

*Citation:*

L.S. Ornstein, The clustering tendency of the molecules at the critical point, in:  
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in the Physical Laboratory, had proved already that the substance we had under consideration is paramagnetic.

For the moment these principal points may suffice. Perhaps we will discuss these questions when publishing further experimental results.

We gladly use the occasion to thank Prof. VAN ROMBURGH for his kindness in putting his preparation at our disposal.

*Summary.*

1. A new method is described to measure with the aid of thermopile and galvanometer the extinction of liquid-crystalline substances.

2. The very different influence on the extinction of a vertical (longitudinal) and a horizontal (transversal) magnetic field is traced.

3. An explanation of the observed phenomena is drawn in outline whereby the principal supposition is that the wall of glass directs the particles in planes parallel, directs them according to the lines of force.

*Physical Laboratory, Institute for Theoretical Physics.*

*Utrecht, October 1916.*

**Physics.** — “*The clustering tendency of the molecules at the critical point*”. By Prof. L. S. ORNSTEIN. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of May 27, 1916).

In a former communication by Dr. F. ZERNIKE and the author<sup>1)</sup> the arrangement of the molecules in space using a new method of probability is described, more accurately than this was possible in the considerations of VON SMOLUCHOWSKI and EINSTEIN; by this method it was also possible to calculate the opalescence at the critical point itself, which was impossible with the formulas of KEESOM-EINSTEIN.

We introduced a function  $f$ , defined in the following way. Suppose that space is divided into a great number of elements of volume  $dV_0, dV_1, \dots, dV_s$ , etc. The numbers  $r_0, r_1, r_s$ , etc. may represent the deviations of the average number of molecules in these elements. Then, if the *deviations* in all the surrounding elements of the working sphere are *given* ( $r_1, r_s$ , etc.), the average deviation in the element  $dV_0$  may be represented by:

<sup>1)</sup> Accidental deviations of density and the opalescence at the critical point of a single substance. These Proc. XVII, p. 793, 1914.

$$\bar{v}_0 = f_{01} v_1 dV_1 + f_{02} v_2 dV_2 + \dots \quad (1)$$

The coefficients  $f_{01}$ , etc. indicate the correlation of the elements. In a homogeneous phase they will only depend on the distance between the elements, whereas in a capillary transitory layer the function will be different.

As we published our paper we met with difficulties in the kinetic deduction of formula (1), owing to the fact that we tried to work with mathematically infinitely small elements of volume. As Dr. ZERNIKE<sup>1)</sup> has now solved another difficulty adhering to our considerations it is worth demonstrating that a deduction from statistical mechanics of (1) is possible. In this way it will be possible to indicate the physical meaning of function  $f$  and to prove that  $\int f dV$  taken with respect to the working sphere is at the critical point equal to unity, which formerly was demonstrated by an artifice.

Starting from (12) of the cited paper the proof of formula (1) is very simple.

The number of the systems (3), for which in the elements  $dV_\tau$  and  $dV_\sigma$  the deviations of the mean number of particles amount to  $v_\tau$  and  $v_\sigma$  was found to be:

$$\xi = C \omega^n \rho^{-n} e^{\frac{1}{2\Theta} n \rho \sum \varphi_{\sigma\tau}} + \frac{1}{2} \sum_{\sigma} \left( -\frac{1}{v} + \frac{1}{v} \frac{d}{d\rho} \rho^2 \frac{d \log \omega}{d\rho} + \frac{\varphi_{00}}{\Theta dV} \right) v_\sigma^2 + \sum_{\sigma} \sum_{\tau} \varphi_{\sigma\tau} \frac{v_\sigma v_\tau}{dV} \dots \quad (2)$$

In this formula  $\rho$  represents the number of molecules per unit of volume  $\left(\frac{n}{V}\right)$ ,  $\varphi_{\sigma\tau}$  is the mutual potential energy for a couple of molecules the one of which is lying in the element  $\rho$ , the other in the element  $\tau$ ,  $\omega$  is the function defined in my Thesis.

Now considering that the quantity  $\frac{a}{\Theta dV}$  or  $\sum \rho \frac{\varphi_{\sigma\tau}}{\Theta}$  (as appears from the equation of state) is of the order of the unity, every term of the form  $\frac{\varphi_{\sigma\tau}}{\Theta dV}$  will be small with respect to unity. Hence we may develop in the exponential function the part containing in  $v_\tau$  and  $v_\sigma$  and write (summarising unimportant terms in the constant  $D$ ):

$$\xi = D e^{\frac{1}{2} \sum_{\sigma} \left( -\frac{1}{v} + \frac{1}{v} \frac{d}{d\rho} \rho^2 \frac{d \log \omega}{d\rho} \right) v_\sigma^2} \left( 1 + \sum_{\sigma} \frac{\varphi_{00} v_\sigma^2}{2\Theta dV} + \sum_{\sigma} \sum_{\tau} \frac{\varphi_{\sigma\tau}}{\Theta dV} v_\sigma v_\tau \right) \quad (3)$$

<sup>1)</sup> The clustering tendency of the molecules in the critical state and the extinction of light caused thereby. These Proc. XVIII, p. 1520. 1916.

