Linda E. Reichl

A Modern Course in Statistical Physics

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4th revised and updated edition

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Bose–Einstein condensates;
courtesy of Daniel J. Heinzen

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Preface to the Fourth Edition

A Modern Course in Statistical Physics has gone through several editions. The first edition was published in 1980 by University of Texas Press. It was well received because it contained a presentation of statistical physics that synthesized the best of the american and european "schools" of statistical physics at that time. In 1997, the rights to *A Modern Course in Statistical Physics* were transferred to John Wiley & Sons and the second edition was published. The second edition was a much expanded version of the first edition, and as we subsequently realized, was too long to be used easily as a textbook although it served as a great reference on statistical physics. In 2004, Wiley-VCH Verlag assumed rights to the second edition, and in 2007 we decided to produce a shortened edition (the third) that was explicitly written as a textbook. The third edition appeared in 2009.

Statistical physics is a fast moving subject and many new developments have occurred in the last ten years. Therefore, in order to keep the book "modern", we decided that it was time to adjust the focus of the book to include more applications in biology, chemistry and condensed matter physics. The core material of the book has not changed, so previous editions are still extremely useful. However, the new fourth edition, which is slightly longer than the third edition, changes some of its focus to resonate with modern research topics.

The first edition acknowledged the support and encouragement of Ilya Prigogine, who directed the Center for Statistical Mechanics at the U.T. Austin from 1968 to 2003. He had an incredible depth of knowledge in many fields of science and helped make U.T. Austin an exciting place to be. The second edition was dedicated to Ilya Prigogine "for his encouragement and support, and because he has changed our view of the world." The second edition also acknowledged another great scientist, Nico van Kampen, whose beautiful lectures on stochastic processes, and critically humorous view of everything, were an inspiration and spurred my interest statistical physics. Although both of these great people are now gone, I thank them both.

The world exists and is stable because of a few symmetries at the microscopic level. Statistical physics explains how thermodynamics, and the incredible complexity of the world around us, emerges from those symmetries. This book attempts to tell the story of how that happens.

Austin, Texas January 2016 *L. E. Reichl*

1
Introduction

Thermodynamics, which is a macroscopic theory of matter, emerges from the symmetries of nature at the microscopic level and provides a universal theory of matter at the macroscopic level. Quantities that cannot be destroyed at the microscopic level, due to symmetries and their resulting conservation laws, give rise to the *state variables* upon which the theory of thermodynamics is built.

Statistical physics provides the microscopic foundations of thermodynamics. At the microscopic level, many-body systems have a huge number of states available to them and are continually sampling large subsets of these states. The task of statistical physics is to determine the macroscopic (measurable) behavior of many-body systems, given some knowledge of properties of the underlying microscopic states, and to recover the thermodynamic behavior of such systems.

The field of statistical physics has expanded dramatically during the last half-century. New results in quantum fluids, nonlinear chemical physics, critical phenomena, transport theory, and biophysics have revolutionized the subject, and yet these results are rarely presented in a form that students who have little background in statistical physics can appreciate or understand. This book attempts to incorporate many of these subjects into a basic course on statistical physics. It includes, in a unified and integrated manner, the foundations of statistical physics and develops from them most of the tools needed to understand the concepts underlying modern research in the above fields.

There is a tendency in many books to focus on equilibrium statistical mechanics and derive thermodynamics as a consequence. As a result, students do not get the experience of traversing the vast world of thermodynamics and do not understand how to apply it to systems which are too complicated to be analyzed using the methods of statistical mechanics. We will begin in Chapter 2, by deriving the equations of state for some simple systems starting from our knowledge of the microscopic states of those systems (the *microcanonical ensemble*). This will give some intuition about the complexity of microscopic behavior underlying the very simple equations of state that emerge in those systems.

In Chapter 3, we provide a thorough grounding in thermodynamics. We review the foundations of thermodynamics and thermodynamic stability theory and devote a large part of the chapter to a variety of applications which do not involve phase transitions, such as heat engines, the cooling of gases, mixing, osmosis,

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chemical thermodynamics, and batteries. Chapter 4 is devoted to the thermodynamics of phase transitions and the use of thermodynamic stability theory in analyzing these phase transitions. We discuss first-order phase transitions in liquid–vapor–solid transitions, with particular emphasis on the liquid–vapor transition and its critical point and critical exponents. We also introduce the Ginzburg–Landau theory of continuous phase transitions and discuss a variety of transitions which involve broken symmetries. And we introduce the critical exponents which characterize the behavior of key thermodynamic quantities as a system approaches its critical point.

In Chapter 5, we derive the probability density operator for systems in thermal contact with the outside world but isolated chemically (the *canonical ensemble*). We use the canonical ensemble to derive the thermodynamic properties of a variety of model systems, including semiclassical gases, harmonic lattices and spin systems. We also introduce the concept of scaling of free energies as we approach the critical point and we derive values for critical exponents using Wilson renormalization theory for some particular spin lattices.

In Chapter 6, we derive the probability density operator for open systems (the *grand canonical ensemble*), and use it to discuss adsorption processes, properties of interacting classical gases, ideal quantum gases, Bose–Einstein condensation, Bogoliubov mean field theory, diamagnetism, and super-conductors.

The discrete nature of matter introduces fluctuations about the average (thermodynamic) behavior of systems. These fluctuations can be measured and give valuable information about decay processes and the hydrodynamic behavior of many-body systems. Therefore, in Chapter 7 we introduce the theory of Brownian motion which is the paradigm theory describing the effect of underlying fluctuations on macroscopic quantities. The relation between fluctuations and decay processes is the content of the so-called fluctuation–dissipation theorem which is derived in this chapter. We also derive Onsager's relations between transport coefficients, and we introduce the mathematics needed to introduce the effect of causality on correlation functions. We conclude this chapter with a discussion of thermal noise and Landauer conductivity in ballistic electron waveguides.

Chapter 8 is devoted to hydrodynamic processes for systems near equilibrium. We derive the Navier–Stokes equations from the symmetry properties of a fluid of point particles, and we use the derived expression for entropy production to obtain the transport coefficients for the system. We also use the solutions of the linearized Navier–Stokes equations to predict the outcome of light-scattering experiments. We next derive a general expression for the entropy production in binary mixtures and use this theory to describe thermal and chemical transport processes in mixtures, and in electrical circuits. We conclude Chapter 8 with a derivation of hydrodynamic equations for superfluids and consider the types of sound that can exist in such fluids.

In Chapter 9, we derive microscopic expressions for the coefficients of diffusion, shear viscosity, and thermal conductivity, starting both from mean free path arguments and from the Boltzmann and Lorentz–Boltzmann equations. We obtain explicit microscopic expressions for the transport coefficients of a hard-sphere gas.

Finally, in Chapter 10 we conclude with the fascinating subject of nonequilibrium phase transitions. We show how nonlinearities in the rate equations for chemical reaction–diffusion systems lead to nonequilibrium phase transitions which give rise to chemical clocks, nonlinear chemical waves, and spatially periodic chemical structures, while nonlinearities in the Rayleigh–Bénard hydrodynamic system lead to spatially periodic convection cells.

The book contains Appendices with background material on a variety of topics. Appendix A, gives a review of basic concepts from probability theory and the theory of stochastic processes. Appendix B reviews the theory of exact differentials which is the mathematics underlying thermodynamics. In Appendix C, we review ergodic theory. Ergodicity is a fundamental ingredient for the microscopic foundations of thermodynamics. In Appendix D, we derive the second quantized formalism of quantum mechanics and show how it can be used in statistical mechanics. Appendix E reviews basic classical scattering theory. Finally, in Appendix F, we give some useful math formulas and data. Appendix F also contains solutions to some of the problems that appear at the end of each chapter.

The material covered in this textbook is designed to provide a solid grounding in the statistical physics underlying most modern physics research topics.

2
Complexity and Entropy

2.1
Introduction

Thermodynamics and statistical physics describe the behavior of systems with many interacting degrees of freedom. Such systems have a huge number of microscopic states available to them and they are continually passing between these states. The reason that we can say anything about the behavior of such systems is that symmetries (and conservation laws) exist that must be respected by the microscopic dynamics of these systems.

If we have had a course in Newtonian mechanics or quantum mechanics, then we are familiar with the effects of conservation laws on the dynamics of classical or quantum systems. However, in such courses, we generally only deal with very special systems (usually integrable systems) that have few degrees of freedom. We seldom are taught the means to deal with the complexity that arises when interacting systems have many degrees of freedom. Fortunately, nature has given us a quantity, called *entropy*, that is a measure of complexity. Thermodynamics shows us that entropy is one of the essential building blocks, together with conservation laws, for describing the macroscopic behavior of complex systems. The tendency of systems to maximize their entropy gives rise to effective forces (entropic forces). Two examples of entropic forces are the pressure of an ideal gas and the tension in an elastic band.

In this chapter, we focus on tools for measuring the complexity of systems with many degrees of freedom. We first describe methods for counting microscopic states. Then we introduce the measure of complexity, the entropy, that will play a fundamental role in everything we discuss in the remainder of the book.

2.2
Counting Microscopic States

The first step in counting the number of microscopic states, for a given system, is to identify what these states are. Once the states are identified, we can start the counting process. It is useful to keep in mind two very important counting

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principles [125, 146, 183]:

1. *Addition principle*: If two operations are mutually exclusive and the first can be done in m ways while the second can be done in n ways, then one or the other can be done in $m + n$ ways.
2. *Multiplication principle*: If an operation can be performed in n ways, and after it is performed in any one of these ways a second operation is performed which can be performed in any one of m ways, then the two operations can be performed in $n \times m$ ways.

Let us consider some very simple examples which illustrate the use of these counting principles. As a first example (Exercise 2.1), we count the number of distinct signals that a ship can send if it has one flagpole and four distinct (distinguishable) flags. The number of distinct signals depends on the rules for distinguishing different signals.

Exercise 2.1

A ship has four distinct flags, $\boxed{W}$, $\boxed{X}$, $\boxed{Y}$, and $\boxed{Z}$, that it can run up its flagpole. How many different signals can it send (assuming at least one flag must be on the flagpole to create a signal)? Consider two different rules for defining a signal (a state): (a) the order of the flags on the flagpole is important and (b) the order of the flags is not important. (Note that the cases of one flag, two flags, three flags, and four flags on the flag pole are *mutually exclusive*. Therefore, we must find the number of signals for each case and add them.)

(a) *Order of flags important.* With one flag there are $4!/(4-1)! = 4$ signals, with two flags $4!/(4-2)! = 12$ signals, with three flags $4!/(4-3)! = 24$ signals, with four flags $4!/(4-4)! = 24$ signals, for a total of $4 + 12 + 24 + 24 = 64$ signals.

(b) *Order of flags not important*. With one flag there are $4!/((4-1)!1!) = 4$ signals, with two flags $4!/((4-2)!2!) = 6$ signals, with three flags $4!/((4-3)!3!) = 4$ signals, with four flags $4!/((4-4)!4!) = 1$ signal, for a total of $4 + 6 + 4 + 1 = 15$ signals.

In Exercise 2.1(a), the number of signals is given by the number of *permutations* of the flags, while for Exercise 2.1(b) the number of signals corresponds to the number of *combinations* of flags. Below we discuss these two quantities in more detail.

A *permutation* is any arrangement of a set of N distinct objects in a definite order. *The number of different permutations of N distinct objects is $N!$* To prove this, assume that we have N ordered spaces and N distinct objects with which to fill them. The first space can be filled N ways, and after it is filled, the second space can be filled in $(N-1)$ ways, etc. Thus, the N spaces can be filled in $N(N-1)(N-2) \times \cdots \times 1 = N!$ ways.

The number of different permutations of N objects taken R at a time is $N!/(N-R)!$. To prove this, let us assume we have R ordered spaces to fill. Then the first can be filled in N ways, the second in $(N-1)$ ways, …, and the Rth in

$(N-R+1)$ ways. The total number of ways P_{R}^{N} that R ordered spaces can be filled using N distinct objects is $P_{\mathrm{R}}^{N} = N(N-1) \times \cdots \times (N-R+1) = N!/(N-R)!$.

A *combination* is a selection of N distinct objects without regard to order. *The number of different combinations of N objects taken R at a time is* $N!/((N-R)!R!)$. R distinct objects have $R!$ permutations. If we let C_{R}^{N} denote the number of combinations of N distinct objects taken R at a time, then $R!C_{\mathrm{R}}^{N} = P_{\mathrm{R}}^{N}$ and $C_{\mathrm{R}}^{N} = N!/((N-R)!R!)$.

Exercise 2.2

A bus has seven seats facing forward, F, and six seats facing backward, B, so that $F/B \rightarrow (\cap\cap\cap\cap\cap\cap\cap)/(\cup\cup\cup\cup\cup\cup)$. Nine (distinct) students get on the bus, but three of them refuse to sit facing backward. In how many different ways can the nine students be distributed among the seats on the bus?

Answer: Three students must face forward. The number of ways to seat three students in the seven forward facing seats is equal to the number of permutations of seven objects taken three at a time or $7!/(7-3)! = 210$. After these three students are seated, the number of ways to seat the remaining six students among the remaining ten seats is equal to the number of permutations of ten objects taken six at a time or $10!/(10-6)! = 151\,200$. Now using the *multiplication principle*, we find that the total number of distinct ways to seat the students is $(210) \times (151\,200) = 31\,752\,000$, which is an amazingly large number.

It is also useful to determine the number of distinct permutations of N objects when some of them are identical and indistinguishable. The number of permutations of a set of N objects which contains n_1 identical elements of one kind, n_2 identical elements of another kind, …, and n_k identical elements of a kth kind is $N!/(n_1!n_2!\cdots n_k!)$, where $n_1 + n_2 + \cdots + n_k = N$. A simple example of this is given in Exercise 2.3.

Exercise 2.3

(a) Find the number of permutations of the letters in the word, ENGINEERING.
(b) In how many ways are three E's together?
(c) In how many ways are (only) two E's together.

Answer: (a) The number of permutations is $(11!/3!3!2!2!) = 277\,200$, since there are 11 letters but two identical pairs (I and G) and two identical triplets (E and N).

(b) The number of permutations with three E's together = the number of permutations of ENGINRING = $(9!/3!2!2!) = 15\,120$.

(c) The number of ways that only two E's are together = $8 \times (15\,120) = 120\,960$, since there are eight ways to insert EE into ENGINRING and its permutations.

When we are considering a physical system with N particles, the number of microscopic states can be enormous for even moderate values of N. In Exercise 2.4, we count the number of different microscopic magnetic states available to a collection of N spin-1/2 particles.

Exercise 2.4

Consider a system of N spin-1/2 particles lined up in a row. Distinct states of the N-particle system, have different spatial ordering of the spins-up ↑ and spins-down ↓. For $N = 10$, one such state might be ↑↓↓↑↓↑↑↑↓↑. How many microscopic states (different configurations of the N particle spin system) does this system have?

Answer: Use the *multiplication principle*. The first spin has two configurations, ↑ and ↓. After the configuration of the first spin is set, the second spin can exist in one of these two configurations, and so on. Thus, the total number of microscopic states is $2 \times 2 \times \cdots \times 2 = 2^N$. For $N = 10$, the number of microscopic states is 1024. For $N = 1000$ the number of microscopic states is $1.071\,51 \times 10^{301}$. For a small magnetic crystal with $N = 10^{23}$ atoms, the number of microscopic spin states is so large that it is beyond comprehension.

Exercise 2.5

Take a bag of N distinct coins (each coin from a different country and each having one side with the picture of a head on it) and dump them on the floor. How many different ways can the coins have n heads facing up?

Answer: First ask a different question. How many different ways can N distinct coins be assigned to n pots (one coin per pot)? There are N distinct ways to assign a coin to the first pot and, after that is done, $N - 1$ distinct ways to assign the remaining $N - 1$ coins to the second pot, …, and $N - n + 1$ ways to assign the remaining coins to the nth pot. Thus, the total number of distinct ways to assign the N coins to n pots is $N \times (N - 1) \times \ldots \times (N - n + 1) = N!/(N - n)!$. Now note that permutation of the coins, among the pots, doesn't give a different answer, so we must divide by $n!$. Thus, the number of distinct ways to assign n heads to N distinct coins is $\mathcal{N}(n) = N!/(n!(N - n)!)$.

As we will see, these counting rules are extremely important when we attempt to count the different microscopic states available to a quantum system containing N particles. The symmetry properties of the Liouville operator or Hamiltonian operator, under interchange of the particles, determines whether the particles are identical or distinct. The number of microscopic states available to the system, and therefore its physical properties, are very different for these two cases. Consider the example discussed in Exercise 2.5. If we have N distinct coins and drop them on the floor, the number of distinct ways to assign n "heads" to the coins (have n "heads" face up) is $\mathcal{N}(n) = N!/(n!(N - n)!)$. However, if the coins are identical (all US quarters) the number of distinct ways that n "heads" can face up is $\mathcal{N}(n) = 1$.

The question of whether the particles comprising a system are distinct or identical has measurable physical consequences because the number of microscopic states available to the system is very different for the two cases. As we have seen, the number of microscopic states available to a collection of N particles is generally huge.

2.3
Probability

Once we have identified the microscopic states of a system, we can ask what might be observed in an experiment. Because the number of microscopic states associated with a macroscopic system is so large, the outcome of an experiment generally will be different every time it is performed. However, if we perform an experiment many times, we can begin to assign quantitative weights (probabilities) to the various outcomes, consistent with the probabilities associated with the microscopic states. This relation between the outcome of experiments and the probabilities assigned to those outcomes is the content of the Central Limit Theorem (see Appendix A).

The simplest situation (and one very common in nature) is one in which the microscopic states are all equally likely to occur. Then, if we have N microscopic states, x_j $(j = 1, \ldots, N)$, the probability that the state x_j appears as a result of an experiment is $P(x_j) = 1/N$. The entire collection of microscopic states, with their assigned probabilities, forms a *sample space* $\mathcal{S}$.

An *event* is the outcome of an experiment, and it can involve one or more microscopic states. Let us consider two events, A and B, each of which involves several microscopic states. Let $P(A)$ $(P(B))$ denote the probability that event A (B) occurs as the outcome of the experiment. The probability $P(A)$ $(P(B))$ is the sum of the probabilities of all the microscopic states that comprise the event A (B). If the event includes the entire sample space then $P(\mathcal{S}) = 1$ and, if the event includes no elements of the sample space so $A = \emptyset$ ($\emptyset$ denotes an empty set), then $P(\emptyset) = 0$.

The *union* of events A and B (denoted $A \cup B$) contains all microscopic states that participate in both events. The *intersection* of events A and B (denoted $A \cap B$) contains all microscopic states shared by the two events. Therefore, the probability that both events occur as a result of an experiment is the probability of the union, which can be written

$$P(A \cup B) = P(A) + P(B) - P(A \cap B) , \tag{2.1}$$

where $P(A \cap B)$ is the probability associated with microscopic states in the intersection. When we add the probabilities $P(A)$ and $P(B)$, we count the states $A \cap B$ twice, so we correct this mistake by subtracting off one factor of $P(A \cap B)$.

If the two events A and B are *mutually exclusive*, then they have no microscopic states in common and

$$P(A \cup B) = P(A) + P(B) . \tag{2.2}$$

We can partition the sample space $\mathcal{S}$ into a complete set of mutually exclusive events $A_1, A_2, \ldots, A_m$ so that $A_1 \cup A_2 \cup \cdots \cup A_m = S$. Then, the probabilities associated with the m events satisfy the condition

$$P(A_1) + P(A_2) + \cdots + P(A_m) = 1 . \tag{2.3}$$

This partitioning of the sample space will prove extremely useful in subsequent chapters.

Exercise 2.6

Three distinguishable coins (labeled a, b, and c) are tossed. The coins are each *fair* so "heads" (h) and "tails" (t) are equally likely. (a) Find the probability of getting *no* heads. (b) Find the probability of getting *at least two* heads. (c) Show that the event *heads on coin a* and the event *tails on coins b and c* are independent. (d) Show that the event *only two coins heads* and the event *three coins heads* are dependent and mutually exclusive. (e) Find the conditional probability that, given heads on coin a, coin b will be tails.

Answer: Construct a sample space of the following equally probable events: $(a, b, c) = \{(\mathrm{h}, \mathrm{h}, \mathrm{h}), (\mathrm{h}, \mathrm{h}, \mathrm{t}), (\mathrm{h}, \mathrm{t}, \mathrm{h}), (\mathrm{h}, \mathrm{t}, \mathrm{t}), (\mathrm{t}, \mathrm{h}, \mathrm{h}), (\mathrm{t}, \mathrm{h}, \mathrm{t}), (\mathrm{t}, \mathrm{t}, \mathrm{h}), (\mathrm{t}, \mathrm{t}, \mathrm{t})\}$. (a) The probability of no heads = 1/8. (b) The probability of at least two heads = 1/2. (c) Define event A = "heads on the first coin." Define event B = "tails on the last two coins." Then $P(A) = 1/2$ and $P(B) = 1/4$. The union, $A \cup B$ has probability, $P(A \cup B) = 5/8$. Thus, the probability of the intersection is $P(A \cap B) = P(A) + P(B) - P(A \cup B) = 1/8 = P(A) \times P(B)$. Thus, the events, A and B are independent. (d) Define event C = "only two coins heads." Define event D = "three coins heads." Then $P(C) = 3/8$ and $P(D) = 1/8$. The union, $C \cup D$ has probability, $P(C \cup D) = 1/2$. Thus, the probability of the intersection is $P(C \cap D) = P(C) + P(D) - P(C \cup D) = 0 \neq P(C) \times P(D)$. Thus, the events C and D are dependent and are mutually exclusive. (e) Use as the sample space all events with *heads on coin a*. This new sample space has four states. The conditional probability that, given coin a is heads, then coin b will be tails is 1/2.

The events A and B are *independent* if

$$P(A \cap B) = P(A)P(B) . \tag{2.4}$$

Note that *independent* events have some microscopic states in common because $P(A \cap B) \neq 0$. It is important to note that *independent events are not mutually exclusive events.*

Another important quantity is the *conditional probability* $P(B|A)$, defined as the probability of event A, using event B as the sample space (rather than S). The conditional probability is defined by the equation

$$P(B|A) = \frac{P(A \cap B)}{P(B)} . \tag{2.5}$$

Since $P(A \cap B) = P(B \cap A)$, we find the useful relation

$$P(A)P(A|B) = P(B)P(B|A) . \tag{2.6}$$

From Eqs. (2.4) and (2.5), we see that, *if A and B are independent*, then

$$P(B|A) = P(A) . \tag{2.7}$$

In Exercise 2.6, we illustrate all these aspects of probability theory for a simple coin-toss experiment.

In the next sections, we consider several different physical systems and determine how the number of microscopic states, and their probability distributions, depend on physical parameters of those systems.

2.4
Multiplicity and Entropy of Macroscopic Physical States

For a dynamical system with N interacting particles ($3N$ degrees of freedom in 3D space), there will be a very large multiplicity $\mathcal{N}_N$ (number) of *microscopic states* available to the system. In addition, a few conservation laws will allow us to define a set of *macroscopic states* that are parametrized by the values of the conserved quantities. Two of the most important conserved quantities associated with an interacting many-body system are the particle number (assuming no chemical reactions occur) and the total energy of the system. However, there can be other conserved quantities. For example, for a lattice of spin-1/2 particles, the spin is a measure of a conserved internal angular momentum of each particle. Spin cannot be destroyed by interactions between the particles or with external forces. Therefore, the spin provides an additional parameter (along with particle number and total energy) that can be used to specify the state of an N-particle spin lattice. We can assign a macroscopic variable, the number n of "spins up," to the system. Each value of the macroscopic variable n has a *multiplicity* of $\mathcal{N}_N(n)$ microscopic states associated to it.

The total energy is generally proportional to the number of degrees of freedom of the system. When we discuss thermodynamics we also need a measure of the multiplicity of a system that is proportional to the number of degrees of freedom. That quantity is the *entropy*, S. The entropy of an N-particle system with energy E and macroscopic states characterized by a parameter n, is defined

$$S(N, E, n) = k_{\mathrm{B}} \ln(\mathcal{N}_N(E, n)) . \tag{2.8}$$

The quantity $k_{\mathrm{B}} = 1.38 \times 10^{-23}\,\mathrm{J/K}$ is Boltzmann's constant. This expression for the entropy implicitly assumes that all microscopic states with the same values of N, E, and n have the same weight. Another way to say this is that all such microscopic states are equally probable.

The fact that all microscopic states with the same energy are equally probable, derives from the *ergodic theorem*, which has its origins in classical mechanics. A classical mechanical system is ergodic if it spends equal times in equal areas of the mechanical energy surface. All fully chaotic mechanical systems have this property, and it is the foundation upon which statistical mechanics is built. It underlies everything we talk about in this book.

In subsequent sections, we will compute the multiplicity and entropy of the four physical systems; a spin system, a polymer chain, an Einstein solid, and an ideal gas.

2.5
Multiplicity and Entropy of a Spin System

Consider a collection of N spin-1/2 atoms arranged on a lattice. The spin is a measure of quantized angular momentum internal to the atom. Spin-1/2 atoms have a magnetic moment and magnetic field associated with them due to the intrinsic charge currents that give rise to the spin. Generally when an array of spin-1/2 atoms is arranged on a lattice, the various atoms will interact with one another via their magnetic fields. These interactions give rise to many interesting properties of such lattices, including phase transitions. We will discuss these in later sections of the book.

2.5.1
Multiplicity of a Spin System

Since the atoms are fixed to their respective lattice sites, they can be distinguished by their position on the lattice and therefore are distinct. Let n denote the number of atoms with spin up (↑). Note that for this problem, the method of counting microscopic states is the same as that for the bag of N coins in Exercise 2.5. The number of distinct ways to assign n spins "up" is the same as the number of distinct ways that N distinct objects can be assigned to n pots, assuming their ordering among the pots does not matter. Thus, the multiplicity of the macroscopic state "n spins up" is

$$\mathcal{N}_N(n) = \frac{N!}{n!(N-n)!} \; . \tag{2.9}$$

This is the number of microscopic states available to the lattice for the given value of n. As a check, let us sum over all possible values $n = 0, 1, \dots, N$. If we make use of the binomial theorem

$$(a+b)^N = \sum_{n=0}^{N} \frac{N!}{n!(N-n)!} a^{N-n} b^n \; , \tag{2.10}$$

and set $a = b = 1$ we can use Eq. (2.9) to obtain the total number of microstates

$$\mathcal{N}_N = \sum_{n=0}^{N} \mathcal{N}_N(n) = \sum_{n=0}^{N} \frac{N!}{n!(N-n)!} = 2^N \; . \tag{2.11}$$

Thus, the sum of all the microstates contained in the macrostates gives 2^N, as it should. Note that our ability to *count* the number of microscopic states is due to the fact that the angular momentum intrinsic to the atoms is quantized and is a consequence of the quantum nature of matter.

Let us now focus on the limit $N \to \infty$, and consider the behavior of the *fraction of microstates*, $\mathcal{F}_N(n) = (\mathcal{N}_N(n))/(\mathcal{N}_N)$ with n spins "up,"

$$\mathcal{F}_N(n) = \frac{N!}{n!(N-n)!}\frac{1}{2^N} = \frac{N!}{n!(N-n)!}\left(\frac{1}{2}\right)^n\left(\frac{1}{2}\right)^{N-n} \; . \tag{2.12}$$

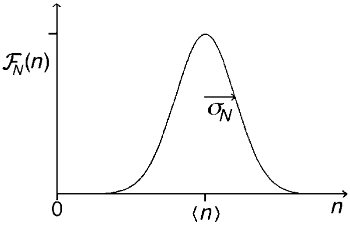

Figure 2.1 A plot of the fraction of microscopic states, $\mathcal{F}_N(n)$ that belong to the macroscopic state "n spins up," plotted as a function of n. The macroscopic state $n = \langle n \rangle = N/2$ contains the most microscopic states. As N increases, the ratio $\sigma_N/\langle n \rangle$ decreases as $1/\sqrt{N}$, and the macrostate $n = \langle n \rangle$ begins to dominate the physical properties of the system.

If all microstates are equally probable, then $\mathcal{F}_N(n)$ is the probability of finding the chain of N spin-1/2 particles with n spins "up," and is given by the binomial distribution (see Appendix A). For large N, the binomial distribution can be approximated by a Gaussian distribution (this is derived in Appendix A) so we can write

$$\mathcal{F}_N(n) \approx \frac{1}{\sigma_N\sqrt{2\pi}} \exp\left[-\frac{(n-\langle n \rangle)^2}{2\sigma_N^2}\right] , \tag{2.13}$$

where $\langle n \rangle = N/2$ is the peak of the distribution and $\sigma_N = \sqrt{N}/2$ is a measure of its width. Notice that $\lim_{N\to\infty} \sigma_N/\langle n \rangle = 0$. Thus, for very large N, to good approximation, the macrostate with $n = \langle n \rangle$ governs the physical properties of the system.

If we plot the fraction $\mathcal{F}_N(n)$ of microscopic states having n spins up (see Figure 2.1), we find that it is sharply peaked about the value $n = \langle n \rangle$. As the number of degrees of freedom tend to infinity ($N \to \infty$), the physical properties of the system become determined by that one value of the macroscopic variable $n = \langle n \rangle$, and this is called the equilibrium state of the system. The tendency of a macrostate to be dominated by a single most-probable value of its parameter, in the limit of a large number of degrees of freedom, is universal to all systems whose interactions have short range. It is a manifestation of the Central Limit Theorem (Appendix A) and is the basis for the universal behavior found in thermodynamic systems.

2.5.2
Entropy of Spin System

The entropy of a spin lattice (with N spin-1/2 particles) that has n spins up is given by Eqs. (2.8) and (2.9) and can be written

$$S(N,n) = k_{\mathrm{B}} \ln\left[\frac{N!}{n!(N-n)!}\right] . \tag{2.14}$$

For large N ($N > 10$), we can use Stirling's approximations,

$$N! \approx \sqrt{2\pi N} N^N \mathrm{e}^{-N} \quad \text{and} \quad \ln(N!) \approx N\ln(N) - N , \tag{2.15}$$

to simplify the factorials. The entropy then takes the form

$$S(N,n) \approx k_{\mathrm{B}} \ln\left[\frac{N^N}{n^n(N-n)^{N-n}}\right] . \tag{2.16}$$

The form of the entropy in Eq. (2.16) is easier to deal with than Eq. (2.14) because it does not depend on factorials.

In the limit $N \to \infty$, the entropy is well approximated by the value

$$S(N, \langle n\rangle) \approx k_{\mathrm{B}} \ln \left[\frac{N^N}{\langle n\rangle^{\langle n\rangle}(N - \langle n\rangle)^{N-\langle n\rangle}} \right] , \tag{2.17}$$

which is called the entropy of the *equilibrium state* of the system. If no external magnetic fields are present, then $\langle n\rangle = N/2$, and we find

$$S(N, \langle n\rangle) \approx N k_{\mathrm{B}} \ln 2 . \tag{2.18}$$

In this case, because the spins are independent of one another, the total entropy of the system is just N times the entropy of a single spin. Note that the entropy is *additive* because the entropy of the whole system is the sum of the entropies of the independent parts of the system.

2.5.2.1 Entropy and Fluctuations About Equilibrium

In the limit $N \to \infty$, the entropy is equal to $S(N, \langle n\rangle)$, which is the equilibrium value of the entropy. However, in the real world we never reach the limit $N = \infty$. Any given system always has a finite number of particles and there will be macroscopic states with $n \neq \langle n\rangle$. Therefore, there will be fluctuations in the entropy about the equilibrium value $S(N, \langle n\rangle)$. Since the multiplicity of the macroscopic states with $n \neq \langle n\rangle$ is always less than that of the state with $n = \langle n\rangle$, fluctuations away from equilibrium must cause the value of the entropy to decrease. Thus, for systems with fixed energy, the entropy takes its maximum value at equilibrium.

The spin system considered above has zero magnetic energy so we have suppressed the energy dependence of the entropy. If all microscopic states with the same energy, particle number, and number of spins-up are equally probable, then the probability $P_N(n)$ of finding the system in the macrostate, (N, n) is simply the *fraction of microstates*, $\mathcal{F}_N(n) = (\mathcal{N}_N(n))/\mathcal{N}_N$ with parameters N, n. Therefore, we can write

$$P_N(n) = \mathcal{F}_N(n) = \frac{\mathcal{N}_N(n)}{\mathcal{N}_N} = \frac{1}{\mathcal{N}_N} \exp\left(\frac{1}{k_{\mathrm{B}}} S(N, n) \right) . \tag{2.19}$$

Thus, the entropy, written as a function of the macroscopic variable n, can be used to determine the probability of fluctuations in the value of n away from the equilibrium state $n = \langle n\rangle$.

2.5.2.2 Entropy and Temperature

In the absence of a magnetic field, the spin lattice has zero magnetic energy. However, if a magnetic flux density $\mathcal{B}$ is present and directed upward, then spin-up lattice sites have energy $-\mu\mathcal{B}$ and spin-down lattice sites have energy $+\mu\mathcal{B}$, where μ is the magnetic moment of the atoms. In the limit of large N, we can make the replacement $n \to \langle n\rangle$ and the energy becomes a *thermodynamic* energy. Then the total magnetic energy takes the form

$$\langle E\rangle = -\mu\langle n\rangle\mathcal{B} + \mu(N - \langle n\rangle)\mathcal{B} = \mu\mathcal{B}(N - 2\langle n\rangle) , \tag{2.20}$$

and the magnetization is

$$\langle M\rangle = \mu\,(2\langle n\rangle - N)\ . \tag{2.21}$$

The physical properties of the system are determined by the equilibrium value $n = \langle n\rangle$. Note that, in the presence of a magnetic field, the average number of spins-up $\langle n\rangle$ will be shifted away from its value for the field-free case but, using Eq. (2.20), it can be written in terms of the magnetic energy

$$\langle n\rangle = \frac{N}{2} - \frac{\langle E\rangle}{2\mu\mathcal{B}}\ . \tag{2.22}$$

The entropy can be written in terms of the average energy and number of atoms on the lattice. If we combine Eqs. (2.14) and (2.22) and use Stirling's approximation in Eq. (2.15), the entropy takes the form

$$\begin{aligned} S(N,\langle E\rangle,\mathcal{B}) \approx k_{\mathrm{B}} N \ln N - k_{\mathrm{B}}\left(\frac{N}{2} - \frac{\langle E\rangle}{2\mu\mathcal{B}}\right)\ln\left(\frac{N}{2} - \frac{\langle E\rangle}{2\mu\mathcal{B}}\right) \\ - k_{\mathrm{B}}\left(\frac{N}{2} + \frac{\langle E\rangle}{2\mu\mathcal{B}}\right)\ln\left(\frac{N}{2} + \frac{\langle E\rangle}{2\mu\mathcal{B}}\right)\ . \end{aligned} \tag{2.23}$$

Note that, both the average energy and entropy are proportional to the number of degrees of freedom.

Let us now introduce a result from thermodynamics that we will justify in the next chapter. The rate at which the entropy changes as we change the thermodynamic energy is related to the temperature T of the system (in kelvin) so that

$$\left(\frac{\partial S}{\partial\langle E\rangle}\right)_{\mathcal{B},N} = \frac{1}{T}\ . \tag{2.24}$$

At very low temperature (in kelvin), a small change in energy can cause a large change in the entropy of the system. At high temperature, a small change in energy causes a very small change in the entropy.

We can use Eq. (2.24) to determine how the thermodynamic energy of the system varies with temperature. We need to take the derivative of $S(N,\langle E\rangle)$ with respect to $\langle E\rangle$ holding N and $\mathcal{B}$ constant. Then with a bit of algebra, we obtain

$$\left(\frac{\partial S}{\partial\langle E\rangle}\right)_{\mathcal{B},N} = \frac{k_{\mathrm{B}}}{2\mu\mathcal{B}}\ln\left(\frac{N - \langle E\rangle/(\mu\mathcal{B})}{N + \langle E\rangle/(\mu\mathcal{B})}\right) = \frac{1}{T}\ . \tag{2.25}$$

Solving for $\langle E\rangle$, we finally obtain

$$\langle E\rangle(N,T,\mathcal{B}) = -N\mu\mathcal{B}\tanh\left(\frac{\mu\mathcal{B}}{k_{\mathrm{B}}T}\right) \approx -\frac{N\mu^2\mathcal{B}^2}{k_{\mathrm{B}}T}\ , \tag{2.26}$$

to lowest order in $\mathcal{B}$. We have just demonstrated the power of thermodynamics in allowing us to relate seemingly unrelated physical quantities. However, having entered the realm of thermodynamics, the thermodynamic energy $\langle E\rangle(N,T,\mathcal{B})$, now contains information about thermal properties of the system.

We can also obtain the magnetization $\langle M\rangle$ of this system. We find

$$\langle M\rangle = \frac{N\mu^2\mathcal{B}}{k_{\mathrm{B}}T}\,, \tag{2.27}$$

to lowest order in $\mathcal{B}$. Equation (2.27) is equation of state for the magnetic system. The magnetization can also be found from the entropy, but we will need to develop the full machinery of thermodynamics in order to see how this can be done properly. The equation of state relates the mechanical and thermal properties of a system, and generally can be determined from measurements in the laboratory on the system in question. It is one of the most common and important relationships that we can know about most physical systems.

The magnetic equation of state (2.28) is often written in terms of the number of *moles* $\mathfrak{n}$ of atoms in the system. The total number of moles is related to the total number of atoms on the lattice via Avogadro's number $N_{\mathrm{A}} = 6.022\times 10^{23}$. Avogadro's number is the number of atoms in one mole of atoms or $N = \mathfrak{n}N_{\mathrm{A}}$. Then the magnetic equation of state takes the form

$$\langle M\rangle = \frac{\mathfrak{n}D_{\mathrm{m}}\mathcal{B}}{T}\,, \tag{2.28}$$

where $D_{\mathrm{m}} = N_{\mathrm{A}}\mu^2/k_{\mathrm{B}}$ is a parameter determined by fundamental constants and the magnetic moment of the atoms in the particular system being considered.

2.6
Entropic Tension in a Polymer

A very simple model of a polymer consists of a freely jointed chain (FJC) of N non-interacting directed links, each of length ℓ. The links are numbered from 1 to N, and each link is equally probable to be either left pointing (←) or right pointing (→). The net length X of the polymer chain is defined as the net displacement from the unattached end of link 1 to the unattached end of link N so $X = n_{\mathrm{R}}\ell - n_{\mathrm{L}}\ell$, where n_{L} (n_{R}) is the number of left (right) pointing links, and $N = n_{\mathrm{R}} + n_{\mathrm{L}}$.

This system is mathematically analogous to the chain of spin-1/2 particles in Section 2.5. The multiplicity of microscopic states with n_{R} links to the right is

$$\mathcal{N}_N(n_{\mathrm{R}}) = \frac{N!}{n_{\mathrm{R}}!(N-n_{\mathrm{R}})!}\,. \tag{2.29}$$

The total number of microscopic states is 2^N. Assuming that all microscopic states are equally probable, the probability of finding a polymer that has a total of N links with n_{R} right-directed links is

$$P_N(n_{\mathrm{R}}) = \frac{1}{2^N}\frac{N!}{n_{\mathrm{R}}!(N-n_{\mathrm{R}})!} = \frac{N!}{n_{\mathrm{R}}!(N-n_{\mathrm{R}})!}p^{n_{\mathrm{R}}}q^{N-n_{\mathrm{R}}}\,, \tag{2.30}$$

where $p = q = 1/2$. This probability is a binomial distribution (see Appendix A). The average number of right-pointing links n_{R} is given by

$$\langle n_{\mathrm{R}} \rangle = \sum_{n_{\mathrm{R}}=0}^{N} n_{\mathrm{R}} P_N(n_{\mathrm{R}}) = pN = \frac{N}{2}\,, \tag{2.31}$$

so the average number of left pointing links is $\langle n_{\mathrm{L}} \rangle = N - \langle n_{\mathrm{R}} \rangle = N/2$ and the average net length of the polymer is $\langle X \rangle = 0$. In the limit $N \to \infty$ the probability distribution in Eq. (2.30) approaches a Gaussian narrowly peaked about $n_{\mathrm{R}} = \langle n_{\mathrm{R}} \rangle = N/2$. Thus, most of the polymers are tightly and randomly coiled.

The entropy of the collection of polymers with n_{R} right-pointing links is

$$S = k_{\mathrm{B}} \ln \left[\frac{N!}{n_{\mathrm{R}}!(N - n_{\mathrm{R}})!} \right] \approx k_{\mathrm{B}}[N \ln N - n_{\mathrm{R}} \ln n_{\mathrm{R}} - (N - n_{\mathrm{R}}) \ln(N - n_{\mathrm{R}})\,], \tag{2.32}$$

where we have used Stirling's approximation. If we plot the entropy as a function of n_{R}, the curve has an extremum whose location is given by the condition

$$\frac{\mathrm{d}S}{\mathrm{d}n_{\mathrm{R}}} = k_{\mathrm{B}} \ln \left(\frac{N - n_{\mathrm{R}}}{n_{\mathrm{R}}} \right) = 0\,. \tag{2.33}$$

This has the solution $n_{\mathrm{R}} = N/2$, so the state of maximum entropy (the peak of the curve) occurs for $n_{\mathrm{R}} = N/2$ and $X = 0$. Thus, the collection of the most tightly curled-up polymers have the maximum entropy.

In the absence of interactions, all microscopic states have the same energy. The tension J of the polymer can be related to the displacement X via the thermodynamic relation $J = -T(\partial S/\partial X)_{E,N}$. But we can write $n_{\mathrm{R}} = X/(2\ell) + N/2$ so $J = -T/(2\ell)(\partial S/\partial n_{\mathrm{R}})_{U,N}$. We use the expression for the entropy to find the tension J in the chain, as a function of X. We obtain

$$J = -\frac{k_{\mathrm{B}} T}{2\ell} \ln \left(\frac{N - n_{\mathrm{R}}}{n_{\mathrm{R}}} \right) = -\frac{k_{\mathrm{B}} T}{2\ell} \ln \left(\frac{N - X/\ell}{N + X/\ell} \right) \approx \frac{k_{\mathrm{B}} T}{N\ell^2} X + \ldots \tag{2.34}$$

In the last term, we have expanded J in powers of $X/N\ell$ (which is only valid if $X/N\ell \ll 1$). For the case $X/N\ell \ll 1$, we have obtained $J \approx k_{\mathrm{B}} T/(N\ell^2) X + \ldots$, which is Hooke's law for the elastic force needed to stretch the polymer. The force constant is $k = k_{\mathrm{B}} T/(N\ell^2)$. The tension J is an entropic force (per unit length). If the chain is stretched to maximum length, it will have very few microscopic states available. On the average, it will contract back to a length where it maximizes the entropy (multiplicity of states).

The theory described here is a random walk model for polymer coiling in one space dimension. The results would be different if we considered the random walk in three space dimensions. Nevertheless, this type of one-dimensional entropic elasticity has been observed in polymers. One example is the macromolecule DNA, which is a very long molecule, with lengths on the order of tens of millimeters (although it is generally coiled into a complex structure). There are short segments of the molecule (with lengths of order 50 nm) whose elasticity, for small deviations from equilibrium, is well described by the FJC model described above. For these short segments in DNA, the force constant associated with Hook's law is found to be $k = 0.1\,\text{pN}$ [11].

2.7
Multiplicity and Entropy of an Einstein Solid

Einstein developed a very simple model for mechanical vibrations on a lattice. This model is called the *Einstein solid* and consists of a three dimensional lattice which contains $N/3$ lattice sites, with one atom attached to each lattice site. Each atom can oscillate about its lattice site in three independent spatial directions, (x, y, z). Thus, each lattice site contains three independent oscillators. The entire lattice contains a total of N oscillators, which are assumed to be harmonic oscillators, all having the same radial frequency ω. The vibrations of the solid are due to these N harmonic oscillators. A single harmonic oscillator has an energy $E = (1/2)\hbar\omega + q\hbar\omega$, where $\hbar$ is Planck's constant, $(1/2)\hbar\omega$ is the zero-point energy of the harmonic oscillator, and $q = 0, 1, 2, \ldots, \infty$ is an integer. A harmonic oscillator has zero point energy because of the Heisenberg uncertainty relation $\Delta p_x \Delta x \geq \hbar$, which arises from the wave nature of particles. The oscillator can never come to rest because that would cause $\Delta x \to 0$ and $\Delta p_x \to 0$, which can not be satisfied quantum mechanically.

For a lattice with N harmonic oscillators, the total vibrational energy can be written

$$E(N, q) = \frac{1}{2} N\hbar\omega + q\hbar\omega\ , \tag{2.35}$$

where $q = 0, 1, 2, \ldots, \infty$ is again an integer. The oscillators are independent of one another and can be in different states of motion. If the lattice has a total energy $E(N, q)$, the q quanta of energy can be distributed among the N harmonic oscillators in many different ways.

2.7.1
Multiplicity of an Einstein Solid

Let us assume that "q quanta on the lattice" is a macroscopic state, and let us determine the multiplicity of this macroscopic state [190]. We need to determine how many ways q quanta can be distributed among N distinct pots. This is straightforward if we draw a picture. Represent a quantum of energy by an "x" and N pots by $N - 1$ vertical lines. For example, if $q = 9$ and $N = 6$, then one way to distribute the quanta is represented by the picture $\{xx|xxx||x|xx|x\}$. We can determine all possible ways to distribute $q = 9$ quanta among $N = 6$ pots by finding the number permutations of nine "x"s and five vertical lines. More generally, the number of ways to distribute q quanta among N pots is the total number of permutations of q "x"s with $N-1$ vertical lines. This number is the multiplicity $\mathcal{N}(q)$ of the macrostate "q quanta on the lattice" and is given by

$$\mathcal{N}_N(q) = \frac{(N+q-1)!}{q!(N-1)!} . \tag{2.36}$$

If there is only one quantum of vibrational energy on the lattice and the lattice has $N = 12$ oscillators (four lattice sites), then it can be placed in the $N = 12$ oscillators in $\mathcal{N}_{12}(1) = 12$ different ways. However, if there are $q = 12$ quanta on the lattice of $N = 12$ oscillators, they can be distributed among the oscillators in $\mathcal{N}_{12}(12) = 1\,352\,078$ different ways. Generally, we are interested in a piece of a crystal which typically has $N = 10^{23}$ oscillators. Then, if there are enough quanta on the lattice to excite even a small fraction of the oscillators, the number of microscopic states available is amazingly large. It is clear that we need a way to make contact with measurable quantities, and thermodynamics will give us that. Note again that our ability to count the number of vibrational states available to the lattice is a consequence of quantum mechanics and the quantization of vibrational energy.

2.7.2
Entropy of the Einstein Solid

For the Einstein solid, we have one less macroscopic parameter than for the spin system. In the spin system, in the absence of a magnetic field, all microscopic configurations have the same energy. However, for the spin system we have another parameter, n, (due to spin conservation) which is the number of spins-up on the lattice and we can use it to construct different macroscopic states depending on the value of n. For the Einstein solid, for a fixed number of harmonic oscillators N, we only have the parameter q which is the number of quanta of oscillation energy and is proportional to the energy E. Therefore, for the Einstein solid, we have only one macroscopic state, determined by the value of q, and many microscopic states given by the number of ways to distribute the q quanta among the N harmonic oscillators.

If we use Eqs. (2.8) and (2.36), the entropy of the Einstein solid is given by

$$S(N,q) = k_\mathrm{B} \ln\left[\frac{(N+q-1)!}{q!(N-1)!}\right] \approx k_\mathrm{B} \ln\left[\frac{(N+q)^{N+q}}{N^N q^q}\right] , \tag{2.37}$$

where we have assumed that N and q are large and we have used Stirling's approximation Eq. (2.15). We can now use thermodynamics to relate the energy to the temperature via the relation

$$\left(\frac{\partial S}{\partial E}\right)_N = \frac{1}{\hbar\omega}\left(\frac{\partial S}{\partial q}\right)_N = \frac{1}{T} , \tag{2.38}$$

where, in the middle term, we have used the relation between E and q given in Eq. (2.35). If we take the derivative of the entropy, as indicated in Eq. (2.38), and solve for the energy, we obtain

$$E(N,T) = \frac{1}{2}N\hbar\omega + \frac{N\hbar\omega \mathrm{e}^{-\beta\hbar\omega}}{(1-\mathrm{e}^{-\beta\hbar\omega})}\,, \tag{2.39}$$

where $\beta = 1/(k_{\mathrm{B}}T)$. As we shall see in the chapter on thermodynamics, the heat capacity of the Einstein solid can be written

$$C_N = \left(\frac{\partial E}{\partial T}\right)_N = \frac{N(\hbar\omega)^2 \mathrm{e}^{-\beta\hbar\omega}}{k_{\mathrm{B}}T^2(1-\mathrm{e}^{-\beta\hbar\omega})^2}\,. \tag{2.40}$$

In the limit $T \to 0$, the heat capacity of the Einstein solid goes to zero exponentially as a function of temperature T. This result provided an important breakthrough in our understanding of the effect of quantum mechanics on the thermal properties of solids at low temperature. Classical physics could not explain the experimentally observed fact that the heat capacity of solids do tend to zero as the temperature tends to 0 K. The heat capacity given by the Einstein solid is not quite correct. The heat capacity of real solids goes to zero as T^3, not exponentially. The reason for this will become clear when we consider a Debye solid, which allows lattice sites to be coupled.

2.8
Multiplicity and Entropy of an Ideal Gas

We now consider an ideal gas of N particles in a box of volume $V = L^3$. State-counting in this system is different from the spin system and Einstein solid because the particles in the gas move freely through the box. If the gas particles have no distinguishing internal characteristics such as different mass or different spin, they are *indistinguishable*. For the spin system and the Einstein solid, particles are attached to specific lattice sites and remain there, so they are distinguishable and distinct.

2.8.1
Multiplicity of an Ideal Gas

We want to determine the multiplicity of states available to an ideal gas of N particles. By ideal gas we mean the real gas density is low enough that the energy of interaction between the particles is negligible. The key to obtaining a countable set of microscopic states is to remember that this system is intrinsically quantum mechanical and that the quantum states available to each particle occupy a finite size region of phase space whose size is determined by Planck's constant, h. Since the particles move in three dimensional configuration space, the number of degrees of freedom of the system is $D = 3N$ and the momentum of each particle has three independent components. The total energy of the gas can be written

$$E = \sum_{j=1}^{3N} \frac{p_j^2}{2m}\ , \tag{2.41}$$

where the sum is over all $3N$ components of momentum, p_j is one of the $3N$ components of momentum, and m is the mass of each particle.

The volume of phase space available to a single quantum state of the gas is $\Delta p_1 \Delta x_1 \times \cdots \times \Delta p_{3N} \Delta x_{3N} = h^{3N}$, where h is Planck's constant. The volume of phase space $\Omega^{(D)}(E)$ that has energy less than E can be written $\Omega^{(D)}(E) = V^N \Omega_p^{(D)}(E)$, where we have explicitly separated the spatial volume V from the volume of the momentum coordinates. This is possible because there are no external fields present and interactions between the particles are neglected.

It is useful to begin with a very simple case. Let us first obtain the phase space volume available to one particle ($N = 1$) in two dimensional configuration space and $D = 2$ degrees of freedom. The energy of the particle is $E = 1/(2m)(p_x^2 + p_y^2)$. Therefore, we can write $p_x^2 + p_y^2 = 2mE = R^2$, where R is the radius of the allowed circle in momentum space. The area (volume) within the circle in momentum space is $\Omega_p^{(2)}(E) = \pi(\sqrt{2mE})^2 = \pi 2mE$. Thus, the volume of phase space with energy less than or equal to E is $\Omega^{(2)}(E) = L^2 \pi 2mE$.

In a similar manner, we can determine the volume of phase space $\Omega^{(D)}(E) = V^N \Omega_p^{(D)}(E)$ that has energy less than or equal to E for the case of N particles in a box of volume V. For $D = 3N$ degrees of freedom, Eq. (2.41) can be written in the form $p_1^2 + \cdots + p_\mathrm{D}^2 = 2mE = R^2$. The volume in momentum space with energy less than or equal to E can be written in the form $\Omega_p^D(E) = A_\mathrm{D} R^D = A_\mathrm{D}(R^2)^{D/2}$, where A_D is an unknown constant. It is useful to write $(\mathrm{d}\Omega_p^{(D)}(E))/(\mathrm{d}R^2) = A_\mathrm{D} D/2R^{D-2}$ and, therefore,

$$\int_0^\infty \mathrm{d}R^2 \frac{\mathrm{d}\Omega_p^{(D)}(E)}{\mathrm{d}R^2} \mathrm{e}^{-R^2} = A_\mathrm{D} \frac{D}{2} \Gamma\left(\frac{D}{2}\right)\ , \tag{2.42}$$

where $\Gamma(x)$ is the Gamma function.

To determine the constant A_D, compute $\Omega_p^D(E)$ in another way. Note that

$$\Omega_p^{(D)}(E) = \int_{-\infty}^{\infty} \mathrm{d}p_1 \cdots \int_{-\infty}^{\infty} \mathrm{d}p_\mathrm{D} \Theta\left(R^2 - p_1^2 - \cdots - p_\mathrm{D}^2\right)\ , \tag{2.43}$$

where $\Theta(R^2 - p_1^2 - \cdots - p_\mathrm{D}^2)$ is the Heaviside function. (Heaviside functions have the property that $\Theta(x) = 0$ if $x < 0$, $\Theta(x) = 1$ if $x > 0$, and $\Theta(x) = 1/2$ if $x = 0$.) Because the derivative of a Heaviside function is a Dirac delta function, $\delta(x) = \mathrm{d}\Theta(x)/\mathrm{d}x$, we can write

$$\frac{\mathrm{d}\Omega_p^{(D)}(E)}{\mathrm{d}R^2} = \int_{-\infty}^{\infty} \mathrm{d}p_1 \cdots \int_{-\infty}^{\infty} \mathrm{d}p_\mathrm{D} \delta\left(R^2 - p_1^2 - \cdots - p_\mathrm{D}^2\right)\ . \tag{2.44}$$

Now note that

$$\int_0^\infty \mathrm{d}R^2 \frac{\mathrm{d}\Omega_p^{(D)}(E)}{\mathrm{d}R^2} \mathrm{e}^{-R^2} = \int_{-\infty}^{\infty} \mathrm{d}p_1 \cdots \int_{-\infty}^{\infty} \mathrm{d}p_\mathrm{D} \mathrm{e}^{-(p_1^2+p_2^2+\cdots+p_\mathrm{D}^2)} = \pi^{D/2} . \tag{2.45}$$

If we equate Eqs. (2.42) and (2.45), we obtain $A_\mathrm{D} = 2\pi^{D/2}/(D\Gamma(D/2))$.

Using the above results we find that, for an ideal gas with $D = 3N$ degrees of freedom, the total volume of phase space with energy equal to or less than energy E is

$$\Omega^{(D)}(E) = V^N \Omega_p^{(D)}(E) = V^N A_\mathrm{D}(R^2)^{D/2} = \frac{V^N(2\pi mE)^{3N/2}}{(3N/2)!} , \tag{2.46}$$

where we have assumed that $3N$ is an even integer and the Gamma function can be written $\Gamma(n+1) = n!$.

We now can determine the multiplicity $\mathcal{N}_N(E)$ of the microstates of the ideal gas with energy less than or equal to E. We divide the phase space volume $\Omega^{(D)}(E)$ by the volume h^{3N} of a single quantum state of the N particle gas. Since the particles are indistinguishable, we must also divide by $N!$ to avoid over counting states. We then obtain

$$\mathcal{N}_N(E) = \frac{V^N(2\pi mE)^{3N/2}}{N!h^{3N}(3N/2)!} . \tag{2.47}$$

As we shall see later, the factor $N!$ is essential to obtain the correct equation of state for an ideal classical gas of indistinguishable particles.

2.8.2
Entropy of an Ideal Gas

The entropy of an ideal gas is determined by the number of microscopic states with energy E and not the number of microscopic states with energy less than or equal to E, which was obtained in Eq. (2.47). However, as we will now show, in the limit $N \to \infty$, these two numbers give values of the entropy that are the same, to good approximation. Let us first divide phase space into a sequence of energy shells, each of width ΔE. The phase space volume of the shell at energy E is $\Omega_{\Delta E}(E)$. We can then write a sequence of inequalities between the sizes of these various volumes such that

$$\Omega_{\Delta E}(E) < \Omega^{(D)}(E) < (E/\Delta E)\Omega_{\Delta E}(E) . \tag{2.48}$$

Next note that $\ln(\Omega_{\Delta E}(E)) \sim D$, $\ln(\Omega^{(D)}(E)) \sim D$ and $\ln E \sim \ln D$. Therefore, for a very large number of degrees of freedom (10^{23}), we can assume that $\ln(\Omega_{\Delta E}(E)) \approx \ln(\Omega^{(D)}(E))$ and the multiplicity $\mathcal{N}_N(E)$, derived in Eq. (2.47), can be used to obtain the entropy of an ideal gas.

The entropy of an ideal gas can now be written

$$S = k_\mathrm{B} \ln(\mathcal{N}_N(E)) = k_\mathrm{B} \ln\left[\frac{V^N(2\pi mE)^{3N/2}}{N!h^{3N}(3N/2)!}\right] . \tag{2.49}$$

This formula can be simplified if we use Stirling's approximation. Then the entropy takes the form

$$S = \frac{5}{2} N k_\mathrm{B} + N k_\mathrm{B} \ln \left[\frac{V}{N} \left(\frac{4\pi m E}{3h^2 N} \right)^{3/2} \right] . \tag{2.50}$$

Equation (2.50) is called the Sackur–Tetrode equation and gives the entropy of an ideal gas of indistinguishable particles.

We can obtain a relation between the energy and temperature of an ideal gas from the Sackur–Tetrode equation using the thermodynamic equation

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_{V,N} = \frac{3}{2} \frac{N k_\mathrm{B}}{E} , \tag{2.51}$$

where the last term was obtained by taking the derivative of Eq. (2.50). Therefore, $E = (3/2) N k_\mathrm{B} T$. The pressure of the ideal gas can be obtained from the entropy using another thermodynamic relation

$$\frac{P}{T} = \left(\frac{\partial S}{\partial V} \right)_{E,N} = \frac{N k_\mathrm{B}}{V} , \tag{2.52}$$

where, again, the last term was obtained by taking the derivative of Eq. (2.50). Thus, we obtain $PV = N k_\mathrm{B} T$, which is the equation of state of an ideal gas.

2.9
Problems

Problem 2.1 A bus has nine seats facing forward and eight seats facing backward. In how many ways can seven passengers be seated if two refuse to ride facing forward and three refuse to ride facing backward?

Problem 2.2 Find the number of ways in which eight persons can be assigned to two rooms (A and B) if each room must have at least three persons in it.

Problem 2.3 Find the number of permutations of the letters in the word, MONOTONOUS. In how many ways are four O's together? In how many ways are (only) 3 O's together?

Problem 2.4 In how many ways can five red balls, four blue balls, and four white balls be placed in a row so that the balls at the ends of the row are the same color?

Problem 2.5 Various six digit numbers can be formed by permuting the digits 666655. All arrangements are equally likely. Given that a number is even, what is the probability that two fives are together?

Problem 2.6 Fifteen boys go hiking. Five get lost, eight get sunburned, and six return home without problems. (a) What is the probability that a sunburned boy got lost? (b) What is the probability that a lost boy got sunburned?

Problem 2.7 A deck of cards contains 52 cards, divided equally among four suits, Spades (S), Clubs (C), Diamonds (D), and Hearts (H). Each suit has 13 cards which are designated: (2, 3, 4, 5, 6, 7, 8, 9, 10, J, Q, K, A). Assume that the deck is always well shuffled so it is equally likely to receive any card in the deck, when a card is dealt. (a) If a dealt hand consists of five cards, how many different hands can one be dealt (assume the cards in the hand can be received in any order)? (b) If the game is poker, what is the probability of being dealt a Royal Flush (10, J, Q, K, and A all of one suit)? (c) If one is dealt a hand with seven cards, and the first four cards are spades, what is the probability of receiving at least one additional spade?

Problem 2.8 A fair six-sided die is thrown N times and the result of each throw is recorded. (a) If the die is thrown $N = 12$ times, what is the probability that odd numbers occur three times? If it is thrown $N = 120$ times, what is the probability that odd numbers occur 30 times? Use the binomial distribution. (b) Compute the same quantities as in part (a) but use the Gaussian distribution. (*Note*: For part (a) compute your answers to four places.) (c) Plot the binomial and Gaussian distributions for $N = 2$ and $N = 12$.

Problem 2.9 A gas of N identical particles is free to move among M distinguishable lattice sites on a lattice with volume V, such that each lattice site can have at most one particle at any time. The density of lattice sites is $\mu = M/V$. Assume that $N \ll M$ and that all configurations of the lattice have the same energy. (a) Compute the entropy of the gas. (b) Find the equation of state of the gas. (*Note*: the pressure of an ideal gas is an example of an entropic force.)

Problem 2.10 An Einstein solid (in 3D space) has 100 lattice sites and 300 phonons, each with energy $\hbar\omega = 0.01$ eV. (a) What is the entropy of the solid (give a number)? (b) What is the temperature of the solid (give a number)?

Problem 2.11 A system consists of N noninteracting, distinguishable two-level atoms. Each atom can exist in one of two energy states, $E_0 = 0$ or $E_1 = \varepsilon$. The number of atoms in energy level, E_0, is n_0 and the number of atoms in energy level, E_1, is n_1. The internal energy of this system is $U = n_0E_0 + n_1E_1$. (a) Compute the multiplicity of microscopic states. (b) Compute the entropy of this system as a function of internal energy. (c) Compute the temperature of this system. Under what conditions can it be negative? (d) Compute the heat capacity for a fixed number of atoms, N.

Problem 2.12 A lattice contains N normal lattice sites and N interstitial lattice sites. The lattice sites are all distinguishable. N identical atoms sit on the lattice, M on the interstitial sites, and $N - M$ on the normal sites ($N \gg M \gg 1$). If an atom occupies a normal site, it has energy $E = 0$. If an atom occupies an interstitial site, it has energy $E = \varepsilon$. Compute the internal energy and heat capacity as a function of temperature for this lattice.

Problem 2.13 Consider a lattice with N spin-1 atoms with magnetic moment μ. Each atom can be in one of three spin states, $S_z = -1, 0, +1$. Let n_{-1}, n_0, and n_1 denote the respective number of atoms in each of those spin states. Find the total entropy and the configuration which maximizes the total entropy. What is the maximum entropy? (Assume that no magnetic field is present, so all atoms have the same energy. Also assume that atoms on different lattice sites cannot be exchanged, so they are distinguishable.)

Problem 2.14 A system consists of $N = 3$ particles, distributed among four energy levels, with energies $E_0 = 0$, $E_1 = 1$, $E_2 = 2$, and $E_3 = 3$. Assume that the total energy of the system is $E = 5$. Answer questions (a), (b), and (c) below for the following two cases: (I) The N particles and the four energy levels are distinguishable; and (II) the N particles are indistinguishable, but levels with different energy are distinguishable. (a) Compute the multiplicity of microstates. (b) What is the probability of finding two particles occupying energy levels E_2? (c) Given that one particle occupies energy level E_3, what is the probability that one particle occupies energy level E_2?

3
Thermodynamics

3.1
Introduction

The science of thermodynamics began with the observation that matter in the aggregate can exist in macroscopic states which are stable and do not change in time. Once a system reaches its equilibrium state, the system will remain forever in that state unless some external influence acts to change it. This inherent stability and reproducibility of the equilibrium states can be seen everywhere in the world around us.

Thermodynamics has been able to describe, with remarkable accuracy, the macroscopic behavior of a huge variety of systems over the entire range of experimentally accessible temperatures (10^{-9} to 10^6 K). It provides a truly universal theory of matter in the aggregate. And yet, the entire subject is based on only four laws [183, 220], which may be stated rather simply as follows:

Zeroth Law	*Two bodies, each in equilibrium with a third body, are in equilibrium with each other.*
First Law	*Energy is conserved.*
Second Law	*Heat flows spontaneously from high temperature to low temperature.*
Third Law	*It is not possible to reach the coldest temperature using a finite set of reversible steps.*

Even though these laws sound rather simple, their implications are vast and give us important tools for studying the behavior and stability of systems in equilibrium and, in some cases, of systems far from equilibrium.

The state of thermodynamic equilibrium can be specified completely in terms of a few parameters – called *state variables*. State variables emerge from the conservation laws governing the underlying dynamics of these systems. State variables may be either *extensive* or *intensive*. Extensive variables always change in value when the size (spatial extent and number of degrees of freedom) of the system is changed, and intensive variables do not.

Certain pairs of intensive and extensive state variables occur together because they correspond to generalized forces and displacements which appear in expres-

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sions for thermodynamic work. Examples of such extensive and intensive pairs include, respectively, volume, V, and pressure, P; magnetization, $\boldsymbol{M}$, and magnetic field, $\boldsymbol{H}$; length, L, and tension, J; area, A, and surface tension, σ; electric polarization, $\boldsymbol{P}$, and electric field, $\boldsymbol{E}$. The relation of these state variables to underlying conservation laws is direct in some cases. For example, the existence of magnetization is related to the conservation of the internal angular momentum of atoms and electric polarization is related to the conservation of electric charge.

The pair of state variables related to heat content of a thermodynamic system are the temperature, T, which is intensive, and the entropy, S, which is extensive. There is also a pair of state variables associated with "chemical" properties of a system. They are the number of particles N (number of moles $\mathfrak{n}$) which is extensive, and the chemical potential per particle (per mole), μ, which is intensive. If there is more than one type of particle in the system, then there will be a particle number or mole number and chemical potential associated with each type of particle.

Other state variables used to describe the thermodynamic behavior of a system are the various response functions, such as heat capacity, C; compressibility, κ; magnetic susceptibility, χ; and various thermodynamic potentials, such as the internal energy, U; enthalpy, H; Helmholtz free energy, A; Gibbs free energy, G; and the grand potential, Ω. We shall become acquainted with these state variables in subsequent sections.

If we change the thermodynamic state of our system, the amount by which the state variables change must be independent of the path taken. If this were not so, the state variables would contain information about the history of the system. It is precisely this property of state variables which makes them so useful in studying changes in the equilibrium state of various systems. *Mathematically, changes in state variables correspond to exact differentials.* The mathematics of exact differentials is reviewed in Appendix B.

It is useful to distinguish between three types of thermodynamic systems. An *isolated system* is one which is surrounded by an insulating wall, so that no heat or matter can be exchanged with the surrounding medium. A *closed system* is one which is surrounded by a conducting wall that allows heat to be exchanged with the surrounding medium, but not matter. An *open system* is one which allows both heat and matter exchange with the surrounding medium. If the insulating/conducting wall can move, then mechanical work can be exchanged with the surrounding medium.

It is possible to change from one equilibrium state to another. Such changes can occur reversibly or irreversibly. A reversible change is one for which the system always remains infinitesimally close to the thermodynamic equilibrium – that is, is performed quasi-statically. Such changes can always be reversed and the system brought back to its original thermodynamic state without causing any changes in the thermodynamic state of the universe. For each step of a reversible process, the state variables have a well-defined meaning.

An irreversible or spontaneous change from one equilibrium state to another is one in which the system does not stay infinitesimally close to equilibrium during each step. Such changes often occur rapidly and give rise to flows and "friction" effects. After an irreversible change the system cannot be brought back to its original thermodynamic state without causing a change in the thermodynamic state of the universe.

3.2
Energy Conservation

There is a store of energy in a thermodynamic system, called the internal energy U. Infinitesimal changes $\mathrm{d}U$ in internal energy content can occur by causing the system to do mechanical work, $đW$ or by adding heat, $đQ$, to the system. The internal energy can also be changed by adding particles of types $j = 1, 2, \ldots, \nu$ to the system causing infinitesimal changes in the internal energy equal to $\sum_{j=1}^{\nu} \mu_j \, \mathrm{d}N_j$, where μ_j is the chemical potential of particles of type j and $\mathrm{d}N_j$ is the infinitesimal change in the number of type j particles. We use the notation, $đW$, to indicate that the differential $đW$ is not exact (see Appendix B). The quantities $đQ$ and $đW$ are not exact differentials because they depend on the path taken (on the way in which heat is added or work is done). The quantities $\mathrm{d}N_j$ are exact differentials.

The change in the internal energy that results from these thermal, mechanical, and chemical processes is given by

$$\mathrm{d}U = đQ - đW + \sum_{j=1}^{\nu} \mu_j \, \mathrm{d}N_j \,. \tag{3.1}$$

The work, $đW$, may be due to changes in any relevant extensive "mechanical" variable. In general it can be written

$$đW = P \, \mathrm{d}V - J \, \mathrm{d}L - \sigma \, \mathrm{d}A - \boldsymbol{E} \cdot \mathrm{d}\boldsymbol{P} - \boldsymbol{H} \cdot \mathrm{d}\boldsymbol{M} - \phi \, \mathrm{d}e \,, \tag{3.2}$$

where $\mathrm{d}U$, $\mathrm{d}V$, $\mathrm{d}L$, $\mathrm{d}A$, $\mathrm{d}\boldsymbol{P}$, $\mathrm{d}\boldsymbol{M}$, and $\mathrm{d}e$ are exact differentials. The magnetization $\boldsymbol{M}$ and the magnetic field $\boldsymbol{H}$ are related to the magnetic flux density $\boldsymbol{B}$ by the equation $\boldsymbol{B} = \mu_0 \boldsymbol{H} + \boldsymbol{M}$, where μ_0 is the permeability of free space. The definition of the first five terms in Eq. (3.2) was discussed in Section 3.1. The term, $-\phi \, \mathrm{d}e$, is the work the system does if it has an electric potential, ϕ, and increases its charge by an amount, $\mathrm{d}e$. We may think of $-P$, J, σ, $\boldsymbol{E}$, $\boldsymbol{H}$ and ϕ as generalized forces, and we may think of $\mathrm{d}V$, $\mathrm{d}L$, $\mathrm{d}A$, $\mathrm{d}\boldsymbol{P}$, $\mathrm{d}\boldsymbol{M}$, and $\mathrm{d}e$ as generalized displacements.

It is useful to introduce a generalized mechanical force, Y, which denotes quantities such as, $-P$, J, σ, $\boldsymbol{E}$, $\boldsymbol{H}$, and ϕ, and a generalized displacement, X, which denotes the corresponding displacements, V, L, A, $\boldsymbol{P}$, $\boldsymbol{M}$, and e, respectively. Then $đW = -Y \, \mathrm{d}X$ and the first law of thermodynamics can be written in the form

$$\mathrm{d}U = đQ + Y \, \mathrm{d}X + \sum_{j=1}^{\nu} \mu_j \, \mathrm{d}N_j \,. \tag{3.3}$$

Note that μ_j is a chemical force and dN_j is a chemical displacement. Note also that the pressure, P, has a different sign from the other generalized forces. If we increase the pressure, the volume increases, whereas if we increase the force, Y, for all other cases, the extensive variable, X, decreases.

3.3
Entropy

The second law of thermodynamics is of immense importance for many reasons [24, 47, 183]. We can use it to compute the maximum possible efficiency of an engine that transforms heat into work. It also enables us to introduce a new state variable, the entropy S, which is conjugate to the temperature. The entropy gives us a measure of the degree of thermal disorder in a system and also gives us a means for determining the stability of equilibrium states. In addition, it provides an important link between reversible and irreversible processes.

3.3.1
Carnot Engine

The second law is most easily discussed in terms of a universal heat engine first introduced by Carnot. The construction of all heat engines is based on the observation that, if heat is allowed to flow from a high temperature to a lower temperature, part of the heat can be turned into work. Carnot observed that temperature differences can disappear spontaneously without producing work. Therefore, the most efficient heat engines must be those whose cycles consist only of reversible steps, thereby eliminating wasteful heat flows. There are many ways to construct reversible heat engines, and they generally have different levels of efficiency. However, Carnot found the most efficient of all possible heat engines.

The Carnot heat engine is universal because, not only is it the most efficient of all heat engines, but *the efficiency of the Carnot engine is independent of the materials used to run it.* The Carnot engine consists of the four steps shown in Figure 3.1. These include:

1. Isothermal (constant temperature) absorption of heat ΔQ_{12} from a reservoir at a high temperature T_h (we use Δ to indicate a finite rather than an infinitesimal amount of heat) (the process 1 → 2).
2. Adiabatic (constant heat content) change in temperature from T_h to the lower value T_c (the process 2 → 3).
3. Isothermal expulsion of heat ΔQ_{43} into a reservoir at temperature T_c (the process 3 → 4).
4. Adiabatic return of the state at temperature T_c to the state at temperature T_h (the process 4 → 1).

The work done by the engine during one complete cycle can be found by integrating the differential element of work $Y\,dX$ about the entire cycle and, there-

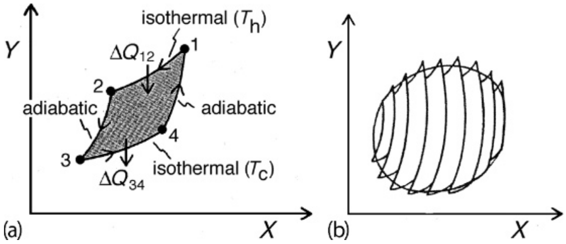


Figure 3.1 (a) A Carnot engine which runs on a substance with state variables, X and Y. The heat absorbed is ΔQ_{12} and the heat ejected is ΔQ_{43}. The shaded area is equal to the work done during the cycle. The whole process takes place reversibly. (b) An arbitrary reversible heat engine is composed of many infinitesimal Carnot engines. The area enclosed by the curve is equal to the work done by the heat engine.

fore, the net work ΔW_{tot} done by the engine is given by the shaded area in Figure 3.1a.

The efficiency η of any heat engine is given by the ratio of the net work done ΔW_{tot} to heat absorbed ΔQ_{abs} so, in general, the efficiency of a heat engine is given by $\eta = (\Delta W_{\text{tot}})/(\Delta Q_{\text{abs}})$.

For the Carnot engine, heat is only absorbed during the process 1 → 2, so the efficiency of the Carnot engine (CE) can be written

$$\eta_{\text{CE}} = \frac{\Delta W_{\text{tot}}}{\Delta Q_{12}} . \tag{3.4}$$

The internal energy U is a state variable and, therefore, the total change ΔU_{tot} for one complete cycle of the engine must be zero because completion of the cycle returns the system to the thermodynamic state it started in. The first law then enables us to write

$$\Delta U_{\text{tot}} = \Delta Q_{\text{tot}} - \Delta W_{\text{tot}} = 0 \tag{3.5}$$

and thus

$$\Delta W_{\text{tot}} = \Delta Q_{\text{tot}} = \Delta Q_{12} + \Delta Q_{34} = \Delta Q_{12} - \Delta Q_{43} . \tag{3.6}$$

If we combine Eqs. (3.4) and (3.6), we can write the efficiency of the Carnot engine in the form

$$\eta_{\text{CE}} = 1 - \frac{\Delta Q_{43}}{\Delta Q_{12}} . \tag{3.7}$$

A 100% efficient engine is one which converts all the heat it absorbs into work. However, as we shall see, no such engine can exist in nature because real engines do not operate in a completely reversible manner.

Carnot engines can operate using any of a variety of substances (examples are left as problems). In Exercise 3.1, we compute the efficiency of a Carnot engine which uses an ideal gas as an operating substance. However, regardless of the operating substance, all Carnot engines have the same efficiency.

The Kelvin temperature scale T was introduced by W. Thomson (Lord Kelvin) and is a universal temperature scale because it is based on the universality of the Carnot engine. It is defined as

$$\frac{\Delta Q_{43}}{\Delta Q_{12}} = \frac{T_c}{T_h}\,, \tag{3.8}$$

where T_h (T_c) is the hottest (coldest) temperature reached by the Carnot engine. The units of degree Kelvin (K) are the same as degree Celsius (°C). The ice point and boiling points of water, at one atmosphere pressure are defined to be 0 °C and 100 °C, respectively. The triple point of water is 0.01 °C and occurs at a pressure of 611.73 Pa. The relation between degree Celsius, t_c, and degree Kelvin, T, is $T = (t_c + 273.15)$. The triple point of water is fixed at $T = 273.16\,\text{K}$.

We can use the Carnot engine to define a new state variable called the *entropy*. All Carnot engines have an efficiency

$$\eta_{\text{CE}} = 1 - \frac{\Delta Q_{43}}{\Delta Q_{12}} = 1 - \frac{T_c}{T_h} \tag{3.9}$$

regardless of operating substance. Using Eq. (3.9), we can write the following relation for a Carnot cycle:

$$\frac{\Delta Q_{12}}{T_h} + \frac{\Delta Q_{34}}{T_c} = 0 \tag{3.10}$$

(note that $\Delta Q_{34} = -\Delta Q_{43}$).

Equation (3.10) can be generalized to the case of an arbitrary *reversible* heat engine because we can consider such an engine as being composed of a sum of many infinitesimal Carnot cycles (cf. Figure 3.1b). For an arbitrary reversible heat engine we have

$$\oint \frac{đQ}{T} = 0\,, \tag{3.11}$$

and, therefore,

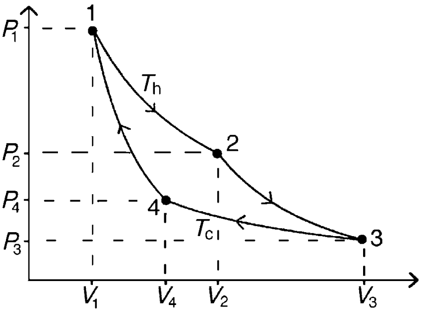
$$\mathrm{d}S \equiv \frac{đQ}{T} \tag{3.12}$$

is an exact differential. The quantity S, is called the *entropy* and is a state variable because the integral of $\mathrm{d}S$ about a closed path gives zero.

Exercise 3.1

Compute the efficiency of a Carnot cycle which uses a monatomic ideal gas as an operating substance. Use the equation of state of a monatomic ideal gas $PV = \mathfrak{n}RT$ and the internal energy $U = (3/2)\mathfrak{n}RT$.

Answer: The Carnot cycle for an ideal gas is shown in the figure below.



(a) Let us first consider the *isothermal paths* 1 → 2 and 3 → 4. Since the temperature is constant along these paths, $\mathrm{d}T = 0$ and $\mathrm{d}U = (3/2)nR\,\mathrm{d}T = 0$. Thus, along the path 1 → 2, $đQ = đW = nRT_\mathrm{h}(\mathrm{d}V/V)$. The heat absorbed/ejected along the paths 1 → 2 and 3 → 4 are

$$\Delta Q_{12} = nRT_\mathrm{h}\int_{V_1}^{V_2}\frac{\mathrm{d}V}{V} = nRT_\mathrm{h}\ln\left(\frac{V_2}{V_1}\right) \quad \text{and} \quad \Delta Q_{34} = nRT_\mathrm{c}\ln\left(\frac{V_4}{V_3}\right),$$

respectively. Since $V_2 > V_1$, $\Delta Q_{12} > 0$ and heat is absorbed along the path 1 → 2. Since $V_3 > V_4$, $\Delta Q_{34} < 0$ and heat is ejected along the path 3 → 4.

(b) Let us next consider the *adiabatic paths* 2 → 3 and 4 → 1. Along the adiabatic path, $đQ = 0 = \mathrm{d}U + P\,\mathrm{d}V = (3/2)nR\,\mathrm{d}T + P\,\mathrm{d}V$. If we make use of the equation of state, we find $(3/2)\,\mathrm{d}T/T = -\mathrm{d}V/V$. We now integrate to find $T^{3/2}V$ = constant for an adiabatic process. Thus, along the paths 2 → 3 and 4 → 1, respectively, we have $T_\mathrm{c}V_3^{2/3} = T_\mathrm{h}V_2^{2/3}$ and $T_\mathrm{c}V_4^{2/3} = T_\mathrm{h}V_1^{2/3}$ which gives $V_3/V_4 = V_2/V_1$. Because U is a state variable, for the entire cycle we can write $\Delta U_\mathrm{tot} = \Delta Q_\mathrm{tot} - \Delta W_\mathrm{tot} = 0$. Thus $\Delta W_\mathrm{tot} = \Delta Q_\mathrm{tot} = \Delta Q_{12} + \Delta Q_{34}$. The efficiency of the Carnot cycle is

$$\eta = \frac{\Delta W_\mathrm{tot}}{\Delta Q_{12}} = 1 + \frac{\Delta Q_{34}}{\Delta Q_{12}} = 1 - \frac{T_\mathrm{c}}{T_\mathrm{h}}\frac{\ln(V_3/V_4)}{\ln(V_2/V_1)} = 1 - \frac{T_\mathrm{c}}{T_\mathrm{h}}\,.$$

No heat engine, operating between the same high and low temperatures, can be more efficient than a Carnot engine. Thus, an engine which runs between the same two reservoirs but contains spontaneous or irreversible processes in some part of the cycle will have a lower efficiency. Therefore, for an irreversible heat engine we can write

$$\frac{\Delta Q_{43}}{\Delta Q_{12}} > \frac{T_\mathrm{c}}{T_\mathrm{h}} \quad \text{and} \quad \frac{\Delta Q_{12}}{T_\mathrm{h}} - \frac{\Delta Q_{43}}{T_\mathrm{c}} < 0\,. \tag{3.13}$$

For an arbitrary heat engine which contains an irreversible part, Eq. (3.13) gives the very important relation

$$\oint \frac{đQ}{T} < 0 \ : \tag{3.14}$$

For an irreversible process, $đQ/T$ can no longer be considered an exact differential.

A system may evolve between two thermodynamic states either by a reversible path or by a spontaneous, irreversible path. For any process, reversible or irreversible, the entropy change depends only on the initial and final thermodynamic equilibrium states of the system, since the entropy is a state variable. If the system evolves between the initial and final states via a reversible path, we can compute the entropy change along that path using thermodynamic relations. However, if the system evolves via an irreversible path, then we must construct a hypothetical reversible path between the initial and final states in order to use the equations of thermodynamics to compute the entropy change during the spontaneous process.

For an irreversible path between two thermodynamic states, the heat absorbed by the system will be less than the heat absorbed along a reversible path between the same two thermodynamic states. Therefore, $\int_{\mathrm{irrev}} đQ/T < \int_{\mathrm{rev}} đQ/T$. This means that *for an irreversible process,* $\int_{\mathrm{irrev}} đQ/T$ *does not contain all contributions to the entropy change.* Some of it comes from the disorder created by spontaneity. This result is usually written in the form

$$\mathrm{d}S = \frac{đQ}{T} + \mathrm{d}_i S \,, \tag{3.15}$$

where $\mathrm{d}_i S$ denotes the *entropy production* due to spontaneous processes. For a reversible process, $\mathrm{d}_i S = 0$ so the entropy change is entirely due to a flow of heat into or out of the system. For a spontaneous (irreversible) process, $\mathrm{d}_i S > 0$.

For an isolated system we have $đQ = 0$, and we obtain the important relation

$$\mathrm{d}S = \mathrm{d}_i S \geq 0 \,, \tag{3.16}$$

where the equality holds for a reversible process and the inequality holds for a spontaneous or irreversible process. Since the equilibrium state is, by definition, a state which is stable against spontaneous changes, Eq. (3.16) tells us that, for an isolated system, *the equilibrium state is a state of maximum entropy.* As we shall see, this fact gives an important criterion for determining the stability of the equilibrium state for an isolated system.

3.3.2
The Third Law

An alternative statement of the third law – *It is impossible to reach absolute zero in a finite number of steps if a reversible process is used* – is easily demonstrated by means of a plot in the S–T plane [24, 47, 196]. In Figure 3.2 we have plotted S

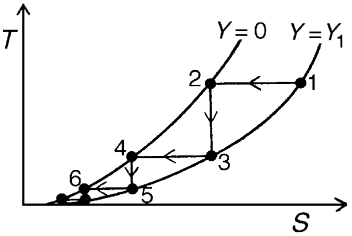


Figure 3.2 The fact that curves $Y = 0$ and $Y = Y_1$ must approach the same point (the third law) makes it impossible to reach absolute zero by a finite number of reversible steps.

versus T for two states whose generalized forces have values $Y = 0$ and $Y = Y_1$. (A specific example might be a paramagnetic salt with $Y = H$.) We can cool the system by alternating between the two states, adiabatically and isothermally. From the identities in Appendix B, we write

$$\left(\frac{\partial T}{\partial Y}\right)_{S,N} = -\left(\frac{\partial T}{\partial S}\right)_{Y,N}\left(\frac{\partial S}{\partial Y}\right)_{T,N} . \tag{3.17}$$

As we shall show in Section 3.7, thermal stability requires that $C_{Y,N}/T = (\partial S/\partial T)_Y \geq 0$. Equation (3.17) tells us that if T decreases as Y increases adiabatically, then S must decrease as Y decreases isothermally, as shown in Figure 3.2. For the process $1 \to 2$ we change from state $Y = Y_1$ to state $Y = 0$ isothermally, thus squeezing out heat, and the entropy decreases. For process $2 \to 3$, we increase Y adiabatically from $Y = 0$ to $Y = Y_1$ and thus decrease the temperature. We can repeat these processes as many times as we wish. However, as we approach $T = 0\,\mathrm{K}$, we know by the third law that the two curves must approach the same point and must therefore begin to approach each other, thus making it impossible to reach $T = 0\,\mathrm{K}$ in a finite number of steps.

Another consequence of the third law is that certain derivatives of the entropy must approach zero as $T \to 0\,\mathrm{K}$. Let us consider a process at $T = 0\,\mathrm{K}$ such that $Y \to Y + \mathrm{d}Y$ and $X \to X + \mathrm{d}X$. Then the change in entropy if Y, T, and N are chosen as independent variables is (assume $\mathrm{d}N = 0$) $\mathrm{d}S = (\partial S/\partial Y)_{N,T=0}\,\mathrm{d}Y$ or if X, T, and N are chosen as independent we obtain $\mathrm{d}S = (\partial S/\partial X)_{N,T=0}\,\mathrm{d}X$. Thus, if the states $(Y, T = 0\,\mathrm{K})$ and $(Y + \mathrm{d}Y, T = 0\,\mathrm{K})$ or the states $(X, T = 0\,\mathrm{K})$ and $(X + \mathrm{d}X, T = 0\,\mathrm{K})$ are connected by a reversible process, we must have $\mathrm{d}S = 0$ (third law) and therefore

$$\left(\frac{\partial S}{\partial Y}\right)_{N,T=0} = 0 \quad \text{and} \quad \left(\frac{\partial S}{\partial X}\right)_{N,T=0} = 0 . \tag{3.18}$$

Equation (3.18) appears to be satisfied by real substances.

3.4
Fundamental Equation of Thermodynamics

The entropy plays a central role in both equilibrium and nonequilibrium thermodynamics. It can be thought of as a measure of the disorder in a system. As we have seen in Chapter 2, entropy is obtained microscopically by state counting.

The entropy of an isolated system is proportional to the logarithm of the number of microscopic states available to the system.

From Eqs. (3.3) and (3.12), the entropy must be an extensive, additive quantity since $\mathrm{d}U$ has that property and T is intensive. If a system is composed of a number of independent subsystems, then the entropy of the whole system will be the sum of the entropies of the subsystems. This additive property of the entropy is expressed mathematically by the relation

$$S(\lambda U, \lambda X, \{\lambda N_i\}) = \lambda S(U, X, \{N_i\}) . \tag{3.19}$$

That is, the entropy is a first-order homogeneous function of the extensive state variables of the system. If we increase *all* the extensive state variables by a factor λ, then the entropy must also increase by a factor λ. It is easy to check that the Sackur–Tetrode equation in Eq. (2.50) (the entropy of an ideal gas) has this property.

Differential changes in the entropy are related to differential changes in the extensive state variables through *the combined first and second laws of thermodynamics*:

$$T\,\mathrm{d}S \geq đQ = \mathrm{d}U - Y\,\mathrm{d}X - \sum_{j=1}^{\nu} \mu_j\,\mathrm{d}N_j . \tag{3.20}$$

The equality (inequality) holds if changes in the thermodynamic state are reversible (irreversible). Equations (3.19) and (3.20) now enable us to define the *Fundamental Equation* of thermodynamics. Let us take the derivative of λS with respect to λ:

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}\lambda}(\lambda S) = {}& \left(\frac{\partial S}{\partial \lambda U}\right)_{X,\{N_j\}} \frac{\mathrm{d}}{\mathrm{d}\lambda}(\lambda U) + \left(\frac{\partial S}{\partial \lambda X}\right)_{U,\{N_j\}} \frac{\mathrm{d}}{\mathrm{d}\lambda}(\lambda X) \\ & + \sum_{j=1}^{\nu} \left(\frac{\partial S}{\partial \lambda N_j}\right)_{U,X,\{N_{i\neq j}\}} \frac{\mathrm{d}(\lambda N_j)}{\mathrm{d}\lambda} .\end{aligned} \tag{3.21}$$

However, from (3.20) we see that

$$\left(\frac{\partial S}{\partial U}\right)_{X,\{N_j\}} = \frac{1}{T} , \quad \left(\frac{\partial S}{\partial X}\right)_{U,\{N_j\}} = -\frac{Y}{T} , \quad \left(\frac{\partial S}{\partial N_j}\right)_{U,X,\{N_{i\neq j}\}} = -\frac{\mu_j}{T} . \tag{3.22}$$

The first, second, and third relations in Eq. (3.22) are called the thermal, mechanical, and chemical *equations of state*, respectively. If we now combine Eqs. (3.21) and (3.22), we obtain

$$TS = U - XY - \sum_{j=1}^{\nu} \mu_j N_j . \tag{3.23}$$

Equation (3.23) is called the *Fundamental Equation of thermodynamics* (it is also known as *Euler's equation*).

If we take the differential of Eq. (3.23) and subtract Eq. (3.20) (we will take the reversible case), we obtain another important equation,

$$S\,\mathrm{d}T + X\,\mathrm{d}Y + \sum_{j=1}^{\nu} N_j\,\mathrm{d}\mu_j = 0\,, \tag{3.24}$$

which is called the *Gibbs–Duhem* equation. The Gibbs–Duhem equation relates differentials of intensive state variables.

For a monatomic system ($\nu = 1$), these equations simplify if we work with densities. Let us work with molar densities. For a single component system, the Fundamental Equation can be written $TS = U - YX - \mu\mathfrak{n}$ and the combined first and second laws (for reversible processes) can be written $T\,\mathrm{d}S = \mathrm{d}U - Y\,\mathrm{d}X - \mu\,\mathrm{d}\mathfrak{n}$. Let us now introduce the molar entropy, $s = S/\mathfrak{n}$, the molar density, $x = X/\mathfrak{n}$, and the molar internal energy, $u = U/\mathfrak{n}$. Then the Gibbs–Duhem equation takes the form $\mathrm{d}\mu = -s\,\mathrm{d}T - x\,\mathrm{d}Y$ and, therefore, the chemical potential is a function only of intensive variables $\mu = \mu(T, Y)$. The fundamental equation is $Ts = u - Yx - \mu$ and the combined first and second laws become (for reversible processes) $T\,\mathrm{d}s = \mathrm{d}u - Y\,\mathrm{d}x$. Thus, $(\partial s/\partial u)_x = 1/T$ and $(\partial s/\partial x)_u = -Y/T$.

Exercise 3.2

The entropy of $\mathfrak{n}$ moles of a monatomic ideal gas is given by the Sackur–Tetrode equation in Eq. (2.50). The mechanical equation of state is $PV = \mathfrak{n}RT$ and the internal energy is $U = (3/2)\mathfrak{n}RT$. Compute the chemical potential of the ideal gas.

Answer: Starting from Eq. (2.50), molar entropy can be written in the form

$$s = \frac{5}{2}R + R\ln\left[\frac{T^{5/2}}{P}\right] + R\ln\left[\left(\frac{2\pi m}{h^2}\right)^{3/2} k_{\mathrm{B}}^{5/2}\right]\,.$$

From the Gibbs–Duhem equation in Eq. (3.24), we have $(\partial\mu/\partial T)_P = -s$ and $(\partial\mu/\partial P)_T = v = RT/P$. If we integrate these we obtain the following expression for the molar chemical potential:

$$\mu = -RT\ln\left[\frac{(k_{\mathrm{B}}T)^{5/2}}{P}\left(\frac{2\pi m}{h^2}\right)^{3/2}\right]\,.$$

Exercise 3.3

Mixing of distinct molecules provides an example of a spontaneous process that leads to entropy increase without heat exchange. Consider an isolated rigid container of volume V which is divided into l compartments of equal volume V/l. The walls of the compartments are massless, rigid, and conduct heat so the temperature T is the same in all compartments. Each compartment contains $\mathfrak{n}$ moles of a different kind of molecule A_j ($j = 1, \dots, l$) and the system is in equilibrium. If the walls of the compartments are suddenly removed and the system is allowed to come back to equilibrium, what is the change in the entropy of the system?

Answer: (a) Initially, the pressure is the same in each compartment and is given by $P_j^{(\mathrm{i})} = \mathfrak{n}RT/(V/l)$. Also, the internal energy is the same in each compartment and is $U_j = (3/2)\mathfrak{n}RT$. The entropy of the initial equilibrium state is the sum of the entropies of the gases in each compartment. Using the Sackur–Tetrode equation, it can be written as

$$S_{\mathrm{initial}} = l\frac{5}{2}\mathfrak{n}R + \sum_{j=1}^{l} \mathfrak{n}R \ln\left[\frac{T^{5/2}}{P_j^{(\mathrm{i})}}\right] + \mathfrak{n}lR \ln\left[\left(\frac{2\pi m}{h^2}\right)^{3/2} k_{\mathrm{B}}^{5/2}\right] .$$

(b) The pressure of the gas of each type of molecule, after the walls are removed, is $P_j^{(\mathrm{f})} = \mathfrak{n}RT/V$, because each type of gas now fills the entire volume V. The internal energy and temperature of the gases don't change because, for an ideal gas, they are independent of volume and the entire system is isolated. The total pressure of the mixed gas is $P = \sum_{j=1}^{l} P_j^{(\mathrm{f})}$ ($P_j^{(\mathrm{f})}$ is called the partial pressure of molecules of type j). The entropy of the mixed gas is

$$S_{\mathrm{final}} = l\frac{5}{2}\mathfrak{n}R + \sum_{j=1}^{l} \mathfrak{n}R \ln\left[\frac{T^{5/2}}{P_j^{(\mathrm{f})}}\right] + \mathfrak{n}lR \ln\left[\left(\frac{2\pi m}{h^2}\right)^{3/2} k_{\mathrm{B}}^{5/2}\right] .$$

The change in the entropy is

$$\Delta S_{\mathrm{mix}} = S_{\mathrm{final}} - S_{\mathrm{initial}} = \sum_{j=1}^{l} \mathfrak{n}R \ln\left[\frac{P_j^{(\mathrm{i})}}{P_j^{(\mathrm{f})}}\right] = \mathfrak{n}lR \ln l .$$

The quantity ΔS_{mix} is called the entropy of mixing. If the particles were all identical, we would not have a summation in the expression for S_{final}, but a single term involving final pressure $P^{(\mathrm{f})} = \mathfrak{n}lRT/V$ and the entropy would not change. This difference in behavior of identical and distinct particles is called the *Gibbs paradox*. The origin of this difference lies in quantum mechanics and the fact that the number of microscopic states available to identical particles is different from the number of microscopic states available to the same number of distinct particles.

3.5
Thermodynamic Potentials

In conservative mechanical systems, such as a spring or a mass raised in a gravitational field, work can be stored in the form of potential energy and subsequently retrieved [24, 145, 183]. *Under certain circumstances* the same is true for thermodynamic systems. We can store energy in a thermodynamic system by doing work on it through a reversible process, and we can eventually retrieve that energy in the form of work. The energy which is stored and retrievable in the form of work is called the *free energy*. There are as many different forms of free energy in a thermodynamic system as there are combinations of constraints. In this section, we shall discuss the five most common ones: internal energy, U; the enthalpy, H; the Helmholtz free energy, A; the Gibbs free energy, G; and the grand potential, Ω. These quantities play a role analogous to that of the potential energy in a spring when their respective dependent variables are held fixed and, for that reason, they are also called the *thermodynamic potentials*.

3.5.1
Internal Energy

The combined first and second laws of thermodynamics (Eq. (3.20)) yield the following expression for the total differential of the internal energy $U(S, X, \{N_j\})$,

$$\mathrm{d}U \leq T\,\mathrm{d}S + Y\,\mathrm{d}X + \sum_{j=1}^{\nu} \mu_j\,\mathrm{d}N_j\,, \tag{3.25}$$

where T, Y, and μ_j are considered to be functions of S, X, and $\{N_j\}$ and can be expressed as partial differentials of the internal energy (see Table 3.1). The equality holds for reversible changes, and the inequality holds for changes which are spontaneous. The internal energy is a thermodynamic potential or free energy because for processes carried out reversibly in an isolated, closed system at fixed S, X and $\{N_j\}$, the change in internal energy is equal to the maximum amount of work that can be done on or by the system.

Table 3.1 The equations for internal energy changes in a closed, isolated system.

Internal energy	$U(S, X, \{N_j\})$
Total Differential	$\mathrm{d}U = T\,\mathrm{d}S + Y\,\mathrm{d}X + \sum_{j=1}^{\nu} \mu_j\,\mathrm{d}N_j$
Fundamental Equation	$U = TS + YX + \sum_{j=1}^{\nu} \mu_j N_j$
Equations of State	$T = \left(\frac{\partial U}{\partial S}\right)_{X,\{N_j\}}$
$Y = \left(\frac{\partial U}{\partial X}\right)_{S,\{N_j\}}$	$\mu_j = \left(\frac{\partial U}{\partial N_j}\right)_{S,X,\{N_{l\neq j}\}}$
Maxwell Relations	
$\left(\frac{\partial T}{\partial X}\right)_{S,\{N_j\}} = \left(\frac{\partial Y}{\partial S}\right)_{X,\{N_j\}}$	$\left(\frac{\partial T}{\partial N_j}\right)_{S,X,\{N_{l\neq j}\}} = \left(\frac{\partial \mu_j}{\partial S}\right)_{X,\{N_j\}}$
$\left(\frac{\partial Y}{\partial N_j}\right)_{S,X,\{N_{l\neq j}\}} = \left(\frac{\partial \mu_j}{\partial X}\right)_{S,\{N_j\}}$	$\left(\frac{\partial \mu_j}{\partial N_i}\right)_{S,X,\{N_{l\neq i}\}} = \left(\frac{\partial \mu_i}{\partial N_j}\right)_{S,X,\{N_{l\neq j}\}}$

For a substance with a single type of particle, the equations in Table 3.1 simplify if we work with densities. Let $u = U/\mathfrak{n}$ denote the molar internal energy. Then the Fundamental Equation can be written $u = Ts + Yx + \mu$, where s is the molar entropy and x is a molar density. The combined first and second laws (for reversible processes) are $\mathrm{d}u = T\,\mathrm{d}s + Y\,\mathrm{d}x$. Therefore, we obtain the identities $T = (\partial u/\partial s)_x$ and $Y = (\partial u/\partial x)_s$, and the Maxwell relations reduce to $(\partial T/\partial x)_s = (\partial Y/\partial s)_x$.

If a process takes place in which no work is done on or by the system, no matter is exchanged with the outside world, and the entropy of the system doesn't change, then Eq. (3.25) becomes

$$(\mathrm{d}U)_{S,X,\{N_j\}} \leq 0 \tag{3.26}$$

and the internal energy either does not change (reversible process) or decreases (spontaneous process). Since a system in equilibrium cannot change its state spontaneously, we see that *an equilibrium state at fixed* S, X, and $\{N_j\}$ *is a state of minimum internal energy.*

3.5.2
Enthalpy

The enthalpy, $H(S, Y, \{N_j\})$, is a thermodynamic potential for systems which are thermally isolated and closed but mechanically coupled to the outside world. It is obtained from the fundamental equation for the internal energy by adding to the internal energy an additional energy $-XY$ due to the mechanical coupling:

$$H \equiv U - XY = ST + \sum_j \mu_j N_j\,. \tag{3.27}$$

The addition of the term $-XY$ has the effect of changing the independent variables from (S, X, N_j) to (S, Y, N_j) and is called a *Legendre transformation*. If we take the differential of Eq. (3.27) and combine it with Eq. (3.25), we obtain the following equation for the exact differential of the enthalpy

$$\mathrm{d}H \leq T\,\mathrm{d}S - X\,\mathrm{d}Y + \sum_j \mu_j\,\mathrm{d}N_j\,. \tag{3.28}$$

The quantities T, X and $\{\mu_j\}$ are functions of S, Y and $\{N_j\}$ and can be expressed in terms of partial derivatives of the enthalpy as shown in Table 3.2.

For a substance with a single type of molecule, the equations in Table 3.2 become particularly simple if we work with densities. Let $h = H/\mathfrak{n}$ denote the molar enthalpy. Then the fundamental equation for the molar enthalpy can be written $h = u - xY = sT + \mu$. The exact differential of the molar enthalpy is $\mathrm{d}h = T\,\mathrm{d}s - x\,\mathrm{d}Y$ (for reversible processes), which yields the identities $T = (\partial h/\partial s)_Y$ and $x = (\partial h/\partial Y)_s$. Maxwell's relations reduce to $(\partial T/\partial Y)_s = -(\partial x/\partial s)_Y$. In Exercise 3.4, we compute the enthalpy for a monatomic ideal gas in terms of its natural variables s and Y.

Table 3.2 The equations for enthalpy changes in a system mechanically coupled to the outside world but closed to thermal and material exchange.

Enthalpy	$\boldsymbol{H(S, Y, \{N_j\})}$
Total Differential	$\mathrm{d}H = T\,\mathrm{d}S - X\,\mathrm{d}Y + \sum_{j=1}^{\nu} \mu_j\,\mathrm{d}N_j$
Fundamental Equation	$H = U - XY = TS + \sum_{j=1}^{\nu} \mu_j N_j$
Equations of State	$T = \left(\frac{\partial H}{\partial S}\right)_{Y,\{N_j\}}$
$X = -\left(\frac{\partial H}{\partial Y}\right)_{S,\{N_j\}}$	$\mu_j = \left(\frac{\partial H}{\partial N_j}\right)_{S,Y,\{N_{l\neq j}\}}$
Maxwell Relations	
$\left(\frac{\partial T}{\partial Y}\right)_{S,\{N_j\}} = -\left(\frac{\partial X}{\partial S}\right)_{Y,\{N_j\}}$	$\left(\frac{\partial T}{\partial N_j}\right)_{S,Y,\{N_{l\neq j}\}} = \left(\frac{\partial \mu_j}{\partial S}\right)_{Y,\{N_j\}}$
$\left(\frac{\partial X}{\partial N_j}\right)_{S,Y,\{N_{l\neq j}\}} = -\left(\frac{\partial \mu_j}{\partial Y}\right)_{S,\{N_j\}}$	$\left(\frac{\partial \mu_j}{\partial N_i}\right)_{S,Y,\{N_{l\neq i}\}} = \left(\frac{\partial \mu_i}{\partial N_j}\right)_{S,Y,\{N_{l\neq j}\}}$

Exercise 3.4

Compute the enthalpy for $\mathfrak{n}$ moles of a monatomic ideal gas and express it in terms of its natural variables. Assume the entropy is given by the Sackur–Tetrode equation $S = (5/2)\mathfrak{n}R + nR\ln[(V/V_0)(\mathfrak{n}_0/\mathfrak{n})(T/T_0)^{3/2}]$ and the mechanical equation of state is $PV = \mathfrak{n}RT$.

Answer: If we combine the Sackur–Tetrode equation and the equation of state, we can write the molar entropy in terms of temperature and pressure so that $s = (5/2)R + R\ln[(P_0/P)(T/T_0)^{5/2}]$. Now since $\mathrm{d}h = T\,\mathrm{d}s + v\,\mathrm{d}P$ we have

$$\left(\frac{\partial h}{\partial P}\right)_s = v = +\frac{RT}{P} \quad \text{and} \quad \left(\frac{\partial h}{\partial s}\right)_P = T = T_0\left(\frac{P}{P_0}\right)^{2/5} \mathrm{e}^{(s-s_0)/s_0} .$$

If we integrate, we find $h = (5/2)RT_0(P/P_0)^{2/5}\mathrm{e}^{(s-s_0)/s_0} = (5/2)RT$. In terms of temperature, the molar enthalpy is $h = (5/2)RT$. Note that there is an easier way to obtain these results. The molar internal energy is $u = (3/2)RT$. The fundamental equation for the molar enthalpy is $h = u + vP$. Since $v = RT/P$, we obtain $h = (5/2)RT$ and $H = (5/2)\mathfrak{n}RT$.

If a process takes place at constant S, Y, and $\{N_j\}$, then

$$(\mathrm{d}H)_{S,Y,\{N_j\}} \leq 0 . \tag{3.29}$$

Since the equilibrium state cannot change spontaneously, we find that *the equilibrium state at fixed S, Y, and* $\{N_j\}$ *is a state of minimum enthalpy.*

3.5.3
Helmholtz Free Energy

For processes carried out at constant T, X, and $\{N_j\}$, the Helmholtz free energy corresponds to a thermodynamic potential. The Helmholtz free energy, A, is useful for systems which are closed and thermally coupled to the outside world but are mechanically isolated (held at constant X). We obtain the Helmholtz free energy from the internal energy by adding a term $-ST$ due to the thermal coupling:

$$A = U - ST = YX + \sum_{j=1}^{\nu} \mu_j N_j \, . \tag{3.30}$$

The addition of $-ST$ is a Legendre transformation which changes the independent variables from $(S, X, \{N_j\})$ to $(T, X, \{N_j\})$. If we take the differential of Eq. (3.30) and use Eq. (3.25), we find

$$\mathrm{d}A \leq -S\,\mathrm{d}T + Y\,\mathrm{d}X + \sum_{j=1}^{\nu} \mu_j\,\mathrm{d}N_j \, . \tag{3.31}$$

The equations of state and the Maxwell relations that result from Eq. (3.31) are given in Table 3.3.

Let us consider a monatomic substance and let $a = A/\mathfrak{n}$ denote the molar Helmholtz free energy. Then the fundamental equation for the molar Helmholtz free energy is $a = u - sT = xY + \mu$, where $u = U/\mathfrak{n}$, $s = S/\mathfrak{n}$ and $x = X/\mathfrak{n}$. The combined first and second laws (for reversible processes) can be written $\mathrm{d}a = -s\,\mathrm{d}T + Y\,\mathrm{d}x$ so that $s = -(\partial a/\partial T)_x$ and $Y = (\partial a/\partial x)_T$. Maxwell's relations re-

Table 3.3 The equations for changes in the Helmholtz free energy in a system thermally coupled to the outside world but closed to mechanical energy and chemical exchange.

Helmholtz free energy	$\boldsymbol{A(T, X, \{N_j\})}$
Total Differential	$\mathrm{d}A = -S\,\mathrm{d}T + Y\,\mathrm{d}X + \sum_{j=1}^{\nu} \mu_j\,\mathrm{d}N_j$
Fundamental Equation	$A = U - ST = XY + \sum_{j=1}^{\nu} \mu_j N_j$
Equations of State	$T = -\left(\frac{\partial A}{\partial T}\right)_{X,\{N_j\}}$
$Y = \left(\frac{\partial A}{\partial X}\right)_{T,\{N_j\}}$	$\mu_j = \left(\frac{\partial A}{\partial N_j}\right)_{T,X,\{N_{l\neq j}\}}$
Maxwell Relations	
$\left(\frac{\partial S}{\partial X}\right)_{T,\{N_j\}} = -\left(\frac{\partial Y}{\partial T}\right)_{X,\{N_j\}}$	$\left(\frac{\partial S}{\partial N_j}\right)_{T,X,\{N_{l\neq j}\}} = -\left(\frac{\partial \mu_j}{\partial T}\right)_{X,\{N_j\}}$
$\left(\frac{\partial Y}{\partial N_j}\right)_{T,X,\{N_{l\neq j}\}} = \left(\frac{\partial \mu_j}{\partial X}\right)_{T,\{N_j\}}$	$\left(\frac{\partial \mu_j}{\partial N_i}\right)_{T,X,\{N_{l\neq i}\}} = \left(\frac{\partial \mu_i}{\partial N_j}\right)_{T,X,\{N_{l\neq j}\}}$

duce to $(\partial s/\partial x)_T = -(\partial Y/\partial T)_x$. In Exercise 3.4, we compute that Helmholtz free energy for a monatomic ideal gas in terms of its natural variables.

If no work is done for a process occurring at fixed T, X, and $\{N_j\}$, Eq. (3.31) becomes

$$(\mathrm{d}A)_{T,X,\{N_j\}} \le 0 \,. \tag{3.32}$$

Thus, *an equilibrium state at fixed T, X, and* $\{N_j\}$ *is a state of minimum Helmholtz free energy.*

Exercise 3.5

Compute the Helmholtz free energy for $\mathfrak{n}$ moles of a monatomic ideal gas and express it in terms of its natural variables. The mechanical equation of state is $PV = \mathfrak{n}RT$ and the Sackur–Tetrode equation for the entropy can be written $S = (5/2)\mathfrak{n}R + \mathfrak{n}R\ln[(V/V_0)(\mathfrak{n}_0/\mathfrak{n})(T/T_0)^{3/2}]$.

Answer: Since $\mathrm{d}a = -s\,\mathrm{d}T - P\,\mathrm{d}v$ we have

$$\left(\frac{\partial a}{\partial T}\right)_v = -s = -\frac{5}{2}R - R\ln\left[\frac{v}{v_0}\left(\frac{T}{T_0}\right)^{3/2}\right]$$

and

$$\left(\frac{\partial a}{\partial v}\right)_T = -P = -\frac{RT}{v} \,.$$

If we integrate, we find $a = -RT - RT\ln\left[(v/v_0)(T/T_0)^{3/2}\right]$ and $A = -\mathfrak{n}RT - \mathfrak{n}RT\ln\left[(V/V_0)\cdot(\mathfrak{n}_0/\mathfrak{n})(T/T_0)^{3/2}\right]$.

3.5.4
Gibbs Free Energy

For processes carried out at constant T, Y and $\{N_j\}$, the Gibbs free energy corresponds to the thermodynamic potential. Such a process is coupled both thermally and mechanically to the outside world. We obtain the Gibbs free energy, $G(T, Y, \{N_j\})$, from the internal energy U by adding terms $-ST$ and $-XY$ due to the thermal and mechanical coupling, respectively,

$$G = U - TS - XY = \sum_{j=1}^{v} \mu_j N_j \,. \tag{3.33}$$

In this way we change from the independent variables $(S, X, \{N_i\})$ for the internal energy to the independent variables $(T, Y, \{N_i\})$ for the Gibbs free energy. If we take the differential of Eq. (3.33) and use Eq. (3.25), we obtain

$$\mathrm{d}G \le -S\,\mathrm{d}T - X\,\mathrm{d}Y + \sum_j \mu_j\,\mathrm{d}N_j \,. \tag{3.34}$$

Table 3.4 The equations for changes in the Gibbs free energy in a system thermally coupled and mechanically coupled to the outside world but closed to chemical exchange.

Gibbs free energy	**$G(T, Y, \{N_j\})$**
Total Differential	$\mathrm{d}G = -S\,\mathrm{d}T - X\,\mathrm{d}Y + \sum_{j=1}^{\nu} \mu_j\,\mathrm{d}N_j$
Fundamental Equation	$G = U - TS - YX = \sum_{j=1}^{\nu} \mu_j N_j$
Equations of State	$S = -\left(\frac{\partial G}{\partial T}\right)_{Y,\{N_j\}}$
$X = -\left(\frac{\partial G}{\partial Y}\right)_{T,\{N_j\}}$	$\mu_j = \left(\frac{\partial G}{\partial N_j}\right)_{T,Y,\{N_{l\neq j}\}}$
Maxwell Relations	
$\left(\frac{\partial S}{\partial Y}\right)_{T,\{N_j\}} = \left(\frac{\partial X}{\partial T}\right)_{Y,\{N_j\}}$	$\left(\frac{\partial S}{\partial N_j}\right)_{T,Y,\{N_{l\neq j}\}} = -\left(\frac{\partial \mu_j}{\partial T}\right)_{Y,\{N_j\}}$
$\left(\frac{\partial X}{\partial N_j}\right)_{T,Y,\{N_{l\neq j}\}} = -\left(\frac{\partial \mu_j}{\partial Y}\right)_{T,\{N_j\}}$	$\left(\frac{\partial \mu_j}{\partial N_i}\right)_{T,Y,\{N_{l\neq i}\}} = \left(\frac{\partial \mu_i}{\partial N_j}\right)_{T,Y,\{N_{l\neq j}\}}$

The equations of state and Maxwell equations for the Gibbs free energy are given in Table 3.4.

Let us consider a monomolecular substance and let $g = G/\mathfrak{n}$ denote the molar Gibbs free energy. Then the fundamental equation for the molar Gibbs free energy is $g = u - sT - xY = \mu$ and the molar Gibbs free energy is equal to the chemical potential (for a monomolecular substance). The combined first and second laws (for reversible processes) can be written $\mathrm{d}g = -s\,\mathrm{d}T - x\,\mathrm{d}Y$ so that $s = -(\partial g/\partial T)_Y$ and $x = -(\partial g/\partial Y)_T$. Maxwell's relations reduce to $(\partial s/\partial Y)_T = +(\partial x/\partial T)_Y$. For a monatomic substance, the molar Gibbs free energy is equal to the chemical potential.

Exercise 3.6

Consider a system which has the capacity to do work, $\text{đ}W = -Y\,\mathrm{d}X + \text{đ}W'$. Assume that processes take place spontaneously so that $\mathrm{d}S = 1/T\text{đ}Q + \mathrm{d}_iS$, where d_iS, is the entropy change due to the spontaneity of the process. Show that $-(\mathrm{d}G)_{Y,T} = \text{đ}W' + T\,\mathrm{d}_iS$, so that, at fixed Y and T, all the Gibbs free energy is available to do work for reversible processes but only part of it is available to do work for spontaneous processes.

Answer: From the fundamental equation for the Gibbs free energy, we know that $\mathrm{d}G = \mathrm{d}U - X\,\mathrm{d}Y - Y\,\mathrm{d}X - T\,\mathrm{d}S - S\,\mathrm{d}T$. Also we know that $\mathrm{d}U = \text{đ}Q + Y\,\mathrm{d}X - \text{đ}W'$, so we can write $\mathrm{d}G = \text{đ}Q - \text{đ}W' - X\,\mathrm{d}Y - T\,\mathrm{d}S - S\,\mathrm{d}T$. For fixed Y and T we have $(\mathrm{d}G)_{Y,T} = \text{đ}Q - \text{đ}W' - T\,\mathrm{d}S$. Now remember that $\mathrm{d}S = 1/T\text{đ}Q + \mathrm{d}_iS$. Then we find $(\mathrm{d}G)_{Y,T} = -\text{đ}W' - T\,\mathrm{d}_iS$.

For a process at fixed T, Y, and $\{N_j\}$ we obtain

$$(\mathrm{d}G)_{T,Y,\{N_j\}} \leq 0 \,, \tag{3.35}$$

and we conclude that *an equilibrium state at fixed T, Y, and $\{N_j\}$ is a state of minimum Gibbs free energy.*

3.5.5
Grand Potential

The Grand Potential is a thermodynamic potential that is extremized for a system in thermal and chemical equilibrium with the surrounding environment but is mechanically isolated. It describes systems that are held at the same temperature and chemical potential as the environment. It is a thermodynamic potential energy for processes carried out in open systems where particle number can vary but T, X, and $\{\mu_j\}$ are kept fixed.

The grand potential, Ω, can be obtained from the internal energy U by adding terms to U that are due to thermal and chemical coupling of the system to the outside world:

$$\Omega = U - TS - \sum_{j=1}^{\nu} \mu_j N_j = XY \,. \tag{3.36}$$

The Legendre transformation in Eq. (3.36) changes the independent variables from $(S, X, \{N_t\})$ for the internal energy to $(T, X, \{\mu_j\})$ for the grand potential.

Table 3.5 The equations for changes in the Grand Potential in a system thermally and chemically coupled to the outside world.

Grand potential	$\boldsymbol{\Omega(T, X, \{\mu_j\})}$
Total Differential	$\mathrm{d}\Omega = -S\,\mathrm{d}T + Y\,\mathrm{d}X - \sum_{j=1}^{\nu} N_j\,\mathrm{d}\mu_j$
Fundamental Equation	$\Omega = U - TS - \sum_{j=1}^{\nu} \mu_j N_j = XY$
Equations of State	$S = -\left(\frac{\partial \Omega}{\partial T}\right)_{X,\{\mu_j\}}$
$Y = \left(\frac{\partial \Omega}{\partial X}\right)_{T,\{\mu_j\}}$	$N_j = -\left(\frac{\partial \Omega}{\partial \mu_j}\right)_{T,X,\{\mu_{l\neq j}\}}$
Maxwell Relations	
$\left(\frac{\partial S}{\partial X}\right)_{T,\{\mu_j\}} = -\left(\frac{\partial Y}{\partial T}\right)_{X,\{\mu_j\}}$	$\left(\frac{\partial S}{\partial \mu_j}\right)_{T,Y,\{\mu_{l\neq j}\}} = \left(\frac{\partial N_j}{\partial T}\right)_{X,\{\mu_j\}}$
$\left(\frac{\partial Y}{\partial \mu_j}\right)_{T,X,\{\mu_{l\neq j}\}} = -\left(\frac{\partial N_j}{\partial X}\right)_{T,\{\mu_j\}}$	$\left(\frac{\partial N_j}{\partial \mu_i}\right)_{T,X,\{\mu_{l\neq i}\}} = \left(\frac{\partial N_i}{\partial \mu_j}\right)_{T,X,\{\mu_{l\neq j}\}}$

If we take the differential of Eq. (3.36) and combine it with the differential $\mathrm{d}U$ in Eq. (3.25), we obtain

$$\mathrm{d}\Omega \leq -S\,\mathrm{d}T + Y\,\mathrm{d}X - \sum_j N_j\,\mathrm{d}\mu_j\,. \tag{3.37}$$

The equations of state and Maxwell relations that result from the fact that $\mathrm{d}\Omega$ is an exact differential, are listed in Table 3.5.

For a process at fixed T, X, and $\{\mu_j\}$, we obtain

$$(\mathrm{d}\Omega)_{T,X,\{\mu_j\}} \leq 0\,. \tag{3.38}$$

Thus, *an equilibrium state at fixed T, X, and $\{\mu_j\}$ is a state of minimum grand potential.*

3.6
Response Functions

The response functions are the thermodynamic quantities most accessible to experiment. They give us information about how a specific state variable changes as other independent state variables are changed under controlled conditions. As we shall see in later chapters, they also provide a measure of the size of fluctuations in a thermodynamic system. The response functions can be divided into (a) thermal response functions, such as heat capacities, (b) mechanical response functions, such as compressibility and susceptibility, and (c) chemical response functions. We shall introduce some thermal and mechanical response functions in this section.

3.6.1
Thermal Response Functions (Heat Capacity)

The heat capacity, C, is a measure of the amount of heat needed to raise the temperature of a system by a given amount. In general, it is defined as the derivative, $C = (\text{đ}Q/\mathrm{d}T)$. When we measure the heat capacity, we try to fix all independent variables except the temperature. Thus, there are as many different heat capacities as there are combinations of independent variables, and they each contain different information about the system. We shall derive the heat capacity at constant X and $\{N_j\}$, $C_{X,\{N_j\}}$, and we shall derive the heat capacity at constant Y and $\{N_j\}$, $C_{Y,\{N_j\}}$. We will derive these heat capacities in two different ways, first from the first law and then from the definition of the entropy.

To obtain an expression of $C_{X,\{N_j\}}$, we shall assume that X, T, and $\{N_j\}$ are independent variables. Then the first law, $\text{đ}Q = \mathrm{d}U - Y\,\mathrm{d}X - \sum_j \mu_j\,\mathrm{d}N_j$, can be written

$$\text{đ}Q = \left(\frac{\partial U}{\partial T}\right)_{X,\{N_j\}} \mathrm{d}T + \left[\left(\frac{\partial U}{\partial X}\right)_{T,\{N_j\}} - Y\right] \mathrm{d}X + \sum_j \left[\left(\frac{\partial U}{\partial N_j}\right)_{T,X,\{N_{i\neq j}\}} - \mu_j\right] \mathrm{d}N_j \,. \tag{3.39}$$

For constant X and $\{N_j\}$, we have $[\text{đ}Q]_{X,\{N_j\}} = C_{X,\{N_j\}}\,\mathrm{d}T$ and we find

$$C_{X,\{N_j\}} = \left(\frac{\partial U}{\partial T}\right)_{X,\{N_j\}} \tag{3.40}$$

for the heat capacity at constant X and $\{N_j\}$.

To obtain an expression for $C_{Y,\{N_j\}}$, we shall assume that Y, T, and $\{N_j\}$ are independent variables. Then we can write

$$\mathrm{d}X = \left(\frac{\partial X}{\partial T}\right)_{Y,\{N_j\}} \mathrm{d}T + \left(\frac{\partial X}{\partial Y}\right)_{T,\{N_j\}} \mathrm{d}Y + \sum_j \left(\frac{\partial X}{\partial N_j}\right)_{T,Y,\{N_{i\neq j}\}} \mathrm{d}N_j \,. \tag{3.41}$$

If we substitute the expression for $\mathrm{d}X$ into Eq. (3.39), and hold Y and $\{N_j\}$ fixed so that $\mathrm{d}Y = 0$ and $\{\mathrm{d}N_j = 0\}$, we obtain

$$[\text{đ}Q]_{Y,\{N_j\}} = \left\{C_{X,\{N_j\}} + \left[\left(\frac{\partial U}{\partial X}\right)_{T,\{N_j\}} - Y\right]\left(\frac{\partial X}{\partial T}\right)_{Y,\{N_j\}}\right\} \mathrm{d}T \tag{3.42}$$

Since $[\text{đ}Q]_{Y,\{N_j\}} = C_{Y,\{N_j\}}\,\mathrm{d}T$ and we obtain

$$C_{Y,\{N_j\}} = C_{X,\{N_j\}} + \left[\left(\frac{\partial U}{\partial X}\right)_{T,\{N_j\}} - Y\right]\left(\frac{\partial X}{\partial T}\right)_{Y,\{N_j\}} \tag{3.43}$$

for the heat capacity at constant Y and $\{N_j\}$.

For a monatomic substance, these equations simplify. Let us write them in terms of molar quantities. We can write the heat capacity in the form $C_{X,\mathfrak{n}} = (\partial U/\partial T)_{X,\mathfrak{n}} = \mathfrak{n}(\partial u/\partial T)_x$, where $u = U/\mathfrak{n}$ is the molar internal energy and $x = X/\mathfrak{n}$ is a molar density of the mechanical extensive variable. The molar heat capacity is then $c_x = (\partial u/\partial T)_x$ so that $C_{X,\mathfrak{n}} = \mathfrak{n}c_x$. Similarly, let us note that $(\partial X/\partial T)_{Y,\mathfrak{n}} = \mathfrak{n}(\partial x/\partial T)_Y$ and $(\partial U/\partial X)_{T,\mathfrak{n}} = \mathfrak{n}(\partial u/\partial x)_T$. Therefore, the molar heat capacity at constant Y is $c_Y = c_x + [(\partial u/\partial x)_T - Y](\partial x/\partial T)_Y$.

It is useful to rederive expressions for $C_{X,\{N_j\}}$ and $C_{Y,\{N_j\}}$ from the entropy using the definition $\text{đ}Q = T\,\mathrm{d}S$. Let us first assume that T, X, and $\{N_j\}$ are independent. Then for a reversible process, we obtain

$$\text{đ}Q = T\left(\frac{\partial S}{\partial T}\right)_{X,\{N_j\}} \mathrm{d}T + T\left(\frac{\partial S}{\partial X}\right)_{T,\{N_j\}} \mathrm{d}X + \sum_j T\left(\frac{\partial S}{\partial N_j}\right)_{T,X,\{N_{i\neq j}\}} \mathrm{d}N_j \,. \tag{3.44}$$

For a process which occurs at constant X and $\{N_j\}$, Eq. (3.44) becomes

$$[\text{đ}Q]_{X,\{N_j\}} = T\left(\frac{\partial S}{\partial T}\right)_{X,\{N_j\}} \mathrm{d}T\,, \tag{3.45}$$

and therefore

$$C_{X,\{N_j\}} = T\left(\frac{\partial S}{\partial T}\right)_{X,\{N_j\}} = -T\left(\frac{\partial^2 A}{\partial T^2}\right)_{X,\{N_j\}}\,. \tag{3.46}$$

The second term uses the fact that $S = -T\,(\partial A/\partial T)_{X,\{N_j\}}$ (see Table 3.3).

Let us now assume that T, Y, and $\{N_j\}$ are independent. For a reversible process, we can write

$$\text{đ}Q = T\left(\frac{\partial S}{\partial T}\right)_{Y,\{N_j\}} \mathrm{d}T + T\left(\frac{\partial S}{\partial Y}\right)_{T,\{N_j\}} \mathrm{d}Y + \sum_j T\left(\frac{\partial S}{\partial N_j}\right)_{T,Y,\{N_{i\neq j}\}} \mathrm{d}N_j\,. \tag{3.47}$$

If we combine Eqs. (3.41) and (3.44), and hold Y and $\{N_j\}$ fixed, we can write

$$[\text{đ}Q]_{Y,\{N_j\}} = T\left[\left(\frac{\partial S}{\partial T}\right)_{X,\{N_j\}} + \left(\frac{\partial S}{\partial X}\right)_{T,\{N_j\}}\left(\frac{\partial X}{\partial T}\right)_{Y,\{N_j\}}\right]\mathrm{d}T\,. \tag{3.48}$$

If we now compare Eqs. (3.47) and (3.48), we find

$$\begin{aligned} C_{Y,\{N_j\}} &= T\left(\frac{\partial S}{\partial T}\right)_{Y,\{N_j\}} = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_{Y,\{N_j\}} \\ &= C_{X,\{N_j\}} + T\left(\frac{\partial S}{\partial X}\right)_{T,\{N_j\}}\left(\frac{\partial X}{\partial T}\right)_{Y,\{N_j\}}\,. \end{aligned} \tag{3.49}$$

The top line in Eq. (3.49) uses the relation $S = -T\,(\partial G/\partial T)_{Y,\{N_j\}}$ (see Table 3.4).

We can obtain some additional useful identities from the above equations. If we use the Maxwell relation $(\partial S/\partial X)_{T,\{N_j\}} = -\,(\partial Y/\partial T)_{X\{N_j\}}$ (see Table 3.3) and Eqs. (3.43), and (3.49), we obtain the identity

$$\left(\frac{\partial S}{\partial X}\right)_{T,\{N_j\}} = \frac{1}{T}\left[\left(\frac{\partial U}{\partial X}\right)_{T,\{N_j\}} - Y\right] = -\left(\frac{\partial Y}{\partial T}\right)_{X,\{N_j\}}\,. \tag{3.50}$$

Therefore,

$$\left(\frac{\partial^2 Y}{\partial T^2}\right)_{X,\{N_j\}} = -\frac{1}{T}\left(\frac{\partial C_{X,\{N_j\}}}{\partial X}\right)_{T,\{N_j\}}\,, \tag{3.51}$$

where we have used identity $\left(\partial/\partial T\,(\partial S/\partial X)_{T,\mathfrak{n}}\right)_{X,\mathfrak{n}} = \left(\partial/\partial X\,(\partial S/\partial T)_{X,\mathfrak{n}}\right)_{T,\mathfrak{n}}$ and Eq. (3.50).

For a monatomic substance, it is fairly easy to show that the molar heat capacity at constant molar density, x, is $c_x = T(\partial s/\partial T)_x = -T(\partial^2 a/\partial T^2)_x$, and the molar heat capacity at constant Y is $c_Y = T(\partial s/\partial T)_Y = -T(\partial^2 a/\partial T^2)_Y$. We also obtain the useful identities $(\partial s/\partial x)_T = (1/T)[(\partial u/\partial x)_T - Y] = -(\partial Y/\partial T)_x$ and $(\partial^2 Y/\partial T^2)_x = -(1/T)(\partial c_x/\partial x)_T$.

3.6.2
Mechanical Response Functions

There are three mechanical response functions which are commonly used. They are the *isothermal susceptibility*,

$$\chi_{T,\{N_j\}} = \left(\frac{\partial X}{\partial Y}\right)_{T,\{N_j\}} = -\left(\frac{\partial^2 G}{\partial Y^2}\right)_{T,\{N_j\}} , \tag{3.52}$$

the *adiabatic susceptibility*,

$$\chi_{S,\{N_j\}} = \left(\frac{\partial X}{\partial Y}\right)_{S,\{N_j\}} = -\left(\frac{\partial^2 H}{\partial Y^2}\right)_{S,\{N_j\}} , \tag{3.53}$$

and the *thermal expansivity*,

$$\alpha_{Y,\{N_j\}} = \left(\frac{\partial X}{\partial T}\right)_{Y,\{N_j\}} . \tag{3.54}$$

Using the identities in Section 3.5, the thermal and mechanical response functions can be shown to satisfy the identities

$$\chi_{T,\{N_j\}}(C_{Y,\{N_j\}} - C_{X,\{N_j\}}) = T(\alpha_{Y,\{N_j\}})^2 , \tag{3.55}$$

$$C_{Y,\{N_j\}}(\chi_{T,\{N_j\}} - \chi_{S,\{N_j\}}) = T(\alpha_{Y,\{N_j\}})^2 , \tag{3.56}$$

and

$$\frac{C_{Y,\{N_j\}}}{C_{X,\{N_j\}}} = \frac{\chi_{T,\{N_j\}}}{\chi_{S,\{N_j\}}} . \tag{3.57}$$

The derivation of these identities is left as a homework problem.

For PVT systems, the mechanical response functions have special names. Quantities closely related to the isothermal and adiabatic susceptibilities are the *isothermal compressibility*,

$$\kappa_{T,\{N_j\}} = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,\{N_j\}} = -\frac{1}{V}\left(\frac{\partial^2 G}{\partial P^2}\right)_{T,\{N_j\}} , \tag{3.58}$$

and *adiabatic compressibility*,

$$\kappa_{S,\{N_j\}} = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{S,\{N_j\}} = -\frac{1}{V}\left(\frac{\partial^2 H}{\partial P^2}\right)_{S,\{N_j\}} , \tag{3.59}$$

respectively. The *thermal expansivity* for a PVT is defined slightly differently from above. It is

$$\alpha_{P,\{N_j\}} = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P,\{N_j\}} . \tag{3.60}$$

For a monatomic PVT system the mechanical response functions become even simpler if written in terms of densities. The isothermal and adiabatic compressibilities are $\kappa_T = -(1/v)(\partial v/\partial P)_T$ and $\kappa_s = -(1/v)(\partial v/\partial P)_s$, respectively, where $v = V/\mathfrak{n}$ and $s = S/\mathfrak{n}$ are the molar volume and molar entropy, respectively. The thermal expansivity is $\alpha_P = (1/v)(\partial v/\partial T)_P$.

Exercise 3.7

Gases are composed of atoms or molecules that have a repulsive core and a weak attractive region surrounding the repulsive core. The van der Waals equation of state

$$\left(P + \frac{a\mathfrak{n}^2}{V^2}\right)(V - \mathfrak{n}b) = \mathfrak{n}RT$$

gives corrections to the ideal gas equation of state due to these interactions. The parameter a accounts for a reduction in pressure due to the attractive interaction and b reduces the volume available to the particles because of the repulsive core. (a) Compute the molar heat capacity c_P, (b) the adiabatic compressibility κ_S, and (c) the thermal expansivity α_P for a van der Waals gas. Assume a monatomic gas so that $c_{V,\mathfrak{n}} = 3R/2$.

Answer: (a) First note that from Eq. (3.51) and the van der Waals equation, we have the relation $\left(\partial C_{V,\mathfrak{n}}/\partial V\right)_{T,\mathfrak{n}} = T\left(\partial^2 P/\partial T^2\right)_{V,\mathfrak{n}} = 0$, which shows that $C_{V,\mathfrak{n}}$ is independent of V. We can compute c_P using Eq. (3.43). From the van der Waals equation of state and Eq. (3.50), we find

$$\left(\frac{\partial v}{\partial T}\right)_P = R\left[\frac{RT}{v-b} - \frac{2\alpha(v-b)}{v^3}\right]^{-1} \quad \text{and} \quad \left(\frac{\partial u}{\partial v}\right)_T = \frac{\alpha}{v^2} ,$$

where $v = V/n$. If we combine Eq. (3.43) and the above equations, and use the van der Waals equation of state, we obtain

$$c_p = \frac{3}{2}R + R\left[1 - \frac{2\alpha(v-b)^2}{RTv^3}\right]^{-1} .$$

(b) The derivation of the adiabatic compressibility, κ_s is more involved. We first find the entropy. Note that $(\partial s/\partial T)_v = 3R/(2T)$ and $(\partial s/\partial v)_T = (\partial P/\partial T)_v = R/(v-b)$. If we integrate, we obtain the molar entropy $s = R\ln[(v-b)T^{3/2}] +$ constant. Using the van der Waals equation, we obtain

$$s = \frac{5}{2}R + R\ln\left[(v-b)^{5/2}\left(P + \frac{\alpha}{v^2}\right)^{3/2}\right] + \text{constant} .$$

If we now take the derivative of s with respect to P holding s fixed, we obtain

$$\kappa_s = -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_s = \left[\frac{5}{3}\frac{RTv}{(v-b)^2} - \frac{2\alpha}{v^2}\right]^{-1} .$$

(c) The thermal expansivity α_P is easy to compute. If we take the derivative of the van der Waals equation with respect to T holding P fixed, we find

$$\alpha_P = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P = R\left[\frac{RT}{(v-b)} - \frac{2\alpha(v-b)}{v^3}\right]^{-1} .$$

3.7
Stability of the Equilibrium State

The entropy of an isolated system takes its maximum value at equilibrium. If the system has a finite number of particles, the thermodynamic quantities describe the *average* behavior of the system and there can be spontaneous fluctuations away from this average behavior. Fluctuations away from equilibrium must cause the entropy to decrease. If this were not the case, the system could spontaneously move to a new equilibrium state with a higher entropy because of fluctuations. For a system in a stable equilibrium state this, by definition, cannot happen.

We can use the fact that the entropy must be maximum for an isolated system to obtain conditions for local equilibrium and for local stability of equilibrium systems [67, 109, 183]. We will restrict ourselves to PVT systems. However, our arguments also apply more generally to YXT systems.

3.7.1
Conditions for Local Equilibrium in a PVT System

Let us consider a mixture of l types of particles in an isolated box with total volume, V_{T}, total internal energy U_{T}, total entropy S_{T}, and total number of particles $N_{j,\mathrm{T}}$ of type j. Assume that the box is divided into two parts, A and B, by a conducting porous wall which is free to move and through which particles can pass. With this type of dividing wall there is a free exchange of heat, mechanical energy, and particles between A and B. One can think of A and B as two different parts of a fluid (gas or liquid), or perhaps as a solid (part A) in contact with its vapor (part B). We shall assume that no chemical reactions occur. Since the box is closed and isolated, we can write

$$U_{\mathrm{T}} = \sum_{\alpha=\mathrm{A,B}} U_\alpha\,, \quad V_{\mathrm{T}} = \sum_{\alpha=\mathrm{A,B}} V_\alpha\,, \quad S_{\mathrm{T}} = \sum_{\alpha=\mathrm{A,B}} S_\alpha\,, \quad N_{j,\mathrm{T}} = \sum_{\alpha=\mathrm{A,B}} N_{j,\alpha}\,, \tag{3.61}$$

where U_α, V_α, S_α, and $N_{j,\alpha}$ are the internal energy, volume, entropy, and total number of particles of type j in compartment α, respectively.

Let us now assume that spontaneous fluctuations can occur in the energy, volume, and particle number of each cell subject to the constraints

$$\Delta U_{\mathrm{T}} = \Delta V_{\mathrm{T}} = \Delta N_{j,\mathrm{T}} = 0 \tag{3.62}$$

so that $\Delta U_{\mathrm{A}} = -\Delta U_{\mathrm{B}}$, $\Delta V_{\mathrm{A}} = -\Delta V_{\mathrm{B}}$, and $\Delta N_{j,\mathrm{A}} = -\Delta N_{j,\mathrm{B}}$. As long as the system is not near a phase transition, the fluctuations will be small. Then changes in the entropy, due to these fluctuations, can be expanded in a Taylor series to first order in the fluctuations and can be written

$$\Delta S_{\mathrm{T}} = \sum_{\alpha=\mathrm{A,B}} \left[\left(\frac{\partial S_\alpha}{\partial U_\alpha} \right)^0_{V_\alpha,\{N_{j,\alpha}\}} \Delta U_\alpha + \left(\frac{\partial S_\alpha}{\partial V_\alpha} \right)^0_{U_\alpha,\{N_{j,\alpha}\}} \Delta V_\alpha \right.$$
$$\left. + \sum_{j=1}^{l} \left(\frac{\partial S_\alpha}{\partial N_{j,\alpha}} \right)^0_{U_\alpha,V_\alpha,\{N_{k\neq j,\alpha}\}} \Delta N_{j,\alpha} \right] + \ldots \tag{3.63}$$

where the superscript “0” denotes absolute equilibrium. From Eqs. (3.22) and (3.62), we can write Eq. (3.63) in the form

$$\Delta S_{\mathrm{T}} = \left(\frac{1}{T^0_{\mathrm{A}}} - \frac{1}{T^0_{\mathrm{B}}} \right) \Delta U_{\mathrm{A}} + \left(\frac{P^0_{\mathrm{A}}}{T^0_{\mathrm{A}}} - \frac{P^0_{\mathrm{B}}}{T^0_{\mathrm{B}}} \right) \Delta V_{\mathrm{A}}$$
$$- \sum_{j=1}^{l} \left(\frac{\mu^0_{j,\mathrm{A}}}{T^0_{\mathrm{A}}} - \frac{\mu^0_{j,\mathrm{B}}}{T^0_{\mathrm{B}}} \right) \Delta N_{j,\mathrm{A}} + \ldots , \tag{3.64}$$

where T^0_α and P^0_α are the equilibrium temperature and pressure, respectively, of the material in compartment α, and $\mu^0_{j,\alpha}$ is the equilibrium chemical potential of particles of type j in compartment α.

For a system in equilibrium, the entropy is a maximum. Therefore, any spontaneous changes must cause the entropy to decrease. However, ΔU_{A}, ΔV_{A}, and $\Delta N_{j,\mathrm{A}}$ can be positive or negative. Thus, in order to ensure that $\Delta S_{\mathrm{T}} \leq 0$, we must have

$$T^0_{\mathrm{A}} = T^0_{\mathrm{B}} , \quad P^0_{\mathrm{A}} = P^0_{\mathrm{B}} , \quad \text{and} \quad \mu^0_{j,\mathrm{A}} = \mu^0_{j,\mathrm{B}} \quad \text{for} \quad j = 1, \ldots , l . \tag{3.65}$$

Equations (3.65) give the conditions for local equilibrium in a system in which no chemical reactions occur. Thus, *if the interface between* A *and* B *can transmit heat, mechanical energy, and particles of all types, then the two systems must have the same temperature, pressure, and chemical potential for each type of particle in order to be in equilibrium.* It is important to note that if the partition cannot pass particles of type, i, then $\Delta N_{i,\mathrm{A}} = \Delta N_{i,\mathrm{B}} = 0$ and we can have $\mu^0_{i,\mathrm{A}} \neq \mu^0_{i,\mathrm{B}}$. If the partition is nonporous and fixed in position so no particles can pass and no mechanical work can be transmitted, then we can have $P^0_{\mathrm{A}} \neq P^0_{\mathrm{B}}$ and $\mu^0_{j,\mathrm{A}} \neq \mu^0_{j,\mathrm{B}}$ ($j = 1, \ldots , l$) and still have equilibrium.

3.7.2
Conditions for Local Stability in a PVT System

Stability of the equilibrium state places certain conditions on the sign of the response functions. To see this, let us again consider a closed isolated box with volume V_{T}, total entropy S_{T}, total internal energy U_{T}, and a total number of particles $N_{j,\mathrm{T}}$ of type j, where $j = 1, \ldots , \nu$. We shall assume that the box is divided into l cells which can exchange thermal energy, mechanical energy, and particles.

We shall denote the equilibrium volume, entropy, internal energy, and number of particles of type j for the αth cell by V_α^0, S_α^0, U_α^0, and $N_{j,\alpha}^0$, respectively. The equilibrium pressure, temperature, and chemical potentials of the various cells are P^0, T^0, and μ_j^0, respectively (they must be the same for all the cells). As we have seen in Section 3.7.1, when we expand the total entropy in terms of fluctuations ΔU_α, ΔV_α, and $\Delta N_{j,\alpha}$, first-order terms are zero. Thus, the changes in the entropy, to second order in fluctuations, can be written

$$\Delta S_{\mathrm{T}} = \frac{1}{2}\sum_{\alpha=1}^{l}\left[\Delta\left(\frac{1}{T}\right)_\alpha \Delta U_\alpha + \Delta\left(\frac{P}{T}\right)_\alpha \Delta V_\alpha - \sum_{j=1}^{\nu}\Delta\left(\frac{\mu_j}{T}\right)_\alpha \Delta N_{j,\alpha}\right] + \dots\ , \tag{3.66}$$

which is a compact way to write the many terms that contribute to second order. The fluctuations ΔU_α, ΔV_α, and $\Delta N_{j,\alpha}$ are defined as $\Delta U_\alpha = U_\alpha - U_\alpha^0$, $\Delta V_\alpha = V_\alpha - V_\alpha^0$, and $\Delta N_{j,\alpha} = N_{j,\alpha} - N_{j,\alpha}^0$ and denote the deviation of the quantities U_α, V_α, and $N_{j,\alpha}$ from their absolute equilibrium values, U_α^0, V_α^0, and $N_{j,\alpha}^0$, respectively. For $l = 1$, there will be nine terms.

Exercise 3.8

A spherical droplet of liquid floats in equilibrium with its gas phase (neglect gravity) in a large room with volume $V_{\mathrm{tot}} = V_{\mathrm{l}} + V_{\mathrm{g}}$, where V_{l} (V_{g}) is the volume of the liquid (gas). The droplet has radius R and surface tension σ. (For water $\sigma = 0.072\,\mathrm{N/m}$ at $T = 25\,°\mathrm{C}$.) The gas and liquid are free to exchange heat and molecules, so the temperature and chemical potential are uniform throughout the system. Find the condition for mechanical equilibrium.

Answer: The condition for chemical equilibrium is $\mu_{\mathrm{g}}(T, P_{\mathrm{g}}) = \mu_{\mathrm{l}}(T, P_{\mathrm{l}})$, where μ_{l} (μ_{g}) is the chemical potential of the liquid (gas) and P_{l} (P_{g}) is the pressure of the liquid (gas). Since we are dealing with a system of fixed total volume, temperature and chemical potential, it is convenient to use the grand potential. The grand potential for the entire system can be written

$$\Omega = -P_{\mathrm{g}}V_{\mathrm{g}} - P_{\mathrm{l}}V_{\mathrm{l}} + \sigma A = -\left(V_{\mathrm{tot}} - \frac{4}{3}\pi R^3\right)P_{\mathrm{g}} - \frac{4}{3}\pi R^3 P_{\mathrm{l}} + \sigma 4\pi R^2\ .$$

For a system at equilibrium with fixed temperature, total volume, and chemical potential, the grand potential must be a minimum so the condition for thermodynamic equilibrium is $(\mathrm{d}\Omega/\mathrm{d}R)_{T,V_{\mathrm{tot}},\mu} = 0$. Therefore, when the interface between two parts of a thermodynamic system has a surface tension and the surface has curvature, the condition for mechanical equilibrium takes the form

$$P_{\mathrm{l}} - P_{\mathrm{g}} = \frac{2\sigma}{R}\ .$$

The pressures in the two parts of the system need not be equal.

To obtain the full expansion of Eq. (3.66) in terms of fluctuations ΔU_α, ΔV_α, and $\Delta N_{j,\alpha}$, note that

$$\Delta\left(\frac{1}{T}\right)_\alpha = \Delta\left(\frac{\partial S_\alpha}{\partial U_\alpha}\right)_{V_\alpha,\{N_{j,\alpha}\}}, \quad \Delta\left(\frac{P}{T}\right)_\alpha = \Delta\left(\frac{\partial S_\alpha}{\partial V_\alpha}\right)_{U_\alpha,\{N_{j,\alpha}\}},$$
$$\text{and} \quad \Delta\left(\frac{\mu_j}{T}\right)_\alpha = -\Delta\left(\frac{\partial S_\alpha}{\partial N_{j,\alpha}}\right)_{U_\alpha,V_\alpha,\{N_{i\neq j,\alpha}\}}. \tag{3.67}$$

We can expand $\Delta\left(\partial S_\alpha/\partial U_\alpha\right)_{V_\alpha,\{N_{j,\alpha}\}}$ in terms of fluctuations ΔU_α, ΔV_α, and $\Delta N_{j,\alpha}$ as follows:

$$\Delta\left(\frac{\partial S_\alpha}{\partial U_\alpha}\right)_{V_\alpha,\{N_{j,\alpha}\}} \equiv \left(\frac{\partial^2 S}{\partial U^2}\right)^0_{V,\{N_j\}} \Delta U_\alpha + \left[\frac{\partial}{\partial V}\left(\frac{\partial S}{\partial U}\right)_{V,\{N_j\}}\right]^0_{U,\{N_j\}} \Delta V_\alpha$$
$$+ \sum_{j=1}^{\nu}\left[\frac{\partial}{\partial N_j}\left(\frac{\partial S}{\partial U}\right)_{V,\{N_j\}}\right]^0_{U,V,\{N_{k\neq j}\}} \Delta N_{j,\alpha}. \tag{3.68}$$

The quantities $\Delta(\partial S_\alpha/\partial V_\alpha)_{U_\alpha,\{N_{j,\alpha}\}}$ and $\Delta(\partial S_\alpha/\partial N_{j,\alpha})_{U_\alpha,V_\alpha,\{N_{k\neq j,\alpha}\}}$ can be expanded in a similar manner. In Eq. (3.68), the superscripts 0 on partial derivatives indicate that they are evaluated at absolute equilibrium.

It is useful to write Eq. (3.66) in a slightly different form. If we use the combined first and second laws to relate the fluctuations as $T^0\Delta S = \Delta U + P^0\Delta V - \sum_{j=1}^{\nu}\mu_j^0\Delta N_j$, then we find

$$\Delta S_{\mathrm{T}} = -\frac{1}{2T^0}\sum_{\alpha=1}^{l}\left(\Delta T_\alpha\Delta S_\alpha - \Delta P_\alpha\Delta V_\alpha + \sum_{j=1}^{\nu}\Delta\mu_{j,\alpha}\Delta N_{j,\alpha}\right) + \cdots, \tag{3.69}$$

where T^0 is the equilibrium temperature of the system. Equation (3.69) gives the entropy change, due to spontaneous fluctuations, in a completely general form. This expression for ΔS_{T}, can be expanded in terms of any set of independent variables we choose.

Let us now obtain stability conditions for the PVT system. For simplicity, we will assume that only one kind of particle exists in the system and we will assume that different parts of the system cannot exchange particles. Then $\Delta N_\alpha = 0$. Let us choose T and V as the independent variables. With these assumptions, we can write

$$[\Delta S_\alpha]_{N_\alpha} = \left(\frac{\partial S}{\partial T}\right)^0_{V,N}\Delta T_\alpha + \left(\frac{\partial S}{\partial V}\right)^0_{T,N}\Delta V_\alpha, \tag{3.70}$$

and

$$[\Delta P_\alpha]_{N_\alpha} = \left(\frac{\partial P}{\partial T}\right)^0_{V,N}\Delta T_\alpha + \left(\frac{\partial P}{\partial V}\right)^0_{T,N}\Delta V_\alpha. \tag{3.71}$$

If we substitute Eqs. (3.70), (3.71), and the constraint $\Delta N_\alpha = 0$ into Eq. (3.69), and use the Maxwell relation $(\partial S/\partial V)_{T,N} = (\partial P/\partial T)_{V,N}$ for the Helmholtz free energy (see Table 3.3), the entropy change becomes

$$\Delta S_{\mathrm{T}} = -\frac{1}{2T^0}\sum_{\alpha=1}^{l}\left[\left(\frac{\partial S}{\partial T}\right)^0_{V,N}(\Delta T_\alpha)^2 - \left(\frac{\partial P}{\partial V}\right)^0_{T,N}(\Delta V_\alpha)^2\right] + \cdots \tag{3.72}$$

Because the fluctuations ΔT_α and ΔV_α are independent, the requirement that $\Delta S_{\mathrm{T}} \le 0$ for a stable equilibrium state leads to the requirements that

$$C_{V,N} = T\left(\frac{\partial S}{\partial T}\right)_{V,N} \ge 0 \quad \text{and} \quad \kappa_{T,N} = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,N} \ge 0\,. \tag{3.73}$$

The constraints in Eq. (3.73) are a realization of Le Châteliers's famous principle: *If a system is in stable equilibrium, then any spontaneous change in its parameters must bring about processes which tend to restore the system to equilibrium.*

The first constraint in Eq. (3.73), $C_{V,N} \ge 0$, is the condition for *thermal stability*. It tells us that if a small excess of heat is added to a volume element of fluid, the temperature of the volume element must increase relative to its surroundings so that some of the heat will flow out again. This requires that the heat capacity be positive. If the heat capacity were negative, the temperature would decrease and even more heat would flow in, thus leading to an instability. A similar analysis shows that $C_{P,N} \ge 0$. From Eq. (3.56), we obtain the condition

$$C_{P,N} > C_{V,N} \ge 0\,. \tag{3.74}$$

The second constraint in Eq. (3.73), $\kappa_{T,N} \ge 0$, is a condition for *mechanical stability*. If a small volume element of fluid spontaneously increases, the pressure of the fluid inside the fluid element must decrease relative to its surroundings so that the larger pressure of the surroundings will stop the growth of the volume element. This requires that the compressibility be positive. A similar analysis shows that $\kappa_{S,N} \ge 0$. From the analog of Eq. (3.56) for PVT systems, we can show that

$$\kappa_{T,N} > \kappa_{S,N} \ge 0\,. \tag{3.75}$$

We can also obtain conditions for chemical stability. If we expand Eq. (3.69) in terms of fluctuations ΔT, ΔP and ΔN_j, and hold P and T fixed, we obtain the following condition for *chemical stability*

$$(\boldsymbol{\Delta N})^{\mathrm{T}} \cdot \overline{\boldsymbol{\mu}} \cdot (\boldsymbol{\Delta N}) = \sum_{i=1}^{\nu}\sum_{j=1}^{\nu}\left(\frac{\partial \mu_j}{\partial N_i}\right)^0_{T,P,\{N_{k\neq i}\}}\Delta N_i \Delta N_j \ge 0\,, \tag{3.76}$$

where ΔN_i and ΔN_j are independent and arbitrary variations,

$$\overline{\boldsymbol{\mu}} = \begin{pmatrix} \mu_{1,1} & \mu_{1,2} & \cdots & \mu_{1,l} \\ \mu_{2,1} & \mu_{2,2} & \cdots & \mu_{2,l} \\ \vdots & \vdots & \ddots & \vdots \\ \mu_{l,1} & \mu_{l,2} & \cdots & \mu_{\nu,\nu} \end{pmatrix}, \quad (\boldsymbol{\Delta N}) = \begin{pmatrix} \Delta N_1 \\ \Delta N_2 \\ \vdots \\ \Delta N_\nu \end{pmatrix} \tag{3.77}$$

$(\boldsymbol{\Delta N})^{\mathrm{T}}$ denotes the transpose of $(\boldsymbol{\Delta N})$, and $\mu_{j,i} \equiv (\partial\mu_j/\partial N_i)^0_{T,P,\{N_{k\neq i}\}}$. Because of the Maxwell relation $\mu_{j,i} = \mu_{i,j}$ (see Table 3.4), the matrix $\overline{\boldsymbol{\mu}}$ is symmetric. In addition, in order to satisfy the condition for chemical stability, the matrix $\overline{\boldsymbol{\mu}}$ must be a positive definite matrix. A symmetric matrix is positive definite if $\mu_{ii} > 0$ $(i = 1, \ldots, l)$ and if every principal minor is positive or zero.

It is important to note that a thermodynamically stable state may not be a state of thermodynamic equilibrium unless the appropriate free energy is minimum. A thermodynamically stable state which is not an equilibrium state is sometimes called a *metastable* state. It can exist in nature but eventually will decay to an absolute equilibrium state.

3.7.3
Implications of the Stability Requirements for the Free Energies

The stability conditions place restrictions on the derivatives of the thermodynamic potentials. Before we show this, it is useful to introduce the concept of concave and convex functions [193]:

1. A function $f(x)$ is *convex* if $\mathrm{d}^2 f(x)/\mathrm{d}x^2 \geq 0$ for all x (cf. Figure 3.3). For any x_1 and x_2 the chord joining the points $f(x_1)$ and $f(x_2)$ lies above or on the curve $f(x)$ for all x in the interval $x_1 < x < x_2$. If $\mathrm{d}f(x)/\mathrm{d}x$ exists at a given point, the tangent at that point always lies below the function except at the point of tangency.
2. A function $f(x)$ is *concave* if the function $-f(x)$ is convex.

From Table 3.3 and the stability conditions in Eqs. (3.74) and (3.75), we can write

$$\left(\frac{\partial^2 A}{\partial T^2}\right)_{V,\{N_j\}} = -\left(\frac{\partial S}{\partial T}\right)_{V,\{N_j\}} = -\frac{C_{V,\{N_j\}}}{T} < 0\,, \tag{3.78}$$

$$\left(\frac{\partial^2 A}{\partial V^2}\right)_{T,\{N_j\}} = -\left(\frac{\partial P}{\partial V}\right)_{T,\{N_j\}} = \frac{1}{V\kappa_{T,\{N_j\}}} > 0\,. \tag{3.79}$$

The Helmholtz free energy is a concave function of temperature and a convex function of volume.

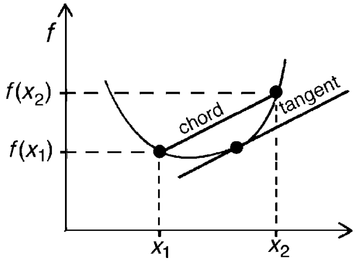


Figure 3.3 The function $f(x)$ is a convex function of x.

From Table 3.4 and the stability conditions in Eqs. (3.74) and (3.75), we can write

$$\left(\frac{\partial^2 G}{\partial T^2}\right)_{P,\{N_j\}} = -\left(\frac{\partial S}{\partial T}\right)_{P,\{N_j\}} = -\frac{C_{P,\{N_j\}}}{T} < 0\,, \tag{3.80}$$

$$\left(\frac{\partial^2 G}{\partial P^2}\right)_{T,\{N_j\}} = \left(\frac{\partial V}{\partial P}\right)_{T,\{N_j\}} = -V\kappa_{T,\{N_j\}} < 0\,. \tag{3.81}$$

Thus, *the Gibbs free energy is a concave function of temperature and a concave function of pressure.*

Exercise 3.9

A mixture of particles, A and B, has a Gibbs free energy of the form

$$G = \mathfrak{n}_A\mu_A^0(P,T) + \mathfrak{n}_B\mu_B^0(P,T) + RT\mathfrak{n}_A\ln x_A + RT\mathfrak{n}_B\ln x_B + \lambda\frac{\mathfrak{n}_A\mathfrak{n}_B}{\mathfrak{n}}\,,$$

where $\mathfrak{n} = \mathfrak{n}_A + \mathfrak{n}_B$, $x_A = \mathfrak{n}_A/\mathfrak{n}$, and $x_B = \mathfrak{n}_B/\mathfrak{n}$ ($\mathfrak{n}$ indicates mole number), μ_A^0 and μ_B^0 are functions only of P and T. Plot the region of thermodynamic instability in the $x_A{-}T$ plane.

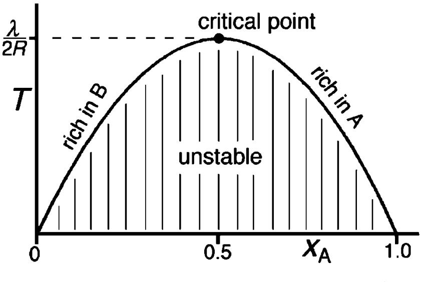
Answer: (a) For chemical stability, the matrix $\begin{pmatrix}\mu_{A,A} & \mu_{A,B}\\ \mu_{B,A} & \mu_{B,B}\end{pmatrix}$ must be symmetric positive definite. This requires that $(\partial\mu_A/\partial\mathfrak{n}_A)_{P,T,\mathfrak{n}_B} > 0$, $(\partial\mu_B/\partial\mathfrak{n}_B)_{P,T,\mathfrak{n}_A} > 0$, and $(\partial\mu_A/\partial\mathfrak{n}_B)_{P,T,\mathfrak{n}_A} = (\partial\mu_B/\partial\mathfrak{n}_A)_{P,T,\mathfrak{n}_B} < 0$. The chemical potential of the A-type particle is

$$\mu_A = \left(\frac{\partial G}{\partial\mathfrak{n}_A}\right)_{P,T,\mathfrak{n}_B} = \mu_A^0(P,T) + RT\ln x_A + \lambda\frac{\mathfrak{n}_B}{\mathfrak{n}} - \lambda\frac{\mathfrak{n}_A\mathfrak{n}_B}{\mathfrak{n}^2}\,.$$

A condition for thermodynamic stability is

$$\left(\frac{\partial\mu_A}{\partial\mathfrak{n}_A}\right)_{P,T,\mathfrak{n}_B} = \frac{RT}{x_A}\frac{\mathfrak{n}_B}{\mathfrak{n}^2} - 2\frac{\lambda\mathfrak{n}_B}{\mathfrak{n}^2} + 2\frac{\lambda\mathfrak{n}_A\mathfrak{n}_B}{\mathfrak{n}^3} > 0\,,$$

or $x_A^2 - x_A + RT/(2\lambda) > 0$. For $T > \lambda/(2R)$, this is always satisfied. A plot of $T = (2\lambda/R)(x_A - x_A^2)$ is given below.



The shaded region corresponds to $x_A^2 - x_A + RT/(2\lambda) < 0$ and is thermodynamically unstable. The unshaded region is thermodynamically stable. For $T < \lambda/(2R)$, two values of x_A satisfy the condition $x_A^2 - x_A + RT/(2\lambda) > 0$ for each value of T. These two values of x_A lie outside and on either side of the shaded region and are the mole fractions of two coexisting phases of the binary mixture, one rich in A and the other rich in B. For $T > \lambda/(2R)$, only one value of x_A satisfies the condition $x_A^2 - x_A + RT/(2\lambda) > 0$, so only one phase of the substance exists.

The form of the Gibbs and Helmholtz free energies for a magnetic system is not so easy to obtain. However, Griffiths [74] has shown that for a system of uncharged particles with spin, $G(T, H)$ is a concave function of T and H and $A(T, M)$ is a concave function of T and convex function of M.

3.7.4
Correlations Between Fluctuations

The probability distribution of fluctuations about absolute equilibrium can be written in terms of the entropy function associated with those fluctuations (see Eq. (2.19)). We can generalize Eq. (2.19) to include simultaneous fluctuations in several macroscopic variables. Then we can use Eq. (3.69) to determine the probability density for fluctuations in thermodynamic quantities about the equilibrium state.

Let us consider a closed isolated system with energy E. We shall assume that the macroscopic state of the system is describable in terms of n independent macroscopic state variables $A_i (i = 1, 2, \dots, n)$. Let $\Gamma(E, A_1, \dots, A_n)$ denote the number of microstates with energy E and parameters $A_1, \dots, A_n$. Then the probability that the system is in a macroscopic state described by parameters $E, A_1, \dots, A_n$, is given by

$$P(E, A_1, \dots, A_n) = \frac{\Gamma(E, A_1, \dots, A_n)}{\Gamma(E)} , \tag{3.82}$$

where $\Gamma(E)$ is the total number of microscopic states with energy E. The entropy of the system in a state with parameters $(E, A_1, \dots, A_n)$ is given by

$$S(E, A_1, \dots, A_n) = k_B \ln[\Gamma(E, A_1, \dots, A_n)] . \tag{3.83}$$

Hence

$$P(E, A_1, \dots, A_n) = \frac{1}{\Gamma(E)} \exp\left[\frac{1}{k_B} S(E, A_1, \dots, A_n)\right] . \tag{3.84}$$

The entropy will be a maximum when the system is in an equilibrium state, $A_1^0, \dots, A_n^0$. Any fluctuation about the equilibrium state must cause the entropy to decrease. If we let α_i denote the fluctuations

$$\alpha_i = A_i - A_i^0 , \tag{3.85}$$

then we can expand the entropy about its equilibrium value to obtain

$$S(E, A_1, \dots, A_n) = S\left(E, A_1^0, \dots, A_n^0\right) - \frac{1}{2} \sum_{i=1}^{n} \sum_{j=1}^{n} g_{ij} \alpha_i \alpha_j + \cdots , \tag{3.86}$$

where

$$g_{ij} \equiv -\left(\frac{\partial^2 S}{\partial A_i \partial A_j}\right)_{A_i=A_i^0;A_j=A_j^0} . \tag{3.87}$$

We assume that the fluctuations about the equilibrium state are small so we can terminate the expansion of the entropy at second order. This approximation is not good near a phase transition where fluctuations can become very large. The matrix g_{ij} is positive definite since the entropy must decrease and it is symmetric since the quantities, A_i, are state variables. Equation (3.86) contains no terms which are first order in A_i to ensure that spontaneous fluctuations about the equilibrium do not cause an increase in the entropy. Equilibrium is a state of maximum entropy.

We can now substitute Eqs. (3.86) into Eqs. (3.84) and obtain the following expression for the probability distribution of fluctuations about the equilibrium state,

$$P(\boldsymbol{\alpha}) = \sqrt{\frac{\det|\overline{\boldsymbol{g}}|}{(2\pi k_{\mathrm{B}})^n}} \exp\left(-\frac{1}{2k_{\mathrm{B}}} \sum_{i=1}^{n} \sum_{j=1}^{n} g_{ij}\alpha_i\alpha_j\right) , \tag{3.88}$$

where $\boldsymbol{\alpha}$ denotes the $1 \times n$ column matrix composed of elements α_j and $\overline{\boldsymbol{g}}$ denotes the $n \times n$ square symmetric matrix composed of matrix elements $g_{i,j}$. The quantity, $\det|\overline{\boldsymbol{g}}|$, is the determinant of the matrix $\overline{\boldsymbol{g}}$. The probability $P(\boldsymbol{\alpha})$ is normalized to one

$$\int_{-\infty}^{\infty} \mathrm{d}\boldsymbol{\alpha} P(\boldsymbol{\alpha}) \equiv \int_{-\infty}^{\infty} \mathrm{d}\alpha_1 \times \cdots \times \int_{-\infty}^{\infty} \mathrm{d}\alpha_n P(\boldsymbol{\alpha}) = 1 \tag{3.89}$$

(see Exercise A.7). Since only small fluctuations are assumed to be probable, there is no difficulty in extending the limits of integration in Eq. (3.89) from $-\infty$ to $+\infty$.

We often want to find expectation values of various moments of the fluctuations. To do this, it is convenient to introduce a more general integral,

$$I(\boldsymbol{\beta}) \equiv \sqrt{\frac{\det|\overline{\boldsymbol{g}}|}{(2\pi k_{\mathrm{B}})^n}} \int_{-\infty}^{\infty} \mathrm{d}\boldsymbol{\alpha} \exp\left(-\frac{1}{2k_{\mathrm{B}}}\boldsymbol{\alpha}^{\mathrm{T}} \cdot \overline{\boldsymbol{g}} \cdot \boldsymbol{\alpha} + \boldsymbol{\beta}^{\mathrm{T}} \cdot \boldsymbol{\alpha}\right) = \mathrm{e}^{\frac{1}{2}k_{\mathrm{B}}\boldsymbol{\beta}^{\mathrm{T}} \cdot \overline{\boldsymbol{g}}^{-1} \cdot \boldsymbol{\beta}} , \tag{3.90}$$

where $\boldsymbol{\beta}$ is $1 \times n$ column matrix and $\boldsymbol{\alpha}^{\mathrm{T}}$ and $\boldsymbol{\beta}^{\mathrm{T}}$ denote the transpose of $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$, respectively (see Exercise A.8). The moment, $\langle\alpha_i\alpha_j\rangle$, is defined as

$$\langle\alpha_i\alpha_j\rangle = \lim_{\boldsymbol{\beta}\to 0}\left(\frac{\partial^2}{\partial\beta_i\partial\beta_j} I(\boldsymbol{\beta})\right) = k_{\mathrm{B}}(\overline{\boldsymbol{g}}^{-1})_{ij} . \tag{3.91}$$

Since the probability density, $P(\boldsymbol{\alpha})$, is a multivariant Gaussian with zero mean, the first moment, $\langle\alpha_i\rangle = 0$, and all higher moments can be expressed in terms of the moments $\langle\alpha_i^2\rangle$ and $\langle\alpha_i\alpha_j\rangle$ (see Exercise A.8).

Let us now apply this formalism to a PVT system. We consider a monatomic fluid in a closed isolated box with volume, V_{T}, total entropy, S_{T}, total energy, E_{T}, total number of particles, N_{T}, and total mass, M_{T}. We shall assume that the box is divided into l cells of equal size and that at equilibrium the volume, entropy, internal energy, and mass of particles in the ith cell are $V_{\mathrm{i}} = V_0, S_i, U_i$, and M_i, respectively. The total volume of the box is then $V_{\mathrm{T}} = lV_0$. The equilibrium pressure, temperature, and chemical potential of the whole system are denoted P°, T°, and μ°, respectively.

From Eq. (3.69), the entropy change due to deviations in various thermodynamic quantities from their equilibrium state can be written

$$\Delta S_{\mathrm{T}} = \frac{1}{2T_0} \sum_{i=1}^{l} \left(-\Delta T_{\mathrm{i}} \Delta S_i + \Delta P_{\mathrm{i}} \Delta V_{\mathrm{i}} - \Delta \mu_i \Delta M_i \right) , \tag{3.92}$$

where we now use the mass of particles in the ith cell as the extensive chemical state variable (as opposed to particle number or mole number) and the chemical potential has appropriate units for that choice.

We next obtain an expression for ΔS_{T} in terms of a set of independent variables. Let us first pull the volume dependence out of the expression for ΔS_{T}. We will write $S = V_0 s$ and $M = V_0 \rho$, where s is entropy/volume and ρ is mass/volume. Let us next note that the Gibbs–Duhem equation, when written in terms of mass density, ρ, takes the form $\rho\, \mathrm{d}\mu = -s\, \mathrm{d}T + \mathrm{d}P$ so the fluctuations satisfy the relation $\rho \Delta\mu = -s\Delta T + \Delta P$. Therefore, $\Delta T \Delta S - \Delta P \Delta V + \Delta\tilde{\mu}\Delta M = V_0(\Delta T \Delta s + \Delta\mu\Delta\rho)$. The differential of the Helmholtz free energy/volume, a, satisfies the equation $\mathrm{d}a = -s\, \mathrm{d}T + \mu\, \mathrm{d}\rho$, so $(\partial\mu/\partial T)_\rho = -(\partial s/\partial\rho)_{\mathrm{T}}$. If we now choose temperature T and mass density ρ as independent variables, we obtain

$$\Delta T \Delta S - \Delta P \Delta V + \Delta\mu\Delta M = V_0 \left[\frac{c_\rho}{T^\circ} (\Delta T)^2 + \left(\frac{\partial\mu}{\partial\rho} \right)_T^0 (\Delta\rho)^2 \right] , \tag{3.93}$$

where c_ρ is the equilibrium specific heat.

We can write the probability of a fluctuation $\boldsymbol{\alpha}^{\mathrm{T}} = (\{\Delta T_{\mathrm{i}}\}, \{\Delta\rho_i\})$ in the form

$$P(\{\Delta T_{\mathrm{i}}, \Delta\rho_i\}) = \sqrt{\frac{\left(V_0 c_\rho / T^{\circ 2}\right)^l \left[(V_0/T^\circ)(\partial\mu/\partial\rho)_{\mathrm{T}}^0\right]^l}{(2\pi k_{\mathrm{B}})^{2l}}}$$

$$\times \exp\left\{ -\frac{1}{2k_{\mathrm{B}}} \sum_{i=1}^{l} \left[\frac{V_0 c_\rho}{T^{\circ 2}} (\Delta T_{\mathrm{i}})^2 + \frac{V_0}{T^\circ} \left(\frac{\partial\mu}{\partial\rho} \right)_T^0 (\Delta\rho_i)^2 \right] \right\} , \tag{3.94}$$

(see Eq. (3.88)), where we have used the fact that $g_{i,j} = (V_0 c_\rho)/T^{\circ 2}$ if $i = j$ and $1 \le i \le l$; $g_{i,j} = (V_0/T^\circ)(\partial\mu/\partial\rho)_{\mathrm{T}}^0$ if $i = j$ and $l + 1 \le i \le 2l$; and $g_{i,j} = 0$ otherwise, and we have written the determinant of $\bar{\boldsymbol{g}}$ under the square root. From Eq. (3.91), we obtain expressions for moments of the fluctuations inside various cells

$$\langle \Delta\rho_j \Delta T_k \rangle = \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \mathrm{d}(\Delta\rho_1) \cdots \mathrm{d}(\Delta\rho_{\mathrm{l}})\,\mathrm{d}(\Delta T_1) \ldots \mathrm{d}(\Delta T_{\mathrm{l}}) \times P(\{\Delta T_{\mathrm{i}}, \Delta\rho_i\}) \Delta\rho_j \Delta T_k = 0\,, \tag{3.95}$$

$$\langle (\Delta\rho_j)^2 \rangle = \frac{k_{\mathrm{B}} T^\circ}{V_0} \left[\left(\frac{\partial\mu}{\partial\rho} \right)_{\mathrm{T}}^{0} \right]^{-1}, \tag{3.96}$$

$$\langle (\Delta T_j)^2 \rangle = \frac{T^{\circ 2} k_{\mathrm{B}}}{V_0 c_\rho}\,, \tag{3.97}$$

and

$$\langle \Delta\rho_j \rangle = \langle \Delta T_j \rangle = 0\,. \tag{3.98}$$

Note that the variances in temperature and density fluctuations are inversely proportional to response functions. We have found that fluctuations in temperature and density are statistically independent. Pressure and entropy fluctuations are also statistically independent, but fluctuations in most other pairs of thermodynamic variables are not statistically independent.

It is important to note that, in Eqs. (3.95)–(3.98), we found no correlation between various cells. This result was built into the theory because Eq. (3.92) contains no information about coupling between cells. In real systems, there is coupling between cells. This can be included in the theory by expressing ΔS_i and ΔP_{i} in terms of temperature and volume variations in other cells and not just those of cell *i*. The more general expression will then contain coupling constants which reflect the strength of the coupling between the cells.

In this section, we have analyzed fluid systems by dividing them into discrete cells. This, of course, is a rather artificial way to proceed, but it is conceptually very simple and gives us good intuition about which thermodynamic quantities govern the behavior of fluctuations about the equilibrium state. It is a simple matter to change the summations over discrete cells to integrations over continuously varying densities, provided that the spatial variations have sufficiently long wavelengths (vary slow enough). We shall look at the spatial dependence of fluctuations in later chapters.

3.8
Cooling and Liquefaction of Gases

The molecules that compose neutral gases interact via a potential that has a hard core and a short-ranged attractive region. If such a gas is allowed to expand freely, it must do work against the attractive forces and its temperature will decrease.

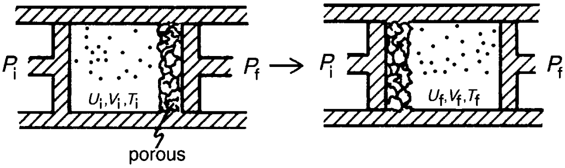


Figure 3.4 The Joule–Kelvin effect. Throttling of a gas through a porous plug can cause cooling or heating.

This effect can be used to cool a gas, although the amount of cooling that occurs via this mechanism alone is very small. (An ideal gas will have no temperature change during free expansion.) Throttling of a gas through a porous plug or a small constriction provides a much more efficient means of cooling than free expansion and is the basis of most liquification machines [220]. The throttling process in its simplest form is depicted in Figure 3.4. A gas initially at a pressure, P_i, temperature, T_i, and volume, V_i, is forced through a porous plug into another chamber, maintained at pressure, $P_f < P_i$. All chambers and the plug are insulated so $\Delta Q = 0$ for the process. The gas inside the plug is forced through narrow twisting chambers irreversibly. Work must be done to force the gas through the plug. Even though the entire process is irreversible, we can use thermodynamics to relate the initial and final states.

The net work done by the gas is

$$\Delta W = \int_0^{V_f} P_f \, dV + \int_{V_i}^{0} P_i \, dV = P_f V_f - P_i V_i \, . \tag{3.99}$$

From the first law, $\Delta U = -\Delta W$ since $\Delta Q \equiv 0$. Thus,

$$H_i = U_i + P_i V_i = U_f + P_f V_f = H_f \, . \tag{3.100}$$

Thus, the throttling process is one which takes place at constant enthalpy.

Let us now construct a hypothetical reversible path to describe the constant enthalpy process. For each differential change along the reversible path, we have (assuming the total particle number remains constant) $[dH]_{\mathfrak{n}} = 0 = T\, dS + V\, dP$. We see that the increase in entropy due to the throttling process is accompanied by a decrease in pressure. It is convenient to use temperature and pressure as independent variables rather than entropy and pressure. We therefore expand the entropy $[dS]_{\mathfrak{n}} = (\partial S/\partial T)_{P,\mathfrak{n}}\, dT + (\partial S/\partial P)_{T,\mathfrak{n}}\, dP$ and obtain

$$[dH]_{\mathfrak{n}} = 0 = C_{P,\mathfrak{n}}\, dT + \left[V - T \left(\frac{\partial V}{\partial T} \right)_{P,\mathfrak{n}} \right] dP \, . \tag{3.101}$$

In Eq. (3.101) we have used Eq. (3.50). Equation (3.101) can be rewritten in the form $dT = (\partial T/\partial P)_{H,\mathfrak{n}}\, dP$, where $(\partial T/\partial P)_{H,\mathfrak{n}}$ is the *Joule–Kelvin coefficient* and is defined

$$\left(\frac{\partial T}{\partial P} \right)_{H,\mathfrak{n}} = -\frac{(\partial H/\partial P)_{T,\mathfrak{n}}}{(\partial H/\partial T)_{P,\mathfrak{n}}} = \frac{1}{C_{P,\mathfrak{n}}} \left[T \left(\frac{\partial V}{\partial T} \right)_{P,\mathfrak{n}} - V \right] \, . \tag{3.102}$$

Let us now compute the Joule–Kelvin coefficient for various gases. For an ideal gas, $(\partial V/\partial T)_{P,\mathfrak{n}} = V/T$ and therefore the Joule–Kelvin coefficient, $(\partial T/\partial P)_{H,\mathfrak{n}} = 0$. There will be no temperature change during the throttling process for an ideal gas. Furthermore, since $T_{\mathrm{i}} = T_{\mathrm{f}}$ for ideal gases, $P_{\mathrm{f}} V_{\mathrm{f}} = P_{\mathrm{i}} V_{\mathrm{i}}$ and no net work will be done ($\Delta W = 0$).

For a van der Waals gas, assuming that $C_{V,n} = 3/2nR$, we find

$$\left(\frac{\partial T}{\partial P}\right)_{H,\mathfrak{n}} = \frac{1}{R}\left[\frac{2a}{RT}\left(\frac{v-b}{v}\right)^2 - b\right] \Big/ \left[\frac{5}{2} - \frac{3a}{RTv}\left(\frac{v-b}{v}\right)^2\right] , \tag{3.103}$$

where $v = V/\mathfrak{n}$ is the molar volume. Equation (3.103) is straightforward to obtain from the right-hand term in Eq. (3.102) using the Maxwell relation $(\partial S/\partial X)_{T,N} = -(\partial Y/\partial T)_{X,N}$ (see Table 3.3) and Eq. (3.49). For an interacting gas, such as the van der Waals gas, the Joule–Kelvin coefficient can change sign. This is easiest to see if we consider low densities so that $RTv \gg a$ and $v \gg b$. Then

$$\left(\frac{\partial T}{\partial P}\right)_{H,\mathfrak{n}} \approx \frac{2}{5R}\left[\frac{2a}{RT} - b\right] . \tag{3.104}$$

For low temperatures $(\partial T/\partial P)_{H,\mathfrak{n}} > 0$, and gases cool in the throttling process, but at high temperatures, we have $(\partial T/\partial P)_{H,\mathfrak{n}} < 0$, and they heat up. Two effects determine the behavior of the Joule–Kelvin coefficient. On the one hand, the gas expands, which gives rise to cooling. On the other hand, work can be done on or by the gas. If $P_{\mathrm{i}} V_{\mathrm{i}} > P_{\mathrm{f}} V_{\mathrm{f}}$, then net work is done on the gas, which causes heating. If $P_{\mathrm{i}} V_{\mathrm{i}} < P_{\mathrm{f}} V_{\mathrm{f}}$, then net work is done by the gas, which causes cooling.

The inversion temperature (the temperature at which the sign of μ_{JK} changes) for the Joule–Kelvin coefficient will be a function of pressure. Since $C_{P,n} > 0$, the condition for inversion (from Eq. (3.102)) is $(\partial V/\partial T)_{P,\mathfrak{n}} = V/T$ or, for a van der Waals gas (cf. Eq. (3.103)),

$$\frac{2a}{RT}\left(\frac{v-b}{v}\right)^2 = b . \tag{3.105}$$

We can use the van der Waals equation of state to write Eq. (3.105) in terms of pressure and temperature. First solve Eq. (3.105) for v as a function R, T, a, and b,

Table 3.6 Van der Waals constants for some simple fluids [124].

	a (Pa m^6/mol^2)	**b (m^3/mol)**
H_2	0.024 53	0.000 026 51
He	0.003 456	0.000 023 70
CO_2	0.3658	0.000 042 86
H_2O	0.5537	0.000 030 49
O_2	0.1382	0.000 031 86
N_2	0.1370	0.000 038 7

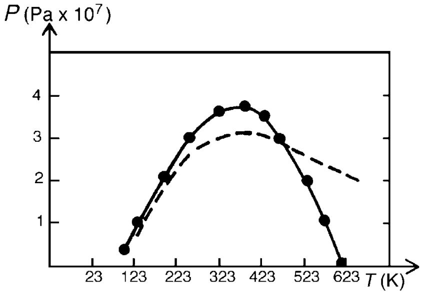


Figure 3.5 A plot of the inversion temperature versus pressure for the Joule–Kelvin coefficient of N_2. The solid line is the experimental curve [220]. The dashed line is the curve predicted by the van der Waals equation for $a = 0.1408\,\mathrm{Pa\,m^6/mol^2}$ and $b = 0.000\,039\,13\,\mathrm{m^3/mol}$.

and substitute into the van der Waals equation. This gives

$$P = \frac{2}{b}\sqrt{\frac{2aRT}{b}} - \frac{3RT}{2b} - \frac{a}{b^2}\,. \tag{3.106}$$

The inversion curve predicted by the van der Waals equation has the shape of a parabola with a maximum at $T_{\max}^{\mathrm{VW}} = 8a/9bR$. For CO_2, $T_{\max}^{\mathrm{VW}} = 911\,\mathrm{K}$ while the experimental value [24] is $T_{\max} = 1500\,\mathrm{K}$. For H_2, $T_{\max}^{\mathrm{VW}} = 99\,\mathrm{K}$ while the experimental value is $T_{\max} = 202\,\mathrm{K}$. In Figure 3.5, we plot the van der Waals and the experimental inversion curves for N_2. The van der Waals equation predicts an inversion curve which lies below the experimental curve but qualitatively has the correct shape. For nitrogen at $P = 10^5\,\mathrm{Pa}$, $\mu_{\mathrm{JK}} = 1.37 \times 10^{-7}\,\mathrm{K/Pa}$ at $T = 573\,\mathrm{K}$, $\mu_{\mathrm{JK}} = 1.27 \times 10^{-6}\,\mathrm{K/Pa}$ at $T = 373\,\mathrm{K}$, $\mu_{\mathrm{JK}} = 6.40 \times 10^{-6}\,\mathrm{K/Pa}$ at $T = 173\,\mathrm{K}$, and $\mu_{\mathrm{JK}} = 2.36 \times 10^{-5}\,\mathrm{K/Pa}$ at $T = 93\,\mathrm{K}$. (For experimental value of the Joule–Kelvin coefficient for other substances, see the International Critical Tables [207].) We see that the cooling effect can be quite large for throttling.

At times the Joule–Kelvin effect can lead to serious difficulties. For example, highly compressed H_2, which has a low inversion temperature, can ignite spontaneously when leaking from a damaged container, because of Joule–Kelvin heating.

3.9
Osmotic Pressure in Dilute Solutions

Each spring, when the weather begins to warm up, sap rises in trees and the yearly cycle of life starts again. The rising of sap is one of many examples in biological systems of the phenomenon called *osmosis*. One can easily demonstrate the effect in the laboratory. Take a beaker of water and partially immerse a long tube (open at both ends) in it and let it stand vertically. The water levels of the tube and of the beaker will be the same. Next, close off the bottom end of the tube with a membrane which is permeable to water but not sugar. The water levels will still be the same in the tube and the beaker. Now add a bit of sugar to the water in the tube. Additional water will begin to enter the tube through the membrane, and

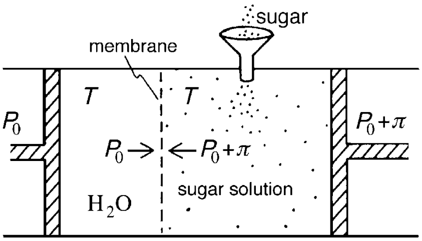


Figure 3.6 A schematic representation of osmosis.

the level of the sugar solution will rise a distance h above the level of the water in the beaker. The excess pressure created in the tube, $\pi = \rho_s hg$, is called the *osmotic pressure* (ρ_s is the density of the sugar solution and g is the acceleration of gravity). After equilibrium is reached, the pressure at the surface of the pure water will be P_A (atmospheric pressure) and the pressure in the sugar solution, at the same level, will be $P_A + \rho_s hg$. The membrane must sustain the unbalanced force between the pure water and the sugar solution.

We can show the same phenomenon in another way (cf. Figure 3.6). Consider a system consisting of pure water, separated by a permeable (to water) membrane from a solution of sugar and water. The entire system is kept at a fixed temperature T, and the membrane is rigid and fixed in place. At equilibrium, there will be an imbalance in the pressures of the two sides. If P_0 is the pressure of the pure water, than the sugar solution will have a pressure $P = P_0 + \pi$, where π is the *osmotic pressure*. This imbalance of pressures is possible because the membrane is rigid and cannot transmit mechanical energy. Since the water is free to move through the membrane, the chemical potential of the pure water must be equal to the chemical potential of the water in the sugar solution.

Let us write the thermodynamic relations for this system. First consider the sugar solution. A differential change in the Gibbs free energy, $G = G(P, T, \mathfrak{n}_w, \mathfrak{n}_s)$, of the sugar solution (with $\mathfrak{n}_w$ moles of water and $\mathfrak{n}_s$ moles of sugar) can be written

$$dG = -S\,dT + V\,dP + \mu_w\,d\mathfrak{n}_w + \mu_s\,d\mathfrak{n}_s\,, \tag{3.107}$$

where $S = -(\partial G/\partial T)_{P,\mathfrak{n}_w,\mathfrak{n}_s}$ is the entropy of the solution, $V = (\partial G/\partial P)_{T,\mathfrak{n}_w,\mathfrak{n}_s}$ is the volume of the solution, and $\mu_w = (\partial G/\partial \mathfrak{n}_w)_{P,T,\mathfrak{n}_s}$ and $\mu_s = (\partial G/\partial \mathfrak{n}_s)_{P,T,\mathfrak{n}_w}$ are the chemical potentials of the water and sugar, respectively, in the solution. The chemical potentials are intensive and depend only on ratios $\mathfrak{n}_s/\mathfrak{n}_w$. It is convenient to introduce mole fractions

$$x_w = \frac{\mathfrak{n}_w}{\mathfrak{n}_w + \mathfrak{n}_s} = \frac{1}{1 + \mathfrak{n}_s/\mathfrak{n}_w} \quad \text{and} \quad x_s = \frac{\mathfrak{n}_s}{\mathfrak{n}_w + \mathfrak{n}_s} = \frac{\mathfrak{n}_s/\mathfrak{n}_w}{1 + \mathfrak{n}_s/\mathfrak{n}_w}\,. \tag{3.108}$$

Since $x_w + x_s = 1$, the chemical potentials can be written as a function of mole fraction, x_s. Thus, $\mu_w = \mu_w(P, T, x_s)$ and $\mu_s = \mu_s(P, T, x_s)$.

At equilibrium, the chemical potentials of the pure water and the water in the sugar solution will be equal. If we let $\mu_w^{(0)}(P_0, T)$ denote the chemical potential of the pure water, we can write

$$\mu_w^{(0)}(P_0, T) = \mu_w(P, T, x_s) \tag{3.109}$$

as the condition for thermodynamic equilibrium.

We want to obtain an expression for the osmotic pressure in terms of measurable quantities. We will assume that the solution is dilute so that $\mathfrak{n}_s/\mathfrak{n}_w \ll 1$ and $x_s \approx \mathfrak{n}_s/\mathfrak{n}_w \ll 1$. We can construct a fairly simple model to describe the solution. We write the Gibbs free energy of the solution in the form

$$\begin{aligned} G(P, T, \mathfrak{n}_s, \mathfrak{n}_w) = {} & \mathfrak{n}_w \mu_w^{(0)}(P, T) + \mathfrak{n}_s \mu_s^{(0)}(P, T) - \lambda \frac{\mathfrak{n}_s \mathfrak{n}_w}{\mathfrak{n}} \\ & + \mathfrak{n}_w RT \ln x_w + \mathfrak{n}_s RT \ln x_s \, . \end{aligned} \tag{3.110}$$

The chemical potential $\mu_w^{(0)}$ ($\mu_s^{(0)}$) contains contributions to the Gibbs free energy due to the presence of water (sugar) molecules and due to self-interactions. The term $-\lambda(\mathfrak{n}_s \mathfrak{n}_w/\mathfrak{n})$ gives the contribution to the free energy due to interactions between sugar and water molecules. The last two terms on the right give contributions to the free energy due to mixing. The chemical potential of the water in the solution can now be written (see Exercise 3.3).

$$\mu_w(P, T, x_s) = \left(\frac{\partial G}{\partial \mathfrak{n}_w} \right)_{P,T,\mathfrak{n}_s} = \mu_w^{(0)}(P, T) - \lambda x_s^2 + RT \ln(1 - x_s) \, , \tag{3.111}$$

where $\mu_w^{(0)}(P, T)$ is the chemical potential of pure water at pressure P and temperature T. For a dilute solution, $x_s = \mathfrak{n}_s/\mathfrak{n} \ll 1$ and $\ln(1 - x_s) = -x_s - 1/2 x_s^2 - \cdots$ Thus, to lowest order in $x_s = \mathfrak{n}_s/\mathfrak{n}$, we find

$$\mu_w(P, T, x_s) \approx \mu_w^{(0)}(P, T) - x_s RT \tag{3.112}$$

for the chemical potential of water in a dilute sugar solution.

We now can find an expression for the osmotic pressure, $\pi = P - P_0$. Let us note that water, as well as most liquids, is very incompressible. The compressibility, κ_T, of water at 0 °C is $\kappa_T = 4.58 \times 10^{-10}\ \mathrm{m^2/N}$. Therefore the quantity $\left(\partial \mu_w^0/\partial P\right)_{T,\mathfrak{n}_w} = (\partial V^0/\partial \mathfrak{n}_w)_{T,P} \equiv v_w^0$ (v_w^0 is the partial molar volume of water in the absence of solute and V^0 is the volume of water in the absence of solute) remains approximately constant for small changes in pressure. With this observation we can integrate $\left(\partial \mu_w^0/\partial P\right)_{T,\mathfrak{n}_w}$ to find

$$\mu_w^0(P, T) - \mu_w^0(P_0, T) \approx v_w^0(P - P_0) = v_w^0 \pi \, . \tag{3.113}$$

The change in the volume of water as we increase the number of moles is proportional to the number of moles so that $V^0 = \mathfrak{n}_w v_w^0$. Also, for very small concentrations of solute, we can assume that the change in the volume of water due to the presence of the solute is negligible so that $V^0 \approx V$, where V is the volume of the mixture. Then we can combine Eqs. (3.109), (3.112), and (3.113) to obtain

$$\pi \approx \frac{\mathfrak{n}_s RT}{V} \, . \tag{3.114}$$

Equation (3.114) is called *van't Hoff's law* and, surprisingly, looks very much like the ideal gas law, although we are by no means dealing with a mixture of ideal gases. Equation (3.114) is well verified for all dilute neutral solvent–solute systems.

