Substitution of σ_1 from Eq. (A2) into Eq. (12a) and the equating of coefficients of $\exp i\nu t$ gives

$$A_+=\frac{\sigma_0[\varphi_1(\omega-\tilde{\eta}_{12})+\tilde{\eta}_{11}\varphi_2+i\nu\varphi_2]}{-\nu^2+i(\tilde{\eta}_{11}+\tilde{\eta}_{22})\nu+\omega'^2}, \tag{A4}$$

where

$$\varphi_i=\mathbf{a}_i\cdot\boldsymbol{\varphi}. \tag{A5}$$

From Eq. (A4) we obtain

$$\mathrm{Re}A_+=(\sigma_0/D)[\varphi_1(\omega-\tilde{\eta}_{12})(\omega'^2-\nu^2)+\varphi_2(\tilde{\eta}_{22}\nu^2+\tilde{\eta}_{11}\omega'^2)], \tag{A6}$$

and

$$\mathrm{Im}A_+=i(\sigma_0/D)\nu[-\varphi_1(\tilde{\eta}_{11}+\tilde{\eta}_{22})(\omega-\tilde{\eta}_{12})+\varphi_2(\omega^2-\nu^2-\tilde{\eta}_{12}^2-\tilde{\eta}_{11}^2)], \tag{A7}$$

where

$$D=(\omega'^2-\nu^2)^2+\nu^2(\tilde{\eta}_{11}+\tilde{\eta}_{22})^2. \tag{A8}$$

Setting

$$\sigma_2=B_+e^{i\nu t}+B_-e^{-i\nu t}, \tag{A9}$$

with

$$B_-=B_+^*, \tag{A10}$$

we obtain, in an entirely analogous manner

$$\mathrm{Re}B_+=(\sigma_0/D)[\varphi_2(\omega+\tilde{\eta}_{12})(\omega'^2-\nu^2)-\varphi_1(\tilde{\eta}_{11}\nu^2+\tilde{\eta}_{22}\omega'^2)], \tag{A11}$$

and

$$\mathrm{Im}B_+=-i\nu(\sigma_0/D)[\varphi_2(\tilde{\eta}_{11}+\tilde{\eta}_{22})(\omega+\tilde{\eta}_{12})+\varphi_1(\omega^2-\nu^2-\tilde{\eta}_{12}^2-\tilde{\eta}_{22}^2)]. \tag{A12}$$

APPENDIX B

The average power P absorbed by the TLS from the field is given by $\langle\mathfrak{F}\cdot\mathbf{d}\rangle_{\mathrm{av}}$, where $\mathfrak{F}$ is the field vector. Since

$$\mathfrak{F}=-(\hbar/2\mu)\mathbf{f}, \tag{A13}$$

we have, from Eq. (1),

$$P=-\tfrac{1}{2}\hbar\textstyle\sum_i\langle f_i\dot{\sigma}_i\rangle_{\mathrm{av}}, \tag{A14}$$

which is Eq. (13) of the text. In first order, σ_3 is constant, and we therefore have, for a weak field.

$$P=-\tfrac{1}{2}\hbar\langle f_1\dot{\sigma}_1+f_2\dot{\sigma}_2\rangle_{\mathrm{av}}=-i\hbar\nu(\varphi_1\,\mathrm{Im}A_++\varphi_2\,\mathrm{Im}B_+). \tag{A15}$$

Utilizing Eqs. (A7) and (A12), we obtain

$$P=-\hbar\nu^2(\tilde{\eta}_{11}+\tilde{\eta}_{22})(\sigma_0/D)[\omega(\varphi_1^2+\varphi_2^2)+\tilde{\eta}_{12}(\varphi_2^2-\varphi_1^2)+\varphi_1\varphi_2(\tilde{\eta}_{11}-\tilde{\eta}_{22})], \tag{A16}$$

which—with the notational definitions of Eqs. (7), and in dyadic notation—is identical to Eq. (15).

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Theory of Thermal Transport Coefficients*

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A simple proof of the usual correlation-function expressions for the thermal transport coefficients in a resistive medium is given. This proof only requires the assumption that the phenomenological equations in the usual form exist. It is a "mechanical" derivation in the same sense that Kubo's derivation of the expression for the electrical conductivity is. That is, a purely Hamiltonian formalism with external fields is used, and one never has to make any statements about the nature or existence of a local equilibrium distribution function, or how fluctuations regress. For completeness the analogous formulas for the viscosity coefficients and the heat conductivity of a simple fluid are given.

I. INTRODUCTION

In recent years there has been considerable interest in certain general formulas for transport coefficients. These formulas express the transport coefficients in terms of certain correlation functions and are in principle more general than the use of any transport equation. Such general expressions seem to have been first given by Green[1] for transport in fluids. For the electrical transport coefficients the analogous formulas seem first to have been published by Kubo.[2] Since the latter's formula for the electrical conductivity tensor is perhaps the most widely used of these formulas, they are often known as "Kubo" formulas.

In obtaining such formulas, two different approaches have been used. For the electrical conductivity problem one can simply study the linear response of the system to an external electrical field and calculate the currents that flow. This leads unambiguously to Kubo's formula for the electrical conductivity tensor and seems very hard to object to. Such derivations we will call "mechanical" because they arise from studying a problem with a well-defined Hamiltonian (that of system plus interaction with external field). On the other hand, to obtain, say, the thermal conductivity, there exists no mechanical formulation, since there is no

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[1] M. S. Green, J. Chem. Phys. **20**, 1281 (1952); **22**, 398 (1954). From a quite different point of view, equivalent formulas were obtained by H. Mori, Phys. Rev. **112**, 1829 (1958).

[2] R. Kubo, J. Phys. Soc. Japan **12**, 570 (1957); R. Kubo, M. Yokota, and S. Nakajima, *ibid.*, p. 1203.

Hamiltonian which describes a thermal gradient. (The temperature is a statistical property of the system.) In this case, the derivations have been carried out using local variables (variables describing macroscopic but small portions of the system) and some assumptions about how these variables develop in time. In Green's derivation, the assumption is essentially that such variables are controlled by a Markoff process; in Mori's derivation the form of the "local equilibrium distribution" is assumed. Although these derivations are not as rigorous as Kubo's mechanical one, they are quite plausible, and there has been little doubt that the resulting formulas are correct. Recently, however, such formulas have been questioned by Prigogine,[3] Cohen,[4] and their co-workers on the basis of a model of an imperfect gas at low densities. Since the Green-Kubo-Mori (GKM) formulas are being applied widely (especially in solid-state physics), we attempt in this paper to put them on a more solid basis. That is, we show that it is possible to give them an essentially mechanical derivation, analogous to the Kubo formula for the electrical conductivity.

To understand what is involved in such a derivation we first consider the problem of the self-diffusion coefficient. This is quite difficult to obtain by a direct mechanical argument. However, we may proceed as follows. First calculate the electrical conductivity tensor similarly to Kubo, then use the Einstein relationship[5] between the diffusion coefficient and the electrical conductivity tensor. The Einstein relationship is quite general, depending only on the existence of the phenomenological equations relating current, electrical field, and concentration gradient, and may hardly be doubted. Similarly, to study the thermal-transport phenomena we may introduce a field (essentially an inhomogeneous gravitational field) which causes energy or heat currents to flow. After the coefficients which relate this field to the currents are obtained, an argument analogous to the Einstein argument relating electrical conductivity to diffusion is again used, and in this way the thermal coefficients are obtained.

In Sec. II we shall carry out the process in more detail for the diffusion coefficient, and in Sec. III the derivation of the GKM formulas for the thermal-transport coefficients will be given. In Appendix A, some necessary formulas from equilibrium statistical mechanics are derived, while in Appendix B the "mechanical" derivations of the viscosity and heat-conductivity coefficients for a simple fluid are given.

II. RESPONSE TO AN ELECTRIC FIELD

For simplicity we shall restrict ourselves to a one-component system of particles of charge e. Let an external electrostatic potential φ be gradually turned on, so that the electrostatic potential at a point $\mathbf{r}$ is

$$\varphi=\varphi(\mathbf{r})e^{st}, \tag{1.1}$$

where s is a small positive quantity. If the Hamiltonian of the system is without field is H, then the total Hamiltonian H_T is given by

$$H_T=H+Fe^{st}, \tag{1.2}$$

where

$$F=\int\rho(\mathbf{r})\varphi(\mathbf{r})d\mathbf{r}, \tag{1.3}$$

and $\rho(\mathbf{r})$ is the charge-density operator for the system, i.e.,

$$\rho(\mathbf{r})=en(\mathbf{r}), \tag{1.4}$$

where $n(\mathbf{r})$ is the number-density operator.

