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from which follows:

$$\alpha = T\frac{d^2 X_x{}^t}{dT^2}$$

$$2\beta = T\frac{d^2 a}{dT^2}$$

$$2\beta + \gamma = T\frac{d^2 b}{dT^2}$$

The functions of temperature $\alpha\,\beta\,\gamma$ can be calculated from the formulae of BORN so that X'_x a and b can be determined. In a more detailed communication we will communicate this calculation itself also.

Delft, June 1916.   *Phys. Lab. of the T. H. S.*

Physics. — "*The influence of accidental deviations of density on the equation of state.*" By Prof. L. S. ORNSTEIN and Dr. F. ZERNIKE. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of June 24, 1916).

In their article in the Encyclopädie der mathematischen Wissenschaften the following statement by Prof. KAMERLINGH ONNES and Dr. KEESOM is found :

"Da bei der Annäherung an den kritischen Punkt Liquid—Gas die von den BOLTZMANN-GIBBS'schen Prinzipien beherrschten Dichteunterschiede (Schwarmbildung Nr 48*f*), der bis ∞ ansteigenden Zusammendrückbarkeit der Substanz wegen, besonders hervortreten, ist zu erwarten, dasz bei der Entwicklung der Zustandsgleichung für die Umgebung des kritischen Punktes nach jenen Prinzipien Glieder auftreten werden, die mit der grossen Zusammendrückbarkeit in der Nähe des kritischen Punktes zusammenhängen. Diese Glieder werden wahrscheinlich durch die Art der Abweichung der Zusammendrückbarkeit in dem kritischen Gebiet (∞ im kritischen Punkt und von diesem aus, soweit sie das realisirbare homogene Gebiet betrifft, allseitig schnell abfallend) für dasselbe ein besondere Bedeutung erlangen, während sie für benachbarte Gebiete nicht mehr in Betracht kommen. Während eine allmählige Verschiebung oder Verzerrung, die sich durch das ganze Diagramm durchzieht, wie z. B. eine kontinuirliche Aenderung von a_w, b_w oder R_w, sich experimentell nicht besonders zeigen würde, werden die betreffende Glieder in der Zustandsgleichung in der Nähe des kritischen Punktes demgemäss zum Schluss führen können, dass die Eigenschaften in diesem Gebiet in beobacht-

barer Weise abweichen von den Eigenschaften, die man durch Inter-
polation zwischen Zuständen, die um den kritischen herumliegen,
aber weiter von ihm entfernt bleiben, erwarten sollte."

KAMERLINGH ONNES and KEESOM assert to have found deviations
pointing to suchlike causes and they have tried to account for the
special phenomena at the critical point by adding a function of
disturbance to the equation of state which takes specially large
values in the critical point.

In this contribution we will try to point out that there can be
no question about a function of disturbance caused by the accidental
deviations of density.

In deducing the equation of state we will use the method of the
virial. The virial theorem takes the form

$$2L + \Sigma \overline{(x_h X_h + y_k Y_h + z_h Z_k)} + \Sigma \Sigma \overline{r_{hk} F (r_{hk})} = 0$$

if L is the kinetic energy, the coordinates of the molecules are
$x_h, y_h, z_h,$ the distance between the centres of a pair of molecules
h and k is r_{hk}, the external forces are $X_h Y_h Z_h$ and the force
between the pair of molecules $h \cdot k$ is $F(z_{hk})$. If the pressure is the
only external force, the second average may be represented by
$- 3p V$, whereas the average kinetic energy depends on the abso-
lute temperature in the known way. [1])

We will now take into consideration the second sum. Suppose
the volume V containing n molecules to be divided into a large number
of elements dv_k; let the mean density in these elements be ϱ. Now
consider a system in which the density in the different elements can
be represented by $\varrho + v_k$. Then the contribution by the elements
dv_k and dv_h to the sum mentioned above amounts to

$$(\varrho + v_k) (\varrho + v_h) r_{hk} F (r_{hk}) dv_k dv_h.$$

By integrating this expression with respect to dv_h and dv_k over
the volume V we get, passing to the mean values, twice the
required sum. Taking the averages the terms ϱv_h and ϱv_k will not
contribute, the average of $v_h = v_k$ being zero.