Exercise 3.10

An experiment is performed in which the osmotic pressure of a solution, containing $\mathfrak{n}_{\mathrm{suc}}$ moles of sucrose ($C_{12}H_{22}O_{11}$) and 1 kg of water (H_2O), is found to have the following values [85]: (a) for $\mathfrak{n}_{\mathrm{suc}} = 0.1$, $\pi = 2.53 \times 10^5$ Pa, (b) for $\mathfrak{n}_{\mathrm{suc}} = 0.2$, $\pi = 5.17 \times 10^5$ Pa, and (c) for $\mathfrak{n}_{\mathrm{suc}} = 0.3$, $\pi = 7.81 \times 10^5$ Pa. Compute the osmotic pressure of this system using van't Hoff's law. How do the computed values compare with the measured values?

Answer: The molecular weight of water (H_2O) is $M_{H_2O} = 18\,\mathrm{g/mol}$. Therefore, 1 kg of water contains 55.56 mol of water. The molar volume of water is $v_{H_2O} = 18 \times 10^{-6}\,\mathrm{m^3/mol}$. The osmotic pressure of the solution, according to van't Hoff's law, is

$$\pi = \frac{\mathfrak{n}_{\mathrm{suc}}}{55.56} \frac{(8.317\,\mathrm{J/K})(303\,\mathrm{K})}{18 \times 10^{-6}\,\mathrm{m^3/mol}} .$$

The computed values are as follows: (a) For $\mathfrak{n}_{\mathrm{suc}} = 0.1$, $\pi = 2.52 \times 10^5$ Pa, (b) for $\mathfrak{n}_{\mathrm{suc}} = 0.2$, $\pi = 5.04 \times 10^5$ Pa, and (c) for $\mathfrak{n}_{\mathrm{suc}} = 0.3$, $\pi = 7.56 \times 10^5$ Pa. The predictions of van't Hoff's law are good for a dilute solution of sucrose in water, but begin to deviate as the mole fraction of sucrose increases.

3.10
The Thermodynamics of Chemical Reactions

Chemical reactions involve the breaking and formation of electrical bonds between constituent atoms or parts of a molecule involved in the reaction. The manner in which atoms are joined together to form molecules is important for determining their thermodynamic properties. The two major types of chemical bonds are *covalent* bonds and *ionic* bonds. The strongest bonds are the covalent bonds, formed by the mutual sharing of electron pairs. In the molecule H_2, for example, the two hydrogen atoms are held together by a covalent bond. Ionic bonds involve the transfer of electrons from one atom to another, thus leaving one atom positively charged and the other atom negatively charged. The molecule is then held together by the electrostatic attraction of the two oppositely charged ions. In the sodium chloride molecule NaCl, for example, Na loses an electron and Cl gains an electron and the electrical attraction between Na^+ and Cl^- holds the molecule together. There is a whole range of chemical bonds between the two extremes of covalent and ionic bonds. For example, *polar* bonds involve the unequal sharing of electrons between the atoms that comprise the molecule and this can give rise to an electric dipole moment in the molecule. The water molecule H_2O, is held together by a covalent bond, but since the oxygen molecule is larger than the hydrogen atom the concentration of negative charge is greater around the oxygen atom than around the hydrogen atoms. As a consequence, the water molecule has a permanent electric dipole moment $d_e = 6.2 \times 10^{-30}\,\mathrm{C \cdot m}$.

When we deal with chemical reactions, we generally deal with large quantities of molecules breaking and reforming their chemical bonds. Regardless of the type of bonds involved, the macroscopic properties of all chemical reactions can be described by thermodynamics. In this section, we will limit our considerations to reactions involving electrically neutral species. The thermodynamics of ionic solutions (the flow of charged ions in electrically neutral solutions) requires a slight generalization of the discussion in this section [81, 95, 189].

Chemical reactions, in systems containing several species of molecules (which we will call A_1, A_2, A_3, and A_4), change the identity of the molecules through inelastic collisions. A typical case might be one where molecules A_1 and A_2 collide inelastically to form molecules A_3 and A_4. Conversely, molecules A_3 and A_4 can collide inelastically to form molecules A_1 and A_2. Collisions between molecules occur at random and can be either elastic or inelastic. For an inelastic collision to occur, the two molecules must have sufficient energy to overcome any potential barriers to the reaction which might exist. Chemical equilibrium [171, 172, 208] occurs when the rate of production of each chemical species is equal to its rate of depletion through chemical reactions. The chemical reactions themselves never stop, even at equilibrium.

In the early part of this century a Belgium scientist, de Donder, found that it was possible to characterize each chemical reaction by a single variable ξ, called the *degree of reaction*. In terms of ξ, it is then possible to determine when the Gibbs free energy has reached its minimum value (chemical reactions usually take place in systems with fixed temperature and pressure) and therefore when the chemical system reaches chemical equilibrium. The concept of degree of reaction assumes that we can generalize the concept of Gibbs free energy to systems out of equilibrium.

3.10.1
The Affinity

Let us consider a chemical reaction of the form

$$-\nu_1 A_1 - \nu_2 A_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \nu_3 A_3 + \nu_4 A_4 \tag{3.115}$$

The quantities ν_1, ν_2, ν_3, and ν_4 are called *stoichiometric coefficients*; ν_j is the number of molecules of type *j* needed for the reaction to take place. By convention, ν_1 and ν_2 are negative. The constant k_1 is the rate constant for the forward reaction, and k_2 is the rate constant for the backward reaction.

Since we generally deal with large quantities of molecules undergoing chemical reactions, it is convenient to describe changes in the amounts of each species of molecule in terms of moles. Let $\mathrm{d}\mathfrak{n}_j$ denote the change in the number of moles of a molecule of type *j*. It is possible to characterize the changes $\mathrm{d}\mathfrak{n}_j$ for a given chemical reaction in terms of the single parameter, ξ, called the *degree of reaction*. We will use the convention that $\mathrm{d}\xi > 0$ for reactions proceeding to the right and $\mathrm{d}\xi < 0$ for reactions proceeding to the left. Any changes in the concentrations due to the reaction can therefore be written

$$\mathrm{d}\mathfrak{n}_1 = \nu_1\,\mathrm{d}\xi\,, \quad \mathrm{d}\mathfrak{n}_2 = \nu_2\,\mathrm{d}\xi\,, \quad \mathrm{d}\mathfrak{n}_3 = \nu_3\,\mathrm{d}\xi\,, \quad \mathrm{d}\mathfrak{n}_4 = \nu_4\,\mathrm{d}\xi\,. \tag{3.116}$$

These changes in the thermodynamic properties of a system, due to a given chemical reaction, can be characterized by a single variable ξ.

From Table 3.4 and Eq. (3.116), differential changes in the Gibbs free energy may be written

$$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}P + \sum_{j=1}^{m}\mu_j\,\mathrm{d}\mathfrak{n}_j = -S\,\mathrm{d}T + V\,\mathrm{d}P + \sum_{j=1}^{m}\mu_j\nu_j\,\mathrm{d}\xi\,, \tag{3.117}$$

where the sum is over the species which participate in the reaction and m is the number of species that participate in the reaction (for the reaction in (3.115) $m = 4$). Therefore,

$$\left(\frac{\partial G}{\partial \xi}\right)_{P,T} = \sum_{j=1}^{m}\mu_j\nu_j \equiv \mathcal{A}\,. \tag{3.118}$$

The quantity $\mathcal{A} \equiv \sum_{j=1}^{m}\mu_j\nu_j$ is called the *affinity* (in some books the affinity is defined with an opposite sign). At chemical equilibrium, the Gibbs free energy must be a minimum,

$$\left(\frac{\partial G}{\partial \xi}\right)_{P,T}^{0} = \mathcal{A}^0 = 0 \tag{3.119}$$

(the superscript 0 denotes equilibrium) and, therefore, at chemical equilibrium the affinity must be zero.

At constant P and T, the Gibbs free energy, G, must always decrease as the system moves toward chemical equilibrium (at equilibrium G is a minimum). Therefore,

$$[\mathrm{d}G]_{P,T} = \left(\frac{\partial G}{\partial \xi}\right)_{P,T}\mathrm{d}\xi < 0\,. \tag{3.120}$$

If the reaction goes to the right, then $\mathrm{d}\xi > 0$ and $\mathcal{A} < 0$. If the reaction goes to the left, then $\mathrm{d}\xi < 0$ and $\mathcal{A} > 0$. This decrease in the Gibbs free energy is due to spontaneous entropy production resulting from the chemical reactions.

If there are r chemical reactions in the system involving species, j, then there will be r parameters, ξ_k, needed to describe the rate of change of the number of moles, $\mathfrak{n}_j$:

$$\mathrm{d}\mathfrak{n}_j = \sum_{k=1}^{r}\nu_{jk}\,\mathrm{d}\xi_k\,. \tag{3.121}$$

The sum over k is over all chemical reactions in which molecules of type j participate.

Table 3.7 Values of the chemical potential, μ^0, for some molecules in the gas phase at pressure $P_0 = 1$ atm and temperature $T_0 = 298$ K [189].

Molecule	**μ^0 (kcal/mol)**
H_2	0.00
HI	0.31
I_2	4.63
N_2	0.00
NO_2	12.39
NH_3	−3.98
N_2O_4	23.49

Using ideal gas laws, some useful relations can be obtained for reactions in the gas phase. Consider a gas composed of four different kinds of molecules which undergo the reaction in Eq. (3.115). If the partial pressure of the ith constituent is P_i, the chemical potential of the ith constituent can be written in the form

$$\mu_j(P_j, T) = \mu_j^0(P_0, T_0) - RT \ln\left(\frac{P_0 T^{5/2}}{P_j T_0^{5/2}}\right) , \tag{3.122}$$

where $\mu_j^0(P_0, T_0)$ is the chemical potential of the jth constituent at pressure P_0 and temperature T_0. Values of μ_i^0, with $P_0 = 1$ atm and $T_0 = 298$ K, have been tabulated for many kinds of molecules [189]. Some of these are listed in Table 3.7.

If we use Eq. (3.122), the Gibbs free energy can be written

$$\begin{aligned} G(T, P, \xi) = {} & \sum_j \mathfrak{n}_j \mu_j^0(P_0, T_0) \\ & - \sum_j \mathfrak{n}_j RT \ln\left(\frac{P_0 T^{5/2}}{P T_0^{5/2}}\right) + RT \ln\left(x_1^{\mathfrak{n}_1} x_2^{\mathfrak{n}_2} x_3^{\mathfrak{n}_3} x_4^{\mathfrak{n}_4}\right) , \end{aligned} \tag{3.123}$$

and the affinity can be written

$$\mathcal{A}(T, P, \xi) = \sum_j \nu_j \mu_j^0(P_0, T_0) - \sum_j \nu_j RT \ln\left(\frac{P_0 T^{5/2}}{P T_0^{5/2}}\right) + RT \ln\left(\frac{x_3^{\nu_3} x_4^{\nu_4}}{x_1^{|\nu_1|} x_2^{|\nu_2|}}\right) , \tag{3.124}$$

where T and $P = \sum_j P_j$ are the temperature and pressure, respectively, at which the reaction occurs and $x_j = P_j/P = \mathfrak{n}_j/\mathfrak{n}$ are the mole fractions of the constituent chemicals.

For "ideal gas reactions" the equilibrium concentrations of the reactants can be deduced from the condition that at equilibrium the affinity is zero, $A^0 = 0$. From (3.124) this gives the equilibrium condition

$$\ln\left(\frac{x_3^{\nu_3} x_4^{\nu_4}}{x_1^{|\nu_1|} x_2^{|\nu_2|}}\right) = \sum_i \nu_i \ln\left(\frac{P_0 T^{5/2}}{P T_0^{5/2}}\right) - \frac{1}{RT} \sum_i \nu_i \mu_i^0(P_0, T_0) . \tag{3.125}$$

Equation (3.125) is called the *law of mass action*. As we shall show in Exercise 3.11, we can use it to compute the value of the degree of reaction, and therefore the mole fractions, at which chemical equilibrium occurs as a function of pressure and temperature.

We can deduce a number of useful results regarding the approach to chemical equilibrium. First, let us note that

$$\left(\frac{\partial^2 G}{\partial \xi^2}\right)^0_{P,T} = \left(\frac{\partial \mathcal{A}}{\partial \xi}\right)^0_{P,T} > 0\,. \tag{3.126}$$

Equation (3.126) is a statement of the fact that the Gibbs free energy, considered as a function of P, T, and ξ, is minimum at equilibrium for fixed T and P.

From the fundamental equation, $H = G + TS$, we obtain several important relations. First, let us note that at equilibrium, since $(\partial G/\partial \xi)^0_{P,T} = 0$, we have

$$\left(\frac{\partial H}{\partial \xi}\right)^0_{P,T} = T\left(\frac{\partial S}{\partial \xi}\right)^0_{P,T}\,. \tag{3.127}$$

Thus, changes in enthalpy are proportional to the changes in entropy. The left-hand side of Eq. (3.127) is called the *heat of reaction*. It is the heat absorbed per unit reaction in the neighborhood of equilibrium. For an *exothermic reaction*, $(\partial H/\partial \xi)^0_{P,T}$ is negative. For an *endothermic reaction*, $(\partial H/\partial \xi)^0_{P,T}$ is positive. Equation (3.127) can also be written (see Table 3.4)

$$\left(\frac{\partial H}{\partial \xi}\right)^0_{P,T} = -T\left(\frac{\partial \mathcal{A}}{\partial T}\right)^0_{P,\xi}\,, \tag{3.128}$$

where we have used the relation

$$-T\left[\frac{\partial}{\partial \xi}\left(\frac{\partial G}{\partial T}\right)_{P,\xi}\right]_{P,T} = -T\left[\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial \xi}\right)_{P,T}\right]_{P,\xi}\,.$$

For an “ideal gas reaction,” we can use Eqs. (3.124) and (3.128) to obtain an explicit expression for the heat of reaction. We find

$$\left(\frac{\partial H}{\partial \xi}\right)^0_{P,T} = \frac{5}{2}\sum_j \nu_j RT + \sum_j \nu_j RT \ln\left(\frac{P_0 T^{5/2}}{P T_0^{5/2}}\right) - RT\ln\left(\frac{x_3^{\nu_3} x_4^{\nu_4}}{x_1^{|\nu_1|} x_2^{|\nu_2|}}\right)\,. \tag{3.129}$$

If the total number of particles changes during the reaction ($\sum_j \nu_j \neq 0$), there will be contributions to the heat of reaction from two sources: (1) There will be a change in the heat capacity of the gas due to the change in particle number, and (2) there will be a change in the entropy due to the change in the mixture of the particles. If the total number of particles remains unchanged ($\sum_i \nu_i = 0$), the only contribution to the heat of reaction will come from the change in the mixture of particles (assuming we neglect changes to the heat capacity due to changes in the internal structure of the molecules).

Let us now obtain some other general properties of chemical reactions. From the chain rule (see Appendix B), we can write

$$\left(\frac{\partial \xi}{\partial T}\right)_{P,\mathcal{A}} = -\frac{(\partial \mathcal{A}/\partial T)_{P,\xi}}{(\partial \mathcal{A}/\partial \xi)_{P,T}} = \frac{1}{T}\frac{(\partial H/\partial \xi)_{P,T}}{(\partial \mathcal{A}/\partial \xi)_{P,T}} . \tag{3.130}$$

The denominator in Eq. (3.130) is always positive. Thus, at equilibrium any small increase in temperature causes the reaction to shift in a direction in which heat is absorbed.

Let us next note the Maxwell relation, $(\partial \mathcal{A}/\partial P)_{T,\xi} = (\partial V/\partial \xi)_{P,T}$, which enables us to write

$$\left(\frac{\partial \xi}{\partial P}\right)_{T,\mathcal{A}} = -\frac{(\partial \mathcal{A}/\partial P)_{T,\xi}}{(\partial \mathcal{A}/\partial \xi)_{P,T}} = -\frac{(\partial V/\partial \xi)_{P,T}}{(\partial \mathcal{A}/\partial \xi)_{P,T}} \tag{3.131}$$

(we have used identities from Appendix B). At equilibrium an increase in pressure at fixed temperature will cause the reaction to shift in a direction which decreases the total volume.

Exercise 3.11

Consider the reaction $N_2O_4 \rightleftharpoons 2NO_2$ which occurs in the gas phase. Start initially with one mole of N_2O_4 and no NO_2 and let $n_{N_2O_4} = 1 - \xi$ and $n_{NO_2} = 2\xi$. For $P_0 = 1\,\text{atm}$ and $T_0 = 298\,\text{K}$, $\mu^0_{N_2O_4} = 23.49\,\text{kcal/mol}$ and $\mu^0_{NO_2} = 12.39\,\text{kcal/mol}$. Assume that the reaction occurs at temperature T and pressure P. Use ideal gas equations for the chemical potential. (a) Compute and plot the affinity, $A(T, P, \xi)$, as a function of the degree of reaction, ξ, for $P = P_0$ and for $T = T_0$ and $T = 2T_0$. (b) What is the degree of reaction, ξ, at chemical equilibrium for $P = 1\,\text{atm}$ and temperature $T = 298\,\text{K}$ and how many moles of N_2O_4 and NO_2 are present at equilibrium? (c) If initially the volume is V_0, what is the volume at equilibrium for $P = 1\,\text{atm}$ and $T = 298\,\text{K}$? (d) What is the heat of reaction for $P = 1\,\text{atm}$ and $T = 298\,\text{K}$?

Answer: The mole fractions are $x_{N_2O_4} = (1 - \xi)/(1 + \xi)$ and $x_{NO_2} = 2\xi/(1 + \xi)$.

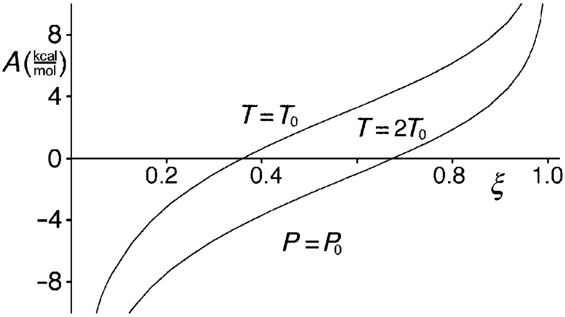
(a) The affinity is

$$A(T, P) = \sum_i \nu_i \mu_i^0(P_0, T_0) - \sum_i \nu_i RT \ln\left(\frac{P_0 T^{5/2}}{P T_0^{5/2}}\right) + RT \ln\left[\frac{(2\xi)^2}{1-\xi}(1+\xi)\right] .$$

Plots of $A(T, P)$ are given in the figure.

(b) Chemical equilibrium occurs for $\mathcal{A} = 0$. From the plot for $T = T_0$, at equilibrium the degree of reaction is $\xi_{eq} \approx 0.166$. Thus, at equilibrium $n_{N_2O_4} = 0.834$ and $n_{NO_2} = 0.332$. At equilibrium the mole fractions are $x_{N_2O_4} = 0.834/1.166 = 0.715$ and $x_{NO_2} = 0.332/1.166 = 0.285$.

(c) Initially $n_{N_2O_4} = 1\,\text{mol}$ and $n_{NO_2} = 0\,\text{mol}$ so one mol of gas is present. At chemical equilibrium, $n_{N_2O_4} = 0.834\,\text{mol}$ and $n_{NO_2} = 0.332\,\text{mol}$ so 1.166 mol of gas is present. The reaction occurs at temperature T_0 and pressure P_0. Therefore, the initial volume is $V_0 = 1RT_0/P_0$ and the equilibrium volume is $V = 1.166RT_0/P_0 = 1.166V_0$.



(d) If the reaction occurs at $T = T_0$ and $P = P_0$, the heat of reaction is

$$\left(\frac{\partial H}{\partial \xi}\right)^0_{P,T} = \frac{5}{2}RT_0 - RT_0 \ln\left(\frac{x^2_{NO_2}}{x_{N_2O_4}}\right)$$

$$= \frac{5}{2}RT_0 - RT_0 \ln\left(\frac{0.285^2}{0.715}\right) = 4.68RT_0 \,.$$

It is useful to note that much basic information about a given chemical reaction can be obtained using the lists of "Standard Thermodynamic Properties of Chemical Substances" found in [124]. These lists tabulate the standard molar Gibbs free energy Δg°, enthalpy Δh°, entropy s°, and heat capacity c°_p at $T = 298.15\,\text{K}$ and $P = 1.0\,\text{bar}$. The standard molar Gibbs free energy Δg° (enthalpy Δh°) is the Gibbs free energy (enthalpy) of formation of one mole of a given substance at $T = 298.15\,\text{K}$ and $P = 1.0\,\text{bar}$. By convention, elements in their most stable states at $T = 298.15\,\text{K}$ and $P = 1.0\,\text{bar}$ have zero Gibbs free energy (enthalpy). The standard molar entropy is defined relative to the entropy of a pure crystal of the given substance at $T = 0\,\text{K}$. For a pure crystal, at $T = 0\,\text{K}$, $s^\circ = 0$.

As an example of the use of these numbers, consider the chemical reaction $O_2 + 2H_2 \rightarrow 2H_2O$ at $T = 298.15\,\text{K}$ and $P = 1.0\,\text{bar}$. From the tables of "Standard Thermodynamic Properties of Chemical Substances" in [124], the molar Gibbs free energies of gaseous O_2 and H_2 and liquid H_2O are $\Delta g^\circ_{O_2} = 0$, $\Delta g^\circ_{H_2} = 0$, and $\Delta g^\circ_{H_2O} = -237.1\,\text{kJ/mol}$, respectively. The change in molar Gibbs free energy is $\Delta g^\circ_{\text{total}} = 2\Delta g^\circ_{H_2O} - \Delta g^\circ_{H_2} - \Delta g^\circ_{O_2} = -474.2\,\text{J/mol}$ and it decreases. Therefore, this reaction occurs spontaneously because it attempts to minimize the Gibbs free energy (approach equilibrium).

The molar enthalpies are $\Delta h^\circ_{O_2} = 0$, $\Delta h^\circ_{H_2} = 0$ and $\Delta h^\circ_{H_2O} = -285.8\,\text{kJ/mol}$. The change in enthalpy is $\Delta h^\circ_{\text{total}} = 2\Delta h^\circ_{H_2O} - \Delta h^\circ_{H_2} - \Delta h^\circ_{O_2} = -571.6\,\text{J/mol}$. $\Delta h^\circ_{\text{total}}$ shows that a large amount of heat is released in this reaction, which explains why this reaction is used to fuel rockets.

The molar entropies are $s^\circ_{O_2} = 205.2\,\text{kJ/(mol K)}$, $s^\circ_{H_2} = 130.7\,\text{kJ/(mol K)}$ and $s^\circ_{H_2O} = 70\,\text{kJ/(mol K)}$. The change in entropy is $s^\circ_{\text{total}} = 2s^\circ_{H_2O} - s^\circ_{H_2} - s^\circ_{O_2} = -195.9\,\text{kJ/(mol K)}$. Entropy decreases because the reaction has gone from a mixture to a pure substance and the H_2O has condensed into a liquid.

3.11
The Thermodynamics of Electrolytes

Electrolytes are substances that ionize when dissolved in certain solvents, such as water. Once the substance dissociates into ions in the solution, it has the capacity to conduct electricity or to create an electric potential energy gradient in the system [42, 81, 189]. When we consider a mixture of charged particles in the presence of an electrostatic potential ϕ, the definition of the chemical potential must be expanded to include the contribution to the energy required to add a particle with charge q to the mixture in the presence of the field. Let us assume there are N different kinds of charged particle in the mixture. Particles $j = 1, \dots, m$ are ions with charge $q_j = ez_j$, where z_j is the valency or charge of the ion and e is the charge of a proton. Particles $j = m+1, \dots, N$ are neutral (uncharged). Then differential changes in the internal energy density (internal energy per unit volume $u = U/V$) can be written

$$\mathrm{d}u = T\,\mathrm{d}s + \sum_{j=1}^{m} \mu_j^{\mathrm{e}}\,\mathrm{d}c_j + \sum_{j=m+1}^{N} \mu_j\,\mathrm{d}c_j \,, \tag{3.132}$$

where $s = S/V$, $c_j = n_j/V$ is the molar concentration of type j particles, $\mu_j^{\mathrm{e}} = \mu_j + z_j\phi F$ is the electrochemical potential, and F is the amount of charge in one mole of protons and is called a *Faraday* ($1\,\mathrm{F} = 96.485\,\mathrm{C/mol}$). For charged particles, equilibrium occurs when the electrochemical potentials of each species are equal.

A particularly important type of charged mixture (the type considered in this section) contains charged ions in an electrically neutral solution. Such systems are common in biological systems and form the basis for the construction of batteries. Let us consider the behavior of dilute solutions of a salt (the solute), such as NaCl, $CaCl_2$, $AgNO_3$, or $Cu(NO_3)_2$ in water (the solvent). If we denote the negative ion (the anion) as A^- and the positive ion (the cation) as C^+, the dissociation of the salt into charged ions can be denoted

$$\mathrm{A}_{\nu_{\mathrm{a}}}\mathrm{C}_{\nu_{\mathrm{c}}} \rightleftharpoons \nu_{\mathrm{a}}\mathrm{A}^- + \nu_{\mathrm{c}}\mathrm{C}^+ \tag{3.133}$$

(e. g., $\mathrm{CaCl_2} \rightleftharpoons 2\mathrm{Cl}^- + \mathrm{Ca}^{2+}$), where ν_{a} and ν_{c} are the stoichiometric coefficients for the dissociation. (We could also have $\mathrm{Ag} \to \mathrm{Ag}^+ + \mathrm{e}^-$ in an aqueous solution.) The condition for equilibrium is

$$\mu_{\mathrm{ac}} = \nu_{\mathrm{a}}\mu_{\mathrm{a}}^{\mathrm{e}} + \nu_{\mathrm{c}}\mu_{\mathrm{c}}^{\mathrm{e}} \,, \tag{3.134}$$

where $\mu_{\mathrm{a}}^{\mathrm{e}}(\mu_{\mathrm{c}}^{\mathrm{e}})$ is the electrochemical potential of ion, $\mathrm{A}^-(\mathrm{C}^+)$ and μ_{ac} is the chemical potential of the undissociated salt. Electrical neutrality of the fluid requires that $\nu_{\mathrm{a}}z_{\mathrm{a}} + \nu_{\mathrm{c}}z_{\mathrm{c}} = 0$, where $z_{\mathrm{a}}e(z_{\mathrm{c}}e)$ is the charge of the ion, $\mathrm{A}^-(\mathrm{C}^+)$, and e is the proton charge.

The chemical potential of the salt in aqueous solution is extremely complicated, but experiments show that it can be written in the form

$$\mu_{\mathrm{ac}}(P, T, x_{\mathrm{ac}}) = \mu_{\mathrm{ac}}^0(P, T) + RT \ln \alpha_{\mathrm{ac}} \,, \tag{3.135}$$

where α_{ac} is called the *activity* and $\mu^0_{\mathrm{ac}}(P, T)$ is the chemical potential of the salt in aqueous solution at temperature T and pressure P in the limit of infinite dilution ($\mu^0_{\mathrm{ac}}(P, T)$ is *proportional* to the energy needed to add one salt molecule to pure water).

We can relate the activity, α_{ac}, for the salt molecule to activities for the ions. We define $\alpha_{\mathrm{ac}} = \alpha_{\mathrm{a}}^{\nu_{\mathrm{a}}} \alpha_{\mathrm{c}}^{\nu_{\mathrm{c}}}$. Then

$$\ln(\alpha_{\mathrm{ac}}) = \nu_{\mathrm{a}} \ln(\alpha_{\mathrm{a}}) + \nu_{\mathrm{c}} \ln(\alpha_{\mathrm{c}}) \,. \tag{3.136}$$

The quantities α_{a} and α_{c} are defined to be the activities of the anion and cation, respectively. It is found experimentally that in the limit of infinite dilution, $\alpha_{\mathrm{a}} = f_{\mathrm{a}} c_{\mathrm{a}}$ and $\alpha_{\mathrm{c}} = f_{\mathrm{c}} c_{\mathrm{c}}$, where c_{a} and c_{c} are the concentrations (mol/volume) of the anions and cations, respectively. The quantities f_{c} and f_{c} are called *activity coefficients*. In the limit $c_i \to 0$, $f_i \to 1 (i = \mathrm{a, c})$. Solutions for which $f_{\mathrm{c}} = 1$ and $f_{\mathrm{a}} = 1$ are said to be *ideal*.

The condition for equilibrium, Eq. (3.134), for *ideal solutions* is satisfied if we define the electrochemical potentials of the ions to be

$$\mu^{\mathrm{e}}_j = \mu^0_j(P, T) + RT \ln c_j + z_j F \phi \tag{3.137}$$

where $j = \{\mathrm{a, c}\}$. Two important applications of the thermodynamics of electrolytes concerns the functioning of batteries and biological cells. We first consider batteries and then biological cells.

3.11.1
Batteries and the Nernst Equation

A simple battery consists of two "half-cells." Each half-cell contains a pure metal electrode immersed in a dilute aqueous solution of the corresponding salt (e. g., an Ag electrode with a dilute solution of $AgNO_3$ or a Cu electrode with a dilute solution of $Cu(NO_3)_2$).

For a half-cell with a silver (Ag) electrode, the salt dissociates into a dilute solution of Ag^+ and $NO_3{}^-$ ions, and an equilibrium is set up between the silver ions on the electrode and those in the solution. Either silver ions dissolve from the electrode into the solution, leaving excess electrons on the electrode, or silver ions in the solution can attach to the electrode leaving it with a net positive charge. In either case, a charged bilayer is set up at the interface between the electrode and the solution causing an electric potential energy difference between the solution and the electrode.

For simplicity, consider two half-cells, with silver electrodes, which we label $\mathcal{I}$ and $\mathcal{II}$. When the whole system is at equilibrium, the chemical potential of the silver ions in solution and silver ions on the electrode must be equal. The chemical potential on the electrode in $\mathcal{I}$ can be written $\mu^{\mathcal{I}}_{\mathrm{Ag}^+}(s) = \mu^{0,\mathcal{I}}_{\mathrm{Ag}^+}(s) + zF\Phi_{\mathcal{I}}$, since it is pure solid silver. The chemical potential of ions in the solution in $\mathcal{I}$ is $\mu^{\mathcal{I}}_{\mathrm{Ag}^+}(\ell) = \mu^{0,\mathcal{I}}_{\mathrm{Ag}^+}(\ell) + RT \ln[c_{\mathcal{I}}] + zF\phi_{\mathcal{I}}$. Similar expressions can be written for half-cell $\mathcal{II}$. The quantities $\mu^{0,\mathcal{I}}_{\mathrm{Ag}^+}(s)$ and $\mu^{0,\mathcal{I}}_{\mathrm{Ag}^+}(\ell)$ are the energies required to add one silver ion to the silver electrode and an infinitely dilute solution, respectively, $\Phi_{\mathcal{I}}$ and $\phi_{\mathcal{I}}$ are the electric potentials on the electrode and in the solution, respectively, and $c_{\mathcal{I}}$ is the concentration of silver ions in the solution.

The conditions for equilibrium between the silver ions on the electrode and the solution, in each of the half-cells, can be written

$$\mu^{0,\mathcal{I}}_{\mathrm{Ag}^+}(s) + zF\Phi_{\mathcal{I}} = \mu^{0,\mathcal{I}}_{\mathrm{Ag}^+}(\ell) + RT\ln c_{\mathcal{I}} + zF\phi_{\mathcal{I}} \, , \tag{3.138}$$

$$\mu^{0,\mathcal{II}}_{\mathrm{Ag}^+}(s) + zF\Phi_{\mathcal{II}} = \mu^{0,\mathcal{II}}_{\mathrm{Ag}^+}(\ell) + RT\ln c_{\mathcal{II}} + zF\phi_{\mathcal{II}} \, . \tag{3.139}$$

Now note that $\mu^{0,\mathcal{I}}_{\mathrm{Ag}^+}(s) = \mu^{0,\mathcal{II}}_{\mathrm{Ag}^+}(s)$, since they both apply to pure silver, and $\mu^{0,\mathcal{I}}_{\mathrm{Ag}^+}(\ell) = \mu^{0,\mathcal{II}}_{\mathrm{Ag}^+}(\ell)$ since they both apply to infinitely dilute solutions. Assume that electrical contact is made (via a salt-bridge for example) between the solutions in the two half-cells so that the electric potential energies of the solutions is the same. Then $\phi_{\mathcal{I}} = \phi_{\mathcal{II}}$, but the concentrations and temperatures need not be the same. We can now subtract Eqs. (3.138) and (3.139) and obtain

$$\Phi_{\mathcal{I}} - \Phi_{\mathcal{II}} = \frac{RT}{zF}\ln\left(\frac{c_{\mathcal{I}}}{c_{\mathcal{II}}}\right) = (0.0257\,\mathrm{V})\ln\left(\frac{c_{\mathcal{I}}}{c_{\mathcal{II}}}\right) \, . \tag{3.140}$$

Equation (3.140) is the Nernst equation. It relates the difference in the electric potential energy of the electrodes to the difference in the concentrations of silver ions in the two solutions. This electric potential difference can be measured with a volt meter. For example, if $c_{\mathcal{I}} = 2c_{\mathcal{II}}$ then $\Phi_{\mathcal{I}} - \Phi_{\mathcal{II}} = 0.0178$ V and a small voltage difference has been created between the two electrodes when thermodynamic equilibrium exists between the two half-cells. Thus, we have created a battery, although a rather weak one.

There are a number of different metals that can be used for batteries. The absolute potential on an electrode cannot be measured without changing the chemistry of the half-cell, so all voltages have been standardized relative to a *standard hydrogen half-cell*. A standard hydrogen half-cell uses a porous platinum electrode that serves as a catalyst for the reaction $\mathrm{H}_2 \rightarrow 2\mathrm{H}^+ + 2\mathrm{e}^-$. The platinum electrode is partially submerged in a dilute sulfuric acid ($\mathrm{H_2SO_4}$) solution at a temperature of $T = 298$ K. Hydrogen gas (H_2), at a pressure of $P = 1.0$ bar, flows over the porous platinum (see Figure 3.7) catalyzing the reaction. The concentration of hydrogen ions (H^+) in the solution is maintained at $c_{\mathrm{H}} = 1.0\,\mathrm{M} = 1.0\,\mathrm{mol/dm^3}$. This standard hydrogen half-cell is connected to a half-cell containing a solid metal electrode and corresponding salt solution (e. g. Cu and $\mathrm{Cu_2SO_4}$ or Zn and $\mathrm{Zn(NO_3)_2}$). The connection between the solutions is made via a "salt-bridge," so the potentials in the solutions can equilibrate. The concentration of the metal ion (let us assume Cu^{2+}) is also maintained at $c_{\mathrm{Cu}} = 1.0\,\mathrm{M} = 1.0\,\mathrm{mol/dm^3}$. The potential energy difference between the "hydrogen" (platinum) electrode and the Cu electrode, $\Delta\Phi^0 = \Phi^0_{\mathrm{Cu}} - \Phi^0_{\mathrm{H}}$, is measured. The potential $\Phi^0_{\mathrm{H}} \equiv 0$, by convention. In this way, the *standard electrode potential* Φ^0 of various metal half-cells can be determined and tabulated. Some *standard electrode potentials* include $\Phi^0_{\mathrm{Li}} = -3.03$ V, $\Phi^0_{\mathrm{Zn}} = -0.76$ V, $\Phi^0_{\mathrm{Fe}} = -0.44$ V, $\Phi^0_{\mathrm{H}} = 0.0$ V, $\Phi^0_{\mathrm{Cu}} = +0.34$ V, $\Phi^0_{\mathrm{Ag}} = +0.80$ V, and $\Phi^0_{\mathrm{Au}} = +1.50$ V.

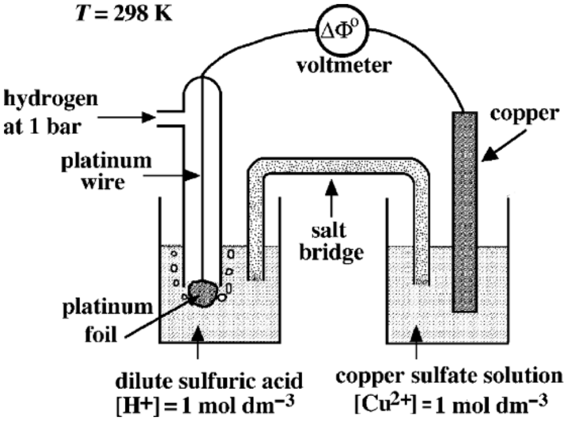


Figure 3.7 The standard hydrogen cell used to measure the *standard electrode potential* of various metals (in this case Cu).

The Nernst equation can also be used to determine the variation of a metal electrode potential from it's *standard value* Φ^0 by an analysis similar to that in Eqs. (3.138)–(3.140). We compute equilibrium conditions between the standard metal half-cell (metal ion concentration $c = 1.0$ M) and the standard hydrogen half-cell, and then we compute equilibrium conditions between the metal half-cell with metal ion concentration c and the standard hydrogen half-cell. If we then eliminate the parameters related to the standard hydrogen half-cell, we obtain

$$\Phi = \Phi^0 + \frac{RT}{zF} \ln[c] \,, \tag{3.141}$$

where Φ is the potential of the metal electrode, for metal ion concentration c, and Φ^0 is the *standard electrode potential* of the metal.

The *standard electrode potentials* can be used to determine the potential difference of two different metal half-cells. For example, a battery consisting of a Cu half-cell connected to a Zn half-cell, under standard conditions, can generate a voltage $\Phi^0_{\mathrm{Cu}} - \Phi^0_{\mathrm{Zn}} = +0.34\,\mathrm{V} - (-0.76\,\mathrm{V}) = 1.10\,\mathrm{V}$.

3.11.2
Cell Potentials and the Nernst Equation

Sports drinks contain electrolytes, such as potassium chloride KCl and sodium chloride NaCl, to help maintain the balance of cations (K^+ and Na^+) and anions (Cl^-) needed for proper cell function. All animal cells are surrounded by a lipid bilayer that is largely inert but contains embedded proteins that form selective ion channels. For example, potassium channels allow passage of potassium ions but effectively block passage of other types of ions. An aqueous solution of K^+, Na^+, and Cl^- ions outside a cell with potassium channels will allow the passage of 1000 potassium ions into the interior of the cell for every Na^+ ion allowed passage. As a consequence of this selective flow of potassium ions, an electric potential energy difference is established across the cell wall. Lipid bilayers have a width of about $\Delta d = 8\,\text{nm}$ and have a capacitance of about $C = 2.0\,\mu\text{F/cm}^3$. They can sustain a potential energy difference of up to about 0.2 V before breaking down.

When the system is in equilibrium, the electrochemical potential of K^+ inside, μ_K^in, and outside, μ_K^out, the cell must be equal. This equilibrium condition allows us to derive a Nernst equation that relates the potassium concentrations inside and outside the cell to the potential energy difference across the cell wall. The chemical potential inside the cell is $\mu_\text{K}^\text{in} = \mu_\text{K}^{0,\text{in}} + RT \ln c_\text{K}^\text{in} + z_\text{K} F \phi_\text{in}$, where ϕ_in is the electric potential inside the cell and $z_\text{K} = 1$ is the charge of potassium ions. Outside the cell the chemical potential is $\mu_\text{K}^\text{out} = \mu_\text{K}^{0,\text{out}} + RT \ln c_\text{K}^\text{out} + z_\text{K} F \phi_\text{out}$. Since $\mu_\text{K}^{0,\text{out}} \approx \mu_\text{K}^{0,\text{in}}$ is the energy needed to add one potassium ion to an infinitely dilute solution, we can equate these equations and obtain

$$\Delta\phi = \phi_\text{in} - \phi_\text{out} = \frac{RT}{z_\text{K} F} \ln\left(\frac{c_\text{K}^\text{out}}{c_\text{K}^\text{in}}\right) . \tag{3.142}$$

The potential energy difference, $\Delta\phi$, needed to maintain the potassium concentration difference is called the *Nernst potential* or *equilibrium* potential. For a body temperature of $T = 98\,°\text{C} = 295.6\,\text{K}$ the potential difference across the walls of a cell with only potassium channels is $\Delta\phi \approx (0.0255\,\text{V}) \ln\left(c_\text{K}^\text{out}/c_\text{K}^\text{in}\right)$.

The potassium channel is only one of several types of channels that exist in membranes. There are also sodium channels, calcium channels, and other types of ion channels. In addition, there are ion pumps, which play an active role in maintaining a potential difference across cell walls, and often these processes act together. The Nernst equation only applies when equilibrium exists between the intracellular and extracellular fluids.

3.12
Problems

Problem 3.1 Electromagnetic radiation in an evacuated vessel of volume V at equilibrium with the walls at temperature T (blackbody radiation) behaves like a gas of photons having internal energy $U = aVT^4$ and pressure $P = 1/3aT^4$, where a is Stefan's constant. (a) Plot the closed curve in the P–V plane for a Carnot cycle using blackbody radiation. (b) Derive *explicitly* the efficiency of a Carnot engine which uses blackbody radiation as its working substance.

Problem 3.2 A Carnot engine uses a paramagnetic substance as its working substance. The equation of state is $M = \mathfrak{n}DH/T$, where M is the magnetization, H is the magnetic field, $\mathfrak{n}$ is the number of moles, D is a constant determined by the type of substance, and T is the temperature. (a) Show that the internal energy U, and therefore the heat capacity C_M, can only depend on the temperature and not the magnetization. Let us assume that $C_M = C = \text{constant}$. (b) Sketch a typical

Carnot cycle in the M–H plane. (c) Compute the total heat absorbed and the total work done by the Carnot engine. (d) Compute the efficiency of the Carnot engine.

Problem 3.3 Find the efficiency of the engine shown in Figure 3.8a. Assume that the operating substance is an ideal monatomic gas. Express your answer in terms of V_1 and V_2. (The processes $1 \rightarrow 2$ and $3 \rightarrow 4$ are adiabatic. The processes $4 \rightarrow 1$ and $2 \rightarrow 3$ occur at constant volume.)

Problem 3.4 One kilogram of water is compressed isothermally at 20 °C from 1 to 20 atm. (a) How much work is required? (b) How much heat is ejected? Assume that the average isothermal compressibility of water during this process is $\kappa_T = 0.5 \times 10^{-4}/\text{atm}$ and the average thermal expansivity of water during this process is $\alpha_P = 2 \times 10^{-4}/°\text{C}$.

Problem 3.5 Compute the efficiency of the heat engine shown in Figure 3.8b. The engine uses a rubber band whose equation of state is $J = \alpha L T$, where α is a constant, J is the tension, L is the length, and T is the temperature in kelvins. The heat capacity is a constant, $C_{L,M} = C$. Assume the mass M is held fixed.

Problem 3.6 A heat engine uses blackbody radiation as its operating substance. The equation of state for blackbody radiation is $P = 1/3aT^4$ and the internal energy is $U = aVT^4$, where $a = 7.566 \times 10^{-16}\,\text{J}/(\text{m}^3\,\text{K}^4)$ is Stefan's constant, P is pressure, T is temperature, and V is volume. The engine cycle consists of three steps. Process $1 \rightarrow 2$ is an expansion at constant pressure $P_1 = P_2$. Process $2 \rightarrow 3$ is a decrease in pressure from P_2 to P_3 at constant volume $V_2 = V_3$. Process $3 \rightarrow 1$ is an adiabatic contraction from volume V_3 to V_1. Assume that $P_1 = 3.375P_3$, $T_1 = 2000\,\text{K}$, and $V_1 = 10^{-3}\,\text{m}^3$. (a) Express V_2 in terms of V_1 and $T_1 = T_2$ in terms of T_3. (b) Compute the work done during each part of the cycle. (c) Compute the heat absorbed during each part of the cycle. (d) What is the efficiency of this heat engine (get a number)? (e) What is the efficiency of a Carnot engine operating between the highest and lowest temperatures.

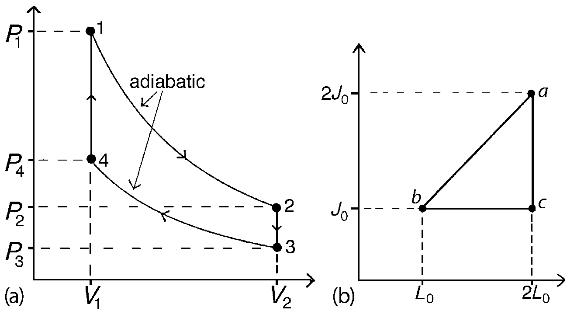


Figure 3.8 (a) Figure for P3.3. (b) Figure for P3.5.

Problem 3.7 Experimentally one finds that for a rubber band

$$\left(\frac{\partial J}{\partial L}\right)_{\mathrm{T},M} = \frac{aT}{L_0}\left[1+2\left(\frac{L_0}{L}\right)^3\right] \quad \text{and}$$

$$\left(\frac{\partial J}{\partial T}\right)_{L,M} = \frac{aL}{L_0}\left[1-\left(\frac{L_0}{L}\right)^3\right],$$

where J is the tension, $a = 1.0 \times 10^3\,\mathrm{dyn/K}$, and $L_0 = 0.5\,\mathrm{m}$ is the length of the band when no tension is applied. The mass M of the rubber band is held fixed. (a) Compute $(\partial L/\partial T)_{J,M}$ and discuss its physical meaning. (b) Find the equation of state and show that $\mathrm{d}J$ is an exact differential. (c) Assume that the heat capacity at constant length is $C_L = 1.0\,\mathrm{J/K}$. Find the work necessary to stretch the band reversibly and adiabatically to a length of 1 m. Assume that when no tension is applied, the temperature of the band is $T = 290\,\mathrm{K}$. What is the change in temperature?

Problem 3.8 Blackbody radiation in a box of volume V and at temperature T has internal energy $U = aVT^4$ and pressure $P = 1/3aT^4$, where a is the Stefan–Boltzmann constant. (a) What is the fundamental equation for blackbody radiation (the entropy)? (b) Compute the chemical potential.

Problem 3.9 For a low-density gas the virial expansion can be terminated at first order in the density and the equation of state is

$$P = \frac{Nk_\mathrm{B}T}{V}\left[1 + \frac{N}{V}B_2(T)\right],$$

where $B_2(T)$ is the second virial coefficient. The heat capacity will have corrections to its ideal gas value. We can write it in the form

$$C_{V,N} = \frac{3}{2}Nk_\mathrm{B} - \frac{N^2k_\mathrm{B}}{V}F(T).$$

(a) Find the form that $F(T)$ must have in order for the two equations to be thermodynamically consistent. (b) Find $C_{P,N}$. (c) Find the entropy and internal energy.

Problem 3.10 Prove that

$$C_{Y,N} = \left(\frac{\partial H}{\partial T}\right)_{Y,N} \quad \text{and} \quad \left(\frac{\partial H}{\partial Y}\right)_{T,N} = T\left(\frac{\partial X}{\partial T}\right)_{Y,N} - X.$$

Problem 3.11 Compute the entropy, enthalpy, Helmholtz free energy, and Gibbs free energy of a paramagnetic substance and write them explicitly in terms of their natural variables when possible. Assume that the mechanical equation of state is $m = (DH/T)$ and that the molar heat capacity at constant magnetization is $c_\mathrm{m} = c$, where m is the molar magnetization, H is the magnetic field, D is a constant, c is a constant, and T is the temperature.

Problem 3.12 Prove that (a) $\kappa_T(C_P - C_V) = TV\alpha_P^2$ and (b) $(C_P/C_V) = (\kappa_T/\kappa_S)$.

Problem 3.13 Show that $T\,\mathrm{d}s = c_x(\partial T/\partial Y)_x\,\mathrm{d}Y + c_Y(\partial T/\partial x)_Y\,\mathrm{d}x$, where $x = X/n$ is the amount of extensive variable, X, per mole, c_x is the heat capacity per mole at constant x, and c_Y is the heat capacity per mole at constant Y.

Problem 3.14 Compute the heat capacity at constant magnetic field $C_{H,\mathfrak{n}}$, the susceptibilities $\chi_{T,\mathfrak{n}}$ and $\chi_{S,\mathfrak{n}}$, and the thermal expansivity $\alpha_{\mathrm{H},\mathfrak{n}}$ for a magnetic system, given that the mechanical equation of state is $M = \mathfrak{n}D\mathrm{H}/T$ and the heat capacity is $C_{M,\mathfrak{n}} = \mathfrak{n}c$, where M is the magnetization, H is the magnetic field, $\mathfrak{n}$ is the number of moles, D is a constant, c is the molar heat capacity, and T is the temperature.

Problem 3.15 A material is found to have a thermal expansivity $\alpha_P = R/Pv + a/RT^2v$ and an isothermal compressibility $\kappa_T = 1/v(Tf(P) + (b/P))$, where $v = V/n$ is the molar volume. (a) Find $f(P)$. (b) Find the equation of state. (c) Under what conditions is this material mechanically stable?

Problem 3.16 Compute the efficiency of the two reversible heat engines in Figure 3.9a,b. Which engine is the most efficient? (Note that these are not Carnot cycles. The efficiency of a heat engine is $\eta = \Delta W_{\mathrm{total}}/\Delta Q_{\mathrm{absorbed}}$.)

Problem 3.17 It is found for a gas that $\kappa_T = Tvf(P)$ and $\alpha_P = Rv/P + Av/T^2$, where T is the temperature, v is the molar volume, P is the pressure, A is a constant, and $f(P)$ is an unknown function of P. (a) What is $f(P)$? (b) Find $v = v(P, T)$.

Problem 3.18 A boy blows a soap bubble of radius R which floats in the air a few moments before breaking. What is the difference in pressure between the air inside the bubble and the air outside the bubble when (a) $R = 1$ cm and (b) $R = 1$ mm? The surface tension of the soap solution is $\sigma = 25$ dyn/cm. (Note that soap bubbles have two surfaces.)

Problem 3.19 Imagine a droplet of water, in equilibrium with its vapor, placed on a wire frame that can stretch the surface area of the droplet, keeping the temperature fixed. Assume that the whole system, droplet, frame, and vapor is contained in a fixed total volume V and kept at temperature T. The grand potential of the system can be written $\Omega = \Omega_0 + \Omega_s$, where $\Omega_s = \sigma A$ is the surface grand potential, σ is the surface tension, A is the surface area of the liquid, and Ω_0 is the grand potential of the remainder of the system. Neglect contributions from the frame and

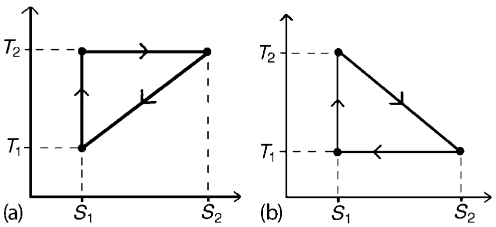


Figure 3.9 Figure for P3.16.

changes in the volume of the water droplet as it is stretched. The surface tension of water can be written

$$\sigma = \sigma_0 \left(1 - \frac{t}{t'}\right)^n ,$$

where $\sigma_0 = 75.5\,\text{dyn/cm}$ is the surface tension at temperature, $t = 0\,°\text{C}$, $n = 1.2$, and $t' = 368\,°\text{C}$. (a) Compute the internal energy per unit area of the surface assuming that the number of surface atoms, $N_\text{s} = 0$. (b) Plot the surface area and the surface internal energy per unit area for the temperature interval $t = 0\,°\text{C}$ to $t = t'$.

Problem 3.20 A stochastic process, involving three fluctuating quantities, x_1, x_2, and x_3, has a probability distribution

$$P(x_1, x_2, x_3) = C \exp\left[-\frac{1}{2}\left(2x_1^2 + 2x_1x_2 + 4x_2^2 + 2x_1x_3 + 2x_2x_3 + 2x_3^2\right)\right] ,$$

where C is the normalization constant. (a) Write probability distribution in the form $P(x_1, x_2, x_3) = C \exp(-1/2\boldsymbol{x}^\text{T} \cdot \boldsymbol{g} \cdot \boldsymbol{x})$, where $\boldsymbol{g}$ is a 3×3 symmetric matrix, $\boldsymbol{x}$ is a column matrix with matrix elements x_i, $i = 1, 2, 3$, and $\boldsymbol{x}^\text{T}$ is its transpose. Obtain the matrix $\boldsymbol{g}$ and its inverse $\boldsymbol{g}^{-1}$. (b) Find the eigenvalues λ_i $(i = 1, 2, 3)$ and orthonormal eigenvectors of $\boldsymbol{g}$ and obtain the 3×3 orthogonal matrix $\boldsymbol{O}$ that diagonalizes the matrix $\boldsymbol{g}$ (get numbers for all of them). Using this orthogonal matrix, we can write $\boldsymbol{x}^\text{T} \cdot \boldsymbol{g} \cdot \boldsymbol{x} = \boldsymbol{x}^\text{T} \cdot \boldsymbol{O}^\text{T} \cdot \boldsymbol{O} \cdot \boldsymbol{g} \cdot \boldsymbol{O}^\text{T} \cdot \boldsymbol{O} \cdot \boldsymbol{x} = \boldsymbol{a}^\text{T} \cdot \bar{\Lambda} \cdot \boldsymbol{a} = \sum_{i=1}^{3} \lambda_i a_i^2$, where $\boldsymbol{O} \cdot \boldsymbol{g} \cdot \boldsymbol{O}^\text{T} = \bar{\Lambda}$ is a 3×3 diagonal matrix with matrix elements $(\bar{\Lambda})_{i,j} = \lambda_i \delta_{i,j}$ and $\boldsymbol{O} \cdot \boldsymbol{x} = \boldsymbol{a}$ is a column matrix with elements a_i $(i = 1, 2, 3)$. (c) Compute the normalization constant, C. (d) Compute the moments $\langle x_i \rangle$ $(i = 1, 2, 3)$, $\langle x_i x_j \rangle$ $(i = 1, 2, 3, j = 1, 2, 3)$, $\langle x_1^2 x_2 x_3 \rangle$ and $\langle x_1 x_2^2 x_3 \rangle$. (Note that Exercises A.7 and A.8 might be helpful.)

Problem 3.21 A monatomic fluid in equilibrium is contained in a large insulated box of volume V. The fluid is divided (conceptually) into m cells, each of which has an average number N_0 of particles, where N_0 is large (neglect coupling between cells). Compute the variance of fluctuations of enthalpy per particle $h = H/N$ fluctuations. $\langle (\Delta h_i)^2 \rangle$, in the ith cell. (*Hint*: Use pressure P and entropy per particle $s = S/N$ as independent variables.)

Problem 3.22 A monatomic fluid in equilibrium is contained in a large insulated box of volume V. The fluid is divided (conceptually) into m cells, each of which has an average number of particles N_0, where N_0 is large (neglect coupling between cells). Compute the variance in fluctuations of internal energy per particle $u = U/N$, $\langle (\Delta u_i)^2 \rangle$, in the ith cell. (*Hint*: Use temperature T and volume per particle $v = V/N$ as independent variables.)

Problem 3.23 A monatomic fluid in equilibrium is contained in a large insulated box of total volume V. The fluid is divided conceptually into m cells, each with approximately the same average number of particles, N_0, where N_0 is large (neglect coupling between cells). Compute the variance, $\langle (\Delta s_i)^2 \rangle$ $(s = S/N$ is the entropy per particle), the variance $\langle (\Delta v_i)^2 \rangle$ $(v = V/N$ is the volume per particle), and the correlation between them $\langle(\Delta s_i \Delta v_i)\rangle$ in the ith cell (neglect interaction between neighboring cells). Where possible express your answers in terms of response functions, equilibrium temperature T_0, and equilibrium densities.

Problem 3.24 A van der Waals gas can be cooled by free expansion. Since no work is done and no heat is added during free expansion, the internal energy remains constant. An infinitesimal change in volume $\mathrm{d}V$ causes an infinitesimal temperature change in $\mathrm{d}T$, where

$$\mathrm{d}T = \left(\frac{\partial T}{\partial V}\right)_{U,\mathfrak{n}} \mathrm{d}V \,.$$

(a) Compute the Joule coefficient $(\partial T/\partial V)_{U,\mathfrak{n}}$ for a van der Waals gas (note that the heat capacity $C_{V,\mathfrak{n}}$ is independent of volume and use $C_{V,\mathfrak{n}} = 3/2\mathfrak{n}R$). (b) Compute the change in temperature of one mole of oxygen (O_2) and one mole of carbon dioxide (CO_2) if they each expand from an initial volume $V_\mathrm{i} = 10^{-3}\,\mathrm{m}^3$ at temperature $T_\mathrm{i} = 300\,\mathrm{K}$ to a final volume $V_\mathrm{f} = \infty$. (For O_2 the van der Waals constant is $a = 0.1382\,\mathrm{Pa\,m^6/mol^2}$ and for CO_2 it is $a = 0.3658\,\mathrm{Pa\,m^6/mol^2}$.)

Problem 3.25 Consider a gas obeying the Dieterici equation of state,

$$P = \frac{nRT}{(V - \mathfrak{n}b)} \exp\left(-\frac{\mathfrak{n}a}{VRT}\right) ,$$

where a and b are constants. (a) Compute the Joule coefficient $(\partial T/\partial V)_{U,\mathfrak{n}}$. (b) Compute the Joule–Kelvin coefficient $(\partial T/\partial P)_{H,\mathfrak{n}}$. (c) For the throttling process, find an equation for the inversion curve and sketch it. What is the maximum inversion temperature?

Problem 3.26 Two containers, each of volume V, contain ideal gas held at temperature T and pressure P. The gas in chamber 1 consists of $N_{1,a}$ molecules of type a and $N_{1,b}$ molecules of type b. The gas in chamber 2 consists of $N_{2,a}$ molecules of type a and $N_{2,b}$ molecules of type b. Assume that $N_{1,a} + N_{1,b} = N_{2,a} + N_{2,b}$. The gases are allowed to mix so the final temperature is T and the final pressure is P. (a) Compute the entropy of mixing. (b) What is the entropy of mixing if $N_{1,a} = N_{2,a}$ and $N_{1,b} = N_{2,b}$. (c) What is the entropy of mixing if $N_{1,a} = N_{2,b}$ and $N_{1,b} = N_{2,a} = 0$. Discuss your results for (b) and (c).

Problem 3.27 An insulated box with fixed total volume V is partitioned into m insulated compartments, each containing an ideal gas of a different molecular species. Assume that each compartment has the same pressure but a different number of moles, a different temperature, and a different volume. (The thermodynamic variables for the ith compartment are $(P, \mathfrak{n}_i, T_\mathrm{i}, V_\mathrm{i})$.) If all partitions are suddenly removed and the system is allowed to reach equilibrium: (a) Find the final temperature and pressure, and the entropy of mixing. (Assume that the particles are monatomic.) (b) For the special case of $m = 2$ and parameters $\mathfrak{n}_1 = 1\,\mathrm{mol}$, $T_1 = 300\,\mathrm{K}$, $V_1 = 1\,\mathrm{l}$, $\mathfrak{n}_2 = 3\,\mathrm{mol}$, and $V_2 = 2\,\mathrm{l}$, obtain numerical values for all parameters in part (a).

Problem 3.28 A tiny sack made of membrane permeable to water but not NaCl (sodium chloride) is filled with a 1% solution (by weight) of NaCl and water and is immersed in an open beaker of pure water at 38 °C at a depth of 1 ft. (a) What osmotic pressure is experienced by the sack? (b) What is the total pressure of the solution in the sack (neglect surface tension)? Assume that the sack is small enough that the pressure of the surrounding water can be assumed constant. (An example of such a sack is a human blood cell.)

Problem 3.29 Hemoglobin is a protein, carried by red blood cells, that transports oxygen from the lungs to tissue throughout the body. A $m = 21.5 \times 10^{-3}$ g sample of hemoglobin protein is dissolved in water at a temperature of 5 °C to form a 1.5 ml solution. The osmotic pressure of the solution is found to be $\pi = 0.00475$ atm. What is the molecular weight (in atomic mass units) of the hemoglobin molecule? (Historically, the molecular weight of the hemoglobin molecule was first determined by measuring osmotic pressure of such solutions.)

Problem 3.30 A biological molecule of unknown mass can be prepared in pure powdered form. If 15 g of this powder is added to a container with 1 L of water at $T = 300$ K, which is initially at atmospheric pressure, the pressure inside the container increases to $P = 1.3$atm. (a) What is the molecular weight of the biological molecules? (b) What is the mass of each molecule expressed in atomic units?

Problem 3.31 A solution of particles A and B has a Gibbs free energy

$$G(P, T, \mathfrak{n}_A, \mathfrak{n}_B) = \mathfrak{n}_A g_A(P, T) + \mathfrak{n}_B g_B(P, T) + \frac{1}{2}\lambda_{AA}\frac{\mathfrak{n}_A^2}{\mathfrak{n}} + \frac{1}{2}\lambda_{BB}\frac{\mathfrak{n}_B^2}{\mathfrak{n}} + \lambda_{AB}\frac{\mathfrak{n}_A\mathfrak{n}_B}{\mathfrak{n}} + \mathfrak{n}_A RT \ln x_A + \mathfrak{n}_B RT \ln x_B \,. \tag{3.143}$$

Initially, the solution has $\mathfrak{n}_A$ moles of A and $\mathfrak{n}_B$ moles of B. (a) If an amount, $\Delta\mathfrak{n}_B$, of B is added keeping the pressure and temperature fixed, what is the change in the chemical potential of A? (b) For the case $\lambda_{AA} = \lambda_{BB} = \lambda_{AB}$, does the chemical potential of A increase or decrease?

Problem 3.32 Consider the hypothetical reaction $2XY_2 \rightleftharpoons 2XY + Y_2$, which occurs in the gas phase. Start initially with two moles of XY_2 and zero moles each of XY and Y_2. Assume the reaction occurs at temperature T and pressure P. Use ideal gas equations for the chemical potential. The chemical potentials for these molecules in the gas phase at $T = 298.15$ K and $P = 1$ bar are $\mu_{XY_2} = -394.37$ J/mol, $\mu_{XY} = -137.17$ J/mol, and $\mu_{Y_2} = 0$. (a) Compute and plot the Gibbs free energy, $G(T, P, \xi)$, as a function of the degree of reaction ξ for (i) $P = 1$ bar and $T = 298.15$ K and (ii) $P = 1$ bar and $T = 398.15$ K. (b) Compute and plot the affinity $A(T, P, \xi)$, as a function of the degree of reaction ξ for (i) $P = 1$ bar and $T = 298.15$ K and (ii) $P = 1$ bar and $T = 398.15$ K. (c) What is the degree of reaction ξ at chemical equilibrium for $P = 1$ bar and $T = 298.15$ K? How many moles of XY_2, XY, and Y_2 are present at equilibrium? (d) If initially the volume of the gas was V_0, what is the volume at equilibrium for $P = 1$ bar and $T = 298.15$ K? (e) What is the heat of reaction for $P = 1$ bar and $T = 298.15$ K?

Problem 3.33 Consider the reaction

$$2\mathrm{HI} \rightleftharpoons \mathrm{H}_2 + \mathrm{I}_2$$

which occurs in the gas phase. Start initially with 2 mol of HI and 0 mol each of H_2 and I_2. Assume that the reaction occurs at temperature T and pressure P. Use ideal gas equations for the chemical potential. (a) Compute and plot the Gibbs free energy, $G(T, P, \xi)$, as a function of the degree of reaction, ξ, for (i) $P = 1$ atm and $T = 298$ K and (ii) $P = 1$ atm and $T = 596$ K. (b) Compute and plot the affinity, $A(T, P, \xi)$, as a function of the degree of reaction, ξ, for (i) $P = 1$ atm and $T = 298$ K and (ii) $P = 1$ atm and $T = 596$ K. (c) What is the degree of reaction, ξ, at chemical equilibrium for $P = 1$ atm and temperature $T = 298$ K? How many moles of HI, H_2, and I_2 are present at equilibrium? (d) If initially the volume is V_0, what is the volume at equilibrium for $P = 1$ atm and $T = 298$ K? (e) What is the heat of reaction for $P = 1$ atm and $T = 298$ K?

Problem 3.34 Consider the reaction

$$2\mathrm{NH}_3 \rightleftharpoons \mathrm{N}_2 + 3\mathrm{H}_2$$

which occurs in the gas phase. Start initially with 2 mol of NH_3 and 0 mol each of H_2 and N_2. Assume that the reaction occurs at temperature T and pressure P. Use ideal gas equations for the chemical potential. (a) Compute and plot the Gibbs free energy, $G(T, P, \xi)$, as a function of the degree of reaction, ξ, for (i) $P = 1$ atm and $T = 298$ K and (ii) $P = 1$ atm and $T = 894$ K. (b) Compute and plot the affinity, $A(T, P, \xi)$, as a function of the degree of reaction, ξ, for (i) $P = 1$ atm and $T = 298$ K and (ii) $P = 1$ atm and $T = 894$ K. (c) What is the degree of reaction, ξ, at chemical equilibrium for $P = 1$atm and temperature $T = 894$ K? How many moles of NH_3, H_2, and N_2 are present at equilibrium? (d) If initially the volume is V_0, what is the volume at equilibrium for $P = 1$ atm and $T = 894$ K? (e) What is the heat of reaction for $P = 1$ atm and $T = 894$ K?

4
The Thermodynamics of Phase Transitions

4.1
Introduction

A thermodynamic system can exist in a number of different phases and the macroscopic behavior of these various phases can differ dramatically. Generally, systems become more ordered as temperature is lowered because forces of cohesion begin to overcome thermal motion and atoms can rearrange themselves into more ordered states. Phase changes occur abruptly at some critical temperature, although evidence that a phase change will occur can be found on a macroscopic scale as the critical temperature is approached. In this chapter we will be concerned with the thermodynamics of phase transitions – that is, the description of phase transitions in terms of macroscopic variables. In later chapters we shall study them from a microscopic point of view.

The first step in analyzing phase changes is to map out the phase diagram for the system. At a transition point, two (or more) phases can coexist in equilibrium with each other. Since phases can exchange thermal and mechanical energy and matter, equilibrium occurs when the chemical potentials of the phases become equal for given values of Y and T. From this equilibrium condition, we can determine the maximum number of phases that can coexist and, in principle, find an equation for the regions of coexistence (the Clausius–Clapeyron equation, for example).

Phase transitions can be divided into two classes according the behavior of the Gibbs free energy. Phase transitions with discontinuous first derivatives of the Gibbs free energy (taken with respect to T and Y) are called *first-order phase transitions*. Phase transitions with continuous first derivatives, but discontinuous higher order derivatives, are called *continuous phase transitions*. We give examples of both in this chapter.

Classical fluids provide some of the most familiar examples of first-order phase transitions. The vapor–liquid, vapor–solid, and liquid–solid transitions are all first order. For these phase transitions, we can use the Clausius–Clapeyron equation to find explicit approximate equations for the coexistence curves. Since the vapor–liquid transition terminates in a critical point, we will focus on this transition and compare the observed behavior of the vapor–liquid coexistence region to that predicted by the van der Waals equation.

A Modern Course in Statistical Physics, 4. Edition. Linda E. Reichl.

A binary mixture of molecules in the fluid state provides a different example of a first-order phase transition. For such systems, below a certain critical temperature we can have a physical separation of the mixture into two fluids, each of which is rich in one of the types of molecules.

Superconductors and superfluids are especially interesting from the standpoint of thermodynamics because they exhibit phase transitions that depend on the quantum statistics of the particles. In the absence of a magnetic field, the transition of electrons in a metal, from a normal to a superconducting state, is a continuous phase transition. It is quantum mechanical in nature and results from a macroscopic condensation of pairs of electrons into a single quantum state. The superfluid transitions in liquid He^3 and liquid He^4 are of similar quantum origin. The superfluid transitions in liquid He^3 involve pairs of "dressed" He^3 atoms which condense, on a macroscopic scale, into a single quantum state. In liquid He^4 a macroscopic number of "dressed" He^4 atoms condense into the ground state. When liquid He^3 and liquid He^4 are mixed together, they form a binary mixture which can undergo both a continuous superfluid phase transition and a first-order binary phase transition.

A continuous phase transition is accompanied by a change in the symmetry properties of the two phases. Ginzburg and Landau developed a general theory of continuous symmetry-breaking phase transitions which involves an analytic expansion of the free energy in terms of the order parameter. We shall discuss the Ginzburg–Landau theory in this chapter and show how it can be applied to magnetic systems at the Curie point and to superfluid and superconducting systems.

The critical point plays a unique role in the theory of phase transitions. At a critical point, some thermodynamic variables can become infinite. Critical points occur in a huge variety of systems, but regardless of the particular substance or mechanical variable involved, there appears to be a universality in the behavior of all systems as they approach their critical points. One of the best ways to characterize the approach to a critical point is by means of critical exponents. We shall define critical exponents in this chapter and give explicit examples of some of them for the liquid–vapor transition in simple fluids and for the Curie point.

4.2
Coexistence of Phases: Gibbs Phase Rule

The *Gibbs phase rule* tells us how many phases can coexist, for a system in thermodynamic equilibrium. Generally, coexisting phases are in thermal and mechanical equilibrium and can exchange matter. Under these conditions, the temperature and chemical potentials of the phases must be equal (cf. Section 3.7) and there will be a condition expressing mechanical equilibrium. For example, for a simple PVT system, the pressures of the two phases will be equal (if surface tension can be neglected).

For simplicity, let us first consider a YXT system which is pure (composed of one kind of particle). For a pure system, two phases, I and II, can coexist at a fixed value

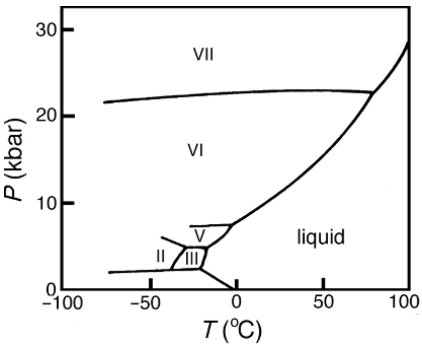


Figure 4.1 Coexistence curves for the solid and liquid phases of water. In accordance with the Gibbs phase rule, no more than three phases can coexist [21] (based on [172]).

of Y and T if their respective chemical potentials are equal $\mu^{\mathrm{I}}(Y, T) = \mu^{\mathrm{II}}(Y, T)$. (The chemical potentials are functions only of intensive variables.) This gives us a relation between the values of Y and T for which the phases can coexist, $Y = Y(T)$ and in the $Y{-}T$ plane it defines a *coexistence curve* for the two phases.

If the pure system has three phases, I, II, and III, they can only coexist at a single point in the $Y{-}T$ plane (the triple point). Three coexisting phases must satisfy the equations $\mu^{\mathrm{I}}(Y, T) = \mu^{\mathrm{II}}(Y, T) = \mu^{\mathrm{III}}(Y, T)$. Since we have two equations and two unknowns, the triple point is uniquely determined. For a pure system, four phases cannot coexist, because we would then have three equations and two unknowns and there would be no solution. *For a mixture of l different types of particles, at most $l + 2$ phases can coexist.*

As an example of the Gibbs phase rule for pure substances, we show the coexistence curves for various solid phases of water (cf. Figure 4.1). We see that although water can exist in many different solid phases, no more than three phases can coexist at a given temperature and pressure.

4.3
Classification of Phase Transitions

As we change the independent intensive variables $(Y, T, x_1, \dots, x_l)$ of a system, we reach values of the variables for which a phase change can occur. At such points the chemical potentials of the phases must be equal and the phases can coexist.

The fundamental equation for the Gibbs free energy, in a system with l different kinds of molecules, is $G = \sum_{j=1}^{l} \mathfrak{n}_j \mu_j$, where $\mathfrak{n}_j$ is the number of moles of the jth constituent and μ_j is its chemical potential (see Table 3.4). For processes which occur at constant Y and T, changes in the Gibbs free energy can be written

$$[\mathrm{d}G]_{Y,T} = \sum_{j=1}^{l} \mu_j \,\mathrm{d}\mathfrak{n}_j \,. \tag{4.1}$$

Thus, at a phase transition, the derivatives $\mu_j = \left(\partial G/\partial \mathfrak{n}_j\right)_{Y,T,\{\mathfrak{n}_{i\neq j}\}}$ in the two phases must be equal. However, no restriction is placed on the derivatives

$X = -(\partial G/\partial Y)_{T,\{n_j\}}$ and $S = -(\partial G/\partial T)_{Y,\{n_j\}}$. The behavior of these derivatives is used to classify phase transitions. If the derivatives $(\partial G/\partial Y)_{T,\{n_j\}}$ and $(\partial G/\partial T)_{Y,\{n_j\}}$ are discontinuous at the transition point (i. e., if the extensive variable X and the entropy S have different values in the two phases), the transition is called *first order*. If the derivatives $(\partial G/\partial T)_{Y,\{n_j\}}$ and $(\partial G/\partial Y)_{T,\{n_j\}}$ are continuous at the transition but higher order derivatives are discontinuous, then the phase transition is *continuous*. (The terminology "*n*th-order phase transition" was introduced by Ehrenfest to indicate a phase transition for which the *n*th derivative of G was the first discontinuous derivative. However, for some systems, higher order derivatives are infinite, and the theory proposed by Ehrenfest breaks down for those cases.)

In Figure 4.2, we plot the Gibbs free energy for a first-order transition in a PVT system. For such a system the Gibbs free energy must be a concave function of P and T (cf. Section 3.7). A discontinuity in $(\partial G/\partial P)_{T,\{n_j\}}$ means that there is the discontinuity in the volume of the two phases,

$$\Delta V = V^{\mathrm{I}} - V^{\mathrm{II}} = \left(\frac{\partial G}{\partial P}\right)^{\mathrm{I}}_{T,\{n_j\}} - \left(\frac{\partial G}{\partial P}\right)^{\mathrm{II}}_{T,\{n_j\}} , \tag{4.2}$$

and a discontinuity in $(\partial G/\partial T)_{P,\{n_j\}}$ means there is a discontinuity in the entropy of the two phases,

$$\Delta S = S^{\mathrm{I}} - S^{\mathrm{II}} = \left(\frac{\partial G}{\partial T}\right)^{\mathrm{II}}_{P,\{n_j\}} - \left(\frac{\partial G}{\partial T}\right)^{\mathrm{I}}_{P,\{n_j\}} . \tag{4.3}$$

Since the Gibbs free energy is the same for both phases at the transition, the fundamental equation $H = G + TS$ shows that the enthalpy of the two phases is dif-

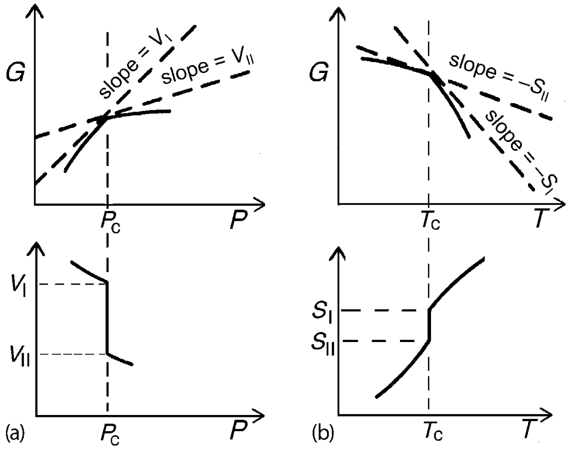


Figure 4.2 Typical behavior for the Gibbs free energy at a first-order phase transition. Plots of (a) G vs P and V versus P, and (b) G versus T and S versus T.

ferent,

$$\Delta H = H^{\mathrm{I}} - H^{\mathrm{II}} = T\Delta S \,, \tag{4.4}$$

for a first-order phase transition. The enthalpy difference, ΔH, is also called the *latent heat*.

For a continuous phase transition, the Gibbs free energy is continuous but its slope changes rapidly. This in turn leads to a peaking in the heat capacity at the transition point. For a continuous transition, there is no abrupt change in the entropy or the extensive variable (as a function of Y and T) at the transition.

In the subsequent sections we shall give examples of first-order and continuous phase transitions.

4.4
Classical Pure PVT Systems

A classical pure PVT system is a system composed of only one type of molecule that can exist in solid, liquid, and/or vapor phases [116, 196, 220]. This class of PVT system does not include the isotopes of helium, He^3 or He^4 at low temperature where they have superfluid phases, but it is typical of most other pure substances. Since we deal with pure substances in this section, it is convenient to describe their phase transitions in terms of molar densities.

4.4.1
Phase Diagrams

A typical set of coexistence curves for pure substances is given in Figure 4.3a. Point A on the diagram is the *triple point*, the point at which the gas, liquid, and solid phases can coexist. Point C is the *critical point*, the point at which the vaporization curve terminates. The fact that the vaporization curve has a critical point means that we can go continuously from a gas to a liquid without ever going through a phase transition, if we choose the right path. The fusion curve does not have a critical point (none has ever been found). We must go through a phase transition in going from the liquid to the solid state. This difference between the gas–liquid and liquid–solid transitions indicates that there is a fundamental difference between liquid–solid transition and the liquid–gas transition. The difference lies in their symmetry properties. Solids exhibit spatial ordering, while liquids and gases do not. (We will use "vapor" and "gas" interchangeably.)

The transitions from gas to liquid phase, from liquid to solid phase, and from gas to solid phase are all first-order transitions and are accompanied by a latent heat and a change in volume. In Figure 4.3b, we have drawn the phase diagram in the P–v plane. The dashed lines are lines of constant temperature. We notice that the slope of the dashed lines is negative, $(\partial P/\partial v)_T < 0$. This is a statement of the stability condition, $\kappa_T > 0$ (cf. Section 3.7). In the region of coexistence of phases,

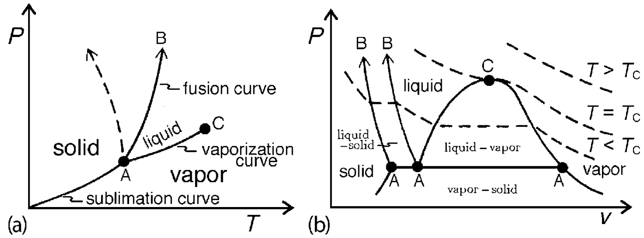


Figure 4.3 (a) Coexistence curves for a typical pure PVT system. Point A is the triple point and point C is the critical point. The dashed line is an example of a fusion curve with negative slope. (b) A plot of the coexistence regions for a typical PVT system. All the phase transitions here are first order. The dashed lines represent isotherms.

the isotherms (dashed lines) are always flat, indicating that in these regions the change in volume occurs for constant P and T.

4.4.2
Coexistence Curves: Clausius–Clapeyron Equation

The molar Gibbs free energies (the chemical potentials), $g = G/\mathrm{n}$, of two coexisting phases (which we call I and II) of a monatomic PVT system must be equal. If we change the pressure and temperature at which the two phases coexist (i. e., if we move to a new point on the coexistence curve), the molar Gibbs free energy of the two phases must change by equal amounts. Thus, $[\mathrm{d}g^{\mathrm{I}}]_{\mathrm{coexist}} = [\mathrm{d}g^{\mathrm{II}}]_{\mathrm{coexist}}$ and, using Table 3.4, we can write

$$v^{\mathrm{I}}\,\mathrm{d}P - s^{\mathrm{I}}\,\mathrm{d}T = v^{\mathrm{II}}\,\mathrm{d}P - s^{\mathrm{II}}\,\mathrm{d}T \tag{4.5}$$

along the coexistence curve, where v is the molar volume and s is the molar entropy. Thus,

$$\left(\frac{\mathrm{d}P}{\mathrm{d}T}\right)_{\mathrm{coex}} = \frac{s^{\mathrm{I}} - s^{\mathrm{II}}}{v^{\mathrm{I}} - v^{\mathrm{II}}} = \frac{\Delta s}{\Delta v} = \frac{\Delta h}{T\Delta v} \tag{4.6}$$

along the coexistence curve, where $\Delta s = s^{\mathrm{I}} - s^{\mathrm{II}}$ ($\Delta v = v^{\mathrm{I}} - v^{\mathrm{II}}$) is the difference in the molar entropy (molar volume) of the two phases. In the right-most term in Eq. (4.6), we have introduced the latent heat, $\Delta h = T\Delta s$ (cf. Table 3.2). Equation (4.6) is called the *Clausius–Clapeyron equation*. The latent heat, Δh, is the heat absorbed per mole in the transition from phase II to phase I.

It is useful to consider the Clausius–Clapeyron equation for each of the three coexistence curves in Figure 4.3. We first consider the *vaporization curve*. If we evacuate a chamber and partially fill it with a pure substance, then for the temperatures and pressures along the coexistence curve (the *vaporization curve*) from the triple point to the critical point (point A to point C in Figure 4.3a) the vapor and liquid phases will coexist in the chamber. In the absence of gravity, droplets of liquid will coexist with vapor. For a given temperature T, the pressure of the vapor and liquid is called the *saturated vapor pressure*. The Clausius–Clapeyron equation tells us how the vapor pressure changes as a function of temperature along the coexistence curve.

We can obtain a rather simple equation for the vaporization curve if we make some approximations. Let us assume that changes in the molar volume of the liquid may be neglected relative to changes in the molar volume of the vapor (gas) as we move along the coexistence curve, and let us assume the vapor obeys the ideal gas law. Then $\Delta v \approx RT/P$, and the Clausius–Clapeyron equation for the vapor pressure curve takes the form

$$\left(\frac{\mathrm{d}P}{\mathrm{d}T}\right)_{\text{coex}} = \frac{P\Delta h_{\text{lg}}}{RT^2} , \tag{4.7}$$

where Δh_{lg} is the *latent heat of vaporization*. If we assume that the latent heat of vaporization is roughly constant over the range of temperatures considered, we can integrate Eq. (4.7) from (P_0, T_0) to (P, T) along the coexistence curve to obtain

$$P = P_0 \exp\left[\frac{\Delta h_{\text{lg}}(T - T_0)}{RTT_0}\right] . \tag{4.8}$$

Thus, as the temperature is increased, the vapor pressure increases exponentially along the vaporization curve. Conversely, if we increase the pressure, the temperature of coexistence (boiling point) increases.

Exercise 4.1

Prove that the latent heat must always be positive (heat is absorbed) when making a transition from a low-temperature phase to a high-temperature phase.

Answer: Let us assume that phase I is the high-temperature phase and phase II is the low-temperature phase. Since for fixed pressure and temperature the equilibrium state is a state of minimum Gibbs free energy, we must have $G_{\text{I}} < G_{\text{II}}$ above the transition temperature and $G_{\text{I}} > G_{\text{II}}$ below the transition temperature. This implies that $(\partial G_{\text{I}}/\partial T)_{P,\{n_j\}} < (\partial G_{\text{II}}/\partial T)_{P,\{n_j\}}$ both above and below the transition temperature. Therefore $S_{\text{I}} = -(\partial G_{\text{I}}/\partial T)_{P,\{n_j\}} > S_{\text{II}} = -(\partial G_{\text{II}}/\partial T)_{P,\{n_j\}}$ and $\Delta S = T\Delta H$ is always positive in going from the low-temperature phase to the high-temperature phase.

The fusion curve does not terminate at a critical point but can have either positive or negative slope. The Clausius–Clapeyron equation for the liquid–solid transition is

$$\left(\frac{\mathrm{d}P}{\mathrm{d}T}\right)_{\text{coex}} = \frac{\Delta h_{\text{sl}}}{T\Delta v_{\text{sl}}} , \tag{4.9}$$

where Δv_{sl} is the change in molar volume in going from the solid to the liquid phase and Δh_{sl} is the *latent heat of fusion*. If the volume of the solid is greater than that of the liquid, then Δv_{sl} will be negative and the slope, $(\mathrm{d}P/\mathrm{d}T)_{\text{coex}}$, will be negative (the dashed line in Figure 4.3a).

For the case of a fusion curve with positive slope (the solid line in Figure 4.3a), if we increase the pressure at a fixed temperature, we simply drive the system deeper into the solid phase. However, if the fusion curve has a negative slope, then increasing the pressure at fixed temperature can drive the system into the liquid phase. Water is an example of a system whose fusion curve has negative slope.

Exercise 4.2

Compute the molar heat capacity of a vapor along the vaporization curve.

Answer: Along the vaporization curve there is only one independent variable, which we choose to be the temperature. In general, the entropy of the vapor is a function of both the pressure and temperature, but along the vaporization curve the pressure is related to the temperature by the Clausius–Clapeyron equation. The molar heat capacity along the vaporization curve can be written

$$c_{\mathrm{coex}} = T\left(\frac{\partial s}{\partial T}\right)_{\mathrm{coex}} = c_P - T\left(\frac{\partial v}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_{\mathrm{coex}} ,$$

where we have used identities in Appendix B and Table 3.4 ($(\partial s/\partial P)_T = -(\partial v/\partial T)_P$). The molar heat capacity, c_P, is the heat capacity of the vapor held at constant pressure as we approach the coexistence curve. If we use the ideal gas equation of state to describe the properties of the vapor phase and if we use the Clausius–Clapeyron equation, we obtain the following expression for the molar heat capacity along the coexistence curve, $c_{\mathrm{coex}} = c_P - ((\Delta h_{\mathrm{lg}})/T)$.

If a solid is placed in an evacuated chamber and maintained at some pressure and temperature along the sublimation curve, a vapor will coexist in equilibrium with the solid phase. If we again assume that the gas phase obeys the ideal gas equation of state, then the volume of the solid can be neglected and $\Delta v_{\mathrm{sg}} = RT/P$, is the change in molar volume in going from the solid to the gas phase. The Clausius–Clapeyron equation for the sublimation curve can then be written

$$\left(\frac{\mathrm{d}P}{\mathrm{d}T}\right)_{\mathrm{coex}} = \frac{P\Delta h_{\mathrm{sg}}}{RT^2} , \tag{4.10}$$

where Δh_{sg} is the *latent heat of sublimation*. If the vapor pressure is known over a small temperature interval, then the latent heat of sublimation can be obtained from Eq. (4.10). We can rewrite Eq. (4.10) in the form

$$\Delta h_{\mathrm{sg}} = -R\frac{\mathrm{d}\ln(P)}{\mathrm{d}(1/T)} . \tag{4.11}$$

Then Δh_{sg} is proportional to the slope of the curve, $\ln P$ versus $1/T$.

Exercise 4.3

Two crystalline forms of calcium carbonate, $CaCO_3$, are called calcite and aragonite. At $T_0 = 298\,\text{K}$ and $P_0 = 1.0\,\text{bar}$, calcite and aragonite have molar Gibbs free energy $g_c^\circ = -1128.8\,\text{kJ}$ and $g_a^\circ = -1127.8\,\text{kJ}$, molar entropy $s_c^\circ = 92.9\,\text{J/K}$ and $s_a^\circ = 88.7\,\text{J/K}$, and molar volume $v_c^\circ = 36.93 \times 10^{-6}\,\text{m}^3$ and $v_a^\circ = 34.15 \times 10^{-6}\,\text{m}^3$, respectively [190]. (a) At $T = T_0$ and $P = P_0$, which form is stable? (b) At what temperature does a phase transition occur between the two substances when $P = P_0$? (c) At what pressure does the phase transition occur when $T = T_0$?

Answer: (a) At $T_0 = 298\,\text{K}$, calcite is stable because $g_c < g_a$.

(b) At fixed $P = P_0$, $[\mathrm{d}g]_P = -s\,\mathrm{d}T$ so $g_c(T_1, P_0) - g_c(T_0, P_0) \approx s_c^\circ(T_1 - T_0)$ and $g_a(T_1, P_0) - g_a(T_1, P_0) \approx s_a^\circ(T_1 - T_0)$ (assuming s is slowly varying). Let $\Delta g = g_a - g_c$ and $\Delta s = s_a - s_c$ so $\Delta g(T_1, P_0) - \Delta g^\circ \approx \Delta s^\circ(T_1 - T_0)$. The phase transition occurs when $\Delta g(T_1, P_0) = 0$ or $T_1 \approx T_0 + \Delta g^\circ/\Delta s^\circ = 298\,\text{K} + 1000\,\text{kJ}/(-4.2\,\text{J/K}) = 59.9\,\text{K}$.

(c) The Clausius–Clapeyron equation for this transition is $\mathrm{d}P/\mathrm{d}T \approx \Delta s^\circ/\Delta v^\circ = 15.1\,\text{bar/K}$ so $\mathrm{d}P \approx (15.1\,\text{bar/K})\ \mathrm{d}T$. If we integrate, with lower limit at the transition point ($T_1 = 59.9\,\text{K}$, $P_0 = 1.0\,\text{bar}$), we find $P_2 - P_0 = (15.1\,\text{bar/K})(T_0 - T_1)$. At $T = T_0$, the transition occurs at $P_2 = 3.6\,\text{kbar}$.

4.4.3

Liquid–Vapor Coexistence Region

The liquid–vapor coexistence region culminates in a critical point and will be of special interest later. Therefore, it is useful at this point to examine this coexistence region more closely [116, 196]. Let us redraw the coexistence curve (vaporization curve) for the liquid–vapor transition in the P–v plane (cf. Figure 4.4). The isotherms for stable thermodynamic states are indicated by the solid lines. As we decrease the molar volume of the gas with temperature fixed at $T_0 < T_c$, the pressure increases until we reach the coexistence curve (point A). At point A, the vapor starts to condense and the pressure remains fixed until all vapor has changed to liquid (point B). Then the pressure begins to rise again.

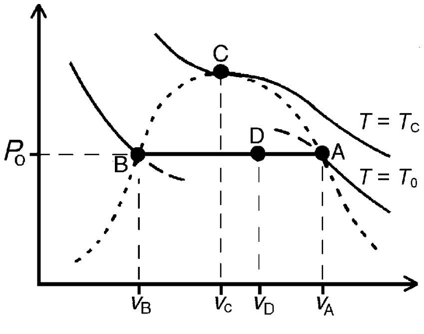


Figure 4.4 The coexistence curve for the vapor–liquid coexistence region for a pure PVT system.

4.4.3.1 Lever Rule

The amounts of liquid and vapor which coexist are given by the *lever rule*. Let us consider a system with temperature $T_0 < T_c$, pressure P_0, total volume V_D. The liquid and vapor phases coexist. The total volume V_D and total mole number n can be written $V_D = n_g v_g + n_l v_l$ and $n = n_g + n_l$, respectively, where v_g (v_l) is the molar volume of the gas (liquid) and n_g (n_g) is the number of moles of gas (liquid). The total molar volume, $v_D = V_D/n$, is given in terms of the molar volume v_l of the liquid at point B, and the molar volume v_g of vapor (gas) at point A, by $v_D = x_l v_l + x_g v_g$, where x_l is the mole fraction of liquid at point D and x_g is the mole fraction of gas at point D. If we multiply v_D by $x_l + x_g \equiv 1$, we find

$$\frac{x_l}{x_g} = \frac{(v_g - v_D)}{(v_D - v_l)} . \tag{4.12}$$

Equation (4.12) is called *the lever rule*. It tells us that the ratio of the mole fractions of liquid to gas at point D is equal to the inverse ratio of the distance between point D and points A and B.

Exercise 4.4

In the neighborhood of the triple point of ammonia (NH_3), the equation for the sublimation curve is $\ln(P) = 27.79 - 3726/T$ and the equation for the vaporization curve is $\ln(P) = 24.10 - 3005/T$, where P is measured in Pascals and T is measured in Kelvin. (a) Compute the temperature and pressure of the triple point. (b) What is the latent heat of sublimation? What is the latent heat of vaporization?

Answer: (a) At the triple point, the pressure and temperature of the vapor, liquid, and solid are the same. Therefore, the equation for the triple point temperature, T_t, is $27.79 - 3726/T_t = 24.10 - 3005/T_t$ or $T_t = 195.4\,\mathrm{K}$. The triple point pressure, P_t, is $P_t = 6.13\,\mathrm{kPa}$.

(b) The slope of the sublimation curve is $(\partial P/\partial T)_{\mathrm{coex}} \approx (P\Delta h_{sg})/(RT^2) = (3726P)/T^2$. Therefore, $\Delta h_{sg} = 3726R \approx 31\,\mathrm{kJ/mol}$. The slope of the vaporization curve is $(\partial P/\partial T)_{\mathrm{coex}} \approx (P\Delta h_{lg})/(RT^2) = (3005P)/T^2$. Therefore, $\Delta h_{lg} = 3005R \approx 25\,\mathrm{kJ/mol}$.

As long as $(\partial v/\partial P)_T < 0$, the system is mechanically stable (see Section 3.7). If we continue the isotherm, T_0, past the points A and B (the dashed line), we obtain curves which are mechanically stable but no longer correspond to a minimum of free energy. States along the dashed line at point A correspond to supercooled vapor states, while those along the dashed line at point B correspond to superheated liquid states. Such states are metastable and can be produced in the laboratory for very pure samples.

4.4.3.2 Law of Corresponding States

The actual shape of the coexistence curve in the T–ρ plane (ρ is the mass density) has been given by Guggenheim [76] for a variety of classical pure substances and is reproduced in Figure 4.5. Guggenheim plots the coexistence curve in terms of

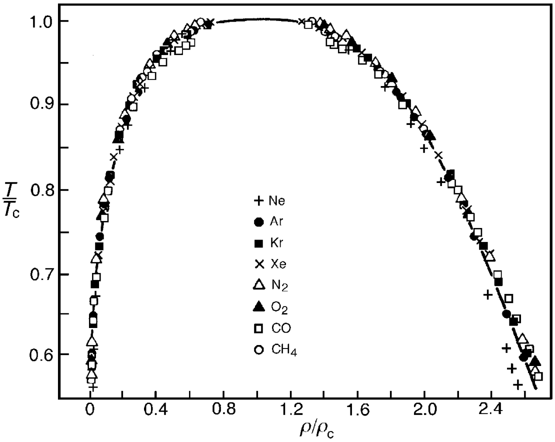


Figure 4.5 Experimental vapor–liquid coexistence curve for a variety of substances. The plot is of the reduced temperature versus reduced density (based on [76]).

the reduced quantities T/T_c and ρ/ρ_c, where T_c and ρ_c are the critical temperature and mass density, respectively, of a given substance (T_c and ρ_c are different for each substance). Most classical substances, when plotted in terms of reduced temperature and density, lie in approximately the same curve. This is an example of the so-called *law of corresponding states*, which says that all classical pure fluids, when described in terms of reduced quantities, obey the same equation of state.

It is found from experiment that the reduced densities of the liquid and gas phases along the coexistence curves obey the following equations:

$$\frac{\rho_l + \rho_g}{2\rho_c} = 1 + \frac{3}{4}\left(1 - \frac{T}{T_c}\right) \quad \text{and} \quad \frac{\rho_l - \rho_g}{\rho_c} = \frac{7}{2}\left(1 - \frac{T}{T_c}\right)^{1/3} . \tag{4.13}$$

These equations will be useful later.

4.4.3.3 Response Functions in the Coexistence Region

It is possible to obtain expressions for response functions in the coexistence region. As an example, we will consider the molar heat capacity, c_v, for a liquid and vapor coexisting at a fixed molar volume, v_D (cf. Figure 4.4). If we neglect any effects of gravity, then the system will consist of droplets of liquid in equilibrium with and floating in vapor. The internal energy per mole of the liquid at point D is $u_l(v_B, T_0)$ and that of the vapor at point D is $u_g(v_A, T_0)$ (the thermodynamic properties of the liquid and the vapor at point D are the same as on their respective sides of the coexistence curve). The total internal energy at point D is $U_{tot} = n_g u(v_g, T_0) + n_l u(v_l, T_0)$ and the total internal energy per mole at point D is

$$u_{tot} = x_g u(v_g, T_0) + x_l u(v_l, T_0) , \tag{4.14}$$

where $v_g = v_A$, $v_l = v_B$, and n_g and n_l are the number of moles of gas and liquid, respectively, at point D.

Let us now look at the variation of the internal energy with temperature along a line of fixed molar volume at point D (the molar heat capacity at point D),

$$c_v = \left(\frac{\partial u_{\mathrm{tot}}}{\partial T}\right)_{v_D} = x_g\left(\frac{\partial u_g}{\partial T}\right)_{\mathrm{coex}} + x_l\left(\frac{\partial u_l}{\partial T}\right)_{\mathrm{coex}} + (u_l - u_g)\left(\frac{\partial x_l}{\partial T}\right)_{\mathrm{coex}}, \tag{4.15}$$

where we have used the fact that $\mathrm{d}x_l = -\,\mathrm{d}x_g$. Equation (4.15) can be expressed in terms of directly measurable quantities. There are several steps involved which we itemize below.

1. First consider the quantity $(\partial u_l/\partial T)_{\mathrm{coex}}$. Using identities from Appendix B, we can write

$$\left(\frac{\partial u_l}{\partial T}\right)_{\mathrm{coex}} = \left(\frac{\partial u_l}{\partial T}\right)_{v_l} + \left(\frac{\partial u_l}{\partial v_l}\right)_T\left(\frac{\partial v_l}{\partial T}\right)_{\mathrm{coex}} = c_{v_l} + \left(\frac{\partial u_l}{\partial v_l}\right)_T\left(\frac{\partial v_l}{\partial T}\right)_{\mathrm{coex}}, \tag{4.16}$$

where c_{v_l} is the molar heat capacity of the liquid at point B. Similarly,

$$\left(\frac{\partial u_g}{\partial T}\right)_{\mathrm{coex}} = c_{v_g} + \left(\frac{\partial u_g}{\partial v_g}\right)_T\left(\frac{\partial v_g}{\partial T}\right)_{\mathrm{coex}}, \tag{4.17}$$

where c_{v_g} is the molar heat capacity of the vapor at point A.

2. Next consider the difference $\Delta u = u_g - u_l$ between the molar internal energies of the gas and liquid. From the Clausius–Clapeyron equation (4.6) and the fundamental equation for the enthalpy (see Table 3.2), we can write

$$\left(\frac{\mathrm{d}P}{\mathrm{d}T}\right)_{\mathrm{coex}} = \frac{\Delta h}{T\Delta v} = \frac{\Delta u}{T\Delta v} + \frac{\Delta(Pv)}{T\Delta v} = \frac{\Delta u}{T\Delta v} + \frac{P}{T}, \tag{4.18}$$

where $\Delta h = h_g - h_l$ and $\Delta v = v_g - v_l$ ($\Delta P = 0$ because the pressure of the two coexisting phases are the same). Therefore,

$$\Delta u = u_g - u_l = \left\{\left[T\left(\frac{\mathrm{d}P}{\mathrm{d}T}\right)_{\mathrm{coex}} - P\right](v_g - v_l)\right\}_{\mathrm{coex}}. \tag{4.19}$$

3. Finally, let us consider the quantity $(\partial x_l/\partial T)_{\mathrm{coex}}$. Since the total molar volume at point D can be written $v_D = x_g v_g + x_l v_l$, we can write

$$\left(\frac{\partial v_D}{\partial T}\right)_{v_D} = 0 = (v_l - v_g)\left(\frac{\partial x_l}{\partial T}\right)_{\mathrm{coex}} + x_g\left(\frac{\partial v_g}{\partial T}\right)_{\mathrm{coex}} + x_l\left(\frac{\partial v_l}{\partial T}\right)_{\mathrm{coex}}. \tag{4.20}$$

Here we have used the fact that as we vary the temperature along the line v_D = constant, the liquid and vapor vary along their respective sides of the coexistence curve. We can rewrite Eq. (4.20) in the form

$$\left(\frac{\partial x_l}{\partial T}\right)_{\mathrm{coex}} = \frac{1}{(v_g - v_l)}\left[x_g\left(\frac{\partial v_g}{\partial T}\right)_{\mathrm{coex}} + x_l\left(\frac{\partial v_l}{\partial T}\right)_{\mathrm{coex}}\right] . \tag{4.21}$$

We can combine Eqs. (4.15), (4.17), (4.19), and (4.21) to obtain the following expression for the heat capacity along the line v_D = constant;

$$\begin{aligned} c_v = x_g c_{v_g} + x_l c_{v_l} + x_g\left(\frac{\partial u_g}{\partial v_g}\right)_T\left(\frac{\partial v_g}{\partial T}\right)_{\mathrm{coex}} + x_l\left(\frac{\partial u_l}{\partial v_l}\right)_T\left(\frac{\partial v_l}{\partial T}\right)_{\mathrm{coex}} \\ - \left[T\left(\frac{\mathrm{d}P}{\mathrm{d}T}\right)_{\mathrm{coex}} - P\right]\left[x_g\left(\frac{\partial v_g}{\partial T}\right)_{\mathrm{coex}} + x_l\left(\frac{\partial v_l}{\partial T}\right)_{\mathrm{coex}}\right] . \end{aligned} \tag{4.22}$$

We now can make two final changes to Eq. (4.22). We can use the identity

$$\left(\frac{\partial u_g}{\partial v_g}\right)_T = T\left(\frac{\partial P_g}{\partial T}\right)_{v_g} - P \tag{4.23}$$

and an analogous identity for $(\partial u_l/\partial v_l)_T$ (cf. (3.50)). Also, we can write

$$\left(\frac{\partial P}{\partial T}\right)_{v_g} = \left(\frac{\partial P}{\partial T}\right)_{\mathrm{coex}} - \left(\frac{\partial P}{\partial v_g}\right)_T\left(\frac{\partial v_g}{\partial T}\right)_{\mathrm{coex}} \tag{4.24}$$

and an analogous expression for $(\partial P/\partial T)_{v_l}$. If Eqs. (4.23) and (4.24) and the analogous expressions for the liquid are substituted into Eq. (4.22), we find

$$c_v = x_g\left[c_{v_g} - T\left(\frac{\partial P}{\partial v_g}\right)_T\left(\frac{\partial v_g}{\partial T}\right)^2_{\mathrm{coex}}\right] + x_l\left[c_{v_l} - T\left(\frac{\partial P}{\partial v_l}\right)_T\left(\frac{\partial v_l}{\partial T}\right)^2_{\mathrm{coex}}\right] . \tag{4.25}$$

All quantities in Eq. (4.25) are measurable, and therefore a numerical value for the heat capacity can be obtained without much difficulty. Equation (4.25) will be useful later when we consider critical exponents.

The heat capacity at constant volume is finite in the coexistence region. However, the heat capacity at constant pressure is infinite in the coexistence region. If we add heat to a system with coexisting liquid and vapor phases and keep the pressure fixed, liquid will turn to vapor but the temperature will not change. Thus, $c_P = \infty$ in the coexistence region, while c_v can remain finite.

4.4.4

The van der Waals Equation

The van der Waals equation, $P = (\mathfrak{n}RT)/(N - \mathfrak{n}b) - (a\mathfrak{n}^2)/V^2$, was first derived by van der Waals in his doctoral dissertation in 1873. The parameters a and b account for attractive and repulsive forces, respectively, between molecules in a fluid (see Table 4.1 for values of a and b for some simple fluids). It is the simplest equation of state which exhibits many of the essential features of the liquid–vapor phase transition. The van der Waals equation is cubic in the molar volume and can be written in the form

$$v^3 - \left(b + \frac{RT}{P}\right)v^2 + \frac{a}{P}v + \frac{ab}{P} = 0\,, \tag{4.26}$$

where $v = V/\mathfrak{n}$. An isotherm of the van der Waals equation is plotted in Figure 4.6a. For small values of T and P, the cubic equation has three distinct real roots (three values of v) for each value of P and T (this case is shown in Figure 4.6a). As T increases, the roots coalesce at a critical temperature, T_c, and above T_c two of the roots become imaginary and therefore unphysical. As $T \to \infty$, (4.26) reduces to the ideal gas equation of state, $v = RT/P$.

The critical point is the point at which the roots of Eq. (4.26) coalesce. It is also the point at which the critical isotherm ($T = T_\mathrm{c}$) has a vanishing slope $(\partial P/\partial v)_{T=T_\mathrm{c}} = 0$ and an inflection point $(\partial^2 P/\partial v^2)_{T=T_\mathrm{c}} = 0$, so the curve changes from convex to concave and $(\partial^2 P/\partial v^2)_T$ changes sign. If we use the fact that

$$\left(\frac{\partial P}{\partial v}\right)_{T=T_\mathrm{c}} = 0 \quad \text{and} \quad \left(\frac{\partial^2 P}{\partial v^2}\right)_{T=T_\mathrm{c}} = 0 \tag{4.27}$$

Table 4.1 Values of specific enthalpy, specific entropy, and specific volume of H_2O along the liquid and gas coexistence curves from the triple point to the critical point [70]. (Note that 1 dm = 10^{-1} m.)

t (°C)	P (bar)	h_l (kJ/kg)	h_g (kJ/kg)	s_l (kJ/(kg K))	s_g (kJ/(kg K))	v_l (dm³/kg)	v_g (dm³/kg)
0.01	0.006	0	2502	0	9.158	1.000	206163
25	0.0317	104.8	2547	0.3674	8.559	1.003	43402
50	0.123	209.3	2592	0.704	8.078	1.012	12046
100	1.013	419.1	2676	1.307	7.355	1.044	1673
150	4.760	632.2	2745	1.842	6.836	1.091	392.5
200	15.55	852.4	2791	2.331	6.428	1.157	127.2
250	39.78	1086	2800	2.793	6.071	1.251	50.04
300	85.93	1345	2751	3.255	5.708	1.404	21.65
350	165.4	1672	2568	3.780	5.218	1.741	8.798
374.15	221.2	2107	2107	4.443	4.443	3.170	3.170

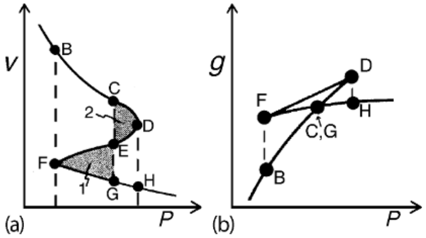


Figure 4.6 (a) A sketch of a typical van der Waals isotherm for $T < T_c$. The line from D to F corresponds to mechanically unstable states. The area, CDE, is labeled 2, and the area EFG is labeled 1. (b) A plot of the molar Gibbs free energy as a function of pressure for the isotherm in Figure 4.6a.

at the critical point, then we obtain the following values for the temperature T_c, pressure P_c, and molar volume v_c, at the critical point:

$$P_c = \frac{a}{27b^2}\,, \quad v_c = 3b\,, \quad T_c = \frac{8a}{27bR}\,. \tag{4.28}$$

If we introduce reduced variables $\overline{P} = P/P_c$, $\overline{T} = T/T_c$, and $\overline{v} = v/v_c$, then we may write the van der Waals equation in the form

$$\left(\overline{P} + \frac{3}{\overline{v}^2}\right)(3\overline{v} - 1) = 8\overline{T}\,. \tag{4.29}$$

It is important to note that Eq. (4.29) is independent of a and b. We are now measuring pressure, volume, and temperature in terms of their fractional distance from the critical point. The values of v_c, T_c, and P_c will differ for different gases, but *all gases obey the same equation if they are the same fractional distance from their respective critical points* – that is, if they have the same values of $\overline{P} = P/P_c$, $\overline{T} = T/T_c$, and $\overline{v} = v/v_c$. Thus, we see again the *law of corresponding states.*

An unphysical aspect of the van der Waals equation is its prediction of positive slope, $(\partial P/\partial v)_T$, for certain segments of the isotherms below T_c (the segment between D and F in Figure 4.6a). This region corresponds to mechanically unstable thermodynamic states. However, the unphysical parts of the P–V curve can be removed by use of the *Maxwell construction,* which we will now describe.

We can write the equation for infinitesimal changes in the molar Gibbs free energy in the form $\mathrm{d}g = -s\,\mathrm{d}T + v\,\mathrm{d}P$. If we follow one of the isotherms so $\mathrm{d}T = 0$, we can determine how g varies with pressure along that isotherm. In Figure 4.6a, we plot the molar volume as a function of pressure along a typical van der Waals isotherm, and in Figure 4.6b, we plot the molar Gibbs free energy as a function of pressure for the isotherm in Figure 4.6a. Along the isotherm the difference in molar Gibbs free energy between any two points is equal to the area under the curve, $v = v(P)$, between those two points:

$$g_2 - g_1 = \int_{P_1}^{P_2} v(P)\,\mathrm{d}P\,. \tag{4.30}$$

The Gibbs free energy increases and is concave between A and D. Between D and F it decreases and is convex. Then between F and I it becomes concave again and increases. Between D and F the states are mechanically unstable since mechanical stability requires that g be concave (see Section 3.7). The regions from A to D and from F to I are both mechanically stable since g is concave. However, only the curve ACI in Figure 4.6b corresponds to states in thermodynamic equilibrium because for these states the Gibbs free energy is a minimum. The states FCD are metastable. The equilibrium states thus correspond to those states whose Gibbs free energy has values lying along the curve ACI. To obtain the equilibrium states on the isotherm between C and G we must draw a straight line (line of constant pressure) between them, since this is the only way the Gibbs free energy will remain constant in going from C to G. The physical isotherm (isotherm containing equilibrium states) is the line BCEGH in Figure 4.6a.

Before we can complete our construction of isotherms, we must decide where C and G lie. For the points C and G, the molar Gibbs free energies are equal. Thus, $g_{\mathrm{G}} - g_{\mathrm{C}} = \int_{P_{\mathrm{C}}}^{P_{\mathrm{G}}} v(P)\,\mathrm{d}P = 0$ so

$$0 = \int_{P_{\mathrm{C}}}^{P_{\mathrm{D}}} v(P)\,\mathrm{d}P + \int_{P_{\mathrm{D}}}^{P_{\mathrm{E}}} v(P)\,\mathrm{d}P + \int_{P_{\mathrm{E}}}^{P_{\mathrm{F}}} v(P)\,\mathrm{d}P + \int_{P_{\mathrm{F}}}^{P_{\mathrm{G}}} v(P)\,\mathrm{d}P \tag{4.31}$$

or, after rearranging,

$$\int_{P_{\mathrm{C}}}^{P_{\mathrm{D}}} v(P)\,\mathrm{d}P - \int_{P_{\mathrm{E}}}^{P_{\mathrm{D}}} v(P)\,\mathrm{d}P = \int_{P_{\mathrm{F}}}^{P_{\mathrm{E}}} v(P)\,\mathrm{d}P - \int_{P_{\mathrm{F}}}^{P_{\mathrm{G}}} v(P)\,\mathrm{d}P\,. \tag{4.32}$$

The left-hand side is equal to Area 2 in Figure 4.6a and the right-hand side is equal to Area 1. Thus, the line from C to G must be drawn so that *Area 1 = Area 2*. If this is done, the curve BCEGH gives the equilibrium states of the system. This requirement of equal areas is called the *Maxwell construction*. Using the Maxwell construction, we obtain the equilibrium isotherms from the van der Waals equation and the curves for metastable states.

4.4.5
Steam Engines – The Rankine Cycle

The steam engines historically have provided much of the power that has driven the growth of modern civilization. They continue to be one of our most important sources of power because coal-based power plants or modern nuclear power plants use steam engines to change heat into electrical power. Water is plentiful, chemically stable and poses no health risks. Water and steam have relatively large heat capacities and latent heat, making them good heat sponges. The steam engine cycle runs through the liquid–vapor coexistence region of the water phase diagram. Water is converted to steam which then drives a turbine or piston.

A basic steam engine generally consists of a boiler, a condenser, a pump, and a turbine or piston. A reversible version of the steam engine, called the Rankine

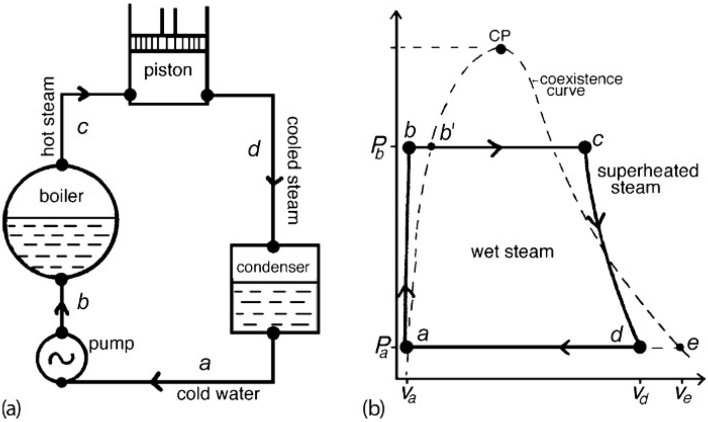


Figure 4.7 (a) The basic elements of a steam engine. (b) The Rankine cycle.

cycle, is shown in Figure 4.7a and b [220]. The Rankine cycle runs through the closed cycle $a \to b \to c \to d \to a$ in Figure 4.7b as follows

$a \to b$: Cold water is pumped adiabatically from low temperature T_a and pressure P_a to slightly higher temperature T_b and much higher pressure P_b ($T_a < T_b$, $P_a \ll P_b$).

$b \to c$: Water at high pressure P_b and cold temperature T_b is heated at constant pressure P_b to the boiling point $T_{b'}$, then turned into steam at constant pressure P_b and temperature $T_{b'}$ and then further heated to a superheated (dry steam) state at pressure P_b and temperature T_c ($T_b \ll T_{b'} \ll T_\mathrm{c}$).

$c \to d$: Superheated steam at pressure P_b and temperature T_c flows into a compartment where it expands approximately adiabatically against a piston or turbine blades until its pressure and temperature drop to approximately P_a and temperature T_d ($T_d \ll T_\mathrm{c}$) forming wet steam.

$d \to a$: Wet steam at pressure P_a and temperature T_d condenses into water at pressure P_a and temperature T_a, and the cycle is complete.

For the Rankine cycle, an amount of heat/mass ΔQ_{bc} is absorbed, but over a range of temperatures, and an amount of heat/mass ΔQ_{da} is ejected. For the part of the process $a \to b$, there is only a slight decrease $\Delta v_{ab} = v_b - v_a$ in the volume/mass of the water since water is very incompressible. Because the processes $b \to c$ and $d \to a$ occur at constant pressure, the heat/mass absorbed and ejected can be expressed in terms of the change in enthalpy/mass h of the water. (Note that $\mathrm{d}h = T\,\mathrm{d}s + v\,\mathrm{d}P$, where s is the entropy/mass. If $\mathrm{d}P = 0$ we have $\mathrm{d}h = T\,\mathrm{d}s = \mathrm{d}q$.) Thus, $\Delta Q_{bc} = h_\mathrm{c} - h_b$ and $\Delta Q_{da} = h_a - h_d$.

Since the Rankine cycle is reversible, the change in the internal energy for the complete cycle is $\Delta U_\mathrm{tot} = \Delta Q_\mathrm{tot} - \Delta W_\mathrm{tot} = 0$. Thus, the work/mass done by the engine is $\Delta W_\mathrm{tot} = \Delta Q_\mathrm{tot} = \Delta Q_{bc} + \Delta Q_{da} = \Delta Q_{bc} - \Delta Q_{ad}$. The efficiency of the

Table 4.2 Truncated Steam Table – Values of specific enthalpy (kJ/kg), specific entropy (kJ/kg K), and specific volume (dm^3/kg) of H_2O as functions of pressure (bar) and temperature (°C) for subsaturated water and super-heated steam (separated by dots) [70]. (Note that 1 dm $= 10^{-1}$ m. The dots separate data for subsaturated water from data for super-heated steam.)

$P \downarrow \backslash t \rightarrow$		100	200	250	300	350	400	450	500
20	h	420	853 …	2902	3025	3139	3249	3358	3467
20	s	1.31	2.33 …	6.55	6.77	6.960	7.13	7.286	7.432
20	v	1.04	1.16 …	111	126	138.6	151	163.4	175.6
50	h	423	854	1086 …	2926	3072	3194	3318	3434
50	s	1.30	2.33	2.79 …	6.21	6.455	6.65	6.822	6.977
50	v	1.04	1.15	1.25 …	45.3	51.94	57.8	63.25	68.49
100	h	427	856	1086	1343 …	2926	3100	3244	3375
100	s	1.30	2.32	2.78	3.25 …	5.949	6.22	6.424	6.576
100	v	1.04	1.15	1.24	1.40 …	22.42	26.4	29.74	32.76

Rankine cycle can be written

$$\eta = \frac{\Delta W_{\mathrm{tot}}}{\Delta Q_{bc}} = \frac{\Delta Q_{bc} - \Delta Q_{ad}}{\Delta Q_{bc}} = \frac{h_{\mathrm{c}} - h_b - h_d + h_a}{h_{\mathrm{c}} - h_b} \,. \tag{4.33}$$

The process $a \rightarrow b$ is reversible and adiabatic so $\mathrm{d}h = v\,\mathrm{d}P$ and $h_b - h_a = \int_{P_a}^{P_b} v\,\mathrm{d}P \approx v_{\mathrm{w}}(P_b - P_a)$, where v_{w} is the approximately constant volume/mass of water during the transition $a \rightarrow b$. The quantity $v_{\mathrm{w}}(P_b - P_a)$ is called the *feed-pump* contribution. Thus, the efficiency of the Rankine engine can be written

$$\eta = \frac{h_{\mathrm{c}} - h_d - v_{\mathrm{w}}(P_b - P_a)}{h_{\mathrm{c}} - h_a - v_{\mathrm{w}}(P_b - P_a)} \,. \tag{4.34}$$

The quantity h_d is the enthalpy of water in the coexistence region. It can be found as follows. The point e in Figure 4.7b is on the vapor side of the coexistence curve at temperature T_a and pressure P_a. The Gibbs free energy per unit mass at point d is $g_d = h_d - T_a s_d$ and at point e it is $g_e = h_e - T_a s_e$. Because the process $c \rightarrow d$ is reversible and adiabatic we have $s_{\mathrm{c}} = s_d$. If we use the fact that $g_e = g_d$ we can write $h_d = h_e - T_a(s_e - s_{\mathrm{c}})$. All these quantities can be found in *steam tables* [70] (see Tables 4.1 and 4.2).

Exercise 4.5

A steam engine outputs superheated steam at a temperature of $T = 250\,°\mathrm{C}$ and pressure $P = 20\,\mathrm{bar}$. After the steam has driven engine turbines, it is liquified in a condenser at a temperature of $T = 25\,°\mathrm{C}$. (a) Compute the efficiency of the steam engine assuming that it operates on a Rankine cycle. (b) Compute the efficiency of a Carnot engine operating between the same high and low temperatures.

Answer: (a) Referring to the Rankine cycle in Figure 4.7b, assume that the temperature at points a and e is $T_a = T_e = 25\,°\mathrm{C} = 298\,\mathrm{K}$, since both points lie on (opposite sides of) the coexistence curve. From Table 4.1, the pressure at points a and e is $P_a = P_e = 0.0317\,\mathrm{bar} = 3.17 \times 10^3\,\mathrm{Pa}$. The specific volume of water at point a is $v_a = 1.003\,\mathrm{dm}^3/\mathrm{kg} = 1.003 \times 10^{-3}\,\mathrm{m}^3/\mathrm{kg}$. Assume that the pressure at points b and c is $P_b = P_c = 20\,\mathrm{bar} = 2.0 \times 10^6\,\mathrm{Pa}$, and the temperature at point c is $T_c = 250\,°\mathrm{C} = 523\,\mathrm{K}$. The efficiency of the Rankine cycle is

$$\eta = \frac{h_c - h_d - v_a(P_b - P_a)}{h_c - h_a - v_a(P_b - P_a)} \quad \text{with} \quad h_d = h_e - T_a(s_e - s_c)\,.$$

From Table 4.1, the specific enthalpy and entropy at point e are $h_e = 2547\,\mathrm{kJ/kg}$ and $s_e = 8.56\,\mathrm{kJ/(kg\,K)}$, respectively. From Table 4.2, the specific enthalpy and entropy at point c are $h_c = 2902\,\mathrm{kJ/kg}$ and $s_c = 6.55\,\mathrm{kJ/(kg\,K)}$, respectively. Thus, the feed-pump term gives $v_a(P_b - P_a) = 1.97\,\mathrm{kJ/kg}$. The enthalpy at point d is $h_d = h_e - T_a(s_e - s_c) = 1948\,\mathrm{kJ/kg}$. The efficiency of the Rankine cycle (using the above formula) is $\eta = 0.34$. (b) The efficiency of a Carnot engine operating between $T_{\mathrm{cold}} = 298\,\mathrm{K}$ and $T_{\mathrm{hot}} = 523\,\mathrm{K}$ is $\eta_{\mathrm{Carnot}} = 0.43$.

4.5
Binary Mixtures

If we consider a fluid which is a mixture of several different types of interacting particles, a phase transition can occur in which there is a physical separation of the fluid into regions containing different concentrations of the various types of particles [83, 106, 172, 188]. The simplest example of this type of phase transition occurs for binary mixtures.

The Gibbs free energy for a binary mixture composed of $\mathfrak{n}_1$ moles of type 1 particles and $\mathfrak{n}_2$ moles of type 2 particles is $G(T, P, \mathfrak{n}_1, \mathfrak{n}_2) = \mathfrak{n}_1\mu_1 + \mathfrak{n}_2\mu_2$ and differential changes in the Gibbs free energy can be written $\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}P + \mu_1\,\mathrm{d}\mathfrak{n}_1 + \mu_2\,\mathrm{d}\mathfrak{n}_2$ (see Table 3.4). The molar Gibbs free energy is $g = G/\mathfrak{n} = x_1\mu_1 + x_2\mu_2$, where $\mathfrak{n} = \mathfrak{n}_1 + \mathfrak{n}_2$ and x_1 and x_2 are the mole fractions of particles of type 1 and 2, respectively. It is straightforward to show that

$$\mathrm{d}g = -s\,\mathrm{d}T + v\,\mathrm{d}P + (\mu_1 - \mu_2)\,\mathrm{d}x_1\,, \tag{4.35}$$

so that $g = g(T, P, x_1)$.

The chemical potential of type 1 particles is

$$\mu_1 = \left(\frac{\partial G}{\partial \mathfrak{n}_1}\right)_{P,T,\mathfrak{n}_2} = g + (1 - x_1)\left(\frac{\partial g}{\partial x_1}\right)_{P,T} \tag{4.36}$$

and the chemical potential of type 2 particles is

$$\mu_2 = \left(\frac{\partial G}{\partial \mathfrak{n}_2}\right)_{P,T,\mathfrak{n}_1} = g - x_1\left(\frac{\partial g}{\partial x_1}\right)_{P,T}\,, \tag{4.37}$$

where we have used the fact that $\left(\partial x_1/\partial \mathfrak{n}_1\right)_{\mathfrak{n}_2} = x_2/\mathfrak{n}$ and $\left(\partial x_1/\partial \mathfrak{n}_2\right)_{\mathfrak{n}_1} = -x_1/\mathfrak{n}$. From Eqs. (4.35)–(4.37), we see that the chemical potential depends on the mole numbers $\mathfrak{n}_1$ and $\mathfrak{n}_2$, only through its dependence on the mole fraction, x_1.

We can also show that

$$\left(\frac{\partial \mu_1}{\partial x_1}\right)_{P,T} = (1 - x_1)\left(\frac{\partial^2 g}{\partial x_1^2}\right)_{P,T} \quad \text{and} \quad \left(\frac{\partial \mu_2}{\partial x_1}\right)_{P,T} = -x_1\left(\frac{\partial^2 g}{\partial x_1^2}\right)_{P,T} \tag{4.38}$$

From Eq. (4.38) and the stability conditions in Section 3.7, namely $\left(\partial \mu_1/\partial \mathfrak{n}_1\right)_{P,T,\mathfrak{n}_2} > 0$ we find that the molar Gibbs free energy must satisfy the conditions

$$\left(\frac{\partial^2 g}{\partial x_1^2}\right)_{P,T} > 0 \quad \text{and} \quad \left(\frac{\partial \mu_2}{\partial x_1}\right)_{P,T} < 0\,. \tag{4.39}$$

Thus, *for chemical stability, the molar Gibbs free energy must be a convex function of the mole fraction.*

4.5.1
Equilibrium Conditions

For a binary mixture to be in equilibrium, the chemical potentials of the two types of particle must be equal. This equality of chemical potentials of the two types of particle gives us a condition for locating the coexistence curve when a phase separation occurs. For type 1 particles we have $\mu_1^{\mathrm{I}} = \mu_1^{\mathrm{II}}$ or

$$g^{\mathrm{I}} + \left(1 - x_1^{\mathrm{I}}\right)\left(\frac{\partial g}{\partial x_1}\right)_{P,T}^{\mathrm{I}} = g^{\mathrm{II}} + \left(1 - x_1^{\mathrm{II}}\right)\left(\frac{\partial g}{\partial x_1}\right)_{P,T}^{\mathrm{II}}\,, \tag{4.40}$$

and for type 2 particles we have $\mu_2^{\mathrm{I}} = \mu_2^{\mathrm{II}}$ or

$$g^{\mathrm{I}} - x_1^{\mathrm{I}}\left(\frac{\partial g}{\partial x_1}\right)_{P,T}^{\mathrm{I}} = g^{\mathrm{II}} - x_1^{\mathrm{II}}\left(\frac{\partial g}{\partial x_1}\right)_{P,T}^{\mathrm{II}}\,, \tag{4.41}$$

where I and II denote the two phases. If we combine Eqs. (4.40) and (4.41), we can write the conditions for equilibrium in the form

$$\left(\frac{\partial g}{\partial x_1}\right)_{P,T}^{\mathrm{I}} = \left(\frac{\partial g}{\partial x_1}\right)_{P,T}^{\mathrm{II}} \quad \text{and} \quad g^{\mathrm{I}} - g^{\mathrm{II}} = \left(x_1^{\mathrm{I}} - x_1^{\mathrm{II}}\right)\left(\frac{\partial g}{\partial x_1}\right)_{P,T}^{\mathrm{I}}\,. \tag{4.42}$$

Equations (4.42) tell us that the equilibrium points in the (g, x_1) plane have equal slopes, and they have a common tangent. These two conditions enable us to locate the coexistence curve.

In Figure 4.8a, we show a sketch of the molar Gibbs free energy which illustrates these various properties. It shows a region where two phases can coexist.

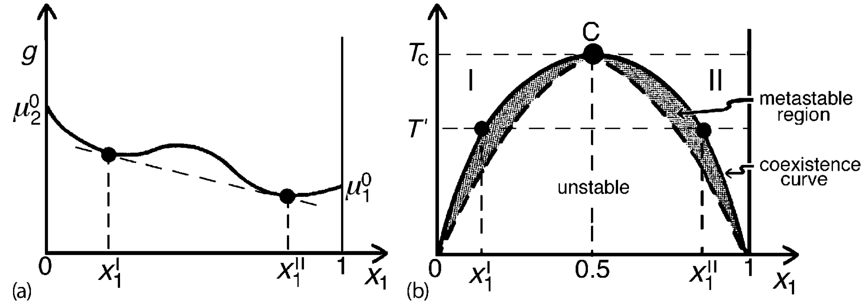


Figure 4.8 (a) A sketch of the molar Gibbs free energy of a phase-separated binary mixture. The two points with common tangent are equilibrium states. (b) The phase diagram for a binary mixture. Point C is the critical point.

The points that have a common tangent are the equilibrium points. The concave region in the middle is unstable. In a test tube, the heavier phase will sink to the bottom and the lighter one will float to the top.

As long as $(\partial\mu_2/\partial x_1)_{P,T} < 0$, the binary mixture will be chemically stable and exist in one phase. However, if $(\partial\mu_2/\partial x_1)_{P,T} > 0$ the system has an unstable region and phase separation occurs. The critical point for this phase separation is given by $(\partial\mu_2/\partial x_1)^{\rm c}_{P,T} = 0$. The critical point is the point where the x_1 first becomes a double-valued function of μ_1 or μ_2 as the temperature is changed. That is, two different values of x_1 give the same value of the chemical potential. Thus, in analogy to the liquid–vapor critical point (with $P \to \mu_2$ and $v \to x_1$), the critical point is a point of inflection of the curve $\mu_2 = \mu_2(T, P, x_1)$ for T and P constant. Therefore, we have the additional condition that $(\partial^2\mu_2/\partial x_1^2)^{\rm c}_{P,T} = 0$ at the critical point.

A sketch of the coexistence curve, and the curve separating stable from unstable states is given in Figure 4.8b. The region outside and above the coexistence curve corresponds to allowed single-phase equilibrium states. Below the coexistence curve is a coexistence region in which two equilibrium states with different concentrations of type 1 particles can coexist at the same temperature. The shaded region corresponds to metastable states. These are single-phase states which are not in thermodynamic equilibrium but are chemically stable. All single-phase states below the dashed line are unstable and cannot be realized in nature. Let us follow the horizontal line at temperature, $T' < T_{\rm c}$, in Figure 4.8b. At $x_1 = 0$, we have a system consisting only of type 2 particles. As we start adding type 1 particles, the concentration of type 1 particles increases until we reach the coexistence curve at point I. At this point, the system separates into two phases, one in which type 1 particles have concentration $x_1^{\rm I}$ and another in which type 1 particles have concentration $x_1^{\rm II}$. As we increase the number of type 1 particles relative to type 2 particles, the amount of phase II increases and the amount of phase I decreases until we reach the coexistence curve at point II. At point II, phase I has disappeared and we again have a single-phase equilibrium state of concentration, $x_1^{\rm II}$.

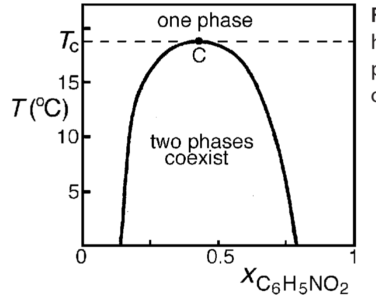


Figure 4.9 The phase diagram for a mixture of *n*-hexane and nitrobenzene ($C_6H_5NO_2$) at atmospheric pressure. The solid line is the coexistence curve (based on [172]).

Exercise 4.6

Consider a binary mixture of particles of types 1 and 2, whose molar Gibbs free energy is given by

$$g = x_1\mu_1^0 + x_2\mu_2^0 + RTx_1 \ln x_1 + RTx_2 \ln x_2 + \lambda x_1 x_2$$

where x_1 and x_2 are the mole fractions of particles of types 1 and 2, respectively. (a) For the case when $\mu_1^0 = 1.0$, $\mu_2^0 = 1.05$, $RT = 0.39$, and $\lambda = 1$, what are x_1^{I} and x_1^{II}? (b) Use conditions $(\partial\mu_1/\partial x_1)_{P,T}^c = (\partial^2\mu_1/\partial x_1^2)_{P,T}^c = 0$ to locate the critical point.

Answer: (a) In the expression for the molar Gibbs free energy let $x_2 = 1 - x_1$ and find points with equal slope $\mathrm{d}g/\mathrm{d}x_1$ *and* a common tangent. This can be done graphically and gives equilibrium concentrations $x_1^{\mathrm{I}} = 0.13$ and $x_1^{\mathrm{II}} = 0.87$.

(b) The chemical potential, μ_2, is $\mu_2 = \mu_2^0(P, T) + RT \ln(1 - x_1) + \lambda x_1^2$. Therefore, at the critical point we have $(\partial\mu_2/\partial x_1)_{P,T}^c = -RT/(1 - x_1) + 2\lambda x_1 = 0$ and $(\partial^2\mu_2/\partial x_1^2)_{P,T}^c = -RT/(1 - x_1)^2 + 2\lambda = 0$. If we solve these two equations for T and x_1, we find that the critical point is located at $x_1 = 1/2$ and $T = \lambda/2R$.

We see that there many analogies between the liquid–gas transition and the separation of a binary mixture into two phases. An example of a system exhibiting this type of behavior is a mixture of *n*-hexane and nitrobenzene at atmospheric pressure. The phase diagram for this system is given in Figure 4.9.

4.6
The Helium Liquids

Helium atoms, because of their small mass and weak attraction, remain in the liquid state for a wide range of pressures and temperatures down to the lowest measured values. The helium atom occurs in nature in two stable isotopic forms, He^3 and He^4. He^3, with nuclear spin (1/2), obeys Fermi–Dirac statistics; while He^4, with nuclear spin 0, obeys Bose–Einstein statistics. At very low temperatures, where quantum effects become important, He^3 and He^4 provide two of the few examples in nature of quantum liquids.

Chemically, He^3 and He^4 are virtually identical. The primary difference between them is a difference in mass. However, at low temperatures the two systems exhibit very different behavior due to the difference in their statistics. Liquid He^4, which is a boson liquid, exhibits a rather straightforward transition to a superfluid state at 2.19 K. Liquid He^3 also undergoes a transition to a superfluid state, but at a much lower temperature (2.7×10^{-3} K). The mechanism for the superfluid transition in liquid He^3 is quite different from that of liquid He^4.

When He^3 and He^4 are combined to form a binary mixture, a new type of phase point occurs (called a *tricritical point*) in which a λ-line connects to the critical point of a binary phase transition.

4.6.1
Liquid He^4

He^4 was first liquefied in 1908 by Kamerlingh Onnes at a temperature of 4.215 K at a pressure of 1 atm [101, 127, 218]. Unlike the classical liquids we described in Section 4.4, it has two triple points. The coexistence curves for liquid He^4 are shown in Figure 4.10a (compare them with the coexistence curve for a classical liquid in Figure 4.5). He^4 at low temperature has four phases. The solid phase only appears for pressures above 25 atm, and the transition between the liquid and solid phases is first order. The liquid phase continues down to temperatures approaching $T = 0$ K. However, there are in fact two liquid phases. As the normal liquid [liquid He(I)] is cooled, a line of λ-points occurs at about $T = 2$ K (the exact temperature depends on the pressure), indicating that a continuous symmetry-breaking phase transition occurs at this line. There is a triple point at each end of the λ-line. The symmetry that is broken is gauge symmetry. The specific heat of liquid He^4 along the λ-line is shown in Figure 4.10b. We can see that it has the lambda shape characteristic of a continuous phase transition.

The phase diagram of He^4 provides a good example of the third law. The vapor–liquid and solid–liquid coexistence curves approach the P-axis with zero slope. This is a consequence of the third law.

Below the λ-line, the liquid phase (which was called liquid He(II) by Keesom and Wolfke [99]) begins to exhibit very strange properties. In 1938, Kapitza [94]

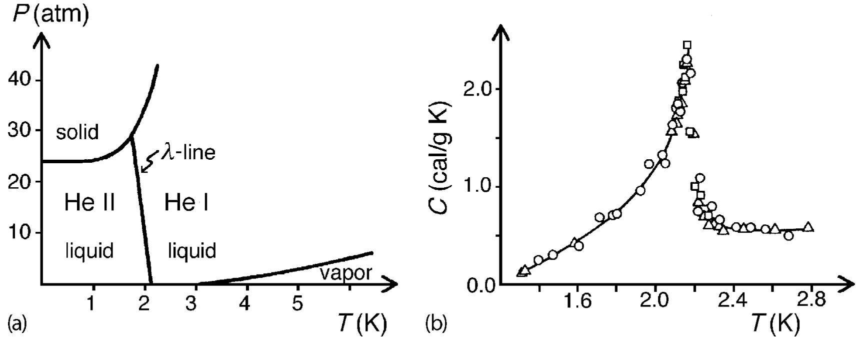


Figure 4.10 (a) The coexistence curves for He^4. (b) The specific heat of He^4 at vapor pressure at the λ-point [127].

and Allen and Misener [3] simultaneously published data that showed abnormally low viscosity in HeII (Kapitza called it a "superfluid"). Indeed, the first experimenters who worked with HeII, found that it was able to leak out of their containers through cracks so tiny that even He^4 gas could not leak through them. This apparently frictionless flow is a consequence of the fact that the condensed phase is a highly coherent macroscopic quantum state. The thermodynamic behavior of the liquid involves an unusual coupling of thermal and mechanical effects that are described below.

4.6.1.1 **Thermomechanical Effect**

The thermodynamic behavior of liquid He^4 below the λ-line can be modeled in terms of two interpenetrating fluids. One fluid (superfluid) can flow through tiny cracks and carries no entropy. The other fluid (normal fluid) behaves normally. The fact that the superfluid carries no entropy leads to interesting behavior that can be described with classical thermodynamics.

Let us consider two vessels A and B, insulated from the outside world and filled with liquid He^4 at a temperature below 2.19 K. We assume that A and B are connected by a capillary so thin that only the superfluid can pass through it (cf. Figure 4.11a). This means that the total entropy must remain constant if no irreversible processes take place. We also assume that the total mass and total volume of the system remain constant. Under these conditions, the equilibrium state is a state of minimum internal energy.

We can obtain the condition for equilibrium between the vessels if we assume that matter can flow between them but entropy cannot. The total internal energy will be denoted U_{T}, and u_l will denote internal energy per kilogram (specific internal energy) in vessel l. The total internal energy is then given by $U_{\mathrm{T}} = \sum_{l=\mathrm{A,B}} M_l u_l$, where M_l is the total mass of liquid He^4 in vessel l. At equilibrium, the total internal energy must be a minimum. Thus,

$$\delta U_{\mathrm{T}} = 0 = \sum_{l=\mathrm{A,B}} (u_l \delta M_l + M_l \delta u_l) . \tag{4.43}$$

Let us now assume that the total volume, V_l, and the total entropy, S_l, of liquid He^4 in vessel l (for $l = \mathrm{A, B}$) are constant (this is possible because only superfluid can flow between the vessels and superfluid carries no entropy). The entropy of liquid He^4 in vessel l can be written $S_l = M_l s_l$, where M_l and s_l are the total mass and specific entropy of liquid He^4 in vessel l. Similarly, $V_l = M_l v_{\mathrm{l}}$, where v_{l} is the specific volume of liquid He^4 in vessel l. Since S_l and V_l are constants, we can

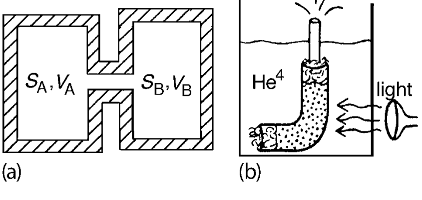


Figure 4.11 (a) Two vessels containing liquid He^4 below 2.19 K and connected by a very fine capillary. Only superfluid can pass between the two vessels. (b) The fountain effect.

write $\delta S_l = M_l \delta s_l + s_l \delta M_l = 0$ and $\delta V_l = M_l \delta v_1 + v_1 \delta M_l = 0$. Therefore,

$$\delta s_l = -s_l \frac{\delta M_l}{M_l} \quad \text{and} \quad \delta v_1 = -v_1 \frac{\delta M_l}{M_l} \,. \tag{4.44}$$

Let us now expand the differential, δu_l, in (4.43) in terms of specific entropy and specific volume. Equation (4.43) then takes the form

$$\sum_{l=\mathrm{A,B}} \left\{ u_l \delta M_l + M_l \left[\left(\frac{\partial u_l}{\partial s_l} \right)_{v_1} \delta s_l + \left(\frac{\partial u_l}{\partial v_1} \right)_{s_l} \delta v_1 \right] \right\} = 0 \,. \tag{4.45}$$

If we note that $(\partial u / \partial s)_v = T$ and $(\partial u / \partial v)_\mathrm{s} = -P$ and make use of Eq. (4.44), we obtain

$$\sum_{l=\mathrm{A,B}} (u_l - s_l T_l + v_1 P_l) \delta M_l = \sum_{l=\mathrm{A,B}} \mu_l \delta M_l = 0 \,, \tag{4.46}$$

where μ_l is the chemical potential of liquid He^4 in vessel l. Since the total mass is conserved, we can write $\delta M_\mathrm{A} = -\delta M_\mathrm{B}$ and we obtain the equilibrium condition

$$\mu_\mathrm{A}(T_\mathrm{A}, P_\mathrm{A}) = \mu_\mathrm{B}(T_\mathrm{B}, P_\mathrm{B}) \,. \tag{4.47}$$

Since matter can flow between the two vessels, the chemical potentials in the two vessels must be equal. However, heat cannot be exchanged and the volume cannot change (no mechanical energy transfer), so the pressure and temperature of the two vessels need not be the same.

We can now vary the temperature and pressure in one of the vessels (vessel A, for example) in such a way that the two vessels remain in equilibrium. The change in chemical potential in vessel A is

$$\Delta \mu_\mathrm{A} = -s \Delta T_\mathrm{A} + v \Delta P_\mathrm{A} \,, \tag{4.48}$$

where $s = -(\partial \mu / \partial T)_P$ and $v = (\partial \mu / \partial P)_T$. But to maintain equilibrium, we must have $\Delta \mu_\mathrm{A} = 0$ so the chemical potentials of the two vessels remain equal. Therefore,

$$\Delta P_\mathrm{A} = \frac{s}{v} \Delta T_\mathrm{A} \,. \tag{4.49}$$

Thus, a change in temperature of vessel A must be accompanied by a change in pressure of vessel A. If the temperature increases, the pressure will increase. This is called the *thermomechanical effect*.

The thermomechanical effect is most dramatically demonstrated in terms of the fountain effect. Imagine a small elbow tube filled with very fine powder, with cotton stuffed in each end. Assume that a long, thin capillary tube is put in one end and the elbow tube is immersed in liquid He^4 at a temperature below 2.19 K. If we now irradiate the elbow tube with a burst of light, the pressure of helium in the elbow tube will increase and helium will spurt out of the capillary tube (cf. Figure 4.11b). This is called the *fountain effect* and is a consequence of Eq. (4.49).

When helium in the elbow tube is heated by radiation, superfluid will flow into the elbow tube to equalize the chemical potentials and increase the pressure in the elbow tube. It is interesting that in the fountain effect there is a spontaneous flow of matter from a cooler to hotter vessel. However, since the superfluid does not carry entropy, this does not violate the second law.

4.6.2
Liquid He^3

The He^3 atom is the rarer of the two helium isotopes [123, 137, 211]. Its relative abundance in natural helium gas is one part in a million. Therefore, in order to obtain it in large quantities, it must be "grown" artificially from tritium solutions through β-decay of the tritium atom. Thus, He^3 was not obtainable in large enough quantities to study until the late 1940s and it was first liquefied in 1948 by Sydoriack, Grilly, and Hammel [195]. Since the He^3 atom has only 3/4 the mass of a He^4 atom, it has a larger zero point energy than the He^4 atom. As a result, He^3 boils at a temperature about 25% lower than He^4, and it requires a pressure about 25% greater than that of He^4 to solidify.

The phase diagram for He^3 (on the same scale as that for He^4) is given in Figure 4.12a. On this scale there appears to be no transition to a superfluid state. There is, however, a minimum in the liquid–solid coexistence curve. This is attributed to the spin of the He^3 atom. At low temperature the spin lattice of the He^3 solid has a higher entropy than the liquid. The entropy difference, $\Delta S = S_{\text{liquid}} - S_{\text{solid}}$, is positive at high temperature, vanishes at about $T = 0.3\,\text{K}$ and becomes negative below 0.3 K. Since volume differences remain virtually unchanged, the Clausius–Clapeyron equation $\mathrm{d}P/\mathrm{d}T = \Delta S/\Delta V$ leads to a positive slope at high temperature and a negative slope at low temperature. At low temperature, if the third law is to be satisfied, the slope of the liquid–solid coexistence curve must become flat as $T \to 0\,\text{K}$.

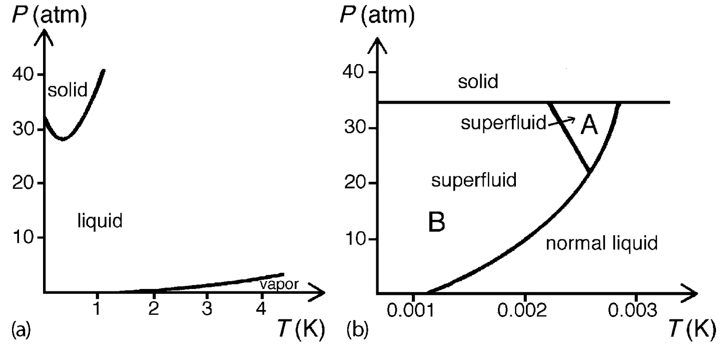


Figure 4.12 (a) Coexistence curves for He^3. (b) Coexistence curves for superfluid phases of He^3 when no magnetic field is applied [99].

Superfluidity was first observed in liquid He^3 in 1971 by Osheroff, Richardson, and Lee [159]. In 1997, they received the Nobel prize for this work. The transition occurs at 2.7×10^{-3} K at a pressure of about 34 atm. The phase diagram for a small temperature interval is shown in Figure 4.12b. There are, in fact, several superfluid phases in liquid He^3, depending on how the bound pairs orient themselves. The so-called A-phase is an anisotropic phase. The He^3 atoms (more accurately He^3 atoms "dressed" by interactions with the surrounding medium) form bound pairs with a spin $s = 1$ and relative angular momentum, $l = 1$, which means the spatial distribution of the pairs is flattened and have structure. The fact that the bound pairs in the A-phase have structure leads to many fascinating effects. The B-phase is a more isotropic phase. The bound pairs have spin $s = 0$ and relative angular momentum, $l = 0$, so the spatial distribution of the pairs is spherical. This phase has many features in common with the superfluid phase of a superconductor. If we apply a magnetic field to liquid He^3, a third superfluid phase appears. The transition between the normal and superfluid phases appears to be continuous, while that between the A and B superfluid phases appears to be first order.

4.6.3
Liquid He^3-He^4 Mixtures

When He^3 and He^4 are mixed together and condensed to the liquid state, some interesting phenomena occur. We will let x_3 denote the mole fraction of He^3. In 1949, Abraham, Weinstock, and Osborne [1] showed that He^3-He^4 mixtures can undergo a transition to a superfluid state. In this early experiment, they found that the λ-line extended from $T = 2.19$ K for $x_3 = 0$ to about $T = 1.56$ K for $x_3 = 0.282$. Later experiments extended the λ-line down to $T = 0.87$ K for $x_3 = 0.67$ (cf. Figure 4.13).

In 1954, Prigogine, Bingen, and Bellemans [171] predicted the existence of a phase separation of liquid He^3-He^4 mixtures into an He^3-rich phase and an He^4-rich phase. This phase separation was found in 1956 by Walters and Fair-

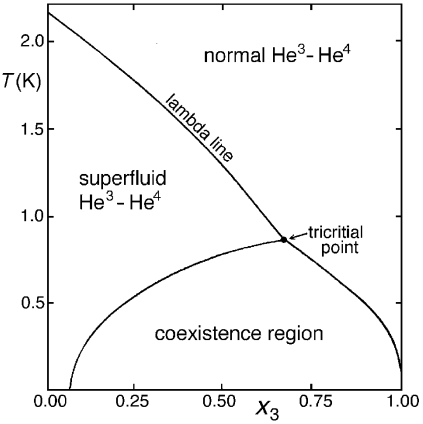


Figure 4.13 The phase diagram for a liquid He^3-He^4 mixture plotted as a function of temperature T and mole fraction x_3 of He^3.

bank [206], using nuclear magnetic resonance techniques. The critical point for this binary phase transition lies at the end of the λ-line at $T = 0.87$ K and $x_3 = 0.67$. The phase transition along the λ-line is second order. The binary phase separation is a first-order phase transition. In 1982, the region of metastable states for this first-order phase transition was measured by Alpern, Benda, and Leiderer [4]. The end point of the λ-line is the critical point of the first-order binary phase transition. It was first called a *tricritical point* by Griffiths [75]. In a *suitable space*, it is the meeting point of three lines of second-order phase transitions. One line is the λ-line and the other two are lines of critical points associated with the first-order phase transition. Thus, the tricritical point is different from the triple points we have seen in classical fluids.

4.7
Superconductors

Superconductivity was first observed in 1911 by Kamerlingh Onnes [126, 154, 197]. He found that the resistance to current flow in mercury drops to zero at about 4.2 K (cf. Figure 4.14). At first this was interpreted as a transition to a state with infinite conductivity. However, infinite conductivity imposes conditions on the magnetic field which were not subsequently observed. The relation between the electric current $\boldsymbol{J}$ and the applied electric field $\boldsymbol{E}$ in a metal is given by Ohm's law $\boldsymbol{J} = \sigma\boldsymbol{E}$, where σ is the conductivity. The electric field $\boldsymbol{E}$ is related to the magnetic field $\boldsymbol{B}$ by Faraday's law, $\nabla_r \times \boldsymbol{E} = -\partial\boldsymbol{B}/\partial t$. If we combine these two laws we get $\nabla_r \times \boldsymbol{J}/\sigma = -\partial\boldsymbol{B}/\partial t$. Therefore, infinite conductivity, $\sigma \to \infty$, implies that $\partial\boldsymbol{B}/\partial t = 0$. This in turn implies that the state of the system depends on its history. If we first cool the sample below the transition temperature and then apply an external magnetic field, $\boldsymbol{H}$, surface currents must be created in the sample to keep any field from entering the sample, since $\boldsymbol{B}$ must remain zero inside. However, if we place the sample in the $\boldsymbol{H}$-field before cooling, a $\boldsymbol{B}$-field is created inside. Then, if we cool the sample, the $\boldsymbol{B}$-field must stay inside. Thus, the final states depend on how we prepare the sample. With the hypothesis of infinite conductivity, the state below the transition temperature cannot be a thermodynamic state since it depends on history.

In 1933, Meissner and Ochsenfeld [135] cooled a monocrystal of tin in a magnetic field and found that the field inside the sample was expelled below the transition point for tin indicating a transition to a state of perfect diamagnetism, $\boldsymbol{B} = 0$ inside the sample. It is now known that superconductors are perfect diamagnets.

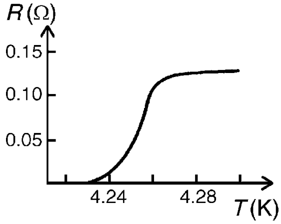


Figure 4.14 The resistance of mercury drops to zero at about 4.2 K (based on [154]).

When superconducting metals are cooled below their transition point in the presence of a magnetic field, currents are set up on the surface of the sample in such a way that the magnetic fields created by the currents cancel any magnetic fields initially inside the medium. Thus, $\boldsymbol{B} = 0$ inside a superconducting sample regardless of the history of its preparation.

No electric field is necessary to cause a current to flow in a superconductor. A magnetic field is sufficient. In a normal conductor, an electric field causes electrons to move at a constant average velocity because interaction with lattice impurities acts as a friction which removes energy from the electron current. In a superconductor, an electric field accelerates part of the electrons in the metal because no significant frictional effects act to slow them down. This behavior is reminiscent of the frictionless superflow observed in liquid He^4 below 2.19 K. Indeed, the superfluid flow in He^4 and the supercurrents in superconductors are related phenomena. The origin of the apparently frictionless flow in both cases lies in quantum mechanics. Electrons in a superconducting metal can experience an effective attractive interaction due to interaction with lattice phonons. Because of this attraction, a fraction of the electrons (we never know which ones) can form "bound pairs." The state of minimum free energy is the one in which the bound pairs all have the same quantum numbers. Thus, the bound pairs form a single macroscopically occupied quantum state which acts coherently and forms the condensed phase. Any friction effects due to lattice impurities must act on the entire phase (which will contain many pairs and have a large mass) and not on a single pair. Thus, when an electric field is applied, the condensed phase moves as a whole and is not slowed significantly by frictional effects.

If a superconductor is placed in a large enough external magnetic field, the superconducting state can be destroyed. A plot of magnetic induction, B, versus applied field, H, appears as in Figure 4.15a. For applied field, H, with a value less than some temperature-dependent critical value, $H_{\text{coex}}(T)$, the system is a perfect diamagnet. That is, the permeability $\mu = 0$ and therefore $B = 0$. However, for $H > H_{\text{coex}}(T)$ the system becomes normal and $B = \mu H$. (For normal metals $\mu \approx \mu_0$, where μ_0 is the permeability of the vacuum.) Thus, inside the sample $B = 0$ if $H < H_{\text{coex}}(T)$ and $B = \mu_0 H$ if $H > H_{\text{coex}}(T)$.

The field, $H_{\text{coex}}(T)$ lies on the coexistence curve for the two phases. It has been measured as a function of the temperature and has roughly the same behavior for most metals (cf. Figure 4.15b). The coexistence curve for the normal and superconducting phases is well approximated by the equation

$$H_{\text{coex}}(T) = H_0\left(1 - \frac{T^2}{T_c^2}\right) , \tag{4.50}$$

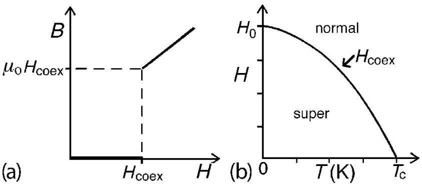


Figure 4.15 (a) A plot of the magnetic induction, $\boldsymbol{B}$, versus the applied magnetic field, H, in a superconductor (b) The coexistence curve for normal and superconducting states.

where T_c is the critical temperature when no external fields are present. The slope $(\mathrm{d}H/\mathrm{d}T)_\mathrm{coex} = 0$ at $T = 0\,\mathrm{K}$ and is negative at $T = T_\mathrm{c}$. The phase diagram for a superconducting metal has analogies to the vapor–liquid transition in a PVT system, if we let H_coex replace the specific volume. Inside the coexistence curve, condensate begins to appear.

Along the coexistence curve, the chemical potentials of the superconducting and normal phases must be equal and, therefore, any changes in the chemical potentials must be equal. Thus, along the coexistence curve $-s_n\,\mathrm{d}T - B_n\,\mathrm{d}H = -s_\mathrm{s}\,\mathrm{d}T - B_\mathrm{s}\,\mathrm{d}H$ and

$$s_n - s_\mathrm{s} = -\mu_0 H_\mathrm{coex}(T)\left(\frac{\mathrm{d}H}{\mathrm{d}T}\right)_\mathrm{coex} , \tag{4.51}$$

where we have used the fact that $B_\mathrm{s} = 0$ and $B_n = \mu_0 H_\mathrm{coex}(T)$ on the coexistence curve. Equation (4.51) is the Clausius–Clapeyron equation for superconductors. Here $s_{n(s)}$ is the entropy per unit volume of the normal (superconducting) phase. We see that the transition has a latent heat (is first order) for all temperatures except $T = T_\mathrm{c}$ where $H_\mathrm{coex} = 0$. When no external magnetic fields are present, the transition is continuous.

The change in the heat capacity per unit volume at the transition is

$$(c_n - c_\mathrm{s})_\mathrm{coex} = \left[T\frac{\partial(s_n - s_\mathrm{s})}{\partial T}\right]_\mathrm{coex} = 2\mu_0\frac{H_0^2}{T_\mathrm{c}}\left(\frac{T}{T_\mathrm{c}} - \frac{3T^3}{T_\mathrm{c}^3}\right) . \tag{4.52}$$

We have used Eq. (4.50) to evaluate the derivatives $(\mathrm{d}H/\mathrm{d}T)_\mathrm{coex}$. At low temperatures the heat capacity of the normal phase is higher than that of the superconducting phase. At $T = T_\mathrm{c}$ (the critical point) the heat capacity is higher in the superconductor and has a finite jump, $(c_\mathrm{s} - c_n)_{T=T_\mathrm{c}} = (4\mu_0/T_\mathrm{c})H_0^2$. It is worthwhile nothing that as $T \to 0$, $(s_\mathrm{s} - s_n) \to 0$ since $(\mathrm{d}H/\mathrm{d}T)_\mathrm{coex} \to 0$ as $T \to 0$. This is in agreement with the third law of thermodynamics.

4.8
Ginzburg–Landau Theory

In the late 1930s, Ginzburg and Landau proposed a mean field theory of continuous phase transitions which relates the order parameter to the underlying symmetries of the system. First-order phase transitions may or may not involve the breaking of a symmetry of the system. For example, in the liquid–solid and vapor–solid transitions, the translational symmetry of the high-temperature phase (liquid or vapor) is broken, but for the vapor–liquid transition no symmetry of the system is broken. Solids may also exhibit first-order phase transitions in which the lattice structure undergoes a sudden rearrangement from one symmetry to another and the state of the solid changes discontinuously.

At a continuous phase transition, the slope of the free energy curve changes continuously and a symmetry is always broken. In such transitions, a new macroscopic parameter (the order parameter) appears in the less symmetric phase. The order parameter may be a scalar, a vector, a tensor, a complex number or some other quantity. The form of the order parameter is determined by the type of symmetry that is broken [118]. For example, in the transition from a paramagnetic to a ferromagnetic system, rotational symmetry is broken because a spontaneous magnetization occurs which defines a unique direction in space. The order parameter is a vector. In the transition from normal liquid He^4 to superfluid liquid He^4, gauge symmetry is broken. The order parameter is a complex scalar. In a solid, the lattice might begin to undergo a gradual reorientation as the temperature is lowered. The order parameter is the change in the spatially varying number density. In continuous transitions, one phase will always have a lower symmetry than the other. Usually the lower temperature phase is less symmetric, but this need not always be the case.

All transitions which involve a broken symmetry and a continuous change in the slope of the free energy curve can be described within the framework of a mean field theory due to Ginzburg and Landau [118]. Ginzburg–Landau theory does not describe all features of continuous phase transitions correctly, but it does give us a good starting point for understanding such transitions.

4.8.1
Continuous Phase Transitions

We will let η denote the order parameter and let ϕ denote the free energy and write

$$\phi(T, Y, f) = \phi_0(T, Y) + \alpha_2(T, Y)\eta^2 + \alpha_3(T, Y)\eta^3 + \alpha_4(T, Y)\eta^4 + \cdots - f\eta \,, \tag{4.53}$$

where f is the force conjugate to the order parameter and coefficients $\alpha_i(Y, T)$ depend on the details of the transition. There is no term in Eq. (4.53) which is first order in η because that would ensure a nonzero value for the order parameter above the transition point. The molar free energy, $\phi_0(T, Y)$, describes the thermodynamic quantities not directly involved in the transition and generally will depend on other state variables. The value of the order parameter, η, that is realized in nature, is the one that gives a minimum of the free energy.

A continuous phase transition can occur if the cubic term in Eq. (4.53) cannot appear and if no external field is present. The free energy then takes the form

$$\phi(T, Y, \eta) = \phi_0(T, Y) + \alpha_2(T, Y)\eta^2 + \alpha_4(T, Y)\eta^4 + \cdots \tag{4.54}$$

The dependence of $\alpha_2(T, Y)$ on temperature is chosen so that for temperatures above and at the critical temperature, the free energy will only be minimized for $\eta = 0$, while below the critical temperature it will be minimized for $|\eta| > 0$.

In general, the free energy will be minimum if

$$\left(\frac{\partial \phi}{\partial \eta}\right)_{T,Y} = 0 \quad \text{and} \quad \left(\frac{\partial^2 \phi}{\partial \eta^2}\right)_{T,Y} \geq 0 \,. \tag{4.55}$$

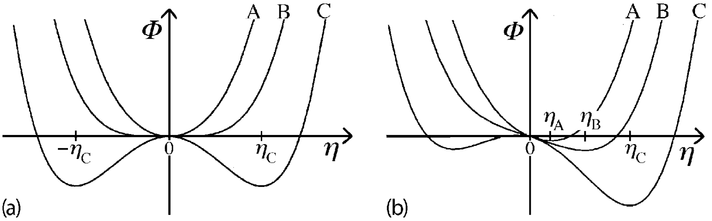


Figure 4.16 The behavior of the free energy for $\alpha_4 = 4.0$. (a) The free energy $\phi = \alpha_2\eta^2 + \alpha_4\eta^4$. For the curves (A) $\alpha_2 = 0.6$, (B) $\alpha_2 = 0.0$, and (C) $\alpha_2 = -0.6$. In the figure, the nonzero equilibrium order parameter is $\eta_C = 2.7386$. (b) The free energy, $\phi = \alpha_2\eta^2 + \alpha_4\eta^4 - f\eta$ for $f = 0.06$, and (A) $\alpha_2 = 0.6$, (B) $\alpha_2 = 0.0$, and (C) $\alpha_2 = -0.6$. $\eta_A = 0.0485$, $\eta_B = 0.1554$, and $\eta_C = 0.2961$ give the location of the minima of the curves.

Equations (4.55) give us conditions that must be satisfied for equilibrium states. *Global stability* requires that $\alpha_4(T, Y) > 0$ and ensures that, as we increase η to very large values, the free energy will continue to increase.

The critical point occurs when $\alpha_2(T, Y) = 0$. This happens at a temperature $T = T_c(Y)$. If the critical temperature is a function of another variable, Y, then there will be a line of critical points in the (T, Y) plane. If we choose $\alpha_2(T, Y) > 0$ for $T > T_c(Y)$ and $\alpha_2(T, Y) < 0$ for $T < T_c(Y)$, then the free energy, Φ, will have its minimum value at $\eta = 0$ when $T > T_c(Y)$ and will have its minimum value for $\eta \neq 0$ when $T < T_c(Y)$. Since the free energy must vary continuously through the transition point, at $T = T_c(Y)$ we must have $\alpha_2(T_c, Y) = 0$. We can combine all this information if we write $\alpha_2(T, Y)$, in the neighborhood of the transition point, in the form

$$\alpha_2(T, Y) = \alpha_0(T, Y)(T - T_c(Y)) , \tag{4.56}$$

where α_0 is a slowly varying function of T and Y.

In Figure 4.16a, we sketch the free energy for three values of α_2. In curve (A), the free energy has a minimum for $\eta = 0$. Curve (B) shows the critical point. The free energy becomes flattened in the neighborhood of $\eta = 0$. In curve (C), the free energy has minima at $\eta = \pm\eta_0 \neq 0$. The system will randomly select one of these two nonzero values of the order parameter, η, below the critical point. The region on curve (C) for which $(\partial^2\phi/\partial\eta^2)_{T,Y} < 0$ corresponds to a region of unstable states. The free energy has *extrema* when

$$\left(\frac{\partial\phi}{\partial\eta}\right)_{T,Y} = 2\alpha_2\eta + 4\alpha_4\eta^3 = 0 \tag{4.57}$$

and therefore when

$$\eta = 0 \quad \text{or} \quad \eta = \pm\sqrt{\frac{-\alpha_2}{2\alpha_4}} = \pm\sqrt{\frac{\alpha_0}{2\alpha_4}(T_c - T)} . \tag{4.58}$$

When $T > T_c$, the *minimum* occurs for $\eta = 0$. When $T < T_c$, the *minimum* occurs for $\eta = \pm\sqrt{(\alpha_0/2\alpha_4)(T_c - T)}$. Thus, below the critical temperature, the order parameter is nonzero and increases as $\sqrt{T_c - T}$. From the above discussion, the free

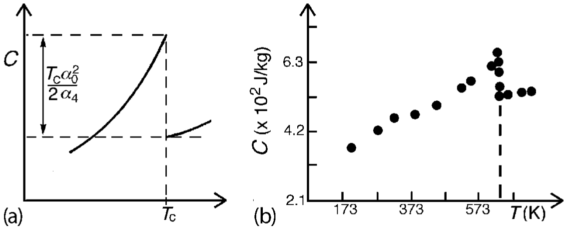


Figure 4.17 (a) The jump in the heat capacity at the critical point (lambda point) as predicted by Ginzburg–Landau theory. (b) The specific heat of nickel in the neighborhood of the Curie point. The dashed line gives the Curie point (based on [120].).

energy takes the following form:

$$\phi(T, Y, \eta) = \begin{cases} \phi_0(T, Y) & \text{for} \quad T > T_c \\ \phi_0(T, Y) - \frac{\alpha_0^2(T_c - T)^2}{4\alpha_4} & \text{for} \quad T < T_c \end{cases} , \tag{4.59}$$

where we have suppressed the dependence of T_c on Y and the dependence of α_0 and α_4 on T and Y.

The molar heat capacity is $c_Y = -T\left(\partial^2\phi/\partial T^2\right)_Y$. If we neglect derivatives of α_0 and α_4 (we assume that they vary slowly with temperature), we find that the molar heat capacity has a finite jump at the critical point:

$$c_Y\left(T_c^-\right) - c_Y\left(T_c^+\right) = \frac{T_c\alpha_0^2}{2\alpha_4} . \tag{4.60}$$

The jump in the heat capacity has the shape of a λ, as shown in Figure 4.17a, and therefore the critical point for a continuous phase transition is sometimes called a λ-point.

If we turn on an external force, f, which couples to the order parameter, then the continuous phase transition is destroyed. In the presence of an external force, the free energy has the form

$$\phi'(T, Y, f) = \phi(T, Y, \eta) - f\eta = \phi_0(T, Y) + \alpha_2\eta^2 + \alpha_4\eta^4 + \cdots - f\eta , \tag{4.61}$$

where $\alpha_2 = \alpha_2(T, Y)$ and $\alpha_4 = \alpha_4(T, Y)$. The order parameter is nonzero for all temperatures. A plot of the free energy in the presence of a force is shown in Figure 4.16b for the same parameters as Figure 4.16a.

From Eq. (4.61), we can obtain the susceptibility,

$$\chi = \left(\frac{\partial\eta}{\partial f}\right)_{T,Y} = -\left(\frac{\partial^2\phi'}{\partial f^2}\right)_{T,Y} . \tag{4.62}$$

The equilibrium state is a solution of the equation

$$\left(\frac{\partial\phi'}{\partial\eta}\right)_{T,Y} = 2\alpha_2\eta + 4\alpha_4\eta^3 - f = 0 . \tag{4.63}$$

If we take the derivative of Eq. (4.63) with respect to f and solve for $(\partial\eta/\partial f)_{T,Y}$, we obtain

$$\chi(f) = \left(\frac{\partial\eta}{\partial f}\right)_{T,Y} = \frac{1}{2\alpha_2 + 12\alpha_4\eta^2} \,. \tag{4.64}$$

In the limit, $f \to 0$, $\eta = 0$ for $T > T_\mathrm{c}$ and $\eta = \sqrt{-\alpha_2/2\alpha_4}$ for $T < T_\mathrm{c}$. Therefore, in the limit $f \to 0$ the susceptibility will be different above and below the critical point. We find

$$\chi = \lim_{f\to 0}\left(\frac{\partial\eta}{\partial f}\right)_{T,Y} = \begin{cases} \frac{1}{2\alpha_0(T-T_\mathrm{c})} & \text{for} \quad T > T_\mathrm{c}\,, \\ \frac{1}{4\alpha_0(T_\mathrm{c}-T)} & \text{for} \quad T < T_\mathrm{c}\,. \end{cases} \tag{4.65}$$

Note that the susceptibility diverges at the critical point.

4.8.2
First-Order Transitions

If the order parameter is a scalar, then there is no reason to exclude a third-order term in the molar free energy, ϕ. Also, if the order parameter is a second-order tensor, there are ways to contract a product of three such tensors to yield a scalar and again the free energy can have a third-order term. Such systems cannot exhibit a continuous transition. To see why, let us write the free energy in the form

$$\phi(T, Y, \eta) = \phi_0(T, Y) + \alpha_2\eta^2 + \alpha_3\eta^3 + \alpha_4\eta^4 + \cdots \,, \tag{4.66}$$

where $\alpha_2 = \alpha_2(T, Y)$, $\alpha_3 = \alpha_3(T, Y)$, and $\alpha_4 = \alpha_4(T, Y)$.

The extrema of the free energy are given by the equation $(\partial\phi/\partial\eta)_{T,Y} = 0$, which has solutions $\eta = 0$ and $\eta = (-3\alpha_3 \pm \sqrt{9\alpha_3^2 - 32\alpha_2\alpha_4})/8\alpha_4$. As long as $9\alpha_3^2 - 32\alpha_2\alpha_4 < 0$, the only minimum of the free energy occurs at $\eta = 0$ because other values of η will be complex and therefore unphysical. When $9\alpha_3^2 - 32\alpha_2\alpha_4 > 0$,

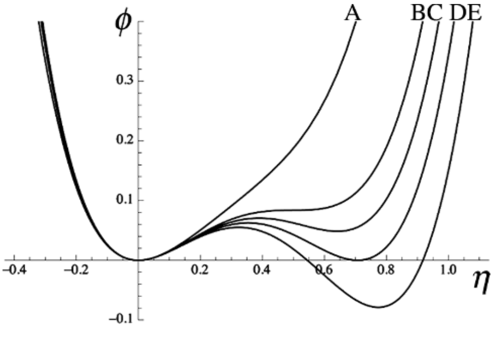


Figure 4.18 The behavior of the free energy, $\phi = \alpha_2\eta^2 + \alpha_3\eta^3 + \alpha_4\eta^4$, for $\alpha_2 = 2.0$, $\alpha_4 = 4.0$, and (A) $\alpha_3 = -4.5$, (B) $\alpha_3 = -5.333$, (C) $\alpha_3 = -5.5$, (D) $\alpha_3 = -5.6568$, and (E) $\alpha_3 = -5.85$. In the figure, $\eta_\mathrm{E} = 0.7738$.

two minima and one maximum can exist. A plot of the free energy for $\alpha_2 > 0$, $\alpha_4 > 0$, and a range of values of α_3 is given in Figure 4.18. For curves A, B, and C the state of minimum free energy (the equilibrium state) occurs for $\eta = 0$. Curve D shows the behavior of the free energy at the critical temperature for this system. At this point the equilibrium state shifts from one with order parameter $\eta = 0$ to one with order parameter $\eta = \eta_{\mathrm{D}}$. Therefore, this is a discontinuous transition and is of the type one expects for a first-order transition. The transition point for the first-order transition (curve D in Figure 4.18) is easily found. It must satisfy the conditions $\phi - \phi_0 = 0$ and $(\partial\phi/\partial\eta)_{T,Y} = 0$. These two conditions give $\eta = -\alpha_3/2\alpha_4$ and $\alpha_2 = \alpha_3^2/4\alpha_4$. Therefore, the first-order transition occurs when $\alpha_2 > 0$, and therefore it occurs before any continuous transition as the temperature is lowered. If $\alpha_3 < 0$, then it occurs for a positive value of the order parameter. If $\alpha_3 > 0$, then it occurs for a negative value of the order parameter.

4.8.3
Some Applications of Ginzburg–Landau Theory

In this section, we discuss three applications of Ginzburg–Landau theory: superfluids, magnetic systems, and superconductors.

4.8.3.1 Superfluids

The phase transition from normal to superfluid phase is a transition in which gauge symmetry is broken. A gauge transformation is a transformation that changes the phase of all wave functions in the system. It is generated by the number operator. The transition from normal to superfluid in liquid He^4 is an example of a continuous phase transition which involves broken gauge symmetry. The order parameter, η, is the macroscopic wave function, Ψ, for the condensed phase. The free energy can be written

$$\phi(T, P, \Psi) = \phi_0(T, P) + \alpha_2|\Psi|^2 + \alpha_4|\Psi|^4 + \cdots \ , \tag{4.67}$$

where $\alpha_2(T, P) = \alpha_0(T, P)(T - T_{\mathrm{c}})$ and $\alpha_0(T, P)$ and $\alpha_4(T, P)$ are slowly varying functions of T and P. The order parameter, $\Psi = 0$, above the critical temperature, and $\Psi = \mathrm{e}^{\mathrm{i}\theta}\sqrt{(\alpha_0/2\alpha_4)(T_{\mathrm{c}} - T)}$ below the critical temperature. The phase factor, θ, can be chosen to be zero as long as no currents flow in the system. For liquid He^4 (see Figure 4.10a), there is a line of continuous transition points in the (P, T) plane. In Figure 4.10b, the heat capacity has a finite lambda-shaped jump as we pass through the line of critical points.

4.8.3.2 The Curie Point

The transition from a paramagnetic to ferromagnetic system is one of the simplest examples of a continuous phase transition. A system which exhibits this behavior is a magnetic solid, such as nickel, whose lattice sites contain atoms with a magnetic moment. The critical temperature is called the Curie temperature. Above the Curie temperature, the magnetic moments are oriented at random and there is no net magnetization. However, as the temperature is lowered, magnetic interaction energy between lattice sites becomes more important than randomizing thermal energy. Below the Curie temperature, the magnetic moments became ordered on the average and a spontaneous magnetization appears. The symmetry that is broken at the Curie point is rotation symmetry. Above the Curie point, the paramagnetic system is rotationally invariant, while below it the spontaneous magnetization selects a preferred direction in space. The order parameter for this continuous phase transition is the magnetization, $\boldsymbol{M}$. The magnetization is a vector and changes sign under time reversal. The free energy is a scalar and does not change sign under time reversal. If a magnetic field, $\boldsymbol{H}$, is applied to the system, the Ginzburg–Landau free energy can be written in the form

$$\phi(T,\boldsymbol{H}) = \phi_0(T) - \boldsymbol{M}\cdot\boldsymbol{H} + \alpha_2\boldsymbol{M}\cdot\boldsymbol{M} + \alpha_4(\boldsymbol{M}\cdot\boldsymbol{M})^2 + \cdots \ , \tag{4.68}$$

where the coefficients α_2 and α_4 have the same properties as described above. For the case when the applied field $\boldsymbol{H}$ equals 0, the magnetization $\boldsymbol{M}$ equals 0 above the Curie temperature and $\boldsymbol{M} = \pm\sqrt{(\alpha_0/2\alpha_4)(T_\mathrm{c} - T)}\hat{\boldsymbol{e}}_M$ below the Curie temperature, where $\hat{\boldsymbol{e}}_M$ is a unit vector which gives the direction of the magnetization vector. The actual direction of the magnetization vector, if $\boldsymbol{H} = 0$, will be determined by random fluctuations or outside influences. The heat capacity at the Curie point exhibits the characteristic λ-shaped peak. As an example, the λ-point in nickel is shown in Figure 4.17b.

4.8.3.3 **Superconductors**

The condensed phase in a superconductor corresponds to a macroscopically occupied quantum state and therefore the order parameter is a complex scalar function (a macroscopic "wave function") which we denote as Ψ. Gauge symmetry is broken in the transition to the superconducting phase. We can use Ginzburg–Landau theory to determine the shape and width of the interface between normal and condensed phases.

Under a gauge transformation, the order parameter Ψ changes its phase. However, the free energy must remain invariant under the gauge transformation. Therefore, if no magnetic fields are present, the Ginzburg–Landau expression for the free energy per unit volume has the form

$$\phi(\boldsymbol{r}, T) = \phi_n(T) + \alpha_2(T)|\Psi(\boldsymbol{r})|^2 + \alpha_4(T)|\Psi(\boldsymbol{r})|^4 + \frac{1}{2m}\left|\mathrm{i}\hbar\nabla_r\Psi(\boldsymbol{r})\right|^2 \ , \tag{4.69}$$

where $\hbar$ is Planck's constant, $|\Psi|^2 = \Psi^*\Psi$, and m is the mass of the superconducting electron pairs.

The total free energy, $\Phi(T)$, can be found by integrating $\phi(\boldsymbol{r}, T)$ over the entire volume so that

$$\Phi(T) = \int \mathrm{d}\boldsymbol{r}\left[\phi_n(T) + \alpha_2(T)|\Psi(\boldsymbol{r})|^2 + \alpha_4(T)|\Psi(\boldsymbol{r})|^4 + \frac{1}{2m}\left|\mathrm{i}\hbar\nabla_r\Psi(\boldsymbol{r})\right|^2\right] \ . \tag{4.70}$$

We now extremize the total free energy with respect to variations in Ψ^* by setting $\delta\Phi = \int \delta\phi/\delta\Psi^* \delta\Psi^* = 0$. This gives

$$\alpha_2 \Psi + 2\alpha_4 \Psi|\Psi|^2 - \frac{\hbar^2}{2m}\nabla_{\boldsymbol{r}}^2 \Psi(\boldsymbol{r}) = 0\,, \tag{4.71}$$

where we have performed an integration by parts and have assumed that both Ψ and the normal component of $\nabla_{\boldsymbol{r}}\Psi$ are zero at the surface of the volume of integration. Current flow involving condensed electron pairs in the superconductor is given by $\boldsymbol{J}(\boldsymbol{r}) = e\hbar/(2mi)(\Psi^*\nabla_{\boldsymbol{r}}\Psi - \Psi\nabla_{\boldsymbol{r}}\Psi^*)$. In the absence of a magnetic or electric field $\boldsymbol{J}(\boldsymbol{r}) = 0$ and we can assume that the order parameter Ψ is real.

We can now determine how the order parameter $\Psi(\boldsymbol{r})$ varies in space at the interface between a normal region and a condensed region. For simplicity, assume that the spatial variation of $\Psi(\boldsymbol{r})$ is along the z-direction so that $\Psi = \Psi(z)$. We introduce the dimensionless function $f(z) = \Psi\sqrt{\alpha_4/2|\alpha_2|}$. Then Eq. (4.71) takes the form

$$-\xi^2(T)\frac{\mathrm{d}^2 f}{\mathrm{d}z^2} - f + f^3 = 0\,, \tag{4.72}$$

where $\xi(T) = \sqrt{\hbar^2/2m|\alpha_2|}$ is the *Ginzburg–Landau coherence length*. Let us assume that the sample extends from $z = -\infty$ to $z = +\infty$ and the region from $z = -\infty$ to $z = 0$ is normal (contains no condensate) so $f(z = 0) = 0$. We further assume that deep inside the condensed phase the order parameter takes its maximum value $\Psi(z \to \infty) = \sqrt{|\alpha_2|2\alpha_4}$ so $f(z \to \infty) = 1$.

We can now solve Eq. (4.72). First multiply by $\mathrm{d}f/\mathrm{d}z$, rearrange terms and integrate to obtain

$$-\xi^2(T)\left(\frac{\mathrm{d}f}{\mathrm{d}z}\right)^2 = f^2 - \frac{1}{2}f^4 + C\,, \tag{4.73}$$

where C is an integration constant. Next require that $\mathrm{d}f/\mathrm{d}x = 0$ and $f = 1$ at $z = \infty$. This gives $C = -1/2$ and Eq. (4.73) takes the form

$$-\xi^2(T)\left(\frac{\mathrm{d}f}{\mathrm{d}z}\right)^2 = \frac{1}{2}(1 - f^2)^2\,. \tag{4.74}$$

We can solve Eq. (4.74) to obtain $f(z) = \tanh(z/\sqrt{2\xi})$ for $z \geq 0$ and $f(z) = 0$ for $z < 0$. Thus, most of the spatial variation of the order parameter occurs within a distance $z = 2\xi(T)$ of the boundary between the normal and condensed phases. Near a critical point $\xi(T)$ becomes very large.

4.9
Critical Exponents

The critical point is the point at which the order parameter of a new phase begins to grow continuously from zero [58, 82, 193]. As we approach the critical point from above (higher temperature), microscopic regions become ordered and fluctuate, although the order parameter on the average remains zero. These microscopic ordered regions grow and become very large as the critical point is approached. Just below the critical point, the order parameter of the new phase assumes a nonzero average value.

4.9.1
Definition of Critical Exponents

The behavior of thermodynamic systems, as they approach their critical point, appears to be universal. This can best be seen in terms of their critical exponents. As one approaches the critical point, various thermodynamic functions may diverge or go to zero or even remain finite. We therefore introduce an expansion parameter $\varepsilon = (T - T_c)/T_c$ that is a measure of the distance from the critical point. Near the critical point all thermodynamic functions can be written in the form

$$f(\varepsilon) = A\varepsilon^{\lambda}(1 + B\varepsilon^{y} + \cdots) \tag{4.75}$$

where $y > 0$. The critical exponent for the function $f(\varepsilon)$ is defined

$$\lambda = \lim_{\varepsilon \to 0} \frac{\ln f(\varepsilon)}{\ln \varepsilon} \, . \tag{4.76}$$

If λ is negative, $f(\varepsilon)$ diverges at the critical point. If λ is positive, $f(\varepsilon)$ goes to zero at the critical point.

The case where $\lambda = 0$ may correspond to several different possibilities; for example, it may correspond to a logarithmic divergence $f(\varepsilon) = A|\ln \varepsilon| + B$ or to a dependence on ε of the form $f(\varepsilon) = A + B\varepsilon^{1/2}$. For such cases a modified exponent is introduced. If j is the smallest integer for which $\mathrm{d}^j f(\varepsilon)/\mathrm{d}\varepsilon^j = f^{(j)}(\varepsilon)$ diverges, then

$$\lambda' = j + \lim_{\varepsilon \to 0} \frac{\ln |f^{(j)}(\varepsilon)|}{\ln \varepsilon} \, . \tag{4.77}$$

Although we have chosen to write ε in terms of temperature, we can also introduce critical exponents for quantities such as pressure, density, magnetic field, and so on. Thus, there are a number of different critical exponents that can be defined for a system, depending on how the critical point is approached. We give some examples below.

4.9.2
The Critical Exponents for Pure PVT Systems

There are four critical exponents that are commonly used to describe the bulk thermodynamic properties of PVT systems. Below, we define them and give their experimental values.

1. *Degree of the Critical Isotherm, δ.* The deviation of the pressure $(P - P_c)$ from its critical value varies *at least* as the fourth power of $(V - V_c)$ as the critical point is approached along the critical isotherm. It is convenient to express this fact by introducing a critical exponent, δ, such that

   $$\frac{P - P_c}{P_c^0} \equiv A_\delta \left| \frac{\rho - \rho_c}{\rho_c} \right|^\delta \operatorname{sign}(\rho - \rho_c) \,, \quad T = T_c \,, \tag{4.78}$$

   where P_c is the critical pressure, ρ_c is the critical density, A_δ is a constant, and P_c^0 is the pressure of an ideal gas at the critical density and temperature. Experimentally it is found that $6 > \delta_{\text{exp}} \geq 4$. The exponent δ is called the *degree of the critical isotherm.*
2. *Degree of the Coexistence Curve, β.* Guggenheim [76] has shown that the deviation $(T - T_c)$ varies approximately as the third power of $(V - V_c)$ as the critical point is approached along either side of the coexistence curve. One quantifies this by introducing a critical exponent β, such that

   $$\frac{\rho_l - \rho_g}{\rho_c} = A_\beta (-\varepsilon)^\beta \,, \tag{4.79}$$

   where ρ_l is the density of liquid at temperature $T < T_c$, ρ_g is the density of gas at temperature $T < T_c$, each evaluated on the coexistence curve, and A_β is a constant. The quantity $\rho_l - \rho_g$ is the order parameter of the system. It is zero above the critical point and nonzero below it. The exponent β is called the *degree of the coexistence curve* and is found from experiment to have values $\beta_{\text{exp}} \approx 0.34$.
3. *Heat Capacity, α.* The heat capacity at constant volume appears to have a logarithmic divergence for $T \to T_c$ along the critical isochore $(V = V_c)$. The critical exponent for heat capacity is denoted α and is defined as follows:

   $$C_V = \begin{cases} A'_\alpha (-\varepsilon)^{-\alpha'}, & T < T_c \,, \quad \rho = \rho_c \\ A_\alpha (+\varepsilon)^{-\alpha}, & T > T_c \,, \quad \rho = \rho_c \,, \end{cases} \tag{4.80}$$

   where A'_α and A_α are constants. The exponents α and α' are found experimentally to have values $\alpha_{\text{exp}} \sim 0.1$ and $\alpha'_{\text{exp}} \sim 0.1$.
4. *Isothermal Compressibility, γ.* The isothermal compressibility diverges approximately as a simple pole:

   $$\frac{\kappa_T}{\kappa_T^0} = \begin{cases} A'_\gamma (-\varepsilon)^{-\gamma'}, & T < T_c \,, \quad \rho = \rho_l(T) \quad \text{or} \quad \rho_g(T) \\ A_\gamma (+\varepsilon)^{-\gamma} \,, & T > T_c \,, \quad \rho = \rho_c \,, \end{cases} \tag{4.81}$$

   where A'_γ and A_γ are constants. For $T < T_c$ one approaches the critical point along the coexistence curve; for $T > T_c$ one approaches it along the critical isochore. Typical experimental values are $\gamma'_{\text{exp}} \sim 1.2$ and $\gamma_{\text{exp}} \sim 1.3$.

It is possible to obtain inequalities between the critical exponents using thermodynamic arguments. We shall give an example here. Equation (4.25) can be rewritten in terms of the mass density as

$$c_v = x_g c_{v_g} + x_l c_{v_l} + \frac{x_g T}{\rho_g^3 \kappa_T^g}\left(\frac{\partial \rho_g}{\partial T}\right)^2_{\text{coex}} + \frac{x_l T}{\rho_l^3 \kappa_T^l}\left(\frac{\partial \rho_l}{\partial T}\right)^2_{\text{coex}} , \tag{4.82}$$

where c_v, c_{v_g} and c_{v_l} are now specific heats (heat capacity per kilogram), and κ_T is the isothermal compressibility. All terms on the right-hand side of Eq. (4.82) are positive. Thus, we can write

$$c_v \geq \frac{x_g T}{\rho_g^3 \kappa_T^g}\left(\frac{\partial \rho_g}{\partial T}\right)^2_{\text{coex}} . \tag{4.83}$$

As the critical point is approached for fixed volume, $x_g \to (1/2), \rho_g \to \rho_c$ (ρ_c is the critical density), κ_T diverges as $(T_c - T)^{-\gamma'}$ (cf. Eq. (4.81)), and $(\partial \rho_g / \partial T)_{\text{coex}}$ diverges as $(T_c - T)^{\beta - 1}$ if we assume that $[(1/2)(\rho_l + \rho_g) - \rho_c]$ goes to zero more slowly than $(\rho_l - \rho_g)$ (cf. Eq. (4.13)). Thus,

$$c_v \geq \frac{1}{2}\frac{T_c B (T_c - T)^{\gamma' + 2\beta - 2}}{\rho_c^3} , \tag{4.84}$$

where B is a constant, so that $\ln c_v \geq (2 - \gamma' - 2\beta)|\ln(-\varepsilon)|$. If we next divide by $|\ln(-\varepsilon)|$ and take the limit $T \to T_c^-$, we find

$$\alpha' + 2\beta + \gamma' \geq 2 . \tag{4.85}$$

The inequality in Eq. (4.85) is roughly satisfied by real fluids. If we choose $\alpha' = 0.1, \beta = 1/3$, and $\gamma' = 1.3$, then $\alpha' + 2\beta + \gamma' \approx 2$. Equation (4.85) is called the *Rushbrook inequality*.

4.9.3

The Critical Exponents for the Curie Point

For magnetic systems, exponents α, β, γ, and δ can be defined in analogy with pure fluids. The coexistence curve for a ferromagnetic system is given in Figure 4.19a. Below some critical temperature the spins begin to order spontaneously. The coexistence curve separates the two directions of magnetization. In Figure 4.19b, we plot some isotherms of the magnetic system. It is helpful to refer to these curves when defining the various exponents.

1. *Degree of the Critical Isotherm, δ.* The exponent δ describes the variation of magnetization with magnetic field along the critical isotherm

$$\frac{H}{H_c^0} = B_\delta \left|\frac{M_H(T_c)}{M_0(0)}\right|^\delta , \tag{4.86}$$

where $H_c^0 = k_B T / m_0, M_0(0)$ is the magnetization in zero field at zero temperature, m_0 is the magnetic moment per spin, and B_δ is a proportionality constant. Experimentally, $4 \leq \delta_{\text{exp}} \leq 6$, in agreement with the values of δ_{exp} for pure fluids.

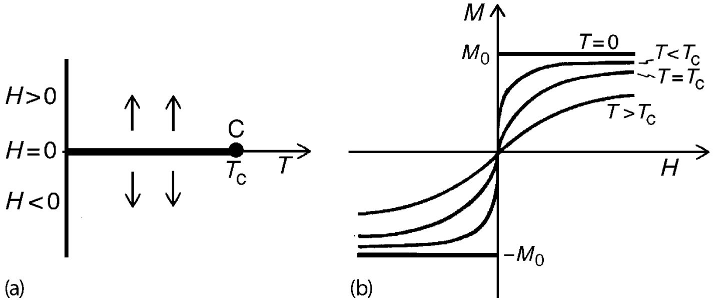


Figure 4.19 (a) Coexistence curve for a typical magnetic system. Below the Curie point the magnetization occurs spontaneously. The curve $H = 0$ separates the two possible orientations of the magnetization. (b) A sketch of the isotherms for a ferromagnetic system.

2. *Magnetization Exponent, β.* In a magnetic system, the exponent β describes how the magnetization approaches its value at the critical point when no external field is present. It is defined as follows:

$$\frac{M_0(T)}{M_0(0)} = B_\beta(-\epsilon)^\beta \,, \tag{4.87}$$

where B_β is a constant. For magnetic systems, $\beta_{\text{exp}} \approx 1/3$ as it is for fluids.