The density matrix (ρ_T) at any instant of time is given by ($\hbar=1$)

$$i(\partial\rho_T/\partial t)=[H_T,\rho_T]. \tag{1.5}$$

Since we are interested in the *linear* response to the field, we may write

$$\rho_T=\rho+fe^{st}, \tag{1.6}$$

where ρ is the equilibrium density matrix for the system (corresponding to its condition when the field is turned on at $t=-\infty$) and f is linear in the external field. Substituting (1.6) in (1.5) and retaining only linear terms, we obtain

$$[H,f]-isf=C, \tag{1.7}$$

where

$$C=[\rho,F]. \tag{1.8}$$

As may easily be verified by going to the representation where H is diagonal, the solution of (1.7) is given by

$$f=i\int_0^\infty dte^{-st}C(-t), \tag{1.9}$$

where for a general operator A, $A(t)$ is defined by

$$A(t)=e^{iHt}Ae^{-iHt}. \tag{1.10}$$

Similarly, we verify at once that

$$C=i\rho\int_0^\beta d\beta'\dot{F}(-i\beta'), \tag{1.11}$$

$$\dot{F}=i[H,F]=\int d\mathbf{r}\dot{\rho}(\mathbf{r})\varphi(\mathbf{r}), \tag{1.12}$$

$\beta=1/kT$, where T is the original equilibrium temperature at $t=-\infty$. This is true when ρ is represented by a grand canonical distribution, which we shall assume from now on. Therefore,

$$f=-\rho\int_0^\infty dte^{-st}\int_0^\beta d\beta'\dot{F}(-t-i\beta'). \tag{1.13}$$

The charge-density operator is given by

$$\rho(\mathbf{r})=e\sum_j\delta(\mathbf{r}-\mathbf{r}_j), \tag{1.14}$$

[3] I. Prigogine and G. Severne, Phys. Letters **6**, 177 (1963).
[4] E. G. D. Cohen, Phys. Letters **5**, 192 (1963). Professor Cohen has kindly informed me that since the publication of his Letter a computational error has been found in his work, and now he obtains agreement with the Kubo type formula.
[5] A. Einstein, Ann. Physik **17**, 549 (1905).

where $\mathbf{r}_j$ is the position of the jth particle. From this, the equation of continuity follows at once:

$$\dot{\rho}(\mathbf{r})+\nabla\cdot\mathbf{j}(\mathbf{r})=0, \qquad (1.15)$$

where $\mathbf{j}(\mathbf{r})$ is the current-density operator

$$\mathbf{j}(\mathbf{r})=(e/2)\sum_j(\mathbf{v}_j\delta(\mathbf{r}-\mathbf{r}_j)+\delta(\mathbf{r}-\mathbf{r}_j)\mathbf{v}_j). \qquad (1.16)$$

Here $\mathbf{v}_j$ is the velocity operator for the jth particle. If we assume velocity-independent interactions among the particles and no external magnetic field, for example,

$$\mathbf{v}_j=\mathbf{p}_j/m, \qquad (1.17)$$

then

$$\dot{F}=\int d\mathbf{r}[-\nabla\cdot\mathbf{j}(\mathbf{r})]\varphi(\mathbf{r})$$

$$=\int d\mathbf{r}\mathbf{j}(\mathbf{r})\cdot\nabla\varphi(r)=-\int d\mathbf{r}\mathbf{j}(\mathbf{r})\cdot\mathbf{E}(r), \qquad (1.18)$$

where $\mathbf{E}(\mathbf{r})$ is the electric field at $\mathbf{r}$.

Since the average current density at $\mathbf{r}$ is given by (apart from a factor e^{st}; we shall not write such factors explicitly from now on)

$$\langle\mathbf{j}(\mathbf{r})\rangle=\mathrm{Tr}[f\mathbf{j}(\mathbf{r})], \qquad (1.19)$$

we have

$$\langle j_\alpha(\mathbf{r})\rangle=+\int_0^\infty dte^{-st}\int_0^\beta d\beta'\int d\mathbf{r}'$$
$$\times\langle j_\gamma(\mathbf{r}',-t-i\beta')j_\alpha(\mathbf{r})\rangle_0E_\gamma(\mathbf{r}'), \qquad (1.20)$$

where

$$\langle A\rangle_0\equiv\mathrm{Tr}(\rho A)$$

and γ is summed on x, y, z.

This general formula (1.20) gives the current density which flows in response to the turning on of an arbitrary spacially varying electric field. Now what interests us for the phenomenological theory is the response to a field which is slowly varying, i.e., whose variation is negligible over a distance containing many particles. Since everything is linear in the field, we may confine ourselves to a single Fourier component of the potential

$$\varphi(\mathbf{r})=\varphi_\mathbf{q}e^{i\mathbf{q}\cdot\mathbf{r}}. \qquad (1.21)$$

For a homogeneous system the response must have this same spacial dependence.

Writing

$$j_{\mathbf{q}\alpha}=\int d\mathbf{r}e^{-i\mathbf{q}\cdot\mathbf{r}}j_\alpha(\mathbf{r})$$
$$=\tfrac{1}{2}\sum_j(v_{j\alpha}e^{-i\mathbf{q}\cdot\mathbf{r}}+e^{-i\mathbf{q}\cdot\mathbf{r}_j}v_{j\alpha}), \qquad (1.22)$$

we obtain, for the only non-negligible Fourier component of the current density,

$$\langle j_{\mathbf{q}\alpha}\rangle=\int_0^\infty dt\,e^{-st}\int_0^\beta d\beta'\langle j_{-\mathbf{q},\gamma}(-t-i\beta')j_{\mathbf{q}\alpha}\rangle_0E_{\gamma\mathbf{q}}, \qquad (1.23)$$

where

$$E_{\gamma\mathbf{q}}=-iq_\gamma\varphi_\mathbf{q}. \qquad (1.24)$$

We are interested in the limit of (1.23) as q and s approach zero, if we want to derive the phenomenological transport coefficients.

Now depending on how this limit is performed, we get very different results. This may be seen at and from the phenomenological equations. These are

$$\langle j_\alpha(\mathbf{r})\rangle=\sigma_{\alpha\gamma}E_\gamma(\mathbf{r})-D_{\alpha\gamma}\nabla_\gamma\langle\rho(\mathbf{r})\rangle, \qquad (1.25)$$

the first term being the current induced by the electric field, the second being the diffusion current caused by concentration gradients. Substituting (1.25) in the equation of continuity we obtain for $\langle\rho_q\rangle$, the qth Fourier component of the induced charge density,

$$\langle\rho_\mathbf{q}\rangle=-[V\sigma_{\alpha\gamma}q_\alpha q_\gamma/(s+D_{\alpha\gamma}q_\alpha q_\gamma)]\varphi_\mathbf{q}, \qquad (1.26)$$

$$\langle j_{\mathbf{q}\alpha}\rangle=V\{\sigma_{\alpha\gamma}-D_{\alpha\gamma}[\sigma_{\alpha'\gamma'}q_{\alpha'}q_{\gamma'}/(s+D_{\alpha'\gamma'}q_{\alpha'}q_{\gamma'})]\}E_{\mathbf{q}\gamma}. \qquad (1.27)$$

V is the volume of the system.

We now consider two limits: (a) the "rapid" case, where q,s approaches zero, but q approaches zero first; (b) the "slow" case, in which s approaches zero, then q does. To be more specific, in (a), $s\gg D_{\alpha\gamma}q_\alpha q_\gamma$; in (b), $s\ll D_{\alpha\gamma}q_\alpha q_\gamma$.

In the "rapid" case we see that

$$\langle\rho_\mathbf{q}\rangle\sim q^2/s=0, \qquad (1.28)$$

$$\langle j_{\mathbf{q}\alpha}\rangle=V\sigma_{\alpha\gamma}E_{\mathbf{q}\gamma}+O(q^2/s)$$
$$=V\sigma_{\alpha\gamma}E_{\mathbf{q}\gamma}. \qquad (1.29)$$

In the rapid case, the system stays homogeneous (doesn't have time to adjust to the spacially varying potential). The electrical conductivity tensor is obtained, using (1.29) from (1.23) by letting q go to zero, then s. That is,

$$\sigma_{\alpha\gamma}=\lim_{s\to0}\frac{1}{V}\int_0^\infty dt\,e^{-st}\int_0^\beta d\beta'\langle j_{0\gamma}(-t-i\beta')j_{0\alpha}\rangle_0, \qquad (1.30)$$

which is just the usual Kubo formula.[6]

On the other hand, in the slow case, no current can flow since it corresponds to a perfectly well-defined static periodic potential applied to the system. For such a case we will have a situation of thermal equilibrium in which, of course, no bulk currents flow. Therefore, from (1.26) and (1.27) with $\langle j_{\mathbf{q}\alpha}\rangle=0$, we get

$$\sigma_{\alpha\gamma}=D_{\alpha\gamma}(\sigma_{\alpha'\gamma'}q_{\alpha'}q_{\gamma'}/D_{\alpha'\gamma'}q_{\alpha'}q_{\gamma'}), \qquad (1.31)$$

$$\langle\rho_\mathbf{q}\rangle=-(V\sigma_{\alpha'\gamma'}q_{\alpha'}q_{\gamma'}/D_{\alpha'\gamma'}q_{\alpha'}q_{\gamma'})\varphi_\mathbf{q}. \qquad (1.32)$$

[6] In the case of Coulomb interactions between the particles, some care is necessary in going to the $q=0$ limit. This well-known difficulty [see, for example, V. Ambegaokar and W. Kohn, Phys. Rev. 117, 423 (1960)] is related to the fact that a longitudinal external field is screened by the charged particles while a transverse one is not, so they have different $q=0$ limits. The simplest correct procedure is than to consider a transverse field (as in Appendix B) and proceed to the $q=0$ limit for it.

