Citation:

Accidental deviations of density and opalescence at the critical point of a single substance, in:
KNAW, Proceedings, 17 II, 1914, pp. 793-806

$$E \cos pt = RI \cos(pt+\beta) - \frac{\pi^2}{p8H^2I} l \sin(pt+\beta) \Sigma \frac{1}{s^2} \frac{1}{(n_s^2-p^2)}$$

from which I can be found. The sum in the second member can be put in a way analogous to that of § 3, into a form identical with (18). Our result does not agree with that of CREHORE (compare p. 214). In our solution the retardation of phase is the same for all vibrations, which is not the case in CREHORE's paper.

It may be observed that in our problem we have to do with a system of an infinite number of variables in which a dissipation-function couples the variables; for eliminating J from (12) and (13), we obtain

$$\ddot{\varphi}_s + n_s^2 \varphi = -\frac{8H^2}{s\pi\varrho R} \Sigma \frac{\dot{\varphi}_s}{s}.$$

The dissipation F takes the form

$$F = \frac{8H^2}{\pi^2\varrho R}\left(\Sigma \frac{\dot{\varphi}_s}{s}\right)^2.$$

Groningen, Sept. 1914.

Physics. — "*Accidental deviations of density and opalescence at the critical point of a single substance.*" By Dr. L. S. ORNSTEIN and F. ZERNIKE. (Communicated by Prof. H. A. LORENTZ.)

(Communicated in the meeting of September 26, 1914).

1. The accidental deviations for a single substance as well as for mixtures have been treated by SMOLUCHOWSKI [1]) and EINSTEIN [2]) with the aid of BOLTZMANN's principle; by ORNSTEIN [3]) with the aid of statistical mechanics. It appears as if the considerations used and the results obtained remain valid in the critical point. SMOLUCHOWSKI has applied the formula found for the probability of a deviation to the critical point itself, and has found for the average deviation of density

$$\bar{\delta} = \frac{1.13}{\sqrt[4]{v}}.$$

He has used this formula to express in terms of the mean density

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[1]) M. SMOLUCHOWSKI, Theorie Cinétique de l'opalescence. Bull. Crac 1907 p. 1057. Ann. der Phys. Bd. 25, 1908, p. 205. Phil. Mag. 1912. On opalescence of gases in the critical state. W. H. KEESOM, Ann. der Phys. 1911 p. 591.

[2]) A. EINSTEIN. Ann. der Phys. Bd. 33, 1910, p. 1276.

[3]) ORNSTEIN, These Proc., **15**, p. 54 (1912).

the accidental deviations in a cube, the side of which is equal to the wave-length of the light used in the experiments on opalescence.

Now there is a difficulty with this formula, to which, indeed, lead also the considerations of EINSTEIN as well as statistical mechanics when worked out in an analogous way for the critical point. In all these cases the mutual independence of the elements of volume is presupposed. Now, let there be given for the element of volume v the mean square of deviation *viz.* $\overline{(n-\overline{n})^2}$. Consider p equal contiguous elements of volume v_1, v_2, etc., in which n_1, n_2, etc. particles are situated, $\overline{n_1}, \overline{n_2}$ etc. indicating the mean values of these numbers.

Hence in the volume $V = v_1 + v_2 + \ldots$ there are $N = n_1 + n_2 + \ldots$ particles.

For the mean value of N we have

$$\overline{N} = \overline{n_1} + \overline{n_2} + \ldots$$

subsequently

$$\overline{(N - \overline{N})^2} = \overline{\{(n_1 - \overline{n_1}) + (n_2 - \overline{n_2}) + \ldots\}^2} = p\,\overline{(n - \overline{n})^2}$$

since, the elements of volume being supposed independent of each other, the means of the double products vanish. So we find for the deviation of density that the product of volume and mean square of deviation must be a constant.