3. *The Heat Capacity, α.* For magnetic systems, the coefficients α and α' are defined as follows:

$$C_H(H=0) = \begin{cases} B'_\alpha(-\epsilon)^{-\alpha'} \,, & T < T_{\text{c}} \,, \\ B_\alpha \epsilon^{-\alpha} \,, & T > T_{\text{c}} \,, \end{cases} \tag{4.88}$$

where B_α and B'_α are constants. Experimentally, one finds $\alpha_{\text{exp}} \sim \alpha'_{\text{exp}} \sim 0$.

4. *The Magnetic Susceptibility, γ.* The magnetic susceptibility in the vicinity of the critical point can be written

$$\frac{\chi_T}{\chi_T^0} = \begin{cases} B'_\gamma(-\epsilon)^{-\gamma'} \,, & T < T_{\text{c}} \,, \quad H = 0 \,, \\ B_\gamma \epsilon^{-\gamma} \,, & T > T_{\text{c}} \,, \quad H = 0 \,, \end{cases} \tag{4.89}$$

where B'_γ and B_γ are constants and χ_T^0 is the susceptibility of a noninteracting system at the critical temperature. From experiment $\gamma_{\text{exp}} \sim 1.3$.

The striking feature about the critical exponents for fluids and for magnetic systems is that the values are roughly the same. Indeed, there appears to be a great similarity in the way in which many systems approach their critical points.

The critical exponents can be computed fairly easily starting from mean field theories such as the van der Waals equation of state or Ginzburg–Landau theory. All mean field theories give similar results. The common feature of these theories is that they assume that the particles move in a mean field due to all other particles. The mean field theories do not properly take into account the effects of short-ranged correlations at the critical point and do not give the correct results for the critical exponents. We shall return to this point when we discuss Wilson renormalization theory of critical points.

4.9.4
The Critical Exponents for Mean Field Theories

In this section, we compute the critical exponents, α, β, δ, and γ for a gas whose equation of state is given by the van der Waals equation.

The van der Waals equation, in terms of reduced variables, is $(\overline{P} + (3/\overline{v}^2))(3\overline{v} - 1) = 8\overline{T}$. In order to examine the neighborhood of the critical point, we introduce expansion parameters $\varepsilon = (T/T_c) - 1$, $\omega = (v/v_c) - 1$, and $\pi = (P/P_c) - 1$. In terms of these parameters, the van der Waals equation can be written

$$\left[(1+\pi) + \frac{3}{(1+\omega)^2}\right][3(\omega+1) - 1] = 8(1+\varepsilon)\,. \tag{4.90}$$

If we solve for π, we find

$$\pi = \frac{8\varepsilon + 16\varepsilon\omega + 8\varepsilon\omega^2 - 3\omega^3}{2 + 7\omega + 8\omega^2 + 3\omega^3}\,. \tag{4.91}$$

We can use this expression to obtain the critical exponents.

1. *The degree of the critical isotherm*, δ. Let $\varepsilon = 0$ in Eq. (4.91) and expand π in powers of ω. This gives

   $$\pi = -\frac{3}{2}\omega^3 + \cdots \tag{4.92}$$

   The degree of the critical isotherm is $\delta = 3$.
2. *The isothermal compressibility exponent*, γ. Let us compute $(\partial\pi/\partial\omega)_\varepsilon$ and then set $\omega = 0$. We obtain

   $$\left(\frac{\partial\pi}{\partial\omega}\right)_\varepsilon = -6\varepsilon \tag{4.93}$$

   for $\omega = 0$. The critical exponent, γ, is $\gamma = 1$.
3. *The degree of the coexistence curve*, β. In the neighborhood of the critical point, the van der Waals equation can be written

   $$\pi = 4\varepsilon - 6\varepsilon\omega + 9\varepsilon\omega^2 - \frac{3}{2}\omega^3 + \cdots \tag{4.94}$$

   The values of ω on either side of the coexistence curve can be found from two conditions along the isotherm:
   (i) The condition that the pressure and temperature of the liquid and gas in the coexistence region be equal $(\overline{P}(\overline{v}_l) = \overline{P}(\overline{v}_g))$ yields

   $$-\frac{3}{2}\omega_l^3 - 6\varepsilon\omega_l + 9\varepsilon\omega_l^2 = -\frac{3}{2}\omega_g^3 - 6\varepsilon\omega_g + 9\varepsilon\omega_g^2\,, \tag{4.95}$$

   where $\omega_{\text{ł}} = (v_{\text{ł}}/v_c) - 1$ and $\omega_g = (v_g/v_c) - 1$. If we note that ω_l is negative and write $\omega_l = -\tilde{\omega}_l$ and $\omega_g = +\tilde{\omega}_g$, then Eq. (4.95) gives

   $$4\varepsilon\left(\tilde{\omega}_l + \tilde{\omega}_g\right) + 6\varepsilon\left(\tilde{\omega}_l^2 - \tilde{\omega}_g^2\right) + \tilde{\omega}_l^3 + \tilde{\omega}_g^3 = 0\,; \tag{4.96}$$

(ii) The molar Gibbs free energy of the liquid and gas phases are equal so that $\int_{v_\mathrm{g}}^{v_\mathrm{l}} v\,\mathrm{d}P = 0$, which can also be written

$$\int\limits_{\omega_\mathrm{g}}^{\omega_\mathrm{l}} \mathrm{d}\omega(1+\omega)\left(-6\varepsilon + 18\omega\varepsilon - \frac{9}{2}\omega^2 + \cdots\right)$$
$$\approx -6\varepsilon(\omega_\mathrm{l} - \omega_\mathrm{g}) + 6\varepsilon\left(\omega_\mathrm{l}^2 - \omega_\mathrm{g}^2\right) - \frac{3}{2}\left(\omega_\mathrm{l}^3 - \omega_\mathrm{g}^3\right) + \cdots = 0 \qquad (4.97)$$

so that

$$4\varepsilon(\tilde{\omega}_\mathrm{l} + \tilde{\omega}_\mathrm{g}) + 4\varepsilon\left(\tilde{\omega}_\mathrm{l}^2 - \tilde{\omega}_\mathrm{g}^2\right) + \tilde{\omega}_\mathrm{l}^3 + \tilde{\omega}_\mathrm{g}^3 = 0\,. \qquad (4.98)$$

In order for Eqs. (4.96) and (4.98) to be consistent, we must have $\tilde{\omega}_\mathrm{g} = \tilde{\omega}_\mathrm{l}$. If we plug this into Eqs. (4.96) or (4.98), and let $\tilde{\omega}_\mathrm{l} = \tilde{\omega}_\mathrm{g} = \tilde{\omega}$, then $\tilde{\omega}^2 \approx -4\varepsilon$. Note that ε is negative. Thus,

$$\tilde{\omega}_\mathrm{g} \approx \tilde{\omega}_\mathrm{l} = 2|\varepsilon|^{1/2} \qquad (4.99)$$

and the degree of the coexistence curve is $\beta = 1/2$.

4. *The heat capacity exponent*, α. The jump in the heat capacity can be obtained from Eq. (4.25). Let us approach the critical point along the critical isochore, $v = v_\mathrm{c}$. Then as $T \to T_\mathrm{c}$, $x_\mathrm{l} \approx x_\mathrm{g} \to 1/2$ and $c_{v_\mathrm{g}} \to c_{v_\mathrm{l}}$. Thus, the jump in the heat capacity is given by

$$c_{v_\mathrm{c}}\left(T_\mathrm{c}^-\right) - c_{v_\mathrm{c}}\left(T_\mathrm{c}^+\right)$$
$$= \lim_{T\to T_\mathrm{c}}\left\{-\frac{T}{2}\left[\left(\frac{\partial P_\mathrm{g}}{\partial v_\mathrm{g}}\right)_T\left(\frac{\partial v_\mathrm{g}}{\partial T}\right)_\mathrm{coex}^2 + \left(\frac{\partial P_\mathrm{l}}{\partial v_\mathrm{l}}\right)_T\left(\frac{\partial v_\mathrm{l}}{\partial T}\right)_\mathrm{coex}^2\right]\right\}\,. \qquad (4.100)$$

Along the coexistence curve $(\partial\bar{v}/\partial\bar{T})_\mathrm{coex} = \pm|\varepsilon|^{-1/2}$, where the minus sign applies to the liquid and the plus sign applies to the gas. From Eqs. (4.94) and (4.99) we find

$$\left(\frac{\partial\bar{P}_\mathrm{l}}{\partial\bar{v}_\mathrm{l}}\right)_T \equiv \left(\frac{\partial\bar{P}_\mathrm{g}}{\partial\bar{v}_\mathrm{g}}\right)_T = 6|\varepsilon| - \frac{9}{2}\omega^2 - 18\omega|\varepsilon| + \cdots = -12|\varepsilon| \pm O(|\varepsilon|^{3/2})\,. \qquad (4.101)$$

If we note that $(P_\mathrm{c}v_\mathrm{c}/RT_\mathrm{c}) = (3/8)$, we find

$$c_{v_\mathrm{c}}\left(T_\mathrm{c}^-\right) - c_{v_\mathrm{c}}\left(T_\mathrm{c}^+\right) = \frac{9}{2}R + O(\varepsilon)\,. \qquad (4.102)$$

Thus, the van der Waals equation predicts a finite jump in the heat capacity at the critical point and therefore it predicts $\alpha' = \alpha = 0$.

4.10
Problems

Problem 4.1 A condensible vapor has a molar entropy $s = s_0 + R\ln[C(v - b)(u + (a/v))^{5/2}]$, where C and s_0 are constants. (a) Compute the equation of state. (b) Compute the molar heat capacities, c_v and c_P. (c) Compute the latent heat between liquid and vapor phases at temperature T in terms of the temperature T, the gas constant R, and the liquid and gas molar volumes v_l and v_g. How can you find explicit values of v_l and v_g if you need to?

Problem 4.2 Find the coefficient of thermal expansion, $\alpha_{\mathrm{coex}} = 1/v(\partial v/\partial T)_{\mathrm{coex}}$, for a gas maintained in equilibrium with its liquid phase. Find an approximate explicit expression for α_{coex}, using the ideal gas equation of state. Discuss its behavior.

Problem 4.3 Prove that the slope of the sublimation curve of a pure substance at the triple point must be greater than that of the vaporization curve at the triple point.

Problem 4.4 Approximately, how much pressure must be applied to an ice cube to make it melt at temperature $T = -1.5\,°\mathrm{C}$? (Note that the latent heat of fusion of H_2O is $L_\mathrm{f} = 3.33 \times 10^5\,\mathrm{J/kg}$, the density of water is $\rho_\mathrm{w} = 1.0 \times 10^3\,\mathrm{kg/m^3}$, and the density of ice is $\rho_\mathrm{I} = 0.917 \times 10^3\,\mathrm{kg/m^3}$.)

Problem 4.5 Consider the vaporization curve for liquid mercury. The latent heat of vaporization, L (in J/mol) varies slowly with pressure, but has significant variation with temperature and can be written $L = (7724 - 0.9768T)R$, where R is the gas constant and T is measured in kelvin. It is known that at atmospheric pressure ($P_{\mathrm{atm}} = 1.013 \times 10^5\,\mathrm{Pa}$) mercury begins to vaporize at temperature $T = 630\,\mathrm{K}$. (a) Plot the vaporization curve for mercury between temperatures $T = 500\,\mathrm{K}$ and $T = 650\,\mathrm{K}$. (b) At what pressure does mercury begin to vaporize when $T = 530\,\mathrm{K}$? (*Hint*: The volume of the liquid mercury can be neglected relative to that of the vapor and the vapor can be treated as an ideal gas.)

Problem 4.6 Two phases of solid carbon are called graphite and diamond. At standard temperature ($T_0 = 298\,\mathrm{K}$) and standard pressure ($P_0 = 1.0\,\mathrm{bar}$), the difference in the molar Gibbs free energy for these two phases is $\Delta g = g_\mathrm{G} - g_\mathrm{D} = -2.9\,\mathrm{kJ/mol}$, so graphine is the stable phase at standard temperature and pressure (STP). At STP, the difference in molar volume is $\Delta v = v_\mathrm{G} - v_\mathrm{D} = 1.9 \times 10^{-6}\mathrm{m^3/mol}$, and the difference in molar entropy is $\Delta s = s_\mathrm{G} - s_\mathrm{D} = 3.4\,\mathrm{J/(K\,mol)}$. (a) If temperature is held fixed at $T = T_0 = 298\,\mathrm{K}$, estimate the pressure at which a phase transition occurs and diamond becomes the most stable form of the crystal. (b) At temperature $T = 398\,\mathrm{K}$, at approximately what pressure does the phase transition from graphine to diamond occur?

Problem 4.7 One kilogram of superheated steam, at temperature $t = 350°\mathrm{C}$, pressure $P = 100\,\mathrm{bar}$, and specific entropy $s = 5.949\,\mathrm{kJ/(kg\,K)}$, is expanded reversibly and adiabatically to form wet steam at $t = 200\,°\mathrm{C}$ and pressure $P = 15.55\,\mathrm{bar}$. The specific entropy of water vapor and liquid water *on the coexistence curve* at $t = 200\,°\mathrm{C}$ are $s_{\mathrm{g}} = 6.428\,\mathrm{kJ/(kg\,K)}$ and $s_{\mathrm{l}} = 2.331\,\mathrm{kJ/(kg\,K)}$, respectively. The specific enthalpy of water vapor (gas) and liquid water *on the coexistence curve* at $t = 200\,°\mathrm{C}$ are $h_{\mathrm{g}} = 2791\,\mathrm{kJ/kg}$ and $h_{\mathrm{l}} = 852.4\,\mathrm{kJ/kg}$. (a) What is the specific enthalpy of the wet steam at $t = 200\,°\mathrm{C}$? (b) What fraction of the wet steam is liquid water?

Problem 4.8 Consider a monatomic fluid along its liquid–gas coexistence curve. Compute the rate of change of chemical potential along the coexistence curve, $(\mathrm{d}\mu/\mathrm{d}T)_{\mathrm{coex}}$, where μ is the chemical potential and T is the temperature. Express your answer in terms of s_{l}, v_{l} and s_{g}, v_{g}, which are the molar entropy and molar volume of the liquid and gas, respectively.

Problem 4.9 A system in its solid phase has a Helmholtz free energy per mole, $a_{\mathrm{s}} = B/Tv^3$, and in its liquid phase it has a Helmholtz free energy per mole, $a_{\mathrm{l}} = A/Tv^2$, where A and B are constants, v is the volume per mole, and T is the temperature. (a) Compute the molar Gibbs free energy density of the liquid and solid phases. (b) How are the molar volumes, v, of the liquid and solid related at the liquid–solid phase transition? (c) What is the slope of the coexistence curve in the P–T plane?

Problem 4.10 Deduce the Maxwell construction using stability properties of the Helmholtz free energy rather than the Gibbs free energy.

Problem 4.11 For a van der Waals gas, plot the isotherms in the $\overline{P}$–$\overline{V}$ plane ($\overline{P}$ and $\overline{V}$ are the reduced pressure and volume) for reduced temperatures $\overline{T} = 0.5$, $\overline{T} = 1.0$, and $\overline{T} = 1.5$. For $\overline{T} = 0.5$, is $\overline{P} = 0.1$ the equilibrium pressure of the liquid–gas coexistence region?

Problem 4.12 Medium size steam-based power stations in the Middle East typically output superheated steam at a temperature of $t = 496\,°\mathrm{C}$ and condense it at a temperature of $t = 38\,°\mathrm{C}$. (a) Compute the efficiency of these power stations assuming that they operate on a Rankine cycle. (b) Compute the efficiency of a Carnot engine operating between the same high and low temperatures. (*Hint*: you will need to estimate values for specific enthalpy, entropy and volume by extrapolating between data points in the steam tables.)

Problem 4.13 Consider a binary mixture composed of two types of particles, A and B. For this system the fundamental equation for the Gibbs free energy is $G = \mathfrak{n}_{\mathrm{A}}\mu_{\mathrm{A}} + \mathfrak{n}_{\mathrm{B}}\mu_{\mathrm{B}}$, the combined first and second laws are $\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}P + \mu_A\,\mathrm{d}\mathfrak{n}_{\mathrm{A}} + \mu_{\mathrm{B}}\,\mathrm{d}\mathfrak{n}_{\mathrm{B}}$ (S is the total entropy and V is the total volume of the system), and the chemical potentials μ_{A} and μ_{B} are intensive so that $\mu_{\mathrm{A}} = \mu_{\mathrm{A}}(P, T, x_{\mathrm{A}})$ and $\mu_{\mathrm{B}} = \mu_{\mathrm{B}}(P, T, x_{\mathrm{A}})$, where x_{A} is the mole fraction of A. Use these facts to derive the relations

$$s\,\mathrm{d}T - v\,\mathrm{d}P + \sum_{\alpha=\mathrm{A,B}} x_\alpha\,\mathrm{d}\mu_\alpha = 0$$

and

$$\sum_{\alpha=A,B} x_\alpha(\mathrm{d}\mu_\alpha + s_\alpha\,\mathrm{d}T - v_\alpha\,\mathrm{d}P) = 0\,,$$

where $s = S/\mathfrak{n}$, $v = V/\mathfrak{n}$, $\mathfrak{n} = \mathfrak{n}_\mathrm{A} + \mathfrak{n}_\mathrm{B}$, $s_\alpha = (\partial S/\partial\mathfrak{n}_\alpha)_{P,T,\mathfrak{n}_{\beta\neq\alpha}}$, and $v_\alpha = (\partial V/\partial\mathfrak{n}_\alpha)_{P,T,\mathfrak{n}_{\beta\neq\alpha}}$ with $\alpha = A, B$ and $\beta = A, B$.

Problem 4.14 Consider liquid mixture (l) of particles A and B coexisting in equilibrium with vapor mixture (g) of particles A and B. Show that the generalization of the Clausius–Clapeyron equation for the coexistence curve between the liquid and vapor phases when the mole fraction of A in the liquid phase is held fixed is given by

$$\left(\frac{\mathrm{d}P}{\mathrm{d}T}\right)_{x_\mathrm{A}^\mathrm{l}} = \frac{x_\mathrm{A}^\mathrm{g}\left(s_\mathrm{A}^\mathrm{g} - s_\mathrm{A}^\mathrm{l}\right) + x_\mathrm{B}^\mathrm{g}\left(s_\mathrm{B}^\mathrm{g} - s_\mathrm{B}^\mathrm{l}\right)}{x_\mathrm{A}^\mathrm{g}\left(v_\mathrm{A}^\mathrm{g} - v_\mathrm{A}^\mathrm{l}\right) + x_\mathrm{B}^\mathrm{g}\left(v_\mathrm{B}^\mathrm{g} - v_\mathrm{B}^\mathrm{l}\right)}\,,$$

where $s_\alpha = (\partial S/\partial\mathfrak{n}_\alpha)_{P,T,n_{\beta\neq\alpha}}$ and $v_\alpha = (\partial V/\partial\mathfrak{n}_\alpha)_{P,T,\mathfrak{n}_{\beta\neq\alpha}}$ with $\alpha = \mathrm{A, B}$ and $\beta = \mathrm{A, B}$. (*Hint*: Equations from Problem 4.13 are useful.)

Problem 4.15 A PVT system has a line of continuous phase transitions (a lambda line) separating two phases, I and II, of the system. The molar heat capacity c_P and the thermal expansivity α_P are different in the two phases. Compute the slope $(\mathrm{d}P/\mathrm{d}T)_\mathrm{coex}$ of the λ line in terms of the temperature T, the molar volume v, $\Delta c_P = c_P^\mathrm{I} - c_P^\mathrm{II}$, and $\Delta\alpha_P = \alpha_P^\mathrm{I} - \alpha_P^\mathrm{II}$.

Problem 4.16 Assume that two vessels of liquid He^4, connected by a *very* narrow capillary, are maintained at constant temperature; that is, vessel A is held at temperature T_A, and vessel B is held at temperature T_B. If an amount of mass, ΔM, is transferred reversibly from vessel A to vessel B, how much heat must flow out of (into) each vessel? Assume that $T_\mathrm{A} > T_\mathrm{B}$.

Problem 4.17 Water has a latent heat of vaporization, $\Delta h = 540\,\mathrm{cal/g}$. One mole of steam is kept at its condensation point under pressure at $T = 373\,\mathrm{K}$. The temperature is then lowered to $T = 336\,\mathrm{K}$, keeping the volume fixed. What fraction of the steam condenses into water? (Treat the steam as an ideal gas and neglect the volume of the water.)

Problem 4.18 The molar free energy of a spin system can be written

$$\begin{aligned}\phi(T,H) = \phi_0(T) &- \frac{1}{2}Jm^2 \\ &+ \frac{1}{2}k_\mathrm{B}T[(1+m)\ln(1+m) + (1-m)\ln(1-m)] - mH\end{aligned}$$

where J is the interaction strength, m is the net magnetization per mole, $\phi_0(T)$ is the molar free energy in the absence of a net magnetization, H is an applied magnetic field, k_B is Boltzmann's constant, and T is the temperature. (a) Compute the critical temperature (called the Curie temperature). (b) Compute the linear magnetic susceptibility of this system. (*Hint*: Only consider temperatures in the neighborhood of the critical point where m is small.)

Problem 4.19 A liquid crystal is composed of molecules which are elongated (and often have flat segments). It behaves like a liquid because the locations of the center-of-mass of the molecules have no long-range order. It behaves like a crystal because the orientation of the molecules does have long-range order. The order parameter for a liquid crystal is given by the dyatic $\boldsymbol{S} = \eta(\boldsymbol{nn} - 1/3\boldsymbol{I})$, where $\boldsymbol{n}$ is a unit vector (called the director) which gives the average direction of alignment of the molecules. The free energy of the liquid crystal can be written

$$\phi = \phi_0 + \frac{1}{2}AS_{ij}S_{ij} - \frac{1}{3}BS_{ij}S_{jk}S_{ki} + \frac{1}{4}CS_{ij}S_{ij}S_{kl}S_{kl}$$

where $A = A_0(T - T^*)$, A_0, B and C are constants, $\boldsymbol{I}$ is the unit tensor so $\hat{\boldsymbol{x}}_i \cdot \boldsymbol{I} \cdot \hat{\boldsymbol{x}}_j = \delta_{ij}$, $S_{ij} = \hat{\boldsymbol{x}}_i \cdot \boldsymbol{S} \cdot \hat{\boldsymbol{x}}_j$, and the summation is over repeated indices. The quantities $\hat{\boldsymbol{x}}_i$ are the unit vectors $\hat{\boldsymbol{x}}_1 = \hat{\boldsymbol{x}}$, $\hat{\boldsymbol{x}}_2 = \hat{\boldsymbol{y}}$, and $\hat{\boldsymbol{x}}_3 = \hat{\boldsymbol{z}}$. (a) Perform the summations in the expression for Φ and write Φ in terms of η, A, B, C. (b) Compute the critical temperature T_c at which the transition from isotropic liquid to liquid crystal takes place, and compute the magnitude of the order parameter η at the critical temperature. (c) Compute the difference in entropy between the isotropic liquid ($\eta = 0$) and the liquid crystal at the critical temperature.

Problem 4.20 The equation of state of a gas is given by the Berthelot equation $(P + a/Tv^2)(v - b) = RT$. (a) Find values of the critical temperature T_c, the critical molar volume v_c, and the critical pressure P_c, in terms of a, b, and R. (b) Does the Berthelot equation satisfy the law of corresponding states? (c) Find the critical exponents β, δ, and γ from the Berthelot equation.

Problem 4.21 A mixture of particles A and B have a molar Gibbs free energy of the form

$$g = x_A\mu_A^\circ(P, T) + x_B\mu_B^\circ(P, T) + RTx_A \ln x_A + RTx_B \ln x_B + \lambda x_A x_B\ ,$$

where $\mu_A^\circ(P, T)$ and $\mu_B^\circ(P, T)$ are the chemical potentials of pure A and pure B, respectively, at pressure P and temperature T, R is the gas constant, x_A and x_B are the mole fractions of A and B, respectively, and λ measures the strength of coupling between A and B. In terms of dimensionless parameters, $\overline{g} = g/\lambda$, $\overline{\mu}_A^\circ(P, T) = \mu_A^\circ(P, T)/\lambda$, $\overline{\mu}_B^\circ(P, T) = \mu_B^\circ(P, T)/\lambda$, and $\tau = RT/\lambda$, the molar Gibbs free energy takes the form

$$\overline{g} = x_A\overline{\mu}_A^\circ(P, T) + x_B\overline{\mu}_B^\circ(P, T) + \tau x_A \ln x_A + \tau x_B \ln x_B + x_A x_B\ .$$

Assume that $\overline{\mu}_B^\circ = 0.45$ and $\overline{\mu}_A^\circ = 0.40$.

(a) Find the critical temperature τ_c at which phase separation occurs and plot the curve separating the chemically stable from unstable regions in the τ–x_A plane.

(b) For $\tau = 1/2.6$, find equilibrium values of x_A on the coexistence curve.

(c) For $\tau = 1/3.6$, find equilibrium values of x_A on the coexistence curve.

(d) On the same plot as in (a), plot (sketch) the coexistence curve. You can estimate its location based on your results in (b) and (c).

Problem 4.22 For a binary mixture of particles of type 1 and 2, the Gibbs free energy is $G = \mathfrak{n}_1\mu_1 + \mathfrak{n}_2\mu_2$ and differential changes in the Gibbs free energy are $\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}P + \mu_1\,\mathrm{d}\mathfrak{n}_1 + \mu_2\,\mathrm{d}\mathfrak{n}_2$. The Gibbs free energy of the mixture is assumed to be

$$G = \mathfrak{n}_1\mu_1^0(P, T) + \mathfrak{n}_2\mu_2^0(P, T) + RT\mathfrak{n}_1 \ln x_1 + RT\mathfrak{n}_2 \ln x_2 + \lambda\mathfrak{n}x_1x_2 ,$$

where $\mu_1^0 = \mu_2^0$ are the chemical potentials of the pure substances. In the region in which the binary mixture separates into two phases, I and II with concentrations x_1^{I} and x_1^{II}, find the equation, $(\partial x_1^{\mathrm{I}}/\partial T)_P$ for the coexistence curve. Write your answer in terms of x_1^{I} and $\tau = T/T_{\mathrm{c}}$ where $T_{\mathrm{c}} = \lambda/2R$.

Problem 4.23 Consider a mixture of molecules of type A and B to which a *small* amount of type C molecules is added. Assume that the Gibbs free energy of the resulting tertiary system is given by

$$\begin{aligned} G(P, T, \mathfrak{n}_{\mathrm{A}}, \mathfrak{n}_{\mathrm{B}}, \mathfrak{n}_C) = {} & \mathfrak{n}_{\mathrm{A}}\mu_{\mathrm{A}}^0 + \mathfrak{n}_{\mathrm{B}}\mu_{\mathrm{B}}^0 + \mathfrak{n}_C\mu_C^0 \\ & + RT\mathfrak{n}_{\mathrm{A}} \ln x_{\mathrm{A}} + RT\mathfrak{n}_{\mathrm{B}} \ln x_{\mathrm{B}} + RT\mathfrak{n}_C \ln x_C \\ & + \lambda\mathfrak{n}_{\mathrm{A}}\mathfrak{n}_{\mathrm{B}}/\mathfrak{n} + \lambda_1\mathfrak{n}_{\mathrm{A}}\mathfrak{n}_C/\mathfrak{n} + \lambda_1\mathfrak{n}_{\mathrm{B}}\mathfrak{n}_C/\mathfrak{n} , \end{aligned}$$

where $\mathfrak{n} = \mathfrak{n}_{\mathrm{A}} + \mathfrak{n}_{\mathrm{B}} + \mathfrak{n}_{\mathrm{C}}$, $\mathfrak{n}_{\mathrm{C}} \ll \mathfrak{n}_{\mathrm{A}}$, and $\mathfrak{n}_{\mathrm{C}} \ll \mathfrak{n}_{\mathrm{B}}$. The quantities $\mu_{\mathrm{A}}^0 = \mu_{\mathrm{A}}^0(P, T)$, $\mu_{\mathrm{B}}^0 = \mu_{\mathrm{B}}^0(P, T)$, and $\mu_c^0 = \mu_{\mathrm{C}}^0(P, T)$ are the chemical potentials of pure A, B, and C, respectively, at pressure P and temperature T. For simplicity, assume that $\mu_{\mathrm{A}}^0 = \mu_{\mathrm{B}}^0 = \mu_{\mathrm{C}}^0$. To lowest order in the mole fraction x_{C}, compute the shift in the critical temperature and critical mole fraction of A due to the presence of C.

Problem 4.24 Compute the equilibrium vapor pressure of a monomolecular gas in equilibrium with a spherical droplet of liquid of the same substance, as a function of the radius R of the droplet and for fixed temperature. Assume the gas phase is well described by the ideal gas equation of state and the liquid can be assumed to be incompressible. Use the fact that for mechanical equilibrium $P_{\mathrm{l}} - P_{\mathrm{g}} = 2\sigma/R$, where P_{l} (P_{g}) is the pressure of the liquid (gas) and σ is the surface tension.

5
Equilibrium Statistical Mechanics I – Canonical Ensemble

5.1
Introduction

The entropy of *weakly* interacting systems can be obtained by counting the microscopic states available to those systems at a given energy. Then, assuming that all *microscopic* states have equal weight (are equally probable), we can assign probability distributions to *macroscopic* states that emerge due to underlying conservation laws, and we can compute average properties of these macroscopic quantities. In Chapter 2, the thermodynamic properties of noninteracting spin lattices, polymers, the Einstein solid and a classical ideal gas were derived in this manner. The assumption that all microscopic states with the same energy are equally probable can be justified in terms of the underlying Newtonian dynamics governing the system, provided that the dynamics is *ergodic* (see Appendix C). Hard-sphere gases have been rigorously proven to be ergodic. Chaotic dynamical systems are ergodic. Ergodicity forms the dynamical basis of statistical mechanics.

For a closed isolated system, such as those considered in Chapter 2, the entropy is determined by the number of microscopic states available to the system, and is defined $S = k_{\mathrm{B}} \ln[\mathfrak{N}(E)]$, where $k_{\mathrm{B}} = 1.38 \times 10^{-23}$ J/K is the Boltzmann constant and $\mathfrak{N}(E)$ is the number of microscopic states with energy E. The entropy must be an additive function of extensive variables, it must be positive, and it must have a maximum value at equilibrium. We can also write the entropy in terms of the probability density operator $\hat{\rho}$ (see Appendix A) and, in this form, it is called the *Gibbs entropy* and is given by

$$S = -k_{\mathrm{B}} \mathrm{Tr}(\hat{\rho} \ln \hat{\rho}) \,. \tag{5.1}$$

The trace, Tr, is taken over any complete orthonormal set of basis states.

For closed, isolated systems, the equilibrium probability density, must be a function of the Hamiltonian, $\hat{\rho} = \hat{\rho}(\hat{H})$ so it commutes with the Hamiltonian $\hat{H}$ and therefore does not vary in time. Let $|E, n\rangle$ denote a set of states of energy E with respect to which the density operator is diagonal. The integer, n, takes values $n = 1, \dots, N(E)$, where $N(E)$ is the total number of states with energy E. The probability to find the system in state $|E, n\rangle$ is $P_n = \langle E, n|\hat{\rho}|E, n\rangle$, and the entropy can

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be written

$$S = -k_{\mathrm{B}} \mathrm{Tr}(\hat{\rho} \ln \hat{\rho}) = -k_{\mathrm{B}} \sum_{n=1}^{N(E)} P_n \ln P_n \,. \tag{5.2}$$

We can determine the set of probabilities, $\{P_n\}$, which extremize the entropy subject to the constraint, $\mathrm{Tr}(\hat{\rho}) = \sum_{n=1}^{N(E)} P_n = 1$. The simplest way to do this is to use Lagrange multipliers. Since we have one constraint, we need one Lagrange multiplier, which we call α_0. We then require the following variation to be zero:

$$\delta \left[\sum_{n=1}^{N(E)} (\alpha_0 P_n - k_{\mathrm{B}} P_n \ln P_n) \right] = \sum_{n=1}^{N(E)} (\alpha_0 - k_{\mathrm{B}} - k_{\mathrm{B}} \ln P_n) \delta P_n = 0 \,. \tag{5.3}$$

Since the variation, δP_n, is arbitrary we must have $\alpha_0 - k_{\mathrm{B}} - k_{\mathrm{B}} \ln P_n = 0$ or $P_n = \exp(\alpha_0/k_{\mathrm{B}} - 1) =$ constant. The Lagrange multiplier, α_0, is determined by the normalization condition, $\mathrm{Tr}(\hat{\rho}) = \sum_{n=1}^{N(E)} P_n = 1$. We find that the probability, P_n, is given by

$$P_n = \frac{1}{N(E)} \,. \tag{5.4}$$

Thus, the probability distribution which extremizes the Gibbs entropy is the one for which all states of the same energy are equally probable. This is called the *microcanonical ensemble*. If we substitute Eq. (5.4) into Eq. (5.2), we find that the entropy is given by

$$S = k_{\mathrm{B}} \ln N(E) \,, \tag{5.5}$$

as we expect.

If we wish to derive thermodynamic quantities under a variety of different external constraints, we must have the ability to describe the microscopic behavior of systems under those constraints. *Isolated closed systems* have fixed total energy and fixed particle number. *Closed systems* have fixed particle number but varying energy so only the average energy is specified. *Open systems* can have varying particle number and energy. The probability density for closed systems (called the canonical ensemble) will be determined below. The probability density for open systems will be derived in Chapter 6. Once the equilibrium probability density for a system is known, the problem of computing thermodynamic quantities is straightforward.

We begin by computing the partition function and the probability density operator for closed systems. We then use them to obtain the thermodynamic properties of semiclassical gases, and we obtain the thermodynamic properties of solids using approximations developed by Debye to account for the interactions between atoms in the solid. The Debye model of a solid uses phonon collective modes as a basis for counting microscopic states and obtains results that are in good agreement with experiment at low temperatures.

We next compute the thermodynamic properties of an Ising spin lattice. We can obtain exact expressions for the thermodynamic properties of one-dimensional spin lattices, and we use a mean field model to obtain approximate expressions for the thermodynamic properties of higher dimensional spin lattices. We show that, near critical points, fluctuations become correlated over a wide region of space, indicating that long-range order has set in.

As thermodynamic systems approach a critical point, we must have a systematic way of treating thermodynamic functions in the neighborhood of the critical point. Such a method exists and is called *scaling*. The idea of scaling can be expressed mathematically by saying that the thermodynamic functions are *homogeneous functions* of their distance from the critical point. As we shall see, scaling underlies all theories of critical phenomena and enables us to compute microscopic expressions for critical exponents. The scaling behavior of thermodynamic functions near a critical point has been verified experimentally.

5.2
Probability Density Operator – Canonical Ensemble

A closed nonisolated system can exchange heat with its surroundings and as a consequence will have a fluctuating total energy. We therefore need to find a probability density which corresponds to an extremum of the entropy for such systems.

In order to obtain the probability density operator for a closed nonisolated system we extremize the Gibbs entropy subject to two constraints. We require that the probability density operator, $\hat{\rho}$, be normalized to one, and we require that the average energy be fixed to some value $\langle E\rangle$, so that

$$\mathrm{Tr}_N(\hat{\rho}) = 1 \quad \text{and} \quad \mathrm{Tr}_N(\hat{H}_N\hat{\rho}) = \langle E\rangle \,. \tag{5.6}$$

If we introduce the Lagrange multipliers, α_0 and α_E, we can find the probability density operator, $\hat{\rho}$, which extremizes the entropy subject to the constraints in Eq. (5.6). The extremization condition is

$$\begin{aligned}&\delta[\mathrm{Tr}_N(\alpha_0\hat{\rho} + \alpha_E\hat{H}_N\hat{\rho} - k_{\mathrm{B}}\hat{\rho}\ln\hat{\rho})]\\ &\quad = \mathrm{Tr}_N\{[(\alpha_0 - k_{\mathrm{B}})\hat{I} + \alpha_E\hat{H}_N - k_{\mathrm{B}}\ln\hat{\rho}]\delta\hat{\rho}\} = 0\,,\end{aligned} \tag{5.7}$$

where $\hat{I}$ is the unit operator. Since $\delta\hat{\rho}$ is arbitrary, we must have

$$(\alpha_0 - k_{\mathrm{B}})\hat{I} + \alpha_E\hat{H}_N - k_{\mathrm{B}}\ln\hat{\rho} = 0\,, \tag{5.8}$$

and therefore

$$\hat{\rho} = \exp\left[\left(\frac{\alpha_0}{k_{\mathrm{B}}} - 1\right)\hat{I} + \frac{\alpha_E}{k_{\mathrm{B}}}\hat{H}_N\right]\,. \tag{5.9}$$

The two Lagrange multipliers, α_0 and α_E, can be determined from the constraints in Eqs. (5.6). From Eqs. (5.6) and (5.9) we find

$$Z_N(\alpha_E) \equiv \exp\left(1 - \frac{\alpha_0}{k_{\mathrm{B}}}\right) = \mathrm{Tr}\left(\mathrm{e}^{\alpha_E\hat{H}_N/k_{\mathrm{B}}}\right)\,. \tag{5.10}$$

The quantity $Z_N(T)$ is called the *partition function*.

We next determine the Lagrange multiplier, α_E. Let us multiply Eq. (5.8) by $\hat{\rho}$ and take the trace. We obtain

$$\mathrm{Tr}_N[(\alpha_0 - k_\mathrm{B})\hat{\rho} + \alpha_E \hat{H}_N \hat{\rho} - k_\mathrm{B}\hat{\rho}\ln\hat{\rho}] = -k_\mathrm{B}\ln[Z_N(\alpha_E)] + \alpha_E\langle E\rangle + S = 0\,, \tag{5.11}$$

where we have made use of the constraints in Eq. (5.6), and the definitions of the partition function in Eq. (5.10) and the Gibbs entropy Eq. (5.1). From Table 3.3, the fundamental equation for the Helmholtz free energy can be written $A - U + ST = 0$. If we note that the internal energy is $U = \langle E\rangle$, then we can make the identification $\alpha_E = -1/T$ and we find that the Helmholtz free energy is

$$A = -k_\mathrm{B} T\ln[Z_N(T)]\,. \tag{5.12}$$

The *partition function*, $Z_N(T)$, takes the form

$$Z_N(T) = \mathrm{e}^{-\beta A} = \mathrm{Tr}_N(\mathrm{e}^{-\beta\hat{H}_N})\,, \tag{5.13}$$

where $\beta = 1/(k_\mathrm{B}T)$. The probability density operator can be written

$$\hat{\rho} = \mathrm{e}^{-\beta(\hat{H}_N - A)} = \frac{\mathrm{e}^{-\beta\hat{H}_N}}{\mathrm{Tr}_N(\mathrm{e}^{-\beta\hat{H}_N})}\,. \tag{5.14}$$

Equation (5.14) is the probability density for the *canonical ensemble*. The trace is evaluated using any convenient complete orthonormal set of N-particle basis states.

Equation (5.12) is the fundamental equation for a closed system. From it we can obtain all thermodynamic quantities. For example, the entropy is given by $S = -(\partial A/\partial T)_{X,N}$. The generalized force is given by $Y = (\partial A/\partial X)_{T,N}$. The chemical potential is given by $\mu = (\partial A/\partial N)_{T,X}$. Another useful relation for the internal energy is $U = (\partial\beta A/\partial\beta)_{X,N}$.

5.2.1
Energy Fluctuations

In the canonical ensemble the temperature T is fixed and the *average energy*, $U = \langle E\rangle$, is fixed. However, because there can be a flow of energy in and out of this system, it is important to know how large fluctuations in the energy (about the average energy, $\langle E\rangle$) will be. Let us therefore compute the variance of the energy fluctuations. We first write the normalization condition

$$\mathrm{Tr}_N(\mathrm{e}^{\beta[A(T,X,N)-\hat{H}_N]}) = 1\,. \tag{5.15}$$

If we differentiate Eq. (5.15) twice with respect to β, we find

$$0 = \mathrm{Tr}_N\left\{\left[\left(\frac{\partial^2\beta A}{\partial\beta^2}\right)_{X,N} + \left(-\hat{H}_N + \left(\frac{\partial\beta A}{\partial\beta}\right)_{X,N}\right)^2\right]\mathrm{e}^{\beta[A(T,X,N)-\hat{H}_N]}\right\}\,. \tag{5.16}$$

This gives

$$\langle E^2\rangle - \langle E\rangle^2 = -\left(\frac{\partial^2 \beta A}{\partial \beta^2}\right)_{X,N} = k_{\mathrm{B}} T^2 C_{X,N} \,, \tag{5.17}$$

where $C_{X,N}$ is the heat capacity at constant X and N. The heat capacity $C_{X,N}$ and average energy $\langle E\rangle$ are each proportional to N. Therefore, the fractional deviation behaves as

$$\frac{\sqrt{\langle E^2\rangle - \langle E\rangle^2}}{\langle E\rangle} \sim N^{-1/2} \tag{5.18}$$

and goes to zero as the number of degrees of freedom becomes infinite. This means that the fluctuations in energy become very small relative to the magnitude of the energy itself. In the thermodynamic limit, most microstates will have an energy approximately equal to the average energy, $U = \langle E\rangle$, and the canonical ensemble becomes equivalent to the microcanonical ensemble.

In evaluating the trace in Eq. (5.13) we must distinguish between systems of indistinguishable particles and systems of distinguishable particles. A system of N indistinguishable particles, by definition, has the property that the Hamiltonian and all other physical observables remain invariant under permutation of the particles. We will consider both cases below.

5.3
Semiclassical Ideal Gas of Indistinguishable Particles

For systems of identical particles, we must evaluate the trace in Eq. (5.13) either in terms of complete sets of symmetrized or antisymmetrized N-body position or momentum eigenstates, or in terms of the "number" representation. The fact that, in the canonical ensemble, the number of particles is restricted to N makes the particle number representation unwieldy when using the canonical ensemble. For a semiclassical gas, some of the quantum effects contained in the symmetrized and antisymmetrized states are negligible and expressions for the partition function can be simplified considerably.

5.3.1
Approximations to the Partition Function for Semiclassical Ideal Gases

The trace of the probability density for a set of N identical particles may be written (see Appendix D)

$$\begin{aligned}\mathrm{Tr}_N(\hat{\rho}) &= \mathfrak{C}_\alpha \sum_{k_1,\dots,k_N} {}^{(\alpha)}\langle k_1, k_2, \dots, k_N|\hat{\rho}|k_1, k_2, \dots, k_N\rangle^{(\alpha)} \\ &= \frac{1}{N!}\sum_{k_1,\dots,k_N} \langle k_1, \dots, k_N|\hat{\rho}|k_1, \dots, k_N\rangle^{(\pm)} = 1 \,,\end{aligned} \tag{5.19}$$

where $k_j = (\boldsymbol{k}_j, \sigma_j)$ denotes the momentum and spin of a particle, $\alpha = A, S$, and $\mathfrak{C}_\alpha$ is a counting factor the prevents the summation from overcounting states. The symmetrized and antisymmetrized states $|k_1, k_2, \dots, k_N\rangle^{(\alpha)}$ form a complete orthonormal set, and

$$|k_1, \dots, k_N\rangle^{(\pm)} = \sum_P (\pm 1)^P |k_1, \dots, k_N\rangle \tag{5.20}$$

where $\sum_P$ denotes the sum over all $N!$ permutations of the moment/spin variables k_j.

It is instructive to evaluate the partition function $Z_N(T)$ for the (unrealistic) case of $N = 3$ noninteracting identical particles in a box of volume $V = L^3$. For simplicity, we neglect any spin or other internal degrees of freedom. The Hamiltonian for this three-body ideal gas is $\hat{H}_3 = \hat{p}_1^2/(2m) + \hat{p}_2^2/(2m) + \hat{p}_3^2/(2m)$, where $\hat{\boldsymbol{p}}_j = \hbar\hat{\boldsymbol{k}}_j$ is the momentum operator for the jth particle and $\hat{\boldsymbol{k}}_j$ is the wavevector of the jth particle.

The partition function for a single particle is $Z_1(T) = \mathrm{Tr}_1\{\exp[-\beta\hat{p}^2/(2m)]\} = \sum_{\boldsymbol{k}} \langle \boldsymbol{k}| \exp[-\beta\hbar^2\hat{k}^2/(2m)]|\boldsymbol{k}\rangle$. The particle is confined to a cubic box of volume $V = L^3$. We can use the momentum eigenstates, which have periodic boundary conditions, to evaluate the trace. The allowed wavevectors are

$$\boldsymbol{k} = \frac{2\pi n_x}{L}\hat{\boldsymbol{e}}_x + \frac{2\pi n_y}{L}\hat{\boldsymbol{e}}_y + \frac{2\pi n_z}{L}\hat{\boldsymbol{e}}_z\,, \tag{5.21}$$

where n_x, n_y, and n_z are integers $-\infty \le n_x \le \infty$, etc. The momentum eigenstates, in the position basis, are

$$\psi_{n_x,n_y,n_z}(x, y, z) = \frac{1}{L^{3/2}} \mathrm{e}^{\frac{\pi 2\pi n_x x}{L}} \mathrm{e}^{\frac{\pi 2\pi n_y y}{L}} \mathrm{e}^{\frac{\pi 2\pi n_z z}{L}}\,. \tag{5.22}$$

The single particle partition function can then be written

$$Z_1(T) = \sum_{n_x=-\infty}^{\infty} \sum_{n_y=-\infty}^{\infty} \sum_{n_z=-\infty}^{\infty} \exp\left[-\beta\frac{4\pi^2\hbar^2}{2mL^2}\left(n_x^2 + n_y^2 + n_z^2\right)\right]\,. \tag{5.23}$$

If the volume, V, is very large compared to microscopic length scales, we can change the summation to an integration in Eq. (5.23). We write $\sum_{n_x=-\infty}^{\infty} = \int_{-\infty}^{\infty} \mathrm{d}n_x$, and make a change of variables, $p_x = 2\pi n_x\hbar/L$. The quantity, $2\pi\hbar/L \approx 0$ is very small so an integer change in n_x gives a very small change in p_x, and we find

$$\begin{aligned} Z_1(T) &= \frac{L^3}{8\pi^3\hbar^3} \int_{-\infty}^{\infty} \mathrm{d}p_x \int_{\infty}^{\infty} \mathrm{d}p_y \int_{-\infty}^{\infty} \mathrm{d}p_z \exp\left[-\frac{\beta}{2m}\left(p_x^2 + p_y^2 + p_z^2\right)\right] \\ &= \frac{V}{\lambda_T^3}\,, \end{aligned} \tag{5.24}$$

where

$$\lambda_T = \frac{h}{\sqrt{2\pi m k_{\mathrm{B}} T}} \tag{5.25}$$

is the *thermal wavelength* and has units of length. The thermal wavelength is a measure of the distance over which the particles maintain phase coherence in the gas.

A straightforward calculation shows that a three-body partition function can be written

$$\begin{aligned}Z_3(T) &= \mathrm{Tr}_3(\mathrm{e}^{-\beta\hat{H}}) = \frac{1}{3!}\sum_{\boldsymbol{k}_1,\boldsymbol{k}_2,\boldsymbol{k}_3} \langle \boldsymbol{k}_1, \boldsymbol{k}_2, \boldsymbol{k}_3, |\hat{\rho}| \boldsymbol{k}_1, \boldsymbol{k}_2, \boldsymbol{k}_3\rangle^{(\pm)} \\ &= \frac{1}{3!}\left(\frac{V}{\lambda_T^3}\right)^3 \left[1 \pm \frac{3}{2^{3/2}}\left(\frac{\lambda_T^3}{V}\right) + \frac{2}{3^{3/2}}\left(\frac{\lambda_T^3}{V}\right)^2\right] . \end{aligned} \tag{5.26}$$

The semiclassical limit corresponds to high temperatures and/or low densities (large V). In that case, we can neglect terms proportional to λ_T^3/V and we obtain the semiclassical partition function for a gas of three identical particles:

$$Z_3(T) \approx \frac{1}{3!}\left(\frac{V}{\lambda_T^3}\right)^3 . \tag{5.27}$$

This is equivalent to neglecting the permuted terms in Eq. (5.26) and writing

$$Z_3(T) = \frac{1}{3!}\sum_{k_1,\ldots,k_3} \langle \boldsymbol{k}_1, \boldsymbol{k}_2, \boldsymbol{k}_3 | \mathrm{e}^{-\beta\hat{H}} | \boldsymbol{k}_1, \boldsymbol{k}_2, \boldsymbol{k}_3\rangle \tag{5.28}$$

for the three-body partition function.

Symmetrized and antisymmetrized states must be used when computing the partition function for systems of identical particles at low temperatures and/or high densities where quantum effects strongly influence the translational degrees of freedom. However, for moderately high temperatures and/or moderate densities, for a gas of N identical particles, the partition function takes the approximate form

$$Z_N(T) \approx \frac{1}{N!}\sum_{k_1,\ldots,k_N} \langle k_1, \ldots, k_N | \mathrm{e}^{-\beta\hat{H}} | k_1, \ldots, k_N\rangle , \tag{5.29}$$

where we now neglect the contributions from permuted states. In doing so, we are neglecting terms of order, $(N/V)\lambda_T^3$. Thus, the semiclassical limit gives an approximate partition function:

$$Z_N(T) \approx \frac{1}{N!}\left(\frac{V}{\lambda_T^3}\right)^N . \tag{5.30}$$

The factor $N!$ in Eq. (5.30) is exactly the counting factor used in the microcanonical ensemble for indistinguishable particles. It resolves the Gibbs paradox. Equation (5.30) gives a good description of a semiclassical gas of N identical particles.

For a semiclassical ideal gas with no internal degrees of freedom, the partition function is

$$Z_N(T,V) = \frac{1}{N!}\left(\frac{V}{\lambda_T^3}\right)^N \approx \left(\frac{eV}{N\lambda_T^3}\right)^N , \tag{5.31}$$

where we have made use of *Stirling's approximation*, $N! \approx (N/e)^N$. The Helmholtz free energy is

$$A = -k_\mathrm{B} T \ln Z_N = -Nk_\mathrm{B} T - Nk_\mathrm{B} T \ln\left[\frac{V}{N}\left(\frac{\hbar^2}{2\pi m k_\mathrm{B} T}\right)^{-3/2}\right] . \tag{5.32}$$

The entropy is

$$S = -\left(\frac{\partial A}{\partial T}\right)_{V,N} = \frac{5}{2}Nk_\mathrm{B} + nk_\mathrm{B} \ln\left[\frac{V}{N}\left(\frac{\hbar^2}{2\pi m k_\mathrm{B} T}\right)^{-3/2}\right] , \tag{5.33}$$

which is just the Sackur–Tetrode equation.

Let us now consider a gas of noninteracting molecules which have internal degrees of freedom which can absorb energy. Such internal degrees of freedom might include the rotational and vibrational motions of the molecule and electronic or nuclear excitations. For such a system, the Hamiltonian of the ith molecule can be written $\hat{H}_j = \hat{p}_j^2/(2m) + \hat{H}_{j(\mathrm{rot})} + \hat{H}_{j(\mathrm{vib})} + \hat{H}_{j(\mathrm{elec})} + \hat{H}_{j(\mathrm{nuc})}$, where $\hat{H}_{j(\mathrm{rot})}$, $\hat{H}_{j(\mathrm{vib})}$, $\hat{H}_{j(\mathrm{elec})}$, and $\hat{H}_{j(\mathrm{nuc})}$ denote the rotational, vibrational, electronic, and nuclear internal degrees of freedom, respectively. We have assumed that these various internal degrees of freedom are uncoupled from one another. For a gas of N noninteracting particles in a box of volume V, in the semiclassical limit the partition function can be written

$$Z_N(V,T) = \frac{1}{N!}\mathrm{Tr}_N\left(\mathrm{e}^{-\beta\sum_{i=1}^N\left(\frac{\hat{p}_i^2}{2m}+\hat{H}_{i(\mathrm{rot})}+\hat{H}_{i(\mathrm{vib})}+\hat{H}_{i(\mathrm{el})}+\hat{H}_{i(\mathrm{nuc})}\right)}\right) . \tag{5.34}$$

The partition function takes a particularly simple form for this system *if the Hamiltonians in Eq.* (5.34) *commute with one another*. Then we find

$$Z_N(T,V) = \frac{1}{N!}\left(Z_{1(\mathrm{tr})}Z_{1(\mathrm{rot})}Z_{1(\mathrm{vib})}Z_{1(\mathrm{elec})}Z_{1(\mathrm{nuc})}\right)^N , \tag{5.35}$$

where $Z_{1(\mathrm{tr})} = \mathrm{Tr}_1(\mathrm{e}^{-\beta\hat{p}^2/(2m)})$, $Z_{1(\mathrm{rot})} = \mathrm{Tr}_1(\mathrm{e}^{-\beta\hat{H}_{1}(\mathrm{rot})})$, and so on. The trace, Tr_1 is taken over a complete set of single particle states appropriate for the Hamiltonian appearing under it.

In Exercise 5.1, we compute the thermodynamic properties for a semiclassical gas of N identical spin-1/2 particles in a magnetic field. In Exercise 5.2, we consider the effect of rotational degrees of freedom on the thermodynamic properties of a gas.

Exercise 5.1

A box of volume, $V = L^3$, contains an ideal gas of N identical atoms, each of which has spin, $s = 1/2$, and magnetic moment, μ. A magnetic field, $\boldsymbol{B}$, is applied to the system. (a) Compute the partition function for this system. (b) Compute the internal energy and the heat capacity. (c) What is the magnetization?

Answer: (a) The partition function takes the form $Z_N = (1/N!)(Z_{1(\mathrm{tr})})^N \cdot (Z_{1(\mathrm{mag})})^N$, where $Z_{1(\mathrm{tr})} = V/\lambda_T^3$. Each atom has magnetic energy $E(s) = -(1/2)s\mu B$, where $s = \pm 1$. The magnetic partition function for a single atom is $Z_{1(\mathrm{mag})} = \sum_{s=\pm 1} \mathrm{e}^{-s\beta\mu B/2} = 2\cosh\left[(\beta\mu B)/2\right]$. The partition function for the gas is $Z_N = (1/N!)\left(2V/\lambda_T^3\right)^N \cosh^N\left[(\beta\mu B)/2\right]$.
(b) The internal energy is given by

$$U = -\left(\partial \ln Z_N/\partial\beta\right) = 3/2 N k_\mathrm{B} T - 1/2 N\mu B \tanh\left[(\beta\mu B)/2\right] .$$

The heat capacity is

$$C_{V,N} = \left(\frac{\partial U}{\partial T}\right)_{V,N,B} = \frac{3}{2} N k_\mathrm{B} + N k_\mathrm{B} \left(\beta\mu B/2\right)^2 \operatorname{sech}^2\left[(\beta\mu B)/2\right] .$$

(c) The magnetization is given by $M = -(\partial\Phi/\partial B)_{T,N}$, where Φ is the free energy this system (the translational part is like a Helmholtz free energy, a function of T, V, and N, and the magnetic part is like a Gibbs free energy, a function of T, B, and N). The free energy of the combined system doesn't have a name so we call it Φ. Then $\Phi = -k_\mathrm{B} T \ln Z_N$ and $M = -\left(\partial\Phi/\partial B\right)_{T,N} = (1/2)N\mu \tanh\left[(\beta\mu B)/2\right]$.

5.3.2
Maxwell–Boltzmann Distribution

We consider a dilute semiclassical gas of N particles contained in a volume V. We assume that the gas is in equilibrium and that the interaction energy between particles is negligible compared to the kinetic energy of the particles. The particle number density $n(\boldsymbol{k})$ is defined (see Appendix D)

$$n(\boldsymbol{k}_1) = \langle \boldsymbol{k}_1 | \hat{\rho} | \boldsymbol{k}_1 \rangle = \frac{1}{(N-1)!} \sum_{\boldsymbol{k}_2,\ldots,\boldsymbol{k}_N}^{(\pm)} \langle \boldsymbol{k}_1, \boldsymbol{k}_2, \ldots, \boldsymbol{k}_N | \hat{\rho} | \boldsymbol{k}_1, \boldsymbol{k}_2, \ldots, \boldsymbol{k},_N \rangle \tag{5.36}$$

and the density operator $\hat{\rho}$ is defined $\hat{\rho} = \exp(\sum_j^N \hat{p}_j^2/(2m))/\mathrm{Tr}[\exp(\sum_j^N \hat{p}_j^2/(2m))]$. With some algebra we can write

$$n(\boldsymbol{k}) = N\frac{\lambda_T^3}{V} \exp\left(-\frac{\hbar^2 k^2}{2 m k_\mathrm{B} T}\right) . \tag{5.37}$$

Note that $n(\boldsymbol{k})$ is normalized to the number of particles so that $\sum_{\boldsymbol{k}} n(\boldsymbol{k}) = N$.

Exercise 5.2

A single molecule has rotational kinetic energy $\hat{H}_{\mathrm{rot}} = \hat{L}^2/(2I)$, where $\hat{\boldsymbol{L}}$ is the angular momentum operator and I is the moment of inertia of the molecule. The rotational partition function, for a single particle, is given by $Z_1^{\mathrm{rot}} = \sum_{l=0}^{\infty}(2l + 1)\exp[-\beta k_{\mathrm{B}}\theta l(l+1)]$, where l is the angular momentum quantum number, $2l + 1$ is the multiplicity of states with angular momentum l, and $\theta_{\mathrm{R}} = \hbar^2/(2Ik_{\mathrm{B}})$ is the rotational temperature. The CO molecule has a rotational temperature $\theta_{\mathrm{CO}} = 2.8\,\mathrm{K}$ and atomic mass of $M_{\mathrm{CO}} = 28$. A semiclassical ideal gas, consisting of one mole of CO molecules, is contained in a box of volume $V = 1.0\,\mathrm{m}^3$ and cooled to a temperature of $T = 3.0\,\mathrm{K}$ (assume the molecules remain in the gas phase under these conditions). What fraction of the internal energy is associated with the rotational degrees of freedom (a) at $T = 3.0\,\mathrm{K}$ (b) at $T = 300\,\mathrm{K}$?

Answer: The partition function for this gas is $Z = (1/N!)\left(V/\lambda_T^3\right)^N (Z_1^{\mathrm{rot}})^N$. The thermal wavelength is $\lambda_T = h/\sqrt{2\pi m_{\mathrm{CO}} k_{\mathrm{B}} T}$, where m_{CO} is the mass of a single CO molecule. The Helmholtz free energy is $A = -k_{\mathrm{B}}T\ln Z = A_{\mathrm{trans}} + A_{\mathrm{rot}}$ with $A_{\mathrm{trans}} = -Nk_{\mathrm{B}}T - Nk_{\mathrm{B}}T\ln\left[V/(N\lambda_T^3)\right]$ and $A_{\mathrm{rot}} = -k_{\mathrm{B}}TN\ln Z_1^{\mathrm{rot}}$. The internal energy is $U = (\partial\beta A/\partial\beta)_{V,N}$. The internal energy associated with translational degrees of freedom is $U_{\mathrm{trans}} = (3/2)Nk_{\mathrm{B}}T$. The internal energy associated with rotational degrees of freedom is $U_{\mathrm{rot}} = (N/Z_1^{\mathrm{rot}})\sum_{l=0}^{\infty}(2l+1)k_{\mathrm{B}}\theta l(l+1)\mathrm{e}^{-\beta k_{\mathrm{B}}\theta l(l+1)}$.

(a) For temperature $T = 3.0\,\mathrm{K}$, only the first few terms in the summations give nonnegligible contributions, and we obtain $U_{\mathrm{rot}} = 1.95Nk_{\mathrm{B}}$. The fraction of internal energy that is rotational is $U_{\mathrm{rot}}/(U_{\mathrm{rot}} + U_{\mathrm{trans}}) = 0.30$.

(b) For temperature $T = 300\,\mathrm{K}$, $U_{\mathrm{rot}} \approx Nk_{\mathrm{B}}T$ so $U_{\mathrm{rot}}/(U_{\mathrm{rot}} + U_{\mathrm{trans}}) = 2/3$.

The Maxwell Boltzmann distribution $F(\boldsymbol{v})$ is the probability density to find a particle in the velocity interval $\boldsymbol{v} \to \boldsymbol{v} + \mathrm{d}\boldsymbol{v}$. We can obtain $F(\boldsymbol{v})$ from $n(\boldsymbol{k})$ by a change of variables

$$\begin{aligned}\sum_{\boldsymbol{k}} n(\boldsymbol{k}) &= \frac{V}{(2\pi)^3}\int \mathrm{d}\boldsymbol{k}\, n(\boldsymbol{k}) = \frac{N}{(2\pi m k_{\mathrm{B}}T)^{3/2}}\int \mathrm{d}\boldsymbol{p}\exp\left(-\frac{p^2}{2mk_{\mathrm{B}}T}\right)\\ &= N\left(\frac{m}{2\pi k_{\mathrm{B}}T}\right)^{3/2}\int \mathrm{d}\boldsymbol{v}\exp\left(-\frac{mv^2}{2k_{\mathrm{B}}T}\right) \equiv N\int \mathrm{d}\boldsymbol{v}F(\boldsymbol{v})\,.\end{aligned} \tag{5.38}$$

The Maxwell–Boltzmann distribution

$$F(\boldsymbol{v}) = \left(\frac{m}{2\pi k_{\mathrm{B}}T}\right)^{3/2}\int \mathrm{d}\boldsymbol{v}\exp\left(-\frac{mv^2}{2k_{\mathrm{B}}T}\right) \tag{5.39}$$

is normalized to one so that $\int \mathrm{d}\boldsymbol{v}F(\boldsymbol{v}) = 1$.

5.4
Interacting Classical Fluids

For fluids at high enough temperature that quantum statistics do not play an important role, expressions for and calculation of the partition function can be simplified, considerably [27, 61, 85, 134]. Let us assume that we have a classical fluid consisting of N particles with mass m whose dynamics is determined by a Hamiltonian of the form $\hat{H} = \hat{T}^N + \hat{V}^N$, where

$$\hat{T}^N(\{\hat{\boldsymbol{p}}^N\}) = \sum_{i=1}^{N} \frac{\hat{p}_i^2}{2m} \quad \text{and} \quad \hat{V}^N(\{\hat{\boldsymbol{r}}^N\}) = \sum_{(ij)=1}^{N(N-1)/2} V(\hat{\boldsymbol{r}}_{ij}) \,, \tag{5.40}$$

are the kinetic and potential energy operators, respectively, and $\hat{\boldsymbol{r}}_{ij} = \hat{\boldsymbol{r}}_i - \hat{\boldsymbol{r}}_j$ is the relative displacement operator of particles, i and j.

The partition function can be written

$$Z_N(T) = \mathrm{Tr}(\mathrm{e}^{-\beta(\hat{T}^N + \hat{V}^N)}) = \mathrm{Tr}(\mathrm{e}^{-\beta\hat{T}^N}\mathrm{e}^{-\beta\hat{V}^N}) + \mathrm{O}\{\beta^2[\hat{T}^N, \hat{V}^N]\} \,, \tag{5.41}$$

where O{ … } denotes terms depending on the commutator

$$[\hat{T}^N, \hat{V}^N] = -\mathrm{i}\hbar/(2m) \sum_{j=1}^{N} [\boldsymbol{p}_j \cdot (\nabla_{\boldsymbol{r}_j} \hat{V}^N) + (\nabla_{\boldsymbol{r}_j} \hat{V}^N) \cdot \boldsymbol{p}_j]$$

and on β^2. If we neglect contributions from these terms in Eq. (5.41), the partition function takes the form

$$Z_N(T) = \mathrm{Tr}(\mathrm{e}^{-\beta(\hat{T}^N + \hat{V}^N)}) \approx \mathrm{Tr}(\mathrm{e}^{-\beta\hat{T}^N}\mathrm{e}^{-\beta\hat{V}^N}) \,. \tag{5.42}$$

By neglecting the commutator in Eq. (5.41), we neglect contributions due to the noncommutivity of $\hat{\boldsymbol{p}}_j$ and $\hat{\boldsymbol{r}}_j$ and β^2. Such terms, at high enough temperature, can be neglected.

We can now compute the partition function. In the position basis it is

$$\begin{aligned} Z_N(T) &= \frac{1}{N!}\int \mathrm{d}\boldsymbol{r}_1 \ldots \int \mathrm{d}\boldsymbol{r}_N \langle \boldsymbol{r}_1, \ldots, \boldsymbol{r}_N | \mathrm{e}^{-\beta\hat{T}^N}\mathrm{e}^{-\beta\hat{V}^N} | \boldsymbol{r}_1, \ldots, \boldsymbol{r}_N \rangle \\ &= \frac{1}{N!}\int \mathrm{d}\boldsymbol{r}_1 \ldots \int \mathrm{d}\boldsymbol{r}_N \langle \boldsymbol{r}_1, \ldots, \boldsymbol{r}_N | \mathrm{e}^{-\beta\hat{T}^N} | \boldsymbol{r}_1, \ldots \boldsymbol{r}_N \rangle \mathrm{e}^{-\beta V^N(\{\boldsymbol{r}^N\})} \,. \end{aligned} \tag{5.43}$$

Next insert a complete set of momentum eigenstates and perform the momentum integration. This gives

$$\begin{aligned} Z_N(T) &= \frac{1}{N!}\int \mathrm{d}\boldsymbol{r}_1 \ldots \int \mathrm{d}\boldsymbol{r}_N \sum_{\boldsymbol{k}_1,\ldots,\boldsymbol{k}_N} \mathrm{e}^{-\beta\hat{T}^N(\{\boldsymbol{k}^N\})}\mathrm{e}^{-\beta V^N(\{\boldsymbol{r}^N\})} \\ &\quad \times |\langle \boldsymbol{r}_1, \ldots, \boldsymbol{r}_N | \boldsymbol{k}_1, \ldots, \boldsymbol{k}_N \rangle|^2 = \frac{1}{N!}\frac{1}{\lambda_T^{3N}} Q_N(T, V) \,, \end{aligned} \tag{5.44}$$

where we have used the fact that $|\langle \boldsymbol{r}_1, \ldots, \boldsymbol{r}_N | \boldsymbol{k}_1, \ldots, \boldsymbol{k}_N \rangle|^2 = V^{-N}$ (see Appendix D) and

$$Q_N(T, V) = \int \mathrm{d}\boldsymbol{r}_1 \ldots, \int \mathrm{d}\boldsymbol{r}_N \mathrm{e}^{-\beta V^N(\{\boldsymbol{r}^N\})} \tag{5.45}$$

is called the *configuration integral*.

5.4.1
Density Correlations and the Radial Distribution Function

One of the simplest quantities to compute is the internal energy, $U(T, V, N)$. The internal energy is just the average value of the Hamiltonian and can be written

$$U(T, V, N) = \langle \hat{H} \rangle = \frac{3}{2} N k_{\mathrm{B}} T + \frac{1}{2} \int \mathrm{d}\boldsymbol{r}_1\, \mathrm{d}\boldsymbol{r}_2\, V(\boldsymbol{r}_{12}) n_2^N(\boldsymbol{r}_1, \boldsymbol{r}_2)\,, \tag{5.46}$$

where $n_{(2)}^N(\boldsymbol{r}_1, \boldsymbol{r}_2)$ is the reduced two-body density matrix (see Appendix D). The term $(3/2)N k_{\mathrm{B}} T$ is the kinetic contribution to the internal energy, and the remaining term is the contribution due to the interaction between the particles.

The expression for the internal energy simplifies considerably for systems whose particles interact via spherically symmetric potentials, $V(\boldsymbol{r}_{ij}) = V(r_{ij})$, where $r_{ij} = |\boldsymbol{r}_i - \boldsymbol{r}_j|$ is the magnitude of the relative displacement. Then the two-particle reduced density matrix takes the form $n_2^N(\boldsymbol{r}_1, \boldsymbol{r}_2) = n_2^N(r_{12})$. If we change the integration variables to relative, $\boldsymbol{r}_{ij}$, and center-of-mass, $\boldsymbol{R}_{ij} = (\boldsymbol{r}_i + \boldsymbol{r}_j)/2$, coordinates and let $n_2^N(r_{12}) = (N/V)^2 g_2^N(r_{ij})$, then we can integrate over the center-of-mass coordinates and find

$$U(T, V, N) = \frac{3}{2} N k_{\mathrm{B}} T + \frac{1}{2} \frac{N^2}{V} \int 4\pi r^2\, \mathrm{d}r V(r) g_2^N(r)\,, \tag{5.47}$$

where $r = r_{12}$. The function $g_2^N(r)$ is called the *radial distribution function*. The radial distribution function completely characterizes the behavior of a classical fluid of spherically symmetric particles. It also has a direct physical interpretation. The quantity $(N/V) g(r) 4\pi r^2\, \mathrm{d}r$ is the average number of particles in a spherical shell of width $r \to r + \mathrm{d}r$ at a distance r from any particle in the fluid.

The radial distribution function $g_2^N(r)$ is closely related to the density correlation function $C_{nn}(\boldsymbol{r})$ for the fluid, which is defined

$$C_{nn}(\boldsymbol{r}) = \frac{1}{N} \int \mathrm{d}\boldsymbol{r}' \langle \hat{n}(\boldsymbol{r}' + \boldsymbol{r}) \hat{n}(\boldsymbol{r}') \rangle\,, \tag{5.48}$$

where the density phase function is defined $\hat{n}(\boldsymbol{r}) = \sum_{i=1}^N \delta(\hat{\boldsymbol{r}}_i - \boldsymbol{r})$. In order to verify this relationship, it is useful to compute the Fourier transform $S_{nn}(\boldsymbol{k})$ of $C_{nn}(\boldsymbol{r})$, which is called the *structure function*. The structure function $S_{nn}(\boldsymbol{k})$ can be determined from neutron scattering experiments in which slow neutrons scatter from atomic nuclei in a liquid. The angular dependence of the scattered neutrons is measured, and this information can be used to construct the structure function of the liquid.

The structure function $S_{nn}(\boldsymbol{k})$ can be expressed in terms of the radial distribution function. First note that

$$S_{nn}(\boldsymbol{k}) = \frac{1}{N}\int \mathrm{d}\boldsymbol{r}\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}\int \mathrm{d}\boldsymbol{r}'\langle\hat{n}(\boldsymbol{r}'+\boldsymbol{r})\hat{n}(\boldsymbol{r}')\rangle = \frac{1}{N}\sum_{i=1}^{N}\sum_{j=1}^{N}\langle\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot(\hat{\boldsymbol{r}}_i-\hat{\boldsymbol{r}}_j)}\rangle\,, \tag{5.49}$$

where we have made use of Eq. (5.48) and, in the last term, we have integrated over $\boldsymbol{r}$ and $\boldsymbol{r}'$. If we evaluate the average $\langle\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot(\hat{\boldsymbol{r}}_i-\hat{\boldsymbol{r}}_j)}\rangle$ in the canonical ensemble, we find

$$\begin{aligned}
S_{nn}(\boldsymbol{k}) &= \frac{1}{N}\frac{1}{Q_N(V,T)}\sum_{i=1}^{N}\sum_{j=1}^{N}\int \mathrm{d}\boldsymbol{r}_1\cdots\int \mathrm{d}\boldsymbol{r}_N\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{r}_i-\boldsymbol{r}_j)}\mathrm{e}^{-\beta V(\boldsymbol{r}^N)}\\
&= \frac{1}{N}\left(N + \frac{1}{Q_N(V,T)}\sum_{(i\neq j)}^{N(N-1)}\int \mathrm{d}\boldsymbol{r}_1\cdots\int \mathrm{d}\boldsymbol{r}_N\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{r}_i-\boldsymbol{r}_j)}\mathrm{e}^{-\beta V(\boldsymbol{r}^N)}\right)\\
&= 1 + \frac{1}{N}\int \mathrm{d}\boldsymbol{r}_1\int \mathrm{d}\boldsymbol{r}_2\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_{ij}}n_2^N(\boldsymbol{r}_1,\boldsymbol{r}_2) = 1 + \frac{N}{V}\int \mathrm{d}\boldsymbol{r}_{12}\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_{12}}g_2^N(r_{12})\,.
\end{aligned} \tag{5.50}$$

The minimum value of the wavevector, $\boldsymbol{k}$, is determined by the size of the box. In the limit $N \to \infty$ and $V \to \infty$ with $n = N/V =$ constant, the length of the wavevector can be zero. We can separate this contribution from the remainder of the integral. We find

$$S_{nn}(\boldsymbol{k}) = 1 + n\delta(\boldsymbol{k}) + n\int \mathrm{d}\boldsymbol{r}_{12}\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_{12}}(g_2^N(r_{12}) - 1)\,. \tag{5.51}$$

The integration over angles in Eq. (5.51) can be performed to finally give

$$S_{nn}(\boldsymbol{k}) = 1 + n\delta(\boldsymbol{k}) + \frac{4\pi n}{k}\int r\,\mathrm{d}r\sin(kr)(g_2^N(r) - 1)\,. \tag{5.52}$$

The structure function can be measured in neutron scattering experiments, and the term $n\delta(\boldsymbol{k})$ is the contribution due to coherent forward scattering.

In Figure 5.1 we show the structure function and the radial distribution function obtained from neutron scattering experiments on liquid ^{36}Ar at 85 K. The radial distribution function goes to zero at about the hard-core radius of ^{36}Ar, indicating that no particles can penetrate the hard core. It has a maximum at about the distance of the minimum of the attractive potential between nearest-neighbor argon atoms in the liquid. The next peak is due to the high probability of finding next nearest neighbors at that position, and so on.

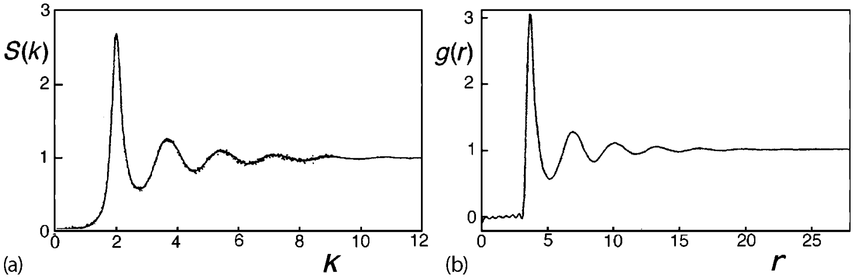

Figure 5.1 (a) The structure function, $S(k) = S_{nn}(k)$, versus k (in Å^{-1}) for liquid ^{36}Ar at 85\,K obtained from neutron scattering experiments. The dots are data points. The solid line is a best fit to the data. (b) The radial distribution function, $g(r)$, versus r (in Å) obtained from the data in (a). Reprinted, by permission, from [219].

5.4.2
Magnetization Density Correlations

For the case of a fluid whose particles have spin and a magnetic moment, the magnetization density operator $\hat{m}(\boldsymbol{r})$ and total magnetization operator $\hat{\boldsymbol{M}}$ are defined

$$\hat{m}(\boldsymbol{r}) = \mu \sum_{j=1}^{N} \hat{s}_j \delta(\hat{\boldsymbol{r}}_j - \boldsymbol{r}) , \quad \text{and} \quad \hat{\boldsymbol{M}} = \int \mathrm{d}\boldsymbol{r} \hat{m}(\boldsymbol{r}) = \mu \sum_{j=1}^{N} \hat{s}_j , \tag{5.53}$$

respectively, where N is the number of particles, μ is the magnetic moment, $\hat{s}_j$ is the spin operator for the jth particle, and $\hat{\boldsymbol{r}}_j$ is the position operator for the jth particle. If a magnetic induction field, $\boldsymbol{B}(\boldsymbol{r})$, is present, the total Hamiltonian can be written

$$\hat{H} = \sum_{i=1}^{N} \frac{\hat{p}_i^2}{2m} + \sum_{(ij)=1}^{N(N-1)/2} \mathrm{V}(\hat{\boldsymbol{r}}_{ij}; \hat{s}_i, \hat{s}_j) - \int \mathrm{d}\boldsymbol{r} \hat{m}(\boldsymbol{r}) \cdot \boldsymbol{B}(\boldsymbol{r}) . \tag{5.54}$$

The average magnetization, in the presence of the magnetic induction field is

$$\langle \boldsymbol{M} \rangle_{\boldsymbol{B}} = \mathrm{Tr}(\hat{\boldsymbol{M}} \mathrm{e}^{-\beta\hat{H}}) / \mathrm{Tr}(\mathrm{e}^{-\beta\hat{H}}) . \tag{5.55}$$

If we let $\hat{M}_\alpha$ $(\alpha = x, y, z)$ denote the αth component of the magnetization operator $\hat{\boldsymbol{M}}$, then the (α, α') component of the magnetic susceptibility matrix can be written

$$\chi_{\alpha,\alpha'} = \left(\frac{\partial \langle M_\alpha \rangle_{\boldsymbol{B}}}{\partial B_{\alpha'}} \right)_{T,N,B=0} = \beta \langle (\hat{M}_\alpha - \langle \hat{M}_\alpha \rangle)(\hat{M}_{\alpha'} - \langle \hat{M}_{\alpha'} \rangle) \rangle . \tag{5.56}$$

Note that the susceptibility $\chi_{\alpha,\alpha'}$, as we have defined it, is a linear susceptibility and is independent of the applied magnetic field. It contains information about magnetic properties of the unperturbed equilibrium system.

Let us now introduce magnetization density fluctuations $\delta\hat{m}_\alpha(\boldsymbol{r}) = \hat{m}_\alpha(\boldsymbol{r}) - \langle \hat{m}_\alpha(\boldsymbol{r}) \rangle$. Then the correlation function $C_{\alpha,\alpha'}(\boldsymbol{r}_1, \boldsymbol{r}_2)$ for magnetization density fluctuations at points $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ in the fluid can be written

$$\begin{aligned} C_{\alpha,\alpha'}(\boldsymbol{r}_1, \boldsymbol{r}_2) &= \langle \delta\hat{m}_\alpha(\boldsymbol{r}_1)\delta\hat{m}_{\alpha'}(\boldsymbol{r}_2)\rangle = \langle \delta\hat{m}_\alpha(\boldsymbol{r}_1 - \boldsymbol{r}_2)\delta\hat{m}_{\alpha'}(\boldsymbol{0})\rangle \\ &\equiv C_{\alpha,\alpha'}(\boldsymbol{r}_1 - \boldsymbol{r}_2) , \end{aligned} \tag{5.57}$$

where we have made use of the fact that the equilibrium correlation function, in the absence of spatially varying external fields, will depend on the relative displacement of two points in the fluid and not on their absolute position.

It is useful to introduce the Fourier transform of the correlation function, the magnetic structure function $G_{\alpha,\alpha'}(\boldsymbol{k})$,

$$\begin{aligned} G_{\alpha,\alpha'}(\boldsymbol{k}) &= \int \mathrm{d}\boldsymbol{r} \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}} C_{\alpha,\alpha'}(\boldsymbol{r}) = \frac{1}{V}\int \mathrm{d}\boldsymbol{r}_1 \int \mathrm{d}\boldsymbol{r}_2 \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{r}_1-\boldsymbol{r}_2)} \langle \delta\hat{m}_\alpha(\boldsymbol{r}_1)\delta\hat{m}_{\alpha'}(\boldsymbol{r}_2)\rangle \\ &= \frac{1}{V}\langle \delta\hat{m}_\alpha(\boldsymbol{k})\delta\hat{m}_{\alpha'}(-\boldsymbol{k})\rangle , \end{aligned} \tag{5.58}$$

where we have made use of the Fourier decomposition of spatially varying magnetic fluctuations $\delta\hat{m}_\alpha(\boldsymbol{r}) = (1/V)\sum_{\boldsymbol{k}} \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}\delta\hat{m}_\alpha(\boldsymbol{k})$. From these results we see that the magnetic susceptibility can be written in terms of the infinite wavelength component of the magnetic structure factor $\chi_{\alpha,\alpha'} = \beta V G_{\alpha,\alpha'}(\boldsymbol{k} = \boldsymbol{0}) = \beta V \int \mathrm{d}\boldsymbol{r} C_{\alpha,\alpha'}(\boldsymbol{r})$.

In Chapter 4, we found that the magnetic susceptibility becomes infinite as we approach the critical point of a magnetic phase transition. Thus, near the critical point, the correlation function will have a large long-wavelength component, indicating that long-range order has begun to occur.

5.5
Heat Capacity of a Debye Solid

In simple atomic crystals, the long-range attractive forces between atoms hold the atoms of the crystal in place at some fixed lattice spacing, although the atoms can undergo oscillations (vibrations) about their lattice positions. The short-range repulsive forces between atoms make crystals virtually incompressible. While the potential which governs the oscillations is anharmonic, to lowest approximation, in deriving the heat capacity, we can treat it as harmonic. If the crystal has N atoms, it will have $3N$ degrees of freedom and the Hamiltonian can be written in the form

$$\hat{H} = \sum_{i=1}^{3N} \frac{\hat{p}_i^2}{2m} + \sum_{(i,j)}^{N(N-1)/2} \kappa_{i,j}\hat{q}_i\hat{q}_j , \tag{5.59}$$

where p_i and q_i are the momentum and the displacement from the lattice site, respectively, of the ith degree of freedom, m is the mass of the atom, and $\kappa_{i,j}$ contains information about interaction between neighboring atoms. Hamiltonians like the one in Eq. (5.59), can be transformed to normal mode coordinates

$(\hat{P}_1, \dots, \hat{P}_{3N}, \hat{Q}_1, \dots, \hat{Q}_{3n})$ via a canonical transformation and written in the form

$$\hat{H} = \sum_{\alpha=1}^{3N} \frac{\hat{P}_\alpha^2}{2m} + \sum_{\alpha=1}^{3N} \frac{m\omega_\alpha^2}{2} \hat{Q}_\alpha^2 \,. \tag{5.60}$$

The lattice now consists of a collection of independent harmonic oscillators that correspond to sound waves or phonons on the lattice. The thermodynamic properties of such a lattice can be computed exactly [183]. However, Debye proposed a very simple continuum approximation to the lattice that well describes the low-temperature thermodynamic behavior of the lattice.

In this section we shall compute the heat capacity for a three-dimensional harmonically coupled lattice using the continuum approximation first proposed by Debye [10, 38, 40]. Consider a rectangular lattice with sides of lengths L_x, L_y, and L_z. We will assume that the sound waves form standing waves with wavelengths $2L_x/l_x$, $2L_y/l_y$, and $2L_z/l_z$ in the x-, y-, and z-directions, respectively, where l_x, l_y, and l_z are integers ($l_x = 1, 2, \dots, \infty$, etc.). The αth sound mode will have a dispersion relation of the form

$$\omega_\alpha^2 = c^2 \left[\left(\frac{\pi l_{x\alpha}}{L_x} \right)^2 + \left(\frac{\pi l_{y\alpha}}{L_y} \right)^2 + \left(\frac{\pi l_{z\alpha}}{L_z} \right)^2 \right] , \tag{5.61}$$

where c is the speed of sound. The Hamiltonian operator takes the form

$$\hat{H} = \sum_{\alpha=1}^{3N} \hbar\omega_\alpha \left(\hat{n}_\alpha + \frac{1}{2}\hat{1} \right) , \tag{5.62}$$

where $\hat{n}_\alpha$ is the number operator for energy quanta (phonons) in the αth normal mode. Let $|n_\alpha\rangle$ be the eigenvector of the number operator, $\hat{n}_\alpha$. Then $\hat{n}_\alpha|n_\alpha\rangle = n_\alpha|n_\alpha\rangle$, where $n_\alpha = 0, 1, \dots, \infty$.

The partition function can be written

$$Z_N(T) = \mathrm{Tr}_N(\mathrm{e}^{-\beta\hat{H}}) = \sum_{n_1=0}^{\infty} \dots \sum_{n_{3N}=0}^{\infty} \mathrm{e}^{-\beta \sum_{\alpha=1}^{3N} \hbar\omega_\alpha (\hat{n}_\alpha + \frac{1}{2})} = \prod_{\alpha=1}^{3N} \frac{\mathrm{e}^{-\beta\hbar\omega_\alpha/2}}{1 - \mathrm{e}^{-\beta\hbar\omega_\alpha}} \,. \tag{5.63}$$

The average energy is

$$\langle E \rangle = -\frac{\partial \ln Z_N}{\partial \beta} = \sum_{\alpha=1}^{3N} \frac{\hbar\omega_\alpha}{2} + \sum_{\alpha=1}^{3N} \frac{\hbar\omega_\alpha}{\mathrm{e}^{\beta\hbar\omega_\alpha} - 1} \,. \tag{5.64}$$

Since the average energy can also be written $\langle E \rangle = \langle \sum_{\alpha=1}^{3N} \hbar\omega_\alpha(\hat{n}_\alpha + 1/2) \rangle$, comparison with Eq. (5.64) shows that the average number of quanta in the αth phonon mode is

$$\langle \hat{n}_\alpha \rangle = \frac{1}{\mathrm{e}^{\beta\hbar\omega_\alpha} - 1} \,, \tag{5.65}$$

which is Planck's formula.

The allowed values of ω_α in Eq. (5.61) consist of discrete points in a three-dimensional frequency space. The distance between points in the x-direction is $\pi c/L_x$, in the y-direction it is $\pi c/L_y$, and in the z-direction it is $\pi c/L_z$. The volume per point in frequency space is therefore $(\pi c)^3/V$, where $V = L_x L_y L_z$ is the volume of the crystal. The number points per unit volume in frequency space is $V/(\pi c)^3$. The total number of allowed values of ω_α less than some value ω is given by $(1/8)(4\pi\omega^3/3)(V/(\pi c)^3)$, where $(1/8)(4\pi\omega^3/3)$ is the volume of $1/8$ of a sphere of radius ω (the phonon frequency is positive). Thus, the number of allowed frequencies in the range $\omega \to \omega + \mathrm{d}\omega$ is given by

$$\mathrm{d}\nu = \frac{V}{2\pi^2 c^3}\omega^3\,\mathrm{d}\omega\,. \tag{5.66}$$

In general, there will be two transverse sound modes and one longitudinal sound mode since crystals can sustain both longitudinal and transverse sound modes (a fluid can only sustain longitudinal sound modes). The transverse and longitudinal sound modes in a crystal propagate at different velocities, which we shall denote as c_t and c_l, respectively. If the three different sound modes are taken into account, the number of allowed frequencies $\mathrm{d}\nu$ in the interval, $\omega \to \omega + \mathrm{d}\omega$, is

$$\mathrm{d}\nu = \frac{V}{2\pi^2}\left(\frac{2}{c_\mathrm{t}^3} + \frac{1}{c_\mathrm{l}^3}\right)\omega^2\,\mathrm{d}\omega\,. \tag{5.67}$$

Since there is a minimum wavelength allowed on the lattice due to the finite spacing of the atoms, there will be a cutoff frequency, ω_D (the Debye frequency). We can then determine the Debye frequency by relating it to the total number of sound modes,

$$3N = \int_1^{3N} \mathrm{d}\nu = \frac{V}{2\pi^2}\left(\frac{2}{c_\mathrm{t}^3} + \frac{1}{c_\mathrm{l}^3}\right)\int_0^{\omega_\mathrm{D}} \omega^2\,\mathrm{d}\omega = \frac{V}{2\pi^2}\left(\frac{2}{c_\mathrm{t}^3} + \frac{1}{c_\mathrm{l}^3}\right)\frac{\omega_\mathrm{D}^3}{3}\,. \tag{5.68}$$

If we solve for ω_D^3, we find that the Debye frequency is given by

$$\omega_\mathrm{D}^3 = \frac{18N\pi^2}{V}\left(\frac{2}{c_\mathrm{t}^3} + \frac{1}{c_\mathrm{l}^3}\right)^{-1}\,. \tag{5.69}$$

The density of states can be written

$$g(\omega) = \frac{\mathrm{d}\nu}{\mathrm{d}\omega} = \frac{V\omega^2}{2\pi^2}\left(\frac{2}{c_\mathrm{t}^3} + \frac{1}{c_\mathrm{l}^3}\right) = \frac{9N\omega^2}{\omega_\mathrm{D}^3}\,. \tag{5.70}$$

Once we are given the density of states, $g(\omega)$, the average energy is given by

$$\langle E\rangle = \frac{1}{2}\int_0^{\omega_\mathrm{D}} \hbar\omega g(\omega)\,\mathrm{d}\omega + \int_0^{\omega_\mathrm{D}} \hbar\omega n(\omega) g(\omega)\,\mathrm{d}\omega\,. \tag{5.71}$$

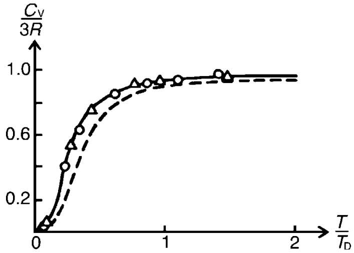

Figure 5.2 The solid line is the heat capacity curve predicted by Debye theory. The dashed line is that predicted for an Einstein solid. The circles and triangles are experimental values for the heat capacity of Al ($T_D = 390$ K) and Cu ($T_D = 315$ K), respectively (based on [38]).

We then find

$$\langle E \rangle = \frac{9N\hbar\omega_D}{8} + \frac{9N}{\omega_D^3}\int_0^{\omega_D} \frac{\hbar\omega^3\,\mathrm{d}\omega}{\mathrm{e}^{\beta\hbar\omega}-1} . \tag{5.72}$$

The heat capacity is

$$C_N = \frac{9Nk_B}{\hbar^2\beta^2\omega_D^3}\int_0^{\omega_D} \mathrm{d}\omega \frac{(\beta\hbar\omega)^4\mathrm{e}^{\beta\hbar\omega}}{(\mathrm{e}^{\beta\hbar\omega}-1)^2} = \frac{9Nk_B}{(\hbar\beta\omega_D)^3}\int_0^{T_D/T} \mathrm{d}x \frac{x^4\mathrm{e}^x}{(\mathrm{e}^x-1)^2} , \tag{5.73}$$

where the Debye temperature, T_D, is defined $T_D = \hbar\omega_D/k_B$. In the limit $T \to 0$, the heat capacity becomes approximately

$$C_N \approx \frac{9Nk_B}{(\hbar\beta\omega_D)^3}\int_0^{\infty} \mathrm{d}x \frac{x^4\mathrm{e}^x}{(\mathrm{e}^x-1)^2} = \frac{12Nk_B\pi^4T^3}{5T_D^3} . \tag{5.74}$$

These results are in good qualitative agreement with the experimentally observed heat capacity of many solids at low temperature. We give two examples in Figure 5.2 where we have plotted the prediction of Debye theory and have compared it to experimental results for aluminum and copper (using the appropriate Debye temperatures for those substances). Experimentally, one finds that at high temperatures the heat capacity, C_N, is roughly constant with $C_N \approx 3Nk_B = 3\mathfrak{n}R$, where $\mathfrak{n}$ is the number of moles and R is the gas constant. However, as the temperature approaches $T = 0$ K, the heat capacity goes to zero as T^3.

It is interesting to compare the density of states for an Einstein solid, a Debye solid, and the density of states obtained from experiment on real solids. For the Einstein solid, all phonon modes have a single frequency and therefore the density of states is $g(\omega) = 3N\delta(\omega - \omega_0)$, where ω_0 is the frequency of all the phonon modes. In real solids, the phonon modes have a distribution of frequencies, and this is more accurately taken into account by the Debye (continuum) theory. In Figure 5.3a, we compare the density of states for the Einstein solid and the Debye solid.

The density of states of solids can be measured using neutron scattering techniques. Neutrons interact with the nuclei of atoms in the solid and are scattered by phonons, which are the normal modes of the atomic oscillations. In Figure 5.3b we show the density of states for aluminum. The low-frequency contribution looks like the Debye result, but at high frequencies the Debye density of states is completely inadequate.

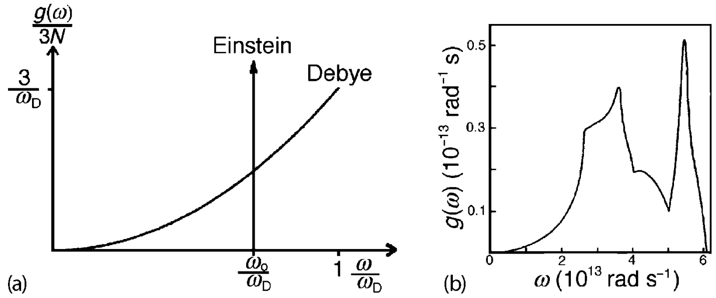

Figure 5.3 (a) Plots of the density of states of Einstein and Debye solids. (b) The density of states for aluminum, obtained from neutron scattering experiments. Reprinted, by permission, from [194].

5.6
Order–Disorder Transitions on Spin Lattices

One of the simplest systems that exhibits a phase transition is the Ising system [89] which consists of a lattice of N spin-1/2 objects with magnetic moment μ. Each lattice site can interact with the magnetic fields of their nearest neighbors and with any external applied magnetic fields that might be present. The Hamiltonian for an Ising lattice can be written

$$H = \sum_{\{ij\}} \epsilon_{ij} s_i s_j - \mu B \sum_{i=1}^{N} s_i \,, \tag{5.75}$$

where $\sum_{ij}$ denotes the sum over nearest-neighbor pairs ij (one must be careful to count each pair only once), ϵ_{ij} is the magnetic interaction energy between nearest neighbors i and j, s_i is the z-component of spin at the ith lattice site, and B is the external magnetic field. For spin-1/2 objects, $s_i = +1$ (-1) if the spin of site i is oriented in the positive (negative) z-direction. There is no kinetic energy in Eq. (5.75). *The Hamiltonian only contains information about spin orientation and the spatial distribution of lattice sites.* If $\epsilon_{ij} < 0$, then for $B = 0$ the lattice will have its lowest energy when all the lattice sites have spin up or all the lattice sites have spin down (ferromagnetic), both cases being equally probable. If $B \neq 0$, then the configuration in which all lattice sites are oriented with spin up will be energetically favored. Similarly, if $\epsilon_{ij} > 0$, then for $B = 0$ the configuration in which neighboring spins are oriented opposite to one another will be favored (antiferromagnetic).

The partition function for this spin lattice can be written

$$Z_N(T) = \sum_{\text{all config}} \exp\left(-\beta \sum_{\{ij\}} \epsilon_{ij} s_i s_j + \beta \mu B \sum_{i=1}^{N} s_i \right) , \tag{5.76}$$

where $\sum_{\text{all config}}$ denotes the sum over all 2^N possible different configurations of spin on the lattice. The partition function introduces an additional influence, that of thermal energy, $k_B T$. While the magnetic interaction energy will cause the spins on the lattice to become ordered, the thermal energy, $k_B T$, will tend to randomize the spins on the lattice. It is these two competing influences that lead to an *order–disorder phase transition* on the spin lattice. At low temperature, the lattice will be ordered. As we raise the temperature, at some point the order disappears and the spins become randomly oriented.

The system described by the partition function (5.76) was originally used by Ising [89] as a model for ferromagnetism, but it also has been used to describe lattice gases and binary alloys. The model also has applications outside of physics. It has been used to model learning [36] and information storage [29] in neural networks. In molecular biology, it has been used to model cooperative conformational changes due to ligand binding in macromolecules [72], and heat denaturation of DNA [35]. It has been used in biology to model cultural isolation [91].

The Ising model can be solved exactly for the case of lattices with one or two space dimensions, and analytic expressions for its thermodynamic properties can be found for those cases. However, no one has ever succeeded in solving it analytically in three dimensions. In one dimension it does not exhibit a phase transition at finite temperature, but in two dimensions it does. In one dimension the lattice does not have enough nearest neighbors for the ordering effects of the interaction energy to compete effectively with the disordering thermal energy. However, for two or more spatial dimensions it does. The Ising model was first solved in two dimensions by Onsager [96, 97, 156]. It is one of the few exactly soluble models which exhibit a phase transition.

In this section, we will first obtain exact expressions for the thermodynamic properties of a one-dimensional Ising lattice. The one-dimensional lattice does not exhibit a phase transition at finite temperature. However, the method of solution contains some ideas that are used to solve the much more difficult case of a two-dimensional lattice. Because of space constraints, we will not attempt to solve the two-dimensional case but we will give the exact expression for the specific heat for a two-dimensional square lattice and show how the phase transition occurs for this system. In this section, we will also compute the thermodynamic properties of an Ising lattice with d-dimensions in the mean field approximation. The mean field approximation of the d-dimensional lattice does have a phase transition at finite temperature.

5.6.1
Exact Solution for a One-Dimensional Lattice

Let us consider a one-dimensional periodic lattice that consists of N lattice sites evenly spaced. We will assume that all nearest neighbors have the same interaction energy, $\epsilon_{ij} = -\epsilon$, so that the configuration with lowest energy is one in which the spins are totally aligned. The periodicity of the lattice is imposed by assuming that $s_{i+N} = s_i$. The total energy for a given configuration, $\{s_i\}$, is

$$E\{s_i\} = -\epsilon \sum_{i=1}^{N} s_i s_{i+1} - \mu B \sum_{i=1}^{N} s_i \,. \tag{5.77}$$

The partition function can be written

$$Z_N(T, B) = \sum_{s_1=\pm 1} \cdots \sum_{s_N=\pm 1} \exp\left\{\beta \sum_{i=1}^{N} \left[\epsilon s_i s_{i+1} + \frac{1}{2}\mu B(s_i + s_{i+1})\right]\right\} , \quad (5.78)$$

where we have used the fact that $\sum_{i=1}^{N} s_i = 1/2 \sum_{i=1}^{N}(s_i + s_{i+1})$ for a periodic lattice. It is now convenient to introduce a 2×2 matrix,

$$\overline{\boldsymbol{P}} = \begin{pmatrix} \mathrm{e}^{\beta(\epsilon+\mu B)} & \mathrm{e}^{-\beta\epsilon} \\ \mathrm{e}^{-\beta\epsilon} & \mathrm{e}^{\beta(\epsilon-\mu B)} \end{pmatrix} , \quad (5.79)$$

whose matrix elements are defined as

$$\langle s_i|\overline{\boldsymbol{P}}|s_{i+1}\rangle = \mathrm{e}^{\beta[\epsilon s_i s_{i+1} + \frac{1}{2}\mu B(s_i + s_{i+1})]} . \quad (5.80)$$

The partition function may then be written

$$\begin{aligned} Z_N(T, B) &= \sum_{s_1=\pm 1} \cdots \sum_{s_N=\pm 1} \langle s_1|\overline{\boldsymbol{P}}|s_2\rangle\langle s_2|\overline{\boldsymbol{P}}|s_3\rangle \cdots \langle s_N|\overline{\boldsymbol{P}}|s_1\rangle \\ &= \sum_{s_1=\pm 1} \langle s_1|\overline{\boldsymbol{P}}^N|s_1\rangle = \mathrm{Tr}(\overline{\boldsymbol{P}}^N) = \lambda_+^N + \lambda_-^N = \lambda_+^N \left[1 + \left(\frac{\lambda_-}{\lambda_+}\right)^N\right] , \end{aligned} \quad (5.81)$$

where $\lambda_\pm$ are the eigenvalues of the matrix $\overline{\boldsymbol{P}}$. We shall use the convention $\lambda_+ > \lambda_-$. The eigenvalues of $\overline{\boldsymbol{P}}$ are easily found to be

$$\lambda_\pm = \mathrm{e}^{\beta\epsilon}\left[\cosh(\beta\mu B) \pm \sqrt{\cosh^2(\beta\mu B) - 2\mathrm{e}^{-2\beta\epsilon}\sinh(2\beta\epsilon)}\right] . \quad (5.82)$$

In the limit $N \to \infty$, only the largest eigenvalue, λ_+, contributes to the thermodynamic quantities. This is easily seen if we note that the Gibbs free energy per site is

$$g(T, B) = \lim_{N\to\infty} \frac{1}{N} G_N(T, B) = -k_\mathrm{B} T \lim_{N\to\infty} \frac{1}{N} \ln Z_n(T, B) = -k_\mathrm{B} T \ln \lambda_+ . \quad (5.83)$$

In Eq. (5.83), we have used the fact that $\lim_{N\to\infty}(\lambda_-/\lambda_+)^N = 0$. Thus, the Gibbs free energy per site is

$$g(T, B) = -\epsilon - k_\mathrm{B} \ln\left[\cosh(\beta\mu B) + \sqrt{\cosh^2(\beta\mu B) - 2\mathrm{e}^{-2\beta\epsilon}\sinh(2\beta\epsilon)}\right] . \quad (5.84)$$

The order parameter is given by

$$\langle s\rangle = -\left(\frac{\partial g}{\partial \mu B}\right)_\mathrm{T} = \frac{\sinh(\beta\mu B)}{\sqrt{\cosh^2(\beta\mu B) - 2\mathrm{e}^{-2\beta\epsilon}\sinh(2\beta\epsilon)}} . \quad (5.85)$$

From Eq. (5.85) we see that the one-dimensional Ising model cannot exhibit a phase transition because when $B \to 0$ the order parameter also goes to zero. Hence, no spontaneous nonzero value of the order parameter is possible.

5.6.2
Mean Field Theory for a d-Dimensional Lattice

We can obtain analytic expressions for the thermodynamic properties of a d-dimensional Ising lattice using the mean field approximation first introduced by Weiss [209]. In the mean field approximation, the Hamiltonian of a d-dimensional spin lattice with N lattice sites can be written

$$\hat{H} = -\frac{1}{2}\sum_{i=1}^{N} \nu\epsilon\langle s\rangle s_i - \mu B \sum_{i=1}^{N} s_i = -\sum_{i=1}^{N} E(\epsilon, B) s_i \ , \tag{5.86}$$

where ϵ is the coupling constant, ν is the number of nearest-neighbor spins, and $E(\epsilon, B) = (1/2)\nu\epsilon\langle s\rangle + \mu B$. The factor of $1/2$ ensures that we don't count the same pair of spins twice. The quantity $\langle s\rangle \equiv \langle s_i\rangle$ is the average spin per site. The quantity $\nu\epsilon\langle s\rangle s_i$ is an average magnetic interaction energy between site i and its nearest neighbors, assuming that the neighbors all have spin $\langle s\rangle$. As we shall show below, the average spin per site, $\langle s\rangle$, must be determined in a self-consistent manner.

The partition function can be written

$$Z_N = \left(\sum_{s_i=\pm 1} \mathrm{e}^{\beta E s_i}\right)^N = (2\cosh(\beta E))^N \ . \tag{5.87}$$

The Gibbs free energy per site is

$$g(\epsilon, B) = -k_\mathrm{B} T \lim_{N\to\infty}\left(\frac{1}{N}\ln Z_N\right) = -k_\mathrm{B} T \ln[2\cosh(\beta E)] \ . \tag{5.88}$$

The probability $P(s_i)$ that site i has spin s_i is

$$P(s_i) = \frac{\mathrm{e}^{\beta E s_i}}{\sum_{s_i=\pm 1} \mathrm{e}^{\beta E s_i}} = \frac{\mathrm{e}^{\beta E s_i}}{2\cosh(\beta E)} \ . \tag{5.89}$$

Note that the probability $P(s_i)$ depends on $\langle s\rangle$, which must be determined self-consistently.

The average magnetization of the lattice is given by

$$\langle M\rangle = N\mu\langle s\rangle \ , \tag{5.90}$$

where

$$\langle s\rangle = \frac{\sum_{s_i=\pm 1} s_i \mathrm{e}^{\beta E s_i}}{\sum_{s_j=\pm 1} \mathrm{e}^{\beta E s_j}} = \tanh(\beta E) = \tanh\left[\beta\left(\frac{1}{2}\nu\epsilon\langle s\rangle + \mu B\right)\right] \ . \tag{5.91}$$

The magnetization is the order parameter for the spin lattice. If $B = 0$, the magnetization will be zero for the high-temperature paramagnetic phase of the lattice (randomly ordered spins) and it will be nonzero at lower temperatures where the spins have spontaneously aligned.

We can determine the critical temperature, T_c, at which the lattice starts to become ordered as temperature is lowered (the Curie point) from the expression for the average spin per site, $\langle s\rangle$. Let us write $\langle s\rangle$ for the case $B = 0$;

$$\langle s\rangle = \tanh\left(\frac{1}{2}\beta\nu\epsilon\langle s\rangle\right) = \tanh\left(\frac{\nu\epsilon\langle s\rangle}{2k_B T}\right) . \tag{5.92}$$

We must solve Eq. (5.92) for $\langle s\rangle$. This can be done graphically by plotting $f_1 \equiv \langle s\rangle$ versus $\langle s\rangle$ and $f_2 \equiv \tanh(\alpha\langle s\rangle)$ versus $\langle s\rangle$ on the same graph. The solution to Eq. (5.92) is given by those points where the two curves cross – that is, where $f_1 = f_2$. In Figures 5.4a and 5.4b, we plot f_1 and f_2 versus $\langle s\rangle$ for $\alpha < 1$ and $\alpha > 1$, respectively. For the case $\alpha < 1$, there is only one crossing point and it is at $\langle s\rangle = 0$. For $\alpha > 1$, there are three crossing points, at $\langle s\rangle = 0$ and at $\langle s\rangle = \pm s_0$. The free energy per site for these various cases is

$$g(\epsilon, 0) = \begin{cases} -k_B T \ln 2 & \text{if} \quad \langle s\rangle = 0 , \\ -k_B T \ln\left[2\cosh\left(\frac{1}{2}\beta\nu\epsilon s_0\right)\right] & \text{if} \quad \langle s\rangle = \pm s_0 . \end{cases} \tag{5.93}$$

Thus, the values, $\langle s\rangle = \pm s_0$ (when they are solutions to Eq. (5.92)) describe possible states of thermodynamic equilibrium since they minimize the free energy. The transition point (critical point) occurs at $\alpha = 1$ in Figure 5.4 and therefore when $\nu\epsilon/(2k_B T) = 1$. Thus, the critical temperature in the mean field approximation is $T = T_c = \nu\epsilon/(2k_B)$. In Figure 5.5a, we plot the order parameter $\langle s\rangle$, versus T/T_c.

We see that mean field theory predicts a phase transition at a finite temperature for a d-dimensional lattice. This does not agree with our exact result for the case $d = 1$ (cf. Section 5.6.1) where we found no phase transition at finite temperature. Mean field theory gives too high an estimate of the critical temperature for spatial dimensions, $d \leq 3$. It gives good estimates for $d \geq 4$ which is not of physical interest but is of mathematical interest.

Let us next examine the behavior of the heat capacity in the neighborhood of the critical temperature. The internal energy for $B = 0$ is

$$U = -\frac{1}{Z_N}\frac{\partial Z_N}{\partial\beta} = -\frac{1}{2}N\nu\epsilon\langle s\rangle^2 . \tag{5.94}$$

The heat capacity is

$$C_N = \left(\frac{\partial U}{\partial T}\right)_N = -k_B\beta^2\left(\frac{\partial U}{\partial\beta}\right)_N = Nk_B\nu\epsilon\beta^2\langle s\rangle\left(\frac{\partial\langle s\rangle}{\partial\beta}\right)_N . \tag{5.95}$$

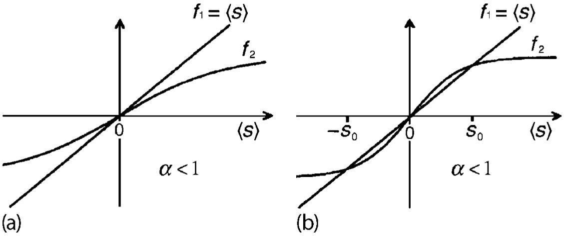

Figure 5.4 Plots of $f_1 \equiv \langle s\rangle$ versus $\langle s\rangle$ and $f_2 \equiv \tanh(\alpha\langle s\rangle)$ versus $\langle s\rangle$. (a) $\alpha < 1$. (b) $\alpha > 1$.

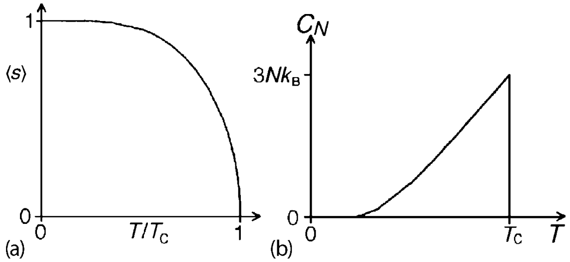

Figure 5.5 (a) A plot of the order parameter, $\langle s\rangle$, versus the reduced temperature, T/T_c. (b) A plot of the heat capacity, C_N, as a function of temperature in the neighborhood of the critical point.

But

$$\left(\frac{\partial\langle s\rangle}{\partial\beta}\right)_N = \operatorname{sech}^2\left(\beta\frac{\nu\epsilon}{2}\langle s\rangle\right)\left[\frac{\nu\epsilon}{2}\langle s\rangle + \beta\frac{\nu\epsilon}{2}\left(\frac{\partial\langle s\rangle}{\partial\beta}\right)_N\right] \tag{5.96}$$

so

$$\left(\frac{\partial\langle s\rangle}{\partial\beta}\right)_N = \frac{\nu\epsilon\langle s\rangle}{3\cosh^2\left(\beta\frac{\nu\epsilon}{2}\langle s\rangle\right) - \beta\nu\epsilon}\,. \tag{5.97}$$

The heat capacity finally takes the form

$$C_N = \frac{Nk_B\beta^2\nu^2\epsilon^2\langle s\rangle^2}{2\cosh^2\left(\beta\frac{\nu\epsilon}{2}\right) - \beta\nu\epsilon} = \frac{2Nk_B\langle s\rangle^2(T_c/T)^2}{\left(\cosh^2(\langle s\rangle T_c/T) - T_c/T\right)}\,. \tag{5.98}$$

In Figure 5.5b, we plot the heat capacity as a function of temperature. We see that the heat capacity has a finite jump at the critical temperature. It reaches a maximum value of $3Nk_B$ at $T = T_c$.

The final quantity we wish to compute is the magnetic susceptibility, $\chi_{T,N}(B)$. The magnetic susceptibility is defined as

$$\chi_{T,N}(B) = \left(\frac{\partial\langle M\rangle}{\partial B}\right)_{T,N} = N\mu\left(\frac{\partial\langle s\rangle}{\partial B}\right)_{T,N}\,. \tag{5.99}$$

From (5.91) we can write

$$\left(\frac{\partial\langle s\rangle}{\partial B}\right)_{T,N} = \operatorname{sech}^2\left(\beta\frac{\nu\epsilon}{2}\langle s\rangle + \beta\mu B\right)\left[\beta\frac{\nu\epsilon}{2}\left(\frac{\partial\langle s\rangle}{\partial B}\right)_{T,N} + \beta\mu\right] \tag{5.100}$$

or

$$\left(\frac{\partial\langle s\rangle}{\partial B}\right)_{T,N} = \frac{2\beta\mu}{2\cosh^2\left(\beta\frac{\nu\epsilon}{2}\langle s\rangle + \beta\mu B\right) - \beta\nu\epsilon}\,. \tag{5.101}$$

The magnetic susceptibility, $\chi_{T,N}(B)$, is then given by

$$\chi_{T,N}(B) = \frac{2\beta N\mu^2}{2\cosh^2\left(\beta\frac{\nu\epsilon}{2}\langle s\rangle + \beta\mu B\right) - \beta\nu\epsilon}\,. \tag{5.102}$$

The magnetic susceptibility in the limit $B = 0$ is

$$\chi_{T,N}(0) = \frac{2\beta N\mu^2}{2\cosh^2\left(\beta\frac{\nu\epsilon}{2}\langle s\rangle\right) - \beta\nu\epsilon} = \frac{2N\mu^2}{\nu\epsilon}\frac{(T_\mathrm{c}/T)}{\cosh^2(\langle s\rangle T_\mathrm{c}/T) - T_\mathrm{c}/T}\,, \tag{5.103}$$

with $\langle s\rangle$ given by Eq. (5.92). Examination of Eq. (5.103) shows that the magnetic susceptibility has an infinite jump at the critical point.

The results we have obtained in this section for the thermodynamic properties of a spin lattice in the neighborhood of the phase transition are qualitatively similar to the results we obtained in Chapter 4 using mean field theories. Using statistical mechanics to obtain these results allows us to compute various constants that appear in the thermodynamic expressions in terms of microscopic interaction energies and magnetic moments. As we shall see in subsequent sections, where we give some exact results for the two-dimensional spin lattice and use renormalization theory, mean field theory gives a rough qualitative picture of the phase transition, but it is not quantitatively correct.

5.6.3
Mean Field Theory of Spatial Correlation Functions

Let us now use a version of Ginzburg–Landau mean field theory to write a phenomenological expression for the partition function of a spin lattice

$$Z_N(T) = \sum_{\{m_1\}} \mathrm{e}^{-V\Phi(m_1)}\,, \tag{5.104}$$

where $\Phi(m_1)$ is the free energy density of the system, $\mathrm{e}^{-V\Phi(m_1)}$ is proportional to the probability to find the lattice in configuration $\{m_1\}$, and the summation is over all possible configurations of the lattice. We assume that, at temperature $T > T_\mathrm{c}$, $\langle m_1\rangle = 0$ and $\Phi(m_1)$ must be an even function of m_1.

If the lattice is very large, we can let the discrete spatial variation of the local magnetization density become continuous so $m_\alpha \to m(\boldsymbol{r})$. For small fluctuations away from equilibrium we can write

$$\begin{aligned}\Phi\{\delta m(\boldsymbol{r})\} = \phi(T) + \frac{1}{2}C_1(T)\int_V \mathrm{d}\boldsymbol{r}(\delta m(\boldsymbol{r}))^2 \\ + \frac{1}{2}C_2(T)\int_V \mathrm{d}\boldsymbol{r}(\nabla\delta m(\boldsymbol{r}))\cdot(\nabla\delta m(\boldsymbol{r})) + \ldots\,,\end{aligned} \tag{5.105}$$

where $\phi(T)$ is the nonmagnetic free energy density. Let us next note that

$$\int_V \mathrm{d}\boldsymbol{r}(\delta m(\boldsymbol{r}))^2 = \frac{1}{V}\sum_{\boldsymbol{k}} \delta m(\boldsymbol{k})\delta m(-\boldsymbol{k})\,, \tag{5.106}$$

where $\delta m(-\boldsymbol{k}) = \delta m^*(\boldsymbol{k})$ and

$$\int_V \mathrm{d}\boldsymbol{r}(\nabla\delta m(\boldsymbol{r}))\cdot(\nabla\delta m(\boldsymbol{r})) = \frac{1}{V}\sum_{\boldsymbol{k}} k^2\delta m(\boldsymbol{k})\delta m(-\boldsymbol{k})\,. \tag{5.107}$$

The free energy can then be written

$$\Phi\{\delta m(\boldsymbol{k})\} = \phi(T) + \frac{1}{V}\sum_{\boldsymbol{k}}(C_1(T) + k^2C_2(T))\delta m(\boldsymbol{k})\delta m(-\boldsymbol{k})\,. \tag{5.108}$$

We can use this free energy to obtain the probability for a fluctuation $\delta m(\boldsymbol{k})$ to occur. It is

$$P(\delta m(\boldsymbol{k})) = C\exp\left[-\frac{1}{2}\left(C_1(T) + k^2C_2(T)\right)|\delta m(\boldsymbol{k})|^2\right]\,, \tag{5.109}$$

where C is a normalization constant. Given the probability density in Eq. (5.109), we can compute the static structure function. We obtain

$$G(\boldsymbol{k}) = \int_{\infty}^{\infty}\mathrm{d}|\delta m(\boldsymbol{k})||\delta m(\boldsymbol{k})|^2P(\delta m(\boldsymbol{k})) = \frac{1}{C_1 + C_2k^2}\,. \tag{5.110}$$

The static susceptibility is given by

$$\chi = \beta VG(\boldsymbol{k}=0) = \frac{\beta V}{C_1}\,. \tag{5.111}$$

Near a phase transition, the susceptibility behaves as $\chi \approx (T - T_\mathrm{c})^{-1}$. Therefore, $C_1 \approx (T - T_\mathrm{c})$.

The static correlation function is given by

$$C(\boldsymbol{r}) = \frac{1}{V}\sum_{\boldsymbol{k}} G(\boldsymbol{k})\mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}} = \int\frac{\mathrm{d}\boldsymbol{k}}{(2\pi)^3}\frac{\mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}}{\left(C_1 + C_2k^2\right)} = \frac{1}{4\pi C_2r}\mathrm{e}^{-r\sqrt{C_1/C_2}}\,. \tag{5.112}$$

The correlation function has a correlation length $\xi \approx \sqrt{C_2/C_1}$. Since $C_1 \sim (T - T_\mathrm{c})$ near a critical point, the correlation length $\xi \approx \sqrt{C_2/(T - T_\mathrm{c})}$ goes to infinity as $(T - T_\mathrm{c})^{-1/2}$ as we approach a critical point. Therefore, at the critical point the spatial correlations between fluctuations extend across the entire system.

5.6.4
Exact Solution to Ising Lattice for $d = 2$

The two-dimensional Ising model is one of the simplest systems that exhibit a phase transition and one of the few for which the thermodynamic properties can be obtained exactly [156, 183, 186]. Although we will not derive the exact solution here, we will write the partition function and then give the exact result for the heat capacity.

We consider a planar lattice of N spin-1/2 objects with magnetic moment μ. A planar lattice is one that can be laid out flat in a two-dimensional plane without any bonds intersecting (a lattice with periodic boundary conditions is not planar). Each lattice site can interact with the magnetic fields of its nearest neighbors. The Hamiltonian for a two dimensional planar lattice can be written

$$H = -\sum_{\{i,j\}} J(s_i s_j - 1)\,, \tag{5.113}$$

where $\{i, j\}$ denotes the sum over nearest neighbors, i and j, J is the magnetic interaction energy between nearest neighbors, and s_j is the z-component of spin at the jth lattice site. The factor, -1, merely shifts the zero point of energy. The quantity $s_j = +1(-1)$ if the spin of site j is oriented in the positive (negative) direction. The partition function can be written

$$Z_N(T) = \sum_{a.c.} \exp\left(\sum_{(i,j)} K(s_i s_j - 1)\right) = \mathrm{e}^{-N_{nn}K} \sum_{s_1=\pm 1} \cdots \sum_{s_N=\pm 1} \prod_{(i,j)} \mathrm{e}^{K s_i s_j} \tag{5.114}$$

where $K = \beta J$, $\sum_{a.c.}$ denotes the sum over all 2^N possible configurations of spin on the lattice, and N_{nn} is the number of nearest neighbor pairs. The sum $\sum_{(i,j)}$ and product $\prod_{(i,j)}$ are taken only over nearest neighbor pairs. The mathematics involved in obtaining expressions for thermodynamic properties of the planar lattice is challenging. We only give the results here.

For an infinite square 2D planar lattice, the specific heat (heat capacity per lattice site) is

$$\begin{aligned} c(T) = \frac{2}{\pi} k_{\mathrm{B}} K^2 \coth^2(2K) \Big\{ & 2\boldsymbol{K}(\kappa) - 2\boldsymbol{E}(\kappa) \\ & -2\operatorname{sech}^2(2K)\left[\frac{\pi}{2} + (2\tanh(2K) - 1)\boldsymbol{K}(\kappa)\right]\Big\} \end{aligned} \tag{5.115}$$

where $\kappa = 2\sinh(2K)/\cosh^2(2K)$ and $\boldsymbol{K}(\kappa)$ ($\boldsymbol{E}(\kappa)$) is the complete elliptic integral of the first kind (second kind) [23]. The complete elliptic integral of the first kind has a singularity at $\kappa = 1$ and the phase transition occurs at this point. The temperature at which the phase transition occurs is therefore given by the condition

$$\kappa_{\mathrm{c}} = \frac{2\sinh(2K_{\mathrm{c}})}{\cosh^2(2K_{\mathrm{c}})} = 1\,. \tag{5.116}$$

This gives a critical temperature $T_{\mathrm{c}} = 2.269 J/k_{\mathrm{B}}$. In Figure 5.6a, we plot the specific heat as a function of K (note that K is proportional to the inverse temperature).

Ising-like transitions have been measured in the two-dimensional Ising-like anti-ferromagnets, K_2CoF_4 and Rb_2CoF_4. These substances behave like two-dimensional spin systems because they consist of strongly coupled antiferromagnetic CoF_2 planes separated by weakly coupled planes containing the remaining molecules. In Figure 5.6b, we show two measurements of the heat capacity of Rb_2CoF_4. We see the characteristic Ising-like singularity in the heat capacity.

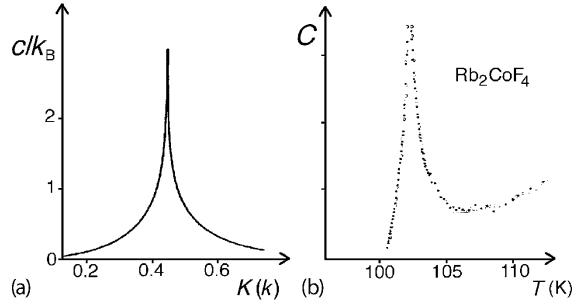

Figure 5.6 (a) The specific heat for the 2D planar Ising lattice, as a function of K. The phase transition occurs at $K_c = 1/2.269 = 0.4407$. (b) The heat capacity of Rb_2CoF_4 (given in arbitrary units) as a function of temperature T (measured in kelvin). Two sets of experimental data are shown. Reprinted, by permission, from [88].

5.7
Scaling

As we approach the critical point, the distance over which fluctuations are correlated approaches infinity and all effects of the finite lattice spacing are wiped out. There are no natural length scales left. Thus we might expect that, as we change the distance from the critical point (e. g., by changing the temperature), we do not change the form of the free energy but only *its scale*. The idea of scaling underlies all critical exponent calculations [179, 193]. To understand scaling, we must first introduce the concept of a homogeneous function.

5.7.1
Homogeneous Functions

A function $F(\lambda x)$ is homogeneous if, for all values of λ, we obtain

$$F(\lambda x) = g(\lambda)F(x) . \tag{5.117}$$

The general form of the function $g(\lambda)$ can be found easily. We first note that

$$F(\lambda \mu x) = g(\lambda \mu)F(x) = g(\lambda)g(\mu)F(x) \tag{5.118}$$

so that

$$g(\lambda \mu) = g(\lambda)g(\mu) . \tag{5.119}$$

If we take the derivative with respect to μ, we find

$$\frac{\partial}{\partial \mu} g(\lambda \mu) = \lambda g'(\lambda \mu) = g(\lambda)g'(\mu) , \tag{5.120}$$

where $g'(\mu) \equiv \mathrm{d}g(\mu)/\,\mathrm{d}\mu$. We next set $\mu = 1$ and $g'(1) = p$. Then

$$\lambda g'(\lambda) = p g(\lambda) . \tag{5.121}$$

If we integrate from 1 to λ and note that $g(1) = 1$, we find $g(\lambda) = \lambda^p$. Thus,

$$F(\lambda x) = \lambda^p F(x) \tag{5.122}$$

and $F(x)$ is said to be a homogeneous function of degree p. In Eq. (5.122), if we let $\lambda = x^{-1}$, we obtain

$$F(x) = F(1)x^p \; . \tag{5.123}$$

Thus, the homogeneous function $F(x)$ has power-law dependence on its arguments.

Let us now consider a homogeneous function of two variables $f(x, y)$. Such a function can be written in the form

$$f(\lambda^p x, \lambda^q y) = \lambda f(x, y) \tag{5.124}$$

and is characterized by two parameters, p and q. It is convenient to write $f(x, y)$ in another form. We will let $\lambda = y^{-1/q}$. Then

$$f(x, y) = y^{1/q} f\left(\frac{x}{y^{p/q}}, 1\right) \; , \tag{5.125}$$

and we see that the homogeneous function, $f(x, y)$, depends on x and y only through the ratio $x/y^{p/q}$ aside from a multiplicative factor. We can now apply these ideas to thermodynamic quantities near the critical point.

5.7.2
Widom Scaling

When a phase transition occurs in a thermodynamic system, singular behavior occurs in some thermodynamic response functions, and the nature of the singularity can be quantified in terms of the critical exponents. Widom [212] obtained relations between different critical exponents by assuming that the “singular” part of the free energy scales. We will use magnetic systems to illustrate Widom scaling and we will assume that a magnetic induction field, $\boldsymbol{B}$, is present.

Let us write the free energy per lattice site of a magnetic system in terms of a regular part, $g_{\mathrm{r}}(T, \boldsymbol{B})$, that does not change in any significant way as we approach the critical point, and a singular part, $g_{\mathrm{s}}(\varepsilon, \boldsymbol{B})$, that contains the important singular behavior of the system in the neighborhood of the critical point. Then

$$g(T, \boldsymbol{B}) = g_{\mathrm{r}}(T, \boldsymbol{B}) + g_{\mathrm{s}}(\varepsilon, \boldsymbol{B}) \; , \tag{5.126}$$

where $\varepsilon = (T - T_{\mathrm{c}})/T_{\mathrm{c}}$ and T_{c} is the critical temperature.

We shall assume that the singular part of the free energy is a generalized homogeneous function of its parameters,

$$g_{\mathrm{s}}(\lambda^p \varepsilon, \lambda^q B) = \lambda g_{\mathrm{s}}(\varepsilon, B) \; . \tag{5.127}$$

We now write the free energy as a function of the magnitude of $\boldsymbol{B}$. For the systems considered here, its direction does not play an important role. The critical exponents can be expressed in terms of p and q.

Let us first find an expression for the critical exponent β, which quantifies the behavior of the order parameter in the neighborhood of the critical point, and is defined (see Eq. (4.87))

$$M(\varepsilon, B = 0) \sim (-\varepsilon)^{\beta} \, . \tag{5.128}$$

If we differentiate Eq. (5.127) with respect to B, we obtain

$$\lambda^q M(\lambda^p \varepsilon, \lambda^q B) = \lambda M(\varepsilon, B) \, . \tag{5.129}$$

If we next let $\lambda = (-\varepsilon)^{-1/p}$ and set $B = 0$, we obtain

$$M(\varepsilon, 0) = (-\varepsilon)^{(1-q)/p} M(-1, 0) \, . \tag{5.130}$$

Thus,

$$\beta = \frac{1-q}{p} \tag{5.131}$$

and we have obtained a relation between the critical exponent β and Widom scaling exponents p and q.

Let us next determine the exponent δ (the degree of the critical isotherm), which is defined (see Eq. (4.86)) as

$$M(0, B) = |B|^{1/\delta} \operatorname{sign} B \, . \tag{5.132}$$

If we set $\varepsilon = 0$ and $\lambda = B^{-1/q}$ in Eq. (5.129), we obtain

$$M(0, B) = B^{(1-q)/q} M(0, 1) \, . \tag{5.133}$$

Thus,

$$\delta = \frac{q}{1-q} \tag{5.134}$$

and we related the critical exponent δ to the Widom scaling exponent q.

The magnetic susceptibility is obtained from the thermodynamic relation (see Eq. (4.89))

$$\chi = -\left(\frac{\partial^2 g}{\partial B^2}\right)_T \sim \begin{cases} (-\varepsilon)^{-\gamma'} , & T < T_{\mathrm{c}} \, , \\ (\varepsilon)^{-\gamma} , & T > T_{\mathrm{c}} \, . \end{cases} \tag{5.135}$$

By differentiating Eq. (5.129) twice with respect to B, we can write

$$\lambda^{2q} \chi(\lambda^p \varepsilon, \lambda^q B) = \lambda \chi(\varepsilon, B) \, . \tag{5.136}$$

If we now set $B = 0$ and let $\lambda = (\varepsilon)^{-1/p}$, we find

$$\chi(\varepsilon, 0) = \varepsilon^{(1-2q)/p} \chi(1, 0) \, . \tag{5.137}$$

Thus, the critical exponent for the susceptibility is

$$\gamma = \frac{2q - 1}{p} , \tag{5.138}$$

and we have related the critical exponent γ to the Widom scaling exponents p and q. By a similar calculation, we find that $\gamma = \gamma'$.

The heat capacity at constant B is given by (see Eq. (4.88))

$$C_B = -T \left(\frac{\partial^2 g}{\partial T^2} \right)_B \sim (\varepsilon)^{-\alpha} . \tag{5.139}$$

From Eq. (5.127), we obtain

$$\lambda^{2p} C_B(\lambda^p \varepsilon, \lambda^q B) = \lambda C_B(\varepsilon, B) . \tag{5.140}$$

If we set $B = 0$ and $\lambda = (\varepsilon)^{-1/p}$, we find

$$C_B(\varepsilon, 0) = \varepsilon^{(1-2p)/p} C_B(1, 0) , \tag{5.141}$$

and therefore

$$\alpha = 2 - \frac{1}{p} \tag{5.142}$$

and the critical exponent α is related to the Widom scaling exponent p. By a similar calculation we find $\alpha = \alpha'$.

In Eqs. (5.131), (5.134), (5.138), and (5.142), we have obtained the four critical exponents, α, β, γ, and δ, in terms of the two Widom scaling exponents p and q. If we combine Eqs. (5.131), (5.134), and (5.138), we find

$$\gamma' = \gamma = \beta(\delta - 1) . \tag{5.143}$$

From Eqs. (5.131), (5.134), and (5.142) we find

$$\alpha + \beta(\delta + 1) = 2 . \tag{5.144}$$

Thus, the Widom scaling assumption allows us to obtain *exact* relations between the critical exponents. These relations agree with mean field theory ($\alpha = 0$, $\beta = 1/2$, $\delta = 3$, $\gamma = 1$) as one can easily check. They also agree with experimentally obtained values of the critical exponents which generally differ from mean field results (cf. Table 5.1).

For later reference, it is useful to express p and q in terms of the critical exponents. We find

$$p = \frac{1}{\beta} \frac{1}{(\delta + 1)} \tag{5.145}$$

and

$$q = \delta \frac{1}{(\delta + 1)} . \tag{5.146}$$

The scaling property for systems near the critical point has been verified experimentally for fluids [152] and magnetic systems [193].

5.7.3
Kadanoff Scaling

Kadanoff [93] showed how to use the idea of scaling to obtain important information about the Ising model. Let us consider a d-dimensional Ising system with nearest-neighbor coupling (Γ nearest neighbors). The Hamiltonian is

$$H\{S\} = -K \sum_{(ij)}^{\Gamma N/2} S_i S_j - B \sum_{i=1}^{N} S_i \,, \tag{5.147}$$

where N is the number of lattice sites and $S_i = \pm 1$ is the spin on lattice site i. We will divide the lattice into blocks of lattice sites with block edges of length La, where a is the distance between lattice sites (cf. Figure 5.7a). We choose L so that $La \ll \xi$ where ξ is the correlation length of spin fluctuations on the lattice (cf. (5.112)). The total number of spins in each block is L^d. The total number of blocks is NL^{-d}. The total spin in block I is

$$S'_{\mathrm{I}} = \sum_{i \in \mathrm{I}} S_i \,. \tag{5.148}$$

Since L is chosen so that $La \ll \xi$, the spins in each block will be highly correlated and it is likely that they will be aligned to some extent. In view of this, it is useful to define a new spin variable, S_{I}, through the relation

$$S'_{\mathrm{I}} = Z S_{\mathrm{I}} \,, \tag{5.149}$$

where $S_{\mathrm{I}} = \pm 1$, $Z = L^y$ and y is a parameter to be determined.

Spins interact with nearest-neighbor spins, so blocks should also interact with nearest-neighbor blocks. Thus, the block Hamiltonian will be of the form

$$H\{S_{\mathrm{L}}\} = -K_{\mathrm{L}} \sum_{(\mathrm{IJ})}^{\Gamma N L^{-d}/2} S_{\mathrm{I}} S_{\mathrm{J}} - B_{\mathrm{L}} \sum_{\mathrm{I}=1}^{NL^{-d}} S_{\mathrm{I}} \,, \tag{5.150}$$

where K_{L} is the new effective interaction between nearest-neighbor blocks. The block Hamiltonian looks exactly like the site Hamiltonian except that all quantities

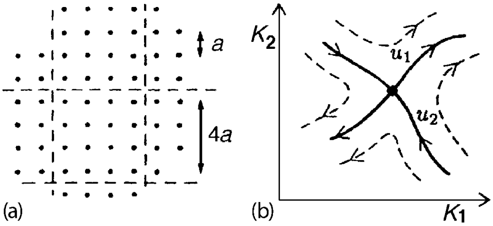

Figure 5.7 (a) Decomposition of a square lattice into square blocks whose sides have length $La = 4a$. (b) A hyperbolic fixed point with its eigencurves and the flow of points in the neighborhood of the fixed point.

are rescaled. Therefore, we expect the free energy per block, $g(\varepsilon_{\mathrm{L}}, B_{\mathrm{L}})$, to have the same functional form as the free energy per site, $g(\varepsilon, B)$. Since there are L^d sites per block, we have

$$g(\varepsilon_{\mathrm{L}}, B_{\mathrm{L}}) = L^d g(\varepsilon, B) \,. \tag{5.151}$$

If we rescale our system and describe it in terms of blocks rather than sites, we reduce the effective correlation length (measured in units of La) and therefore we move farther away from the critical point. Thus, the correlation length will behave as

$$\xi_{\mathrm{L}}(\varepsilon_{\mathrm{L}}, B_{\mathrm{L}}) = L^{-1}\xi(\varepsilon, B) \,. \tag{5.152}$$

Since rescaling moves us away from the critical point, the temperature ε and magnetic field B must also rescale. We assume that

$$\varepsilon_{\mathrm{L}} = \varepsilon L^x \,, \tag{5.153}$$

where x is a positive parameter. Similarly,

$$B\sum_{i=1}^{N} S_i = B\sum_{\mathrm{I}=1}^{NL^{-d}}\sum_{i\in\mathrm{I}} S_i = B\sum_{\mathrm{I}=1}^{NL^{-d}} S'_{\mathrm{I}} = BZ\sum_{\mathrm{I}=1}^{NL^{-d}} S_{\mathrm{I}} \,, \tag{5.154}$$

so that

$$B_{\mathrm{L}} = BZ = L^y B \,. \tag{5.155}$$

Equation (5.150) now becomes

$$g(L^x\varepsilon, L^y B) = L^d g(\varepsilon, B) \,. \tag{5.156}$$

If we compare Eqs. (5.156) and (5.127), we find $x = pd$ and $y = qd$. Thus,

$$q < 1 \tag{5.157}$$

in agreement with experiment.

The Kadanoff view of scaling allows us to introduce two new critical exponents which are associated with the spatial correlations of spin fluctuations in the system. The block correlation function is defined

$$C(r_{\mathrm{L}}, \varepsilon_{\mathrm{L}}) = \langle S_{\mathrm{I}} S_{\mathrm{J}}\rangle - \langle S_{\mathrm{I}}\rangle\langle S_{\mathrm{J}}\rangle \,, \tag{5.158}$$

where r_{L} is the distance between blocks I and J in units of La. We can write Eq. (5.158) as

$$\begin{aligned} C(r_{\mathrm{L}}, \varepsilon_{\mathrm{L}}) &= Z^{-2}[\langle S'_{\mathrm{I}} S'_{\mathrm{J}}\rangle - \langle S'_{\mathrm{I}}\rangle\langle S'_{\mathrm{J}}\rangle] && (5.159)\\ &= Z^{-2}\sum_{i\in\mathrm{I}}\sum_{j\in\mathrm{J}}[\langle S_i S_j\rangle - \langle S_i\rangle\langle S_j\rangle] && (5.160)\\ &= Z^{-2}(L^d)^2[\langle S_i S_j\rangle - \langle S_i\rangle\langle S_j\rangle] = Z^{-2}(L^d)^2 C(r, \varepsilon) \,, && (5.161)\end{aligned}$$

where r is the distance between sites i and j on different blocks. The distances r_{L} and r are related by the expression

$$r_{\mathrm{L}} = L^{-1} r \,, \tag{5.162}$$

and we write

$$C(L^{-1} r, \varepsilon L^{x}) = L^{2(d-y)} C(r, \varepsilon) \,. \tag{5.163}$$

If we choose $L = r/a$, the correlation function takes the form

$$C(r, \varepsilon) = \left(\frac{r}{a}\right)^{2(y-d)} C\left[a, \varepsilon \left(\frac{r}{a}\right)^{x}\right] . \tag{5.164}$$

We can now introduce two new exponents for the correlation function. We first define a critical exponent, ν, for the correlation length as

$$\xi \sim (T - T_{\mathrm{c}})^{-\nu} \,. \tag{5.165}$$

For mean field theories $\nu = 1/2$. From Eq. (5.112) we see that the correlation function away from the critical point depends on r and ε in the combination $r/\xi = r\varepsilon^{\nu}$. In Eq. (5.164) the correlation function depends on r and ε in the combination εr^{x}. Thus,

$$x = pd = \nu^{-1} \,. \tag{5.166}$$

At the critical point, $\varepsilon = 0$ and the correlation function varies as

$$C(r, 0) \sim (r)^{2(y-d)} \,. \tag{5.167}$$

In three dimensions, we expect the correlation function at the critical point to behave as

$$C(r, 0) \sim \left(\frac{1}{r}\right)^{1+\eta} \,, \tag{5.168}$$

where η is another new exponent. For mean field theories, $\eta = 0$. In d-dimensions, $C(r, 0)$ varies as

$$C(r, 0) = \left(\frac{1}{r}\right)^{(d-2+\eta)} \tag{5.169}$$

and we can make the identification

$$(d - 2 + \eta) = 2(d - y) = 2d(1 - q) \,. \tag{5.170}$$

Thus, the exponents for the correlation function can be written in terms of the exponents for the thermodynamic quantities we have already considered. From Eqs. (5.142) and (5.166) we find

$$\nu = \frac{2 - \alpha}{d} \tag{5.171}$$

and from Eqs. (5.146) and (5.170) we find,

$$\eta = 2 - d\left(\frac{\delta - 1}{\delta + 1}\right) = 2 - \frac{d\gamma}{2\beta + \gamma} \,. \tag{5.172}$$

Thus, Kadanoff scaling allows us to obtain two new critical exponents and new identities between all the exponents.

5.8
Microscopic Calculation of Critical Exponents

The Kadanoff picture of scaling was given firm mathematical foundation by Wilson [215], who developed a technique for computing the critical exponents microscopically. We shall outline Wilson's procedure for the case of spin systems whose spatial lattice structure is self-similar, and then we apply it to a self-similar triangular planar lattice (see also [13, 59, 128, 179, 216, 217]). The use of self-similar lattices provides the simplest way to illustrate the techniques used in renormalization theory. For most systems found in nature, the lattice structure is not self-similar and a different method can be used to obtain critical exponents using self-similar spin blocks based on wavelength components of the thermodynamic quantities. At the end of this section, we shall briefly describe the scaling approach based on wavelengths and then give results.

5.8.1
General Theory

Let us consider a system described by the partition function

$$Z(\boldsymbol{K}, N) = \sum_{\{S_i\}} \exp[-\mathcal{H}(\boldsymbol{K}, \{S_i\}, N)] \,. \tag{5.173}$$

The effective Hamiltonian, $\mathcal{H}(\boldsymbol{K}, \{S_i\}, N)$ (which includes temperature), can be written in the form

$$\mathcal{H}(\boldsymbol{K}, \{S_i\}, N) = K_0 + K_1 \sum_i S_i + K_2 \sum_{(i,j)}^{[1]} S_i S_j + K_3 \sum_{(i,j)}^{[2]} S_i S_j + K_4 \sum_{(i,j,k)}^{[1]} S_i S_j S_k + \cdots \,, \tag{5.174}$$

where $\boldsymbol{K}$ is an infinite-dimensional vector containing all coupling constants, and the summation $\sum^{[i]}$ means that only (ith) nearest neighbors are included. The coupling constants, K_i, contain the temperature. For the Ising model, $K_1 = -\beta B, K_2 = -\beta J$ where J is the strength of the coupling between spins, and $K_3 = K_4 = \cdots = 0$.

We can introduce blocks and let S_{I} denote the total spin of the Ith block and σ_{I} denote the spins internal to block I. Thus, we can write

$$Z(\boldsymbol{K}, N) = \sum_{\{S_{\mathrm{I}}, \sigma_{\mathrm{I}}\}} \exp[-\mathcal{H}(\boldsymbol{K}, \{S_{\mathrm{I}}, \sigma_{\mathrm{I}}\}, N)] \tag{5.175}$$

$$= \sum_{\{S_{\mathrm{I}}\}} \exp[-\mathcal{H}(\boldsymbol{K}_{\mathrm{L}}, \{S_{\mathrm{I}}\}, NL^{-d})] = Z(\boldsymbol{K}_{\mathrm{L}}, NL^{-d}) \,, \tag{5.176}$$

where we have summed over spins interior to each block. Since the new partition function has the same functional form as the old one, we can write the following expression for the free energy density per site:

$$g(\boldsymbol{K}) = \lim_{N\to\infty} \frac{1}{N} \ln Z(\boldsymbol{K}, N) = \lim_{N\to\infty} \frac{1}{N} \ln Z(\boldsymbol{K}_{\mathrm{L}}, NL^{-d}) = L^{-d} g(\boldsymbol{K}_{\mathrm{L}}) . \quad (5.177)$$

The coupling constant vectors, $\boldsymbol{K}$ and $\boldsymbol{K}_{\mathrm{L}}$, of the site spin and block spin systems, respectively, will be related by a transformation,

$$\boldsymbol{K}_{\mathrm{L}} = \boldsymbol{T}(\boldsymbol{K}) , \quad (5.178)$$

where $\boldsymbol{K}_{\mathrm{L}}$ will be a vector whose elements are nonlinear functions of the components of $\boldsymbol{K}$. Since our new Hamiltonian is identical in form to the old one, we can repeat the process and transform to larger blocks nL. After n transformations, we find

$$\boldsymbol{K}_{nL} = \boldsymbol{T}(\boldsymbol{K}_{(n-1)L}) . \quad (5.179)$$

If the system is not critical, there will be a finite correlation range. Thus, when we transform to larger blocks the effective correlation range appears to shrink and we move away from the critical point. However, when the system is critical, the correlation range is infinite and we reach a fixed point of the transformation. At the fixed point, the transformation $\boldsymbol{T}$ can no longer change the vector $\boldsymbol{K}$. Thus, the critical point occurs for values of the coupling constant vectors, $\boldsymbol{K}^*$, which satisfy the condition

$$\boldsymbol{K}^* = \boldsymbol{T}(\boldsymbol{K}^*) . \quad (5.180)$$

The sequence of transformations $\boldsymbol{T}$ is called the renormalization group (although $\boldsymbol{T}$ only has properties of a semigroup).

It is useful to illustrate the behavior of $\boldsymbol{K}$ for the case of a two-dimensional vector, $\boldsymbol{K} = (K_1, K_2)$. Equation (5.179) can be thought to describe the motion of $\boldsymbol{K}$ in $\boldsymbol{K}$ space (the space of components of $\boldsymbol{K}$) as we change block size. To locate a critical point in $\boldsymbol{K}$ space, we must locate the fixed points of Eq. (5.179). Let us assume that a fixed point of the transformation $\boldsymbol{K}_{\mathrm{L}} = \boldsymbol{T}(\boldsymbol{K})$ occurs at $\boldsymbol{K}^* = (K_1^*, K_2^*)$. We will want to know how the vector $\boldsymbol{K}$ moves in the neighborhood of the point $\boldsymbol{K}^*$. We must linearize Eq. (5.179) about $\boldsymbol{K}^*$. We will let $\delta\boldsymbol{K}_{\mathrm{L}} = (\boldsymbol{K}_{\mathrm{L}} - \boldsymbol{K}^*)$ and $\delta\boldsymbol{K} = (\boldsymbol{K} - \boldsymbol{K}^*)$. Then for small $\delta\boldsymbol{K}_{\mathrm{L}}$ and $\delta\boldsymbol{K}$ we get a linearized transformation

$$\delta\boldsymbol{K}_{\mathrm{L}} = \overline{\boldsymbol{A}} \cdot \delta\boldsymbol{K} , \quad (5.181)$$

where

$$\overline{\boldsymbol{A}} = \begin{pmatrix} \dfrac{\partial K_{1L}}{\partial K_1} & \dfrac{\partial K_{1L}}{\partial K_2} \\ \dfrac{\partial K_{2L}}{\partial K_1} & \dfrac{\partial K_{2L}}{\partial K_2} \end{pmatrix}_{(K_1^*, K_2^*)} . \quad (5.182)$$

We next find the eigenvalues and eigenvectors of the matrix $\overline{\boldsymbol{A}}$. Since $\overline{\boldsymbol{A}}$, in general, will be nonsymmetric, its left and right eigenvectors will be different. The right eigenvectors can be mapped

$$\delta \boldsymbol{u}_{\mathrm{L}} = \overline{\overline{\Lambda}}\, \delta \boldsymbol{u} \,, \tag{5.183}$$

where $\overline{\overline{\Lambda}}$ (the matrix of eigenvalues) and $\delta \boldsymbol{u}$ (the right eigenvector) can be written

$$\overline{\Lambda} = \begin{pmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{pmatrix} \quad \text{and} \quad \delta \boldsymbol{u} = \begin{pmatrix} \delta u_1 \\ \delta u_2 \end{pmatrix} , \tag{5.184}$$

respectively.

The eigenvalues λ_1 and λ_2 of the matrix $\overline{\boldsymbol{A}}$ determine the behavior of trajectories in the neighborhood of the fixed point. In Figure 5.7b, we have drawn the case of a hyperbolic fixed point and its eigencurves. Points along the eigencurves move as

$$\delta u_{nL,1} = (\lambda_1)^n \delta u_1 \ , \tag{5.185}$$

$$\delta u_{nL,2} = (\lambda_2)^n \delta u_2 \ . \tag{5.186}$$

Thus, for $\lambda > 1$ the point moves away from the fixed point under the transformation, and for $\lambda < 1$ it moves toward the fixed point. The dashed lines represent the trajectories of points which do not lie on the eigencurves. For a hyperbolic fixed point, they will always move away from the fixed point after many transformations. All systems with vectors $\boldsymbol{K}$ lying on an eigencurve with eigenvalue $\lambda < 1$ are critical, since with enough transformations they will come arbitrarily close to the fixed point. Such systems are said to exhibit "universality." The behavior of a point along an eigencurve with $\lambda > 1$ is reminiscent of the actual behavior of noncritical systems. As we increase the block size, we move away from the critical point. Thus, an eigenvalue $\lambda > 1$ is called relevant and its eigenvector is identified as one of the physical quantities (ε or B, for example) which measure the distance of the system from the critical point.

In general, we write the singular part of the free energy density in terms of the eigenvectors δu_i and eigenvalues λ_i as follows:

$$g_{\mathrm{s}}(\delta u_1, \delta u_2, \delta u_3, \ldots) = L^{-d} g_{\mathrm{s}}(\lambda_1 \delta u_1, \lambda_2 \delta u_2, \lambda_3 \delta u_3, \ldots) \tag{5.187}$$

(cf. Eq. (5.177)). This looks very much like Widom scaling. Indeed, for the case of an Ising system for which there are two relevant physical parameters which measure the distance of the system from the critical point, we expect that two of the eigenvalues will be relevant, let us say $\lambda_1 > 1$ and $\lambda_2 > 1$. If we compare Eq. (5.187) with Widom scaling of the Ising model in Eq. (5.127), we can make the identification $\delta u_1 = \varepsilon$ and $\delta u_2 = B$. Thus, $\lambda = L^d$ (Kadanoff scaling),

$$\lambda_1 = (L^d)^p \Rightarrow p = \frac{\ln \lambda_1}{d \ln L} \quad \text{and} \quad \lambda_2 = (L^d)^q \Rightarrow q = \frac{\ln \lambda_2}{d \ln L} \ . \tag{5.188}$$

If we now use Eqs. (5.145) and (5.146), we have expressed the critical exponents in terms of the relevant eigenvalues.

5.8.2
Application to Triangular Lattice

Let us now compute the critical exponents for 3-spin blocks on the triangular planar lattice for the two-dimensional nearest-neighbor Ising model (see Figure 5.8a) [151]. We will retain terms to lowest order in $\langle V\rangle$. The Hamiltonian can be written

$$H = -K\sum_{ij} s_i s_j - B\sum_i s_i \,. \tag{5.189}$$

We assign to a single block (block I in Figure 5.8b) a spin given by $S_\mathrm{I} = \mathrm{sign}(s_1^\mathrm{I} + s_2^\mathrm{I} + s_3^\mathrm{I})$. Therefore, $S_\mathrm{I} = +1$ for the following configurations:

$$(\alpha = 1; \downarrow\uparrow\uparrow)(\alpha = 2; \uparrow\downarrow\uparrow)(\alpha = 3; \uparrow\uparrow\downarrow)(\alpha = 4; \uparrow\uparrow\uparrow)\,. \tag{5.190}$$

The internal spin degrees of freedom are defined, $\sigma_\mathrm{I}^\alpha = |s_1^\mathrm{I} + s_2^\mathrm{I} + s_3^\mathrm{I}|_\alpha$. For configurations defined above we have: $\sigma_\mathrm{I}^1 = \sigma_\mathrm{I}^2 = \sigma_\mathrm{I}^3 = 1$, and $\sigma_\mathrm{I}^4 = 3$.

The partition function can be written

$$Z(K_\mathrm{L}, N) = \sum_{\{S_\mathrm{I}\}} \exp[-H(\boldsymbol{K}_\mathrm{L}, \{S_\mathrm{I}\})] = \sum_{\{S_\mathrm{I}\}}\sum_{\{\sigma_\mathrm{I}\}} \exp[-H(\boldsymbol{K}, \{S_\mathrm{I}, \sigma_\mathrm{I}\})]\,. \tag{5.191}$$

Now define

$$H(\boldsymbol{K}, \{S_\mathrm{I}, \sigma_\mathrm{I}\}) = H_0(\boldsymbol{K}, \{S_\mathrm{I}, \sigma_\mathrm{I}\}) + V(\boldsymbol{K}, \{S_\mathrm{I}, \sigma_\mathrm{I}\})\,, \tag{5.192}$$

where

$$H_0(\boldsymbol{K}, \{S_\mathrm{I}, \sigma_\mathrm{I}\}) = -K\sum_\mathrm{I}\sum_{i\in\mathrm{I}}\sum_{j\in\mathrm{I}} s_i s_j \tag{5.193}$$

and

$$V(K, \{S_\mathrm{I}, \sigma_\mathrm{I}\}) = -K\sum_{I\neq J}\sum_{i\in\mathrm{I}}\sum_{j\in J} s_i s_j - B\sum_\mathrm{I}\sum_{i\in\mathrm{I}} s_i\,. \tag{5.194}$$

We next define the expectation value

$$\langle A(\{S_\mathrm{I}\})\rangle = \frac{\sum_{\sigma_\mathrm{I}} A(\{S_\mathrm{I}, \sigma_\mathrm{I}\}) \exp[-H_0(\boldsymbol{K}, \{S_\mathrm{I}, \sigma_\mathrm{I}\})]}{\sum_{\sigma_\mathrm{I}} \exp[-H_0(\boldsymbol{K}, \{S_\mathrm{I}, \sigma_\mathrm{I}\})]}\,. \tag{5.195}$$

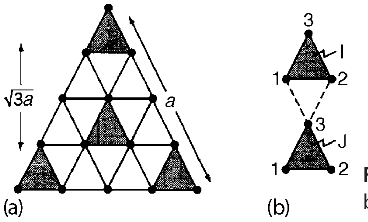

Figure 5.8 (a) The planar triangle lattice. (b) Coupling between neighboring blocks.

Note that

$$\sum_{S_{\mathrm{I}},\sigma_{\mathrm{I}}} \mathrm{e}^{-(H_0+V)} = \sum_{S_{\mathrm{I}}} \left[\left(\sum_{\sigma_{\mathrm{I}}} \mathrm{e}^{-H_0} \right) \sum_{\sigma_{\mathrm{I}}} \frac{\mathrm{e}^{-H_0}}{\left(\sum_{\sigma_{\mathrm{I}}} \mathrm{e}^{-H_0} \right)} \mathrm{e}^{-V} \right] . \tag{5.196}$$

If we now perform the summation over σ_{I} in the left-hand term, we can equate arguments under the summation $\sum_{S_{\mathrm{I}}}$ and write

$$\exp[-H(\boldsymbol{K}_{\mathrm{L}}, \{S_{\mathrm{I}}\})] = \left(\sum_{\sigma_{\mathrm{I}}} \exp[-H_0(\boldsymbol{K}, \{S_{\mathrm{I}}, \sigma_{\mathrm{I}}\})] \right) \langle \mathrm{e}^{-V} \rangle \tag{5.197}$$

$$\approx \left(\sum_{\sigma_{\mathrm{I}}} \mathrm{e}^{-H_0} \right) \left(\mathrm{e}^{\langle V \rangle + \frac{1}{2}[\langle V^2 \rangle - \langle V \rangle^2]} + \cdots \right) , \tag{5.198}$$

where we have expanded $\langle \mathrm{e}^{-V} \rangle$ in a cumulant expansion (see Appendix A). We can perform the summations in the unperturbed part to get

$$[Z_0(\boldsymbol{K})]^M = \sum_{\sigma_{\mathrm{I}}} \exp[-H_0(\boldsymbol{K}, \{S_{\mathrm{I}}, \sigma_{\mathrm{I}}\})] , \tag{5.199}$$

where M is the number of blocks and $Z_0(\boldsymbol{K})$ is the partition function of a single block and can be computed explicitly to obtain

$$Z_0(\boldsymbol{K}) = \sum_{\sigma_{\mathrm{I}}} \exp\left[K \left(s_1^{\mathrm{I}} s_2^{\mathrm{I}} + s_1^{\mathrm{I}} s_3^{\mathrm{I}} + s_2^{\mathrm{I}} s_3^{\mathrm{I}} \right) \right] = \mathrm{e}^{3K} + 3\mathrm{e}^{-K} , \tag{5.200}$$

for $S_{\mathrm{I}} = +1$ and $S_{\mathrm{I}} = -1$. The interaction is $V_{\mathrm{IJ}} = -K(s_1^{\mathrm{I}} s_3^{\mathrm{J}} + s_2^{\mathrm{I}} s_3^{\mathrm{J}})$ (see Figure 5.8). The average value of a single spin index is

$$\langle s_3^{\mathrm{J}} \rangle = Z_0(K)^{-1} \sum_{\sigma_{\mathrm{I}}} s_3^{\mathrm{J}} \exp\left[K \left(s_1^{\mathrm{J}} s_2^{\mathrm{J}} + s_2^{\mathrm{J}} s_3^{\mathrm{J}} + s_3^{\mathrm{J}} s_1^{\mathrm{J}} \right) \right]$$

$$= Z_0(K)^{-1} S_{\mathrm{J}} (\mathrm{e}^{3K} + \mathrm{e}^{-K}) . \tag{5.201}$$

In order to obtain the result in Eq. (5.201), construct diagrams of the eight spin configurations of block I and separate them according to their total spin S_{I}. When configurations with the same total spin S_{I} are added, several terms cancel.

If we take the logarithm of Eq. (5.197), we obtain

$$\begin{aligned} H(K_{\mathrm{L}}, B_{\mathrm{L}}\{S_{\mathrm{I}}\}) &= M \ln(Z_0(K)) + \langle V \rangle + \frac{1}{2}[\langle V^2 \rangle - \langle V^2 \rangle] \cdots \\ &= M \ln(Z_0(K)) - 2K \sum_{I \neq J} \left(\frac{\mathrm{e}^{3K} + \mathrm{e}^{-K}}{\mathrm{e}^{3K} + 3\mathrm{e}^{-K}} \right)^2 S_{\mathrm{I}} S_{\mathrm{J}} \\ &\quad - 3 \sum_{\mathrm{I}} \left(\frac{\mathrm{e}^{3K} + \mathrm{e}^{-K}}{\mathrm{e}^{3K} + 3\mathrm{e}^{-K}} \right) S_{\mathrm{I}} B + \cdots , \end{aligned} \tag{5.202}$$

where we have retained terms up to $\langle V \rangle$. Thus, the Hamiltonian for the blocks has been written in the form

$$H(K_{\rm L}, B_{\rm L}, \{S_{\rm I}\}) = -K_{\rm L} \sum_{\rm IJ} S_{\rm I} S_{\rm J} - B_{\rm L} \sum_{\rm I} S_{\rm I} \,. \tag{5.203}$$

If we now compare Eqs. (5.202) and (5.203), we find

$$K_{\rm L} = 2K \left(\frac{{\rm e}^{3K} + {\rm e}^{-K}}{{\rm e}^{3K} + 3{\rm e}^{-K}} \right)^2 \tag{5.204}$$

and

$$B_{\rm L} = 3B \left(\frac{{\rm e}^{3K} + {\rm e}^{-K}}{{\rm e}^{3K} + 3{\rm e}^{-K}} \right) . \tag{5.205}$$

Fixed points occur for ($K^* = 0$, $B^* = 0$) and for ($K^* = K_{\rm f}$, $B^* = 0$), where $K_{\rm f}$ is the solution to the equation

$$\frac{1}{2} = \left(\frac{{\rm e}^{3K_{\rm f}} + {\rm e}^{-K_{\rm f}}}{{\rm e}^{3K_{\rm f}} + 3{\rm e}^{-K_{\rm f}}} \right)^2 . \tag{5.206}$$

Equation (5.206) has eight solutions, only one of which is real and positive. This solution gives $K_{\rm f} = \frac{1}{4} \ln(1 + 2\sqrt{2}) \approx 0.3356$. Thus, the fixed points occur for ($K^* = 0$, $B^* = 0$) and for ($K^* = 0.3356$, $B^* = 0$). The ($K^* = 0$, $B^* = 0$) fixed point corresponds to infinite temperature since K is proportional to $\beta = (k_{\rm B} T)^{-1}$.

Let us next consider the fixed point, ($K^* = 0.3356$, $B^* = 0$). If we let $K = 0.3356 + \delta K$ and $B = \delta B$ and linearize Eqs. (5.204) and (5.205) in δK and δB, we obtain

$$\delta K_{\rm L} = 1.623 \delta K \quad \text{and} \quad \delta B_{\rm L} = 2.121 \delta B \,, \tag{5.207}$$

so the eigenvalues are $\lambda_K = 1.623$ and $\lambda_B = 2.121$. The Widom scaling exponents become

$$p = \frac{\ln(\lambda_K)}{2\ln(\sqrt{3})} = 0.441 \quad \text{and} \quad q = \frac{\ln(\lambda_B)}{2\ln(\sqrt{3})} = 0.684 \,. \tag{5.208}$$

The critical exponents are

$$\begin{aligned} \alpha &= 2 - \frac{1}{p} = -0.27 \,, \qquad \beta = \frac{1-q}{p} = 0.72 \,, \\ \gamma &= \frac{2q-1}{p} = 0.83 \,, \quad \text{and} \quad \delta = \frac{q}{1-q} = 2.2 \,. \end{aligned} \tag{5.209}$$

The exact solution of this two-dimensional Ising model yields $(\lambda_K)_{\rm exact} = 1.73$ and $(\lambda_B)_{\rm exact} = 2.80$. Thus, we are close for λ_K but our calculation of λ_B is not very good. It is possible to carry the calculation to higher orders in $\langle V^n \rangle$. In so doing, more elements of the vector, $\boldsymbol{K}$, are introduced and better agreement with the exact results is obtained.

5.8.3
The S^4 Model

Most spin lattices do not have spatial self-similar structure so a more general method of scaling was developed that focuses on wavelength components of spatial correlation functions. A widely used model for wavelength-based scaling is the S^4-model. We derive the S^4-model here, and we give results of the scaling process, but we do not explicitly discuss how the scaling process unfolds. More discussion can be found in [128, 179, 183, 216].

Let us consider a d-dimensional cubic Ising lattice with N lattice sites. The partition function can be written in the form

$$Z(K) = \sum_{\{s_n\}} \exp\left(K \sum_{\boldsymbol{n}} \sum_{\boldsymbol{e}} S_{\boldsymbol{n}} S_{\boldsymbol{n}+\boldsymbol{e}} \right) , \tag{5.210}$$

where $K = \beta J$ is the effective interaction and $\boldsymbol{e}$ is the vector indicating the positions of various nearest neighbors of the site, $\boldsymbol{n}$. The summation is over all possible configurations of the lattice. We can change the summation to an integration if we introduce a weighting factor $W(S_{\boldsymbol{n}}) = \delta(S_{\boldsymbol{n}}^2 - 1)$. Then Eq. (5.210) can be written

$$Z(K) = \left[\prod_{\boldsymbol{m}} \int_{-\infty}^{\infty} \mathrm{d}S_{\boldsymbol{m}} \, W(S_{\boldsymbol{m}}) \right] \exp\left(K \sum_{\boldsymbol{n}} \sum_{\boldsymbol{e}} S_{\boldsymbol{n}} S_{\boldsymbol{n}+\boldsymbol{e}} \right) , \tag{5.211}$$

where the product is taken over all lattice sites. The partition function is now in a form that allows some generalization.

Let us choose the weighting factor in a slightly different form,

$$W(S_{\boldsymbol{n}}) = \mathrm{e}^{-(b/2)S_{\boldsymbol{n}}^2 - uS_{\boldsymbol{n}}^4} . \tag{5.212}$$

Note that if we choose $b = -4u$, then $W(S_{\boldsymbol{n}}) = \mathrm{e}^{-u(S_{\boldsymbol{n}}^2-1)^2}$, which is a softened version of the exact weighting function, $W(S_{\boldsymbol{n}}) = \delta(S_{\boldsymbol{n}}^2 - 1)$. With the weighting factor in Eq. (5.212), the partition function takes the form

$$Z(K) = \left[\prod_{\boldsymbol{m}} \int_{-\infty}^{\infty} \mathrm{d}S_{\boldsymbol{m}} \right] \exp\left[\mathcal{H}\right] , \tag{5.213}$$

where the effective Hamiltonian $\mathcal{H}$ can be written

$$\begin{aligned} \mathcal{H} &= K \sum_{\boldsymbol{n}} \sum_{\boldsymbol{e}} S_{\boldsymbol{n}} S_{\boldsymbol{n}+\boldsymbol{e}} - \sum_{\boldsymbol{n}} \frac{b}{2} S_{\boldsymbol{n}}^2 + u S_{\boldsymbol{n}}^4 \\ &= \frac{1}{2} K \sum_{\boldsymbol{n}} \left[{\sum_{\boldsymbol{e}}}' (S_{\boldsymbol{n}+\boldsymbol{e}} - S_{\boldsymbol{n}})^2 + \left(\frac{b}{K} - 2d \right) S_{\boldsymbol{n}}^2 \right] + u \sum_{\boldsymbol{n}} S_{\boldsymbol{n}}^4 \end{aligned} \tag{5.214}$$

and the sum $\sum_{\boldsymbol{e}}'$ is restricted to positive values of $\boldsymbol{e}$. Note that $\sum_{\boldsymbol{e}}' = d$ for a cubic lattice.

We next rewrite the effective Hamiltonian in terms of wavelength components of the spin field $S_{\boldsymbol{n}}$, where $S_{\boldsymbol{n}}$ denotes the spin at point $\boldsymbol{x} = \boldsymbol{n}a$ on the lattice (we will now assume an infinitely large cubic lattice with spacing a between lattice sites). The Fourier amplitude $S(\boldsymbol{k})$ of the spin field is defined

$$S(\boldsymbol{k}) = a^d \sum_{\boldsymbol{n}} S_{\boldsymbol{n}} \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{n}a} \,. \tag{5.215}$$

The components k_i ($i = 1, \dots, d$) of the wavevectors $\boldsymbol{k}$ can only take on values in the range $-\pi/a < k_i < \pi/a$ since wavelengths smaller than the lattice spacing are not allowed. It is useful to note the identities

$$\left(\frac{a}{2\pi}\right)^d \int_{-\pi/a}^{\pi/a} \mathrm{d}k_1 \dots \int_{-\pi/a}^{\pi/a} \mathrm{d}k_d \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{n}a} = \delta_{\boldsymbol{n},\boldsymbol{0}} \quad \text{and} \quad a^d \sum_{\boldsymbol{n}} \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{n}a} = \delta(\boldsymbol{k}) \,. \tag{5.216}$$

When written in terms of the Fourier amplitudes, the effective Hamiltonian $\mathcal{H}$ takes the form

$$\begin{aligned}\mathcal{H} = {} & \frac{K}{2}\left(\frac{1}{2\pi a}\right)^d \int \mathrm{d}\boldsymbol{k} {\sum_{\boldsymbol{e}}}' |S(\boldsymbol{k})|^2 |\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{n}a} - 1|^2 \\ & + \frac{K}{2}\left(\frac{b}{K} - 2d\right)\left(\frac{1}{2\pi a}\right)^d \int \mathrm{d}\boldsymbol{k} |S(\boldsymbol{k})|^2 \\ & + \frac{u}{a^d}\left(\frac{1}{2\pi}\right)^{4d} \int \mathrm{d}\boldsymbol{k}_1 \int \mathrm{d}\boldsymbol{k}_2 \int \mathrm{d}\boldsymbol{k}_3 \int \mathrm{d}\boldsymbol{k}_4 \\ & \times S(\boldsymbol{k}_1)S(\boldsymbol{k}_2)S(\boldsymbol{k}_3)S(\boldsymbol{k}_4)\delta(\boldsymbol{k}_1 + \boldsymbol{k}_2 + \boldsymbol{k}_3 + \boldsymbol{k}_4) \,. \end{aligned} \tag{5.217}$$

Near the critical point spin fluctuations begin to exhibit long-range order and only long wavelength (small wavevector) contributions to $\mathcal{H}$ are important. With this in mind, the expression for $\mathcal{H}$ can be simplified to some extent. Note that $\sum_{\boldsymbol{e}}' |\boldsymbol{k} \cdot \boldsymbol{e}|^2 = k^2$ so that $|\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{n}a} - 1|^2 \approx k^2 a^2$ for small k. Then the effective Hamiltonian can be written in the form

$$\begin{aligned}\mathcal{H}(r, u', \{S'\}) = {} & \frac{1}{2}\left(\frac{1}{2\pi}\right)^d \int \mathrm{d}\boldsymbol{k}(r + k^2)|S'(\boldsymbol{k})|^2 \\ & + u'\left(\frac{1}{2\pi}\right)^{4d} \int \mathrm{d}\boldsymbol{k}_1 \int \mathrm{d}\boldsymbol{k}_2 \int \mathrm{d}\boldsymbol{k}_3 \int \mathrm{d}\boldsymbol{k}_4 \\ & \times S'(\boldsymbol{k}_1)S'(\boldsymbol{k}_2)S'(\boldsymbol{k}_3)S'(\boldsymbol{k}_4)\delta(\boldsymbol{k}_1 + \boldsymbol{k}_2 + \boldsymbol{k}_3 + \boldsymbol{k}_4) \,, \end{aligned} \tag{5.218}$$

where $S'(\boldsymbol{k}) = S(\boldsymbol{k})(Ka^{2-d})^{1/2}$, $r = (b/K - 2d)a^{-2}$ and $u' = (Ka^{2-d})^{-2}$. The partition function takes the form

$$Z(r, u', \{S'\}) = \int \mathrm{D}S' \mathrm{e}^{\mathcal{H}(r,u',\{S'\})} \,, \tag{5.219}$$

where $\mathrm{D}S'$ denotes a function integral over all values of spin variables $S'(\boldsymbol{k})$.

Equations (5.218) and (5.219) are called the S^4 model because of the quartic dependence on the spin variables. They form the starting point for the renormalization theory based on the S^4 model. When $u' = 0$, the model is called the Gaussian model. The renormalization procedure is the same as that used in previous sections for the self-similar lattices, except that now the block Hamiltonians are formed in terms of their dependence on intervals of values of wavevectors k_i. A renormalization map is constructed for the variables r and u'.

In Table 5.1, we compare results for values of the critical exponents obtained from experiment, from mean field theory, the exact Ising model (with results obtained numerically), and the S^4 model. For $d = 3$ the S^4 model gives very good agreement with experiment and with exact Ising values of the exponents. For $d = 4$ (not listed in Table 5.1), mean field theories and the S^4 model give the same results ($d = 4$ is unphysical but mathematically interesting).

5.9
Problems

Problem 5.1 The magnetization operator for the ith atom in a lattice containing N atoms is $\hat{M}_i = \mu \hat{S}_{i,z}$, where μ is the magnetic moment and $\hat{S}_{i,z}$ is the spin of the ith atom. Neglecting interactions between the particles, the Hamiltonian (energy) of the lattice is $\hat{H} = -\hat{M}_T B$, where B is an applied magnetic field and $\hat{M}_T = \sum_{i=1}^{N} \hat{M}_i$ is the total magnetization of the lattice. Derive an expression for the variance $\langle M_T^2 \rangle_{\text{eq}}$ in terms of a thermodynamic response function. Which response function is it?

Problem 5.2 Use the canonical ensemble to compute the entropy, internal energy, and heat capacity of the Einstein solid.

Problem 5.3 Two distinguishable three-level atoms on a lattice can each have energies $0, \epsilon, 2\epsilon$. Thus, the two-atom system can exist in nine different states with energies $E_j (j = 1, \dots, 9)$, where $E_1 = 0$, $E_2 = E_3 = \epsilon$, and $E_4 = E_5 = E_6 = 2\epsilon$, $E_7 = E_8 = 3\epsilon$ and $E_9 = 4\epsilon$. Find the probabilities f_j of the nine configurations

Table 5.1 Values of critical exponents from experiment and various theories.

Critical Exponent	Experimental Value	Exact Ising ($d = 3$)	Mean Field Theory	S^4 Model ($d = 3$)
α	0–0.2	0.12	0	0.17
β	0.3–0.4	0.31	1/2	0.33
δ	4–5	5.2	3	4
γ	1.2–1.4	1.25	1	1.17
ν	0.6–0.7	0.64	1/2	0.58
η	0.1	0.056	0	0

($j = 1, \dots, 9$), assuming that they extremize the entropy $S = -k_B \sum_{j=1}^{9} f_j \ln f_j$ subject to the conditions that the probability be normalized $\sum_{j=1}^{9} f_j = 1$ and the average energy be $\sum_{j=1}^{9} E_j f_j = \frac{3}{2}\epsilon$.

Problem 5.4 A system has three distinguishable molecules at rest, each with a quantized magnetic moment which can have z-components $+1/2\mu$ or $-1/2\mu$. Find an expression for the distribution function, f_i (i denotes the ith configuration), which maximizes entropy subject to the conditions $\sum_i f_i = 1$ and $\sum_i M_{i,z} f_i = \gamma\mu$, where $M_{i,z}$ is the magnetic moment of the system in the ith configuration. For the case $\gamma = 1/2$, compute the entropy and compute f_i.

Problem 5.5 What is the partition function for a van der Waals gas with N particles? Note that the result is phenomenological and might involve some guessing. It is useful to compare it to the partition function for an ideal gas. Remember that the particles are indistinguishable, so when using the partition function one must insert a counting factor. Use this partition function to compute the internal energy, $U(N, T, V)$, the pressure, $P(N, T, V)$, and the entropy, $S(U, V, N)$.

Problem 5.6 Consider a solid surface to be a two-dimensional lattice with N_s sites. Assume that N_a atoms ($N_a \ll N_s$) are adsorbed on the surface, so that each lattice site has either zero or one adsorbed atom. An adsorbed atom has energy $E = -\varepsilon$, where $\varepsilon > 0$. Assume the atoms on the surface do not interact with one another. If the surface is at temperature T, compute the chemical potential of the adsorbed atoms as a function of T, ε, and N_a/N_s (use the canonical ensemble).

Problem 5.7 Consider a two-dimensional lattice in the x–y plane with sides of length L_x and L_y which contains N atoms (N very large) coupled by nearest-neighbor harmonic forces. (a) Compute the Debye frequency for this lattice. (b) In the limit $T \to 0$, what is the heat capacity?

Problem 5.8 The CO molecule has a rotational temperature $\theta = \hbar^2/(2Ik_B) = 2.8\,\mathrm{K}$, where I is the moment of inertia of the CO molecule. The rotational partition function for one molecule is $Z_1^{\text{rot}} = \sum_{l=0}^{\infty}(2l+1)\mathrm{e}^{-l(l+1)\theta/T}$. (a) If one mole of CO molecules could freely rotate at temperature $T = 3.2\,\mathrm{K}$, what is their total rotational entropy? (b) What is the rotational entropy of one mole of CO molecules at temperature $T = 320\,\mathrm{K}$? (*Hint*: At high temperature, where many angular momenta contribute, $Z_1^{\text{rot}} \approx \int_0^{\infty} \mathrm{d}l(2l+1)\mathrm{e}^{-l(l+1)\theta/T}$.) (c) What is the translational entropy of one mole of CO molecules in a box of volume $V = 1.0\,\mathrm{m}^3$ at temperature $T = 320\,\mathrm{K}$?

Problem 5.9 The ClF molecule has a rotational temperature $\theta_R = \hbar^2/(2Ik_B) = 0.737\,\mathrm{K}$, where I is the moment of inertia of the molecule. A gas consisting of one mole of ClF molecules is contained in a box of volume $V = 10^{-3}\,\mathrm{m}^3$ and is cooled to a temperature of $T = 2\,\mathrm{K}$ (assume the molecules remain in the gas phase under these conditions). (a) At $T = 2\,\mathrm{K}$, what fraction of the internal energy of the gas is associated with the rotational degrees of freedom? (b) At $T = 250\,\mathrm{K}$, what fraction of the internal energy of the gas is associated with the rotational degrees of freedom?

Problem 5.10 The vibrational frequency of the I_2 molecule is $f = 6.42 \times 10^{12}\, s^{-1}$. The vibrational temperature is $\theta^{\mathrm{vib}}_{I_2} = \frac{hf}{k_B} = 308\,\mathrm{K}$. The rotational temperature is $\theta^{\mathrm{rot}}_{I_2} = 0.0538\,\mathrm{K}$. Consider a gas of N I_2 molecules at temperature $T = 300\,\mathrm{K}$. (a) What fraction of the molecules is in the vibrational ground state and what fraction have one vibrational quantum of energy? (b) What percentage of the total internal energy of the gas is: (1) translational?; (2) vibrational?; (3) rotational?.

Problem 5.11 A dilute gas, composed of a mixture of N_{I} iodine atoms I and N_{I_2} iodine molecules I_2, is confined to a box of volume $V = 1.0\,\mathrm{m}^3$ at temperature $T = 300\,\mathrm{K}$. The rotational temperature of the iodine molecules is $\theta_{\mathrm{rot}} = 0.0537\,\mathrm{K}$ (for simplicity we neglect vibrational modes). (a) Compute the chemical potentials, μ_{I} and μ_{I_2}, of the iodine atoms and molecules, respectively. (b) The numbers of the iodine atoms and molecules can change via chemical reactions with one another. The condition for chemical equilibrium is $\mu_{\mathrm{I}_2} = 2\mu_{\mathrm{I}}$. Use this condition to find the ratio $N_{\mathrm{I}}^2/N_{\mathrm{I}_2}$ when the gas is in equilibrium. (c) Does the inclusion of the rotational degree of freedom increase or decrease the number of I_2 molecules at chemical equilibrium.

Problem 5.12 A cubic box (with infinitely hard walls) of volume $V = L^3$ contains an ideal gas of N rigid HCl molecules (assume that the effective distance between the H atom and the Cl atom is $d = 1.3\,\text{Å}$. (a) If $L = 1.0\,\mathrm{cm}$, what is the spacing between translational energy levels? (b) Write the partition function for this system (include both translation and rotational contributions). At what temperature do rotational degrees of freedom become important? (c) Write expressions for the Helmholtz free energy, the entropy, and the heat capacity of this system for temperatures where the rotational degrees of freedom make a significant contribution.

Problem 5.13 An ideal gas is composed of N "red" atoms of mass m, N "blue" atoms of mass m, and N "green" atoms of mass m. Atoms of the same color are indistinguishable. Atoms of different color are distinguishable. (a) Use the canonical ensemble to compute the entropy of this gas. (b) Compute the entropy of an ideal gas of $3N$ "red" atoms of mass m. Does it differ from that of the mixture? If so, by how much?

Problem 5.14 An ideal gas, in a box of volume V, consists of a mixture of N_{r} "red" and N_{g} "green" atoms, both with mass m. Red atoms are distinguishable from green atoms. The green atoms have an internal degree of freedom that allows the atom to exist in two energy states, $E_{\mathrm{g},1} = p^2/(2m)$ and $E_{\mathrm{g},2} = p^2/(2m) + \Delta$. The red atoms have no internal degrees of freedom. Compute the chemical potential of the "green" atoms.

Problem 5.15 Consider a one-dimensional lattice with N lattice sites and assume that the ith lattice site has spin $s_i = \pm 1$. The Hamiltonian describing this lattice is $H = -\varepsilon \sum_{i=1}^{N} s_i s_{i+1}$. Assume periodic boundary conditions, so $s_{N+1} \equiv s_1$. Compute the correlation function, $\langle s_1 s_2 \rangle$. How does it behave at very high temperature and at very low temperature?

Problem 5.16 In the mean field approximation to the Ising lattice, the order parameter, $\langle s \rangle$, satisfies the equation $\langle s \rangle = \tanh(\langle s \rangle T_c/T)$, where $T_c = \nu\varepsilon/2k_B$ with ε the strength of the coupling between lattice sites and ν the number of nearest neighbors. (a) Show that $\langle s \rangle$ has the following temperature dependence: (i) $\langle s \rangle \approx 1 - 2e^{-2T_c/T}$ if $T \sim 0$ K, and (ii) $\langle s \rangle \approx \sqrt{3(1 - T/T_c)}$ if $T \sim T_c$. (b) Compute the jump in the heat capacity at $T = T_c$. (c) Compute the magnetic susceptibility, $\chi_{T,N}(B = 0)$, in the neighborhood of $T = T_c$ for both $T > T_c$ and $T < T_c$. What is the critical exponent for both cases?

Problem 5.17 Consider a magnetic system whose free energy, near the critical point, scales as $\lambda^5 g(\epsilon, B) = g(\lambda^2\epsilon, \lambda^3 B)$. Compute (a) the degree of the coexistence curve, (b) the degree of the critical isotherm, (c) the critical exponent for the magnetic susceptibility, and (d) the critical exponent for the heat capacity. Do your results agree with values of the critical exponents found in experiments?

Problem 5.18 A one-dimensional lattice of spin-1/2 lattice sites can be decomposed into blocks of three spins each. Use renormalization theory to determine whether or not a phase transition can occur on this lattice. If a phase transition does occur, what are its critical exponents? Retain terms in the block Hamiltonian to order $\langle V \rangle$, where V is the coupling between blocks.

Problem 5.19 Find the critical exponents for five spin blocks on a square lattice for the two-dimensional nearest-neighbor Ising model. Retain terms to lowest order in $\langle V \rangle$, where V is the interaction energy between blocks (cf. Figure 5.9).

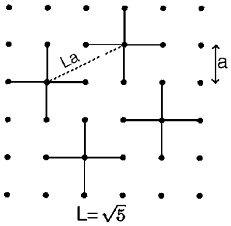

Figure 5.9 Problem 5.19.

Problem 5.20 The order-disorder phase transition on a two-dimensional triangular lattice can be analyzed in terms of a two-dimensional Ising model with seven spins as shown in Figure 5.10. In all calculations, only retain terms to lowest order in $\langle V \rangle$. Assume the nearest-neighbor spacing between lattice sites is a. (a) Compute Z_0. (b) Compute $\langle s_1 \rangle$ (the central spin in the block in Figure 5.10 and $\langle s_4 \rangle$ (an outer spin in the block shown in Figure 5.10). (c) Construct the renormalization map and find its relevant fixed point. (d) Linearize the renormalization map about its relevant fixed point and find its eigenvalues. (e) Compute the Widom scaling exponents p and q. (f) Compute the critical exponents $\alpha, \beta, \gamma, \delta$. (*Note*: Each block has $2^7 = 128$ spin configurations. Blocks with $S_\mathrm{I} = +1$ have 64 configurations. The various $S_\mathrm{I} = +1$ configurations can be grouped so that each group gives a term in Z_0. These groupings also make the derivation of $\langle s_1 \rangle$ and $\langle s_1 \rangle$ straightforward.)

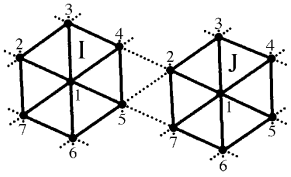

Figure 5.10 Problem 5.20.

6
Equilibrium Statistical Mechanics II – Grand Canonical Ensemble

6.1
Introduction

When a system is open to the surrounding environment, both the energy and particle number of the system can fluctuate. In that case, the system will be in equilibrium with the environment if the temperature and chemical potential (of each kind of particle) are the same in the system and the environment. The probability distribution and the thermodynamic properties of particles in open systems are given by the grand canonical ensemble, which we derive and discuss in this chapter.

The process of *adsorption* provides an important classical example of a thermodynamic process in an open system and is easily analyzed in the grand canonical ensemble. Adsorption occurs when a fluid mixture (gas or liquid) is in contact with a solid surface that can selectively bind (at multiple sites) one type of molecule in the fluid. For adsorption, the system consists of the binding sites and the fluid is the environment. We will use the grand canonical ensemble to derive adsorption isotherms.

The theory of interacting semiclassical fluids (composed of neutral particles) is also easily described in the grand canonical ensemble. For such systems, the interparticle potential has a hard core and a weak attractive region so perturbation expansions in terms of the potential are not convergent. For the case of dilute or moderately dense fluids, the only small parameter is the density and, therefore it is useful to express thermodynamic quantities in terms of density (virial) expansions. We shall use the grand canonical ensemble to derive microscopic expressions for the virial coefficients in the density expansion of the equation of state of interacting classical fluids. We shall apply these results to fluids whose particles interact via hard-core potentials, square-well potentials, and the Lennard-Jones 6–12 potential, and we will compare them with experiment.

The grand canonical ensemble is especially suitable for describing systems with broken gauge symmetry because particle number can fluctuate. We will use the grand canonical ensemble to compute the thermodynamic properties of ideal quantum gases, both Bose–Einstein and Fermi–Dirac. An ideal Bose–Einstein gas is composed of indistinguishable bosons. At very low temperatures, it can exhibit

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a phase transition (even though the particles do not interact) in which a macroscopic number of particles condense into the lowest energy state. For the case of interacting bosons, Bogoliubov mean field theory can be used to obtain equilibrium properties of the condensate at very low temperatures. An ideal Fermi–Dirac gas does not exhibit a phase transition because no two fermions can have the same set of quantum numbers (the Pauli exclusion principle). Therefore, at low temperature the fermions fill all the low energy states and even at $T = 0\,\mathrm{K}$ some particles can have a very high energy. If coulomb interactions are neglected, an ideal Fermi–Dirac gas of electrons provides a simple model that can explain both the paramagnetic and diamagnetic properties of many condensed matter systems.

If we allow an attraction between fermions, then they can form bound pairs that can condense in momentum space. This is what happens to electrons in a superconductor. In a superconducting solid, electrons interact with lattice phonons and with one another through a phonon-mediated interaction which is attractive in the neighborhood of the Fermi surface. The fermion pairs condense in momentum space and act coherently, thus giving rise to the unusual superconducting properties observed in such systems. We derive microscopic expressions for the energy gap and the heat capacity of such systems at the end of this chapter.

6.2
The Grand Canonical Ensemble

An open system can exchange both heat and matter with its surroundings, causing both energy and particle number to fluctuate. To obtain the equilibrium probability density in such a fluctuating environment, we use the method of Lagrange multipliers to extremize the Gibbs entropy subject to the following three constraints. We require that the normalization take the form

$$\mathrm{Tr}(\hat{\rho}) = 1\,. \tag{6.1}$$

We require that the average energy have a fixed value, $\langle E \rangle$, so that

$$\mathrm{Tr}(\hat{H}\hat{\rho}) = \langle E \rangle\,. \tag{6.2}$$

And finally, we require that the average particle number have a fixed value, $\langle N \rangle$, so that

$$\mathrm{Tr}(\hat{N}\hat{\rho}) = \langle N \rangle\,, \tag{6.3}$$

where $\hat{N}$ is the total particle number operator.

We can find the probability density operator, $\hat{\rho}$, that extremizes the Gibbs entropy subject to the constraints in Eqs. (6.1)–(6.3). The extremization condition is

$$\begin{aligned}&\delta[\mathrm{Tr}(\alpha_0\hat{\rho} + \alpha_E\hat{H}\hat{\rho} + \alpha_N\hat{N}\hat{\rho} - k_\mathrm{B}\hat{\rho}\ln\hat{\rho})]\\ &\quad = \mathrm{Tr}\{[(\alpha_0 - k_\mathrm{B})\hat{I} + \alpha_E\hat{H} + \alpha_N\hat{N} - k_\mathrm{B}\ln(\hat{\rho})]\delta\hat{\rho}\} = 0\,,\end{aligned} \tag{6.4}$$

where α_0, α_E, and α_N are Lagrange multipliers. Since $\delta\hat{\rho}$ is arbitrary, we have

$$(\alpha_0 - k_\mathrm{B})\hat{I} + \alpha_E \hat{H} + \alpha_N \hat{N} - k_\mathrm{B} \ln \hat{\rho} = 0 \,. \tag{6.5}$$

We can now use Eq. (6.5) and the three constraints, Eqs. (6.1)–(6.3) to determine the Lagrange multipliers. The normalization condition, Eq. (6.1), allows us to introduce the grand partition function. If we take the trace of Eq. (6.4), we can write

$$Z(\alpha_E, \alpha_N) \equiv \exp\left(\frac{\alpha_0}{k_\mathrm{B}} - 1\right) = \mathrm{Tr}\left[\exp\left(\frac{\alpha_E}{k_\mathrm{B}}\hat{H} + \frac{\alpha_N}{k_\mathrm{B}}\hat{N}\right)\right] , \tag{6.6}$$

which relates α_0 to α_E and α_N. To determine α_E and α_N, let us multiply Eq. (6.5) by $\hat{\rho}$ and take the trace. We find

$$-k_\mathrm{B} \ln[Z(\alpha_E, \alpha_N)] + \alpha_E \langle E\rangle + \alpha_N \langle N\rangle + S = 0 \,. \tag{6.7}$$

If we compare Eq. (6.7) to the fundamental equation for the grand potential, $\Omega = U - TS - \mu N$ (cf. Table 3.5), we can make the identifications, $\alpha_E = -1/T$ and $\alpha_N = \mu/T$, and

$$\Omega(T, \mu) = -k_\mathrm{B} T \ln Z_\mu(T) \,. \tag{6.8}$$

The *grand partition function* can now be written

$$Z_\mu(T) = \mathrm{e}^{-\beta\Omega(T,\mu)} = \mathrm{Tr}\left(\mathrm{e}^{-\beta(\hat{H}-\mu\hat{N})}\right) , \tag{6.9}$$

with $\beta = 1/k_\mathrm{B}T$, and the probability density operator can be written

$$\hat{\rho} = \mathrm{e}^{-\beta(\hat{H}-\mu\hat{N}-\Omega)} = \frac{\mathrm{e}^{-\beta(\hat{H}-\mu\hat{N})}}{\mathrm{Tr}\left(\mathrm{e}^{-\beta(\hat{H}-\mu\hat{N})}\right)} \,. \tag{6.10}$$

Equation (6.10) is the probability density operator for the *grand canonical ensemble.*

Although we have not written it explicitly, the grand potential will generally depend on a generalized displacement, X, whose form is determined by the mechanical properties of the system being considered. For a gas, $X = V$ is the volume and, for a magnetic system, $X = M$ is the magnetization. Once we know the grand partition function, we can compute the grand potential, and from it we can obtain all thermodynamic quantities. The entropy is given by $S = -(\partial\Omega/\partial T)_{X,\mu}$. The generalized force is given by $Y = (\partial\Omega/\partial X)_{T,\mu}$. The average particle number is given by $\langle N\rangle = -(\partial\Omega/\partial\mu)_{T,X}$.

6.2.1
Particle Number Fluctuations

In the grand canonical ensemble, the temperature T and chemical potential μ are fixed and the average energy $\langle E\rangle$ and average particle number $\langle N\rangle$ are fixed. However, because there can be a flow of energy and particles in and out of the system, it is important to determine the size of energy and particle number fluctuations. The derivation of the variance in energy fluctuations is similar to the derivation given in Section 5.2, so here we only derive the variance in particle number fluctuations. We first write the normalization condition in the form

$$\mathrm{Tr}\left(\mathrm{e}^{\beta[\Omega(T,\mu)-\hat{H}+\mu\hat{N}]}\right)=1\,. \tag{6.11}$$

If we differentiate Eq. (6.11) twice with respect to μ, we can obtain

$$\langle N^2\rangle-\langle N\rangle^2=-k_{\mathrm{B}}T\left(\frac{\partial^2\Omega}{\partial\mu^2}\right)_{T,X}=k_{\mathrm{B}}T\left(\frac{\partial\langle N\rangle}{\partial\mu}\right)_{T,X}\,. \tag{6.12}$$

Thus, the fractional deviation behaves as

$$\frac{\sqrt{\langle N^2\rangle-\langle N\rangle^2}}{\langle N\rangle}\sim N^{-1/2}\,. \tag{6.13}$$

As the average number of particles increases, the size of the fluctuations in particle number becomes small compared to the size of the average particle number. For very large $\langle N\rangle$, most microstates will have a particle number approximately equal to $\langle N\rangle$ and we retrieve the canonical ensemble.