Equation (1.31) may only be satisfied if for arbitrary $\mathbf{q}$ if

$$\sigma_{\alpha\gamma}=aD_{\alpha\gamma}\,, \tag{1.33}$$

where a is some constant independent of q.

$$a=-\sigma_{\alpha'\gamma'}q_{\alpha'}q_{\gamma'}/D_{\alpha'\gamma'}q_{\alpha'}q_{\gamma'}\,,$$
$$\langle\rho_{\mathbf{q}}\rangle=-Va\varphi_{\mathbf{q}}\,. \tag{1.34}$$

Now since $\langle\rho_q\rangle$ is the charge density for a system in equilibrium in a static external potential with Fourier coefficient φ_q, it may be calculated by equilibrium statistical mechanics. Therefore, a is an equilibrium property of the system. A straightforward calculation, which is given in Appendix A, yields

$$a=e^2/(\partial\mu/\partial n)_T\,, \tag{1.35}$$

where μ is the chemical potential regarded as a function of the temperature and equilibrium particle density n.

Combining (1.35) and (1.33) we get the usual Einstein relationship, which, combined with (1.30), gives the "Kubo" formula for the self-diffusion tensor $D_{\alpha\gamma}$.

Although none of the results of this section are new, the method used to derive them may be taken over with only minor modifications to obtain the thermal transport coefficients.

III. CALCULATION OF THE THERMAL TRANSPORT COEFFICIENTS

Just as the space- and time-varying external electric potential produced electric currents and density variations, so a varying gravitational field will produce, in principle,[7] energy flows and temperature fluctuations. The reason for this is that an energy density $h(\mathbf{r})$ behaves as if it had a mass density $h(\mathbf{r})/c^2$, as far as its interaction with a gravitation field goes. Calling the gravitational potential $-c^2\psi(\mathbf{r},t)$, we have an interaction term in the Hamiltonian of the form

$$\int h(\mathbf{r})\psi(\mathbf{r},t)d\mathbf{r}\,,$$

where $h(\mathbf{r})$ is the Hamiltonian density of the unperturbed system. Clearly a varying ψ will give rise to a varying energy density, which, in turn, will correspond to a varying temperature. We shall see this in more detail below.

Turning on simultaneously a φ and a ψ, which vary as e^{st}, we again obtain a total Hamiltonian of the form (1.2), except that now F is given by

$$F=\int\rho(\mathbf{r})\varphi(\mathbf{r})d\mathbf{r}+\int h(\mathbf{r})\psi(\mathbf{r})d\mathbf{r}\,. \tag{2.1}$$

The entire analysis of Sec. II is still valid, leading to (1.13), where $\dot{F}$ is now given by

$$\dot{F}=\int\dot{\rho}(\mathbf{r})\varphi(\mathbf{r})d\mathbf{r}+\int\dot{h}(\mathbf{r})\psi(\mathbf{r})d\mathbf{r}\,. \tag{2.2}$$

Again, as in (1.15) we may write

$$\dot{h}(\mathbf{r})+\nabla\cdot\mathbf{j}^E(\mathbf{r})=0\,, \tag{2.3}$$

where $j^E(\mathbf{r})$ is the energy-current-density operator for the unperturbed system. For a simple system of interacting particles we may take

$$h(\mathbf{r})=\tfrac{1}{2}\textstyle\sum_j(h_j\delta_j+\delta_jh_j)\,, \tag{2.4}$$

where

$$\delta_j=\delta(\mathbf{r}-\mathbf{r}_j)\,,$$
$$h_j=(p_j^2/2m)+V_j+\tfrac{1}{2}\sum_{j'\neq j}u_{jj'}\,,$$

V_j being the interaction energy between the jth particle and an external fixed field, $u_{jj'}$ the velocity-independent interaction between the jth and j'th particles. In this case $\mathbf{j}_\alpha{}^E(\mathbf{r})$ may be written

$$\begin{aligned}j_\alpha{}^E(\mathbf{r})=\tfrac{1}{2}\sum_j(h_jj_{j\alpha}(\mathbf{r})+j_{j\alpha}(\mathbf{r})h_j)\\+(1/8m){\sum_{j,j'}}'\,[(p_{j\alpha}+p_{j'\alpha})x_{jj'}{}^\gamma F_{jj'}{}^\gamma\delta_j\\+\delta_jx_{jj'}{}^\gamma F_{jj'}{}^\gamma(p_{j\alpha}+p_{j'\alpha})]\,,\end{aligned} \tag{2.5}$$

$$j_{j\alpha}(\mathbf{r})=(1/2m)(p_{j\alpha}\delta_j+\delta_jp_{j\alpha})\,,$$
$$F_{jj'}{}^\gamma=-\partial u_{jj'}/\partial x_j{}^\gamma\,.$$

(These expressions make an error of the order qa, where a is the range of the interparticle potential and q the propagation vector of the disturbance in the system.[8])

Now $\mathbf{j}(\mathbf{r})$ and $\mathbf{j}^E(\mathbf{r})$ are not the total current densities, the expressions for the current densities being modified by the interaction with the external fields. Call the time-dependent average charge density $\langle\rho(\mathbf{r};t)\rangle$;

$$\begin{aligned}\langle\rho(\mathbf{r};t)\rangle&=\mathrm{Tr}(\rho_T\rho(\mathbf{r}))\,,\\ \partial\langle\rho(\mathbf{r};t)\rangle/\partial t&=\mathrm{Tr}[(\partial\rho_T/\partial t)\rho(\mathbf{r})]\\&=\mathrm{Tr}\rho_Ti[H_T,\rho(\mathbf{r})]\,.\end{aligned} \tag{2.6}$$

Since the total charge is conserved, we may write

$$i[H_T,\rho(\mathbf{r})]=-\nabla\cdot\mathbf{j}^T(\mathbf{r})\,. \tag{2.7}$$

The $\langle j^T(r;t)\rangle$ computed from this equation will satisfy the equation of continuity. Similarly, if $h_T(\mathbf{r})$ is the total energy density, we have

$$\begin{aligned}\langle h_T(\mathbf{r};t)\rangle&=\mathrm{Tr}(\rho_Th_T)\,,\\ \partial\langle h_T(r;t)\rangle/\partial t&=\mathrm{Tr}(\rho_T\{i[H_T,h_T(\mathbf{r})]+(\partial h_T/\partial t)\})\,.\end{aligned} \tag{2.8}$$

Again, by energy conservation, we may write

$$i[H_T,h_T(\mathbf{r})]=-\nabla\cdot\mathbf{j}^{ET}(\mathbf{r})\,. \tag{2.9}$$

This term represents the energy flux in the system,

[7] These effects are actually extremely small, far too small to be observed in any ordinary experiment. They were first considered by A. Einstein, Ann. Physik **38**, 443 (1912). See also R. C. Tolman, Phys. Rev. **35**, 904 (1930) and R. C. Tolman and P. Ehrenfest, *ibid.* **36**, 1791 (1930). (I am indebted to Professor G. Uhlenbeck for calling these interesting references to my attention.) Although the effect is very small, in practice we are only interested in questions of principle, and an arbitrarily small effect is just as good as a large one. In fact, if the gravitational field didn't exist, one could invent one for the purposes of this paper.

[8] See H. Mori, Ref. 1, pp. 1838–1839.

whereas the second term $(\partial h_T/\partial t)$ represents the rate of increase of energy of the system due to the work done on it by the external forces.

Direct calculation gives

$$\mathbf{j}^T(\mathbf{r})=\mathbf{j}(\mathbf{r})+e^{st}\psi(\mathbf{r})\mathbf{j}(\mathbf{r}), \tag{2.10}$$

$$\mathbf{j}^{ET}(\mathbf{r})=\mathbf{j}^E(\mathbf{r})+e^{st}(\varphi(\mathbf{r})j(\mathbf{r})+2\psi(\mathbf{r})\mathbf{j}^E(\mathbf{r})). \tag{2.11}$$

If we are taking only the linear terms of the response in φ and ψ, then the corrections to $\mathbf{j}$ and $\mathbf{j}^E$ that arise in this manner do not contribute, since the average currents in the equilibrium distribution are zero.