Indeed the above-mentioned formula of probability for the deviations of density is so far inexact, as the terms of higher order appearing in it are at variance with the mutual independence of the elements of volume, which underlies the deduction of the frequency-law. In fact this deduction is only valid for such large elements of volume that these terms are no more of any influence. It is easily seen that this limit, above which the formula is valid, increases indefinitely in approaching the critical point. This explains also mathematically the wrong dependence on v found for the mean deviation in the critical point itself.

Now one could try to deduce the formula to a farther approximation. However, also the supposition of independence of the elements of volume is inexact in case these are small, and it would thus be impossible to ascertain how far the formula would yet differ from reality.[1]

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[1] A deduction of the inequalities in which the inexact terms of higher order do not at all appear, is given by ZERNIKE in his thesis, which will shortly appear. As this deduction too uses the independence alluded to, the objection mentioned holds here also.

The remark of EINSTEIN (l.c. p. 1285) that there would be no principal difficulty

2. Now, in order to avoid the difficulties mentioned, it is necessary to take into account the influence of deviations in the one element on the state in another. Let us divide the system into infinitely small elements of volume. A molecule is considered to lie in the element when its centre is situated in it. We consider an element dv_0 in the origin of coordinates. Around this element we imagine the sphere of attraction i.e. the region in which a molecule must lie when it is to have any influence on the state in dv_0. We determine the numbers of molecules for the elements of the sphere of attraction in giving the deviations ν_1, ν_2 etc. from the mean number of molecules per unit of volume.

We suppose the mean value of the density ν_0, when ν_1 etc. are given, to be a linear function of the deviations ν_1 etc., i.e. we put[1])

$$\overline{\nu_0} = C + f_1\nu_1 dv_1 + f_2\nu_2 dv_2 + \cdot \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Taking the mean value of ν_0 over all possible values of ν_1, it appears immediately that $C = 0$, hence

$$\overline{\nu_0} = f_1\nu_1 dv_1 + f_2\nu_2 dv_2 + \cdot \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The coefficients f denote the coupling of the elements, they only depend on the relative coordinates, i.e. here, on $x\, y\, z$. That the influence of an element, when the density is given, must be proportional to its size is immediately seen by considering the influence of uniting two elements in (2).

We shall now write the sum (2) as an integral. For the density in the element $dx\, dy\, dz$ we put ν_{xyz}; further, we can dispose of f in such a way that $f(0,0,0) = 0$. Then for (2) we get

$$\overline{\nu_0} = \iiint_{-\infty}^{+\infty} \nu_{xyz} f(x,y,z)\, dx dy dz \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The integration may be extended here from $-\infty$ to $+\infty$, f being zero outside the sphere of action [2]).

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in extending his deduction to a further approximation, is therefore mistaken. On the contrary, the consideration of higher terms so long as the independence is made use of, will not lead to anything.

[1]) Putting things more generally, we could write a series in ν_1 etc. instead of (1). However, for the purpose we have in view, (1) is sufficient.

[2]) The quantity ν can only take the values $1-adv$ and $-adv$, hence ν is a discontinuous function of the coordinates. One might be inclined therefore, to continue writing a sum instead of the integral (3) and to solve the problem dealt with in the text with the aid of this sum. In doing so one gets sum-formulae which are wholly analogous to the integrals we used. However, we prefer introducing the integral, as the discontinuous function ν has entirely disappeared from formula (6) only the function g appearing in it, which is continuous when the function f is

On the contrary, if v_0 is given, $\bar{v}$ has another value for the surrounding elements, than if $v_0 = 0$. Be in the element at xyz

$$\bar{v}_{xyz} = g(x, y, z, v_0 dv_0) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and let us try to determine the function g, the function f being given.

Now take the mean of formula (3), a fixed value v_1 being ascribed to v in a certain element $dx_1\, dy_1\, dz_1$.