The number of systems for which  $v_\tau$  has every possible value and the other  $v$ 's of the sphere of action have given values is found to be:

$$\bar{\zeta}_\tau = \frac{DV \sqrt{2\pi}}{\sqrt{\left(\frac{1}{v} - \frac{1}{v} \frac{d}{dQ} \varrho^2 \frac{d \log \omega}{dQ}\right)}} e^{\frac{1}{2} \sum_{\tau \neq \sigma} \left(-\frac{1}{v} + \frac{1}{v} \frac{d}{dQ} \varrho^2 \frac{d \log \omega}{dQ}\right) v_\tau^2} \quad (4)$$

The mean value of  $v_\tau$  with given value of  $v_\tau$  ( $\tau \neq \sigma$ ) in the sphere of action now becomes

$$\sum_\tau v_\tau \bar{\zeta}_\tau = D \sum_{\tau \neq \sigma} \frac{\varphi_{\tau\tau}}{\Theta dV} v_\tau \frac{\sqrt{2\pi}}{\sqrt{\left(\frac{1}{v} - \frac{1}{v} \frac{d}{dQ} \varrho^2 \frac{d \log \omega}{dQ}\right)}} e^{\frac{1}{2} \sum_{\tau \neq \sigma} \left(-\frac{1}{v} + \frac{1}{v} \frac{d}{dQ} \varrho^2 \frac{d \log \omega}{dQ}\right) v_\tau^2} \quad (5)$$

From this follows

$$\bar{v}_\sigma = \frac{\sum v_\sigma \bar{\zeta}_\sigma}{\sum \bar{\zeta}_\sigma} = \sum_\tau v_\tau \frac{\varphi_{\tau\tau}}{\Theta dV} \frac{v}{\left(1 - \frac{d}{dQ} \varrho^2 \frac{d \log \omega}{dQ}\right)} = \sum \frac{\varphi_{\tau\tau}}{\Theta \left(1 - \frac{d}{dQ} \varrho^2 \frac{d \log \omega}{dQ}\right)} v_\tau \quad (6)$$

Thus we have now proved (1) whereas for  $f_{\tau\tau}$  we find

$$f_{\tau\tau} = \frac{\varphi_{\tau\tau}}{\Theta \left(1 - \frac{d}{dQ} \varrho^2 \frac{d \log \omega}{dQ}\right)} \dots \dots \dots (7)$$

In my Thesis I have demonstrated that the pressure in an element may be represented by

$$\frac{p}{\Theta} = \varrho - \varrho^2 \frac{d \log \omega}{dQ} - \frac{d\varrho^2}{2\Theta}$$

Thus we have

$$f_{\tau\tau} = \frac{\varphi_{\tau\tau}}{\frac{dp}{dQ} + d\varrho} \dots \dots \dots (8)$$

According to the meaning of  $\varphi_{\tau\tau}$ ,  $\int \varphi_{\tau\tau} dV$  taken with respect to the sphere of action equals  $\alpha$  (in a homogeneous medium); we get therefore for  $F$

$$F = \int f_{\tau\tau} dV = \frac{\varrho \alpha}{\frac{dp}{dQ} + \varrho \alpha} \dots \dots \dots (9)$$

For the critical point  $\frac{dp}{dQ} = 0$  and therefore  $F = 1$ . It is worth

noticing that in the deduction of (8) the fact that we have a homogeneous system has not been used. The given relation holds also in a capillary layer. However  $f_{\tau}$  will depend on a parameter in the direction of the layer (for  $\frac{dp}{d\rho}$  depends on it). The consideration may easily be extended to the case of a mixture and the capillary layers in a mixture. It will be possible then to develop MANDELSTAMM's <sup>1)</sup> considerations on the diffuse reflection at the layer of contact between two liquid phases in the critical point of mixture more exactly than he himself has done.

*Utrecht, Mei 1916.*

**Physics.** — “*The dilatation of solid bodies by heat.*” By Prof. H. A. LORENTZ.

(Communicated in the meeting of October 30, 1915.)

When in the theory of specific heat the idea had been worked out that the heat motion of solid bodies consists in vibrations of the particles under the influence of the same forces that give rise to the phenomena of elasticity, DEBYE <sup>2)</sup> successfully attacked the problem of thermal dilatation. In his theory, which has been further developed by M. J. M. VAN EVERDINGEN <sup>3)</sup>, it is shown that this phenomenon may be accounted for in a satisfactory way by adding in the expression for the potential energy of the body terms which are of the third order with respect to the displacements of the particles.

In the present paper considerations similar to those of DEBYE and VAN EVERDINGEN are presented in a form that is perhaps somewhat simpler.

§ 1. We shall suppose the body to be isotropic or crystallized in the regular system. Let  $S$  be its surface and  $v$  its volume at the temperature  $T$  and under a uniform pressure  $p$ . We can imagine that the particles lying on the surface are kept fixed in the positions about which they vibrate and that, when this has been done, the

<sup>1)</sup> Ann. der Phys. 42.

<sup>2)</sup> P. DEBYE, Zustandsgleichung und Quantenhypothese, Wolfskehl-Vorträge, Göttingen, 1913, p. 17; Leipzig, Teubner.

<sup>3)</sup> M. I. M. VAN EVERDINGEN, De toestandsvergelijking van het isotrope, vaste lichaam. Proefschrift, Utrecht, 1914.