Proceeding just as in Sec. II, we therefore obtain

$$\begin{aligned}\langle j_{\mathbf{q}\alpha}\rangle&=\int_0^\infty dt\, e^{-st}\int_0^\beta d\beta'[\langle j_{-\mathbf{q}\gamma}(-t-i\beta')j_{\mathbf{q}\alpha}\rangle_0 E_{\gamma\mathbf{q}}\\&\quad+\langle \mathbf{j}_{\mathbf{q}\gamma}{}^E(-t-i\beta')j_{\mathbf{q}\alpha}\rangle_0(-iq_\gamma\psi_\mathbf{q})],\\ \langle j_{\mathbf{q}\alpha}{}^E\rangle&=\int_0^\infty dt\, e^{-st}\int_0^\beta d\beta'[\langle \mathbf{j}_{\mathbf{q}\gamma}(-t-i\beta')j_{\mathbf{q}\alpha}{}^E\rangle_0 E_{\gamma\mathbf{q}}\\&\quad+\langle j_{-\mathbf{q}\gamma}{}^E(-t-i\beta')j_{\mathbf{q}\alpha}{}^E\rangle_0(-iq_\gamma\psi_\mathbf{q})].\end{aligned} \tag{2.12}$$

Once more we consider the "rapid" and "slow" cases. To see what these limits mean in this case, we use the phenomenological equations in the form[9]

$$\begin{aligned}j_\alpha(\mathbf{r})&=L_{\alpha\gamma}{}^{(1)}\left[E_\gamma-\frac{1}{e}T\nabla_\gamma\left(\frac{\mu}{T}\right)\right]\\&\quad+L_{\alpha\gamma}{}^{(2)}T\nabla_\gamma\left(\frac{1}{T}\right)+\tilde{L}_{\alpha\gamma}{}^{(2)}(-\nabla_\gamma\psi),\\ j_\alpha{}^E(\mathbf{r})&=L_{\alpha\gamma}{}^{(3)}\left[E_\gamma-\frac{1}{e}T\nabla_\gamma\left(\frac{\mu}{T}\right)\right]\\&\quad+L_{\alpha\gamma}{}^{(4)}T\nabla_\gamma\left(\frac{1}{T}\right)+\tilde{L}_{\alpha\gamma}{}^{(4)}(-\nabla_\gamma\psi).\end{aligned} \tag{2.13}$$

The chemical potential μ which appears here is defined as the same function of the slowly varying particle density and temperature as it is in equilibrium.

Taking the qth Fourier component of (2.13), we have

$$j_{\mathbf{q}\alpha}=-iq_\gamma\left\{L_{\alpha\gamma}{}^{(1)}\left[\varphi_\mathbf{q}+\frac{1}{e}\frac{T_0}{V}\left(\frac{\mu}{T}\right)_\mathbf{q}\right]-L_{\alpha\gamma}{}^{(2)}\frac{T_0}{V}\left(\frac{1}{T}\right)_\mathbf{q}+\tilde{L}_{\alpha\gamma}{}^{(2)}\psi_\mathbf{q}\right\}V, \tag{2.14}$$

[9] See, for example, A. H. Wilson, *The Theory of Metals* (Cambridge University Press, Cambridge, 1953), Chap. VIII. These are the standard phenomenological equations which already include the Einstein relationship between the conductivity and a diffusion constants. To them we have added a general term proportional to $(-\nabla\psi)$, since the gravitational driving force must be proportional to the gravitational field, for slowly varying fields.

$$j_{\mathbf{q}\alpha}{}^E=-iq_\gamma\left\{L_{\alpha\gamma}{}^{(3)}\left[\varphi_\mathbf{q}+\frac{1}{e}\frac{T_0}{V}\left(\frac{\mu}{T}\right)_\mathbf{q}\right]-L_{\alpha\gamma}{}^{(4)}\frac{T_0}{V}\left(\frac{1}{T}\right)_\mathbf{q}+\tilde{L}_{\alpha\gamma}{}^{(4)}\psi_\mathbf{q}\right\}V, \tag{2.15}$$

where T_0 is the equilibrium temperature.

In the "slow" case, we are in equilibrium and no currents flow. Therefore the curly brackets must vanish when $(\mu/T)_\mathbf{q}$ and $(1/T)_\mathbf{q}$ are given by their equilibrium values in the external potentials $\varphi_\mathbf{q}$ and $\psi_\mathbf{q}$. These are easily calculated (see Appendix A) and are given by

$$\varphi_\mathbf{q}+(T_0/eV)(\mu/T)_\mathbf{q}=0, \tag{2.16}$$

$$\psi_\mathbf{q}-T_0(1/V)(1/T)_\mathbf{q}=0. \tag{2.17}$$

Therefore, the vanishing of the currents in equilibrium is the same as

$$\tilde{L}_{\alpha\gamma}{}^{(2)}=L_{\alpha\gamma}{}^{(2)}, \tag{2.18}$$

$$\tilde{L}_{\alpha\gamma}{}^{(4)}=L_{\alpha\gamma}{}^{(4)}. \tag{2.19}$$

These relationships are the thermal analogs of the Einstein relationship between conductivity and diffusion coefficients.

Now the entire point of this paper is that we may calculate $\tilde{L}_{\alpha\gamma}{}^{(2)}$, $L_{\alpha\gamma}{}^{(3)}$, and $\tilde{L}_{\alpha\gamma}{}^{(4)}$ at once by proceeding to the "rapid" limit. In this case, since $\nabla\cdot\mathbf{j}$ and $\nabla\cdot\mathbf{j}^E$ are proportional to q^2, the equations of continuity for charge and energy flow tell us at once that

$$\begin{aligned}\langle\rho_\mathbf{q}\rangle&=O(q^2/s)\to 0,\\ \langle h_\mathbf{q}\rangle&=O(q^2/s)\to 0.\end{aligned} \tag{2.20}$$

That is, the external fields are varying too rapidly for the particle and energy density to vary. Therefore, the temperature and chemical potential, which may be regarded as functions of the particle and energy densities, are also constant. In the "rapid" case we therefore have

$$\begin{aligned}(1/T)_\mathbf{q}&=0,\\ (\mu/T)_\mathbf{q}&=0.\end{aligned} \tag{2.21}$$

Thus, for this case, we must have

$$\begin{aligned}j_{\mathbf{q}\alpha}&=-iq_\gamma\{L_{\alpha\gamma}{}^{(1)}\varphi_\mathbf{q}+\tilde{L}_{\alpha\gamma}{}^{(2)}\psi_\mathbf{q}\}V,\\ j_{\mathbf{q}\alpha}{}^E&=-iq_\gamma\{L_{\alpha\gamma}{}^{(3)}\varphi_\mathbf{q}+\tilde{L}_{\alpha\gamma}{}^{(4)}\psi_\mathbf{q}\}V.\end{aligned} \tag{2.22}$$

Comparison with (2.12) yields

$$\begin{aligned}L_{\alpha\gamma}{}^{(1)}&=\lim_{s\to0}\frac{1}{V}\int_0^\infty e^{-st}dt\int_0^\beta d\beta'\langle j_{0\gamma}(-t-i\beta')j_{0\alpha}\rangle_0,\\ \tilde{L}_{\alpha\gamma}{}^{(2)}&=\lim_{s\to0}\frac{1}{V}\int_0^\infty e^{-st}dt\int_0^\beta d\beta'\langle j_{0\gamma}{}^E(-t-i\beta')j_{0\alpha}\rangle_0,\\ L_{\alpha\gamma}{}^{(3)}&=\lim_{s\to0}\frac{1}{V}\int_0^\infty e^{-st}dt\int_0^\beta d\beta'\langle j_{0\gamma}(-t-i\beta')j_{0\alpha}{}^E\rangle_0,\\ \tilde{L}_{\alpha\gamma}{}^{(4)}&=\lim_{s\to0}\frac{1}{V}\int_0^\infty e^{-st}dt\int_0^\beta d\beta'\langle j_{0\gamma}{}^E(-t-i\beta')j_{0\alpha}{}^E\rangle_0.\end{aligned} \tag{2.23}$$

If we now take $\psi=0$ in (2.13) and use (2.18) and (2.19), we have the usual phenomenological equations, with the transport coefficients L given by (2.23). These are the usual GKM results obtained previously by assumptions about the form of the local equilibrium distribution function or the regression of fluctuations. No such assumptions were necessary here.