It is useful to write Eq. (6.12) in terms of the isothermal compressibility. From the chain rule in Appendix B, $(\partial N/\partial\mu)_{T,V}=-(\partial N/\partial V)_{T,\mu}(\partial V/\partial\mu)_{T,N}$. From Table 3.5, $(\partial\mu/\partial V)_{T,N}=-(\partial P/\partial N)_{T,V}$. Also, $(\partial P/\partial N)_{T,V}=-(\partial P/\partial V)_{T,N}$ $(\partial V/\partial N)_{T,P}$. If we now combine these equations and note that $(\partial N/\partial V)_{T,\mu}=(\partial N/\partial V)_{T,P}=\langle N\rangle/V$ since $\mu=\mu(T,P)$, we find

$$\langle N^2\rangle-\langle N\rangle^2=k_{\mathrm{B}}T\left(\frac{\partial\langle N\rangle}{\partial\mu}\right)_{T,X}=-k_{\mathrm{B}}T\frac{\langle N\rangle^2}{V^2}\left(\frac{\partial\langle V\rangle}{\partial P}\right)_{T,N}=\frac{k_{\mathrm{B}}T\langle N\rangle^2}{V}\kappa_T\,. \tag{6.14}$$

Thus, the variance in particle number fluctuations is proportional to the isothermal compressibility. Near a critical point, the compressibility can become infinite and, therefore, fluctuations in the particle number (or density) become very large.

6.2.2
Ideal Classical Gas

The equation of state for an ideal classical gas of indistinguishable particles, of mass m, can be computed starting from the grand canonical ensemble. The Hamiltonian of an ideal gas, in the absence of external fields, consists only of kinetic energy $\hat{H}_0=\sum_{j=1}^{N}\hbar^2\hat{k}_j^2/(2m)$. In general, when evaluating the trace for a fluid of indistinguishable particles, we can ether use a complete set of symmetrized or antisymmetrized N-body momentum/energy eigenstates or we can use the number representation (see Appendix D). Since we are interested in the classical limit, it is most convenient to use the momentum/energy eigenstates.

In general, the grand partition function can be written

$$Z_\mu(T,V) = \sum_{N=0}^{\infty} \mathfrak{C}_{\alpha,N} \sum_{k_1,\ldots,k_N} {}^{(\alpha)}\langle k_1, k_2, \ldots, k_N | \mathrm{e}^{-\beta(\hat{H}_0 - \mu\hat{N})} | k_1, k_2, \ldots, k_N \rangle^{(\alpha)} \,, \tag{6.15}$$

where $\alpha = A, S$, $\mathfrak{C}_{\alpha,N}$ is a counting factor the prevents the summation from overcounting states, and $|k_1, k_2, \ldots, k_N\rangle^{(\alpha)}$ are symmetrized ($\alpha = S$) or antisymmetrized ($\alpha = A$) states (see Appendix D).

As discussed in Section 5.3, in the classical limit contributions due to the symmetrization or antisymmetrization can be neglected and the grand partition function takes the form

$$\begin{aligned} Z_\mu(T,V) &= \sum_{N=0}^{\infty} \frac{1}{N!} \sum_{k_1,\ldots,k_N} \langle k_1, k_2, \ldots, k_N | \mathrm{e}^{-\beta(\hat{H}_0 - \mu\hat{N})} | k_1, k_2, \ldots, k_N \rangle \\ &= \sum_{N=0}^{\infty} \frac{\mathrm{e}^{\beta\mu N}}{N!} \frac{V^N}{\lambda_T^{3N}} = \exp\left(\mathrm{e}^{\beta\mu} \frac{V}{\lambda_T^3} \right) . \end{aligned} \tag{6.16}$$

The pressure is

$$P = -\frac{\Omega}{V} = \frac{k_\mathrm{B} T}{V} \ln Z_\mu(T,V) = k_\mathrm{B} T \frac{\mathrm{e}^{\beta\mu}}{\lambda_T^3} . \tag{6.17}$$

The average particle number is

$$\langle N \rangle = -\left(\frac{\partial \Omega}{\partial \mu} \right)_{T,V} = \frac{V \mathrm{e}^{-\beta\mu}}{\lambda_T^3} . \tag{6.18}$$

If we combine Eqs. (6.17) and (6.18), we obtain the classical equation of state $PV = \langle N \rangle k_\mathrm{B} T$ for an ideal gas of indistinguishable particles.

6.3
Adsorption Isotherms

The adsorption of atoms and molecules from a gas or liquid onto a surface is a process of great importance for biological function and for processes that involve the storage of molecules or the removal of contaminants from a gas or liquid. The adsorption process can be classified as physisorption (from van der Waals forces) or chemisorption (characteristic of covalent bonding).

One material commonly used for storage or cleaning of gases and liquids is *activated carbon*, which is a form of carbon processed to have small pores that significantly increase its surface area. Activated carbon is widely used to remove pollutants from air or water or store gases, such as natural gas or hydrogen. The pollutants or gases adhere to the surface and then can be retrieved by raising the temperature of the carbon surface.

The adsorption of oxygen molecules, O_2, by myoglobin or hemoglobin is an example of a biologically important adsorption process. Myoglobin is a protein that is found in muscles and hemoglobin is a protein found in the blood. Hemoglobin is responsible for transporting oxygen from the lungs to the muscles. Both myoglobin and hemoglobin contain a complex organic group of molecules called the heme that contains an iron ion. Myoglobin contains one heme group and hemoglobin contains four heme groups. Oxygen in the lungs is adsorbed onto the heme groups in hemoglobin and then is transported to the myoglobin molecules. The adsorption of oxygen on myoglobin takes place in solution, but one can obtain a rough estimate of the chemical potential of oxygen in solution from its chemical potential in the atmosphere, which is in equilibrium with the oxygen in solution. The atmosphere is approximately 21% oxygen so at one atmosphere the partial pressure of oxygen is $P_{O_2} = 0.21$ bar. Given P_{O_2}, we can use the ideal gas expression to obtain the chemical potential of O_2 in the atmosphere.

Let us now obtain an expression for the fraction of surface sites that have adsorbed molecules. We consider an adsorbing surface (the *adsorbent*), with N adsorbing sites, in contact with a gaseous mixture containing an *adsorbate* molecule, “M” at partial pressure P_M. Let us assume that the adsorption sites are distinguishable and don’t interact with each other, and let us assume that each site can only adsorb one molecule. The adsorption occurs because the “M” molecule can become bound to the site with a binding energy, $-\epsilon$. *The system will be in equilibrium when the chemical potential of the molecules* “M” *in the gas is equal to the chemical potential of the adsorbed molecules* “M” *at the sites.*

The grand partition function, for the case when there are N binding sites and any number $0 \le n \le N$ of “M” molecules bound to the sites, is given by

$$\mathcal{Z}(T,\mu) = \sum_{n=0}^{N} \frac{N!}{(N-n)!n!} e^{-\beta(-n\epsilon - n\mu)} = (1 + e^{\beta(\epsilon+\mu)})^N \,, \tag{6.19}$$

where $\frac{N!}{(N-n)!n!}$ is the number of different ways that n identical “M” molecules can be attached to N distinct sites and $E(n) = -n\epsilon$ is the total binding energy when molecules are attached to n of the N sites. The fact that the molecules don’t interact allows the grand partition function to factor into a product of single-site grand partition functions,

$$\mathcal{Z}_1(T,\mu) = 1 + e^{\beta(\epsilon+\mu)} \,. \tag{6.20}$$

The probabilities that a given site is empty, f_0, or occupied, f_1, are given by

$$f_0 = \frac{1}{1 + e^{\beta(\epsilon+\mu)}} \quad \text{and} \quad f_1 = \frac{e^{\beta(\epsilon+\mu)}}{1 + e^{\beta(\epsilon+\mu)}} \,, \tag{6.21}$$

respectively.

Let us now assume that the gas mixture is well described by the ideal gas equation of state and that the adsorbate molecules “M” in the gas mixture have a partial pressure P_M and mass m. The chemical potential of the adsorbate molecules in the gas is

$$\mu = -k_B T \ln\left(\frac{k_B T}{P_M \lambda_T^3}\right), \tag{6.22}$$

where $\lambda_T^3 = \left(\frac{h^2}{2m\pi k_B T}\right)^{3/2}$. If we now combine Eqs. (6.21) and (6.22), we can write the following expression for the fraction of surface sites with adsorbed "M" molecules

$$f_M = \frac{P_M}{\frac{k_B T}{\lambda_T^3} e^{-\beta\epsilon} + P_M}. \tag{6.23}$$

Equation (6.23) is called the *Langmuir adsorption isotherm* and gives the fraction of occupied sites as a function of the partial pressure of the adsorbate molecules for a fixed temperature.

In Figure 6.1, we have plotted the fraction of myoglobin molecules with adsorbed O_2, as a function of partial pressure of O_2 for several different temperatures. The partial pressure of O_2 in the atmosphere, at $T = 0\,°C$, is $P_{O_2} = 0.21$ bar = 159 Torr. The data fits the Langmuir adsorption isotherm very well and indicates that most myoglobin molecules contain adsorbed oxygen.

When the adsorption sites can adsorb more than one molecule, the Langmuir adsorption isotherm is no longer adequate to describe the fraction of adsorbed molecules, and other adsorption isotherms have been developed to describe these more complex situations. It is interesting to compare the O_2 adsorption isotherms for myoglobin and hemoglobin, which can adsorb as many as four O_2 molecules. In Figure 6.2, we show the isotherms for myoglobin and hemoglobin at temperature $T = 310$ K as a function of the partial pressure of oxygen. The adsorption isotherm for hemoglobin is significantly different from that of myoglobin because

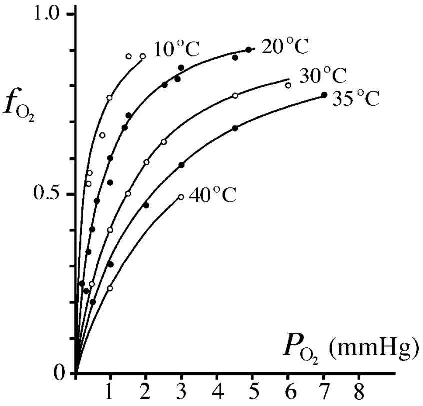

Figure 6.1 The fraction f_{O_2} of myoglobin molecules with adsorbed oxygen, as a function of partial pressure P_{O_2} of oxygen, for several different temperatures (based on [187]).

the binding energy of the heme sites, on a given hemoglobin molecule, is a function of the number of oxygen molecules already adsorbed on that hemoglobin molecule. We can still use the grand canonical ensemble to determine the fraction of adsorbed molecules, as long as the adsorption sites on *different* hemoglobin molecules remain independent. An example of this more general use of the grand canonical ensemble is given in Exercise 6.1.

Exercise 6.1

Consider a hypothetical molecule "P" that has two heme sites that can bind an oxygen molecule O_2. The binding energies E_n when zero, one, and two O_2 are bound to the molecule are $E_0 = 0$, $E_1 = -0.51$, and $E_2 = -1.05$ eV, respectively. Assume that $N = 1000$ "P" molecules are in equilibrium with air at $T = 310$ K and the partial pressure of O_2 in air is $P_{O_2} = 0.2$ bar. Assume that the "P" molecules are independent of one another. How many "P" molecules have (a) zero O_2 molecules attached; (b) one O_2 molecule attached; (c) two O_2 molecules attached?

Answer: The grand partition function for O_2 in contact with a single "P" molecule is

$$\mathcal{Z}_1 = 1 + 2e^{-\beta(E_1 - \mu_{O_2})} + e^{-\beta(E_2 - 2\mu_{O_2})}$$

(note that there are two ways to attach one O_2 to the "P" molecule). For $T = 310$ K, $\lambda_T = 0.175 \times 10^{-10}$ m and $k_B T = 0.0267$ eV, the chemical potential of O_2 is $\mu_{O_2} = -0.468$ eV. Therefore, $e^{-\beta(E_1 - \mu_{O_2})} = 4.82$, $e^{-\beta(E_2 - 2\mu_{O_2})} = 71.50$, and $\mathcal{Z}_1 = 1 + 2(4.82) + 71.50 = 82.14$. The probability to find a "P" molecule with n O_2 bound to it, for $n = 0, 1, 2$ is $P_0 = \frac{1}{\mathcal{Z}_1} = 0.012$, $P_1 = 2e^{-\beta(E_1 - \mu_{O_2})}/\mathcal{Z}_1 = 0.117$, and $P_2 = e^{-\beta(E_2 - 2\mu_{O_2})}/\mathcal{Z}_1 = 0.870$. On the average, the numbers N_n of "P" molecules with $n = 0, 1, 2$ O_2 molecules attached are given by $N_0 = NP_0 = 12$, $N_1 = NP_1 = 117$, and $N_2 = NP_2 = 870$.

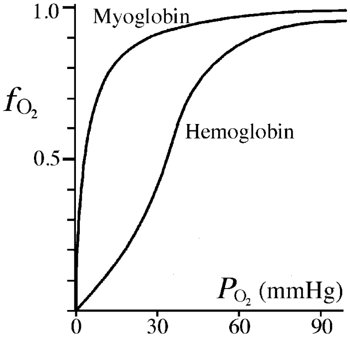

Figure 6.2 A comparison of the oxygen adsorption isotherms, at $T = 310$ K, as a function of the partial pressure of oxygen (based on [64]).

6.4
Virial Expansion for Interacting Classical Fluids

The first step in obtaining tractable microscopic expressions for the thermodynamic properties of interacting fluids is to find a small parameter that can be used as an expansion parameter. For dilute or moderately dense gases, such a parameter is the density. In this section we shall first obtain a microscopic expression for the virial (density) expansion of the equation of state for a classical fluid, and then we compare the predictions of the microscopic theory to experimental results [84, 85, 130, 134, 201].

6.4.1
Virial Expansion and Cluster Functions

Let us consider a classical gas of identical particles of mass m that interact via two-body short-ranged forces. We shall assume that the potential has a large repulsive core and short-ranged attraction (cf. Figure 6.3). For a semiclassical fluid, we can use the approximations in Section 5.4 and write the grand partition function in the form

$$Z_\mu(T, V) = \sum_{N=0}^{\infty} \frac{1}{N!} \frac{1}{\lambda_T^{3N}} e^{\beta N \mu} Q_N(V, T)\,, \tag{6.24}$$

where the momentum integrations have been performed and the configuration integral, $Q_N(V, T)$, is defined in Eq. (5.45).

If the interparticle potential V_{ij} has an infinite hard core at short interparticle separation, it can not be used as an expansion parameter. However, we can introduce a function f_{ij} that is not divergent,

$$f_{ij} = e^{-\beta V_{ij}} - 1\,. \tag{6.25}$$

The function f_{ij} becomes zero outside the range of the interaction. Furthermore, in the region of the hard core, where $\mathrm{V}_{ij} \approx \infty$, the function $f_{ij} = -1$ (cf. Figure 6.3).

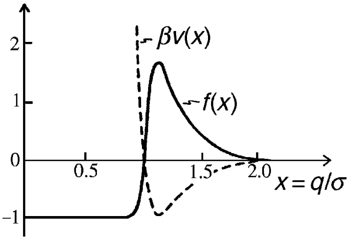

Figure 6.3 The dashed line is a plot of a typical interparticle potential, $v(x)$ (Lennard-Jones 6–12), the solid line is a plot of $f(x) = e^{-\beta v(x)} - 1$, and σ is a measure of the hard-core radius ($v(1) = 0$). The plots are given for a fixed temperature.

In terms of the function f_{ij}, the configuration integral can be written as

$$Q_N(V,T) = \int \cdots \int \mathrm{d}\boldsymbol{r}_1 \cdots \mathrm{d}\boldsymbol{r}_N \, W_N(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N)\,, \tag{6.26}$$

where

$$W_N(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N) = \prod_{(ij)}^{N(N-1)/2} (1 + f_{ij}) \tag{6.27}$$

and the product is taken over all pairs of particles (ij). There are $N(N-1)/2$ such pairs. The first few terms are given by $W_1 = 1$, $W_2(\boldsymbol{r}_1, \boldsymbol{r}_2) = (1 + f_{12})$, $W_3(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3) = (1 + f_{12})(1 + f_{13})(1 + f_{23})$ and so on.

It was shown by Ursell [203] that the grand partition function can be written in terms of a cumulant expansion (see Appendix A), such that

$$\begin{aligned} Z_\mu(T,V) &= \sum_{N=0}^{\infty} \frac{1}{N!} \frac{1}{\lambda_T^{3N}} \mathrm{e}^{\beta N \mu} \int \cdots \int \mathrm{d}\boldsymbol{r}_1 \cdots \mathrm{d}\boldsymbol{r}_N \, W_N(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N) \\ &= \exp\left[\sum_{l=1}^{\infty} \frac{1}{l!} \frac{1}{\lambda_T^{3l}} \mathrm{e}^{\beta l \mu} \int \cdots \int \mathrm{d}\boldsymbol{r}_1 \cdots \mathrm{d}\boldsymbol{r}_l U_l(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_l) \right] \,, \end{aligned} \tag{6.28}$$

where $U_l(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_l)$ is called a *cluster function* or *Ursell function*.

When written in terms of cluster functions, the grand potential takes a simple form:

$$\begin{aligned} \Omega(V,T,\mu) &= -k_{\mathrm{B}} T \ln Z_\mu(T,V) \\ &= -k_{\mathrm{B}} T \sum_{l=1}^{\infty} \frac{1}{l!} \frac{1}{\lambda_T^{3l}} \mathrm{e}^{\beta l \mu} \int \cdots \int \mathrm{d}\boldsymbol{r}_1 \cdots \mathrm{d}\boldsymbol{r}_l U_l(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_l)\,. \end{aligned} \tag{6.29}$$

If we know the function $W_N(\boldsymbol{r}, \ldots, \boldsymbol{r}_N)$, then we can easily find the cluster functions $U_N(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N)$. We expand (6.28) in powers of $\lambda_T^{-3} \exp(\beta\mu)$ and equate coefficients. We then obtain the following hierarchy of equations:

$$\begin{aligned} U_1(\boldsymbol{r}_1) &= W_1(\boldsymbol{r}_1)\,, \\ U_2(\boldsymbol{r}_1, \boldsymbol{r}_2) &= W_2(\boldsymbol{r}_1, \boldsymbol{r}_2) - W_1(\boldsymbol{r}_1) W_1(\boldsymbol{r}_2)\,, \\ U_3(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3) &= W_3(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3) - W_1(\boldsymbol{r}_1) W_2(\boldsymbol{r}_2, \boldsymbol{r}_3) \\ &\quad - W_1(\boldsymbol{r}_2) W_2(\boldsymbol{r}_1, \boldsymbol{r}_3) - W_1(\boldsymbol{r}_3) W_2(\boldsymbol{r}_1, \boldsymbol{r}_2) \\ &\quad + 2 W_1(\boldsymbol{r}_1) W_1(\boldsymbol{r}_2) W_1(\boldsymbol{r}_3)\,, \end{aligned} \tag{6.30}$$

and so on. From Eqs. (6.27) and (6.30) we can find the first few cluster functions. They are $U_1(\boldsymbol{r}_1) = 1$, $U_2(\boldsymbol{r}_1, \boldsymbol{r}_2) = f_{12}$, and $U_3(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3) = f_{12} f_{13} + f_{12} f_{23} + f_{13} f_{23} + f_{12} f_{13} f_{23}$ and so on. The function $U_N(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N)$ depends on all *connected* clusters of N particles.

The integrals over cluster functions $U_N(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N)$ are always proportional to the volume due to integration over the center-of-mass of each cluster. Therefore, we can introduce an intensive quantity

$$b_l(T) = \frac{1}{Vl!} \int \cdots \int \mathrm{d}\boldsymbol{r}_1 \cdots \mathrm{d}\boldsymbol{r}_l U_l(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_l) , \tag{6.31}$$

where $b_l(T)$ is called a *cluster integral*. When written in terms of $b_l(T)$, the expression for the grand potential, $\Omega(V, T, \mu)$, in Eq. (6.29) is explicitly proportional to the volume.

$$\Omega(V, T, \mu) = -Vk_\mathrm{B}T \sum_{l=1}^{\infty} \frac{b_l(T)\mathrm{e}^{\beta l \mu}}{\lambda_T^{3l}} . \tag{6.32}$$

The pressure takes the form

$$P = -\frac{\Omega(V, T, \mu)}{V} = k_\mathrm{B}T \sum_{l=1}^{\infty} \frac{b_l(T)\mathrm{e}^{\beta l \mu}}{\lambda_T^{3l}} \tag{6.33}$$

and the particle density is given by

$$\frac{\langle N \rangle}{V} = -\frac{1}{V}\left(\frac{\partial \Omega}{\partial \mu}\right)_{V,T} = \sum_{l=1}^{\infty} \frac{l b_l(T)\mathrm{e}^{\beta l \mu}}{\lambda_T^{3l}} . \tag{6.34}$$

The virial expansion of the equation of state is an expansion in powers of the density,

$$\frac{PV}{\langle N \rangle k_\mathrm{B}T} = \sum_{l=1}^{\infty} B_l(T) \left(\frac{\langle N \rangle}{V}\right)^{l-1} . \tag{6.35}$$

If we combine Eqs. (6.33), (6.34), and (6.35), we obtain

$$\sum_{l=1}^{\infty} \frac{b_l(T)\mathrm{e}^{\beta l \mu}}{\lambda_T^{3l}} \left(\sum_{n=1}^{\infty} \frac{n b_n(T)\mathrm{e}^{\beta n \mu}}{\lambda_T^{3n}}\right)^{-1} = \sum_{l'=1}^{\infty} B_{l'} \left(\sum_{n'=1}^{\infty} \frac{n' b_{n'}(T)\mathrm{e}^{\beta n' \mu}}{\lambda_T^{3n'}}\right)^{l'-1} . \tag{6.36}$$

If we now expand both sides of Eq. (6.36) and equate coefficients of equal powers of $\lambda_T^{-3} \exp(\beta\mu)$, we obtain the following expressions for the first three virial coefficients:

$$\begin{aligned} B_1(T) &= b_1(T) = 1 , \\ B_2(T) &= -b_2(T) , \\ B_3(T) &= 4b_2^2(T) - 2b_3(T) , \end{aligned} \tag{6.37}$$

and so on. The higher order terms in the virial expansion are determined by larger and larger clusters of particles.

6.4.2
The Second Virial Coefficient, $B_2(T)$

The second virial coefficient gives the correction to the ideal gas equation of state due to two-body clustering [85]. For very dilute gases, two-body clusters give, by far, the dominant contribution from interactions in the fluid and it is sufficient to terminate the virial expansion at second order.

From Eqs. (6.31), and (6.37), the second virial coefficient can be written

$$B_2(T) = -\frac{1}{2V}\int d\boldsymbol{r}_1\, d\boldsymbol{r}_2 f(\boldsymbol{r}_{12}) = -\frac{1}{2}\int d\boldsymbol{r}_{12}(e^{-\beta V(\boldsymbol{r}_{12})} - 1)\,, \tag{6.38}$$

where we have changed to center-of-mass ($\boldsymbol{R} = (\boldsymbol{r}_1 + \boldsymbol{r}_2)/2$) and relative ($\boldsymbol{r}_{12} = \boldsymbol{r}_1 - \boldsymbol{r}_2$) coordinates and have integrated over the center-of-mass. The behavior of the second virial coefficient has been studied for a variety of interparticle potentials. For very simple potentials it can be computed analytically, and for realistic potentials it must be computed numerically. We shall focus on three potentials that historically have been important in understanding the behavior of the virial coefficients. They are the hard-sphere potential (see Exercise 6.1), the square-well potential, and the Lennard-Jones 6–12 potential (cf. Figure 6.4).

6.4.2.1 Square-Well Potential

The square-well potential (shown in Figure 6.4a) has the form

$$\mathrm{V}_{\mathrm{SW}}(q) = \begin{cases} \infty & \text{if} \quad 0 < q < \sigma\,, \\ -\varepsilon & \text{if} \quad \sigma < q < R\sigma\,, \\ 0 & \text{if} \quad R\sigma < q\,. \end{cases} \tag{6.39}$$

This potential has a hard core of radius, σ, and a square attractive region of depth ε and width $(R-1)\sigma$. The second virial coefficient can be computed analytically and has the form

$$B_2(T)_{\mathrm{SW}} = \frac{2\pi\sigma^3}{3}[1 - (R^3 - 1)(e^{\beta\varepsilon} - 1)]\,. \tag{6.40}$$

Note that $B_2(T)_{\mathrm{SW}}$ differs from $B_2(T)_{\mathrm{HC}}$ by a temperature-dependent term (see Exercise 6.1). At low temperatures, $B_2(T)_{\mathrm{SW}}$ is negative and at high temperatures

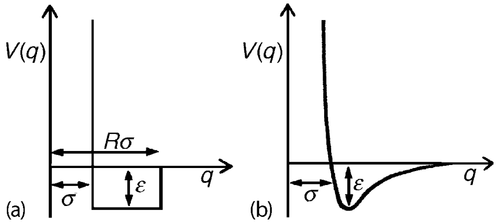

Figure 6.4 Sketch of (a) the square-well potential and (b) the Lennard-Jones 6–12 potential.

it becomes positive. At low temperatures the attractive interaction energy due to the square well can compete with the thermal energy, $k_B T$, and causes a lowering of the pressure relative to the ideal gas value. At high temperature the hard core becomes dominant and the pressure increases relative to that of an ideal gas.

We can write $B_2(T)_{SW}$ in a reduced form if we let $B^*(T)_{SW} = B(T)_{SW}/b_0$, where $b_0 = 2\pi\sigma^3/3$ and $T^* = k_B T/\varepsilon$. Then we find

$$B_2^*(T)_{SW} = [1 - (R^3 - 1)(e^{1/T^*} - 1)] . \tag{6.41}$$

Equation (6.41) will be useful when we compare the square-well results to experiment.

6.4.2.2 **Lennard-Jones 6–12 Potential**

A potential which gives a very good approximation to the interaction between atoms is the Lennard-Jones 6–12 potential,

$$V_{LJ}(q) = 4\varepsilon \left[\left(\frac{\sigma}{q}\right)^{12} - \left(\frac{\sigma}{q}\right)^{6}\right] \tag{6.42}$$

(cf. Figure 6.4b). The Lennard-Jones potential has a gradually sloping hard core, which takes account of the fact that particles with high energy can, to some extent, penetrate the hard core. When $q = \sigma$, we obtain $V_{LJ}(\sigma) = 0$. Thus, $q = \sigma$ is the radius of the hard core because at $q = \sigma$ the potential changes from repulsive to attractive. The minimum of the Lennard-Jones potential occurs at $q = 2^{1/6}\sigma$. The value of the potential at the minimum is $V_{LJ}(2^{1/6}\sigma) = -\varepsilon$, so ε is the depth of the Lennard-Jones potential.

The second virial coefficient for the Lennard-Jones potential can be found analytically in the form of a series expansion. If we integrate Eq. (6.38) by parts and introduce the notation $x = q/\sigma$, $T^* = k_B T/\varepsilon$, and $B_2^*(T)_{LJ} = B_2(T)_{LJ}/b_0$, we find

$$B_2^*(T)_{LJ} = \frac{4}{T^*} \int_0^\infty \mathrm{d}x x^2 \left[\frac{12}{x^{12}} - \frac{6}{x^6}\right] \exp\left\{-\frac{4}{T^*}\left[\left(\frac{1}{x}\right)^{12} - \left(\frac{1}{x}\right)^{6}\right]\right\} . \tag{6.43}$$

If we expand $\exp[4/T^*(1/x)^6]$ in an infinite series, each term of the series can be computed analytically and we obtain the following expansion for $B_2^*(T)_{LJ}$:

$$B_2^*(T)_{LJ} = -\sum_{n=0}^{\infty} \frac{2}{4n!} \Gamma\left(\frac{2n-1}{4}\right)\left(\frac{1}{T^*}\right)^{((2n+1)/4)} , \tag{6.44}$$

where $\Gamma(x)$ is the Gamma Function. The expansion for $B_2^*(T)_{LJ}$ converges rapidly for $T^* > 4$, but more slowly for lower values of T^*. Values of $B_2^*(T)_{LJ}$ for T^* ranging from 0.3 to 400 are given in Table 6.1.

In Figure 6.5 we plot $B_2^*(T)$ versus T^* for both the square-well potential and the Lennard-Jones potential. We also give experimental values of $B_2^*(T)$ for a variety of substances. The Lennard-Jones potential gives values of $B_2^*(T)$ in good

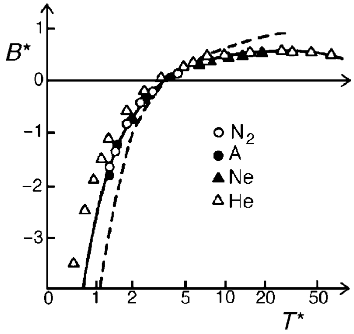

Figure 6.5 The reduced second virial coefficient. The solid line is the calculated curve for the Lennard-Jones 6–12 potential. The dashed line is the calculated curve for the square-well potential (for $R = 1.6$). The points are experimental values for the gases listed (based on [85]).

Table 6.1 Values of the Reduced Second Virial Coefficient versus the Reduced Temperature for the Lennard-Jones Potential.

T^*	B_2^*	T^*	B_2^*
0.30	−27.8806	4.00	+0.1154
0.40	−13.7988	4.50	+0.1876
0.50	−8.7202	5.00	+0.2433
0.70	−4.7100	10.00	+0.4609
1.00	−2.5381	20.00	+0.5254
1.50	−1.2009	30.00	+0.5269
2.00	−0.6276	40.00	+0.5186
2.50	−0.3126	50.00	+0.5084
3.00	−0.1152	100.00	+0.4641
3.50	+0.0190	400.00	+0.3583

agreement with experimental results. At high temperatures, $B_2^*(T)_{\mathrm{LJ}}$ and the experimental points for He gas exhibit a maximum while $B_2^*(T)_{\mathrm{SW}}$ does not. The maximum in $B_2^*(T)_{\mathrm{LJ}}$ occurs because at high temperatures, particles can penetrate into the hard core and lower the amount of excluded volume. The square-well potential has a hard core with infinite slope and cannot account for this effect. The data points for He deviate from the classical results at low temperature. These deviations are due to quantum effects not included in the semiclassical approximation to the grand partition function. The second virial coefficients for all classical gases, when plotted in terms of reduced quantities, are identical. This is an example of the law of corresponding states.

The parameters $\varepsilon/k_{\mathrm{B}}$ and σ can be obtained from experimental values for the second virial coefficient for various substances. Thus, measurements of the virial coefficients of real gases provide an extremely important source of information about interparticle potential for various molecules. It is important to note that, although the Lennard-Jones 6–12 potential is perhaps the most widely used interparticle potential, there are many other forms of potential that may be used to compute the virial coefficients, and some of them give better agreement with experimental results over a wider range of temperature than does the Lennard-Jones potential.

Computation of the third virial coefficient is more challenging but still can be done for some simple potentials. However, new effects can enter [183], such as three-body forces which are not included in the examples given here.

Exercise 6.2

Compute the second virial coefficient, $B_2(T)$, for a hard-sphere gas of atoms of radius, R, confined to a box of volume, V. Write the equation of state for this gas as a virial expansion to first order in the density.

Answer: The second virial coefficient, $B_2(T)$, is defined as

$$B_2(T) = -\frac{1}{V}\frac{1}{2!}\int \mathrm{d}\boldsymbol{r}_1 \int \mathrm{d}\boldsymbol{r}_2 (\mathrm{e}^{-\beta V(\boldsymbol{r}_{21})} - 1)\,,$$

where $\boldsymbol{r}_{21} = \boldsymbol{r}_2 - \boldsymbol{r}_1$. For hard spheres $V(\boldsymbol{r}_{21}) = \infty$ for $r_{21} < R$ and $V(\boldsymbol{r}_{21}) = 0$ for $r_{21} > R$. We can make a change of variables and let $\boldsymbol{r} = \boldsymbol{r}_{21} = \boldsymbol{r}_2 - \boldsymbol{r}_1$ and $\boldsymbol{R} = (1/2)(\boldsymbol{r}_1 + \boldsymbol{r}_2)$. If we then integrate over $\boldsymbol{R}$, we obtain

$$B_2(T) = -\frac{1}{2}\int \mathrm{d}\boldsymbol{r}(\mathrm{e}^{-\beta V(\boldsymbol{r})} - 1) = +2\pi \int_0^R \mathrm{d}r r^2 = \frac{2\pi R^3}{3} \equiv b_0\,.$$

The equation of state of a hard-sphere gas, to second order in the density, is

$$\frac{PV}{Nk_\mathrm{B}T} = 1 + b_0\frac{N}{V} + \cdots$$

6.5
Blackbody Radiation

All material bodies emit electromagnetic radiation. The emitted radiation is distributed over a range of frequencies and the peak of the distribution moves to higher frequencies as the temperature of the material is increased. This is why a piece of iron looks grey at room temperature but, as it is heated, it begins to glow red through yellow to white with increasing temperature.

Let us now imagine a totally closed empty box whose walls are maintained at temperature T. The radiation emitted from the walls inside the box come to thermodynamic equilibrium with the walls and form a gas of noninteracting photons with temperature T. If a *small* hole (so small that it does not change the distribution of radiation inside the box) is cut into the wall of the box, radiation will escape and have a frequency distribution equal to that of the photon gas in the box. Any radiation that enters the hole from outside will be absorbed by the interior walls and will never escape. Thus, the hole is a perfect absorber of radiation and appears black from the outside. The emitted equilibrium radiation is thus called blackbody radiation.

We can compute the thermodynamic properties of blackbody radiation. Let us assume that the box containing the blackbody radiation has volume $V = L^3$. The allowed photon energies, inside the box, are determined by the standing waves formed by the electromagnetic field in the box. The photon energies are $\hbar\omega_i = \hbar c|\boldsymbol{k}_i|$, where $\boldsymbol{k}_i$ is the wavevector of the ith standing wave. Since photons have no mass, the gas will have chemical potential, $\mu = 0$.

Since there are an infinite number of standing waves allowed, the grand partition function is

$$Z_\mu(T) = \sum_{n_1=0}^{\infty} \cdots \sum_{n_\infty=0}^{\infty} \exp\left(-\beta \sum_{i=1}^{\infty} n_i \hbar\omega_i\right) = \prod_{i=1}^{\infty} \frac{1}{1 - \mathrm{e}^{-\beta\hbar\omega_i}} \,. \tag{6.45}$$

The grand potential is

$$\Omega(T) = -PV = k_\mathrm{B} T \sum_{i=1}^{\infty} \ln(1 - \mathrm{e}^{-\beta\hbar\omega_i}) \,. \tag{6.46}$$

Because the chemical potential is zero, the internal energy is simply given by $U = ((\beta\partial\Omega(T))/\partial\beta)_V$. Then

$$U = \sum_{i=1}^{\infty} \hbar\omega_i n(\omega_i) = \sum_{i=1}^{\infty} \frac{\hbar\omega_i}{(\mathrm{e}^{\beta\hbar\omega_i} - 1)} \,, \tag{6.47}$$

where $n(\omega_i) = (\mathrm{e}^{\beta\hbar\omega_i} - 1)^{-1}$ gives the number of photons with frequency ω_i and is called the Planck distribution.

We can change the summation to an integration in the following way. The standing waves have wavevectors, $\boldsymbol{k} = (n_x\pi/L)\hat{\boldsymbol{e}}_x + (n_y\pi/L)\hat{\boldsymbol{e}}_y + (n_z\pi/L)\hat{\boldsymbol{e}}_z$. These correspond to allowed frequencies, ω, such that

$$\omega^2 = c^2k^2 = c^2\left[\left(\frac{n_x\pi}{L}\right)^2 + \left(\frac{n_y\pi}{L}\right)^2 + \left(\frac{n_z\pi}{L}\right)^2\right] \,. \tag{6.48}$$

If we imagine a lattice of allowed frequencies, $\omega = ck$, the spacing per point in ω space is $c\pi/L$. The volume per point is $(c\pi/L)^3$. The number of points per unit volume is $(L/c\pi)^3$.

The number, ν of allowed frequencies less than some value ω is therefore

$$\nu = \frac{1}{8}\frac{4}{3}\pi\omega^3\left(\frac{L}{c\pi}\right)^3 = \frac{L^3\omega^3}{6c^3\pi^2} \,. \tag{6.49}$$

For each allowed frequency of the electromagnetic field, there are two transverse modes. Thus, $\sum_{i=1}^{\infty} = 2\int \mathrm{d}\nu = (L^3/\pi^2 c^3)\int_0^\infty \omega^2\,\mathrm{d}\omega$. The pressure therefore becomes

$$P = -\frac{k_\mathrm{B}T}{\pi^2 c^3}\int_0^\infty \omega^2\,\mathrm{d}\omega \ln\left(1 - \mathrm{e}^{-\beta\hbar\omega}\right) . \tag{6.50}$$

If we integrate by parts, we find

$$P = \frac{\hbar}{3c^3\pi^2}\int_0^\infty \omega^3\,\mathrm{d}\omega \frac{1}{\mathrm{e}^{-\beta\hbar\omega} - 1} = \frac{\pi^2 k_\mathrm{B}^4 T^4}{45 c^3 \hbar^3} = \frac{1}{3} a T^4 , \tag{6.51}$$

where $a = \pi^2 k_\mathrm{B}^4/(15c^3\hbar^3)$ is Stefan's constant. Similarly, the internal energy takes the form

$$U = \frac{L^3}{\pi^2 c^3}\int_0^\infty \omega^2\,\mathrm{d}\omega \frac{\hbar\omega}{\mathrm{e}^{\beta\hbar\omega} - 1} = aVT^4 . \tag{6.52}$$

The energy density (energy per unit volume) in each frequency component of the blackbody radiation is

$$u(\omega) = \frac{\omega^2}{\pi^2 c^3}\frac{\hbar\omega}{(\mathrm{e}^{\beta\hbar\omega} - 1)} . \tag{6.53}$$

Equation (6.53) is called Planck's law of radiation.

Exercise 6.3

Consider a noninteracting gas of two-level atoms immersed in, and in equilibrium with, blackbody radiation at temperature T. Each atom has ground state energy E_1 and excited state energy E_2, with N_1 (N_2) atoms in the ground state (excited) state. At equilibrium, the ratio $N_2/N_1 = \mathrm{e}^{-\beta\epsilon}$, where $\epsilon = E_2 - E_1$. For an excited atom in a vacuum, the probability/time of spontaneous emission of a photon is $\dot{p}_\mathrm{sp} = A$. In the presence of the radiation field, the probability/time to absorb a photon with energy $\epsilon = \hbar\omega$ is $\dot{p}_\mathrm{abs} = Bu(\omega)$ and the probability/time to emit (stimulated emission) such a photon is $\dot{p}_\mathrm{st} = B'u(\omega)$, where $u(\omega) = \omega^2/(\pi^2 c^3)\hbar\omega/(\mathrm{e}^{\beta\hbar\omega} - 1)$ is Planck's radiation law. Compute A, B, and B' when the atoms are in equilibrium with the radiation field.

Answer: If the atoms are in equilibrium with the radiation field, there should be no change in the average number of excited and ground state atoms, even though individual atoms are continually emitting and absorbing photons. The time rate of change of the number of atoms in the ground state can be written

$$\frac{\mathrm{d}N_1}{\mathrm{d}t} = AN_2 + B'u(\omega)N_2 - Bu(\omega)N_1 = 0 .$$

Since $N_2 = N_1\mathrm{e}^{-\beta\epsilon} = N_1\mathrm{e}^{-\beta\hbar\omega}$, this can be written $A = (B\mathrm{e}^{\beta\hbar\omega} - B')u(\omega)$. The left-hand side does not depend on temperature and, therefore, the right-hand side must also be independent of temperature. This requires $B = B'$. Then $B = \pi^2 c^3/(\hbar\omega^3)A$ and $\dot{p}_{\text{abs}} = \dot{p}_{\text{st}} = An(\omega) = A/(\mathrm{e}^{\beta\hbar\omega} - 1)$. The coefficients A and B are called Einstein A and B coefficients [50].

6.6
Ideal Quantum Gases

When a collection of indistinguishable particles forms a gas at a temperature low enough for the thermal wavelength to become larger than the average distance between particles, the statistics of the particles starts to play a crucial role in determining the thermodynamic behavior of the gas. All known particles obey either Bose–Einstein or Fermi–Dirac statistics. At very low temperatures, Bose–Einstein and Fermi–Dirac gases behave in completely different ways. At high temperatures, all ideal gases, regardless of statistics become more alike in their thermodynamic behavior.

For an ideal gas of indistinguishable particles with mass m, the grand partition function can be written

$$Z_\mu(T, V) = \mathrm{Tr}(\mathrm{e}^{-\beta(\hat{H}_0 - \mu\hat{N})}) , \tag{6.54}$$

where $\hat{H}_0$ is the kinetic energy operator and $\hat{N}$ is the total particle number operator.

We shall assume that the gas is contained in a "box" with periodic boundary conditions. We will let the volume of the "box" be $V = L_x L_y L_z$, where L_x, L_y, and L_z are the lengths of the sides of the box in the x-, y-, and z-directions, respectively. The momentum operator for a single particle can be written $\hat{\boldsymbol{p}}_l = \hbar\hat{\boldsymbol{k}}_l$, where

$$\boldsymbol{k}_l = \left(\frac{2\pi l_x}{L_x}\boldsymbol{e}_x + \frac{2\pi l_y}{L_y}\boldsymbol{e}_y + \frac{2\pi l_z}{L_z}\boldsymbol{e}_z \right) , \tag{6.55}$$

is the wavevector of the particle, l_x, l_y, and l_z are integers each ranging from $-\infty$ to ∞, and $\boldsymbol{e}_x$, $\boldsymbol{e}_y$, and $\boldsymbol{e}_z$ are unit vectors in the x-, y-, and z-directions, respectively. Let us denote the set of integers, $\boldsymbol{l} = (l_x, l_y, l_z)$. The kinetic energy for a single particle in the state $\boldsymbol{l} = (l_x, l_y, l_z)$ is given by

$$\varepsilon_l = \frac{\hbar^2}{2m}\left(\frac{4\pi^2 l_x^2}{L_x^2} + \frac{4\pi^2 l_y^2}{L_y^2} + \frac{4\pi^2 l_z^2}{L_z^2} \right) . \tag{6.56}$$

Because we need to keep the full effect of the quantum statistics, it is easiest to evaluate the trace in Eq. (6.54) in the number representation (see Appendix D). In the number representation, the Hamiltonian operator can be written

$$\hat{H}_0 = \sum_{\boldsymbol{l}} \varepsilon_l \hat{a}^\dagger_{\boldsymbol{k}_l} \hat{a}_{\boldsymbol{k}_l} , \tag{6.57}$$

where $\hat{a}^{\dagger}_{\boldsymbol{k}_l}$ and $\hat{a}_{\boldsymbol{k}_l}$, respectively, create and annihilate a particle with wavevector $\boldsymbol{k}_l$. As discussed in Appendix D, these operators act on the number basis states $|n_l\rangle$ such that $\hat{a}^{\dagger}_{\boldsymbol{k}_l}|n_l\rangle = \sqrt{n_l+1}|n_l+1\rangle$ and $\hat{a}_{\boldsymbol{k}_l}|n_l\rangle = \sqrt{n_l}|n_l-1\rangle$. The combination $\hat{n}_l = \hat{a}^{\dagger}_{\boldsymbol{k}_l}\hat{a}_{\boldsymbol{k}_l}$ is just the number operator since $\hat{a}^{\dagger}_{\boldsymbol{k}_l}\hat{a}_{\boldsymbol{k}_l}|n_l\rangle = \sqrt{n_l}\hat{a}^{\dagger}_{\boldsymbol{k}_l}|n_l-1\rangle = n_l|n_l\rangle$. The operators $\hat{a}^{\dagger}_{\boldsymbol{k}_l}$ and $\hat{a}_{\boldsymbol{k}_l}$ obey boson or fermion commutation relations (see Appendix D) depending on the type of particle being considered.

The trace in Eq. (6.54) is taken with respect to a complete set of number basis states $|\{n_l\}\rangle \equiv |n_{-\infty,-\infty,-\infty}, \ldots, n_{-1,0,0}, n_{0,0,0}, n_{1,0,0}, \ldots, n_{\infty,\infty,\infty}\rangle$. Thus we can write

$$Z_\mu(T,V) = \prod_l \left(\sum_{n_l}\right) \langle\{n_l\}|\mathrm{e}^{-\beta(\hat{H}_0-\mu\hat{N})}\{n_l\}\rangle \tag{6.58}$$

where

$$\prod_l \left(\sum_{n_l}\right) = \sum_{n_{-\infty,-\infty,-\infty}} \times \cdots \times \sum_{n_{-1,0,0}} \sum_{n_{0,0,0}} \sum_{n_{1,0,0}} \times \cdots \times \sum_{n_{\infty,\infty,\infty}} . \tag{6.59}$$

Equation (6.58) can be rewritten in the form

$$Z_\mu(T,V,\mu) = \prod_l \left\{ \sum_{n_l} \exp[-\beta n_l(\varepsilon_l - \mu)] \right\} . \tag{6.60}$$

The difference between Bose–Einstein and Fermi–Dirac particles lies in the numbers of particles that can occupy a given energy eigenstate. For a gas of identical Bose–Einstein particles there is no restriction on the number of particles that can have a given set of quantum numbers, l_x, l_y, and l_z. Therefore, the summation over n_l in Eq. (6.60), for Bose–Einstein particles, must include the possibility that any number of particles, n_l, ranging from 0 to ∞, can occupy the momentum state, $\boldsymbol{p}_l$. This will be true for each different momentum state. Thus, for a Bose–Einstein gas the grand partition function is

$$Z_{\mathrm{BE}}(T,V,\mu) = \prod_l \left\{ \sum_{n_l=0}^{\infty} \exp[-\beta n_l(\varepsilon_l - \mu)] \right\} . \tag{6.61}$$

In Eq. (6.61) we have not explicitly included the possibility that the particles have (integer) spin or other internal degrees of freedom. However, it is straightforward to include them.

For a gas of identical Fermi–Dirac particles, the Pauli exclusion principle restricts the number of particles, n_l, which can occupy a given state, $\boldsymbol{l}$, to $n_l = 0$ or $n_l = 1$. Thus, for a Fermi–Dirac gas the grand partition function becomes

$$Z_{\mathrm{FD}}(T,V,\mu) = \prod_l \left\{ \sum_{n_l=0}^{1} \exp[-\beta_{n_l}(\varepsilon_l - \mu)] \right\} . \tag{6.62}$$

In writing the grand partition function for the Fermi–Dirac gas, we have not explicitly included the (half-integer) spin or other internal degrees of the freedom of the particles. We will do this in a later section, where we describe the behavior of Fermi–Dirac gases in more detail.

6.7
Ideal Bose–Einstein Gas

The grand partition function for a Bose–Einstein ideal gas in Eq. (6.8) implicitly assumes that the bosons have spin $s = 0$, so spin degrees of freedom do not have to be taken into account. We can perform the summation inside the brackets in Eq. (6.61), using the relation $(1-x)^{-1} = \sum_{n=0}^{\infty} x^n$. We obtain

$$Z_{\mathrm{BE}}(T, V, \mu) = \prod_{\boldsymbol{l}} \left(\sum_{n_{\boldsymbol{l}}=0}^{\infty} \mathrm{e}^{-\beta n_{\boldsymbol{l}}(\varepsilon_{\boldsymbol{l}}-\mu)} \right) = \prod_{\boldsymbol{l}} \left(\frac{1}{1-\mathrm{e}^{-\beta(\varepsilon_{\boldsymbol{l}}-\mu)}} \right) . \tag{6.63}$$

The grand potential then can be written

$$\Omega_{\mathrm{BE}}(T, V, \mu) = -k_{\mathrm{B}} T \ln Z_{\mathrm{BE}}(T, V, \mu) = k_{\mathrm{B}} T \sum_{\boldsymbol{l}} \ln(1-\mathrm{e}^{-\beta(\varepsilon_{\boldsymbol{l}}-\mu)}) . \tag{6.64}$$

The average number of particles in the gas is

$$\langle N \rangle = -\left(\frac{\partial \Omega_{\mathrm{BE}}}{\partial \mu} \right)_{T,V} = \sum_{\boldsymbol{l}} \frac{1}{\mathrm{e}^{\beta(\varepsilon_{\boldsymbol{l}}-\mu)^{-1}}} = \sum_{\boldsymbol{l}} \langle n_{\boldsymbol{l}} \rangle , \tag{6.65}$$

where $\langle n_{\boldsymbol{l}} \rangle$ is the average number of particles in the state $\boldsymbol{l}$ and is defined

$$\langle n_{\boldsymbol{l}} \rangle = \frac{1}{\mathrm{e}^{\beta(\varepsilon_{\boldsymbol{l}}-\mu)-1}} = \frac{z}{\mathrm{e}^{\beta\varepsilon_{\boldsymbol{l}}} - z} . \tag{6.66}$$

The quantity $z = \mathrm{e}^{\beta\mu}$ is called the *fugacity*.

At low temperature, an ideal Bose–Einstein gas can undergo a phase transition. We get our first indication of this by looking at the distribution of particles among the energy levels. Since the exponential $\mathrm{e}^{\beta\varepsilon_{\boldsymbol{l}}}$ can only have values $1 \leq \mathrm{e}^{\beta\varepsilon_{\boldsymbol{l}}} \leq \infty$, the fugacity must have values $0 \leq z \leq 1$. Otherwise, $\langle n_{\boldsymbol{l}} \rangle$ could become negative, and that is unphysical since $\langle n_{\boldsymbol{l}} \rangle$ is the average number of particles in energy level $\varepsilon_{\boldsymbol{l}}$. Thus, for a Bose–Einstein gas the chemical potential, $\mu = k_{\mathrm{B}} T \ln(z)$, must be negative or zero. For the state with quantum numbers $\boldsymbol{l} = \boldsymbol{0}$, the energy, $\varepsilon_{\boldsymbol{0}} = 0$, and the average particle number, $\langle n_{\boldsymbol{0}} \rangle$, is given by

$$\langle n_{\boldsymbol{0}} \rangle = \frac{z}{1-z} . \tag{6.67}$$

Since $\lim_{z\to 1} \langle n_{\boldsymbol{0}} \rangle = \infty$, the state with zero energy can become macroscopically occupied as $z \to 1$. This is precisely what happens at the phase transition.

Let us now compute some thermodynamic quantities for the Bose–Einstein gas. We first compute the average particle number $\langle N \rangle = \sum_{\boldsymbol{l}} \langle n_{\boldsymbol{l}} \rangle$, where $\sum_{\boldsymbol{l}} =$

$\sum_{l_x=-\infty}^{\infty}\sum_{l_y=-\infty}^{\infty}\sum_{l_z=-\infty}^{\infty}$. It is useful to change the summation $\sum_{\boldsymbol{l}}$ to an integration. However, from Eq. (6.66) we see that the term in the sum with $l_x = 0$, $l_y = 0$, and $l_z = 0$ can become infinite as $z \to 1$, so it must be removed from the sum before we do this.

We can change the summation to an integration if we note the energy dispersion relation $\epsilon = p^2/(2m)$ and the relation between momentum and wave vector $\boldsymbol{p} = \hbar\boldsymbol{k}$. Then we find $\sum_{\boldsymbol{l}} \to \int \mathrm{d}\boldsymbol{l} = (V/h^3)\int \mathrm{d}\boldsymbol{p} = \int \mathrm{d}\epsilon g(\epsilon)$ where $g(\epsilon) = (m^{3/2}V\sqrt{\epsilon})/(2\pi^2\hbar^3)$ is the density of states and $V = L_xL_yL_z$.

Let us assume that $L_x > L_y > L_z$ so the lowest nonzero energy state is $\epsilon_{1,0,0} = 4\pi^2\hbar^2/(2mL_x^2)$. If we remove the term in the sum with $l_x = 0$, $l_y = 0$, and $l_z = 0$, the average particle number can be written

$$\langle N\rangle = \frac{z}{1-z} + \frac{Vm^{3/2}}{\sqrt{2}\pi^2\hbar^3}\int_{\frac{4\pi^2\hbar^2}{2mL_x^2}}^{\infty} \mathrm{d}\epsilon\epsilon^{1/2}\frac{z}{\exp(\beta\epsilon)-z} \tag{6.68}$$

or

$$\langle N\rangle = \frac{z}{1-z} + \frac{4\pi V}{(2\pi\hbar)^3}\int_{2\pi\hbar/L_x}^{\infty} p^2\,\mathrm{d}p\frac{z}{\exp[\beta p^2/(2m)]-z}\,, \tag{6.69}$$

where we have made the change of variables $\epsilon = p^2/(2m)$. Similarly, we can write the grand potential in the form

$$\Omega_{\mathrm{BE}}(T,V,\mu) = k_{\mathrm{B}}T\ln(1-z) + \frac{4\pi Vk_{\mathrm{B}}T}{(2\pi\hbar)^3} \times \int_{2\pi\hbar/L_x}^{\infty} p^2\,\mathrm{d}p\ln\{1-z\exp[-\beta p^2/(2m)]\}\,, \tag{6.70}$$

where we again have separated out the point at the origin. Note that

$$\lim_{L\to\infty}\int_0^{2\pi\hbar/L_x} p^2\,\mathrm{d}p\ln\{1-z\exp[-\beta p^2/(2m)]\} = 0\,, \tag{6.71}$$

so the lower limits on the integration can be set to zero in Eqs. (6.68)–(6.70).

It is useful to introduce dimensionless variables. If we let $x^2 = \beta p^2/(2m)$, and note that $\Omega = -PV$, the pressure of the Bose–Einstein gas can be written,

$$P = -\frac{\Omega_{\mathrm{BE}}}{V} = -\frac{k_{\mathrm{B}}T}{V}\ln(1-z) + \frac{k_{\mathrm{B}}T}{\lambda_T^3}g_{5/2}(z)\,, \tag{6.72}$$

where $\lambda_T = (2\pi\hbar^2/(mk_{\mathrm{B}}T))^{1/2}$ is the thermal wavelength and

$$g_{5/2}(z) = -\frac{4}{\sqrt{\pi}}\int_0^{\infty} x^2\,\mathrm{d}x\ln(1-z\mathrm{e}^{-x^2}) = \sum_{\alpha=1}^{\infty}\frac{z^{\alpha}}{\alpha^{5/2}}\,. \tag{6.73}$$

In Eq. (6.73), the summation is obtained by expanding the integrand in powers of z and integrating each term. The thermal wavelength λ_T is the deBroglie wavelength of a quantum particle with kinetic energy $k_B T$, and it is a measure of the spread of a wave function of the particles. When λ_T becomes of the same order of, or greater than, the average interparticle spacing, quantum effects begin to dominate.

Exercise 6.4

An ideal gas of bosons of mass m is confined to a harmonic potential (harmonic trap) which gives each boson a potential energy $V(\boldsymbol{r}) = 1/2m(\omega_1^2 x^2 + \omega_2^2 y^2 + \omega_3^2 z^2)$. (a) Compute the density of states. (b) Write an expression for the average particle number.

Answer: The energy levels available to each boson can be written $E_{l_1,l_2,l_3} = \hbar(l_1\omega_1 + l_2\omega_2 + l_3\omega_3) + E_0$, where $0 \le l_j \le \infty$ $(j = 1, 2, 3)$ and $E_0 = \hbar/2(\omega_1 + \omega_2 + \omega_3)$ is the zero point energy. Assume that a boson has energy E and let $\epsilon = E - E_0$ be the difference between that energy and the zero-point energy and let $\epsilon_j = \hbar l_j \omega_j$ $(j = 1, 2, 3)$. The states with energy ϵ lie in the plane $\epsilon = \epsilon_1 + \epsilon_2 + \epsilon_3$. The number of states $\eta(\epsilon)$ with energy ϵ is $\eta(\epsilon) = \int_0^\epsilon \mathrm{d}\epsilon_1 \int_0^{\epsilon-\epsilon_1} \mathrm{d}\epsilon_2 \int_0^{\epsilon-\epsilon_1-\epsilon_2} \mathrm{d}\epsilon_3 = \epsilon^3/(6\hbar^3\omega_1\omega_2\omega_3)$. The density of states is $g(\epsilon) = \mathrm{d}\eta(\epsilon)/\mathrm{d}\epsilon = \epsilon^2/(2\hbar^3\omega_1\omega_2\omega_3)$.

The average particle number can be written $\langle N \rangle = \sum_l \{z/[\exp(\beta E) - z]\}$. When $\mu = E_0$ and $l_1 = l_2 = l_3 = 0$, this can become infinite. Therefore, we must remove the term with $l_1 = l_2 = l_3 = 0$. We then obtain

$$\langle N \rangle = \frac{z}{e^{\beta E_0} - z} + \frac{1}{2\hbar^3\omega_1\omega_2\omega_3} \int_0^\infty \mathrm{d}\epsilon\,\epsilon^2 \left(\frac{z}{\exp[\beta(\epsilon + E_0)] - z} \right) .$$

We also obtain an equation for the average particle density,

$$\langle n \rangle = \frac{\langle N \rangle}{V} = \frac{1}{V}\frac{z}{1-z} + \frac{1}{\lambda_T^3} g_{3/2}(z) , \tag{6.74}$$

where

$$g_{3/2}(z) = z\frac{\mathrm{d}}{\mathrm{d}z} g_{5/2}(z) = \frac{4}{\sqrt{\pi}} \int_0^\infty x^2\,\mathrm{d}x \frac{z}{e^{x^2} - z} = \sum_{\alpha=1}^{\infty} \frac{z^\alpha}{\alpha^{3/2}} . \tag{6.75}$$

The quantities $g_{5/2}(z)$ and $g_{3/2}(z)$, which appear in Eqs. (6.72) and (6.74), are well-behaved functions of z. We plot them in Figure 6.6a. Both $g_{5/2}(z)$ and $g_{3/2}(z)$ remain bounded and approach finite values,

$$g_{5/2}(1) = \zeta\left(\frac{5}{2}\right) \approx 1.342\ldots \quad \text{and} \quad g_{3/2}(1) = \zeta\left(\frac{3}{2}\right) \approx 2.612\ldots , \tag{6.76}$$

as $z \to 1$, where $\zeta(5/2)$ and $\zeta(3/2)$ are Riemann zeta functions.

Finally, let us examine the functions $-(1/V)\ln(1-z)$ and $(1/V)[z/(1-z)]$ which appear in Eqs. (6.72) and (6.74). In Eq. (6.74), we fix $\langle n\rangle$ and T and let $V\to\infty$ and $z\to 1$. In the neighborhood of $z=1$, we will write $z = 1 - 1/(n_0 V)$, where n_0 is a constant, so $z\to 1$ in a systematic manner as $V\to\infty$. Then it is easy to see that

$$\lim_{V\to\infty}\left[-\frac{1}{V}\ln(1-z(V))\right] = 0 \quad \text{and} \quad \lim_{V\to\infty}\left(\frac{1}{V}\frac{z(V)}{1-z(V)}\right) = n_0 \,. \tag{6.77}$$

Thus, in the limit $V\to\infty$, we can neglect the contribution to pressure due to the term $-(1/V)\ln(1-z)$, but we must retain the contribution to the average particle density due to the term $(1/V)[z/(1-z)]$. We next examine the behavior of the function $(1/V)[z/(1-z)]$. In Figure 6.6b, we plot $(1/V)[z/(1-z)]$, as a function of z for increasing values of the volume, V. Note that for any given value V, it always becomes infinite as $z\to 1$. The larger the volume, the closer z must be to $z=1$ before the term $(1/V)[z/(1-z)]$ becomes significant.

Let us now take the thermodynamic limit in Eqs. (6.72) and (6.74). We let $V\to\infty$ and $\langle N\rangle\to\infty$ so that $\langle n\rangle = \langle N\rangle/V$ remains finite. The pressure then takes the form

$$P = \begin{cases} \frac{k_B T}{\lambda_T^3} g_{5/2}(z) & \text{if} \quad z < 1\,, \\ \frac{k_B T}{\lambda_T^3} g_{5/2}(1) & \text{if} \quad z = 1\,. \end{cases} \tag{6.78}$$

The average particle density takes the form

$$\langle n\rangle = \frac{\langle N\rangle}{V} = \begin{cases} \frac{1}{\lambda_T^3} g_{3/2}(z) & \text{if} \quad z < 1\,, \\ n_0 + \frac{1}{\lambda_T^3} g_{3/2}(1) & \text{if} \quad z = 1\,. \end{cases} \tag{6.79}$$

A somewhat exaggerated plot of $\langle n\rangle\lambda_T^3$, $n_0\lambda_T^3$, and $g_{3/2}(z)$ as a function of z is shown in Figure 6.7a. The plot is actually done at large but finite volume, so the growth of $n_0\lambda_T^3$ can be seen more clearly. The main contribution to the growth

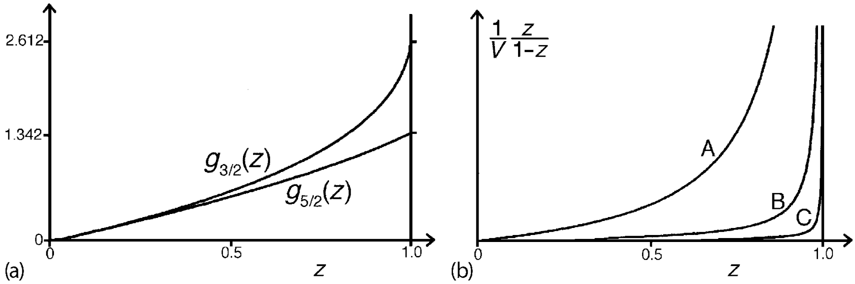

Figure 6.6 (a) Plots of $g_{5/2}(z)$ and $g_{3/2}(z)$ versus z. (b) Plots of $1/V[z/(1-z)]$ versus z for (A) $V=10$, (B) $V=100$, (C) $V=1000$.

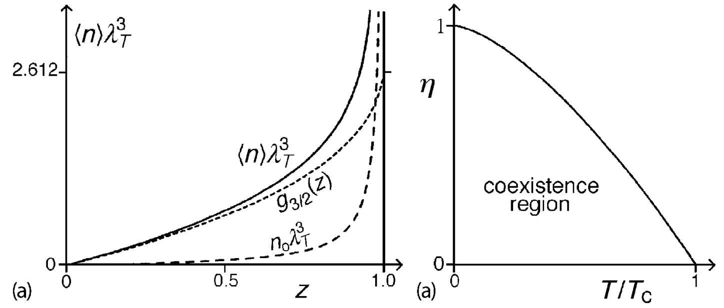

Figure 6.7 (a) Plots of $\langle n\rangle\lambda_T^3$, $g_{3/2}(z)$, and $n_0\lambda_T^3$ versus z. (The contribution of $n_0\lambda_T^3$ for $z < 1$ has been exaggerated by taking $V = 100$ rather than $V = \infty$.) (b) A plot of the order parameter, $\eta = n_0/\langle n\rangle$, versus temperature, T, for Bose–Einstein condensation.)

of the quantity $\langle n\rangle\lambda_T^3$ comes from $g_{3/2}(z)$ until z approaches $z = 1$. Then as $z \to 1$, $g_{3/2}(z)$ approaches a constant and $n_0\lambda_T^3$ determines the further growth of $\langle n\rangle\lambda_T^3$. This is *Bose–Einstein condensation*. What we are seeing as $z \to 1$ is the macroscopic condensation of particles into lowest energy state of the gas. The number density, n_0, of particles in the zero energy state, ε_0, becomes macroscopic in size.

The high-temperature behavior of the Bose–Einstein gas is readily obtained. At high temperature, $z \to 0$ and we only need to keep the first few terms in expansions of $g_{5/2}(z)$, $g_{3/2}(z)$, and $g_{1/2}(z)$ in powers of z. From Eq. (6.79) we obtain the average density,

$$\langle n\rangle = \frac{\langle N\rangle}{V} = \frac{1}{\lambda_T^3}\left(z + \frac{1}{2^{3/2}}z^2 + \dots\right) \tag{6.80}$$

and from Eq. (6.78) the pressure is

$$P = \frac{k_B T}{\lambda_T^3}\left(z + \frac{1}{2^{5/2}}z^2 + \dots\right). \tag{6.81}$$

We can revert the series in Eq. (6.80), and write z as a function of $\langle n\rangle$. If we substitute this series into Eq. (6.81), we obtain the virial expansion for an ideal boson gas. If we keep only the lowest-order term in z in Eqs. (6.80) and (6.81), we obtain the equation of state for an ideal classical gas, $P = \langle n\rangle k_B T$, and the specific heat $c_n = 3\langle n\rangle k_B/2$. Thus, at high temperature the Bose–Einstein gas behaves like an ideal classical gas.

6.7.1
Bose–Einstein Condensation

Bose–Einstein condensation begins to occur when the fugacity, $z \to 1$ (the chemical potential $\mu(T, \langle n\rangle) = k_B T \ln(z) \to 0$) so the temperature and average particle number satisfy the condition

$$\langle n\rangle\lambda_T^3 = g_{3/2}(1) \approx 2.612 \tag{6.82}$$

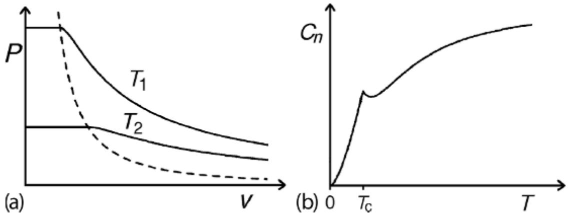

Figure 6.8 (a) A plot of the coexistence curve (dashed line) and some isotherms in the *P*–*v* plane for the phase transition in a Bose–Einstein gas. (b) A plot of the heat capacity per unit volume for a Bose–Einstein ideal gas as a function of the temperature. The temperature, T_c, is the critical temperature for the onset of Bose–Einstein condensation.

(cf. Eq. (6.79)). Equation (6.82) enables us to write the critical particle density, $\langle n\rangle_c$ (the particle density at which condensation occurs), as a function of temperature:

$$\langle n\rangle_c = \frac{1}{\langle v\rangle_c} = \frac{g_{3/2}(1)}{\lambda_T^3} \approx 2.612\left(\frac{mk_BT}{2\pi\hbar^2}\right)^{3/2}, \tag{6.83}$$

where $\langle v\rangle_c$ is the critical volume per particle. The critical temperature, T_c (the temperature at which condensation occurs), as a function of particle density is given by

$$\lambda_{T_c}^3 = \frac{g_{3/2}(1)}{\langle n\rangle} \quad \text{or} \quad T_c = \left(\frac{2\pi\hbar^2}{mk_B}\right)\left(\frac{\langle n\rangle}{g_{3/2}(1)}\right)^{2/3} \approx \left(\frac{2\pi\hbar^2}{mk_B}\right)\left(\frac{\langle n\rangle}{2.612}\right)^{2/3}. \tag{6.84}$$

The order parameter, η, for Bose–Einstein condensation is the fraction of particles in the condensed phase, $\eta = n_0/\langle n\rangle$. From Eqs. (6.79) and (6.84), we can write

$$\eta = \frac{n_0}{\langle n\rangle} = 1 - \frac{g_{3/2}(1)}{\langle n\rangle\lambda_T^3} = 1 - \frac{\lambda_{T_c}^3}{\lambda_T^3} = 1 - \left(\frac{T}{T_c}\right)^{3/2}. \tag{6.85}$$

A plot of the order parameter as a function of temperature is given in Figure 6.7b.

Equation (6.82) also determines the shape of the coexistence curve between the "normal" phase and the "condensed" phase of the gas. From Eq. (6.78), we see that for particle densities, $\langle n\rangle > \langle n\rangle_c$, the pressure becomes independent of particle density. If we now use Eq. (6.83), we can write the critical pressure, P_c, as a function of the critical volume per particle, $\langle v\rangle_c$:

$$P_c = \frac{2\pi\hbar^2 g_{5/2}(1)}{m(g_{3/2}(1))^{5/3}}\frac{1}{\langle v\rangle_c^{5/3}}. \tag{6.86}$$

A plot of the coexistence curve, Eq. (6.86), together with some isotherms in the *P*–*v* plane, is given in Figure 6.8a. In the region under the dashed curve, both condensed particles and noncondensed particles can coexist.

Another quantity of great interest in the neighborhood of a phase transition is the heat capacity. From Table 3.5, the entropy per unit volume is $s = (\partial S/\partial V)_{T,\mu} =$

$(\partial P/\partial T)_{V,\mu}$ (note that $s = (\partial S/\partial V)_{T,\mu}$ only if the gas is composed of a single type of particle). Therefore, from (6.78) we can compute the entropy and we obtain

$$s = \left(\frac{\partial P}{\partial T}\right)_{V,\mu} = \begin{cases} k_B \frac{5}{2}\frac{1}{\lambda_T^3} g_{5/2}(z) - k_B \langle n \rangle \ln z & \text{if} \quad z < 1\,, \\ k_B \frac{5}{2}\frac{1}{\lambda_T^3} g_{5/2}(1) & \text{if} \quad z = 1 \end{cases} \tag{6.87}$$

(we have made use of Eq. (6.79)). The Bose–Einstein gas clearly obeys the third law of thermodynamics. In the limit $T \to 0$ K, the entropy approaches zero with temperature dependence, $T^{3/2}$. We can also compute the heat capacity/volume, $c_n = T(\partial s/\partial T)_n$. Note that, when computing c_n, we hold n fixed and not μ. The computation of c_n requires the following quantity,

$$\left(\frac{\partial \beta\mu}{\partial T}\right)_n = -\frac{3}{2T}\frac{g_{3/2}(z)}{g_{1/2}(z)}\,. \tag{6.88}$$

Equation (6.88) is obtained by differentiating (6.79) with respect to T holding $\langle n \rangle$ fixed. The computation of c_n is then straightforward. We find

$$c_n = T\left(\frac{\partial s}{\partial T}\right)_n = \begin{cases} k_B \frac{15}{4}\frac{1}{\lambda_T^3} g_{5/2}(z) - \langle n \rangle k_B \frac{9}{4}\frac{g_{3/2}(z)}{g_{1/2}(z)} & \text{if} \quad z < 1\,, \\ k_B \frac{15}{4}\frac{1}{\lambda_T^3} g_{5/2}(1)\,, & \text{if} \quad z = 1\,. \end{cases} \tag{6.89}$$

In Figure 6.8b, we plot c_n for the Bose–Einstein gas. The location of the critical point is clear in the plot. In the high-temperature limit, the heat capacity approaches a constant value as we would expect for a classical ideal gas.

6.7.2
Experimental Observation of Bose–Einstein Condensation

The second-order phase transition in liquid ^{4}He$_2$, from the normal state (HeI) to the superfluid state (HeII), is thought to be related to Bose–Einstein condensation. However, liquid helium is very dense and strongly interacting and therefore is very different from an ideal gas. As a consequence, there has been no direct proof that the superfuid transition in ^{4}He$_2$ is, indeed, a form of Bose–Einstein condensation.

However, true Bose–Einstein condensation was recently observed in dilute gases of alkali atoms. It was first observed in a gas of rubidium atoms (^{87}Rb$_{37}$) in 1995 [6] at a temperature of $T = 1.7 \times 10^{-7}$ K. A few months later, Bose–Einstein condensation in a gas of sodium atoms (^{23}Na$_{11}$) [37] at a temperature of $T = 2 \times 10^{-6}$ K was reported. In the rubidium experiment, at the lowest temperatures achieved, about 2000 atoms formed the condensate. In the sodium experiment, which used slightly different techniques for trapping and cooling the gas, about $\times 10^5$ atoms remained in the condensate (a condensate with 2×10^5 ^{87}Rb$_{37}$ atoms was later obtained by a different group [80]). In 2001, the Nobel prize was awarded to Wieman and Cornell [6] for the rubidium experiment and Ketterle [37] for the sodium experiment (and for their subsequent studies of the properties of these condensates). Since these early experiments, Bose–Einstein condensation has been observed in $^7\mathrm{Li}_3$ [20] and $^1\mathrm{H}_1$ [62], and in a number of different laboratories around the world.

Neutral alkali atoms have equal numbers of electrons and protons (both spin-1/2 particles), so their statistics is determined by the number of neutrons (a spin-1/2 particle) in their nucleus. If an atom has an even (odd) number of neutrons, it is a boson (fermion). The alkali atoms, $^{87}\mathrm{Rb}_{37}$ and $^{23}\mathrm{Na}_{11}$, have an odd number of protons and an even number of neutrons, making them bosons. For alkali atoms, all but one of the electrons occupy closed shells. The remaining electron is in an s-orbital. For both $^{87}\mathrm{Rb}_{37}$ and $^{23}\mathrm{Na}_{11}$, the interaction between the atoms is repulsive. However, in these experiments the temperature is very low and the gas is dilute so the thermal wavelength is greater than the average interparticle spacing, and much greater than the range of the interaction. Thus, the atomic interactions play a very small role in the condensation process.

In both of the experiments [6] and [37], the gas was confined in an MOT (a magneto-optical trap), which is composed of a spatially varying magnetic field and laser radiation. Such devices can both cool and trap the gas [166]. The optical trap is formed with a magnetic field which interacts with the magnetic moment of the atoms and effectively confines the gas in a three-dimensional harmonic potential well. The critical temperature for Bose–Einstein condensation can be estimated for such systems. From Exercise 6.3, the critical particle number for Bose–Einstein condensation in a harmonic trap is

$$\langle N\rangle_\mathrm{c} = \frac{1}{2\hbar^3\omega_1\omega_2\omega_3}\int_0^\infty \mathrm{d}\epsilon\,\epsilon^2 \frac{1}{\exp(\beta\epsilon)-1} = \frac{k_\mathrm{B}^3 T^3 \zeta(3)}{\hbar^3\omega_1\omega_2\omega_3}\,, \tag{6.90}$$

where $\zeta(3) = 1.202$ is the Riemann zeta function and ω_1, ω_2, ω_3 are the frequencies of the harmonic trap (see Exercise 6.3). We can also write the critical temperature T_c in terms of the number of particles in the harmonic trap,

$$T_\mathrm{c} = \left(\frac{\langle N\rangle\omega_1\omega_2\omega_3}{1.202}\right)^{1/3}\frac{\hbar}{k_\mathrm{B}}\,. \tag{6.91}$$

(In Exercise 6.4, we estimate the condensation temperature of sodium for the experiment reported in [37].)

Exercise 6.5

Compute the Bose–Einstein condensation temperature for a gas of $N = 2\times10^6$ sodium atoms in an asymmetric harmonic trap with oscillation frequencies $f_1 = 235$, $f_2 = 410$, and $f_3 = 745\,\mathrm{Hz}$.

Answer: The condensation temperature is given by $T_\mathrm{c} = ((\langle N\rangle\omega_1\omega_2\omega_3)/1.202)^{1/3}\hbar/k_\mathrm{B}$, where $\omega_j = 2\pi f_j$. Plugging in $\hbar = 1.0546\times10^{-34}\,\mathrm{J\,s}$, $k_\mathrm{B} = 1.3807\times10^{-23}\,\mathrm{J/K}$, $\langle N\rangle = 2\times10^6$, $\omega_1 = 2\pi(235)\,\mathrm{rad/s}$, $\omega_2 = 2\pi(410)\,\mathrm{rad/s}$, and $\omega_3 = 2\pi(745)\,\mathrm{rad/s}$, we obtain $T_\mathrm{c} = 2.0\times10^{-6}\,\mathrm{K}$ [37].

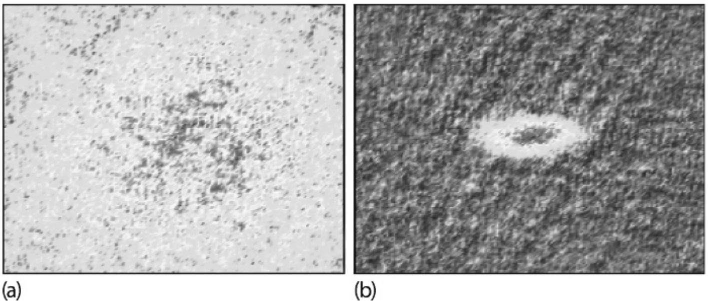

Figure 6.9 Ballistic motion of rubidium atoms after they have been released from a harmonic trap for (a) temperature above condensation ($T = 755$ nK and $N = 1.1 \times 10^7$ particles); (b) temperature below condensation ($T = 169$ nK and $N = 9.2 \times 10^5$ condensed particles). In (a) the cloud is thermal and in (b) the cloud has the shape of the ground state of the trap and shows little expansion (Figures from D.J. Heinzen).

Bose–Einstein condensation for atoms in harmonic traps is observed by performing the experiment several times, each at a different final temperature. In a given experiment, once the final temperature is reached, the trap magnetic field is turned off and the subsequent ballistic motion of the atoms is observed. If the final temperature is above the condensation temperature, the energy of the atoms has a thermal distribution and the cloud of atoms expands in a thermal manner (see Figure 6.9a). If the temperature is below the condensation temperature, most atoms will be in the quantum ground state of the harmonic trap. They will hardly move when the magnetic field is turned off and they will form an asymmetric cloud (see Figure 6.9b), reflecting the fact that the ground state of a spatially asymmetric harmonic potential is spatially asymmetric.

6.8
Bogoliubov Mean Field Theory

Bose-Einstein condensates created in the laboratory are not ideal gases. They are gases of interacting bosons with very low temperature and density. A mean field theory that accounts for the interactions between bosons, and describes many properties of real BECs, was developed by Bogoliubov [17, 73, 167, 168]. As a first step in deriving the Bogoliubov mean field theory, we must add an interaction term to the kinetic energy in Eq. (6.57). Then the Hamiltonian, in the number representation, takes the form (see Appendix D)

$$\hat{H} = \sum_{\boldsymbol{k}} \frac{\hbar^2 k^2}{2m} \hat{\alpha}^\dagger_{\boldsymbol{k}} \hat{\alpha}_{\boldsymbol{k}} + \frac{1}{2V} \sum_{\boldsymbol{k}_1,\boldsymbol{k}_2,\boldsymbol{k}_3,\boldsymbol{k}_4} \langle \boldsymbol{k}_1, \boldsymbol{k}_2 | \hat{V} | \boldsymbol{k}_3, \boldsymbol{k}_4 \rangle \hat{\alpha}^\dagger_{\boldsymbol{k}_1} \hat{\alpha}^\dagger_{\boldsymbol{k}_2} \hat{\alpha}_{\boldsymbol{k}_4} \hat{\alpha}_{\boldsymbol{k}_3} , \tag{6.92}$$

where V is the volume of the BEC, $\boldsymbol{k}_i$ are the wavevectors of the particles, and $\hat{V} = \hat{V}(r)$ is the interaction potential energy between bosons (r is the relative displacement). The operator $\hat{\alpha}^\dagger_{\boldsymbol{k}}$ ($\hat{\alpha}_{\boldsymbol{k}}$) creates (annihilates) a particle with momentum $\hbar\boldsymbol{k}$. The particle creation and annihilation operators satisfy the boson commutation relations $[\hat{\alpha}_{\boldsymbol{k}_1}^\dagger, \hat{\alpha}_{\boldsymbol{k}_2}^\dagger] = \delta_{\boldsymbol{k}_1,\boldsymbol{k}_2}$, where $\delta_{\boldsymbol{k}_1,\boldsymbol{k}_2}$ is the product of three Kronecker delta functions, one for each component of the momentum.

At very low temperatures, the particles have very little energy so collisions between particles can be described solely in terms of the scattering length a of the collision process. It is therefore possible to replace the detailed potential energy between particles by the "contact" potential energy $\mathrm{V}(r) = g\delta(r)$, where $g = 4\pi\hbar^2\mathsf{a}/m$ (see Appendix E). Then the Hamiltonian takes the form

$$\hat{H} = \sum_{\boldsymbol{k}} \frac{\hbar^2 k^2}{2m} \hat{\alpha}_{\boldsymbol{k}}^\dagger \hat{\alpha}_{\boldsymbol{k}} + \frac{g}{2V} \sum_{\boldsymbol{k}_1,\boldsymbol{k}_2,\boldsymbol{k}_3,\boldsymbol{k}_4} \delta_{\boldsymbol{k}_1+\boldsymbol{k}_2-\boldsymbol{k}_3-\boldsymbol{k}_4} \hat{\alpha}_{\boldsymbol{k}_1}^\dagger \hat{\alpha}_{\boldsymbol{k}_2}^\dagger \hat{\alpha}_{\boldsymbol{k}_4} \hat{\alpha}_{\boldsymbol{k}_3} \,. \tag{6.93}$$

The summations run over all single-particle states for both positive and negative components of $\boldsymbol{k}_i$.

At very low temperature, a macroscopic number of particles N_0 will be condensed into the lowest energy state $\boldsymbol{k} = 0$. However, since the particles can interact, particles can enter and leave the condensate via interactions, so even at $T = 0\mathrm{K}$ not all particles will have wavevector $\boldsymbol{k} = \boldsymbol{0}$. If $\Delta N = N - N_0$ is the number of excited particles, then typically $\Delta N/N \sim 0.01$ at $T = 0\,\mathrm{K}$. Since there are a macroscopic number of particles in the ground state, we can approximate the operators $\hat{\alpha}_{\boldsymbol{0}}$ and $\hat{\alpha}_{\boldsymbol{0}}^\dagger$ by the *number* $\sqrt{N_0}$, and neglect their operator character.

We now write the particle creation and annihilation operators in the form $\hat{\alpha}_{\boldsymbol{0}}^\dagger = \hat{\alpha}_{\boldsymbol{0}} = \sqrt{N_0}$ for $\boldsymbol{k} = \boldsymbol{0}$ and $\hat{\alpha}_{\boldsymbol{k}}^\dagger = \hat{a}_{\boldsymbol{k}}^\dagger$, $\hat{\alpha}_{\boldsymbol{k}} = \hat{a}_{\boldsymbol{k}}$ for $\boldsymbol{k} \neq \boldsymbol{0}$. Then, keeping terms to second order in $\hat{a}_{\boldsymbol{k}}^\dagger$ and $\hat{a}_{\boldsymbol{k}}$ (and requiring momentum conservation), the Bogoliubov mean field Hamiltonian can be written the form

$$\hat{H} = \frac{gN_0^2}{2V} + \frac{1}{2}\sum_{\boldsymbol{k}\neq\boldsymbol{0}} \left[(\epsilon_k + \nu)\left(\hat{a}_{\boldsymbol{k}}^\dagger \hat{a}_{\boldsymbol{k}} + \hat{a}_{-\boldsymbol{k}}^\dagger \hat{a}_{-\boldsymbol{k}}\right) + \varDelta\left(\hat{a}_{\boldsymbol{k}}^\dagger \hat{a}_{-\boldsymbol{k}}^\dagger + \hat{a}_{-\boldsymbol{k}} \hat{a}_{\boldsymbol{k}}\right)\right] , \tag{6.94}$$

where $\epsilon_k = \hbar^2 k^2/(2m)$, $\nu = 2gN_0/V$, and $\varDelta = gN_0/V$. Note that $\varDelta$ is the order parameter for the condensed phase. The particle number operator can be written $\hat{N} = N_0 + \sum_{\boldsymbol{k}\neq\boldsymbol{0}} \hat{a}_{\boldsymbol{k}}^\dagger \hat{a}_{\boldsymbol{k}}$. The quantities ν and $\varDelta$ depend on temperature and density of the gas. However, in the limit $T \to 0\,\mathrm{K}$, this dependence can be neglected, as a first approximation. However, for higher temperatures, this dependence cannot be neglected (we discuss this further below).

Let us now consider the thermodynamic properties of the gas. Using Bogoliubov mean field theory, the grand potential can be written

$$\varOmega = -k_{\mathrm{B}} T \ln\left[\mathrm{Tr}\left(\mathrm{e}^{-\beta(K_0+\hat{K})}\right)\right] \tag{6.95}$$

where $K_0 = gN_0^2/(2V) - \mu N_0$ and

$$\hat{K} = \sum_{\boldsymbol{k}} \left[(\epsilon_k + \nu - \mu)\, \hat{a}_{\boldsymbol{k}}^\dagger \hat{a}_{\boldsymbol{k}} + \frac{\varDelta}{2}\left(\hat{a}_{\boldsymbol{k}}^\dagger \hat{a}_{-\boldsymbol{k}}^\dagger + \hat{a}_{-\boldsymbol{k}} \hat{a}_{\boldsymbol{k}}\right)\right] . \tag{6.96}$$

We can "diagonalize" $\hat{K}$ using the Bogoliubov transformation

$$\hat{a}_{\boldsymbol{k}}^\dagger = (u_k \hat{b}_{\boldsymbol{k}}^\dagger - v_k \hat{b}_{-\boldsymbol{k}}) \quad \text{and} \quad \hat{a}_{\boldsymbol{k}} = (u_k \hat{b}_{\boldsymbol{k}} - v_k \hat{b}_{-\boldsymbol{k}}^\dagger) \,, \tag{6.97}$$

where $\hat{b}_{\boldsymbol{k}}^{\dagger}$ and $\hat{b}_{\boldsymbol{k}}$ are *bogolon* creation and annihilation operators, respectively (bogolons are collective excitations in the BEC). The bogolon creation and annihilation operators satisfy the boson commutation relations $[\hat{b}_{\boldsymbol{k}}, \hat{b}_{\boldsymbol{k}}^{\dagger}] = 1$, and this requirement leads to the condition that $u_k^2 - v_k^2 = 1$. The Bogoliubov transformation diagonalizes $\hat{K}$, so that

$$\hat{K} = \sum_{\boldsymbol{k} \neq 0} E_k \hat{b}_{\boldsymbol{k}}^{\dagger} \hat{b}_{\boldsymbol{k}} + \frac{1}{2} \sum_{\boldsymbol{k} \neq 0} \left[E_k - \left(\epsilon_k + \nu - \mu \right) \right] , \tag{6.98}$$

if u_k, v_k, and the bogolon excitation energy E_k are defined

$$u_k = \frac{1}{\sqrt{2}} \sqrt{\frac{\epsilon_k + \nu - \mu}{E_k} + 1}, \quad v_k = \frac{1}{\sqrt{2}} \sqrt{\frac{\epsilon_k + \nu - \mu}{E_k} - 1} \tag{6.99}$$

and

$$E_k = \sqrt{\left(\epsilon_k + \nu - \mu \right)^2 - \Delta^2} \tag{6.100}$$

(derivation of E_k, u_k, v_k is left as a homework problem).

A Bose–Einstein condensate has no gap in its energy spectrum. This differs from a superconductor, which does have a gap due to the binding energy of the bound electron pairs that must form in order for condensation to take place. As was pointed out by Hugenholtz and Pines [86], the requirement for a gapless spectrum imposes a condition on the chemical potential, namely $\mu = \nu - \Delta$. The bogolon excitation energy then takes the form

$$E_k = \sqrt{\left(\epsilon_k + \Delta \right)^2 - \Delta^2} \tag{6.101}$$

and the parameters u_k and v_k are given by.

$$u_k = \frac{1}{\sqrt{2}} \sqrt{\frac{\epsilon_k + \Delta}{E_k} + 1} \quad \text{and} \quad v_k = \frac{1}{\sqrt{2}} \sqrt{\frac{\epsilon_k + \Delta}{E_k} - 1} \, . \tag{6.102}$$

Note that the bogolon spectrum is phonon-like ($E_k \sim k$) at very low energies and particle-like ($E_k \sim k^2$) at higher energies.

The grand potential can now be written

$$\begin{aligned} \Omega = & -k_{\mathrm{B}} T \ln \left[\mathrm{Tr} \left(\mathrm{e}^{-\beta K_0} \right) \right] - k_{\mathrm{B}} T \ln \left[\mathrm{Tr} \left(\mathrm{e}^{-\beta \sum_{\boldsymbol{k} \neq 0} E_k \hat{b}_{\boldsymbol{k}}^{\dagger} \hat{b}_{\boldsymbol{k}}} \right) \right] \\ & - k_{\mathrm{B}} T \ln \left[\mathrm{Tr} \left(\mathrm{e}^{-\frac{\beta}{2} \sum_{\boldsymbol{k} \neq 0} \left[E_k - \left(\epsilon_k + \Delta \right) \right)\right]} \right) \right] \end{aligned} \tag{6.103}$$

or

$$\Omega = -\frac{g N_0^2}{2V} + k_{\mathrm{B}} T \sum_{\boldsymbol{k} \neq 0} \ln \left(1 - \mathrm{e}^{-\beta E_k} \right) + \frac{1}{2} \sum_{\boldsymbol{k} \neq 0} E_k - \left(\epsilon_k + \Delta \right) . \tag{6.104}$$

The last term in Eq. (6.104), which contributes to the ground state energy, has an ultra-violet divergence. However, the divergence is a consequence of the approximations made in deriving the simple mean field Hamiltonian in Eq. (6.94). This divergence can be removed by keeping additional contributions and then gives a negligible contribution to the properties of the BEC (see [73] for further discussion), so we neglect this term in the subsequent discussion.

We can now rewrite the thermodynamic expressions using these approximations. The average particle number takes the form

$$\langle N\rangle = N_0 + \sum_{\boldsymbol{k}\neq 0}\frac{\epsilon_k + \Delta}{E_k}\frac{1}{\mathrm{e}^{\beta E_k}-1} \tag{6.105}$$

and the entropy is given by

$$S = \left(\frac{\partial\Omega}{\partial T}\right)_{V,\mu} = -k_\mathrm{B}\sum_{\boldsymbol{k}\neq 0}\ln(1-\mathrm{e}^{\beta E_k}) + \sum_{\boldsymbol{k}\neq 0}\frac{E_k}{T}\frac{1}{\mathrm{e}^{\beta E_k}-1}\ . \tag{6.106}$$

The pressure is given by $P = -\frac{\Omega}{V}$ so that

$$P = \frac{gN_0^2}{2V^2} - \frac{k_\mathrm{B}T}{V}\sum_{\boldsymbol{k}\neq 0}\ln\left(1-\mathrm{e}^{-\beta E_k}\right)\ . \tag{6.107}$$

The heat capacity can be obtained from the expression for the entropy. We obtain

$$C_{V,N} = \left(\frac{\partial S}{\partial T}\right)_{V,N} = \frac{1}{k_\mathrm{B}T^2}\sum_{\boldsymbol{k}\neq 0}E_k^2\frac{\mathrm{e}^{\beta E_k}}{\left(\mathrm{e}^{\beta E_k}-1\right)^2}\ . \tag{6.108}$$

Let us examine the behavior of these quantities at ultra-low temperature. We first introduce dimensionless units. We write energy in units of $E_\mathsf{a} = k_\mathrm{B}T_\mathsf{a} \equiv \hbar^2/(2m\mathsf{a}^2)$, which is the energy of a particle with wavelength of order of the s-wave scattering length. Ultra-low energy means that most particles have thermal energy $k_\mathrm{B}T$ much lower than E_a. This requires temperatures $T \ll T_\mathsf{a}$. In terms of dimensionless units, the bogolon energy is

$$E_k = \sqrt{\left(\frac{\hbar^2k^2}{2m}+\Delta\right)^2-\Delta^2} = \frac{\hbar^2}{2m\mathsf{a}^2}\sqrt{\left(\kappa^2+\mathsf{d}\right)^2-\mathsf{d}^2} \tag{6.109}$$

where $\kappa = k\mathsf{a}$ is a dimensionless measure of the wavelength of the particles (relative to the scattering length), and $\mathsf{d} = 8\pi\mathsf{a}^3N_0/V$ is a dimensionless measure of the density of the particles. Both κ and d are small for an ultra-low temperature dilute gas. If we expand the bogolon energy for $\kappa \ll \mathsf{d}$, we obtain

$$E_k = k_\mathrm{B}T_\mathsf{a}\left(\sqrt{2\mathsf{d}}\kappa + \frac{\kappa^3}{2\sqrt{2\mathsf{d}}} + \ldots\right) = k_\mathrm{B}T_\mathsf{a}\sqrt{2\mathsf{d}}\left(\kappa + \frac{\kappa^3}{4\mathsf{d}} + \ldots\right) \tag{6.110}$$

For Rubidium, some typical numbers are $m = 87\ \mathrm{u} = 1.44\times10^{-25}$ kg, $\mathsf{a} = 105a_0 = 5.0\times10^{-9}$ m, $T = 7.25\times10^{-9}$ K (from experiment), $k_\mathrm{B}T = 1.0\times10^{-31}$ J, $\mathsf{d} = 1.0\times$

10^{-5}, and $k_B T_a = \hbar^2/(2ma^2) = 1.44 \times 10^{-30}$ J. Note that the temperature quoted above for the experiment does not quite put us in the ultra-low temperature limit in the sense that $T \ll T_a$.

We now compute various thermodynamic quantities in the ultra-low temperature limit $T \ll T_a$. First consider the heat capacity. Assuming a very large volume for the gas, we can change the summation to an integration and write

$$C_{N,V} = \frac{1}{k_B T^2} \sum_{k \neq 0} E_k^2 \frac{e^{\beta E_k}}{(e^{\beta E_k} - 1)^2} = \frac{1}{k_B T^2} 4\pi \frac{V}{(2\pi)^3} \int_0^\infty dk k^2 E_k^2 \frac{e^{\beta E_k}}{(e^{\beta E_k} - 1)^2} . \tag{6.111}$$

For $T \ll T_a$, we make the approximation $E_k = k_B T_a \sqrt{2d}\kappa$. Then the heat capacity takes the form

$$\begin{aligned} C_{N,V} &\approx \frac{4\pi}{k_B T^2} \frac{V}{(2\pi)^3} \frac{2d k_B^2 T_a^2}{a^3} \int_0^\infty d\kappa \kappa^4 \frac{e^{T_a \sqrt{2d}\kappa/T}}{(e^{T_a \sqrt{2d}\kappa/T} - 1)^2} \\ &= k_B V \frac{\pi^2}{\sqrt{2}15} \frac{1}{a^3 d^{3/2}} \left(\frac{T}{T_a} \right)^3 . \end{aligned} \tag{6.112}$$

Thus, the heat capacity at ultra-low temperature goes to zero as T^3 when $T \to 0$ K, which is the same as a gas of photons or phonons. The pressure can be written

$$\begin{aligned} P &= \frac{g}{2} \left(\frac{N_0}{V} \right)^2 + \frac{k_B T}{(2\pi)^3} \frac{4\pi}{a^3} \int d\kappa \kappa^2 \ln \left(1 - e^{-T_a \sqrt{2d}\kappa/T} \right) \\ &= \frac{g}{2} \left(\frac{N_0}{V} \right)^2 - \frac{k_B \pi^2 T^4}{189 \sqrt{2} a^3 T_a^3 d^{3/2}} \end{aligned} \tag{6.113}$$

so at $T = 0$ K there is a residual pressure proportional to the scattering length.

The Bogoliubov mean field theory, derived here, gives good agreement with experiment for ultra-low temperature BECs. A generalization of the theory, called the HFB-Popov approximation (HFB is Hartree–Fock Bogoliubov) [43, 73] allows for the self-consistent variation of the mean fields ν and Δ with temperature and density. Predictions of the HFB-Popov approximation have been shown to describe well the results of experiment for the temperature range $0 \leq T/T_c \leq 0.6$ K [43, 78], where T_c is the critical temperature of the BEC.

6.9
Ideal Fermi–Dirac Gas

We now examine the thermodynamic behavior of a gas of indistinguishable, noninteracting, spin $s = 1/2$ fermions with mass m. For simplicity, we shall assume the gas is in a cubic box so $L_x = L_y = L_z = L$. In order to include the effects of spin, we must generalize the expression for the grand partition function given in Eq. (6.62). Spin 1/2 particles can exist in two spin states, $s_z = \pm\hbar/2$. Therefore, each energy level can be occupied with up to two particles (one particle for each of the two spin states) and not violate the Pauli exclusion principle. We will let $n_{\boldsymbol{l},\sigma}$ denote the number of particles with quantum numbers $\boldsymbol{l} = (l_x, l_y, l_z)$ and spin σ, where $\sigma = \uparrow (\downarrow)$ for $s_z = +\hbar/2(-\hbar/2)$. The grand partition function takes the form

$$\begin{aligned} Z_{\mathrm{FD}}(T, V, \mu) &= \prod_{\boldsymbol{l}=0}^{\infty} \left(\sum_{n_{\boldsymbol{l}\uparrow}=0}^{1} \mathrm{e}^{-\beta n_{\boldsymbol{l},\uparrow}(\varepsilon_1 - \mu)} \sum_{n_{\boldsymbol{l},\downarrow}=0}^{1} \mathrm{e}^{-\beta n_{\boldsymbol{l},\downarrow}(\varepsilon_{\boldsymbol{l}} - \mu)} \right) \\ &= \prod_{\boldsymbol{l}} (1 + \mathrm{e}^{-\beta(\varepsilon_{\boldsymbol{l}} - \mu)})^2 \; . \end{aligned} \tag{6.114}$$

The power of 2 is due to the fact that there are two possible spin states for each set of quantum numbers, $\boldsymbol{l}$. If we are dealing with a gas of spin-s fermions, then there will be $g = 2s + 1$ spin states for each value of $\boldsymbol{l}$ and the grand partition function takes the form

$$Z_{\mathrm{FD}}(T, V, \mu) = \prod_{\boldsymbol{l}} (1 + \mathrm{e}^{-\beta(\varepsilon_{\boldsymbol{l}} - \mu)})^g \; . \tag{6.115}$$

The grand potential is then given by

$$\Omega_{\mathrm{FD}}(T, V, \mu) = -k_{\mathrm{B}} T \ln Z_{\mathrm{FD}}(T, V, \mu) = -k_{\mathrm{B}} T g \sum_{\boldsymbol{l}} \ln(1 + \mathrm{e}^{-\beta(\varepsilon_{\boldsymbol{l}} - \mu)}) \; . \tag{6.116}$$

The average number of particles in the Fermi–Dirac gas is

$$\langle N \rangle = -\left(\frac{\partial \Omega_{\mathrm{FD}}}{\partial \mu} \right)_{T,V} = \sum_{\boldsymbol{l}} \frac{g}{\mathrm{e}^{\beta(\varepsilon_{\boldsymbol{l}} - \mu)} + 1} = \sum_{\boldsymbol{l}} \langle n_{\boldsymbol{l}} \rangle \; , \tag{6.117}$$

where $\langle n_{\boldsymbol{l}} \rangle$ is the average number of particles with quantum numbers $\boldsymbol{l}$ and is defined

$$\langle n_{\boldsymbol{l}} \rangle = \frac{g}{\mathrm{e}^{\beta(\varepsilon_{\boldsymbol{l}} - \mu)} + 1} = \frac{gz}{\mathrm{e}^{\beta \varepsilon_{\boldsymbol{l}}} + z} \; . \tag{6.118}$$

The quantity $z = \mathrm{e}^{\beta\mu}$ is the fugacity. For Fermi–Dirac particles, the fugacity can take on the entire range of values $0 \leq z \leq \infty$, and the average particle number can take on a range of value $0 \leq \langle n_{\boldsymbol{l}} \rangle \leq g$. In Figure 6.10a, we plot $\langle n_{\boldsymbol{l}} \rangle$ as a function of $\varepsilon_{\boldsymbol{l}}$ at low temperature (solid line) and at $T = 0\,\mathrm{K}$ (dashed line). We see that at low temperature the particles completely fill all the states with lowest energy. Only those states at higher energy are partly occupied. At zero temperature, all states below a cutoff energy, $\varepsilon_{\mathrm{f}} = \mu_0$ are occupied (ε_{f} is called the *Fermi energy*). The momentum, $p_{\mathrm{f}} = \sqrt{2m\varepsilon_{\mathrm{f}}}$, is called the *Fermi momentum*. The distribution of particles in momentum space at low temperature is like a "sea" with all the lower states filled with particles. Only particles in states near the "top" of the "sea" can

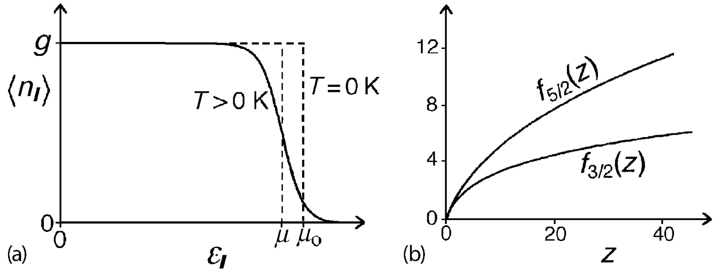

Figure 6.10 (a) Plots of the average occupation number, $\langle n_l \rangle$, as a function of energy, ε_l, at very low temperature. The solid line is a plot for $T > 0$ K, and the dashed line is a plot for $T = 0$ K. μ is the chemical potential. (b) Plots of $f_{5/2}(z)$ and $f_{3/2}(z)$ versus z.

change their state. For this reason this distribution of particles at low temperatures is called the *Fermi sea*.

Let us now compute the thermodynamic properties of the Fermi–Dirac gas. For large enough volume, V, we can change the summation, $\sum_l$, to an integration,

$$\sum_l \approx \frac{4\pi V}{(2\pi\hbar)^3}\int_0^\infty p^2\,\mathrm{d}p\,. \tag{6.119}$$

The grand potential then takes the form

$$\Omega_{\mathrm{FD}}(T, V, \mu) = -PV = -\frac{4\pi k_{\mathrm{B}} T V}{(2\pi\hbar)^3}\int_0^\infty p^2\,\mathrm{d}p\,\ln\left(1 + z\mathrm{e}^{\beta p^2/(2m)}\right). \tag{6.120}$$

Similarly, the average particle number can be written

$$\langle N \rangle = \frac{4\pi g V}{(2\pi\hbar)^3}\int_0^\infty p^2\,\mathrm{d}p\left(\frac{z}{\mathrm{e}^{\beta p^2/(2m)} + z}\right). \tag{6.121}$$

Let us now make the change of variables, $x^2 = \beta p^2/(2m)$, in Eqs. (6.120) and (6.121). The pressure of the Fermi–Dirac gas takes the form

$$P = -\frac{\Omega_{\mathrm{FD}}}{V} = \frac{g k_{\mathrm{B}} T}{\lambda_T^3} f_{5/2}(z)\,, \tag{6.122}$$

where λ_T is the thermal wavelength $\lambda_T = h/\sqrt{2\pi m k_{\mathrm{B}} T}$ (see Eq. (5.25)) and the function $f_{5/2}(z)$ is defined as

$$f_{5/2}(z) = \frac{4}{\sqrt{\pi}}\int_0^\infty x^2\,\mathrm{d}x\,\ln\left(1 + z\mathrm{e}^{-x^2}\right) = \sum_{\alpha=1}^{\infty}(-1)^{\alpha+1}\frac{z^\alpha}{\alpha^{5/2}}\,. \tag{6.123}$$

The average particle density can be written

$$\langle n \rangle = \frac{\langle N \rangle}{V} = \frac{g}{\lambda_T^3} f_{3/2}(z)\,, \tag{6.124}$$

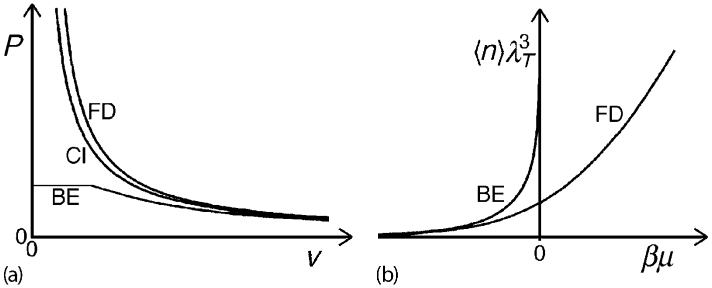

Figure 6.11 (a) Plots of the pressure of a Fermi–Dirac (FD), a Bose–Einstein (BE), and a classical (Cl) ideal gas as a function of volume per particle assuming the particles have the same mass and neglecting spin. One isotherm for each gas is shown. The temperatures of the three isotherms are the same. (b) Plots of $\langle n\rangle\lambda_T^3$ versus $\beta\mu$ for a Bose–Einstein (BE) and Fermi–Dirac (FD) gas.

where

$$f_{3/2}(z) = z\frac{\mathrm{d}}{\mathrm{d}z}f_{5/2}(z) = \frac{4}{\sqrt{\pi}}\int_0^\infty x^2\,\mathrm{d}x\frac{z}{\mathrm{e}^{x^2}+z} = \sum_{\alpha=1}^{\infty}(-1)^{\alpha+1}\frac{z^\alpha}{\alpha^{3/2}}\,. \tag{6.125}$$

In Figure 6.10b, we plot $f_{5/2}(z)$ and $f_{3/2}(z)$ as a function of z.

It is interesting to compare the pressure of an ideal Fermi gas with that of an ideal classical gas and an ideal Bose–Einstein gas. In Figure 6.11a, we plot P versus the average volume per particle, $v = \langle n\rangle^{-1}$ and show one isotherm of the same temperature for each gas. For the Fermi–Dirac gas we set $g = 1$ so we are comparing only the effect of statistics. The pressure of the Bose–Einstein gas is dramatically lower than the classical or Fermi–Dirac gas for small v. This happens because in a Bose–Einstein gas at low v (below the critical volume per particle) a macroscopic number of particles condense into the zero momentum state and can no longer contribute to the pressure. Conversely, the pressure of the Fermi–Dirac gas always lies a little above that of the classical gas, because the Fermi–Dirac gas will contain more particles at higher momentum (due to the Pauli exclusion principle) and will have a higher pressure than the classical gas.

It is useful to examine the behavior of the quantity, $\langle n\rangle\lambda_T^3$, as a function of the chemical potential, μ. In Figure 6.11b, we plot $\langle n\rangle\lambda_T^3$ versus the product, $\beta\mu$, for both a Fermi–Dirac and Bose–Einstein ideal gas. We see that the chemical potential of the Bose–Einstein gas remains negative and that the dominant growth in $\langle n\rangle\lambda_T^3$ occurs as $\mu \to 0$. For the Fermi–Dirac gas the product, $\beta\mu$, can be positive or negative and the dominant growth in $\langle n\rangle\lambda_T^3$ occurs when $\beta\mu$ is positive. The chemical potential for a Fermi–Dirac gas approaches a positive finite constant as $T \to 0\,\mathrm{K}$.

We can revert the series expansion of $\langle n\rangle\lambda_T^3/g$ (see Eqs. (6.124) and (6.125)) and obtain a series expansion for the fugacity z in terms of $\langle n\rangle\lambda_T^3/g$,

$$z = \mathrm{e}^{\beta\mu} = \frac{\langle n\rangle\lambda_T^3}{g} + \frac{1}{2^{3/2}}\left(\frac{\langle n\rangle\lambda_T^3}{g}\right)^2 + \left(\frac{1}{2^2} - \frac{1}{3^{3/2}}\right)\left(\frac{\langle n\rangle\lambda_T^3}{g}\right)^3 + \cdots \tag{6.126}$$

The coefficients of various powers of the quantity, $\langle n\rangle\lambda_T^3/g$, will always be positive. Thus, as $T \to \infty$, $z \to 0$ and the product, $\beta\mu$, must be large and negative. At high temperature, where $\beta \to 0$, the chemical potential $\mu \to -\infty$. For low temperatures, $z \to \infty$ and $\beta\mu \to \infty$. Since $\beta \to \infty$, in the limit $T \to 0$ the chemical potential can remain finite and indeed it does.

Let us now compute the thermodynamic properties of the ideal Fermi–Dirac gas at low temperatures. We first examine the behavior of $f_{3/2}(z)$, which we write in the form

$$f_{3/2}(z) = \frac{4}{\sqrt{\pi}}\int_0^\infty \mathrm{d}x \frac{x^2}{\mathrm{e}^{x^2-\nu}+1} = \frac{2}{\sqrt{\pi}}\int_0^\infty \mathrm{d}y \frac{\sqrt{y}}{\mathrm{e}^{y-\nu}+1}$$
$$= \frac{4}{3\sqrt{\pi}}\int_0^\infty \mathrm{d}y\, y^{3/2}\frac{\mathrm{e}^{y-\nu}}{(1+\mathrm{e}^{y-\nu})^2} \,. \tag{6.127}$$

We have let $y = x^2$ and $\nu = \beta\mu$ in the second integral and we have integrated by parts in the last integral. The function $\Delta(y,\nu) \equiv \mathrm{e}^{y-\nu}/(1+\mathrm{e}^{y-\nu})^2$, which appears in the last integral, is essentially the derivative of the occupation number $\langle n_l\rangle$, and at low temperature is sharply peaked about $y = \nu = \beta\mu$ where the strongest variation in $\langle n_l\rangle$ occurs (cf. Figure 6.12a). Thus, to perform the integration in Eq. (6.127), we may expand $y^{3/2}$ in a Taylor series about $y = \nu$. If we then let $t = (y-\nu)$, we can write $f_{3/2}(z)$ as

$$f_{3/2}(z) = \frac{4}{3\sqrt{\pi}}\int_{-\nu}^\infty \mathrm{d}t \frac{\mathrm{e}^t}{(1+\mathrm{e}^t)^2}\left(\nu^{3/2} + \frac{3}{2}\nu^{1/2}t + \frac{3}{8}\nu^{-1/2}t^2 + \cdots\right) \,. \tag{6.128}$$

The contribution from the lower limit in the integral will be of order $\mathrm{e}^{-\beta\mu}$. At low temperatures we can neglect it and extend the lower limit to $-\infty$ so that

$$f_{3/2}(z) = \frac{4}{3\sqrt{\pi}}\int_{-\infty}^\infty \mathrm{d}t \frac{\mathrm{e}^t}{(1+\mathrm{e}^t)^2}\left(\nu^{3/2} + \frac{3}{2}\nu^{1/2}t + \frac{3}{8}\nu^{-1/2}t^2 + \cdots\right) \,. \tag{6.129}$$

To evaluate Eq. (6.129), we must evaluate integrals of the form

$$I_n = \int_{-\infty}^\infty \mathrm{d}t \frac{t^n\mathrm{e}^t}{(1+\mathrm{e}^t)^2} \,. \tag{6.130}$$

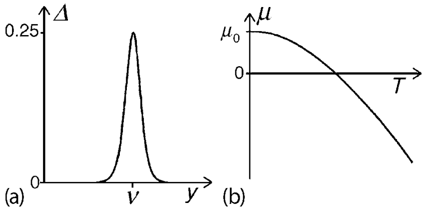

Figure 6.12 (a) A plot of $\Delta(y,v) \equiv e^{y-v}/(1+e^{y-v})^2$ versus y. (b) A plot of the chemical potential of a Fermi–Dirac gas as a function of temperature for fixed particle density.

The result is $I_n = 0$ for n odd, $I_0 = 1$, and $I_n = (n-1)!(2n)(1-2^{1-n})\zeta(n)$ for n even, where $\zeta(n)$ is a Riemann zeta function ($\zeta(2) = \pi^2/6$, $\zeta(4) = \pi^4/90$, $\zeta(6) = \pi^6/945$), etc.

We can use the above results to obtain an expansion for the quantity $\langle n\rangle\lambda_T^3/g$ which is valid at low temperature. From Eqs. (6.124), (6.129) and (6.130), we find

$$\langle n\rangle\frac{\lambda_T^3}{g} = \frac{4}{3\sqrt{\pi}}\left[(\beta\mu)^{3/2} + \frac{\pi^2}{8}(\beta\mu)^{-1/2} + \cdots\right] . \tag{6.131}$$

If we take the limit $T \to 0\,\mathrm{K}$ in (6.131), we find the following density-dependent expression for the chemical potential

$$\mu(T=0) = \mu_0 \equiv \varepsilon_F = \frac{\hbar^2}{2m}\left(\frac{6\pi^2\langle n\rangle}{g}\right)^{2/3} . \tag{6.132}$$

The chemical potential, $\mu_0 \equiv \varepsilon_F$, at $T = 0\,\mathrm{K}$ is also called the *Fermi energy*, because at $T = 0\,\mathrm{K}$ it is the maximum energy that a particle in the gas can have (cf. Figures 6.10a and 6.12b). At very low temperatures, only particles within a distance, $k_B T$, of the Fermi surface can participate in physical processes in the gas, because they can change their momentum state. Particles lower down in the Fermi sea have no empty momentum states available for them to jump to and do not contribute to changes in the thermodynamic properties. Equation (6.131) may be reverted to find the chemical potential a a function of temperature and density. The result is

$$\mu = \varepsilon_F\left[1 - \frac{\pi^2}{12}\left(\frac{k_B T}{\varepsilon_F}\right)^2 + \cdots\right] . \tag{6.133}$$

Thus, the chemical potential approaches a finite constant as $T \to 0\,\mathrm{K}$.

The internal energy, $U = \langle\hat{H}\rangle = \sum_l \varepsilon_l n_l$, can be computed in a similar manner. At low temperature, it is given by

$$U = \frac{3}{5}\langle N\rangle\varepsilon_F\left[1 + \frac{5\pi^2}{12}\left(\frac{k_B T}{\varepsilon_F}\right)^2 + \cdots\right] . \tag{6.134}$$

From Eq. (6.134) we obtain the heat capacity of the ideal Fermi–Dirac gas in the limit $T \to 0\,\mathrm{K}$. We find

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{V,\langle N\rangle} = \frac{\langle N\rangle\pi^2}{2}\frac{k_B^2 T}{\varepsilon_F} + \cdots . \tag{6.135}$$

Thus, the heat capacity of an ideal Fermi–Dirac gas depends linearly on the temperature at very low temperatures and goes to zero at $T = 0\,\mathrm{K}$ in accordance with the third law. It is important to note, however, that particles in an ideal Fermi–Dirac gas can have a large zero-point momentum and, therefore, a large pressure and energy even at $T = 0\,\mathrm{K}$. This is a result of the Pauli exclusion principle.

Exercise 6.6

The isotope $^3\mathrm{He}_2$ is a fermion with spin $s = 1/2$. It remains a liquid over a wide range of pressures down to $T = 0\,\mathrm{K}$. Consider one mole of liquid $^3\mathrm{He}_2$. At very low temperature its heat capacity has the same temperature dependence as that of an ideal Fermi gas and can be written $C_{V,N} \approx (2.8\,\mathrm{K}^{-1})N_\mathrm{A}k_\mathrm{B}T = (23\,\mathrm{J/K})T$. Find the temperature at which the entropy associated with the spins becomes greater than the entropy associated with the thermal properties of the gas.

Answer: The heat capacity associated with thermal motion can be written $C_{V,N} = T(\partial S/\partial T)_{V,N}$ so $S_\mathrm{th} = (2.8\,\mathrm{K}^{-1})N_\mathrm{A}k_\mathrm{B}T$. The entropy of N_A spin 1/2 particles is $S_\mathrm{spin} = k_\mathrm{B}N_\mathrm{A}\ln 2$. These entropies become equal when $(2.8\,\mathrm{K}^{-1})N_\mathrm{A}k_\mathrm{B}T = k_\mathrm{B}N_\mathrm{A}\ln 2$ so $T = 0.24\,\mathrm{K}$. At this temperature, the slope of the coexistence curve changes sign.

It is a simple matter to show that at high temperatures, all quantities approach values expected for an ideal classical gas. The procedure for deriving the classical ideal gas equation of state is the same as that for an ideal boson gas (see Section 6.7).

6.10
Magnetic Susceptibility of an Ideal Fermi Gas

The magnetic susceptibility of matter is largely determined by its electron dynamics. When a magnetic field is applied to a molecule or to condensed matter, the magnetic field inside the material is either enhanced (paramagnetic material) or reduced (diamagnetic material). Systems whose electron states have unpaired spins are generally paramagnetic. Systems with paired electron spin states are generally diamagnetic. The origins of these two types of magnetic response are very different. In paramagnetic systems, electron states have a net magnetic moment and this magnetic moment interacts with the magnetic field to create an enhanced magnetization. When electron spins are paired, there is no net magnetic moment and it is the orbital motion of the electrons, induced by the Lorentz force, that gives rise to diamagnetic effects. The origins of paramagnetism and diamagnetism can be demonstrated fairly easily for an ideal electron gas. Below we consider these two effects separately.

6.10.1
Paramagnetism

Let us consider an ideal electron gas in the presence of a magnetic flux density $\boldsymbol{B}$. The grand partition function can be written

$$Z_{\mathrm{FD}} = \prod_{\ell=0}^{\infty} \prod_{\sigma_\ell=\pm 1} \ln\left[1 + \exp(-\beta(\epsilon_\ell - \mu_{\mathrm{B}}\sigma_\ell B - \mu)\right] , \tag{6.136}$$

where the Bohr magneton, $\mu_{\mathrm{B}} = e\hbar/(2m)$, is the magnetic moment of the electron. The grand potential can be written

$$\begin{aligned} \Omega_{\mathrm{FD}} &= -k_{\mathrm{B}}T \ln[Z_{\mathrm{FD}}] = -k_{\mathrm{B}}T \sum_{l=0}^{\infty} \sum_{\sigma_l=\pm 1} \ln\left(1 + z^{(\sigma_\ell)} \mathrm{e}^{-\beta\epsilon_\ell}\right) \\ &= \frac{Vk_{\mathrm{B}}T}{\lambda_T^3}\left(f_{5/2}(z^{(+1)}) + f_{5/2}(z^{(-1)})\right) , \end{aligned} \tag{6.137}$$

where $z^{(\pm 1)} = \mathrm{e}^{\beta\mu}\mathrm{e}^{\pm\mu_{\mathrm{B}}B}$. The average particle number is

$$\langle N\rangle = -\left(\frac{\partial\Omega}{\partial\mu}\right)_{T,V,B} = \frac{V}{\lambda_T^3}\left(f_{3/2}(z^{(+1)}) + f_{3/2}(z^{(-1)})\right) \tag{6.138}$$

and the magnetization is

$$\langle M\rangle = -\left(\frac{\partial\Omega}{\partial B}\right)_{T,V,\mu} = \frac{\mu_{\mathrm{B}}V}{\lambda_T^3}\left(f_{3/2}(z^{(+1)}) - f_{3/2}(z^{(-1)})\right) . \tag{6.139}$$

Thus, there will be a net magnetization if the occupation numbers of the "spin-up" states differ from those of the "spin-down" states.

We can easily find the magnetization at high temperature where $z = \mathrm{e}^{\beta\mu} \to 0$, because we can expand both the average particle number and the magnetization in powers of z. Furthermore, we will consider the case of a weak magnetic field and expand in powers of B. We then obtain the particle density

$$\langle n\rangle = \frac{\langle N\rangle}{V} = \frac{2}{\lambda_T^3}\mathrm{e}^{\beta\mu}(\mathrm{e}^{+\beta\mu_{\mathrm{B}}B} + \mathrm{e}^{-\beta\mu_{\mathrm{B}}B}) = \frac{2}{\lambda_T^3}\mathrm{e}^{\beta\mu} + \mathcal{O}(B^2) \tag{6.140}$$

and the magnetization density

$$\frac{\langle M\rangle}{V} = \frac{2\mu_{\mathrm{B}}^2}{k_{\mathrm{B}}T\lambda_T^3}\mathrm{e}^{\beta\mu}B + \mathcal{O}(B^3) , \tag{6.141}$$

where $\mathcal{O}(B^n)$ indicates terms of order B^n and higher. If we now combine Eqs. (6.140) and (6.141), we obtain

$$\frac{\langle M\rangle}{V} = \frac{\langle n\rangle\mu_{\mathrm{B}}^2}{k_{\mathrm{B}}T}B , \tag{6.142}$$

and we find that the magnetic susceptibility at high temperature and weak magnetic field is $\chi = \langle n\rangle\mu_{\mathrm{B}}^2/(k_{\mathrm{B}}T)$. Since it is positive, the system is paramagnetic. We can also obtain the magnetic susceptibility in the limit $T \to 0$, but this is left as a homework problem.

6.10.2
Diamagnetism

Diamagnetism results from the orbital motion of electrons in the presence of a static magnetic field. The magnetic susceptibility, due to orbital motion, was first computed for an ideal Fermi gas by Landau [114] and is called "Landau diamagnetism." Diamagnetism is a quantum mechanical effect and does not occur in a classical gas [122].

The Lorentz force on an electron with charge $-e$ and mass m in the presence of a magnetic flux density $\boldsymbol{B}$ is $\boldsymbol{F} = -e\boldsymbol{v} \times \boldsymbol{B}$, where $\boldsymbol{v}$ is the velocity of the electron. Let us consider the static magnetic field along the z-axis, so that $\boldsymbol{B} = B\hat{\boldsymbol{e}}_z$. The Lorentz force provides the centripetal force that allows the electron to maintain a circular orbit with radius R and angular velocity $\omega_{\mathrm{c}} = v/R$. Newton's equation for the centripetal motion is $evB = m\omega_{\mathrm{c}}^2 R$, so the angular velocity is $\omega_{\mathrm{c}} = eB/m$.

Let us now consider a degenerate electron gas in a cubic box with volume $V = L^3$ in the presence of the magnetic flux density $\boldsymbol{B} = B\hat{\boldsymbol{e}}_z$. We introduce the magnetic vector potential $\boldsymbol{A}$ whose curl is the magnetic flux density $\boldsymbol{B} = \nabla \times \boldsymbol{A}$. There is some freedom in our choice of the vector potential. For example, $\boldsymbol{A} = -yB\hat{\boldsymbol{e}}_x$ and $\boldsymbol{A} = 1/2(-yB\hat{\boldsymbol{e}}_x + xB\hat{\boldsymbol{e}}_y)$ both give the same magnetic flux density $\boldsymbol{B} = B\hat{\boldsymbol{e}}_z$.

The Hamiltonian for an electron in the presence of the magnetic flux density $\boldsymbol{B}$ can be written $\hat{H} = 1/(2m)(\hat{\boldsymbol{p}} + e\boldsymbol{A})^2$, where $\hat{\boldsymbol{p}}$ is the canonical momentum operator and $\hat{\boldsymbol{v}} = (\hat{\boldsymbol{p}} + e\boldsymbol{A})/m$ is the velocity of the electrons. The Schrödinger equation for the electron energy eigenfunctions $\psi_E(\boldsymbol{r})$ and eigenvalues E is then given by

$$\hat{H}\psi_E(\boldsymbol{r}) = \frac{1}{2m}(-\mathrm{i}\hbar\nabla_{\boldsymbol{r}} + e\boldsymbol{A})^2\psi_E(\boldsymbol{r}) = E\psi_E(\boldsymbol{r}) \tag{6.143}$$

where $\hat{\boldsymbol{p}} = -\mathrm{i}\hbar\nabla_{\boldsymbol{r}}$ is the momentum operator in the position basis. Let us write the vector potential as $\boldsymbol{A} = -yB\hat{\boldsymbol{e}}_x$ and assume a solution to the Schrödinger equation of the form $\psi_E(\boldsymbol{r}) = \mathrm{e}^{\mathrm{i}k_x x}\mathrm{e}^{\mathrm{i}k_z z}\phi(y)$. The Schrödinger equation then becomes

$$-\frac{\hbar^2}{2m}\frac{\partial^2\phi(y)}{\partial y^2} + \frac{1}{2}m\omega_{\mathrm{c}}^2\left(y - y_0\right)^2\phi(y) = \Delta E\phi(y) \tag{6.144}$$

where $y_0 = \hbar k_x/eB$, $\omega_{\mathrm{c}} = eB/m$, $\Delta E = (E - \hbar^2 k_z^2/(2m)$ is the energy of the electron motion in the x–y plane and $\hbar^2 k_z^2/(2m)$ is the kinetic energy of the electron due to its motion along the z-axis. Equation (6.144) is the eigenvalue equation for a harmonic oscillator that oscillates about the point $y = y_0$ with oscillation frequency ω_{c}. The allowed energies of this harmonic motion are $\Delta E_n = \hbar\omega_{\mathrm{c}}(n + 1/2)$, with $n = 0, 1, 2, \ldots$. The energy levels ΔE_n for elections in the x–y plane are called *Landau levels* and describe the quantized motion of the electrons in the presence of the external magnetic field. The wavevectors k_x and k_z are quantized and have values $k_j = 2\pi\ell_j/L$ where $j = x, z$ and $\ell_j = 0, \pm1, \pm2, \ldots$.

The electron motion in the x–y plane is highly degenerate because of the dependence of the point $y = y_0$ on k_x. This dependence means that the origin of the oscillator can change its position in increments $\delta y_0 = \hbar 2\pi/(eBL)$, without changing the energy of the oscillator. Since the length of the box in the x-direction is L, the number of such positions is $\mathcal{N} = L/\delta y_0 = eBL^2/(2\pi\hbar)$, where BL^2 is the total magnetic flux through the x–y-plane.

Having determined the energy levels of an electron in the presence of the magnetic field, we can now write the grand potential per unit volume in the form

$$\frac{\Omega(T, V, \mu)}{V} = -k_{\mathrm{B}} T g \frac{eB}{4\pi^2\hbar} \int\limits_{-\infty}^{\infty} \mathrm{d}k_z \sum_{n=0}^{\infty} \ln\left\{1 + \mathrm{e}^{-\beta\left[\frac{\hbar^2 k_z^2}{2m} + \hbar\omega_{\mathrm{c}}\left(n+\frac{1}{2}\right) - \mu\right]}\right\} , \tag{6.145}$$

where g is the spin degeneracy of the electrons (we have not included the interaction of the magnetic field with the electron spins in this expression). Equation (6.145) includes the degeneracy $\mathcal{N} = eBL^2/(2\pi\hbar)$ of the Landau levels.

At high temperatures, we can use the approximation $\ln(1 + x) \approx x - 1/2x^2 + \ldots$ and approximate the grand potential by the first-order term in the logarithm. We then have

$$\begin{aligned} \frac{\Omega(T, V, \mu)}{V} &\approx -k_{\mathrm{B}} T g \frac{eB}{4\pi^2\hbar} \int\limits_{-\infty}^{\infty} \mathrm{d}k_z \sum_{n=0}^{\infty} \mathrm{e}^{-\beta\left[\frac{\hbar^2 k_z^2}{2m} + \hbar\omega_{\mathrm{c}}\left(n+\frac{1}{2}\right) - \mu\right]} \\ &= -k_{\mathrm{B}} T g \frac{eB}{4\pi^2\hbar} \sqrt{\frac{2\pi m}{\beta\hbar^2}} \mathrm{e}^{+\beta\mu} \frac{\mathrm{e}^{-\beta\hbar\omega_{\mathrm{c}}/2}}{1 - \mathrm{e}^{-\beta\hbar\omega_{\mathrm{c}}}} . \end{aligned} \tag{6.146}$$

Since we are interested in the magnetic susceptibility, we only need contributions to lowest order in B. Let us note that $\mathrm{e}^{-x}/(1 - \mathrm{e}^{-2x}) \approx 1/(2x) - x/12 + \ldots$ for $x \ll 1$. Remembering that $\omega_{\mathrm{c}} = eB/m$, we obtain

$$\begin{aligned} \frac{\Omega(T, V, \mu)}{V} &= -k_{\mathrm{B}} T g \frac{eB}{4\pi^2\hbar} \sqrt{\frac{2\pi m}{\beta\hbar^2}} \mathrm{e}^{+\beta\mu} \left(\frac{1}{\beta\hbar\omega_{\mathrm{c}}} - \frac{1}{24}\beta\hbar\omega_{\mathrm{c}} + \ldots\right) \\ &= -k_{\mathrm{B}} T g \frac{\mathrm{e}^{+\beta\mu}}{\lambda_T^3} \left(1 - \frac{1}{6}\left(\frac{e\hbar}{2m}\right)^2 \left(\frac{B}{k_{\mathrm{B}} T}\right)^2 + \ldots\right) . \end{aligned} \tag{6.147}$$

The average particle density is

$$\langle n \rangle = -\frac{1}{V}\left(\frac{\partial\Omega}{\partial\mu}\right)_{T,V} = g\frac{\mathrm{e}^{+\beta\mu}}{\lambda_T^3}(1 - \ldots) \tag{6.148}$$

so the grand potential density can be written

$$\frac{\Omega(T, V, \mu)}{V} = -k_{\mathrm{B}} T \langle n \rangle \left[1 - \frac{1}{6}\left(\frac{e\hbar}{2m}\right)^2 \left(\frac{B}{k_{\mathrm{B}} T}\right)^2 + \ldots\right] . \tag{6.149}$$

The isothermal magnetic susceptibility is

$$\chi_T = -\frac{1}{V}\left(\frac{\partial^2 \Omega}{\partial B^2}\right)_{T,\langle n\rangle} = -\frac{\langle n\rangle \mu_{\mathrm{B}}^2}{3k_{\mathrm{B}}T} + \dots \tag{6.150}$$

where $\mu_{\mathrm{B}} = e\hbar/(2m)$ is the Bohr magneton. Thus, the magnetic susceptibility is negative, indicating that the effect of the orbital motion of the electrons, in the presence of a magnetic field is diamagnetic. However, if we combine the paramagnetic and diamagnetic susceptibilities for the Fermi gas, we see that the combined susceptibility is positive, indicating that the Fermi gas is paramagnetic.

6.11
Momentum Condensation in an Interacting Fermi Fluid

Electrons in a conducting solid are free to wander through the lattice and form a Fermi fluid. At low temperatures the electrons form a Fermi sea and only those near the Fermi surface affect the thermodynamic properties of the electron fluid. The electrons do experience a mutual Coulomb repulsion which is screened, however, by lattice ions. As first noted by Frohlich [63], electrons in the neighborhood of the Fermi surface can also experience a lattice-phonon-mediated effective attraction (two electrons may in effect be attracted to one another because they are both attracted to the same lattice ion). Cooper [32] showed that this effective attraction at the Fermi surface could cause bound pairs of electrons to form, and these pairs could then condense in momentum space, giving rise to a phase transition in the interacting Fermi fluid. Bardeen, Schrieffer, and Cooper (BCS) [12] showed that this momentum space condensation of *Cooper pairs* is the origin of superconductivity in materials. In 1972, they received the Nobel Prize for this work.

We shall derive the thermodynamic properties of a condensed Fermi fluid using mean field theory [197]. It is found experimentally that Cooper pairs have zero total angular momentum and zero total spin. If the pairs are not undergoing a net translation through the fluid (no supercurrent), then the paired electrons will have equal and opposite momentum and opposite spin components. We shall assume that all other electrons behave like an ideal gas. With these assumptions, we can write the Hamiltonian of the electron fluid in the form

$$\hat{H} = \sum_{\boldsymbol{k},\lambda} \varepsilon_{\boldsymbol{k}} \hat{a}^{\dagger}_{\boldsymbol{k},\lambda} \hat{a}_{-\boldsymbol{k},\lambda} + \sum_{\boldsymbol{k}} \sum_{\boldsymbol{k}'} V_{\boldsymbol{k},\boldsymbol{k}'} \hat{a}^{\dagger}_{\boldsymbol{k},\uparrow} \hat{a}^{\dagger}_{-\boldsymbol{k},\downarrow} \hat{a}_{-\boldsymbol{k}',\downarrow} \hat{a}_{\boldsymbol{k}',\uparrow} , \tag{6.151}$$

where $\varepsilon_{\boldsymbol{k}} = \hbar^2 k^2/(2m)$, and λ denotes the z-component of spin of a given electron and takes values $\lambda = \uparrow$ or $\lambda = \downarrow$ (spin component $+1/2\hbar$ or $-1/2\hbar$, respectively). The operators, $\hat{a}^{\dagger}_{\boldsymbol{k},\lambda}$ and $\hat{a}_{\boldsymbol{k},\lambda}$, respectively create and annihilate an electron with momentum $\hbar\boldsymbol{k}$ and spin component λ (cf. Appendix D). They satisfy fermion anticommutation relations,

$$\left[\hat{a}_{\boldsymbol{k}}, \hat{a}^{\dagger}_{\boldsymbol{k}'}\right]_{+} = \delta_{\boldsymbol{k},\boldsymbol{k}'} , \quad \left[\hat{a}_{\boldsymbol{k}}, \hat{a}_{\boldsymbol{k}'}\right]_{+} = 0 , \quad \left[\hat{a}^{\dagger}_{\boldsymbol{k}}, \hat{a}^{\dagger}_{\boldsymbol{k}'}\right]_{+} = 0 . \tag{6.152}$$

The interaction term in Eq. (6.151) destroys a pair of electrons with momenta $\hbar\boldsymbol{k}'$ and $-\hbar\boldsymbol{k}'$ and opposite spin components, and it creates a pair of electrons with momenta $\hbar\boldsymbol{k}$ and $-\hbar\boldsymbol{k}$ and opposite spin components.

Since the electrons only experience an attraction at the Fermi surface, the interaction energy, $V_{\boldsymbol{k},\boldsymbol{k}'}$, can be written

$$V_{\boldsymbol{k},\boldsymbol{k}'} = \begin{cases} -V_0 & \text{for} \quad |\mu - \varepsilon_{\boldsymbol{k}}| \le \Delta\varepsilon\,, \quad |\mu - \varepsilon_{\boldsymbol{k}'}| \le \Delta\varepsilon\,, \\ 0 & \text{otherwise}\,, \end{cases} \tag{6.153}$$

where V_0 is a positive constant, μ is the chemical potential of the Fermi fluid, and $\Delta\varepsilon$ is a small energy interval of order $k_{\mathrm{B}}T$.

We now introduce the mean field approximation. We write the Hamiltonian in the form

$$\hat{H}_{\mathrm{mf}} = \sum_{\boldsymbol{k},\lambda} \varepsilon_{\boldsymbol{k}} \hat{a}^{\dagger}_{\boldsymbol{k},\lambda} \hat{a}_{\boldsymbol{k},\lambda} + \sum_{\boldsymbol{k}} \Delta^{*} \hat{a}_{-\boldsymbol{k},\downarrow} \hat{a}_{\boldsymbol{k},\uparrow} + \sum_{\boldsymbol{k}} \Delta \hat{a}^{\dagger}_{\boldsymbol{k},\uparrow} \hat{a}^{\dagger}_{-\boldsymbol{k},\downarrow}\,, \tag{6.154}$$

where

$$\Delta \equiv -V_0 \sum_{\boldsymbol{k}}{}' \left\langle \hat{a}_{-\boldsymbol{k},\downarrow} \hat{a}_{\boldsymbol{k},\downarrow} \right\rangle\,, \quad \text{and} \quad \Delta^{*} \equiv -V_0 \sum_{\boldsymbol{k}}{}' \left\langle \hat{a}^{\dagger}_{\boldsymbol{k},\uparrow} \hat{a}^{\dagger}_{-\boldsymbol{k},\downarrow} \right\rangle\,. \tag{6.155}$$

The prime on the summation, $\sum'_{\boldsymbol{k}}$, means that the summation is restricted to a distance, $\Delta\varepsilon$, on either side of the Fermi surface. The average, $\langle \hat{a}_{-\boldsymbol{k},\downarrow} \hat{a}_{\boldsymbol{k},\uparrow} \rangle$, is defined as

$$\langle \hat{a}_{-\boldsymbol{k},\downarrow} \hat{a}_{\boldsymbol{k},\uparrow} \rangle = \mathrm{Tr}(\hat{\rho}\, \hat{a}_{-\boldsymbol{k},\downarrow} \hat{a}_{\boldsymbol{k},\uparrow})\,, \tag{6.156}$$

and the density operator, $\hat{\rho}$, is defined

$$\hat{\rho} = \frac{\mathrm{e}^{-\beta(\hat{H}_{\mathrm{mf}} - \mu\hat{N})}}{\mathrm{Tr}(\mathrm{e}^{-\beta(\hat{H}_{\mathrm{mf}} - \mu\hat{N})})}\,. \tag{6.157}$$

The average, $\langle \hat{a}^{\dagger}_{\boldsymbol{k},\uparrow} \hat{a}^{\dagger}_{-\boldsymbol{k},\downarrow} \rangle$, is similarly defined. The particle number operator, $\hat{N}$, is given by

$$\hat{N} = \sum_{\boldsymbol{k},\lambda} \hat{a}^{\dagger}_{\boldsymbol{k},\lambda} \hat{a}_{\boldsymbol{k},\lambda}\,, \tag{6.158}$$

as we would expect. The quantity Δ is called the *gap function* and, in general, may be real or complex. The gap function is real ($\Delta = \Delta^{*}$) if no supercurrent is present and that is the case we consider here (the dependence on $\boldsymbol{k}$ and $-\boldsymbol{k}$ indicates that the total momentum of the pair is zero). The gap function Δ is the order parameter for the phase transition and is a measure of the average binding energy of all the Cooper pairs. If a macroscopic number of Cooper pairs form, then $\langle \hat{a}^{\dagger}_{\boldsymbol{k},\uparrow} \hat{a}^{\dagger}_{-\boldsymbol{k},\downarrow} \rangle = \langle \hat{a}^{\dagger}_{\boldsymbol{k},\uparrow} \hat{a}^{\dagger}_{-\boldsymbol{k},\downarrow} \rangle \approx n_{\mathrm{c}}$, where n_{c} is the average number of Cooper pairs in the fluid.

The Hamiltonian, $\hat{H}_{\mathrm{mf}}$, does not commute with the number operator $\hat{N}$ if $\Delta \neq 0$. This means that the system does not conserve the particle (electron) number and the gauge symmetry is broken. If a macroscopic number of Cooper pairs form, the total energy of the system is lowered. The phase transition occurs when the thermal energy $k_{\mathrm{B}}T$, which tends to break Cooper pairs apart, becomes less important than the phonon-mediated attraction between electrons.

It is useful to introduce an effective Hamiltonian

$$\hat{K} = \sum_{\boldsymbol{k}} \xi_{\boldsymbol{k}} \left(\hat{a}^{\dagger}_{\boldsymbol{k},\uparrow} \hat{a}_{\boldsymbol{k},\uparrow} - \hat{a}_{-\boldsymbol{k},\downarrow} \hat{a}^{\dagger}_{-\boldsymbol{k},\downarrow} \right) + \sum_{\boldsymbol{k}} \Delta \hat{a}_{-\boldsymbol{k},\downarrow} \hat{a}_{\boldsymbol{k},\uparrow} + \sum_{\boldsymbol{k}} \Delta \hat{a}^{\dagger}_{\boldsymbol{k},\uparrow} \hat{a}^{\dagger}_{-\boldsymbol{k},\downarrow} , \tag{6.159}$$

where

$$\xi_{\boldsymbol{k}} = \varepsilon_{\boldsymbol{k}} - \mu = \frac{\hbar^2 k^2}{2m} - \mu , \tag{6.160}$$

and we have made use of the fermion anticommutation relations. The effective Hamiltonian, $\hat{K}$, differs from $\hat{H}_{\mathrm{mf}} - \mu\hat{N}$ only by a constant term. Therefore, the density operator can be written

$$\hat{\rho} = \frac{\mathrm{e}^{\beta\hat{K}}}{\mathrm{Tr}(\mathrm{e}^{-\beta\hat{K}})} . \tag{6.161}$$

The effective Hamiltonian, $\hat{K}$, can be written in matrix form:

$$\hat{K} = \sum_{\boldsymbol{k}} \boldsymbol{\alpha}^{\dagger}_{\boldsymbol{k}} \overline{\boldsymbol{K}}_{\boldsymbol{k}} \boldsymbol{\alpha}_{\boldsymbol{k}} , \tag{6.162}$$

where

$$\overline{\boldsymbol{K}}_{\boldsymbol{k}} \equiv \begin{pmatrix} \xi_{\boldsymbol{k}} & \Delta \\ \Delta & -\xi_{\boldsymbol{k}} \end{pmatrix} , \quad \boldsymbol{\alpha}_{\boldsymbol{k}} = \begin{pmatrix} \hat{a}_{\boldsymbol{k},\uparrow} \\ \hat{a}^{\dagger}_{-\boldsymbol{k},\uparrow} \end{pmatrix} , \quad \boldsymbol{\alpha}^{\dagger}_{\boldsymbol{k}} = \left(\hat{a}^{\dagger}_{\boldsymbol{k},\uparrow} \; \hat{a}_{-\boldsymbol{k},\downarrow} \right) . \tag{6.163}$$

Bogoliubov [18] showed that the effective Hamiltonian, $\hat{K}$, can be diagonalized by means of a unitary transformation which preserves the fermion anticommutation relations. In so doing, we obtain a Hamiltonian for uncoupled excitations (called bogolons) of the system. To diagonalize the effective Hamiltonian, we introduce a 2 × 2 unitary matrix,

$$\overline{\boldsymbol{U}}_{\boldsymbol{k}} \equiv \begin{pmatrix} u_{\boldsymbol{k}} & v_{\boldsymbol{k}} \\ -v_{\boldsymbol{k}} & u_{\boldsymbol{k}} \end{pmatrix} . \tag{6.164}$$

Since $\overline{\boldsymbol{U}}^{\dagger}_{\boldsymbol{k}} \overline{\boldsymbol{U}}_{\boldsymbol{k}} = \overline{\boldsymbol{U}}_{\boldsymbol{k}} \overline{\boldsymbol{U}}^{\dagger}_{\boldsymbol{k}} = \overline{1}$ (unitarity), we must have $u^2_{\boldsymbol{k}} + v^2_{\boldsymbol{k}} = 1$. We also introduce the vectors

$$\boldsymbol{\Gamma}_{\boldsymbol{k}} = \begin{pmatrix} \hat{\gamma}_{\boldsymbol{k},0} \\ \hat{\gamma}^{\dagger}_{\boldsymbol{k},1} \end{pmatrix} , \quad \boldsymbol{\Gamma}^{\dagger}_{\boldsymbol{k}} = \left(\hat{\gamma}^{\dagger}_{\boldsymbol{k},0} \hat{\gamma}_{\boldsymbol{k},1} \right) , \tag{6.165}$$

which are related to the vectors, $\overline{\alpha}_{\boldsymbol{k}}$, via the unitary transformation

$$\boldsymbol{\alpha}_{\boldsymbol{k}} = \overline{\boldsymbol{U}}_{\boldsymbol{k}} \boldsymbol{\Gamma}_{\boldsymbol{k}} . \tag{6.166}$$

The physical significance of the vectors, $\overline{\Gamma}_{\boldsymbol{k}}$, will become clear below. It is easy to show that since $\hat{a}^{\dagger}_{\boldsymbol{k},\lambda}$ and $\hat{a}_{\boldsymbol{k},\lambda}$ obey fermion anticommutation relations, the operators, $\hat{\gamma}^{\dagger}_{\boldsymbol{k},i}$ and $\hat{\gamma}_{\boldsymbol{k},i}$ ($i = 0, 1$), must also obey fermion anticommutation relations

$$\left[\hat{\gamma}_{\boldsymbol{k},i}, \hat{\gamma}^{\dagger}_{\boldsymbol{k}',i'}\right]_{+} = \delta_{\boldsymbol{k},\boldsymbol{k}'}\delta_{i,i'}\,, \quad \left[\hat{\gamma}_{\boldsymbol{k},i}\hat{\gamma}_{\boldsymbol{k}',i'}\right]_{+} = \left[\hat{\gamma}^{\dagger}_{\boldsymbol{k},i}, \hat{\gamma}^{\dagger}_{\boldsymbol{k}',i'}\right]_{+} = 0\,. \tag{6.167}$$

If we revert Eq. (6.166), we see that $\hat{\gamma}_{\boldsymbol{k},0}$ decreases the momentum of the system by $\hbar\boldsymbol{k}$ and lowers the spin by $\hbar$ (it destroys a particle with quantum numbers, $(\boldsymbol{k}, \uparrow)$, and creates one with quantum numbers, $(-\boldsymbol{k}, \downarrow)$, whereas $\hat{\gamma}_{\boldsymbol{k},1}$ increases the momentum of the system by $\hbar\boldsymbol{k}$ and raises the spin by $\hbar$.

We now require that the unitary matrix, $\overline{\boldsymbol{U}}_{\boldsymbol{k}}$, diagonalize the effective Hamiltonian, $\hat{K}$. That is,

$$\overline{\boldsymbol{U}}^{\dagger}_{\boldsymbol{k}}\overline{\boldsymbol{K}}_{\boldsymbol{k}}\overline{\boldsymbol{U}}_{\boldsymbol{k}} = \overline{\boldsymbol{E}}_{\boldsymbol{k}} \quad \text{with} \quad \overline{\boldsymbol{E}}_{\boldsymbol{k}} = \begin{pmatrix} E_{\boldsymbol{k},0} & 0 \\ 0 & E_{\boldsymbol{k},1} \end{pmatrix}\,. \tag{6.168}$$

We find that $E_{\boldsymbol{k},0} = E^{\mathrm{o}}_{\boldsymbol{k}}$ and $E_{\boldsymbol{k},1} = -E^{\mathrm{o}}_{\boldsymbol{k}}$ with

$$E^{\mathrm{o}}_{\boldsymbol{k}} = \sqrt{\xi^{x}_{\boldsymbol{k}} + \Delta^2}\,. \tag{6.169}$$

With this transformation, we have succeeded in reducing the interacting Fermi gas of electrons to an ideal Fermi gas of bogolons. In terms of bogolon operators, the effective Hamiltonian takes the form

$$\begin{aligned}\hat{K} &= \sum_{\boldsymbol{k}} \boldsymbol{\alpha}^{\dagger}_{\boldsymbol{k}}\bar{\boldsymbol{U}}_{\boldsymbol{k}}\overline{\boldsymbol{U}}^{\dagger}_{\boldsymbol{k}}\overline{\boldsymbol{K}}_{\boldsymbol{k}}\overline{\boldsymbol{U}}_{\boldsymbol{k}}\overline{\boldsymbol{U}}^{\dagger}_{\boldsymbol{k}}\boldsymbol{\alpha}_{\boldsymbol{k}} = \sum_{\boldsymbol{k}} \boldsymbol{\gamma}^{\dagger}_{\boldsymbol{k}}\overline{\boldsymbol{E}}_{\boldsymbol{k}}\boldsymbol{\gamma}_{\boldsymbol{k}} \\ &= \sum_{\boldsymbol{k}} \left(E_{\boldsymbol{k},0}\hat{\gamma}^{\dagger}_{\boldsymbol{k},0}\hat{\gamma}_{\boldsymbol{k},0} - E_{\boldsymbol{k},1}\hat{\gamma}^{\dagger}_{\boldsymbol{k},1}\hat{\gamma}_{\boldsymbol{k},1} + E_{\boldsymbol{k},1}\right)\,. \end{aligned} \tag{6.170}$$

The bogolons are collective modes and play a role analogous to that of phonons in a Debye solid, although their dispersion relation is quite different.

We can now obtain a self-consistent equation for the gap function, Δ. First note that

$$\left\langle \hat{\gamma}^{\dagger}_{\boldsymbol{k},0}\hat{\gamma}_{\boldsymbol{k},0} \right\rangle = \frac{1}{1 + \mathrm{e}^{\beta E_{\boldsymbol{k},0}}} = \frac{1}{2}\left[1 - \tanh\left(\frac{\beta E_{\boldsymbol{k},0}}{2}\right)\right] \tag{6.171}$$

and

$$\left\langle \hat{\gamma}^{\dagger}_{\boldsymbol{k},1}\hat{\gamma}_{\boldsymbol{k},1} \right\rangle = \frac{1}{1 + \mathrm{e}^{-\beta E_{\boldsymbol{k},1}}} = \frac{1}{2}\left[1 + \tanh\left(\frac{\beta E_{\boldsymbol{k},1}}{2}\right)\right]\,. \tag{6.172}$$

Then

$$\begin{aligned}\left\langle \boldsymbol{\alpha}_{\boldsymbol{k}}\boldsymbol{\alpha}_{\boldsymbol{k}}^{\dagger}\right\rangle &= \begin{pmatrix} 1-\left\langle \hat{a}_{\boldsymbol{k},\uparrow}^{\dagger}\hat{a}_{\boldsymbol{k},\uparrow}\right\rangle & -\left\langle \hat{a}_{-\boldsymbol{k},\downarrow}\hat{a}_{\boldsymbol{k},\uparrow}\right\rangle \\ -\left\langle \hat{a}_{\boldsymbol{k},\uparrow}^{\dagger}\hat{a}_{-\boldsymbol{k},\downarrow}^{\dagger}\right\rangle & \left\langle \hat{a}_{-\boldsymbol{k},\downarrow}^{\dagger}\hat{a}_{-\boldsymbol{k},\downarrow}\right\rangle \end{pmatrix} \\ &= \overline{\boldsymbol{U}}_{\boldsymbol{k}} \begin{pmatrix} 1-\left\langle \hat{\gamma}_{\boldsymbol{k},0}^{\dagger}\hat{\gamma}_{\boldsymbol{k},0}\right\rangle & 0 \\ 0 & \left\langle \hat{\gamma}_{\boldsymbol{k},1}^{\dagger}\hat{\gamma}_{\boldsymbol{k},1}\right\rangle \end{pmatrix} \overline{\boldsymbol{U}}_{\boldsymbol{k}}^{\dagger} \\ &= \frac{1}{2}\overline{\mathbf{1}} + \frac{1}{2E_{\boldsymbol{k}}^{\mathrm{o}}}\overline{\boldsymbol{U}}_{\boldsymbol{k}} \begin{pmatrix} E_{\boldsymbol{k}}^{\mathrm{o}} & 0 \\ 0 & -E_{\boldsymbol{k}}^{\mathrm{o}} \end{pmatrix} \overline{\boldsymbol{U}}_{\boldsymbol{k}}^{\dagger} \tanh\left(\frac{\beta E_{\boldsymbol{k}}^{\mathrm{o}}}{2}\right) \\ &= \frac{1}{2}\overline{\mathbf{1}} + \frac{1}{2E_{\boldsymbol{k}}^{\mathrm{o}}}\overline{\boldsymbol{K}}_{\boldsymbol{k}} \tanh\left(\frac{\beta E_{\boldsymbol{k}}^{\mathrm{o}}}{2}\right) . \end{aligned} \tag{6.173}$$

We can equate off-diagonal matrix elements and write

$$-\langle \hat{a}_{-\boldsymbol{k},\downarrow}\hat{a}_{\boldsymbol{k},\uparrow}\rangle = \frac{\Delta_{\boldsymbol{k}}}{2E_{\boldsymbol{k}}^{\mathrm{o}}} \tanh\left(\frac{\beta E_{\boldsymbol{k}}^{\mathrm{o}}}{2}\right) . \tag{6.174}$$

If we multiply (6.174) by $V_{\boldsymbol{k},\boldsymbol{k}'}$, integrate over $\boldsymbol{k}$, we obtain

$$1 = V_0 {\sum_{\boldsymbol{k}}}' \frac{1}{2E_{\boldsymbol{k}}^{\mathrm{o}}} \tanh\left(\frac{\beta E_{\boldsymbol{k}}^{\mathrm{o}}}{2}\right) . \tag{6.175}$$

Under the primed summation the bogolon energy can be written $E_{\boldsymbol{k}}^{\mathrm{o}} = \sqrt{\xi_{\boldsymbol{k}}^2 + \Delta^2}$. Equation (6.175) is the equation for the gap function Δ and is called the *gap equation*. Solutions of the gap equation correspond to extrema of the free energy. The solution that minimizes the free energy corresponds to the stable thermodynamic state.

Let us now determine some properties of the gap function from Eq. (6.175). For large volume, V, we can change the summation to an integration

$$\sum_{\boldsymbol{k}} \approx \frac{V}{2\pi^2}\int_0^\infty \mathrm{d}k k^2 = \frac{m^{3/2}V}{\sqrt{2}\pi^2\hbar^3}\int_{-\mu}^{\infty} \mathrm{d}\xi_{\boldsymbol{k}}\sqrt{\xi_{\boldsymbol{k}}+\mu} . \tag{6.176}$$

The summation, $\sum_{\boldsymbol{k}}'$ can be written

$${\sum_{\boldsymbol{k}}}' \approx \frac{m^{3/2}V}{\sqrt{2}\pi^2\hbar^3}\int_{-\Delta\varepsilon}^{\Delta\varepsilon} \sqrt{\varepsilon_{\mathrm{f}}}\,\mathrm{d}\xi_{\boldsymbol{k}} \approx N(0)\int_{-\Delta\varepsilon}^{\Delta\varepsilon} \mathrm{d}\xi_{\boldsymbol{k}} , \tag{6.177}$$

where we have set $\mu \approx \varepsilon_{\mathrm{f}}$ (ε_{f} is the Fermi energy) and $N(0) = mVk_{\mathrm{f}}/(2\pi^2\hbar^2)$ is the density of states at the Fermi surface for a single spin state (cf. Exercise 6.3). We can now write (6.175) in the form

$$1 = V_0 N(0)\int_0^{\Delta\varepsilon} \mathrm{d}\xi_{\boldsymbol{k}} \frac{\tanh\left[\frac{\beta}{2}\sqrt{\xi_{\boldsymbol{k}}^2 + \Delta(T)^2}\right]}{\sqrt{\xi_{\boldsymbol{k}}^2 + \Delta(T)^2}} . \tag{6.178}$$

Equation (6.178) determines the temperature dependence of the gap, $\Delta(T)$, and can be used to find the transition temperature.

The energy of bogolons (measured from the Fermi surface) with momentum $\hbar\boldsymbol{k}$ is $E_{\boldsymbol{k}} = \sqrt{\xi_{\boldsymbol{k}}^2 + \Delta(T)^2}$. It takes a finite amount of energy to excite them, regardless of their momentum, because there is a gap in the energy spectrum. At the critical temperature, T_c, the gap goes to zero and the excitation spectrum reduces to that of an ideal Fermi gas. The critical temperature can be obtained from Eq. (6.178). It is the temperature at which the gap becomes zero. Thus, at the critical temperature we have

$$\begin{aligned} 1 &= V_0 N(0) \int_0^{\Delta\varepsilon} \mathrm{d}\xi_{\boldsymbol{k}} \frac{\tanh(\beta\xi_{\boldsymbol{k}}/2)}{\xi_{\boldsymbol{k}}} = N(0)V_0 \int_0^{\beta_c\Delta\varepsilon/2} \mathrm{d}x \frac{\tanh x}{x} \\ &= N(0)V_0 \ln\left(\frac{\alpha}{2}\beta_c\Delta\varepsilon\right) , \end{aligned} \tag{6.179}$$

where $\beta_c = (k_B T_c)^{-1}$, $\alpha = 2.267\,73$, and we have used the fact that

$$\int_0^b \frac{\tanh x}{x} \mathrm{d}x = \ln(\alpha b) , \tag{6.180}$$

for $b > 100$. Thus, Eq. (6.179) holds when $\beta_c\Delta\varepsilon/2 > 100$. This means that $N(0)V_0 < 0.184$ and therefore use of Eq. (6.179) restricts us to fairly weakly coupled systems. From Eqs. (6.179) and (6.180) we obtain

$$k_B T_c = \frac{\alpha}{2}\Delta\varepsilon \mathrm{e}^{-1/(N(0)V_0)} , \tag{6.181}$$

for $\beta_c\Delta\varepsilon/2 > 100$. Thus, the critical temperature, T_c, varies exponentially with the strength of the attractive interaction.

We can also use Eq. (6.178) to find the gap, $\Delta(0) \equiv \Delta_0$, at $T = 0\,\mathrm{K}$. Since $\tanh(\infty) = 1$, we can write

$$1 = V_0 N(0) \int_0^{\Delta\varepsilon} \mathrm{d}\xi_{\boldsymbol{k}} \frac{1}{\sqrt{\xi_{\boldsymbol{k}}^2 + \Delta_0^2}} = V_0 N(0) \sinh^{-1}\left(\frac{\Delta_\varepsilon}{\Delta_0}\right) , \tag{6.182}$$

or

$$\Delta_0 = \frac{\Delta_\varepsilon}{\sinh[1/(V_0 N(0))]} \approx 2\Delta\varepsilon \mathrm{e}^{-1/(N(0)V_0)} . \tag{6.183}$$

The right-most expression for Δ_0 applies for weakly coupled systems when $N(0)V_0 < 0.184$. Comparing Eqs. (6.181) and (6.183), we obtain the following relation between the critical temperature and the zero temperature gap *for weakly coupled systems*:

$$\frac{\Delta_0}{k_B T_c} = \frac{4}{\alpha} = 1.764 . \tag{6.184}$$

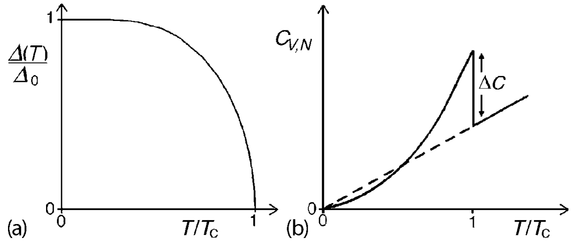

Figure 6.13 (a) A plot of the ratio $\Delta(T)/\Delta_0$ versus the reduced temperature, T/T_c, for a weakly coupled system. (b) A sketch of the heat capacity for a superconductor. The straight dashed line gives the heat capacity in the absence of interaction (ideal Fermi gas). The solid line shows the jump in the heat capacity at the critical point and the exponential decay for temperatures below the critical point.

Equation (6.184) is in good agreement with experimental values of this ratio for superconductors. Equation (6.178) may be solved numerically to obtain a plot of the gap as a function of temperature. We show the behavior of $\Delta(T)$ in Figure 6.13a for weakly coupled systems.

Since bogolons form an ideal gas, the bogolon entropy can be written in the form

$$S = -2k_B \sum_{\boldsymbol{k}} [n_{\boldsymbol{k}} \ln(n_{\boldsymbol{k}}) + (1 - n_{\boldsymbol{k}}) \ln(1 - n_{\boldsymbol{k}})] , \tag{6.185}$$

where $n_{\boldsymbol{k}} = (1 + \mathrm{e}^{\beta E_{\boldsymbol{k}}})^{-1}$. The heat capacity, $C_{V,N}$, is easy to find from Eq. (6.185). Let us first note that for a Fermi gas at very low temperature we have $\mu \approx \varepsilon_f$, where ε_f is the Fermi energy, and $(\partial\mu/\partial T)_{V,\langle N\rangle} \approx 0$. Thus,

$$\begin{aligned} C_{V,N} = T\left(\frac{\partial S}{\partial T}\right)_{V,\langle N\rangle} &\approx 2\beta k_\beta \sum_{\boldsymbol{k}} \frac{\partial n_{\boldsymbol{k}}}{\partial\beta} \ln\left(\frac{n_{\boldsymbol{k}}}{1 - n_{\boldsymbol{k}}}\right) \\ &= -2\beta k_B \sum_{\boldsymbol{k}} \frac{\partial n_{\boldsymbol{k}}}{\partial E_{\boldsymbol{k}}} \left(E_{\boldsymbol{k}}^2 + \frac{1}{2}\beta \frac{\partial \Delta_{\boldsymbol{k}}^2}{\partial\beta}\right) . \end{aligned} \tag{6.186}$$

We can now examine the heat capacity, both at the critical temperature and in the limit $T \to 0\,\mathrm{K}$.

Let us first look at the neighborhood of the critical point. The first term in Eq. (6.186) is continuous at $T = T_c$, but the second term is not since $\partial|\Delta_{\boldsymbol{k}}|^2/\partial\beta$ has a finite value for $T < T_c$ but is zero for $T > T_c$. Near $T = T_c$, we may let $E_{\boldsymbol{k}} \to |\xi_{\boldsymbol{k}}|$. Then the heat capacity just below the critical temperature is

$$C_{V,N}^{<} \approx -2\beta_c k_B \sum_{\boldsymbol{k}} \frac{\partial n_{\boldsymbol{k}}}{\partial \xi_{\boldsymbol{k}}} \left[\xi_{\boldsymbol{k}}^2 + \frac{1}{2}\beta_c \left(\frac{\partial \Delta_{\boldsymbol{k}}^2}{\partial\beta}\right)_{T=T_c}\right] , \tag{6.187}$$

and just above the critical temperature it is

$$C_{V,N}^{>} \approx -2\beta_c k_B \sum_{\boldsymbol{k}} \frac{\partial n_{\boldsymbol{k}}}{\partial \xi_{\boldsymbol{k}}} \xi_{\boldsymbol{k}}^2 . \tag{6.188}$$

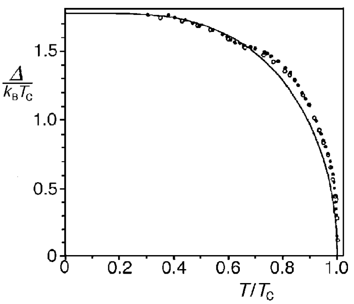

Figure 6.14 Variation of $\Delta/k_B T_c$ with reduced temperature, T/T_c, for tin. The data points are obtained from ultrasonic acoustic attenuation measurements [18] for two different frequencies. The solid line is BCS theory. Reprinted, by permission, from [144].

The discontinuity in the heat capacity at the critical temperature is

$$\Delta C_{V,N} = C^{<}_{V,\langle N\rangle} - C^{>}_{V,\langle N\rangle} = -\beta_c^2 k_B \sum_{\boldsymbol{k}}{}' \left(\frac{\partial \Delta^2}{\partial \beta}\right)_{T=T_c} \frac{\partial n_{\boldsymbol{k}}(\xi_{\boldsymbol{k}})}{\partial \xi_{\boldsymbol{k}}}$$
$$= -k_B \beta_c^2 N(0) \left(\frac{\partial \Delta^2}{\partial \beta}\right)_{T=T_c} = N(0) \left(\frac{\partial \Delta^2}{\partial T}\right)_{T=T_c} . \qquad (6.189)$$

Thus, the heat capacity has a finite discontinuity at the critical temperature, as we would expect for a mean field theory.

Mean field theory gives a surprisingly good description of the behavior of real superconductors. In Figure 6.14 we show experimental measurements of the gap function, Δ, as a function of temperature for tin. The solid line is the mean field theory of Bardeen, Cooper, and Schrieffer. The experimental points, which are obtained from ultrasonic acoustic attenuation measurements [144], fit it very well.

6.12
Problems

Problem 6.1 A monatomic dilute gas, in a box of volume V, obeys the Dieterici equation of state $P = nRT/(V - nb)\exp(-na/(VRT))$, where n is mole number, a and b are constants determined by the type of molecules in the gas. (a) Find the second virial coefficient for this gas and express it in terms of a and b. (b) Compute the constants a and b for a gas of particles that interacts via a two-body potential $V(r)$ that has an infinite hard core and an attractive square-well potential region such that $V(r) = \infty$ for $r < \sigma$, $V(r) = -\epsilon$ for $\sigma \le r \le \lambda\sigma$, and $V(r) = 0$ for $r > \lambda\sigma$, where r is the relative displacement of a pair of particles. (c) The constants a and b for a gas of CO_2 molecules are $a = 0.3658\,\mathrm{Pa\,m^6/mol^2}$ and $b = 0.000\,042\,86\,\mathrm{m^3/mol}$ (see Table 3.6, Section 3.8). Assuming that $\lambda = 2$ obtain estimates for the radius σ and binding energy ϵ (in eVs) for CO_2.

Problem 6.2 Consider $N = 1000$ hypothetical molecules "M" each of which has three heme sites that can bind an oxygen molecule O_2. The binding energies E_n when n O_2 are bound are $E_0 = 0$, $E_1 = -0.49$ eV, $E_2 = -1.02$ eV, and $E_3 = -1.51$ eV. Assume that the "M" molecules are in equilibrium with air at $T = 310$ K and the partial pressure of O_2 in air is $P_{O_2} = 0.2$ bar. Also assume that the "M" molecules don't interact with each other and air can be treated as an ideal gas. Of the $N = 1000$ "PP" molecules present, how many will have (a) zero O_2 molecules bound to them; (b) one O_2 molecule bound to them; (c) two O_2 molecules bound to them; (d) three O_2 molecules bound to them?

Problem 6.3 Compute the second virial coefficient for a gas that interacts via the potential

$$\mathrm{V}(\boldsymbol{q}) = \begin{cases} \infty & \text{if} \quad q < R\,, \\ \frac{\varepsilon}{R(\lambda-1)}(q-\lambda R) & \text{if} \quad R \leq q \leq \lambda R\,, \\ 0 & \text{if} \quad q > \lambda R\,. \end{cases}$$

Problem 6.4 Consider a classical gas in a box of volume V. Compute the second virial coefficient, B_2, for the Gaussian model, $f(q_{ij}) = \mathrm{e}^{-aq_{ij}^2}$, where $a^{-1/2} \ll V^{1/2}$. Sketch the effective potential, $\beta V(q_{ij})$.

Problem 6.5 Compute the second coefficient for the weakly coupled particles with potential $V(\boldsymbol{q}) = V_0$ for $q \leq R$ and $V(\boldsymbol{q}) = 0$ for $q > R$.

Problem 6.6 The density of states of an ideal Bose–Einstein gas in a cubic box of volume V is

$$g(E) = \begin{cases} \alpha E^3 & \text{if} \quad E > 0\,, \\ 0 & \text{if} \quad E < 0\,, \end{cases}$$

where α is a constant. Compute the critical temperature for Bose–Einstein condensation.

Problem 6.7 (a) Compute the Bose–Einstein condensation temperature for a gas of $N = 4 \times 10^4$ rubidium atoms in an asymmetric harmonic trap with oscillation frequencies $f_1 = 120$ Hz, $f_2 = 120/\sqrt{8}$ Hz, and $f_3 = 120/\sqrt{8}$ Hz. (b) If condensation occurred at the same temperature in a cubic box, what is the volume of the box?

Problem 6.8 Liquid helium ($^4He_2$) undergoes a superfluid transition at a temperature of $T = 2.16$ K. At this temperature it has a mass density of $\rho = 0.145\,\mathrm{g/cm^3}$. Make the (rather drastic) assumption that liquid helium behaves like an ideal gas and compute the critical temperature for Bose–Einstein condensation.

Problem 6.9 An ideal Bose–Einstein gas consists of noninteracting bosons of mass m which have an internal degree of freedom which can be described by assuming that the bosons are two-level atoms. Bosons in the ground state have energy $E_0 = p^2/(2m)$, while bosons in the excited state have energy $E_1 = p^2/(2m) + \Delta$, where p is the momentum and Δ is the excitation energy. Assume that $\Delta \gg k_B T$. Compute the Bose–Einstein condensation temperature, T_c, for this gas of two-level bosons. Does the existence of the internal degree of freedom raise or lower the condensation temperature?

Problem 6.10 Compute the Clausius–Clapeyron equation for an ideal Bose–Einstein gas and sketch the coexistence curve. Show that the line of transition points in the P–v plane obeys the equation

$$Pv^{5/3} = \frac{2\pi\hbar^2}{m} \frac{g_{5/2}(1)}{(g_{3/2}(1))^{5/3}} .$$

Problem 6.11 Show that the pressure, P, of an ideal Bose–Einstein gas can be written in the form $P = \alpha u$, where u is the internal energy per unit volume and α is a constant. (a) What is u? (b) What is α?

Problem 6.12 (a) For a BEC, prove that

$$H = \sum_k \left[\mathcal{E}_k \hat{a}_k^\dagger \hat{a}_k + \frac{\Delta}{2}\left(\hat{a}_{-k}^\dagger \hat{a}_k^\dagger + \hat{a}_{-k}\hat{a}_k\right)\right] = \sum_k E_k \hat{b}_k^\dagger \hat{b}_k + \frac{1}{2}\sum_k (E_k - \mathcal{E}_k)$$

using the Bogoliubov transformation $\hat{a}_k^\dagger = u_k \hat{b}_k^\dagger - v_k \hat{b}_{-k}$ and $\hat{a}_k = u_k \hat{b}_k - v_k \hat{b}_{-k}^\dagger$. (b) Using the requirement that $[\hat{a}_k \hat{a}_k^\dagger - \hat{a}_k^\dagger \hat{a}_k] = 1$ and $[\hat{b}_k \hat{b}_k^\dagger - \hat{b}_k^\dagger \hat{b}_k] = 1$, find explicit expressions for E_k, u_k, and v_k in terms of $\mathcal{E}_k$ and Δ.

Problem 6.13 Electrons in a piece of copper metal can be assumed to behave like an ideal Fermi gas. Copper metal in the solid state has a mass density of $9\,\mathrm{g/cm^3}$. Assume that each copper atom donates one electron to the Fermi gas. Assume the system is at $T = 0\,\mathrm{K}$. (a) Compute the Fermi energy, ε_F, of the electron gas. (b) Compute the Fermi "temperature", $T_F = \varepsilon_F / k_B$.

Problem 6.14 A two-dimensional electron gas can be formed at the interface of GaAs/AlGaAs semiconductors. The effective mass of the electrons is $m = 0.067 m_e$, where m_e is the mass of the electron in free space. Treat the electrons like an ideal Fermi gas of particles with spin-1/2 and mass m in a two-dimensional box with area $A = L^2$. (a) What is the density of states of the electron gas? (b) If the electron density is $N/A = 2.0 \times 10^{13}/\mathrm{cm}^2$, what is the Fermi energy of the two-dimensional electron gas?

Problem 6.15 The density of states of an ideal Fermi–Dirac gas is

$$g(E) = \begin{cases} D & \text{if} \quad E > 0\,, \\ 0 & \text{if} \quad E < 0\,, \end{cases}$$

where D is a constant. (a) Compute the Fermi energy. (b) Compute the heat capacity at very low temperature.

Problem 6.16 Compute the magnetization of an ideal gas of spin-1/2 fermions in the presence of a magnetic field. Assume that the fermions each have magnetic moment μ_e. Find an expression for the magnetization in the limit of weak magnetic field and $T \to 0\,\mathrm{K}$.

Problem 6.17 Show that the entropy for an ideal Fermi–Dirac ideal gas (neglecting spin) can be written in the form

$$S = -k_B \sum_l \left\{ \langle n_l \rangle \ln[\langle n_l] + (1 - \langle n_l \rangle) \ln[1 - \langle n_l \rangle] \right\} ,$$

where $\langle n_1 \rangle = (e^{\beta(\varepsilon_1 - \mu)} + 1)^{-1}$.

Problem 6.18 One mole of a dilute gas of He^3 atoms (which are spin-1/2 fermions) at temperature $T = 140\,\mathrm{K}$ is contained in a box of volume $V = 1.0\,\mathrm{cm}^3$. (a) Compute the lowest order (in density) correction to the classical ideal gas pressure. (b) What fraction of the total pressure is due to the Fermi statistics of the atoms?

Problem 6.19 In the grand canonical ensemble, the variance in particle number is $\langle N^2 \rangle - \langle N \rangle^2 = 1/\beta(\partial \langle N \rangle / \partial \mu)_{T,}$. (a) Compute $\langle N^2 \rangle - \langle N \rangle^2$ for a classical ideal gas. (b) Compute $\langle N^2 \rangle - \langle N \rangle^2$ for a Bose–Einstein ideal gas at fairly high temperature (keep corrections to the classical result to first order in the particle density). How and why is your result different from the classical ideal gas result? (c) Compute $\langle N^2 \rangle - \langle N \rangle^2$ for a Fermi–Dirac ideal gas at a fairly high temperature (keep corrections to the classical result to first order in the particle density). How and why is your result different from the classical ideal gas result?

Problem 6.20 To lowest order in the density, find the difference in the pressure and isothermal compressibility between an ideal boson and an ideal fermion gas. Assume that the fermions and bosons have the same mass and both are spinless. (*Note*: You are now considering fairly high temperature.)

Problem 6.21 Show that near the critical temperature the gap function, $\Delta(T)$, in a weakly coupled, condensed Fermi fluid (superconductor) in the mean field approximation has temperature dependence

$$\frac{\Delta(T)}{\Delta(0)} = 1.74 \left(1 - \frac{T}{T_c}\right)^{1/2} ,$$

where T_c is the critical temperature and $\Delta(0)$ is the gap function at $T = 0\,\mathrm{K}$.

Problem 6.22 The unitary matrix, $\overline{\boldsymbol{U}}_k \equiv \begin{pmatrix} u_k & v_k \\ -v_k & u_k \end{pmatrix}$, diagonalizes the effective Hamiltonian $\overline{\boldsymbol{K}}_k \equiv \begin{pmatrix} \varepsilon_k & \Delta \\ \Delta & -\varepsilon_k \end{pmatrix}$. Compute v_k and u_k.

7
Brownian Motion and Fluctuation–Dissipation

7.1
Introduction

We now begin to discuss the dynamics of many-body systems that are out of equilibrium and we develop tools to describe the processes by which they decay back to equilibrium. These systems generally have 10^{23} degrees of freedom that decay rapidly (on the time scale of a few collision times). However, a few of these degrees of freedom decay very slowly due to conservation laws at the microscopic level. It is these slowly decaying modes that we will be most concerned about. We will find that these same decay processes also govern the dynamical behavior of fluctuations in systems that are at equilibrium.

The dynamics of a Brownian particle provides a paradigm for describing equilibrium and nonequilibrium processes. When a relatively massive particle (like a grain of pollen) is immersed in a fluid, it is observed to undergo rapid, random motion, even when it is in thermodynamic equilibrium with the fluid. The agitated motion of the Brownian particle is a consequence of random "kicks" that it receives from density fluctuations in the equilibrium fluid, and these density fluctuations are a consequence of the discrete (atomic) nature of matter. Thus, Brownian motion provides evidence on the macroscopic scale of the fluctuations that are continually occurring in equilibrium systems.

A phenomenological theory of Brownian motion can be obtained by writing Newton's equation of motion for the massive particle and including in it a systematic friction force and a random force that mimics the effects of the many degrees of freedom of the fluid in which the massive particle is immersed. The equation of motion for the Brownian particle is called the Langevin equation. Given the Langevin equation for a Brownian motion process, we can obtain an equation for the time evolution of the probability distribution of the Brownian particle, called the Fokker–Planck equation. We will derive the Fokker–Planck equation and we will solve it for Brownian motion with one spatial degree of freedom in the presence of strong friction.

In 1932, Onsager showed that the time reversibility of Newtonian dynamics (or quantum mechanics) imposes certain relations between decay (to equilibrium) processes in a complex system. Onsager's relations are important because they

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provide a link between different types of decay processes and thereby reduce the number of experiments that must be performed in order to measure decay properties of a system. In this chapter we will derive Onsager's relations.

Fluctuations about the equilibrium state decay *on the average* according to the same macroscopic laws that govern the decay of a nonequilibrium system to the equilibrium state. If we can probe equilibrium fluctuations, we have a means of probing the decay processes in a system. Linear response theory provides a tool for probing equilibrium fluctuations by applying a weak external field which couples to the system. The system responds to the field in a manner that depends entirely on the spectrum of the equilibrium fluctuations. The response to the dynamic field is measured by the susceptibility matrix. The fluctuation–dissipation theorem links the susceptibility matrix to the correlation matrix for equilibrium fluctuations. According to the fluctuation–dissipation theorem, the spectrum of equilibrium fluctuations determines the rate of absorption of energy from the external field.

Our derivation of Onsager's relations and of the fluctuation–dissipation theorem in this chapter are very general. We do however illustrate the fluctuation–dissipation theorem by applying it to classical Brownian motion. In Chapter 8, we will discuss these theories again in the context of hydrodynamics.

In the last section of this chapter, we derive linear response theory for quantum systems starting from microscopic theory. We then use this theory to obtain the conductance of ballistic electrons in a one-dimensional wire connected to electron reservoirs. We show that this simple quantum system can absorb power from an applied field.

7.2
Brownian Motion

Brownian motion provides evidence, on the "macroscopic" scale, for the atomic nature of matter on the "microscopic" scale. The discreteness of matter causes fluctuations in the matter density which, in turn, causes observable effects on the motion of the Brownian particle. This can be seen if one immerses a large particle (usually about one micron in diameter) in a fluid with the same density as the particle. When viewed under a microscope, the large particle (the Brownian particle) appears to be in a state of agitation, undergoing rapid and random movements. Early in the nineteenth century, the biologist Robert Brown wrote a paper on this phenomenon [22] which received wide attention [49, 51, 164], and as a result it was named after him.

In this section we derive the theory of Brownian motion starting from the Langevin equations of motion for a Brownian particle. We focus on a large particle (the Brownian particle) immersed in a fluid of much smaller atoms. The motion of the large particle is much slower than that of the atoms and is the result of random and rapid kicks due to density fluctuations in the fluid. Since the time scales of the Brownian motion and the atomic motions are vastly different, we can separate them and focus on the behavior of the Brownian particle. The effect of the fluid on the Brownian particle can be reduced to that of a random force and a systematic friction acting on the Brownian particle.

The theory of Brownian motion provides a paradigm for treating many-body systems in which a separation of time scales can be identified between some of the degrees of freedom. This is the reason we consider it in some detail here.

7.2.1
Langevin Equation

Consider a particle of mass m and radius a, immersed in a fluid of particles of mass m_{f} ($m_{\mathrm{f}} \ll m$) and undergoing Brownian motion. The fluid gives rise to a retarding force (friction) that is proportional to the velocity, and a random force, $\xi(t)$, due to random density fluctuations in the fluid. The equation of motion for the Brownian particle can be written

$$\frac{\mathrm{d}v(t)}{\mathrm{d}t} = -\frac{\gamma}{m} v(t) + \frac{1}{m}\xi(t) , \tag{7.1}$$

where $v(t)$ is the velocity of the particle at time t and γ is the friction coefficient. Equation (7.1) is called the *Langevin equation*.

We will assume that $\xi(t)$ is a Gaussian white noise process with zero mean so that $\langle \xi(t)\rangle_\xi = 0$. The noise is assumed to be Markovian and stationary and the average, $\langle\rangle_\xi$, is an average with respect to the probability distribution of realizations of the stochastic variable $\xi(t)$. We will not write the probability distribution explicitly. The assumption that the noise is *white* means that the noise is delta-correlated,

$$\langle \xi(t_1)\xi(t_2)\rangle_\xi = g\delta(t_2 - t_1) , \tag{7.2}$$

and therefore it is not possible to represent a single realization of $\xi(t)$ in terms of a continuously drawn line (although it is possible to do so with $v(t)$). The weighting factor, g, is a measure of the strength of the noise. Because the noise is *Gaussian* with zero mean, correlation functions with an odd number of terms, $\xi(t)$, are zero and correlation functions with an even number of terms, $\xi(t)$, can be expressed in terms of sums of products of the pairwise correlation function, $\langle \xi(t_1)\xi(t_2)\rangle_\xi$. For example,

$$\begin{aligned}\langle \xi(t_1)\xi(t_2)\xi(t_3)\xi(t_4)\rangle_\xi &= \langle \xi(t_1)\xi(t_2)\rangle_\xi \langle \xi(t_3)\xi(t_4)\rangle_\xi \\ &\quad + \langle \xi(t_1)\xi(t_3)\rangle_\xi \langle \xi(t_2)\xi(t_4)\rangle_\xi + \langle \xi(t_1)\xi(t_4)\rangle_\xi \langle \xi(t_2)\xi(t_3)\rangle_\xi .\end{aligned} \tag{7.3}$$

This is a realization of Wick's theorem in a classical system (see Exercise A.7).

Assume that at time $t = 0$, the velocity and displacement of the Brownian particle are $v(0) = v_0$ and $x(0) = x_0$, respectively. Then its velocity and displacement at time t are

$$v(t) = v_0 \mathrm{e}^{-(\gamma/m)t} + \frac{1}{m}\int_0^t \mathrm{d}s \mathrm{e}^{-(\gamma/m)(t-s)}\xi(s) \tag{7.4}$$

and

$$x(t) = x_0 + \frac{m}{\gamma}(1 - \mathrm{e}^{-(\gamma/m)t})v_0 + \frac{1}{\gamma}\int_0^t \mathrm{d}s(1 - \mathrm{e}^{-(\gamma/m)(t-s)})\xi(s)\,, \tag{7.5}$$

respectively. Equations (7.4) and (7.5) give $v(t)$ and $x(t)$ for a single realization of $\xi(t)$. Since $\xi(t)$ is a stochastic variable, $v(t)$ and $x(t)$ are also stochastic variables whose properties are determined by $\xi(t)$.

7.2.2
Correlation Function and Spectral Density

We can obtain the velocity autocorrelation function from Eqs. (7.2) and (7.4). If we make use of the fact that $\langle v_0\xi(t)\rangle_\xi = 0$, then we can write

$$\begin{aligned}\langle v(t_2)v(t_1)\rangle_\xi &= v_0^2\mathrm{e}^{-(\gamma/m)(t_2+t_1)}\\ &\quad + \frac{g}{m^2}\int_0^{t_2}\mathrm{d}s_2\int_0^{t_1}\mathrm{d}s_1\,\delta(s_2 - s_1)\mathrm{e}^{(\gamma/m)(s_1-t_1)}\mathrm{e}^{(\gamma/m)(s_2-t_2)}\,. \end{aligned}\tag{7.6}$$

We can perform the integration in Eq. (7.6). For $t_2 > t_1$, we obtain

$$\langle v(t_2)v(t_1)\rangle_\xi = \left(v_0^2 - \frac{g}{2m\gamma}\right)\mathrm{e}^{-(\gamma/m)(t_2+t_1)} + \frac{g}{2m\gamma}\mathrm{e}^{-(\gamma/m)(t_2-t_1)}\,. \tag{7.7}$$

For $t_1 > t_2$, we obtain a similar result but with the order of t_1 and t_2 interchanged in the last exponent. Therefore, for arbitrary t_1 and t_2 we can write

$$\langle v(t_2)v(t_1)\rangle_\xi = \left(v_0^2 - \frac{g}{2m\gamma}\right)\mathrm{e}^{-(\gamma/m)(t_2+t_1)} + \frac{g}{2m\gamma}\mathrm{e}^{-(\gamma/m)(|t_2-t_1|)}\,. \tag{7.8}$$

Note the absolute value sign on the last exponent.

We can also obtain the variance in the displacement. If we use Eqs. (7.2) and (7.5) and the fact that $\langle x_0\xi(t)\rangle_\xi = 0$, we can write

$$\begin{aligned}\langle (x(t) - x_0)^2\rangle_\xi &= \frac{m^2}{\gamma^2}\left(v_0^2 - \frac{g}{2m\gamma}\right)(1 - \mathrm{e}^{-(\gamma/m)t})^2\\ &\quad + \frac{g}{\gamma^2}\left[t - \frac{m}{\gamma}(1 - \mathrm{e}^{-(\gamma/m)t})\right]\,. \end{aligned}\tag{7.9}$$

Thus, after a long time the variance goes as $\langle (x(t_2) - x_0)^2\rangle_\xi = (g/\gamma^2)t$ (neglecting some constant terms).

We can determine the value of g for a Brownian particle in equilibrium with a fluid. Take the "thermal" average $\langle\rangle_T$ of Eq. (7.8). By the equipartition theorem, $(1/2)m\langle v_0^2\rangle_T = (1/2)k_\mathrm{B}T$, where k_B is Boltzmann's constant and T is the temperature in kelvin. If the Brownian particle is in equilibrium, its velocity autocorrelation function must be stationary and can only depend on time differences $t_1 - t_2$.

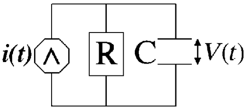
Therefore, we must have $g = 2m\gamma v_0^2$ so the first term on the right in Eq. (7.8) is removed. If we now take the thermal average of Eq. (7.8), we see that we must have $g = 2\gamma k_\mathrm{B} T$. The correlation function can then be written

$$\langle\langle v(t_2)v(t_1)\rangle_\xi\rangle_T = \frac{k_\mathrm{B}T}{m}\mathrm{e}^{-(\gamma/m)(|t_2-t_1|)} . \tag{7.10}$$

The absolute value on the time difference ensures that correlations always decay as the time difference increases. This means that information about the initial velocity of the Brownian particle decays away exponentially.

Exercise 7.1

Electrons in an electrical circuit at temperature T undergo Brownian motion (thermal agitation) which is a fundamental source of noise in such circuits. Consider the simple circuit shown in the figure, which consists of a capacitor C in parallel with a resistor R. Electrons in the resistor provide a fluctuating current $i(t)$, whose average is zero $\langle i(t)\rangle = 0$ but whose fluctuations about the average are delta-correlated $\langle i(t+\tau)i(t)\rangle_i = g\delta(\tau)$, where g is the noise strength. By the equipartition theorem, the average electrical energy in the capacitor is $(1/2)C\langle V^2\rangle_T = (1/2)k_\mathrm{B}T$. (a) Compute the noise strength g. (b) Compute the voltage correlation function $\langle\langle V(t_2)V(t_1)\rangle_i\rangle_T$.



Answer: The voltage across the capacitor is a solution of the circuit equation $i(t) = V(t)/R + C\mathrm{d}V(t)/\mathrm{d}t$ and is given by $V(t) = V(0)\mathrm{e}^{-t/RC} + (1/C)\int_0^\infty \mathrm{d}t_1 \mathrm{e}^{-(t-t_1)/RC} i(t_1)$. Using the fact that $\langle i(t+\tau)i(t)\rangle_i = g\delta(\tau)$, the voltage correlation function takes the form

$$\langle V(t_2)V(t_1)\rangle_i = \left(V(0)^2 - \frac{gR}{2C}\right)\mathrm{e}^{-(t_2+t_1)/RC} + \frac{gR}{2C}\mathrm{e}^{-|t_2-t_1|/RC} .$$

If the system is assumed to be in thermal equilibrium and we take the thermal average of $\langle V(t_2)V(t_1)\rangle_i$, the thermal average can only depend on the time difference $|t_2 - t_1|$. Therefore, by the equipartition theorem, we can set $\langle V(0)^2\rangle_T = k_\mathrm{B}T/C = gR/(2C)$, and the noise strength is given by $g = 2k_\mathrm{B}T/R = 2k_\mathrm{B}TG$, where $G = 1/R$ is the conductivity. Thus, the current correlation function and the voltage correlation function take the forms

$$\langle\langle i(t+\tau)i(t)\rangle_i\rangle_T = 2k_\mathrm{B}TG\delta(\tau) \quad \text{and} \quad \langle\langle V(t_2)V(t_1)\rangle_i\rangle_T = \frac{k_\mathrm{B}T}{C}\mathrm{e}^{-|t_2-t_1|/RC} ,$$

respectively. The electrical noise induced by the Brownian motion of electrons in a circuit was measured by Johnson [92] and was used by him to determine the value of Boltzmann's constant k_B.

For the case when the Brownian particle is in equilibrium with the fluid, the variance of the displacement becomes

$$\langle\langle(x(t)-x_0)^2\rangle_\xi\rangle_T = \frac{2k_\mathrm{B}T}{\gamma}\left[t-\frac{m}{\gamma}(1-\mathrm{e}^{-(\gamma/m)t})\right], \tag{7.11}$$

where we have assumed that $\langle x_0\rangle_T = \langle v_0\rangle_T = 0$ and that x_0 and v_0 are statistically independent so that $\langle x_0 v_0\rangle = 0$. Thus, after a long time, $\langle\langle(x(t)-x_0)^2\rangle_\xi\rangle_T = (2k_\mathrm{B}T/\gamma)t$ and the *diffusion coefficient* becomes $D = k_\mathrm{B}T/\gamma$. The friction coefficient, γ, can also be determined from properties of the fluid and hydrodynamics. For large spherical Brownian particles, we can assume that the fluid sticks to the surface. The friction coefficient is then the Stokes friction, $\gamma = 6\pi\eta a$, where η is the shear viscosity of the fluid and a is the radius of the Brownian particle.

The spectral density is the Fourier transform of the correlation function (this is the content of the Weiner–Khintchine Theorem which is discussed later in this Chapter) and contains information about the frequency spectrum of fluctuations about the equilibrium state. The spectral density is given by

$$S_{v,v}(\omega) = \int_{-\infty}^{\infty} \mathrm{d}\tau \mathrm{e}^{-\mathrm{i}\omega\tau}\langle v(t_1+\tau)v(t_1)\rangle_{\xi,T} = \int_{-\infty}^{\infty} \mathrm{d}\tau \mathrm{e}^{-\mathrm{i}\omega\tau} C_{v,v}(\tau)\,. \tag{7.12}$$

For the case of simple Brownian motion with a velocity autocorrelation given by (7.10), the spectral density is given by

$$S_{vv}(\omega) = \frac{2k_\mathrm{B}T}{m}\frac{\gamma/m}{\omega^2+(\gamma/m)^2} \tag{7.13}$$

and corresponds to a Lorentzian curve that is peaked at $\omega = 0$ with a half-width of γ/m. White noise has a very different spectrum. Its spectral density is

$$S_{\xi,\xi}(\omega) = \int_{-\infty}^{\infty} \mathrm{d}\tau \mathrm{e}^{-\mathrm{i}\omega\tau}\langle \xi(t_1+\tau)\xi(t_1)\rangle_\xi = g = 2\gamma k_\mathrm{B}T\,, \tag{7.14}$$

and contains all frequencies with equal weight.