In x, y, z, according to (4)

$$\bar{v}_{xyz} = g(x-x_1, y-y_1, z-z_1, v_1\, dx_1 dy_1 dz_1) \quad . \quad . \quad . \quad . \quad (5)$$

For the first member we therefore get

$$\bar{V}_0 = g(x_1, y_1, z_1, v_1 dx_1 dy_1 dz_1)$$

as f and g do not depend on the direction of the line joining the elements. In the integral, (5) cannot be applied to the element $dx_1\, dy_1\, dz_1$; however, this element gives

$$v_1 f(x_1, y_1, z_1)\, dx_1 dy_1 dz_1$$

Further taking $g\,(0, 0, 0)$ zero, as it may arbitrarily be chosen, we get

$$g(x_1,y_1,z_1,v_1 dx_1 dy_1 dz_1) = \iiint\limits_{-\infty}^{+\infty} g(x-x_1,y-y_1,z-z_1,v_1 dx_1 dy_1 dz_1) f(xyz)\, dxdydz + \\ + v_1 f(x_1,y_1,z_1)\, dx_1 dy_1 dz_1.$$

This is true for all values of $v_1\, dx_1\, dy_1\, dz_1$, hence g must contain this quantity as a factor, and we obtain

$$g(x_1,y_1,z_1) - \iiint\limits_{-\infty}^{+\infty} g(x-x_1, y-y_1, z-z_1)\, f(xyz)\, dxdydz = f(x_1,y_1,z_1)$$

Now put $x - x_1 = \xi$, $y - y_1 = \eta$, $z - z_1 = \zeta$, and omit the index, then for g we get the integral equation

$$g(x,y,z) - \iiint\limits_{-\infty}^{+\infty} f(x+\xi, y+\eta, z+\zeta)\, g(\xi\eta\zeta)\, d\xi d\eta d\zeta = f(xyz). \quad . \quad (6)$$

For g we have

$$\bar{v}_{xyz} = g(xyz)\, v_0\, dv_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

from which it appears immediately that

$$\overline{v_{xyz}\, v_0} = g(xyz)\, \overline{v_0^2}\, dv_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

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continuous. The integral-formulae obtained in this way are easier to deal with mathematically, and besides the integral equation (6) has been solved, this being not so easily found from the analogous sum-formula.

Now let us consider more closely the coefficient of g in (8).

Let a molecules be present in the unit of volume, then the mean number of molecules in dv is equal to adv. If we take dv very small, there may be no or one molecule in it. The chance for one molecule is, therefore, adv; for none $1 - adv$. In the first case $\boldsymbol{v} = \frac{1}{dv} - a$, in the latter it is $-a$, thus

[illegible]

$$\overline{\boldsymbol{v}^2} = \frac{a}{dv} - a^2$$

or

$$\overline{\boldsymbol{v}^2}dv = a \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Introducing this into (8), we find for the two elements $x_\sigma y_\sigma z_\sigma$ and $x_\tau y_\tau z_\tau$

$$\overline{\boldsymbol{v}_\sigma \boldsymbol{v}_\tau} = ag(x_\sigma - x_\tau, y_\sigma - y_\tau, z_\sigma - z_\tau) \quad . \quad . \quad . \quad . \quad . \quad (10)$$

This result can be used to indicate the values of $\overline{(N - \overline{N})^2} = \overline{\Delta N^2}$ for any volume.

We have

$$\Delta N = \int \boldsymbol{v} dv$$

$$\overline{\Delta N^2} = \iint\limits_{VV} \overline{\boldsymbol{v}_\sigma{}^2}\, dv_\sigma\, dv_\tau + \iint\limits_{VV} \overline{\boldsymbol{v}_\sigma \boldsymbol{v}_\tau}\, dx_\sigma\, dy_\sigma\, dz_\sigma\, dx_\tau\, dy_\tau\, dz_\tau$$

from which applying (9) and (10)

$$\overline{\Delta N^2} = aV + a \iint\limits_{VV} g\,(x_\sigma - x_\tau, y_\sigma - y_\tau, z_\sigma - z_\tau)\, dx_\sigma\, dy_\sigma\, dz_\sigma\, dx_\tau\, dy_\tau\, dz_\tau\,.$$