APPENDIX A

We consider a system in equilibrium at temperature T having a Hamiltonian $H+F$, when F is given by (2.1). Then the distribution function is

$$\rho_T=e^{-\beta(H-\mu N+F)}/\mathrm{Tr}e^{-\beta(H-\mu N+F)}. \tag{A1}$$

To the first order in F, if $\langle F\rangle_0=0$, this is well known

$$\rho_T=\rho-\rho\int_0^\beta d\beta' F(-i\beta'), \tag{A2}$$

where ρ is the equilibrium distribution for a system with Hamiltonian H. Taking external fields with only a $\mathbf{q}$ component ($\mathbf{q}\neq 0$), we obtain at once

$$\begin{aligned}\langle\rho_{-\mathbf{q}}\rangle&=-\int_0^\beta d\beta'[\langle\rho_{-\mathbf{q}}(-i\beta')\rho_{\mathbf{q}}\rangle_0\varphi_{\mathbf{q}}+\langle\rho_{-\mathbf{q}}(-i\beta')h_{\mathbf{q}}\rangle_0\psi_{\mathbf{q}}],\\ \langle h_{-\mathbf{q}}\rangle&=-\int_0^\beta d\beta'[\langle\rho_{-\mathbf{q}}(-i\beta')h_{\mathbf{q}}\rangle_0\varphi_{\mathbf{q}}+\langle h_{-\mathbf{q}}(-i\beta')h_{\mathbf{q}}\rangle_0\psi_{\mathbf{q}}].\end{aligned} \tag{A3}$$

Now when $\mathbf{q}$ is zero, $\rho_{\mathbf{q}}$ and $h_{\mathbf{q}}$ become simply the total number of particles and the Hamiltonian, respectively. Since both of these commute with the Hamiltonian we have

$$\begin{aligned}\rho_{-\mathbf{q}}(-i\beta')&=\rho_{-\mathbf{q}}[1+O(q)],\\ h_{-\mathbf{q}}(-i\beta')&=h_{-\mathbf{q}}[1+O(q)],\end{aligned} \tag{A4}$$

as $\mathbf{q}$ approaches zero. Therefore for very small $\mathbf{q}$ we have

$$\begin{aligned}\langle\rho_{\mathbf{q}}\rangle&=-\beta[\langle\rho_{-\mathbf{q}}\rho_{\mathbf{q}}\rangle_0\varphi_{\mathbf{q}}+\langle\rho_{-\mathbf{q}}h_{\mathbf{q}}\rangle_0\psi_{\mathbf{q}}],\\ \langle h_{q}\rangle&=-\beta[\langle\rho_{-\mathbf{q}}h_{\mathbf{q}}\rangle_0\varphi_{q}+\langle h_{-\mathbf{q}}h_{\mathbf{q}}\rangle_0\psi_{\mathbf{q}}].\end{aligned} \tag{A5}$$

To calculate these quantities, consider first

$$\langle\rho_{-\mathbf{q}}\rho_{\mathbf{q}}\rangle_0=e^2\langle n_{-\mathbf{q}}n_{\mathbf{q}}\rangle_0, \tag{A6}$$

where $n_{\mathbf{q}}$ is the Fourier component of the particle-density operator. Let us introduce a volume $V_S=L_S^3$ centered around the origin, where $V_S\ll V$. Call N_S the operator giving the number of particles in V_S.

$$N_S=\textstyle\sum_j f(\mathbf{r}_j), \tag{A7}$$

where

$$\begin{aligned}f(\mathbf{r})&=1 \quad \mathbf{r}\text{ in } V_S,\\ &=0 \text{ otherwise}.\end{aligned} \tag{A8}$$

Write

$$f(\mathbf{r})=(1/V)\sum_{q\mathbf{q}} fe^{-i\mathbf{q}\cdot\mathbf{r}}, \tag{A9}$$

$$f_{\mathbf{q}}=\int d\mathbf{r}f(\mathbf{r})e^{+i\mathbf{q}\cdot\mathbf{r}}. \tag{A10}$$

Then

$$N_S=(1/V)\sum_{\mathbf{q},j} f_{\mathbf{q}}e^{-i\mathbf{q}\cdot\mathbf{r}_j}=(1/V)\sum_{\mathbf{q}} f_{\mathbf{q}}n_{\mathbf{q}}. \tag{A11}$$

Therefore

$$\begin{aligned}\langle N_S^2\rangle_0&=(1/V^2)\sum_{\mathbf{q},\mathbf{q}'} f_{\mathbf{q}'}f_{\mathbf{q}}\langle n_{\mathbf{q}'}n_{\mathbf{q}}\rangle_0\\ &=(1/V^2)\sum_{\mathbf{q}} f_{-\mathbf{q}}f_{\mathbf{q}}\langle n_{-\mathbf{q}}n_{\mathbf{q}}\rangle_0\\ &=(1/V^2)\sum_{\mathbf{q}\neq 0} f_{-\mathbf{q}}f_{\mathbf{q}}\langle n_{-\mathbf{q}}n_{\mathbf{q}}\rangle_0+(1/V^2)f_0^2N^2.\end{aligned} \tag{A12}$$

However,

$$\langle N_S\rangle=(1/V)f_0N, \tag{A13}$$

so that

$$\langle N_S^2\rangle_0-\langle N_S\rangle_0^2=(1/V^2)\sum_{\mathbf{q}\neq 0} f_{-\mathbf{q}}f_{\mathbf{q}}\langle n_{-\mathbf{q}}n_{\mathbf{q}}\rangle_0. \tag{A14}$$

Now $f_{\mathbf{q}}$ approaches zero when $q\gg 1/L_S$. Therefore, if $\langle n_{-\mathbf{q}}n_{\mathbf{q}}\rangle_0$ has a limit as q approaches zero, we can choose L_S such that

$$\langle N_S\rangle_0^2-\langle N_S\rangle_0^2=\Big((1/V^2)\sum_{\mathbf{q}\neq 0} f_{-\mathbf{q}}f_{\mathbf{q}}\Big)\lim_{\mathbf{q}\to 0}\langle n_{-\mathbf{q}}n_{\mathbf{q}}\rangle_0. \tag{A15}$$

Since

$$\int d\mathbf{r}f^2(\mathbf{r})=\int d\mathbf{r}f(\mathbf{r})=V_S=\frac{1}{V}\sum_{\mathbf{q}} f_{-\mathbf{q}}f_{\mathbf{q}}, \tag{A16}$$

we have

$$\lim_{\mathbf{q}\to 0}\langle n_{-\mathbf{q}}n_{\mathbf{q}}\rangle_0=V[(\langle N_S^2\rangle_0-\langle N_S\rangle_0^2)/V_S]. \tag{A17}$$

On the other hand, the particle fluctuation in a macroscopic but small subsystem of a macroscopic system may be calculated by using the grand partition function for a system of the same density.

Therefore,

$$\lim_{\mathbf{q}\to 0}\langle n_{-\mathbf{q}}n_{\mathbf{q}}\rangle_0=V[(\langle N^2\rangle_0-\langle N\rangle_0^2)/V]. \tag{A18}$$

Using well-known results from the theory of the grand partition function,

$$e^{-\beta\Omega(\beta,\alpha)}=\mathrm{Tr}(e^{-\beta H+\alpha N}), \tag{A19}$$

where $\alpha=\mu\beta$, we have

$$\begin{aligned}\langle N^2\rangle_0-\langle N\rangle_0^2&=-\partial^2(\Omega\beta)/\partial\alpha^2,\\ \lim_{\mathbf{q}\to 0}\langle n_{-\mathbf{q}}n_{\mathbf{q}}\rangle_0&=-\partial^2(\beta\Omega)/\partial\alpha^2.\end{aligned} \tag{A20}$$

Similarly,

$$\lim_{\mathbf{q}\to 0}\langle n_{-\mathbf{q}}h_{\mathbf{q}}\rangle_0=\langle HN\rangle_0-\langle H\rangle_0\langle N\rangle_0=\partial^2(\beta\Omega)/\partial\alpha\partial\beta, \tag{A21}$$

$$\lim_{\mathbf{q}\to 0}\langle h_{-\mathbf{q}}n_{\mathbf{q}}\rangle_0=\langle HN\rangle_0-\langle H\rangle_0\langle N\rangle_0=\partial^2(\beta\Omega)/\partial\alpha\partial\beta, \tag{A22}$$

$$\lim_{\mathbf{q}\to 0}\langle h_{-\mathbf{q}}h_{\mathbf{q}}\rangle_0=\langle H^2\rangle_0-\langle H\rangle_0^2=-\partial^2(\beta\Omega)/\partial\beta^2. \tag{A23}$$

Using

$$\bar{N}=-(\partial\Omega/\partial\mu)_T=-\partial(\beta\Omega)/\partial\alpha\,,$$
$$U=\partial(\beta\Omega)/\partial\beta\,, \qquad \text{(A24)}$$

and calling the particle and energy density n and u, respectively, we obtain

$$\lim_{q\to 0}\langle n_{-q}n_q\rangle_0=V[\partial n(\beta,\alpha)/\partial\alpha]\,, \qquad \text{(A25)}$$

$$\lim_{q\to 0}\langle n_{-q}h_q\rangle_0=\lim_{q\to 0}\langle h_{-q}n_q\rangle_0=V[\partial u(\beta\alpha)/\partial\alpha]$$
$$=-V[\partial n(\beta\alpha)/\partial\beta]\,, \qquad \text{(A26)}$$

$$\lim_{q\to 0}\langle h_{-q}h_q\rangle_0=-V[\partial u(\beta\alpha)/\partial\beta]. \qquad \text{(A27)}$$