7.3
The Fokker–Planck Equation

The Fokker–Planck equation [65, 185, 205] is the equation governing the time evolution of the probability density for the Brownian particle. It is a second-order differential equation and is exact for the case when the noise acting on the Brownian particle is Gaussian white noise. The derivation of the Fokker–Planck equation is a two step process. We first derive the equation of motion for the probability density, $\rho(x, v, t)$, to find the Brownian particle in the interval, $x \to x + \mathrm{d}x$ and

$v \to v + \mathrm{d}v$, at time, t, for one realization of the random force, $\xi(t)$. We then obtain an equation for $P(x, v, t) = \langle \rho(x, v, t) \rangle_\xi$, the average of $\rho(x, v, t)$ over many realizations of the random force, $\xi(t)$. The probability density, $P(x, v, t)$, is the macroscopically observed probability density for the Brownian particle. Its dynamical evolution is governed by the Fokker–Planck equation.

Exercise 7.2

Consider a Brownian particle of mass m which is attached to a harmonic spring with force constant k and is constrained to move in one dimension. The Langevin equations are

$$\frac{\mathrm{d}v}{\mathrm{d}t} = -\frac{\gamma}{m} v - \omega_0^2 x + \frac{1}{m} \xi(t) \quad \text{and} \quad \frac{\mathrm{d}x}{\mathrm{d}t} = v \, ,$$

where $\omega_0 = \sqrt{k/m}$. Let x_0 and v_0 be the initial position and velocity, respectively, of the Brownian particle and assume that it is initially in equilibrium with the fluid. By the equipartition theorem, $(1/2)m\langle v_0^2 \rangle_T = (1/2)k_\mathrm{B} T$ and $(1/2)\omega_0^2 \langle x_0^2 \rangle_T = (1/2)k_\mathrm{B} T$. Assume that x_0 and v_0 are statistically independent so $\langle x_0 v_0 \rangle_T = 0$. (a) Show that a condition for the process to be stationary is that the noise strength is $g = 4\gamma k_\mathrm{B} T$. (b) Compute the velocity correlation function, $\langle \langle v(t_2) v(t_1) \rangle_\xi \rangle_T$.

Answer: The Langevin equations can be solved and give the following expression for the velocity at time t:

$$v(t) = v_0 \mathrm{e}^{-\Gamma t} w(t) - \frac{\omega_0^2}{\Delta} x_0 \mathrm{e}^{-\Gamma t} \sinh(\Delta t) + \frac{1}{m} \int_0^t \mathrm{d}t' \xi(t') \mathrm{e}^{-\Gamma(t-t')} w(t - t') \, ,$$

where $w(t) = \cosh(\Delta t) - (\Gamma/\Delta) \sinh(\Delta t)$, $\Gamma = \gamma/m$, and $\Delta = \sqrt{\Gamma^2 - \omega_0^2}$. If we use the fact that $\langle x_0 v_0 \rangle_T = 0$ and assume that $t_2 > t_1$, the velocity correlation function can be written

$$\begin{aligned}
\langle \langle v(t_2) v(t_1) \rangle_\xi \rangle_T &= \mathrm{e}^{-\Gamma(t_2+t_1)} w(t_2) w(t_1) \langle v_0^2 \rangle_T \\
&\quad + \frac{\omega_0^4}{\Delta^2} \langle x_0^2 \rangle_T \mathrm{e}^{-\Gamma(t_2+t_1)} \sinh(\Delta t_2) \sinh(\Delta t_1) \\
&\quad + \frac{g}{m^2} \int_0^{t_1} \mathrm{d}t \mathrm{e}^{-\Gamma(t_2+t_1-2t)} w(t_2 - t) w(t_1 - t) \, .
\end{aligned}$$

If we choose $g = 4\gamma k_\mathrm{B} T$ then after some algebra we obtain a stationary correlation function

$$\langle \langle v(t_2) v(t_1) \rangle_\xi \rangle_T = \frac{k_\mathrm{B} T}{m} \mathrm{e}^{-\Gamma(t_2-t_1)} \left[\cosh[\Delta(t_2 - t_1)] - \frac{\Gamma}{\Delta} \sinh[\Delta(t_2 - t_1)] \right] \, .$$

A similar calculation for $t_1 > t_2$ yields the same answer but with $t_1 \leftrightarrow t_2$. Thus,

$$\langle \langle v(t_1 + \tau) v(t_1) \rangle_\xi \rangle_T = \frac{k_\mathrm{B} T}{m} \mathrm{e}^{-\Gamma|\tau|} \left[\cosh(\Delta \tau) - \frac{\Gamma}{\Delta} \sinh(\Delta |\tau|) \right] \, .$$

7.3.1
Probability Flow in Phase Space

Let us obtain the probability to find the Brownian particle in the interval $x \to x + \mathrm{d}x$ and $v \to v + \mathrm{d}v$ at time, t. We will consider the space of coordinates, $\boldsymbol{X} = (x, v)$, (x and v being the displacement and velocity of the Brownian particle, respectively), where $-\infty < x < \infty$ and $-\infty < v < \infty$. The Brownian particle is located in the infinitesimal area, $\mathrm{d}x\,\mathrm{d}v$, with probability, $\rho(x, v, t)\,\mathrm{d}x\,\mathrm{d}v$. We may view the probability distribution as a fluid whose density at point, (x, v), is given by $\rho(x, v, t)$ (cf. Appendix A). The speed of the fluid at point, (x, v), is given by $\dot{\boldsymbol{X}} = (\dot{x}, \dot{v})$. Since the Brownian particle must lie somewhere in this space, we have the condition

$$\int_{-\infty}^{\infty} \mathrm{d}x \int_{-\infty}^{\infty} \mathrm{d}v \rho(x, v, t) = 1\,. \tag{7.15}$$

Let us now consider a fixed finite area, A_0, in (x, v) space. The probability to find the Brownian particle in this area is $P(A_0) = \int_{A_0} \mathrm{d}x\,\mathrm{d}v \rho(x, v)$. Since the Brownian particle cannot be destroyed, any change in the probability contained in A_0 must be due to a flow of probability through the sides of A_0. Thus,

$$\frac{\partial}{\partial t} P(A_0) = \frac{\partial}{\partial t} \iint_{A_0} \mathrm{d}x\,\mathrm{d}v \rho(x, v, t) = -\oint_{L_0} \rho(x, v, t) \dot{\boldsymbol{X}} \cdot \mathrm{d}\boldsymbol{S_0}\,, \tag{7.16}$$

where $\mathrm{d}\boldsymbol{S_0}$ denotes a differential surface element along the edge of area A_0, $\rho\dot{\boldsymbol{X}}$ is the probability current through the edge, and L_0 is the line around the edge of area element, A_0. We can use Gauss's theorem to change the surface integral into an area integral, $\oint_{L_0} \rho(x, v, t)\dot{\boldsymbol{X}} \cdot \mathrm{d}\boldsymbol{S_0} = \int_{A_0} \mathrm{d}x\,\mathrm{d}v \boldsymbol{\nabla}_X \cdot (\dot{\boldsymbol{X}}\rho(x, v, t))$, where $\boldsymbol{\nabla}_X$ denotes the gradient, $\boldsymbol{\nabla}_X = (\partial/\partial x, \partial/\partial v)$. We find

$$\frac{\partial}{\partial t} \iint_{A_0} \mathrm{d}x\,\mathrm{d}v \rho(x, v, t) = -\int_{A_0} \mathrm{d}x\,\mathrm{d}v \boldsymbol{\nabla}_X \cdot (\dot{\boldsymbol{X}}\rho(x, v, t))\,. \tag{7.17}$$

Since the area, A_0, does not change with time, we can take the time derivative inside the integral. Since the area, A_0, is arbitrary, we can equate integrands of the two integrals in Eq. (7.17). Then we find that

$$\frac{\partial \rho(t)}{\partial t} = -\boldsymbol{\nabla}_X \cdot (\dot{\boldsymbol{X}}\rho(t)) = -\frac{\partial(\dot{x}\rho(t))}{\partial x} - \frac{\partial(\dot{v}\rho(t))}{\partial v}\,, \tag{7.18}$$

where we have let $\rho(t) = \rho(x, v, t)$.

7.3.2
Probability Flow for Brownian Particle

Let us assume that the Brownian particle moves in the presence of a potential, $V(x)$. The Langevin equations are then

$$\frac{\mathrm{d}v(t)}{\mathrm{d}t} = -\frac{\gamma}{m}v(t) + \frac{1}{m}F(x) + \frac{1}{m}\xi(t) \quad \text{and} \quad \frac{\mathrm{d}x(t)}{\mathrm{d}t} = v(t)\,, \tag{7.19}$$

where the force, $F(x) = -\mathrm{d}V(x)/\mathrm{d}x$. If we substitute these equations into Eq. (7.18), we find

$$\frac{\partial\rho(t)}{\partial t} = -\hat{L}_0\rho(t) - \hat{L}_1(t)\rho\,, \tag{7.20}$$

where the differential operators, $\hat{L}_0$ and $\hat{L}_1$ are defined

$$\hat{L}_0 = v\frac{\partial}{\partial x} - \frac{\gamma}{m} - \frac{\gamma}{m}v\frac{\partial}{\partial v} + \frac{1}{m}F(x)\frac{\partial}{\partial v} \quad \text{and} \quad \hat{L}_1 = \frac{1}{m}\xi(t)\frac{\partial}{\partial v}\,. \tag{7.21}$$

Since $\xi(t)$ is a stochastic variable, the time evolution of $\rho(x, v, t)$ will be different for each realization of $\xi(t)$.

When we observe an actual Brownian particle we are observing the average effect of the random force on it. Therefore, we introduce an *observable* probability, $P(x, v, t)\,\mathrm{d}x\,\mathrm{d}v$, to find the Brownian particle in the interval $x \to x + \mathrm{d}x$ and $v \to v + \mathrm{d}v$. We define this observable probability to be

$$P(x, v, t) = \langle\rho(x, v, t)\rangle_\xi\,. \tag{7.22}$$

We now must find the equation of motion for $P(x, v, t)$.

Since the random force, $\xi(t)$, has zero mean and is a Gaussian white noise, the derivation of $P(x, v, t)$ is straightforward and very instructive. It only takes a bit of algebra. We first introduce a new probability density, $\sigma(t)$, such that

$$\rho(t) = \mathrm{e}^{-\hat{L}_0 t}\sigma(t)\,. \tag{7.23}$$

Using (7.20), it is easy to show that $\sigma(t)$ obeys the equation of motion

$$\frac{\partial\sigma(t)}{\partial t} = -\hat{V}(t)\sigma(t)\,, \tag{7.24}$$

where $\hat{V}(t) = \mathrm{e}^{+\hat{L}_0 t}\hat{L}_1(t)\mathrm{e}^{-\hat{L}_0 t}$. Equation (7.24) has the formal solution

$$\sigma(t) = \exp\left(\int_0^t \mathrm{d}t'\,\hat{V}(t')\right)\sigma(0)\,. \tag{7.25}$$

Let us now expand the exponential in Eq. (7.25) in a power series. Using the identity, $\mathrm{e}^x = \sum_{n=0}^{\infty} x^n/n!$, we obtain

$$\sigma(t) = \left[\sum_{n=0}^{\infty}\frac{(-1)^n}{n!}\left(\int_0^t \mathrm{d}t'\,\hat{V}(t')\right)^n\right]\sigma(0)\,. \tag{7.26}$$

We now can take the average, $\langle\rangle_\xi$, of Eq. (7.26). Because the noise, $\xi(t)$, has zero mean and is Gaussian, Wick's theorem applies (see Exercise A.8). Only even values of n will remain,

$$\langle\sigma(t)\rangle_\xi = \left[\sum_{n=0}^{\infty}\frac{1}{2n!}\left\langle\left(\int_0^t \mathrm{d}t'\,\hat{V}(t')\right)^{2n}\right\rangle_\xi\right]\sigma(0)\,, \tag{7.27}$$

and the average, $\langle(\int_0^t \mathrm{d}t'\,\hat{V}(t'))^{2n}\rangle_\xi$ will decompose into $2n!/(n!2^n)$ identical terms, each containing a product of n pairwise averages, $\langle\int_0^t \mathrm{d}t_i\,\hat{V}(t_i)\int_0^t \mathrm{d}t_j\,\hat{V}(t_j)\rangle_\xi$. Thus, Eq. (7.27) takes the form

$$\langle\sigma(t)\rangle_\xi = \left[\sum_{n=0}^{\infty}\frac{1}{n!}\left(\frac{1}{2}\int_0^t \mathrm{d}t_2\int_0^t \mathrm{d}t_1\langle\hat{V}(t_2)\hat{V}(t_1)\rangle_\xi\right)^n\right]\sigma(0)\,. \tag{7.28}$$

We can now sum this series to obtain

$$\langle\sigma(t)\rangle_\xi = \exp\left(\frac{1}{2}\int_0^t \mathrm{d}t_2\int_0^t \mathrm{d}t_1\langle\hat{V}(t_2)\hat{V}(t_1)\rangle_\xi\right)\sigma(0)\,. \tag{7.29}$$

Let us compute the integral in Eq. (7.29),

$$\begin{aligned}
&\frac{1}{2}\int_0^t \mathrm{d}t_2\int_0^t \mathrm{d}t_1\langle\hat{V}(t_2)\hat{V}(t_1)\rangle_\xi \\
&= \frac{g}{2m^2}\int_0^t \mathrm{d}t_2\int_0^t \mathrm{d}t_1\delta(t_2-t_1)\mathrm{e}^{+\hat{L}_0 t_2}\frac{\partial}{\partial v}\mathrm{e}^{-\hat{L}_0(t_2-t_1)}\frac{\partial}{\partial v}\mathrm{e}^{-\hat{L}_0 t_1} \\
&= \frac{g}{2m^2}\int_0^t \mathrm{d}t_1\mathrm{e}^{+\hat{L}_0 t_1}\frac{\partial^2}{\partial v^2}\mathrm{e}^{-\hat{L}_0 t_1}\,.
\end{aligned} \tag{7.30}$$

If we substitute Eq. (7.30) into Eq. (7.29) and take the derivative of Eq. (7.29) with respect to time, t, we find the following equation of motion for $\langle\sigma(t)\rangle_\xi$,

$$\frac{\partial\langle\sigma(t)\rangle_\xi}{\partial t} = \frac{g}{2m^2}\mathrm{e}^{+\hat{L}_0 t}\frac{\partial^2}{\partial v^2}\mathrm{e}^{-\hat{L}_0 t}\langle\sigma(t)\rangle_\xi\,. \tag{7.31}$$

With this result, we can obtain the equation of motion of $P(x,v,t) = \langle\rho(x,v,t)\rangle_\xi$.

Let us note that $\langle\rho(t)\rangle_\xi = \mathrm{e}^{-\hat{L}_0 t}\langle\sigma(t)\rangle_\xi$ and take the derivative of $\langle\rho(t)\rangle_\xi$ with respect to time, t. We then obtain

$$\frac{\partial\langle\rho(t)\rangle_\xi}{\partial t} = -\hat{L}_0\langle\rho(t)\rangle_\xi + \mathrm{e}^{-\hat{L}_0 t}\frac{\partial\langle\sigma(t)\rangle_\xi}{\partial t} = -\hat{L}_0\langle\rho(t)\rangle_\xi + \frac{g}{2m^2}\frac{\partial\langle\rho(t)\rangle_\xi}{\partial v^2}\,, \tag{7.32}$$

where we have used Eq. (7.31). If we combine Eqs. (7.21), (7.22), and (7.32), the equation for the observable probability density, $P(x, v, t)$, takes the form

$$\frac{\partial P}{\partial t} = -v\frac{\partial P}{\partial x} + \frac{\partial}{\partial v}\left[\left(\frac{\gamma}{m}v - \frac{1}{m}F(x)\right)P\right] + \frac{g}{m^2}\frac{\partial^2 P}{\partial v^2} . \tag{7.33}$$

Equation (7.33) is the *Fokker–Planck equation* for the observable probability, $P(x, v, t) \cdot \mathrm{d}x\,\mathrm{d}v$, to find the Brownian particle in the interval $x \to x + \mathrm{d}x$ and $v \to v + \mathrm{d}v$ at time, t.

It is important to note that the Fokker–Planck equation conserves probability. We can write it in the form of a *continuity equation*

$$\frac{\partial P}{\partial t} = -\boldsymbol{\nabla} \cdot \boldsymbol{J} , \tag{7.34}$$

where $\boldsymbol{\nabla} = \hat{\boldsymbol{e}}_x \partial/\partial x + \hat{\boldsymbol{e}}_v \partial/\partial v$ is a gradient operator acting on the (x, v) phase space and $\boldsymbol{J}$ is the probability current or flux,

$$\boldsymbol{J} = \hat{\boldsymbol{e}}_x vP - \hat{\boldsymbol{e}}_v\left(\frac{\gamma}{m}vP - \frac{1}{m}F(x)P + \frac{g}{m^2}\frac{\partial P}{\partial v}\right) , \tag{7.35}$$

in the (x, v) phase space. By the same arguments used in Eqs. (7.16) and (7.17), we see that any change in the probability contained in a given area of the (x, v) phase space must be due to flow of probability through the sides of the area, and therefore the probability is a conserved quantity. It cannot be created or destroyed locally.

In this section we have derived the Fokker–Planck equation for a Brownian particle which is free to move in one spatial dimension. The Fokker–Planck equation can be generalized easily to three spatial dimensions, although in three spatial dimensions it generally cannot be solved analytically.

Below we consider Brownian motion in the limit of very large friction. For this case, detailed balance holds and we can begin to understand some of the complex phenomena governing the dynamics of the Fokker–Planck equation.

7.3.3
The Strong Friction Limit

Let us consider a Brownian particle moving in one dimension in a potential well, $V(x)$, and assume that the friction coefficient, γ is very large so that the velocity of the Brownian particle relaxes to its stationary state very rapidly. Then we can neglect time variations in the velocity (set $\mathrm{d}v/\mathrm{d}t \approx 0$) in the equation for the relaxation of the spatial position of the Brownian particle. With this assumption, the Langevin equation (7.19) reduces to

$$\frac{\mathrm{d}x(t)}{\mathrm{d}t} = \frac{1}{\gamma}F(x) + \frac{1}{\gamma}\xi(t) , \tag{7.36}$$

where $F(x) = -\mathrm{d}V(x)/\mathrm{d}x$. From Eq. (7.18), the equation of motion for the density, $\rho(x, t)$, is given by

$$\frac{\partial \rho(t)}{\partial t} = -\frac{\partial(\dot{x}\rho)}{\partial x} = -L_0\rho(t) - L_1(t)\rho , \tag{7.37}$$

where differential operators, L_0 and L_1, are defined

$$\hat{L}_0 = \frac{1}{\gamma}\frac{\partial F(x)}{\partial x} + \frac{1}{\gamma}F(x)\frac{\partial}{\partial x} \quad \text{and} \quad \hat{L}_1 = \frac{1}{\gamma}\xi(t)\frac{\partial}{\partial x} \,. \tag{7.38}$$

If we now substitute these definitions for $\hat{L}_0$ and $\hat{L}_1$ into (7.29), take the derivative with respect to time t, and note that $P(x,t) = \langle \rho(t) \rangle_\xi$, we obtain

$$\frac{\partial P(x,t)}{\partial t} = \frac{1}{\gamma}\frac{\partial}{\partial x}\left(\frac{\mathrm{d}V}{\mathrm{d}x}P(x,t) + \frac{g}{2\gamma}\frac{\partial P(x,t)}{\partial x}\right) = -\frac{\partial J}{\partial x}\,, \tag{7.39}$$

where we have let $F(x) = -\mathrm{d}V(x)/\mathrm{d}x$. The quantity $J = 1/\gamma((\mathrm{d}V/\mathrm{d}x)P + g/\gamma\,(\mathrm{d}P/\mathrm{d}x))$ is the probability current. Equation (7.39) is now a Fokker–Planck equation for the probability density, $P(x,t)$, to find the Brownian particle in the interval, $x \to x + \mathrm{d}x$, at time, t, for the case of strong friction. Because Eq. (7.39) has the form of a continuity equation, the probability is conserved.

For the case of a "free" Brownian particle, one for which $V(x) = 0$, the Fokker–Planck reduces to the *diffusion equation*

$$\frac{\partial P(x,t)}{\partial t} = \frac{g}{2\gamma^2}\frac{\partial^2 P(x,t)}{\partial x^2} = D\frac{\partial^2 P(x,t)}{\partial x^2}\,, \tag{7.40}$$

where $D = g/2\gamma^2 = k_\mathrm{B}T/\gamma$ is the diffusion coefficient since $g = 2\gamma k_\mathrm{B}T$. If we introduce the Fourier transform of $P(x,t)$,

$$P(x,t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} \mathrm{d}k\mathrm{e}^{-\mathrm{i}kx} f(k,t)\,, \tag{7.41}$$

then the Fourier amplitude, $f(k,t)$ satisfies the equation of motion

$$\frac{\partial f(k,t)}{\partial t} = -Dk^2 f(k,t)\,. \tag{7.42}$$

This has a solution $f(k,t) = \mathrm{e}^{-Dk^2 t}$ and yields a probability density

$$P(x,t) = \sqrt{\frac{1}{4\pi Dt}}\exp\left(\frac{-x^2}{4Dt}\right)\,. \tag{7.43}$$

It is interesting to note that Einstein who, unaware of the phenomenon of Brownian motion, was looking for a way to confirm the atomic nature of matter and obtained a relation between the diffusion coefficient, D, and the atomic properties of matter. This relation is $D = RT/(N_\mathrm{A}6\pi\eta a)$, where R is the gas constant, $N_\mathrm{A} = 6.02 \times 10^{23}\ \mathrm{mol}^{-1}$ is Avogadro's number, T is the temperature in kelvin, η is the viscosity, and a is the radius of the Brownian particle [49, 51]. It has since been confirmed by many experiments on Brownian motion [164].

7.3.3.1 Spectral Decomposition of the Fokker–Planck Equation

For the case of strong friction, we can obtain a spectral decomposition of the probability density, $P(x, t)$. Let us first introduce a rescaled time $\tau = t/\gamma$, and write the Fokker–Planck equation as

$$\frac{\partial P(x,\tau)}{\partial \tau} = \frac{\mathrm{d}^2 V}{\mathrm{d}x^2} P + \frac{\mathrm{d}V}{\mathrm{d}x}\frac{\partial P}{\partial x} + \frac{g}{2\gamma}\frac{\partial^2 P}{\partial x^2} = -\hat{L}_{\mathrm{FP}} P(x,\tau)\,. \tag{7.44}$$

The operator, $\hat{L}_{\mathrm{LP}} = \mathrm{d}^2 V/\mathrm{d}x^2 + \mathrm{d}V/\mathrm{d}x \partial/\partial x + g/(2\gamma)\partial^2/\partial x^2$, is a nonself-adjoint operator because of its dependence on the first-order partial derivative. However, it is possible to rewrite the Fokker–Planck equation in terms of a self-adjoint operator via a simple transformation. Then the solutions become more intuitive.

Let us write the probability in the form

$$P(x,\tau) = \mathrm{e}^{\frac{-\gamma V(x)}{g}}\, \Psi(x,\tau)\,, \tag{7.45}$$

where $\Psi(x, \tau)$ is a function to be determined. If we now substitute into (7.44), we obtain the following equation for $\Psi(x, \tau)$

$$\frac{\partial \Psi(x,\tau)}{\partial \tau} = \left[\frac{1}{2}\frac{\mathrm{d}^2 V}{\mathrm{d}x^2} - \frac{\gamma}{2g}\left(\frac{\mathrm{d}V}{\mathrm{d}x}\right)^2\right]\Psi(x,\tau) + \frac{g}{2\gamma}\frac{\partial^2 \Psi}{\partial x^2} = -\hat{H}_{\mathrm{FP}}\Psi(x,\tau)\,. \tag{7.46}$$

The operator, $\hat{H}_{\mathrm{FP}} = -(1/2(\mathrm{d}^2 V/\mathrm{d}x^2) - \gamma/(2g)(\mathrm{d}V/\mathrm{d}x)^2) - g/(2\gamma)\partial^2/\partial x^2$, is a self-adjoint operator and we can use well-established techniques for dealing with such operators.

We will let $\phi_n(x)$ and λ_n denote the nth eigenfunction and eigenvalue, respectively, of H_{FP} so that $H_{\mathrm{FP}}\phi_n(x) = \lambda_n \phi_n(x)$. The eigenfunctions form a complete set and can be made orthonormal so that

$$\int_{-\infty}^{\infty} \mathrm{d}x \phi_{n'}(x)\phi_n(x) = \delta_{n',n}\,. \tag{7.47}$$

We can expand $\Psi(x, t)$ in terms of the eigenfunctions and eigenvalues of $\hat{H}_{\mathrm{FP}}$,

$$\Psi(x,\tau) = \sum_{n=0}^{\infty} a_n \mathrm{e}^{-\lambda_n \tau}\phi_n(x)\,. \tag{7.48}$$

The eigenvalues are real and must have zero or positive values in order that the probability remains finite.

The operator $\hat{H}_{\mathrm{FP}}$ has at least one zero eigenvalue, which we denote $\lambda_0 = 0$, and a corresponding eigenfunction, $\phi_0(x)$, which satisfies the equation

$$\left[\frac{1}{2}\frac{\mathrm{d}^2 V}{\mathrm{d}x^2} - \frac{\gamma}{2g}\left(\frac{\mathrm{d}V}{\mathrm{d}x}\right)^2\right]\phi_0(x) + \frac{g}{2\gamma}\frac{\partial^2 \phi_0(x)}{\partial x^2} = 0\,. \tag{7.49}$$

Equation (7.49) has the solution

$$\phi_0(x) = C\mathrm{e}^{\frac{-\gamma V(x)}{g}} , \tag{7.50}$$

where C is a normalization constant. This is just the transformation used in Eq. (7.45). Therefore we can now combine Eqs. (7.45), (7.48), and (7.50) and write the probability as

$$P(x, \tau) = \phi_0^2(x) + \sum_{n=1}^{\infty} a_n \mathrm{e}^{-\lambda_n \tau} \phi_0(x) \phi_n(x) . \tag{7.51}$$

In this form, the probability is conserved due to the orthonormality of the eigenstates. If we integrate Eq. (7.51) over x, we obtain

$$\int_{-\infty}^{\infty} \mathrm{d}x P(x, \tau) = \int_{-\infty}^{\infty} \mathrm{d}x \phi_0(x)^2 = 1 . \tag{7.52}$$

The coefficients, a_n, can be determined from the initial conditions. Let us assume that we are given $P(x, 0)$. Then we write

$$P(x, 0) = \phi_0^2(x) + \sum_{n=1}^{\infty} a_n \phi_0(x) \phi_n(x) . \tag{7.53}$$

If we now divide through by $\phi_0(x)$, multiply by $\phi_{n_0}(x)$, and integrate over x we obtain

$$a_{n_0} = \int_{-\infty}^{\infty} \mathrm{d}x \frac{\phi_{n_0}(x)}{\phi_0(x)} P(x, 0) . \tag{7.54}$$

After a long time, the probability approaches the stationary state

$$P(x, \infty) = \phi_0^2(x) . \tag{7.55}$$

There are several examples of Fokker–Planck equations with one variable which can be solved analytically. We will consider one of them in Exercise 7.3 and leave the others as homework problems.

This method can also be extended to Fokker–Planck equations with two or more spatial degrees of freedom when a transformation analogous to Eq. (7.50) can be found that allows us to write the Fokker–Planck equation in terms of a self-adjoint operator. For such cases, it is possible that the dynamics governed by the self-adjoint operator can undergo a transition to chaos. Examples of such cases, have been studied in [5, 105, 141].

Exercise 7.3

Solve the Fokker–Planck equation for the probability distribution $P(x,t)$ of a Brownian particle of mass m in a fluid with strong friction γ in a harmonic potential $V(x) = (1/2)kx^2$, where k is the harmonic force constant. Assume that $P(x,0) = \delta(x - x_{\mathrm{o}})$.

Answer: From Eq. (7.44), the Fokker–Planck equation can be written

$$\frac{\partial P(x,\tau)}{\partial \tau} = kP + kx\frac{\partial P}{\partial x} + \frac{g}{2\gamma}\frac{\partial^2 P}{\partial x^2} .$$

Now make the transformation $P(x,\tau) = \mathrm{e}^{(-\gamma k x^2)/(2g)}\Psi(x,\tau)$ and substitute it into the Fokker–Planck equation to get

$$\frac{1}{k}\frac{\partial \Psi(x,\tau)}{\partial \tau} = \left(\frac{1}{2} - \frac{x^2}{4A}\right)\Psi(x,\tau) + A\frac{\partial^2 \Psi}{\partial x^2}$$

where $A = g/(2k\gamma)$. The operator, $\hat{H}_{\mathrm{FP}} = 1/2 - x^2/(4A) + A\partial^2/\partial x^2$, is self-adjoint and has eigenfunctions $\phi_n(x)$ $(n = 0, 1, 2, \dots, \infty)$ of the form,

$$\phi_n(x) = \frac{1}{\sqrt{2^n n! \sqrt{2\pi A}}} H_n\left[\frac{x}{\sqrt{2A}}\right] \mathrm{e}^{-x^2/4A} ,$$

where $H_n(y)$ is the nth order Hermite polynomial and can be written $H_n(y) = (-1)^n \mathrm{e}^{y^2}(\mathrm{d}^n/\mathrm{d}y^n)\mathrm{e}^{-y^2}$. The Hermite polynomial satisfies the eigenvalue equation $\hat{H}_{\mathrm{FP}}\phi_n(x) = -n\phi_n(x)$ so the nth eigenvalue is $\lambda_n = -n$. The spectral decomposition of $P(x,\tau)$ is now given by

$$P(x,\tau) = \sum_{n=0}^{\infty} a_n \mathrm{e}^{-nk\tau}\phi_0(x)\phi_n(x) .$$

For initial distribution $P(x,0) = \delta(x - x_{\mathrm{o}})$ we have $a_n = \phi_n(x_{\mathrm{o}})/\phi_0(x_{\mathrm{o}})$. Thus,

$$\begin{aligned} P(x,\tau) &= \sum_{n=0}^{\infty} \mathrm{e}^{-nk\tau}\frac{\phi_0(x)}{\phi_0(x_{\mathrm{o}})}\phi_n(x)\phi_n(x_{\mathrm{o}}) \\ &= \frac{1}{\sqrt{2\pi A}}\mathrm{e}^{-x^2/(2A)}\sum_{n=0}^{\infty}\frac{1}{2^n n!}\mathrm{e}^{-nk\tau}H_n\frac{x_{\mathrm{o}}}{\sqrt{2A}}H_n\frac{x}{\sqrt{2A}} \\ &= \frac{1}{\sqrt{2\pi A(1-\mathrm{e}^{-2k\tau})}}\exp\left[\frac{-(x - x_{\mathrm{o}}\mathrm{e}^{-k\tau})^2}{2A(1-\mathrm{e}^{-2k\tau})}\right] , \end{aligned}$$

where in the last term we have used an identity for sums involving Hermite polynomials [143].

7.4
Dynamic Equilibrium Fluctuations

Systems in equilibrium undergo fluctuations about their equilibrium states. Information about these fluctuations is contained in the dynamic correlation function for the equilibrium system, and in the power spectrum of the equilibrium fluctuations. The power spectrum is a quantity often measured in experiments.

Systems which are out of equilibrium generally return to the equilibrium state through a variety of processes which may or may not be coupled to one another. The time reversal invariance of the underlying Newtonian (or quantum) dynamics of the various degrees of freedom puts constraints on the behavior of the dynamic equilibrium fluctuations and the time-dependent correlation functions that characterize these fluctuations. We will derive these constraints using the notation for fluctuations from Section 3.7.4. We denote the macroscopic state variables as $A_1, A_2, \ldots, A_n$ and denote deviations from equilibrium values $A_1^{\mathrm{o}}, A_2^{\mathrm{o}}, \ldots, A_n^{\mathrm{o}}$ of these quantities as $\alpha_i = A_i - A_i^{\mathrm{o}}$ for $i = 1, 2, \ldots, n$. As before, the quantity $\overline{\alpha}$ will denote the $1 \times n$ column matrix composed of elements $\alpha_1, \ldots, \alpha_n$.

The time-reversal invariance of Newtonian dynamics requires that the dynamic correlation functions for macroscopic fluctuations, $\overline{\alpha}$, about the equilibrium state, obey the relations

$$\langle \alpha_i \alpha_j(\tau) \rangle = \langle \alpha_i(\tau) \alpha_j \rangle \,. \tag{7.56}$$

Equation (7.56) tells us that the correlation between a fluctuation α_i at time $t = 0$ and a fluctuation α_j at time $t = \tau$ is the same as that of a fluctuation α_j at time $t = 0$ and a fluctuation α_i at time $t = \tau$. The quantities α_i and α_j can correspond to fluctuations in the same state variables at different points in space. Thus, Eq. (7.56) can also be turned into an equation relating correlations between space- and time-dependent fluctuations.

To establish Eq. (7.56), we note that the correlation matrix $\langle \boldsymbol{\alpha}\boldsymbol{\alpha}(\tau) \rangle$ can be written

$$\langle \boldsymbol{\alpha}\boldsymbol{\alpha}(\tau) \rangle \equiv \iint \mathrm{d}\boldsymbol{\alpha}\, \mathrm{d}\boldsymbol{\alpha}' \boldsymbol{\alpha}\boldsymbol{\alpha}' P(\boldsymbol{\alpha}, 0; \boldsymbol{\alpha}', \tau) = \iint \mathrm{d}\boldsymbol{\alpha}\, \mathrm{d}\boldsymbol{\alpha}' \boldsymbol{\alpha}\boldsymbol{\alpha}' P(\boldsymbol{\alpha}) P(\boldsymbol{\alpha}|\boldsymbol{\alpha}', \tau) \tag{7.57}$$

where $P(\boldsymbol{\alpha}, 0; \boldsymbol{\alpha}', \tau) \equiv P(\boldsymbol{\alpha}) P(\boldsymbol{\alpha}|\boldsymbol{\alpha}', \tau)$ is the joint probability to have a fluctuation $\boldsymbol{\alpha}$ at time $t = 0$ and a fluctuation $\boldsymbol{\alpha}'$ at time $t = \tau$. The quantity $P(\boldsymbol{\alpha}|\boldsymbol{\alpha}', \tau)$ is the conditional probability that the fluctuation has value $\boldsymbol{\alpha}'$ at time $t = \tau$, given that it had value $\boldsymbol{\alpha}$ at time $t = 0$, and $P(\boldsymbol{\alpha})$ is the probability distribution of fluctuations about the equilibrium state. For a closed isolated system,

$$P(\boldsymbol{\alpha}) = \sqrt{\frac{\mathrm{Det}[\overline{\boldsymbol{g}}]}{(2\pi k_{\mathrm{B}})^n}}\, \mathrm{e}^{-\overline{\boldsymbol{g}} \cdot \boldsymbol{\alpha}\boldsymbol{\alpha}/(2k_{\mathrm{B}})} \,, \tag{7.58}$$

and $\langle \boldsymbol{\alpha}\boldsymbol{\alpha} \rangle = k_{\mathrm{B}} \boldsymbol{g}^{-1}$ (see Section 3.7.4).

The change in entropy which results from these fluctuations about the equilibrium state is

$$\Delta S = -\frac{1}{2} \overline{\boldsymbol{g}} : \boldsymbol{\alpha}\boldsymbol{\alpha} \tag{7.59}$$

(see Section 3.7.4). It is useful to introduce a generalized force, $\mathfrak{F}$, for systems out of equilibrium, which is defined as

$$\mathfrak{F} = \overline{\boldsymbol{g}} \cdot \boldsymbol{\alpha} = -\left(\frac{\partial \Delta S}{\partial \boldsymbol{\alpha}}\right) , \tag{7.60}$$

(note the analogy to the equilibrium force $Y = -T(\partial S/\partial X)_{U,N}$) and a generalized current, $\mathfrak{J}$, defined as

$$\mathfrak{J} = \frac{\mathrm{d}\boldsymbol{\alpha}}{\mathrm{d}t} . \tag{7.61}$$

Then the time rate of change of the entropy due to fluctuations is

$$\frac{\mathrm{d}\Delta S}{\mathrm{d}t} = -\mathfrak{J}^{\mathrm{T}} \cdot \mathfrak{F} \tag{7.62}$$

(T denotes transpose). For a resistor held at constant temperature, where $\mathfrak{J}$ is the electric current and $\mathfrak{F}$ is an electric field, (7.62) is proportional to the rate at which energy is dissipated through Joule heating. The quantity α, in that case, could represent a fluctuation in the electron density away from the equilibrium density. Such a fluctuation would induce to a fluctuating electric field $\mathfrak{F}$.

We must now remember that $\boldsymbol{\alpha}$ is a macroscopic variable. Thus, for each value of $\boldsymbol{\alpha}$ there are many possible microscopic states of the system. We can relate the joint probability distribution $P(\boldsymbol{\alpha}, 0; \boldsymbol{\alpha}', \tau)$ for fluctuations $\boldsymbol{\alpha}$ at time $t = 0$ and $\boldsymbol{\alpha}'$ at time $t = \tau$ to the microscopic joint probability density in the following way:

$$\begin{aligned} P(\boldsymbol{\alpha}, 0; \boldsymbol{\alpha}', \tau) = P(\boldsymbol{\alpha})P(\boldsymbol{\alpha}|\boldsymbol{\alpha}', \tau) &= \frac{1}{\Omega_{\Delta E}(E)} \int\limits_{\substack{(\boldsymbol{\alpha}\to\boldsymbol{\alpha}+\mathrm{d}\boldsymbol{\alpha}) \\ (E\to E+\Delta E)}} \mathrm{d}\boldsymbol{q}^N \, \mathrm{d}\boldsymbol{p}^N \\ &\times \int\limits_{(\boldsymbol{\alpha}'\to\boldsymbol{\alpha}'+\mathrm{d}\boldsymbol{\alpha}')} \mathrm{d}\boldsymbol{q}'^N \, \mathrm{d}\boldsymbol{p}'^N P(\boldsymbol{p}^N, \boldsymbol{q}^N | \boldsymbol{p}'^N, \boldsymbol{q}'^N, \tau) . \end{aligned} \tag{7.63}$$

In Eq. (7.63) we have used the fact that the equilibrium probability density for a closed isolated system, $P(\boldsymbol{p}^N, \boldsymbol{q}^N) = \Omega_{\Delta E}(E)^{-1}$, where $\Omega_{\Delta E}(E)$ is the volume of the energy shell (see Chapter 2). The phase space integrations are restricted to the energy shell and to trajectories with values of $\overline{\alpha}$ and $\overline{\alpha}'$ appearing in the left-hand side of Eq. (7.63); $P(\boldsymbol{p}^N, \boldsymbol{q}^N | \boldsymbol{p}'^N, \boldsymbol{q}'^N, \tau)$ is the conditional probability that a system can be in a state $(\boldsymbol{p}'^N, \boldsymbol{q}'^N)$ at time $t = \tau$, given that it was in the state $(\boldsymbol{p}^N, \boldsymbol{q}^N)$ at time $t = 0$. Since classical systems are completely deterministic, we must have

$$\begin{aligned} P(\boldsymbol{p}^N, \boldsymbol{q}^N | \boldsymbol{p}'^N, \boldsymbol{q}'^N, \tau) = {} & \delta[\boldsymbol{q}'^N - \boldsymbol{q}^N - \Delta\boldsymbol{q}^N(\boldsymbol{p}^N, \boldsymbol{q}^N, \tau)] \\ & \times \delta[\boldsymbol{p}'^N - \boldsymbol{p}^N - \Delta\boldsymbol{p}^N(\boldsymbol{p}^N, \boldsymbol{q}^N, \tau)] , \end{aligned} \tag{7.64}$$

where $\Delta\boldsymbol{q}^N$ and $\Delta\boldsymbol{p}^N$ are uniquely determined from Hamilton's equations.

Because Hamilton's equations are causal and time-reversal invariant, reversal of all momenta in the system will cause the system to retrace its steps. This implies that

$$P(\boldsymbol{q}^N, \boldsymbol{p}^N | \boldsymbol{q}'^N, \boldsymbol{p}'^N, \tau) = P(\boldsymbol{q}'^N, -\boldsymbol{p}'^N | \boldsymbol{q}^N, -\boldsymbol{p}^N, \tau) . \tag{7.65}$$

We can now combine Eqs. (7.63)–(7.65) to obtain a microscopic detailed balance

$$f(\boldsymbol{\alpha})P(\boldsymbol{\alpha}|\boldsymbol{\alpha}', \tau) = f(\boldsymbol{\alpha}')P(\boldsymbol{\alpha}'|\boldsymbol{\alpha}, \tau) . \tag{7.66}$$

From Eq. (7.66), Eq. (7.56) follows easily.

7.4.1
Regression of Fluctuations

We can use Eq. (7.56) to find relations between the rates at which various fluctuations α_i decay, on the average, back to the equilibrium state. These are called Onsager relations [155]. Let us first introduce the conditional average $\langle \boldsymbol{\alpha}(t)\rangle_{\boldsymbol{\alpha}_0}$, which is the average value of $\boldsymbol{\alpha}$ at time t, given that the initial value of $\boldsymbol{\alpha}$ was $\boldsymbol{\alpha}_0$. We then can write

$$\langle \boldsymbol{\alpha}(t)\rangle_{\boldsymbol{\alpha}_0} \equiv \int \mathrm{d}\boldsymbol{\alpha}\boldsymbol{\alpha}P(\boldsymbol{\alpha}_0|\boldsymbol{\alpha}, t) \tag{7.67}$$

for the conditional average.

Onsagar assumed that, *on the average*, the fluctuations decay according to the same linear laws that govern the decay to equilibrium of systems which are driven slightly out of equilibrium by external forces. Thus, the average fluctuation, $\langle \boldsymbol{\alpha}(t)\rangle_{\boldsymbol{\alpha}_0}$, obeys an equation of the form

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle \boldsymbol{\alpha}(t)\rangle_{\boldsymbol{\alpha}_0} = -\overline{\boldsymbol{M}} \cdot \langle \boldsymbol{\alpha}(t)\rangle_{\boldsymbol{\alpha}_0} , \tag{7.68}$$

where $\overline{\boldsymbol{M}}$ is an $n \times n$ matrix. Equation (7.68) has the solution

$$\langle \boldsymbol{\alpha}(t)\rangle_{\boldsymbol{\alpha}_0} = \mathrm{e}^{-\overline{\boldsymbol{M}}t} \cdot \boldsymbol{\alpha}_0 . \tag{7.69}$$

The time derivative in Eq. (7.68) must be used with caution. It is defined in the following sense:

$$\frac{\mathrm{d}\langle \boldsymbol{\alpha}(t)\rangle_{\boldsymbol{\alpha}_0}}{\mathrm{d}t} \equiv \frac{\langle \boldsymbol{\alpha}(t+\tau)\rangle_{\boldsymbol{\alpha}_0} - \langle \boldsymbol{\alpha}(t)\rangle_{\boldsymbol{\alpha}_0}}{\tau} , \tag{7.70}$$

where τ is a small time interval whose values are bounded by inequalities,

$$T_0 \ll \tau \ll T . \tag{7.71}$$

The quantity T_0 is the time between collisions, and T is the time it takes the fluctuation to decay to equilibrium. The limitation in Eq. (7.71) rules out fluctuations which are too small – that is, fluctuations which decay to equilibrium in a few collision times. Similarly, (7.71) is not valid when the fluctuation has just been created. It takes a few collision times for it to settle down to a macroscopic decay.

Equation (7.56) imposes a condition on the matrix $\overline{\boldsymbol{M}}$. If we expand Eq. (7.69) for short times,

$$\langle \boldsymbol{\alpha}(t)\rangle_{\boldsymbol{\alpha}_0} = \boldsymbol{\alpha}_0 - t\overline{\boldsymbol{M}} \cdot \boldsymbol{\alpha}_0 + O(t^2) , \tag{7.72}$$

and substitute it into Eq. (7.56), we obtain

$$\langle \boldsymbol{\alpha}_0 \overline{\boldsymbol{M}} \cdot \boldsymbol{\alpha}_0 \rangle = \langle \overline{\boldsymbol{M}} \cdot \boldsymbol{\alpha}_0 \boldsymbol{\alpha}_0 \rangle \,. \tag{7.73}$$

If we now use the fact that $\overline{\boldsymbol{M}} \cdot \boldsymbol{\alpha} = \boldsymbol{\alpha}^{\mathrm{T}} \cdot \overline{\boldsymbol{M}}^{\mathrm{T}}$ and use Eq. (3.91) for the variance in the fluctuations, we obtain

$$\overline{\boldsymbol{g}}^{-1} \cdot \overline{\boldsymbol{M}}^{\mathrm{T}} = \overline{\boldsymbol{M}} \cdot \overline{\boldsymbol{g}}^{-1} \,, \tag{7.74}$$

where T denotes the transpose. We can define a new matrix

$$\overline{\boldsymbol{L}} \equiv \overline{\boldsymbol{M}} \cdot \overline{\boldsymbol{g}}^{-1} \,. \tag{7.75}$$

Then Eq. (7.74) becomes

$$\overline{\boldsymbol{L}} = \overline{\boldsymbol{L}}^{\mathrm{T}} \quad \text{or} \quad L_{ij} = L_{ji} \,. \tag{7.76}$$

Equations (7.76) are called *Onsagar's relations*. Note that since the matrices $\overline{\boldsymbol{g}}$ and $\overline{\boldsymbol{L}}$ are symmetric, the matrix $\overline{\boldsymbol{M}}$ is symmetric.

If we make use of the generalized force $\boldsymbol{\mathfrak{F}} = \overline{\boldsymbol{g}} \cdot \boldsymbol{\alpha}$ (cf. Eq. (7.60)), the time rate of change of the fluctuation can be written

$$\frac{\mathrm{d}}{\mathrm{d}t} \langle \boldsymbol{\alpha}(t) \rangle_{\boldsymbol{\alpha}_0} = -\overline{\boldsymbol{L}} \cdot \langle \boldsymbol{\mathfrak{F}}(t) \rangle_{\boldsymbol{\alpha}_0} \,. \tag{7.77}$$

Equation (7.76) is a generalized Ohm's Law. It is so useful that Onsagar received a Nobel prize for deriving it. The matrix $\overline{\boldsymbol{L}}$ is a matrix of transport coefficients. Equation (7.77) tells us that a force resulting from a fluctuation α_i can cause a flux of A_j, and a force arising from a fluctuation α_j can cause a flux of A_i. Equation (7.76) tells us that the transport coefficients for the two processes are the same. For example, a particle concentration gradient can drive a heat current, and a temperature gradient can drive a particle current. The transport coefficients for the two processes are the same although the processes physically appear to be very different. For the case of a conductor, α could represent a fluctuation in the electron density and L would be the conductance.

7.4.2
Wiener–Khintchine Theorem

The Wiener–Khintchine theorem [39, 103, 214] makes the connection between the correlation matrix for time-dependent fluctuations about the equilibrium state and the spectral density matrix for these fluctuations. Equilibrium systems are governed by stationary distribution functions and this imposes certain conditions on correlation functions for fluctuations about the equilibrium state. Below we first discuss the conditions stationarity imposes on the time-dependent correlation matrices and then we derive the Wiener–Khintchine theorem.

Let us consider the time-dependent correlation matrix, $\langle \boldsymbol{\alpha}(\tau)\boldsymbol{\alpha}(0)\rangle$, for a system governed by a stationary distribution function (such as a system in equilibrium). The correlation matrix has the property

$$\overline{\boldsymbol{C}}_{\boldsymbol{\alpha}\boldsymbol{\alpha}}(\tau) \equiv \langle \boldsymbol{\alpha}(\tau)\boldsymbol{\alpha}(0)\rangle = \langle \boldsymbol{\alpha}(t+\tau)\boldsymbol{\alpha}(t)\rangle = \langle \boldsymbol{\alpha}(-\tau)\boldsymbol{\alpha}\rangle^{\mathrm{T}} = \overline{\boldsymbol{C}}_{\boldsymbol{\alpha}\boldsymbol{\alpha}}(-\tau)^{\mathrm{T}} , \quad (7.78)$$

where we have let $t = -\tau$ and T denotes the transpose of the correlation matrix. From the condition of microscopic reversibility, we know that $\langle \boldsymbol{\alpha}(\tau)\boldsymbol{\alpha}\rangle = \langle \boldsymbol{\alpha}\boldsymbol{\alpha}(\tau)\rangle$ and, therefore,

$$\overline{\boldsymbol{C}}_{\boldsymbol{\alpha}\boldsymbol{\alpha}}(\tau) = \overline{\boldsymbol{C}}_{\boldsymbol{\alpha}\boldsymbol{\alpha}}(\tau)^{\mathrm{T}} . \quad (7.79)$$

Furthermore, from Section 3.7.4, we have $\overline{C}_{\boldsymbol{\alpha}\boldsymbol{\alpha}}(0) = \langle \boldsymbol{\alpha}\boldsymbol{\alpha}\rangle = k_{\mathrm{B}}\overline{\boldsymbol{g}}^{-1}$, where $\overline{\boldsymbol{g}}^{-1}$ depends on the thermodynamic response functions. From Eqs. (7.69) and (7.78) the correlation matrix can be written

$$\overline{\boldsymbol{C}}_{\boldsymbol{\alpha}\boldsymbol{\alpha}}(\tau) = \int \mathrm{d}\boldsymbol{\alpha}_0 P(\boldsymbol{\alpha}_0)\boldsymbol{\alpha}_0 \langle \boldsymbol{\alpha}(\tau)\rangle_{\boldsymbol{\alpha}_0} = k_{\mathrm{B}}\overline{\boldsymbol{g}}^{-1} \cdot \mathrm{e}^{-\overline{\boldsymbol{M}}|\tau|} \quad (7.80)$$

since $\overline{\boldsymbol{M}}$ is a self-adjoint matrix ($|\tau|$ indicates the absolute value of τ).

We now introduce the spectral density matrix and show that it is the Fourier transform of the correlation matrix. Let us first introduce a slight modification of the time series $\boldsymbol{\alpha}(t)$ as follows:

$$\boldsymbol{\alpha}(t;\mathcal{T}) \equiv \begin{cases} \boldsymbol{\alpha}(t) & |t| < \mathcal{T} , \\ 0 & |t| > \mathcal{T} \end{cases} \quad (7.81)$$

such that $\lim_{\mathcal{T}\to\infty} \boldsymbol{\alpha}(t;\mathcal{T}) = \boldsymbol{\alpha}(t)$. We next introduce the Fourier transform of $\boldsymbol{\alpha}(t;\mathcal{T})$:

$$\boldsymbol{\alpha}(\omega;\mathcal{T}) = \int_{-\infty}^{\infty} \mathrm{d}t\boldsymbol{\alpha}(t;\mathcal{T})\mathrm{e}^{\mathrm{i}\omega t} = \int_{-\mathcal{T}}^{\mathcal{T}} \mathrm{d}t\boldsymbol{\alpha}(t;\mathcal{T})\mathrm{e}^{\mathrm{i}\omega t} . \quad (7.82)$$

Since the fluctuations, $\boldsymbol{\alpha}(t)$, are real, we find

$$\boldsymbol{\alpha}^*(\omega;\mathcal{T}) = \boldsymbol{\alpha}(-\omega;\mathcal{T}) \quad (7.83)$$

(* denotes complex conjugate).

The spectral density matrix is defined as

$$\overline{\boldsymbol{S}}_{\boldsymbol{\alpha}\boldsymbol{\alpha}}(\omega) = \lim_{\mathcal{T}\to\infty} \frac{1}{\mathcal{T}}\boldsymbol{\alpha}^*(\omega;\mathcal{T})\boldsymbol{\alpha}(\omega;T) . \quad (7.84)$$

Combining Eqs. (7.82) and (7.83) we can write

$$\overline{\boldsymbol{S}}_{\boldsymbol{\alpha}\boldsymbol{\alpha}}(\omega) = \int_{-\infty}^{\infty} \mathrm{d}\tau\mathrm{e}^{\mathrm{i}\omega\tau} \lim_{\mathcal{T}\to\infty} \frac{1}{\mathcal{T}} \int_{-\infty}^{\infty} \mathrm{d}t\boldsymbol{\alpha}(t;\mathcal{T})\boldsymbol{\alpha}(t+\tau;\mathcal{T}) . \quad (7.85)$$

If we now invoke the ergodic theorem (Appendix C), we can equate the time average in Eq. (7.85) to the phase average of the fluctuations:

$$\langle \boldsymbol{\alpha}\boldsymbol{\alpha}(\tau)\rangle = \lim_{\mathcal{T}\to\infty} \frac{1}{\mathcal{T}} \int\limits_{-\infty}^{\infty} \boldsymbol{\alpha}(t;\mathcal{T})\boldsymbol{\alpha}(t+\tau;\mathcal{T})\,\mathrm{d}t\,. \tag{7.86}$$

Then Eqs. (7.85) and (7.86) lead to the relation

$$\overline{\boldsymbol{S}}_{\boldsymbol{\alpha}\boldsymbol{\alpha}}(\omega) = \int\limits_{-\infty}^{\infty} \mathrm{d}\tau \mathrm{e}^{\mathrm{i}\omega\tau}\langle \boldsymbol{\alpha}\boldsymbol{\alpha}(\tau)\rangle = \int\limits_{-\infty}^{\infty} \mathrm{d}\tau \mathrm{e}^{\mathrm{i}\omega\tau}\overline{\boldsymbol{C}}_{\boldsymbol{\alpha}\boldsymbol{\alpha}}(\tau)\,. \tag{7.87}$$

Thus, the spectral density matrix is the Fourier transform of the correlation matrix. Equation (7.87) is called the *Wiener–Khintchine theorem.*

7.5
Linear Response Theory and the Fluctuation–Dissipation Theorem

Fluctuations in an equilibrium system decay, *on the average*, according to the same linear macroscopic laws that describe the decay of the system from a nonequilibrium state to the equilibrium state. If we can probe the equilibrium fluctuations, we have a means of probing the transport processes in the system. The fluctuation–dissipation theorem shows that it is possible to probe the equilibrium fluctuations by applying a weak external field which couples to particles in the medium but yet is too weak to affect the medium. The system will respond to the field and absorb energy from the field in a manner which depends entirely on the spectrum of the equilibrium fluctuations. According to the fluctuation–dissipation theorem, the spectrum of the equilibrium fluctuations and the rate of absorption of energy from the external field can be expressed in terms of a response matrix.

In this section we derive the fluctuation–dissipation theorem [39]. We first introduce linear response theory and use the assumption of causality to obtain a relation between the real and imaginary parts of the dynamic susceptibility matrix, which is the Fourier transform of the response matrix. We then obtain a relation between the dynamic susceptibility matrix and the correlation matrix, and we obtain an expression for power absorption in terms of the dynamic susceptibility matrix. This gives us a relation between the fluctuations in an equilibrium system and energy absorbed by that system when an external field is applied.

7.5.1
The Response Matrix

Let us assume that weak external forces, $\boldsymbol{F} = (F_1, F_2, \ldots, F_n)^{\mathrm{T}}$, are applied to a system and that these forces couple to the state variables, $(A_1, A_2, \ldots, A_n)$, causing them to deviate from their equilibrium values by the amounts, $\alpha_i = A_i - A_i^{\circ}$,

$i = 1, \ldots, n$. We shall assume also that the deviations from equilibrium of the state variables depend linearly on the applied forces (linear response). Then we can write

$$\langle \boldsymbol{\alpha}(t) \rangle_F = \int_{-\infty}^{\infty} dt' \overline{\boldsymbol{K}}(t - t') \cdot \boldsymbol{F}(t') = \int_{-\infty}^{\infty} \overline{\boldsymbol{K}}(\tau) \cdot \boldsymbol{F}(t - \tau)\, d\tau \,. \tag{7.88}$$

The matrix $\overline{\boldsymbol{K}}(t - t')$ is real and is called the *response matrix*. Since the response must be causal (the response cannot precede the force which causes it), $\overline{\boldsymbol{K}}(t - t')$ must satisfy the causality condition,

$$\overline{\boldsymbol{K}}(t - t') = 0 \,, \quad t - t' < 0 \,. \tag{7.89}$$

We shall assume that the response matrix relaxes fast enough that the integral

$$\int_{0}^{\infty} \overline{\boldsymbol{K}}(t)\, dt < \infty \tag{7.90}$$

is finite. Physically, this means that a finite force must give rise to a finite response. Since Eq. (7.88) is linear in the force, its Fourier transform has a very simple form. If we note that

$$\langle \boldsymbol{\alpha}(t) \rangle_F = \frac{1}{2\pi} \int_{-\infty}^{\infty} \langle \boldsymbol{\alpha}(\omega) \rangle_F e^{-i\omega t}\, d\omega \tag{7.91}$$

and use similar expressions relating $\boldsymbol{F}(\tau)$ to $\boldsymbol{F}(\omega)$, we obtain

$$\langle \boldsymbol{\alpha}(\omega) \rangle_F = \overline{\chi}(\omega) \cdot \boldsymbol{F}(\omega) \,, \tag{7.92}$$

where

$$\overline{\chi}(\omega) = \int_{-\infty}^{\infty} \overline{\boldsymbol{K}}(t) e^{i\omega t}\, dt \tag{7.93}$$

is the dynamic susceptibility. We have also used the definition for the delta function, $\delta(t) = (1/2\pi)\int_{-\infty}^{\infty} d\omega e^{-i\omega t}$. Thus, a frequency component $\boldsymbol{F}(\omega)$ of the force can only excite a response with the same frequency. This will not be true if the response function depends on the force (nonlinear response).

The fact that $\overline{\boldsymbol{K}}(t)$ is causal ($\overline{\boldsymbol{K}}(t) = 0$ for $t < 0$ and $\overline{\boldsymbol{K}}(t) \neq 0$ for $t > 0$) imposes conditions on the structure of $\overline{\chi}(\omega)$. The inverse transform of (7.93) gives

$$\overline{\boldsymbol{K}}(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \overline{\chi}(\omega) e^{-i\omega t}\, d\omega \,. \tag{7.94}$$

Generally such integrals can be solved by contour integration in the complex ω-plane. For $t < 0$, the contour must be closed in the upper half complex ω-plane so the contribution from the semicircle at infinity is zero. In order for $\overline{\boldsymbol{K}}(t) = 0$ for $t < 0$, the dynamic susceptibility $\overline{\chi}(\omega)$ can have no poles in the upper half complex ω-plane. For $t > 0$, $\overline{\chi}(\omega)$ can have any number of poles in the lower half complex ω-plane, depending on the detailed dynamics of the process. (Note: two excellent references on contour integration are [132] and [192].)

Exercise 7.4

Compute the dynamic susceptibility for a Brownian particle of mass m in the presence of white noise $\xi(t)$ and fluid friction γ.

Answer: The Langevin equation for the Brownian particle in the presence of a driving force $F(t)$ is $m\mathrm{d}v(t)/\mathrm{d}t + \gamma v(t) = \xi(t) + F(t)$. If we take the average with respect to the noise, we obtain $m(\mathrm{d}\langle v(t)\rangle_\xi)/\mathrm{d}t + \gamma\langle v(t)\rangle_\xi = F(t)$. Assume the Brownian particle receives a "kick" at time $t = 0$ so $F(t) = F_0\delta(t)$. Then $\langle v(t)\rangle_\xi = K(t)F_0$. The equation for the response function $K(t)$ takes the form $m\mathrm{d}K(t)/\mathrm{d}t + \gamma K(t) = \delta(t)$. This equation has the solution $K(t) = (1/m)\mathrm{e}^{-\gamma t/m}\,\Theta(t)$, where $\Theta(t)$ is the Heaviside function (note that $\delta(t) = \mathrm{d}\Theta/\mathrm{d}t$). The Fourier transform of $K(t)$ gives the dynamic susceptibility $\chi(\omega) = (-\mathrm{i}m\omega + \gamma)^{-1}$. Note that $\chi(\omega)$ has a pole in the lower half complex ω-plane, which is consistent with its causal response to the force field.

7.5.2
Causality

Causality enables us to obtain a relation between the real and imaginary parts of the dynamic susceptibility. We can show this relationship in the following way. Define a matrix $\overline{\boldsymbol{G}}(z)$ such that

$$\overline{\boldsymbol{G}}(z) \equiv \frac{\overline{\chi}(z)}{z - u}\,, \tag{7.95}$$

where $z = \omega + \mathrm{i}\epsilon$ and u is real. Causality requires that $\overline{\chi}(z)$ have no poles in the upper half z-plane. Integrate $\overline{\boldsymbol{G}}(z)$ over a contour C' (cf. Figure 7.1) so that C'

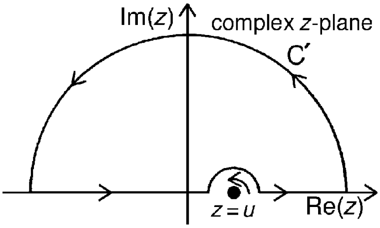


Figure 7.1 Integration contour used to obtain the Kramers–Kronig relations.

encloses no poles of $\overline{\mathbf{G}}(z)$. Then

$$\oint_{C'} \overline{\mathbf{G}}(z)\,\mathrm{d}z = \oint_{C'} \frac{\overline{\chi}(z)}{z-u}\,\mathrm{d}z = 0\,. \tag{7.96}$$

Since $\overline{\chi}(z) \to 0$ as $\varepsilon \to \infty$ there will be no contribution from the semicircle at infinity. Thus,

$$\begin{aligned}\oint_{C'} \frac{\overline{\chi}(z)}{z-u}\,\mathrm{d}z = \int_{-\infty}^{u-r} \frac{\overline{\chi}(\omega)}{\omega-u}\,\mathrm{d}\omega + \int_{u+r}^{\infty} \mathrm{d}\omega \frac{\overline{\chi}(\omega)}{\omega-u} + \mathrm{i}r \\ \times \int_{\pi}^{0} \mathrm{d}\phi \mathrm{e}^{\mathrm{i}\phi} \frac{\overline{\chi}(u+r\mathrm{e}^{\mathrm{i}\phi})}{u+r\mathrm{e}^{\mathrm{i}\phi}-u} = 0\,.\end{aligned} \tag{7.97}$$

It is useful to introduce the Cauchy principal part,

$$P\int_{-\infty}^{\infty} \mathrm{d}\omega \frac{\overline{\chi}(\omega)}{\omega-u} \equiv \lim_{r\to 0}\left[\int_{-\infty}^{u-r} \mathrm{d}\omega \frac{\overline{\chi}(\omega)}{\omega-u} + \int_{u+r}^{\infty} \mathrm{d}\omega \frac{\overline{\chi}(\omega)}{\omega-u}\right]. \tag{7.98}$$

Equation (7.97) then gives

$$P\int_{-\infty}^{\infty} \mathrm{d}\omega \frac{\overline{\chi}(\omega)}{\omega-u} = -\lim_{r\to 0}\int_{\pi}^{0} \mathrm{i}\,\mathrm{d}\phi\overline{\chi}(u+r\mathrm{e}^{\mathrm{i}\phi}) = \mathrm{i}\pi\overline{\chi}(u) \tag{7.99}$$

or

$$\overline{\chi}(u) = \frac{1}{\pi\mathrm{i}}P\int_{-\infty}^{\infty} \frac{\overline{\chi}(\omega)\,\mathrm{d}\omega}{\omega-u}\,. \tag{7.100}$$

Equation (7.100) is a consequence of causality and allows us to relate the real part, $\overline{\chi}'(\omega)$, and the imaginary part, $\overline{\chi}''(\omega)$, of the dynamic susceptibility matrix. Let us write

$$\overline{\chi}(\omega) = \overline{\chi}'(\omega) + \mathrm{i}\overline{\chi}''(\omega) \tag{7.101}$$

and make use of Eq. (7.100). We then obtain the following relations between $\overline{\chi}'(\omega)$ and $\overline{\chi}''(\omega)$:

$$\overline{\chi}'(u) = \frac{1}{\pi}P\int_{-\infty}^{\infty} \frac{\overline{\chi}''(\omega)}{\omega-u}\,\mathrm{d}\omega \tag{7.102}$$

and

$$\overline{\chi}''(u) = -\frac{1}{\pi}P\int_{-\infty}^{\infty} \frac{\overline{\chi}'(\omega)}{\omega-u}\,\mathrm{d}\omega\,. \tag{7.103}$$

Equations (7.102) and (7.103) are called the *Kramers–Kronig relations* [112]. They enable us to compute the real part of $\overline{\chi}(\omega)$ if we know the imaginary part and vice versa. As we shall see, the imaginary part of $\overline{\chi}(\omega)$ often can be obtained from experiment.

Exercise 7.5

Verify the Kramers–Kronig relations for the dynamic susceptibility in Exercise 7.4.

Answer: The dynamic susceptibility is $\chi(\omega) = (-\mathrm{i}m\omega + \gamma)^{-1}$. Its real part is $\chi'(\omega) = (\gamma/m)/(\omega^2 + \gamma^2)$ and its imaginary part is $\chi''(\omega) = (\omega/m)/(\omega^2 + \gamma^2)$. Using the Kramers–Kronig relations, we can write

$$\chi'(u) = \frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{\chi''(\omega)}{\omega - u} \mathrm{d}\omega = \frac{1}{\pi} \lim_{\varepsilon \to 0} \int_{-\infty}^{\infty} \frac{\omega - u}{(\omega - u)^2 + \epsilon^2} \frac{\omega/m}{\omega^2 + \gamma^2} \mathrm{d}\omega = \frac{\gamma/m}{u^2 + \gamma^2} .$$

The integrand has poles at $\omega = u \pm \mathrm{i}\epsilon$ and at $\omega = \pm \mathrm{i}\gamma$. A contour integration that picks up one pole of each type gives the above result.

7.5.2.1 Piece-Wise Constant Force

Everything we have done to this point is completely general. Let us now obtain an explicit expression of the response for the case of a constant force which acts for an infinite length of time and then is abruptly shut off at time $t = 0$. The force we consider has the form

$$\boldsymbol{F}(t) = \begin{cases} \boldsymbol{F}_o & \text{for} \quad t < 0 \\ 0 & \text{for} \quad t > 0 . \end{cases} \tag{7.104}$$

The Fourier transform of the force is

$$\begin{aligned} \boldsymbol{F}(\omega) &= \boldsymbol{F}_o \int_{-\infty}^{0} \mathrm{e}^{\mathrm{i}\omega t} \mathrm{d}t = \lim_{\varepsilon \to 0} \boldsymbol{F}_o \int_{-\infty}^{0} \mathrm{e}^{\mathrm{i}zt} \mathrm{d}t \\ &= \lim_{\varepsilon \to 0} \boldsymbol{F}_o \frac{1}{\mathrm{i}z} = (-\mathrm{i}) \lim_{\varepsilon \to 0} \boldsymbol{F}_o \left[\frac{\omega}{\omega^2 + \varepsilon^2} + \frac{\mathrm{i}\varepsilon}{\omega^2 + \varepsilon^2} \right] , \end{aligned} \tag{7.105}$$

where $z = \omega - \mathrm{i}\epsilon$. If we now use the following definitions for the Cauchy principal part and the Dirac delta function, respectively,

$$P\left(\frac{1}{\omega}\right) = \lim_{\varepsilon \to 0} \frac{\omega}{\omega^2 + \varepsilon^2} \quad \text{and} \quad \delta(\omega) = \frac{1}{\pi} \lim_{\varepsilon \to 0} \frac{\varepsilon}{\omega^2 + \varepsilon^2} , \tag{7.106}$$

we obtain

$$\boldsymbol{F}(\omega) = \boldsymbol{F}_o \left[P\left(\frac{1}{\mathrm{i}\omega}\right) + \pi\delta(\omega) \right] . \tag{7.107}$$

From Eqs. (7.88) and (7.92), the response can be written in the form

$$\langle \boldsymbol{\alpha}(t) \rangle_{\boldsymbol{F}} = \frac{1}{2\pi} \int_{-\infty}^{\infty} \mathrm{d}\omega \mathrm{e}^{-\mathrm{i}\omega t} \overline{\boldsymbol{\chi}}(\omega) \cdot \tilde{\boldsymbol{F}}(\omega) . \tag{7.108}$$

It is useful to write the response in a slightly different form. In Eq. (7.100) we replace $\overline{\chi}(u)$ by $\mathrm{e}^{\pm \mathrm{i}ut}\overline{\chi}(u)$ and write

$$\mathrm{e}^{-\mathrm{i}ut}\overline{\chi}(u) = \frac{1}{\mathrm{i}\pi} P \int_{-\infty}^{\infty} \frac{\mathrm{e}^{-\mathrm{i}\omega t}\overline{\chi}(\omega)\,\mathrm{d}\omega}{\omega - u}\,, \quad t < 0 \tag{7.109}$$

and

$$\mathrm{e}^{\mathrm{i}ut}\overline{\chi}(u) = \frac{1}{\mathrm{i}\pi} P \int_{-\infty}^{\infty} \frac{\mathrm{e}^{\mathrm{i}\omega t}\overline{\chi}(\omega)\,\mathrm{d}\omega}{\omega - u}\,, \quad t > 0\,. \tag{7.110}$$

Then, for $t < 0$, Eq. (7.109) yields the expression

$$\overline{\chi}(0) = \frac{1}{\mathrm{i}\pi} P \int_{-\infty}^{\infty} \mathrm{d}\omega \frac{\mathrm{e}^{-\mathrm{i}\omega t}\overline{\chi}(\omega)}{\omega}\,, \tag{7.111}$$

and, for $t > 0$, Eq. (7.110) yields the expression

$$\overline{\chi}(0) = \frac{1}{i\pi} P \int_{-\infty}^{\infty} \mathrm{d}\omega \frac{\mathrm{e}^{\mathrm{i}\omega t}\overline{\chi}(\omega)}{\omega}\,. \tag{7.112}$$

For $t < 0$, the response takes the form

$$\langle \boldsymbol{\alpha}(t) \rangle_{F} = \frac{1}{2\pi} \int_{-\infty}^{\infty} \mathrm{d}\omega \mathrm{e}^{-\mathrm{i}\omega t}\overline{\chi}(\omega) \cdot \boldsymbol{F}_{\mathrm{o}} \left[P\left(\frac{1}{\mathrm{i}\omega}\right) + \pi\delta(\omega) \right] = \overline{\chi}(0) \cdot \boldsymbol{F}_{\mathrm{o}}\,. \tag{7.113}$$

For $t > 0$, the response can be written

$$\langle \boldsymbol{\alpha}(t) \rangle_{F} = \frac{1}{\mathrm{i}\pi} P \int_{-\infty}^{\infty} \mathrm{d}\omega \frac{\overline{\chi}(\omega) \cdot \boldsymbol{F}_{\mathrm{o}}}{\omega} \cos(\omega t)\,. \tag{7.114}$$

If we combine Eqs. (7.113) and (7.114), the response is

$$\langle \boldsymbol{\alpha}(t) \rangle_{\overline{F}} = \begin{cases} \overline{\chi}(0) \cdot \boldsymbol{F}_{\mathrm{o}} & \text{for} \quad t < 0 \\ \frac{1}{\mathrm{i}\pi} P \int_{-\infty}^{\infty} \mathrm{d}\omega \frac{\overline{\chi}(\omega) \cdot \boldsymbol{F}_{\mathrm{o}}}{\omega} \cos(\omega t) & \text{for} \quad t > 0\,. \end{cases} \tag{7.115}$$

Thus, while the force is turned on, the response is constant. When it is turned off, the response becomes time-dependent. The variables $A_1, \ldots, A_n$ begin to decay back to their equilibrium values.

7.5.3
The Fluctuation–Dissipation Theorem

The fluctuation–dissipation theorem relates the response matrix to the correlation matrix for equilibrium fluctuations. As a result, a weak external field can be used as a probe of equilibrium fluctuations.

To derive the fluctuation–dissipation theorem, let us consider a system to which a constant force $\boldsymbol{F}_\text{o}$ is applied from $t = -\infty$ to $t = 0$ and switched off at $t = 0$. We first write the response, $\langle \boldsymbol{\alpha}(t)\rangle_{\boldsymbol{F}_\text{o}}$, for times $t \geq 0$ in terms of the conditional average $\langle \boldsymbol{\alpha}(t)\rangle_{\boldsymbol{\alpha}_0}$,

$$\langle \boldsymbol{\alpha}(t)\rangle_{\boldsymbol{F}_\text{o}} = \int \mathrm{d}\boldsymbol{\alpha}_0 P(\boldsymbol{\alpha}_0, \boldsymbol{F}_\text{o})\langle \boldsymbol{\alpha}(t)\rangle_{\boldsymbol{\alpha}_0} \quad \text{for} \quad t \geq 0\,, \tag{7.116}$$

where $P(\boldsymbol{\alpha}_0, \boldsymbol{F}_\text{o})$ is the probability distribution for fluctuations $\boldsymbol{\alpha}_0$ at time $t = 0$ in the presence of a constant external field, $\boldsymbol{F}_\text{o}$. For times $t > 0$, the field is no longer turned on and we can write

$$\langle \boldsymbol{\alpha}(t)\rangle_{\boldsymbol{\alpha}_0} = \mathrm{e}^{-\overline{\boldsymbol{M}}t} \cdot \boldsymbol{\alpha}_0 \quad \text{for} \quad t \geq 0 \tag{7.117}$$

(cf. Eq. (7.69)). Combining Eqs. (7.116) and (7.117), we obtain

$$\begin{aligned}\langle \boldsymbol{\alpha}(t)\rangle_{\boldsymbol{F}_\text{o}} &= \mathrm{e}^{-\overline{\boldsymbol{M}}t} \cdot \int \mathrm{d}\boldsymbol{\alpha}_0 P(\boldsymbol{\alpha}_0, \boldsymbol{F}_\text{o})\boldsymbol{\alpha}_0 = \mathrm{e}^{-\overline{\boldsymbol{M}}t} \cdot \langle \boldsymbol{\alpha}(0)\rangle_{\boldsymbol{F}_\text{o}} \\ &= \mathrm{e}^{-\overline{\boldsymbol{M}}t} \cdot \overline{\boldsymbol{\chi}}(0) \cdot \boldsymbol{F}_\text{o} = \frac{1}{\mathrm{i}\pi} P \int_{-\infty}^{\infty} \mathrm{d}\omega \cos(\omega t) \frac{\overline{\boldsymbol{\chi}}(\omega)}{\omega} \cdot \boldsymbol{F}_\text{o}\,,\end{aligned} \tag{7.118}$$

where we have used Eq. (7.115). Thus, we find

$$\mathrm{e}^{-\overline{\boldsymbol{M}}t} \cdot \overline{\boldsymbol{\chi}}(0) = \frac{1}{\mathrm{i}\pi} P \int_{-\infty}^{\infty} \mathrm{d}\omega \cos(\omega t) \frac{\overline{\boldsymbol{\chi}}(\omega)}{\omega}\,. \tag{7.119}$$

If we remember that

$$\overline{\boldsymbol{C}}_{\boldsymbol{\alpha\alpha}}(t) = \langle \boldsymbol{\alpha}(t)\boldsymbol{\alpha}\rangle = \mathrm{e}^{-\overline{\boldsymbol{M}}|t|} \cdot \langle \boldsymbol{\alpha\alpha}\rangle\,, \tag{7.120}$$

(cf. Eq. (7.80)) we may combine Eqs. (7.118) and (7.119) to obtain

$$\overline{\boldsymbol{C}}_{\boldsymbol{\alpha\alpha}}(t) = \frac{1}{\mathrm{i}\pi} P \int_{-\infty}^{\infty} \mathrm{d}\omega \cos(\omega t) \frac{\overline{\boldsymbol{\chi}}(\omega)}{\omega} \cdot \overline{\boldsymbol{\chi}}^{-1}(0) \cdot \langle \boldsymbol{\alpha\alpha}\rangle \tag{7.121}$$

for $t > 0$. Thus, we have obtained a relation between the dynamic susceptibility matrix, $\overline{\boldsymbol{\chi}}(\omega)$, and the equilibrium correlation function $\overline{\boldsymbol{C}}_{\boldsymbol{\alpha\alpha}}(t)$ for fluctuations. Equation (7.121) is the famous *fluctuation–dissipation theorem*. It gives a relation between the linear response function and the correlation function for equilibrium fluctuations.

Exercise 7.6

Given the dynamic susceptibility $\chi(\omega) = (-\mathrm{i}m\omega + \gamma)^{-1}$ for simple Brownian motion (see Exercise 7.4) and the thermal average $\langle v_o^2\rangle_T = k_\text{B}T/m$, use the fluctuation–dissipation theorem to obtain the velocity autocorrelation function.

Answer: The fluctuation–dissipation theorem Eq. (7.121) says the correlation function is given by

$$\frac{\gamma}{m}\frac{k_{\mathrm{B}}T}{\mathrm{i}\pi}P\int_{-\infty}^{\infty}\mathrm{d}\omega\frac{\chi(\omega)}{\omega}\cos(\omega t)=\frac{\gamma}{m}\frac{k_{\mathrm{B}}T}{\pi}\lim_{\epsilon\to0}\int_{-\infty}^{\infty}\mathrm{d}\omega\frac{\omega}{\omega^2+\epsilon^2}\chi''(\omega)\cos(\omega t)$$

$$=\frac{\gamma k_{\mathrm{B}}T}{m\pi}\lim_{\epsilon\to0}\int_{-\infty}^{\infty}\mathrm{d}\omega\frac{\omega^2\mathrm{e}^{\mathrm{i}\omega t}}{(\omega^2+\epsilon^2)(\omega^2+(\gamma/m)^2)}=\frac{k_{\mathrm{B}}T}{m}\mathrm{e}^{-\gamma t/m}\,.$$

In the second term, the real part of $\chi(\omega)$ does not contribute because it makes the integrand an odd function of ω.

Exercise 7.7

Prove that $\overline{\boldsymbol{\chi}}(0)=\overline{\boldsymbol{g}}^{-1}/T$, where $\overline{\boldsymbol{g}}$ is the matrix whose matrix element is $g_{ij}=(\partial^2S/\partial\alpha_i\partial\alpha_j)_U$.

Answer: The external field, $\boldsymbol{F}_{\mathrm{o}}$, does work on the system and increases its internal energy by an amount $\mathrm{d}U=\boldsymbol{F}_{\mathrm{o}}\cdot\mathrm{d}\boldsymbol{\alpha}$. We can expand the differential of the entropy $\mathrm{d}S$ and use internal energy and state variables $\boldsymbol{\alpha}$ as independent variables, $\mathrm{d}S=(\partial S/\partial U)_{\boldsymbol{\alpha}}\,\mathrm{d}U+(\partial S/\partial\boldsymbol{\alpha})_U\cdot\mathrm{d}\boldsymbol{\alpha}$. But $(\partial S/\partial U)_{\boldsymbol{\alpha}}=1/T$ and $(\partial S/\partial\boldsymbol{\alpha})_U=-\overline{\boldsymbol{g}}\cdot\boldsymbol{\alpha}$. Therefore, we can write $\mathrm{d}S=\left((\boldsymbol{F}_{\mathrm{o}})/T-\overline{\boldsymbol{g}}\cdot\boldsymbol{\alpha}\right)\cdot\mathrm{d}\boldsymbol{\alpha}$. For a constant force, $\langle\boldsymbol{\alpha}\rangle=\overline{\boldsymbol{\chi}}(0)\cdot\boldsymbol{F}_{\mathrm{o}}$ is the expectation value of $\langle\boldsymbol{\alpha}\rangle$ rather than zero, and the entropy will have its maximum for $\boldsymbol{\alpha}=\overline{\boldsymbol{\chi}}(0)\cdot\boldsymbol{F}_{\mathrm{o}}$. Thus, we have $\partial S/\partial\boldsymbol{\alpha}=(\boldsymbol{F}_{\mathrm{o}})/T-\overline{\boldsymbol{g}}\cdot\boldsymbol{\alpha}$, and the condition that entropy be maximum at $\boldsymbol{\alpha}=\overline{\boldsymbol{\chi}}(0)\cdot\boldsymbol{F}_{\mathrm{o}}$ yields $(\partial S/\partial\boldsymbol{\alpha})_{\boldsymbol{\alpha}=\overline{\boldsymbol{\chi}}(0)\cdot\boldsymbol{F}_{\mathrm{o}}}=(1/T)\,\boldsymbol{F}_{\mathrm{o}}-\overline{\boldsymbol{g}}\cdot\overline{\boldsymbol{\chi}}(0)\cdot\boldsymbol{F}_{\mathrm{o}}=0$ or $\overline{\boldsymbol{\chi}}(0)=(1/T)\,\overline{\boldsymbol{g}}^{-1}$.

7.5.4
Power Absorption

The work done on the medium by an external force $\boldsymbol{F}$ to change $\boldsymbol{\alpha}$ by an amount $\mathrm{d}\boldsymbol{\alpha}$ is

$$\text{đ}W=-\boldsymbol{F}\cdot\mathrm{d}\boldsymbol{\alpha}\,. \tag{7.122}$$

The average rate at which work is done on the medium is just the power $P(t)$ absorbed by the medium:

$$P(t)=\left\langle\frac{\text{đ}W}{\mathrm{d}t}\right\rangle_{\boldsymbol{F}}=-\boldsymbol{F}(t)\cdot\langle\dot{\boldsymbol{\alpha}}(t)\rangle_{\boldsymbol{F}}=-\boldsymbol{F}(t)\cdot\frac{\mathrm{d}}{\mathrm{d}t}\int_{-\infty}^{\infty}\mathrm{d}t'\overline{\boldsymbol{K}}(t-t')\cdot\boldsymbol{F}(t')\,. \tag{7.123}$$

If we write the right-hand side in terms of Fourier transforms $\overline{\chi}(\omega)$ and $\boldsymbol{F}(\omega)$, we obtain

$$P(t) = \mathrm{i}\left(\frac{1}{2\pi}\right)^2 \int\limits_{-\infty}^{\infty} \mathrm{d}\omega \int\limits_{-\infty}^{\infty} \mathrm{d}\omega' \omega' \boldsymbol{F}(\omega) \cdot \overline{\chi}(\omega') \cdot \boldsymbol{F}(\omega') \mathrm{e}^{-\mathrm{i}(\omega+\omega')t} \,. \tag{7.124}$$

We can now compute the power absorbed and the total energy absorbed for various types of external forces.

7.5.4.1 **Delta Function Force**

Let us assume that at time $t = 0$ a delta function force is applied. Then,

$$\boldsymbol{F}(t) = \boldsymbol{F}_0 \delta(t) \quad \text{and} \quad \boldsymbol{F}(\omega) = \boldsymbol{F}_0 \,. \tag{7.125}$$

Substituting into Eq. (7.124), we obtain

$$P(t) = \mathrm{i}\left(\frac{1}{2\pi}\right)^2 \int\limits_{-\infty}^{\infty} \mathrm{d}\omega \int\limits_{-\infty}^{\infty} \mathrm{d}\omega' \omega' \overline{\chi}(\omega') : \boldsymbol{F}_0 \boldsymbol{F}_0 \mathrm{e}^{-\mathrm{i}(\omega+\omega')t} \,. \tag{7.126}$$

(*Note*: $\boldsymbol{F} \cdot \overline{\chi}(\omega) \cdot \boldsymbol{F} \equiv \overline{\chi}(\omega) : \boldsymbol{F}\boldsymbol{F}$.) We can find the total energy absorbed by integrating over all times:

$$W_{\mathrm{abs}} = \int\limits_{-\infty}^{\infty} P(t)\,\mathrm{d}t = -\left(\frac{1}{2\pi}\right) \int\limits_{-\infty}^{\infty} \mathrm{d}\omega \omega \overline{\chi}''(\omega) \colon \boldsymbol{F}_0 \boldsymbol{F}_0 \,, \tag{7.127}$$

where $\overline{\chi}''(\omega)$ is the imaginary part of the dynamic susceptibility matrix. Since the total energy absorbed must be a real quantity, only the imaginary part of $\overline{\chi}(\omega)$ contributes.

Exercise 7.8

Find the total energy absorbed by the fluid when a simple Brownian particle (see Exercise 7.3) is hit by a delta function force $F(t) = F_{\mathrm{o}} \delta(t)$.

Answer: The instantaneous absorbed power is $P(t) = -F(t)\langle v(t)\rangle_{\mathrm{F}}$. The total energy absorbed is

$$W_{\mathrm{abs}} = \int\limits_{-\infty}^{\infty} P(t)\,\mathrm{d}t = -\int\limits_{0}^{\infty} \mathrm{d}t F_{\mathrm{o}} \delta(t) K(t) F_{\mathrm{o}} = -\frac{F_{\mathrm{o}}^2}{2m}$$

where we have used the fact that $K(t) = 0$ for $t < 0$ and $\int_0^\infty \mathrm{d}t \delta(t) = 1/2$.

7.5.4.2 **Oscillating Force**

Now let us consider a monochromatic oscillating force of the form

$$\boldsymbol{F}(t) = \boldsymbol{F}_0 \cos(\omega_0 t) = \frac{1}{2} \boldsymbol{F}_0 \left(\mathrm{e}^{\mathrm{i}\omega_0 t} + \mathrm{e}^{-\mathrm{i}\omega_0 t}\right) \,. \tag{7.128}$$

Then $\boldsymbol{F}(\omega) = \pi\boldsymbol{F}_0(\delta(\omega+\omega_0)+\delta(\omega-\omega_0))$ and the power absorbed can be written

$$P(t) = -\frac{1}{4}\left[(-\mathrm{i}\omega_0)(\mathrm{e}^{-\mathrm{i}2\omega_0 t}+1)\overline{\boldsymbol{\chi}}(\omega_0) + (\mathrm{i}\omega_0)(\mathrm{e}^{\pi 2\omega_0 t}+1)\overline{\boldsymbol{\chi}}(-\omega_0)\right] : \boldsymbol{FF}\,. \tag{7.129}$$

As we can see, the instantaneous power absorption oscillates in time. We can find the average power absorbed by taking the time average of Eq. (7.129) over one period T of oscillation:

$$P_T = \frac{\omega_0}{\pi}\int\limits_0^{\pi/\omega_0} \mathrm{d}t P(t) = \frac{\mathrm{i}\omega_0}{4}\left[\overline{\boldsymbol{\chi}}(\omega_0) - \overline{\boldsymbol{\chi}}(-\omega_0)\right] : \boldsymbol{FF} = \frac{\omega_0}{2}\overline{\boldsymbol{\chi}}''(\omega_0) : \boldsymbol{FF}\,, \tag{7.130}$$

where $\overline{\boldsymbol{\chi}}''(\omega_0)$ is the imaginary part of $\overline{\boldsymbol{\chi}}(\omega_0)$. For this case we see that the average power absorbed depends on the imaginary part of the response matrix. In principle, the average power absorbed can be measured, and therefore $\overline{\boldsymbol{\chi}}''(\omega_0)$ can be measured for all ω_0. The Kramers–Kronig relations allow us to obtain the real part of $\overline{\boldsymbol{\chi}}(\omega_0)$ once we know $\overline{\boldsymbol{\chi}}''(\omega_0)$.

The fluctuation–dissipation theorem relates $\overline{\boldsymbol{\chi}}(\omega)$ to the correlation matrix $\overline{\boldsymbol{C}}_{\boldsymbol{\alpha\alpha}}(\tau)$ for equilibrium fluctuations and therefore also relates $\overline{\boldsymbol{\chi}}(\omega)$ to the spectral density matrix, $\overline{\boldsymbol{S}}_{\boldsymbol{\alpha\alpha}}(\omega)$, of equilibrium fluctuations. Thus, by applying a weak external field to a system, we can probe the equilibrium fluctuations.

7.6
Microscopic Linear Response Theory

It is possible to derive the linear response matrix directly from microscopic theory [113]. In this section, we show how to do that for one of the simplest electric circuits, a ballistic electron waveguide. We first derive a general formula for the change in the density operator when an external field is applied. We then use it to derive the conductance of the electron waveguide.

7.6.1
Density Operator Perturbed by External Field

Let us consider a system to which we apply an external field that couples to microscopic densities in the system. We consider the case of an applied electric potential that couples to electron densities in a conductor. The total Hamiltonian of the system in the presence of the external field can be written

$$\hat{H}(t) = \hat{H}_0 + \Delta\hat{H}(t)\,, \tag{7.131}$$

where $\hat{H}_0$ is the Hamiltonian of the system in the absence of the field and $\Delta\hat{H}(t)$ is the contribution to the Hamiltonian due to the external field. We assume that the external field is turned on at time $t = -\infty$. The density operator, $\hat{\rho}(t)$, in the presence of the field, satisfies the equation of motion (see Appendix A)

$$\mathrm{i}\hbar \frac{\partial \hat{\rho}(t)}{\partial t} = [\hat{H}(t), \hat{\rho}(t)] \, . \tag{7.132}$$

Let us write the total density operator in the form

$$\hat{\rho}(t) = \hat{\rho}_{\mathrm{eq}} + \Delta\hat{\rho}(t) \, , \tag{7.133}$$

where $\Delta\hat{\rho}(t)$ is the change in the state of the system due to the external field and $\hat{\rho}_{\mathrm{eq}} = \mathrm{e}^{-\beta\hat{H}_0}/\mathrm{Tr}(\mathrm{e}^{-\beta\hat{H}_0})$ is the equilibrium density operator when no external field is present. Since $[\hat{H}_0, \hat{\rho}_{\mathrm{eq}}] = 0$, we find

$$\mathrm{i}\hbar \frac{\partial \hat{\rho}(t)}{\partial t} = [\Delta\hat{H}(t), \hat{\rho}_{\mathrm{eq}}] + [\hat{H}_0, \Delta\hat{\rho}(t)] + [\Delta\hat{H}(t), \Delta\hat{\rho}(t)] \, . \tag{7.134}$$

To obtain an expression for $\Delta\hat{\rho}(t)$ linear in the applied field, we neglect the nonlinear term, $[\Delta\hat{H}(t), \Delta\hat{\rho}(t)]$, and write

$$\mathrm{i}\hbar \frac{\partial \Delta\hat{\rho}(t)}{\partial t} = [\Delta\hat{H}(t), \hat{\rho}_{\mathrm{eq}}] + [\hat{H}_0, \Delta\hat{\rho}(t)] \, . \tag{7.135}$$

We can solve Eq. (7.135) for $\Delta\hat{\rho}(t)$. First write

$$\Delta\hat{\rho}(t) = \mathrm{e}^{-\mathrm{i}\hat{H}_0 t/\hbar} \Delta\hat{\rho}_{\mathrm{I}}(t) \mathrm{e}^{\mathrm{i}\hat{H}_0 t/\hbar} \tag{7.136}$$

and plug this expression into Eq. (7.135). Then the equation for $\Delta\hat{\rho}_{\mathrm{I}}(t)$ is

$$\mathrm{i}\hbar \frac{\partial \Delta\hat{\rho}_{\mathrm{I}}(t)}{\partial t} = \left[\mathrm{e}^{-\mathrm{i}\hat{H}_0 t/\hbar} \Delta\hat{H}(t) \mathrm{e}^{\mathrm{i}\hat{H}_0 t/\hbar}, \hat{\rho}_{\mathrm{eq}}\right] \, . \tag{7.137}$$

We can integrate (7.137). If we assume that $\Delta\hat{\rho}_{\mathrm{I}}(-\infty) = 0$, we find

$$\Delta\hat{\rho}_{\mathrm{I}}(t) = \frac{1}{\mathrm{i}\hbar} \int\limits_{-\infty}^{t} \mathrm{d}t' \left[\mathrm{e}^{-\mathrm{i}\hat{H}_0 t'/\hbar} \Delta\hat{H}(t') \mathrm{e}^{\mathrm{i}\hat{H}_0 t'/\hbar}, \hat{\rho}_{\mathrm{eq}}\right] \tag{7.138}$$

and

$$\Delta\hat{\rho}(t) = \frac{1}{\mathrm{i}\hbar} \int\limits_{-\infty}^{t} \mathrm{d}t' \left[\mathrm{e}^{\mathrm{i}\hat{H}_0(t-t')\hbar} \Delta\hat{H}(t') \mathrm{e}^{-\mathrm{i}\hat{H}_0(t-t')/\hbar}, \hat{\rho}_{\mathrm{eq}}\right] \, . \tag{7.139}$$

We can use Eqs. (7.133) and (7.139) to find the average value of any desired quantity in the presence of a weak field.

7.6.2
The Electric Conductance

We compute the conductance of a ballistic electron waveguide. Electron waveguides can be formed at the interface of semiconducting materials such as GaAs/

AlGaAs. Electrons at the interface form a two-dimensional Fermi gas. One-dimensional flow can be achieved by using gates (negatively charged structures) on the outside of the materials to induce electrostatic walls at the interface. The walls can be aligned so the electrons are forced to flow through one-dimensional channels at the interface. In real ballistic electron waveguides, the two transverse degrees of freedom are confined to small widths which only allow one or a few transverse quantum states to be excited for the energies available to the electrons in these systems [34]. The effect of these transverse degrees of freedom is to cause the conductance of the wire to increase in discrete jumps (an effect called conductance quantization) as the energy of the electrons is increased. These jumps in conductance occur because with increasing energy more and more transverse modes can be excited resulting in an increase in the number of conduction channels available to the electrons.

We consider a wire of length L that is attached to an electron reservoir on its left and an electron reservoir on its right. We assume that electron energies are low enough that only one state is excited in each of the two transverse directions. The reservoirs are infinitely large and each contains an electron gas distributed according to the Fermi distribution. Generally the reservoirs can have different temperature T and chemical potential μ. We assume that the shape of the interface between the reservoir and the wire is such that electrons from the reservoir can enter the wire with minimal chance of reflection back into the reservoir [119].

Electrons flowing in a one-dimensional wire between the two reservoirs produce a current in the wire. The allowed momentum states in the wire are $k_n = (2\pi n)/L$, where n is an integer that can take values $n = \pm 1, \pm 2, \dots, \pm\infty$. We will use creation and annihilation operators to describe electrons that enter the wire from the two reservoirs. We let $\hat{a}^{\dagger}_{\mathrm{L},n}$ ($\hat{a}_{\mathrm{L},n}$) create (annihilate) electrons entering the wire from the left reservoir [16]. Similarly, we let $\hat{a}^{\dagger}_{\mathrm{R},n}$ ($\hat{a}_{\mathrm{R},n}$) create (annihilate) electrons entering the wire from the right reservoir. The creation and annihilation operators satisfy the Fermi anti-commutation relation

$$\hat{a}^{\dagger}_{\alpha,n}\hat{a}_{\alpha',n'} + \hat{a}_{\alpha',n'}\hat{a}^{\dagger}_{\alpha,n} = \delta_{\alpha,\alpha'}\delta_{n,n'} , \tag{7.140}$$

where $\alpha = \mathrm{L, R}$. The operator that annihilates electrons at point x and time t (the field operator) in the wire can be written

$$\hat{\psi}(x,t) = \frac{1}{\sqrt{L}}\sum_{n=1}^{\infty} \mathrm{e}^{-\mathrm{i}E_n t/\hbar}\left(\hat{a}_{\mathrm{L},n}\mathrm{e}^{\mathrm{i}k_n x} + \hat{a}_{\mathrm{R},n}\mathrm{e}^{-\mathrm{i}k_n x}\right) , \tag{7.141}$$

where $E_n = \hbar^2 k_n^2/(2m) = (2\pi)^2\hbar^2 n^2/(2mL^2)$ is the energy of an electron with wavevector k_n.

In terms of the field operators, the electron current operator at point x and time t is given by

$$\hat{J}(x,t) = \frac{e\hbar}{2mi}\left(\hat{\psi}^{\dagger}(x,t)\frac{\mathrm{d}\hat{\psi}(x,t)}{\mathrm{d}x} - \frac{\mathrm{d}\hat{\psi}^{\dagger}(x,t)}{\mathrm{d}x}\hat{\psi}(x,t)\right) . \tag{7.142}$$

If we substitute the field operator into the expression for the current, we can write (after some algebra)

$$\hat{J}(x,t) = \sum_{n'=1}^{\infty} \sum_{n=1}^{\infty} \mathrm{e}^{\mathrm{i}(E_{n'}-E_n)t/\hbar} \hat{J}_{n',n}(x) , \tag{7.143}$$

where

$$\begin{aligned}\hat{J}_{n',n}(x) = \frac{e\hbar}{2mL} \Big[&(k_{n'} + k_n)\hat{a}^{\dagger}_{\mathrm{L},n'}\hat{a}_{\mathrm{L},n}\mathrm{e}^{-\mathrm{i}(k_{n'}-k_n)x} \\ &+ (k_{n'} - k_n)\hat{a}^{\dagger}_{\mathrm{L},n'}\hat{a}_{\mathrm{R},n}\mathrm{e}^{-\mathrm{i}(k_{n'}+k_n)x} - (k_{n'} - k_n)\hat{a}^{\dagger}_{\mathrm{R},n'}\hat{a}_{\mathrm{L},n}\mathrm{e}^{\mathrm{i}(k_{n'}+k_n)x} \\ &-(k_{n'} + k_n)\hat{a}^{\dagger}_{\mathrm{R},n'}\hat{a}_{\mathrm{R},n}\mathrm{e}^{\mathrm{i}(k_{n'}-k_n)x} \Big] .\end{aligned} \tag{7.144}$$

Let us now assume that a *weak localized* electric potential pulse is applied to the center of the wire such that

$$\Delta\hat{H}(t) = \mathrm{e}\int_{-\infty}^{\infty} \mathrm{d}x V(x,t)\hat{\psi}(x)\hat{\psi}(x) , \tag{7.145}$$

where $V(x,t) = V(x)\cos(\omega_0 t)$. We assume that $V(x) \to 0$ rapidly as $|x| \to \infty$ and that time variations in $V(x,t)$ are slow enough (ω_0 is small enough) that any induced magnetic fields can be neglected. The potential pulse will induce a current in the wire. The average value of this current is given by

$$\langle J(x,t)\rangle = \mathrm{Tr}(\hat{J}(x)\hat{\rho}(t)) = \mathrm{Tr}(\hat{J}(x)\hat{\rho}_{\mathrm{eq}}) + \mathrm{Tr}(\hat{J}(x)\Delta\hat{\rho}(t)) . \tag{7.146}$$

The equilibrium probability density operator for electrons in reservoir α, where $\alpha = \mathrm{L, R}$, is $\hat{\rho}_\alpha = \mathrm{e}^{\beta\hat{K}_\alpha}/\mathrm{Tr}(\mathrm{e}^{\beta\hat{K}_\alpha})$ where $\hat{K}_\alpha = \hat{H}_\alpha - \mu\hat{N} = \sum_n (E_n - \mu)\hat{a}^{\dagger}_{\alpha,n}\hat{a}_{\alpha,n}$. The reservoirs are independent of each other. Therefore, the total equilibrium distribution of the system can be written $\hat{\rho}_{\mathrm{eq}} = \hat{\rho}_{\mathrm{L}}\hat{\rho}_{\mathrm{R}}$.

Exercise 7.9

Compute the average current in the wire for the case when no pulse is applied but the temperature and chemical potential of the two reservoirs are different.

Answer: If we use the definitions of the current in Eqs. (7.143) and (7.144), and use Wick's theorem (see Appendix D) to compute the average of products of creation and annihilation operators, we find

$$\mathrm{Tr}\left(\hat{\rho}_\alpha \hat{a}^{\dagger}_{\alpha',n'}\hat{a}_{\alpha'',n}\right) = \delta_{\alpha,\alpha'}\delta_{\alpha',\alpha''}\delta_{n,n'} f_\alpha(E_n) , \tag{7.147}$$

where $f_\alpha(E_n) = (1 + \mathrm{e}^{\beta_\alpha(E_n-\mu_\alpha)})^{-1}$ is the Fermi distribution of electrons in the αth reservoir. It is now straightforward to show that the average current is

$$\langle J(x,t)\rangle = \mathrm{Tr}\left(\hat{\rho}_{\mathrm{L}}\hat{\rho}_{\mathrm{R}}\hat{J}(x,t)\right) = \frac{\mathrm{e}\hbar}{mL}\sum_{n=1}^{\infty} k_n(f_{\mathrm{L}}(E_n) - f_{\mathrm{R}}(E_n)) .$$

For the case when the reservoirs have the same temperature and chemical potential, $f_{\mathrm{L}}(E_n) = f_{\mathrm{R}}(E_n)$ and $\langle J(x,t)\rangle = 0$ because electrons flow to the left and to the right at the same rate. (Note that $\mathrm{Tr}(\hat\rho_\alpha \hat a_{\alpha,n}) = \mathrm{Tr}(\hat\rho_\alpha \hat a^\dagger_{\alpha,n}) = 0$.)

When the temperature and chemical potential of the left and right reservoirs are the same, the average current is zero $\mathrm{Tr}(\hat\rho_{\mathrm{eq}}\hat J(x,t)) = 0$ (see Exercise (7.147)). Therefore, $\langle J(x,t)\rangle = \mathrm{Tr}(\hat J(x)\Delta\hat\rho(t))$ and

$$\begin{aligned}\mathrm{Tr}(\hat J(x)\Delta\hat\rho(t)) &= \frac{1}{\mathrm{i}\hbar}\int_{-\infty}^{t} \mathrm{d}t'\,\mathrm{Tr}\left(\hat J(x)\left[\mathrm{e}^{\mathrm{i}\hat H_0(t-t')\hbar}\Delta\hat H(t')\mathrm{e}^{-\mathrm{i}\hat H_0(t-t')/\hbar}, \hat\rho_{\mathrm{eq}}\right]\right)\\ &= \frac{1}{i\hbar}\int_{-\infty}^{t} \mathrm{d}t'\,\mathrm{Tr}\left(\hat\rho_{\mathrm{eq}}\left[\hat J(x,t), \Delta\hat{\mathfrak{H}}(t')\right]\right) \end{aligned} \tag{7.148}$$

where

$$\Delta\hat{\mathfrak{H}}(t) = \mathrm{e}^{\mathrm{i}\hat H_0 t/\hbar}\Delta\hat H(t)\mathrm{e}^{-\mathrm{i}\hat H_0 t/\hbar} = \mathrm{e}\int_{-\infty}^{\infty} \mathrm{d}x V(x,t)\hat\psi^\dagger(x,t)\hat\psi(x,t)\,, \tag{7.149}$$

$$\hat\psi(x,t) = \mathrm{e}^{\mathrm{i}\hat H_0 t/\hbar}\hat\psi(x)\mathrm{e}^{-\mathrm{i}\hat H_0 t/\hbar} \quad \text{and} \quad \hat J(x,t) = \mathrm{e}^{\mathrm{i}\hat H_0 t/\hbar}\hat J(x)\mathrm{e}^{-\mathrm{i}\hat H_0 t/\hbar}\,. \tag{7.150}$$

To obtain the last term in Eq. (7.148), we have cyclically permuted operators under the trace and we have used the fact that $\hat H_0$ commutes with $\hat\rho_{\mathrm{eq}}$.

Let us now consider $\Delta\hat{\mathfrak{H}}(t)$. We can write

$$\hat\psi^\dagger(x,t)\hat\psi(x,t) = \sum_{n_1=1}^{\infty}\sum_{n_2=1}^{\infty} \mathrm{e}^{\mathrm{i}(E_1-E_2)t/\hbar}\frac{2m}{\mathrm{i}\mathrm{e}\hbar}\frac{1}{(k_1^2-k_2^2)}\frac{\mathrm{d}\hat J_{n_1,n_2}}{\mathrm{d}x}\,, \tag{7.151}$$

where $\hat J_{n_1,n_2}$ is defined in Eq. (7.144). It is then straightforward to show, after a bit of algebra, that

$$\Delta\hat{\mathfrak{H}}(t') = \frac{\hbar}{\mathrm{i}\mathrm{e}}\sum_{n_1=1}^{\infty}\sum_{n_2=1}^{\infty}\frac{\mathrm{e}^{\mathrm{i}(E_1-E_2)t'/\hbar}}{E_1-E_2}\int_{-\infty}^{\infty}\mathrm{d}x V(x,t')\frac{\mathrm{d}\hat J_{n_1,n_2}(x)}{\mathrm{d}x}\,. \tag{7.152}$$

If we integrate Eq. (7.152) by parts over x, and use the fact that $V(x,t) \to 0$ as $|x| \to \infty$, we obtain

$$\Delta\hat{\mathfrak{H}}(t') = \frac{\hbar}{\mathrm{i}\mathrm{e}}\sum_{n_1=1}^{\infty}\sum_{n_2=1}^{\infty}\frac{\mathrm{e}^{\mathrm{i}(E_1-E_2)t'/\hbar}}{E_1-E_2}\int_{-\infty}^{\infty}\mathrm{d}x\mathcal{E}(x,t')\hat J_{n_1,n_2}(x)\,, \tag{7.153}$$

where $\mathcal{E}(x,t) = -\mathrm{d}V(x,t)/\mathrm{d}x$ is the electric field associated with the potential pulse. We can combine these results and write the average current in the form

$$\langle J(x,t)\rangle = \mathrm{e}\mathrm{Tr}(\hat J(x)\Delta\hat\rho(t)) = \int_{-\infty}^{t}\mathrm{d}t'\int_{-\infty}^{\infty}\mathrm{d}x'\sigma(x,x';t-t')\mathcal{E}(x',t')\,, \tag{7.154}$$

where $\sigma(x, x'; t - t')$ is the conductivity and is defined

$$\sigma(x, x'; t - t') = -\frac{1}{\mathrm{e}^2} \sum_{n_1=1}^{\infty} \sum_{n_2=1}^{\infty} \sum_{n_3=1}^{\infty} \sum_{n_4=1}^{\infty} \mathrm{e}^{\mathrm{i}(E_1 - E_2)t/\hbar} \mathrm{e}^{\mathrm{i}(E_3 - E_4)t'/\hbar} \times \frac{1}{E_3 - E_4} \mathrm{Tr}\left(\hat{\rho}_{\mathrm{eq}} \left[\hat{J}_{n_1,n_2}(x), \hat{J}_{n_3,n_4}(x')\right]\right) \Theta(t - t') . \tag{7.155}$$

We have used the notation $k_1 \equiv k_{n_1}$ and $E_1 \equiv E_{n_1}$. *The conductivity is determined by the equilibrium correlation function for charge currents.* Note that causality requires that $\sigma(x, x'; t - t') = 0$ for $t < t'$, and we have explicitly included this causality requirement by inserting a Heaviside function $\Theta(t - t')$ into the expression for $\sigma(x, x'; t - t')$ in (7.155). The conductivity must also satisfy the condition

$$\int_0^{\infty} \mathrm{d}t \sigma(x, x'; t) < \infty \tag{7.156}$$

so a finite force induces a finite response in the system.

We can use Eq. (7.144) and Wick's theorem to compute the current autocorrelation function,

$$\mathrm{Tr}\left[\hat{\rho}_{\mathrm{eq}} \left(\hat{J}_{n_1,n_2}(x), \hat{J}_{n_3,n_4}(x')\right)\right] = 2\left(\frac{\mathrm{e}\hbar}{2mL}\right)^2 \cos[(k_1 - k_2)(x - x')] \times \delta_{n_1,n_4} \delta_{n_2,n_3} (k_1 + k_2)^2 (f_1 - f_2) , \tag{7.157}$$

where $f_1 = f(E_1)$. If we substitute Eq. (7.157) into Eq. (7.155), we obtain

$$\sigma(x, x'; t - t') = -2\left(\frac{\hbar}{2mL}\right)^2 \sum_{n_1=1}^{\infty} \sum_{n_2=1}^{\infty} \mathrm{e}^{\mathrm{i}(E_1 - E_2)(t - t')/\hbar} \Theta(t - t') \times \cos\left[(k_1 - k_2)(x - x')\right] \left(\frac{f_1 - f_2}{E_1 - E_2}\right) (k_1 + k_2)^2 . \tag{7.158}$$

Note that the conductivity depends only on $x - x'$ and $t - t'$ as is expected for a correlation function averaged over the stationary equilibrium distribution function.

Because we are dealing with linear response, each frequency component of the driving field excites only that same frequency component of the current. Therefore, it is particularly useful to compute the Fourier transform of $\sigma(x, x'; t)$. Because the conductivity in Eq. (7.155) is oscillatory, in order to satisfy Eq. (7.156) we must insert a convergence factor into the Fourier transform. Then the Fourier transform of the conductivity is given by

$$\begin{aligned}\sigma(x,x';\omega) &= \lim_{\delta\to 0}\int_0^\infty \mathrm{d}t e^{\mathrm{i}(\omega+\mathrm{i}\delta)t}\sigma(x,x';t)\\ &= \lim_{\delta\to 0}\left[-2\mathrm{i}\left(\frac{e\hbar}{2mL}\right)^2\sum_{n_1=1}^{\infty}\sum_{n_2=1}^{\infty}(k_1+k_2)^2\right.\\ &\left.\times\left(\frac{f_1-f_2}{E_1-E_2}\right)\frac{\cos[(k_1-k_2)(x-x')]}{(\omega+E_2/\hbar-E_1/\hbar+i\delta)}\right] . \qquad (7.159)\end{aligned}$$

The average current can now be written

$$\langle J(x,t)\rangle = \frac{1}{2\pi}\int_{-\infty}^{\infty}\mathrm{d}\omega \mathrm{e}^{-\mathrm{i}\omega t}\int_{-\infty}^{\infty}\mathrm{d}x'\sigma(x,x';\omega)\tilde{\mathcal{E}}(x',\omega) , \qquad (7.160)$$

where $\tilde{\mathcal{E}}(x',\omega)$ is the Fourier transform of $\mathcal{E}(x,t)$. The quantity $J(x,\omega)=\int_{-\infty}^{\infty}\mathrm{d}x'$ $\sigma(x,x';\omega)\tilde{\mathcal{E}}(x',\omega)$ is the component of the current with frequency ω, and is the microscopic expression for Ohm's Law for this system.

7.6.3
Power Absorption

Let us assume that the applied electric field is oscillatory so that $\mathcal{E}(x,t) = \mathcal{E}(x)\cos(\omega_0 t)$. We can compute the average power P_T absorbed by the system over one period $T=2\pi/\omega_0$ of the applied pulse. The average power absorbed is just the Joule heating of the wire during one period and is given by

$$P_T = \frac{1}{T}\int_0^T \mathrm{d}t\int_{-\infty}^{\infty}\mathrm{d}x\mathcal{E}(x,t)\langle J(x,t)\rangle . \qquad (7.161)$$

If we substitute Eqs. (7.159) and (7.160) into Eq. (7.161) and perform the integrations over x, x', ω and t, we obtain

$$\begin{aligned}P_T = \frac{-\mathrm{i}}{2}\left(\frac{e\hbar}{2mL}\right)^2\lim_{\delta\to 0}&\left[\sum_{n_1=1}^{\infty}\sum_{n_2=1}^{\infty}(k_1+k_2)^2\frac{f_1-f_2}{E_1-E_2}|\tilde{\mathcal{E}}(k_1-k_2)|^2\right.\\ &\left.\times\left\{\frac{1}{-\omega_0+E_2/\hbar-E_1/\hbar+\mathrm{i}\delta}+\frac{1}{\omega_0+E_2/\hbar-E_1/\hbar+\mathrm{i}\delta}\right\}\right] ,\end{aligned} \qquad (7.162)$$

where $|\tilde{\mathcal{E}}(k_1-k_2)|^2 = \int\mathrm{d}x\int\mathrm{d}x'\mathcal{E}(x)\mathcal{E}(x')\cos[(k_1-k_2)(x-x')]$. If the wire is sufficiently long, we can change the summation over momentum states to an integration over energy of the electrons so that $\sum_{n=1}^{\infty}\to L/(2\pi)\int_0^{\infty}\mathrm{d}k$, where $k=2\pi n/L$. In this limit the spectrum becomes continuous. (As pointed out by

Datta [34], the spectrum can be continuous for one of two reasons. If the wire is infinitely long ($L \to \infty$) the spectrum is, by definition, continuous. However, coupling of the finite wire to the reservoirs will give the energies of electrons in the wire a width because electrons placed in the wire can only live there for a finite time.) We can then use the definition

$$\lim_{\delta\to 0}\left(\frac{1}{\hbar\omega_0 + E_2 - E_1 + \mathrm{i}\hbar\delta}\right) = P\left(\frac{1}{\hbar\omega_0 + E_2 - E_1}\right) - \mathrm{i}\pi\delta(\hbar\omega_0 + E_2 - E_1)\,. \tag{7.163}$$

If we now interchange the dummy variables k_1 and k_2, the principal parts in Eq. (7.162) cancel and we find

$$P_T = \frac{-\pi\hbar}{2}\left(\frac{\mathrm{e}\hbar}{4m\pi}\right)^2 \int_0^\infty \mathrm{d}k_1 \int_0^\infty \mathrm{d}k_2 (k_1 + k_2)^2 \frac{f_1 - f_2}{E_1 - E_2} |\tilde{\mathcal{E}}(k_1 - k_2)|^2 \\ \times [\delta(-\hbar\omega_0 + E_2 - E_1) + \delta(\hbar\omega_0 + E_2 - E_1)]\,. \tag{7.164}$$

Finally, interchange k_1 and k_2 in the second delta function to obtain

$$P_T = -\pi\hbar\left(\frac{\mathrm{e}\hbar}{4m\pi}\right)^2 \int_0^\infty \mathrm{d}k_1 \int_0^\infty \mathrm{d}k_2 (k_1 + k_2)^2 \left(\frac{f_1 - f_2}{E_1 - E_2}\right) |\tilde{\mathcal{E}}(k_1 - k_2)|^2 \\ \times \delta(E_2 - E_1 - \hbar\omega_0)\,. \tag{7.165}$$

We can now rewrite this as

$$P_T = -\pi\hbar\left(\frac{\mathrm{e}\hbar}{4m\pi}\right)^2 \int_0^\infty \mathrm{d}E \int_0^\infty \mathrm{d}k_1 \int_0^\infty \mathrm{d}k_2 \left(\frac{f(E) - f(E - \hbar\omega_0)}{\hbar\omega_0}\right) \\ \times (k_1 + k_2)^2 |\tilde{\mathcal{E}}(k_1 - k_2)|^2 \delta(E - E_2)\delta(E - E_1 - \hbar\omega_0)\,. \tag{7.166}$$

For $\hbar\omega_0 \ll E_\mathrm{f}$ and $T \to 0$, $\big((f(E) - f(E - \hbar/\omega_0))(\hbar\omega_0)\big) \to -\delta(E - E_\mathrm{f})$. Also,

$$\delta(E - E_\mathrm{f}) = \frac{2m}{\hbar^2}\delta\left(k^2 - k_\mathrm{f}^2\right) = \frac{2m}{\hbar^2}\frac{1}{2}k_\mathrm{f}[\delta(k - k_\mathrm{f}) + \delta(k + k_\mathrm{f})]\,. \tag{7.167}$$

Using these relations, the average power takes the form

$$P_T = \frac{\mathrm{e}^2}{16\pi\hbar}\frac{\left(k_\mathrm{f} + \sqrt{k_\mathrm{f}^2 - 2m\omega_0/\hbar}\right)}{k_\mathrm{f}\sqrt{k_\mathrm{f}^2 - 2m\omega_0/\hbar}}\left|\tilde{\mathcal{E}}\left(\sqrt{k_\mathrm{f}^2 - \frac{2m\omega_0}{\hbar}} - k_\mathrm{f}\right)\right|^2\,. \tag{7.168}$$

For $(m\omega_0)/\hbar \ll k_\mathrm{f}$, this becomes

$$P_T \approx \frac{\mathrm{e}^2}{8\pi\hbar k_\mathrm{f}}\left|\tilde{\mathcal{E}}\left(\frac{2m\omega_0}{\hbar k_\mathrm{f}}\right)\right|^2\,. \tag{7.169}$$

Thus, the system does absorb power from the applied pulse. This power absorption comes from the fact that the spectrum is continuous. Any energy that is absorbed from the applied field to form a current in the wire will be carried down the infinite wire (or into the reservoirs) and can never return.

7.7
Thermal Noise in the Electron Current

If we apply a voltage difference V between the two reservoirs, but keep the temperature of the reservoirs the same, there will be a nonzero average current $\langle J\rangle = GV$ between the two reservoirs, where $G = e^2/h$ is the Landauer conductivity of the quantum wire (see Problem 7.8).

The thermal noise in the electron current is measured by the correlation function for *current fluctuations* in the wire. Current fluctuations occur because the electrons come out of the reservoirs in discrete units and therefore the current, at any given instant, may be greater or less than the average. To determine the thermal noise, we must compute the correlation function for fluctuations of the current about its average value, $C_{J,J}(x,x';t-t') = \langle(\hat{J}(x,t)-\langle J\rangle)(\hat{J}(x',t')-\langle J\rangle)\rangle$. For the case where the reservoirs have the same temperature and chemical potential, the wire will have zero average current and the correlation function takes the form

$$C_{J,J}(x,x';t-t') = \langle \hat{J}(x,t)\hat{J}(x',t')\rangle = \mathrm{Tr}\left[\hat{\rho}_{\mathrm{L}}\hat{\rho}_{\mathrm{R}}\hat{J}(x,t)\hat{J}(x',t)\right] . \tag{7.170}$$

If we substitute the expression for the current operator $\hat{J}(x,t)$, given in Eqs. (7.143) and (7.144), into Eq. (7.170) and use Wick's theorem to evaluate the trace (see Appendix D), we obtain

$$C_{J,J}(x,x';t-t') = \left(\frac{e\hbar}{2mL}\right)^2 \sum_{n_1=1}^{\infty}\sum_{n_2=1}^{\infty} e^{i(E_1-E_2)(t-t')/\hbar} C_{n_1,n_2}(x-x') \tag{7.171}$$

where

$$\begin{aligned} C_{n_1,n_2}(x-x') = {} & 2(k_1+k_2)^2 f_1(1-f_2)\cos\left[(k_1-k_2)(x-x')\right] + (k_1-k_2)^2 \\ & \times\left[(1-f_1)(1-f_2)e^{-i(k_1+k_2)(x-x')} + f_1 f_2 e^{+i(k_1+k_2)(x-x')}\right] . \end{aligned} \tag{7.172}$$

Let us now compute the power spectrum of these fluctuations,

$$\begin{aligned} S_{J,J}(x,x';\omega) &= \int_{-\infty}^{\infty} d\tau e^{-i\omega\tau} C_{J,J}(x,x';t-t') \\ &= 2\pi\left(\frac{e\hbar}{2mL}\right)^2 \sum_{n_1=1}^{\infty}\sum_{n_2=1}^{\infty} \delta\left(\omega - \frac{E_1}{\hbar} + \frac{E_2}{\hbar}\right) C_{n_1,n_2}(x-x') . \end{aligned} \tag{7.173}$$

If we look at the continuum limit $L \to \infty$ and low frequency limit $\omega \to 0$ of the power spectrum, and remember that

$$\sum_{n=1}^{\infty} \to \frac{L}{2\pi} \int_0^{\infty} \mathrm{d}k = \frac{L}{2\pi} \frac{\sqrt{m}}{\hbar\sqrt{2}} \int_0^{\infty} \frac{\mathrm{d}E}{\sqrt{E}} \tag{7.174}$$

and (since $k > 0$) $\delta\left((E_1 - E_2)/\hbar\right) = m/(\hbar k)\delta(k_1 - k_2)$, we obtain

$$\lim_{\omega\to 0} S_{J,J}(x, x'; \omega) = \frac{2e^2 k_B T}{h} = 2Gk_B T\,, \tag{7.175}$$

where $G = \mathrm{e}^2/h$ is the Landauer conductance. Thus, in this limit we obtain the same noise spectrum as for the classical circuit in Exercise 7.1, except that the classical conductance $G = 1/R$, where R is the resistance, is replaced by the Landauer conductance.

7.8
Problems

Problem 7.1 Compute the spectral density, $S_{v,v}(\omega)$, for the harmonically bound Brownian particle considered in Exercise 7.2. Plot the velocity correlation function, $C_{v,v}(\tau)$, and spectral density $S_{v,v}(\omega)$ for the case $\omega_0 > \Gamma$ (this corresponds to an *underdamped* Brownian particle).

Problem 7.2 A Brownian particle of mass m is attached to a harmonic spring with force constant, k, and is driven by an external force, $F(t)$. The particle is constrained to move in one dimension. The Langevin equation is

$$m\frac{\mathrm{d}^2x(t)}{\mathrm{d}t^2} + \gamma\frac{\mathrm{d}x(t)}{\mathrm{d}t} + m\omega_0^2 x(t) = \xi(t) + F(t)\,,$$

where $\omega_0 = k/m$, γ is the friction constant, and $\xi(t)$ is a Gaussian white noise with zero mean, $\langle\xi(t)\rangle_\xi = 0$. Here $\langle\rangle_\xi$ denotes the average over values of the random force. Consider the overdamped case. (a) Compute the equilibrium correlation function, $\langle\langle x(t)x(0)\rangle_\xi\rangle_T$, starting from the Langevin equation above with $F(t) = 0$. Let $\langle\rangle_T$ denote the thermal average over the initial position and velocity of the Brownian particle. Assume that $\langle x(0)v(0)\rangle_T = 0$ and $\langle x(0)^2\rangle_T = k_B T/(m\omega_0^2)$. (b) Show that the dynamic susceptibility for the Brownian oscillator is $\chi(\omega) = (-m\omega^2 + m\omega_0^2 - \mathrm{i}\gamma\omega)^{-1}$. Use the fluctuation–dissipation theorem,

$$\langle x(t)x(0)\rangle = \frac{k_B T}{\mathrm{i}\pi} P \int_{-\infty}^{\infty} \frac{1}{\omega}\chi(\omega)\cos(\omega t)\,,$$

to compute the equilibrium correlation function. Do your results in (a) and (b) agree?

Problem 7.3 Consider the "short time" relaxation of a free Brownian particle. The Langevin equation for the velocity is $m\mathrm{d}v/\mathrm{d}t = -\gamma v + \xi(t)$. (a) Find the Fokker–Planck equation for the probability, $P(v,t)\,\mathrm{d}v$, to find the Brownian particle with velocity, $v \to v + \mathrm{d}v$, at time t. (b) Solve the Fokker–Planck equation, assuming that at time, $t = 0$, the velocity is $v = v_0$. (*Hint*: Use the transform in Section 7.3.3.1 to write the Fokker–Planck in terms of a Hermitian operator. The eigenfunctions of that operator will be Hermite polynomials.)

Problem 7.4 The magnetization $M(t)$ of a spin system is driven out of equilibrium by a magnetic field $H(t)$ and obeys the Langevin equation of motion

$$\frac{\mathrm{d}M(t)}{\mathrm{d}t} + \Gamma M(t) = \xi(t) - \Gamma\chi_0 H(t)\,,$$

where $\xi(t)$ is a delta-correlated white noise with zero mean that is due to background magnetic field fluctuations and Γ is a positive constant. (a) Compute the linear response function, $K(t)$, which is defined through the equation $\langle M(t)\rangle_\xi = \int_{-\infty}^{\infty}\mathrm{d}t' K(t-t')H(t')$. (b) Compute the equilibrium dynamic correlation function $\langle M(t)M(0)\rangle_{\mathrm{eq}}$. (c) What is χ_0?

Problem 7.5 A Brownian particle of mass m is attached to a harmonic spring with force constant, k, and is driven by an external force, $F(t)$. The particle is constrained to move in one dimension. The Langevin equation is

$$m\frac{\mathrm{d}^2x(t)}{\mathrm{d}t^2} + \gamma\frac{\mathrm{d}x(t)}{\mathrm{d}t} + m\omega_0^2 x(t) = \xi(t) + F(t)\,,$$

where $\omega_0^2 = k/m$, γ is the friction constant, and $\xi(t)$ is a Gaussian white noise with zero mean. The equation of motion of the average position, $\langle x(t)\rangle_{\mathrm{F}}$, in the presence of the external force, $F(t)$, is

$$m\frac{\mathrm{d}^2\langle x(t)\rangle_{\mathrm{F}}}{\mathrm{d}t^2} + \gamma\frac{\mathrm{d}\langle x(t)\rangle_{\mathrm{F}}}{\mathrm{d}t} + m\omega_0^2\langle x(t)\rangle_{\mathrm{F}} = F(t)\,.$$

(a) Compute and plot the linear response function, $K(t)$, where $\langle x(t)\rangle_{\mathrm{F}} = \int_{-\infty}^{\infty} K(t-t')F(t')\,\mathrm{d}t'$. (b) Compute the total energy absorbed for the case of a driving force, $F(t) = F_0\delta(t)$.

Problem 7.6 Consider a dilute solution composed of a polar molecule solute in a nonpolar solvent (polar molecules are molecules with a permanent electric dipole). The electric polarization $P(t)$ of this fluid is driven out of equilibrium by an electric field $E(t)$ and obeys the Langevin equation of motion

$$\frac{dP(t)}{\mathrm{d}t} + 5P(t) = \xi(t) + 5aE(t)\,,$$

where $\xi(t)$ is a delta-correlated white noise (due to background magnetic fluctuations) with zero mean $\langle\xi(t)\rangle = 0$, and a is a constant. (a) Compute the linear response function $K(t)$. (b) Compute the dynamic susceptibility $\chi(\omega)$ and find its limit as $\omega \to 0$, where $1/2C\langle Q(0)^2\rangle_T = \frac{1}{2}k_{\mathrm{B}}T$ from the equipartition theorem.

Problem 7.7 The equation for the potential drop around an RC circuit connected in series is

$$RI(t)+\frac{1}{C}Q(t)=V(t)+\xi(t)\,,$$

where $I(t)=\mathrm{d}Q(t)/\mathrm{d}t$ is the current, $Q(t)$ is the charge, R is the resistance, C is the capacitance, $V(t)$ is a potential drop induced in the circuit, and $\xi(t)$ is a random potential (noise) drop due to the Brownian motion of electrons in the resistor. The random potential is "delta" correlated so $\langle\xi(t)\xi(t')\rangle=g\delta(t-t')$ and it has zero average $\langle\xi(t)\rangle=0$, where g is the strength of the random noise. (a) For the case when $V(t)=0$, the potential across the capacitor is the random potential generated by thermal motion of electrons in the resistor. Compute the strength g of the random noise. (Note that the average energy of the capacitor is $1/2C\langle Q(0)^2\rangle_T=1/2k_\mathrm{B}T$, due to the equipartition theorem. (b) Compute the linear response function $K(t)$, where $K(t)$ is defined from the equation $\langle Q(t)\rangle=\int_\infty^\infty \mathrm{d}t'K(t-t')V(t')$, and compute the dynamic susceptibility $\chi(\omega)$, where $\chi(\omega)=\int_{-\infty}^\infty \mathrm{d}tK(t)\mathrm{e}^{\mathrm{i}\omega t}$. (c) Compute the equilibrium correlation function $\langle Q(t)Q(0)\rangle_T$ for the charge on the capacitor, starting from the fluctuation-dissipation theorem which can be written

$$C_{Q,Q}(t)=\frac{1}{\mathrm{i}\pi}\int\limits_{-\infty}^{\infty}\mathrm{d}\omega P\left(\frac{1}{\omega}\right)\cos(\omega t)\chi(\omega)\chi^{-1}(0)\langle Q(0)^2\rangle_T\,,$$

where $1/(2C)\langle Q(0)^2\rangle_T=1/2k_\mathrm{B}T$ from the equipartition theorem.

Problem 7.8 The Langevin equation for the angular velocity $\Omega(t)$ of a large Brownian particle, with moment of inertia $I=3$, in equilibrium with a fluid, is given by

$$3\frac{\mathrm{d}\Omega(t)}{\mathrm{d}t}+7\Omega(t)=\xi(t)+\tau(t)\,,$$

where $\xi(t)$ is a Gaussian white noise torque and $\tau(t)$ is an external torque. Use the Fluctuation–Dissipation Theorem

$$C_{\Omega\Omega}(t)=\frac{1}{\mathrm{i}\pi}P\int\limits_{-\infty}^{\infty}\mathrm{d}\omega\cos(\omega t)\frac{\chi(\omega)}{\omega}\chi^{-1}(0)\langle\Omega^2\rangle_T\,,$$

where $\langle\Omega^2\rangle_T=k_\mathrm{B}T/I$, to compute the angular velocity autocorrelation function $C_{\Omega\Omega}(t)$ (no other method will be accepted).

Problem 7.9 A paramagnetic system sits in a constant external field, $H_0\hat{\boldsymbol{z}}$, and therefore has constant magnetization, $M_0\hat{\boldsymbol{z}}$. Assume that this is the equilibrium configuration of the system and that a small uniform time-dependent magnetic field, $H_1(t)=H_1\cos(\omega_0 t)\hat{\boldsymbol{x}}$ is applied to the system. The magnetization then becomes time-dependent. Its equation of motion can be written

$$\frac{\mathrm{d}\langle\boldsymbol{M}\rangle}{\mathrm{d}t}=-\gamma\langle\boldsymbol{M}\rangle\times\boldsymbol{H}(t)-D(\langle\boldsymbol{M}\rangle)$$

(these are called Bloch equations), where $\langle \boldsymbol{M} \rangle = \mathrm{Tr}(\hat{\rho}\boldsymbol{M}) = M_x(t)\hat{\boldsymbol{e}}_x + M_y(t)\hat{\boldsymbol{e}}_y + (M_0 - M_z(t))\hat{\boldsymbol{e}}_z$, $\boldsymbol{H}(t) = H_0\hat{\boldsymbol{e}}_z + H_1(t)\hat{\boldsymbol{e}}_x$, and $D(\langle \boldsymbol{M} \rangle)$ is a damping term due to interactions between particles in the medium. The constant γ equals $g\mu/\hbar$, where g is the Lande g-factor and μ is the magnetic moment of particles in the system. (a) Write the equations of motion for $M_x(t)$, $M_y(t)$, and $M_z(t)$, assuming $D_x = M_x/T_2$, $D_y = M_y/T_2$, and $D_z = M_z/T_1$. The equations you derive will be nonlinear functions of H_1, M_x, M_y, and M_z. (b) Assume that H_1, M_x, M_y, and M_z are small, so the equations can be linearized. If we define the response matrix, $\overline{\boldsymbol{K}}(t)$, from the equation $\langle \boldsymbol{M}(t) \rangle = \int_{-\infty}^{\infty} \mathrm{d}t' \overline{\boldsymbol{K}}(t - t') \cdot \boldsymbol{H}(t')$, find $\chi_{xx}(\omega)$ and $K_{xx}(t)$. Write the expression for $\chi_{xx}(\omega)$ in the limits $1/T_1 \to 0$ and $1/T_2 \to 0$. (c) Compute the average power absorbed during the period $T = 2\pi/\omega_0$. (Note that $\hat{\boldsymbol{e}}_x\hat{\boldsymbol{e}}_y$, and $\hat{\boldsymbol{e}}_z$ are unit vectors in the x-, y-, and z-directions, respectively.)

Problem 7.10 Consider a casual function, $g(t)$, such that $g(t) = 0$ for $t < 0$ and $g(t) \neq 0$ for $t > 0$. Let $\tilde{g}_{\mathrm{L}}(z) = \int_0^{\infty} \mathrm{d}t \cdot \mathrm{e}^{-zt} g(t)$ be the Laplace transform. Let $\tilde{g}_{\mathrm{F}}(\omega) = \int_{-\infty}^{\infty} \mathrm{d}t\, \mathrm{e}^{\mathrm{i}\omega t} g(t)$ be the Fourier transform. Show that

$$\tilde{g}_{\mathrm{L}}(z) = \int_{\infty}^{\infty} \frac{\mathrm{d}\omega}{2\pi} \frac{\tilde{g}_{\mathrm{F}}(\omega)}{z + \mathrm{i}\omega} = \tilde{g}_{\mathrm{F}}(\mathrm{i}z) ,$$

and show that the inverse transforms give the correct behavior for $g(t)$.

Problem 7.11 Prove that

$$\langle \alpha(t) \rangle = 2\mathrm{i} \int_{-\infty}^{t} \mathrm{d}t' \overline{K}''(t - t') \cdot \overline{F}(t')$$

where $\overline{K}''(t)$ is the Fourier transform of $\overline{\chi}''(\omega)$. This form of the linear response is commonly seen in the literature. [Note that the identity

$$\lim_{\eta \to 0} \frac{1}{\omega' - \omega \mp \mathrm{i}\eta} = P \frac{1}{\omega' - \omega} \pm \mathrm{i}\pi\delta(\omega' - \omega) ,$$

and the spectral representation of the Heaviside function

$$\theta(t - t') = -\lim_{\eta \to 0} \int_{-\infty}^{\infty} \frac{\mathrm{d}\omega}{(2\pi\mathrm{i})} \frac{\mathrm{e}^{-\mathrm{i}\omega(t - t')}}{\omega + i\eta}$$

are useful.]

Problem 7.12 Consider a 1D ballistic waveguide which is coupled to low-temperature electron reservoirs with Fermi distributions $f_{\mathrm{L}}(E_n)$ and $f_{\mathrm{R}}(E_n)$ on the left and right ends, respectively. Assume that the temperatures of the reservoirs are the same but that the left reservoir has an electric potential energy bias $-eV$, where e is the electron charge. Assume the waveguide has a length L that is very large so you can take the limit $L \to \infty$, and keep only the lowest-order term in V. Compute the average current in the waveguide and show that the conductivity of the waveguide is given by $G = e^2/h$, where h is Planck's constant.

8
Hydrodynamics

8.1
Introduction

When a fluid is disturbed from its equilibrium state, quantities that are not conserved at the microscopic level (and are not order parameters) decay rapidly to their equilibrium values. After a very short time (a few collision times in a gas) only microscopically conserved quantities and order parameters, remain out of equilibrium. Therefore, densities of conserved quantities and order parameters entirely characterize the nonequilibrium behavior of the fluid after long times. The equations of motion for these long-lived quantities are called the *hydrodynamic equations*. Some examples of conserved quantities are the particle number, momentum, and energy. Examples of order parameters may include spontaneous average magnetization, or a complex function characterizing a superfluid state. If there are inhomogeneities in the densities of conserved quantities, then particles, momentum, and kinetic energy must be transported from one part of the fluid to another to achieve equilibrium. Therefore, very-long-wavelength disturbances will take a long time to relax, whereas short-wavelength disturbances relax more quickly. This dependence of relaxation time on wavelength is a characteristic of hydrodynamic processes.

Hydrodynamic equations describe long-wavelength, low-frequency phenomena in a large variety of systems, including dilute gases, liquids, liquid crystals, superfluids, and chemically reacting systems. For complex systems, transport processes are often coupled. For example, in a mixture, it is possible to have a temperature gradient drive a particle current and a concentration gradient drive a heat current. Some systems can have as many as 10 or 20 (or more) transport coefficients to describe the decay to equilibrium from the hydrodynamic regime. Onsager showed that some of these transport processes can be linked due to the time-reversal invariance of dynamics at the microscopic level. In this chapter, we will show how the hydrodynamic equations can be derived from a knowledge of the thermodynamics and symmetry properties of a system.

The hydrodynamic equations for a fluid can explain the spectral properties of light scattered from the fluid. Incident light waves polarize particles in the fluid and they re-emit the light. Density fluctuations cause the emitted light to be

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scattered. By measuring the spectrum of the scattered light we can measure the spectrum of density fluctuations. We will find that density fluctuations are of two types: thermal density fluctuations due to fluctuations in the local entropy and mechanical density fluctuations due to damped sound waves. For low-frequency and long-wavelength fluctuations, the spectrum of scattered light can be obtained from the linearized hydrodynamic equations, and, therefore, light scattering experiments give us a means of measuring transport coefficients in the fluid.

In this chapter, we also develop the hydrodynamic theory of mixtures and apply it to Brownian motion and to systems with thermally induced particle diffusion. The hydrodynamics of mixtures also gives us insight regarding transport processes that occur when temperature and potential differences are maintained across electrical circuits composed of different metals coupled together.

Finally, in the last section of this chapter, we derive the hydrodynamic equations for superfluids which contain an additional degree of freedom due to the complex order parameter that emerges when the superfluid phase transition takes place. The appearance of the order parameter enables a thermal "sound" mode to emerge called second sound. The emergence of second sound is related to the fact that the condensed phase of a superfluid does not carry entropy.

8.2
Navier–Stokes Hydrodynamic Equations

The Navier–Stokes equations describe the macroscopic behavior of an isotropic fluid of point particles out of equilibrium [8, 39, 115]. They include balance equations for densities of quantities that are conserved during collision processes (particle number, momentum, energy) and the balance equation for the entropy density. Entropy is not a conserved quantity. For a fluid in which irreversible processes can occur, there will be an entropy source term. The entropy source term in a fluid is the hydrodynamic equivalent of the Joule heating which occurs in an electric circuit. The entropy source term enables us to identify generalized forces and currents in the fluid. The *conductance* in a fluid (the proportionality constant between force and resulting current) is called a *transport coefficient*. Once the transport coefficients for the fluid have been identified, we can write the Navier–Stokes equations.

8.2.1
Balance Equations

Balance equations govern the flow of various densities in a fluid. In our discussion of hydrodynamic flow, we will be particularly interested in balance equations for mass density, momentum density, energy density, and entropy density. However, balance equations can also describe the flow of probability density in phase space.

Let us consider a continuous medium which moves with velocity $\boldsymbol{v}(\boldsymbol{r}, t)$ at point $\boldsymbol{r}$ and time t. The displacement $\boldsymbol{r} = (x_1, x_2, x_3)$ is measured with respect to a reference frame O_r fixed in space. A second frame of reference frame $O_{\boldsymbol{z}}$ moves with the fluid. At time $t = 0$, the two frames coincide. We select a “fluid particle,” which at time $t = 0$ is located at point $\boldsymbol{r}(0)$ in frame O_r and at point $\boldsymbol{z} = (z_1, z_2, z_3)$ in frame $O_{\boldsymbol{z}}$. Because the frames coincide at time $t = 0$, $\boldsymbol{r}(0) = \boldsymbol{z}$. Assume that frame $O_{\boldsymbol{z}}$ moves freely with the fluid and the fluid particle always has displacement $\boldsymbol{z}$ with respect to $O_{\boldsymbol{z}}$. The position of the fluid particle at time t in frame $O_{\boldsymbol{r}}$ is $\boldsymbol{r}(t) = \boldsymbol{r}(\boldsymbol{z}, t)$, where $\boldsymbol{z} = \boldsymbol{r}(0)$ is the initial position of the fluid particle (see Figure 8.1).

Now assume the fluid carries some quantity D, which could be mass, probability, entropy or some other quantity. At time t, observer $O_{\boldsymbol{z}}$ sees density $\mathfrak{D}'(\boldsymbol{z}, t)$ in the neighborhood of the fluid particle and observer $O_{\boldsymbol{r}}$ sees density $\mathfrak{D}(\boldsymbol{r}(t), t)$ in the neighborhood of the fluid particle, such that $\mathfrak{D}(\boldsymbol{r}(t), t) = \mathfrak{D}'(\boldsymbol{z}, t)$. The time rate of change of the density in the neighborhood of the fluid particle can be written

$$\left(\frac{\partial \mathfrak{D}'}{\partial t}\right)_{z} = \left(\frac{\partial \mathfrak{D}}{\partial t}\right)_{r} + \left(\frac{\partial \mathfrak{D}}{\partial \boldsymbol{r}}\right)_{t} \left(\frac{\partial \boldsymbol{r}}{\partial t}\right)_{z} , \tag{8.1}$$

where $\boldsymbol{v} = (\partial \boldsymbol{r}/\partial t)_{\boldsymbol{z}}$ is the velocity of the fluid particle. Here $\left(\partial \mathfrak{D}'/\partial t\right)_{\boldsymbol{z}}$ is the time rate of change of the density as seen by an observer moving with the fluid particle and is denoted $\mathrm{d}/\mathrm{d}t$. The quantity $(\partial \mathfrak{D})/\partial t)_r$ is the time rate of change of the density as seen by an observer fixed in space and is denoted $\partial/\partial t$. The relation between these two time derivatives is written

$$\frac{\mathrm{d}}{\mathrm{d}t} = \frac{\partial}{\partial t} + \boldsymbol{v} \cdot \nabla_r . \tag{8.2}$$

The derivative $\mathrm{d}/\mathrm{d}t$ is called the *convective time derivative.*

If the fluid is compressible, the volume of the fluid particle can change with the flow. Consider a volume element $\mathrm{d}V_0 = \mathrm{d}\boldsymbol{z} = \mathrm{d}\boldsymbol{r}(0)$ at time $t = 0$. At time t it can be written $\mathrm{d}V_t = \mathrm{d}\boldsymbol{r}(t) = \mathfrak{J}(\boldsymbol{r}(t); \boldsymbol{z})\,\mathrm{d}\boldsymbol{z}$, where $\mathfrak{J}(\boldsymbol{r}(t); \boldsymbol{z})$ is the Jacobian of the transformation from time $t = 0$ to time t, and is the determinant of the 3×3 matrix formed from the derivatives $\partial x_i(t)/\partial z_j$. Using properties of derivatives of determinants, we can show that the Jacobian evolves in time according to the

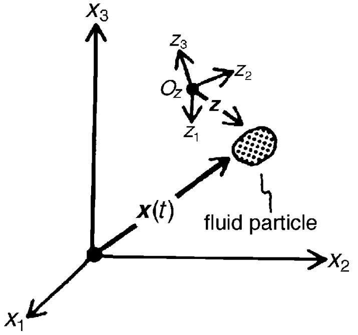

Figure 8.1 Coordinates of a fluid particle at time t.

equation

$$\frac{\mathrm{d}\mathfrak{J}}{\mathrm{d}t} = \mathfrak{J}\nabla_r \cdot \boldsymbol{v} \, . \tag{8.3}$$

If the fluid is incompressible, then $\nabla_r \cdot \boldsymbol{v} = 0$ and the volume element remains constant in time.

These properties of fluid flow will be useful below where we derive the balance equations for the mass, momentum, energy, and entropy densities for an isotopic fluid of point particles.

8.2.1.1 Mass Density Equations

In the absence of chemical reactions, the number of particles in the fluid is conserved. For nonrelativistic processes, the total mass of the particles is also conserved. If we consider a volume element of the fluid, $V(t)$ (with a given set of fluid particles), which moves with the fluid, the amount of mass inside this volume element must remain constant. Let $\rho = \rho(\boldsymbol{r}, t)$ denote the mass density (mass per unit volume) and let M denote the total mass in the volume, $V(t)$. Then

$$\frac{\mathrm{d}M}{\mathrm{d}t} = \frac{\mathrm{d}}{\mathrm{d}t} \int\limits_{V(t)} \rho \, \mathrm{d}V_t = \frac{\mathrm{d}}{\mathrm{d}t} \int\limits_{V_0} \rho \mathfrak{J} \, \mathrm{d}V_0 \, , \tag{8.4}$$

where, in the last term, we have written the integral in terms of coordinates at time $t = 0$ and $\mathfrak{J}$ is the Jacobian of the transformation from coordinates at time $t = 0$ to time t. We can now take the time derivative inside the integral and write

$$\frac{\mathrm{d}M}{\mathrm{d}t} = \int\limits_{V_0} \left(\frac{\mathrm{d}\rho}{\mathrm{d}t} \mathfrak{J} + \rho \nabla_r \cdot \boldsymbol{v} \mathfrak{J} \right) \mathrm{d}V_0 = \int\limits_{V(t)} \left(\frac{\mathrm{d}\rho}{\mathrm{d}t} + \rho \nabla_r \cdot \boldsymbol{v} \right) \mathrm{d}V_t = 0 \, , \tag{8.5}$$

where we have used Eq. (8.3) and $\boldsymbol{v} = \boldsymbol{v}(\boldsymbol{r}, t)$ is the average velocity of the fluid at point $\boldsymbol{r}$ and time t. Since the volume element, $V(t)$, is arbitrary, the integrand must be zero and we find

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} + \rho \nabla_r \cdot \boldsymbol{v} = 0 \, . \tag{8.6}$$

If we use Eq. (8.2) for the "convective" derivative $\mathrm{d}/\mathrm{d}t$, we can also write

$$\frac{\partial \rho}{\partial t} + \nabla_r \cdot (\rho \boldsymbol{v}) = 0 \, . \tag{8.7}$$

The quantity, $\boldsymbol{J} \equiv \rho \boldsymbol{v}$ is the mass current or mass flux and has units mass/area · time. It is also a momentum density. The derivative, $\mathrm{d}\rho / \mathrm{d}t$, gives the time rate of change of the mass density for an observer moving with the fluid. The derivative, $\partial \rho / \partial t$, gives the time rate of change of the mass density for an observer at a fixed point in space. Equation (8.7) is sometimes called the *continuity equation* and sometimes called the *mass balance equation* for the fluid. It is a direct consequence of the conservation of mass in the fluid.

8.2.1.2 Momentum Balance Equation

The total momentum, $\boldsymbol{P}(t) = \int_{V(t)} \rho \boldsymbol{v}\, \mathrm{d}V_t$ of the volume $V(t)$, evolves according to Newton's law. The time rate of change of the momentum, $\boldsymbol{P}(t)$, must be equal to the sum of the forces acting on the volume element, $V(t)$. Therefore, we can write the equation of motion of the fluid element in the form

$$\frac{\mathrm{d}\boldsymbol{P}(t)}{\mathrm{d}t} = \frac{\mathrm{d}}{\mathrm{d}t}\int\limits_{V(t)} \rho \boldsymbol{v}\, \mathrm{d}V_t = \int\limits_{V(t)} \rho \boldsymbol{F}\, \mathrm{d}V_t + \int\limits_{S(t)} \boldsymbol{f}\, \mathrm{d}S_t\,, \tag{8.8}$$

where $\boldsymbol{F}$ is an external force per unit mass which couples to the particles inside the volume element (an electric or magnetic field for example), $\boldsymbol{f}$ is a force per unit area acting on the walls of the volume element, and $S(t)$ denotes the surface of the volume element, $V(t)$. The surface force, $\boldsymbol{f}$, is due to the fluid surrounding the volume element. It will always have a component perpendicular to the surface of $V(t)$, and for a nonideal fluid (a fluid with dissipation) it will have a component tangent to the surface.

If we write a differential surface area element as a vector, $\mathrm{d}\boldsymbol{S}$, directed outward perpendicular to the surface, then we can write $\boldsymbol{f}\,\mathrm{d}S = \mathrm{d}\boldsymbol{S}\cdot\overline{\boldsymbol{P}}$, where $\overline{\boldsymbol{P}}$ is the pressure tensor, $\boldsymbol{f} = \hat{\boldsymbol{n}}\cdot\overline{\boldsymbol{P}}$, and $\hat{\boldsymbol{n}}$ is a unit vector directed outward perpendicular to the surface so $\mathrm{d}\boldsymbol{S} = \mathrm{d}S\hat{\boldsymbol{n}}$. The pressure tensor has nine components. In Cartesian coordinates it can be written $\overline{\boldsymbol{P}} = P_{xx}\hat{\boldsymbol{e}}_x\hat{\boldsymbol{e}}_x + P_{xy}\hat{\boldsymbol{e}}_x\hat{\boldsymbol{e}}_y + \cdots + P_{zz}\hat{\boldsymbol{e}}_z\hat{\boldsymbol{e}}_z$, where $\hat{\boldsymbol{e}}_x$, $\hat{\boldsymbol{e}}_y$, and $\hat{\boldsymbol{e}}_z$ are unit vectors in the x-, y-, and z-directions, respectively. The unit vector, $\hat{\boldsymbol{n}}$, can be written $\hat{\boldsymbol{n}} = n_x\hat{\boldsymbol{e}}_x + n_y\hat{\boldsymbol{e}}_y + n_z\hat{\boldsymbol{e}}_z$, where n_x, n_y, and n_z are components of $\hat{\boldsymbol{n}}$ in the x-, y-, and z-directions, respectively. Note that the ith component of the vector, $\boldsymbol{f}$, can be written $f_i = \sum_j n_j P_{ji}$, where $i = x, y, z$ and $j = x, y, z$. If we use Gauss's theorem, we can write

$$\int\limits_{S(t)} \mathrm{d}\boldsymbol{S}_t \cdot \overline{\boldsymbol{P}} = \int\limits_{V(t)} \mathrm{d}V_t \nabla_r \cdot \overline{\boldsymbol{P}}\,. \tag{8.9}$$

Here $\nabla_r \cdot \overline{\boldsymbol{P}}$ is a vector whose ith component is $(\nabla_r \cdot \overline{\boldsymbol{P}})_i = \sum_j \partial_j P_{ji}$, where $\partial_x = \partial/\partial x$, $\partial_y = \partial/\partial y$, and $\partial_z = \partial/\partial z$. The argument of Eq. (8.8) must satisfy the equation

$$\frac{\mathrm{d}\rho\boldsymbol{v}}{\mathrm{d}t} + \rho\boldsymbol{v}(\nabla_r \cdot \boldsymbol{v}) = \rho\boldsymbol{F} + \nabla_r \cdot \overline{\boldsymbol{P}}\,. \tag{8.10}$$

For an ideal fluid (no dissipation) the only force on the walls of $V(t)$ is due to the hydrostatic pressure, $P = P(\boldsymbol{r}, t)$, which is always perpendicular to the walls and pointed inward. Thus, for an ideal fluid we have $\boldsymbol{f} = -P\hat{\boldsymbol{n}}$ and $\overline{\boldsymbol{P}} = -P\overline{\boldsymbol{U}}$ ($\overline{\boldsymbol{U}}$ is the unit tensor, $\overline{\boldsymbol{U}} = \hat{\boldsymbol{e}}_x\hat{\boldsymbol{e}}_x + \hat{\boldsymbol{e}}_y\hat{\boldsymbol{e}}_y + \hat{\boldsymbol{e}}_z\hat{\boldsymbol{e}}_z$). For a nonideal fluid, there is also a dissipative contribution, $\overline{\Pi}$, to the pressure tensor and Eq. (8.10) takes the form

$$\frac{\mathrm{d}\rho\boldsymbol{v}}{\mathrm{d}t} + \rho\boldsymbol{v}(\nabla_r \cdot \boldsymbol{v}) = \rho\boldsymbol{F} - \nabla_r P - \nabla_r \cdot \overline{\boldsymbol{\Pi}} \tag{8.11}$$

since $\nabla_r \cdot P\overline{\boldsymbol{U}} = \nabla_r P$. The tensor $\overline{\boldsymbol{\Pi}}$ is called the *stress tensor*. If we make use of the convective time derivative, $\mathrm{d}/\mathrm{d}t = \partial/\partial t + \boldsymbol{v}\cdot\nabla$, we can also write Eq. (8.11) in the form

$$\frac{\partial \rho \boldsymbol{v}}{\partial t} + \nabla_r \cdot (P\overline{\boldsymbol{U}} + \rho \boldsymbol{v}\boldsymbol{v} + \overline{\boldsymbol{\Pi}}) = \rho \boldsymbol{F}\,. \tag{8.12}$$

The term $\rho\boldsymbol{v}\boldsymbol{v}$ is the momentum flux and is a nine-component dyatic tensor, $\rho\boldsymbol{v}\boldsymbol{v} = \rho v_x v_x \hat{\boldsymbol{e}}_x\hat{\boldsymbol{e}}_x + \rho v_x v_y \hat{\boldsymbol{e}}_x\hat{\boldsymbol{e}}_y + \cdots + \rho v_z v_z \hat{\boldsymbol{e}}_z\hat{\boldsymbol{e}}_z$. Equations (8.11) and (8.12) are alternative versions of the *momentum balance equation* for an isotropic fluid of point particles. Equation (8.11) describes the time rate of change of momentum density as seen by an observer moving with the fluid, and Eq. (8.12) describes the time rate of change of momentum density as seen by an observer at a fixed point in space.

Exercise 8.1

Show that an arbitrary tensor, $\overline{\boldsymbol{T}}$, can be decomposed into three orthogonal components.

Answer: In cartesian coordinates we can write the nine component tensor in the form $\overline{\boldsymbol{T}} = T_{xx}\hat{\boldsymbol{e}}_x\hat{\boldsymbol{e}}_x + T_{xy}\hat{\boldsymbol{e}}_x\hat{\boldsymbol{e}}_y + \cdots + T_{zz}\hat{\boldsymbol{e}}_z\hat{\boldsymbol{e}}_z$. The nine terms in $\bar{\boldsymbol{T}}$ can be regrouped into three orthogonal quantities

$$\overline{\boldsymbol{T}} = \frac{1}{3}\mathrm{Tr}(\hat{\boldsymbol{T}})\overline{\boldsymbol{U}} + \overline{\boldsymbol{T}}^s + \overline{\boldsymbol{T}}^a\,,$$

where $\overline{\boldsymbol{U}} = \hat{\boldsymbol{e}}_x\hat{\boldsymbol{e}}_x + \hat{\boldsymbol{e}}_y\hat{\boldsymbol{e}}_y + \hat{\boldsymbol{e}}_z\hat{\boldsymbol{e}}_z$ is the unit tensor and $\mathrm{Tr}(\overline{\boldsymbol{T}}) = T_{xx} + T_{yy} + T_{zz}$. $\overline{\boldsymbol{T}}^s$ is a symmetric tensor with zero trace and is defined as

$$\overline{\boldsymbol{T}}^s = \frac{1}{2}(\overline{\boldsymbol{T}} + \overline{\boldsymbol{T}}^{\mathrm{T}}) - \frac{1}{3}\mathrm{Tr}(\overline{\boldsymbol{T}})\overline{\boldsymbol{U}}\,,$$

where $\overline{\boldsymbol{T}}^{\mathrm{T}}$ is the transpose of $\overline{\boldsymbol{T}}$, $T^s_{xx} = 2/3T_{xx} - 1/3T_{yy} - 1/3T_{zz}$, and $T^s_{xy} = 1/2(T_{xy} + T_{yx})$. $\overline{\boldsymbol{T}}^a$ is an antisymmetric tensor with zero trace and is defined as

$$\overline{\boldsymbol{T}}^a = \frac{1}{2}(\overline{\boldsymbol{T}} - \overline{\boldsymbol{T}}^{\mathrm{T}})\,,$$

where $T^a_{xx} = 0$ and $T^a_{xy} = 1/2(T_{xy} - T_{yx})$. If we introduce a second tensor, $\overline{\boldsymbol{V}}$, then it also can be decomposed in the manner described above. The scalar product of the two tensors can be written

$$\overline{\boldsymbol{T}} : \overline{\boldsymbol{V}} = \frac{1}{3}[\mathrm{Tr}(\overline{\boldsymbol{T}})][\mathrm{Tr}(\overline{\boldsymbol{V}})] + \bar{\boldsymbol{T}}^s : \overline{\boldsymbol{V}}^s + \overline{\boldsymbol{T}}^a : \bar{\boldsymbol{V}}^a\,.$$

One can also show that $\overline{\boldsymbol{U}} : \overline{\boldsymbol{T}}^s = \overline{\boldsymbol{U}} : \bar{\boldsymbol{T}}^a = \overline{\boldsymbol{T}}^s : \overline{\boldsymbol{V}}^a = 0$. Thus, the tensor, $\overline{\boldsymbol{T}}$, has been decomposed into three independent orthogonal components.

8.2.1.3 Energy and Entropy Balance Equations

The energy and entropy balance equations are easy to write down. We let ϵ denote the energy per unit mass, and let ρe denote the energy per unit volume of the fluid. For the case when the external force has the form $\boldsymbol{F} = -\nabla_r \phi$ (ϕ is a potential energy per unit mass), the energy density can be written $\rho e = \rho u + 1/2\rho v^2 + \rho\phi$, where u is the internal energy per unit mass. Thus, the energy density has contributions from thermodynamic processes in the fluid, the kinetic energy of the fluid, and the external potential energy.

Since the energy inside the volume element cannot be created or destroyed by collisions (for a fluid of point particles), the only way the energy inside the volume element can change is by flow through the walls of $V(t)$. The balance equation for the total energy can be written

$$\frac{\partial \rho e}{\partial t} + \nabla_r \cdot \left(\boldsymbol{J}_\mathrm{e}^\mathrm{R} + \boldsymbol{J}_\mathrm{e}^\mathrm{D}\right) = 0\,, \tag{8.13}$$

where $\boldsymbol{J}_\mathrm{e}^\mathrm{R}$ is the reactive (nondissipative) energy current and $\boldsymbol{J}_\mathrm{e}^\mathrm{D}$ is the dissipative energy current. Both $\boldsymbol{J}_\mathrm{e}^\mathrm{R}$ and $\boldsymbol{J}_\mathrm{e}^\mathrm{D}$ have yet to be determined.

The entropy balance equation can be written in an analogous fashion. However, now we must take account of the fact that entropy can be created inside the volume $V(t)$ due to spontaneous processes. Let s denote the entropy per unit mass (the specific entropy) and ρs denote the entropy per unit volume. The entropy balance equation then becomes

$$\frac{\partial \rho s}{\partial t} + \nabla_r \cdot \left(\boldsymbol{J}_\mathrm{s}^\mathrm{R} + \boldsymbol{J}_\mathrm{s}^\mathrm{D}\right) = \sigma_\mathrm{s}\,, \tag{8.14}$$

where $\boldsymbol{J}_\mathrm{s}^\mathrm{R}$ is the reactive entropy current, $\boldsymbol{J}_\mathrm{s}^\mathrm{D}$ is the dissipative entropy current, and σ_s is an entropy source term due to dissipative processes inside of $V(t)$. The explicit forms of $\boldsymbol{J}_\mathrm{s}^\mathrm{R}$, $\boldsymbol{J}_\mathrm{s}^\mathrm{D}$, and σ_s will be determined in the next section.

8.2.2
Entropy Source and Entropy Current

Let us assume that deviations from thermodynamic equilibrium occur on very large length scales compared to microscopic distances. Then locally the system will be in equilibrium, but the actual values of thermodynamic quantities vary slowly in space and time. The fundamental equation for the internal energy is $\rho u = T\rho s - P + \rho\mu$, where μ is the chemical potential. If we take the differential of this equation and use the Gibbs–Duhem equation, $\rho\,\mathrm{d}\mu + \rho s\,\mathrm{d}T - \mathrm{d}P = 0$, we find $\mathrm{d}(\rho u) = T\,\mathrm{d}(\rho s) + \mu\,\mathrm{d}\rho$. Therefore, we can write

$$\begin{aligned}\frac{\mathrm{d}\rho u}{\mathrm{d}t} - T\frac{\mathrm{d}\rho s}{\mathrm{d}t} - \mu\frac{\mathrm{d}\rho}{\mathrm{d}t} &= \frac{\partial \rho u}{\partial t} - T\frac{\partial \rho s}{\partial t} - \mu\frac{\partial \rho}{\partial t}\\ &+ \boldsymbol{v}\cdot\nabla_r(\rho u) - T\boldsymbol{v}\cdot\nabla_r(\rho s) - \mu\boldsymbol{v}\cdot\nabla_r(\rho) = 0\,,\end{aligned} \tag{8.15}$$

where we have made use of the convective time derivative. Let us next note that

$$\begin{aligned}
&\boldsymbol{v} \cdot \nabla_{\boldsymbol{r}}(\rho \boldsymbol{u}) - T\boldsymbol{v} \cdot \nabla_{\boldsymbol{r}}(\rho s) - \mu \boldsymbol{v} \cdot \nabla_{\boldsymbol{r}}\rho \\
&= \nabla_{\boldsymbol{r}} \cdot [(\rho u - T\rho s - \rho\mu)\boldsymbol{v}] + \rho s \boldsymbol{v} \cdot \nabla_{\boldsymbol{r}} T + \rho \boldsymbol{v} \cdot \nabla_{\boldsymbol{r}}\mu + P\nabla_{\boldsymbol{r}} \cdot \boldsymbol{v} \\
&= \boldsymbol{v} \cdot (\rho s \nabla_{\boldsymbol{r}} T + \rho \nabla_{\boldsymbol{r}}\mu - \nabla_{\boldsymbol{r}} P) = 0\,,
\end{aligned} \tag{8.16}$$

where we have used the fundamental equation, $\rho u = T\rho s - P + \rho\mu$. The last term is zero because of the Gibbs–Duhem equation, $\rho\,\mathrm{d}\mu + \rho s\,\mathrm{d}T - \mathrm{d}P = 0$. Therefore,

$$\frac{\mathrm{d}\rho u}{\mathrm{d}t} - T\frac{\mathrm{d}\rho s}{\mathrm{d}t} - \mu\frac{\mathrm{d}\rho}{\mathrm{d}t} = \frac{\partial \rho u}{\partial t} - T\frac{\partial \rho s}{\partial t} - \mu\frac{\partial \rho}{\partial t} = 0\,. \tag{8.17}$$

Let us now assume, for simplicity, that all external forces are zero so that $\boldsymbol{F} = 0$. Then the total energy per unit volume is $\rho e = \rho u + 1/2\rho v^2$, and we can write

$$\frac{\partial \rho e}{\partial t} = \frac{\partial \rho u}{\partial t} + \boldsymbol{v} \cdot \frac{\partial \rho \boldsymbol{v}}{\partial t} - \frac{1}{2}v^2\frac{\partial \rho}{\partial t}\,. \tag{8.18}$$

If we combine Eqs. (8.17) and (8.18), we find

$$T\frac{\partial \rho s}{\partial t} = \frac{\partial \rho e}{\partial t} - \boldsymbol{v} \cdot \frac{\partial \rho \boldsymbol{v}}{\partial t} + \left(\frac{1}{2}v^2 - \mu\right)\frac{\partial \rho}{\partial t}\,. \tag{8.19}$$

We can now obtain an expression for the entropy current and source. If we combine Eqs. (8.7), (8.12), (8.13), and (8.19), we obtain

$$T\frac{\partial \rho s}{\partial t} = -\nabla_{\boldsymbol{r}} \cdot \left(\boldsymbol{J}_{\mathrm{e}}^{\mathrm{R}} + \boldsymbol{J}_{\mathrm{e}}^{\mathrm{D}}\right) + \boldsymbol{v}[\nabla_{\boldsymbol{r}} \cdot (P\overline{\boldsymbol{U}} + \rho\boldsymbol{v}\boldsymbol{v} + \overline{\boldsymbol{\Pi}})] - \left(\frac{1}{2}v^2 - \mu\right)\nabla_{\boldsymbol{r}} \cdot (\rho\boldsymbol{v})\,. \tag{8.20}$$

This equation can be simplified further. Note that

$$\boldsymbol{v} \cdot [\nabla_{\boldsymbol{r}} \cdot (\rho\boldsymbol{v}\boldsymbol{v})] = \sum_i \sum_j v_i \nabla_j(\rho v_j v_i) = \sum_i \sum_j \left[\rho v_i v_j(\nabla_j v_i) + v_i^2 \nabla_j(\rho v_j)\right]\,. \tag{8.21}$$

Note also that

$$\nabla_j\left(\rho v_j \frac{1}{2}v_i^2\right) = \frac{1}{2}v_i^2\nabla_j(\rho v_j) + \rho v_j v_i \nabla_j v_i\,. \tag{8.22}$$

If we combine Eqs. (8.21) and (8.22), we find

$$\boldsymbol{v} \cdot \left[\nabla_{\boldsymbol{r}} \cdot (\rho\boldsymbol{v}\boldsymbol{v})\right] = \frac{1}{2}v^2\nabla_{\boldsymbol{r}} \cdot (\rho\boldsymbol{v}) + \frac{1}{2}\nabla_{\boldsymbol{r}} \cdot (\rho v^2\boldsymbol{v})\,. \tag{8.23}$$

We now substitute Eq. (8.23) into Eq. (8.20), make use of the Gibbs–Duhem relation, $\rho s\nabla_{\boldsymbol{r}} T + \rho\nabla_{\boldsymbol{r}}\mu - \nabla_{\boldsymbol{r}} P = 0$, and rearrange terms. We then obtain

$$T\frac{\partial \rho s}{\partial t} = -\nabla_{\boldsymbol{r}} \cdot \left(\boldsymbol{J}_{\mathrm{e}}^{\mathrm{R}} + \boldsymbol{J}_{\mathrm{e}}^{\mathrm{D}} - \rho\mu''\boldsymbol{v} - \overline{\boldsymbol{\Pi}} \cdot \boldsymbol{v}\right) + \rho s\boldsymbol{v} \cdot \nabla_{\boldsymbol{r}} T - \overline{\boldsymbol{\Pi}} : \nabla_{\boldsymbol{r}}\boldsymbol{v}\,, \tag{8.24}$$

where $\overline{\boldsymbol{\Pi}} : \nabla_{\boldsymbol{r}}\boldsymbol{v} \equiv \sum_i \sum_j \Pi_{ij}\nabla_i v_j$ and $\mu'' = \mu + 1/2v^2$. We can write Eq. (8.24) in the form of a balance equation. If we divide through by the temperature, we can rearrange terms to obtain

$$\frac{\partial \rho s}{\partial t} = -\nabla_r \cdot \left(\frac{\boldsymbol{J}_{\mathrm{e}}^{\mathrm{R}} + \boldsymbol{J}_{\mathrm{e}}^{\mathrm{D}} - \rho\mu''\boldsymbol{v} - \overline{\boldsymbol{\Pi}} \cdot \boldsymbol{v}}{T} \right) + \left(\boldsymbol{J}_{\mathrm{e}}^{\mathrm{R}} + \boldsymbol{J}_{\mathrm{e}}^{\mathrm{D}} - \rho\mu''\boldsymbol{v} - \rho s T \boldsymbol{v} - \overline{\boldsymbol{\Pi}} \cdot \boldsymbol{v} \right) \cdot \nabla_{\boldsymbol{r}} \left(\frac{1}{T} \right) - \frac{1}{T} \overline{\boldsymbol{\Pi}} : \nabla_{\boldsymbol{r}}\boldsymbol{v} \,. \tag{8.25}$$

We can simplify Eq. (8.25) still further if we consider its form for a nondissipative fluid.

Exercise 8.2

In orthogonal curvilinear coordinates the gradient is

$$\nabla = \frac{\hat{\boldsymbol{e}}_1}{h_1}\frac{\partial}{\partial u_1} + \frac{\hat{\boldsymbol{e}}_2}{h_2}\frac{\partial}{\partial u_2} + \frac{\hat{\boldsymbol{e}}_3}{h_3}\frac{\partial}{\partial u_3} \,,$$

where the coordinates are u_1, u_2, and u_3, the scale factors are h_1, h_2, and h_3, and the unit vectors are $\hat{\boldsymbol{e}}_1$, $\hat{\boldsymbol{e}}_2$, and $\hat{\boldsymbol{e}}_3$. In terms of these coordinates, the velocity can be written $\boldsymbol{v} = v_1\hat{\boldsymbol{e}}_1 + v_2\hat{\boldsymbol{e}}_2 + v_3\hat{\boldsymbol{e}}_3$. The unit vectors $\hat{\boldsymbol{e}}_i$ are related to the Cartesian unit vectors $\hat{\boldsymbol{e}}_\alpha$ $(\alpha = x, y, z)$ as $\hat{\boldsymbol{e}}_i = \sum_\alpha R_{i,\alpha}(u_1, u_2, u_3)\hat{\boldsymbol{e}}_\alpha$. The dyatic tensor, $\nabla_{\boldsymbol{r}}\boldsymbol{v}$ then takes the form

$$\nabla_{\boldsymbol{r}}\boldsymbol{v} = \sum_i \sum_j \frac{\hat{\boldsymbol{e}}_i\hat{\boldsymbol{e}}_j}{h_i}\frac{\partial v_j}{\partial u_i} + \sum_i \sum_j \sum_k \sum_\alpha \frac{\hat{\boldsymbol{e}}_i\hat{\boldsymbol{e}}_k}{h_i} v_j \frac{\partial R_{j,\alpha}}{\partial u_i} R^{-1}_{\alpha,k} \,.$$

Write the dyatic tensor $\nabla_{\boldsymbol{r}}\boldsymbol{v}$ for the special case of cylindrical coordinates $u_1 = r$, $u_2 = \phi$, and $u_3 = z$ with scale factors $h_1 = 1$, $h_2 = r$, and $h_3 = 1$ and unit vectors $\hat{\boldsymbol{e}}_1 = \hat{\boldsymbol{e}}_{\mathrm{r}}$, $\hat{\boldsymbol{e}}_2 = \hat{e}_\phi$, and $\hat{\boldsymbol{e}}_3 = \hat{\boldsymbol{e}}_z$.

Answer: In cylindrical coordinates we have

$$\begin{pmatrix} \hat{\boldsymbol{e}}_r \\ \hat{\boldsymbol{e}}_\phi \\ \hat{\boldsymbol{e}}_z \end{pmatrix} = \begin{pmatrix} \cos(\phi) & \sin(\phi) & 0 \\ -\sin(\phi) & \cos(\phi) & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \hat{\boldsymbol{e}}_x \\ \hat{\boldsymbol{e}}_y \\ \hat{\boldsymbol{e}}_z \end{pmatrix} .$$

Therefore, we find

$$\nabla_r\boldsymbol{v} = \hat{\boldsymbol{e}}_r\hat{\boldsymbol{e}}_r\frac{\partial v_r}{\partial r} + \hat{\boldsymbol{e}}_r\hat{\boldsymbol{e}}_\phi\frac{\partial v_\phi}{\partial r} + \hat{\boldsymbol{e}}_r\hat{\boldsymbol{e}}_z\frac{\partial v_z}{\partial r} + \hat{\boldsymbol{e}}_\phi\hat{\boldsymbol{e}}_r\left(\frac{1}{r}\frac{\partial v_r}{\partial \phi} - \frac{v_\phi}{r}\right) + \hat{\boldsymbol{e}}_\phi\hat{\boldsymbol{e}}_\phi\left(\frac{1}{r}\frac{\partial v_\phi}{\partial \phi} + \frac{v_r}{r}\right) + \hat{\boldsymbol{e}}_\phi\hat{\boldsymbol{e}}_z\frac{1}{r}\frac{\partial v_z}{\partial \phi} + \hat{\boldsymbol{e}}_z\hat{\boldsymbol{e}}_r\frac{\partial v_r}{\partial z} + \hat{\boldsymbol{e}}_z\hat{\boldsymbol{e}}_\phi\frac{\partial v_\phi}{\partial z} + \hat{\boldsymbol{e}}_z\hat{\boldsymbol{e}}_z\frac{\partial v_z}{\partial z} \,.$$

Consider a fluid in which no dissipative processes occur. By definition, the stress tensor $\overline{\boldsymbol{\Pi}} = 0$ and the dissipative energy current $\boldsymbol{J}_{\text{e}}^{\text{D}} = 0$ for such a fluid. Also there will be no entropy source term. Therefore, from Eq. (8.25) the reactive energy current must be given by

$$\boldsymbol{J}_{\text{e}}^{\text{R}} \equiv \rho\mu''\boldsymbol{v} + \rho sT\boldsymbol{v} = \rho\left(h + \frac{1}{2}v^2\right)\boldsymbol{v} = \rho\left(u + P + \frac{1}{2}v^2\right)\boldsymbol{v}\,, \tag{8.26}$$

where h is the enthalpy per unit mass. If we substitute Eq. (8.26) into Eq. (8.25) and set $\overline{\Pi} = 0$ and $\boldsymbol{J}_{\epsilon}^{\text{D}} = 0$, we obtain the entropy balance equation for a nondissipative fluid,

$$\frac{\partial \rho s}{\partial t} = -\nabla_{\boldsymbol{r}} \cdot (\rho s\boldsymbol{v})\,. \tag{8.27}$$

The entropy current in a nondissipative fluid is $\rho s\boldsymbol{v}$.

If we substitute the definition of the reactive energy current, $\boldsymbol{J}_{\text{e}}^{\text{R}}$, into Eq. (8.24), we obtain the final form of the entropy balance equation for a dissipative fluid:

$$\frac{\partial \rho s}{\partial t} = -\nabla_{\boldsymbol{r}} \cdot \left(\rho s\boldsymbol{v} + \boldsymbol{J}_{\text{s}}^{\text{D}}\right) - \frac{1}{T}\boldsymbol{J}_{\text{s}}^{\text{D}} \cdot \nabla_{\boldsymbol{r}} T - \frac{1}{T}\overline{\boldsymbol{\Pi}} : \nabla_{\boldsymbol{r}}\boldsymbol{v}\,, \tag{8.28}$$

where the dissipative entropy current, $\boldsymbol{J}_{\text{s}}^{\text{D}}$, is

$$\boldsymbol{J}_{\text{s}}^{\text{D}} = \frac{1}{T}\left(\boldsymbol{J}_{\text{e}}^{\text{D}} - \overline{\boldsymbol{\Pi}} \cdot \boldsymbol{v}\right). \tag{8.29}$$

The entropy source in a dissipative fluid is

$$\sigma_{\text{s}} = -\frac{1}{T}\boldsymbol{J}_{\text{s}}^{\text{D}} \cdot \nabla_{\boldsymbol{r}} T - \frac{1}{T}\overline{\boldsymbol{\Pi}} : \nabla_{\boldsymbol{r}}\boldsymbol{v}\,. \tag{8.30}$$

One can easily check that the quantity $\boldsymbol{J}_{\text{s}}^{\text{D}} \cdot \nabla_{\boldsymbol{r}} T + \overline{\boldsymbol{\Pi}} : \nabla_{\boldsymbol{r}}\boldsymbol{v}$ has units (energy/(volume · time)). It is the hydrodynamic version of Joule heating. In an electric circuit, Joule heating is given by $\boldsymbol{J} \cdot \boldsymbol{E}$, where $\boldsymbol{E}$ is the electric field and $\boldsymbol{J}$ is the electric current, and is the (energy/(volume · time)) dissipated in the electric circuit. We see that the hydrodynamic entropy production has the same form if we identify $\boldsymbol{J}_{\text{s}}^{\text{D}}$ and $\overline{\boldsymbol{\Pi}}$ as the generalized currents and $\nabla_{r} T$ and $\nabla_{r}\boldsymbol{v}$ as the generalized forces driving those currents.

In an electric circuit the electric current and the electric field (driving force) are related by Ohm's law, $\boldsymbol{J} = \sigma\boldsymbol{E}$, where σ is the conductivity of the medium. Hydrodynamic media also have a version of Ohm's law in which the driving forces are linearly related to the currents. In hydrodynamic systems the "conductivities" are called "transport coefficients." In the next section we will obtain the transport coefficients for an isotropic fluid of point particles, and in so doing we will be able to write the Navier–Stokes equations for the fluid.

8.2.3
Transport Coefficients

Transport coefficients are the generalized conductivities of a hydrodynamic system. Before we can determine how many transport coefficients are needed for our isotropic fluid of point particles, we must determine how many independent driving forces and currents there are in the fluid. In the last section, we found that the generalized driving forces are $\nabla_r T$ and $\nabla_r \boldsymbol{v}$ and the generalized currents are $\boldsymbol{J}_{\mathrm{s}}^{\mathrm{D}}$ and $\overline{\boldsymbol{\Pi}}$. Both $\nabla_r \boldsymbol{v}$ and $\overline{\boldsymbol{\Pi}}$ are nine-component tensors, and each can be decomposed into three orthogonal parts. For example, we can write the dyatic, $\nabla_r \boldsymbol{v}$, in the form (see Exercise 8.1)

$$\nabla_r \boldsymbol{v} = \frac{1}{3}(\nabla_r \cdot \boldsymbol{v})\overline{U} + [\nabla_r \boldsymbol{v}]^s + [\nabla_r \boldsymbol{v}]^a \,. \tag{8.31}$$

In Cartesian coordinates, we have

$$[\nabla_r \boldsymbol{v}]^s_{ij} = \frac{1}{2}(\partial_j v_i + \partial_i v_j) - \frac{1}{3}\delta_{ij}\nabla_r \cdot \boldsymbol{v} \quad \text{and} \quad [\nabla_r \boldsymbol{v}]^a_{ij} = \frac{1}{2}(\partial_j v_i - \partial_i v_j) \,. \tag{8.32}$$

Similarly, we can write the stress tensor as

$$\overline{\boldsymbol{\Pi}} = \frac{1}{3}[\mathrm{Tr}(\overline{\boldsymbol{\Pi}})]\overline{\boldsymbol{U}} + \overline{\boldsymbol{\Pi}}^s + \overline{\boldsymbol{\Pi}}^a \,. \tag{8.33}$$

For an isotropic fluid of point particles (or particles which interact via a spherically symmetric potential), the antisymmetric part of the stress tensor is identically zero. The antisymmetric "force," $[\nabla_r \boldsymbol{v}]^a = \nabla_r \times \boldsymbol{v}$, is the curl of the velocity and is the contribution from vortex motion in the fluid. For a fluid of particles coupled by spherically symmetric forces, there is no coupling of rotational motion of the particles to vortex motion of the fluid. Energy from the fluid can't be dissipated by transforming angular momentum of the fluid into angular momentum of the particles so $\overline{\boldsymbol{\Pi}}^a \equiv 0$. For a fluid of particles which interact via nonspherically symmetric forces, there will be coupling between angular momentum and translational flow [183].

In order to write "Ohm's law" for the fluid, we shall make use of Curie's principle, which states that, *in an isotropic fluid, a given force cannot drive a current of a different tensor character*. Let us note that there are four independent generalized forces in the fluid, each with a different tensor character. They are $\nabla_r T$, a polar vector; $[\nabla_r \boldsymbol{v}]^s$, a symmetric tensor; $\nabla_r \cdot \boldsymbol{v}$, a scalar: and $[\nabla_r \boldsymbol{v}]^a = \nabla_r \times \boldsymbol{v}$, an axial vector. (Polar vectors and axial vectors behave differently under inversion through the origin of coordinates. Polar vectors change their sign. Axial vectors do not.) Since the antisymmetric part of the stress tensor is zero for a fluid of point particles, the axial vector cannot drive a current. Thus, an isotropic fluid of point particles has three generalized forces. They are $\nabla_r T$, $\nabla_r \cdot \boldsymbol{v}$, and $[\nabla_r \boldsymbol{v}]^s$ and they drive the generalized currents, $\boldsymbol{J}_{\mathrm{s}}^{\mathrm{D}}$, $\Pi \equiv (1/3)\mathrm{Tr}(\overline{\boldsymbol{\Pi}})$, and $\overline{\boldsymbol{\Pi}}^s$, respectively. Since these forces all have different tensor character, we find the following generalization of Ohm's law for the fluid:

$$\boldsymbol{J}_{\mathrm{s}}^{\mathrm{D}} = -\frac{K}{T}\nabla_r T \,, \tag{8.34}$$

where K is the *coefficient of thermal conductivity*,

$$\overline{\boldsymbol{\Pi}}^s = -2\eta[\nabla_r \boldsymbol{v}]^s \,, \tag{8.35}$$

where η is the *coefficient of shear viscosity*, and

$$\Pi = -\zeta \nabla_r \cdot \boldsymbol{v} \,, \tag{8.36}$$

where ζ is the *coefficient of bulk viscosity*.

Exercise 8.3

Write the pressure tensor $\boldsymbol{P} = \sum_{i,j} P_{i,j} \hat{\boldsymbol{e}}_i \hat{\boldsymbol{e}}_j$ for an incompressible fluid in: (a) cylindrical coordinates where $i = r, \phi, z$ and $j = r, \phi, z$; (b) spherical coordinates where $i = r, \theta, \phi$ and $j = r, \theta, \phi$.

Answer: (a) In cylindrical coordinates

$$\begin{aligned}
P_{r,r} &= -P + 2\eta \frac{\partial v_r}{\partial r} \,, \quad P_{\phi,\phi} = -P + 2\eta \left(\frac{1}{r} \frac{\partial v_\phi}{\partial \phi} + \frac{v_r}{r} \right) \,, \\
P_{z,z} &= -P + 2\eta \frac{\partial v_z}{\partial z} \,, \quad P_{r,\phi} = \eta \left(\frac{1}{r} \frac{\partial v_r}{\partial \phi} + \frac{\partial v_\phi}{\partial r} - \frac{v_\phi}{r} \right) \,, \\
P_{z,\phi} &= \eta \left(\frac{\partial v_\phi}{\partial z} + \frac{1}{r} \frac{\partial v_z}{\partial \phi} \right), \quad P_{r,z} = \eta \left(\frac{\partial v_z}{\partial r} + \frac{\partial v_r}{\partial z} \right) \,.
\end{aligned}$$

(b) In spherical coordinates

$$\begin{aligned}
P_{r,r} &= -P + 2\eta \frac{\partial v_r}{\partial r} \,, \quad P_{\phi,\phi} = -P + 2\eta \left(\frac{1}{r\sin(\theta)} \frac{\partial v_\phi}{\partial \phi} + \frac{v_r}{r} + \frac{v_\theta \cot(\theta)}{r} \right), \\
P_{\theta,\theta} &= -P + 2\eta \left(\frac{1}{r} \frac{\partial v_\theta}{\partial \theta} + \frac{v_r}{r} \right), \quad P_{\theta,\phi} = \eta \left(\frac{1}{r\sin(\theta)} \frac{\partial v_\theta}{\partial \phi} + \frac{1}{r} \frac{\partial v_\phi}{\partial \theta} - \frac{v_\phi \cot(\theta)}{r} \right), \\
P_{r,\theta} &= \eta \left(\frac{1}{r} \frac{\partial v_r}{\partial \theta} + \frac{\partial v_\theta}{\partial r} - \frac{v_\theta}{r} \right), \quad P_{\phi,r} = \eta \left(\frac{\partial v_\phi}{\partial r} + \frac{1}{r\sin(\theta)} \frac{\partial v_r}{\partial \phi} - \frac{v_\phi}{r} \right).
\end{aligned}$$

If we use Eqs. (8.34)–(8.36), the entropy source term takes the form

$$\sigma_{\mathrm{s}} = \frac{K}{T^2} |\nabla_r T|^2 + 2\frac{\eta}{T} |[\nabla_r \boldsymbol{v}]^s|^2 + \frac{\zeta}{T} |\nabla_r \cdot \boldsymbol{v}|^2 \,, \tag{8.37}$$

where $|\nabla_r T|^2 = (\nabla_r T) \cdot (\nabla_r T)$ and $|[\nabla_r \boldsymbol{v}]^s|^2 = [\nabla_r \boldsymbol{v}]^s : [\nabla_r \boldsymbol{v}]^s$. The mass balance, momentum balance, and entropy balance equations take the form

$$\frac{\partial \rho}{\partial t} + \nabla_r \cdot (\rho \boldsymbol{v}) = 0 \,, \tag{8.38}$$

$$\frac{\partial \rho \boldsymbol{v}}{\partial t} + \nabla_r \cdot (\rho \boldsymbol{v} \boldsymbol{v}) = -\nabla_r P + \eta \nabla_r^2 \boldsymbol{v} + \left(\zeta + \frac{1}{3}\eta \right) \nabla_r (\nabla_r \cdot \boldsymbol{v}) \,, \tag{8.39}$$

and

$$\frac{\partial \rho s}{\partial t} + \nabla_r \cdot \left(\rho s \boldsymbol{v} + \boldsymbol{J}_{\mathrm{s}}^{\mathrm{D}} \right) = \frac{K}{T^2} |\nabla_r T|^2 + 2\frac{\eta}{T} |[\nabla_r, \boldsymbol{v}]^s|^2 + \frac{\zeta}{T} (\nabla_r \cdot \boldsymbol{v})^2 \,, \tag{8.40}$$

respectively, where we have used the fact that

$$\nabla_r \cdot \overline{\boldsymbol{\Pi}} = -\eta \nabla_r^2 \boldsymbol{v} - \left(\zeta + \frac{1}{3}\eta\right) \nabla_r(\nabla_r \cdot \boldsymbol{v}) \,. \tag{8.41}$$

The derivation of the specific form of Eq. (8.39) is given in Exercise 8.3. Equations (8.38)–(8.40) collectively are called the *Navier–Stokes equations* or hydrodynamic equations. They describe the hydrodynamic behavior of an isotropic fluid of point particles. In the next section we describe how to solve the linearized version of these equations.

8.3
Linearized Hydrodynamic Equations

The hydrodynamic equations, (8.38)–(8.40), depend nonlinearly on the thermodynamic variables and the average velocity. This makes them very difficult to solve and one generally must resort to numerical methods to solve them. However, if we restrict ourselves to the neighborhood of absolute equilibrium, then we can look at the behavior of small deviations from the equilibrium state, and it is possible to linearize the hydrodynamic equations [60]. The linearized hydrodynamic equations describe the behavior of the fluid if it is only slightly displaced from absolute equilibrium. They are also useful in describing the behavior of fluctuations for a fluid in equilibrium.

8.3.1
Linearization of the Hydrodynamic Equations

Let ρ_0, T_0, s_0, and P_0, denote the equilibrium mass density, temperature, specific entropy, and pressure, respectively. Close to the equilibrium state, we can write $\rho(\boldsymbol{r}, t) = \rho_0 + \Delta\rho(\boldsymbol{r}, t)$, $T = T_0 + \Delta T(\boldsymbol{r}, t)$, $s(\boldsymbol{r}, t) = s_0 + \Delta s(\boldsymbol{r}, t)$, and $P(\boldsymbol{r}, t) = P_0 + \Delta P(\boldsymbol{r}, t)$, respectively. The quantities $\Delta\rho$, ΔT, Δs and ΔP, denote deviations from equilibrium. The average velocity, $\boldsymbol{v}(\boldsymbol{r}, t)$, is zero at equilibrium, so it is already first order in deviation from equilibrium. If we now substitute these expansions into the hydrodynamic equations (8.38)–(8.40), and only retain terms to first order in deviations from equilibrium, we find

$$\frac{\partial \Delta\rho}{\partial t} + \rho_0 \nabla_r \cdot \boldsymbol{v} = 0 \,, \tag{8.42}$$

$$\rho_0 \frac{\partial \boldsymbol{v}}{\partial t} = -\nabla_r \Delta P + \eta \nabla_r^2 \boldsymbol{v} + \left(\zeta + \frac{1}{3}\eta\right) \nabla_r(\nabla_r \cdot \boldsymbol{v}) \,, \tag{8.43}$$

and

$$\rho_0 \frac{\partial \Delta s}{\partial t} = \frac{K}{T_0} \nabla_r^2 \Delta T \,. \tag{8.44}$$

To obtain the final form of Eq. (8.44), we have used Eq. (8.38) to eliminate two terms and we have used Eq. (8.40).

The momentum balance equation, (8.43), is actually three equations since the velocity has three components. Thus, we have five equations but we have seven unknowns, $\Delta\rho$, Δs, ΔT, ΔP, v_x, v_y, and v_z. We can use thermodynamics to reduce the number of unknowns to five since the quantities $\Delta\rho$, Δs, ΔT, and ΔP are related by thermodynamic equations. We can choose two of them to be independent and expand the other two in terms of them. The choice of the two independent variables depends on the problem of interest.

Let us choose $\Delta\rho$ and ΔT to be independent. Then we can write

$$\Delta s(\boldsymbol{r}, t) = \left(\frac{\partial s}{\partial \rho}\right)_T^0 \Delta\rho(\boldsymbol{r}, t) + \left(\frac{\partial s}{\partial T}\right)_\rho^0 \Delta T(\boldsymbol{r}, t) \tag{8.45}$$

and

$$\Delta P(\boldsymbol{r}, t) = \left(\frac{\partial P}{\partial \rho}\right)_T^0 \Delta\rho(\boldsymbol{r}, t) + \left(\frac{\partial P}{\partial T}\right)_\rho^0 \Delta T(\boldsymbol{r}, t) \, . \tag{8.46}$$

The linearized hydrodynamic equations take the form

$$\frac{\partial \Delta\rho}{\partial t} + \rho_0 \nabla_r \cdot \boldsymbol{v} = 0 \, , \tag{8.47}$$

$$\rho_0 \frac{\partial \boldsymbol{v}}{\partial t} = -\left(\frac{\partial P}{\partial \rho}\right)_T^0 \nabla_r \Delta\rho - \left(\frac{\partial P}{\partial T}\right)_\rho^0 \nabla_r \Delta T + \eta \nabla_r^2 \boldsymbol{v} + \left(\zeta + \frac{1}{3}\eta\right) \nabla_r (\nabla_r \cdot \boldsymbol{v}) \, , \tag{8.48}$$

and

$$\rho_0 \left(\frac{\partial s}{\partial \rho}\right)_T^0 \frac{\partial \Delta\rho}{\partial t} + \rho_0 \left(\frac{\partial s}{\partial T}\right)_\rho^0 \frac{\partial \Delta T}{\partial t} = \frac{K}{T_0} \nabla_r^2 \Delta T \, . \tag{8.49}$$

Equations (8.47)–(8.49) form a set of coupled equations that describe the behavior of small deviations from absolute equilibrium.