This holds for every size and form of V. Elaborating it for a cube with side l the dependence on V is seen more clearly. Putting $x_\sigma - x_\tau = \xi$, $y_\sigma - y_\tau = \eta$, $z_\sigma - z_\tau = \zeta$, and integrating only for $\xi\eta\zeta$ positive, by which $^1/_8$ of the integral in question is found then, we get

$$\overline{\Delta N^2} = \overline{N} + 8a \int_0^l\!\!\int_0^l\!\!\int_0^l g\,(\xi\eta\zeta) \int_\xi^l\!\!\int_\eta^l\!\!\int_\zeta^l dx_\sigma\, dy_\sigma\, dz_\sigma \qquad d\xi\ d\eta\ d\zeta$$

$$= \overline{N} + 8a \int_0^l\!\!\int_0^l\!\!\int_0^l (l^3 - l^2)(\xi + \eta + \zeta) + l\,(\xi\eta + \eta\zeta + \zeta\xi) - \xi\eta\zeta)\, g\, d\xi\, d\eta\, d\zeta.$$

Hence

$$\frac{\overline{\Delta N^2}}{\overline{N}} = 1 + \iiint\limits_{-l}^{+l} g\,(xyz)\,dxdydz - 3\iiint\limits_{-l}^{+l} \frac{|x|}{l}\,g\,dxdydz$$

$$+ 3\iiint\limits_{-l}^{+l} \frac{x^2}{l^2}\,g\,dx\,dy\,dz - \iiint\limits_{-l}^{+l} \frac{|x^3|}{l^3}\,g\,dx\,dy\,dz.$$

Every integral in this formula is always smaller than the preceding one. If l is large with respect to the distance for which g has an appreciable value, there remains only the first integral. For any great volume we have

$$\frac{\overline{\Delta N^2}}{\overline{N}} = 1 + \iiint\limits_{-\infty}^{+\infty} g\,dx\,dy\,dz \quad . \; . \; . \; . \; . \quad (11)$$

3. In trying to determine the function f by means of statistical mechanics, we meet with difficulties. Still something may be found about the quantities $\overline{\nu_\sigma \nu_\tau}$ by applying the statistic-mechanical method to our problem. Indeed statistical mechanics permit to introduce a mutual action of the elements of volume.

We will avail ourselves of a canonical ensemble. We suppose the molecules to be spherical and rigid, and to attract each other for distances which are great with respect to their size. Elements small with respect to the sphere of attraction therefore may still contain a great number of molecules. But now we drop the supposition of the sphere of attraction being homogeneously filled for all systems (or at least for by far the greater part of them) [1].

In calculating the number of the various distributions, we must, for the potential energy of attraction, take into account the mutual action of the elements; whereas, in calculating the exclusion of definite configurations of centres, we may neglect the fact that there is some correlation on the borders of the elements. For the dimensions of the elements have been supposed large with respect to the molecular diameter.

The mutual potential energy of the $\nu + \tau$ molecules contained in an element dv, will be represented by

$$-\tfrac{1}{2}\,\frac{(\nu+\tau)^2}{dv}\,\varphi_{00}$$

in this formula ν represents the number of molecules contained in the volume dv for the most frequent system. In this system the distribution is homogeneous.

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[1] Cf Ornstein, Toepassing der Statistische mechanica van Gibbs op molekulair-theoretische vraagstukken. Diss. Leiden 1908, p. 43 and p. 110.

Of course, the potential energies will not strictly be the same for different configurations within the elements, but we shall neglect this complication. Further we will represent the mutual potential energy for the two elements σ and ϱ by

$$-\frac{(v+\tau_\sigma)(v+\tau_\varrho)\,\varphi_{\varrho\sigma}}{dv}$$

all elements of volume being put equal.