Further, we have

$$\left(\frac{\mu}{T}\right)_q=\left[\frac{\partial(\mu/T)}{\partial n}\right]_u\langle n_q\rangle+\left[\frac{\partial(\mu/T)}{\partial u}\right]_n\langle h_q\rangle$$
$$=k\left[\left(\frac{\partial\alpha}{\partial n}\right)_u\langle n_q\rangle+\left(\frac{\partial\alpha}{\partial u}\right)_n\langle h_q\rangle\right] \qquad \text{(A28)}$$

and

$$\left(\frac{1}{T}\right)_q=k\left[\left(\frac{\partial\beta}{\partial n}\right)_u\langle n_q\rangle+\left(\frac{\partial\beta}{\partial u}\right)_n\langle h_q\rangle\right]. \qquad \text{(A29)}$$

Using (A25)–(A29) and (A5) in (A28) and (A27), we obtain at once

$$(\mu/T)_q=-(V/T)e\varphi_q\,, \qquad \text{(A30)}$$

$$(1/T)_q=(V/T)\psi_q\,, \qquad \text{(A31)}$$

which are (2.16) and (2.17).

These relationships are also quite easily obtained by considering the probability of a fluctuation of energy and density, and making use of the Boltzmann relationship between the probability of such a fluctuation and the entropy of the system when it has the corresponding number and energy densities.

If $\psi_q=0$, $(1/T)_q=0$, the temperature is uniform in equilibrium. Then

$$\left(\frac{\mu}{T}\right)_q=\frac{1}{T}\left(\frac{\partial\mu}{\partial n}\right)_T\langle n_q\rangle=\frac{1}{eT}\left(\frac{\partial\mu}{\partial n}\right)_T\langle\rho_q\rangle. \qquad \text{(A32)}$$

Using (A30), we have for this case

$$\langle\rho_q\rangle=-Ve^2\varphi_q/(\partial\mu/\partial n)_T\,, \qquad \text{(A33)}$$

which is just (1.35).

APPENDIX B

In this appendix we consider the transport coefficients (viscosity, heat conductivity) for a simple fluid. In the main text we considered the situation appropriate to solid-state physics where impurities, phonons, or some other mechanism gives rise to a resistive behavior. Here we investigate a simple monatomic liquid where the Hamiltonian conserves momentum. (Such a system would have infinite static electrical conductivity, for example, and therefore the procedure given in the text does not apply.)

The procedure is nonetheless essentially the same as before. We assume that the phenomenological equations in the usual form exist. Then by studying the response to external fields we obtain expressions for the coefficients appearing in these equations. The phenomenological equations for a simple fluid are, of course, the standard equations of hydrodynamics. These are[10]

$$\partial\rho_m/\partial t+\nabla_\beta(\rho_m v_\beta)=0\,, \qquad \text{(B1)}$$

$$\rho_m[(\partial/\partial t)+v_\beta\nabla_\beta]v_\alpha=F_\alpha-\nabla_\alpha p+\nabla_\beta\sigma_{\alpha\beta}'\,, \qquad \text{(B2)}$$

$$\rho_m T[(\partial/\partial t)+v_\beta\nabla_\beta]S_m=\sigma_{\alpha\beta}'\nabla_\beta v_\alpha+\nabla_\beta(K\nabla_\beta T)\,. \qquad \text{(B3)}$$

In these equations ρ_m is the mass density, v_α the local velocity, F_α the external force per unit volume, p the local pressure, S_m the local intropy per unit mass, T the local temperature. Further,

$$\sigma_{\alpha\beta}'=\eta(\nabla_\beta v_\alpha+\nabla_\alpha v_\beta)+(\zeta-\tfrac{2}{3}\eta)\delta_{\alpha\beta}\nabla_\gamma v_\gamma\,. \qquad \text{(B4)}$$

The quantities η and ζ are known as the shear and bulk viscosity, respectively, and K is the thermal conductivity.

In the linear approximation these equations become

$$(\partial\rho_m/\partial t)+\rho_m^0\nabla_\beta v_\beta=0\,, \qquad \text{(B5)}$$

$$\rho_m^0(\partial v_\alpha/\partial t)=F_\alpha-\nabla_\alpha p+\nabla_\beta\sigma_{\alpha\beta}'\,, \qquad \text{(B6)}$$

$$(\partial/\partial t)(u-w_0 n)=K\nabla^2 T\,, \qquad \text{(B7)}$$

where ρ_m^0, w_0 are the equilibrium density and enthalpy per particle, respectively; u and n are the local energy and number densities.

Imagine that the external force is given by an external electric field, and that the particles have unit charge. Then

$$F_\alpha=n_0E_\alpha$$
$$=n_0E_{q\alpha}e^{iq\cdot r}e^{st}\,, \qquad \text{(B8)}$$

if the field has one Fourier component, which we turn on slowly. Fourier analyzing (B5)–(B7) and dropping the factor e^{st}, we obtain (where m is the mass of the particles)

$$sn_q+iq_\beta n_0 v_{q\beta}=0\,, \qquad \text{(B9)}$$

$$sv_{q\alpha}=VE_{q\alpha}-\frac{1}{n_0}iq_\alpha p_q$$
$$-\frac{1}{n_0}\left[\eta q^2 v_{q\alpha}+\left(\zeta+\frac{\eta}{3}\right)q_\alpha(q_q v_{q\beta})\right], \qquad \text{(B10)}$$

$$s(u_q-w_0n_q)=Kq^2T_q\,. \qquad \text{(B11)}$$

Again we shall consider the "rapid" case, where $q\to 0$ and $s\to 0$, but $q\to 0$ first. Then clearly the leading

[10] See, for example, L. D. Landau and E. M. Lifshitz, *Fluid Mechanics* (Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1959), pp. 2, 48, 185.

terms are given by

$$v_{q\alpha}{}^0 = VE_{q\alpha/ms},$$
$$n_q{}^0 = (-iq_\beta v_{q\beta}{}^0/s)n_0, \qquad \text{(B12)}$$
$$u_q{}^0 = w_0 n_q{}^0 = -w_0(iq_\beta \sigma_{q\beta}{}^0/s).$$

Further,

$$p_q = (\partial p/\partial n)_u{}^0 n_q + (\partial p/\partial u)_n{}^0 u_q, \qquad \text{(B13)}$$

so that

$$p_q{}^0 = [(\partial p/\partial n)_u{}^0 + w_0(\partial p/\partial u)_n{}^0] n_q{}^0 \equiv C_0 n_q{}^0. \qquad \text{(B14)}$$

Substituting (B12) and (B14) into the terms proportional to q^2 in (B10), we obtain

$$s\rho_m{}^0 v_{q\alpha} = NE_{q\alpha} - \frac{n_0 C_0 V}{ms^2} q_\alpha(q_\beta E_{q\beta}) - \frac{V}{ms}\left[\eta q^2 E_{\beta\alpha} + \left(\zeta + \frac{\eta}{3}\right) q_\alpha(\alpha_\beta E_\beta)\right]. \qquad \text{(B15)}$$

We consider two cases: (a) transverse case or $\mathbf{q}\perp\mathbf{E}$; (b) longitudinal case, $\mathbf{q}\|\mathbf{E}$. We have

$$s\rho_m{}^0 v_{q\alpha} = NE_{q\alpha} - (V\eta/m)(q^2/s)E_{q\alpha} \quad \text{(transverse case)}, \qquad \text{(B16)}$$

$$s\rho_m{}^0 v_{q\alpha} = NE_{q\alpha} - (n_0 C_0 V/m)(q^2/s^2)E_{q\alpha} - \frac{V[\zeta + (4\eta/3)]}{m}\frac{q^2}{s}E_{q\alpha} \quad \text{(longitudinal case)}. \qquad \text{(B17)}$$

If we compare (B16) and (B17) to the results we obtain by imagining an external electric field applied to the system, using first-order perturbation theory and expanding to order q^2, we must obtain expressions for the viscosity coefficients η and $\zeta + 4\eta/3$.