Given that we have linearized equations, we can obtain dispersion relations for various processes in the fluid. As a first step, let us Fourier transform the space dependence of the linearized hydrodynamic equations. We let $\Delta\rho(\boldsymbol{r}, t) = (1/2\pi)^3 \int \mathrm{d}\boldsymbol{k} \rho_{\boldsymbol{k}}(t) \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}$ so that $\rho_{\boldsymbol{k}}(t) = \int \mathrm{d}\boldsymbol{r} \Delta\rho(\boldsymbol{r}, t) \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}$, with similar transforms for $\boldsymbol{v}(\boldsymbol{r}, t)$ and $\Delta T(\boldsymbol{r}, t)$. If we substitute these expressions into Eqs. (8.47)–(8.49), we find

$$\frac{\partial \rho_{\boldsymbol{k}}}{\partial t} - \mathrm{i}\rho_0 \boldsymbol{k} \cdot \boldsymbol{v}_{\boldsymbol{k}} = 0 \, , \tag{8.50}$$

$$\rho_0 \frac{\partial \boldsymbol{v}_{\boldsymbol{k}}}{\partial t} = \mathrm{i}\left(\frac{\partial P}{\partial \rho}\right)_T^0 \boldsymbol{k} \rho_{\boldsymbol{k}} + \mathrm{i}\left(\frac{\partial P}{\partial T}\right)_\rho^0 \boldsymbol{k} T_{\boldsymbol{k}} - \eta k^2 \boldsymbol{v}_{\boldsymbol{k}} - \left(\zeta + \frac{1}{3}\eta\right) \boldsymbol{k}(\boldsymbol{k} \cdot \boldsymbol{v}_{\boldsymbol{k}}) \, , \tag{8.51}$$

and

$$\rho_0 \left(\frac{\partial s}{\partial \rho}\right)_T^0 \frac{\partial \rho_{\boldsymbol{k}}}{\partial t} + \rho_0 \left(\frac{\partial s}{\partial T}\right)_\rho^0 \frac{\partial T_{\boldsymbol{k}}}{\partial t} = -\frac{K}{T_0} k^2 T_{\boldsymbol{k}} \, , \tag{8.52}$$

where $\rho_{\boldsymbol{k}} = \rho_{\boldsymbol{k}}(t)$, $T_{\boldsymbol{k}} = T_{\boldsymbol{k}}(t)$, and $\boldsymbol{v}_{\boldsymbol{k}} = \boldsymbol{v}_{\boldsymbol{k}}(t)$.

We can simplify Eqs. (8.50)–(8.52) still further. Let us divide the velocity into longitudinal (parallel to $\boldsymbol{k}$) and transverse (perpendicular to $\boldsymbol{k}$) components:

$$\boldsymbol{v}_{\boldsymbol{k}}(t) = v_{\boldsymbol{k}}^{\parallel}(t)\hat{\boldsymbol{k}} + \boldsymbol{v}_{\boldsymbol{k}}^{\perp}(t)\,, \tag{8.53}$$

where $\boldsymbol{k}\cdot\boldsymbol{v}_{\boldsymbol{k}}^{\perp}(t) \equiv 0$ and $\boldsymbol{k}\cdot\boldsymbol{v}_{\boldsymbol{k}}(t) \equiv k v_{\boldsymbol{k}}^{\parallel}(t)$. The component $k v_{\boldsymbol{k}}^{\parallel}(t)$ is the amplitude of a longitudinal velocity variation (in the direction $\boldsymbol{k}$) that has wavelength $\lambda = 2\pi/k$. The velocity vector, $\boldsymbol{v}_{\boldsymbol{k}}^{\perp}(t)$, is a two-component vector which describes velocity variations with wavelength $\lambda = 2\pi/k$, but transverse (perpendicular) to the direction of $\boldsymbol{k}$.

The transverse and longitudinal components of the average velocity decouple in the linearized hydrodynamic equations and evolve according to different equations of motion. From Eqs. (8.50)–(8.53), we can write

$$\frac{\partial \rho_{\boldsymbol{k}}}{\partial t} - i\rho_0 k v_{\boldsymbol{k}}^{\parallel} = 0\,, \tag{8.54}$$

$$\rho_0 \frac{\partial v_{\boldsymbol{k}}^{\parallel}}{\partial t} = \mathrm{i}k\left(\frac{\partial P}{\partial \rho}\right)_T^0 \rho_{\boldsymbol{k}} + \mathrm{i}k\left(\frac{\partial P}{\partial T}\right)_\rho^0 T_{\boldsymbol{k}} - \left(\zeta + \frac{4}{3}\eta\right) k^2 v_{\boldsymbol{k}}^{\parallel}\,, \tag{8.55}$$

$$\rho_0\left(\frac{\partial s}{\partial \rho}\right)_T^0 \frac{\partial \rho_{\boldsymbol{k}}}{\partial t} + \rho_0\left(\frac{\partial s}{\partial T}\right)_\rho^0 \frac{\partial T_{\boldsymbol{k}}}{\partial t} = -\frac{K}{T_0} k^2 T_{\boldsymbol{k}}\,, \tag{8.56}$$

and

$$\rho_0 \frac{\partial \boldsymbol{v}_{\boldsymbol{k}}{}^{\perp}}{\partial t} = -\eta k^2 \boldsymbol{v}_{\boldsymbol{k}}^{\perp}\,. \tag{8.57}$$

Equations (8.54)–(8.56) govern the evolution of the coupled heat and sound modes (sound consists of longitudinal oscillations of the fluid). Equation (8.57) governs the evolution of shear modes (transverse velocity oscillations).

If we want to solve the hydrodynamic equations for a given set of initial conditions $\rho_{\boldsymbol{k}}(0)$, $T_{\boldsymbol{k}}(0)$, and $\boldsymbol{v}_{\boldsymbol{k}}(0)$, it is useful to introduce the Laplace transform

$$\tilde{\rho}_{\boldsymbol{k}}(z) = \int_0^\infty \mathrm{d}t\,\rho_{\boldsymbol{k}}(t)\mathrm{e}^{-zt} \quad \text{and} \quad \rho_{\boldsymbol{k}}(t) = \frac{1}{2\pi\mathrm{i}}\int_{\delta-\mathrm{i}\infty}^{\delta+\mathrm{i}\infty} \mathrm{d}z\,\tilde{\rho}_{\boldsymbol{k}}(z)\mathrm{e}^{zt}\,, \tag{8.58}$$

where δ is a positive number. The Laplace transform of the time derivative is

$$\int_0^\infty \mathrm{d}t \frac{\partial \rho_{\boldsymbol{k}}(t)}{\partial t}\mathrm{e}^{-zt} = -\rho_{\boldsymbol{k}}(0) + z\tilde{\rho}_{\boldsymbol{k}}(z)\,. \tag{8.59}$$

Similar Laplace transforms can be written for the other variables.

Let us now Laplace transform Eqs. (8.54)–(8.57). We find

$$z\tilde{\rho}_{\boldsymbol{k}}(z) - \mathrm{i}\rho_0 k \tilde{v}^{\parallel}_{\boldsymbol{k}}(z) = \rho_{\boldsymbol{k}}(0)\,, \tag{8.60}$$

$$\rho_0 z \tilde{v}^{\parallel}_{\boldsymbol{k}}(z) - \mathrm{i}k \left(\frac{\partial P}{\partial \rho}\right)^0_T \tilde{\rho}_{\boldsymbol{k}}(z) - \mathrm{i}k \left(\frac{\partial P}{\partial T}\right)^0_\rho \tilde{T}_{\boldsymbol{k}}(z) + \left(\zeta + \frac{4}{3}\eta\right) k^2 \tilde{v}^{\parallel}_{\boldsymbol{k}}(z)$$
$$= \rho_0 v^{\parallel}_{\boldsymbol{k}}(0)\,, \tag{8.61}$$

$$\rho_0 z \left(\frac{\partial s}{\partial \rho}\right)^0_T \tilde{\rho}_{\boldsymbol{k}}(z) + \rho_0 z \left(\frac{\partial s}{\partial T}\right)^0_\rho \tilde{T}_{\boldsymbol{k}}(z) + \frac{K}{T_0} k^2 \tilde{T}_{\boldsymbol{k}}(z)$$
$$= \rho_0 \left(\frac{\partial s}{\partial \rho}\right)^0_T \rho_{\boldsymbol{k}}(0) + \rho_0 \left(\frac{\partial s}{\partial T}\right)^0_\rho T_{\boldsymbol{k}}(0)\,, \tag{8.62}$$

and

$$\rho_0 z \tilde{\boldsymbol{v}}^{\perp}_{\boldsymbol{k}}(z) + \eta k^2 \tilde{\boldsymbol{v}}^{\perp}_{\boldsymbol{k}}(z) = \rho_0 \boldsymbol{v}^{\perp}_{\boldsymbol{k}}(0)\,. \tag{8.63}$$

We can simplify these equations as follows. First note that $(\partial P/\partial \rho)^0_s = (\partial P/\partial \rho)^0_T + (\partial P/\partial T)^0_\rho (\partial T/\partial \rho)^0_s$, where $c_0 = \sqrt{(\partial P/\partial \rho)^0_s}$ is the speed of sound. Also note the thermodynamic identities

$$\left(\frac{\partial P}{\partial \rho}\right)^0_T = \frac{c_0^2}{\gamma} \quad \text{and} \quad \left(\frac{\partial P}{\partial T}\right)^0_\rho = \frac{\rho_0 c_0^2 \alpha_P}{\gamma} = \frac{\rho_0}{T_0}\frac{c_P - c_\rho}{\alpha_P}\,, \tag{8.64}$$

where $c_\rho = T_0(\partial s/\partial T)^0_\rho$ and $c_P = T_0(\partial s/\partial T)^0_{\mathrm{P}}$ are the specific heats at constant density and pressure, respectively, $\alpha_P = -1/\rho_0(\partial \rho/\partial T)^0_P$ is the thermal expansivity, and $\gamma = c_P/c_\rho$. Note the Maxwell relation, $(\partial s/\partial \rho)^0_T = -1/\rho_0^2(\partial P/\partial T)^0_\rho$. Also, let us introduce the *longitudinal kinetic viscosity*, ν_1, the *transverse kinetic viscosity*, ν_τ, and the *thermal diffusivity*, χ, which are defined

$$\nu_1 = \frac{1}{\rho_0}\left(\zeta + \frac{4}{3}\eta\right), \quad \nu_\tau = \frac{\eta}{\rho_0}\,, \quad \text{and} \quad \chi = \frac{K}{\rho_0 c_P}\,, \tag{8.65}$$

respectively. Then Eqs. (8.60)–(8.63) take the form

$$z\tilde{\rho}_k(z) - \mathrm{i}\rho_0 k \tilde{v}^{\parallel}_{\boldsymbol{k}}(z) = \rho_k(0)\,, \tag{8.66}$$

$$\left(z + \nu_1 k^2\right) \tilde{v}^{\parallel}_{\boldsymbol{k}}(z) - \mathrm{i}k\frac{c_0^2}{\gamma\rho_0}\tilde{\rho}_{\boldsymbol{k}}(z) - \mathrm{i}k\frac{c_0^2\alpha_P}{\gamma}\tilde{T}_{\boldsymbol{k}}(z) = v^{\parallel}_{\boldsymbol{k}}(0)\,, \tag{8.67}$$

$$-z\frac{c_0^2\alpha_P}{\rho_0\gamma}\tilde{\rho}_{\boldsymbol{k}}(z) + \frac{c_\rho}{T_0}(z + \gamma\chi k^2)\tilde{T}_{\boldsymbol{k}}(z) = -\frac{c_0^2\alpha_P}{\rho_0\gamma}\rho_{\boldsymbol{k}}(0) + \frac{c_\rho}{T_0}T_{\boldsymbol{k}}(0)\,, \tag{8.68}$$

and

$$(z + \nu_\tau k^2)\tilde{\boldsymbol{v}}^{\perp}_{\boldsymbol{k}}(z) = \boldsymbol{v}^{\perp}_{\boldsymbol{k}}(0)\,. \tag{8.69}$$

Solving the linearized hydrodynamic equations is now simply a matter of doing some algebra. Since the transverse modes completely decouple from the longitudinal modes, we will consider them separately below.

Exercise 8.4

A rough infinitely long cylinder of radius a lies along the z-axis and is immersed in an incompressible fluid. The cylinder rotates with a constant angular velocity ω. The fluid sticks to the outer surface of the cylinder and, at the surface, moves with the same velocity as the surface of the cylinder. (a) Find the velocity $\boldsymbol{v}(r, \phi, z)$ of the fluid, assuming that $\boldsymbol{v} \to 0$ as $r \to \infty$. (b) Replace the cylinder by a singular region such that the fluid velocity abruptly goes to zero for $r < a$ and compute the *vorticity* $\boldsymbol{\nabla} \times \boldsymbol{v}$ of the fluid when this singular region is present.

Answer: (a) If we take the curl of the Navier–Stokes equations, we find $\nabla^2 \boldsymbol{\nabla} \times \boldsymbol{v} = 0$. Since the cylinder is infinitely long, symmetry considerations restrict the fluid velocity to the form $\boldsymbol{v} = v_\phi(r)\hat{\boldsymbol{e}}_\phi$. Then $\nabla^2 \boldsymbol{\nabla} \times \boldsymbol{v} = \mathrm{d}^2/\mathrm{d}r^2(1/r\mathrm{d}(rv_\phi)/\mathrm{d}r) = 0$. If we require that the fluid velocity be zero at $r = \infty$, then this has the solution $v_\phi(r) = C/r$, where C is a constant. Next require that the fluid velocity and the surface of the cylinder have the same velocity, namely $v_\phi(a) = C/a = \omega a$. This gives $C = \omega a^2$ and $v_\phi(r) = \omega a^2/r$. (b) We can write the fluid velocity for the case where the fluid velocity abruptly goes to zero for $r < a$. Then, we have $\boldsymbol{v} = (\omega a^2/r)\theta(r - a)\hat{\boldsymbol{e}}_\phi$, where $\theta(r - a)$ is a Heaviside function. The vorticity of the fluid for this case is $\boldsymbol{\nabla} \times \boldsymbol{v} = \omega a \delta(r - a)\hat{\boldsymbol{e}}_z$. The singularity in the fluid flow at $r = a$ gives rise to a non zero vorticity. The singular region extends along the entire z-axis and is called a *vortex line*. This example *roughly* models the behavior of a tornado or hurricane.

8.3.2
Transverse Hydrodynamic Modes

Let us assume that the Fourier components of the transverse velocity at time $t = 0$ are known to be $\boldsymbol{v}_{\boldsymbol{k}}^{\perp}(0)$. Then from Eq. (8.69) we have

$$\tilde{\boldsymbol{v}}_{\boldsymbol{k}}^{\perp}(z) = \frac{\boldsymbol{v}_{\boldsymbol{k}}^{\perp}(0)}{z + v_\tau k^2} . \tag{8.70}$$

The Fourier components of the transverse velocity at time t are

$$\boldsymbol{v}_{\boldsymbol{k}}^{\perp}(t) = \frac{1}{2\pi \mathrm{i}} \int_{\delta - \mathrm{i}\infty}^{\delta + \mathrm{i}\infty} \mathrm{d}z \frac{\boldsymbol{v}_{\boldsymbol{k}}^{\perp}(0)\mathrm{e}^{zt}}{z + v_\tau k^2} = \boldsymbol{v}_{\boldsymbol{k}}^{\perp}(0)\mathrm{e}^{-v_\tau k^2 t} . \tag{8.71}$$

In order to obtain the final result in Eq. (8.71), we have changed the integration along the line $z = \delta + \mathrm{i}y$ (with y varying from $-\infty$ to $+\infty$) to a contour integration with the contour shown in Figure 8.2. We see that any transverse velocity variations in the fluid decay in time and cannot propagate. The short-wavelength disturbances decay faster than the long-wavelength disturbances. This wavelength dependence of the decay time is the signature of a hydrodynamic mode.

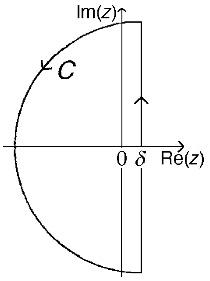

Figure 8.2 The contour, C, used to integrate (8.71).

8.3.3
Longitudinal Hydrodynamic Modes

The time evolution of the longitudinal modes can be determined from Eqs. (8.66)–(8.68). Let us first write them in the following matrix from:

$$\begin{pmatrix} z & -\mathrm{i}\rho_0 k & 0 \\ -\frac{\mathrm{i}kc_0^2}{\gamma\rho_0} & [z+\nu_1 k^2] & -\frac{\mathrm{i}kc_0^2\alpha_P}{\gamma} \\ -z\frac{c_0^2\alpha_P}{\rho_0\gamma} & 0 & \frac{c_\rho}{T_0}[z+\gamma\chi k^2] \end{pmatrix} \begin{pmatrix} \tilde{\rho}_{\boldsymbol{k}}(z) \\ \tilde{v}^{\parallel}_{\boldsymbol{k}}(z) \\ \tilde{T}_{\boldsymbol{k}}(z) \end{pmatrix}$$

$$= \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ -\frac{c_0^2\alpha_P}{\rho_0\gamma} & 0 & \frac{c_\rho}{T_0} \end{pmatrix} \begin{pmatrix} \Delta\rho_{\boldsymbol{k}}(0) \\ v^{\parallel}_{\boldsymbol{k}}(0) \\ \Delta T_{\boldsymbol{k}}(0) \end{pmatrix} . \tag{8.72}$$

If we multiply by the inverse of the matrix on the left in Eq. (8.72), we obtain

$$\begin{pmatrix} \tilde{\rho}_{\boldsymbol{k}}(z) \\ \tilde{v}^{\parallel}_{\boldsymbol{k}}(z) \\ \tilde{T}_{\boldsymbol{k}}(z) \end{pmatrix} = \frac{\overline{M}}{D(\boldsymbol{k},z)} \begin{pmatrix} \Delta\rho_{\boldsymbol{k}}(0) \\ v_{\boldsymbol{k}}(0) \\ -\frac{c_0^2\alpha_P}{\rho_0\gamma}\Delta\rho_{\boldsymbol{k}}(0) + \frac{c_\rho}{T_0}\Delta T_{\boldsymbol{k}}(0) \end{pmatrix} , \tag{8.73}$$

where $D(\boldsymbol{k},z)$ is the determinant of the 3×3 matrix on the left in Eq. (8.72), and $\overline{M}/D(\boldsymbol{k},z)$ is its inverse. The determinant $D(\boldsymbol{k},z)$, can be written

$$D(\boldsymbol{k},z) = \frac{c_\rho}{T_0}\left[z^3 + z^2\left(\nu_1+\gamma\chi\right)k^2 + z\left(\gamma\chi\nu_1 k^4 + c_0^2 k^2\right) + c_0^2\chi k^4\right] . \tag{8.74}$$

The matrix, $\overline{M}$, which appears in Eq. (8.73) can be written

$$\overline{M} = \begin{pmatrix} \frac{c_\rho}{T_0}(z+\nu_1 k^2)(z+\gamma\chi k^2) & \frac{\mathrm{i}k\rho_0 c_\rho}{T_0}(z+\gamma\chi k^2) & -\frac{\rho_0\alpha_P c_0^2 k^2}{\gamma} \\ \frac{\mathrm{i}kc_\rho c_0^2}{\rho_0 T_0}(z+\chi k^2) & \frac{c_\rho}{T_0}z(z+\gamma\chi k^2) & \mathrm{i}kz\frac{\alpha_P c_0^2}{\gamma} \\ \frac{c_0^2\alpha_P}{\rho_0\gamma}z(z+\nu_1 k^2) & \mathrm{i}kz\frac{c_0^2\alpha_P}{\gamma} & z^2+z\nu_1 k^2 + k^2\frac{c_0^2}{\gamma} \end{pmatrix} . \tag{8.75}$$

Before we use Eqs. (8.73) and (8.75) to solve the equations of motion, it is useful to look more closely at the determinant, Eq. (8.74).

To second order in k, the three roots of the equation $D(\boldsymbol{k}, z) = 0$, are given by $z_1 = -\chi k^2$ and $z_\pm = \pm \mathrm{i} c_0 k - 1/2k^2[\nu_l + \chi(\gamma - 1)]$. Therefore, for long-wave-length disturbances (small k), $D(\boldsymbol{k}, z)$ is approximately given by

$$D(\boldsymbol{k}, z) \approx \frac{c_\rho}{T_0}(z + \chi k^2)(z + \mathrm{i} k c_0 + \Gamma k^2)(z - \mathrm{i} k c_0 + \Gamma k^2) , \tag{8.76}$$

where $\Gamma = 1/2[\nu_l + \chi(\gamma - 1)]$ and we have neglected terms of higher order in k.

The dissipative fluid has three longitudinal normal modes. The time evolution of the density, longitudinal velocity, and temperature variations each contain contributions from all three longitudinal normal modes. One of the longitudinal normal modes is primarily a heat mode and has a decay rate given by z_1. The other two longitudinal normal modes are primarily damped sound modes. The sound modes can propagate but eventually will be damped out by dissipative processes in the fluid, both viscous and thermal.

The time evolution of the density, longitudinal velocity, and temperature variations can be obtained by performing the following integration:

$$\begin{pmatrix} \rho_{\boldsymbol{k}}(t) \\ v^{\parallel}_{\boldsymbol{k}}(t) \\ T_{\boldsymbol{k}}(t) \end{pmatrix} = \frac{1}{2\pi \mathrm{i}} \int\limits_{\delta - \mathrm{i}\infty}^{\delta + \mathrm{i}\infty} \mathrm{d}z \mathrm{e}^{zt} \begin{pmatrix} \rho_{\boldsymbol{k}}(z) \\ v^{\parallel}_{\boldsymbol{k}}(z) \\ T_{\boldsymbol{k}}(z) \end{pmatrix} . \tag{8.77}$$

In Exercise 8.5, we obtain the time dependence of Fourier components of the density under special conditions.

Exercise 8.5

Compute $\rho_{\boldsymbol{k}}(t)$ assuming that at time $t = 0$ we have $\rho_{\boldsymbol{k}}(0) \neq 0$, $v^{\parallel}_{\boldsymbol{k}}(0) = 0$, and $T_{\boldsymbol{k}}(0) = 0$. Write the amplitude of the evolution to lowest order in k.

Answer: From Section 8.3.3 we can write

$$\tilde{\rho}_{\boldsymbol{k}}(z) = \left(\frac{[z + \nu_l k^2][z + \gamma\chi k^2] + c_0^2 k^2(\gamma - 1)/\gamma}{[z + \chi k^2][z + \mathrm{i} c_0 k + \Gamma k^2][z - \mathrm{i} c_0 k + \Gamma k^2]} \right) \rho_{\boldsymbol{k}}(0) .$$

The density at time t is

$$\rho_{\boldsymbol{k}}(t) = \frac{1}{2\pi \mathrm{i}} \int\limits_{\delta - \mathrm{i}\infty}^{\delta + \mathrm{i}\infty} \mathrm{d}z \tilde{\rho}_{\boldsymbol{k}}(z) \mathrm{e}^{zt} .$$

If, after the integration, we retain terms in the coefficients of time-dependent terms to zeroth order in k, $\rho_{\boldsymbol{k}}(t)$ reduces to

$$\rho_{\boldsymbol{k}}(t) \approx \left[\left(1 - \frac{1}{\gamma} \right) \mathrm{e}^{-\chi k^2 t} + \frac{1}{\gamma} \mathrm{e}^{-\Gamma k^2 t} \cos(c_0 k t) \right] \rho_{\boldsymbol{k}}(0) .$$

Thus, the initial disturbance in the density is eventually damped out. The long-wavelength components are the last to go.

8.3.4
Dynamic Correlation Function and Spectral Density

The dynamic density correlation function for a fluid in a box of volume V may be written

$$C_{nn}(\boldsymbol{\rho}, \tau) = \frac{1}{N} \int \mathrm{d}\boldsymbol{r} \langle n(\boldsymbol{r} + \boldsymbol{\rho}, \tau) n(\boldsymbol{r}, 0) \rangle_T \,, \tag{8.78}$$

where N is the total number of particles. The spectral density (also called the dynamic structure factor) is given by

$$S_{nn}(\boldsymbol{k}, \Omega) = \int \mathrm{d}\boldsymbol{\rho} \int\limits_{-\infty}^{\infty} \mathrm{d}\tau C_{nn}(\boldsymbol{\rho}, \tau) \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{\rho}} \mathrm{e}^{-\mathrm{i}\Omega_\tau} \,. \tag{8.79}$$

For a fluid of point particles in equilibrium, the average, $\langle \rangle_T$, is taken over the equilibrium distribution. We can compute both the dynamic correlation function and the spectral density for a fluid of point particles in equilibrium.

Let us first write the density variations as $n(\boldsymbol{r}, t) = n_0 + \Delta n(\boldsymbol{r}, t)$, where $n_0 = \langle n(\boldsymbol{r}, t) \rangle_T = N/V$, is the equilibrium density and $\Delta n(\boldsymbol{r}, t)$ describes fluctuations about equilibrium such that $\langle \Delta n(\boldsymbol{r}, t) \rangle_T = 0$. If we substitute $n(\boldsymbol{r}, t) = n_0 + \Delta n(\boldsymbol{r}, t)$ into the expression for the correlation function, we obtain

$$\begin{aligned} C_{nn}(\boldsymbol{\rho}, \tau) &= \frac{1}{N} \int \mathrm{d}\boldsymbol{r} \langle n(\boldsymbol{r} + \boldsymbol{\rho}, t) n(\boldsymbol{r}, 0) \rangle_T \,, \\ &= n_0 + \frac{1}{N} \int \mathrm{d}\boldsymbol{r} \langle \Delta n(\boldsymbol{r} + \boldsymbol{\rho}, t) \Delta n(\boldsymbol{r}, 0) \rangle_T \,. \end{aligned} \tag{8.80}$$

Let us introduce the Fourier series expansion of the density

$$\Delta n(\boldsymbol{r}, t) = \frac{1}{V} \sum_{\boldsymbol{k}} \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}} n_{\boldsymbol{k}}(t) \quad \text{with} \quad n_{\boldsymbol{k}}(t) = \int \mathrm{d}\boldsymbol{r} \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}} \Delta n(\boldsymbol{r}, t) \,, \tag{8.81}$$

and of the correlation function

$$C_{nn}(\boldsymbol{k}, \tau) = \int \mathrm{d}\boldsymbol{\rho} \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{\rho}} C_{nn}(\boldsymbol{\rho}, \tau) = N\delta_{\boldsymbol{k},0} + \frac{1}{N} \langle n_{\boldsymbol{k}}(t) n_{-\boldsymbol{k}}(0) \rangle_T \,. \tag{8.82}$$

To obtain the last term in Eq. (8.82), we have substituted the Fourier expansion of the density, Eq. (8.81), into Eq. (8.80) and have used the identity $(1/V) \int \mathrm{d}\boldsymbol{r} \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}} = \delta_{\boldsymbol{k},0}$, where $\delta_{\boldsymbol{k},0}$ is the Kronecker delta function. From equilibrium fluctuation theory in Section 3.7.4, we know that temperature and density fluctuations are statistically independent. Therefore, $\langle \Delta n_{\boldsymbol{k}}(0) \Delta T_{-\boldsymbol{k}}(0) \rangle_T = 0$. Also, we will assume that velocity fluctuations are statistically independent of density fluctuations. Therefore, any contributions to the density at time t, due to fluctuations in velocity or temperature at time $t = 0$, will disappear when the average, $\langle \rangle_T$, is taken. As a result, we can use the solution for the density, $\rho_{\boldsymbol{k}}(t) \equiv m n_{\boldsymbol{k}}(t)$, obtained in Exercise 8.5 to determine the time evolution of the density correlation function. We can write

$$C_{nn}(\boldsymbol{k},t) = N\delta_{\boldsymbol{k},0} + \frac{1}{m^2N}\langle n_{\boldsymbol{k}}(0)n_{-\boldsymbol{k}}(0)\rangle_T \times \left[\left(1-\frac{1}{\gamma}\right)\mathrm{e}^{-\chi^{k^2}|t|} + \frac{1}{\gamma}\mathrm{e}^{-\Gamma k^2|t|}\cos(c_0kt)\right] . \tag{8.83}$$

The absolute value of the time appears in Eq. (8.83) because it is the correlation function for a stationary process. We must remember that Eq. (8.83) is an approximate expression for the density correlation function. Some terms proportional to the wavevector have been neglected. We shall leave it as a homework problem to determine the size of these neglected terms.

Let us now consider the spectral density function. If we substitute Eq. (8.80) into Eq. (8.79) and make use of Eqs. (8.82) and (8.83), we find

$$S_{nn}(\boldsymbol{k},\Omega) = 2\pi N\delta(\Omega)\delta_{\boldsymbol{k},0} + \frac{1}{m^2N}\langle n_{\boldsymbol{k}}(0)n_{-\boldsymbol{k}}(0)\rangle\left[\left(1-\frac{1}{\gamma}\right)\frac{2\chi k^2}{\Omega^2+\chi^2k^4} + \frac{1}{\gamma}\left(\frac{\Gamma k^2}{(\Omega-c_0k)^2+\Gamma^2k^4} + \frac{\Gamma k^2}{(\Omega+c_0k)^2+\Gamma^2k^4}\right)\right] , \tag{8.84}$$

where we have used the fact that $1/2\pi\int_{-\infty}^{\infty}\mathrm{d}t\mathrm{e}^{\mathrm{i}\Omega t} = \delta(\Omega)$. Away from the critical point, the correlation function, $\langle n_{\boldsymbol{k}}(0)n_{-\boldsymbol{k}}(0)\rangle$, is independent of $\boldsymbol{k}$ and proportional to the compressibility. Near the critical point it behaves like $(C+k^2)^{-1}$, where $C \sim (T-T_{\mathrm{c}})$ (cf. Eq. (5.112)).

The spectral density for an isotropic fluid has three terms of the form

$$f(\Omega) = \frac{2\Delta}{\Delta^2 + (\Omega-\Omega')^2} , \tag{8.85}$$

where $f(\Omega)$ is a Lorentzian centered at frequency, Ω', with half-width at one-half maximum given by Δ. Therefore, the spectral density, as a function of frequency, has three peaks. One is centered at $\Omega = 0$ with width χk^2 and is due to the thermal hydrodynamic mode. This is called the *Rayleigh peak*. The other two are centered at $\Omega = \pm c_0k$ with width, Γk^2. They are called the *Brillouin peaks*.

8.4
Light Scattering

A light wave incident on a simple fluid induces oscillating dipoles in the particles of the fluid. These oscillating dipoles reemit spherical light waves. If the medium is homogeneous, all scattered light waves cancel except those in the forward direction. However, if density fluctuations exist in the fluid, light will be scattered in directions other than the forward direction [15, 33, 108, 147].

From the late 1800s until 1928, light scattering experiments involved measurement of the *intensity* of scattered light as a function of angle with respect to the incident direction. In 1928, Raman measured the *spectrum* of light inelastically scattered from gases using conventional light sources, and he found frequency shifts in the scattered light due to internal degrees of freedom of the molecules. One of the sharpest conventional light sources is the 6438 Å line of cadmium, but it has a line width of order 6×10^8 Hz which swamps many details of the spectrum of the inelastically scattered light. Also, conventional light sources are very weak so experiments often last 10–12 h. A revolution in the subject occurred in the early 1960s with the development of lasers. The neon–helium laser had a monochromatic light source with a line width of order 1 Hz and a very high power. Light scattering experiments can now measure dynamical events on time scales ranging from 10^{-1} to 10^{-15} s.

Since equilibrium fluctuations in a fluid decay, on the average, according to the laws of hydrodynamics, it is possible to obtain information about transport coefficients by scattering light (or particles) off of equilibrium fluctuations. In 1934, Landau and Placzek [115] showed that it is possible to obtain the time dependence of the density autocorrelation function for a fluid from the hydrodynamic equations. Later, van Hove [204] was able to relate the differential cross section for scattering of neutrons from a fluid to the density autocorrelation function of the fluid, thus establishing another method for probing equilibrium fluctuations. In this section we shall obtain an expression for the intensity of light scattered from a fluid in terms of the hydrodynamic modes.

Density fluctuations are both thermal and mechanical in origin. Thermal density fluctuations result from damped temperature or entropy waves, while mechanical density fluctuations result from sound waves in the fluid. Light which scatters from density fluctuations will be unshifted in frequency, while light which scatters from the sound waves will undergo a frequency shift (Doppler shift).

In general, sound waves in the fluid have a wide range of wavevectors and frequencies. However, for a given scattering angle, θ, only selected sound modes will contribute to the scattering. Light will scatter from the wave-fronts of the sound waves and must satisfy the Bragg condition (cf. Figure 8.3)

$$2\lambda_s \sin\frac{\theta}{2} = \lambda_0 \,, \tag{8.86}$$

where λ_s is the wavelength of the sound and λ_0 is the wavelength of the incident light. The wavevector of the light wave will be shifted by an amount

$$\Delta k = 2k_0 \sin\frac{\theta}{2} \,, \tag{8.87}$$

where $k_0 = 2\pi/\lambda_0$. The frequency of the scattered light will be Doppler-shifted by

$$\Omega = \omega - \omega_0 = \pm v_s \Delta k = \pm\frac{2\omega_0 v_s}{c} \sin\frac{\theta}{2} \,, \tag{8.88}$$

where $\omega_0 = ck_0$, v_s is the speed of sound in the fluid, and c is the speed of light.

In the sections below, we find an expression relating the intensity of scattered light to the correlation function for density fluctuations in the fluid.

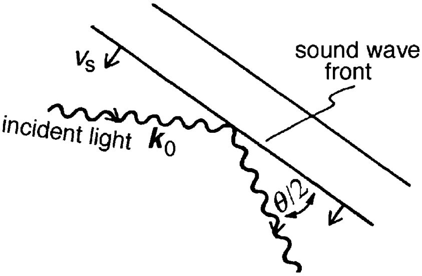

Figure 8.3 Light scattered from a sound wavefront.

8.4.1
Scattered Electric Field

We wish to find an expression for the intensity of light scattered from a simple fluid of identical particles [90, 198]. We shall assume that a monochromatic light wave,

$$\boldsymbol{E}(\boldsymbol{r}, t) = \boldsymbol{E}_0 \mathrm{e}^{\mathrm{i}(\boldsymbol{k}_0 \cdot \boldsymbol{r} - \omega_0 t)} , \tag{8.89}$$

impinges on the fluid, and that the fluid particles have a polarizability α. The induced polarization gives rise to a dipole moment density $\mathcal{P}(\boldsymbol{r}, t)$ such that

$$\mathcal{P}(\boldsymbol{r}, t) = \alpha \boldsymbol{E}(\boldsymbol{r}, t) \sum_{i=1}^{N} \delta(\boldsymbol{r} - \boldsymbol{q}_i(t)) , \tag{8.90}$$

where $\boldsymbol{q}_i(t)$ is the position of the ith particle at time t. In writing Eq. (8.90) we have neglected multiple scattering effects because we are assuming the polarization is induced entirely by the external field.

The easiest way to obtain the amplitude of the scattered light is to introduce the Hertz potential $\boldsymbol{Z}(\boldsymbol{r}, t)$. This is done in the following way. The electric field $\boldsymbol{E}(\boldsymbol{r}, t)$ is defined in terms of the usual scalar potential $\phi(\boldsymbol{r}, t)$ and vector potential $\boldsymbol{A}(\boldsymbol{r}, t)$ as

$$\boldsymbol{E} = -\nabla_r \phi - \frac{\partial \boldsymbol{A}}{\partial t} . \tag{8.91}$$

In the Lorentz gauge, the scalar and vector potentials satisfy the equations

$$\nabla_r^2 \boldsymbol{A} - \varepsilon\mu \frac{\partial^2 \boldsymbol{A}}{\partial t^2} = -\mu \boldsymbol{J} = -\varepsilon\mu \frac{\partial \mathcal{P}}{\partial t} , \tag{8.92}$$

and

$$\nabla_r^2 \phi - \varepsilon\mu \frac{\partial^2 \phi}{\partial t^2} = -\frac{\rho}{\varepsilon} = \nabla_r \cdot \mathcal{P} , \tag{8.93}$$

where μ is the permeability of the medium and ε is the permittivity of the medium, $\boldsymbol{J}$ is the electric current, and ρ is the electric charge density. For the system we are considering, the source of electric current and electric charge is the dipole moment density, $\mathcal{P}(\boldsymbol{r}, t)$. We now introduce the Hertz potential, $\boldsymbol{Z}(\boldsymbol{r}, t)$ [198] by means of the equations

$$\boldsymbol{A} = \varepsilon\mu \frac{\partial \boldsymbol{Z}}{\partial t} \quad \text{and} \quad \phi = -\nabla_r \cdot \boldsymbol{Z} \,. \tag{8.94}$$

Comparing Eqs. (8.92)–(8.94), we find that $\boldsymbol{Z}(\boldsymbol{r}, t)$ satisfies the following equation:

$$\nabla_r^2 \boldsymbol{Z} - \varepsilon\mu \frac{\partial^2 \boldsymbol{Z}}{\partial t^2} = -\mathcal{P} \,. \tag{8.95}$$

Thus, we have an equation of motion for the Hertz potential in which the polarization acts as a source.

Given Eq. (8.95) we can write the Hertz potential for the scattered light wave. The retarded solution to Eq. (8.95) is given by

$$\boldsymbol{Z}(\boldsymbol{r}, t) = \frac{1}{4\pi} \int \mathrm{d}\boldsymbol{r}' \int\limits_{-\infty}^{\infty} \mathrm{d}t' \frac{\mathcal{P}(\boldsymbol{r}', t')}{|\boldsymbol{r}' - \boldsymbol{r}|} \delta\left(t' - t + \frac{|\boldsymbol{r}' - \boldsymbol{r}|}{c}\right) \tag{8.96}$$

(cf. [90]). We next introduce the Fourier expansion of the delta function and obtain

$$\begin{aligned} \boldsymbol{Z}(\boldsymbol{r}, t) = \frac{1}{2}\left(\frac{1}{2\pi}\right)^2 \int \mathrm{d}\boldsymbol{r}' \int\limits_{-\infty}^{\infty} \mathrm{d}t' \int\limits_{-\infty}^{\infty} \mathrm{d}\omega' \frac{\mathcal{P}(\boldsymbol{r}', t')}{|\boldsymbol{r}' - \boldsymbol{r}|} \\ \times \exp\left[\mathrm{i}\omega'\left(t' - t + \frac{|\boldsymbol{r}' - \boldsymbol{r}|}{c}\right)\right] \end{aligned} \tag{8.97}$$

for the outgoing wave. The outgoing electric field is related to $\boldsymbol{Z}(\boldsymbol{r}, t)$ through the expression

$$\boldsymbol{E}'(\boldsymbol{r}, t) = \nabla_r(\nabla_r \cdot \boldsymbol{Z}) - \varepsilon\mu \frac{\partial^2 \boldsymbol{Z}}{\partial t^2} \tag{8.98}$$

(cf. Eqs. (8.91) and (8.94)).

We only need an expression for the scattered light far from the source. If we remember that $\boldsymbol{r}'$ is restricted to the region of the dipoles and $\boldsymbol{r}$ is the coordinate of the observer so $r' \ll r$, we can make the following approximation:

$$|\boldsymbol{r} - \boldsymbol{r}'| \approx r - \hat{\boldsymbol{e}}_r \cdot \boldsymbol{r}'^{\cdot} + \cdots \,, \tag{8.99}$$

where $\hat{\boldsymbol{e}}_r$ is the unit vector $\hat{\boldsymbol{e}}_r = \boldsymbol{r}/|\boldsymbol{r}|$. If we substitute Eqs. (8.90) and (8.99) into Eq. (8.97), we obtain

$$\begin{aligned} \boldsymbol{Z}(\boldsymbol{r}, t) \approx \frac{1}{2}\left(\frac{1}{2\pi}\right)^2 \frac{\alpha \boldsymbol{E}_0}{r} \int \mathrm{d}\boldsymbol{r}' \int\limits_{-\infty}^{\infty} \mathrm{d}t' \int\limits_{-\infty}^{\infty} \mathrm{d}\omega' \mathrm{e}^{\mathrm{i}(\boldsymbol{k}_0 \cdot \boldsymbol{r}' - \omega_0 t')} \sum_{i=1}^{N} \delta(\boldsymbol{r}' - \boldsymbol{q}_i(t')) \\ \times \exp\left[\mathrm{i}\omega'\left(t' - t + \frac{r}{c} - \frac{\boldsymbol{r} \,\hat{\cdot}\, \boldsymbol{r}'}{c}\right)\right] \,. \end{aligned} \tag{8.100}$$

We next substitute Eq. (8.100) into Eq. (8.98) and neglect terms of order r'/r and smaller. We then obtain the following expression for the scattered electric field:

$$\begin{aligned}\boldsymbol{E}'(\boldsymbol{r},t) &= \frac{1}{2}\left(\frac{1}{2\pi}\right)^2 \frac{\alpha}{c^2 r}\left[\boldsymbol{E}_0 - \hat{\boldsymbol{r}}\left(\hat{\boldsymbol{r}}\cdot\boldsymbol{E}_0\right)\right]\int \mathrm{d}\boldsymbol{r}' \int_{-\infty}^{\infty}\mathrm{d}t' \int_{-\infty}^{\infty}\mathrm{d}\omega'\,\omega'^2 \\ &\quad \times \exp\left[\mathrm{i}(\boldsymbol{k}_0\cdot\boldsymbol{r}' - \omega_0 t')\right]\exp\left[\mathrm{i}\omega'\left(t' - t + \frac{r}{c} - \frac{1}{c}\hat{\boldsymbol{r}}\cdot\boldsymbol{r}'\right)\right] n(\boldsymbol{r}',t')\,,\end{aligned} \tag{8.101}$$

where

$$n(\boldsymbol{r}',t') \equiv \sum_{i=1}^{N}\delta(\boldsymbol{r}' - \boldsymbol{q}_i(t')) \tag{8.102}$$

is the microscopic density of particles in the medium and we remember that the speed of light is $c = 1/\sqrt{\varepsilon_0\mu_0}$.

8.4.2
Intensity of Scattered Light

The spectral intensity of scattered light is defined as (cf. Eq. (7.84))

$$I(\boldsymbol{r},\omega) \equiv \lim_{\mathcal{T}\to\infty}\frac{1}{2\mathcal{T}}\sqrt{\frac{\varepsilon_0}{\mu_0}}\boldsymbol{E}'(\boldsymbol{r},\omega;\mathcal{T})\cdot\boldsymbol{E}'^*(\boldsymbol{r},\omega;\mathcal{T})\,, \tag{8.103}$$

where

$$\boldsymbol{E}'(\boldsymbol{r},\omega;\mathcal{T}) = \int_{-\infty}^{\infty}\mathrm{d}t\,\mathrm{e}^{\mathrm{i}\omega t}\boldsymbol{E}'(\boldsymbol{r},t)\theta(\mathcal{T} - |t|) \tag{8.104}$$

and $\theta(\mathcal{T} - |t|)$ is a Heaviside function. Because equilibrium systems are ergodic, we can equate the time average to the equilibrium thermal average. We combine Eqs. (8.103) and (8.104) to obtain

$$\begin{aligned}I(\boldsymbol{r},\omega) &= \lim_{\mathcal{T}\to\infty}\frac{1}{2\mathcal{T}}\sqrt{\frac{\varepsilon_0}{\mu_0}}\int_{-\infty}^{\infty}\mathrm{d}t\int_{-\infty}^{\infty}\mathrm{d}t'\,\mathrm{e}^{\mathrm{i}\omega(t-t')} \\ &\quad \times \boldsymbol{E}'(\boldsymbol{r},t)\cdot\boldsymbol{E}'^*(\boldsymbol{r},t')\theta(\mathcal{T} - |t|)\theta(\mathcal{T} - |t'|) \\ &= \frac{1}{2}\sqrt{\frac{\varepsilon_0}{\mu_0}}\int_{-\infty}^{\infty}\mathrm{d}\tau\,\mathrm{e}^{\mathrm{i}\omega\tau}\lim_{\mathcal{T}\to\infty}\frac{1}{\mathcal{T}}\int_{-\mathcal{T}}^{\mathcal{T}}\mathrm{d}t'\boldsymbol{E}'(\boldsymbol{r},t'+\tau)\cdot\boldsymbol{E}'^*(\boldsymbol{r},t') \\ &= \frac{1}{2}\sqrt{\frac{\varepsilon_0}{\mu_0}}\int_{-\infty}^{\infty}\mathrm{d}\tau\,\mathrm{e}^{\mathrm{i}\omega\tau}\langle\boldsymbol{E}'(\boldsymbol{r},\tau)\cdot\boldsymbol{E}'^*(\boldsymbol{r},0)\rangle_T\,.\end{aligned} \tag{8.105}$$

The thermal average $\langle\rangle_T$ in Eq. (8.105) is taken with respect to a stationary equilibrium ensemble. Now substitute (8.101) into (8.105), to obtain

$$\begin{aligned} I(\boldsymbol{r},\omega) &= \\ &\frac{1}{8}\sqrt{\frac{\varepsilon_0}{\mu_0}}\left(\frac{\alpha}{4\pi^2 c^2 r}\right)^2 E_0^2\sin^2(\phi)\int \mathrm{d}\boldsymbol{r}'\int \mathrm{d}\boldsymbol{r}''\int_{-\infty}^{\infty}\mathrm{d}t'\int_{-\infty}^{\infty}\mathrm{d}t''\int_{-\infty}^{\infty}\mathrm{d}\omega' \\ &\times\int_{-\infty}^{\infty}\mathrm{d}\omega''\int_{-\infty}^{\infty}\mathrm{d}\tau\,\omega'^2\omega''^2\mathrm{e}^{\mathrm{i}\omega\tau}\mathrm{e}^{\mathrm{i}(\boldsymbol{k}_0\cdot\boldsymbol{r}'-\omega_0 t')}\mathrm{e}^{-\mathrm{i}(\boldsymbol{k}_0\cdot\boldsymbol{r}''-\omega_0 t'')} \\ &\times\exp\left[\mathrm{i}\omega'\left(t'-\tau+\frac{r}{c}-\frac{1}{c}\hat{\boldsymbol{r}}\cdot\boldsymbol{r}'\right)\right]\exp\left[-\mathrm{i}\omega''\left(t''+\frac{r}{c}-\frac{1}{c}\hat{\boldsymbol{r}}\cdot\boldsymbol{r}''\right)\right] \\ &\times\langle n(\boldsymbol{r}',t')n(\boldsymbol{r}'',t'')\rangle_T\,, \end{aligned}\tag{8.106}$$

where we have let $\hat{\boldsymbol{r}}\cdot\boldsymbol{E}_0 = E_0\cos\phi$. We next integrate over τ and ω'. This gives

$$\begin{aligned} I(\boldsymbol{r},\omega) &= \\ &\frac{1}{16}\sqrt{\frac{\varepsilon_0}{\mu_0}}\left(\frac{\alpha}{2\pi c^2 r}\right)^2 E_0^2\sin^2(\phi)\int \mathrm{d}\boldsymbol{r}'\int \mathrm{d}\boldsymbol{r}''\int_{-\infty}^{\infty}\mathrm{d}t'\int_{-\infty}^{\infty}\mathrm{d}t''\int_{-\infty}^{\infty}\mathrm{d}\omega''\omega''^2\omega^2 \\ &\times\mathrm{e}^{\mathrm{i}(\boldsymbol{k}_0\cdot\boldsymbol{r}'-\omega_0 t')}\mathrm{e}^{-\mathrm{i}(\boldsymbol{k}_0\cdot\boldsymbol{r}''-\omega_0 t'')}\exp\left[\mathrm{i}\omega\left(t'+\frac{r}{c}-\frac{1}{c}\hat{\boldsymbol{r}}\cdot\boldsymbol{r}'\right)\right] \\ &\times\exp\left[-\mathrm{i}\omega''\left(t''+\frac{r}{c}-\frac{1}{c}\hat{\boldsymbol{r}}\cdot\boldsymbol{r}''\right)\right]\langle n(\boldsymbol{r}',t')n(\boldsymbol{r}'',t'')\rangle_T\,. \end{aligned}\tag{8.107}$$

Let us note that $\langle n(\boldsymbol{r}',t')n(\boldsymbol{r}'',t'')\rangle$ can only depend on the differences $\tau' = t' - t''$ and $\boldsymbol{\rho} = \boldsymbol{r}' - \boldsymbol{r}''$. If we make the change of variables $\tau = t' - t''$ and $\boldsymbol{\rho} = \boldsymbol{r}' - \boldsymbol{r}''$, we find

$$\begin{aligned} I(\boldsymbol{r},\omega) = {}&\frac{1}{8}\sqrt{\frac{\varepsilon_0}{\mu_0}}\left(\frac{\alpha}{2\pi r c^2}\right)^2 E_0^2\sin^2(\phi)\int \mathrm{d}\boldsymbol{\rho}\int \mathrm{d}\boldsymbol{r}''\int_{-\infty}^{\infty}\mathrm{d}\tau\,\omega^4\mathrm{e}^{-\mathrm{i}(\omega_0-\omega)\tau} \\ &\times\exp\left[\mathrm{i}\left(\boldsymbol{k}_0-\mathrm{i}\frac{\omega}{c}\hat{\boldsymbol{r}}\right)\cdot\boldsymbol{\rho}\right]\langle n(\boldsymbol{r}''+\boldsymbol{\rho},\tau)n(\boldsymbol{r}'')\rangle_T\,. \end{aligned}\tag{8.108}$$

We next introduce the dynamic density correlation function

$$C(\boldsymbol{\rho},\tau) \equiv \frac{1}{N}\int \mathrm{d}\boldsymbol{r}'\langle n(\boldsymbol{r}'+\boldsymbol{\rho},\tau)n(\boldsymbol{r}',0)\rangle_T\,,\tag{8.109}$$

where N is the number of particles in the fluid. In terms of these quantities, the intensity may be written

$$\begin{aligned} I(\boldsymbol{r},\omega) &= \frac{1}{4}I_0\omega^4\left(\frac{\alpha}{2\pi c^2 r}\right)^2 N\sin^2(\phi)\int \mathrm{d}\boldsymbol{\rho}\int \mathrm{d}\tau C(\boldsymbol{\rho},\tau) \\ &\quad\times\exp\left[\mathrm{i}\left(\boldsymbol{k}_0-\frac{\omega_0}{c}\hat{\boldsymbol{r}}\right)\cdot\boldsymbol{\rho}\right]\mathrm{e}^{-\mathrm{i}(\omega_0-\omega)\tau} \\ &= \frac{1}{4}I_0\omega^4\left(\frac{\alpha}{2\pi c^2 r}\right)^2 N\sin^2(\phi)S_{nn}(\boldsymbol{k},\Omega)\,, \end{aligned}\tag{8.110}$$

where $S_{nn}(\boldsymbol{k},\Omega)$ is the spectral density function (see Eq. (8.79)), $I_0 = (1/2)\sqrt{\varepsilon_0/\mu_0}\,E_0^2$, $\boldsymbol{k} = \boldsymbol{k}_0 - \omega_0/c\hat{\boldsymbol{r}}$, and $\Omega = \omega_0 - \omega$.

An expression for the spectral density function, $S_{nn}(\boldsymbol{k},\Omega)$, for an isotropic fluid was obtained in Eq. (8.84). If we use that result, we find that the intensity of scattered light for an isotropic fluid can be written

$$\begin{aligned} I(\boldsymbol{r},\omega) = {} & \frac{1}{4} I_0 \omega^4 \left(\frac{\alpha}{2\pi c^2 r}\right)^2 \sin^2(\phi) \Bigg\{ 2\pi N^2 \delta(\Omega)\delta_{k,0} \\ & + \frac{1}{m^2}\langle n_{\boldsymbol{k}}(0) n_{-\boldsymbol{k}}(0)\rangle \left[\frac{\gamma-1}{\gamma}\frac{2\chi k^2}{\Omega^2+\chi^2 k^4} \right. \\ & \left. \left. + \frac{1}{\gamma}\left(\frac{\Gamma k^2}{(\Omega - c_0 k)^2 + \Gamma^2 k^4} + \frac{\Gamma k^2}{(\Omega + c_0 k)^2 + \Gamma^2 k^4} \right) \right] \right\} , \end{aligned} \tag{8.111}$$

where $\gamma = (c_P/c_\rho)$, χ is the thermal diffusivity, $\Gamma = 1/2[\nu_l + \chi(\gamma - 1)]$, and ν_l is the longitudinal kinetic viscosity. In a typical light scattering experiment for a simple liquid, $c_0 \approx 10^5$ cm/s, $k \approx 10^5\ \text{cm}^{-1}$, $\chi k/c_0 \approx 10^{-2}$–$10^{-3}$, and $\nu_t k/c_0 \approx 10^{-2}$–$10^{-3}$.

Thus, we see that the scattered light spectral intensity will have peaks at frequencies $\Omega = \omega_0$ and $\Omega = \omega_0 \pm c_0 k$. The central peak ($\Omega = \omega_0$) is due to scattering from thermal density fluctuations. It is called the *Rayleigh peak*. The two side peaks ($\Omega = \omega_0 \pm c_0 k$) are due to scattering of light from mechanical density fluctuations (sound waves) in the fluid. They are called *Brillouin peaks*.

The ratio of the intensity, I_{th}, of light scattered from thermal density fluctuations to the intensity, I_{mech}, of light scattered from mechanical density fluctuations is given by

$$\frac{I_{\text{th}}}{I_{\text{mech}}} = \gamma - 1 = \frac{c_P - c_\rho}{c_\rho} = \frac{\kappa_T - \kappa_S}{\kappa_S} , \tag{8.112}$$

where κ_T is the isothermal compressibility and κ_S is the adiabatic compressibility. Since $c_P \to \infty$ and $\kappa_T \to \infty$ as we approach the critical point, we expect the Rayleigh peak to become very large compared to the Brillouin peaks.

In Figure 8.4, we show experimental plots for the intensity of light scattered from CO_2 at an angle of 90° with respect to the incident direction. The CO_2 is at a temperature 2.7 °C below the critical temperature. Note that the Rayleigh peak is very wide and high (not all of it is shown) compared to the Brillouin peaks. This is because the system is close to the critical point.

8.5
Friction on a Brownian particle

In Section 7.2, we reviewed the theory of Brownian motion for the case in which a Brownian particle of radius, R, is assumed to move under the influence of the Stokes friction, $6\pi\eta R$, and a random white noise. In this section, we derive the Stokes friction using the linearized hydrodynamic equations (8.42) and (8.43). For simplicity, we will consider an *incompressible fluid* so that $\nabla_r \cdot \boldsymbol{v}_\omega = 0$. If we Fourier

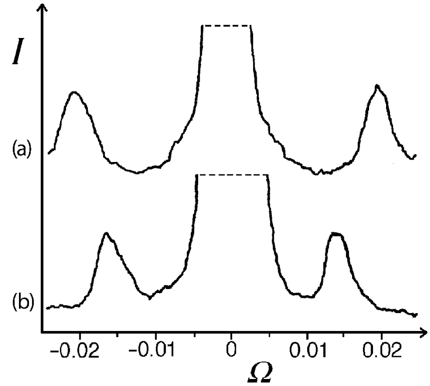

Figure 8.4 Intensity of light scattered from CO_2 at an angle of 90° from the incident direction, shown as a function of frequency shift, Ω. The CO_2 is 2.7 °C below the critical point. (a) Light scattered from CO_2 liquid. (b) Light scattered from CO_2 vapor. Reprinted, by permission, from [33].

transform the time dependence of the hydrodynamic equations, the equation for the Fourier component of the velocity flow reduces to

$$-\mathrm{i}\omega\rho_0 \boldsymbol{v}_\omega(\boldsymbol{r}) = -\nabla_{\boldsymbol{r}} P_\omega(\boldsymbol{r}) - \eta \nabla_{\boldsymbol{r}} \times (\nabla_{\boldsymbol{r}} \times \boldsymbol{v}_\omega(\boldsymbol{r})) \tag{8.113}$$

where we have used the vector identity, $\nabla_{\boldsymbol{r}}^2 \boldsymbol{v} = \nabla_{\boldsymbol{r}}(\nabla_{\boldsymbol{r}} \cdot \boldsymbol{v}) - \nabla_{\boldsymbol{r}} \times (\nabla_{\boldsymbol{r}} \times \boldsymbol{v})$ (see Appendix F).

Let us now assume that a spherical Brownian particle of radius, R, moves through the fluid along the z-direction with velocity, $\boldsymbol{u}_\omega = u_\omega \hat{\boldsymbol{e}}_z$, where the unit vector $\hat{\boldsymbol{e}}_z = \cos(\theta)\hat{\boldsymbol{e}}_r - \sin(\theta)\hat{\boldsymbol{e}}_\theta$. We also assume that the surface of the Brownian particle is very rough so the fluid sticks to its surface. At the surface of the Brownian particle, the velocity of the fluid equals the velocity of the surface. In the rest frame of the particle, the fluid velocity, $\boldsymbol{v}_\omega^{rf}(R)$, at the particle surface is $\boldsymbol{v}_\omega^{rf}(R) = \boldsymbol{v}_\omega(R) - \boldsymbol{u}_\omega = 0$ so $\boldsymbol{v}_\omega(R) = \boldsymbol{u}_\omega$. This gives the additional boundary condition $\boldsymbol{v}_\omega(\boldsymbol{r}) \to 0$ as $r \to \infty$.

In order to determine the force exerted on the Brownian particle by the fluid, we first find the velocity distribution of the fluid in the presence of the moving Brownian particle. Once the velocity distribution is known, the force on the Brownian particle is given by

$$\boldsymbol{F} = \oint \mathrm{d}\boldsymbol{S} \cdot \bar{\boldsymbol{P}} = \oint \mathrm{d}S\hat{\boldsymbol{r}} \cdot \bar{\boldsymbol{P}}\,, \tag{8.114}$$

where $\bar{\boldsymbol{P}}$ is the pressure tensor (cf. Section 8.2.1.2) and $\mathrm{d}\boldsymbol{S}$ is a surface area element directed normal to the surface of the Brownian particle.

We can use some vector identities (see Appendix F) to help solve Eq. (8.113). The velocity, $\boldsymbol{v}_\omega$, is a polar vector and can be written in the form $\boldsymbol{v}_\omega = \nabla_{\boldsymbol{r}} \times \boldsymbol{A}_\omega$, where $\boldsymbol{A}_\omega$ is an axial vector. There are two vectors in the problem from which we can build the vector $\boldsymbol{A}_\omega$. They are the radial vector, $\boldsymbol{r}$, and the velocity, $\boldsymbol{u}_\omega$. Let us write $\boldsymbol{A}_\omega = (\nabla_{\boldsymbol{r}} g(r)) \times \boldsymbol{u}_\omega = \nabla_{\boldsymbol{r}} \times (g(r)\boldsymbol{u}_\omega)$, where $g(r)$ is a function of the distance, r, from the center of the Brownian particle. The fluid velocity can then be written

$$\boldsymbol{v}_\omega = \nabla_{\boldsymbol{r}} \times \nabla_{\boldsymbol{r}} \times (g(r)\boldsymbol{u}_\omega) \quad \text{and} \quad \nabla_{\boldsymbol{r}} \times \boldsymbol{v}_\omega(\boldsymbol{r}) = -\nabla_{\boldsymbol{r}}^2(\nabla_{\boldsymbol{r}} \times g(r)\boldsymbol{u}_\omega)\,. \tag{8.115}$$

The boundary conditions on the fluid velocity require that $g(r) \to 0$ as $r \to \infty$.

We now take the curl of Eq. (8.113) and obtain

$$-\mathrm{i}\omega\rho_0 \nabla_{\boldsymbol{r}} \times \boldsymbol{v}_\omega = -\eta \nabla_{\boldsymbol{r}} \times \nabla_{\boldsymbol{r}} \times (\nabla_{\boldsymbol{r}} \times \boldsymbol{v}_\omega) = \eta \nabla_{\boldsymbol{r}}^2(\nabla_{\boldsymbol{r}} \times \boldsymbol{v}_\omega)\,. \tag{8.116}$$

If we use the expression for $\boldsymbol{v}_\omega(\boldsymbol{r})$ in Eq. (8.115), and the vector identities in Appendix F, Eq. (8.116) reduces to

$$(k^2 \nabla_{\boldsymbol{r}}^2 \nabla_{\boldsymbol{r}} g(r) + \nabla_{\boldsymbol{r}}^4 \nabla_{\boldsymbol{r}} g(r)) \times \boldsymbol{u}_\omega = 0\,, \tag{8.117}$$

where $k^2 = \mathrm{i}\omega\rho_0/\eta$ and $k = \sqrt{\omega\rho_0}2\eta(1+\mathrm{i})$. Thus, we must solve the equation,

$$\nabla_{\boldsymbol{r}}(\nabla_{\boldsymbol{r}}^4 g(r) + k^2 \nabla_{\boldsymbol{r}}^2 g(r)) = 0\,, \tag{8.118}$$

subject to the boundary conditions of the problem. If we integrate Eq. (8.118) once, we obtain

$$\nabla_{\boldsymbol{r}}^4 g(r) + k^2 \nabla_{\boldsymbol{r}}^2 g(r) = C\,, \tag{8.119}$$

where C is an integration constant. Because of the boundary conditions on the fluid, the solution to Eq. (8.119) will be such that $\nabla_{\boldsymbol{r}}^2 g(r)$ and all derivatives of $\nabla_{\boldsymbol{r}}^2 g(r)$ go to zero at $r = \infty$. This also means that $C = 0$.

The boundary conditions at $r = \infty$ are satisfied by the solution

$$\nabla_{\boldsymbol{r}}^2 g(r) = \frac{1}{r^2}\frac{\partial}{\partial r} r^2 \frac{\partial g}{\partial r} = \frac{c_1}{r}\mathrm{e}^{\mathrm{i}kr}\,, \tag{8.120}$$

where c_1 is a constant. Let us now integrate Eq. (8.120) once to find

$$\frac{\partial g}{\partial r} = \frac{1}{r^2}\left[c_1 \mathrm{e}^{\mathrm{i}kr}\left(\frac{r}{\mathrm{i}k} + \frac{1}{k^2}\right) + c_2\right]\,. \tag{8.121}$$

From Eq. (8.115), the fluid velocity can be written

$$\boldsymbol{v}_\omega(\boldsymbol{r}) = -\hat{\boldsymbol{r}}\frac{2u_\omega \cos(\theta)}{r}\frac{\partial g}{\partial r} + \hat{\theta}\frac{u_\omega \sin(\theta)}{r}\left(\frac{\partial g}{\partial r} + r\frac{\partial^2 g}{\partial r^2}\right)\,. \tag{8.122}$$

The constants, c_1 and c_2 in Eq. (8.121) can be found from the "stick" boundary condition at the surface of the Brownian particle, $\boldsymbol{v}_\omega(R, \theta) = \boldsymbol{u}_\omega$. This boundary condition, together with Eqs. (8.121) and (8.122), yields

$$c_1 = -\frac{3R}{2}\mathrm{e}^{-\mathrm{i}kR} \quad \text{and} \quad c_2 = \frac{R^3}{2}\left(-1 + -\frac{3}{\mathrm{i}kR} + \frac{3}{k^2R^2}\right)\,. \tag{8.123}$$

To find the drag force on the Brownian particle, we must perform the integration in Eq. (8.114). The first step is to write the pressure tensor. The hydrostatic pressure $P_\omega(\boldsymbol{r})$ can be found from Eq. (8.113). The gradient of the hydrostatic pressure is

$$\nabla_{\boldsymbol{r}} P_\omega(\boldsymbol{r}) = \mathrm{i}\omega\rho_0 \boldsymbol{v}_\omega(\boldsymbol{r}) - \eta\nabla_{\boldsymbol{r}} \times (\nabla_{\boldsymbol{r}} \times \boldsymbol{v}_\omega(\boldsymbol{r})) \,. \tag{8.124}$$

If we use the results from Eqs. (8.121)–(8.123) (with $\mathrm{i}\omega\rho_0 = \eta k^2$), to find an explicit expression for $\nabla_{\boldsymbol{r}} P_\omega(\boldsymbol{r})$, we can then integrate that expression to obtain

$$P = \eta u_\omega \cos(\theta) \left(\frac{3R}{2r^2} - \frac{3\mathrm{i}kR^2}{2r^2} - \frac{k^2R^3}{2r^2} \right) \,. \tag{8.125}$$

From Eq. (8.114), the drag force on the Brownian particle is given by

$$\boldsymbol{F} = R^2 \int_0^\pi \sin(\theta)\,\mathrm{d}\theta \int_0^{2\pi} \mathrm{d}\phi \left(P_{rr}\hat{\boldsymbol{e}}_r + P_{r\theta}\hat{\boldsymbol{e}}_\theta + P_{r\phi}\hat{\boldsymbol{e}}_\phi \right) \,. \tag{8.126}$$

For the spherical Brownian particle $P_{r\phi} = 0$ and the components, P_{rr} and $P_{r\theta}$, of the pressure tensor are given by

$$P_{rr} = P - 2\eta \frac{\partial v_r}{\partial r} \quad \text{and} \quad P_{r\theta} = -\eta \left(\frac{1}{r}\frac{\partial v_r}{\partial \theta} + \frac{\partial v_\theta}{\partial r} - \frac{v_\theta}{r} \right) \,. \tag{8.127}$$

On the surface of the Brownian particle, $(\partial v_r/\partial r)_{r=R} = 0$, so

$$P_{rr} = \eta u_\omega \cos(\theta) \left(\frac{3}{2R} - \frac{3\mathrm{i}k}{2} - \frac{k^2R}{2} \right) \quad \text{and}$$
$$P_{r\theta} = -\eta u_\omega \sin(\theta) \left(\frac{3}{2R} - \frac{3\mathrm{i}k}{2} \right) \tag{8.128}$$

on the surface.

We can now substitute these results into Eq. (8.126) and integrate. However, before we do the integration we must expand the unit vectors, $\hat{\boldsymbol{e}}_r$ and $\hat{\boldsymbol{e}}_\theta$ in terms of Cartesian unit vectors. The directions of $\hat{\boldsymbol{e}}_r$ and $\hat{\boldsymbol{e}}_\theta$ vary over the surface while the Cartesian unit vectors do not. Note that $\hat{\boldsymbol{e}}_r = \sin(\theta)\cos(\phi)\hat{\boldsymbol{e}}_x + \sin(\theta)\sin(\phi)\hat{\boldsymbol{e}}_y + \cos(\theta)\hat{\boldsymbol{e}}_z$ and $\hat{\boldsymbol{e}}_\theta = \cos(\theta)\cos(\phi)\hat{\boldsymbol{e}}_x + \cos(\theta)\sin(\phi)\hat{\boldsymbol{e}}_y - \sin(\theta)\hat{\boldsymbol{e}}_z$. If we perform the integration in Eq. (8.126), we obtain

$$\boldsymbol{F} = 6\pi\eta u_\omega \hat{\boldsymbol{e}}_z \left(1 - \mathrm{i}kR - \frac{k^2R^2}{9} \right) \,. \tag{8.129}$$

In the limit that the frequency $\omega \to 0$, the drag force reduces to the usual Stokes friction force, namely, $\boldsymbol{F} = 6\pi\eta u R\hat{\boldsymbol{z}}$. The Stokes friction can only be used to describe Brownian particles which are moving very slowly, and generally works well for Brownian particles that are large and massive relative to the particles that compose the fluid in which they are immersed. However, when describing the Brownian motion of individual atoms or molecules, the frequency-dependent terms generally cannot be neglected and memory effects become important. In Section 8.6, we compute the velocity autocorrelation function for a Brownian particle which is undergoing rapid random motion.

8.6
Brownian Motion with Memory

In Section 8.5, we derived frequency-dependent corrections to the Stokes friction on a particle undergoing Brownian motion. The frequency-dependent terms become important for small Brownian particles, which can be strongly agitated by density fluctuations in the surrounding medium. This became apparent in the 1960s, when molecular dynamics simulations by Rahman [178] of liquid argon showed significant deviations from exponential behavior in the velocity autocorrelation function of argon atoms. In Figure 8.5, we compare Rahman's results for the decay of the velocity autocorrelation function of argon atoms in liquid argon to the exponential decay expected for the case of Brownian motion with white noise and a constant friction coefficient. There is a significant difference in the detailed behavior of the two cases.

Subsequent to the work of Rahman, Alder and Wainwright [2] used computer simulations to obtain the velocity autocorrelation function for hard-sphere particles in a hard-sphere gas. They also found deviations from exponential behavior. One of the more striking features they found was a long time tail in the velocity autocorrelation function. In the long time limit, the velocity autocorrelation function decayed as $t^{-3/2}$ rather than exponentially with time. Alder and Wainwright were able to pinpoint the reason for the discrepancy. They observed vortices in the flow pattern around the Brownian particle. As the Brownian particle moved through the fluid, it left a memory of its motion which could influence its later movement. This complicated flow around the Brownian particle is a direct consequence of hydrodynamics.

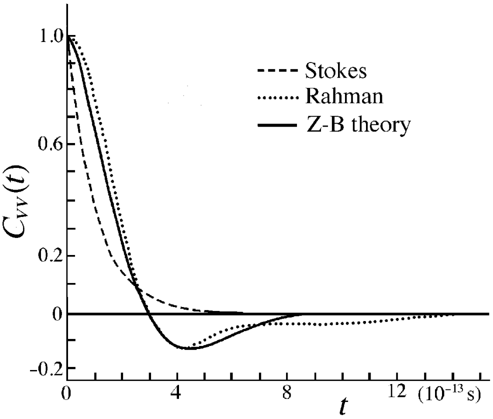

Figure 8.5 The velocity autocorrelation function for argon atoms in liquid argon. The dotted line is the numerical simulation of Rahman. The dashed line is the exponential decay predicted by Brownian motion theory using the constant Stokes friction coefficient. The solid line is the Zwanzig–Bixon (Z-B) theoretical result. Reprinted, by permission, from [222].

As we can see from Eq. (8.129), the friction force for a Brownian particle in a fluid depends on frequency, and this means that the Brownian particle velocity has memory. We can generalize the Langevin equation Eq. (7.1) to include memory effects by writing it in the form

$$m\frac{\mathrm{d}v(t)}{\mathrm{d}t} + \int_{-\infty}^{\infty} \alpha(t-t')v(t')\,\mathrm{d}t' = F_{\mathrm{rand}}(t)\,, \tag{8.130}$$

where $\alpha(t)$ is a time-dependent friction coefficient whose Fourier transform is given by Eq. (8.129). Namely,

$$\alpha(\omega) = \int_{-\infty}^{\infty} \mathrm{d}t\alpha(t)\mathrm{e}^{\mathrm{i}\omega t} = 6\pi\eta R\left(1 - \mathrm{i}kR - \frac{k^2R^2}{9}\right)\,, \tag{8.131}$$

where $k^2 = \mathrm{i}\rho_0\omega/\eta$. The friction force is assumed to be causal so that $\alpha(t) = 0$ for $t < 0$ and $\alpha(t) \neq 0$ for $t > 0$. In Eq. (8.131), $F_{\mathrm{rand}}(t)$ is the random force of the medium on the Brownian particle. We assume that the random force has zero average value, $\langle F_{\mathrm{rand}}(t)\rangle_F = 0$, where $\langle\rangle_F$ is an average over realizations of the random force. Because there is memory, the random force will not be "white."

If we make use of Eq. (8.131), the Fourier transform of Eq. (8.130) can be written

$$-\mathrm{i}m'\omega\tilde{v}(\omega) + \zeta\tilde{v}(\omega) - \zeta\Delta\mathrm{i}\sqrt{\mathrm{i}\omega}\tilde{v}(\omega) = \tilde{F}_{\mathrm{rand}}(\omega)\,, \tag{8.132}$$

where $\Delta = \sqrt{R^2\rho_0/\eta}$, $m' = m + 1/2M$, $\zeta = 6\pi\eta R$, and $M = 4/3\pi\rho_0 R^3$ is the mass of the displaced fluid. If we take the inverse Fourier transform of Eq. (8.132), we find

$$m'\frac{\mathrm{d}v(t)}{\mathrm{d}t} + \zeta v(t) + \frac{\zeta\Delta}{\sqrt{\pi}}\int_{-\infty}^{t} \mathrm{d}\tau\frac{1}{\sqrt{t-\tau}}\frac{\mathrm{d}v}{\mathrm{d}\tau} = F_{\mathrm{rand}}(t)\,. \tag{8.133}$$

Equation (8.133) is the Langevin equation for a Brownian particle of radius, R, in an incompressible fluid assuming "stick" boundary conditions. Note that there is a dressing of the mass of the Brownian particle.

Let us now construct the velocity autocorrelation function $C_{vv}(t) \equiv \langle\langle v(t)\rangle_F\, v(0)\rangle_T$, for the Brownian particle, where $\langle\rangle_T$ denotes a thermal average over the initial conditions. We first average Eq. (8.133) over the random force and obtain

$$m'\frac{\mathrm{d}\langle v(t)\rangle_F}{\mathrm{d}t} + \zeta\langle v(t)\rangle_F + \frac{\zeta\Delta}{\sqrt{\pi}}\int_{-\infty}^{t} \mathrm{d}\tau\frac{1}{\sqrt{t-\tau}}\frac{\mathrm{d}\langle v(s)\rangle_F}{\mathrm{d}\tau} = 0\,. \tag{8.134}$$

We then must solve for $\langle v(t)\rangle_F$, given the initial condition, $\langle v(0)\rangle_F = v(0)$. This is most easily done by means of a Laplace transform.

First take the Laplace transform of the third term in Eq. (8.134) (see Appendix F). We write

$$g(t) \equiv \int_{-\infty}^{t} \mathrm{d}\tau \frac{1}{\sqrt{t-\tau}} \frac{\mathrm{d}f(\tau)}{\mathrm{d}\tau} = \frac{1}{2\pi \mathrm{i}} \int_{-\infty}^{t} \frac{\mathrm{d}\tau}{\sqrt{t-\tau}} \int_{\delta-\mathrm{i}\infty}^{\delta+\mathrm{i}\infty} \mathrm{d}z z \mathrm{e}^{z\tau} f(z) \,, \tag{8.135}$$

where we let $f(\tau) \equiv \langle v(\tau) \rangle_F$ and we have inserted the Laplace transform of $\mathrm{d}f/\mathrm{d}\tau$. If we now interchange the order of the integration over τ and z and note that $\int_{-\infty}^{t} \mathrm{d}\tau (t-\tau)^{-1} \mathrm{e}^{-z(t-\tau)} = \sqrt{\pi/z}$ for $t > \tau$, we obtain

$$g(t) = \frac{1}{2\pi \mathrm{i}} \int_{\delta-\mathrm{i}\infty}^{\delta+\mathrm{i}\infty} \mathrm{d}z \sqrt{\pi z} \mathrm{e}^{zt} f(z) \quad \text{and} \quad \tilde{g}(z) = \sqrt{\pi z} \tilde{f}(z) \,, \tag{8.136}$$

where $\tilde{g}(z)$ and $\tilde{f}(z)$ are the Laplace transforms of $g(t)$ and $f(t)$, respectively.

We can now substitute the above results into Eq. (8.134) and obtain

$$\left(m'z + \zeta + \zeta \Delta \sqrt{z}\right) \langle \tilde{v}(z) \rangle_F = m' v(0) \,. \tag{8.137}$$

If we solve for $\langle \tilde{v}(z) \rangle_F$, we can write the velocity autocorrelation function in the form

$$C_{vv}(t) = \frac{1}{2\pi \mathrm{i}} \int_{\delta-\mathrm{i}\infty}^{\delta+\mathrm{i}\infty} \mathrm{d}z \mathrm{e}^{zt} \frac{m' \langle v(0)^2 \rangle_T}{m'z + \zeta + \zeta \Delta \sqrt{z}} \,, \tag{8.138}$$

where $m' \langle v(0)^2 \rangle_T / 2 = k_\mathrm{B} T/2$ denotes the thermal average of the kinetic energy for Brownian motion in one space dimension. Note that the thermal average involves the dressed mass m' of the Brownian particle. The velocity autocorrelation function then becomes

$$C_{vv}(t) = \frac{k_\mathrm{B} T}{2\pi \mathrm{i}} \int_{\delta-\mathrm{i}\infty}^{\delta+\mathrm{i}\infty} \mathrm{d}z \mathrm{e}^{zt} \frac{1}{m'z + \zeta + \zeta \Delta \sqrt{z}} \,. \tag{8.139}$$

The integrand in Eq. (8.139) has a branch point at $z = 0$. We draw the branch cut along the negative real axis as shown in Figure 8.6. Then we integrate along the contour, C_2. The contribution from the small semicircle at the origin is zero

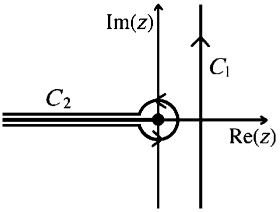

Figure 8.6 Branch cut and integration contours. C_1 is the Bromwich contour.

because there is no pole at the origin. The correlation function is then found to be

$$C_{vv}(t) = \frac{k_B T}{\pi}\int_0^\infty \mathrm{d}x e^{-x|t|}\frac{\zeta\Delta\sqrt{x}}{(\zeta - m'x)^2 + \zeta^2\Delta^2 x}\,, \tag{8.140}$$

where $x = -\mathrm{Re}(z)$. This integral must be evaluated numerically. However, we can obtain an approximate analytic expression for the long time behavior of $C_{vv}(t)$ because it is determined by small values of x. Thus, by expanding the integrand in powers of $\sqrt{x}$, we obtain

$$C_{vv}(t) = \frac{k_B T\delta}{\pi\zeta}\int_0^\infty \mathrm{d}x\sqrt{x}e^{-x|t|} + \ldots = \frac{D\Delta}{2\sqrt{\pi}|t|^{3/2}} + \ldots\,, \tag{8.141}$$

where $D = k_B T/(6\pi\eta R)$ is the Einstein diffusion coefficient. Note that $C_{vv}(t)$ has a long time tail. It decays with time as $t^{-3/2}$.

We can also compute the variance of the Brownian particle. Let us remember that $x(t) - x(0) = \int_0^t \mathrm{d}t' v(t')$. Then for a Brownian particle in equilibrium with the surrounding fluid,

$$\begin{aligned}\langle\Delta x^2(t)\rangle &= \langle(x(t) - x(0))^2\rangle = \int_0^t \mathrm{d}t_1\int_0^t \mathrm{d}t_2\langle v(t_1)v(t_2)\rangle \\ &= \left(\int_{t/2}^{t}\mathrm{d}T\int_{2(T-t)}^{2(t-T)}\mathrm{d}\tau + \int_0^{t/2}\mathrm{d}T\int_{-2T}^{2T}\mathrm{d}\tau\right)C_{vv}(\tau) \\ &= 2\int_0^t \mathrm{d}\tau\int_{\tau/2}^{t-T/2}\mathrm{d}T C_{vv}(\tau) = 2\int_0^t \mathrm{d}\tau(t-\tau)C_{vv}(\tau)\,.\end{aligned} \tag{8.142}$$

In the second line, we have made a change in the variables, $\tau = t_2 - t_1$ and $T = (1/2)(t_1 + t_2)$. In the third line, we have changed the order of integration. For example, $\int_{t/2}^t \mathrm{d}T\int_0^{2(t-T)}\mathrm{d}\tau = \int_0^t \mathrm{d}\tau\int_{t/2}^{t-\tau/2}\mathrm{d}T$. For long times the variance then takes the form

$$\langle\Delta x^2(t)\rangle = 2Dt - \frac{4D\Delta}{\sqrt{\pi}}t^{1/2} + \ldots \tag{8.143}$$

It is also useful to define a „time-dependent diffusion coefficient“ given by

$$D(t) \equiv \frac{1}{2}\frac{d\langle\Delta x^2(t)\rangle}{\mathrm{d}t} = D - \frac{D\Delta}{\pi}\sqrt{\frac{\pi}{t}} + \ldots \tag{8.144}$$

Thus, in the very long time limit the diffusion coefficient approaches the expected value.

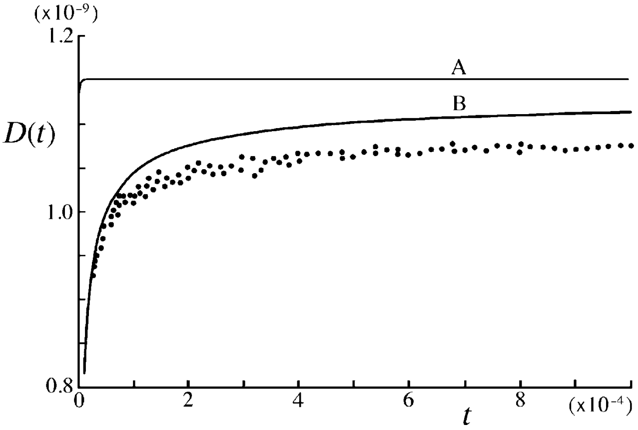

Figure 8.7 Measurement of $D(t)$ (in units of $\mathrm{cm}^2\,\mathrm{s}^{-1}$), versus time (in seconds). Curve A is the prediction for constant friction coefficient. Curve B is the prediction when memory effects are included. The black dots are measurements for a Brownian particle in water. Reprinted by permission from [160].

The diffusion coefficient $D(t)$, for a Brownian particle with radius $R = 1.7$ microns in water, has been measured in light scattering experiments by Paul and Pusey [160]. We show the results in Figure 8.7. Curve A is the result for the case when the friction coefficient, $\alpha = 6\pi\eta R$, has no memory. Curve B is the prediction of Eq. (8.140). The black dots are the result of experiment. While the experimental values qualitatively follow the theoretical predictions, they differ by a systematic quantitative amount. One possible source for these deviations is the rotational degrees of freedom of water. The deviations between theory and experiment have been used to estimate the rotational transport coefficients in water [182].

The velocity autocorrelation function for Argon atoms moving in Argon have been reproduced theoretically by Zwanzig and Bixon [222] using the hydrodynamic equations for a compressible fluid, assuming that the Brownian particle is an Argon atom. A comparison of the results of Zwanzig and Bixon with Rahman's numerical experiments is shown in Figure 8.5. The qualitative agreement is quite impressive. This shows that even on the molecular scale, the conservation laws which give rise to hydrodynamic behavior play a fundamental role. The effect of rotational degrees of freedom of the *fluid* on Brownian motion has been studied in [181]. The effect of hydrodynamic memory on the dielectric response of a Brownian particle in a nonpolar fluid was studied in [191].

8.7
Hydrodynamics of Binary Mixtures

In this section, we will consider some of the key transport processes that occur in binary mixtures [39, 95, 173]. We begin with the derivation the entropy production in binary mixtures. The entropy production determines the type of dissipative processes that can occur in the mixture. We will find that temperature gradients and concentration gradients can each drive both diffusion processes and heat flow. We then consider, in more detail, several types of transport processes commonly found in binary mixtures.

8.7.1
Entropy Production in Binary Mixtures

We consider a fluid that consists of a mixture of two distinguishable types of particle, a and b, with mass m_a and m_b, respectively, and chemical potential μ_a and μ_b, respectively. The fundamental equation for the mixture is

$$\rho u = T\rho s - P + \rho_\mathrm{a}\mu_\mathrm{a} + \rho_\mathrm{b}\mu_\mathrm{b} \,, \tag{8.145}$$

where ρ is the total mass density (mass/volume), u is the internal energy per unit mass, s is the entropy per unit mass, ρ_a (ρ_b) is the mass density of particle of type a (b), and μ_a (μ_b) is the chemical potential per unit mass of particle of type a (b). Note also that $\rho = \rho_\mathrm{a} + \rho_\mathrm{b}$. The Gibbs–Duhem equation is

$$\rho s\,\mathrm{d}T - \mathrm{d}P + \rho_\mathrm{a}\,\mathrm{d}\mu_\mathrm{a} + \rho_\mathrm{b}\,\mathrm{d}\mu_\mathrm{b} = 0 \,. \tag{8.146}$$

If we take the differential of Eq. (8.145) and then combine it with Eq. (8.146), we obtain the following expression for the total differential of the entropy,

$$T\,\mathrm{d}(\rho s) = \mathrm{d}(\rho u) - \mu_\mathrm{a}\,\mathrm{d}\rho_\mathrm{a} - \mu_\mathrm{b}\,\mathrm{d}\rho_\mathrm{b} \,. \tag{8.147}$$

We can write the total particle current in the form

$$\boldsymbol{J} = \rho_\mathrm{a}\boldsymbol{v}_\mathrm{a} + \rho_\mathrm{b}\boldsymbol{v}_\mathrm{b} = \rho\boldsymbol{w} \,, \tag{8.148}$$

where $\boldsymbol{w}$ is the barycentric velocity. We also introduce a diffusive (dissipative) particle current for each particle, defined

$$\boldsymbol{J}_\mathrm{a}^\mathrm{D} = \rho_\mathrm{a}(\boldsymbol{v}_\mathrm{a} - \boldsymbol{w}) \quad \text{and} \quad \boldsymbol{J}_\mathrm{b}^\mathrm{D} = \rho_\mathrm{b}(\boldsymbol{v}_\mathrm{b} - \boldsymbol{w}) \,. \tag{8.149}$$

The diffusive particle currents have the property that $\boldsymbol{J}_\mathrm{a}^\mathrm{D} + \boldsymbol{J}_\mathrm{b}^\mathrm{D} = 0$. The conservation of number of particles of type a and of type b is expressed in terms of the balance equations

$$\frac{\partial \rho_j}{\partial t} = -\nabla_{\boldsymbol{r}} \cdot (\rho_j \boldsymbol{v}_j) = -\nabla_{\boldsymbol{r}} \cdot \left(\boldsymbol{J}_j^\mathrm{D} + \rho_j \boldsymbol{w}\right) \,, \tag{8.150}$$

where $j = \mathrm{a}, \mathrm{b}$. If we add the balance equations for the two types of particles, we obtain the balance equation for the total mass density

$$\frac{\partial \rho}{\partial t} = -\nabla_{\boldsymbol{r}} \cdot \boldsymbol{J} \,. \tag{8.151}$$

The momentum density balance equation can be written

$$\frac{\partial \boldsymbol{J}}{\partial t} = -\nabla_{\boldsymbol{r}} P - \nabla_{\boldsymbol{r}} \cdot \boldsymbol{\Pi}^{\mathrm{D}} \,, \tag{8.152}$$

where P is the hydrostatic pressure and $\boldsymbol{\Pi}^{\mathrm{D}}$ is the (dissipative) stress tensor. The balance equations for the total energy and entropy are

$$\frac{\partial \rho e}{\partial t} + \nabla_{\boldsymbol{r}} \cdot \boldsymbol{J}_e = 0 \quad \text{and} \quad \frac{\partial \rho s}{\partial t} + \nabla_{\boldsymbol{r}} \cdot \boldsymbol{J}_s = \sigma_s \,, \tag{8.153}$$

respectively, where e is the total energy per unit mass, $\boldsymbol{J}_e$ is the total energy current, $\boldsymbol{J}_s$ is the total entropy current, and σ_{s} is the entropy production due to irreversible processes in the fluid.

The total energy consists of the internal energy and kinetic energy due to the fluid flow. We write it

$$\rho e = \rho u + \frac{1}{2}\rho w^2 \,. \tag{8.154}$$

The differential of the total energy can then be written

$$\mathrm{d}\rho e = \mathrm{d}(\rho u) + \boldsymbol{w} \cdot \mathrm{d}\boldsymbol{J} - \frac{1}{2} w^2 \, \mathrm{d}\rho \,. \tag{8.155}$$

Let us now use Eq. (8.147) to write

$$\frac{\mathrm{d}(\rho u)}{\mathrm{d}t} - T\frac{\mathrm{d}(\rho s)}{\mathrm{d}t} - \mu_{\mathrm{a}}\frac{\mathrm{d}\rho_{\mathrm{a}}}{\mathrm{d}t} - \mu_{\mathrm{b}}\frac{\mathrm{d}\rho_{\mathrm{b}}}{\mathrm{d}t} = 0 \,. \tag{8.156}$$

Next let $\mathrm{d}/\mathrm{d}t = \partial/\partial t + \boldsymbol{v} \cdot \nabla_{\boldsymbol{r}}$ in Eq. (8.156). If we use the fundamental equation and the Gibbs–Duhem equation, we can show that

$$\boldsymbol{v} \cdot \left(\nabla_{\boldsymbol{r}}(\rho u) - T\nabla_{\boldsymbol{r}}(\rho s) - \mu_{\mathrm{a}}\nabla_{\boldsymbol{r}}\rho_{\mathrm{a}} - \mu_{\mathrm{b}}\nabla_{\boldsymbol{r}}\rho_{\mathrm{b}}\right) = 0 \,. \tag{8.157}$$

Then we obtain

$$T\frac{\partial(\rho s)}{\partial t} = \frac{\partial(\rho u)}{\partial t} - \mu_{\mathrm{a}}\frac{\partial\rho_{\mathrm{a}}}{\partial t} - \mu_{\mathrm{b}}\frac{\partial\rho_{\mathrm{b}}}{\partial t} \,. \tag{8.158}$$

If we now replace the internal energy by the total energy and use the balance equations, we obtain

$$\begin{aligned} T\frac{\partial(\rho s)}{\partial t} &= \frac{\partial(\rho e)}{\partial t} - \boldsymbol{w} \cdot \frac{\partial \boldsymbol{J}}{\partial t} + \frac{1}{2}w^2\frac{\partial\rho}{\partial t} - \mu_{\mathrm{a}}\frac{\partial\rho_{\mathrm{a}}}{\partial t} - \mu_{\mathrm{b}}\frac{\partial\rho_{\mathrm{b}}}{\partial t} \\ &= -\nabla_{\boldsymbol{r}} \cdot \boldsymbol{J}_e + \boldsymbol{w} \cdot \nabla_{\boldsymbol{r}} P + \boldsymbol{w} \cdot (\nabla_{\boldsymbol{r}} \cdot \boldsymbol{\Pi}^{\mathrm{D}}) - \frac{1}{2}w^2(\nabla_{\boldsymbol{r}} \cdot \boldsymbol{J}) \\ &\quad + \mu_{\mathrm{a}}\nabla_{\boldsymbol{r}} \cdot \boldsymbol{J}_{\mathrm{a}}^{\mathrm{D}} + \mu_{\mathrm{b}}\nabla_{\boldsymbol{r}} \cdot \boldsymbol{J}_{\mathrm{b}}^{\mathrm{D}} + \mu_{\mathrm{a}} \cdot \nabla(\rho_{\mathrm{a}}\boldsymbol{w}) + \mu_{\mathrm{b}} \cdot \nabla(\rho_{\mathrm{b}}\boldsymbol{w}) \,. \end{aligned} \tag{8.159}$$

Next divide by T and rearrange terms. If we use the Gibbs–Duhem equation $\nabla_{\boldsymbol{r}} P = \rho_{\mathrm{a}} \nabla_{\boldsymbol{r}} \mu_{\mathrm{a}} + \rho_{\mathrm{b}} \nabla_{\boldsymbol{r}} \mu_{\mathrm{b}} + \rho s \nabla_{\boldsymbol{r}} T$, we obtain

$$\begin{aligned}\frac{\partial(\rho s)}{\partial t} &= -\nabla_{\boldsymbol{r}} \cdot \left(\frac{\boldsymbol{J}_e - \boldsymbol{w} \cdot \boldsymbol{\Pi}^{\mathrm{D}} - \mu_{\mathrm{a}} \boldsymbol{J}_{\mathrm{a}}^{\mathrm{D}} - \mu_{\mathrm{b}} \boldsymbol{J}_{\mathrm{b}}^{\mathrm{D}} - \rho_{\mathrm{a}} \mu_{\mathrm{a}} \boldsymbol{w} - \rho_{\mathrm{b}} \mu_{\mathrm{b}} \boldsymbol{w}}{T} \right) \\ &\quad - \frac{1}{T} \boldsymbol{\Pi}^{\mathrm{D}} : \nabla_{\boldsymbol{r}} \boldsymbol{w} - \frac{1}{T} \left(\boldsymbol{J}_{\mathrm{a}}^{\mathrm{D}} \cdot \nabla_{\boldsymbol{r}} \mu_{\mathrm{a}} + \boldsymbol{J}_{\mathrm{b}}^{\mathrm{D}} \cdot \nabla_{\boldsymbol{r}} \mu_{\mathrm{b}} \right) \\ &\quad - \frac{1}{T^2} \left[\boldsymbol{J}_e - \rho s T \boldsymbol{w} - \boldsymbol{w} \cdot \boldsymbol{\Pi}^{\mathrm{D}} - \mu_{\mathrm{a}} \boldsymbol{J}_{\mathrm{a}}^{\mathrm{D}} - \mu_{\mathrm{b}} \boldsymbol{J}_{\mathrm{b}}^{\mathrm{D}} - (\rho_{\mathrm{a}} \mu_{\mathrm{a}} + \rho_{\mathrm{b}} \mu_{\mathrm{b}}) \boldsymbol{w} \right] \\ &\quad \times \nabla_{\boldsymbol{r}} T \,. \end{aligned} \tag{8.160}$$

Note that we have now neglected terms that are third order in the barycentric velocity.

Before continuing, it is useful to consider nondissipative fluid flow. If we set the dissipative currents to zero, we obtain

$$\begin{aligned}\frac{\partial(\rho s)}{\partial t} &= -\nabla_{\boldsymbol{r}} \cdot \left(\frac{\boldsymbol{J}_e^{\mathrm{R}} - \rho_{\mathrm{a}} \mu_{\mathrm{a}} \boldsymbol{w} - \rho_{\mathrm{b}} \mu_{\mathrm{b}} \boldsymbol{w}}{T} \right) \\ &\quad - \frac{1}{T^2} (\boldsymbol{J}_e^{\mathrm{R}} - \rho s T \boldsymbol{w} - \rho_{\mathrm{a}} \mu_{\mathrm{a}} \boldsymbol{w} - \rho_{\mathrm{b}} \mu_{\mathrm{b}} \boldsymbol{w}) \cdot \nabla_{\boldsymbol{r}} T \,, \end{aligned} \tag{8.161}$$

where $\boldsymbol{J}_e^{\mathrm{R}}$ is the nondissipative (reactive) part of the energy current. In order for the entropy production to be zero in the nondissipative fluid, the reactive energy current takes the form $\boldsymbol{J}_e^{\mathrm{R}} = \rho s T \boldsymbol{w} + \rho_{\mathrm{a}} \mu_{\mathrm{a}} \boldsymbol{w} + \rho_{\mathrm{b}} \mu_{\mathrm{b}} \boldsymbol{w}$.

The entropy balance equation for the dissipative mixture then takes the form

$$\frac{\partial(\rho s)}{\partial t} = -\nabla_{\boldsymbol{r}} \cdot \left(\rho s \boldsymbol{w} + \boldsymbol{J}_s^{\mathrm{D}} \right) + \sigma_{\mathrm{s}} \tag{8.162}$$

where the reactive and dissipative parts of the entropy current are

$$\boldsymbol{J}_s^{\mathrm{R}} = \rho s \boldsymbol{w} \quad \text{and} \quad \boldsymbol{J}_s^{\mathrm{D}} = \frac{\boldsymbol{J}_e^{\mathrm{D}} - \boldsymbol{w} \cdot \boldsymbol{\Pi}^{\mathrm{D}} - \mu_{\mathrm{a}} \boldsymbol{J}_{\mathrm{a}}^{\mathrm{D}} - \mu_{\mathrm{b}} \boldsymbol{J}_{\mathrm{b}}^{\mathrm{D}}}{T} \tag{8.163}$$

respectively, and the entropy production is given by

$$\sigma_{\mathrm{s}} = -\frac{1}{T} \boldsymbol{J}_s^{\mathrm{D}} \cdot \nabla_{\boldsymbol{r}} T - \frac{1}{T} \boldsymbol{\Pi}^{\mathrm{D}} : \nabla_{\boldsymbol{r}} \boldsymbol{w} - \frac{1}{T} \boldsymbol{J}_{\mathrm{a}}^{\mathrm{D}} \cdot \nabla_{\boldsymbol{r}} \mu_{\mathrm{a}} - \frac{1}{T} \boldsymbol{J}_{\mathrm{b}}^{\mathrm{D}} \cdot \nabla_{\boldsymbol{r}} \mu_{\mathrm{b}} \,. \tag{8.164}$$

Note that the entropy production is again written in terms of products of generalized forces and currents. If we note that $\boldsymbol{J}_{\mathrm{a}}^{\mathrm{D}} + \boldsymbol{J}_{\mathrm{b}}^{\mathrm{D}} = 0$, the last term in σ_{s} can be written

$$\sum_{j=\mathrm{a,b}} \frac{1}{T} \boldsymbol{J}_j^{\mathrm{D}} \cdot \nabla \mu_j = \frac{1}{2T} \left(\boldsymbol{J}_{\mathrm{a}}^{\mathrm{D}} - \boldsymbol{J}_{\mathrm{b}}^{\mathrm{D}} \right) \cdot \nabla (\mu_{\mathrm{a}} - \mu_{\mathrm{b}})$$

and explicitly gives the entropy production due to diffusion of particles a and b. For an isotropic fluid, forces with a given symmetry can only drive currents with the same symmetry. Thus, the entropy current can be driven by both a temperature gradient and a chemical potential gradient. Similarly, particle diffusion can be driven by both a chemical potential gradient and a temperature gradient. The transport coefficients for these processes are related by the Onsager relations discussed in Chapter 7.

8.7.2
Fick's Law for Diffusion

We can derive the diffusion coefficient D, for a dilute solution of solute molecules in a solvent, starting from the expression for the entropy production given in Eq. (8.164). Let us assume that we have a small amount of a solute (which we don't yet specify) dissolved in a solvent (which we assume to be water). Let $\rho_{\mathrm{w}}(\rho_{\mathrm{s}})$ be the density of water (solute) and let $\rho = \rho_{\mathrm{s}} + \rho_{\mathrm{w}}$ be the total density. We assume that the mass density of the solute is much smaller than the mass density of water so that $(\rho_{\mathrm{s}}/\rho_{\mathrm{w}}) \ll 1$. Also, we assume that the fluid is at rest so that $\boldsymbol{w} = 0$, and that the pressure P and temperature T are uniform throughout the fluid. From Eq. (8.164), the entropy production σ is given by

$$T\sigma_s = -\boldsymbol{J}_{\mathrm{w}}^{\mathrm{D}} \cdot [\nabla_{\boldsymbol{r}}\mu_{\mathrm{w}}]_T - \boldsymbol{J}_{\mathrm{s}}^{\mathrm{D}} \cdot [\nabla_{\boldsymbol{r}}\mu_{\mathrm{s}}]_T \,. \tag{8.165}$$

From the Gibbs–Duhem equation, we can write $\rho_{\mathrm{w}}[\nabla_{\boldsymbol{r}}\mu_{\mathrm{w}}]_{T,P} + \rho_{\mathrm{s}}[\nabla_{\boldsymbol{r}}\mu_{\mathrm{s}}]_{T,P} = 0$, when P and T are held constant. If we also use the condition $\boldsymbol{J}_{\mathrm{s}}^{\mathrm{D}} + \boldsymbol{J}_{\mathrm{w}}^{\mathrm{D}} = 0$, Eq. (8.165) can be written

$$T\sigma_s = -\left(\boldsymbol{J}_{\mathrm{s}}^{\mathrm{D}} - \frac{\rho_{\mathrm{s}}}{\rho_{\mathrm{w}}}\boldsymbol{J}_{\mathrm{w}}^{\mathrm{D}}\right) \cdot [\nabla_{\boldsymbol{r}}\mu_{\mathrm{s}}]_{T,P} \,. \tag{8.166}$$

The current that appears in Eq. (8.166) is the diffusion current, $\boldsymbol{J}_{\mathrm{D}} = \boldsymbol{J}_{\mathrm{s}}^{\mathrm{D}} - \rho_{\mathrm{s}}/\rho_{\mathrm{w}}\boldsymbol{J}_{\mathrm{w}}^{\mathrm{D}}$ of solute relative to water.

When written in terms of the diffusion current, the entropy production σ_{s} takes the form

$$T\sigma_s = -\boldsymbol{J}_{\mathrm{D}} \cdot [\nabla_{\boldsymbol{r}}\mu_{\mathrm{s}}]_{T,P} \,. \tag{8.167}$$

We can write the generalized Ohm's Law for this process. The chemical potential of the solute can be written $\mu_{\mathrm{s}} = \mu_{\mathrm{s}}(T, P, x_{\mathrm{s}})$, where x_{s} is the mole fraction of the solute. We can then write

$$\boldsymbol{J}_{\mathrm{D}} = -L_{\mathrm{s}}[\nabla_{\boldsymbol{r}}\mu_{\mathrm{s}}]_{T,P} = -L_{\mathrm{s}}\left(\frac{\partial\mu_{\mathrm{s}}}{\partial x_{\mathrm{s}}}\right)_{P,T} \nabla_{\boldsymbol{r}}x_{\mathrm{s}} \,, \tag{8.168}$$

where L_{s} is a transport coefficient. If we treat the mixture as an *ideal mixture*, the chemical potential takes the form $\mu_{\mathrm{s}} = \mu_{\mathrm{s}}^0 + RT/M_{\mathrm{s}} \ln x_{\mathrm{s}}$, where M_{s} is the molecular mass of the solute, and $\left(\partial/\mu_{\mathrm{s}}\partial x_{\mathrm{s}}\right)_{P,T} = RT/(x_{\mathrm{s}}M_{\mathrm{s}})$. Also note that $\nabla_r x_{\mathrm{s}} = c_{\mathrm{w}}/c^2\nabla_r c_{\mathrm{s}} - c_{\mathrm{s}}/c^2\nabla_r c_{\mathrm{w}}$, where $c_j = n_j/V$ is the concentration (moles/volume) of

Table 8.1 Diffusion coefficients of typical substances in the limit of infinitely dilute aqueous solution ($T = 25\,°C$) [124].

Solute	Formula	D (10^{-5} cm^2 s^{-1})
Acetone	C_3H_6O	1.28
Benzene	C_6H_6	1.02
Ethanol	C_2H_6O	1.24
Methane	CH_4	1.49
Ethylbenzene	C_8H_{10}	0.8

Table 8.2 Diffusion coefficient D of benzene in some typical solvents in the limit of infinitely dilute solution ($T = 25\,°C$) η is the viscosity of the solvent [124].

Solvent	Formula	D (10^{-5} cm^2 s^{-1})	η (10^{-3} Pa s)
1-Butanol	$C_4H_{10}O$	1.00	2.54
Cyclohexane	C_6H_{12}	1.41	0.89
Ethanol	C_2H_6O	1.81	1.07
Heptane	C_7H_{16}	3.91	0.39
Toluene	C_7H_8	2.54	0.56

molecules of type j and $c = c_w + c_s$ is the total concentration. Since we are assuming that $c_s \ll c_w$, to lowest order in c_s/c_w, we can write the diffusion current in the form

$$J'_D = \frac{1}{M_s} J_D = -L_s \frac{RT}{M_s^2 c_s} \nabla_r c_s \equiv -D \nabla_r c_s \,. \tag{8.169}$$

The equation $J'_D = -D\nabla_r c_s$ is *Fick's Law* for diffusion and $D = L_s RT/(M_s^2 c_s)$ is the diffusion coefficient. If we equate the diffusion coefficient D to the Einstein diffusion coefficient for Brownian motion, $D = RT/(N_A \pi \eta a)$, we find $L_s = c_s M_s^2/(N_A \pi \eta a)$, where η is the coefficient of viscosity for water, a is the radius of the solute molecule, and N_A is Avogadro's number. We can obtain a numerical estimate for these quantities. At $T = 25\,°C = 298.15\,K$, the viscosity of water is $\eta \approx 0.9 \times 10^{-3}$ Pa s. For solute molecules with a radius $a = 4\,Å$, the Einstein diffusion coefficient is $D = 0.61 \times 10^{-5}\,\text{cm}^2/\text{s}$. We can compare this with actual measurements of the diffusion coefficient given in Table 8.1 for very dilute aqueous solutions. The value given by the Einstein diffusion coefficient is of the correct order of magnitude.

It is also interesting to see how the diffusion coefficient depends on the nature of the solvent. In Table 8.2, we give the diffusion coefficient for some infinitely dilute solutions of benzene in various solvents.

8.7.3
Thermal Diffusion

If a temperature gradient exists in a mixture of molecules, it can drive diffusion processes. Also, if a concentration gradient exists in a mixture, it can induce a temperature gradient. Diffusion induced by a temperature gradient is called the *thermal diffusion*. The parameter that measures its strength is called the *Soret coefficient*.

Let us consider a binary mixture consisting of water (the solvent) and a solute. We shall assume that the pressure P is uniform throughout the mixture and that the fluid is at rest so that $\boldsymbol{w} = 0$. From Eq. (8.164), the entropy source term (entropy production) σ_{s} is given by

$$\begin{aligned} T\sigma_s &= -\frac{1}{T}\boldsymbol{J}_S^{\mathrm{D}} \cdot \nabla_{\boldsymbol{r}} T - \boldsymbol{J}_{\mathrm{s}}^{\mathrm{D}} \cdot [\nabla_{\boldsymbol{r}}\mu_{\mathrm{s}}]_P - \boldsymbol{J}_{\mathrm{w}}^{\mathrm{D}} \cdot [\nabla_{\boldsymbol{r}}\mu_{\mathrm{w}}]_P \\ &= -\frac{1}{T}\boldsymbol{J}_S^{\mathrm{D}} \cdot \nabla_{\boldsymbol{r}} T - \boldsymbol{J}_{\mathrm{D}} \cdot [\nabla_{\boldsymbol{r}}\mu_{\mathrm{s}}]_P \,, \end{aligned} \tag{8.170}$$

(see Eq. (8.167)) where $\boldsymbol{J}_{\mathrm{D}}$ is the mass current of solute relative to water and $\boldsymbol{J}_S^{\mathrm{D}}$ is the dissipative entropy current. The constitutive equations (generalized Ohm's Laws) for this system can be written

$$\boldsymbol{J}_{\mathrm{D}} = -L_{s,s}[\nabla_{\boldsymbol{r}}\mu_{\mathrm{s}}]_P - L_{s,S}\nabla_{\boldsymbol{r}} T \,, \tag{8.171}$$

$$\boldsymbol{J}_S^{\mathrm{D}} = -L_{S,s}[\nabla_r\mu_{\mathrm{s}}]_P - L_{S,S}\nabla_r T \,, \tag{8.172}$$

where $L_{s,s}$, $L_{s,S}$, $L_{S,s}$ and $L_{S,S}$ are the transport coefficients (Onsager coefficients) associated with this process. Let us again assume that we have a dilute mixture of solute in water so that $[\nabla_{\boldsymbol{r}}\mu_{\mathrm{s}}]_P \approx \left(\partial/\mu_{\mathrm{s}}\partial c_{\mathrm{s}}\right)_P \nabla_{\boldsymbol{r}} c_{\mathrm{s}}$. Then Eqs. (8.171) and (8.172) take the form

$$\boldsymbol{J}_{\mathrm{D}} = -L_{s,s}\left(\frac{\partial\mu_{\mathrm{s}}}{\partial c_{\mathrm{s}}}\right)_P \nabla_r c_{\mathrm{s}} - L_{s,S}\nabla_r T \,, \tag{8.173}$$

$$\boldsymbol{J}_S^{\mathrm{D}} = -L_{S,s}\left(\frac{\partial\mu_{\mathrm{s}}}{\partial c_{\mathrm{s}}}\right)_P \nabla_{\boldsymbol{r}} c_{\mathrm{s}} - L_{S,S}\nabla_r T \,. \tag{8.174}$$

The diffusion coefficient is then $D = (L_{s,s}/M_{\mathrm{s}})\left(\partial/\mu_{\mathrm{s}}\partial c_{\mathrm{s}}\right)_P$. The coefficient of thermal conductivity is $K = L_{S,S}$. In experiments it is found that the coefficient $L_{s,S}$ is linearly proportional to the solute concentration. Therefore, a *coefficient of thermal diffusion* D_T is introduced and is defined so that $L_{s,S} = M_{\mathrm{s}} c_{\mathrm{s}} D_T$. The solute particle flux $\boldsymbol{J}'_{\mathrm{D}} = \boldsymbol{J}_{\mathrm{D}}/M_{\mathrm{s}}$ then takes the form

$$\boldsymbol{J}'_{\mathrm{D}} = -D\nabla_r c_{\mathrm{s}} - c_{\mathrm{s}} D_T \nabla_r T \,. \tag{8.175}$$

The *Soret coefficient* S_T is defined as $S_T = D_T/D = L_{s,q}/(M_{\mathrm{s}} c_{\mathrm{s}} D)$. The Soret coefficient is a measure of the concentration gradient that is set up as the result of a temperature gradient for a system in its steady state. The effect of thermal diffusion is generally small with $D_T \approx 10^{-2}D$ or $D_T \approx 10^{-3}D$. However, it has been used, for example, to separate isotopes Kr^{84} from Kr^{86} and $\mathrm{H}^{35}\mathrm{Cl}$ from $\mathrm{H}^{37}\mathrm{Cl}$ in the gaseous phase [31].

8.8
Thermoelectricity

One may view a metal wire as an electrically neutral system consisting of positively charged metal ions at rest and negatively charged electrons which are free to move through the metal [39, 95, 140, 220]. (Although the carriers of current are negatively charged, we follow the usual convention of depicting the direction of electric current flow to be that of positive charges.) A flux of electrons can carry both a charge current, $I = -FJ_{\mathrm{el}}$, where F is Faraday's constant (the charge of one mole of protons) and J_{el} is electron number current (mol/area · time), and an entropy current, J_S, (or heat current TJ_S). We will assume that the electrons have uniform spatial density, when the system is in equilibrium, because the system is electrically neutral and the density of positive metal ions is fixed. The electrochemical potential of the electrons can be written in the form $\mu_{\mathrm{el}}^{\mathrm{e}} = \mu_{\mathrm{el}}(T) - F\phi$, where $\mu_{\mathrm{el}}(T)$ is the chemical potential of the electrons and ϕ is the electric potential. The entropy source term (entropy production), σ_{s}, which results from the flow of electrons in the metal can be written

$$T\sigma_{\mathrm{s}} = -J_S \nabla_r T - J_{\mathrm{el}} \nabla_r \mu_{\mathrm{el}}^{\mathrm{e}} \,. \tag{8.176}$$

The constitutive equations (generalized Ohm's laws) take the form

$$J_S = -L_{SS} \nabla_r T - L_{SE} \nabla_r \mu_{\mathrm{el}}^{\mathrm{e}} \,, \tag{8.177}$$

$$J_{\mathrm{el}} = -L_{ES} \nabla_r T - L_{EE} \nabla_r \mu_{\mathrm{el}}^{\mathrm{e}} \,. \tag{8.178}$$

As we shall show below, Onsager's relation, $L_{SE} = L_{ES}$, is well verified for this system.

8.8.1
The Peltier Effect

Consider two distinct metals, A and B (copper and iron, for example), are placed in contact at two points (metal junctions) to form a closed circuit. If the metal junctions are kept at the same temperature, but a battery is connected to the circuit and an electric current is passed through the circuit, one junction will become hotter (absorb heat) and the other junction will become colder (emit heat). An amount of heat, $\dot{Q} \equiv h_{\mathrm{P}} I$, ($\dot{Q}$ has units joule/area · time) will be absorbed or emitted (depending on the types of metal at the junction and the direction of current flow). The amount of heat absorbed per unit area per unit time per unit electric current is called the *Peltier heat*, h_{P}, and is written

$$h_{\mathrm{P}} = \left(\frac{\dot{Q}}{I} \right)_{\nabla T = 0} \,. \tag{8.179}$$

The electric current, I, will be continuous at the junction, but the entropy current will be discontinuous due to the absorption or emission of heat. As we show in

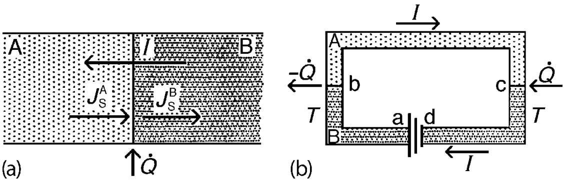

Figure 8.8 The Peltier effect. (a) If an electric current, I, flows through the junction of two metals, A and B, held at uniform temperature, $Q \equiv h_P I$ will be absorbed (or emitted). (b) A circuit at uniform temperature, consisting of two wires, one of metal A and the other of metal B, joined together. A battery is inserted between points a and d, and an electric current, I, is induced in the circuit. At one metal junction, an amount of heat/time, $\dot{Q}$, is absorbed; and at the other metal function, $-\dot{Q}$ is absorbed (emitted).

Figure 8.8a, the relation between the entropy current in metal A and in metal B is given by

$$T J_S^{\mathrm{B}} = T J_S^{\mathrm{A}} - h_{\mathrm{P}} I \,. \tag{8.180}$$

It is useful to consider a specific example. In Figure 8.8b, if metal A is iron and B is copper then junction b cools and junction c becomes hotter. If the current is reversed, then junction c is cooled and junction b becomes hotter. The absorption or emission of heat depends on both the types of metal and the direction of the current. Peltier heat is not a Joule heat since Joule heat depends on the square of the current. Peltier heat is due to the contact potential in the junction. When an electron must "climb" a potential hill in crossing a junction, it will absorb energy, thus causing the junction to cool. When the electron "descends" a potential hill in crossing a junction, it will emit energy, thus causing the junction to heat.

Let us now consider the circuit in Figure 8.8b which contains two junctions between metals A and B (cf. Figure 8.8b). We assume that the entire circuit is kept at temperature T. We connect a battery between points a and d and drive a current, I, in the circuit. If Eqs. (8.177) and (8.178) correctly describe the system, then the electrical current, I, will be accompanied by an entropy current, J_S^{A} $\left(J_S^{\mathrm{B}}\right)$, in metal A (B). We can define an *entropy transport parameter*, S_i^*, for metal i, such that

$$S_i^* = \left(\frac{J_S^i}{J_{\mathrm{el}}^i}\right)_{\nabla T=0} = \frac{L_{SE}^i}{L_{EE}^i} \,, \quad \text{where} \quad i = \mathrm{A}, \mathrm{B} \,. \tag{8.181}$$

S_i^* is a measure of the amount of entropy carried along with the electron current when the temperature in the circuit is uniform. Measurement of the entropy transport parameter enables us to determine the ratio of phenomenological coefficients (L_{SE}/L_{EE}), for each metal.

The Peltier heat, h_{P}, can be expressed in terms of the entropy transport parameters, S_{A}^* and S_{B}^*. Since from (8.181) we have $[J_S^i]_{\nabla_r T=0} = S_i^* [J_{\mathrm{el}}^i]_{\nabla_r T=0} = -S_i^* I/F$, we can use Eq. (8.180) to obtain

$$h_{\mathrm{P}} = \frac{T}{\mathrm{F}} \left(S_{\mathrm{B}}^* - S_{\mathrm{A}}^*\right) \,. \tag{8.182}$$

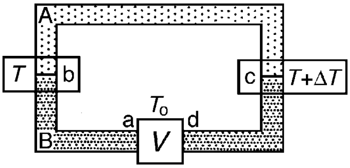

Figure 8.9 The Seebeck effect. A circuit consisting of two wires, one of metal A and the other of metal B, are joined together and the junctions are held at different temperatures, T and $T + \Delta T$. A potentiometer is inserted between points a and d, and a potential difference, $\Delta\phi_{\mathrm{ad}} = \phi_{\mathrm{a}} - \phi_{\mathrm{d}}$, is measured.

Thus, the change in entropy carried by the electrons across the junction has been connected to the heat absorbed at the junction.

8.8.2
The Seebeck Effect

If two different metals A and B are joined to form a closed circuit and if the two metal junctions are kept at different temperatures, T and $T + \Delta T$, an electric current will flow in the circuit. The current exists because the temperature difference has created an electromotive force (EMF) in the circuit due to the fact that the electrons at the two junctions have different chemical potentials. Assume that a potentiometer is inserted at points a and d, rather than a battery, and that the points a and d, and the potentiometer are all maintained at a common temperature, T_0, which lies between T and $T + \Delta T$ (cf. Figure 8.9). For this arrangement there will be no electric current flow so $I = 0$. When $\Delta T \neq 0$, a potential difference, $\Delta\phi_{\mathrm{ad}} = \phi_{\mathrm{a}} - \phi_{\mathrm{d}}$, is measured between points a and d. From Eq. (8.178), $J_{\mathrm{el}} = -L_{ES}\nabla_{\boldsymbol{r}} T - L_{EE}\nabla_{\boldsymbol{r}}\mu^{\mathrm{e}}_{\mathrm{el}} = 0$ so that

$$\left[\nabla_{\boldsymbol{r}}\mu^{\mathrm{e}}_{\mathrm{el}i}\right]_{J_{\mathrm{el}}=0} = -\frac{L^i_{ES}}{L^i_{EE}}\nabla_{\boldsymbol{r}} T = -\frac{L^i_{SE}}{L^i_{EE}}\nabla_{\boldsymbol{r}} T = -S^*_i \nabla_{\boldsymbol{r}} T \,, \tag{8.183}$$

where we have made use of Onsager's relation, $L^i_{SE} = L^i_{ES}$.

We can now obtain a relation between the temperature difference, ΔT, and the potential difference, $\Delta\phi_{\mathrm{ad}} = \phi_{\mathrm{a}} - \phi_{\mathrm{d}}$, measured by the potentiometer. Let x denote the spatial coordinate along the wire. We can integrate Eq. (8.183) along the wire, but it must be done in segments. In Figure 8.9 we have marked points a–d. The change in electrochemical potential as we go from point d to point c is

$$\left(\Delta\mu^{\mathrm{e}}_{\mathrm{el}}\right)_{\mathrm{cd}} = -\int_{T_0}^{T+\Delta T} S^*_{\mathrm{B}}\,\mathrm{d}T \,. \tag{8.184}$$

Similarly,

$$\left(\Delta\mu^{\mathrm{e}}_{\mathrm{el}}\right)_{\mathrm{bc}} = -\int_{T+\Delta T}^{\mathrm{T}} S^*_{\mathrm{A}}\,\mathrm{d}T \,, \quad \text{and} \quad \left(\Delta\mu^{\mathrm{e}}_{\mathrm{el}}\right)_{\mathrm{ab}} = -\int_{T}^{T_0} S^*_{\mathrm{B}}\,\mathrm{d}T \,. \tag{8.185}$$

Table 8.3 Test of the equation $(\mathrm{d}\phi_{\mathrm{ad}})/\mathrm{d}T = h_{\mathrm{P}}/T$ [140, 220].

Thermocouple	T (K)	h_{P}/T (μV/K)	$\mathrm{d}\phi_{\mathrm{ad}}/\mathrm{d}T$ (μV/K)
Cu-Ni	273	18.6	20.4
	302	22.3	21.7
	373	24.4	24.9
Fe-Hg	292	16.7	16.7
	373	15.6	15.4
	456	13.9	13.7

But the change in electrochemical potential from d to a is

$$\left(\Delta\mu_{\mathrm{el}}^{\mathrm{e}}\right)_{\mathrm{da}} = -\left(\Delta\mu_{\mathrm{el}}^{\mathrm{e}}\right)_{\mathrm{cd}} - \left(\Delta\mu_{\mathrm{el}}^{\mathrm{e}}\right)_{\mathrm{bc}} - \left(\Delta\mu_{\mathrm{el}}^{\mathrm{e}}\right)_{\mathrm{ab}} = \int_{T}^{T+\Delta T} \left(S_{\mathrm{B}}^{*} - S_{\mathrm{A}}^{*}\right) \mathrm{d}T \,. \tag{8.186}$$

Since points a and d are at the same temperature, we obtain $(\Delta\mu_{\mathrm{el}}^{\mathrm{e}})_{\mathrm{da}} = -\mathrm{F}\Delta\phi_{\mathrm{da}}$ and

$$\Delta\phi_{\mathrm{ad}} = \phi_{\mathrm{a}} - \phi_{\mathrm{d}} = \frac{1}{F} \int_{T}^{T+\Delta T} (S_{\mathrm{B}}^{*} - S_{\mathrm{A}}^{*})\,\mathrm{d}T \,. \tag{8.187}$$

The potential difference depends only on properties of the metal wires and the temperature difference between the junctions. For very small temperature differences, we can write

$$\frac{\mathrm{d}\phi_{\mathrm{ad}}}{\mathrm{d}T} = \frac{S_{\mathrm{B}}^{*} - S_{\mathrm{A}}^{*}}{F} = \frac{h_{\mathrm{P}}}{T} \,. \tag{8.188}$$

The quantity $(\mathrm{d}\phi_{\mathrm{ad}}/\,\mathrm{d}T)$ is the relative thermoelectric power of metal A against metal B. In order to obtain Eq. (8.188), we had to use Onsager's relation, $L_{SE}^{i} = L_{ES}^{i}$. Therefore, the validity of Eq. (8.188) provides a test of Onsager's relations. In Table 8.3, we compare measured values of $(\mathrm{d}\phi_{\mathrm{ad}}/\,\mathrm{d}T)$ and (h_{P}/T) over a range of temperatures for two different thermocouples. We see that the agreement is quite good.

8.8.3
Thomson Heat

A temperature gradient can be induced in a metal wire by placing opposite ends of the wire in contact with thermal reservoirs at different temperatures. If the wire is connected to a battery, an electric current, I, will flow in the wire. Thomson found that in the presence of the electric current, the original temperature gradient (in the absence of current) can only be maintained if heat, called *Thomson* *heat*, is absorbed (or emitted depending on the direction of current flow) along the wire. Thomson heat is distinct from Joule heat. Thomson showed that in order to maintain a temperature gradient in a wire made of metal A, one must add or subtract an amount of heat, $\mathrm{d}Q = \sigma_{\mathrm{A}}(T)I\,\mathrm{d}T$, for each incremental change in temperature, $\mathrm{d}T$, along a wire of metal A. The quantity

$$\sigma_{\mathrm{A}} = \frac{1}{I}\frac{\mathrm{d}Q}{\mathrm{d}T} \tag{8.189}$$

is called the *Thomson heat*. Thomson heat depends both on the type of metal and the magnitude and direction of the electric current, I.

8.9
Superfluid Hydrodynamics

We can derive hydrodynamic equations for liquid He^4 below the λ line where it is a superfluid (see Section 4.6.1). We assume that the superfluid is composed of two interpenetrating fluids: (1) a normal fluid that behaves somewhat like a classical fluid and has velocity $\boldsymbol{v}_{\mathrm{n}}$ in the laboratory frame and (2) a superfluid which carries no entropy and has velocity $\boldsymbol{v}_{\mathrm{s}}$ in the laboratory frame. We shall first obtain the hydrodynamic equations for the superfluid and then obtain dispersion relations for sound modes [52, 107, 131, 176].

8.9.1
Superfluid Hydrodynamic Equations

The mass balance (mass conservation) equation for the superfluid is given by

$$\frac{\partial \rho}{\partial t} + \nabla_r \cdot \boldsymbol{J} = 0\,, \tag{8.190}$$

where ρ is the total mass density and $\boldsymbol{J}$ is the total momentum density of the fluid. The total mass density can be written $\rho = \rho_{\mathrm{n}} + \rho_{\mathrm{s}}$, where ρ_{n} is the mass density of the normal fluid and ρ_{s} is the mass density of the superfluid. The momentum density of the fluid can be written $\boldsymbol{J} = \rho_{\mathrm{n}}\boldsymbol{v}_{\mathrm{n}} + \rho_{\mathrm{s}}\boldsymbol{v}_{\mathrm{s}}$, where $\boldsymbol{v}_{\mathrm{n}}$ is the normal fluid velocity and $\boldsymbol{v}_{\mathrm{s}}$ is the superfluid velocity. The superfluid and normal fluid phases cannot be separated in configuration space. The superfluid phase results from the condensation of part of the substance into a single quantum state.

The momentum balance equation is

$$\frac{\partial \boldsymbol{J}}{\partial t} + \nabla_r P + \nabla_r \cdot \bar{\bar{\boldsymbol{\Pi}}}^{\mathrm{R}} + \nabla_r \cdot \overline{\overline{\boldsymbol{\Pi}}}^{\mathrm{D}} = 0\,, \tag{8.191}$$

where P is the hydrostatic pressure, $\bar{\bar{\boldsymbol{\Pi}}}^{\mathrm{R}}$ is a reversible part of the stress tensor (momentum current), and $\overline{\overline{\Pi}}^{\mathrm{D}}$ is the dissipative part.

The energy balance equation is

$$\frac{\partial U}{\partial t} + \nabla_r \cdot \left(\boldsymbol{J}_E^{\mathrm{R}} + \boldsymbol{J}_E^{\mathrm{D}}\right) = 0\,, \tag{8.192}$$

where $\boldsymbol{J}_E^{\mathrm{R}}$ and $\boldsymbol{J}_E^{\mathrm{D}}$ are the reversible and dissipative energy currents.

The entropy balance equation is

$$\frac{\partial \rho s}{\partial t} + \nabla_r \cdot \left(\rho s \boldsymbol{v}_\mathrm{n} + \boldsymbol{J}_S^\mathrm{D}\right) = \sigma_\mathrm{s} , \tag{8.193}$$

where s is the specific entropy, $\rho s \boldsymbol{v}_\mathrm{n}$ is the reversible entropy current, $\boldsymbol{J}_S^\mathrm{D}$ is the dissipative entropy current, and σ_s is the entropy production. The reversible entropy current only depends on the normal fluid velocity, $\boldsymbol{v}_\mathrm{n}$, because the superfluid does not carry entropy.

If different regions of a superfluid are connected such that only superfluid can flow between them, they will be in equilibrium (no super fluid flow) when their chemical potentials are equal, even if they do not have the same temperature and pressure (see Eq. (4.47)). Superfluid flow occurs when the chemical potentials are not equal. Thus, we can assume that changes in the superfluid velocity are driven by gradients in the chemical potential and we can write

$$\frac{\mathrm{d}\boldsymbol{v}_\mathrm{s}}{\mathrm{d}t} = \frac{\partial \boldsymbol{v}_\mathrm{s}}{\partial t} + (\boldsymbol{v}_\mathrm{s} \cdot \nabla_r)\boldsymbol{v}_\mathrm{s} = -\nabla_r(\mu^\mathrm{R} + \mu^\mathrm{D}) , \tag{8.194}$$

where $\mathrm{d}\boldsymbol{v}_\mathrm{s}/\mathrm{d}t$ is the convective time derivative of the superfluid, and μ^R and μ^D are reversible and dissipative contributions to the chemical potential, respectively.

It is useful to consider the fluid in the rest frame of the superfluid. Let E_0 denote the energy in the superfluid rest frame. Then differential changes in the energy are given by

$$\mathrm{d}E_0 = \mu\, \mathrm{d}\rho + T\, \mathrm{d}(\rho s) + \boldsymbol{w} \cdot \mathrm{d}\boldsymbol{J}_0 , \tag{8.195}$$

where $\boldsymbol{J}_0 = \boldsymbol{J} - \rho \boldsymbol{v}_\mathrm{s}$ is the momentum density of the fluid in the superfluid rest frame and $\boldsymbol{J}$ is the momentum density in the laboratory frame. The chemical potential is $\mu = (\partial E_0/\partial \rho)_{\rho s, \boldsymbol{J}_0}$. The temperature is $T = (\partial E_0/\partial \rho s)_{\rho, \boldsymbol{J}_0}$. The new quantity, $\boldsymbol{w}$, is a velocity which is defined $\boldsymbol{w} = (\partial E_0/\partial \boldsymbol{J}_0)_{\rho, \rho s}$.

The total energy, E, in the laboratory frame is related to the energy, E_0, in the rest frame of the fluid by a Galilean transformation

$$E = E_0 + \boldsymbol{v}_\mathrm{s} \cdot \boldsymbol{J}_0 + \frac{1}{2}\rho v_\mathrm{s}^2 = E_0 + \boldsymbol{v}_\mathrm{s} \cdot (\boldsymbol{J} - \rho \boldsymbol{v}_\mathrm{s}) + \frac{1}{2}\rho v_\mathrm{s}^2 . \tag{8.196}$$

In the discussion below, we shall consider the fluid to be a function of the variables, $\rho, \rho s, \boldsymbol{J}$, and $\boldsymbol{v}_\mathrm{s}$. From Eqs. (8.195) and (8.196), a differential change in energy, E, can be written

$$\mathrm{d}E = \left(\mu - \boldsymbol{w} \cdot \boldsymbol{v}_\mathrm{s} - \frac{1}{2}v_\mathrm{s}^2\right) \mathrm{d}\rho + T\, \mathrm{d}(\rho s) + (\boldsymbol{w} + \boldsymbol{v}_\mathrm{s}) \cdot \mathrm{d}\boldsymbol{J} + [\boldsymbol{J} - \rho(\boldsymbol{w} + \boldsymbol{v}_\mathrm{s})]\, \mathrm{d}\boldsymbol{v}_\mathrm{s} . \tag{8.197}$$

It is found experimentally that if the velocities of the fluid are too great the superfluid phase can be destroyed. Therefore, the superfluid equations are only useful for low velocities and we can neglect convective contributions to the hydrodynamic equations. As a first step we will reexpress Eq. (8.197) in terms of partial time derivatives rather than total time derivatives since total time derivatives contain contributions due to convection. Thus we write

$$\frac{\partial E}{\partial t} = \left(\mu - \boldsymbol{w}\cdot\boldsymbol{v}_{\mathrm{s}} - \frac{1}{2}v_{\mathrm{s}}^2\right)\frac{\partial \rho}{\partial t} + T\frac{\partial \rho s}{\partial t} + (\boldsymbol{w}+\boldsymbol{v}_{\mathrm{s}})\cdot\frac{\partial \boldsymbol{J}}{\partial t} + [\boldsymbol{J}-\rho(\boldsymbol{w}+\boldsymbol{v}_{\mathrm{s}})]\cdot\frac{\partial \boldsymbol{v}_{\mathrm{s}}}{\partial t}\,. \tag{8.198}$$

As a next step we will substitute the balance equations, Eqs. (8.190)–(8.194), into Eq. (8.198) and eliminate terms which are cubic in the velocity. This gives

$$\begin{aligned} T\frac{\partial \rho s}{\partial t} &= -\nabla_r\cdot\left(\boldsymbol{J}_E^{\mathrm{R}} + \boldsymbol{J}_E^{\mathrm{D}}\right) + \mu\nabla_r\cdot\boldsymbol{J} + (\boldsymbol{w}+\boldsymbol{v}_{\mathrm{s}})\cdot\nabla_r P + (\boldsymbol{w}+\boldsymbol{v}_{\mathrm{s}}) \\ &\quad \times\nabla_r\cdot\overline{\overline{\boldsymbol{\Pi}}}^{\mathrm{D}} + [\boldsymbol{J}-\rho(\boldsymbol{v}+\boldsymbol{w})]\cdot\nabla_r(\mu^{\mathrm{R}}+\mu^{\mathrm{D}})\,. \end{aligned} \tag{8.199}$$

The reversible stress tensor does not appear in Eq. (8.199) because it is a momentum current which is explicitly quadratic in the velocity and therefore leads to contributions in Eq. (8.199) which are cubic in the velocity.

Let us now write the Gibbs–Duhem equation in the superfluid rest frame,

$$\mathrm{d}P = \rho\,\mathrm{d}\mu + \rho s\,\mathrm{d}T + \boldsymbol{J}_0\cdot\mathrm{d}\boldsymbol{w}\,. \tag{8.200}$$

If we substitute the Gibbs–Duhem equation (8.200) into Eq. (8.199) and neglect terms cubic in the velocity, we obtain

$$\begin{aligned} T\frac{\partial \rho s}{\partial t} &= -\nabla_r\cdot\left[\boldsymbol{J}_E^{\mathrm{R}} + \boldsymbol{J}_E^{\mathrm{D}} - \mu\boldsymbol{J} - (\boldsymbol{w}+\boldsymbol{v}_{\mathrm{s}})\cdot\overline{\overline{\boldsymbol{\Pi}}}^{\mathrm{D}}\right] + (\boldsymbol{J}-\rho(\boldsymbol{v}_{\mathrm{s}}+\boldsymbol{w})\cdot\nabla_r(\mu^{\mathrm{R}}-\mu) \\ &\quad + [\boldsymbol{J}-\rho(\boldsymbol{v}_{\mathrm{s}}+\boldsymbol{w})]\cdot\nabla_r\mu^{\mathrm{D}} + \rho s(\boldsymbol{v}_{\mathrm{s}}+\boldsymbol{w})\cdot\nabla_r T - \overline{\overline{\boldsymbol{\Pi}}}^{\mathrm{D}} : \nabla_r(\boldsymbol{v}_{\mathrm{s}}+\boldsymbol{w})\,. \end{aligned} \tag{8.201}$$

There is one final step necessary to put the entropy balance equation into the form Eq. (8.193). If we divide Eq. (8.201) by T and rearrange terms, we find

$$\begin{aligned} \frac{\partial \rho s}{\partial t} &= -\nabla_r\cdot\left[\frac{\boldsymbol{J}_E^{\mathrm{R}} + \boldsymbol{J}_E^{\mathrm{D}} - \mu\boldsymbol{J} - (\boldsymbol{w}+\boldsymbol{v}_{\mathrm{s}})\cdot\overline{\overline{\boldsymbol{\Pi}}}^{\mathrm{D}} - \mu^{\mathrm{D}}\boldsymbol{\lambda}}{T}\right] \\ &\quad + \left[\boldsymbol{J}_E^{\mathrm{R}} + \boldsymbol{J}_E^{\mathrm{D}} - \mu\boldsymbol{J} - (\boldsymbol{w}+\boldsymbol{v}_{\mathrm{s}})\cdot\overline{\overline{\boldsymbol{\Pi}}}^{\mathrm{D}} - \rho s T(\boldsymbol{w}+\boldsymbol{v}_{\mathrm{s}}) - \mu^{\mathrm{D}}\boldsymbol{\lambda}\right]\cdot\nabla_r\frac{1}{T} \\ &\quad + \frac{1}{T}\boldsymbol{\lambda}\cdot\nabla_r(\mu^{\mathrm{R}}-\tilde{\mu}) - \frac{\mu^{\mathrm{D}}}{T}\nabla_r\cdot\boldsymbol{\lambda} - \frac{1}{T}\overline{\overline{\boldsymbol{\Pi}}}^{\mathrm{D}} : \nabla_r(\boldsymbol{w}+\boldsymbol{v}_{\mathrm{s}})\,. \end{aligned} \tag{8.202}$$

To obtain Eq. (8.202), we have used the fact that

$$\frac{1}{T}[\boldsymbol{J}-\rho(\boldsymbol{v}_{\mathrm{s}}+\boldsymbol{w})]\cdot\nabla_r\mu^{\mathrm{D}} = \nabla_r\cdot\frac{\mu^{\mathrm{D}}\boldsymbol{\lambda}}{T} - \frac{\mu^{\mathrm{D}}}{T}\nabla_r\cdot\boldsymbol{\lambda} - \mu^{\mathrm{D}}\boldsymbol{\lambda}\cdot\nabla_r\frac{1}{T}\,, \tag{8.203}$$

where $\boldsymbol{\lambda} = \boldsymbol{J} - \rho(\boldsymbol{v}_{\mathrm{s}} + \boldsymbol{w})$. Equation (8.202) can be simplified further if we first consider the case of a reversible fluid. The fact that the entropy production must be zero for a reversible fluid allows us to give a more precise definition of the reversible currents.

In a reversible fluid, all the dissipative contributions in Eq. (8.202) are zero. The equation for a reversible fluid is then

$$\frac{\partial \rho s}{\partial t} = -\nabla_{\boldsymbol{r}} \cdot \left(\frac{\boldsymbol{J}_E^{\mathrm{R}} - \mu \boldsymbol{J}}{T} \right) + \left[\boldsymbol{J}_E^{\mathrm{R}} - \mu \boldsymbol{J} - \rho s T(\boldsymbol{w} + \boldsymbol{v}_{\mathrm{s}}) \right] \cdot \nabla_{\boldsymbol{r}} \frac{1}{T} + \frac{1}{T} \boldsymbol{\lambda} \cdot \nabla_r (\mu^{\mathrm{R}} - \mu) . \tag{8.204}$$

A reversible fluid, by definition, has no entropy production. This, in turn, means that the reversible energy current must be given by

$$\boldsymbol{J}_E^{\mathrm{R}} = \mu \boldsymbol{J} + \rho s T(\boldsymbol{w} + \boldsymbol{v}_{\mathrm{s}}) , \tag{8.205}$$

and the reversible entropy current is given by

$$\boldsymbol{J}_S^{\mathrm{R}} = \frac{1}{T} \left(\boldsymbol{J}_E^{\mathrm{R}} - \mu \boldsymbol{J} \right) = \rho s (\boldsymbol{w} + \boldsymbol{v}_{\mathrm{s}}) . \tag{8.206}$$

However, the superfluid can't carry entropy so we must have $\boldsymbol{J}_S^{\mathrm{R}} = \rho s \boldsymbol{v}_{\mathrm{n}}$, and this in turn means that

$$\boldsymbol{w} = \boldsymbol{v}_{\mathrm{n}} - \boldsymbol{v}_{\mathrm{s}} . \tag{8.207}$$

Also, $\mu^{\mathrm{R}} = \mu$, so the reversible part of the chemical potential is just the thermodynamic chemical potential. The quantity μ^{D} is a contribution to the chemical potential due to dissipative processes. We can write the equation for the dissipative fluid as

$$\frac{\partial \rho s}{\partial t} = -\nabla_{\boldsymbol{r}} \cdot \left(\rho s \boldsymbol{v}_{\mathrm{n}} + \boldsymbol{J}_S^{\mathrm{D}} \right) - \frac{1}{T} \boldsymbol{J}_S^{\mathrm{D}} \cdot \nabla_r T - \frac{\mu^{\mathrm{D}}}{T} \nabla_r \cdot \boldsymbol{\lambda} - \frac{1}{T} \overline{\boldsymbol{\Pi}}^{\mathrm{D}} : \nabla_{\boldsymbol{r}} \boldsymbol{v}_{\mathrm{s}} , \tag{8.208}$$

where $\boldsymbol{J}_S^{\mathrm{D}} = (\boldsymbol{J}_E^{\mathrm{D}} - \boldsymbol{v}_{\mathrm{n}} \cdot \bar{\boldsymbol{\Pi}}^{\mathrm{D}} - \mu^{\mathrm{D}} \boldsymbol{\lambda})/T$ and $\boldsymbol{\lambda} = \boldsymbol{J} - \rho \boldsymbol{v}_{\mathrm{n}}$.

Let us now write the generalized Ohm's laws for the superfluid. There are two scalar forces, namely, $\nabla_r \cdot \boldsymbol{\lambda}$ and $\nabla_r \cdot \boldsymbol{v}_{\mathrm{n}}$. There is one vector force, $\nabla_r T$, and one symmetric tensor force, $(\nabla_r \boldsymbol{v}_{\mathrm{n}})^{\mathrm{s}}$. We therefore can write

$$\begin{aligned} \Pi^{\mathrm{D}} &= -\zeta_1 \nabla_r \cdot \boldsymbol{\lambda} - \zeta_2 \nabla_r \cdot \boldsymbol{v}_{\mathrm{n}} , \\ \mu^{\mathrm{D}} &= -\zeta_3 \nabla_r \cdot \boldsymbol{\lambda} - \zeta_4 \nabla_r \cdot \boldsymbol{v}_{\mathrm{n}} , \\ \boldsymbol{J}_S^{\mathrm{D}} &= -\frac{K}{T} \nabla_r T , \end{aligned}$$

and

$$(\overline{\boldsymbol{\Pi}}^{\mathrm{D}})^{\mathrm{s}} = -\eta (\nabla_r \boldsymbol{v}_{\mathrm{n}})^{\mathrm{s}} . \tag{8.209}$$

The superfluid has six transport coefficients. From Onsager's relations we have $\zeta_1 = \zeta_4$.

8.9.2
Sound Modes

We now obtain dispersion relations for the various types of sound modes in the absence of dissipation. To obtain sound modes in the nondissipative case, we set all dissipative currents to zero in Eqs. (8.190), (8.191), (8.193), and (8.194) and we linearize about absolute equilibrium. We write $\rho = \rho_0 + \Delta\rho$, $s = s_0 + \Delta s$, $P = P_0 + \Delta P$, where ρ_0, s_0, and P_0 denote the equilibrium density, entropy, and pressure, respectively, and $\Delta\rho = \Delta\rho(\boldsymbol{r}, t)$, $\Delta s = \Delta s(\boldsymbol{r}, t)$, and $\Delta P = \Delta P(\boldsymbol{r}, t)$ denote their deviations from equilibrium. We also neglect all terms to second order in the velocities, $\boldsymbol{v}_\mathrm{n}$ and $\boldsymbol{v}_\mathrm{s}$. The hydrodynamic equations then take the form

$$\frac{\partial \Delta\rho}{\partial t} + \rho_\mathrm{n}^0 \nabla_r \cdot \boldsymbol{v}_\mathrm{n} + \rho_\mathrm{s}^0 \nabla_r \cdot \boldsymbol{v}_\mathrm{s} = 0\,, \tag{8.210}$$

$$\rho_\mathrm{n}^0 \frac{\partial \boldsymbol{v}_\mathrm{n}}{\partial t} + \rho_\mathrm{s}^0 \frac{\partial \boldsymbol{v}_\mathrm{s}}{\partial t} + \nabla_r \Delta P = 0\,, \tag{8.211}$$

$$\rho^0 \frac{\partial \Delta s}{\partial t} + s^0 \frac{\partial \Delta\rho}{\partial t} + \rho^0 s^0 \nabla_r \cdot \boldsymbol{v}_\mathrm{n} = 0\,, \tag{8.212}$$

and

$$\frac{\partial \boldsymbol{v}_\mathrm{s}}{\partial t} + \nabla_r \Delta\mu = 0\,. \tag{8.213}$$

Let us now choose the density and temperature to be our independent thermodynamic variables. Equations (8.210)–(8.213) then become

$$\frac{\partial \Delta\rho}{\partial t} + \rho_\mathrm{n}^0 \nabla_r \cdot \boldsymbol{v}_\mathrm{n} + \rho_\mathrm{s}^0 \nabla_r \cdot \boldsymbol{v}_\mathrm{s} = 0\,, \tag{8.214}$$

$$\rho_\mathrm{n}^0 \frac{\partial \boldsymbol{v}_\mathrm{n}}{\partial t} + \rho_\mathrm{s}^0 \frac{\partial \boldsymbol{v}_\mathrm{s}}{\partial t} + \frac{1}{\rho\kappa_T} \nabla_r \Delta\rho + \left(\frac{\partial P}{\partial T}\right)_\rho^0 \nabla_r \Delta T = 0\,, \tag{8.215}$$

$$\left[s^0 - \frac{1}{\rho^0}\left(\frac{\partial P}{\partial T}\right)_\rho^0\right] \frac{\partial \Delta\rho}{\partial t} + \frac{\rho^0 c_\rho}{T^0} \frac{\partial \Delta T}{\partial t} + \rho^0 s^0 \nabla_r \cdot \boldsymbol{v}_\mathrm{n} = 0\,, \tag{8.216}$$

and

$$\frac{\partial \boldsymbol{v}_\mathrm{s}}{\partial t} + \frac{1}{(\rho^0)^2 \kappa_T} \nabla \Delta\rho - \left[s^0 - \frac{1}{\rho}\left(\frac{\partial P}{\partial T}\right)_\rho^0\right] \nabla \Delta T = 0\,. \tag{8.217}$$

In Eqs. (8.214)–(8.217), we have used the fact that the isothermal compressibility is defined as $\kappa_T = 1/\rho(\partial\rho/\partial P)_T$ and the specific heat is defined $c_\rho = T(\partial s/\partial T)_\rho$. Also $s = -(\partial\tilde{\mu}/\partial T)_P$ and $1/\rho = (\partial\mu/\partial P)_T$, so that $(\partial\mu/\partial T)_\rho = (\partial\mu/\partial T)_P + (\partial\mu/\partial P)_T(\partial P/\partial T)_\rho$ and $(\partial\mu/\partial\rho)_T = (\partial\mu/\partial P)_T(\partial P/\partial\rho)_T = 1/(\rho^2\kappa_T)$.

Equations (8.214)–(8.217) enable us to obtain the dispersion relations for the various types of sound that can exist in an ideal superfluid system. Let us Laplace transform the time-dependent part of the above equations and Fourier transform the space-dependent part. If we note that all contributions from the normal and superfluid velocities are longitudinal, we can write the Fourier–Laplace transform of Eqs. (8.214)–(8.217) in the following matrix form:

$$\begin{pmatrix} z & 0 & -\mathrm{i}k\rho_{\mathrm{n}}^0 & -\mathrm{i}k\rho_{\mathrm{s}}^0 \\ z\left[s^0 - \frac{1}{\rho^0}\left(\frac{\partial P}{\partial T}\right)_{\rho}^{0}\right] & z\frac{\rho^0 c_{\rho}}{T^0} & -\mathrm{i}k\rho^0 s^0 & 0 \\ -\frac{\mathrm{i}k}{\rho^0 \kappa_T} & -\mathrm{i}k\left(\frac{\partial P}{\partial T}\right)_{\rho}^{0} & \rho_{\mathrm{n}}^0 z & \rho_{\mathrm{s}}^0 z \\ -\mathrm{i}\frac{k}{(\rho^0)^2 \kappa_T} & \mathrm{i}k\left[s^0 - \frac{1}{\rho^0}\left(\frac{\partial P}{\partial T}\right)_{\rho^0}\right] & 0 & z \end{pmatrix} \begin{pmatrix} \tilde{\rho}(\boldsymbol{k}, z) \\ \tilde{T}(\boldsymbol{k}, z) \\ \tilde{v}_{\mathrm{n}}(\boldsymbol{k}, z) \\ \tilde{v}_{\mathrm{s}}(\boldsymbol{k}, z) \end{pmatrix}$$

$$= \begin{pmatrix} 1 & 0 & 0 & 0 \\ \left[s^0 - \frac{1}{\rho^0}\left(\frac{\partial P}{\partial T}\right)_{\rho}^{0}\right] & \frac{\rho^0 c_{\rho}}{T} & 0 & 0 \\ 0 & 0 & \rho_{\mathrm{n}}^0 & \rho_{\mathrm{s}}^0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \Delta\rho(\boldsymbol{k}, 0) \\ \Delta T(\boldsymbol{k}, 0) \\ v_n(\boldsymbol{k}, 0) \\ v_{\mathrm{s}}(\boldsymbol{k}, 0) \end{pmatrix} . \tag{8.218}$$

The determinant of the 4×4 matrix,

$$\overline{\boldsymbol{S}}(\boldsymbol{k}, z) = \begin{pmatrix} z & 0 & -\mathrm{i}k\rho_{\mathrm{n}}^0 & -\mathrm{i}k\rho_{\mathrm{s}}^0 \\ z\left[s^0 - \frac{1}{\rho^0}\left(\frac{\partial P}{\partial T}\right)_{\rho}^{0}\right] & z\frac{\rho^0 c_{\rho}}{T^0} & -\mathrm{i}k\rho^0 s^0 & 0 \\ -\frac{\mathrm{i}k}{\rho^0 \kappa_T} & -\mathrm{i}k\left(\frac{\partial P}{\partial T}\right)_{\rho}^{0} & \rho_{\mathrm{n}}^0 z & \rho_{\mathrm{n}}^0 z \\ -\frac{k}{(\rho^0)^2 \kappa_T} & \mathrm{i}k\left[s^0 - \frac{1}{\rho^0}\left(\frac{\partial P}{\partial T}\right)_{\rho}^{0}\right] & 0 & z \end{pmatrix} , \tag{8.219}$$

gives the dispersion relation for sound modes in the fluid. The sound frequencies occur at values of z which satisfy the equation

$$\mathrm{Det}[\overline{\boldsymbol{S}}(\boldsymbol{k}, z)] = -\frac{\rho^0 \rho_{\mathrm{n}}^0 \tilde{c}_{\rho}}{T^0} \left\{ z^4 + \left(\frac{1}{\rho^0 \kappa_T} + \frac{T^0 (s^0)^2 \rho_{\mathrm{s}}^0}{\tilde{c}_{\rho} \rho_{\mathrm{n}}^0} + \frac{T^0}{\tilde{c}_{\rho} (\rho^0)^2} \left[\left(\frac{\partial P}{\partial T} \right)_{\rho}^{0} \right]^2 \right) \right.$$
$$\left. \times k^2 z^2 + \frac{T^0 \rho_{\mathrm{s}}^0 (s^0)^2}{\rho^0 \rho_{\mathrm{n}}^0 \tilde{c}_{\rho} \kappa_T} k^4 \right\} = 0 \, . \tag{8.220}$$

We can simplify the dispersion relation somewhat because the thermal expansivity, α_P, for liquid helium is very small, at least for temperatures well below the transition temperature. This can also be seen in Figure 4.10a. For low enough temperature, the slope, $(\partial P/\partial T)_{\rho}$ is approximately zero. Thus, to good approximation

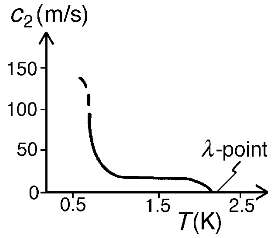

Figure 8.10 Speed of second sound (based on [44]).

we can set

$$\alpha_P = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_P = \kappa_T \left(\frac{\partial P}{\partial T}\right)_\rho \approx 0\,. \tag{8.221}$$

The dispersion relation then simplifies to

$$\begin{aligned} \mathrm{Det}[\bar{\boldsymbol{S}}(\boldsymbol{k}, z)] &\approx -\frac{\rho^0\rho^0_{\mathrm{n}}\tilde{c}_\rho}{T^0}\left\{z^4 + \left(\frac{1}{\rho^0\kappa_T} + \frac{T^0(s^0)^2\rho^0_{\mathrm{s}}}{\tilde{c}_\rho\rho^0_{\mathrm{n}}}\right)k^2z^2 + \frac{T^0\rho^0_{\mathrm{s}}(s^0)^2}{\rho^0\rho^0_{\mathrm{n}}\tilde{c}_\rho\kappa_T}k^4\right\} \\ &= -\frac{\rho^0\rho^0_{\mathrm{n}}\tilde{c}_\rho}{T^0}\left(z^2 + \frac{1}{\rho^0\kappa_T}k^2\right)\left(z^2 + \frac{T^0\rho^0_{\mathrm{s}}(s^0)^2}{\rho^0_{\mathrm{n}}\tilde{c}_\rho}k^2\right) = 0\,. \end{aligned} \tag{8.222}$$

We see from Eq. (8.222) that there are two different types of propagating sound modes in He(II). They are called *first sound* and *second sound*, respectively.

First sound has a dispersion relation, $z = \pm \mathrm{i}c_1 k$, and propagates with speed

$$c_1 = \sqrt{\frac{1}{\rho^0\kappa_T}}\,. \tag{8.223}$$

First sound consists of density waves, similar to sound modes in classical fluids, with one difference. The speed of first sound depends on the isothermal compressibility, while the speed of ordinary sound in classical fluids depends on the adiabatic compressibility. Note that Eq. (8.223) assumes that $(\partial P/\partial T)_\rho \approx 0$.

Second sound has a dispersion relation $z = \pm \mathrm{i}c_2 k$ and propagates with a speed

$$c_2 = \sqrt{\frac{\rho^0_{\mathrm{s}}(s^0)^2T^0}{\tilde{c}_\rho\rho^0_{\mathrm{n}}}}\,. \tag{8.224}$$

Second sound consists of temperature waves which can propagate across the fluid. It was first measured by Peshkov [165], who used an oscillating heat source to set up standing waves in a tube. A plot of the speed of second sound as a function of temperature is given in Figure 8.10. We see that the velocity first peaks at 20.36 m s^{-1} at $T = 1.65$ K and decreases slightly as we lower the temperature, but then increases again and reaches a limiting value of about 150 m s^{-1} at $T = 0$ K.

Measurements of the speed of second sound enable us to obtain a value of the ratio ρ_n^0/ρ^0. If we remember that $\rho = \rho_\mathrm{n}^0 + \rho_\mathrm{s}^0$, Eq. (8.224) takes the form

$$\frac{\rho_\mathrm{n}^0}{\rho^0} = \frac{T^0(s^0)^2}{\tilde{c}_\rho c_2^2 + T^0(s^0)^2} \,. \tag{8.225}$$

From Eq. (8.225), estimates of the hydrodynamic density of the normal fluid can be obtained. Another form of sound occurs when He(II) flows through a porous material. It is called *fourth sound*. Derivation of the dispersion relation of fourth sound is left as a homework problem.

8.10
Problems

Problem 8.1 Prove that

$$\nabla_r \cdot \overline{\Pi} = -\eta \nabla_r^2 \boldsymbol{v} - \left(\zeta + \frac{1}{3}\eta\right) \nabla_r(\nabla_r \cdot \boldsymbol{v}) \tag{8.226}$$

if $\overline{\Pi}^\mathrm{s} = -2\eta[\nabla_r \boldsymbol{v}]^\mathrm{s}$ and $\Pi = -\zeta(\nabla_r \cdot \boldsymbol{v})$ with $\overline{\Pi} = \Pi\overline{\boldsymbol{U}} + \overline{\Pi}^\mathrm{s}$. Note that $\overline{\boldsymbol{U}}$ is the unit tensor.

Problem 8.2 Assume that a viscous fluid flows in a pipe with a circular cross section of radius a. Choose the z-axis to be the direction of motion of the fluid. Assume that the density of the fluid is constant and that the flow is steady. Starting from the hydrodynamic equations, find the equation relating pressure gradients to velocity gradients in the fluid. Describe what is happening in the pipe. (*Note*: For steady flow, the velocity is independent of time, but can vary in space. At the walls the velocity is zero due to friction.)

Problem 8.3 Consider an ideal fluid. Assume that at time $t = 0$ the Fourier amplitudes of the density, velocity, and temperature variations are given by $\rho_{\boldsymbol{k}}(0)$, $\boldsymbol{v}_{\boldsymbol{k}}(0)$, and $T_{\boldsymbol{k}}(0)$, respectively. Compute $\rho_{\boldsymbol{k}}(t)$, $\boldsymbol{v}_{\boldsymbol{k}}(t)$, and $T_{\boldsymbol{k}}(t)$.

Problem 8.4 Consider a fluid of point particles. Assume that at time $t = 0$ the Fourier amplitudes of the coupled longitudinal density, velocity, and temperature variations are given by $\rho_{\boldsymbol{k}}(0)$, $v_{\boldsymbol{k}}^{\parallel}(0)$, and $T_{\boldsymbol{k}}(0)$. Compute $\rho_{\boldsymbol{k}}(t)$, $v_{\boldsymbol{k}}^{\parallel}(t)$, and $T_{\boldsymbol{k}}(t)$, but only keep terms in the amplitudes which are zeroth order in the wavevector, k.

Problem 8.5 Consider an isotropic fluid whose deviation from equilibrium can be described by the linearized Navier–Stokes equations. Assume that at time $t = 0$ the velocity is $\boldsymbol{v}(\boldsymbol{r}, 0) = v_0 \mathrm{e}^{-ar^2}\hat{\boldsymbol{z}}$. Compute $\boldsymbol{v}_{\boldsymbol{k}}^{\perp}(t)$, where $\boldsymbol{v}_{\boldsymbol{k}}^{\perp}(t) = \boldsymbol{v}_{\boldsymbol{k}}(t) - \hat{\boldsymbol{k}} v_{\boldsymbol{k}}^{\parallel}(t)$ and $\boldsymbol{v}_{\boldsymbol{k}}(t)$ is the Fourier transform of $\boldsymbol{v}(\boldsymbol{r}, t)$.

Problem 8.6 Consider an incompressible fluid that is at rest. (a) Starting from the linearized Navier–Stokes equations, derive a closed equation for space-time variations of temperature $\Delta T(\boldsymbol{r}, t)$ in the fluid. (b) If a laser pulse creates a temperature spike $\Delta T(\boldsymbol{r}, 0) = \tau_0 \delta(\boldsymbol{r})$ at point $\boldsymbol{r} = 0$ and time $t = 0$, what is the temperature distribution $\Delta T \boldsymbol{r}, t)$ at time t? (Assume that there are no walls to constrain the fluid). Fourier transform of $\boldsymbol{v}(\boldsymbol{r}, t)$.

Problem 8.7 In an ideal fluid, sound propagation is adiabatic because entropy is constant. Nonideal fluids with very high thermal conductivity K can have a different kind of sound propagation, called isothermal sound. In such fluids, the viscosity can be neglected but the thermal conductivity cannot. (a) Starting from the linearized Navier–Stokes equations, compute the coupled equations for temperature and pressure variations (in space and time) in a non ideal with very large thermal conductivity. (b) Compute the dispersion relation for this type of wave propagation. Write the dispersion relation interns of the speed of adiabatic sound $c_S = \sqrt{(\partial P/\partial \rho)_S}$, the speed of isothermal sound $c_T = \sqrt{(\partial P/\partial \rho)_T}$, the constant pressure heat capacity C_P, and the thermal conductivity K.

Problem 8.8 Consider an isotropic fluid contained in a rectangular box with sides of length $L_x = L$, $L_y = 2L$, and $L_z = 3L$. Assume that the temperature of the fluid at time $t = 0$ has a distribution $T(\boldsymbol{r}, 0)$, but the fluid is initially at rest. Assume that the thermal expansivity of the fluid is very small so that coupling to pressure variations can be neglected. (a) Show that under these conditions the temperature variations satisfy the heat equation, $\partial T(\boldsymbol{r}, t)/\partial t = -\kappa \nabla^2 T(\boldsymbol{r}, t)$. What is κ? (b) If the walls of the box conduct heat and are maintained at temperature, T_0, approximately how long does it take for the system to reach equilibrium. (c) If the walls of the box are insulators, approximately how long does it take for the system to reach equilibrium? (*Hint*: No heat currents flow through the walls of insulators.)

Problem 8.9 At time $t = 0$, water flows in the z-direction between straight parallel walls which are located at $x = 0$ and $x = D = 0.05$ m in the x-direction. The velocity profile at time $t = 0$ is of the form $\boldsymbol{v}(x, y, z, 0) = v_z(x)\hat{\boldsymbol{e}}_z$ and the velocity at the walls is zero so $v_z(0) = v_z(D) = 0$. The shear viscosity of water is $\eta = 3.33 \times 10^{-3}\ \mathrm{N\,s\,m^{-2}}$. The thermal conductivity of water is $K = 0.56\ \mathrm{J/(s\,m\,K)}$. The density of water is $\rho = 10^3\ \mathrm{kg\,m^{-3}}$. Approximately how long does it take for this flow to damp out (what is the decay time)? (Assume that $v_z(x)$ is small enough that the linearized hydrodynamic equations can be used.)

Problem 8.10 Consider an isotropic fluid of point particles. (a) Write the dyatic, $\nabla_r \boldsymbol{v}$, in spherical coordinates. (b) Use your results in (a) to write the stress tensor in spherical coordinates.

Problem 8.11 Compute corrections of order k to the spectral density function of an isotropic fluid of point particles. Estimate the size of these corrections relative to the dominant terms in a light scattering experiment.

Problem 8.12 A monatomic fluid of point particles, of mass m, at time $t = 0$ has a *transverse* average velocity $\boldsymbol{v}_\perp(\boldsymbol{r}, 0) = v_0 \hat{\boldsymbol{z}} \mathrm{e}^{-ax^2}$. (a) Compute the average velocity $\boldsymbol{v}_{\perp}(\boldsymbol{r}, t)$ at time t. (b) Compute the velocity autocorrelation function,

$$C_{\boldsymbol{v}_{\perp},\boldsymbol{v}_{\perp}}(\boldsymbol{q}, T) = \int \mathrm{d}\boldsymbol{r} \langle \boldsymbol{v}_{\perp}(\boldsymbol{r}+\boldsymbol{q}, t)\boldsymbol{v}_{\perp}(\boldsymbol{r}, 0)\rangle_T ,$$

where $\langle v_0^2 \rangle = k_{\mathrm{B}} T/m$. (*Note*: Do all integrations and find an explicit expression).

Problem 8.13 A fixed smooth hard sphere of radius a experiences a drag force $\boldsymbol{F}$ due to the fluid flowing over its surface with a steady velocity $\boldsymbol{u} = u\hat{\boldsymbol{e}}_z$. The drag force is given by $\boldsymbol{F} = \int \mathrm{d}\boldsymbol{S} \cdot \boldsymbol{P}$, where $\mathrm{d}\boldsymbol{S}$ is the surface area element $\mathrm{d}\boldsymbol{S} = \hat{\boldsymbol{e}}_r a^2 \sin(\theta)\,\mathrm{d}\theta\,\mathrm{d}\phi$ perpendicular to the surface of the sphere and $\boldsymbol{P}$ is the pressure tensor. The fact that the surface is smooth means that no force tangent to its surface can be exerted on it so $\hat{\boldsymbol{e}}_r \times [\hat{\boldsymbol{e}}_r \cdot \boldsymbol{\Pi}] = 0$. Also, since the sphere is hard and at rest, the normal component of the fluid at the surface of the sphere $\hat{\boldsymbol{e}}_r \cdot \boldsymbol{v}(r, \theta) = 0$. Compute the drag force $\boldsymbol{F}$ (Stokes friction) on the sphere.

Problem 8.14 A rough spherical particle, of radius R, is immersed in an incompressible fluid. The particle spins with constant angular velocity $\boldsymbol{\Omega} = \Omega\hat{\boldsymbol{e}}_z$, about the z-axis, so at its surface the particle has velocity $\boldsymbol{v}(R) = \boldsymbol{\Omega} \times \boldsymbol{R} = \Omega R \sin\theta \hat{\boldsymbol{e}}_{\varphi}$. The fluid is at rest, except for the local disturbance created by the spinning particle. Compute the torque on the particle due to the surrounding fluid. (*Hint*: Follow the procedure in Section 8.5, but for the case $\omega = 0$. Write the axial vector as $\boldsymbol{A} = g(r)\boldsymbol{\Omega}$ and show that the hydrostatic pressure is zero, so that $\boldsymbol{\nabla}_{\boldsymbol{r}}(\nabla_{\boldsymbol{r}}^2 g(r)) = 0$. Solve for $g(r)$. The torque on the particle is given by $\boldsymbol{\tau} = -\int \mathrm{d}\boldsymbol{S} \cdot \boldsymbol{P} \times \boldsymbol{r}$, where $\boldsymbol{P}$ is the pressure tensor.)

Problem 8.15 The entropy production, σ, in a thermocouple can be written

$$T\sigma = -\boldsymbol{J}_S \cdot \nabla_r T - \boldsymbol{I} \cdot \left(\nabla_r \frac{\mu_{\mathrm{el}}}{\boldsymbol{F}} - \boldsymbol{F}\boldsymbol{E}\right) ,$$

where $\boldsymbol{J}_S$ is the entropy current, $\boldsymbol{I}$ is the current carried by the electrons, F is Faraday's constant, $\boldsymbol{E}$ is the electric field in the metal wires, and μ_{el} is the chemical potential of the electrons. The balance equation for the entropy/volume, s, is $\partial s/\partial t = -\nabla \cdot \boldsymbol{J}_S + \sigma$. The generalized Ohm's laws can be written

$$\boldsymbol{J}_S = -\frac{\lambda}{T}\nabla_r T + \frac{\Gamma}{T}\boldsymbol{I} \quad \text{and} \quad \boldsymbol{E} - \nabla_r \frac{\mu_{\mathrm{el}}}{F} = -\zeta \nabla_r T + R\boldsymbol{I} ,$$

where λ is the coefficient of thermal conductivity at zero electrical current, R is the isothermal electrical resistance, ζ is the differential thermoelectric power, and Γ/T is the entropy transported per unit electric current. (a) Show that the Onsager relation, $L_{SE} = L_{ES}$, implies that $\Gamma = T\zeta$. (b) Show that the entropy balance equation can be written $\partial s/\partial t = \lambda/T\nabla_r^2(T) - \nabla_r \cdot \Gamma\boldsymbol{I}/T + RI^2/T$. The first term on the right is the entropy production due to thermal conductivity. The third term on the right is the entropy production due to Joule heating. The second term on the right is the entropy production due to the Peltier and Thomson effects.

Problem 8.16 Consider the thermocouple shown in Figure 8.4. Replace the potentiometer with a capacitor held at temperature T_0 with wire of metal B attached at points a and d. Show that

$$\frac{\Delta\phi_{\mathrm{ad}}}{\Delta T} = \zeta_{\mathrm{A}} - \zeta_{\mathrm{B}} ,$$

where $\Delta\phi_{\mathrm{ad}} = \phi_{\mathrm{a}} - \phi_{\mathrm{d}}$ is the potential difference across the capacitor and ζ_{A} and ζ_{B} are the differential thermoelectric powers in the two metals (cf. Problem 10.5). Note that in this circuit, there is no electric current.

Problem 8.17 The junction between two metal wires, A and B, in a thermocouple has a circular cross-sectional area, $\pi\rho^2$, where ρ is the radius of the wires. Assume that the transition between the two metals takes place smoothly over a distance, ΔL, so the transition region (the junction) has a volume, $\pi\rho^2\Delta L$. Assume that the temperature is uniform throughout the junction and that an electric current, $\boldsymbol{I}$, is flowing through the junction. From Problem 10.5 the entropy production, σ (entropy/volume · time), is given by

$$\sigma = -\nabla \cdot \frac{\Gamma \boldsymbol{I}}{T} + \frac{RI^2}{T} .$$

In the limit $\Delta L \to 0$, show that the Peltier heat, $\overline{\pi}$ which is just the entropy/(area · time · current) produced (or lost) in the junction, is given by $\overline{\pi} = \Gamma_{\mathrm{B}} - \Gamma_{\mathrm{A}}$.

Problem 8.18 Consider the flow of He(II) through a porous material. Only the superfluid can flow so $\boldsymbol{v}_{\mathrm{n}} = 0$. Also, the porous material exchanges momentum with fluid so that momentum is not conserved and the momentum balance equation cannot be used. Use the linearized nondissipative superfluid hydrodynamic equations to determine the dispersion relation for density oscillations (fourth sound). Show that fourth sound has a speed $c_4 = \sqrt{\rho_{\mathrm{n}}/\rho c_2^2 + \rho_{\mathrm{s}}/\rho c_1^2}$ where c_1 and c_2 are the speeds of first and second sound, respectively. Assume that $(\partial P/\partial T)_\rho = 0$.

Problem 8.19 Derive the wave equations for first sound and second sound in a nondissipative superfluid for the case when $(\partial P/\partial T)_\rho = 0$. Show that only second sound propagates when the momentum density is zero. Show that only first sound propagates when the super fluids and normal fluids move in phase so $\boldsymbol{v}_{\mathrm{n}} = \boldsymbol{v}_{\mathrm{s}}$.

9
Transport Coefficients

9.1
Introduction

Microscopic expressions for the transport coefficients for gases can be derived from kinetic theory. In this chapter, we first derive expressions for the coefficients of self-diffusion, shear viscosity, and thermal conductivity using the simplest possible mean free path arguments. Then to obtain a deeper understanding of transport phenomena, we will derive the transport coefficients from a more rigorous microscopic theory using a “kinetic equation” first derived by Boltzmann.

The Boltzmann equation works extremely well in providing numerical values for the transport coefficients in gases and, to this day, remains one of the great milestones in the history of statistical physics [19]. Much of this chapter is devoted to a study of the Boltzmann equation.

We will apply Boltzmann’s equation to the case of dilute gas containing a mixture of two types of particles which are distinguishable from one another. We will derive microscopic expressions for the coefficients of self-diffusion, shear viscosity, and thermal conductivity. The method we use was introduced by Resibois [184] to derive the transport coefficients in classical gases. It has also provided a simple and elegant way to derive microscopic expressions for transport coefficients in quantum gases [77], and even in Bose–Einstein condensates [78]. The method proceeds as follows. We first derive the linearized hydrodynamic equations from the linearized Boltzmann equation, introducing into them the transport coefficients, and we find the normal mode frequencies of the hydrodynamic equations in terms of the transport coefficients. We next find the hydrodynamic eigenfrequencies of the Boltzmann equation and match these to the normal mode frequencies of the hydrodynamic equations. This gives us the desired microscopic expressions for the transport coefficients.

A Modern Course in Statistical Physics, 4. Edition. Linda E. Reichl.

9.2
Elementary Transport Theory

Before we discuss the full microscopic theory of transport processes based on the Boltzmann equation, it is useful to derive the transport coefficients using very simple mean free path arguments [102, 169]. We will assume that the interaction is very short ranged compared to the mean free path. For a low density gas of N particles contained in a volume V, the interaction energy between particles is negligible compared to the kinetic energy of the particles. The normalized probability density, $F(\boldsymbol{v}_1)$, of finding a particle with velocity, $\boldsymbol{v}_1 \to \boldsymbol{v}_1 + \mathrm{d}\boldsymbol{v}_1$, where $\boldsymbol{v}_1 = \boldsymbol{p}_1/m$, is well described by the *Maxwell–Boltzmann distribution*,

$$F(\boldsymbol{v}_1) = \left(\frac{m\beta}{2\pi}\right)^{3/2} \exp\left(\frac{-\beta m v_1^2}{2}\right) , \tag{9.1}$$

which was derived in Section 5.3.

The Mean Free Path

The *mean free path*, λ, of a particle is the average distance it travels between collisions. We shall assume that collisions occur at random in the gas, so a particle has the same chance of collision in any interval of length $r \to r + \mathrm{d}r$. The average number of collisions per unit length is $1/\lambda$. The probability that a collision occurs in an interval $\mathrm{d}r$ is therefore $\mathrm{d}r/\lambda$.

Let $P_0(r)$ denote the probability that *no collision* occurs in an interval of length r. Then the probability that no collision occurs in an interval of length $r + \mathrm{d}r$ is

$$P_0(r + \mathrm{d}r) = P_0(r)\left(1 - \frac{\mathrm{d}r}{\lambda}\right) . \tag{9.2}$$

The factor $1 - \mathrm{d}r/\lambda$ is the probability that no collision occurs in interval $\mathrm{d}r$. We multiply $P_0(r)$ and $1 - \mathrm{d}r/\lambda$ together because the events “collision in length r” and “collision in length $\mathrm{d}r$” are independent. If we expand the left-hand side of Eq. (9.2) in a Taylor series, we obtain

$$\frac{\mathrm{d}}{\mathrm{d}r} P_0(r) = -\frac{1}{\lambda} P_0(r) \tag{9.3}$$

which has the solution

$$P_0(r) = \mathrm{e}^{-r/\lambda} . \tag{9.4}$$

The probability that no collision occurs in length of path r is a Poisson distribution. The probability that a particle suffers its first collision in an interval $r \to r + \mathrm{d}r$ is $P_0(r)\,\mathrm{d}r/\lambda$. The average distance traveled between collisions is

$$\langle r \rangle = \int_0^\infty r P_0(r) \frac{\mathrm{d}r}{\lambda} = \lambda , \tag{9.5}$$

which is just our original definition of the mean free path.

The Collision Frequency

Consider a gas which contains particles of types A and B. Particles A (B) have mass m_{A} (m_{B}), diameter d_{A} (d_{B}), and number density n_{A} (n_{B}). We assume that each type of particle is distributed uniformly in space but has a velocity distribution given by the Maxwell–Boltzmann distribution (9.1).

The average relative speed between particles A and B is given by

$$\langle v_{\mathrm{r}}\rangle_{\mathrm{AB}} \equiv \int \mathrm{d}\boldsymbol{v}_{\mathrm{A}} \int \mathrm{d}\boldsymbol{v}_{\mathrm{B}} F(\boldsymbol{v}_{\mathrm{A}}) F(\boldsymbol{v}_{\mathrm{B}}) |\boldsymbol{v}_{\mathrm{A}} - \boldsymbol{v}_{\mathrm{B}}| \,. \tag{9.6}$$

The center-of-mass velocity of particles A and B is $\boldsymbol{V}_{\mathrm{cm}} = (m_{\mathrm{A}}\boldsymbol{v}_{\mathrm{A}} + m_{\mathrm{B}}\boldsymbol{v}_{\mathrm{B}})/(m_{\mathrm{A}} + m_{\mathrm{B}})$ and the relative velocity is $\boldsymbol{v}_{\mathrm{r}} = \boldsymbol{v}_{\mathrm{A}} - \boldsymbol{v}_{\mathrm{B}}$. The Jacobian of the transformation from coordinates $\boldsymbol{v}_{\mathrm{A}}$ and $\boldsymbol{v}_{\mathrm{B}}$ to coordinates $\boldsymbol{v}_{\mathrm{r}}$ and $\boldsymbol{V}_{\mathrm{cm}}$ is equal to one. Thus, $\langle v_{\mathrm{r}}\rangle_{\mathrm{AB}}$ can be rewritten

$$\langle v_{\mathrm{r}}\rangle_{\mathrm{AB}} = \left(\frac{\beta M_{\mathrm{AB}}}{2\pi}\right)^{3/2} \left(\frac{\beta \mu_{\mathrm{AB}}}{2\pi}\right)^{3/2} \iint \mathrm{d}\boldsymbol{v}_{\mathrm{r}}\, \mathrm{d}\boldsymbol{V}_{\mathrm{cm}} v_{\mathrm{r}} \mathrm{e}^{-\beta/2(M_{\mathrm{AB}}V_{\mathrm{cm}}^2 + \mu_{\mathrm{AB}} v_{\mathrm{r}}^2)} \,, \tag{9.7}$$

where $M_{\mathrm{AB}} = m_{\mathrm{A}} + m_{\mathrm{B}}$ is the total mass and $\mu_{\mathrm{AB}} = m_{\mathrm{A}} m_{\mathrm{B}}/(m_{\mathrm{A}} + m_{\mathrm{B}})$ is the reduced mass. If we perform the integrations in (9.7), we obtain

$$\langle v_{\mathrm{r}}\rangle_{\mathrm{AB}} = \left(\frac{8 k_{\mathrm{B}} T}{\pi \mu_{\mathrm{AB}}}\right)^{1/2} \tag{9.8}$$

for the average relative speed of particles A and B.

We can now find the frequency of collisions between A particles and B particles. Assume that all B particles in the gas are at rest and an A particle moves through the gas with a speed $\langle v_{\mathrm{r}}\rangle_{\mathrm{AB}}$. The A particle sweeps out a collision cylinder of radius $d_{\mathrm{AB}} = (d_{\mathrm{A}} + d_{\mathrm{B}})/2$ (radius of the sphere of influence) and volume $\pi d_{\mathrm{AB}}^2 \langle v_{\mathrm{r}}\rangle_{\mathrm{AB}} t$ in time t. The number of B particles that particle A collides with in time t is $f_{\mathrm{AB}} t$, where f_{AB} is the collision frequency

$$f_{\mathrm{AB}} = n_{\mathrm{B}} \pi d_{\mathrm{AB}}^2 \langle v_{\mathrm{r}}\rangle_{\mathrm{AB}} \,. \tag{9.9}$$

Therefore, the total number of collisions per unit volume per second, ν_{AB}, between particles of type A and type B is

$$\nu_{\mathrm{AB}} = n_{\mathrm{A}} n_{\mathrm{B}} \pi d_{\mathrm{AB}}^2 \langle v_{\mathrm{r}}\rangle_{\mathrm{AB}} = n_{\mathrm{A}} n_{\mathrm{B}} \pi d_{\mathrm{AB}}^2 \left(\frac{8 k_{\mathrm{B}} T}{\pi \mu_{\mathrm{AB}}}\right)^{1/2} \,. \tag{9.10}$$

From Eq. (9.10) we can easily write down the collision frequency ν_{AA} between identical particles:

$$\nu_{\mathrm{AA}} = \frac{1}{2} n_{\mathrm{A}}^2 \pi d_{\mathrm{AA}}^2 \langle v_{\mathrm{r}}\rangle_{\mathrm{AA}} = \frac{1}{2} n_{\mathrm{A}}^2 \pi d_{\mathrm{AA}}^2 \left(\frac{16 k_{\mathrm{B}} T}{\pi m_{\mathrm{A}}}\right)^{1/2} \,. \tag{9.11}$$

The extra factor of 1/2 enters because the colliding particles are identical and it prevents overcounting.

If we consider a gas of identical particles, then the mean free path, λ, the collision frequency for a single particle, $f_{\mathrm{AA}} = n_{\mathrm{A}}\pi d_{\mathrm{AA}}^2\langle v_{\mathrm{r}}\rangle$, and the average speed, $\langle v\rangle$, are simply related by the equation

$$\lambda = \frac{\langle v\rangle}{f_{\mathrm{AA}}} = \langle v\rangle\tau = \frac{1}{\sqrt{2}n_{\mathrm{A}}\pi d_{\mathrm{AA}}^2}\,, \tag{9.12}$$

where τ is the collision time (the time between collisions), and the average speed, $\langle v\rangle$, is related to the relative speed by the relation $\langle v_{\mathrm{rel}}\rangle = \sqrt{2}\langle v\rangle$.

Tracer Particle Current

Let us consider a gas of particles that are identical in every way except that a small fraction of the particles have a radioactive tracer attached. We shall assume that the density of tracer particles, $n_{\mathrm{T}}(z)$, varies in the z-direction, while the total particle density, n, is held constant. As a first step in obtaining the tracer particle current (number/(area · time)), we draw an imaginary wall in the fluid at $z = 0$ and find the net flux of particles across the wall.

First find the number of particles that hit the wall from above. Consider a segment of the wall, $\mathrm{d}S$, and place the origin of coordinates at the center of $\mathrm{d}S$. Next consider a volume element, $\mathrm{d}V$, of the gas located at position r, θ, ϕ above the wall (see Figure 9.1a). The average number of tracer particles undergoing collisions in $\mathrm{d}V$ per unit time is $f n_{\mathrm{T}}(z)\,\mathrm{d}V = (\langle v\rangle/\lambda)n_{\mathrm{T}}(z)\,\mathrm{d}V$, where f is the collision frequency. Particles in $\mathrm{d}V$ leave in random directions (any direction is equally likely). The fraction of particles that move towards $\mathrm{d}S$ is $\mathrm{d}\Omega/(4\pi)$, where $\mathrm{d}\Omega$ is the solid angle subtended by $\mathrm{d}S$ and $\mathrm{d}\Omega = \mathrm{d}S|\cos\theta|/r^2$. Not all particles leaving $\mathrm{d}V$ in the direction of $\mathrm{d}S$ reach $\mathrm{d}S$. The probability that a tracer particle will reach $\mathrm{d}S$ is $\mathrm{e}^{-r/\lambda}$ (the probability that it will not undergo a collision). Combining the above results, we obtain the following expression for the number of tracer particles, $\mathrm{d}n_{\mathrm{T}}(\boldsymbol{r})$, which collide in $\mathrm{d}V$, leave directed toward $\mathrm{d}S$, and reach $\mathrm{d}S$ without another collision:

$$\mathrm{d}n_{\mathrm{T}}(\boldsymbol{r}) = \frac{\langle v\rangle n_{\mathrm{T}}(z)\,\mathrm{d}V}{\lambda}\frac{\mathrm{d}S|\cos\theta|}{4\pi r^2}\mathrm{e}^{-r/\lambda}\,. \tag{9.13}$$

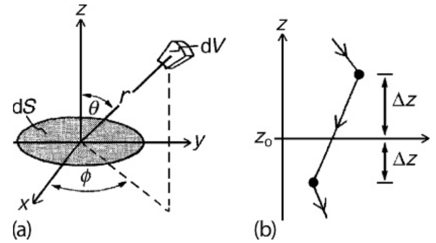

Figure 9.1 (a) Only a fraction of the particles in volume element, dV, reach the surface area element, dS, without undergoing a collision en route. (b) A particle has a collision a distance Δz above the plan and transports property A to another particle a distance Δz below the plane.

The total number hitting a unit area of wall per unit time from above, $\dot{N}_+$, is found by integrating over the entire volume for $z > 0$:

$$\dot{N}_+ = \frac{\langle v \rangle}{4\pi\lambda} \int_0^\infty r^2 \, \mathrm{d}r \int_0^{\pi/2} \sin\theta \, \mathrm{d}\theta \int_0^{2\pi} \mathrm{d}\phi \, n_\mathrm{T}(z) \cos\theta \frac{\mathrm{e}^{-r/\lambda}}{r^2} \,. \tag{9.14}$$

For the case in which the tracer particles are distributed uniformly throughout the gas so $n(z) = \text{constant}$, (9.14) reduces to $\dot{N}_+ = n\langle v \rangle / 4$.

For small variations in tracer density we may expand $n_\mathrm{T}(z)$ in a Taylor series about the origin,

$$n_\mathrm{T}(z) = n_\mathrm{T}(0) + z \left(\frac{\partial n_\mathrm{T}}{\partial z} \right)_0 + \frac{z^2}{2} \left(\frac{\partial^2 n_\mathrm{T}}{\partial z^2} \right)_0 + \cdots \tag{9.15}$$

If $n_\mathrm{T}(z)$ is a slowly varying function of z, then higher order derivatives $(\partial^2 n_\mathrm{T}/\partial z^2)_0$, $(\partial^3 n_\mathrm{T}/\partial z^3)_0$, and so on, will be small. Because of the factor $\mathrm{e}^{-r/\lambda}$ in the integral in Eq. (9.14), only small values of z (values of $z \approx \lambda$) will contribute. Therefore, we can terminate the expansion at $z^2/2(\partial^2 n_\mathrm{T}/\partial z^2)_0$.

The net number of tracer particles moving in the negative z-direction that cross a unit area of the wall per unit time is given by $(\dot{N}_+ - \dot{N}_-)$, where $\dot{N}_-$ is the number crossing a unit area per unit time in the positive z-direction. The expression for $\dot{N}_-$ is the same as for $\dot{N}_+$ except that θ is integrated from $\theta = \pi/2 \to \pi$ and $|\cos\theta|$ is changed to $-\cos\theta$. Therefore,

$$(\dot{N}_+ - \dot{N}_-) = \frac{\langle v \rangle}{4\pi\lambda} \int_0^\infty \mathrm{d}r r^2 \int_0^\pi \sin\theta \, \mathrm{d}\theta \int_0^{2\pi} \mathrm{d}\phi \, n_\mathrm{T}(z) \cos\theta \frac{\mathrm{e}^{-r/\lambda}}{\boldsymbol{r}^2} \,. \tag{9.16}$$

If we substitute Eq. (9.15) into Eq. (9.16), the first and third terms are identically zero and we obtain

$$(\dot{N}_+ - \dot{N}_-) = \frac{\langle v \rangle \lambda}{3} \left(\frac{\partial n_\mathrm{T}}{\partial z} \right)_0 \,. \tag{9.17}$$

If the density increases in the z-direction, then $(\partial n_\mathrm{T}/\partial z)_0 > 0$ and $(\dot{N}_+ - \dot{N}_-) > 0$. Therefore, there will be a net transport of particles in the negative z-direction.

If we let $J_\mathrm{D}(z) = \dot{N}_- - \dot{N}_+$ denote the number of tracer particles crossing a unit area at z in unit time in the positive z-direction, then

$$J_\mathrm{D}(z) = -D \frac{\partial n_\mathrm{T}(z)}{\mathrm{d}z} \,, \tag{9.18}$$

where

$$D = \frac{\langle v \rangle \lambda}{3} \tag{9.19}$$

is the coefficient of self-diffusion.

9.2.1
Transport of Molecular Properties

It is possible to treat all transport processes in a unified manner. Assume that $A = A(z)$ is the *molecular property* to be transported and that it varies in the z-direction. Let us draw an imaginary plane in the gas at $z = z_0$. When a particle crosses the plane, it transports the value of A it obtained in its last collision and transfers it to another particle in its next collision.

Let $A(z_0 + \Delta z)$ be the value of A transported in the negative z-direction across the plane where $\Delta z = a\lambda$ is the distance above the plane where the particle had its last collision (cf. Figure 9.1b), λ is the mean free path and a is a proportionality constant. The average number of particles crossing the plane per unit area per unit time is $n\langle v\rangle$. The net amount of A transported in the positive z-direction per unit area per unit time (the current) is

$$n\langle v\rangle[A(z_0 - \Delta z) - A(z_0 + \Delta z)] = -2n\langle v\rangle \Delta z \frac{\mathrm{d}A}{\mathrm{d}z} = -2an\langle v\rangle\lambda \frac{\mathrm{d}A}{\mathrm{d}z} \, . \quad (9.20)$$

More generally, we can write the current, J_A, as

$$J_\mathrm{A}(z) = -b_\mathrm{A} n\langle v\rangle\lambda \frac{\mathrm{d}A}{\mathrm{d}z} \, , \quad (9.21)$$

where b_A is a proportionality constant. Let us now apply Eq. (9.21) to the cases of self-diffusion, viscosity, and heat conductivity.

Assume that the concentration of tracer particles per particle is $A = n_\mathrm{T}(z)/n$. If the density of tracer particles varies in the z-direction, there will be a concentration gradient $(1/n)(\mathrm{d}n_\mathrm{T}/\mathrm{d}z) = \mathrm{d}A/\mathrm{d}z$ causing them to diffuse through space. If we let $J_\mathrm{A} = J_D$, where J_D is the tracer particle current then, from Eq. (9.21), we obtain

$$J_D(z) = -b_\mathrm{A}\langle v\rangle\lambda \frac{\mathrm{d}n_\mathrm{T}}{\mathrm{d}z} = -D\frac{\mathrm{d}n_\mathrm{T}}{\mathrm{d}z} \, . \quad (9.22)$$

The coefficient of self-diffusion is given by $D = \langle v\rangle\lambda/3$ if we let $b_\mathrm{A} = 1/3$.

If a gas is stirred, one part will move relative to another part. Let us assume that the y-component of the average velocity varies in the z-direction. Then $A(z) = m\langle v_y(z)\rangle$ and $J_\mathrm{A} = J_{zy}$, where J_{zy} is the net flux of the y-component of momentum per unit area per unit time in the z-direction. From Eq. (9.21) we have

$$J_{zy} = -\frac{1}{3}nm\langle v\rangle\lambda \frac{\mathrm{d}\langle v_y(z)\rangle}{\mathrm{d}z} = -\eta \frac{\mathrm{d}\langle v_y(z)\rangle}{\mathrm{d}z} \quad (9.23)$$

where

$$\eta = \frac{1}{3}nm\langle v\rangle\lambda \quad (9.24)$$

is the coefficient of shear viscosity. From Eq. (9.12) we know that $\lambda = (\sqrt{2}n\pi d^2)^{-1}$ for hard spheres of diameter d. Therefore, the coefficient of shear viscosity is

$$\eta = \frac{m\langle v\rangle}{3\sqrt{2}\pi d^2} \quad (9.25)$$

and is independent of density – a somewhat surprising result that is verified by experiment.

If the temperature of the gas varies in the z-direction then

$$A(z) = \frac{1}{2} m \langle v^2(z) \rangle = \frac{3}{2} k_B T(z) \tag{9.26}$$

and $J_A = J_Q$ is the heat current (the net flux of thermal energy per unit area per unit time). Since $b_A = 1/3$, Eq. (9.21) gives

$$J_Q = -K \frac{dT}{dz} , \tag{9.27}$$

where

$$K = \frac{1}{2} n \langle v \rangle \lambda k_B = \frac{1}{3} n m \langle v \rangle \lambda c_v \tag{9.28}$$

is the coefficient of thermal conductivity and c_v is the specific heat.

9.2.2
The Rate of Reaction

When chemical reactions occur in a dilute gas, we can use elementary arguments to obtain a qualitative expression for the rate of the reactions [102]. We cannot simply equate the number of collisions between various molecules to the rate at which they undergo chemical reactions. A simple example will illustrate this. Let us consider the reaction $2HI \rightarrow H_2 + I_2$. The radius of the sphere of influence may be obtained from viscosity data on HI gas ($d = 4 \times 10^{-8}$ cm). At a temperature $T = 700$ K, pressure $P = 1$ atm, the collision frequency is easily computed and yields $\nu_{(HI)^2} = 1.3 \times 10^{28}$/s. If every collision between HI molecules contributed to the reaction, then for a gas containing 10^{23} molecules the reaction would be completed in a fraction of a second. However, experimentally one finds that it takes a much longer time to complete the reaction, the reason being that there is an energy barrier that must be surmounted before a chemical reaction can occur. Not all collisions lead to a reaction.

In order for a reaction of the type $A + B \rightarrow C + D$ to occur, a certain amount of the kinetic energy of A and B must be absorbed during the collision. A and B first form an intermediate state (AB), which then can decay into the products C and D. The intermediate state (AB) is called an *activated complex* and A and B are called the *reactants*. The amount of energy, ε, that must be absorbed in order to form the activated complex is called the *activation energy*.