For the total potential energy we find, in this way

$$-\frac{1}{2dv}\Sigma_\sigma (v+\tau_\sigma)\,\Sigma_\varrho (v+\tau_\varrho)\,\varphi_{\varrho\sigma}.$$

For the frequency ζ of a system with the given distribution of molecules we find

$$\zeta = C\frac{n!}{(v+\tau_1)!(v+\tau_2)!\ldots}(\omega_1 dV)^{\nu+\tau_1}\ldots(\omega_1 dV)^{\nu+\tau_2}\ldots\, e^{\frac{1}{2\Theta dv}\Sigma_\sigma(v+\tau_\sigma)\Sigma_\varrho(v+\tau_\varrho)\varphi_{\varrho\sigma}}.$$

Here ω is the function defined in the quoted dissertation on p. 48. Supposing $\tau \ll v$ and developing, we get,

$$\zeta = C\,\omega^n a^{-n}\, e^{\frac{1}{2\Theta} na\Sigma_\varrho\varphi_{\varrho\sigma} + \frac{1}{2}\Sigma\Sigma\left(-\frac{1}{v}+\frac{1}{v}\frac{d}{da}a^2\frac{d\log\omega}{da}+\frac{\varphi_{00}}{\Theta dv}\right)\tau_\sigma^2 + \frac{\varphi_{\sigma\varrho}}{\Theta dv}\tau_\sigma\tau_\varrho + \ldots} \quad \ldots\ldots\ldots \quad (12)$$

The number of molecules per unit of volume represented there by n, has been put a in this paper. The function ω and the faculties are developed in the same way as in the quoted dissertation. The double sum in the exponent gives the forms $\Sigma_\sigma v\Sigma_\varrho\tau_\varrho\varphi_{\varrho\sigma}$ and $\Sigma\tau_\sigma\Sigma v\varphi_{\rho\sigma}$. These forms are identical, as they consist of the same terms differently arranged, further $\Sigma\varphi_{\rho\sigma}$ is the same for all molecules and $\Sigma\tau_\sigma = 0$, consequently both sums vanish.

The constant C contains the factor $Ne^{\psi/\Theta}$ along with quantities which do not depend on the volume by summing up (12) over all possible values of τ (and taking into account that $\Sigma\tau_\sigma = 0$) we get N, the total number of systems in the ensemble. So we find

$$e^{-\frac{\psi}{\Theta}} = \frac{C'}{\sqrt{\Delta}}\,\omega^n\, V^n\, e^{\frac{n^2}{2\Theta v}\Sigma\varphi_{\rho\sigma}},$$

the quantity Δ being the discriminant of the quadratic form in the exponent.

When we write $\Sigma_\rho\varphi_{\rho\sigma} = \alpha$, we find for the pressure $p = -\frac{\partial\psi}{\partial v}$

$$\frac{p}{\Theta}=\frac{n}{V}+n\frac{d\log\omega}{dV}-\frac{a}{2\Theta}\frac{n^2}{V^2}$$

$\Delta^{-1/2}$ being very small with respect to the other factors, we may neglect its influence in ψ[1]). The equation of state has the same form as VAN DER WAALS' equation. However, the correlation is sensible in the accidental deviation; for it changes the value of $\overline{\tau^2}$; and $\overline{\tau_\sigma\tau_\rho}$, which vanish if the correlation is neglected, obtain values deviating from zero.

Denoting by $\Delta_{\sigma\sigma}$ and by $\Delta_{\sigma\tau}$ the minors of the discriminant, we have

$$\overline{\tau_\sigma^2}=\frac{\Delta_{\sigma\sigma}}{\Delta}(k-1)$$

$$\overline{\tau_\sigma\tau_\rho}=\frac{\Delta_{\sigma\rho}}{\Delta}(k-1)\;^{2})$$

where k is the number of elements into which the volume is divided.