In the first section, we represented the field by a scalar potential. This only corresponds to a longitudinal field. To consider a more general electric field we represent it by a vector potential

$$E_\alpha = -(1/c)(\partial A_\alpha/\partial t), \quad A_\alpha = (-c/s)E_{q\alpha}e^{i\mathbf{q}\cdot\mathbf{r}}e^{st}. \qquad \text{(B18)}$$

This gives a total Hamiltonian

$$H_T = H + Fe^{st},$$

where

$$F = (1/ms)E_{q\alpha}p_\alpha(-\mathbf{q}). \qquad \text{(B19)}$$

Here $p_\alpha(+\mathbf{q})$ is the $\mathbf{q}$th Fourier coefficient of the unperturbed momentum-density operator, which is simply the mass times the unperturbed number current operator. That is,

$$p_\alpha(\mathbf{g}) = \tfrac{1}{2}\sum_j (p_{j\alpha}e^{-i\mathbf{q}\cdot\mathbf{r}_j} + e^{-i\mathbf{q}\cdot\mathbf{r}_j}p_{j\alpha}). \qquad \text{(B20)}$$

Using the same method as in Sec. II, this gives at once that the average value of the momentum density, which is just $\rho_m{}^0 v_{q\alpha}$ in the linear approximation, is

$$\rho_m{}^0 v_{q\alpha} = \frac{1}{S}\left(NE_{q\alpha} - \frac{1}{m}\int_0^\infty dt\, e^{-st}\int_0^\beta d\beta' \times\langle \dot{p}_\gamma(-\mathbf{q}, -t-i\beta')p_\alpha(\mathbf{q})\rangle_0 E_{q\gamma}\right). \qquad \text{(B21)}$$

(The first term arises from the average with the unperturbed density matrix of the change in the momentum density due to the presence of the vector potential.)

Integrating (B21) by parts with respect to t, we obtain at once

$$s\rho_m{}^0 v_{q\alpha} = NE_{q\alpha} - \frac{1}{ms}\int_0^\infty dt\, e^{-st}\int_0^\beta d\beta' \times\langle \dot{p}_\gamma(-\mathbf{q}, -t-i\beta')\dot{p}_\alpha(\mathbf{q})\rangle_0 E_{q\gamma}. \qquad \text{(B22)}$$

Since the total momentum of the system is conserved, we have

$$\dot{p}_\alpha(\mathbf{r}) + \nabla_\gamma P_\alpha{}^\gamma(\mathbf{r}) = 0, \qquad \text{(B23)}$$

where $P_\alpha{}^\gamma(\mathbf{r})$ is the flux of momentum density. For a simple system system this would be given by[11]

$$P_\alpha{}^\gamma(\mathbf{r}) = (1/4m)\sum_j\{p_{\alpha j}p_{\gamma j}\delta_j + \delta_j p_{\alpha j}p_{\gamma j} + p_{\alpha j}\delta_j p_{\gamma j} + p_{\gamma j}\delta_j p_{\alpha j}\} + \tfrac{1}{2}\sum_{j,j'}{}' x_{jj'}{}^\gamma F_{jj'}{}^\alpha \delta_j. \qquad \text{(B24)}$$

In momentum space (B23) becomes

$$\dot{p}_\alpha(q) = -iq_\gamma P_\alpha{}^\gamma(\mathbf{q}). \qquad \text{(B25)}$$

If we insert (B25) in (B22), we obtain

$$s\rho_m{}^0 v_{q\alpha} = NE_{q\alpha} - \frac{q_n q_\delta}{ms}\int_0^\infty dt\, e^{-st}\int_0^\beta d\beta' \times\langle P_\gamma{}^x(-\mathbf{q}, -t-i\beta')P_\alpha{}^\delta(\mathbf{q})\rangle_0 E_{q\gamma}. \qquad \text{(B26)}$$

For the *transverse* case, let us take $\mathbf{E}$ in the x direction, $\mathbf{q}$ in the y direction. Then we obtain

$$s\rho_m{}^0 v_{qx} = NE_{qx} - \frac{q^2}{ms}\int_0^\infty dt\, e^{-st}\int_0^\beta d\beta' \times\langle P_x{}^y(-\mathbf{q}, -t-i\beta')P_x{}^y(\mathbf{q})\rangle_0 E_{qx}. \qquad \text{(B27)}$$

Comparison of (B27) and (B16) gives at once

$$\eta = \frac{1}{V}\lim_{s\to 0}\lim_{q\to 0}\int^\infty dt\, e^{-st}\int_0^\beta d\beta' \times\langle P_x{}^y(-\mathbf{q}, -t-i\beta')P_x{}^y(\mathbf{q})\rangle_0$$
$$= \frac{1}{V}\lim_{s\to 0}\int_0^\infty dt\, e^{-st}\int_0^\beta d\beta' \times\langle \tilde{P}_x{}^y(0, -t-i\beta')\tilde{P}_x{}^y(0)\rangle_0, \qquad \text{(B28)}$$

[11] See H. Mori, Ref. 1, Eq. (6.7).

where for any operator A we write

$$\tilde{A}=A-\langle A\rangle_0. \quad \text{(B29)}$$

This is the standard result for the shear viscosity. For the bulk viscosity one must proceed a little more carefully, as is seen by the existence of the second term in the right-hand side of (B17). This indicates that in the longitudinal case the second term on the right-hand side of (B26) must have a contribution which is $O(1/s^2)$, which must be subtracted out before we can get an expression for $\zeta+4\eta/3$.

In (B26) let us take $\mathbf{q}$, $\mathbf{E}$ in the x direction.

$$s\rho_m{}^0 v_{\mathbf{q}x}=NE_{\mathbf{q}x}-\frac{q^2}{ms}\int_0^\infty dt\, e^{-st}\int_0^\beta d\beta' \times\langle P_x{}^x(-\mathbf{q},-t-i\beta')P_x{}^x(\mathbf{q})\rangle_0 E_{\mathbf{q}x}. \quad \text{(B30)}$$

Now consider

$$A(\mathbf{q})\equiv P_x{}^x(\mathbf{q})-C_1 n_{\mathbf{q}}-C_2 h_{\mathbf{q}}, \quad \text{(B31)}$$

where

$$C_1=(\partial p/\partial n)_u{}^0,\quad C_2=(\partial p/\partial u)_n{}^0. \quad \text{(B32)}$$

Then we have

$$\int_0^\infty dt\, e^{-st}\int_0^\beta d\beta'\langle P_x{}^x(-\mathbf{q},-t-i\beta')P_x{}^x(\mathbf{q})\rangle_0 =\int_0^\infty dt\, e^{-st}\int_0^\beta d\beta'\langle A(-\mathbf{q},-t-i\beta')A(\mathbf{q})\rangle_0+X. \quad \text{(B33)}$$

The remainder X may be written

$$X=(\beta/s)\{\langle P_x{}^x(-\mathbf{q})(C_1n_{\mathbf{q}}+C_2h_{\mathbf{q}})\rangle_0 +\langle(C_1n_{-\mathbf{q}}+C_2h_{-\mathbf{q}})P_x{}^x(\mathbf{q})\rangle_0 -\langle(C_1n_{-\mathbf{q}}+C_2h_{-\mathbf{q}})(C_1n_{\mathbf{q}}+C_2h_{\mathbf{q}})\rangle_0\}, \quad \text{(B34)}$$

since $n_{\mathbf{q}}$ and $h_{\mathbf{q}}$ are constants of the motion up to terms of order q, and we are interested only in the leading term. The last term of (B34) is obtained at once using the results of Appendix A (A25)–(A27).

$$\langle(C_1n_{-\mathbf{q}}+C_2h_{-\mathbf{q}})(C_1n_{\mathbf{q}}+C_2h_{\mathbf{q}})\rangle_0 =V\{[C_1(\partial n/\partial\alpha)_\beta{}^0+C_2(\partial u/\partial\alpha)_\beta{}^0]C_1 -[C_1(\partial n/\partial\beta)_\alpha{}^0+C_2(\partial u/\partial\beta)_\alpha{}^0]C_2\} =V[C_1(\partial p/\partial\alpha)_\beta{}^0-C_2(\partial p/\partial\beta)_\alpha{}^0]=(Vn_0/\beta)C_0, \quad \text{(B35)}$$

since, as one easily sees,

$$(\partial p/\partial\alpha)_\beta{}^0=n_0/\beta,\quad(\partial p/\partial\beta)_\alpha{}^0=-n_0w_0/\beta. \quad \text{(B36)}$$

The second term of (B34) is equal to the first by the usual time-reversal arguments used in proving the Onsager relations. Further, for the longitudinal case,

$$P_x{}^x(-\mathbf{q})=(-m/q^2)(d^2n_{-\mathbf{q}}/dt^2), \quad \text{(B37)}$$

so that (B34) becomes

$$X=2\frac{\beta}{s}\left(\frac{-m}{q^2}\right)\left\langle\frac{d^2n_{-\mathbf{q}}}{dt^2}(C_1n_{\mathbf{q}}+C_2h_{\mathbf{q}})\right\rangle-\frac{Vn_0C_0}{s} =2(\beta/s)(m/q^2)\langle\dot{n}_{-\mathbf{q}}(C_1\dot{n}_{\mathbf{q}}+C_2\dot{h}_{\mathbf{q}})\rangle_0-Vm_0C_0/s =2(\beta/s)(im/q)\langle j_{-qx}(C_1\dot{n}_{\mathbf{q}}+C_2\dot{h}_{\mathbf{q}})\rangle_0-Vm_0C_0/s. \quad \text{(B38)}$$