All of the energy that goes into exciting the activated complex must come from the energy of relative motion of the reactants. Energy in the center-of-mass motion cannot contribute. If ε is the activation energy of the activated complex, then a reaction between A and B can occur only if the relative velocity of A and B is such that

$$\frac{1}{2} \mu_{AB} v_r^2 > \varepsilon . \tag{9.29}$$

Therefore, to find the rate at which reactions between A and B can take place, we must multiply the collision frequency between A and B by the probability that A and B have a relative velocity greater than $\sqrt{2\varepsilon/\mu_{\mathrm{AB}}}$.

The probability that the molecules A and B have center-of-mass velocity in the range $\boldsymbol{V}_{\mathrm{cm}} \to \boldsymbol{V}_{\mathrm{cm}} + \mathrm{d}\boldsymbol{V}_{\mathrm{cm}}$ and a relative velocity in the range $\boldsymbol{v}_{\mathrm{r}} \to \boldsymbol{v}_{\mathrm{r}} + \mathrm{d}\boldsymbol{v}_{\mathrm{r}}$ is given by the Maxwell–Boltzmann distribution $P(\boldsymbol{V}_{\mathrm{cm}}, \boldsymbol{v}_{\mathrm{r}})\,\mathrm{d}\boldsymbol{V}_{\mathrm{cm}}\,\mathrm{d}\boldsymbol{v}_{\mathrm{r}}$, where

$$P(\boldsymbol{V}_{\mathrm{cm}}, \boldsymbol{v}_{\mathrm{r}}) = \left(\frac{\beta M_{\mathrm{AB}}}{2\pi}\right)^{3/2} \left(\frac{\beta \mu_{\mathrm{AB}}}{2\pi}\right)^{3/2} \mathrm{e}^{-(\beta/2)\left(M_{\mathrm{AB}} V_{\mathrm{cm}}^2 + \mu_{\mathrm{AB}} v_{\mathrm{r}}^2\right)} . \tag{9.30}$$

The probability that A and B have a relative velocity in the range $\boldsymbol{v}_{\mathrm{r}} \to \boldsymbol{v}_{\mathrm{r}} + \mathrm{d}\boldsymbol{v}_{\mathrm{r}}$ is found by integrating Eq. (9.30) over the center-of-mass velocity. We then find

$$P(\boldsymbol{v}_{\mathrm{r}})\,\mathrm{d}\boldsymbol{v}_{\mathrm{r}} = \left(\frac{\beta \mu_{\mathrm{AB}}}{2\pi}\right)^{3/2} \mathrm{e}^{-(\beta/2)\mu_{\mathrm{AB}} v_{\mathrm{r}}^2}\,\mathrm{d}\boldsymbol{v}_{\mathrm{r}} . \tag{9.31}$$

The probability that A and B have a relative velocity $v_{\mathrm{r}} > \sqrt{2\varepsilon/\mu_{\mathrm{AB}}}$ is found by integrating Eq. (9.31) from $v_{\mathrm{r}} = \sqrt{2\varepsilon/\mu_{\mathrm{AB}}}$ to $v_{\mathrm{r}} = \infty$ and integrating over all angles. Thus,

$$\begin{aligned} \mathrm{Prob}\left(v_{\mathrm{r}} > \sqrt{\frac{2\varepsilon}{\mu_{\mathrm{AB}}}}\right) &= \left(\frac{\beta \mu_{\mathrm{AB}}}{2\pi}\right)^{3/2} \int_0^{\pi} \mathrm{d}\theta \int_0^{2\pi} \mathrm{d}\phi \int_{\sqrt{2\varepsilon/\mu_{\mathrm{AB}}}}^{\infty} \mathrm{d}v_{\mathrm{r}} \\ &\times v_{\mathrm{r}}^2 \sin\theta \mathrm{e}^{-(\beta/2)\mu_{\mathrm{AB}} v_{\mathrm{r}}^2} = f_{\beta,\varepsilon} \mathrm{e}^{-\beta\varepsilon} . \end{aligned} \tag{9.32}$$

The probability that a reaction takes place depends exponentially on the activation energy. The quantity $f_{\beta,\varepsilon}$ is a function of temperature and activation energy. Its form is not important here.

We can now write the following qualitative expression for the rate of reaction of A and B. The number of reacting molecules, N_{R}, per second per unit volume is

$$\dot{N}_{\mathrm{R}} = K_{\beta,\varepsilon} \nu_{\mathrm{AB}} \mathrm{e}^{-\beta\varepsilon} , \tag{9.33}$$

where ν_{AB} is the collision frequency between molecules A and B, and the coefficient $K_{\beta,\varepsilon}$ depends on activation energy and temperature and may also depend on the geometry of the interacting molecules A and B. We may rewrite Eq. (9.33) in the form of a rate equation. If we let n_{A} denote the number of moles of A per unit volume and use Eq. (9.10), we can write

$$\frac{\mathrm{d}n_{\mathrm{A}}}{\mathrm{d}t} = -K'_{\varepsilon,\beta} d_{\mathrm{AB}}^2 \mathrm{e}^{-\beta\varepsilon} n_{\mathrm{A}} n_{\mathrm{B}} \equiv -k_{\mathrm{AB}} n_{\mathrm{A}} n_{\mathrm{B}} . \tag{9.34}$$

In Eq. (9.34), $K'_{\varepsilon,\beta}$ is a function of ε and β and may depend on the geometry of A and B. The quantity k_{AB} is called the rate constant for the reaction. It depends exponentially on the activation energy. We see that the activation energy is the most important quantity in determining the rate of a chemical reaction, since a small change in ε can cause a large change in k_{AB}. Equation (9.34) gives the rate of decrease of A in the fluid due to the reaction $\mathrm{A} + \mathrm{B} \to \mathrm{C} + \mathrm{D}$.

In general, the expression describing a given chemical reaction is written in the form

$$-\nu_{\mathrm{A}}\mathrm{A} - \nu_{\mathrm{B}}\mathrm{B} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \nu_{\mathrm{C}}\mathrm{C} + \nu_{\mathrm{D}}\mathrm{D}\,, \tag{9.35}$$

where ν_i are the stoichiometric coefficients. The constant k_1 is the rate constant for the forward reaction and k_2 is the rate constant for the backward reaction. The rate of change of A can, in general, be written

$$\frac{\mathrm{d}n_{\mathrm{A}}}{\mathrm{d}t} = -k_1 n_{\mathrm{A}}^{|\nu_{\mathrm{A}}|} n_{\mathrm{B}}^{|\nu_{\mathrm{B}}|} + k_2 n_C^{\nu_c} n_{\mathrm{D}}^{\nu_c}\,, \tag{9.36}$$

where $|\nu_{\mathrm{A}}|$ denotes the absolute value of ν_{A}.

9.3
The Boltzmann Equation

Let us consider a dilute gas of particles of mass, m, which interact via a spherically symmetric potential $V(|\boldsymbol{q}_i - \boldsymbol{q}_j|)$. We shall assume that the time a particle spends between collisions is very much longer than the duration of a collision. We shall describe the behavior of the system in terms of a number density $f(\boldsymbol{p}, \boldsymbol{q}, t)$ rather than a probability density. The distribution function, $f(\boldsymbol{p}, \boldsymbol{q}, t)$, gives the number of particles in the six-dimensional phase space volume element $\boldsymbol{p} \to \boldsymbol{p} + \mathrm{d}\boldsymbol{p}, \boldsymbol{q} \to \boldsymbol{q} + \mathrm{d}\boldsymbol{q}$. It is related to the reduced probability density $\rho_1(\boldsymbol{p}, \boldsymbol{q}, t)$ through the relation

$$f(\boldsymbol{p}, \boldsymbol{q}, t) \equiv N\rho_1(\boldsymbol{p}, \boldsymbol{q}, t)\,, \tag{9.37}$$

where $\rho_1(\boldsymbol{p}, \boldsymbol{q}, t)$ is defined in Appendix A.

Let us now consider a volume element, $\Delta V_1 = \mathrm{d}\boldsymbol{p}_1 \Delta\boldsymbol{r}$, lying in the region $\boldsymbol{p}_1 \to \boldsymbol{p}_1 + \mathrm{d}\boldsymbol{p}_1, \boldsymbol{r} \to \boldsymbol{r} + \Delta\boldsymbol{r}$ of the six-dimensional phase space. We shall assume the volume element $\Delta\boldsymbol{r}$ is large enough to contain many particles and small enough that the distribution function $f(\boldsymbol{p}, \boldsymbol{r}, t)$ does not vary appreciably over $\Delta\boldsymbol{r}$. We wish to find an equation for the rate of change of number of particles in ΔV_1. This change will be due to free streaming of particles into (and out of) ΔV_1 and to scattering of particles into (and out of) ΔV_1 because of collisions. The rate of change of $f(\boldsymbol{p}_1, \boldsymbol{r}, t)$ may be written in the form

$$\frac{\partial f_1}{\partial t} = -\dot{\boldsymbol{r}}_1 \cdot \frac{\partial f_1}{\partial \boldsymbol{r}_1} + \left.\frac{\partial f_1}{\partial t}\right|_{\mathrm{coll}}\,. \tag{9.38}$$

The first term on the right is the contribution due to streaming (flow through the surface of ΔV_1), and the second term is the contribution due to collisions.

If an external field were present, then an additional streaming term of the form $-\dot{\boldsymbol{p}}_1 \cdot \partial f_1/\partial \boldsymbol{p}_1$ would be present on the right.

We shall assume that the gas is dilute enough that only two-body collisions need be considered. Furthermore, we shall assume that all collisions are elastic. In order to write an expression for $\partial f/\partial t|_{\text{coll}}$, we must use ideas from two-body scattering theory. Two-body scattering theory is reviewed in Appendix E.

9.3.1
Derivation of the Boltzmann Equation

Let us denote the rate of particles scattered out of ΔV_1 by $(\partial f_-/\partial t)\Delta \boldsymbol{r}\,\mathrm{d}\boldsymbol{p}_1$. The number of particles in ΔV_1 at time t with coordinates $\boldsymbol{p}_1 \to \boldsymbol{p}_1 + \mathrm{d}\boldsymbol{p}_1$ and $\boldsymbol{r} \to \boldsymbol{r} + \Delta \boldsymbol{r}$ is $f(\boldsymbol{p}_1, \boldsymbol{r}, t)\Delta \boldsymbol{r}\,\mathrm{d}\boldsymbol{p}_1$. All particles of momentum $\boldsymbol{p}_2$ lying within a cylinder of radius b and volume $\mathrm{d}\boldsymbol{q}_2 = 2\pi b\,\mathrm{d}bg\,\mathrm{d}t$ collide with particles $\boldsymbol{p}_1$ in time $\mathrm{d}t$, where $mg = |\boldsymbol{p}_1 - \boldsymbol{p}_2|$. The number of such particles is $f(\boldsymbol{p}_2, \boldsymbol{r}, t)2\pi b\,\mathrm{d}bg\,\mathrm{d}t\,\mathrm{d}\boldsymbol{p}_2$. The total number of collisions, $N\left(\boldsymbol{p}_1\boldsymbol{p}_2 \to \boldsymbol{p}_3\boldsymbol{p}_4\right)$, per unit volume in time $\mathrm{d}t$ between particles of momentum $\boldsymbol{p}_1$ and particles of momentum $\boldsymbol{p}_2$ resulting in new momenta $\boldsymbol{p}_3$ and $\boldsymbol{p}_4$ is given by

$$N\left(\boldsymbol{p}_1\boldsymbol{p}_2 \to \boldsymbol{p}_3\boldsymbol{p}_4\right) = 2\pi g b\,\mathrm{d}b\,\mathrm{d}t f(\boldsymbol{p}_2, \boldsymbol{r}, t) f(\boldsymbol{p}_1, \boldsymbol{r}, t)\,\mathrm{d}\boldsymbol{p}_1\,\mathrm{d}\boldsymbol{p}_2 \tag{9.39}$$

(see Appendix E). In Eq. (9.39) we have assumed that the distribution functions do not change appreciably in position space for the volume element ΔV_1 we are considering. Also, we have assumed that the particles $\boldsymbol{p}_1$ and $\boldsymbol{p}_2$ are completely uncorrelated. This assumption is called *molecular chaos*, or *Stosszahl-Ansatz*.

In analogy to Eq. (9.39) we may write for the inverse scattering process

$$N\left(\boldsymbol{p}_3, \boldsymbol{p}_4 \to \boldsymbol{p}_1, \boldsymbol{p}_2\right) = 2\pi g b\,\mathrm{d}b\,\mathrm{d}t f\left(\boldsymbol{p}_3, \boldsymbol{r}, t\right) f\left(\boldsymbol{p}_4, \boldsymbol{r}, t\right)\mathrm{d}\boldsymbol{p}_3\,\mathrm{d}\boldsymbol{p}_4\,. \tag{9.40}$$

For elastic collisions, $\mathrm{d}\boldsymbol{p}_1\,\mathrm{d}\boldsymbol{p}_2 = \mathrm{d}\boldsymbol{p}_3\,\mathrm{d}\boldsymbol{p}_4$. (This is easily proved if we note that $\mathrm{d}\boldsymbol{p}_1\,\mathrm{d}\boldsymbol{p}_2 = \mathrm{d}\boldsymbol{P}_{1,2}\,\mathrm{d}\boldsymbol{p}_{1,2}$ and $\mathrm{d}\boldsymbol{p}_3\,\mathrm{d}\boldsymbol{p}_4 = \mathrm{d}\boldsymbol{P}_{3,4}\,\mathrm{d}\boldsymbol{p}_{3,4}$. Furthermore, for elastic collisions, $\mathrm{d}\boldsymbol{P}_{1,2} = \mathrm{d}\boldsymbol{P}_{3,4}$ and $p_{1,2}^2\,\mathrm{d}p_{1,2} = p_{3,4}^2\,\mathrm{d}p_{3,4}$. Therefore, $\mathrm{d}\boldsymbol{p}_1\,\mathrm{d}\boldsymbol{p}_2 = \mathrm{d}\boldsymbol{p}_3\,\mathrm{d}\boldsymbol{p}_4$.) We may now combine Eqs. (9.39) and (9.40) to obtain the following expression for the net increase, $(\partial f_1/\partial t)_{\text{coll}}\,\mathrm{d}\boldsymbol{p}_1$, in number of particles with momentum $\boldsymbol{p}_1 \to \boldsymbol{p}_1 + \mathrm{d}\boldsymbol{p}_1$ per unit volume per unit time:

$$\begin{aligned}\left(\frac{\partial f_1}{\partial t}\right)_{\text{coll}}\mathrm{d}\boldsymbol{p}_1 = \mathrm{d}\boldsymbol{p}_1 \int \mathrm{d}\boldsymbol{p}_2 \int \mathrm{d}\Omega g \sigma_{\text{cm}}(b, g) \\ \times \left(f(\boldsymbol{p}_3, \boldsymbol{r}, t) f\left(\boldsymbol{p}_4, \boldsymbol{r}, t\right) - f(\boldsymbol{p}_1, \boldsymbol{r}, t) f(\boldsymbol{p}_2, \boldsymbol{r}, t)\right),\end{aligned} \tag{9.41}$$

where $\mathrm{d}\Omega = \sin(\Theta)\,\mathrm{d}\Theta\,\mathrm{d}\alpha$, σ_{cm} is the center-of-mass collision cross section, and Θ and α are the polar and azimuthal scattering angles, respectively. If we now combine Eqs. (9.38) and (9.41), we obtain

$$\frac{\mathrm{d}f_1}{\partial t} + \dot{\boldsymbol{q}}_1 \cdot \frac{\partial f_1}{\partial \boldsymbol{r}} = \int \mathrm{d}\boldsymbol{p}_2 \int \mathrm{d}\Omega g \sigma_{\text{cm}}(b, g)(f_3 f_4 - f_1 f_2)\,, \tag{9.42}$$

where $f_i = f(\boldsymbol{p}_i, \boldsymbol{r}, t)$. Equation (9.42) is the *Boltzmann equation* [19, 26, 133, 202]. The Boltzmann equation is a nonlinear integrodifferential equation for $f(\boldsymbol{p}_i, \boldsymbol{r}, t)$.

We can write the Boltzmann equation in a form where conservation of energy and momentum is made explicit. It only requires a bit of algebra. The relative velocity before the collision is $\boldsymbol{g} = \boldsymbol{v}_2 - \boldsymbol{v}_1$, and after the collision it is $\boldsymbol{g}' = \boldsymbol{v}_4 - \boldsymbol{v}_3$, where $|\boldsymbol{g}| = |\boldsymbol{g}'| = g$. For simplicity, assume that the initial relative velocity vector, $\boldsymbol{g}$, lies along the z-axis. Then $\boldsymbol{g} = g\hat{\boldsymbol{e}}_z$ and $\boldsymbol{g}' = g\sin(\Theta)\cos(\alpha)\hat{\boldsymbol{e}}_x + g\sin(\Theta)\sin(\alpha)\hat{\boldsymbol{e}}_y + g\cos(\Theta)\hat{\boldsymbol{e}}_z$ (see Appendix E). If we define $\mathrm{d}\Omega = \mathrm{d}(\cos(\Theta))\,\mathrm{d}\alpha$, we can write

$$\begin{aligned} g\,\mathrm{d}\Omega &= \int g'\,\mathrm{d}g'\,\mathrm{d}\Omega\,\delta(g'-g) = \int g'\,\mathrm{d}g'\,\mathrm{d}\Omega\,\delta(g'-g)\int \mathrm{d}\boldsymbol{V}_{3,4}\delta^{(3)}(\boldsymbol{V}_{3,4}-\boldsymbol{V}_{1,2}) \\ &= \frac{m}{2}\iint \mathrm{d}\boldsymbol{V}_{3,4}\,\mathrm{d}\boldsymbol{g}'\,\delta(E_{3,4}-E_{1,2})\delta^{(3)}(\boldsymbol{V}_{3,4}-\boldsymbol{V}_{1,2})\,, \end{aligned} \tag{9.43}$$

where $\mathrm{d}\boldsymbol{g}' = g'^2\,\mathrm{d}g'\,\mathrm{d}\Omega$ and $\boldsymbol{V}_{1,2} = (\boldsymbol{v}_1 + \boldsymbol{v}_2)/2$ is the center-of-mass velocity. We have used the fact that the total kinetic energy can be written

$$E_{1,2} = \frac{m}{2}\left(v_1^2 + v_2^2\right) = m\left(V_{1,2}^2 + \frac{1}{4}g^2\right) = m\left(V_{3,4}^2 + \frac{1}{4}g'^2\right)\,. \tag{9.44}$$

We can also write Eq. (9.43) as

$$g\,\mathrm{d}\Omega = \frac{8}{m}\iint \mathrm{d}\boldsymbol{p}_3 d\boldsymbol{p}_4\delta\left(p_3^2 + p_4^2 - p_1^2 - p_2^2\right)\delta^{(3)}(\boldsymbol{p}_3 + \boldsymbol{p}_4 - \boldsymbol{p}_1 - \boldsymbol{p}_2)\,, \tag{9.45}$$

where we have used the fact that $m^6\,\mathrm{d}\boldsymbol{V}_{3,4}\,\mathrm{d}\boldsymbol{g}' = \mathrm{d}\boldsymbol{p}_3\,\mathrm{d}\boldsymbol{p}_4$ and $\delta(E_{3,4} - E_{1,2})$ $\delta(\boldsymbol{V}_{3,4} - \boldsymbol{V}_{1,2}) = 16m^4\delta(p_1^2 + p_2^2 - p_3^2 - p_4^2)\delta^{(3)}(\boldsymbol{p}_1 + \boldsymbol{p}_2 - \boldsymbol{p}_3 - \boldsymbol{p}_4)$. If we now define

$$\delta^{(4)}_{1,2;3,4} \equiv \frac{8}{m}\delta\left(p_1^2 + p_2^2 - p_3^2 - p_4^2\right)\delta^{(3)}(\boldsymbol{p}_1 + \boldsymbol{p}_2 - \boldsymbol{p}_3 - \boldsymbol{p}_4),\ , \tag{9.46}$$

the Boltzmann equation takes the form

$$\frac{\mathrm{d}f_1}{\partial t} + \boldsymbol{v}_1\cdot\frac{\partial f_1}{\partial \boldsymbol{r}} = \int \mathrm{d}\boldsymbol{p}_2\int \mathrm{d}\boldsymbol{p}_3\int \mathrm{d}\boldsymbol{p}_4\sigma_{\mathrm{cm}}(b,\Theta)\delta^{(4)}_{1,2;3,4}(f_3f_4 - f_1f_2)\,, \tag{9.47}$$

where $\boldsymbol{v}_1 = \dot{\boldsymbol{q}}_1$. Note that we have written the scattering cross section in terms of the polar scattering angle Θ, rather than the impact parameter, b.

9.4
Linearized Boltzmann Equations for Mixtures

We wish to obtain microscopic expressions for the transport coefficients for a two-component mixture whose distribution function varies in time and space according to the Boltzmann equation.

9.4.1
Kinetic Equations for a Two-Component Gas

Let us consider a dilute gas mixture of particles of type A and B which undergo collisions, but no chemical reactions. The Boltzmann equation for type A particles is

$$\frac{\partial f_{1,\mathrm{A}}}{\partial t} + \boldsymbol{v}_1 \cdot \frac{\partial f_{1,\mathrm{A}}}{\partial \boldsymbol{r}} = \sum_{\alpha,\beta,\gamma} \iiint \mathrm{d}\boldsymbol{p}_2\, \mathrm{d}\boldsymbol{p}_3\, \mathrm{d}\boldsymbol{p}_4 \sigma_{\alpha,\beta;\mathrm{A},\gamma}(g,\Theta) \times \delta^{(4)}(1_\mathrm{A}, 2_\gamma; 3_\alpha, 4_\beta) \left(f_{3,\alpha} f_{4,\beta} - f_{1,\mathrm{A}} f_{2,\gamma} \right) , \tag{9.48}$$

and the Boltzmann equation for type B particles is

$$\frac{\partial f_{1,\mathrm{B}}}{\partial t} + \boldsymbol{v}_1 \cdot \frac{\partial f_{1,\mathrm{B}}}{\partial \boldsymbol{r}} = \sum_{\alpha,\beta,\gamma} \iiint \mathrm{d}\boldsymbol{p}_2\, \mathrm{d}\boldsymbol{p}_3\, \mathrm{d}\boldsymbol{p}_4 \sigma_{\alpha,\beta;\mathrm{B},\gamma}(g,\Theta) \times \delta^{(4)}(1_\mathrm{B}, 2_\gamma; 3_\alpha, 4_\beta) \left(f_{3,\alpha} f_{4,\beta} - f_{1,\mathrm{B}} f_{2,\gamma} \right) , \tag{9.49}$$

where the summations over α, β, and γ are over type-A and type-B particles and we have used the notations $f_{1,\mathrm{A}} = f_\mathrm{A}(\boldsymbol{p}_1, \boldsymbol{r}, t)$ and $f_{1,\mathrm{B}} = f_\mathrm{B}(\boldsymbol{p}_1, \boldsymbol{r}, t)$. Since there are no chemical reactions, the number of A and B particles is conserved during collisions. Only the cross sections $\sigma_{\mathrm{A,A;A,A}}$, $\sigma_{\mathrm{A,B;A,B}}$, $\sigma_{\mathrm{B,A;B,A}}$, and $\sigma_{\mathrm{B,B;B,B}}$ are nonzero. The conservation of momentum and kinetic energy now must take account of the possible different mass of type-A and type-B particles so that

$$\delta^{(4)}(1_\mathrm{A}, 2_\gamma; 3_\alpha, 4_\beta) = 8\delta \left(m_\mathrm{A} v_1^2 + m_\gamma v_2^2 - m_\alpha v_3^2 - m_\beta v_4^2 \right) \times \delta^{(3)}(m_\mathrm{A} \boldsymbol{v}_1 + m_\gamma \boldsymbol{v}_2 - m_\alpha \boldsymbol{v}_3 - m_\beta \boldsymbol{v}_4) . \tag{9.50}$$

When computing transport coefficients, it is sufficient to consider systems with small-amplitude disturbance from equilibrium. We therefore linearize the Boltzmann equation in terms of deviations from the equilibrium state of the gas. Denote the type-A (type-B) particle equilibrium distribution by $f_\mathrm{A}^0(\boldsymbol{p}_1)$ ($f_\mathrm{B}^0(\boldsymbol{p}_1)$), where

$$f_j^0(\boldsymbol{p}_1) = n_j \left(\frac{\beta}{2\pi m_j} \right)^{3/2} \mathrm{e}^{-\beta p_1^2/(2m_j)} , \tag{9.51}$$

$j = A, B$, n_j is the particle density, and m_j is the mass of particles of type-j particles.

As a first step in linearizing the Boltzmann equation, we can write

$$f_\mathrm{A}(\boldsymbol{p}_1, \boldsymbol{r}, t) = f_\mathrm{A}^0(\boldsymbol{p}_1)(1 + h_\mathrm{A}(\boldsymbol{p}_1, \boldsymbol{r}, t)) \tag{9.52}$$

and

$$f_\mathrm{B}(\boldsymbol{p}_1, \boldsymbol{r}, t) = f_\mathrm{B}^0(\boldsymbol{p}_1)(1 + h_\mathrm{B}(\boldsymbol{p}_1, \boldsymbol{r}, t)) \tag{9.53}$$

where $h_{\mathrm{A}}(\boldsymbol{p}_1, \boldsymbol{r}, t)$ and $h_{\mathrm{B}}(\boldsymbol{p}_1, \boldsymbol{r}, t)$ denote small amplitude disturbances in the type-A and type-B particle distributions, respectively.

If we substitute Eqs. (9.52) and (9.53) into Eqs. (9.48) and (9.49), and neglect terms of second order or higher in $h_{\mathrm{A}}(\boldsymbol{p}_1, \boldsymbol{r}, t)$, and $h_{\mathrm{B}}(\boldsymbol{p}_1, \boldsymbol{r}, t)$, we obtain

$$\frac{\partial h_{1,\mathrm{A}}}{\partial t} + \boldsymbol{v}_1 \cdot \frac{\partial h_{1,\mathrm{A}}}{\partial \boldsymbol{r}} = \sum_\beta \iiint \mathrm{d}\boldsymbol{p}_2\, \mathrm{d}\boldsymbol{p}_3\, \mathrm{d}\boldsymbol{p}_4 \sigma_{\mathrm{A},\beta;\mathrm{A},\beta}(g, \Theta) f_\beta^0(\boldsymbol{p}_2) \times \delta^{(4)}(1_{\mathrm{A}}, 2_\beta; 3_{\mathrm{A}}, 4_\beta) \left(h_{3,\mathrm{A}} + h_{4,\beta} - h_{1,\mathrm{A}} - h_{2,\beta}\right) \quad (9.54)$$

and

$$\frac{\partial h_{1,\mathrm{B}}}{\partial t} + \boldsymbol{v}_1 \cdot \frac{\partial h_{1,\mathrm{B}}}{\partial \boldsymbol{r}} = \sum_\beta \iiint \mathrm{d}\boldsymbol{p}_2\, \mathrm{d}\boldsymbol{p}_3\, \mathrm{d}\boldsymbol{p}_4 \sigma_{\mathrm{B},\beta;\mathrm{B},\beta}(g, \Theta) f_\beta^0(\boldsymbol{p}_2) \times \delta^{(4)}(1_{\mathrm{B}}, 2_\beta; 3_{\mathrm{B}}, 4_\beta) \left(h_{3,\mathrm{B}} + h_{4,\beta} - h_{1,\mathrm{B}} - h_{2,\beta}\right) . \quad (9.55)$$

In Eqs. (9.54) and (9.55), we have used kinetic energy conservation (contained in $\delta^{(4)}(1_{\mathrm{A}}, 2_\beta; 3_{\mathrm{A}}, 4_\beta)$) to write $f_{\mathrm{A}}^0\left(\boldsymbol{p}_1\right) f_\beta^0\left(\boldsymbol{p}_2\right) = f_{\mathrm{A}}^0(\boldsymbol{p}_3) f_\beta^0(\boldsymbol{p}_4)$. Equations (9.54) and (9.55) are the *linearized Boltzmann equations* for the dilute gas mixture of particles A and B.

We can now decouple diffusion and thermal diffusion effects from viscous and thermal effects. Let us define the total distribution by

$$h^+(\boldsymbol{p}_1, \boldsymbol{r}, t) = h_{\mathrm{A}}(\boldsymbol{p}_1, \boldsymbol{r}, t) + h_{\mathrm{B}}(\boldsymbol{p}_1, \boldsymbol{r}, t) \quad (9.56)$$

and the difference distribution by

$$h^-(\boldsymbol{p}_1, \boldsymbol{r}, t) = h_{\mathrm{A}}(\boldsymbol{p}_1, \boldsymbol{r}, t) - h_{\mathrm{B}}(\boldsymbol{p}_1, \boldsymbol{r}, t) . \quad (9.57)$$

As long as $h^-(\boldsymbol{p}_1, \boldsymbol{r}, t)$ is nonzero, diffusion will occur in the gas.

Exercise 9.1

Assume that the masses of A and B are equal, but their collision cross sections differ and are given by $\sigma_{\mathrm{A,A;A,A}} = \sigma_0 + \sigma_1$, $\sigma_{\mathrm{B,B;B,B}} = \sigma_0 - \sigma_1$, $\sigma_{\mathrm{A,B;A,B}} = \sigma_{\mathrm{B,A;B,A}} = \sigma_0$. Obtain the equations of motion for the total distribution, $h^+(\boldsymbol{p}_1, \boldsymbol{r}, t)$, and for the difference distribution, $h^-(\boldsymbol{p}_1, \boldsymbol{r}, t)$.

Answer: The equations of motion for $h^+(\boldsymbol{p}_1, \boldsymbol{r}, t)$, and $h^-(\boldsymbol{p}_1, \boldsymbol{r}, t)$ can be obtained by adding and subtracting, respectively, Eqs. (9.54) and (9.55). If we add Eqs. (9.54) and (9.55), we obtain

$$\frac{\partial h_1^+}{\partial t} + \boldsymbol{v}_1 \cdot \frac{\partial h_1^+}{\partial \boldsymbol{r}} = \iiint \mathrm{d}\boldsymbol{p}_2\, \mathrm{d}\boldsymbol{p}_3\, \mathrm{d}\boldsymbol{p}_4 2\sigma(g, \Theta) \delta^{(4)}(1, 2; 3, 4) f^0(\boldsymbol{p}_2) \times \left[2\sigma_0 \left(h_3^+ + h_4^+ - h_1^+ - h_2^+\right) + 2\sigma_1 \left(h_3^- + h_4^- - h_1^- - h_2^-\right)\right] . \quad (9.58)$$

If we subtract Eqs. (9.54) and (9.55), we obtain

$$\frac{\partial h_1^-}{\partial t} + \boldsymbol{v}_1 \cdot \frac{\partial h_1^-}{\partial \boldsymbol{r}} = \iiint \mathrm{d}\boldsymbol{p}_2\, \mathrm{d}\boldsymbol{p}_3\, \mathrm{d}\boldsymbol{p}_4 2\sigma(g, \Theta) \delta^{(4)}(1, 2; 3, 4) f^0(\boldsymbol{p}_2) \times \left[2\sigma_0 \left(h_3^- - h_1^-\right) + 2\sigma_1 \left(h_3^+ + h_4^+ - h_1^+ - h_2^+\right)\right] . \quad (9.59)$$

These two equations are coupled because they both depend on h^+ and h^-. However, they have very different behavior. The right-hand side of Eq. (9.58) conserves particle number, energy, and momentum and describes viscous, and thermal transport. The right-hand side of Eq. (9.59) only conserves particle number, and describes diffusion and thermal diffusion in the gas mixture (see Section 8.7).

For simplicity, we assume that particles A and B are distinguishable, but dynamically identical. That is, we assume that they have the same mass, $m_{\mathrm{A}} = m_{\mathrm{B}} = m$ (or mass differences are negligible), and that the cross sections for collisions between A and A, B and B, and A and B particles are the same. Then we can write $\sigma_{\mathrm{A,A;A,A}} = \sigma_{\mathrm{A,B;A,B}} = \sigma_{\mathrm{B,A;B,A}} = \sigma_{\mathrm{B,B;B,B}} = \sigma$. The equations of motion for the total distribution, $h^+(\boldsymbol{p}_1, \boldsymbol{r}, t)$, and for the difference distribution, $h^-(\boldsymbol{p}_1, \boldsymbol{r}, t)$, can be obtained by adding and subtracting, respectively, Eqs. (9.54) and (9.55). If we add Eqs. (9.54) and (9.55), we obtain

$$\begin{aligned}\frac{\partial h_1^+}{\partial t} + \boldsymbol{v}_1 \cdot \frac{\partial h_1^+}{\partial \boldsymbol{r}} = \sum_{\beta} \iiint \mathrm{d}\boldsymbol{p}_2\, \mathrm{d}\boldsymbol{p}_3\, \mathrm{d}\boldsymbol{p}_4 2\sigma(g, \Theta) f^0(\boldsymbol{p}_2) \\ \times \delta^{(4)}(1,2;3,4)\left(h_3^+ + h_4^+ - h_1^+ - h_2^+\right) ,\end{aligned} \tag{9.60}$$

which is the *linearized Boltzmann equation* for the total particle distribution. If we subtract Eqs. (9.54) and (9.55), we obtain

$$\begin{aligned}\frac{\partial h_1^-}{\partial t} + \boldsymbol{v}_1 \cdot \frac{\partial h_1^-}{\partial \boldsymbol{r}} = \sum_{\beta} \iiint \mathrm{d}\boldsymbol{p}_2\, \mathrm{d}\boldsymbol{p}_3\, \mathrm{d}\boldsymbol{p}_4 2\sigma(g, \Theta) f^0(\boldsymbol{p}_2) \\ \times \delta^{(4)}(1,2;3,4)\left(h_3^- - h_1^-\right) ,\end{aligned} \tag{9.61}$$

which is called the *Lorentz–Boltzmann equation* and is the kinetic equation describing diffusion. Note that for this gas mixture of dynamically identical distinguishable particles there is no thermal diffusion, but only viscosity, thermal conductivity and particle diffusion. In subsequent sections, we will obtain microscopic expressions for the coefficients of shear viscosity η, thermal conductivity K, and diffusion D for this gas mixture of dynamically identical distinguishable particles.

9.4.2
Collision Operators

The linearized Boltzmann equation can be written in the form

$$\frac{\partial h_1^+}{\partial t} + \dot{\boldsymbol{r}}_1 \cdot \frac{\partial h_1^+}{\partial \boldsymbol{r}} = \hat{C}_1^+ h_1^+ , \tag{9.62}$$

where $\hat{C}_1^+$ is the *Boltzmann collision operator*. When $\hat{C}_1^+$ acts on an arbitrary function $g(\boldsymbol{p}_1)$, it gives

$$\hat{C}_1^+ g(\boldsymbol{p}_1) = 2 \iiint \mathrm{d}\boldsymbol{p}_2 \, \mathrm{d}\boldsymbol{p}_3 \, \mathrm{d}\boldsymbol{p}_4 \sigma(g, \Theta) \delta^{(4)}_{1,2;3,4} f^0(\boldsymbol{p}_2)(g_3 + g_4 - g_1 - g_2) \, . \tag{9.63}$$

We introduce the following scalar product of two functions $\phi(\boldsymbol{p}_1)$ and $\chi(\boldsymbol{p}_1)$:

$$\langle \phi, \chi \rangle \equiv \left(\frac{\beta}{2\pi m} \right)^{3/2} \int \mathrm{d}\boldsymbol{p}_1 \mathrm{e}^{-\beta p_1^2/(2m)} \phi(\boldsymbol{p}_1) \chi(\boldsymbol{p}_1) \, . \tag{9.64}$$

Using Eq. (9.64) it is easy to show that $\hat{C}^+$ is a self-adjoint operator and that $\langle \Phi, \hat{C}^+ \chi \rangle = \langle \hat{C}^+ \Phi, \chi \rangle$ (proof of these statements are left as problems).

The operator $\hat{C}_p^+$ has five eigenfunctions with eigenvalue zero. They are the five additive constants of the motion: 1, $\boldsymbol{p}$, and $p^2/(2m)$. All other eigenvalues of $\hat{C}_{\boldsymbol{p}}^+$ are negative. We prove this by writing the expectation value of $\hat{C}_{\boldsymbol{p}}^+$ in the form

$$\left\langle \Phi, \hat{C}_{\boldsymbol{p}}^+ \Phi \right\rangle = -\frac{1}{4} \frac{N}{V} \left(\frac{\beta}{2\pi m} \right)^3 \iiiint \mathrm{d}\boldsymbol{p}_1 \, \mathrm{d}\boldsymbol{p}_2 \, \mathrm{d}\boldsymbol{p}_3 \, \mathrm{d}\boldsymbol{p}_4 \mathrm{e}^{-\beta/(2m)(p_1^2 + p_2^2)} \\ \times \delta^{(4)}_{1,2;3,4} \sigma(g, \Theta)(\Phi_3 + \Phi_4 - \Phi_1 - \Phi_2)^2 \tag{9.65}$$

(we leave proof of this as a problem). Thus, $\langle \Phi, \hat{C}_{\boldsymbol{p}}^+ \Phi \rangle$ is less than or equal to zero for an arbitrary function $\Phi(\boldsymbol{p})$. It will be equal to zero only if $(\Phi_3 + \Phi_4 - \Phi_1 - \Phi_2) = 0$. This equation is satisfied if $\Phi(\boldsymbol{p})$ is a linear combination of the five additive constants of motion 1, $\boldsymbol{p}$, and $p^2/(2m)$. Therefore, $\hat{C}_{\boldsymbol{p}}^+$ is a negative semidefinite operator with a nonpositive spectrum of eigenvalues.

The linearized collision operator $\hat{C}_{\boldsymbol{p}}^+$ behaves as a scalar operator with respect to rotations in momentum space. Thus, $\hat{C}_{\boldsymbol{p}}^+ h(\boldsymbol{p})$ transforms in the same way under rotation in momentum space as does $h(\boldsymbol{p})$. Eigenfunctions of $\hat{C}_{\boldsymbol{p}}^+$ have the form

$$\Psi_{r,l,m}(\boldsymbol{p}) = R_{r,l}(p) Y_{l,m} \left(\frac{\boldsymbol{p}}{|\boldsymbol{p}|} \right) , \tag{9.66}$$

where $Y_{l,m}(\boldsymbol{p}/|\boldsymbol{p}|)$ are spherical harmonics.

Let us now solve the linearized Boltzmann equation (9.60) for the case of a spatially homogeneous system. It takes the form

$$\frac{\partial h_1^+}{\partial t} = \hat{C}_1^+ h_1^+ = 2 \iiint \mathrm{d}\boldsymbol{p}_2 \, \mathrm{d}\boldsymbol{p}_3 \, \mathrm{d}\boldsymbol{p}_4 \sigma(g, \Theta) \delta^{(4)}_{1,2;3,4} f_2^0 \left(h_3^+ + h_4^+ - h_1^+ - h_2^+ \right) , \tag{9.67}$$

where $h_1^+ = h^+(\boldsymbol{p}_1, t)$, and so on. We may write the solution to Eq. (9.67) in the form

$$h_1^+(\boldsymbol{p}_1, t) = \sum_{r,l,m} \mathrm{e}^{\lambda_{r,l} t} A_{r,l,m} \Psi_{r,l,m}(\boldsymbol{p}_1) \, . \tag{9.68}$$

The fact that the eigenvalues $\lambda_{r,l}$ must all be negative or zero means that $h_1^+(\boldsymbol{p}_1, t)$ will decay to a time-independent quantity after a long enough time and the system relaxes to equilibrium.

The *Lorentz–Boltzmann equation* can be written in the form

$$\frac{\partial h_1^-}{\partial t} + \dot{\boldsymbol{q}}_1 \cdot \frac{\partial h_1^-}{\partial \boldsymbol{r}} = \hat{C}_1^- h_1^- \,, \tag{9.69}$$

where the Lorentz–Boltzmann collision operator $\hat{C}_1^-$, when acting on an arbitrary function $\Phi(\boldsymbol{p}_1)$ of $\boldsymbol{p}_1$, yields

$$\hat{C}_1^- \Phi(\boldsymbol{p}_1) = 2 \iiint \mathrm{d}\boldsymbol{p}_2 \, \mathrm{d}\boldsymbol{p}_3 \, \mathrm{d}\boldsymbol{p}_4 \sigma(g, \Theta) \delta^{(4)}_{1,2;3,4} f_3^0 (\Phi_3 - \Phi_1) \,. \tag{9.70}$$

The collision operator $\hat{C}_1^-$ differs from $\hat{C}_1^+$ in that it has only one zero eigenvalue, a constant, while the Boltzmann collision operator, $\hat{C}_1^+$, has a fivefold degenerate zero eigenvalue. We can use the Boltzmann and Lorentz–Boltzmann equations to obtain microscopic expressions for the coefficients of self-diffusion, viscosity, and thermal conductivity.

9.5
Coefficient of Self-Diffusion

We shall derive the coefficient of self-diffusion using a method due to Resibois [184] that consists of two steps. In the first step, we derive the linearized hydrodynamic equation from the Lorentz–Boltzmann equation and introduce the self-diffusion coefficient into the hydrodynamic equation using Fick's law. We then can find the dispersion relation for the hydrodynamic diffusion mode. In the second step we use Rayleigh–Schrödinger perturbation theory to obtain the hydrodynamic eigenvalues of the Lorentz–Boltzmann equation. We then match the eigenvalue of the hydrodynamic equation to that of the Lorentz–Boltzmann equation and thereby obtain a microscopic expression for the self-diffusion coefficient.

9.5.1
Derivation of the Diffusion Equation

The difference in A and B particle densities at point $\boldsymbol{r}$ is given by

$$m(\boldsymbol{r}, t) = n_{\mathrm{A}}(\boldsymbol{r}, t) - n_{\mathrm{B}}(\boldsymbol{r}, t) = \int \mathrm{d}\boldsymbol{p}_1 f^0(\boldsymbol{p}_1) h^-(\boldsymbol{p}_1, \boldsymbol{r}, t) \tag{9.71}$$

(at equilibrium this difference is zero). If we multiply the Lorentz–Boltzmann equation by $f^0(\boldsymbol{p}_1)$ and integrate over $\boldsymbol{p}_1$, we obtain

$$\frac{\partial}{\partial t} m(\boldsymbol{r}, t) + \nabla_{\boldsymbol{r}} \cdot \boldsymbol{J}^{\mathrm{D}}(\boldsymbol{r}, t) = 0 \,, \tag{9.72}$$

where $\boldsymbol{J}^{\mathrm{D}}(\boldsymbol{r}, t)$ is the diffusion current and is defined microscopically as

$$\boldsymbol{J}^{\mathrm{D}}(\boldsymbol{r}, t) = \int \mathrm{d}\boldsymbol{p}_1 \frac{\boldsymbol{p}_1}{m} f^0(\boldsymbol{p}_1) h^-(\boldsymbol{p}_1, \boldsymbol{r}, t) \, . \tag{9.73}$$

The contribution from the collision term is identically zero because $C_{\boldsymbol{p}}^{(-)} 1 = 0$. We now introduce the self-diffusion coefficient using Fick's law:

$$\boldsymbol{J}^{\mathrm{D}}(\boldsymbol{r}, t) = -D \nabla_{\boldsymbol{r}} m(\boldsymbol{r}, t) \, . \tag{9.74}$$

If we combine Eqs. (9.72) and (9.74), we obtain the following hydrodynamic equation for the self-diffusion process:

$$\frac{\partial}{\partial t} m(\boldsymbol{r}, t) = D \nabla_{\boldsymbol{r}}^2 m(\boldsymbol{r}, t) \, . \tag{9.75}$$

To find the dispersion relation for hydrodynamic modes we define the Fourier transform

$$m(\boldsymbol{r}, t) = \frac{1}{(2\pi)^4} \int \mathrm{d}\boldsymbol{k} \int \mathrm{d}\omega \tilde{m}(\boldsymbol{k}, \omega) \mathrm{e}^{\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{r} - \omega t)} \, , \tag{9.76}$$

which allows us to study each Fourier component of the diffusion equation separately. If we substitute Eq. (9.76) into Eq. (9.75) we obtain

$$-\mathrm{i}\omega \tilde{m}(\boldsymbol{k}, \omega) + D k^2 \tilde{m}(\boldsymbol{k}, \omega) = 0 \, . \tag{9.77}$$

From Eq. (9.77) we obtain the following dispersion relation for the self-diffusion mode:

$$\omega = -\mathrm{i} D k^2 \, . \tag{9.78}$$

The diffusion frequency is imaginary, which means that the contribution to the density $m(\boldsymbol{r}, t)$ with wavevector k dies out in a time which depends on the diffusion coefficient and the wavevector k:

$$m(\boldsymbol{r}, t) \sim \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}} \mathrm{e}^{-Dk^2 t} \, . \tag{9.79}$$

Very-long-wavelength disturbances take a long time to decay away. This is the characteristic behavior of a hydrodynamic mode. Since the identity of the particles is preserved in each collision, the only way to cause difference in the density of A and B particles to disappear is to physically transport particles from one part of the fluid to another. For very-long-wavelength disturbances the equalization takes a long time since the particles must be transported over long distances.

9.5.2
Eigenfrequencies of the Lorentz–Boltzmann Equation

We can obtain the hydrodynamic eigenfrequencies of the Lorentz–Boltzmann equation by using the Rayleigh–Schrödinger perturbation theory [136]. We can then equate the eigenfrequency of the hydrodynamic equation $\omega = -\mathrm{i}Dk^2$ to the hydrodynamic eigenfrequency of the Lorentz–Boltzmann equation and thereby obtain a microscopic expression for the coefficient of self-diffusion, D.

Since Eq. (9.69) is a linear equation for $h^-(\boldsymbol{p}_1, \boldsymbol{r}, t)$, we can consider each Fourier component separately and write

$$h^-(\boldsymbol{p}, \boldsymbol{r}, t) = |\Psi_n(\boldsymbol{p}, \boldsymbol{k})\rangle_- \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}} \mathrm{e}^{-\mathrm{i}\omega_n t} . \tag{9.80}$$

We then obtain the following eigenvalue equation for $|\Psi_n(\boldsymbol{p}, \boldsymbol{k})\rangle_-$:

$$\left(\hat{C}_p^- - \mathrm{i}k\hat{\boldsymbol{e}}_k \cdot \frac{\boldsymbol{p}}{m}\right) |\Psi_n(\boldsymbol{p}, \boldsymbol{k})\rangle_- = -\mathrm{i}\omega_n^- |\Psi_n(\boldsymbol{p}, \boldsymbol{k})\rangle_- , \tag{9.81}$$

where $\hat{\boldsymbol{e}}_k = \boldsymbol{k}/|\boldsymbol{k}|$ and the eigenfunctions, $|\Psi_n(\boldsymbol{q}, \boldsymbol{k})\rangle_-$, are assumed to be orthonormal. For long-wavelength hydrodynamic disturbances, k will be a small parameter, and we can use Rayleigh–Schrödinger perturbation theory to obtain a perturbation expansion for ω_n in powers of k.

Let us assume that both ω_n^- and $|\Psi_n(\boldsymbol{q}, \boldsymbol{k})\rangle_-$ can be expanded in powers of k. Then

$$\omega_n = \omega_n^{(0)} + k\omega_n^{(1)} + k^2\omega_n^{(2)} + \cdots \tag{9.82}$$

and

$$|\Psi_n\rangle_- = |\Psi_n^{(0)}\rangle_- + k|\Psi_n^{(1)}\rangle_- + k^2|\Psi_n^{(2)}\rangle_- + \cdots \tag{9.83}$$

If we substitute Eqs. (9.82) and (9.83) into Eq. (9.81), we obtain the following expression for quantities $\omega_n^{(0)}$, $\omega_n^{(1)}$ and $\omega_n^{(2)}$:

$$\omega_n^{(0)} = i_-\left\langle \Psi_n^{(0)} \middle| \hat{C}_{\boldsymbol{p}}^- \middle| \Psi_n^{(0)} \right\rangle_- , \quad \omega_n^{(1)} = {}_-\left\langle \Psi_n^{(0)} \middle| \hat{\boldsymbol{e}}_k \cdot \frac{\boldsymbol{p}}{m} \middle| \Psi_n^{(0)} \right\rangle_- \tag{9.84}$$

and

$$\omega_n^{(2)} = {}_-\langle \Psi_n^{(0)} | \left(\hat{\boldsymbol{e}}_k \cdot \frac{\boldsymbol{p}}{m} - \omega_n^{(1)}\right) \left(\frac{-1}{\mathrm{i}\hat{C}_{\boldsymbol{p}}^- + \omega_n^{(0)}}\right) \left(\hat{\boldsymbol{e}}_k \cdot \frac{\boldsymbol{p}}{m} - \omega_n^{(1)}\right) |\Psi_n^{(0)}\rangle_- , \tag{9.85}$$

where the matrix elements are defined as in Eq. (9.64) and $\langle \Psi_{n'}^0 | \Psi_n^0 \rangle \equiv \delta_{n,n'}$. At this point we shall restrict our attention to the eigenvalue which reduces to zero when $k \to 0$. This corresponds to the hydrodynamic mode. There will be only one such eigenvalue of $\hat{C}_{\boldsymbol{p}}^-$.

We will let $|\Psi_1^{(0)}\rangle_-$ denote the eigenfunction of $\hat{C}_{\boldsymbol{p}}^-$ with eigenvalue zero and we normalize it using the scalar product in Eq. (9.64). Then $|\Psi_1^{(0)}\rangle_- = 1$ and we obtain

$$\omega_1^{(0)} = 0 , \quad \omega_1^{(1)} = \frac{1}{m}\left(\frac{\beta}{2\pi m}\right)^{3/2} \int \mathrm{d}\boldsymbol{p}_1 \mathrm{e}^{-\beta p_1^2/(2m)} \hat{\boldsymbol{e}}_k \cdot \boldsymbol{p}_1 \equiv 0 \tag{9.86}$$

and

$$\omega_1^{(2)} = -\frac{1}{m^2}\left(\frac{\beta}{2\pi m}\right)^{3/2} \int \mathrm{d}\boldsymbol{p}_1 \mathrm{e}^{-\beta p_1^2/(2m)} \hat{\boldsymbol{e}}_k \cdot \boldsymbol{p}_1 \frac{1}{i\hat{C}_{\boldsymbol{p}}^-} \hat{\boldsymbol{e}}_k \cdot \boldsymbol{p}_1 \,. \tag{9.87}$$

The hydrodynamic eigenfrequency, ω_1, has the correct hydrodynamic behavior. If we now equate Eqs. (9.78) and (9.82) and use Eqs. (9.86) and (9.87), we find

$$D = -\frac{1}{m^2}\left(\frac{\beta}{2\pi m}\right)^{3/2} \int \mathrm{d}\boldsymbol{p}_1 \mathrm{e}^{-\beta p_1^2/(2m)} \hat{\boldsymbol{e}}_k \cdot \boldsymbol{p}_1 \frac{1}{\hat{C}_{\boldsymbol{p}}^-} \hat{\boldsymbol{e}}_k \cdot \boldsymbol{p}_1 \,. \tag{9.88}$$

Thus, we have obtained a microscopic expression for the self-diffusion coefficient, D. In later sections, we will discuss how to evaluate the integral in (9.88).

9.6
Coefficients of Viscosity and Thermal Conductivity

The Boltzmann collision operator, $\hat{C}_{\boldsymbol{p}}^{(+)}$, has five zero eigenvalues. Therefore, we can derive, from the linearized Boltzmann equation, five linearized hydrodynamic equations: one equation for the total particle density, $n(\boldsymbol{r}, t) = n_N(\boldsymbol{r}, t) + n_{\mathrm{T}}(\boldsymbol{r}, t)$; three equations for the three components of the momentum density, $mn(\boldsymbol{r}, t)\boldsymbol{v}(\boldsymbol{r}, t)$, where $\boldsymbol{v}(\boldsymbol{r}, t)$ is the average velocity; and one equation for the average internal energy density. To find the hydrodynamic eigenfrequencies (which will be expressed in terms of the coefficients of viscosity and thermal conductivity), we find the normal modes of the system of five hydrodynamic equations. We find the five *microscopic* hydrodynamic frequencies of the Boltzmann equation using Rayleigh–Schrödinger perturbation theory. We then can match the five frequencies of the hydrodynamic equations to the five microscopic frequencies and thereby obtain microscopic expressions for the coefficients of viscosity and thermal conductivity.

9.6.1
Derivation of the Hydrodynamic Equations

We now derive the linearized hydrodynamic equations from the linearized Boltzmann equation [60]. The average particle density is defined by

$$n(\boldsymbol{r}, t) = \int \mathrm{d}\boldsymbol{p} f^0(\boldsymbol{p})(1 + h^+(\boldsymbol{p}, \boldsymbol{r}, t)) \,. \tag{9.89}$$

If we multiply Eq. (9.60) by $f^0(\boldsymbol{p}_1)$, integrate over $\boldsymbol{p}_1$, and make use of the fact that $\hat{C}_{\mathrm{p}}^{(+)} 1 = 0$, we obtain

$$\frac{\partial}{\partial t} n(\boldsymbol{r}, t) + \nabla_{\boldsymbol{r}} \cdot \boldsymbol{J}^n(\boldsymbol{r}, t) = 0 \,, \tag{9.90}$$

where $\boldsymbol{J}^n(\boldsymbol{r}, t)$ is the average particle current and is defined as

$$\boldsymbol{J}^n(\boldsymbol{r}, t) = \int \mathrm{d}\boldsymbol{p} \frac{\boldsymbol{p}}{m} f^0(\boldsymbol{p}) h^+(\boldsymbol{p}, \boldsymbol{r}, t) \,. \tag{9.91}$$

It is useful to decompose $\boldsymbol{J}^n(\boldsymbol{r}, t)$ into the product $\boldsymbol{J}^n(\boldsymbol{r}, t) = n(\boldsymbol{n}, t)\boldsymbol{v}(\boldsymbol{r}, t)$. In the linear regime, $\boldsymbol{J}^n(\boldsymbol{r}, t) \approx n_0 \boldsymbol{v}(\boldsymbol{r}, t)$, where n_0 is the equilibrium particle density. Equation (9.90) then becomes

$$\frac{\partial}{\partial t} n(\boldsymbol{r}, t) + n_0 \nabla_{\boldsymbol{r}} \cdot \boldsymbol{v}(\boldsymbol{r}, t) = 0 \,. \tag{9.92}$$

Equation (9.92) is the linearized continuity equation and describes the conservation of total particle number.

If we multiply Eq. (9.60) by $\boldsymbol{p}_1 f^0(\boldsymbol{p}_1)$, integrate over $\boldsymbol{p}_1$, and use the fact that $\hat{C}_{\boldsymbol{p}}^{(+)} \boldsymbol{p} \equiv 0$, we obtain

$$m \frac{\partial}{\partial t} \boldsymbol{J}^n(\boldsymbol{r}, t) = -\nabla_{\boldsymbol{r}} \cdot \overline{\boldsymbol{P}}(\boldsymbol{r}, t) \,, \tag{9.93}$$

where $\overline{\boldsymbol{P}}(\boldsymbol{r}, t)$ is the pressure tensor and is defined

$$\overline{\boldsymbol{P}}(\boldsymbol{r}, t) = \frac{1}{m} \int \mathrm{d}\boldsymbol{p} f^0(\boldsymbol{p}) \boldsymbol{p}\boldsymbol{p} h^+(\boldsymbol{p}, \boldsymbol{r}, t). \tag{9.94}$$

The pressure tensor describes the momentum flux, or current, in the system and contains an irreversible part due to viscous effects.

To obtain the equation for the internal energy density, we must take the average of the thermal kinetic energy $1/(2m)(\boldsymbol{p} - mv(\boldsymbol{r}, t))^2$. However, in the linear approximation, $\boldsymbol{v}(\boldsymbol{r}, t)$ does not contribute. Thus, we can multiply Eq. (9.62) by $p_1^2/(2m)$ and integrate over $\boldsymbol{p}_1$. If we use the fact that $\hat{C}_{\boldsymbol{p}}^{(+)} p^2 \equiv 0$, we obtain

$$\frac{\partial}{\partial t} u(\boldsymbol{r}, t) = -\nabla_{\boldsymbol{r}} \cdot \boldsymbol{J}^u(\boldsymbol{r}, t) \,, \tag{9.95}$$

where $u(r, t)$ is the internal energy per unit volume,

$$u(\boldsymbol{r}, t) = \int \mathrm{d}\boldsymbol{p} \frac{p^2}{2m} f^0(\boldsymbol{p}) h^+(\boldsymbol{p}, \boldsymbol{r}, t) \,, \tag{9.96}$$

and $\boldsymbol{J}^u(\boldsymbol{r}, t)$ is the internal energy current,

$$\boldsymbol{J}^u(\boldsymbol{r}, t) = \int \mathrm{d}\boldsymbol{p} \frac{p^2}{2m} \frac{\boldsymbol{p}}{m} f^0(\boldsymbol{p}) h^+(\boldsymbol{p}, \boldsymbol{r}, t) \,. \tag{9.97}$$

We can write the internal energy density in the form $u(\boldsymbol{r}, t) = n(\boldsymbol{r}, t)e(\boldsymbol{r}, t)$, where $e(\boldsymbol{r}, t)$ is the internal energy per particle. In the linear approximation we find $u(\boldsymbol{r}, t) = n_0 e(\boldsymbol{r}, t) + e_0 n(\boldsymbol{r}, t)$, and Eq. (9.95) takes the form

$$n_0 \frac{\partial}{\partial t} e(\boldsymbol{r}, t) + e_0 \frac{\partial}{\partial t} n(\boldsymbol{r}, t) = -\nabla_{\boldsymbol{r}} \cdot \boldsymbol{J}^u(\boldsymbol{r}, t) \,, \tag{9.98}$$

where e_0 is the equilibrium internal energy per particle. The current $\boldsymbol{J}^u(\boldsymbol{r}, t)$ will contain an irreversible part due to thermal conduction.

As a next step we must write expressions for the pressure tensor, $\overline{\boldsymbol{P}}(\boldsymbol{r}, t)$, and the energy current, $\boldsymbol{J}^u(\boldsymbol{r}, t)$ in terms of transport coefficients. The form that these two quantities must take was discussed in Section 8.2. From Eqs. (8.11), (8.35), and (8.36), we can write the pressure tensor in the form

$$P_{ij}(\boldsymbol{r}, t) = P(\boldsymbol{r}, t)\delta_{ij} - \zeta\delta_{ij}(\nabla_{\boldsymbol{r}} \cdot \boldsymbol{v}) - \eta\left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} - \frac{2}{3}\delta_{ij}\nabla_{\boldsymbol{r}} \cdot \boldsymbol{v}\right), \quad (9.99)$$

where $P(\boldsymbol{r}, t)$ is the hydrostatic pressure, ζ is the coefficient of bulk viscosity, and η is the coefficient of shear viscosity. If we substitute Eq. (9.99) into Eq. (9.93) we obtain, after some rearrangement,

$$mn_0\frac{\partial}{\partial t}\boldsymbol{v}(\boldsymbol{r}, t) = -\nabla_{\boldsymbol{r}}P(\boldsymbol{r}, t) + \eta\nabla_{\boldsymbol{r}}^2\boldsymbol{v}(\boldsymbol{r}, t) + \left(\zeta + \frac{1}{3}\eta\right)\nabla_{\boldsymbol{r}}(\nabla_{\boldsymbol{r}} \cdot \boldsymbol{v}(\boldsymbol{r}, t)) . \quad (9.100)$$

The contribution from the hydrostatic pressure term is reactive, whereas the viscous contribution is dissipative. All terms in Eq. (9.100) are linear in deviations from equilibrium.

Let us now consider the energy equation, Eq. (9.98). The energy current will have a contribution from the convection of internal energy, a contribution involving the pressure which comes from work done in compression or expansion of regions in the fluid, and a contribution from heat conduction (cf. Eq. (8.29)). Thus, in the linear approximation we can write

$$\boldsymbol{J}^u(\boldsymbol{r}, t) = n_0e_0\boldsymbol{v}(\boldsymbol{r}, t) + P_0\boldsymbol{v}(\boldsymbol{r}, t) - K\nabla_{\boldsymbol{r}}T(\boldsymbol{r}, t) , \quad (9.101)$$

where P_0 is the equilibrium pressure, K is the coefficient of thermal conductivity, and $T(\boldsymbol{r}, t)$ is the temperature. If we substitute Eq. (9.101) into Eq. (9.98) and make use of Eq. (9.92), we find

$$n_0\frac{\partial}{\partial t}e(\boldsymbol{r}, t) = -P_0\nabla_{\boldsymbol{r}} \cdot \boldsymbol{v}(\boldsymbol{r}, t) + K\nabla_{\boldsymbol{r}}^2T(\boldsymbol{r}, t) . \quad (9.102)$$

Equation (9.102) simplifies when we write it in terms of the local entropy. If we use the thermodynamic relation $\mathrm{d}e = T\,\mathrm{d}s + P/n^2\,\mathrm{d}n$, we can write

$$\frac{\partial e}{\partial t} = T\frac{\partial s}{\partial t} + \frac{P}{n^2}\frac{\partial n}{\partial t} . \quad (9.103)$$

If we combine Eqs. (9.102) and (9.92), we obtain

$$n_0T_0\frac{\partial}{\partial t}s(\boldsymbol{r}, t) = K\nabla_{\boldsymbol{r}}^2T(\boldsymbol{r}, t) \quad (9.104)$$

where T_0 is the equilibrium temperature and $s(\boldsymbol{r}, t)$ is the local entropy per particle.

The hydrodynamic equations (Eqs. (9.92), (9.100), and (9.104)), which have been derived from the Boltzmann equation with the help of thermodynamic relations, are identical to Eqs. (8.47)–(8.49). If we choose the density, $n(\boldsymbol{r}, t)$, and the temperature, $T(\boldsymbol{r}, t)$, to be the independent variables, the hydrodynamic equations take the form

$$\frac{\partial n}{\partial t} + n_0 \nabla_{\boldsymbol{r}} \cdot \boldsymbol{v} = 0 , \tag{9.105}$$

$$mn_0 \frac{\partial \boldsymbol{v}}{\partial t} = -\left(\frac{\partial P}{\partial n}\right)_T^0 \nabla_{\boldsymbol{r}} n - \left(\frac{\partial P}{\partial T}\right)_n^0 \nabla_{\boldsymbol{r}} T + \eta \nabla_{\boldsymbol{r}}^2 \boldsymbol{v} + \left(\zeta + \frac{1}{3}\eta\right) \nabla_{\boldsymbol{r}} (\nabla_{\boldsymbol{r}} \cdot \boldsymbol{v}) , \tag{9.106}$$

and

$$mn_0 \left(\frac{\partial s}{\partial n}\right)_T^0 \frac{\partial n}{\partial t} + mn_0 \left(\frac{\partial s}{\partial T}\right)_\rho^0 \frac{\partial T}{\partial t} = \frac{K}{T_0} \nabla_{\boldsymbol{r}}^2 T . \tag{9.107}$$

Equations (9.105)–(9.107) are coupled equations for variations in average density, velocity, and temperature.

We now must find normal mode solutions. Since the equations are linear, each Fourier component will propagate independently. Thus, we only need to consider a single Fourier component. We can write

$$n(\boldsymbol{r}, t) = n_{\boldsymbol{k}}(\omega) \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}} , \quad \boldsymbol{v}(\boldsymbol{r}, t) = \boldsymbol{v}_{\boldsymbol{k}}(\omega) \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}} , \quad \text{and} \quad T(\boldsymbol{r}, t) = T_{\boldsymbol{k}}(\omega) \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}} . \tag{9.108}$$

We can also separate the average velocity, $\boldsymbol{v}_{\boldsymbol{k}}$, into a longitudinal part, $\boldsymbol{v}^{\parallel} = v^{\parallel} \hat{\boldsymbol{e}}_{\boldsymbol{k}}$, and a transverse part, $\boldsymbol{v}^{\perp}$ (cf. Section 8.3). The hydrodynamic equation for the transverse velocity, which describes the propagation of shear waves, takes the form

$$(-\mathrm{i}\omega + \nu_{\mathrm{t}} k^2) \tilde{\boldsymbol{v}}_{\boldsymbol{k}}^{\perp}(\omega) = 0 , \tag{9.109}$$

where $\nu_{\mathrm{t}} = \eta / mn_0$ denotes the transverse kinetic viscosity. The dispersion relation for the transverse mode is given by Eq. (9.109). It is

$$\omega = -\mathrm{i}\nu_{\mathrm{t}} k^2 . \tag{9.110}$$

There are two shear modes with this frequency. Thus, we find that the shear waves behave very much like the diffusion waves. Any shear disturbance will be damped out.

The longitudinal modes satisfy the equation

$$\begin{pmatrix} \mathrm{i}\omega & -\mathrm{i}\rho_{\mathrm{o}} k & 0 \\ -\frac{\mathrm{i}kc_0^2}{\gamma\rho_0} & [\mathrm{i}\omega + \nu_{\mathrm{l}} k^2] & -\frac{\mathrm{i}kc_0^2 \alpha_P}{\gamma} \\ -\mathrm{i}\omega \frac{c_0^2 \alpha_P}{\rho_0 \gamma} & 0 & \frac{c_\rho}{T_0} [\mathrm{i}\omega + \gamma\chi k^2] \end{pmatrix} \begin{pmatrix} \tilde{\rho}_{\boldsymbol{k}}(\omega) \\ \tilde{v}_{\boldsymbol{k}}(\omega) \\ \tilde{T}_{\boldsymbol{k}}(\omega) \end{pmatrix} = 0 , \tag{9.111}$$

where $c_0 = \sqrt{(\partial P/\partial(mn_0))_s}$ is the speed of sound, $\alpha_P = -(1/n_0)(\partial n/\partial T)_P$ is the thermal expansivity, $\gamma = \boldsymbol{c}_P/\boldsymbol{c}_\rho$, $\nu_l = (1/\rho_0)(\zeta + 4/3\eta)$ is the longitudinal kinetic viscosity and $\chi = K/(mn_0 c_P)$ (cf. Section 8.3). The dispersion relations for the longitudinal modes can be found by setting the determinant of the matrix in Eq. (9.110) to zero and solving for ω. To second order in wavevector k (small k means long-wavelength disturbances), we find

$$\omega_1 = -\mathrm{i}\left[\frac{Kk^2}{n_0 c_P}\right] \tag{9.112}$$

and

$$\omega_\pm = \pm c_0 k - \frac{\mathrm{i}k^2}{2mn_0}\left[\frac{4}{3}\eta + \zeta + mK\left(\frac{1}{c_v} - \frac{1}{c_P}\right)\right]. \tag{9.113}$$

The first solution (9.112) is purely imaginary and the second two solutions (9.113) are complex.

The wave of frequency ω_1 corresponds predominantly to an entropy (or heat) wave. It is damped out exponentially with time. The waves of frequency $\omega_\pm$ (waves going in opposite directions) correspond to pressure or longitudinal velocity waves (sound waves). These waves propagate but, in the presence of transport processes, they eventually get damped out. Thus, at long wavelengths there are two shear modes, one heat mode, and two sound modes in the fluid. The frequencies in Eqs. (9.110), (9.112), and (9.113) are the normal mode frequencies of the system. These five frequencies, together with the diffusion frequency, Eq. (9.78), give the six normal mode frequencies of this two-component dilute gas.

9.6.2
Eigenfrequencies of the Boltzmann Equation

The second step in deriving microscopic expressions for the thermal conductivity and shear viscosity is to obtain the hydrodynamic eigenfrequencies of the linearized Boltzmann equation. We only need to consider one Fourier component of the linearized Boltzmann equation. If we let

$$h^+(\boldsymbol{p}, \boldsymbol{r}, t) = |\Psi_n(\boldsymbol{p}, \boldsymbol{k})\rangle_+ \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}} \mathrm{e}^{-\mathrm{i}\omega_n t}, \tag{9.114}$$

we obtain the following eigenvalue equation for the eigenvectors:

$$\left(\hat{C}^+_{\boldsymbol{p}} - \mathrm{i}k\hat{\boldsymbol{e}}_k \cdot \frac{\boldsymbol{p}}{m}\right)|\Psi_n(\boldsymbol{p}, \boldsymbol{k})\rangle_+ = -\mathrm{i}\omega_n |\Psi_n(\boldsymbol{p}, \boldsymbol{k})\rangle_+ . \tag{9.115}$$

To obtain a perturbation expansion for ω_n in powers of k, we must first look at the eigenvalue problem for the unperturbed operator $\hat{C}^+_{\boldsymbol{p}}$. We will denote the eigenfunctions of $\hat{C}^+_{\boldsymbol{p}}$ by $|\phi_n\rangle$. Then $\boldsymbol{\hat{C}}^+_{\boldsymbol{p}}|\phi_n\rangle = -\mathrm{i}\omega^0_n|\phi_n\rangle$.

We know that $\hat{C}^+_{\boldsymbol{p}}$ has five zero eigenvalues and we must take this into account when writing a perturbation expansion for eigenstates $|\Psi_n(\boldsymbol{p}, \boldsymbol{k})\rangle_+$. We shall use the method outlined in [136] for writing perturbation expansions when the unperturbed system is degenerate. The orthonormalized eigenfunctions of $\hat{\boldsymbol{C}}_{\boldsymbol{p}}^{+}$, which have eigenvalue zero, are given by

$$|\phi_1\rangle = 1\,, \quad |\phi_2\rangle = \sqrt{\frac{\beta}{m}}p_x\,, \quad |\phi_3\rangle = \sqrt{\frac{\beta}{m}}p_y\,, \quad |\phi_4\rangle = \sqrt{\frac{\beta}{m}}p_z\,, \tag{9.116}$$

and

$$|\phi_5\rangle = \sqrt{\frac{2}{3}}\left(-\frac{3}{2} + \frac{\beta}{2m}p^2\right)\,. \tag{9.117}$$

We shall denote the five eigenfunctions collectively as $|\phi_\alpha\rangle$, where $\alpha = 1, 2, 3, 4$, and 5. All other eigenfunctions will be denoted collectively as $|\phi_\beta\rangle$ where $\beta = 6, \ldots, \infty$. The eigenfunctions $|\phi_n\rangle$ are assumed orthonormal with respect to the scalar product in Eq. (9.64).

Since the eigenfunctions $|\phi_\alpha\rangle$ are degenerate, we must first find the proper linear combination of them to use for the zero-order approximation to the exact eigenfunctions $|\Psi_\alpha\rangle_+$. Therefore, we write

$$|\Psi_\alpha\rangle_+ = \left|\Psi_\alpha^{(0)}\right\rangle_+ + k\left|\Psi_\alpha^{(1)}\right\rangle_+ + k^2\left|\Psi_\alpha^{(2)}\right\rangle_+ + \cdots\,, \tag{9.118}$$

where

$$\left|\Psi_\alpha^{(0)}\right\rangle_+ = \sum_{\alpha'} c_{\alpha\alpha'}\,|\phi_{\alpha'}\rangle\,. \tag{9.119}$$

The process of determining the coefficients $c_{\alpha\alpha'}$ will also give us the first-order term, $\omega_\alpha^{(1)}$, in the perturbation expansion of ω_α:

$$\omega_\alpha = \omega_\alpha^{(0)} + k\omega_\alpha^{(1)} + k^2\omega_\alpha^{(2)} + \cdots \tag{9.120}$$

To find the coefficients $c_{\alpha\alpha'}$ and $\omega_\alpha^{(1)}$, let us first insert the expansions in Eqs. (9.118)–(9.120) into Eq. (9.115) and equate coefficients of terms that are first order in k. We then obtain

$$\hat{\boldsymbol{C}}_{\boldsymbol{p}}^{+}\left|\Psi_\alpha^{(1)}\right\rangle_+ = i\left(-\omega_\alpha^{(1)} + \frac{\hat{\boldsymbol{e}}_k \cdot \boldsymbol{p}}{m}\right)\left|\Psi_\alpha^{(0)}\right\rangle_+\,. \tag{9.121}$$

If we multiply Eq. (9.121) by $\langle\,\phi_{\alpha''}|$, we obtain

$$\omega_\alpha^{(1)}\left\langle\phi_{\alpha''}, \Psi_\alpha^{(0)}\right\rangle_+ = \left\langle\phi_{\alpha''}, (\hat{\boldsymbol{e}}_k \cdot \frac{\boldsymbol{p}}{m})\Psi_\alpha^{(0)}\right\rangle_+ \tag{9.122}$$

(note that since $\hat{C}_{\boldsymbol{p}}^{(+)}$ is self-adjoint, $\langle\phi_{\alpha''}|$ is the adjoint of its dual vector $|\phi_{\alpha''}\rangle$), or, using Eq. (9.119), we obtain

$$\omega_\alpha^{(1)}c_{\alpha\alpha''} = \sum_{\alpha'} W_{\alpha''\alpha'}c_{\alpha\alpha'}\,, \tag{9.123}$$

where

$$W_{\alpha''\alpha'} = \left\langle \phi_{\alpha''} \frac{\hat{\boldsymbol{e}}_k \cdot \boldsymbol{p}}{m} \phi_{\alpha'} \right\rangle = \left(\frac{\beta}{2\pi m}\right)^{3/2} \int \mathrm{d}\boldsymbol{p} \mathrm{e}^{-\beta p^2/(2m)} \phi_{\alpha''}(\boldsymbol{p}) \frac{\hat{\boldsymbol{e}}_k \cdot \boldsymbol{p}}{m} \phi_{\alpha'}(\boldsymbol{p}) . \tag{9.124}$$

If we use the expressions for $|\phi_\alpha\rangle (\alpha = 1, \dots , 5)$ given in Eqs. (9.116) and (9.117) and assume, for simplicity, that $\boldsymbol{k}$ lies along the x-axis so that $\boldsymbol{p} \cdot \hat{\boldsymbol{e}}_k = p_x$, we find by explicit calculation that

$$W_{12} = W_{21} = \left(\frac{1}{m\beta}\right)^{1/2} \quad \text{and} \quad W_{25} = W_{52} = \left(\frac{2}{3}\right)^{1/2} \left(\frac{1}{m\beta}\right)^{1/2} . \tag{9.125}$$

For all other α'' and α', $W_{\alpha''\alpha'} \equiv 0$.

We may obtain values for $\omega_\alpha^{(1)}$ from Eq. (9.123). We first write it in matrix form and set the determinant of the matrix to zero:

$$\det(\bar{W} - \omega^{(1)} \bar{\mathbf{1}}) = 0 . \tag{9.126}$$

If we evaluate the above determinant, we obtain

$$(-\omega^{(1)})^3 \left[(\omega^{(1)})^2 - \frac{5}{3}\frac{1}{m\beta}\right] = 0 . \tag{9.127}$$

From Eq. (9.127) we obtain the following first-order corrections to ω_α,

$$\omega_1^{(1)} = -\omega_2^{(1)} = \left(\frac{5}{3}\frac{1}{m\beta}\right)^{1/2} = c_0 \quad \text{and} \quad \omega_3^{(1)} = \omega_4^{(1)} = \omega_5^{(1)} = 0 . \tag{9.128}$$

In (9.128), $c_0 = \sqrt{5k_\mathrm{B}T/(3m)}$ is the speed of sound of an ideal gas. Notice that we have lifted the degeneracy of only two of the states $|\Psi_\alpha\rangle_+$. We have to go to higher orders in the perturbation expansion to lift the degeneracy in the rest of the states.

Now that we have expressions for $\omega_\alpha^{(1)}$ and $W_{\alpha\alpha'}$, we can use Eq. (9.123) and the orthonormality of the states $|\Psi_\alpha^{(0)}\rangle_+$ to obtain expressions for $c_{\alpha\alpha'}$ and, therefore, for $|\Psi_\alpha^{(0)}\rangle_+$. Substitution of Eqs. (9.125) and (9.128) into Eq. (9.123) gives the following results:

$$\begin{gathered}
c_{13} = c_{14} = c_{23} = c_{24} = c_{32} = c_{42} = c_{52} = 0 , \quad c_{15} = (2/5)^{1/2} , \\
c_{12} = (2/3)^{1/2} c_{11} , \quad c_{25} = -(2/5)^{1/2} , \quad c_{22} = (2/3)^{1/2} c_{21} , \\
c_{35} = -(3/2)^{1/2} c_{31} , \quad c_{45} = -(3/2)^{1/2} c_{41} , \quad \text{and} \quad c_{51} = -(2/3)^{1/2} c_{55} .
\end{gathered}$$

The condition of orthonormality of $|\Psi_\alpha^{(0)}\rangle_+$ gives us $c_{12} = c_{22} = 2^{-1/2}, c_{55} = (3/5)^{1/2}$, and $c_{31} = c_{34} = c_{41} = c_{43} = c_{53} = c_{54} = 0$. We therefore obtain the following expressions for the zeroth order eigenfunctions $|\Psi_\alpha^{(0)}\rangle_+$:

$$|\Psi_1^{(0)}\rangle_+ = \frac{1}{\sqrt{2}}\left[\left(\frac{3}{5}\right)^{1/2}|\phi_1\rangle + |\phi_2\rangle + \left(\frac{2}{5}\right)^{1/2}|\phi_5\rangle\right] , \tag{9.129}$$

$$|\Psi_2^{(0)}\rangle_+ = \frac{1}{\sqrt{2}}\left[\left(\frac{3}{5}\right)^{1/2}|\phi_1\rangle - |\phi_2\rangle + \left(\frac{2}{5}\right)^{1/2}|\phi_5\rangle\right] , \tag{9.130}$$

$$|\Psi_3^{(0)}\rangle_+ = |\phi_3\rangle , \quad |\Psi_4^{(0)}\rangle_+ = |\phi_4\rangle , \tag{9.131}$$

and

$$|\Psi_5^{(0)}\rangle_+ = \sqrt{\frac{2}{5}}\left[-|\phi_1\rangle + \left(\frac{3}{2}\right)^{1/2}|\phi_5\rangle\right] . \tag{9.132}$$

We can now use the states $|\Psi_\alpha^{(0)}\rangle_+$ as the basis states for the perturbation expansion. The general expression for $\omega_n^{(2)}$ has been given in Eq. (9.85). We thus find the following expressions for the five hydrodynamic frequencies:

$$\omega_1 = c_0 k + \mathrm{i}k^2 + \langle\Psi_1^{(0)}|\left(\frac{p_x}{m} - c_0\right)\frac{1}{\hat{C}_{\boldsymbol{p}}^+}\left(\frac{p_x}{m} - c_0\right)|\Psi_1^{(0)}\rangle_+ , \tag{9.133}$$

$$\omega_2 = c_0 k + \mathrm{i}k^2 + \langle\Psi_2^{(0)}|\left(\frac{p_x}{m} + c_0\right)\frac{1}{\hat{C}_{\boldsymbol{p}}^+}\left(\frac{p_x}{m} + c_0\right)|\Psi_2^{(0)}\rangle_+ , \tag{9.134}$$

$$\omega_3 = \mathrm{i}k^2 + \langle\Psi_3^{(0)}|\frac{p_x}{m}\frac{1}{\hat{C}_{\boldsymbol{p}}^+}\frac{p_x}{m}|\Psi_3^{(0)}\rangle_+ , \tag{9.135}$$

$$\omega_4 = \mathrm{i}k^2 + \langle\Psi_4^{(0)}|\frac{p_x}{m}\frac{1}{\hat{C}_{\boldsymbol{p}}^+}\frac{p_x}{m}|\Psi_4^{(0)}\rangle_+ , \tag{9.136}$$

and

$$\omega_5 = \mathrm{i}k^2{}_+\left\langle\Psi_5^{(0)}\middle|\frac{p_x}{m}\frac{1}{\hat{C}_{\boldsymbol{p}}^+}\frac{p_x}{m}\middle|\Psi_5^{(0)}\right\rangle_+ . \tag{9.137}$$

The frequencies ω_1 and ω_2 may be identified with sound modes, frequencies ω_3 and ω_4 may be identified with shear modes, and frequency ω_5 may be identified with the heat mode.

9.6.3
Shear Viscosity and Thermal Conductivity

Given the microscopic expressions for the hydrodynamic frequencies in Eqs. (9.133)–(9.137), we can match them to the frequencies obtained from the linearized, hydrodynamic equations and obtain microscopic expressions for the transport coefficients. If we equate Eqs. (9.110) and (9.135), we find for the shear viscosity

$$\eta = -\frac{n_0\beta}{m^2}\left(\frac{\beta}{2\pi m}\right)^{3/2}\int \mathrm{d}\boldsymbol{p}\mathrm{e}^{-\beta p^2/(2m)} p_y p_x \frac{1}{\hat{C}_{\boldsymbol{p}}^+} p_y p_x . \tag{9.138}$$

If we equate Eqs. (9.112) and (9.137), we obtain for the thermal conductivity

$$K = -\frac{2n_0 c_P}{5m^2}\left(\frac{\beta}{2\pi m}\right)^{3/2} \times \int \mathrm{d}\boldsymbol{p}\mathrm{e}^{-\beta p^2/(2m)}\left(\frac{p^2\beta}{2m}-\frac{5}{2}\right) p_x \frac{1}{\hat{C}^+_{\boldsymbol{p}}} p_x \left(\frac{p^2\beta}{2m}-\frac{5}{2}\right) . \tag{9.139}$$

Note that the shear viscosity is expressed in the form of a momentum current correlation function and the thermal conductivity is expressed in the form of an enthalpy current correlation function.

9.7
Computation of Transport Coefficients

The coefficients of self-diffusion, D, thermal conductivity, K, and shear viscosity, η, may be written in the form

$$D = -\frac{1}{m^2}\left(\frac{\beta}{2\pi m}\right)^{3/2}\int \mathrm{d}\boldsymbol{p}\mathrm{e}^{-\beta p^2/(2m)} p_x \varDelta_x , \tag{9.140}$$

$$K = -\frac{n_0 k_\mathrm{B}}{m^2}\left(\frac{\beta}{2\pi m}\right)^{3/2}\int \mathrm{d}\boldsymbol{p}\mathrm{e}^{-\beta p^2/(2m)}\left(\frac{\beta p^2}{2m}-\frac{5}{2}\right) p_x A_x , \tag{9.141}$$

and

$$\eta = -\frac{n_0 \beta}{m^2}\left(\frac{\beta}{2\pi m}\right)^{3/2}\int \mathrm{d}\boldsymbol{p}\mathrm{e}^{-\beta p^2/(2m)} p_x p_y B_{xy} , \tag{9.142}$$

respectively, where we have used the ideal gas expression for the heat capacity per particle, $c_P = (5/2)k_\mathrm{B}$. The functions D_x, A_x, and B_{xy} satisfy the equations

$$\hat{C}^-_{\boldsymbol{p}}\varDelta_x = p_x , \quad \hat{C}^+_{\boldsymbol{p}}A_x = \left(\frac{\beta p^2}{2m}-\frac{5}{2}\right) \quad \text{and} \quad \hat{C}^+_{\boldsymbol{p}}B_{xy} = p_x p_y . \tag{9.143}$$

These results are identical to the results obtained using the more traditional Chapman–Enskog procedure [26]. In order to obtain numerical values for the transport coefficients, we can expand the unknown functions $\varDelta_x$, A_x, and B_{xy} in terms of a set of orthogonal functions, $S^n_m(x)$, called *Sonine polynomials*, which are closely related to Leguerre polynomials. We describe these polynomials below.

9.7.1
Sonine Polynomials

The Sonine polynomials form a complete set of orthogonal polynomials which may be used to obtain approximate expressions for the transport coefficients. The

Sonine polynomials are defined as

$$S_q^n(x) = \sum_{l=0}^{n} (-1)^l \frac{\Gamma(q+n+1)x^l}{\Gamma(q+l+1)(n-l)!(l!)} , \tag{9.144}$$

where x and q are real numbers, n is an integer, and $\Gamma(q+n+1)$ is a gamma function. The two cases of the gamma function we shall be concerned with are

$$\Gamma(n+1) = n \quad \text{and} \quad \Gamma\left(n+\frac{1}{2}\right) = \frac{1 \cdot 3 \cdot 5 \cdots (2n-3)(2n-1)\sqrt{\pi}}{2^n} . \tag{9.145}$$

The Sonine polynomials for $n = 0$ and $n = 1$ are easily found to be $S_q^0(x) = 1$ and $S_q^1(x) = q + 1 - x$. The Sonine polynomials have the orthogonality property

$$\int_0^\infty \mathrm{d}x \mathrm{e}^{-x} x^q S_q^n(x) S_q^{n'}(x) = \frac{\Gamma(q+n+1)}{n!} \delta_{n,n'} . \tag{9.146}$$

We will use the Sonine polynomials to obtain approximate expressions for the transport coefficients. We consider them one at a time below.

9.7.2
Diffusion Coefficient

The diffusion coefficient D in (9.140) can be expanded in terms of Sonine polynomials, $S_{3/2}^l[\beta p^2/(2m)]$. If we write

$$\Delta_x = \sum_{l=0}^{\infty} d_l p_x S_{3/2}^l \left(\frac{\beta p^2}{2m}\right) , \tag{9.147}$$

then D takes the form

$$D = -\frac{1}{m^2} \left(\frac{\beta}{2\pi m}\right)^{3/2} \sum_{l=0}^{\infty} d_l \int \mathrm{d}\boldsymbol{p} \mathrm{e}^{-\beta p^2/(2m)} p_x^2 S_{3/2}^l \left(\frac{\beta p^2}{2m}\right) = -\frac{d_0}{m\beta} . \tag{9.148}$$

Thus, the self-diffusion coefficient depends only on the coefficient d_0.

We now must find an approximate expression for d_0. Let us substitute Eq. (9.147) into the equation $\hat{C}_{\boldsymbol{p}}^- \Delta_x = p_x$ (see Eq. (9.143)), multiply the resulting expression by $[\beta/(2\pi m)]^{3/2} \mathrm{e}^{-\beta p^2/(2m)}\, S_{3/2}^{l'}[\beta p^2/(2m)] p_x$, and integrate over $\boldsymbol{p}$. We then obtain

$$\sum_{l=0}^{\infty} D_{l',l} d_l = \frac{m}{\beta} \delta_{l',0} , \tag{9.149}$$

where

$$D_{l',l} = \left(\frac{\beta}{2\pi m}\right)^{3/2} \int \mathrm{d}\boldsymbol{p} \mathrm{e}^{-\beta p^2/(2m)} S_{3/2}^{l'} \left(\frac{\beta p^2}{2m}\right) p_x \hat{C}_{\boldsymbol{p}}^- \boldsymbol{S}_{3/2}^l \left(\frac{\beta p^2}{2m}\right) p_x . \tag{9.150}$$

Equation (9.149) is actually an infinite set of equations which determines all the coefficients, d_l.

We can obtain an approximate expression for the self-diffusion coefficient if we use a truncated version of Eq. (9.149). Let us retain only the first $\nu + 1$ terms in the sum and write

$$\sum_{l=0}^{\nu} \overline{D}^{(\nu)}_{l',l} d^{(\nu)}_l = \frac{m}{\beta}\delta_{l',0} \quad \text{for} \quad l' = 0, 1, \ldots, \nu \,. \tag{9.151}$$

The set of coefficients $\overline{D}^{(\nu)}_{l',l}$ form a $(\nu + 1) \times (\nu + 1)$ matrix. The coefficient $d^{(\nu)}_0$ is given by

$$d^{(\nu)}_0 = \frac{m}{\beta}\left([\overline{D}^{(\nu)}]^{-1}\right)_{0,0} \,, \tag{9.152}$$

where $([\overline{D}^{(\nu)}]^{-1})_{0,0}$ is the (0,0) matrix element of the inverse of matrix, $D^{(\nu)}$. The coefficient of self-diffusion now becomes

$$D = -\frac{1}{\beta^2}\lim_{\nu\to\infty}\left([\overline{D}^{(\nu)}]^{-1}\right)_{0,0} \,. \tag{9.153}$$

When the matrix is truncated to lowest order, the self-diffusion coefficient is given by

$$D = -\frac{1}{\beta^2}\frac{1}{D_{00}} = -\frac{1}{\beta^2}\frac{1}{\langle p_x \hat{C}^-_{\boldsymbol{p}} p_x\rangle} \,. \tag{9.154}$$

To second order it is

$$D = -\frac{1}{\beta^2}\frac{1}{D_{00}}\left[1 - \frac{D_{01}D_{10}}{D_{00}D_{11}}\right]^{-1} \,, \tag{9.155}$$

and so on.

The self-diffusion coefficient is straightforward to compute for a hard-sphere gas (see Appendix E). For hard spheres of radius a it is

$$D = -\frac{1}{\beta^2}\frac{1}{\left\langle p_x \hat{C}^-_{\boldsymbol{p}} p_x\right\rangle} = \frac{3}{32}\frac{1}{n_0 a^2}\sqrt{\frac{k_{\mathrm{B}}T}{m\pi}} \,. \tag{9.156}$$

For a dilute gas, it is found that higher order corrections change Eq. (9.156) by only a few percent (cf. [26], page 168).

9.7.3
Thermal Conductivity

The coefficient of thermal conductivity in Eq. (9.141) can be expanded in terms of Sonine polynomials, $S^l_{3/2}[\beta p^2/(2m)]$. If we write

$$A_x = \sum_{l=0}^{\infty} a_l p_x S^l_{3/2}\left(\frac{\beta p^2}{2m}\right) , \tag{9.157}$$

substitute into Eq. (9.141), and perform the integration, we find

$$K = -\frac{n_0 k_{\mathrm{B}}}{m^2}\left(\frac{\beta}{2\pi m}\right)^{3/2}\sum_{l=0}^{\infty} a_l \int \mathrm{d}\boldsymbol{p}\, \mathrm{e}^{-\beta p^2/(2m)}\left[\frac{\beta p^2}{2m}-\frac{5}{2}\right] p_x^2 S^l_{3/2}\left(\frac{\beta p^2}{2m}\right)$$
$$= \frac{5 n_0 k_{\mathrm{B}}}{2m\beta} a_1 \,. \tag{9.158}$$

The thermal conductivity depends on a_1.

Let us next determine a_1. In the equation $\hat{C}^+_{\boldsymbol{p}} A_x = \left[\beta p^2/(2m) - 5/2\right]$ (see Eq. (9.143)), expand A_x in Sonine polynomials, then multiply by the quantity $[\beta/(2\pi m)]^{3/2} \mathrm{e}^{-\beta p^2/(2m)} S^{l'}_{3/2}[\beta p^2/(2m)] p_x$ and integrate over $\boldsymbol{p}$. We obtain

$$\sum_{l=0}^{\infty} \boldsymbol{M}_{l',l} a_l = -\frac{5}{2}\frac{m}{\beta}\delta_{l',1} \,, \tag{9.159}$$

where

$$M_{l',l} = \left(\frac{\beta}{2\pi m}\right)^{3/2}\int \mathrm{d}\boldsymbol{p}\, \mathrm{e}^{-\beta p^2/(2m)} S^{l'}_{3/2}\left(\frac{\beta p^2}{2m}\right) p_x \hat{C}^+_{\boldsymbol{p}} S^l_{3/2}\left(\frac{\beta p^2}{2m}\right) p_x \tag{9.160}$$

and we have used the orthogonality of the Sonine polynomials. Note that since the collision operator, $\hat{C}^+_{\boldsymbol{p}}$, conserves momentum we have $\hat{C}^+_{\boldsymbol{p}} p_x = 0$. Therefore, $M_{l',0} = 0$ and $M_{0,l} = 0$. Equation (9.159) becomes

$$\sum_{l=1}^{\infty} M_{l',l} a_l = -\frac{5}{2}\frac{m}{\beta}\delta_{l',l} \quad \text{for} \quad l' \geq 1 \,. \tag{9.161}$$

We can use the fact that momentum is conserved during the collisions so $\hat{C}^+_{\boldsymbol{p}} p_x = 0$. Therefore, M_{11} becomes

$$M_{11} = -\frac{1}{4}\frac{N}{V}\frac{\beta^2}{4} m^{10}\left(\frac{\beta}{2\pi m}\right)^3 \iint \mathrm{d}\boldsymbol{v}_1\, \mathrm{d}\boldsymbol{v}_2 \mathrm{e}^{-\beta m\left(v_1^2+v_2^2\right)/2}$$
$$\times \int \mathrm{d}(\cos(\Theta))\, \mathrm{d}\alpha g \sigma(\Theta, g)\left(v_{3,x}v_3^2 + v_{4,x}v_4^2 - v_{1,x}v_1^2 - v_{2,x}v_2^2\right)^2 \,, \tag{9.162}$$

where $v_3^2 + v_4^2 = v_1^2 + v_2^2$. In order to evaluate the integral in Eq. (9.162), we introduce the center-of-mass velocity, $\boldsymbol{V}_{\mathrm{cm}} = (1/2)(\boldsymbol{v}_1 + \boldsymbol{v}_2)$, and the relative velocity, $\boldsymbol{g} = \boldsymbol{v}_2 - \boldsymbol{v}_1$, so that $\boldsymbol{v}_1 = \boldsymbol{V}_{\mathrm{cm}} - 1/2\boldsymbol{g}$, $\boldsymbol{v}_2 = \boldsymbol{V}_{\mathrm{cm}} + 1/2\boldsymbol{g}$, $\boldsymbol{v}_3 = \boldsymbol{V}_{\mathrm{cm}} - 1/2\boldsymbol{g}'$, and $\boldsymbol{v}_4 = \boldsymbol{V}_{\mathrm{cm}} + 1/2\boldsymbol{g}'$. Then after some algebra we find

$$v_{3,x}v_3^2 + v_{4,x}v_4^2 - v_{1,x}v_1^2 - v_{2,x}v_2^2 = g'_x(\boldsymbol{g}' \cdot \boldsymbol{V}_{\mathrm{cm}}) - g_x(\boldsymbol{g} \cdot \boldsymbol{V}_{\mathrm{cm}}) \tag{9.163}$$

and

$$M_{11} = -\frac{1}{4}\frac{N}{V}\frac{\beta^2}{4}m^{10}\left(\frac{\beta}{2\pi m}\right)^3 \iint \mathrm{d}\boldsymbol{V}_{\mathrm{cm}}\,\mathrm{d}\boldsymbol{g}\mathrm{e}^{-\beta m\left(V_{\mathrm{cm}}^2+g^2/4\right)}$$
$$\times \int \mathrm{d}(\cos(\Theta))\,\mathrm{d}\alpha g\sigma(\Theta, g)$$
$$\times \left[(g'_x)^2(\boldsymbol{g}'\cdot\boldsymbol{V}_{\mathrm{cm}})^2 - 2g'_x g_x(\boldsymbol{g}'\cdot\boldsymbol{V}_{\mathrm{cm}})(\boldsymbol{g}\cdot\boldsymbol{V}_{\mathrm{cm}}) + g_x^2(\boldsymbol{g}\cdot\boldsymbol{V}_{\mathrm{cm}})^2\right] . \tag{9.164}$$

The collision cross section for hard spheres of radius a is $\sigma(\Theta, g) = a^2$. Let $V_{\mathrm{cm},i}$ ($i = x, y, z$) denote the ith component of the center-of-mass velocity. Then

$$\int \mathrm{d}\boldsymbol{V}_{\mathrm{cm}}\mathrm{e}^{-\beta m V_{\mathrm{cm}}^2} V_{\mathrm{cm},i}V_{\mathrm{cm},j} = \frac{1}{2m\beta}\left(\frac{\pi}{m\beta}\right)^{3/2}\delta_{ij} . \tag{9.165}$$

If we integrate over the center-of-mass velocity in Eq. (9.164), we find

$$M_{11} = -\frac{2}{3}\frac{N}{4V}\frac{\beta^2}{4}m^{10}\left(\frac{\beta}{2\pi m}\right)^3\frac{1}{2m\beta}\left(\frac{\pi}{m\beta}\right)^{3/2} a^2 \int \mathrm{d}\boldsymbol{g}\; g\mathrm{e}^{-\beta m g^2/4}$$
$$\times \int \mathrm{d}(\cos(\Theta))\,\mathrm{d}\alpha[g^4 - (\boldsymbol{g}'\cdot\boldsymbol{g})^2] . \tag{9.166}$$

In Eq. (9.166), we have let $g_x^2 \to 1/3g^2$ inside the integral, since by symmetry $\langle S^1_{3/2}p_x\hat{C}^+_{\boldsymbol{p}}S^1_{3/2}p_x\rangle = \langle S^1_{3/2}p_y\hat{C}^+_{\boldsymbol{p}}S^1_{3/2}p_y\rangle = \langle S^1_{3/2}p_z\hat{C}^+_{\boldsymbol{p}}S^1_{3/2}p_z\rangle$. Now choose the z-axis to lie along $\boldsymbol{g}$. Then $g'_x = g\sin(\Theta)\cos(\alpha)$, $g'_y = g\sin(\Theta)\sin(\alpha)$, $g'_z = g\cos(\Theta)$ and $\boldsymbol{g}'\cdot\boldsymbol{g} = g^2\cos(\Theta)$. First integrate over $\mathrm{d}(\cos(\Theta))\,\mathrm{d}\alpha$. Then integrate over $\mathrm{d}\boldsymbol{g}$. We finally obtain

$$M_{11} = -\frac{64}{3}\frac{n_0 a^2\sqrt{m\pi}}{\beta^{3/2}} , \tag{9.167}$$

and the coefficient of thermal conductivity is given by

$$K = \frac{75}{256a^2}\sqrt{\frac{k_{\mathrm{B}}^3 T}{m\pi}} . \tag{9.168}$$

9.7.4
Shear Viscosity

The shear viscosity in Eq. (9.141) can be written in terms of Sonine polynomials, $S^l_{5/2}[\beta p^2/(2m)]$. If we expand

$$B_{xy} = \sum_{l=0}^{\infty} b_l p_x p_y S^l_{5/2}\left(\frac{\beta p^2}{2m}\right) , \tag{9.169}$$

Table 9.1 Thermal conductivity K in units of 10^{-3} W/(m · K) for some monatomic gases at pressure $P = 10^5$ Pa [124].

Gas	K (at 200 K)	K (at 300 K)	K (at 400 K)
Argon (Ar)	12.4	17.9	22.6
Helium (He)	119.3	156.7	190.6
Krypton (Kr)	6.4	9.5	12.3
Neon (Ne)	37.6	49.8	60.3
Xenon (Xe)	3.6	5.5	7.3

and substitute into Eq. (9.141) we obtain

$$\eta = -\frac{n_0\beta}{m^2}\left(\frac{\beta}{2\pi m}\right)^{3/2}\sum_{l=0}^{\infty} b_l \int \mathrm{d}\boldsymbol{p}\,\mathrm{e}^{-\beta p^2/(2m)} p_x^2 p_y^2 S_{5/2}^{l}\left(\frac{\beta p^2}{2m}\right) = -\frac{n_0 b_0}{\beta}\,. \tag{9.170}$$

Thus, the shear viscosity depends on $\boldsymbol{b}_0$.

In order to determine $\boldsymbol{b}_0$, substitute the expansion Eq. (9.169) for B_{xy} into Eq. (9.143). Then multiply by $[\beta/(2\pi m)]^{3/2}\mathrm{e}^{-\beta p^2/(2m)} S_{5/2}^{l'}[\beta p^2/(2m)]p_x p_y$ and integrate over $\boldsymbol{p}$. Equation (9.143) then takes the form

$$\sum_{l=0}^{\infty} N_{l',l} b_l = \frac{m^2}{\beta^2}\delta_{l',0}\,, \tag{9.171}$$

where

$$N_{l',l} = \left(\frac{\beta}{2\pi m}\right)^{3/2}\int \mathrm{d}\boldsymbol{p}\,\mathrm{e}^{-\beta p^2/(2m)} S_{5/2}^{l'}\left(\frac{\beta p^2}{2m}\right) p_x p_y \hat{C}_{\boldsymbol{p}}^{+} S_{5/2}^{l}\left(\frac{\beta p^2}{2m}\right) p_x p_y\,. \tag{9.172}$$

If we truncate Eq. (9.171) to lowest order, we can write the shear viscosity as

$$\eta = -\frac{n_0 m^2}{\beta^3}\frac{1}{N_{00}} = -\frac{n_0 m^2}{\beta^3}\frac{1}{\langle p_x p_y \hat{C}_{\boldsymbol{p}}^{+} p_x p_y\rangle}\,. \tag{9.173}$$

For a gas of hard spheres of radius a, Eq. (9.173) yields for the shear viscosity

$$\eta = \frac{5}{64a^2}\sqrt{\frac{mk_{\mathrm{B}}T}{\pi}}\,. \tag{9.174}$$

This expression is correct to within a few percent (cf. [26], page 168). Values of the viscosity for some monatomic gases are given in Table 9.2.

It is interesting to compare the viscosity and thermal conductivity. If we take the ratio we find $K/\eta = 15k_{\mathrm{B}}/(4m) = 5/2c_{\mathrm{V}}$, where $c_{\mathrm{V}} = 3k_{\mathrm{B}}/(2m)$ is the specific heat of an ideal monatomic gas. The ratio $K/\eta c_{\mathrm{V}} = 5/2$ is called the *Eucken number*. One can check to see if this relation is satisfied by the monatomic gases in Tables 9.1 and 9.2.

Table 9.2 Viscosity η in units of 10^{-5} P (1 Poise = 0.10 kg/(m s)) for some monatomic gases at pressure $P = 10^5$ Pa [124].

Gas	η (at 200 K)	η (at 300 K)	η (at 400 K)
Argon (Ar)	15.9	22.9	38.8
Helium (He)	15.3	20.0	24.4
Krypton (Kr)	17.1	25.6	33.1
Neon (Ne)	24.3	32.1	38.9
Xenon (Xe)	15.4	23.2	30.7

9.8
Beyond the Boltzmann Equation

Computer experiments have shown that the picture of transport phenomena given by Boltzmann is not complete. The Boltzmann equation predicts exponential decay of the correlation functions, but simple hydrodynamic arguments give a decay of the form $t^{-d/2}$ (long time tail), where d is the dimension of the system. These long time tails are now well established theoretically and have been observed experimentally. (Long time tails in the velocity autocorrelation function of a Brownian particle were derived in Chapter 8.)

Expressions for transport coefficients obtained using the Boltzmann equation are limited to systems with very low density. If we wish to obtain expressions for the transport coefficients at higher densities using microscopic theory, we must begin by writing them in terms of a virial expansion (expansion in powers of the density). The first actual calculation was done by Choh and Uhlenbeck [30]. The Boltzmann equation includes only effects of two-body collisions. Choh and Uhlenbeck computed the contribution to the transport coefficients due to three-body processes. Their result was well behaved. Somewhat later, a number of authors attempted to extend calculations of the transport coefficients to higher order in density. In so doing, they found that all higher order terms are infinite and, therefore, the expansion of the transport coefficients in powers of the density is divergent and ill defined. The divergences in the virial expansion come from secular effects. Resummation of divergent terms [98] leads to well-defined expressions for the transport coefficients but introduces a nonanalytic density expansion for them. The divergences are related to the appearance of long time tails in the correlation functions.

When the most divergent terms in the virial expansion of the transport coefficients are summed together, they give contributions to the current-current correlation functions which decay as $t^{d/2}$ (where d is the number of dimensions) even for low density [45, 46]. In practice, at very low density, the many-body effects give only a very small contribution to the transport coefficients and the Boltzmann equation is adequate. But in principle, they are there and become more important as the density is raised.

9.9
Problems

Problem 9.1 A dilute gas of density n is contained in a cubic box and is in equilibrium with the walls at temperature T. Find the number of particles per unit area per unit time which collide with the walls and have magnitude of velocity greater than v_0.

Problem 9.2 Estimate the value of the coefficient of viscosity of argon gas at 25 °C and 1 atm pressure. Compare your estimate with the experimentally observed value of $\eta = 2.27 \times 10^{-4}\,\mathrm{g\,cm^{-1}\,s^{-1}}$. Argon has an atomic weight of 39.9 and at low temperature forms a closely packed solid with density $\rho = 1.65\,\mathrm{g/cm^3}$.

Problem 9.3 The number density in phase space of an ideal gas can be written

$$f(\boldsymbol{p}, \boldsymbol{r}) = \frac{N}{V}\left(\frac{\beta}{2\pi m}\right)^{3/2} \mathrm{e}^{-\beta p^2/(2m)}(1 + \varepsilon \sin\theta \cos\phi)\,, \tag{9.175}$$

where θ and ϕ are the polar and azimuthal angles, respectively, of the momentum, $\boldsymbol{p}$, measured with respect to the z-axis. (a) Compute the *net* number of particles, per unit area per unit time, that pass through the y–z plane. (b) Compute the *net* number of particles, per unit area per unit time, that pass through the x–z plane.

Problem 9.4 A gas of neon atoms ($^{20}\mathrm{Ne}_{10}$), at temperature $T = 330\,\mathrm{K}$ and pressure $P = 10^5\,\mathrm{Pa}$, is confined to a cubic box of volume $V = 8 \times 10^3\,\mathrm{cm^3}$. Assume the radius of the atoms is approximately $a = 1.5\,\mathrm{Å}$. (a) What is the average speed $\langle v \rangle$ of the neon atoms? (b) What is the mean free path λ of the neon atoms? (c) Compute the coefficient of thermal conductivity using the kinetic theory result ($K_{\mathrm{kth}} = 1/2 n \langle v \rangle \lambda k_{\mathrm{B}}$), where $n = N/V$ is the particle number density, and the result obtained from Boltzmann's equation ($K_{\mathrm{Beq}} = 75 k_{\mathrm{B}}/(256 a^2)\sqrt{k_{\mathrm{B}} T/(m\pi)}$). How do they compare with the experimentally observed value of $K_{\mathrm{exp}} \approx 5 \times 10^{-2}\,\mathrm{W/(m\,K)}$? (d) If a temperature difference of $\Delta T = 3.0\,\mathrm{K}$ is created between two opposite walls of this system, what is the heat current flowing through the gas (in units of $\mathrm{J/(m^2\,s)}$)?

Problem 9.5 The electrons in a cubic sample of metallic solid of volume L^3 and temperature T may be considered to be a highly degenerate ideal Fermi–Dirac gas. Assume the surface of the cube forms a potential energy barrier which is infinitely high, and assume that the electrons have spin $s = 1/2$, mass m, and charge e. (a) What is the number of electrons in the velocity interval, $\boldsymbol{v} \to \boldsymbol{v} + \mathrm{d}\boldsymbol{v}$? (b) Assume that an electrode is attached to the surface which lowers the potential energy to a large but finite value, W, in a small area, A, of the surface. Those electrons which have enough kinetic energy to overcome the barrier can escape the solid. How many electrons per second escape through the area, A? Assume that $W \gg 0$ and use this fact to make simplifying approximations to any integrals you might need to do.

Problem 9.6 (a) Prove that the linearized Boltzmann and Lorentz–Boltzmann collision operators, $\hat{C}^{+}_{\boldsymbol{p}}$ and $\hat{C}^{-}_{\boldsymbol{p}}$, respectively, are self-adjoint. (b) Prove that the scalar products, $\langle \Phi, \hat{C}^{+}\Phi\rangle$ and $\langle \Phi, \hat{C}^{-}\Phi\rangle$, are always less than or equal to zero for arbitrary functions, $\Phi = \Phi(\boldsymbol{p})$.

Problem 9.7 An approximate expression for the Boltzmann collision operator, $\hat{C}$, is

$$\hat{C} = -\gamma\hat{1} + \gamma\sum_{i=1}^{5} |\phi_i\rangle\langle\phi_i| \,, \tag{9.176}$$

where $|\phi_i\rangle$ are the five orthonormal eigenfunctions of $\hat{C}$ with eigenvalue equal to zero. The five eigenfunctions are $|\phi_1\rangle = |1\rangle$, $|\phi_2\rangle = |p_x\rangle$, $|\phi_3\rangle = |p_y\rangle$, $|\phi_4\rangle = |p_z\rangle$, and $|\phi_5\rangle = |5/2 - \beta p^2/(2m)\rangle$. They are orthonormal with respect to the scalar product,

$$\langle\phi(\boldsymbol{p})|\chi(\boldsymbol{p})\rangle = \left(\frac{\beta}{2\pi m}\right)^{3/2}\int \mathrm{d}\boldsymbol{p}\mathrm{e}^{-\beta p^2/(2m)}\phi(\boldsymbol{p})\chi(\boldsymbol{p}) \,. \tag{9.177}$$

1. Compute the coefficient of shear viscosity

   $$\eta = -\lim_{\varepsilon\to 0}\frac{n\beta}{m^2}\left\langle p_x p_y\middle|\frac{1}{\hat{C}+\varepsilon}p_x p_y\right\rangle \,, \tag{9.178}$$

   and the coefficient thermal conductivity,

   $$K = -\lim_{\varepsilon\to 0}\frac{nk_{\mathrm{B}}}{m^2}\left\langle\left(\frac{\beta p^2}{2m}-\frac{5}{2}\right)p_x\middle|\frac{1}{\hat{C}+\varepsilon}p_x\left(\frac{\beta p^2}{2m}-\frac{5}{2}\right)\right\rangle \,, \tag{9.179}$$

   where n is the number density of particles in the gas described by $\hat{C}$ and m is the mass of the particles.
2. What are the units of γ? What are the units of η?

Problem 9.8 The coefficient of diffusion can be written in the form

$$D = -\lim_{\varepsilon\to 0}\frac{1}{m^2}\left(\frac{\beta}{2\pi m}\right)^{3/2}\int \mathrm{d}\boldsymbol{p}\mathrm{e}^{-\beta p^2/(2m)}p_x\frac{1}{\left(\hat{C}^{(-)}_{\boldsymbol{p}}+\varepsilon\right)}p_x \,, \tag{9.180}$$

where $\hat{C}^{(-)}_{\boldsymbol{p}}$ is the Lorentz–Boltzmann collision operator. Replace $\hat{C}^{(-)}_{\boldsymbol{p}}$ by an effective collision operator, $\hat{J}^{(-)}_{\boldsymbol{p}}$, where $\hat{J}^{(-)}_{\boldsymbol{p}}$ acting on an arbitrary function, $h(\boldsymbol{p},\boldsymbol{r},t)$, has the form

$$\hat{J}^{(-)}_{\boldsymbol{p}}h(\boldsymbol{p},\boldsymbol{r},t) = -\gamma h(\boldsymbol{p},\boldsymbol{r},t) + \gamma\left(\frac{\beta}{2\pi m}\right)^{3/2}\int \mathrm{d}\boldsymbol{p}'\mathrm{e}^{-\beta p^2/(2m)}h(\boldsymbol{p}',\boldsymbol{r},t) \,. \tag{9.181}$$

1. Show that $\hat{J}^{(-)}_{\boldsymbol{p}}$ is self-adjoint and negative semidefinite and has one eigenfunction with eigenvalue zero.

2. Use $\hat{J}_{\boldsymbol{p}}^{(-)}$ to obtain an explicit expression for the diffusion coefficient (do all the integrals).
3. What are the units of γ?

Problem 9.9 The coefficient of self-diffusion can be written

$$D = -\frac{1}{m^2}\left(\frac{\beta}{2\pi m}\right)^{3/2} \int \mathrm{d}\boldsymbol{p} \mathrm{e}^{-\beta p^2/(2m)} p_x \Delta_x \,, \tag{9.182}$$

where $\Delta_x = \sum_{l=0}^{\infty} d_l p_x S_{3/2}^l[\beta p^2/(2m)]$. Compute the coefficient of self-diffusion, D, for a gas of hard-sphere particles of radius a, keeping only the lowest-order term ($l = 0$) in the expansion for Δ_x.

Problem 9.10 The coefficient of shear viscosity can be written

$$\eta = -\frac{n_0\beta}{m^2}\left(\frac{\beta}{2\pi m}\right)^{3/2} \int \mathrm{d}\boldsymbol{p} \mathrm{e}^{-\beta p^2/(2m)} p_x p_y B_{xy} \,, \tag{9.183}$$

where $B_{xy} = \sum_{l=0}^{\infty} b_l p_x p_y S_{5/2}^l[\beta p^2/(2m)]$. Compute the coefficient of shear viscosity, η, for a gas of hard-sphere particles of radius a, keeping only the lowest-order term ($l = 0$) in the expansion for B_{xy}.

10
Nonequilibrium Phase Transitions

10.1
Introduction

It is possible to use thermodynamics to analyze the behavior of systems that are far from absolute thermodynamic equilibrium, as long as they are locally in equilibrium. Then the state of the system can be described in terms of thermodynamic densities that vary in space. When thermodynamic systems are held far enough away from absolute equilibrium, nonlinear effects must be included in chemical rate equations or hydrodynamic equations, and these nonlinear effects can open a whole new world of behavior for such systems. Nonlinear equations allow the possibility of multiple solutions, each with different regions of stability. Thus, as we change the parameters of a nonlinear system, it can transition from one type of macroscopic state to another.

Prigogine was the first to prove that near equilibrium (in the linear regime), if one of the thermodynamic forces is held fixed, the stable state of the system is a steady state characterized by a minimum entropy production and it is unique [170, 173]. This state is said to lie on the "thermodynamic branch" of possible states. However, as we move away from the linear regime, nonlinearities in the chemical rate equations or hydrodynamic equations become more important and, at some point, the thermodynamic branch becomes unstable and a nonequilibrium phase transition occurs. The system then changes to a new state that is characterized by an order parameter. Often the change is dramatic. Even if the boundary is held fixed and the steady state in the linear regime is homogeneous or has constant gradients, the new state that appears in the nonlinear regime can oscillate in space and/or in time and often exhibits nonlinear wave motion. Thus, the symmetry of such systems in space and/or time is broken at the phase transition, and the new stable nonequilibrium state exhibits much more structure than the state on the thermodynamic branch. These structures (called *dissipative structures* by Prigogine) require a flow of energy and sometimes a flow of matter and, therefore, a production of entropy to maintain them.

In this chapter, we illustrate the nonequilibrium phase transition with two classic examples, one from chemistry and the other from hydrodynamics. The chemical system is called the Brusselator chemical model, first introduced by Prigogine

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and Lefever [174]. This is the simplest chemical model that can exhibit spatial and temporal *dissipative structures* – that is, oscillations in space and time maintained by the flow of chemicals through the system.

The second example we consider is a purely hydrodynamic system. We show that nonlinearities in the Navier–Stokes equations, in the presence of gravitational forces, can lead to instabilities in fluid flow. The example we consider is called the *Rayleigh–Bénard instability*, and it occurs in a fluid layer in the presence of gravity when the layer is heated from below. When the temperature gradient becomes great enough, the fluid undergoes a transition from an isotropic stationary state to a state whose macroscopic behavior is dominated by stationary spatially periodic convection cells. The hydrodynamic equations can predict the parameter values at which this instability occurs.

10.2
Near Equilibrium Stability Criteria

Thermodynamic systems held out of equilibrium are dissipative because the transport process and chemical reactions that occur away from equilibrium lead to an increase in the entropy of the surrounding world. Prigogine showed that there are stability conditions associated with the entropy production in a nonequilibrium system [67, 150, 170, 173].

As we saw in Chapters 7 and 8, the local entropy production, σ, corresponds to a generalized Joule heating, and can be written as a product of generalized currents and generalized forces such that

$$\sigma_{\mathrm{s}} = -\sum_j \mathfrak{J}_j \cdot \mathfrak{F}_j \,, \tag{10.1}$$

where $\mathfrak{J}_j$ ($\mathfrak{F}_j$) is the jth generalized current (force). Near equilibrium the currents may be approximated by a linear relation (a generalized Ohm's law) of the form

$$\mathfrak{J}_i = -\sum_j L_{i,j} \mathfrak{F}_j \,, \tag{10.2}$$

where $L_{i,j}$ is a symmetric matrix $L_{i,j} = L_{j,i}$ (Onsager's relation). If we substitute Eq. (10.2) in (10.1), we obtain the following expression for the entropy production,

$$\sigma_{\mathrm{s}} = \sum_{i=1}^{\nu} \sum_{j=1}^{\nu} L_{i,j} \mathfrak{F}_i \cdot \mathfrak{F}_j \geq 0 \,, \tag{10.3}$$

so that near equilibrium the entropy production is always positive.

We can now ask under what conditions the entropy production can be minimized. For simplicity, let us consider a case where two independent thermodynamic forces are present so $\nu = 2$ (e.g., a temperature gradient and a chemical potential gradient). The resulting fluxes are also independent. If both forces are allowed to vary independently, the condition for minimum entropy production is

$$\left(\frac{\partial \sigma_{\mathrm{s}}}{\partial \mathfrak{F}_1}\right)_{\mathfrak{F}_2} = 2L_{1,1}\mathfrak{F}_1 + 2L_{1,2}\mathfrak{F}_2 = -2\mathfrak{J}_1 = 0 \tag{10.4}$$

and

$$\left(\frac{\partial \sigma_{\mathrm{s}}}{\partial \mathfrak{F}_2}\right)_{\mathfrak{F}_1} = 2L_{2,2}\mathfrak{F}_2 + 2L_{2,1}\mathfrak{F}_1 = -2\mathfrak{J}_2 = 0 \tag{10.5}$$

(note that we assume that $L_{i,j}$ is constant). When there are no constraints on the forces, the state of minimum entropy production is the equilibrium state, where the forces and currents vanish and the entropy production is zero.

Let us now hold one of the forces fixed and nonzero so $\mathfrak{F}_1 =$ constant (e. g., fix a temperature gradient across the system). Then the condition for minimum entropy production becomes simply

$$\left(\frac{\partial \sigma_{\mathrm{s}}}{\partial \mathfrak{F}_2}\right)_{\mathfrak{F}_1} = 2L_{2,2}\mathfrak{F}_2 + 2L_{2,1}\mathfrak{F}_1 = -2\mathfrak{J}_2 = 0\,. \tag{10.6}$$

Then, $\mathfrak{J}_2 = 0$ but $\mathfrak{J}_1 \neq 0$ and constant. Thus, the state of minimum entropy production is a steady state, a state in which a constant current flows through the system. Furthermore, in the linear regime, such minimum entropy production states are always stable. That is, fluctuations cannot drive the system away from the state of minimum entropy production [170, 173].

As we have just seen, it is possible to create a nonequilibrium steady state by holding one or more thermodynamic forces fixed and nonzero. In the linear regime, the steady state that results is a state of minimum entropy production and is always stable. In the nonlinear regime, we can no longer write the currents as linear functions of the forces and it is no longer possible to prove that the steady state will continue to be stable as we move further into the nonlinear regime. Thus, we have the possibility that the steady states that exist near equilibrium can become unstable as we increase the strength of the nonlinearities, and the system can evolve into a new state that cannot exist close to equilibrium. The transition from the near equilibrium steady state to a new and more ordered state far from equilibrium is called a nonequilibrium phase transition.

The possibility that ordered states could exist far from equilibrium opened a new field of research in the chemical and biological sciences. Living systems may be thought of as chemical systems (although of huge complexity) maintained far from equilibrium. There is now evidence that the formation and maintenance of ordered states far from equilibrium is important for the maintenance of life processes. In 1977, Ilya Prigogine received the Nobel prize in chemistry for laying the foundation of this field of chemistry and for his many contributions to its development.

In the next two sections, we consider two examples of nonequilibrium phase transitions, one in a chemical system and the other in a hydrodynamic system.

10.3
The Chemically Reacting Systems

Chemical systems that are held far from chemical equilibrium (constrained to have a large affinity) can undergo nonequilibrium phase transitions to new states with striking behavior [67, 149, 150, 174, 200]. The new states may be steady states in which the relative concentrations of the constituents vary in space, or they may be spatially homogeneous states in which the concentrations of some constituents vary in time (chemical clocks), or they may be states with nonlinear traveling waves in the concentrations of some constituents. The classic example of such behavior is the Belousov–Zhabotinski reaction [14, 221]. This reaction, which is too complicated to discuss in detail here [56], involves the cerium ion catalyzed oxidation of malonic acid by bromate in a sulfuric acid medium. The reaction is nonlinear because it contains autocatalytic steps. The system, when it is well stirred, can behave like a chemical clock. That is, there is a periodic change in the concentration of Br^- and of the relative concentration Ce^{4+}/Ce^{3+}. The system oscillates between a red and blue color with a period of the order of a minute. Perhaps the most fascinating behavior of this system is the traveling waves in the concentration of Br^- and the relative concentration Ce^{4+}/Ce^{3+} which are observed in shallow unstirred dishes (cf. Figure 10.1).

The Belousov–Zhabotinski reaction appears to be well described by a model which contains three variable intermediates. This model is called the Oregonator and was first introduced by Field and Noyes [56, 57]. However, the qualitative behavior of the type appearing in the Belousov–Zhabotinski reaction also occurs in a simpler model called the Brusselator, first introduced by Prigogine and Lefever [174], which contains two variable intermediates. In this section we shall discuss some properties of the Brusselator.

Figure 10.1 Traveling waves in the chemical concentrations for the Belousov–Zhabotinski reaction. Reprinted, by permission, from [213].

10.3.1

The Brusselator – A Nonlinear Chemical Model

The Brusselator is one of the simplest chemical models of a chemical system that can undergo a nonequilibrium phase transition. It has six different components, four of which are held fixed and two others whose concentrations can vary in space and time. The chemical reaction takes place in four steps and is held far from equilibrium by allowing the reactions to go in one direction only. The four steps are

$$A \overset{k_1}{\rightharpoonup} X\,, \quad B + X \overset{k_2}{\rightharpoonup} Y + D\,, \quad 2X + Y \overset{k_3}{\rightharpoonup} 3X\,, \quad X \overset{k_4}{\rightharpoonup} E\,. \tag{10.7}$$

In practice, A and B are present in excess and D and E are removed as soon as they appear. The rate equations for concentrations c_X and c_Y of X and Y, respectively, can be written

$$\frac{\mathrm{d}c_X}{\mathrm{d}t'} = k_1 c_A - (k_2 c_B + k_4)c_X + k_3 c_X^2 c_Y + D'_1 \nabla_{\boldsymbol{r}}^2 c_X \tag{10.8}$$

and

$$\frac{\mathrm{d}c_Y}{\mathrm{d}t'} = k_2 c_B c_X - k_3 c_X^2 c_Y + D'_2 \nabla_{\boldsymbol{r}}^2 c_Y\,. \tag{10.9}$$

We have allowed the densities to vary in space and have allowed for the possibility of diffusion (D'_1 and D'_2 are the coefficients of diffusion). If we now introduce a change of variables, $t = k_2 t'$, $X = \sqrt{k_3/k_4}\,c_X$, $Y = \sqrt{k_3/k_4}\,c_Y$, $A = \sqrt{k_1^2 k_3/k_4^3}\,c_A$, $B = (k_2/k_4)c_B$, and $D_i = D'_i/k_4$, then Eqs. (10.8) and (10.9) take the form

$$\frac{\mathrm{d}X}{\mathrm{d}t} = A - (B+1)X + X^2 Y + D_1 \nabla_{\boldsymbol{r}}^2 X \tag{10.10}$$

and

$$\frac{\mathrm{d}Y}{\mathrm{d}t} = \mathrm{BX} - X^2 Y + D_2 \nabla_{\boldsymbol{r}}^2 Y\,. \tag{10.11}$$

Equations (10.10) and (10.11) have a spatially uniform steady-state solution of the form

$$X_0 = A \quad \text{and} \quad Y_0 = \frac{B}{A}\,, \tag{10.12}$$

which is the continuation, far from equilibrium, of the steady-state solution that occurs at chemical equilibrium when the reverse reactions in Eq. (10.7) are allowed to occur. That is, the steady state in Eq. (10.12) lies on the "thermodynamic branch" of steady-state solutions. We wish to look for conditions under which the thermodynamic branch becomes unstable and a bifurcation (nonequilibrium phase transition) occurs to a state which may oscillate in space or time.

We can write $X(\boldsymbol{r}, t)$ and $Y(\boldsymbol{r}, t)$ in terms of fluctuations away from the equilibrium steady states so that

$$X(\boldsymbol{r}, t) = A + \delta x(\boldsymbol{r}, t) \quad \text{and} \quad Y(\boldsymbol{r}, t) = \frac{B}{A} + \delta y(\boldsymbol{r}, t) \,, \tag{10.13}$$

where $\delta x(\boldsymbol{r}, t)$ and $\delta y(\boldsymbol{r}, t)$ are small space and time-dependent perturbations. If we substitute Eq. (10.13) into Eqs. (10.10) and (10.11) and linearize them with respect to $\delta x(\boldsymbol{r}, t)$ and $\delta y(\boldsymbol{r}, t)$, we obtain

$$\frac{\mathrm{d}\delta x}{\mathrm{d}t} = \left(B - 1 + D_1 \nabla_{\boldsymbol{r}}^2\right) \delta x + A^2 \delta y \tag{10.14}$$

and

$$\frac{\mathrm{d}\delta y}{\mathrm{d}t} = -B\delta x + \left(-A^2 + D_2 \nabla_{\boldsymbol{r}}^2\right) \delta y \,. \tag{10.15}$$

Since Eqs. (10.14) and (10.15) are linear, it is sufficient to consider one Fourier component of $\delta x(\boldsymbol{r}, t)$ and $\delta y(\boldsymbol{r}, t)$. Before we proceed further, we must specify both the shape of the container in which the reaction takes place and the boundary conditions on the walls of the container.

10.3.2
Boundary Conditions

For simplicity, we shall assume that the reaction takes place in a rectangular container with sides of length L_x, L_y, and L_z. We shall consider two different types of boundary conditions. For Case I, we will hold the concentrations, X and Y, constant on the boundaries. For Case II, we will assume there is no flux of X and Y through the boundaries. Let us consider these two cases separately below.

10.3.2.1 Case I Boundary Conditions

Let us assume the concentrations, X and Y are constant on the boundaries and take on the values

$$X_{\text{bound}} = A \quad \text{and} \quad Y_{\text{bound}} = \frac{B}{A} \tag{10.16}$$

on the boundaries. These boundary conditions can be maintained by allowing a flow of X and Y through the boundaries. A given Fourier component of $\delta x(\boldsymbol{r}, t)$ and $\delta y(\boldsymbol{r}, t)$ can be written

$$\delta x(\boldsymbol{r}, t) = \tilde{x}(\boldsymbol{k}, \omega) \sin(k_x x) \sin(k_y y) \sin(k_z z) \mathrm{e}^{\omega(\boldsymbol{k})t} \tag{10.17}$$

and

$$\delta y(\boldsymbol{r}, t) = \tilde{y}(\boldsymbol{k}, \omega) \sin(k_x x) \sin(k_y y) \sin(k_z z) \mathrm{e}^{\omega(\boldsymbol{k})t} \,, \tag{10.18}$$

where

$$\boldsymbol{k} = \frac{n_x \pi}{L_x} \hat{\boldsymbol{x}} + \frac{n_y \pi}{L_y} \hat{\boldsymbol{y}} + \frac{n_z \pi}{L_z} \hat{\boldsymbol{z}} \,, \tag{10.19}$$

and n_x, n_y, and n_z are integers that can each have values $1, 2, \ldots, \infty$.

10.3.2.2 Case II Boundary Conditions

Let us assume there is no flux of X and Y perpendicular to the boundary surfaces so

$$\hat{\boldsymbol{n}} \cdot \nabla_{\boldsymbol{r}} X = \hat{\boldsymbol{n}} \cdot \nabla_{\boldsymbol{r}} Y = 0 \tag{10.20}$$

on the boundaries, where $\hat{\boldsymbol{n}}$ is normal to the boundaries. A given Fourier component of $\delta x(\boldsymbol{r}, t)$ and $\delta y(\boldsymbol{r}, t)$ can now be written

$$\delta x(\boldsymbol{r}, t) = \tilde{x}(\boldsymbol{k}, \omega) \cos(k_x x) \cos(k_y y) \cos(k_z z) \mathrm{e}^{\omega(\boldsymbol{k})t} , \tag{10.21}$$

and

$$\delta y(\boldsymbol{r}, t) = \tilde{y}(\boldsymbol{k}, \omega) \cos(k_x x) \cos(k_y y) \cos(k_z z) \mathrm{e}^{\omega(\boldsymbol{k})t} , \tag{10.22}$$

where the wavevector $\boldsymbol{k}$ is defined in Eq. (10.19) and n_x, n_y, and n_z can each have values $0, 1, 2, \dots, \infty$.

10.3.3
Stability Analysis

If we substitute the solutions in Eqs. (10.17) and (10.18), or the solutions in Eqs. (10.21) and (10.22), – into Eqs. (10.14) and (10.15), we obtain the following matrix equation

$$\begin{pmatrix} \omega - B + 1 + D_1 k^2 & -A^2 \\ B & \omega + A^2 + D_2 k^2 \end{pmatrix} \begin{pmatrix} \tilde{x} \\ \tilde{y} \end{pmatrix} = 0 . \tag{10.23}$$

An equation for $\omega(\boldsymbol{k})$ is found by setting the determinant of the 2×2 matrix on the left equal to zero. We then have

$$\omega(\boldsymbol{k})^2 + (C_1 - C_2)\omega(\boldsymbol{k}) + A^2 B - C_1 C_2 = 0 , \tag{10.24}$$

where

$$C_1 = B - 1 - k^2 D_1 \quad \text{and} \quad C_2 = A^2 + k^2 D_2 . \tag{10.25}$$

Equation (10.24) has two solutions:

$$\omega^{\pm}(\boldsymbol{k}) = \frac{1}{2} \left(C_1 - C_2 \pm \sqrt{\left(C_1 + C_2\right)^2 - 4A^2 B} \right) . \tag{10.26}$$

From Eq. (10.26), it is easy to see that, depending on the variables D_1, D_2, A, and B, the frequency $\omega(\boldsymbol{k})$ can be either complex or real and the real part can be either positive or negative.

If $\omega(\boldsymbol{k})$ is complex, the component of the perturbation $\delta x(\boldsymbol{r}, t)$ and $\delta y(\boldsymbol{r}, t)$ with wavevector $\boldsymbol{k}$ and frequency $\omega(\boldsymbol{k})$ will oscillate about the steady state Eq. (10.12) with frequency given by the imaginary part of $\omega(\boldsymbol{k})$. The real part of $\omega(\boldsymbol{k})$ determines if the steady state is stable with respect to the perturbation. If the real part of $\omega(\boldsymbol{k})$ is negative, then the perturbation will decay away and the steady state is stable with respect to fluctuations with wavevector $\boldsymbol{k}$ and frequency $\omega(\boldsymbol{k})$. However, if the real part of $\omega(\boldsymbol{k})$ is positive, the perturbation $\delta x(\boldsymbol{r}, t)$ and $\delta y(\boldsymbol{r}, t)$ grows exponentially. Thus, when the real part of $\omega(\boldsymbol{k})$ is positive, a bifurcation or phase transition occurs.

10.3.3.1 **Real Frequency $\omega(\boldsymbol{k})$**

The frequency $\omega(\boldsymbol{k})$ is real when

$$(C_1 + C_2)^2 - 4A^2B > 0 \tag{10.27}$$

(cf. Eq. (10.26)) and $\omega(\boldsymbol{k})$ is positive if

$$C_1C_2 - A^2B > 0 \tag{10.28}$$

or

$$B > B_n = 1 + \frac{D_1}{D_2}A^2 + \frac{A^2}{D_2 n^2 \pi^2}L^2 + \frac{D_1 n^2 \pi^2}{L^2} . \tag{10.29}$$

In this case, there will be no oscillations in time but only in space. A diagram that shows the onset of time-independent spatial oscillations of the concentrations of X and Y is given in Figure 10.2a. The curved line is B_n. The bifurcation first occurs for $B = B_c$, where B_c is the lowest value of B corresponding to an integer value of n. Linear stability analysis can only tell us that a bifurcation to a new spatially oscillating steady state is possible for a particular set of values for the parameters A, B, D_1, D_2, and L. It cannot give us information about the form of the new state. However, for the Brusselator the spatially varying states can be obtained numerically. In Figure 10.2b, we give an example for a one-dimensional system for the following values of the parameters: $B = 4.6$, $A = 2$, $L = 1$, $D_1 = 1.6 \times 10^{-3}$, $D_2 = 6.0 \times 10^{-3}$, $D_2 = 6.0 \times 10^{-3}$, and fixed boundary conditions $X_{\text{bound}} = A$ and $Y_{\text{bound}} = B/A$. The figure shows a state with oscillations in the concentration of X as a function of position.

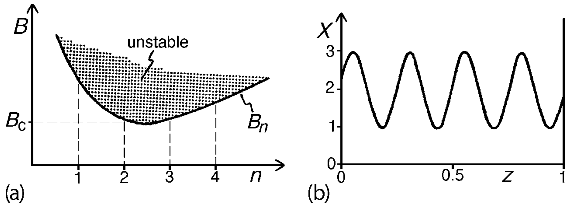

Figure 10.2 (a) Linear stability diagram for the onset of a time-independent dissipative structure. For the case pictured here, as B increases, the first bifurcation occurs at $n = 2$. (b) A steady-state spatial dissipative structure for $B = 4.6, A = 2, L = 1, D_1 = 1.6 \times 10^{-3}$, and $D_2 = 6.0 \times 10^{-3}$. The boundary conditions are fixed at $X = A$ and $Y = B/A$ (based on [150]).

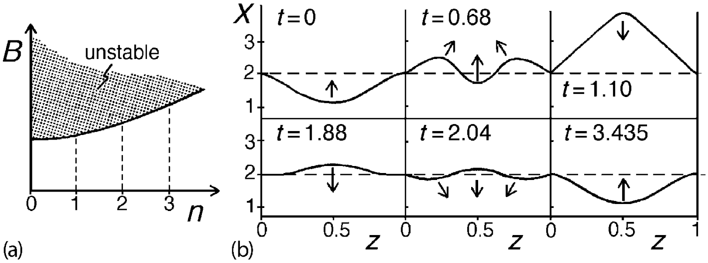

Figure 10.3 (a) Linear stability diagram for the onset of time-dependent dissipative structures. As B is increased, the first bifurcation occurs at $n = 0$ and yields a spatially homogeneous chemical clock. (b) Successive time steps for a dissipative structure with fixed concentrations on the boundary which exhibits oscillations in both space and time. The parameters used are $L = 1$, $A = 2$, $B = 5.45$, $D_1 = 8 \times 10^{-3}$, and $D_2 = 4 \times 10^{-3}$ based on [150].

10.3.3.2 Complex Frequency $\omega(\boldsymbol{k})$

The frequency $\omega(\boldsymbol{k})$ will be complex if

$$D_2 - D_1 \leq \frac{L^2}{n^2\pi^2} . \tag{10.30}$$

In addition, $\omega(\boldsymbol{k})$ will have a positive real part if $C_1 - C_2 > 0$ or if

$$B > A^2 + 1 + \frac{n^2\pi^2}{L^2}(D_1 + D_2) . \tag{10.31}$$

Thus, the curve

$$B_n = A^2 + 1 + \frac{n^2\pi^2}{L^2}(D_1 + D_2) \tag{10.32}$$

denotes the boundary between the region where the steady state Eq. (10.12) is stable and where it is unstable as a function of n.

We note that for the Case II boundary conditions we can have $n = 0$ and, therefore, the possibility of spatially homogeneous oscillations in time of the relative concentrations of X and Y – that is, a chemical clock. For all finite values of n, we have the possibility of a new state which varies in both space and time and therefore may exhibit wave motion. The linear stability diagram for the transition to time-dependent states is given in Figure 10.3a. In Figure 10.3b, we give the results of a computer simulation, of a one-dimensional system, for a state which oscillates in space and time. The solution is reminiscent of a standing wave on a string, but, due to the nonlinearities, it has a much more complicated structure. In two dimensions, computer simulations have shown that traveling waves can exist which are similar to the waves shown in the Belousov–Zhabotinski reaction [150] in Figure 10.1.

10.3.4
Chemical Crystals

Chemical clocks and chemical waves have been realized in the Belousov–Zhabotinski reaction and have been seen in other autocatalytic chemical reactions as well. Chemical “crystals” have been more difficult to achieve experimentally. They were first proposed by Turing [199] in 1952 and were finally realized in the laboratory in 1990 [25]. Chemical “crystals” or Turing structures, as they are now generally called, are stationary chemical concentration patterns (dissipative structures) which can emerge far from chemical equilibrium in nonlinear reaction-diffusion processes. The reason they proved difficult to realize in the laboratory is that they generally require that the diffusion coefficients governing the reaction be very different in value [161]. This was first achieved using a chlorite-malonic acid reaction (CIMA) [157] in a two-dimensional gel. Two different Turing structures formed with the CIMA reaction in a two dimensional gel are shown in Figure 10.4. The Brusselator chemical model can reproduce these structures. The results of a numerical simulation of the Turing structures using parameters for the CIMA chemical reaction are also shown in Figure 10.4. The agreement between the experiment and the simulation is excellent.

Spatially varying steady states, temporally oscillating homogeneous states, and nonlinear traveling waves have been observed in chemical systems. These states, which only become stable far from equilibrium, were called “dissipative structures” by I. Prigogine [67, 150] because their very existence depends upon dissipative processes, such as chemical reactions far from equilibrium or diffusion (if spatial structures occur). They are maintained by production of entropy in the surrounding world and by a related flow of energy and matter through the system. The type of autocatalytic reactions which produce them are abundant in living systems and yet are rare in nonliving systems. Indeed, dissipative structures in living systems play an important role in the maintenance of life processes [148].

10.4
The Rayleigh–Bénard Instability

Nonequilibrium phase transitions are abundant in hydrodynamic systems because they are governed by nonlinear equations [28, 110, 111, 139, 153]. For example, if we let fluid flow in a pipe, we find for low velocities or high viscosities that the flow is smooth and steady. However, as we increase the velocity or decrease the viscosity, we get a transition to turbulent flow. The smooth steady state becomes unstable and a turbulent state becomes favored. As another example, consider a fluid at rest and place it between horizontal parallel plates in the gravitational field. If we put a temperature gradient across the plates (with the hottest plate below) and slowly increase the temperature gradient, we find that at some point the rest state becomes unstable and the fluid breaks into convective flow cells which occur periodically in space. In each cell, fluid rises in one part of the cell and descends in another part. The circulation of fluid repeats itself in each cell. This instability is called the *Rayleigh–Bénard instability* and it is the one we shall study in this section. We will follow closely the classic presentation of Chandrasekhar [28].

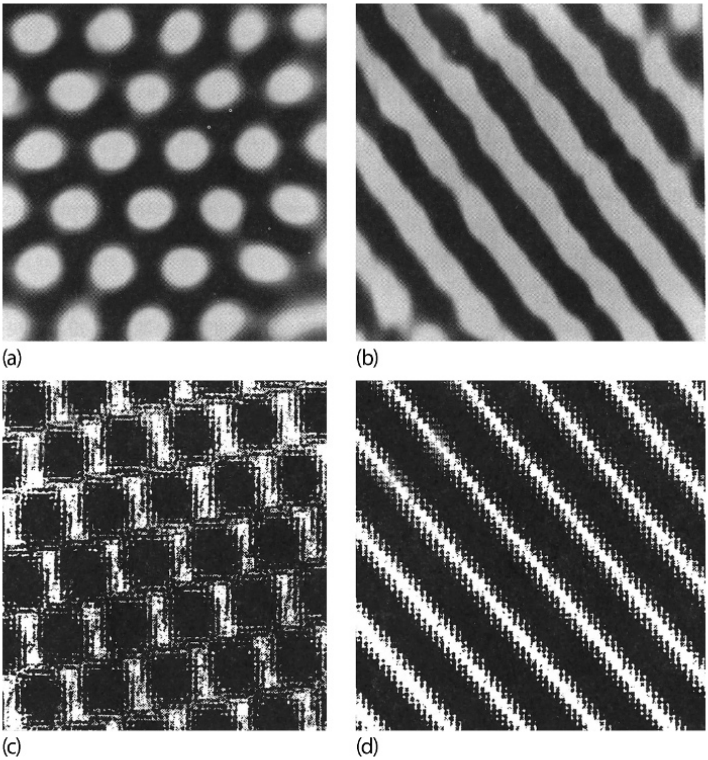

Figure 10.4 Two-dimensional Turing structures. (a) Hexagons and (b) stripes produced with the CIMA chemical reaction in a two-dimensional gel. (c) Hexagons and (d) stripes produced by numerical simulation of Turing structures using the Brusselator chemical model and parameters of the CIMA chemical reaction in a two-dimensional gel. ((a) and (b) reprinted with permission from [177]. (c) and (d) reprinted [41] with kind permission from Elsevier Science – NL, Sara Burgerhart Straat 25, 1055 KV Amsterdam, The Netherlands.)

10.4.1
Hydrodynamic Equations and Boundary Conditions

The Navier–Stokes equations for a monatomic fluid are given in Eqs. (8.38)–(8.40), although we will now include an external force $\rho \boldsymbol{F}$ on the right-hand side of Eq. (8.39). We will consider the case of a fluid at rest and constrained to lie between two parallel plates that extend infinitely far in the x- and y-directions. The distance between the plates is d. We will put a temperature gradient across the plates so that the temperature of the bottom plate is greater than that of the top, and we will assume that a gravitational field acts in the negative z-direction. If d is small enough, any density variations in the system will be due primarily to the temperature gradient (as opposed to gravity) and we can write

$$\rho = \rho_0[1 + \alpha_P(T_0 - T)] , \tag{10.33}$$

where $\alpha_P = -(1/\rho)(\partial\rho/\partial T)_P$ is the thermal expansivity. Heating the bottom more than the top causes the fluid at the top to be denser and heavier and creates the possibility for an instability to occur.

Let us now write the equations for the steady state in the absence of any macroscopic flow; that is, $\boldsymbol{v} = 0$. We obtain

$$\nabla_{\boldsymbol{r}} \cdot \rho\boldsymbol{v} = 0\,, \quad \nabla_{\boldsymbol{r}} P = -\rho g\hat{\boldsymbol{z}}\,, \quad \text{and} \quad \nabla^2_{\boldsymbol{r}} T = 0\,, \tag{10.34}$$

where we have let $\boldsymbol{F} = -g\hat{\boldsymbol{z}}$ and g is the acceleration of gravity. If we note the boundary conditions $T(0) = T_0$ and $T(d) = T_d$, we can solve Eq. (10.34) to obtain the steady-state solutions. We find

$$T(z) = T_0 - az\,, \tag{10.35}$$

$$\rho(z) = \rho_0[1 + \alpha_P(T_0 - T)] = \rho_0(1 + \alpha_P az)\,, \tag{10.36}$$

and

$$P(z) = P_0 - g\rho_0\left(z + \frac{1}{2}\alpha_P az^2\right)\,, \tag{10.37}$$

where a is the temperature gradient, $a = (T_0 - T_d)/d$, and P_0 is the pressure at $z = 0$.

Equations (10.35)–(10.37) are the steady-state solutions in the absence of flow. We wish to determine conditions for which they are stable. As usual, we will perturb the steady-state solutions slightly and study the linearized equations for the perturbations. Thus, we write $T(\boldsymbol{r}, t) = T(z) + \delta T(\boldsymbol{r}, t)$, $P(\boldsymbol{r}, t) = P(z) + \delta P(\boldsymbol{r}, t)$, and $\rho(\boldsymbol{r}, t) = \rho(z) + \delta\rho(\boldsymbol{r}, t)$. The velocity, $\boldsymbol{v}(\boldsymbol{r}, t)$, is a first-order perturbation from equilibrium. Let us further note that the dominant contribution to entropy variations will come from temperature variations. Thus, we write $\delta s = (c_\rho/T)\delta T$, where c_ρ is the specific heat, and we have neglected terms proportional to α_P. If we substitute these expressions into the hydrodynamic equations (8.38)–(8.40), and linearize them in the perturbations δT, δP, $\delta\rho$, and $\boldsymbol{v}$, we find

$$\frac{\partial}{\partial t}\delta\rho = -\nabla_{\boldsymbol{r}} \cdot (\rho(z)\boldsymbol{v})\,, \tag{10.38}$$

$$\frac{\partial}{\partial t}\rho(z)\boldsymbol{v} = -\nabla_{\boldsymbol{r}}(P(z) + \delta P) - \rho g\hat{\boldsymbol{z}} + \eta\nabla^2_{\boldsymbol{r}}\boldsymbol{v} + \left(\zeta + \frac{1}{3}\eta\right)\nabla_{\boldsymbol{r}}(\nabla_{\boldsymbol{r}} \cdot \boldsymbol{v})\,, \tag{10.39}$$

and

$$\frac{\partial}{\partial t}(\rho(z)\tilde{c}_\rho\delta T) = -\nabla_{\boldsymbol{r}} \cdot [\rho(z)\tilde{c}_\rho T(z)\boldsymbol{v} - K\nabla_{\boldsymbol{r}}(T(z) + \delta T)]\,. \tag{10.40}$$

Let us now note that

$$\delta\rho(\boldsymbol{r}, t) = -\rho_0\alpha_P\delta T(\boldsymbol{r}, t) \tag{10.41}$$

(cf. Eq. (10.33)). Then from Eq. (10.38) we have $\nabla_{\boldsymbol{r}} \cdot \boldsymbol{v} \approx \alpha_P$. If we now neglect all terms that depend on α_P except those that appear in the term involving the external field, we obtain

$$\nabla_{\boldsymbol{r}} \cdot \boldsymbol{v} = 0 , \tag{10.42}$$

$$\rho_0 \frac{\partial \boldsymbol{v}}{\partial t} = -\nabla_{\boldsymbol{r}} \delta P + \rho_0 \alpha_P \delta T g \hat{\boldsymbol{z}} + \eta \nabla_{\boldsymbol{r}}^2 \boldsymbol{v} , \tag{10.43}$$

and

$$\frac{\partial}{\partial t} \delta T = a v_z + \frac{K}{\rho_0 \tilde{c}_\rho} \nabla_{\boldsymbol{r}}^2 \delta T . \tag{10.44}$$

The above approximation is called the *Boussinesq approximation.* The consistency of the Boussinesq approximation has been demonstrated by Mihaljan [139]. Equations (10.42)–(10.44) form the starting point of our linear stability analysis.

We can simplify these equations somewhat through the following steps. We first take the curl of Eq. (10.43) to obtain

$$\frac{\partial (\nabla_{\boldsymbol{r}} \times \boldsymbol{v})}{\partial t} = g \alpha_P \nabla_{\boldsymbol{r}} \times (\delta T \hat{\boldsymbol{z}}) + \nu_t \nabla_{\boldsymbol{r}}^2 (\nabla_{\boldsymbol{r}} \times \boldsymbol{v}) , \tag{10.45}$$

where $\nu_t = \eta / \rho_0$. We next take the curl of Eq. (10.45) and note that $\nabla_{\boldsymbol{r}} \times (\nabla_{\boldsymbol{r}} \times \boldsymbol{v}) = \nabla_{\boldsymbol{r}} (\nabla_{\boldsymbol{r}} \cdot \boldsymbol{v}) - \nabla_{\boldsymbol{r}}^2 \boldsymbol{v}$. Using Eq. (10.42), we find

$$\frac{\partial}{\partial t} \nabla_{\boldsymbol{r}}^2 \boldsymbol{v} = -g \alpha_P \nabla_{\boldsymbol{r}} \left(\frac{\partial \delta T}{\partial z} \right) + g \alpha_P \nabla_{\boldsymbol{r}}^2 (\delta T \hat{\boldsymbol{z}}) + \nu \nabla_{\boldsymbol{r}}^4 \boldsymbol{v} . \tag{10.46}$$

In our stability analysis, we shall be interested in instabilities in the z-components of velocity. The equation of motion for the z-component of velocity is given by

$$\frac{\partial}{\partial t} \nabla_{\boldsymbol{r}}^2 v_z = g \alpha_P \left(\frac{\mathrm{d}^2}{\mathrm{d}x^2} + \frac{\mathrm{d}^2}{\mathrm{d}y^2} \right) \delta T + \nu \nabla^4 v_z . \tag{10.47}$$

If an instability occurs in which flow develops in the z-direction, then $v_z \hat{\boldsymbol{z}}$ must change sign as we move in the x- or y-direction (what goes up must come down).

As for the case of the Brusselator, we must specify boundary conditions before we apply the stability analysis. We first note the general boundary conditions that

$$\delta T(x, y, 0; t) = \delta T(x, y, d; t) = 0 \tag{10.48}$$

and

$$v_z(x, y, 0; t) = v_z(x, y, d; t) = 0 . \tag{10.49}$$

In addition to the above general boundary conditions, we have additional constraints on the surfaces at $z = 0$ and $z = d$. We can have either rigid surfaces for which there can be no tangential components of velocity or smooth surfaces where we can have a tangential flow.

10.4.1.1 **Rigid Surface Boundary Conditions**

For a rigid surface we have the boundary conditions

$$\boldsymbol{v}(x, y, 0; t) = \boldsymbol{v}(x, y, d; t) = 0 . \tag{10.50}$$

Since $\boldsymbol{v} = 0$ for all x and y, we find $\mathrm{d}v_x / \mathrm{d}x = \mathrm{d}v_y / \mathrm{d}y = 0$, and thus from Eq. (10.42) we have the additional condition $\mathrm{d}v_z / \mathrm{d}z = 0$.

10.4.1.2 Smooth Surface Boundary Conditions

On a smooth surface there can be horizontal flow but no transport of the horizontal components of velocity in the z-direction. Thus, the components of the stress tensor satisfy the condition

$$\Pi_{xz}(x,y,0;t)=\Pi_{xz}(x,y,d;t)=\Pi_{yz}(x,y,0;t)=\Pi_{yz}(x,y,d;t)=0 \quad (10.51)$$

or

$$\left(\frac{\partial v_x}{\partial z}+\frac{\partial v_z}{\partial x}\right)_{\text{bound}}=0 \quad \text{and} \quad \left(\frac{\partial v_y}{\partial z}+\frac{\partial v_z}{\partial y}\right)_{\text{bound}}=0\,. \quad (10.52)$$

Since $v_z = 0$ for all x and y on the surface, we have

$$\left(\frac{\partial v_z}{\partial x}\right)_{\text{bound}}=\left(\frac{\partial v_z}{\partial y}\right)_{\text{bound}}=0 \quad \text{and} \quad \left(\frac{\partial v_x}{\partial z}\right)_{\text{bound}}=\left(\frac{\partial v_y}{\partial z}\right)_{\text{bound}}=0 \quad (10.53)$$

on the smooth surface.

10.4.2
Linear Stability Analysis

We shall now look for instabilities in v_z, as well as for fluctuations in T which vary in space in the x- and y-directions. Since in the linear stability analysis we work with linearized equations, we only need to consider one Fourier component. Thus, we can write

$$v_z(r,t)=\tilde{V}_z(z)\mathrm{e}^{\mathrm{i}(k_x x+k_y y)}\mathrm{e}^{\omega t} \quad \text{and} \quad T(\boldsymbol{r},t)=\tilde{T}(z)\mathrm{e}^{\mathrm{i}(k_x x+k_y y)}\mathrm{e}^{\omega t}\,, \quad (10.54)$$

where $\tilde{V}_z(z)$ and $\tilde{T}(z)$ are assumed to depend on $\boldsymbol{k}=k_x\hat{\boldsymbol{\imath}}+k_y\hat{\boldsymbol{\jmath}}$ and on ω. Substitution into Eqs. (10.44) and (10.47) yields

$$\omega\tilde{T}=a\tilde{V}_z+\frac{K}{\rho_0\tilde{c}_\rho}\left(\frac{\mathrm{d}^2}{\mathrm{d}z^2}-k^2\right)\tilde{T} \quad (10.55)$$

and

$$\omega\left(\frac{\mathrm{d}^2}{\mathrm{d}z^2}-k^2\right)\tilde{V}_z=-g\alpha_P k^2\tilde{T}+\nu\left(\frac{\mathrm{d}^2}{\mathrm{d}z^2}-k^2\right)^2\tilde{V}_z\,. \quad (10.56)$$

From the general boundary conditions we must have $\tilde{T}(0)=\tilde{T}(d)=0$ and $\tilde{V}_z(0)=\tilde{V}_z(d)=0$. On a rigid surface we have

$$\left.\frac{\mathrm{d}\tilde{V}_z}{\mathrm{d}z}\right|_{z=0}=\left.\frac{\mathrm{d}\tilde{V}_z}{\mathrm{d}z}\right|_{z=d}=0\,. \quad (10.57)$$

On a smooth surface we have

$$\left.\frac{\mathrm{d}^2 \tilde{V}_z}{\mathrm{d}z^2}\right|_{z=0} = \left.\frac{\mathrm{d}^2 \tilde{V}_z}{\mathrm{d}z^2}\right|_{z=d} = 0\,. \tag{10.58}$$

It is convenient to introduce a change of length scale. We will let $\xi = z/d, s = \omega d^2/\nu, \alpha = kd$, and $\mathrm{P} = \nu\rho_0\tilde{c}_\rho/K$ (P is the *Prandtl number*). Then Eqs. (10.55) and (10.56) can be combined and written

$$\left(\frac{\partial^2}{\partial\xi^2} - \alpha^2\right)\left(\frac{\partial^2}{\partial\xi^2} - \alpha^2 - s\right)\left(\frac{\partial^2}{\partial\xi^2} - \alpha^2 - \mathrm{P}s\right)\tilde{V}_z(\xi) = -\mathrm{R}\alpha^2\tilde{V}_z(\xi) \tag{10.59}$$

and an identical equation holds for $\tilde{T}(\xi)$. In (10.59),

$$\mathrm{R} = \frac{g a \rho_0 \tilde{c}_\rho \alpha_P d^4}{\nu K} \tag{10.60}$$

is the *Rayleigh number*.

The transition from the steady state in Eqs. (10.35)–(10.37) to a new steady state (often called a “soft mode” transition when the frequency is real and no temporal oscillations are allowed) occurs when $s = 0$. For $s < 0$, fluctuations are damped. For $s > 0$, they can grow. To find conditions under which the transition occurs, we set $s = 0$ in Eq. (10.59) and find values of R which satisfy the equation

$$\left(\frac{\partial^2}{\partial\xi^2} - \alpha^2\right)^3 \tilde{V}_z(\xi) = -\mathrm{R}\alpha^2\tilde{V}_z(\xi)\,. \tag{10.61}$$

Thus, the whole problem has been reduced to an eigenvalue problem.

We will now solve this eigenvalue problem for smooth boundary conditions and we will compute the lowest value of the Rayleigh number for which an instability can occur. For smooth boundaries at $\xi = 0$ and $\xi = 1$, $\tilde{V}_z(\xi)$ must have the form

$$\tilde{V}_z(\xi) = A \sin n\pi\xi\,, \tag{10.62}$$

where $n = 1, 2, \ldots, \infty$. Substitution into Eq. (10.61) leads to the eigenvalue equation

$$\mathrm{R} = \frac{(n^2\pi^2 + \alpha^2)^3}{\alpha^2}\,. \tag{10.63}$$

The smallest value of R for which an instability can occur is for $n = 1$ or

$$\mathrm{R} = \frac{(\pi^2 + \alpha^2)^3}{\alpha^2}\,. \tag{10.64}$$

If we plot R as a function of α, we find a critical value of α (α is related to the size of cells in the x- and y-directions) for which R takes on its lowest value. To find it analytically we must find the position to the minimum of R. Thus, we set

$$\frac{\partial\mathrm{R}}{\partial\alpha^2} = 3\frac{(\pi^2 + \alpha^2)^2}{\alpha^2} - \frac{(\pi^2 + \alpha^2)^3}{\alpha^4} = 0 \tag{10.65}$$

and obtain

$$\alpha_{\mathrm{c}} = \frac{\pi}{\sqrt{2}} = 2.22\,. \tag{10.66}$$

The critical wavelength (the distance across a cell in the x–y plane) for the onset of instabilities is

$$\lambda_{\mathrm{c}} = \frac{2\pi d}{\alpha} = 2^{3/2} d \tag{10.67}$$

and the critical Rayleigh number is

$$\mathrm{R}_{\mathrm{c}} = \frac{27}{4}\pi^4 = 657.51\,. \tag{10.68}$$

Note that the critical wavelength depends on the size of the container. Thus, we find that a *nonequilibrium phase transition* first occurs, as Rayleigh number is increased, at Rayleigh number $\mathrm{R} = \mathrm{R}_{\mathrm{c}} = 27\pi^4/4$. At this Rayleigh number a mode emerges which has wavevector $\boldsymbol{q} = k_x\hat{\boldsymbol{x}} + k_y\hat{\boldsymbol{y}}$ with magnitude $q^2 = q_{\mathrm{c}}^2 = \pi^2/(2d^2)$.

The case of two smooth surfaces, while easy to analyze, is difficult to realize in experiments. Generally, in experiments one has one smooth surface and one rigid surface, or two rigid surfaces. For these more realistic boundary conditions the analysis proceeds along similar lines but is slightly more complicated [28] and will not be discussed here. For the case of one rigid and one free surface, one finds $\mathrm{R}_{\mathrm{c}} = 1100.65$ and $\alpha_{\mathrm{c}} = 2.68$. For the case of two rigid boundaries, one finds $\mathrm{R}_{\mathrm{c}} = 1707.76$ and $\alpha_{\mathrm{c}} = 3.12$.

Let us now summarize our results. For the region in which the steady state in Eqs. (10.35)–(10.37) is stable, the system is homogeneous in the x- and y-directions. However, at the transition point, convection begins and the system breaks into cells in the x- and y-directions. The cells will have a periodicity in the x- and y-directions which is proportional to d, the distance between the plates. We expect the cell walls to be vertical and that at the cell walls the normal gradient of velocity $v_z(\boldsymbol{r}, t)$ is zero.

The theory we have developed here assumes that the planes are of infinite extent in the x- and y-directions. In practice, the experiments must be done in finite containers. Then the cell pattern that emerges is strongly dependent on the shape of the container. For rectangular containers and circular covered containers, rolls usually form. Square cells can be formed in square containers. In uncovered circular containers, where the effects of surface tension are important, hexagonal cells usually form [111]. In Figure 10.5 we give an example of hexagons, that have been observed experimentally. This transition has also been observed in molecular dynamics experiments on a two-dimensional Rayleigh–Bénard system [129, 175].

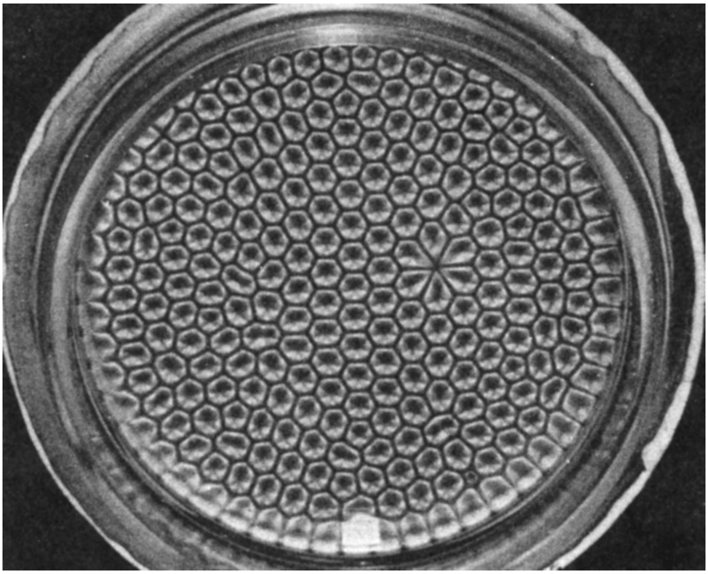

Figure 10.5 Bénard instability. In an opened container where the effects of surface tension are important hexagonal cells usually form. The dark lines indicate vertical motion, and the bright lines indicate predominantly horizontal motion. Reprinted, by permission, from [110].

10.5
Problems

Problem 10.1 Consider the nonlinear chemical reactions

$$A + 2X \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 3X \quad \text{and} \quad X \underset{k4}{\overset{k_3}{\rightleftharpoons}} B$$

(this reaction is called the Schlogl model). (a) Use linear stability theory to locate the stable and unstable steady-state solutions for the Schlogl chemical model. (b) Show that multiple steady states can only occur far from thermodynamic equilibrium.

Problem 10.2 A one-dimensional chemically reacting system has a variable constituent, X, whose rate equation is linear,

$$\frac{\partial c_X}{\partial t} = k c_X - D \nabla_r^2 c_X \, .$$

Assume that the concentration, c_X, is held fixed on the boundaries with values, $c_X = c_0$. Find the steady-state value of c_X as a function of position (D is the diffusion coefficient). Sketch the steady-state solution as a function of position.

Problem 10.3 Write the rate equations for the Brusselator near equilibrium and find the equilibrium values of c_X and c_Y. Find the steady-state solutions for the system near equilibrium (assume it is spatially homogeneous) and show that far from equilibrium (A and B large and D and E eliminated as soon as they are produced) they reduce to the expressions, $X_0 = A$ and $Y_0 = B/A$.

Problem 10.4 Show that the Brusselator admits traveling wave solutions, $c_X(r\theta \pm \nu t)$ and $c_Y(r\theta \pm \nu t)$, for linear motion on a circle, assuming periodic boundary conditions. Find the condition for a bifurcation from the thermodynamic branch to a traveling wave solution using linear stability theory. Show that the velocity, ν, of the waves is a decreasing function of the wave number.

Problem 10.5 A fluid is constrained between two smooth surfaces a distance, d, apart in a gravitational field with a temperature gradient across the fluid. If a Bénard instability develops, show that it is possible to have square cells. Find the horizontal width of the cells in terms of d. Find an expression for the velocity, $\boldsymbol{v}$, of the fluid and sketch the flow in each cell. Assume that, at the cell walls, the fluid flows upward and has its maximum speed.

Appendix A
Probability and Stochastic Processes

A.1
Probability

A.1.1
Definition of Probability

Probability is a quantization of our *expectation* of the outcome of an event or experiment [55, 125, 146]. Suppose that one possible outcome of an experiment is A. Then, the probability of A occurring is $P(A)$ if, out of N identical experiments, we *expect* that $NP(A)$ will result in the outcome A. As N becomes very large ($N \to \infty$) we *expect* that the fraction of experiments which result in A will approach $P(A)$. An important special case is one in which an experiment can result in any of n different equally likely outcomes. If exactly m of these outcomes corresponds to event A, then $P(A) = m/n$.

The concept of a sample space is often useful for obtaining relations between probabilities and for analyzing experiments. The *sample space* of an experiment is a set, S, of elements such that any outcome of the experiment corresponds to one or more elements of the set. An *event* is a subset of a sample space S of an experiment. The probability of an event A can be found by using the following procedure:

a) Set up a sample space S of all possible outcomes.
b) Assign probabilities to the elements of the sample space (the sample points). For the special case of a sample space of N equally likely outcomes, assign a probability $1/N$ to each point.
c) To obtain the probability of an event A, add the probabilities assigned to elements of the subset of S that corresponds to A.

In working with probabilities, some ideas from set theory are useful. The *union* of two events A and B is denoted $A \cup B$. $A \cup B$ is the set of all points belonging to A or B or both (cf. Figure A.1a). The *intersection* of two events is denoted $A \cap B$. $A \cap B$ is the set of all points belonging to both A and B (cf. Figure A.1b). If the events A and B are *mutually exclusive*, then $A \cap B = \emptyset$ where $\emptyset$ is the empty set ($A \cap B = \emptyset$ contains no points) (cf. Figure A.1c).

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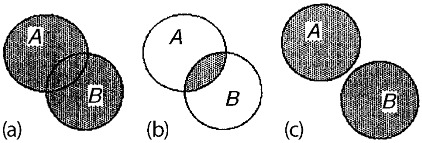

Figure A.1 (a) The shaded area is the union of A and B, $A \cup B$; (b) the shaded area is the intersection of A and B, $A \cap B$; (c) when A and B are mutually exclusive there is no overlap.

We can obtain some useful relations between the probabilities of different events. We shall let $P(A)$ denote the probability that event A is the outcome of an experiment ($P(\emptyset) = 0, P(S) = 1$); we shall let $P(A \cap B)$ denote the probability that *both* events A and B occur as the result of an experiment; and finally we shall let $P(A \cup B)$ denote the probability that event A or event B or both occur as the outcome of an experiment. Then the probability $P(A \cup B)$ may be written

$$P(A \cup B) = P(A) + P(B) - P(A \cap B)\,. \tag{A.1}$$

In writing $P(A) + P(B)$, we take the region $A \cap B$ into account twice. Therefore, we have to subtract a factor $P(A \cap B)$.

If the two events A and B are *mutually exclusive*, then they have no points in common and

$$P(A \cup B) = P(A) + P(B)\,. \tag{A.2}$$

If events $A_1, A_2, \dots, A_m$ are *mutually exclusive* and *exhaustive*, then $A_1 \cup A_2 \cup \cdots \cup A_m = S$ and the m events form a *partition* of the sample space S into m subsets. If $A_1, A_2, \dots, A_m$ form a partition, then

$$P(A_1) + P(A_2) + \cdots + P(A_m) = 1\,. \tag{A.3}$$

We see versions of Eq. (A.3) often in this book.

The events A and B are *independent if and only if*

$$P(A \cap B) = P(A)P(B)\,. \tag{A.4}$$

Note that since $P(A \cap B) \neq 0$, A and B have some points in common. Therefore, independent events are not mutually exclusive events. They are completely different concepts. For mutually exclusive events, $P(A \cap B) = 0$.

The *conditional probability* $P(B|A)$ is the probability that event A occurs as the result of an experiment *if* B also occurs. $P(B|A)$ is defined by the equation

$$P(B|A) = \frac{P(A \cap B)}{P(B)}\,. \tag{A.5}$$

Since $P(A \cap B) = P(B \cap A)$, we find also that

$$P(A)P(A|B) = P(B)P(B|A)\,. \tag{A.6}$$

From Eq. (A.4) we see that if A and B are independent, then

$$P(B|A) = P(A)\,. \tag{A.7}$$

The conditional probability $P(B|A)$ is essentially the probability of event A if we use the set B as the sample space rather than S.

Exercise A.1

Consider a sample space consisting of events A and B such that $P(A) = 3/5$, $P(B) = 2/3$, and $P(A \cup B) = 1$. Compute $P(A \cap B)$, $P(B|A)$, and $P(A|B)$. Are A and B independent?

Answer: From Eq. (A.1), $P(A \cap B) = P(A) + P(B) - P(A \cup B) = 4/15$. But $P(A \cap B) \neq P(A)P(B)$ so A and B are not independent. The conditional probabilities are $P(A|B) = P(A \cap B)/P(A) = 4/9$ and $P(B|A) = P(A \cap B)/P(B) = 2/5$. Thus, $4/9$ of the points in A also belong to B and $2/5$ of the points in B also belong to A.

Exercise A.2

Nine students go camping. Of these students, three get mosquito bites M, five get torn clothes T, and two go unscathed U. (a) What is the probability that a student with mosquito bites has torn clothes? (b) What is the probability that a student with torn clothes has mosquito bites?

Answer: The probability to have torn clothes is $P(T) = 5/9$, to have mosquito bites is $P(M) = 3/9$, and to go unscathed is $P(U) = 2/9$.

(a) If one draws a sample space with nine points in it (one for each student) and assigns the events T, M, and U to the students, then it is easy to see that $P(T \cap M) = 1/9$. Therefore, the probability that a student with mosquito bites also has torn clothes is $P(M|T) = P(T \cap M)/P(M) = (1/9)/(3/9) = 1/3$.

(b) The probability that a student with torn clothes also has mosquito bites is $P(T|M) = P(T \cap M)/P(T) = (1/9)/(5/9) = 1/5$.

(Note that $P(T)P(M) = 15/81 \neq P(T \cap M)$ so T and M are not independent. Note also that $P(M \cap U) = 0$ so M and U are mutually exclusive.)

A.1.2
Probability Distribution Functions

A quantity whose value is a number determined by the outcome of an experiment is called a *stochastic variable* (often it is also called a *random variable*). A stochastic variable, X, on a sample space, S, is a function which maps elements of S into the set of real numbers, $\{R\}$, in such a way that the inverse mapping of every interval in $\{R\}$ corresponds to an event in S (in other words, a stochastic variable is a function which assigns a real number to each sample point). One must be careful to distinguish a stochastic variable (usually denoted by a capital letter X) from its possible realizations, $\{x_i\}$. (It is useful to note that the statement *select at random* means that all selections are equally probable.) Some examples of stochastic variables are (i) the number of heads which appear each time three coins are tossed; (ii) the velocity of each molecule leaving a furnace.

A.1.2.1 **Discrete Stochastic Variables**

Let X be a stochastic variable that has a countable set of realizations, x_i, where $i = 1, 2, \ldots, \nu$ (ν is either a finite integer or $\nu = \infty$). One can introduce a probability space by assigning a probability, $P_X(x_i)$, to each realization, x_i. The set of values, $P_X(x_i)$, is the probability distribution on S and must satisfy the conditions

$$P_X(x_i) \geq 0 \quad \text{and} \quad \sum_{i=1}^{\nu} P_X(x_i) = 1 \,. \tag{A.8}$$

If we can determine the distribution function $P_X(x_i)$ for a stochastic variable X then we have obtained all possible information about it. We usually cannot determine $P_X(x_i)$, but we can often obtain information about the moments of X. The nth moment of X is defined

$$\langle x^n \rangle = \sum_{i=1}^{\nu} x_i^n P_X(x_i) \,. \tag{A.9}$$

Some of the moments have special names. The moment $\langle X \rangle$ is called the *mean value* of X. The combination $\langle X^2 \rangle - \langle X \rangle^2$ is called the *variance* of X, and the quantity

$$\sigma_X = \sqrt{\langle X^2 \rangle - \langle X \rangle^2} \tag{A.10}$$

is called the *standard deviation* of X.

A.1.2.2 **Continuous Stochastic Variables**

In many applications the stochastic variable X can take on a continuous set of values, such as an interval on the real axis. In that case, an interval $\{a \leq x \leq b\}$, corresponds to an event. Let us assume that there exists a piecewise continuous function, $f_X(x)$, such that the probability that X has a value in the interval $(a \leq x \leq b)$ is given by the area under the curve, $f_X(x)$ versus x, between $x = a$ and $x = b$,

$$P_X(a \leq x \leq b) = \int_a^b \mathrm{d}x\, f_X(x) \,. \tag{A.11}$$

Then X is a continuous stochastic variable, $f_X(x)$ is the *probability density* for the stochastic variable, X, and $f_X(x)\,\mathrm{d}x$ is the probability to find the stochastic variable, X, in the interval $x \to x + \mathrm{d}x$. The probability density must satisfy the conditions

$$f_X(x) \geq 0 \quad \text{and} \quad \int_{-\infty}^{\infty} \mathrm{d}x\, f_X(x) = 1 \,, \tag{A.12}$$

where we have assumed that the range of allowed values of X is $-\infty \leq x \leq \infty$. The moments of X are now defined

$$\langle x^n \rangle = \int_{-\infty}^{\infty} \mathrm{d}x x^n f_X(x) \,, \tag{A.13}$$

where $\langle X \rangle$ is the mean value and the variance and standard deviation are defined as before.

A.1.2.3 **Characteristic Function**

If all the moments $\langle X^n \rangle$ are known, then the probability density is completely specified. To see this, we introduce the characteristic function, $\phi_X(k)$, defined as

$$\phi_X(k) = \langle e^{ikx} \rangle = \int_{-\infty}^{\infty} dx e^{ikx} f_X(x) = \sum_{n=0}^{\infty} \frac{(ik)^n \langle x^n \rangle}{n!} . \tag{A.14}$$

The series expansion in Eq. (A.14) is meaningful only if the higher moments, $\langle x^n \rangle$, are small so the series converges. The probability density, $f_X(x)$, is given by the inverse transform

$$f_X(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dk e^{-ikx} \phi_X(k) . \tag{A.15}$$

Thus, it requires all the moments to completely determine the probability density, $f(x)$. Characteristic functions are continuous functions of k and have the property that $\phi_X(0) = 1$, $|\phi_X(k)| \leq 1$, and $\phi_X(-k) = \phi_X^*(k)$ (* denotes complex conjugation). The product of two characteristic functions is always a characteristic function.

If we know the characteristic function we can obtain moments by differentiating:

$$\langle x^n \rangle = \lim_{k \to 0} (-i)^n \frac{d^n \phi_X(x)}{dk^n} . \tag{A.16}$$

Equation (A.16) provides a simple way to obtain moments if we know $\phi_X(k)$.

It is often useful to write the characteristic function, $\phi_X(k)$, in terms of cumulants, $C_n(X)$, rather than expand it directly in terms of moments. The cumulant expansion is defined

$$\phi_X(k) = \exp\left(\sum_{n=1}^{\infty} \frac{(ik)^n}{n!} C_n(X) \right) , \tag{A.17}$$

where $C_n(X)$ is the nth-order cumulant. If we expand Eq. (A.17) in powers of k and equate terms of the same order in k in Eqs. (A.14) and (A.17), we find the following expressions for the first four cumulants:

$$C_1(X) = \langle x \rangle , \tag{A.18}$$

$$C_2(X) = \langle x^2 \rangle - \langle x \rangle^2 , \tag{A.19}$$

$$C_3(X) = \langle x^3 \rangle - 3\langle x \rangle \langle x^2 \rangle + 2\langle x \rangle^3 , \tag{A.20}$$

$$C_4(X) = \langle x^4 \rangle - 3\langle x^2 \rangle^2 - 4\langle x \rangle \langle x^3 \rangle + 12\langle x \rangle^2 \langle x^2 \rangle - 6\langle x \rangle^4 . \tag{A.21}$$

If higher order cumulants rapidly go to zero, we can often obtain a good approximation to $\phi_X(k)$ by retaining only the first few cumulants in Eq. (A.17). We see that $C_1(X)$ is just the mean value of X and $C_2(X)$ is the variance.

Exercise A.3

Consider a system with stochastic variable, X, which has probability density, $f_X(x)$, given by the circular distribution; $f_X(x) = (2/\pi)\sqrt{1-x^2}$ for $|x| \le 1$, and $f_X(x) = 0$ for $|x| > 1$. Find the characteristic function and use it to find the first four moments and the first four cumulants.

Answer: The characteristic function is

$$\phi_X(k) = \frac{2}{\pi}\int_{-1}^{1} \mathrm{d}x e^{\mathrm{i}kx}\sqrt{1-x^2} = \frac{2}{k}J_1(k) \,,$$

(cf. Gradshteyn and Ryzhik [71]) where $J_1(k)$ is a Bessel function. Now expand $f_X(k)$ in powers of k

$$f_X(k) = \frac{2}{k}\left[\frac{k}{2} - \frac{k^3}{16} + \frac{k^5}{384} + \cdots\right] = 1 - \frac{1}{4}\frac{k^2}{2!} + \frac{1}{8}\frac{k^4}{4!} - \cdots \,.$$

From Eq. (A.14), the moments are $\langle x\rangle = \langle x^3\rangle = 0$, $\langle x^2\rangle = 1/4$, and $\langle x^4\rangle = 1/8$. The cumulants are $C_1 = C_3 = 0$, $C_2 = 1/4$, and $C_4 = -1/16$.

A.1.2.4 Jointly Distributed Stochastic Variables

The stochastic variables X and Y are jointly distributed if they are defined on the same sample space, S. The joint probability density $f_{X,Y}(x,y)$ satisfies the conditions

$$0 \le f(x,y) \le 1 \quad \text{and} \quad \int_{-\infty}^{\infty} \mathrm{d}x \int_{-\infty}^{\infty} \mathrm{d}y\, f_{X,Y}(x,y) = 1 \,. \tag{A.22}$$

If we want the reduced distribution function, $f_X(x)$, for the stochastic variable, X, it is defined as

$$f_X(x) = \int_{-\infty}^{\infty} \mathrm{d}y\, f_{X,Y}(x,y) \,. \tag{A.23}$$

We can obtain the reduced probability density, $f_Y(y)$, in a similar manner.

The nth moment of the stochastic variable, X, is defined as

$$\langle x^n\rangle = \int_{-\infty}^{\infty} \mathrm{d}x \int_{-\infty}^{\infty} \mathrm{d}y x^n f_{X,Y}(x,y) \,. \tag{A.24}$$

Joint moments of the stochastic variables, X and Y, are defined as

$$\langle x^m y^n\rangle = \int_{-\infty}^{\infty} \mathrm{d}x \int_{-\infty}^{\infty} \mathrm{d}y x^m y^n f_{X,Y}(x,y) \,. \tag{A.25}$$

A joint moment that is commonly used in the physics literature is the joint *correlation function*

$$\mathrm{Cor}(X, Y) = \frac{\langle (x - \langle x \rangle)(y - \langle y \rangle) \rangle}{\sigma_X \sigma_Y} , \tag{A.26}$$

where σ_X and σ_Y are the standard deviations of the stochastic variables X and Y, respectively. The correlation function, $\mathrm{Cor}(X, Y)$, is dimensionless and is a measure of the degree of dependence of the stochastic variables X and Y on one another. The correlation function has the following properties: (i) $\mathrm{Cor}(X, Y) = \mathrm{Cor}(Y, X)$; (ii) $-1 \leq \mathrm{Cor}(X, Y) \leq 1$; (iii) $\mathrm{Cor}(X, X) = 1$ and $\mathrm{Cor}(X, -X) = -1$; and (iv) $\mathrm{Cor}(aX + b, cY + d) = \mathrm{Cor}(X, Y)$ if $a, c \neq 0$. The notion of the joint correlation function can be extended to any number of stochastic variables.

For two stochastic variables, X and Y, which are *independent*, the following properties hold: (i′) $f_{X,Y}(x, y) = f_X(x) f_Y(y)$; (ii′) $\langle XY \rangle = \langle X \rangle \langle Y \rangle$; (iii′) $\langle (X + Y)^2 \rangle - \langle (X + Y) \rangle^2 = \langle X^2 \rangle - \langle X \rangle^2 + \langle Y^2 \rangle - \langle Y \rangle^2$; and (iv′) $\mathrm{Cor}(X, Y) = 0$. Note that the converse of (iv′) does not necessarily hold. If Cor $(X, Y) = 0$, it does not always means that X and Y are independent.

When we deal with several stochastic variables, we often wish to find the probability density for a new stochastic variable which is a function of the old stochastic variables. For example, if we know the joint probability density, $f_{X,Y}(x, y)$, we may wish to find the probability density for a variable $Z = G(X, Y)$, where $G(X, Y)$ is a known function of X and Y. The probability density, $f_Z(z)$, for the stochastic variable, Z, is defined as

$$f_Z(z) = \int_{-\infty}^{\infty} \mathrm{d}x \int_{-\infty}^{\infty} \mathrm{d}y \delta(z - G(x, y)) f_{X,Y}(x, y) . \tag{A.27}$$

An example is given in Exercise A.4.

A.1.3
Binomial Distributions

We consider the case of a large number, N, of independent experiments, each having two possible outcomes. The probability distribution for one of the outcomes is called the *binomial distribution* [55, 68, 125]. In the limit of large N, the binomial distribution can be approximated by either the Gaussian or the Poisson distribution, depending on the size of the probability of a given outcome during a single experiment. We shall consider all three distributions in this section.

A.1.3.1 The Binomial Distribution

Let us carry out a sequence of N statistically independent trials and assume that each trial can have only one of two outcomes, +1 or −1. Let us denote the probability of outcome, +1, by p and the probability of outcome, −1, by q so that $p + q = 1$.

In a given sequence of N trials, the outcome +1 (−1) can occur n_+ (n_-) times, where $N = n_+ + n_-$. The probability for a given *permutation* of n_+ outcomes, +1, and n_- outcomes, -1, is $p^{n_+}q^{n_-}$ since the N trials are statistically independent. The probability for any *combination* of n_+ outcomes, $+1$, and n_- outcomes, -1, is

$$P_N(n_+) = \frac{N!}{n_+!n_-!}p^{n_+}q^{n_-} \tag{A.28}$$

since a *combination* of n_+ outcomes, $+1$, and n_- outcomes, -1, contains $(N!/n_+!n_-!)$ permutations. The quantity $P_N(n_+)$ in Eq. (A.28) is called the *binomial distribution*.

Exercise A.4

The stochastic variables, X and Y, are independent and have probability densities, $f_X(x) = (1/\sqrt{2\pi})\mathrm{e}^{-(1/2)x^2}$ and $f_Y(y) = (1/\sqrt{2\pi})\mathrm{e}^{-(1/2)y^2}$ with first moments, $\langle x\rangle = \langle y\rangle = 0$, and standard deviations, $\sigma_X = \sigma_Y = 1$. Find the joint probability density $f_{V,W}(v, w)$ for the stochastic variables, $V = X + Y$ and $W = X - Y$. Are V and W independent?

Answer: Since X and Y are independent, Eq. (A.27) gives

$$f_{V,W}(v, w) = \frac{1}{2\pi}\int_{-\infty}^{\infty}\mathrm{d}x\int_{-\infty}^{\infty}\mathrm{d}y\delta(v - v'(x, y))\delta(w - w'(x, y))\mathrm{e}^{-(1/2)(x^2+y^2)} ,$$

where $v'(x, y) = x + y$ and $w'(x, y) = x - y$. Now note that

$$\delta(v - v'(x, y))\delta(w - w'(x, y)) = J\begin{pmatrix} x & y \\ w & v \end{pmatrix}\delta(x - x'(v, w))\delta(y - y'(v, w)) ,$$

where $x'(v, w) = 1/2(v + w)$, $y'(v, w) = 1/2(v - w)$, and $J\begin{pmatrix} x & y \\ w & v \end{pmatrix} = 1/2$ is the Jacobian of the coordinate transformation. Thus, $f_{V,W}(v, w) = 1/4\pi\mathrm{e}^{-(1/4)(v^2+w^2)}$. V and W are independent since $f_{V,W}(v, w)$ is factorizable.

From the binomial theorem, we have the normalization condition

$$\sum_{n_+=0}^{N} P_N(n_+) = \sum_{n_+=0}^{N}\frac{N!}{n_+!(N-n_+)!}p^{n_+}q^{N-n_+} = (p+q)^N = 1 . \tag{A.29}$$

The first moment, or mean value, of outcome $+1$ is

$$\langle n_+\rangle = \sum_{n_+=0}^{N} n_+P_N(n_+) = \sum_{n_+=0}^{N}\frac{n_+N!}{n_+!(N-n_+)!}p^{n_+}q^{N-n_+} = p\frac{\partial}{\partial p}(p+q)^N = pN . \tag{A.30}$$

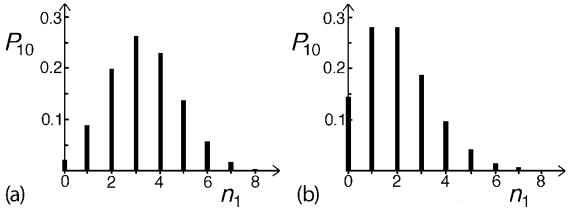

Figure A.2 (a) The binomial distribution for $p = 1/3$ and $N = 10$; for this case, $\langle n_1 \rangle = 10/3$. (b) The Poisson distribution for $\langle n \rangle = a = 2$.

In a similar manner, we obtain for the second moment

$$\langle n_+^2 \rangle = \sum_{n_+=0}^{N} n_+^2 P_N(n_+) = (Np)^2 + Npq \; . \tag{A.31}$$

The variance is given by $\langle n_+^2 \rangle - \langle n_+ \rangle^2 = Npq$, and the standard deviation is

$$\sigma_N = \sqrt{Npq} \; . \tag{A.32}$$

The fractional deviation is

$$\frac{\sigma_N}{\langle n_+ \rangle} = \sqrt{\frac{q}{p}} \frac{1}{\sqrt{N}} \; . \tag{A.33}$$

The fractional deviation is a measure of the deviation of the fraction, n_+/N, of trials with outcome, +1, from its expected value, $\langle n_+ \rangle / N = p$, in any single sequence of N trials. A small value of $\sigma_N / \langle n_+ \rangle$ means that n_+/N will likely be close to p. For $N \to \infty$, $\sigma_N / \langle n_+ \rangle \to 0$ so that $n_1/N \to p$. The binomial distribution, for the case $N = 10$ and $p = 1/3$ is plotted in Figure A.2a. An application of the binomial distribution is given in Exercise A.5.

Exercise A.5

The probability that an archer hits his target is 1/3. If he shoots five times, what is the probability of hitting the target at least three times?

Answer: Let n_+ be the number of hits. Then $N = n_- + n_+ = 5$, $p = 1/3$, and $q = 2/3$. The probability of having n_+ hits in $N = 5$ trials is $P_5(n_+) = 5!/(n_+!(5 - n_+)!)(1/3)^{n_+}(2/3)^{5-n_+}$. The probability of at least three hits $= P_5(3) + P_5(4) + P_5(5) = 51/243 \approx 0.21$.

A.1.3.2 **The Gaussian (or Normal) Distribution**

In the limit of large N and large pN (i.e., p not very small) the binomial distribution approaches a Gaussian distribution. If we make use of Stirling's approximation

$$n! \approx \sqrt{2\pi n} \left(\frac{n}{e} \right)^n \; , \tag{A.34}$$

for $n > 10$, we can write (after a bit of algebra) the following approximation to the binomial distribution

$$P_N(n) \approx \frac{1}{\sqrt{2\pi N}} \left(\frac{n}{N}\right)^{-n-1/2} \left(\frac{N-n}{N}\right)^{n-N-1/2} p^n (1-p)^{N-n} . \tag{A.35}$$

If we use the fact that $\exp(y \ln x) = x^y$, then we can write Eq. (A.35) in the form

$$P_N(n) \approx \frac{1}{\sqrt{2\pi N}} \exp\left[-\left(n+\frac{1}{2}\right)\ln\left(\frac{n}{N}\right) - \left(N-n+\frac{1}{2}\right)\ln\left(\frac{N-n}{N}\right)\right.$$
$$\left. + n\ln(p) + (N-n)\ln(1-p)\right] . \tag{A.36}$$

The binomial distribution $P_N(n)$ exhibits a maximum at $n = \langle n\rangle = Np$ so $\langle n\rangle$ grows at a rate proportional to N. The standard deviation $\sigma_N = \sqrt{pqN}$, which is a measure of the width of $P_N(n)$, only grows at a rate proportional to $\sqrt{N}$. For $N \gg 1$, the width $2\sigma_N$ of the binomial distribution is very small compared to the value of the mean $\langle n\rangle$. Thus, all the values of n that carry significant probability lie in the neighborhood of $\langle n\rangle = pN$ and are very large compared to integer changes in n. Therefore, in the limit $N \to \infty$, it is a good approximation to treat n as a continuous variable.

If we expand the exponent in Eq. (A.36) in a Taylor series about $n = \langle n\rangle$, we obtain the following expression for $P_N(n)$

$$P_N(n) \approx P_N(\langle n\rangle) \exp\left[-\frac{(n-\langle n\rangle)^2}{2Npq} + \frac{(q^2-p^2)(n-\langle n\rangle)^3}{6N^2p^2q^2} + \dots\right] . \tag{A.37}$$

For $(n - \langle n\rangle) \le \sqrt{Npq}$, the terms higher than second order are negligible. For $(n - \langle n\rangle) > \sqrt{Npq}$, $P_N(n)$ falls off exponentially. Thus, for large N, we only need to keep the term which is second order in $(n - \langle n\rangle)$. The binomial distribution then becomes, to good approximation,

$$P_N(n) \approx P_N(\langle n\rangle) \exp\left[-\frac{(n-\langle n\rangle)^2}{2Npq}\right] . \tag{A.38}$$

Exercise A.6

A random walker has a probability $p = 1/2$ $(q = 1/2)$ of taking a step of length d to the right (left), so the probability density for a single step is $P_X(x) = 1/2\delta(x-d) + 1/2\delta(x+d)$. Let $Y_N = X_1 + \dots + X_N$ be the displacement after N steps. Assume that the steps are independent of one another. (a) Find the probability density $P_{Y_N}(y)$ and the first and second moments $\langle y\rangle$ and $\langle y^2\rangle$.