The condition $\Delta=0$ is equivalent to the condition $\frac{dp}{dv}=0$. For if we write down the determinant in some arrangement, and if we add all rows to the first row, we get a determinant of which all terms of the first row have the form

$$-\frac{1}{v}+\frac{1}{v}\frac{d}{da}a^2\frac{dlg\,\omega}{da}+\frac{1}{\Theta dv}\Sigma\varphi_{\sigma\rho}.$$

Strictly speaking, this is not true for some terms at the end of the row, but as we have neglected the action on the borders, we may neglect this fact too. In reality our considerations are only true for an infinitely great volume, where this difficulty disappears, as Δ is then an infinite determinant.

Now if

$$-\frac{1}{v}+\frac{1}{v}a^2\frac{df\omega}{da}+\frac{1}{\Theta dv}\Sigma\varphi_{\sigma\rho}=0$$

then $\Delta=0$.

Or if $\Delta=0$

$$1-\frac{d}{da}a^2\frac{df\omega}{da}+\frac{a}{\Theta}\alpha=0$$

which therefore agrees with $\frac{dp}{dv}=0$.

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[1]) Cf. l. c. p. 129.

[2]) Cf. ORNSTEIN, Accidental deviations in mixtures. These Proceedings **15**, p. 54, (1912).

The quantities $\overline{\tau_\sigma \tau_\rho}$ etc. here found are related to those mentioned above. And though a statistical deduction of the function f entering into details may lead to difficulties, yet it is clear that statistical mechanics yield a correlation analogous to that expressed in g.

If we should wish to continue the deduction of the conditions of the critical point, we should have to use higher powers of τ_σ, which can be done without difficulty; we then find for the second condition $\frac{d^2p}{dv^2} = 0$.

If we drop the supposition that the sphere of attraction is large, we can use the function ϑ, defined in the quoted dissertation. In order to take into account the correlation, we must suppose the integrals

$$\int e^{-\varepsilon_q/\Theta}\, dx_1 \,.\; .\, dz_n\, \tau_\varkappa = \vartheta\,(n_\varkappa)$$

defining ϑ, to depend on n_k for the element in question and also on the numbers of molecules in the surrounding elements. Therefore, in general, the numbers of molecules of all elements will appear in $\vartheta n_\varkappa$, but the influence of distant elements is so small that $\frac{\partial \vartheta n_\varkappa}{\partial n_\sigma}$ can be put zero.

By considerations analogous to those used in the quoted dissertation, we can show that $\vartheta\,(n_\varkappa)$ has the form

$$V_\varkappa^{n_\varkappa}\,(\omega\, \mathfrak{n}_\varkappa, \mathfrak{n}_{\varkappa'}, \mathfrak{n}_{\varkappa''})^{n_\varkappa}$$

in which $\mathfrak{n}_{\varkappa'}\, \mathfrak{n}_{\varkappa''}$ denote the densities (molecular), in the elements with which $V_\varkappa$ is in mutual action. The values of all $\mathfrak{n}_\varkappa$ are equal for the most frequent system.

Now we find for ζ

$$\zeta = C\, V^n\, (\omega\, \mathfrak{n}, \mathfrak{n}, \mathfrak{n}, \mathfrak{n} \ldots)^n\, e^{-P}$$

where P is a quadratic form in the deviations for the various elements, containing squares as well as double products. The form might be easily indicated, but we will omit it, as it is only our purpose to show how in general the statistic-mechanical considerations, changed in the sense of a correlation of elements of volume, lead to formulae analogous to those given in § 2. Here too the mean square of deviation and the means of double products are represented by quotients of minors of the discriminant of P and this quantity itself. Here too for $\frac{dp}{dv} = 0$ the discriminant vanishes.

4. The above considerations can be applied in calculating the critical opalescence. For that purpose we use the simple method indicated by LORENTZ[1]), which consists in superposing the light-vectors caused by the influence of every individual molecule in a point at great distance.

Consider in the substance through which a beam of light passes, a volume V great with respect to the wave-length, and take a distant point P, the direction VP forming an angle φ with the incident ray.