However, in the longitudinal case,

$$C_1\langle\dot{n}_{\mathbf{q}}\rangle+C_2\langle\dot{h}_{\mathbf{q}}\rangle =\int_0^\infty dt\, e^{-st}\int_0^\beta d\beta'\langle j_{-\mathbf{q}x}(-t-i\beta')(C_1\dot{n}_{\mathbf{q}}+C_2\dot{h}_{\mathbf{q}})\rangle_0E_{\mathbf{q}x} =\beta/s\langle j_{-\mathbf{q}x}(C_1\dot{n}_{\mathbf{q}}+C_2\dot{h}_{\mathbf{q}})\rangle_0E_{\mathbf{q}x}, \quad \text{(B39)}$$

since once again $j_{-\mathbf{q}x}$ is a constant of the motion as q goes to zero. Therefore

$$\beta/s\langle j_{-\mathbf{q}x}(C_1\dot{n}_{\mathbf{q}}+C_2\dot{h}_{\mathbf{q}})\rangle_0 =s(C_1\langle n_{\mathbf{q}}\rangle+C_2\langle h_{\mathbf{q}}\rangle)/E_{\mathbf{q}x}=-iqn_0VC_0/ms \quad \text{(B40)}$$

from (B12). Finally,

$$X=Vn_0C_0/s. \quad \text{(B41)}$$

(This result may also be obtained rather tediously by calculating the averages directly.)

Thus (B30) becomes

$$s\rho_m{}^0v_{\mathbf{q}x}=NE_{\mathbf{q}x}-\frac{q^2Vn_0C_0}{ms^2}E_{\mathbf{q}x}-\frac{q^2}{ms}\int_0^\infty dt\, e^{-st}\int_0^\beta d\beta' \times\langle A(-\mathbf{q},-t-i\beta')A(\mathbf{q})\rangle_0E_{\mathbf{q}x}. \quad \text{(B42)}$$

Comparison with (B17) shows that this is of the correct form and therefore that

$$\zeta+\frac{4\eta}{3}=\frac{1}{V}\lim_{s\to0}\lim_{q\to0}\int_0^\infty dt\, e^{-st}\int_0^\beta d\beta' \times\langle A(-q,-t-i\beta')A(q)\rangle_0 =\frac{1}{V}\lim_{s\to0}\int_0^\infty dt\, e^{-st}\int_0^\beta d\beta' \times\langle\tilde{A}(0,-t-i\beta')\tilde{A}(0)\rangle_0. \quad \text{(B43)}$$

This expression for the bulk viscosity coefficient does not agree with the results found in Mori's 1958 work (see Ref. 1), but it does agree with his recent result.[12]

It is also quite easy to obtain an expression for the heat conductivity by a method analogous to that used in Sec. III. We again introduce a field ψ. Let us take the electric field to be zero. The conditions for equilibrium (A30) and (A31) are then

$$(\mu/T)_{\mathbf{q}}=0\quad(1/T)_{\mathbf{q}}=(V/T_0)\psi_{\mathbf{q}}. \quad \text{(B44)}$$

We must add terms to the phenomenological equations such that in equilibrium no currents flow. Clearly that means that in the heat current, instead of $-K\nabla_\beta T$ we must have $-K(\nabla_\beta T+T_0\nabla_\beta\psi)$. Therefore (B7) becomes

$$(\partial/\partial t)(u-w_0n)=K\nabla_\beta(\nabla_\beta T+T_0\nabla_\beta\psi) =K\nabla^2T+T_0K\nabla^2\psi. \quad \text{(B45)}$$

[12] H. Mori, Progr. Theoret. Phys. (Kyoto) 28, 763 (1962).

Again, taking the $\mathbf{q}$th Fourier component and letting everything vary as e^{st}, we obtain

$$s(u_{\mathbf{q}}-w_0n_{\mathbf{q}})=-q^2(KT_{\mathbf{q}}+T_0VK\psi_{\mathbf{q}}).\qquad\text{(B46)}$$

Again considering the "rapid" case $q\to 0$ then $s\to 0$, the variation in temperature itself must be $O(q^2)$ and so may be neglected in (B44). This may be seen by looking at the explicit expressions for $\langle\dot{n}_{\mathbf{q}}\rangle$ or $\langle\dot{h}_{\mathbf{q}}\rangle$ given by perturbation theory with only a $\psi_{\mathbf{q}}$ present. For example,

$$\langle\dot{n}_{\mathbf{q}}\rangle=\int_0^\infty dt\,e^{-st}\int_0^\beta d\beta'\langle j_{-\mathbf{q}\gamma}{}^E(-t-i\beta')\dot{n}_{\mathbf{q}}\rangle(-iq_\gamma\psi_{\mathbf{q}})$$

$$=-q_\delta q_\gamma\int_0^\infty dt\,e^{-st}\int_0^\beta d\beta'\langle j_{-\mathbf{q}\gamma}{}^E(-t-i\beta')j_{\mathbf{q}\delta}\rangle\psi_{\mathbf{q}}$$

$$=-(q_\delta q_\gamma/s)\beta\langle j_{-\mathbf{q}\gamma}{}^E j_{\mathbf{q}\delta}\rangle_0\psi_{\mathbf{q}},$$

$$\langle n_{\mathbf{q}}\rangle\sim(q^2/s^2)\psi_{\mathbf{q}}.$$

Therefore, for the leading term,

$$s(u_{\mathbf{q}}-w_0n_{\mathbf{q}})=-T_0Vq^2K\psi_{\mathbf{q}}.\qquad\text{(B47)}$$

On the other hand, from our general formula we have, taking $\mathbf{q}$ in the x direction,

$$\langle\dot{h}_{\mathbf{q}}-w_0\dot{n}_{\mathbf{q}}\rangle$$

$$=-\int_0^\infty dt\,e^{-st}\int_0^\beta d\beta'\langle\dot{h}_{-\mathbf{q}}(-t-i\beta')(\dot{h}_{\mathbf{q}}-w_0\dot{n}_{\mathbf{q}})\rangle\psi_{\mathbf{q}}$$

$$=-q^2\int_0^\infty dt\,e^{-st}\int_0^\beta d\beta'\langle j_{-\mathbf{q}x}{}^E(-t-i\beta')\times(j_{-\mathbf{q}x}{}^E-w_0j_{\mathbf{q}x})\rangle_0\psi_{\mathbf{q}}.\qquad\text{(B48)}$$

If we define the "thermal" current $j_{\mathbf{q}x}{}^T$ by

$$j_{\mathbf{q}x}{}^T=j_{\mathbf{q}x}{}^E-w_0j_{\mathbf{q}x},\qquad\text{(B49)}$$

then (B46) may be written

$$s\langle h_{\mathbf{q}}-w_0n_{\mathbf{q}}\rangle=-q^2\int_0^\infty dt\,e^{-st}\int_0^\beta d\beta'\times\langle j_{-\mathbf{q}x}{}^T(-t-i\beta')j_{\mathbf{q}x}{}^T\rangle_0\psi_{\mathbf{q}},\qquad\text{(B50)}$$

since the extra $j_{\mathbf{q}x}$ term gives something which goes to zero as q goes to zero. This is because, for a longitudinal electric field only,

$$\int_0^\infty e^{-st}dt\int_0^\beta d\beta'\langle j_{-\mathbf{q}x}(-t-i\beta')j_{\mathbf{q}x}{}^T\rangle_0E_{\mathbf{q}x}=\langle j_{\mathbf{q}}{}^T\rangle$$

$$=(i/q)\langle\dot{h}_{\mathbf{q}}-w_0\dot{n}_{\mathbf{q}}\rangle=(s/q)(\langle h_{\mathbf{q}}\rangle-w_0\langle n_{\mathbf{q}}\rangle)$$

$$=-q^2KT_{\mathbf{q}}=0,\quad\text{when}\quad q=0.$$

Comparing (B45) with (A16) we see that

$$K=\lim_{s\to 0}\lim_{q\to 0}\frac{1}{VT_0}\int_0^\infty dt\,e^{-st}\int_0^\beta d\beta'\times\langle j_{-\mathbf{q}x}{}^T(-t-i\beta')j_{\mathbf{q}x}{}^T\rangle_0\qquad\text{(B51)}$$

$$=\lim_{s\to 0}\frac{1}{VT_0}\int_0^\infty dt\,e^{-st}\int_0^\beta d\beta'\times\langle j_{0x}{}^T(-t-i\beta')j_{0x}{}^T\rangle_0.\qquad\text{(B52)}$$

This is the usual result for the heat conductivity of a liquid.