The contribution

$$\iint \varrho^2 F (r_{hk}) r_{hk} dv_k dv_h$$

is the one taken into account by the usual theory, which neglects
accidental deviations of density, and which therefore takes for ϱ
the mean value, or what comes to the same, the most common
value. Hence the correction for deviations of density appears to be

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[1]) Compare e.g. L. BOLTZMANN, Gastheorie II, p. 141.

$$\iint \overline{v_h \, v_k} \, r_{hk} \, F\left(r_{hk}\right) \, dv_k \, dv_h.$$

Now this integral can be transformed by means of the function g, which we have introduced into our considerations on the opalescence in the critical point. [1])

According to the definition of the function g, the mean value of v_k if v_h is kept constant may be represented by

$$\overline{v_k} = v_h \; g(r_{hk}) \, dv_h.$$

Further we have shown that:

$$\overline{v_k \, v_h} = g\left(r_{hk}\right) \, v_h^2 \, dv_0 = \varrho g\left(r_{hk}\right)$$

(l.c. p. 796) (8).

Introducing this we get

$$\iint \varrho \, r_{hk} \, F\left(r_{hk}\right) \, g\left(r_{hk}\right) \, dv_k \, dv_h.$$

For this we may write

$$n \int r_{hk} \, F\left(r_{hk}\right) \, g\left(r_h \, k\right) \, dv_k$$

as $\int \varrho \, dv_h$ represents the whole number of molecules.

If we proceed to the usual first approximation regarding the terms of the first integral, then we find as equation of state

$$p + \frac{a}{v^2} = \frac{rT}{r}\left(1 + \frac{b}{v}\right) + \frac{1}{6v}\int m g \, \left(r_{hk}\right) \cdot r_{hk} \cdot F\left(r_{hk}\right) \, dv_k$$

where $v = \dfrac{V}{nm}$, and m is the mass of the molecule.

This formula shows that if we take into account the deviations of density, we find a new term in the equation of state. This term however is not equivalent to the function of disturbance of KAMERLINGH ONNES and KEESOM. The special character of the function g in the neighbourhood of the critical point causing the clustering tendency there to become very strong, consists in the fact that this function gets perceptible values for points far outside the sphere of action, so that

for the critical state $\int_0^\infty g \; dv$ does not converge any more. Phenomena connected with this last integral become therefore specially strong at the critical point. For small values of r, inside the sphere of action, g hardly changes when we approach the critical point; and only these values have influence on the found term of correction.

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[1]) L S. ORNSTEIN and F ZERNIKE. The accidental deviations of density and the opalescence in the critical point. These proc. XVII, p. 793.

In this integral the function $F(r_{hk})$ is zero without the sphere of action, therefore this integral has only to be extended to this region. [1] Thus the abnormal character, stated by KAMERLINGH ONNES and KEESOM, cannot be explained by a function of disturbance as a consequence of the accidental deviations.

Physics. — *"Contributions to the research of liquid crystals."* By Dr. W. J. H. MOLL and Prof. L. S. ORNSTEIN. (Communicated by Prof. W. H. JULIUS).

(Communicated in the meeting of October 28, 1916).

1. The extinction of para-azoxyanisol in the magnetic field.

VOIGT has devoted a circumstantial report to the liquid crystals in the Physikalische Zeitschrift XVII 1916. In this report he points specially to the fact that a great uncertainty still exists on the influence exercised by a magnetic field on the extinction. For this reason we further examined the extinction.

We will provisionally explain our method in this communication, and mention some of the results attained, and add a few remarks on a possible explanation of these results.

§ 1. Method of observation.

The extinction was measured with the aid of the galvanometer and the thermopile described by one of us formerly. [2] These sensitive instruments have the great advantage of indicating quickly within two seconds, and so they enable us to follow the changes in the liquid crystals proceeding slowly, but nevertheless so quickly that they must necessarily escape the observer's attention.

These very changes however are of great interest in order to understand the phenomena under consideration.

The substance is heated in a small electric oven, consisting of a strip of copper AA coiled at the two ends with resistance wire. By regulating the current sent through these coils each desired

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[1] According to the explicit calculation of g, executed by one of us, the solid character is denoted by $r^{-1} e^{-kr}$, where $k = 0$ for the critical point. Comp. ZERNIKE, The clustering tendency of the molecules in the critical state and the extinction of light caused thereby. These Proc. XVIII p. 1520.

[2] W. J. H. MOLL. Proc. Kon. Acad. v. Wetensch. May and Nov. 1913: Mrs. KIPP and SONS were so kind as to put the apparatus at our disposal.

84