Answer: The probability density $P_{Y_N}(y)$ is given by

$$P_{Y_N}(y) = \int_{-\infty}^{\infty} \dots \int_{-\infty}^{\infty} \mathrm{d}x_1 \dots \mathrm{d}x_N \delta(y - x_1 - \dots - x_N) P_{X_1}(x_1) \times \dots \times P_{X_N}(x_N) .$$

The characteristic function, $\Phi_{Y_N}(k) = 1/(2\pi)\int \mathrm{d}y\mathrm{e}^{\mathrm{i}ky}P_{Y_N}(y)$, for the random variable Y_N is

$$\Phi_{Y_N}(k) = \int_{-\infty}^{\infty} \dots \int_{-\infty}^{\infty} \mathrm{d}x_1 \dots \mathrm{d}x_N \mathrm{e}^{\mathrm{i}k(x_1+\cdots+x_N)} P_{X_1}(x_1) \times \cdots \times P_{X_N}(x_N)$$

$$= \phi_{X_1}(k) \times \cdots \times \phi_{X_N}(k) = (\cos(kd))^N = \frac{1}{2^N}\sum_{n=0}^{N} \frac{N!}{n!(N-n)!}\mathrm{e}^{\mathrm{i}(2n-N)kd} ,$$

where $\phi_X(k) = 1/(2\pi)\int \mathrm{d}x\mathrm{e}^{\mathrm{i}kx}P_X(x) = \cos(kd)$ is the characteristic function for the random variable X. The first moment is

$$\langle y \rangle = \lim_{k\to 0}\left[(-\mathrm{i})\frac{d\Phi_{Y_N}(k)}{dk}\right] = \lim_{k\to 0}\left[\mathrm{i}Nd(\cos(kd))^{N-1}\sin(kd)\right] = 0 .$$

The second moment is

$$\langle y^2 \rangle = \lim_{k\to 0}\left[(-\mathrm{i})^2\frac{d^2\Phi_{Y_N}(k)}{dk^2}\right] = Nd^2 .$$

The probability density is

$$P_{Y_N}(y) = \int_{-\infty}^{\infty} dk\mathrm{e}^{-\mathrm{i}ky}\Phi_{Y_N}(k) = \frac{1}{2^N}\sum_{n=0}^{N}\frac{N!}{n!(N-n)!}\delta(y-2n+N) .$$

This is a binomial distribution for the probability to find the walker at various points along the y-axis after N steps. In the limit of large N, it approaches a Gaussian distribution centered at $y = 0$ with standard deviation $\sigma_Y = \sqrt{N}d$.

We can now normalize this distribution. Note that the range of allowed values of n is given by $0 \le n \le N$. However, as $N \to \infty$, we find that $P_N(0) \to 0$ and $P_N(N) \to 0$ since $P_N(n)$ goes to zero exponentially fast as we move a distance σ_N away from $n = \langle n \rangle$. Thus, we can extend the range of n to $-\infty \le n \le \infty$ and require that $\sum_0^N P_N(n) \Rightarrow \int_{-\infty}^{\infty} \mathrm{d}n f(n) = 1$, and we find that this limiting case of the binomial distribution yields the Gaussian probability density, $f(n)$, where

$$f(n) = \frac{1}{\sigma\sqrt{2\pi}}\exp\left[-\frac{(n-\langle n \rangle)^2}{2\sigma^2}\right] . \tag{A.39}$$

It is easy to show that $\langle n \rangle = \int_{-\infty}^{\infty} \mathrm{d}n n f(n)$ and $\sigma = \sqrt{\langle n^2 \rangle - \langle n \rangle^2}$. It is important to note that the Gaussian probability density is entirely determined by the first and second moments, $\langle n \rangle$ and $\langle n^2 \rangle$, respectively. The Gaussian distribution is plotted in Chapter 2, Figure 2.1.

Exercise A.7

The multivariant Gaussian distribution with zero mean can be written

$$P_{X_1,\ldots,X_N}(x_1,\ldots,x_N) = \sqrt{\frac{\det(\overline{\boldsymbol{g}})}{(2\pi)^N}}\,\mathrm{e}^{-(1/2)\boldsymbol{x}^{\mathrm{T}}\cdot\overline{\boldsymbol{g}}\cdot\boldsymbol{x}}\ ,$$

where $\overline{\boldsymbol{g}}$ is a symmetric $N \times N$ positive definite matrix, $\boldsymbol{x}$ is a column vector, and the transpose of $\boldsymbol{x}, \boldsymbol{x}^{\mathrm{T}} = (x_1, \ldots, x_N)$, is a row vector. Thus, $\boldsymbol{x}^{\mathrm{T}} \cdot \overline{\boldsymbol{g}} \cdot \boldsymbol{x} = \sum_{i=1}^{N} \sum_{j=1}^{N} g_{ij} x_i x_j$. Show that $P_{X_1,\ldots,X_N}(x_1, \ldots, x_N)$ is normalized to one.

Answer: Since $\overline{\boldsymbol{g}}$ is a symmetric matrix, it can be diagonalized using an orthogonal matrix, $\overline{\boldsymbol{O}}$, where $\overline{\boldsymbol{O}}^{-1} = \overline{\boldsymbol{O}}^{\mathrm{T}}$ and $\overline{\boldsymbol{O}}^{-1} \cdot \overline{\boldsymbol{O}} = \overline{\boldsymbol{I}}$ ($\overline{\boldsymbol{I}}$ is the unit matrix). Note that the determinant of $\overline{\boldsymbol{O}}$ is one, $\det(\overline{\boldsymbol{O}}) = 1$. We can write $\overline{\boldsymbol{O}} \cdot \overline{\boldsymbol{g}} \cdot \overline{\boldsymbol{O}}^{\mathrm{T}} = \overline{\boldsymbol{\Gamma}}$, where $\overline{\boldsymbol{\Gamma}}$ is diagonal ($\overline{\boldsymbol{\Gamma}}_{ii} = \gamma_i$ and $\overline{\boldsymbol{\Gamma}}_{ij} = 0$ for $i \neq j$). The orthogonal matrix, $\overline{\boldsymbol{O}}$, transforms the stochastic variables. We will let $\boldsymbol{\alpha} = \overline{\boldsymbol{O}} \cdot \boldsymbol{x} = (\alpha_1, \ldots, \alpha_N)$. Since $\det(\overline{\boldsymbol{O}}) = 1$, the Jacobian of the transformation is one. Thus, $\mathrm{d}^N\boldsymbol{x} \equiv \mathrm{d}x_1, \ldots, \mathrm{d}x_n = \mathrm{d}\alpha_1, \ldots, \mathrm{d}\alpha_N \equiv \mathrm{d}^N\boldsymbol{\alpha}$. Furthermore, $\boldsymbol{x}^{\mathrm{T}} \cdot \overline{\boldsymbol{g}} \cdot \boldsymbol{x} = \boldsymbol{\alpha}^{\mathrm{T}} \cdot \overline{\boldsymbol{\Gamma}}, \ldots, \boldsymbol{\alpha}$, so we obtain

$$\int \mathrm{d}^N\boldsymbol{x}\mathrm{e}^{-(1/2)\boldsymbol{x}^{\mathrm{T}}\cdot\overline{\boldsymbol{g}}\cdot\boldsymbol{x}} = \int \mathrm{d}^N\boldsymbol{\alpha}\mathrm{e}^{-(1/2)\sum_i^N \gamma_i\alpha_i^2} = \sqrt{\frac{(2\pi)^N}{\gamma_1,\ldots,\gamma_N}} = \sqrt{\frac{(2\pi)^N}{\det(\overline{\boldsymbol{g}})}}\ ,$$

since $\det(\overline{\boldsymbol{g}}) = \det(\overline{\boldsymbol{\Gamma}}) = \gamma_1, \ldots, \gamma_n$.

A.1.3.3 The Poisson Distribution

The Poisson distribution can be obtained from the binomial distribution in the limit $N \to \infty$ and $p \to 0$, such that $Np = a \ll N$ (a is a finite constant). The first moment for the binomial distribution is $\langle n \rangle = Np = a \ll N$ which also locates the neighborhood of the peak value of the distribution. If we use Stirling's approximation Eq. (A.34), and note that the values of n that have largest probability are those for which $n \sim Np \ll N$, then we find $N!/(N-n)! \sim N^n$. Let us further note that

$$\lim_{p\to 0}(1-p)^{N-n} \approx \lim_{p\to 0}(1-p)^N = \lim_{p\to 0}(1-p)^{a/p} \to \mathrm{e}^{-a}\ , \tag{A.40}$$

where we have used the definition $\mathrm{e}^z \equiv \lim_{n\to\infty}(1 + (z/n))^n$. If we combine the above results, the binomial distribution takes the form

$$P(n) = \frac{a^n\mathrm{e}^{-a}}{n!}\ , \tag{A.41}$$

which is called the *Poisson distribution*.

Exercise A.8

The characteristic function for the multivariant Gaussian (see Exercise A.7) is

$$f_{X_1,\ldots,X_N}(k_1,\ldots,k_N) = \sqrt{\frac{\det(\overline{g})}{(2\pi)^N}} \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \mathrm{d}x_1,\ldots,\mathrm{d}x_N \mathrm{e}^{\mathrm{i}\boldsymbol{k}^{\mathrm{T}}\cdot\boldsymbol{x}} \mathrm{e}^{-(1/2)\boldsymbol{x}^{\mathrm{T}}\cdot\overline{g}\cdot\boldsymbol{x}} ,$$

where $\boldsymbol{k}^{\mathrm{T}} = (k_1,\ldots,k_N)$. (a) Compute the characteristic function, $f_{X_1,\ldots,X_N}(k_1,\ldots,k_N)$. (b) Show that the moments, $\langle x_i\rangle = 0$ and that all higher moments can be expressed in terms of products of the moments, $\langle x_i^2\rangle$ and $\langle x_i x_j\rangle$. This is the simplest form of Wick's theorem.

Answer: (a) If we transform the integral into diagonal form, as we did in Exercise A.7, it is straightforward to show that $f_{X_1,\ldots,X_N}\left(k_1,\ldots,k_N\right) = \mathrm{e}^{-(1/2)\boldsymbol{k}^{\mathrm{T}}\cdot\overline{g}^{-1}\cdot\boldsymbol{k}}$.

(b) The first moment is $\langle x_i\rangle = \lim_{k_i\to 0}(-\mathrm{i})(\partial/\partial k_i) f_{X_1,\ldots,X_N}(k_1,\ldots,k_N) = 0$, since the derivative brings down a factor of k_j. In fact, all odd moments will be zero for the same reason. The second moment is easily seen to be $\langle x_i x_j\rangle = \left(\overline{g}^{-1}\right)_{ij}$. Inspection shows that all higher moments depend only on sums of products of factors of the form $\left(\overline{g}^{-1}\right)_{ij}$, and therefore only on sums of products of second moments. More generally, *the average of a product of 2n stochastic variables is equal to the sum of all possible combinations of different pairwise averages of the stochastic variables.* For example,

$$\langle x_1x_2x_3x_4\rangle = \langle x_1x_2\rangle\langle x_3x_4\rangle + \langle x_1x_3\rangle\langle x_2x_4\rangle + \langle x_1x_4\rangle\langle x_2x_3\rangle .$$

(Note that $\langle x_i x_j\rangle = \langle x_j x_i\rangle$.) More generally, if we have $2n$ stochastic variables, the number of terms in the expression for the $2n$th moment, is $(2n)!/n!2^n$. We determine this as follows. There are $(2n)(2n-1)/2$ ways to form the first pair. After that there are $(2n-2)(2n-3)/2$ ways to form the second pair, and so on. After all the pairs are formed in this way, by the multiplication rule, there will be $\prod_{i=0}^{n-1}(2n-2i)[2n-(2i+1)]/2 = (2n)!/2^n$ different combinations of pairs. Of these, $n!$ will be identical because they are different permutations of the same pairs. Thus, the total number of different terms in the expression for $\langle x_1x_2,\ldots,x_{2n}\rangle$ is $(2n)!/(n!2^n)$.

The Poisson distribution applies when many experiments are carried out but the result $n = +1$ has only a very small probability of occurring. The Poisson distribution is normalized to one

$$\sum_0^{\infty} \frac{a^n}{n!}\mathrm{e}^{-a} = \mathrm{e}^{a}\mathrm{e}^{-a} = 1 . \tag{A.42}$$

The first moment, $\langle n\rangle = a$. Note that the Poisson distribution depends only on the first moment, and therefore *it is sufficient to know only the first moment in order to find the probability density for a Poisson process.* In Figure A.2b, we plot the Poisson distribution for $a = 2$.

Exercise A.9

A thin sheet of gold foil (one atom thick) is fired upon by a beam of neutrons. The neutrons are assumed equally likely to hit any part of the foil but only “see” the gold nuclei. Assume that, for a beam containing many neutrons, the average number of hits is two. (a) What is the probability that no hits occur? (b) What is the probability that two hits occur?

Answer: Since the ratio (area nucleus/area atoms) $\approx 10^{-12}$, the probability of a hit is small. Since the number of trials is large, we can use the Poisson distribution. Let n_1 denote the number of hits. Then $\langle n_1 \rangle = 2$ and the Poisson distribution can be written $P(n_1) = \mathrm{e}^{-2}2^{n_1}/n_1!$.

1. The probability that no hits occur is $P(0) = \mathrm{e}^{-2}2^0/0! = 0.135$.
2. The probability that two hits occur is $P(2) = \mathrm{e}^{-2}2^2/2! = 0.27$.

A.1.4
Central Limit Theorem and the Law of Large Numbers

It can be shown that the probability density describing the distribution of outcomes of a large number of events universally approaches a Gaussian form (provided the moments of the distribution for the individual events are finite). This is called the *Central Limit Theorem* and explains why Gaussian distributions are so widely seen in nature [55, 68]. The law of large numbers gives quantitative justification to the use of probabilities.

A.1.4.1 The Central Limit Theorem

The Central Limit Theorem can be stated in a simplified form which has direct relevance to the statistics of measurements. Let us consider a stochastic variable, $Y_N = (1/N)(X_1 + \cdots + X_N) - \langle x \rangle$, which is the deviation from the average of N statistically independent measurements of a stochastic variable, X. We perform measurements of X, whose underlying probability density $f_X(x)$ is not known. We want to find the probability density for the deviation of the average Y_N of all N measurements from the mean value of X.

For simplicity consider the quantity $Z_i = (1/N)(X_i - \langle x \rangle)$ so $Y_N = Z_1 + \cdots + Z_N$. The characteristic function, $\phi_z(k; N)$, for the stochastic variable, $Z_i = (1/N)(X_i - \langle x \rangle)$, can be written

$$\phi_z(k; N) = \int_{-\infty}^{\infty} \mathrm{d}x \mathrm{e}^{\mathrm{i}(k/N)(x-\langle x \rangle)} P_X(x) = 1 - \frac{1}{2}\frac{k^2}{N^2}\sigma_X^2 + \cdots ,$$

where $\sigma_X^2 = \langle x^2 \rangle - \langle x \rangle^2$. For large N and finite variance, higher order terms in the expansion of the right-hand side can be neglected. (Note that the oscillatory character of the integrand ensures that the integral goes to zero for large k.) The characteristic function for Y_N is then

$$\phi_{Y_N}(k) = \left(1 - \frac{1}{2}\frac{k^2}{N^2}\sigma_X^2 + \cdots\right)^N \to \exp\left(-\frac{k^2\sigma_X^2}{2N}\right) \quad \text{as} \quad N \to \infty\,,$$

where we have used the identity $\lim_{N\to\infty}(1 + x/N)^N = \mathrm{e}^x$. Thus,

$$f_{Y_N}(y) \to \frac{1}{2\pi}\int_{-\infty}^{\infty} \mathrm{d}k\mathrm{e}^{\mathrm{i}ky} \exp\left(-\frac{k^2\sigma_X^2}{2N}\right) = \sqrt{\frac{N}{2\pi\sigma_X^2}} \exp\left(-\frac{Ny^2}{2\sigma_X^2}\right)$$

as $N \to \infty$. Regardless of the form of $f_X(x)$, if it has finite moments, the average of a large number of statistically independent measurements of X will be a Gaussian centered at $\langle x\rangle$, with a standard deviation which is $1/\sqrt{N}$ times the standard deviation of the probability density of X. This is a simple example of the *Central Limit Theorem* [68].

A.1.4.2 **Law of Large Numbers**

The law of large numbers underlies the intuitive concept of probability. Much of the content of the law of large numbers is contained in the Central Limit Theorem as applied to measurements. We give a simple version of it here.

The law of large numbers applies to N independent experiments and may be stated as follows: *If an event, A, has a probability, p, of occurring, then the fraction of outcomes, A, approaches p in the limit $N \to \infty$.* The proof has two steps. The first step involves the derivation of the Tchebycheff inequality. The second step uses this inequality to derive the law of large numbers.

The Tchebycheff inequality establishes a relation between the variance and the probability that a stochastic variable can deviate by an arbitrary amount, ε (ε is positive), from its average value. The variance, σ_Z, of a stochastic variable, Z, is written

$$\sigma_Z^2 = \int_{-\infty}^{\infty} \mathrm{d}z(z - \langle z\rangle)^2 P_Z(z)\,. \tag{A.43}$$

If we now delete that range of the variable, z, for which $|z - \langle z\rangle| \leq \varepsilon$, we can write

$$\sigma_Z^2 \geq \int_{-\infty}^{\langle z\rangle-\varepsilon} \mathrm{d}z(z - \langle z\rangle)^2 P_Z(z) + \int_{\langle z\rangle+\varepsilon}^{\infty} \mathrm{d}z(z - \langle z\rangle)^2 P_Z(z)\,. \tag{A.44}$$

Since under the integral $|z - \langle z\rangle| \geq \varepsilon^2$, we can replace $(z - \langle z\rangle)^2$ by ε^2 in Eq. (A.44) and write

$$\sigma_Z^2 \geq \varepsilon^2\left(\int_{-\infty}^{\langle z\rangle-\varepsilon} \mathrm{d}zP_Z(z) + \int_{\langle z\rangle+\varepsilon}^{\infty} \mathrm{d}zP_Z(z)\right) = \varepsilon^2 P(|z - \langle z\rangle| \geq \varepsilon)\,, \tag{A.45}$$

where $P(|z - \langle z\rangle| \geq \varepsilon)$ is the probability that the stochastic variable, Z, deviates from $\langle z\rangle$ by more than $\pm\varepsilon$. From Eq. (A.45), we obtain the Tchebycheff inequality

$$P(|z - \langle z\rangle| \geq \varepsilon) \leq \frac{\sigma_Z^2}{\varepsilon^2} . \tag{A.46}$$

Thus, for fixed variance, σ_Z^2, the probability that Z can differ from its average value by more than $\pm\varepsilon$ decreases as ε^{-2} for increasing ε.

We now come to the law of large numbers. Let us consider N independent measurements of the stochastic variable, Z. Let Y_N be the mean value of the outcomes, $Y_N = (1/N)(Z_1 + \cdots + Z_N)$, where Z_i is the outcome of the ith measurement. The law of large numbers states that the probability that Y_N deviates from $\langle z\rangle$ goes to zero as $N \to \infty$. Thus, $\lim_{N\to\infty} P(|y_N - \langle z\rangle| \geq \varepsilon) = 0$. To prove this, let us first note that $\langle y_N\rangle = \langle z\rangle$. Since we have independent events, the variance, σ_{Y_N}, behaves as $\sigma_{Y_N}^2 = \sigma_Z^2/N$. We now use the Tchebycheff inequality to write

$$P(|y_N - \langle z\rangle| \geq \varepsilon) \leq \frac{\sigma_{Y_N}^2}{\varepsilon^2} = \frac{\sigma_Z^2}{N\varepsilon^2} . \tag{A.47}$$

Thus, we find

$$\lim_{N\to\infty} P(|y_N - \langle z\rangle| \geq \varepsilon) = 0 , \tag{A.48}$$

provided that σ_Z is finite.

The Central Limit Theorem and the Law of Large Numbers discussed above apply to stochastic systems with finite variance. However, there is also a class of random walks that has infinite variance. A random walk on a lattice that has self-similar structure is an example of a random walk with infinite variance. Other examples include the Weierstrass random walk, the Rayleigh–Pearson random walk, and Levy flights [87, 162, 180, 210]. These random walks form fractal-like clusters on all scales, and a different form of Central Limit Theorem can be derived for them.

A.2
Stochastic Processes

We often need to determine how probability distributions evolve in time. Equations governing the flow of probability occur in many forms. Below we consider several of them.

A.2.1
Markov Chains

A Markov chain involves transitions, at discrete times, between values of a discrete stochastic variable, Y. Assume that Y has realizations $\{y_1, \ldots , y_N\}$ and that transitions between these realizations occur at times $t = s\tau$, where $s = 1, 2, \dots, \infty$. Let $P_n(s)$ denote the probability that Y has realization y_n at $t = s$. Let $P(n_1, s_1|n_2, s_2)$ denote the conditional probability that Y has realization y_{n_2} at time s_2, given that it had realization y_{n_1} at time s, then the probability $P_n(s)$ can be written

$$P_n(s+1) = \sum_{m=1}^{N} P_m(s) P(m, s|n, s+1) . \tag{A.49}$$

$P(m, s|n, s+1)$ is called the *transition probability* and contains all necessary information about transition mechanisms in the system. If we note that $P_n(s+1) = \sum_{n_0=1}^{N} P_{n_0}(s_0) P(n_0, s_0|n, s+1)$, we obtain the following equation for the transition probabilities

$$P(n_0, s_0|n, s+1) = \sum_{m=1}^{N} P(n_0, s_0|m, s) P(m, s|n, s+1) . \tag{A.50}$$

A commonly encountered situation is one in which the transition probabilities are independent of time s. We then introduce the transition matrix $Q_{m,n} = P(m, s|n, s+1)$ and can write

$$P_n(s) = \sum_{m=1}^{N} P_m(0) (\boldsymbol{Q}^s)_{m,n} . \tag{A.51}$$

The transition matrix $\boldsymbol{Q}$ is generally not a symmetric matrix, so its left and right eigenvectors will be different. If $\boldsymbol{Q}$ is an $N \times N$ matrix, it will have N eigenvalues λ_j $(j = 1, \dots, N)$, which may or may not be real. The eigenvalues, $\lambda_i (i = 1, \dots, M)$, of $\boldsymbol{Q}$ are given by the condition that $\det|\boldsymbol{Q} - \lambda \boldsymbol{I}| = 0$. The left eigenvector, $\boldsymbol{\chi}_j = (\chi_{j,1}, \dots, \chi_{j,N})$ satisfies the eigenvalue equation $\boldsymbol{\chi}_j \lambda_j = \boldsymbol{\chi}_j \boldsymbol{Q}$, while the right eigenvector $\boldsymbol{\psi}_j = (\psi_{j,1}, \dots, \psi_{j,N})^{\mathrm{T}}$ (T denotes transpose) satisfies the eigenvalue equation $\lambda_j \boldsymbol{\psi}_j = \boldsymbol{Q} \boldsymbol{\psi}_j$. One can show that the left and right eigenvectors are complete $\sum_{m=1}^{N} \boldsymbol{\psi}_j \boldsymbol{\chi}_j^{\mathrm{T}} = \mathbf{1}$ and are orthogonal $\sum_{m=1}^{N} \boldsymbol{\chi}_{j'}^{\mathrm{T}} \boldsymbol{\psi}_j = 0$ for $j' \neq j$. Also the eigenvalues have the property that $|\lambda_j| \leq 1$ and at least one of the eigenvalues (let's say λ_1) always has the value $\lambda_1 = 1$ [183] (we leave the proof of these statements as a homework problem).

We can expand the transition matrix, $\boldsymbol{Q}$, in terms of its left and right eigenvectors so that $Q_{m,n} = \sum_{j=1}^{M} \lambda_j \psi_{j,m} \chi_{j,n}$. Then we obtain the following spectral decomposition of the transition probability

$$P(m, s_0|n, s) = \sum_{j=1}^{M} \lambda_j^{s-s_0} \psi_{j,m} \chi_{j,n} . \tag{A.52}$$

The detailed behavior of the conditional probability and probability $P_n(s)$, as a function of time s, depends on the structure of the transition matrix. We are particularly interested in the case when the transition matrix is *regular*. The transition matrix $\boldsymbol{Q}$ is called *regular* if all elements of some power $\boldsymbol{Q}^N$ (N an integer) are nonzero. If $\boldsymbol{Q}$ is regular, there is only one eigenvalue of $\boldsymbol{Q}$ with eigenvalue $\lambda = 1$ and the probability $P_n(s)$ tends to a unique stationary state P_n^{st} after a long time. In Exercise A.10, we illustrate some of these ideas with an example.

Exercise A.10

Consider two pots, A and B, three red balls and two white balls. Pot A always has two balls and pot B always has three balls. There are three different configurations for the pots: y_1 = (A[RR]; B[WWR]), y_2 = (A[RW]; B[RRW]), y_3 = (A[WW]; B[RRR]), where A[RR] = "pot A has two red balls in it", etc. To transition between y_1, y_2 and y_3, pick a ball out of A and a ball out of B, at random, and interchange them. (a) Compute the transition matrix $\boldsymbol{Q}$ and obtain its eigenvalues and its left and right eigenvectors. (b) Let $\boldsymbol{P}(s) = (p_1(s), p_2(s), p_3(s))$, where $p_n(s)$ is the probability to be in configuration y_n at time s. If $\boldsymbol{P}(0) = (1, 0, 0)$ (start with two red balls in pot A), what is $\boldsymbol{P}(3)$? (c) What is the long-time stationary state $\boldsymbol{P}(\infty)$?

Answer: (a) We can make the following transitions from y_m to y_n with transition probability, $Q_{m,n}$, such that $Q_{1,1} = 0$, $Q_{1,2} = 1$, $Q_{1,3} = 0$, $Q_{2,1} = 1/6$, $Q_{2,2} = 1/2$, $Q_{2,3} = 1/3$, $Q_{3,1} = 0$, $Q_{3,2} = 2/3$, and $Q_{3,3} = 1/3$. Then

$$\boldsymbol{Q} = \begin{pmatrix} 0 & 1 & 0 \\ \frac{1}{6} & \frac{1}{2} & \frac{1}{3} \\ 0 & \frac{2}{3} & \frac{1}{3} \end{pmatrix} \quad \text{and} \quad \boldsymbol{Q}^2 = \begin{pmatrix} \frac{1}{6} & \frac{1}{2} & \frac{1}{3} \\ \frac{1}{12} & \frac{23}{36} & \frac{10}{36} \\ \frac{1}{9} & \frac{20}{36} & \frac{1}{3} \end{pmatrix} .$$

Thus, $\boldsymbol{Q}$ is regular and this system has a unique long-time stationary state. The eigenvalues of $\boldsymbol{Q}$ are $\lambda_1 = 1, \lambda_2 = 1/6$, and $\lambda_3 = -1/3$. The right eigenstates can be written $\boldsymbol{\psi}_1 = (1, 1, 1)^{\mathrm{T}}$, $\boldsymbol{\psi}_2 = (-3/2, -1/4, 1)^{\mathrm{T}}$, and $\boldsymbol{\psi}_3 = (3, -1, 1)^{\mathrm{T}}$. The left eigenstates can be written $\boldsymbol{\chi}_1 = (1/10, 6/10, 3/10)$, $\boldsymbol{\chi}_2 = (-4/15, -4/15, 8/15)$, and $\boldsymbol{\chi}_3 = (1/6, -1/3, 1/6)$.

(b) The probability at time $s = 3$ is

$$\boldsymbol{P}(3) = \boldsymbol{P}(0)\boldsymbol{Q}^3 = (1, 0, 0) \begin{pmatrix} \frac{1}{12} & \frac{23}{36} & \frac{5}{18} \\ \frac{23}{216} & \frac{127}{216} & \frac{11}{36} \\ \frac{5}{54} & \frac{11}{18} & \frac{8}{27} \end{pmatrix} = \left(\frac{1}{12}, \frac{23}{36}, \frac{5}{18} \right) .$$

(c) After a very long time the probability approaches the stationary state $\boldsymbol{P}(\infty) = \lambda_1 \boldsymbol{\psi}_1 \boldsymbol{\chi}_1 = (1/10, 6/10, 3/10)$. At $s = \infty$, the probability to find two red balls in pot A is $p_1 = 1/10$.

A.2.2
The Master Equation

We now consider stochastic processes for which the time interval between events can vary in a continuous manner, but the realizations of the stochastic variable are discrete. For such processes, we must obtain a differential equation for the time dependence of the probability. The time evolution of such processes is governed by the Master Equation [205].

A.2.2.1 Derivation of the Master Equation

We can derive the master equation from Eq. (A.49) for Markov chains. To begin, let us rewrite Eq. (A.49) in the form

$$P_1(n, t + \Delta t) = \sum_{m=1}^{M} P_1(m, t) P_{1|1}(m, t|n, t + \Delta t) . \tag{A.53}$$

The differential equation for $P_1(n, t)$ can be constructed from Eq. (A.53) if we note that

$$\begin{aligned} \frac{\partial P_1(n,t)}{\partial t} &\equiv \lim_{\Delta t \to 0} \left[\frac{P_1(n, t + \Delta t) - P_1(n, t)}{\Delta t} \right] \\ &= \lim_{\Delta t \to 0} \frac{1}{\Delta t} \sum_{m=1}^{M} P_1(m, t)(P_{1|1}(m, t|n, t + \Delta t) - \delta_{m,n}) . \end{aligned} \tag{A.54}$$

Since we will take the limit $\Delta t \to 0$, we can expand the transition probability $P_{1|1}(m, t|n, t + \Delta t)$ in a power series in Δt and keep only the lowest-order term. In order to conserve probability at all times, its most general form is

$$P_{1|1}(m, t|n, t + \Delta t) = \delta_{m,n} \left[1 - \Delta t \sum_{l=1}^{M} w_{m,l}(t) \right] + w_{m,n}(t)\Delta t + \dots , \tag{A.55}$$

where $w_{m,n}(t)$ is the *transition probability rate*. In Eq. (A.55), $w_{m,n}(t)\Delta t$ is the probability of a transition from state m to state n during the time interval $t \to t + \Delta t$. Similarly, $[1 - \sum_{l=1}^{M} w_{m,l}(t)\Delta t]$ is the probability that *no* transition occurs during the time interval $t \to t + \Delta t$. If we now substitute Eq. (A.55) into Eq. (A.54), we obtain

$$\frac{\partial P_1(n,t)}{\partial t} = \sum_{m=1}^{M} [P_1(m, t) w_{m,n}(t) - P_1(n, t) w_{n,m}(t)] . \tag{A.56}$$

Equation (A.56) is called the *master equation*. The master equation gives the rate of change of the probability $P_1(n, t)$ due to transitions into the state n from all other states (first term on the right) and due to transitions out of state n into all other states (second term on the right).

The conditional probability $P_{1|1}(n_0, 0|n, t)$ also satisfies a master equation

$$\frac{\partial P_{1|1}(n_0, 0|n, t)}{\partial t} = \sum_{m=1}^{M} [P_{1|1}(n_0, 0|m, t) w_{m,n}(t) - P_{1|1}(n_0, 0|n, t) w_{n,m}(t)] , \tag{A.57}$$

where $P_{1|1}(n_0, 0|n, t)$ is the probability to find the system in the state n at time t, given that it was in the state n_0 at time $t = 0$. The conditional probability satisfies an initial condition $P_{1|1}(n_0, 0|n, 0) = \delta_{n,n_0}$.

The master equation can be written in a more concise form if we introduce the transition matrix

$$W_{m,n}(t) = w_{m,n}(t) - \delta_{m,n} \sum_{n'=1}^{M} w_{n,n'}(t) . \tag{A.58}$$

The master equation then takes the form

$$\frac{\partial P_1(n, t)}{\partial t} = \sum_{m=1}^{M} P_1(m, t) W_{m,n}(t) . \tag{A.59}$$

From Eq. (A.58), we see that the transition matrix must satisfy the conditions

$$W_{m,n} \geq 0 \quad \text{for} \quad n \neq m \quad \text{and} \quad \sum_{n} W_{m,n} = 0 \quad \text{for each} \quad m . \tag{A.60}$$

Thus, the entries in the rows of $W_{m,n}$ must add to zero. The transition matrix, $W_{m,n}(t)$, in general is not symmetric so its left and right eigenvectors will be different. However, one can often obtain a spectral decomposition of the matrix $W_{m,n}$. However, care must be taken. There may be cases where the eigenvectors of the matrix $W_{m,n}$ do not span the solution space. Then the spectral decomposition cannot be used. However, there is one type of system for which a spectral decomposition can always be done, and that is the case for which the transition rates $w_{m,n}(t)$ satisfy detailed balance.

A.2.2.2 Detailed Balance

The transition rates satisfy *detailed balance* if

$$P^s(n) w_{n,m} = P^s(m) w_{m,n} , \tag{A.61}$$

where $P^s(n) \equiv \lim_{t\to\infty} P_1(n, t)$ is the long-time stationary probability of the system (we assume the transition rates, $w_{m,n}$, are independent of time) and is independent of time. $P^s(n)$ is the left eigenvector of the transition matrix, $W_{m,n}$ with eigenvalue zero. Equation (A.61) tells us that at equilibrium, the flow of probability into level n from level m is equal to the flow of probability from level m to level n. It is useful to note that the state, $P^s(n)$, can be obtained from Eq. (A.61) by iterating. For example, $P^s(2) = P^s(1)(w_{1,2}/w_{2,1}), P^s(3) = P^s(2)(w_{2,3}/w_{3,2}) =$

$P^s(1)(w_{1,2}/w_{2,1})(w_{2,3}/w_{3,2})$ and so on. $P^s(1)$ can then be found by requiring that the probability be normalized to one, $\sum_{n=1}^{M} P^s(n) = 1$.

Given Eq. (A.61), we can show that the dynamical evolution of the master equation is governed by a symmetric matrix. Let us define

$$\begin{aligned} V_{n,m} &= \sqrt{\frac{P^s(n)}{P^s(m)}} W_{n,m} = \sqrt{\frac{P^s(n)}{P^s(m)}} w_{n,m} - \delta_{n,m} \sum_{n'} w_{n,n'} \\ &= \sqrt{\frac{P^s(m)}{P^s(n)}} w_{m,n} - \delta_{n,m} \sum_{n'} w_{m,n'} = V_{m,n} \,, \end{aligned} \tag{A.62}$$

where we have used Eq. (A.61). If we now introduce a new function, $\tilde{P}(n,t) = P_1(n,t)/\sqrt{P^s(n)}$, the master equation takes the form

$$\frac{\partial \tilde{P}(n,t)}{\partial t} = \sum_{m=1}^{M} \tilde{P}(m,t) V_{m,n} \,. \tag{A.63}$$

The solution to the master equation can now be written in terms of a spectral decomposition. It takes the form

$$P_1(n,t) = \sum_{i=0}^{M-1} \sum_{m=1}^{M} \sqrt{\frac{P^s(n)}{P^s(m)}} P_1(m,0) \langle m|\psi_i\rangle \mathrm{e}^{\lambda_i t} \langle \psi_i|n\rangle \,. \tag{A.64}$$

The eigenvalues λ_i must be negative or zero. Let $i = 0$ denote the zero eigenvalue, $\lambda_0 = 0$. Then

$$P^s(n) = \lim_{t\to\infty} P_1(n,t) = \sum_{m=1}^{M} \sqrt{\frac{P^s(n)}{P^s(m)}} P_1(m,0) \langle m|\psi_0\rangle \langle \psi_0|n\rangle \,. \tag{A.65}$$

In order to be consistent we must have $\langle m|\psi_0\rangle = \langle \psi_0|m\rangle = \sqrt{P^s(m)}$, for all m, since $\sum_m P_1(m,0) = 1$. Thus,

$$P_1(n,t) = P^s(n) + \sum_{i=1}^{M-1} \sum_{m=1}^{M} \sqrt{\frac{P^s(n)}{P^s(m)}} P_1(m,0) \langle m|\psi_i\rangle \mathrm{e}^{\lambda_i t} \langle \psi_i|n\rangle \,. \tag{A.66}$$

In Exercise A.11 we give an example of a random walk which obeys detailed balance.

Exercise A.11

Consider an asymmetric random walk on an open-ended lattice with four lattice sites. The transition rates are $w_{1,2} = w_{4,3} = 1$, $w_{2,3} = w_{3,4} = 3/4$, $w_{2,1} = w_{3,2} = 1/4$, and $w_{i,j} = 0$ for all other transitions. (a) Write the transition matrix, $W_{m,n}$, and show that this system obeys detailed balance. (b) Compute the matrix $V_{m,n}$ and find its eigenvalues and eigenvectors. (c) Write $P_1(n,t)$ for the case $P_1(n,0) = \delta_{n,1}$. What is $P_1(2,t)$?

Answer:

1. The transition matrix, $W_{m,n}$, is given by

$$W = \begin{pmatrix} -1 & 1 & 0 & 0 \\ \frac{1}{4} & -1 & \frac{3}{4} & 0 \\ 0 & \frac{1}{4} & -1 & \frac{3}{4} \\ 0 & 0 & 1 & -1 \end{pmatrix} .$$

   It has eigenvalues $\lambda_0 = 0, \lambda_1 = -1 + \sqrt{3}/4, \lambda_2 = -2$, and $\lambda_3 = -1 - \sqrt{3}/4$. The left eigenvector of matrix $W_{m,n}$ with eigenvalue, $\lambda_0 = 0$, is the stationary probability distribution, $P^s = (1/26, 2/13, 6/13, 9/26)$. This system satisfies detailed balance because $P^s(n)w_{n,n+1} = P^s(n+1)w_{n+1,n}$. For example, $P^s(1)w_{1,2} = (1/26)(1) = 1/26$ and $P^s(2)w_{2,1} = (2/13)(1/4) = 1/26$.
2. The matrix $V_{m,n}$ is given by

$$V = \begin{pmatrix} -1 & \frac{1}{2} & 0 & 0 \\ \frac{1}{2} & -1 & \frac{\sqrt{3}}{4} & 0 \\ 0 & \frac{\sqrt{3}}{4} & -1 & \frac{\sqrt{3}}{2} \\ 0 & 0 & \frac{\sqrt{3}}{2} & -1 \end{pmatrix} .$$

   It also has eigenvalues $\lambda_0 = 0, \lambda_1 = -1 + \sqrt{3}/4, y_2 = -2$, and $\lambda_3 = -1 - \sqrt{3}/4$. The orthonormalized eigenstates are

$$\psi_0| = \left(\sqrt{\frac{1}{26}}, \sqrt{\frac{2}{13}}, \sqrt{\frac{6}{13}}, \sqrt{\frac{9}{26}}\right) \approx (0.196, 0.392, 0.679, 0.588) ,$$

$$\psi_1 \approx (0.679, 0.588, -0.196, -0.392) ,$$

$$\psi_2 \approx (-0.196, 0.392, -0.679, 0.588) ,$$

$$\psi_3| \approx (-0.679, 0.588, 0.196, -0.392) .$$

3. For the initial condition, $P_1(n, 0) = \delta_{n,1}$, $P_1(n, t)$ can be written

$$P_1(n, t) = P(n)^s + \sum_{i=1}^{3} \sqrt{\frac{P^s(n)}{P^s(1)}} \psi_i(1) e^{\lambda_i t} \psi_i(n) .$$

   Using the numbers from (b) we find

$$P_1(2, t) \approx 0.154 + (0.799)e^{-0.567t} - (0.154)e^{-2t} - (0.799)e^{-1.433t} .$$

   Note that $P_1(2, 0) = 0$ as it should.

A.2.3
Probability Density for Classical Phase Space

The state of a closed classical system with $3N$ degrees of freedom (e. g., N particles in a three-dimensional box) is completely specified in terms of a set of $6N$ independent real variables $(\boldsymbol{p}^N, \boldsymbol{r}^N)$ ($\boldsymbol{p}^N$ and $\boldsymbol{r}^N$ denote the set of vectors $\boldsymbol{p}^N = (\boldsymbol{p}_1, \boldsymbol{p}_2, \dots, \boldsymbol{p}_N)$ and $\boldsymbol{r}^N = (\boldsymbol{r}_1, \boldsymbol{r}_2, \dots, \boldsymbol{r}_N)$, respectively, where $\boldsymbol{p}_j$ and $\boldsymbol{r}_j$ are the momentum and position of the jth particle). If the state vector $\boldsymbol{X}^N = \boldsymbol{X}^N(\boldsymbol{p}^N, \boldsymbol{r}^N)$ is known at one time, then it is completely determined for any other time from Newton's laws.

If we know the Hamiltonian, $H(\boldsymbol{X}^N)$, for the system, then the time evolution of the quantities $\boldsymbol{p}_j$ and $\boldsymbol{r}_j (j = 1, \dots, N)$ is given by Hamilton's equations,

$$\dot{\boldsymbol{p}}_j \equiv \frac{\mathrm{d}\boldsymbol{p}_j}{\mathrm{d}t} = -\frac{\partial H^N}{\partial \boldsymbol{r}_j} \quad \text{and} \quad \dot{\boldsymbol{r}}_j \equiv \frac{\mathrm{d}\boldsymbol{r}_j}{\mathrm{d}t} = \frac{\partial H^N}{\partial \boldsymbol{p}_j} \; . \tag{A.67}$$

If the Hamiltonian does not depend explicitly on the time, then it is a global constant of the motion and we can write $H^N(\boldsymbol{X}^N) = E$, where the constant, E, is the total energy of the system. In this case the system is called *conservative*.

The state vector $\boldsymbol{X}^N(\boldsymbol{p}^N, \boldsymbol{r}^N)$ specifies a point in the $6N$-dimensional phase space, Γ. As the system evolves in time, the system point $\boldsymbol{X}^N$ traces out a trajectory in Γ-space.

We can consider $\boldsymbol{X}^N$ as a stochastic variable and introduce a probability density $\rho(\boldsymbol{X}^N, t)$ on the phase space, where $\rho(\boldsymbol{X}^N, t)\,\mathrm{d}\boldsymbol{X}^N$ is the probability that the state point, $\boldsymbol{X}^N$, lies in the volume element $\boldsymbol{X}^n \to \boldsymbol{X}^n + \mathrm{d}\boldsymbol{X}^N$ at time t and $\mathrm{d}\boldsymbol{X}^N = \mathrm{d}\boldsymbol{p}_1 \times \dots \times \mathrm{d}\boldsymbol{p}_N\, \mathrm{d}\boldsymbol{r}_1 \times \dots \times \mathrm{d}\boldsymbol{r}_N$. If the phase space were composed of discrete points, then each point would be assigned a probability in accordance with our knowledge of the state of the system at the initial time and then would carry this probability for all time (probability is conserved). Since the state points form a continuum, the normalization condition is

$$\int\limits_{\Gamma} \rho(\boldsymbol{X}^N, t)\,\mathrm{d}\boldsymbol{X}^N = 1 \; , \tag{A.68}$$

where the integration is taken over the entire phase space. If we let $P(R)$ denote the probability of finding the system in region R, then

$$P(R) = \int\limits_{\mathrm{R}} \rho(\boldsymbol{X}^N, t)\,\mathrm{d}\boldsymbol{X}^N \; , \tag{A.69}$$

where the integration is over the region R. Probability behaves like a fluid in phase space so we can use arguments from fluid mechanics to obtain the equation of motion for the probability density. Let $\dot{\boldsymbol{X}}^N = (\dot{\boldsymbol{p}}^N, \dot{\boldsymbol{r}}^N)$ denote the velocity of a state point and consider a small volume element, V_0, at a fixed point in phase space. Since probability is conserved, the decrease in the amount of probability in V_0 per unit time is due to the flow of probability through the surface of V_0. Thus,

$$\frac{\mathrm{d}}{\mathrm{d}t}P(V_0) = \frac{\partial}{\partial t}\int\limits_{V_0} \rho(\boldsymbol{X}^N, t)\,\mathrm{d}\boldsymbol{X}^N = -\oint_{S_0} \rho(\boldsymbol{X}^N, t)\dot{\boldsymbol{X}}^N \cdot \mathrm{d}\boldsymbol{S}^N\,, \tag{A.70}$$

where S_0 denotes the surface of volume element V_0 and $\mathrm{d}\boldsymbol{S}^N$ is a differential area element normal to S_0. If we use Gauss's theorem and change the surface integral to a volume integral, we find

$$\frac{\partial}{\partial t}\int\limits_{V_0} \rho(\boldsymbol{X}^N, t)\,\mathrm{d}\boldsymbol{X}^N = -\int\limits_{V_0} \nabla_{\boldsymbol{X}^N} \cdot [\rho(\boldsymbol{X}^N, t)\dot{\boldsymbol{X}}^N]\,\mathrm{d}\boldsymbol{X}^N\,, \tag{A.71}$$

where $\nabla_{\boldsymbol{X}^N}$ denotes the gradient with respect to phase space variables $\nabla_{\boldsymbol{X}^N} = \left((\partial/\partial \boldsymbol{p}_1), \ldots, (\partial/\partial \boldsymbol{p}_N), (\partial/\partial \boldsymbol{r}_1), \ldots, (\partial/\partial \boldsymbol{r}_N)\right)$. We can take the time derivative inside the integral because V_0 is fixed in space. If we equate arguments of the two integrals in Eq. (A.71), we obtain

$$\frac{\partial}{\partial t}\rho(\boldsymbol{X}^N, t) + \nabla_{\boldsymbol{X}^N} \cdot [\rho(\boldsymbol{X}^N, t)\dot{\boldsymbol{X}}^N] = 0\,. \tag{A.72}$$

Equation (A.72) is the balance equation for the probability density in the $6N$-dimensional phase space.

Using Hamilton's equations we can write

$$\nabla_{\boldsymbol{X}^N} \cdot \dot{\boldsymbol{X}}^N = \left(\frac{\partial \dot{\boldsymbol{p}}^N_{t_0}}{\partial \boldsymbol{p}^N_{t_0}} + \frac{\partial \dot{\boldsymbol{r}}^N_{t_0}}{\partial \boldsymbol{r}^N_{t_0}}\right) \equiv 0\,, \tag{A.73}$$

which tells us that the probability behaves like an incompressible fluid. If we combine Eqs. (A.72) and (A.73), the equation of motion for the probability density takes the form

$$\frac{\partial \rho(\boldsymbol{X}^N, t)}{\partial t} = -\dot{\boldsymbol{X}}^N \cdot \nabla_{\boldsymbol{X}^N}\rho(\boldsymbol{X}^N, t)\,. \tag{A.74}$$

Note that Eq. (A.74) gives the time rate of change of $\rho(\boldsymbol{X}^N, t)$ at a *fixed point* in phase space.

If we use Hamilton's equations, we can write (A.74) in the form

$$\frac{\partial \rho(\boldsymbol{X}^N, t)}{\partial t} = -\hat{\mathcal{H}}^N \rho(\boldsymbol{X}^N, t)\,, \tag{A.75}$$

where the differential operator, $\hat{\mathcal{H}}^N$, is just the Poisson bracket

$$\hat{\mathcal{H}}^N = \sum_{j=1}^{N}\left(\frac{\partial H^N}{\partial \boldsymbol{p}_j} \cdot \frac{\partial}{\partial \boldsymbol{r}_j} - \frac{\partial H^N}{\partial \boldsymbol{r}_j} \cdot \frac{\partial}{\partial \boldsymbol{p}_j}\right). \tag{A.76}$$

Equation (A.75) is often written in the form

$$\mathrm{i}\frac{\partial \rho(\boldsymbol{X}^N, t)}{\partial t} = \hat{L}^N \rho(\boldsymbol{X}^N, t)\,, \tag{A.77}$$

where $\hat{L}^N = -\mathrm{i}\hat{\mathcal{H}}^N$. Equation (A.77) is called the *Liouville equation* and the differential operator, $\hat{L}^N$, is called the *Liouville operator*. The Liouville operator is a Hermitian differential operator.

If we know the probability density, $\rho(\boldsymbol{X}^N, 0)$, at time, $t = 0$, then we may solve Eq. (A.77) to find the probability density, $\rho(\boldsymbol{X}^N, t)$, at time t. The formal solution is

$$\rho(\boldsymbol{X}^N, t) = \mathrm{e}^{-\mathrm{i}\hat{L}^N t}\rho(\boldsymbol{X}^N, 0) . \tag{A.78}$$

A probability density, $\rho_\mathrm{s}(\boldsymbol{X}^N)$, that remains constant in time, must satisfy the condition

$$\hat{L}^N \rho_\mathrm{s}(\boldsymbol{X}^N) = 0 \tag{A.79}$$

and is called a stationary solution of the Liouville equation.

We are generally interested in obtaining the expectation value of phase functions, $O^N(\boldsymbol{X}^N)$. The expectation value of $O^N(\boldsymbol{X}^N)$ is given by

$$\langle O \rangle = \int \mathrm{d}\boldsymbol{X}_1 \cdots \int \mathrm{d}\boldsymbol{X}_N O^N(\boldsymbol{X}^N)\rho(\boldsymbol{X}^N, t) . \tag{A.80}$$

The N-particle probability density, $\rho(\boldsymbol{X}^N, t)$, contains much more information than we would ever need or want. Most quantities we measure experimentally can be expressed in terms of one-body or two-body phase functions. One-body and two-body phase functions are usually written in the form

$$O^N_{(1)}(\boldsymbol{X}^N) = \sum_{i=1}^{N} O(\boldsymbol{X}_i) , \quad \text{and} \quad O^N_{(2)}(\boldsymbol{X}^N) = \sum_{i<j}^{N(N-1)/2} O(\boldsymbol{X}_i, \boldsymbol{X}_j) , \tag{A.81}$$

respectively. An example of a one-body phase function is the kinetic energy, $\sum_{i=1}^{N} p_i^2/2m$, of an N-particle system. An example of a two-body phase function is the potential energy, $\sum_{i<j}^{N(N-1)/2} V(|\boldsymbol{r}_i - \boldsymbol{r}_j|)$, of an N-particle interacting system.

To find the expectation value of a one-body phase function, we only need to know the one-body reduced probability density. Similarly, to find the expectation value of a two-body phase function, we only need to know the two-body reduced probability density. The s-body reduced probability density is given by

$$\rho_\mathrm{s}(\boldsymbol{X}_1, \ldots, \boldsymbol{X}_\mathrm{s}, t) = \int \cdots \int \mathrm{d}\boldsymbol{X}_{s+1}, \ldots, \boldsymbol{X}_N \rho(\boldsymbol{X}_1, \ldots, \boldsymbol{X}_N, t) . \tag{A.82}$$

The expectation value of the one-body phase function is given by

$$\begin{aligned}\langle O_{(1)} \rangle &= \sum_{i=1}^{N} \int \cdots \int \mathrm{d}\boldsymbol{X}_1, \ldots, \mathrm{d}\boldsymbol{X}_N O(\boldsymbol{X}_i)\rho(\boldsymbol{X}^N, t) \\ &= N \int \mathrm{d}\boldsymbol{X}_1 O(\boldsymbol{X}_1)\rho_1(\boldsymbol{X}_1, t) .\end{aligned} \tag{A.83}$$

Similarly, the expectation value of the two-body phase function is

$$\begin{aligned}\langle O_{(2)}\rangle &= \sum_{i<j}^{N(N-1)/2} \int \cdots \int \mathrm{d}\boldsymbol{X}_1, \ldots, \mathrm{d}\boldsymbol{X}_N O(\boldsymbol{X}_i, \boldsymbol{X}_j)\rho(\boldsymbol{X}^N, t) \\ &= \frac{N(N-1)}{2} \iint \mathrm{d}\boldsymbol{X}_1\, \mathrm{d}\boldsymbol{X}_2 O(\boldsymbol{X}_1, \boldsymbol{X}_2)\rho_2(\boldsymbol{X}_1, \boldsymbol{X}_2, t)\,. \end{aligned} \tag{A.84}$$

In Eqs. (A.83) and (A.84), we have assumed that the probability density is symmetric under interchange of particle labels if the Hamiltonian is symmetric.

A.2.4
Quantum Probability Density Operator

For quantum systems, the phase space coordinates do not commute so we cannot introduce a probability density function directly on the phase space. Instead we will introduce a *probability density operator* $\hat{\rho}(t)$. The probability density operator (we shall call it the density operator), contains all possible information about the state of the quantum system. It is a positive definite Hermitian operator. If we know the density operator, $\hat{\rho}(t)$, for a system, we can use it to obtain the expectation value of any observable $\hat{O}$ at time t. The expectation value is defined as

$$\langle O(t)\rangle = \mathrm{Tr}(\hat{O}\hat{\rho}(t))\,, \tag{A.85}$$

where Tr denotes the trace. The density operator is normalized so that

$$\mathrm{Tr}(\hat{\rho}(t)) = 1\,. \tag{A.86}$$

In Eqs. (A.85) and (A.86), the trace can be evaluated using any convenient complete set of states. Let $\{|o_i\rangle\}$ and $\{|a_i\rangle\}$ denote the complete orthonormal sets of eigenstates of the operators, $\hat{O}$ and $\hat{A}$, respectively, and let $\{o_i\}$ and $\{a_i\}$ be the corresponding sets of eigenvalues ($\hat{O}|o_i\rangle = o_i|o_i\rangle$) and ($\hat{A}|a_i\rangle = a_i|a_i\rangle$). The trace can be evaluated in either basis. Thus, we can write

$$\langle O(t)\rangle = \sum_i o_i\langle o_i|\hat{\rho}(t)|o_i\rangle = \sum_i \sum_j \langle a_i|\hat{O}|a_j\rangle\langle a_j|\hat{\rho}(t)|a_i\rangle\,, \tag{A.87}$$

where $o_i = \langle o_i|\hat{O}|o_i\rangle$ and we have used the completeness relation, $\sum_i |a_i\rangle\langle a_i| = \hat{1}$, where $\hat{1}$ is the unit operator. The diagonal matrix element, $\langle a_i|\hat{\rho}(t)|a_i\rangle$, gives the probability to find the system in the state $|a_i\rangle$, at time t. The set of numbers, $\langle a_j|\hat{\rho}(t)|a_i\rangle$, forms a matrix representation of the density operator (called the *density matrix*) with respect to the basis states, $\{|a_i\rangle\}$. The density matrix is a positive definite Hermitian matrix. The off-diagonal matrix element, $\langle a_j|\hat{\rho}(t)|a_i\rangle$ for $i \neq j$, cannot be interpreted as a probability.

The density operator can be used to describe the equilibrium and nonequilibrium states of a many-body system. Consider a quantum system in the state $|\psi(t)\rangle$

which evolves according to the Schrödinger equation,

$$\mathrm{i}\hbar\frac{\partial|\psi(t)\rangle}{\partial t} = \hat{H}|\psi(t)\rangle\,, \tag{A.88}$$

where $\hat{H}$ is the Hamiltonian operator, and $\hbar$ is Planck's constant. The density operator that describes this "pure state" is simply

$$\hat{\rho}(t) = |\psi(t)\rangle\langle\psi(t)|\,. \tag{A.89}$$

A "mixed state" is an incoherent mixture of states $|\psi_i(t)\rangle$:

$$\hat{\rho}(t) = \sum_i p_i|\psi_i(t)\rangle\langle\psi_i(t)|\,, \tag{A.90}$$

where p_i is the probability to be in the state $|\psi_i(t)\rangle$, and the states $|\psi_i(t)\rangle$, each satisfy the Schrödinger equation. Equilibrium and near-equilibrium states of many-body systems are of this type.

Using the Schrödinger equation, the equation of motion of the density operator is easily found to be

$$\mathrm{i}\frac{\partial\hat{\rho}(t)}{\partial t} = \frac{1}{\hbar}[\hat{H},\hat{\rho}(t)] = \hat{L}\hat{\rho}(t)\,, \tag{A.91}$$

where $[\hat{H},\hat{\rho}(t)]$ is the commutator of the Hamiltonian, $\hat{H}$, with $\hat{\rho}(t)$, and the operator $\hat{L} \equiv (1/\hbar)[\hat{H},\ ]$, is proportional to the commutator of $\hat{H}$ with everything on its right. The operator $\hat{L}$ is the quantum version of the *Liouville operator* and is a Hermitian operator. If the density operator is known at time $t = 0$, then its value at time t is given by

$$\hat{\rho}(t) = \mathrm{e}^{-\mathrm{i}\hat{L}t}\hat{\rho}(0) = \mathrm{e}^{-(\mathrm{i}/\hbar)\hat{H}t}\hat{\rho}(0)\mathrm{e}^{+(\mathrm{i}/\hbar)\hat{H}t}\,. \tag{A.92}$$

It is often convenient to expand the density operator in terms of a complete orthonormal set of eigenstates $\{|E_i\rangle\}$ of the Hamiltonian, $\hat{H}$, where E_i is the eigenvalue corresponding to eigenstate $|E_i\rangle$. If we note the completeness relation $\sum_i |E_i\rangle\langle E_i| = \hat{1}$, then Eq. (A.92) takes the form

$$\hat{\rho}(t) = \sum_i\sum_j \langle E_i|\hat{\rho}(0)|E_j\rangle \mathrm{e}^{-(\mathrm{i}/\hbar)(E_i-E_j)t}|E_i\rangle\langle E_j|\,. \tag{A.93}$$

From Eq. (A.93), we see that a stationary state, $\hat{\rho}_{\mathrm{s}}$, occurs when all off-diagonal matrix elements $\langle E_i|\hat{\rho}(0)|E_j\rangle$ (with $i \neq j$), vanish. Thus, the stationary state, $\hat{\rho}_{\mathrm{s}}$, must be diagonal in the energy basis. This can happen if $\hat{\rho}_{\mathrm{s}}$ is a function of the Hamiltonian,

$$\hat{\rho}_{\mathrm{s}} = f(\hat{H})\,. \tag{A.94}$$

For a system with degenerate energy levels, one may still diagonalize both $\hat{\rho}$ and $\hat{H}$ simultaneously by introducing additional invariants of the motion, $\hat{I}$ which commute with each other and with $\hat{H}$. Thus, in general, a stationary state will be a function of all mutually commuting operators, $\hat{H}, \hat{I}_1, \dots, \hat{I}_n$,

$$\hat{\rho}_{\mathrm{s}} = f(\hat{H}, \hat{I}_1, \dots, \hat{I}_n)\,. \tag{A.95}$$

For systems which approach thermodynamic equilibrium, the stationary state may be an equilibrium state.

It is useful to introduce the idea of one- and two-body reduced density matrices. In quantum mechanics, as in classical mechanics, we generally deal with one-body and two-body operators,

$$\hat{O}^N_{(1)} = \sum_{i=1}^{N} \hat{O}_i \quad \text{and} \quad \hat{O}^N_{(2)} = \sum_{i<j}^{N(N-1)/2} \hat{O}_{i,j}\,, \tag{A.96}$$

respectively. The trace of a one-body operator, in the position basis, can be written

$$\begin{aligned}\mathrm{Tr}\left(\hat{O}^N_{(1)}\hat{\rho}\right) &= \sum_{i=1}^{N} \int \mathrm{d}r_1 \cdots \int \mathrm{d}r_N \int \mathrm{d}r'_1 \cdots \int \mathrm{d}r'_N \langle r_1, \dots, r_N|\hat{O}_i|r'_1, \dots, r'_N\rangle \\ &\quad \times \langle r'_1, \dots, r'_N|\hat{\rho}|r_1, \dots, r_N\rangle \\ &\equiv \int \mathrm{d}r_1 \int \mathrm{d}r'_1 \langle r_1|\hat{O}_1|r'_1\rangle\langle r'_1|\hat{\rho}_{(1)}|r_1\rangle\,,\end{aligned} \tag{A.97}$$

where $|r_a, r_b, \cdots, r_l\rangle = |r_a\rangle_1 |r_b\rangle_2 \times \cdots \times |r_l\rangle_N$ with $|r\rangle_i = |\boldsymbol{r}, s_z\rangle_i = |\boldsymbol{r}\rangle_i |s_z\rangle_i$ denoting the eigenstates of both the position operator $\hat{\boldsymbol{r}}_i$ and z-component of spin operator $\hat{s}_{z,i}$ of particle i. The symbol $\int \mathrm{d}r_i$ denotes integration over configuration space and sum over the z-components of spin for particle i. The quantity

$$\langle r'_1|\hat{\rho}_{(1)}(t)|r_1\rangle = N \int \mathrm{d}r_2 \cdots \int \mathrm{d}r_N \langle r'_1, r_2, \dots, r_N|\hat{\rho}|r_1, \dots, r_N\rangle \tag{A.98}$$

is the one-body reduced density matrix.

The two-body reduced density matrix is defined in an analogous manner. The trace of a two-body operator in the position basis can be written

$$\begin{aligned}\mathrm{Tr}\left(\hat{O}^N_{(2)}\hat{\rho}(t)\right) &= \sum_{i<j}^{N(N-1)/2} \int \mathrm{d}r_1 \cdots \int \mathrm{d}r_N \int \mathrm{d}r'_1 \cdots \int \mathrm{d}r'_N \\ &\quad \times \langle r_1, \dots, r_N|\hat{O}_{i,j}|r'_1, \dots, r'_N\rangle\langle r'_1, \dots, r'_N|\hat{\rho}|r_1, \dots, r_N\rangle \\ &\equiv \frac{1}{2}\int \mathrm{d}r_1 \int \mathrm{d}r_2 \int \mathrm{d}r'_1 \int \mathrm{d}r'_2 \langle r_1, r_2|\hat{O}_{1,2}|r'_1, r'_2\rangle\langle r'_1, r'_2|\hat{\rho}_{(2)}|r_1, r_2\rangle\,,\end{aligned} \tag{A.99}$$

where

$$\langle r'_1, r'_2|\hat{\rho}_{(2)}|r_1, r_2\rangle = N(N-1) \int \mathrm{d}r_3 \cdots \int \mathrm{d}r_N \langle r'_1, r'_2, r_3, \dots, r_N|\hat{\rho}|r_1, \dots, r_N\rangle \tag{A.100}$$

is the two-body reduced density matrix.

If we are dealing with a gas of N identical bosons or fermions, then the trace must be taken with respect to symmetrized or anti-symmetrized N-particle states, respectively. For such systems, it is often easier then to work in a second quantized formalism (see Appendix D).

A.3
Problems

Problem A.1 A stochastic variable, X, can have values, $x = 1$ and $x = 3$. A stochastic variable, Y, can have values, $y = 2$ and $y = 4$. Denote the joint probability density, $P_{X,Y}(x, y) = \sum_{i=1,3} \sum_{j=2,4} p_{i,j} \delta(x - i)\delta(y - j)$. Compute the covariance of X and Y for the following two cases: (a) $p_{1,2} = p_{1,4} = p_{3,2} = p_{3,4} = 1/4$; (b) $p_{1,2} = p_{3,4} = 0$ and $p_{1,4} = p_{3,2} = 1/2$. For each case, decide if X and Y are independent.

Problem A.2 The stochastic variables, X and Y, are independent and Gaussian distributed with first moments, $\langle x \rangle = \langle y \rangle = 0$ and standard deviations, $\sigma_X = \sigma_Y = 1$. Find the characteristic function for the random variable, $Z = X^2 + Y^2$, and compute the moments, $\langle z \rangle$, $\langle z^2 \rangle$, and $\langle z^3 \rangle$. Find the first three cumulants.

Problem A.3 A die is loaded so that even numbers occur three times as often as odd numbers. (a) If the die is thrown $N = 12$ times, what is the probability that odd numbers occur three times? If it is thrown $N = 120$ times, what is the probability that odd numbers occur thirty times? Use the binomial distribution. (b) Compute the same quantities as in part (a) but use the Gaussian distribution. (Note: For parts (a) and (b) compute your answers to four places.) (c) Compare your answers for (a) and (b). Plot the binomial and Gaussian distributions for the case $N = 12$.

Problem A.4 A book with 700 misprints contains 1400 pages. (a) What is the probability that one page contains 0 misprints? (b) What is the probability that one page contains 2 misprints?

Problem A.5 Three old batteries and a resistor, R, are used to construct a circuit. Each battery has a probability, p, to generate voltage, $V = v_0$, and a probability, $1 - p$, to generate voltage, $V = 0$. Neglect any internal resistance in the batteries. Find the average power, $\langle V^2 \rangle / R$, dissipated in the resistor if: (a) the batteries are connected in series; (b) the batteries are connected in parallel. In cases (a) and (b), what would be the average power dissipated if all batteries were certain to generate voltage, $V = v_0$? (c) How would you realize the conditions and results of this problem in a laboratory?

Problem A.6 A fair coin (H and T equally probably) is tossed three times. Let X denote the event "H" or "T" *on the first toss*. Let $X = 0$ if "H" occurs first and $X = 1$ if "T" occurs first. Let event Y denote the event "the number of "T"s that occur," so Y takes values 0, 1, 2, or 3. The sample space has eight equally probable points. (a) Compute the probability distribution $P(X)$ (it has two values) and the probability distribution $P(Y)$ (it has four values). (b) Compute the first moments $\langle X \rangle$ and $\langle Y \rangle$, the second moments $\langle X^2 \rangle$ and $\langle Y^2 \rangle$, and the standard deviations σ_X and σ_Y. (c) Compute the covariance $\mathrm{Cov}(X, Y) = \langle (X - \langle X \rangle)(Y - \langle Y \rangle) \rangle$. (d) Compute the correlation $\mathrm{Cor}(X, Y) = \mathrm{Cov}(X, Y)/(\sigma_X \sigma_Y)$. (e) Are the events X and Y independent?

Problem A.7 Consider a random walk in one dimension. In a single step the probability of a displacement between x and $x + \mathrm{d}x$ is given by

$$P(x)\,\mathrm{d}x = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left(-\frac{(x-a)^2}{2\sigma^2}\right) .$$

After N steps the displacement of the walker is $S = X_1 + \cdots + X_N$, where X_i is the displacement during the ith step. Assume the steps are independent of one another. After N steps: (a) what is the probability density for the displacement, S, of the walker; (b) what are the average displacement, $\langle S \rangle$, and the standard deviation of the walker?

Problem A.8 Consider a random walk in one dimension for which the walker at each step is equally likely to take a step with displacement anywhere in the interval, $d - a \leq x \leq d + a$, where $a < d$. Each step is independent of the others. After N steps the walker's displacement is $S = X_1 + \cdots + X_N$, where X_i is his displacement during the ith step. After N steps: (a) what is his average displacement, $\langle S \rangle$; (b) what is his standard deviation?

Problem A.9 Three boys, A, B, and C, stand in a circle and play catch (B stands to the right of A). Before throwing the ball, each boy flips a coin. If "heads" comes up, the boy throws to his right. If "tails" comes up, he throws to his left. The coin of boy A is "fair" (50% heads and 50% tails), the coin of boy B has heads on both sides, and the coin of boy C is weighted (75% heads and 25% tails). (a) Compute the transition matrix, its eigenvalues, and its left and right eigenvectors. (b) If the ball is thrown at regular intervals, approximately what fraction of time does each boy have the ball (assuming they throw the ball many times)? (c) If boy A has the ball to begin with, what is the chance he will have it after two throws?

Appendix B
Exact Differentials

The mathematics of exact differentials governs thermodynamics and the relationships between thermodynamic state variables. In this Appendix, we review key results that are essential when computing thermodynamic quantities.

Consider a function $F = F(x_1, x_2)$ that depends on two independent variables x_1 and x_2. The differential of F is defined as

$$\mathrm{d}F = \left(\frac{\partial F}{\partial x_1}\right)_{x_2} \mathrm{d}x_1 + \left(\frac{\partial F}{\partial x_2}\right)_{x_1} \mathrm{d}x_2 \,, \tag{B.1}$$

where $\left(\partial F/\partial x_1\right)_{x_2}$ is the derivative of F with respect to x_1 holding x_2 fixed. If F and its derivatives are continuous and

$$\left[\frac{\partial}{\partial x_1}\left(\frac{\partial F}{\partial x_2}\right)_{x_1}\right]_{x_2} = \left[\frac{\partial}{\partial x_2}\left(\frac{\partial F}{\partial x_1}\right)_{x_2}\right]_{x_1} \,, \tag{B.2}$$

then $\mathrm{d}F$ is an exact differential. If we denote $c_1 \equiv \left(\partial F/\partial x_1\right)_{x_2}$ and $c_2 \equiv \left(\partial F/\partial x_2\right)_{x_1}$, then the variables c_1 and x_1 and variables c_2 and x_2 are called "conjugate" variables with respect to the function F.

The fact that $\mathrm{d}F$ is exact has the following consequences:

1. The value of the integral $F(\mathrm{B}) - F(\mathrm{A}) = \int_{\mathrm{A}}^{\mathrm{B}} \mathrm{d}F = \int_{\mathrm{A}}^{\mathrm{B}} (c_1\,\mathrm{d}x_1 + c_2\,\mathrm{d}x_2)$ is independent of the path taken between A and B and depends only on the end points A and B.
2. The integral of $\mathrm{d}F$ around a closed path is zero: $\oint_{\text{closed}} \mathrm{d}F = \oint_{\text{closed}} (c_1\,\mathrm{d}x_1 + c_2\,\mathrm{d}x_2) \equiv 0$.
3. If one knows only the differential $\mathrm{d}F$, then the function F can be found to within an additive constant.

If F depends on more than two variables, then the statements given above generalize in a simple way: Let $F = F(x_1, x_2, \dots, x_n)$, then the differential, $\mathrm{d}F$, may be written

$$\mathrm{d}F = \sum_{i=1}^{n} \left(\frac{\partial F}{\partial x_i}\right)_{\{x_{j\neq i}\}} \mathrm{d}x_i \,. \tag{B.3}$$

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The notation $(\partial F/\partial x_i)_{\{x_{j\neq i}\}}$ means that the derivative of F is taken with respect to x_i holding *all* variables *but* x_i constant. For any pair of variables, the following relation holds:

$$\left[\frac{\partial}{\partial x_l}\left(\frac{\partial F}{\partial x_k}\right)_{\{x_{j\neq k}\}}\right]_{\{x_{j\neq l}\}} = \left[\frac{\partial}{\partial x_k}\left(\frac{\partial F}{\partial x_l}\right)_{\{x_{j\neq l}\}}\right]_{\{x_{j\neq k}\}} . \tag{B.4}$$

Given four state variables, x, y, z, and w, where w is a function of any two of the variables x, y, or z, one can obtain the following useful relations along paths for which $F(x, y, z) = 0$:

$$\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{(\partial y/\partial x)_z} . \tag{B.5}$$

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1 . \tag{B.6}$$

$$\left(\frac{\partial x}{\partial w}\right)_z = \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial w}\right)_z . \tag{B.7}$$

$$\left(\frac{\partial x}{\partial y}\right)_z = \left(\frac{\partial x}{\partial y}\right)_w + \left(\frac{\partial x}{\partial w}\right)_y \left(\frac{\partial w}{\partial y}\right)_z . \tag{B.8}$$

Equation (B.6) is called the “chain rule.”

It is a simple matter to derive Eqs. (B.5)–(B.8). We will first consider Eqs. (B.5) and (B.6). Let us choose variables y and z to be independent, $x = x(y, z)$, and then choose x and z to be independent, $y = y(x, z)$, and write the following differentials; $\mathrm{d}x = (\partial x/\partial y)_z\,\mathrm{d}y + (\partial x/\partial z)_y\,\mathrm{d}z$ and $\mathrm{d}y = (\partial y/\partial x)_z\,\mathrm{d}x + (\partial y/\partial z)_x\,\mathrm{d}z$. If we eliminate $\mathrm{d}y$ between these equations, we obtain

$$\left[\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z - 1\right]\mathrm{d}x + \left[\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x + \left(\frac{\partial x}{\partial z}\right)_y\right]\mathrm{d}z = 0 . \tag{B.9}$$

Because $\mathrm{d}x$ and $\mathrm{d}z$ may be varied independently, their coefficients may be set equal to zero separately. The result is Eqs. (B.5) and (B.6).

To derive Eq. (B.7) we let y and z be independent so that $x = x(y, z)$ and write the differential for $\mathrm{d}x$. If we then divide by $\mathrm{d}w$, we obtain

$$\frac{\mathrm{d}x}{\mathrm{d}w} = \left(\frac{\partial x}{\partial y}\right)_z \frac{\mathrm{d}y}{\mathrm{d}w} + \left(\frac{\partial x}{\partial z}\right)_y \frac{\mathrm{d}z}{\mathrm{d}w} . \tag{B.10}$$

For constant z, $\mathrm{d}z = 0$ and we find (B.7).

Finally, to derive Eq. (B.8) we let x be a function of y and w, $x = x(y, w)$. If we write the differential of x, divide it by $\mathrm{d}y$, and restrict the entire equation to constant z, we obtain Eq. (B.8).

When integrating exact differentials, one must be careful not to lose terms. In Exercise B.1, we illustrate a method for integrating exact differentials.

Exercise B.1

Consider the differential $\mathrm{d}\phi = (x^2 + y)\,\mathrm{d}x + x\,\mathrm{d}y$. (a) Show that it is an exact differential. (b) Integrate $\mathrm{d}\phi$ between points A and B using indefinite integrals.

Answer: (a) From the expression $\mathrm{d}\phi = (x^2 + y)\,\mathrm{d}x + x\,\mathrm{d}y$, we can write $(\partial\phi/\partial x)_y = x^2 + y$ and $(\partial\phi/\partial y)_x = x$. Since $[(\partial/\partial y)(\partial\phi/\partial x)_y]_x = [(\partial/\partial x)(\partial\phi/\partial y)_x]_y = 1$, the differential, $\mathrm{d}\phi$, is exact.

(b) We now integrate the differential, $\mathrm{d}\phi$, in a different way. Let us first do the indefinite integrals

$$\int\left(\frac{\partial\phi}{\partial x}\right)_y \mathrm{d}x = \int(x^2 + y)\,\mathrm{d}x = \frac{1}{3}x^3 + xy + K_1(y)\,, \tag{B.11}$$

where $K_1(y)$ is an unknown function of y. Next do the integral

$$\int\left(\frac{\partial\phi}{\partial y}\right)_x \mathrm{d}y = \int x\,\mathrm{d}y = xy + K_2(x)\,, \tag{B.12}$$

where $K_2(x)$ is an unknown function of x. In order for Eqs. (B.11) and (B.12) to be consistent, we must choose $K_2(x) = 1/3x^3 + K_3$ and $K_1(y) = K_3$, where K_3 is a constant. Therefore, $\phi = 1/3x^3 + xy + K_3$ and again, $\phi_\mathrm{B} - \phi_\mathrm{A} = 1/3x_\mathrm{B}^3 + x_\mathrm{B}y_\mathrm{B} - 1/3x_\mathrm{A}^3 - x_\mathrm{A}y_\mathrm{A}$.

Appendix C
Ergodicity

Ergodic theory asks questions which lie at the very foundations of statistical mechanics [53, 54, 163]. The phase space of conservative Newtonian systems is of a very special type because there are no diffusion processes present. For systems with ergodic flow, we can obtain a unique stationary probability density (a constant on the energy surface) which characterizes systems with a fixed energy at equilibrium. However, a system with ergodic flow cannot necessarily reach this equilibrium state if it does not start out there. For decay to equilibrium, we must have at least the additional property of mixing. Mixing systems are ergodic (the converse is not always true, however) and can exhibit random behavior even though Newton's laws are fully deterministic.

Let us now define ergodic flow. Consider a Hamiltonian system with $3N$ degrees of freedom with Hamiltonian $H(\boldsymbol{p}^N, \boldsymbol{r}^N) = E$. If we relabel the momentum coordinates so $p_1 = p_{x,1}, p_2 = p_{y,1}, p_3 = p_{z,1}, p_4 = p_{x,2}, \dots, p_{3N} = p_{z,N}$ (with similar relabeling for the position coordinates), then Hamilton's equations can be written

$$\frac{\mathrm{d}q_1}{(\partial H/\partial p_1)} = \cdots = \frac{\mathrm{d}q_{3N}}{(\partial H/\partial p_{3N})} = \cdots = -\frac{\mathrm{d}p_1}{(\partial H/\partial x_1)} = \cdots = -\frac{\mathrm{d}x_{3N}}{(\partial H/\partial q_{3N})} = \mathrm{d}t\,. \tag{C.1}$$

Equation (C.1) provides $6N - 1$ equations relating phase space coordinates which, when solved, give us $6N - 1$ constants, or integrals, of the motion,

$$f_i(p_1, \dots, p_{3N}, x_1, \dots, x_{3N}) = C_i\,, \tag{C.2}$$

where $i = 1, 2, \dots, 6N - 1$ and C_i is a constant. However, these integrals of the motion can be divided into two kinds: isolating and nonisolating. Isolating integrals define a whole surface in the phase space and are important in ergodic theory, while nonisolating integrals do not define a surface and are unimportant [53]. One of the main problems of ergodic theory is to determine how many isolating integrals a given system has. An example of an isolating integral is the total energy, $H(\boldsymbol{p}^N, \boldsymbol{r}^N) = E$. For N hard-sphere particles in a box, it is the only isolating integral.

Let us consider a system for which the only isolating integral of the motion is the total energy and assume that the system has total energy, E. Then trajectories in Γ

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space (the $6N$-dimensional phase space) which have energy, E, will be restricted to the energy surface, S_E. The energy surface, S_E, is a $(6N-1)$-dimensional "surface" in phase space which exists because of the isolating integral of the motion, $H(p_1, \ldots, p_{3N}, x_1, \ldots, x_{3N}) = E$. The flow of state points on the energy surface is defined to be *ergodic* if almost all points, $\boldsymbol{X}(p_1, \ldots, p_{3N}, x_1, \ldots, x_{3N})$, on the surface move in such a way that they pass through every small finite neighborhood, R_E, on the energy surface. In other words, each point samples small neighborhoods over the entire surface during the course of its motion (a given point, $\boldsymbol{X}(p_1, \ldots, p_{3N}, x_1, \ldots, x_{3N})$ cannot pass through every point on the surface, because a line which cannot intersect itself cannot fill a surface of two or more dimensions). Note that not all points need sample the surface, only "almost all." We can exclude a set of measure zero from this requirement.

A criterion for determining if a system is ergodic was established by Birkhoff and is called the *ergodic theorem*. Let us consider an integrable phase function $f(\boldsymbol{X}^N)$ of the state point $\boldsymbol{X}^N$. We may define a phase average of the function $f(\boldsymbol{X}^N)$ on the energy surface by the equation

$$\langle f \rangle_S = \frac{1}{\Sigma(E)} \int\limits_{S_E} f(\boldsymbol{X}^N)\,\mathrm{d}S_E = \frac{1}{\Sigma(E)} \int\limits_{\Gamma} \delta(H^N(\boldsymbol{X}^N) - E) f(\boldsymbol{X}^N)\,\mathrm{d}\boldsymbol{X}^N , \quad \text{(C.3)}$$

where $\mathrm{d}S_E$ is an area element of the energy surface which is invariant (does not change size) during the evolution of the system and $\Sigma(E)$ is the area of the energy surface and is defined as

$$\Sigma(E) = \int\limits_{S_E} \mathrm{d}S_E = \int\limits_{\Gamma} \delta(H^N(\boldsymbol{X}^N) - E)\,\mathrm{d}\boldsymbol{X}^N . \quad \text{(C.4)}$$

We may define a time average of the function $f(\boldsymbol{X}^N)$ by the equation

$$\langle f \rangle_T = \lim_{T\to\infty} \frac{1}{T} \int\limits_{t_0}^{t_0+T} f(\boldsymbol{X}^N(t))\,\mathrm{d}t \quad \text{(C.5)}$$

for all trajectories for which the time average exists. Birkhoff showed that the time average in Eq. (C.5) exists for all integrable phase functions of physical interest (i. e., for smooth functions).

In terms of averages, the *ergodic theorem* may be stated as follows: *A system is ergodic if for all phase functions, $f(\boldsymbol{X}^N)$: (i) the time average, $\langle f \rangle_T$, exists for almost all $\boldsymbol{X}^N$ (all but a set of measure zero), and (ii) when it exists it is equal to the phase average, $\langle f \rangle_T = \langle f \rangle_S$.*

To determine the form of the invariant area element, $\mathrm{d}S_E$, we write an expression for the volume of phase space, $\Omega(E)$, with energy less than E – that is, the region of phase space for which $0 < H^N(X^N) < E$. We then assume that the phase space can be divided into layers, each with different energy, and that the layers can be arranged in the order of increasing energy. (This is possible for all systems that we will consider.) The volume, $\Omega(E)$, can then be written

$$\Omega(E) = \int_{0<H^N(X^N)<E} \mathrm{d}\boldsymbol{X}^N = \int_{0<H^N(X^N)<E} \mathrm{d}A_H\,\mathrm{d}n_H\,, \tag{C.6}$$

where $\mathrm{d}A_H$ is an area element on a surface of constant energy and $\mathrm{d}n_H$ is normal to that surface. Since $\nabla_x H^N$ is a vector perpendicular to the surface $H^N(X^N) =$ constant, we can write $\mathrm{d}H^N = |\nabla_x H^N|\,\mathrm{d}n_H$ and the volume becomes

$$\Omega(E) = \int_0^E \mathrm{d}H^N \int_{S_H} \frac{\mathrm{d}A_H}{|\nabla_x H^N|}\,. \tag{C.7}$$

If we take the derivative of $\Omega(E)$, we find

$$\frac{\mathrm{d}\Omega(E)}{\mathrm{d}E} = \Sigma(E) = \int_{S_E} \frac{\mathrm{d}A_E}{|\nabla_X H^N|_{H=E}}\,. \tag{C.8}$$

The area, $\Sigma(E)$, is called the *structure function*. If we wish to take the average value of a function $f(\boldsymbol{X}^N)$ over the surface, we can write

$$\langle f\rangle_S = \frac{1}{\Sigma(E)} \int_{S_E} f(\boldsymbol{X}^N) \frac{\mathrm{d}A_E}{|\nabla_X H^N|_{H^N=E}}\,. \tag{C.9}$$

Thus, the differential

$$\mathrm{d}S_E = \frac{\mathrm{d}A_E}{|\nabla_X H^N|_{H^N=E}} \tag{C.10}$$

is the invariant surface area element.

If a system is ergodic, the fraction of time that its state, $X^N(\boldsymbol{p}^N, \boldsymbol{q}^N)$, spends in a given region R_E of the energy surface will be equal to the fraction of the surface S_E occupied by R_E. Let us consider a function $\phi(R_E)$ such that $\phi(R_E) = 1$ when X^N is in R_E and $\phi(R_E) = 0$ otherwise. Then it is easy to see that, for an ergodic system,

$$\lim_{T\to\infty} \frac{\tau_{R_E}}{T} = \frac{\Sigma(R_E)}{\Sigma(E)}\,, \tag{C.11}$$

where τ_{R_E} is the time the trajectory spends in R_E and $\Sigma(R_E)$ is the area occupied by R_E.

A system can exhibit ergodic flow on the energy surface only if there are no other isolating integrals of the motion which prevent trajectories from moving freely on the energy surface. If no other isolating integrals exist, the system is said to be metrically transitive (trajectories move freely on the energy surface). If a system is ergodic, it will spend equal times in equal areas of the energy surface. If we perform measurements to decide where on the surface the system point is, we should find that result. We can also ask for the probability of finding the system in a given region R_E of the energy surface. Since we have nothing to distinguish one region from another, the best choice we can make is to assume that the probability $P(R_E)$ of finding the system in R_E is equal to the fraction of the energy surface occupied by R_E. Thus,

$$P(R_E) = \frac{1}{\Sigma(E)} \int\limits_{R_E} \mathrm{d}S_E = \frac{\Sigma(R_E)}{\Sigma(E)} \,. \tag{C.12}$$

From Eq. (C.12) it is a simple matter to write down a normalized probability density for the energy surface, namely,

$$\rho(\boldsymbol{X}^N, S_E) = \frac{1}{\Sigma(E)} \,. \tag{C.13}$$

Equation (C.13) is called the *fundamental distribution law* by Khintchine and called the *microcanonical ensemble* by Gibbs. Since it is a function only of the energy, it is a stationary state of the Liouville equation (see Appendix A). It says that all states on the energy surface are equally probable. Equation (C.13) forms the foundation upon which all of equilibrium and most of nonequilibrium statistical mechanics are built.

Appendix D
Number Representation

The indistinguishability of particles in a gas comes from the fact that the Hamiltonian and all other physical observables are invariant under permutation of their dynamical variables [138]. This symmetry property of the Hamiltonian leads to a decomposition of the eigenstates of the Hamiltonian and all other states of the system into two types, either symmetric or antisymmetric under permutation of the N particles. Particles with symmetric eigenstates are bosons. Particles with antisymmetric eigenstates are fermions. Experiment shows that systems of particles with integral spin (photons, He^4, etc.) are bosons. Systems of particles with half-integral spin (electrons, protons, He^3, etc.) are fermions.

D.1
Symmetrized and Antisymmetrized States

We often consider systems of N identical particles with spin, confined to a finite or an infinite volume. We will usually consider Hamiltonians which can be decomposed into a kinetic energy and a potential energy,

$$\hat{H}_N = \sum_{i=1}^{N} \frac{\hat{\boldsymbol{p}}_i^2}{2m} + \sum_{i<j=1}^{N(N-1)/2} V(\hat{\boldsymbol{r}}_i, \hat{\boldsymbol{r}}_j; \hat{\boldsymbol{s}}_i \hat{\boldsymbol{s}}_j) , \tag{D.1}$$

where m is the mass of a particle, $\hat{\boldsymbol{p}}_i$ and $\hat{\boldsymbol{r}}_i$ are the momentum and position operators, respectively, for the ith particle, and $\hat{\boldsymbol{s}}_i$ is the spin operator for the ith particle. If a particle has spin, then we must specify not only its momentum or position, but also the component of its spin along some direction in space (we choose the z-direction).

Let the ket, $|\boldsymbol{r}\rangle$, denote the right eigenstate of the position operator, $\hat{\boldsymbol{r}}$, and let the ket, $|\boldsymbol{p}\rangle$, denote the right eigenstate of the momentum operator, $\hat{\boldsymbol{p}}$, so that $\hat{\boldsymbol{r}}|\boldsymbol{r}\rangle = \boldsymbol{r}|\boldsymbol{r}\rangle$ and $\hat{\boldsymbol{p}}|\boldsymbol{p}\rangle = \boldsymbol{p}|\boldsymbol{p}\rangle$. It is useful to write the momentum operator as $\hbar\boldsymbol{k}$, where $\hat{\boldsymbol{k}}$ is the wavevector. Then $\hat{\boldsymbol{p}}|\boldsymbol{k}\rangle = \hbar\hat{\boldsymbol{k}}|\boldsymbol{k}\rangle$. The left eigenstates are found by taking the Hermitian adjoint (denoted by †) of these equations (note that $(\hat{\boldsymbol{r}}|\boldsymbol{r}\rangle)^\dagger = \langle\boldsymbol{r}|\hat{\boldsymbol{r}}^\dagger = \langle\boldsymbol{r}|\hat{\boldsymbol{r}}$, since the position operator is Hermitian, $\hat{\boldsymbol{r}}^\dagger = \hat{\boldsymbol{r}}$). The left and right eigenvectors are orthonormal $\langle\boldsymbol{r}'|\boldsymbol{r}\rangle = \delta(\boldsymbol{r}' - \boldsymbol{r}) = \delta(x' - x)\delta(y' - y)\delta(z' - z)$ and

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$\langle \boldsymbol{k}'|\boldsymbol{k}\rangle = \delta(\boldsymbol{k}' - \boldsymbol{k}) = \delta\left(k'_x - k_x\right)\delta\left(k'_y - k_y\right)\delta\left(k'_z - k_z\right)$. The left and right eigenvectors form complete sets $\int \mathrm{d}\boldsymbol{r}|\boldsymbol{r}\rangle\langle\boldsymbol{r}| = \hat{\mathbf{1}}$ and $\int \mathrm{d}\boldsymbol{k}|\boldsymbol{k}\rangle\langle\boldsymbol{k}| = \hat{\mathbf{1}}$, where the integrations are taken over the entire allowed range of $\boldsymbol{r}$ and $\boldsymbol{k}$, respectively.

D.1.1
Free Particles

For a free particle, the coordinate range is $-\infty < x_i < \infty$, where $i = 1, 2, 3$ and $x_1 = x$, $x_2 = y$ and $x_3 = z$. Also, $-\infty < k_i < \infty$, where $k_1 = k_x$, $k_2 = k_y$ and $k_3 = k_y$. In open space, the momentum eigenvalues are continuous. The momentum operator in the position basis is defined as $\langle \boldsymbol{r}'|\hat{\boldsymbol{p}}|\boldsymbol{r}\rangle = \delta(\boldsymbol{r}' - \boldsymbol{r})(\hbar/\mathrm{i})\nabla_{\boldsymbol{r}}$. Similarly, the position operator in the momentum basis is defined as $\langle \boldsymbol{p}'|\hat{\boldsymbol{r}}|\boldsymbol{p}\rangle = \delta(\boldsymbol{p}' - \boldsymbol{p})(-\hbar/\mathrm{i})\nabla_{\boldsymbol{p}}$.

The momentum eigenstate in the position basis is the solution of the equation

$$\langle \boldsymbol{r}|\hat{\boldsymbol{p}}|\boldsymbol{k}\rangle = \frac{\hbar}{\mathrm{i}}\nabla_{\boldsymbol{r}}\langle \boldsymbol{r}|\boldsymbol{k}\rangle = \hbar\boldsymbol{k}\langle \boldsymbol{r}|\boldsymbol{k}\rangle\ . \tag{D.2}$$

The orthonormalized solution to Eq. (D.2) is

$$\langle \boldsymbol{r}|\boldsymbol{k}\rangle = \phi_{\boldsymbol{k}}(\boldsymbol{r}) = \left(\frac{1}{2\pi}\right)^{3/2} \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}\ . \tag{D.3}$$

The normalized momentum eigenstate in the momentum basis is $\langle \boldsymbol{k}'|\boldsymbol{k}\rangle = \phi_{\boldsymbol{k}}(\boldsymbol{k}') = \delta(\boldsymbol{k} - \boldsymbol{k}')$. Similarly, the normalized position eigenstate in the momentum basis is

$$\langle \boldsymbol{k}|\boldsymbol{r}\rangle = \phi_{\boldsymbol{r}}(\boldsymbol{k}) = \left(\frac{1}{2\pi}\right)^{3/2} \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}} \tag{D.4}$$

and the normalized position eigenstate in the position basis is $\langle \boldsymbol{r}'|\boldsymbol{r}\rangle = \phi_{\boldsymbol{r}}(\boldsymbol{r}') = \delta(\boldsymbol{r} - \boldsymbol{r}')$.

D.1.2
Particle in a Box

Let us now assume that the particle is confined to a cubic box of volume $V = L^3$, and let us assume that the position eigenstates satisfy periodic boundary conditions $\phi_{\boldsymbol{k}}(\boldsymbol{r}) = \phi_{\boldsymbol{k}}(x, y, z) = \phi_{\boldsymbol{k}}(x + n_x L, y + n_y L, z + n_z L)$, where n_x, n_y, and n_z are integers ranging from $-\infty$ to ∞. The wavevector $\hat{\boldsymbol{k}}$ takes on discrete values

$$\boldsymbol{k} = \frac{2\pi}{L}(n_x\hat{\boldsymbol{e}}_x + n_y\hat{\boldsymbol{e}}_y + n_z\hat{\boldsymbol{e}}_z)\ , \tag{D.5}$$

where $\hat{\boldsymbol{e}}_x$, $\hat{\boldsymbol{e}}_x$ and $\hat{\boldsymbol{e}}_x$ are unit vectors in the x-, y-, z-directions, respectively. The eigenvectors $|\boldsymbol{k}\rangle$ of $\hat{\boldsymbol{k}}$ obey the orthogonality condition $\langle \boldsymbol{k}|\boldsymbol{k}'\rangle = \delta^{\mathrm{Kr}}_{\boldsymbol{k},\boldsymbol{k}'}$, where $\delta^{\mathrm{Kr}}_{\boldsymbol{k},\boldsymbol{k}'}$, is the Kronecker delta function. Completeness of the states $|\boldsymbol{r}\rangle$ and $|\boldsymbol{k}\rangle$ gives

$$\int_0^L \mathrm{d}x \int_0^L \mathrm{d}y \int_0^L \mathrm{d}z|\boldsymbol{r}\rangle\langle\boldsymbol{r}| = 1 \quad \text{and} \quad \sum_{n_x=-\infty}^{\infty}\sum_{n_y=-\infty}^{\infty}\sum_{n_z=-\infty}^{\infty} |\boldsymbol{k}\rangle\langle\boldsymbol{k}| = 1\ . \tag{D.6}$$

The wavevector eigenstate in the position basis is then

$$\langle \boldsymbol{r}|\boldsymbol{k}\rangle = \phi_{\boldsymbol{k}}(\boldsymbol{r}) = \frac{1}{L^{3/2}} \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}} \ . \tag{D.7}$$

The position eigenstate in the wavevector basis, $\langle \boldsymbol{k}|\boldsymbol{r}\rangle$, is just the Hermitian adjoint of $\langle \boldsymbol{r}|\boldsymbol{k}\rangle$.

D.1.3
N-Particle Eigenstates

We will let $|r\rangle = |\boldsymbol{r}, s_z\rangle = |\boldsymbol{r}\rangle|s_z\rangle$ denote the eigenstates of both the position operator $\hat{\boldsymbol{r}}$ and the z-component of spin, $\hat{\boldsymbol{s}}_z$ for a single particle, and we will let $|k\rangle = |\boldsymbol{k}, s_z\rangle$ denote the eigenstate of both the wavevector $\hat{\boldsymbol{k}}$ and the z-component of spin. We shall often refer to $|k\rangle$ as a "momentum" eigenstate.

The position eigenstates of the N-body system may be written as the direct product of the position eigenstates of the constituent particles,

$$|r_a, r_b, \ldots, r_l\rangle \equiv |r_a\rangle_1 |r_b\rangle_2 \times \cdots \times |r_l\rangle_N \ . \tag{D.8}$$

On the left-hand side of Eq. (D.8), we use the convention that the positions of the particles labeled from 1 to N are ordered from left to right from 1 to N. Thus, particle 1 has position r_a, particle 2 has position r_b, …, and particle N has position r_l. On the right-hand side of Eq. (D.8), the ket, $|r_a\rangle_i$, is a position eigenstate of particle i. (When we say "position" we include spin if the particle has spin.) A "momentum" (and spin) eigenstate of the N-body system is written

$$|k_a, k_b, \ldots, k_l\rangle \equiv |k_a\rangle_1 |k_b\rangle_2 \times \cdots \times |k_l\rangle_N \ , \tag{D.9}$$

where particle 1 has momentum k_a, particle 2 has position k_b, and so on.

In the position representation, the Hamiltonian takes the form

$$\begin{aligned} H(r_1, \ldots, r_N) &= \langle r_1, \ldots, r_N|\hat{H}_N|r_1, \ldots, r_N\rangle \\ &= \sum_{i=1}^{N} \frac{-\hbar^2}{2m} \nabla^2_{r_i} + \sum_{i<j=1}^{N(N-1)/2} V(\boldsymbol{r}_i, \boldsymbol{r}_j, \boldsymbol{s}_i, \boldsymbol{s}_j) \ . \end{aligned} \tag{D.10}$$

For the case when the Hamiltonian (and the other dynamical variables) are symmetric under interchange of particles, we must use only symmetric or antisymmetric combinations of position or momentum eigenstates when computing expectation values [48, 142]. We will describe these states for the cases of Bose–Einstein and Fermi–Dirac particles separately.

D.1.4
Symmetrized Momentum Eigenstates for Bose–Einstein Particles

By definition, any wave function describing the state of a system containing N identical Bose–Einstein particles must be symmetric under interchange of coordinates of any two particles. Furthermore, any number of bosons can have the same quantum numbers.

Let us first introduce a permutation operator, P_{ij}, such that P_{ij} interchanges the momenta of particles i and j:

$$P_{ij}|k_1, k_2, \dots, k_i, k_j, \dots, k_N\rangle = |k_1, k_2, \dots, k_j, k_i, \dots, k_N\rangle \,. \tag{D.11}$$

We let $\sum_P$ denote the sum over all permutations. For example,

$$\begin{aligned}\sum_P P|k_1, k_2, k_3\rangle = \{&|k_1, k_2, k_3\rangle + |k_2, k_1, k_3\rangle + |k_1, k_3, k_2\rangle \\ &+ |k_3, k_2, k_1\rangle + |k_3, k_1, k_2\rangle + |k_2, k_3, k_1\rangle\} \,.\end{aligned} \tag{D.12}$$

Note that in $|k_2, k_3, k_1\rangle$, particle 1 has momentum k_2, particle 2 has momentum k_3, and particle 3 has momentum k_1.

If, in the ket $|k_1, k_2, \dots, k_N\rangle$, there are n_1 particles with momentum k_1, n_2 particles with momentum k_2, n_3 particles with momentum k_3, and so on, then $\sum_P P|k_1, k_2, k_3\rangle$ contains $N!$ terms, but only $N!/\prod_{\alpha=1}^{\infty} n_\alpha!$ of them are different. If we now use the orthonormality of momentum states,

$$\langle k_a, k_b, \dots, k_l | k'_a, k'_b, \dots, k'_l\rangle = \delta_{k_a,k'_a}\delta_{k_b,k'_b} \times \cdots \times \delta_{k_l,k'_l} \,, \tag{D.13}$$

we find that

$$|k_1, k_2, \dots, k_N\rangle^{(S)} = \frac{1}{\sqrt{N! \prod_{\alpha=1}^{\infty} n_\alpha!}} \sum_P P|k_1, \dots, k_N\rangle \tag{D.14}$$

is a symmetrized orthonormal N-body momentum eigenstate. The symmetrized states have the normalization

$$^{(S)}\langle k_1, k_2, \dots, k_N | k_1, k_2, \dots, k_N\rangle^{(S)} = 1 \tag{D.15}$$

and satisfy the completeness relation

$$\hat{1}^{(S)} = \mathfrak{C}_S \sum_{k_1,\dots,k_N} |k_1, k_2, \dots, k_N\rangle^{(S)(S)}\langle k_1, k_2, \dots, k_N| \,. \tag{D.16}$$

The factor $\mathfrak{C}_S = \prod_{\alpha=1}^{\infty} n_\alpha!/N!$ in front of the summation corrects for the fact that the summation produces $N!/\prod_{\alpha=1}^{\infty} n_\alpha!$ copies of each term.

D.1.5
Antisymmetrized Momentum Eigenstates for Fermi–Dirac Particles

Any wave function describing the state of a system containing N identical Fermi–Dirac particles must be antisymmetric under interchange of coordinates of any two particles. Because of the Pauli exclusion principle, no more than one fermion can have a given set of quantum numbers.

An antisymmetrized momentum eigenstate may be written

$$|k_1, k_2, \dots, k_N\rangle^{(A)} = \frac{1}{\sqrt{N!}} \sum_P (-1)^P P|k_1, \dots, k_N\rangle \,, \tag{D.17}$$

where $(-1)^P = +1$ for an even number of permutations and $(-1)^P = -1$ for an odd number of permutations. For example,

$$\sum_P (-1)^P P|k_1, k_2, k_3\rangle = \{|k_1, k_2, k_3\rangle - |k_2, k_1, k_3\rangle - |k_1, k_3, k_2\rangle - |k_3, k_2, k_1\rangle + |k_3, k_1, k_2\rangle + |k_2, k_3, k_1\rangle\} \,. \quad \text{(D.18)}$$

The antisymmetrized states have the normalization

$$^{(A)}\langle k_1, k_2, \ldots, k_N | k_1, k_2, \ldots, k_N\rangle^{(A)} = 1 \quad \text{(D.19)}$$

and satisfy the completeness relation

$$\hat{1}^{(A)} = \mathfrak{C}_{\mathrm{A}} \sum_{k_1,\ldots,k_N} |k_1, k_2, \ldots, k_N\rangle^{(A)(A)}\langle k_1, k_2, \ldots, k_N| \,, \quad \text{(D.20)}$$

where $\mathfrak{C}_S = 1/N!$ corrects for the fact that the summation produces $N!$ copies of each state. Note that if any two particles have the same momentum and spin, then the state $|k_1, k_2, \ldots, k_N\rangle^{(A)}$ is identically zero. For example, $|k_1, k_1, \ldots, k_N\rangle^{(A)} \equiv 0$.

The wave function $\langle r_1, r_2, \ldots, r_N | k_1, k_2, \ldots, k_N\rangle^{(A)}$ can be written in the form of a determinant,

$$\langle r_1, r_2, \ldots, r_N | k_1, k_2, \ldots, k_N\rangle^{(A)} = \frac{1}{\sqrt{N}} \begin{pmatrix} \langle r_1|k_1\rangle & \langle r_1|k_2\rangle & \cdots & \langle r_1|k_N\rangle \\ \langle r_2|k_1\rangle & \langle r_2|k_2\rangle & \cdots & \langle r_2|k_N\rangle \\ \vdots & \vdots & \ddots & \vdots \\ \langle r_N|k_1\rangle & \langle r_N|k_2\rangle & \cdots & \langle r_N|k_N\rangle \end{pmatrix} , \quad \text{(D.21)}$$

known as the *Slater determinant*.

D.1.6
Partition Functions and Expectation Values

When evaluating the properties of many-body systems, we must compute partition functions and expectation values. Some of these quantities can be simplified as we shall show here.

The trace for an N-particle boson system can be written

$$\begin{aligned} \mathrm{Tr}(\hat{\rho}_N) &= \mathfrak{C}_S \sum_{k_1,\ldots,k_N} {}^{(S)}\langle k_1, k_2, \ldots, k_N|\hat{\rho}_N|k_1, k_2, \ldots, k_N\rangle^{(S)} \\ &= \left(\frac{1}{N!}\right)^2 \sum_{k_1,\ldots,k_N} {}^{(+)}\langle k_1, k_2, \ldots, k_N|\hat{\rho}_N|k_1, k_2, \ldots, k_N\rangle^{(+)} \\ &= \frac{1}{N!} \sum_{k_1,\ldots,k_N} \langle k_1, k_2, \ldots, k_N|\hat{\rho}_N|k_1, k_2, \ldots, k_N\rangle^{(+)} \,, \end{aligned} \quad \text{(D.22)}$$

where

$$|k_1, k_2, \ldots, k_N\rangle^{(+)} \equiv \sum_P P|k_1, k_2, \ldots, k_N\rangle \,. \quad \text{(D.23)}$$

Similarly, for an N-particle fermion system we have

$$\begin{aligned}\mathrm{Tr}(\hat{\rho}_N) &= \mathfrak{C}_A \sum_{k_1,\ldots,k_N} {}^{(A)}\langle k_1, k_2, \ldots, k_N | \hat{\rho}_N | k_1, k_2, \ldots, k_N \rangle^{(A)} \\ &= \frac{1}{N!} \sum_{k_1,\ldots,k_N} \langle k_1, k_2, \ldots, k_N | \hat{\rho}_N | k_1, k_2, \ldots, k_N \rangle^{(-)} ,\end{aligned} \tag{D.24}$$

where

$$|k_1, k_2, \ldots, k_N\rangle^{(-)} \equiv \sum_P (-1)^P P |k_1, k_2, \ldots, k_N\rangle . \tag{D.25}$$

It is useful also to look at expectation values. Let consider the N-particle one-body operator $\hat{O}_N^{(1)} \equiv \sum_{j=1}^{N} \hat{O}_j$, where $\hat{O}_i$ depends only on momentum, coordinate and spin operators for particle *j*. The kinetic energy is an example of such an operator. The expectation value of a one-body operator for a system of N bosons can be written

$$\begin{aligned}\langle \hat{O}^{(1)} \rangle &= \mathrm{Tr}_N \left(\hat{O}_N^{(1)} \hat{\rho}_N \right) = \mathfrak{C}_S \sum_{k_1,\ldots,k_N} {}^{(S)}\langle k_1, k_2, \ldots, k_N | \hat{O}_N^{(1)} \hat{\rho}_N | k_1, k_2, \ldots, k_N \rangle^{(S)} \\ &= \left(\frac{1}{N!} \right)^4 \sum_{k_1,\ldots,k_N} \sum_{k'_1,\ldots,k'_N} \sum_{i=1}^{N} {}^{(+)}\langle k_1, \ldots, k_N | \hat{O}_i | k'_1, \ldots, k'_N \rangle^{(+)} \\ &\quad \times {}^{(+)}\langle k'_1, \ldots, k'_N | \hat{\rho}_N | k_1, \ldots, k_N \rangle^{(+)} \\ &= N \left(\frac{1}{N!} \right)^2 \sum_{k_1,\ldots,k_N} \sum_{k'_1,\ldots,k'_N} \langle k_1, \ldots, k_N | \hat{O}_1 | k'_1, \ldots, k'_N \rangle^{(+)} \\ &\quad \times \langle k'_1, \ldots, k'_N | \hat{\rho}_N | k_1, \ldots, k_N \rangle^{(+)} \\ &= \frac{1}{(N-1)!} \sum_{k'_1} \sum_{k_1,\ldots,k_N} \langle k_1 | \hat{O}_1 | k'_1 \rangle^{(+)} \langle k'_1, k_2, \ldots, k_N | \hat{\rho}_N | k_1, \ldots, k_N \rangle .\end{aligned} \tag{D.26}$$

We can rewrite $\langle \hat{O}^{(1)} \rangle$ in terms of the reduced one-body density matrix $\langle k'_1 | \hat{\rho}_{(1)} | k_1 \rangle$

$$\langle \hat{O}^{(1)} \rangle = \sum_{k'_1} \sum_{k_1} \langle k_1 | \hat{O}_1 | k'_1 \rangle \langle k'_1 | \hat{\rho}_{(1)} | k_1 \rangle . \tag{D.27}$$

The reduced one-body density matrix, $\langle k'_1 | \hat{\rho}_{(1)} | k_1 \rangle$, is defined as

$$\langle k'_1 | \hat{\rho}_{(1)} | k_1 \rangle = \frac{1}{(N-1)!} \sum_{k_2,\ldots,k_N} {}^{(\pm)}\langle k'_1, k_2, \ldots, k_N | \hat{\rho}_N | k_1, \ldots, k_N \rangle , \tag{D.28}$$

where the sign (+) (−) applies to bosons (fermions).

Similarly, we can write an expression for the reduced two-body density matrix $\langle k'_1, k'_2 | \hat{\rho}_{(2)} | k_1, k_2 \rangle$. The N-particle two-body operator can be written $\hat{O}_N^{(2)} \equiv$

$\sum_{i<j}^{N(N-1)/2} \hat{O}_{i,j}$, where $\hat{O}_{i,j}$ depends only on momentum, coordinate, and spin operators for particles i and j. Then

$$\langle \hat{O}^{(2)} \rangle = \mathrm{Tr}\left(\hat{O}_N^{(i,j)} \hat{\rho}_N\right) = \frac{1}{2} \sum_{k_1',k_2'} \sum_{k_1,k_2} \langle k_1, k_2 | \hat{O}_{1,2} | k_1', k_2' \rangle \langle k_1', k_2' | \hat{\rho}_{(2)} | k_1, k_2 \rangle \,, \tag{D.29}$$

where

$$\langle k_1', k_2' | \hat{\rho}_{(2)} | k_1, k_2 \rangle = \frac{1}{(N-2)!} \sum_{k_3,\ldots,k_N}^{(\pm)} \langle k_1', k_2', k_3, \ldots, k_N | \hat{\rho}_N | k_1, k_2, k_3, \ldots, k_N \rangle \,, \tag{D.30}$$

where the sign (+) (−) applies to bosons (fermions).

D.2
The Number Representation

The wave functions $|k_1, \ldots, k_N\rangle$ tell us the momentum state of each particle. However, the states $|k_1, \ldots, k_N\rangle^{(S)(A)}$ contain no such information because they contain permutations of particles among all momentum states listed in the ket. Also, they can be clumsy to work with. Therefore, it is convenient to change representations from one which tells the momentum state of each particle (the momentum representation) to one which tells us the number of particles in each momentum state (the number representation).

D.2.1
The Number Representation for Bosons

The basis states in the number representation are written $|n_1, n_2, \ldots, n_\infty\rangle$, where n_α is the number of particles in the state of momentum and spin k_α. Operators in the number representation are written $\hat{a}_k^+$ and $\hat{a}_k$ and are called creation and annihilation operators, respectively. They are Hermitian conjugates of one another.

The states and operators of the number representation are related to the N-particle states $|k_1, \ldots, k_m\rangle^{(S)}$ as follows:

$$\begin{aligned} |k_1, \ldots, k_m\rangle^{(S)} &= |0, \ldots, n_1, \ldots, n_m, 0 \to 0\rangle \\ &\equiv \frac{1}{\sqrt{\prod_{\alpha=1}^{\infty} n_\alpha!}} \left(\hat{a}_{k_1}^+\right)^{n_1} \left(\hat{a}_{k_2}^+\right)^{n_2} \times \cdots \times \left(\hat{a}_{k_m}^+\right)^{n_m} |0\rangle \,, \end{aligned} \tag{D.31}$$

where $\sum_{i=1}^{m} n_i = N$. We have labeled the momenta in $|k_1, \ldots, k_m\rangle^{(S)}$ from 1 to m. However, it is understood that there are N positions in the ket. Several particles may have the same momentum. The notation $0 \to 0$ means that all occupation numbers after n_m are zero. Note that zeros may be interspersed between occupation numbers $n_1, \dots, n_m$. If we interchange momenta of two particles, the wave function should not change:

$$\begin{aligned}
&|k_1, k_2, \dots, k_m\rangle^{(S)} = |k_2, k_1, \dots, k_m\rangle^{(S)} \\
&= \frac{1}{\sqrt{\prod\limits_{\alpha}^{\infty} n_\alpha!}} \left(\hat{a}^+_{k_1}\right)^{n_1} \left(\hat{a}^+_{k_2}\right)^{n_2} \times \cdots \times \left(\hat{a}^+_{k_m}\right)^{n_m} |0\rangle \\
&= \frac{1}{\sqrt{\prod\limits_{\alpha}^{\infty} n_\alpha!}} \left(\hat{a}^+_{k_1}\right)^{n_1-1} \hat{a}^+_{k_2} \hat{a}^+_{k_1} \left(\hat{a}^+_{k_2}\right)^{n_2-1} \times \cdots \times \left(\hat{a}^+_{k_m}\right)^{n_m} |0\rangle \, . \qquad \text{(D.32)}
\end{aligned}$$

Thus, we find that symmetrization of the wave functions gives

$$\hat{a}^+_{k_1} \hat{a}^+_{k_2} = \hat{a}^+_{k_2} \hat{a}^+_{k_1} \qquad \text{(D.33)}$$

and, therefore, creation operators commute. If we take the Hermitian adjoint of Eq. (D.33), we find $\hat{a}_{k_1} \hat{a}_{k_2} = \hat{a}_{k_2} \hat{a}_{k_1}$, so the annihilation operators also commute.

The wave functions must satisfy the following condition:

$$\begin{aligned}
&{}^{(S)}\langle k_1, k_2, \dots, k_m | k'_1, k'_2, \dots, k'_m\rangle^{(S)} \\
&\equiv \frac{1}{\prod\limits_{\alpha}^{\infty} n_\alpha!} \langle 0 | \hat{a}_{k_m} \times \cdots \times \hat{a}_{k_1} \hat{a}^+_{k'_1} \times \cdots \times \hat{a}^+_{k'_m} |0\rangle \\
&= \begin{cases} 0 & \text{if the sets } [k_1, \dots, k_m] \text{ and } [k'_1, \dots, k'_m] \text{ are not the same .} \\ 1 & \text{if the sets } [k_1, \dots, k_m] \text{ and } [k'_1, \dots, k'_m] \text{ are the same .} \end{cases}
\end{aligned}$$

Equation (D.34) will be satisfied if the state $|0\rangle$ and the creation and annihilation operators have the following properties:

$$\langle 0|0\rangle = 1 \, , \qquad \text{(D.34)}$$

$$\hat{a}_k |0\rangle = 0 \quad \text{for all } k \qquad \text{(D.35)}$$

and

$$[\hat{a}_k, \hat{a}^+_{k'}]_- = \hat{a}_k \hat{a}^+_{k'} - \hat{a}^+_{k'} \hat{a}_k = \delta_{k,k'} \, . \qquad \text{(D.36)}$$

One can easily show that Eq. (D.34) follows from Eqs. (D.34)–(D.36) by doing some examples. One simply commutes each annihilation operator to the right using Eqs. (D.34)–(D.36) as they are needed. The result is Eq. (D.34).

Again, by using Eqs. (D.31), (D.35), and (D.36), we can show that

$$\hat{a}_{k_j} |n_1, \dots, n_j, \dots, n_\infty\rangle = \sqrt{n_j} |n_1, \dots, n_j - 1, \dots, n_\infty\rangle \, , \qquad \text{(D.37)}$$

$$\hat{a}^+_{k_j} |n_1, \dots, n_j, \dots, n_\infty\rangle = \sqrt{n_j + 1} |n_1, \dots, n_j + 1, \dots, n_\infty\rangle \qquad \text{(D.38)}$$

and

$$\langle n_1, \ldots, n_j, \ldots, n_\infty | \hat{a}^+_{k_j} \hat{a}_{k_j} | n_1, \ldots, n_j, \ldots, n_\infty \rangle = n_j \, . \tag{D.39}$$

Equation (D.39) follows from the normalization of the states:

$$\langle n_1, \ldots, n_j, \ldots, n_\infty | n_1, \ldots, n_j, \ldots, n_\infty \rangle = 1 \, . \tag{D.40}$$

When working with N-body systems, we commonly must evaluate one-body operators of the type

$$\hat{O}^N_{(1)} = \sum_{i=1}^{N} O_i(\hat{\boldsymbol{q}}_i, \hat{\boldsymbol{p}}_i, \hat{\boldsymbol{s}}_i) \, . \tag{D.41}$$

(Note that these operators are symmetric under interchange of particle labels.) Some examples are the kinetic energy, the number density, and the particle current. We wish to express these operators in the number representation.

The correspondence between $\hat{O}^N_{(1)}$ and its analog in the number representation is

$$\hat{O}^N_{(1)} \to \hat{O}^{nb}_{(1)} = \sum_{k_a k_b} \langle k_a | \hat{O}_1(\hat{\boldsymbol{q}}_1, \hat{\boldsymbol{p}}_1, \hat{\boldsymbol{s}}_i) | k_b \rangle \hat{a}^+_{k_a} \hat{a}_{k_b} \, . \tag{D.42}$$

To show that Eq. (D.42) is correct, we must show that

$$\begin{aligned} &{}^{(S)}\langle k_1, \ldots, k_m | \hat{O}^N_{(1)} | k'_1, \ldots, k'_m \rangle^{(S)} \\ &\quad = \langle 0, \ldots, n_1, \ldots, n_m, 0 \to 0 | \hat{O}^{nb}_{(1)} | 0, \ldots, n'_1, \ldots, n'_m, 0 \to 0 \rangle \, . \end{aligned} \tag{D.43}$$

We leave this as an exercise.

In going from the momentum representation to the number representation, we thus make the correspondence

$$|k_1, k_2, \ldots, k_m\rangle^{(S)} \to |0, \ldots, n_1, n_2, \ldots, n_m, 0 \to 0\rangle \tag{D.44}$$

and

$$\sum_{i=1}^{N} O_i(\hat{\boldsymbol{q}}_i, \hat{\boldsymbol{p}}_i, \hat{\boldsymbol{s}}_i) \to \sum_{k_a, k_b} \langle k_a | O_1(\hat{\boldsymbol{q}}_1, \hat{\boldsymbol{p}}_1, \hat{\boldsymbol{s}}_1) | k_b \rangle \hat{a}^+_{k_a} \hat{a}_{k_b} \, . \tag{D.45}$$

In practice, the only other type of N-body operators we encounter are two-body operators of the form

$$\hat{O}^N_{(2)} = \sum_{i<j}^{(1/2)N(N-1)} O_{ij}(\hat{\boldsymbol{q}}_i, \hat{\boldsymbol{q}}_j, \hat{\boldsymbol{p}}_i, \hat{\boldsymbol{p}}_j, \hat{\boldsymbol{s}}_i, \hat{\boldsymbol{s}}_j) \, . \tag{D.46}$$

Some examples are the potential energy and the momentum currents (stress tensor). Similarly, we can show that

$$\begin{aligned} &\sum_{i<j}^{(1/2)N(N-1)} O_{ij}(\hat{\boldsymbol{q}}_i, \hat{\boldsymbol{q}}_j, \hat{\boldsymbol{p}}_i, \hat{\boldsymbol{p}}_j, \hat{\boldsymbol{s}}_i, \hat{\boldsymbol{s}}_j) \\ &\quad \to \frac{1}{2} \sum_{k_a k_b k'_a k'_b} \langle k_a k_b | O_{12}(\hat{\boldsymbol{q}}_1 \hat{\boldsymbol{q}}_2 \hat{\boldsymbol{p}}_1 \hat{\boldsymbol{p}}_2 \hat{\boldsymbol{s}}_1 \hat{\boldsymbol{s}}_2) | k'_a k'_b \rangle \hat{a}^+_{k_a} \hat{a}^+_{k_b} \hat{a}_{k'_b} \hat{a}_{k'_a} \, , \end{aligned} \tag{D.47}$$

when going from the coordinate to number representation.

D.2.2
The Number Representation for Fermions

The basis states for fermions are also written $|n_1, n_2, \dots, n_\infty\rangle$, but because of the Pauli exclusion principle the occupation numbers take on values $n_\alpha = 0$ or 1 only. We also introduce creation and annihilation operators $\hat{a}_k^+$ and $\hat{a}_k$, respectively. But they obey different commutation relations.

The correspondence between states in the number representation and antisymmetrized momentum states is

$$|k_1, k_2, \dots, k_N\rangle^{(A)} = |0, \dots, 1_1, 1_2, \dots, 1_N, 0 \to 0\rangle \equiv \hat{a}_{k_1}^+ \hat{a}_{k_2}^+ \times \dots \times \hat{a}_{k_N}^+ |0\rangle \,, \tag{D.48}$$

where we have used the convention $n_\alpha = 1_\alpha$ when the state k_α is filled and zero otherwise. In general, there will be zeros interspersed between the occupation numbers $1_1, 1_2, \dots, 1_N$ on the left-hand side of Eq. (D.48). If we interchange momenta of two particles, the states must change sign:

$$\begin{aligned} |k_1, k_2, \dots, k_N\rangle^{(A)} &= -|k_2, k_1, \dots, k_N\rangle^{(A)} \\ &= \hat{a}_{k_1}^+ \hat{a}_{k_2}^+ \times \dots \times \hat{a}_{k_N}^+ |0\rangle = -\hat{a}_{k_2}^+ \hat{a}_{k_1}^+ \times \dots \times \hat{a}_{k_N}^+ |0\rangle \,. \end{aligned} \tag{D.49}$$

Thus, the creation operators anticommute,

$$\hat{a}_{k_1}^+ \hat{a}_{k_2}^+ = -\hat{a}_{k_2}^+ \hat{a}_{k_1}^+ \,. \tag{D.50}$$

If we take the Hermitian adjoint of Eq. (D.50), we find $\hat{a}_{k_2} \hat{a}_{k_1} = -\hat{a}_{k_1} \hat{a}_{k_2}$, so the annihilation operators also anticommute.

The wave functions must satisfy the condition

$$\begin{aligned} {}^{(A)}\langle k_1, k_2, \dots, k_N | k_1', k_2', \dots, k_N'\rangle^{(A)} &\equiv \langle 0|\hat{a}_{k_N} \times \dots \times \hat{a}_{k_1} \hat{a}_{k_1'}^+ \times \dots \times \hat{a}_{k_N'}^+ |0\rangle \\ &= \begin{cases} 0 & \text{if the sets } \{k_i\} \text{ and } \{k_i'\} \text{ differ ,} \\ +1 & \text{if the sets } \{k_i\} \text{ and } \{k_i'\} \text{ only differ by an even permutation ,} \\ -1 & \text{if the sets } \{k_i\} \text{ and } \{k_i'\} \text{ only differ by an odd permutation .} \end{cases} \end{aligned} \tag{D.51}$$

Equation (D.51) will be satisfied if

$$\langle 0|0\rangle = 1 \,, \tag{D.52}$$

$$\hat{a}_k |0\rangle = 0 \quad \text{for all} \quad k \,, \tag{D.53}$$

and

$$[\hat{a}_k, \hat{a}_k^+]_+ \equiv \hat{a}_k \hat{a}_{k'}^+ + \hat{a}_{k'}^+ \hat{a}_k = \delta_{k,k'} \,. \tag{D.54}$$

For Fermi systems there can be ambiguity in the overall sign of the states. Therefore, *one uses the convention that in the states* $|n_1, n_2, \dots, n_\infty\rangle$ *the occupation numbers are ordered from left to right in order of increasing energy.* We then find that

$$\hat{a}_{k_j}|n_1, n_2, \dots, n_j, \dots, n_\infty\rangle = (-1)^{\Sigma_j}\sqrt{n_j}|n_1, n_2, \dots, (1-n_j), \dots, n_\infty\rangle\,, \tag{D.55}$$

$$\hat{a}^+_{k_j}|n_1, n_2, \dots, n_j, \dots, n_\infty\rangle = (-1)^{\Sigma_j}\sqrt{1-n_j}\,|\,n_1, n_2, \dots, (1+n_j), \dots, n_\infty\rangle\,, \tag{D.56}$$

where $\sum_j \equiv \sum_{l=1}^{j-1} n_l$.

For systems of identical fermions, the same correspondence holds between operators in the coordinate representation and number representation (cf. Eqs. (D.45) and (D.46)) as was found to hold for systems of identical bosons. However, for fermions the creation and annihilation operators anticommute and for bosons they commute.

A similar correspondence holds for the operator $O^N_{(2)}$. However, we must make a brief comment about sign conventions. The correspondence is

$$\begin{aligned}\hat{O}^N_{(2)} &= \sum_{i<j}^{(1/2)N(N-1)} O_{ij}(\hat{\boldsymbol{q}}_i\hat{\boldsymbol{q}}_j\hat{\boldsymbol{p}}_i\hat{\boldsymbol{p}}_j\hat{\boldsymbol{\sigma}}_i\hat{\boldsymbol{\sigma}}_j)\\ &\to \frac{1}{2}\sum_{k_a k_b k'_a k'_b}\langle k_a, k_b|O_{12}(\hat{\boldsymbol{q}}_1\hat{\boldsymbol{q}}_2\hat{\boldsymbol{p}}_1\hat{\boldsymbol{p}}_2\hat{\sigma}_1\hat{\sigma}_2)|k'_a, k'_b\rangle \hat{a}^+_{k_a}\hat{a}^+_{k_b}\hat{a}_{k'_b}\hat{a}_{k'_a}\,.\end{aligned} \tag{D.57}$$

Note that the order of the operators $\hat{a}_{k'_a}$ and $\hat{a}_{k'_b}$ is opposite to the order of k'_a and k'_b in the ket $|k'_a\ k'_b\rangle$. With this convention, the matrix elements whose momenta appear in the same order (of increasing or decreasing energy) on each side have a positive sign.

D.2.3
Thermodynamic Averages of Quantum Operators

We often need to compute average values of operators in the grand canonical ensemble such that $\langle O\rangle = \mathrm{Tr}(\hat{O}\hat{\rho}_0)$, where $\hat{\rho}_0 = \mathrm{e}^{-\beta\hat{K}_0}/\mathrm{Tr}(\mathrm{e}^{-\beta\hat{K}_0})$ and $\hat{K}_0 = \sum_k \epsilon_k \hat{a}^\dagger_k \hat{a}_k$. The quantity $\epsilon_k = \hbar^2k^2/2m - \mu$. The operator $\hat{O}$ may consist of a long string of creation and annihilation operators, $\hat{a}^\dagger_k$ and $\hat{a}_k$, respectively. The first thing to notice is that $\hat{\rho}_0$ is the field theoretic version of a generalized Gaussian distribution. Thus, Wick's theorem can be used to evaluate the trace $\mathrm{Tr}(\hat{O}\hat{\rho}_0)$. Wick's theorem states that *the average of a product of operators is equal to the sum of all possible ways of averaging the product in pairs.*

Before we show how to derive Wick's theorem, we must establish a few properties of the creation and annihilation operators. Let us first define $\hat{a}_k(\tau) =$

$\mathrm{e}^{\tau K_0}\hat{a}_k\mathrm{e}^{-\tau K_0}$. Then, using the boson (upper sign) and fermion (lower sign) commutation relations $[\hat{a}_k, \hat{a}^\dagger_{k'}]_\mp = \delta_{k,k'}$, we can show that

$$\frac{\partial}{\partial\tau}\hat{a}_k(\tau) = \left[\hat{K}_0, \hat{a}_k(\tau)\right]_- = -\epsilon_k\hat{a}_k(\tau) \tag{D.58}$$

and

$$\frac{\partial}{\partial\tau}\hat{a}^\dagger_k(\tau) = \left[\hat{K}_0, \hat{a}^\dagger_k(\tau)\right]_- = \epsilon_k\hat{a}^\dagger_k(\tau)\,. \tag{D.59}$$

Thus,

$$\hat{a}^\dagger_k(\tau) = \mathrm{e}^{\epsilon_k\tau}\hat{a}^\dagger_k \quad \text{and} \quad \hat{a}_k(\tau) = \mathrm{e}^{-\epsilon_k\tau}\,\hat{a}_k\,. \tag{D.60}$$

Also note that

$$\hat{a}_k\mathrm{e}^{-\hat{K}_0\tau} = \mathrm{e}^{-\hat{K}_0\tau}\hat{a}_k\mathrm{e}^{-\epsilon_k\tau} \quad \text{and} \quad \hat{a}^\dagger_k\mathrm{e}^{-\hat{K}_0\tau} = \mathrm{e}^{-\hat{K}_0\tau}\hat{a}^\dagger_k\mathrm{e}^{\epsilon_k\tau}\,. \tag{D.61}$$

Using these results, the expectation value of a product of creation and annihilation operators can be written

$$\left\langle \hat{a}^\dagger_k\hat{a}_{k'}\right\rangle = \mathrm{Tr}\left(\hat{\rho}\hat{a}^\dagger_k\hat{a}_{k'}\right) = \mp\delta_{k,k'} \pm \mathrm{Tr}\left(\hat{\rho}\hat{a}_{k'}\hat{a}^\dagger_k\right) = \mp\delta_{k,k'} \pm \mathrm{e}^{\beta\epsilon_k}\mathrm{Tr}\left(\hat{\rho}\hat{a}^\dagger_k\hat{a}_{k'}\right)\,, \tag{D.62}$$

where we have made use of the commutation relations for bosons (upper sign) and fermions (lower sign). Rearranging terms we obtain

$$\left\langle \hat{a}^\dagger_k\hat{a}_{k'}\right\rangle = \delta_{k,k'}n(k) = \frac{\delta_{k,k'}}{(\mathrm{e}^{\beta\epsilon_k} \mp 1)}\,, \tag{D.63}$$

where $n(k) = (\mathrm{e}^{\beta\epsilon_k} \mp 1)^{-1}$ is the momentum distribution for noninteracting bosons (upper sign) and fermions (lower sign). Furthermore,

$$\left\langle \hat{a}_k\hat{a}^\dagger_{k'}\right\rangle = \delta_{k,k'}(1 \pm n(k))\,, \quad \left\langle \hat{a}_k\hat{a}_{k'}\right\rangle = 0\,, \quad \text{and} \quad \left\langle \hat{a}^\dagger_k\hat{a}^\dagger_{k'}\right\rangle = 0\,. \tag{D.64}$$

If we consider a product of four operators, we evaluate the trace as follows. By successively applying boson or fermion commutation relations, we can write

$$\begin{aligned}\mathrm{Tr}\left(\hat{\rho}\hat{a}^\dagger_{k_1}\hat{a}^\dagger_{k_2}\hat{a}_{k_4}\hat{a}_{k_3}\right) &= -\delta_{k_1,k_4}\mathrm{Tr}\left(\hat{\rho}\hat{a}^\dagger_{k_2}\hat{a}_{k_3}\right) \mp \delta_{k_1,k_3}\mathrm{Tr}\left(\hat{\rho}\hat{a}^\dagger_{k_2}\hat{a}_{k_4}\right)\\ &\quad \pm \mathrm{e}^{-\beta\epsilon_{k_1}}\mathrm{Tr}\left(\hat{\rho}\hat{a}^\dagger_{k_1}\hat{a}^\dagger_{k_2}\hat{a}_{k_4}\hat{a}_{k_3}\right)\,.\end{aligned} \tag{D.65}$$

After rearranging terms, this becomes

$$\mathrm{Tr}\left(\hat{\rho}\;\hat{a}^\dagger_{k_1}\hat{a}^\dagger_{k_2}\hat{a}_{k_4}\hat{a}_{k_3}\right) = \left\langle \hat{a}^\dagger_{k_1}\hat{a}_{k_3}\right\rangle\left\langle \hat{a}^\dagger_{k_2}\hat{a}_{k_4}\right\rangle \pm \left\langle \hat{a}^\dagger_{k_1}\hat{a}_{k_4}\right\rangle\left\langle \hat{a}^\dagger_{k_2}\hat{a}_{k_3}\right\rangle\,. \tag{D.66}$$

The sign in front of a given term in the sum of products of pairwise averages is always positive for bosons but will be negative for fermions if it requires an odd number of permutations to rearrange the product of operators into the appropriate pairs.

If we apply the above procedure to $\mathrm{Tr}(\hat{\rho}\hat{a}^\dagger_{k_1}\hat{a}^\dagger_{k_2}\hat{a}_{k_4}\hat{a}_{k_3}\hat{a}^\dagger_{k_5}\hat{a}^\dagger_{k_6}\hat{a}_{k_7}\hat{a}_{k_8})$, we obtain a sum of 24 terms, each containing a product of pairwise averages.

Appendix E
Scattering Theory

In this Appendix, we first discuss the dynamics of the scattering process and then derive an expression for the scattering cross section [69]. We shall restrict ourselves to elastic scattering processes.

E.1
Classical Dynamics of the Scattering Process

We consider two particles, one with mass m_1 and displacement $\boldsymbol{r}_1(t)$ at time t and another with mass m_2 and displacement $\boldsymbol{r}_2(t)$ at time t. The particles interact via a short-range interaction, $V(|\boldsymbol{r}_2 - \boldsymbol{r}_1|)$. It is useful to introduce the relative displacement, $\boldsymbol{r} = \boldsymbol{r}_2 - \boldsymbol{r}_1$, and the center-of-mass displacement, $\boldsymbol{R} = (m_1/M)\boldsymbol{r}_1 + (m_2/M)\boldsymbol{r}_2$, where $M = m_1 + m_2$ is the total mass. They are related through the equations (cf. Figure E.1a)

$$\boldsymbol{r}_1 = \boldsymbol{R} - \frac{m_2}{M}\boldsymbol{r} \quad \text{and} \quad \boldsymbol{r}_2 = \boldsymbol{R} + \frac{m_1}{M}\boldsymbol{r} \,. \tag{E.1}$$

The momenta of particles 1 and 2 are $\boldsymbol{p}_1$ and $\boldsymbol{p}_2$, respectively. The center-of-mass momentum is $\boldsymbol{P} = \boldsymbol{p} + \boldsymbol{p}_2$. The relative momentum is $\boldsymbol{p} = (m_1/M)\boldsymbol{p}_2 - (m_2/M)\boldsymbol{p}_1$.

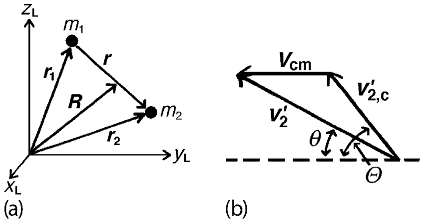

Figure E.1 (a) Relation between lab frame coordinates and center-of-mass and relative coordinates. (b) Relation between lab frame velocity, v'_2, and center-of-mass frame velocity, $v'_{2,c}$, of mass m_2.

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The total Hamiltonian for the system can be written

$$H_{\text{tot}} = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} + V(|\boldsymbol{r}_2 - \boldsymbol{r}_1|) = \frac{P^2}{2M} + \frac{p^2}{2\mu} + V(|\boldsymbol{r}|) = E_{\text{tot}} . \tag{E.2}$$

The Hamiltonian decomposes into a part that depends only on the center-of-mass coordinates, $H_{\text{cm}} = P^2/2M = E_{\text{cm}}$, and a part that depends only on the relative coordinates, $H = p^2/2\mu + V(r) = E$, so $H_{\text{tot}} = H_{\text{cm}} + H$. Therefore, the center-of-mass motion evolves independently from the relative motion. From Hamilton's equation, $\dot{\boldsymbol{P}} = -\partial H_{\text{tot}}/\partial \boldsymbol{R} = 0$, so the center-of-mass momentum, $\boldsymbol{P} = \boldsymbol{p}_1 + \boldsymbol{p}_2$, is a constant of the motion.

We will assume that the scattering is elastic, so the total kinetic energy, $p_1^2/(2m_1) + p_2^2/(2m_2)$, is conserved. Because the potential, $V(|\boldsymbol{r}_2 - \boldsymbol{r}_1|)$, is spherically symmetric (it depends only on the distance, $|\boldsymbol{r}_2 - \boldsymbol{r}_1|$), the total angular momentum vector, $\boldsymbol{L} = \boldsymbol{r}_1 \times \boldsymbol{p}_1 + \boldsymbol{r}_2 \times \boldsymbol{p}_2$, is a constant of the motion.

Let us assume that initially the particles are far apart and free but approach one another with momenta, $\boldsymbol{p}_1$ and $\boldsymbol{p}_2$, in the lab frame. Once they approach close enough to feel the interaction, the scattering process begins and their momenta will be altered. After the collision process is finished, they fly apart with final momenta, $\boldsymbol{p}_1'$ and $\boldsymbol{p}_2'$. Conservation of momentum and of kinetic energy (for elastic processes) then gives

$$\boldsymbol{P}_{\text{cm}} = \boldsymbol{p}_1 + \boldsymbol{p}_2 = \boldsymbol{p}_1' + \boldsymbol{p}_2' \quad \text{and} \quad \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} = \frac{p_1'^2}{2m_1} + \frac{p_2'^2}{2m_2} , \tag{E.3}$$

respectively. One can combine Eq. (E.3) to show that for elastic collisions, the *magnitude* of the relative velocity, $|\boldsymbol{v}_2 - \boldsymbol{v}_1|$, is unchanged by the collision. The relative velocities *before* and *after* the collision are $\boldsymbol{g} = \boldsymbol{v}_2 - \boldsymbol{v}_1$ and $\boldsymbol{g}' = \boldsymbol{v}_2' - \boldsymbol{v}_1'$, respectively. Then for elastic collisions

$$g = |\boldsymbol{g}| = |\boldsymbol{g}'| , \tag{E.4}$$

where g is the magnitude of the relative velocity before and after the collision.

Because angular momentum is conserved, the scattering process occurs in a plane perpendicular to the angular momentum vector. We can choose the z-axis to lie along the angular momentum vector. Then, the scattering process takes place in the x–y plane. If we introduce polar coordinates $x = r\cos(\phi)$ and $y = r\sin(\phi)$, the relative Hamiltonian can be written

$$H = \frac{p^2}{2\mu} + V(r) = \frac{1}{2\mu}\left(p_r^2 + \frac{p_\phi^2}{r^2}\right) + V(r) = E , \tag{E.5}$$

where $p_r = \mu\dot{r}$ and $p_\phi = \mu r^2\dot{\phi}$. Hamilton's equation takes the form

$$\frac{\mathrm{d}p_r}{\mathrm{d}t} = -\frac{\partial H}{\partial r} = \frac{p_\phi^2}{\mu r^3} - \frac{\partial V}{\partial r} , \quad \frac{\mathrm{d}r}{\mathrm{d}t} = \frac{\partial H}{\partial p_r} = \frac{p_r}{\mu} ,$$
$$\frac{\mathrm{d}p_\phi}{\mathrm{d}t} = -\frac{\partial H}{\partial \phi} = 0 , \quad \frac{\mathrm{d}\phi}{\mathrm{d}t} = \frac{\partial H}{\partial p_\phi} = \frac{p_\phi}{\mu r^2} . \tag{E.6}$$

Since $\mathrm{d}p_\phi/\,\mathrm{d}t = 0$, the magnitude of angular momentum, p_ϕ, is a constant of the motion. We therefore set $p_\phi = l$, where l is a constant. Since $\mathrm{d}\phi/\,\mathrm{d}t = l/\mu r^2$, we can write

$$\mathrm{d}\phi = \frac{l}{\mu r^2}\,\mathrm{d}t = \frac{l}{r^2}\frac{\mathrm{d}r}{p_r} = \frac{(l/r^2)\,\mathrm{d}r}{\sqrt{2\mu(E - V(r)) - l^2/r^2}} \,. \tag{E.7}$$

Equation (E.7) relates the polar angle, ϕ, to the distance between the particles at any time during the scattering process.

Let us now consider the scattering process in more detail. Let us assume that at time $t = -\infty$, mass m_1 is at rest at the origin and mass m_2 has coordinates $x = +\infty$ and $y = b$ and is moving parallel to the x-axis in the negative x-direction with a velocity $\mathbf{v}_2 = \mathbf{v}_0 = -v_0\hat{\mathbf{x}}$. The quantity b is the *impact parameter*. Thus, at time $t = -\infty$ we have $(\mathbf{r}_1 = 0, \mathbf{v}_1 = 0, \mathbf{r}_2 = \infty\hat{\mathbf{e}}_x + b\hat{\mathbf{e}}_y, \mathbf{v}_2 = -v_0\hat{\mathbf{e}}_x)$ (cf. Figure E.2a). The center-of-mass velocity is $\mathbf{V}_{\mathrm{cm}} = m_2\mathbf{v}_0/M = \mu\mathbf{v}_0/m_1$ and the relative velocity is $\mathbf{v} = -v_0\hat{\mathbf{e}}_x$. The total angular momentum is $\mathbf{L} = \mathbf{r}_1 \times \mathbf{p}_1 + \mathbf{r}_2 \times \mathbf{p}_2 = -m_2 v_0 b\hat{\mathbf{e}}_z$. The angular momentum can also be divided into center-of-mass angular momentum, $\mathbf{L}_{\mathrm{cm}} = M\mathbf{R} \times \mathbf{V}_{\mathrm{cm}}$, and relative angular momentum, $\mathbf{L}_{\mathrm{rel}} = \mu\mathbf{r} \times \mathbf{v} = \mu b v_0\hat{\mathbf{z}}$, so that $\mathbf{L} = \mathbf{L}_{\mathrm{cm}} + \mathbf{L}_{\mathrm{rel}}$. Since the magnitude of the relative velocity, $g = v_0$, is unchanged by the collision, the impact parameter, b, is the same before and after the collision. Therefore, g and b are intrinsic parameters of the elastic collision processes.

At the end of the scattering event, the particles move apart with constant relative velocity. At time $t = -\infty$ we have $\phi = 0$. At time $t = +\infty$ we have $\phi = \phi_{\mathrm{f}}$. The angle, Θ, between the incident relative velocity and the final relative velocity is called the *scattering angle* and it satisfies the relation $\Theta = \pi - \phi_{\mathrm{f}}$ (cf. Figure E.2b).

It is useful to view the scattering process from the center-of-mass frame of reference, which is the reference frame in which the origin of coordinates is fixed to the center-of-mass and moves with it. In the center-of-mass frame, the displacement of m_1 is $\mathbf{r}_{1,\mathrm{c}} = -m_2\mathbf{r}/M$ and the displacement of m_2 is $\mathbf{r}_{2,\mathrm{c}} = m_1\mathbf{r}/M$. Similarly, their velocities are $\mathbf{v}_{1,\mathrm{c}} = -m_2\mathbf{v}/M$ and $\mathbf{v}_{2,\mathrm{c}} = m_1\mathbf{v}/M$, respectively. The relation between the final velocities $\mathbf{v}'_2$ and $\mathbf{v}'_{2,\mathrm{c}} = m_1\mathbf{g}'/M$, of mass m_2 in the lab frame and center-of-mass frames, respectively, is shown in Figure E.1b. From this figure we can relate the scattering angles, θ and Θ, as seen from the lab and center-of-mass frames, respectively. Equating components of the vectors in Figure E.1b, we find

$$v'_{2,\mathrm{c}}\sin(\Theta) = v'_2\sin(\theta) \quad \text{and} \quad v'_{2,\mathrm{c}}\cos(\Theta) + V_{\mathrm{cm}} = v'_2\cos(\theta) \,. \tag{E.8}$$

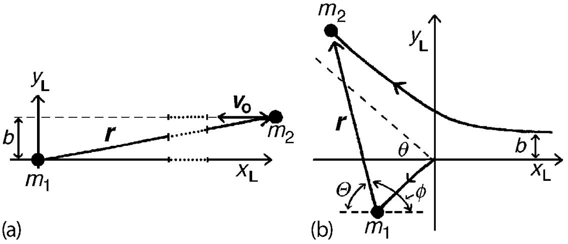


Figure E.2 Scattering in the lab frame. (a) $t = -\infty$. (b) $t = +\infty$.

We can combine these equations to obtain

$$\cos(\theta) = \frac{\xi + \cos(\Theta)}{\sqrt{1 + \xi^2 + 2\xi\cos(\Theta)}} \,, \tag{E.9}$$

where $\xi = V_{\mathrm{cm}}/v'_{2,\mathrm{c}}$. The magnitude of the center-of-mass velocity is $V_{\mathrm{cm}} = \mu v_0/m_1$. Also, for elastic collisions we have $v'_{2,\mathrm{c}} = m_1 v_0/M$ and $\xi = m_2/m_1$. It is useful now to introduce the concept of the scattering cross section.

E.2
The Scattering Cross Section

The scattering problem may be viewed in the lab frame as that of a beam of particles of mass, m_2, incident on a mass, m_1, which is at rest. Let I be the intensity of the incident beam (number of incident particles/(time · area)). Consider a circular area element of the incident beam consisting of those particles with impact parameter in the interval $b \to b + \mathrm{d}b$ and azimuthal angle element $\mathrm{d}\alpha$ (cf. Figure E.3a). These particles are scattered into the solid angle $\mathrm{d}\omega = \sin(\theta)\,\mathrm{d}\theta\,\mathrm{d}\alpha$ in the lab frame and into the solid angle $\mathrm{d}\Omega = \sin(\Theta)\,\mathrm{d}\Theta\,\mathrm{d}\alpha$ in the center-of-mass frame. The angle, α, is the same in the two frames. The number of particles/time, $\mathrm{d}\dot{N}$, scattered into the solid angle $\mathrm{d}\omega = \sin(\theta)\,\mathrm{d}\theta\,\mathrm{d}\alpha$ in the lab frame and into the solid angle $\mathrm{d}\Omega = \sin(\Theta)\,\mathrm{d}\Theta\,\mathrm{d}\alpha$ in the center-of-mass frame is given by (α is the azimuthal angle)

$$\mathrm{d}\dot{N} = Ib\,\mathrm{d}b\,\mathrm{d}\alpha = I\sigma_{\mathrm{lab}}\sin(\theta)\,\mathrm{d}\theta\,\mathrm{d}\alpha = I\sigma_{\mathrm{cm}}\sin(\Theta)\,\mathrm{d}\Theta\,\mathrm{d}\alpha \,, \tag{E.10}$$

where $\sigma_{\mathrm{lab}} = \sigma_{\mathrm{lab}}(g, b)$ and $\sigma_{\mathrm{cm}} = \sigma_{\mathrm{cm}}(g, b)$ are the differential scattering cross sections in the lab and center-of-mass frames, respectively. Equation (E.10) gives the relation between the impact parameter, b, and either the lab frame differential cross section, σ_{lab}, or the center-of-mass differential cross section, σ_{cm}:

$$\sigma_{\mathrm{lab}} = \left|\frac{b\,\mathrm{d}b}{\sin(\theta)\,\mathrm{d}\theta}\right| \quad \text{and} \quad \sigma_{\mathrm{cm}} = \left|\frac{b\,\mathrm{d}b}{\sin(\Theta)\,\mathrm{d}\Theta}\right| \,. \tag{E.11}$$

The differential scattering cross section is independent of α because of the spherical symmetry of the potential. As b increases, θ and Θ decrease. The absolute value signs in Eq. (E.11) are necessary for positive cross sections.

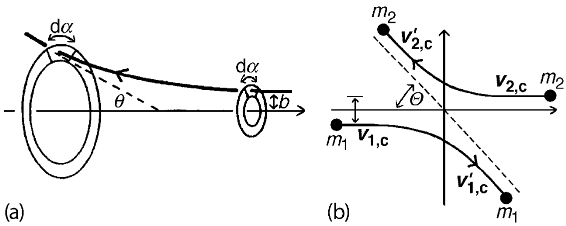


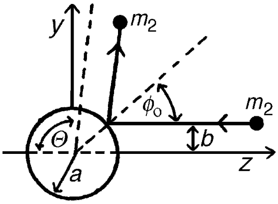
Figure E.3 (a) Relation between the impact parameter and the scattering angle in the lab frame. (b) Scattering process as viewed from the center-of-mass frame. Here $\boldsymbol{v}_{1,\mathrm{c}} = -m_2\boldsymbol{g}/M$, $\boldsymbol{v}'_{1,\mathrm{c}} = -m_2\boldsymbol{g}'/M$, $\boldsymbol{v}_{2,\mathrm{c}} = m_1\boldsymbol{g}/M$, and $\boldsymbol{v}'_{2,\mathrm{c}} = m_1\boldsymbol{g}'/M$.

Exercise E.1

Compute the total scattering cross section for elastic scattering of a point particle of mass m off of a hard sphere of radius a which is fixed in position. Assume that the incident particle has velocity $\boldsymbol{v}_0$ and impact parameter b.

Answer: The fact that the hard sphere is fixed in position means that it, in effect, has an infinite mass and $\boldsymbol{v}_1 = 0$. If we let $m_2 = m$ and $m_1 = \infty$, we find $V_{\mathrm{cm}} = 0$. Therefore, $\xi = 0$ and the scattering angles in the center-of-mass and lab frames are equal, $\cos(\theta) = \cos(\Theta)$. Also the collision cross sections in the center-of-mass and lab frames are equal, $\sigma_{\mathrm{lab}} = \sigma_{\mathrm{cm}}$.

The collision process is shown in the accompanying figure.



Let ϕ_0 be the angle of closest approach. Then the scattering angle is given by $\Theta = \pi - 2\phi_0$. The impact parameter is $b = a\sin(\phi_0) = a\cos(\Theta/2)$ so that, $\mathrm{d}b = -(a/2)\sin(\Theta/2)\,\mathrm{d}\Theta$ and $b\,\mathrm{d}b = -(a^2/2)\sin(\Theta/2)\cos(\Theta/2)\,\mathrm{d}\Theta = -(a^2/4)\sin(\Theta)\,\mathrm{d}\Theta$. Therefore

$$\sigma_{\mathrm{cm}}(b,g) = \left|\frac{b}{\sin(\Theta)}\frac{\mathrm{d}b}{\mathrm{d}\Theta}\right| = \frac{a^2}{4} \,.$$

For this special case, the differential scattering cross section is independent of angle. The scattering is isotropic. The total cross section, σ_{tot}, is given by

$$\sigma_{\mathrm{tot}} = \int_0^{\pi} \sigma_{\mathrm{cm}}(b,g) 2\pi \sin(\Theta)\,\mathrm{d}\Theta = \pi a^2 \,.$$

Thus, the total cross section is just the area of the fixed scatterer as seen by the incoming beam.

The total scattering cross section, σ_{tot}, is given by

$$\sigma_{\mathrm{tot}} = \int_0^{\pi} \sin(\Theta)\,\mathrm{d}\Theta \int_0^{2\pi} \mathrm{d}\alpha\,\sigma_{\mathrm{cm}}(b,g) = \int_0^{\pi} \sin(\theta)\,\mathrm{d}\theta \int_0^{2\pi} \mathrm{d}\alpha\,\sigma_{\mathrm{lab}}(b,g) \,. \tag{E.12}$$

The scattering cross section can be thought of as the effective area cutout of the incident beam by the scattering process. This is clear in Exercise E.1, where we compute the cross section for an incident beam of hard-sphere particles colliding with a fixed hard sphere.

From Eqs. (E.9) and (E.11), the relation between the differential scattering cross sections in the center-of-mass and the lab frames is given by

$$\sigma_{\mathrm{lab}} = \frac{\sigma_{\mathrm{cm}}(1+\xi^2+2\xi\cos(\Theta))^{3/2}}{(1+\xi\cos(\Theta))} . \tag{E.13}$$

In Figure E.3b, we picture the scattering process in the center-of-mass frame of reference. In the center-of-mass frame, the scattering event, $(\boldsymbol{p}_1, \boldsymbol{p}_2) \to \left(\boldsymbol{p}_1', \boldsymbol{p}_2'\right)$, and the reverse scattering event, $\left(\boldsymbol{p}_1', \boldsymbol{p}_2'\right) \to (\boldsymbol{p}_1, \boldsymbol{p}_2)$, are identical except that the directions of the particles are reversed. Therefore, $\sigma_{\mathrm{cm}}(b, g)$ is the differential scattering cross section for both the forward and the reverse scattering events in the center-of-mass frame.

E.3
Quantum Dynamics of Low-Energy Scattering

In the center-of-mass frame, the Schrodinger equation for scattering of two identical particles with mass m, which interact via a spherically symmetric potential, can be written

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi_k(\boldsymbol{r}) + V(r)\psi_k(\boldsymbol{r}) = \frac{\hbar^2 k^2}{2\mu}\psi_k(\boldsymbol{r}) , \tag{E.14}$$

where $\mu = m/2$ is the reduced mass. This can be rewritten in the form

$$(\nabla^2 + k^2)\psi_k(\boldsymbol{r}) = \frac{m}{\hbar^2}V(r)\psi_k(\boldsymbol{r}) , \tag{E.15}$$

and the solution can be written

$$\psi_k(\boldsymbol{r}) = \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}} + \frac{m}{\hbar^2}\int \mathrm{d}\boldsymbol{r}'\, G_k(\boldsymbol{r}|\boldsymbol{r}')V(r')\psi_k(\boldsymbol{r}') , \tag{E.16}$$

where

$$(\nabla^2 + k^2)G_k(\boldsymbol{r}|\boldsymbol{r}') = \delta(\boldsymbol{r}' - \boldsymbol{r}') \tag{E.17}$$

and

$$G_k(\boldsymbol{r}|\boldsymbol{r}') = -\frac{\mathrm{e}^{\mathrm{i}k|\boldsymbol{r}-\boldsymbol{r}'|}}{4\pi|\boldsymbol{r}-\boldsymbol{r}'|} . \tag{E.18}$$

In the asymptotic region, $r \gg r'$ and we can write $|\boldsymbol{r} - \boldsymbol{r}'| \approx r - \boldsymbol{r}\cdot\boldsymbol{r}'/r + \ldots$, and the wave function takes the form

$$\psi_k(\boldsymbol{r}) \approx \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}} - \frac{m}{4\pi\hbar^2 r}\mathrm{e}^{\mathrm{i}kr}\int \mathrm{d}\boldsymbol{r}'\,\mathrm{e}^{-\mathrm{i}\boldsymbol{k}'\cdot\boldsymbol{r}'}V(r')\psi_k(\boldsymbol{r}') , \tag{E.19}$$

where $\boldsymbol{k}' = k\boldsymbol{r}/r$.

Now consider scattering between two identical hard-sphere particles of *diameter* a. Also, consider very low energies so the wavelength of the particles is much longer than the diameter and $k = 2\pi/\lambda \ll \mathsf{a}$. Assume the particles approach along the z-axis and then are scattered in the radial direction. The energy eigenstate will be the superposition of the incident plane wave and the scattered spherical wave and can be written

$$\psi_k(\boldsymbol{r}) = \mathrm{e}^{\mathrm{i}kz} + f(\theta)\frac{\mathrm{e}^{\mathrm{i}kr}}{r}\,, \tag{E.20}$$

where $f(\theta)$ is the scattering amplitude. If we choose $\boldsymbol{k} = k\hat{e}_z$ in Eq. (E.19), then the scattering amplitude can be written

$$f(\theta) = -\frac{m}{4\pi\hbar^2}\int \mathrm{d}\boldsymbol{r}'\mathrm{e}^{-\mathrm{i}\boldsymbol{k}'\cdot\boldsymbol{r}'}V(r')\psi_k(\boldsymbol{r}')\,. \tag{E.21}$$

For hard spheres, when $r \leq \mathsf{a}$, then $V(r) = \infty$ and the wave function can't penetrate this region. This means that the wave function $\psi_k(\boldsymbol{r}) = 0$ for $r \leq \mathsf{a}$. If we now use this condition in Eq. (E.20), we can write

$$\psi_k(a,\theta)) = 0 = \mathrm{e}^{\mathrm{i}k\mathsf{a}} + f(\theta)\frac{\mathrm{e}^{\mathrm{i}k\mathsf{a}}}{\mathsf{a}} \tag{E.22}$$

and we obtain $f(\theta) = -\mathsf{a}$. The quantity a is called the scattering length and is a measure of the spatial distance over which the interaction of the particles takes place.

Let us now consider the case of a *contact potential* between the particles $V(\boldsymbol{r}) = g\delta(\boldsymbol{r})$. If we expand Eq. (E.19) in powers of V, and keep only first-order terms, we get

$$f(\theta) = -\frac{m}{4\pi\hbar^2}g + \ldots \tag{E.23}$$

For hard-sphere scattering $f(\theta) = -\mathsf{a}$ and we find

$$g = \frac{4\pi\hbar^2\mathsf{a}}{m}\,. \tag{E.24}$$

It can be shown [136], using partial wave analysis, that all *very low energy* scattering processes can be described in terms of a single effective scattering length a. The value of the effective scattering length depends on the type of particle. For example, for rubidium ^{87}Rb, $\mathsf{a}_{\mathrm{Rb}} = 105a_0$ and for sodium ^{23}Na, $\mathsf{a}_{\mathrm{Na}} = 55a_0$, where a_0 is the Bohr radius. For very dilute boson gases, at very low temperature, the contact potential energy $V(r) = g\delta(r)$ provides a universal means of representing interactions in the gas.

Appendix F
Useful Math and Problem Solutions

F.1
Useful Mathematics

Some useful series expansions:

$$(a+x)^n = a^n + na^{n-1}x + \frac{n(n-1)}{2!}a^{n-2}x^2 \tag{F.1}$$

$$+ \frac{n(n-1)(n-2)}{3!}a^{n-3}x^3 + \cdots + x^n \tag{F.2}$$

$$(1+x)^{-1} = 1 - x + x^2 - x^3 + x^4 - \dots \tag{F.3}$$

$$\ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + \dots \tag{F.4}$$

$$\mathrm{e}^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \dots \tag{F.5}$$

For series given by $y = b_1x + b_2x^2 + b_3x^3 + \dots$, the reverted series is $x = c_1y + c_2y^2 + c_3y^3 + \dots$, where $b_1c_1 = 1$, $b_1^3c_2 = -b_2$, $b_1^5c_3 = 2b_2^2 - b_1b_2, \dots$

Derivatives commonly used:

$$\frac{\mathrm{d}u^n}{\mathrm{d}x} = nu^{n-1}\frac{\mathrm{d}u}{\mathrm{d}x}\,, \quad \frac{\mathrm{d}}{\mathrm{d}x}\ln(u) = \frac{1}{u}\frac{\mathrm{d}u}{\mathrm{d}x} \tag{F.6}$$

Integrals often encountered:

$$\int_0^\infty \mathrm{d}x x^m \mathrm{e}^{-rx^2} = \frac{\Gamma((m+1)/2)}{2r^{(m+1)/2}} \tag{F.7}$$

$$\int_0^\infty \mathrm{d}x \frac{x}{\mathrm{e}^x - 1} = 1.645 \tag{F.8}$$

$$\int_0^\infty \mathrm{d}x \frac{x^2}{\mathrm{e}^x - 1} = 2.404 \tag{F.9}$$

A Modern Course in Statistical Physics, 4. Edition. Linda E. Reichl.

$$\int_0^\infty \mathrm{d}x \frac{x^3}{\mathrm{e}^x - 1} = 6.494 \tag{F.10}$$

Let $f(\boldsymbol{r})$ and $\boldsymbol{A}(\boldsymbol{r})$ denote scalar and vector functions of displacement $\boldsymbol{r}$. Then the following identities apply,

$$\nabla_r \times \left(\nabla_r \times \boldsymbol{A}\right) = \nabla_r \left(\nabla_r \cdot \boldsymbol{A}\right) - \nabla_r^2 \boldsymbol{A} \,, \tag{F.11}$$

$$\nabla_r \cdot \left(\nabla_r \times \boldsymbol{A}\right) = 0 \,, \tag{F.12}$$

$$\nabla_r \times (f\boldsymbol{A}) = (\nabla_r f) \times \boldsymbol{A} + f(\nabla_r \times \boldsymbol{A}) \,, \tag{F.13}$$

$$\begin{aligned}\nabla_r \times (\boldsymbol{A} \times \boldsymbol{B}) = {} & (\boldsymbol{B} \cdot \nabla_r)\boldsymbol{A} - \boldsymbol{B}(\nabla_r \cdot \boldsymbol{A}) \\ & - (\boldsymbol{A} \cdot \nabla_r)\boldsymbol{B} + \boldsymbol{A}(\nabla_r \cdot \boldsymbol{B}) \,.\end{aligned} \tag{F.14}$$

Consider an **orthogonal curvilinear coordinate frame** for which a differential displacement is $\mathrm{d}\boldsymbol{r} = \sum_{i=1}^3 h_i u_i \hat{\boldsymbol{e}}_i$, where $\hat{\boldsymbol{e}}_i$ is the unit vector in the u_i direction. A volume element in this coordinate frame is written $\mathrm{d}V = h_1 h_2 h_3 \, \mathrm{d}u_1 \, \mathrm{d}u_2 \, \mathrm{d}u_3$. Examples of orthogonal curvilinear coordinates include:

Cartesian coordinates with $(u_1, u_2, u_3) = (x, y, z)$ and $(h_1, h_2, h_3) = (1, 1, 1)$;

Cylindrical coordinates with $(u_1, u_2, u_3) = (r, \phi, z)$ and $(h_1, h_2, h_3) = (1, r, 1)$;

Spherical coordinates with $(u_1, u_2, u_3) = (r, \theta, \phi)$ and $(h_1, h_2, h_3) = (1, r, r \sin\theta)$.

The gradient $\nabla_r f(\boldsymbol{r})$, divergence $\nabla_r \cdot \boldsymbol{A}$, curl $\nabla_r \times \boldsymbol{A}$, and Laplacian $\nabla_r^2 f(\boldsymbol{r})$, respectively, are given by

$$\nabla_r f(\boldsymbol{r}) = \frac{\hat{\boldsymbol{e}}_1}{h_1}\frac{\partial f}{\partial u_1} + \frac{\hat{\boldsymbol{e}}_2}{h_2}\frac{\partial f}{\partial u_2} + \frac{\hat{\boldsymbol{e}}_3}{h_3}\frac{\partial f}{\partial u_3} \,, \tag{F.15}$$

$$\nabla_r \cdot \boldsymbol{A} = \frac{1}{h_1 h_2 h_3}\left[\frac{\partial}{\partial u_1}(h_2 h_3 A_1) + \frac{\partial}{\partial u_2}(h_3 h_1 A_2) + \frac{\partial}{\partial u_3}(h_1 h_2 A_3)\right] \tag{F.16}$$

$$\begin{aligned}\nabla_r \times \boldsymbol{A} = {} & \frac{1}{h_2 h_3}\left[\frac{\partial}{\partial u_2}(h_3 A_3) - \frac{\partial}{\partial u_3}(h_2 A_2)\right]\hat{\boldsymbol{e}}_1 \\ & + \frac{1}{h_1 h_3}\left[\frac{\partial}{\partial u_3}(h_1 A_1) - \frac{\partial}{\partial u_1}(h_3 A_3)\right]\hat{\boldsymbol{e}}_2 \\ & + \frac{1}{h_1 h_3}\left[\frac{\partial}{\partial u_3}(h_1 A_1) - \frac{\partial}{\partial u_1}(h_3 A_3)\right]\hat{\boldsymbol{e}}_2\end{aligned} \tag{F.17}$$

$$\begin{aligned}\nabla_r^2 f(\boldsymbol{r}) = {} & \frac{1}{h_1 h_2 h_3}\left[\frac{\partial}{\partial u_1}\left(\frac{h_2 h_3}{h_1}\frac{\partial f}{\partial u_1}\right)\right. \\ & \left. + \frac{\partial}{\partial u_1}\left(\frac{h_2 h_3}{h_1}\frac{\partial f}{\partial u_1}\right) + \frac{\partial}{\partial u_1}\left(\frac{h_2 h_3}{h_1}\frac{\partial f}{\partial u_1}\right)\right]\end{aligned} \tag{F.18}$$

Throughout the book, we use the following convention when dealing with Fourier transforms. The Fourier transform, $\tilde{f}(\omega)$ of function $f(t)$, and the inverse transform are defined

$$\tilde{f}(\omega) = \int_{-\infty}^{\infty} \mathrm{d}t \, \mathrm{e}^{\mathrm{i}\omega t} f(t) \quad \text{and} \quad f(t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega \mathrm{e}^{-\mathrm{i}\omega t} \tilde{f}(\omega) \,, \tag{F.19}$$

respectively. The Laplace transform $\tilde{f}(z)$ of the function $f(t)$ and its inverse transform are defined

$$f(t) = \frac{1}{2\pi \mathrm{i}} \int_{\delta-\mathrm{i}\infty}^{\delta+\mathrm{i}\infty} \mathrm{d}z\, \mathrm{e}^{zt} \tilde{f}(z) \quad \text{and} \quad \tilde{f}(z) = \int_{0}^{\infty} \mathrm{d}t\, \mathrm{e}^{-zt} f(t)\,, \tag{F.20}$$

respectively. Also, the Laplace transform, and inverse transform, of $\mathrm{d}f/\mathrm{d}t$ are

$$\int_{0}^{\infty} \mathrm{d}t\, \mathrm{e}^{-zt} \frac{\mathrm{d}f(t)}{\mathrm{d}t} = z\tilde{f}(z) - f(0) \quad \text{and} \quad \frac{\mathrm{d}f(t)}{\mathrm{d}t} = \frac{1}{2\pi \mathrm{i}} \int_{\delta-\mathrm{i}\infty}^{\delta+\mathrm{i}\infty} \mathrm{d}z\, \mathrm{e}^{zt} z \tilde{f}(z)\,, \tag{F.21}$$

respectively.

F.2
Solutions for Odd-Numbered Problems

Chapter 2

(1) 3 725 568;
(3) (a) 75 600, (b) 2520, (c) 15 120;
(5) 4/10;
(7) (a) 2 598 960, (b) 1.54×10^{-6}, (c) 0.472;
(9) (a) $S = k_\mathrm{B} \ln\{M!/[N!(M-N)!]\}$, (b) $P \approx Nk_\mathrm{B}T/V$;
(11) (a) Multiplicity $= N!/(n_0!n_1!)$,
(b) $S = k_\mathrm{B} \ln\{(N^N)/[(U/\epsilon)^{U/\epsilon}(N - U/\epsilon)^{N-U/\epsilon}]\}$,
(c) $T = \epsilon/[k_\mathrm{B} \ln(n_0/n_1)]$,
(d) $C = [N\epsilon^2/(k_\mathrm{B}T^2)]\mathrm{e}^{\beta\epsilon}/((1 + \mathrm{e}^{\beta\epsilon})^2)$;
(13) $S = k_\mathrm{B} \ln[N!/(n_{-1}!n_0!n_1!)]$, $S_\mathrm{max} = k_\mathrm{B}N \ln(3)$.

Chapter 3

(1) (a) plot, (b) $\Delta Q_{12} = (4/3)aT_\mathrm{h}^4(V_2 - V_1)$, $\Delta Q_{34} = (4/3)aT_\mathrm{c}^4(V_4 - V_3)$, $\Delta Q_{23} = \Delta Q_{41} = 0$, $\eta = 1 + (\Delta Q_{34}/\Delta Q_{12}) = 1 - (T_\mathrm{c}/T_\mathrm{h})$;
(3) $\eta = 1 - (V_1/V_2)^{2/3}$;
(5) $\eta = \alpha L_0^2/(3\alpha L_0^2 + C_{L,M})$;
(7) (a) $(\partial L/\partial T)_{J,n} = (L/T)(1 - (L_0/L)^3)/[1 + 2(L_0/L)^3]$, (b) $J = (aTL/L_0)(1 - (L_0/L)^3)$, (c) $\Delta T = T - T_0 = 0.005T_0$;
(9) (a) $F(T) = \mathrm{d}(T^2B_2')/\mathrm{d}T$, (b) $C_{P,N} = 3Nk_\mathrm{B}/2 - k_\mathrm{B}(N^2/V)\,\mathrm{d}(T^2B_2')/\mathrm{d}T + Nk_\mathrm{B}\{[1 + (N/V)(B_2 + TB_2')]/(1 + 2(N/V)B_2)\}$, (c) $U = (3/2)Nk_\mathrm{B}T - k_\mathrm{B}(N^2/V)\,T^2B' + U_0$, $S = k_\mathrm{B}N \ln(VT^{3/2}) - k_\mathrm{B}(N^2/V)(B_2 + TB_2') + S_0$
(11) $s = c\ln(u/u_0) - (1/2D)(m^2 - m_0^2) + s_0$, $H = [ncT_0 - (M^2T_0)/(nD)] \exp[(S - S_0)/(nc) + (M^2 - M_0^2)/(2n^2cD)]$, $A = ncT - ncT\ln(T/T_0) + (T/(2nD))(M^2 -$

$M_0^2) - S_0T$, $G = ncT - ncT\ln(T/T_0) - (nD/2)(H^2/T + TH_0^2/T_0^2) - S_0T$;
(15) (a)$F(P) = R/P^2$, (b) $v = (RT/P) - [a/(RT)] - b\ln(P) + v_0$, (c) $b > 0$;
(17) (a) $F(P) = R/P^2$, (b) $v = 1/(A/T - RT/P + C)$;
(19) (a) $(U_s/A) = \sigma_0[(1 - t/t')^{0.2}]\{1 - t/t' + [1.2(273 + t)]/t'\}$, (b) plot;
(21) $\langle \Delta h_i)^2\rangle = (k_BTv)/(N_0\kappa_s) + (k_Bc_PT^2)/N_0$;
(23) $\langle(\Delta s_i)^2\rangle = (c_v^2T_0\kappa_T)/[N_0(c_v\kappa_TT_0 - \alpha_P^2v)]$, $\langle\Delta s_i\Delta v_i\rangle = (c_vT_0\kappa_Tv\alpha_P)/[N_0(c_v\kappa_TT_0 - \alpha_P^2v)]$, $\langle(\Delta v_i)^2\rangle = (c_vT_0^2\kappa_T^2v)/[N_0(c_v\kappa_TT_0 - \alpha_P^2v)]$;
(25) (a) $(\partial T/\partial V)_{U,n} = \{-an^2/[C_{V,n}V(V - nb)]\}\exp[-na/(VRT)]$,
(b) $(\partial T/\partial P)_{H,n} = (V/C_{P,n})(2abn^2 - 2anV + nbRTV)/(anV - abn^2 - RTV^2)$,
(c) $T_{\max} = a/(bR)$;
(27) (a) $T_f = \sum_{i=1}^m x_iT_i$, $P_f = \sum_{i=1}^m P_i$, $\Delta S_{\text{mix}} = (5R/2)\sum_{i=1}^m n_i\ln(T_f/T_i) - R\sum_{i=1}^m n_i\ln(x_i)$, (b) $\Delta S = 2.41R$;
(29) $m_{\text{hemoglobin}} = 6.88 \times 10^4$ u;
(31) (a) $\Delta\mu_A = (1/2)(2\lambda_{AB} - \lambda_{AA} - \lambda_{BB})(x_B^2 - (x_B^0)^2) + RT\ln[(1 - x_B)/(1 - x_B^0)]$, (b) decreases;
(33) (a) $G(T,P) = \sum_i n_i\mu_i^0(P_0, T_0) - \sum_i n_iRT\ln[(T/T_0)^{5/2}(P_0/P)] + RT\ln[(1 - \xi)^{2-2\xi}(\xi/2)^{2\xi}]$, (b) $A(T,P) = 4.01 + RT\ln[(\xi/2)^2/(1 - \xi)^2]$, (c) $\xi_{eq} = 0.064$, $n_{HI}^{eq} = 1.872$, $n_{H_2}^{eq} = 0.064$, $n_{I_2}^{eq} = 0.064$, (d) $\xi_{eq} = 0.064$, $n_{HI}^{eq} = 1.872$, $n_{H_2}^{eq} = 0.064$, $n_{I_2}^{eq} = 0.064$ (no change), (e) $(\partial H/\partial\xi)_{P,T}^0 = 6.76RT_0$.

Chapter 4

(1) (a) $P = RT/(v - b) - (a/v^2)$, (b) $c_P = R\{5/2 + [1 - (2a(v - b)^2)/(v^3RT)]^{-1}\}$, (c) $\ell = RT\ln[(v_g - b)/(v_\ell - b)]$;
(3) $(dP/dT)_{\text{sub}} \to [P_t(\Delta h_{sl} + \Delta h_{lg})]/T_t^2$ and $(dP/dT)_{\text{vap}} \to [P_t(\Delta h_{lg})]/T_t^2$;
(5) (a) plot, (b) $P = 1.1866 \times 10^4$ Pa;
(7) $h_d = 2564$ kJ/kg, $x_\ell = 0.1169$;
(9) (a) $g_s = (4B/T)(TP/3B)^{3/4}$, $g_l = (3A/T)(TP/2A)^{2/3}$, (b) $v_l = 8v_s/9$ and $v_s = (PT/3B)^{3/4}$, (c) $(dP/dT)_{\text{coex}} = (Av_s^3 - Bv_l^2)/[T^2v_l^2v_s^3(v_l - v_s)]$;
(11) (a) plot, (b) not;
(13) derive given eqs.;
(15) $(dP/dT) = \Delta c_p/(vT\Delta\alpha_P)$;
(17) 74%;
(19) (a) $\phi = \phi_0 + (1/3)A\eta^2 - (2/27)B\eta^3 + (1/9)C\eta^4$, (b) $\eta_c = B/(3C)$, (c) $\Delta s = -(A_0B^2)/(27C^2)$;
(21) (a) $T_c = \lambda/(2R)$, (b) $x_A = 0.123$, $x_A = 0.869$, (c) $x_A = 0.0.030$, $x_A = 0.962$;
(23) $T = (\lambda/2R)(1 - x_c)$, $x_a = (1/2) + (x_c/2)$.

Chapter 5

(1) $\chi_{T,N} = -(\partial^2\Phi/\partial B^2)_{T,N} = \beta\langle M_T\rangle_{eq}^2$, magnetic susceptibility;
(3) $f_1 = 0.217$, $f_2 = f_3 = 0.148$, $f_4 = f_5 = f_6 = 0.101$, $f_7 = f_8 = 0.069$, $f_9 = 0.047$;
(5) $Z_N = (1/N!)[(V - Nb)/\lambda_T^3]^N\exp[aN^2/(k_BTV)]$, $P = [Nk_BT/(V - Nb)] - (aN^2/V^2)$, $U = (3/2)Nk_BT - (aN^2/V)$, $S = (5/2)Nk_B + Nk_B\ln[(V - Nb)/(N\lambda_T^3)]$

with $T = [2/(3Nk_\mathrm{B})][U + (aN^2/V)]$;
(7) (a) $\omega_\mathrm{D}^2 = (8N\pi/A)(c_\mathrm{t}^{-2} + c_\mathrm{l}^{-2})^{-1}$, (b) $C \to (28.8Nk_\mathrm{B}T^2)/T_\mathrm{D}^2$;
(9) (a) 0.368, (b) 0.4;
(11) (a) $\mu_\mathrm{I} = -k_\mathrm{B}T\ln[V/(N_\mathrm{I}\lambda_T^3)]$, $\mu_{\mathrm{I}_2} = -k_\mathrm{B}T\ln[2^{3/2}V/(N_{\mathrm{I}_2}\lambda_T^3)] - k_\mathrm{B}T\ln(T/\theta_\mathrm{rot})$, (b) $(N_\mathrm{I}^2/N_{\mathrm{I}_2}) = (V\theta_\mathrm{rot})/(\lambda_T^3 2^{3/2}T)$, (c) increases;
(13) (a) $S_\mathrm{mix} = (15Nk_\mathrm{B}/2) + 3Nk_\mathrm{B}\ln[VT^{3/2}/(N\lambda_0^3)]$, $S_\mathrm{red} = (15Nk_\mathrm{B}/2) + 3Nk_\mathrm{B}\ln[VT^{3/2}/(3N\lambda_0^3)]$, $\Delta S = 3Nk_\mathrm{B}\ln[3]$;
(15) $\langle s_1 s_2\rangle = \tanh(\beta\epsilon)$, $T \to 0$ then $\langle s_1 s_2\rangle \to 1$, $T \to \infty$ then $\langle s_1 s_2\rangle \to 0$;
(17) (a) $\beta = 1$, (b) $\delta = 1.5$, (c) $\gamma = 0.5$, (d) $\alpha = -0.5$, Not agree;
(19) $\alpha = -0.220$, $\beta = 0.605$, $\gamma = 1.010$, $\delta = 2.670$.

Chapter 6

(1) (a) $B_2(T) = (b/N_\mathrm{A}) - [a/(N_\mathrm{A}^2 k_\mathrm{B}T)]$, (b) $a = (2/3)(\pi\sigma^3\epsilon N_\mathrm{A}^2)(\lambda^3 - 1)$, $b = (2/3)\pi\sigma^3 N_\mathrm{A}$, (c) $\sigma = 3.2 \times 10^{-10}$ m, $\epsilon = 0.012\,64$ eV;
(3) $B_2 = 2\pi\{\lambda^3R^3/3 - [R^3(\lambda - 1)/(\beta\epsilon)]\{(\lambda^2 - \exp(\beta\epsilon)) + [(2(\lambda - 1)(\lambda - \exp(\beta\epsilon)))/(\beta\epsilon)] + [(2(\lambda^2 - 1)^2[1 - \exp(\beta\epsilon)])/(\beta^2\epsilon^2)]\}\}$;
(5) $B_2 = -(2/3)\pi f_0 R^3$;
(7) (a) $T_\mathrm{c} = 1.7 \times 10^{-7}$ K, (b) $V = 1.76 \times 10^{-14}$ m^3;
(9) $T_\mathrm{c} = [2\pi\hbar/(mk_\mathrm{B})][(\langle N\rangle/V)/(g_{3/2}(1) + g_{3/2}(\mathrm{e}^{-\beta_\mathrm{c}\Delta})]^{2/3}$, lowers T_c;
(11) $U = ((3\sqrt{\pi}k_\mathrm{B}TV)/(2\sqrt{2}\lambda_T^3))\mathrm{PolyLog}[(5/2), z]$, $\alpha = 2/3$;
(13) (a) $\epsilon_\mathrm{F} = 1.14 \times 10^{-18}$ J, $T_\mathrm{c} = \epsilon_\mathrm{F}/k_\mathrm{B} = 83\,000$ K;
(15) (a) $\epsilon_\mathrm{F} = \langle N\rangle/D$, (b) $C = (\langle N\rangle\pi^2k_\mathrm{B}^2T)/(3\epsilon_f)$;
(17) derive given eq.;
(19) (a)$\langle N^2\rangle - \langle N\rangle^2 = \langle N\rangle$, (b) $\langle N^2\rangle - \langle N\rangle^2 = \langle N\rangle\{1 + [(\langle N\rangle\lambda_T^3)/(2^{3/2}V)] + \dots\}$, (c) $\langle N^2\rangle - \langle N\rangle^2 = \langle N\rangle\{1 - [(\langle N\rangle\lambda_T^3)/(2^{3/2}V)] + \dots\}$;
(21) derive given eq.

Chapter 7

(1) $S_{v,v}(\omega) = (4\gamma k_\mathrm{B}T\omega^2)/[m(\omega_0^2 - 2\delta\omega + \omega^2)(\omega_0^2 + 2\delta\omega + \omega^2)]$, plot;
(3) (a) $(\partial P/\partial t) = (\gamma/m)(\partial(vP)/\partial v) + (g/m^2)(\partial^2P/\partial v^2)$, (b) $P(v, \tau) = \{2\pi A[1 - \exp(-2\tau)]\}^{-1/2}\exp\{-[(v - v_0\exp(-\tau))^2]/[2A(1 - \exp(-2\tau))]\}$;
(5) (a) $K(t) = \{\Theta(t)\exp(-\gamma t/(2m))\sin[\sqrt{\omega_0^2 - \gamma^2/(4m^2)t}]\}/[m\sqrt{\omega_0^2 - \gamma^2/(4m^2)}]$, $W_\mathrm{abs} = -F_0^2/(2m)$;
(7) (a) $g = 2Rk_\mathrm{B}T$, (b) $K(t) = (1/R)\exp[-t/(RC)]\Theta(t)$, (c) $C_{Q,Q}(t) = k_\mathrm{B}TC\exp(-t/RC)$;
(9) (a) $(\mathrm{d}M_x/\mathrm{d}t) = -\gamma M_yH_0 - (M_x/T_2)$, $(\mathrm{d}M_y/\mathrm{d}t) = -\gamma(M_0 - M_z)H_1\cos(\omega_0t) + \gamma M_xH_0 - (M_yT_2)$, $(\mathrm{d}M_z/\mathrm{d}t) = -\gamma M_yH_1\cos(\omega_0t) - (M_zT_1)$, (b) $K_{xx}(t) = \gamma M_0\mathrm{e}^{-t/T_2}\sin(\gamma H_0t)\Theta(t)$, (c) $P(2\pi/\omega_0) = (\omega_0^2\gamma^2M_0H_0H_1^2/T_2)/\{[(1/T_2)^2 + (\gamma H_0)^2 - \omega_0^2]^2 + 4\omega_0^2/T_2^2\}$;
(11) prove given eq.

Chapter 8

(1) prove given eq.;
(3) $\rho_{\boldsymbol{k}}(t) = [1 - (1/\gamma) + (1/\gamma)\cos(kc_0t)]\rho_{\boldsymbol{k}}(0) + \mathrm{i}(\rho_0/c_0)\sin(kc_0t)v_{\boldsymbol{k}}^{\parallel}(0) - (\alpha_P\rho_0/\gamma)[1 - \cos(kc_0t)]T_{\boldsymbol{k}}(0)$, $v_{\boldsymbol{k}}^{\parallel}(t) = +\mathrm{i}(c_0/\rho_0\gamma)\sin(kc_0t)\rho_{\boldsymbol{k}}(0) + \cos(kc_0t)v_{\boldsymbol{k}}^{\parallel}(0) + \mathrm{i}(\alpha_Pc_0/\gamma)\sin(kc_0t)T_{\boldsymbol{k}}(0)$, $T_{\boldsymbol{k}}(t) = +[(1-\gamma)/(\rho_0\gamma\alpha_P)][1 - \cos(kc_0t)]\rho_{\boldsymbol{k}}(0) + \mathrm{i}[(1-\gamma)/(c_0\alpha_P)]\sin(kc_0t)v_{\boldsymbol{k}}^{\parallel}(0) + \{(1/\gamma) + [1 - (1/\gamma)]\cos(kc_0t)\}T_{\boldsymbol{k}}(0)$;
(5) $v_{\boldsymbol{k}}^{\perp}(t) = v_0\sin(\theta)[(\pi/a)^{3/2}]\exp[-k^2/(4a^2)]\exp(-\eta k^2t/\rho_0)$.
(7) (a) $(\partial\rho/\partial T)_P(\partial^2\Delta T/\partial t^2) + (\partial\rho/\partial P)_T(\partial^2\Delta P/\partial t^2) - \nabla^2\Delta P = 0$, $(\partial S/\partial T)_P(\partial\Delta T/\partial t) + (\partial S/\partial P)_T(\partial\Delta P/\partial t) - (K/T_0)\nabla^2\Delta T = 0$, (b) $k^4 - k^2\{[(\mathrm{i}\omega C_p)/K] + (\omega^2/c_T^2)\} + \mathrm{i}\omega^3(C_p/(Kc_S^2)) = 0$;
(9) $\tau = (\rho_0D^2)/(\eta\pi^2) = 253\,\mathrm{s}$;
(11) $S_{\rho,\rho}(\boldsymbol{k},t) = \langle|\rho_{\boldsymbol{k}}(0)|^2\rangle\{[1 - (1/\gamma)]\exp(\chi k^2|t|) + (1/\gamma)\cos(c_0kt)\exp(-\Gamma k^2|t|) + [k/(c_0\gamma)][\Gamma + \chi(\gamma - 1)]\sin(c_0kt)\exp(-\Gamma k^2|t|)\}$, (b) k-correction 10^{-2} smaller;
(13) $F = 4\pi a^2\eta\hat{\boldsymbol{e}}_z$;
(15) $(\Gamma/T) = L_{SE}R$, $L_{ES} = L_{EE}\zeta$, $L_{EE} = 1/R$, $L_{ES} = L_{SE}$ so $\zeta = -\Gamma/T$;
(17) prove given eq.;
(19) show given results.

Chapter 9

(1) $n(v > v_0) = (n_0/\sqrt{2\pi m\beta})(1 + (\beta mv_0^2/2))\exp[-\beta mv_0^2/2]$;
(3) (a) $\mathrm{d}^2n/(\mathrm{d}t\,\mathrm{d}A) = 2N/(3mV)[2m/(\pi\beta)]^{1/2}$, (b) $\mathrm{d}^2n/(\mathrm{d}t\,\mathrm{d}A) = 0$;
(5) (a) $n(\boldsymbol{v}) = 2m^3/h^3\{\exp[\beta((mv^2/2) - \mu)] + 1\}^{-1}$, (b) $j_zA = (4\pi m^2eA/(h^3\beta^2))\exp(-\beta|W - \mu|)$;
(7) (a) $\eta = nk_\mathrm{B}T/\gamma$, (b) $K = 5nk_\mathrm{B}^2T/(2\gamma m)$, (c) $\gamma \sim \mathrm{sec}^{-1}$;
(9) $D = 3/(32n_0a^2)\sqrt{k_\mathrm{B}T/(m\pi)}$.

Chapter 10

(1) (a) Steady state if $x^3 - ax^2 + \kappa x - b = 0$ with $a = k_1c_A/k_2$, $b = k_4c_B/k_2$, $x = c_X$, $\kappa = k_3/k_2$, (b) At equilibrium $(c_B^{\mathrm{eq}}/c_A^{\mathrm{eq}}) = k_4k_2/(k_1k_3)$. Multiple steady states begin to occur at critical point $a_\mathrm{c} > \sqrt{3\kappa}$, $x > a/3$, and $(c_a)_\mathrm{c}/(c_B)_\mathrm{c} > 9k_4k_2/(k_1k_3)$;
(3) $(\mathrm{d}c_X/\mathrm{d}t) = k_1c_A - (k_1' + k_4)c_X + k_2'c_Yc_D - k_2c_Bc_X + k_3c_X^2c_Y - k_3'c_X^3 + k_4'c_E$ and $(\mathrm{d}c_Y/\mathrm{d}t) = -k_2'c_Yc_D + k_2c_Bc_X - k_3c_X^2c_Y + k_3'c_X^3$, (b) Equilibrium $c_X^{\mathrm{eq}} = (k_1c_A + k_4'c_E)/(k_1' + k_4)$ and $c_Y^{\mathrm{eq}} = (k_2c_Bc_X^{\mathrm{eq}} + k_3'(c_X^{\mathrm{eq}})^3)/(k_2'c_D + k_3(c_X^{\mathrm{eq}})^2)$. Far from equil. steady state $c_X^s = k_1c_A/k_4$ and $c_Y^s = k_2c_B/(k_3c_X^s)$. If $X = \sqrt{k_3/k_4}c_X$, $B = k_2c_B/k_4$, $Y = \sqrt{k_3/k_4}c_Y$, $A = \sqrt{k_1^2k_3/k_4^3}c_A$ then $X = A$ and $Y = B/A$;
(5) Smallest Rayleigh number for transition is $\mathrm{R} = [(\pi^2 + \beta^3)/\beta^2]$.
$v_z(\boldsymbol{r}) = A\sin(\pi z/d)\cos(\pi x/(2d))\cos(\pi y/(2d))$, cell size $4d$ across.

Appendix A

(1) (a) $\langle xy\rangle - \langle x\rangle\langle y\rangle = 0$, (b) $\langle xy\rangle - \langle x\rangle\langle y\rangle = -1$ and X and Y not independent;
(3) (a) $P^B_{12}(3) = 0.2581$, $P^B_{120}(30) = 0.0839$, (b) $P^G_{12}(3) = 0.2660$, $P^G_{120}(30) = 0.0841$, (c) plot, values agree ±0.01 for $N = 12$ and ±0.001 for $N = 120$;
(5) (a) $\langle V\rangle/R = 9v_0^2/R$, (b) $\langle V\rangle/R = v_0^2/(9R)$;
(7) (a) $P_S(s) = (1/\sqrt{2\pi N\sigma^2})\exp\{-[(s-Na)^2]/(2N\sigma^2)\}$, (b) $\langle S\rangle = Na$, $\sigma_S = \sqrt{n}\sigma$;
(9) (a) $Q_{1,1} = Q_{2,2} = Q_{3,3} = Q_{2,1} = 0$, $Q_{1,2} = Q_{1,3} = (1/2)$, $Q_{3,1} = 3/4$, $Q_{3,2} = 1/4$. Eigenvalues $\lambda_1 = 1, \lambda_2 = (-1/2) + \mathrm{i}/(2\sqrt{2}), \lambda_2 = (-1/2) - \mathrm{i}/(2\sqrt{2})$. Right eigenvectors $\psi_1 = (1, 1, 1)^{\mathrm{T}}$, $\psi_2 = (-0.222 + 0.786\mathrm{i}, -1.333 - 0.942\mathrm{i}, 1)^{\mathrm{T}}$, $\psi_3 = (-0.222 - 0.786\mathrm{i}, -1.333 + 0.942\mathrm{i}, 1)^{\mathrm{T}}$. Left eigenvectors $\xi_1 = (0.316, 0.263, 0.421)$, $\xi_2 = (-0.421 - 0.019\mathrm{i}, 0.132 + 0.205\mathrm{i}, 0.289 - \mathrm{i}0.186)$, $\xi_3 = (-0.421 + 0.019\mathrm{i}, 0.132 - 0.205\mathrm{i}, 0.289 + \mathrm{i}0.186)$, (b) A has it 6/19, B has it 5/19, C has it 8/19. (c) 3/8.

Table F.1 Name, symbol, atomic number (proton number) for elements in the periodic table shown on back inside cover.

Actinium	Ac	89	Gold	Au	79	Praseodymium	Pr	59
Aluminum	Al	13	Hafnium	Hf	72	Promethium	Pm	61
Americium	Am	95	Hassium	Hs	108	Protoactinium	Pa	91
Antimony	Sb	51	Helium	He	2	Radium	Ra	88
Argon	Ar	18	Holmium	Ho	67	Radon	Rn	86
Arsenic	As	33	Hydrogen	H	1	Roentgenium	Rg	111
Astatine	At	85	Indium	In	49	Rhenium	Re	75
Barium	Ba	56	Iodine	I	53	Rhodium	Rh	45
Berkelium	Bk	97	Iridium	Ir	77	Rubidium	Rb	37
Beryllium	Be	4	Iron	Fe	26	Ruthenium	Ru	44
Bismuth	Bi	83	Krypton	Kr	36	Rutherfordium	Rf	104
Bohrium	Bh	107	Lanthanium	La	57	Samarium	Sm	62
Boron	B	5	Lawrencium	Lr	103	Scandium	Sc	21
Bromine	Br	35	Lead	Pb	82	Seaborgium	Sg	106
Cadmium	Cd	48	Lithium	Li	3	Selenium	Se	34
Calcium	Ca	20	Lutetium	Lu	71	Silicon	Si	14
Californium	Cf	98	Magnesium	Mg	12	Silver	Ag	47
Carbon	C	6	Manganese	Mn	25	Sodium	Na	11
Cerium	Ce	58	Meitnerium	Mt	109	Strontium	Sr	38
Cesium	Cs	55	Mendelevium	Md	101	Sulfur	S	16
Chlorine	Cl	17	Mercury	Hg	80	Tantalum	Ta	73
Chromium	Cr	24	Molybdenum	Mo	42	Technetium	Tc	43
Cobalt	Co	27	Neodymium	Nd	60	Tellurium	Te	52
Copper	Cu	29	Neon	Ne	10	Terbium	Tb	65
Curium	Cm	96	Neptunium	Np	93	Thallium	Tl	81
Darmstadtium	Ds	110	Nickel	Ni	28	Thorium	Th	90
Dubnium	Db	105	Niobium	Nb	41	Thulium	Tm	69
Dysprosium	Dy	66	Nitrogen	N	7	Tin	Sn	50
Einsteinium	Es	99	Nobelium	No	102	Titanium	Ti	22
Erbium	Er	68	Osmium	Os	76	Tungsten	W	74
Europium	Eu	63	Oxygen	O	8	Uranium	U	92
Fermium	Fm	100	Palladium	Pd	46	Vanadium	V	23
Fluorine	F	9	Phosphorus	P	15	Xenon	Xe	54
Francium	Fr	87	Platinum	Pt	78	Ytterbium	Yb	70
Gadolinium	Gd	94	Plutonium	Pu	94	Yttrium	Y	39
Gallium	Ga	31	Polonium	Po	84	Zinc	Zn	30
Germanium	Ge	32	Potassium	K	19	Zirconium	Zr	40

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