All molecules lying in one plane perpendicular to the line which bisects the angle φ, will cause equal phase in P. Take therefore a system of axes with the Z-axis parallel to this line, then the contribution of one molecule will be

$$\beta \sin \frac{2\pi}{\mu\lambda} (ct + 2z \cos \tfrac{1}{2} \varphi)$$

where β depends only on the kind of molecules, on λ and on the distance VP, μ being the index of refraction.

The number of molecules in $dx\, dy\, dz$ amounts to

$$(a + \nu)\, dx\, dy\, dz.$$

The total light-vector in P thus becomes

$$\beta \int\limits_V (a + \nu) \sin \frac{2\pi}{\mu\lambda} (ct + 2z \cos \tfrac{1}{2}\varphi)\, dx\, dy\, dz.$$

and the intensity

$$\beta^2 \frac{c}{\mu\lambda} \int\limits_0^{\mu\lambda/c} dt \iint\limits_{VV} (a + \nu_\sigma)(a + \nu_\tau) \sin \frac{2\pi}{\mu\lambda} (ct + 2z_\sigma \cos \tfrac{1}{2} \varphi)$$
$$\sin \frac{2\pi}{\mu\lambda} (ct + 2z_\tau \cos \tfrac{1}{2} \varphi)$$
$$dx_\sigma\, dy_\sigma\, dz_\sigma\, dx_\tau\, dy_\tau\, dz_\tau.$$

Integrating with resp. to t, we get

$$\frac{1}{2} \beta^2 \iint\limits_{VV} \left\{ a^2 + a(\nu_\sigma + \nu_\tau) + \nu_\sigma \nu_\tau \right\} \cos \left\{ \frac{4\pi}{\mu\lambda} (z_\sigma - z_\tau) \cos \tfrac{1}{2} \varphi \right\} dx_\sigma dy_\sigma dz_\sigma dx_\tau dy_\tau dz_\tau.$$

The mean value of this must be calculated. The term with $\nu_\sigma + \nu_\tau$ vanishes, and that with a^2 yields no contribution proportional to V. We introduce the value of $\overline{\nu_\sigma \nu_\tau}$ from formula (10), and for $\sigma = \tau$ from form. (9). This gives

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[1]) H. A. LORENTZ, On the scattering of light by molecules. These Proceedings **13** p. 92 (1910).

$\cos \tfrac{1}{2}\varphi$

$$\frac{1}{2}\beta^2 a V + \frac{1}{2}\beta^2 a \iint\limits_{V\ V} g\,(x_\sigma - x_\tau,\ y_\sigma - y_\tau,\ z_\sigma - z_\tau) \cos \frac{4\pi}{\mu\lambda}(z_\sigma - z_\tau)\, dx_\sigma \ldots dy_\tau$$

For a great volume one integration over V can be performed (compare the deduction of formula (11)); further we put $aV = \overline{N}$ and for the sake of brevity $\frac{4\pi}{\mu\lambda} \cos \frac{1}{2}\varphi = C$, then we get

$$\frac{1}{2}\beta^2 \overline{N}\left[1 + \iiint\limits_{-\infty}^{+\infty} \cos Cz\, g\,(x, y, z)\, dxdydz\right] \quad . \quad . \quad . \quad (13)$$

The integral appearing here will be represented by G_c, that of formula (11) by G. It will be seen that the deductions criticised in § 1 yield an opalescence proportional to $\overline{\mathfrak{r}^2}$, a quantity which according to the above is proportional to $1 + G$, whereas the opalescence is proportional to $1 + G_c$.

With the aid of the integral-equation (6) we can express G and G_c in the corresponding integrals of the function f, which we will indicate by F and F_c.

Integrating (6) with resp. to xyz from $-\infty$ to $+\infty$, we find

$$\iiint\limits_{-\infty}^{+\infty} g\,(xyz)\, dx\, dy\, dz - \iiint\limits_{-\infty}^{+\infty} g\,(\xi\eta\zeta)\, d\xi\, d\eta\, d\zeta \iiint\limits_{-\infty}^{+\infty} f(x+\xi, y+\eta, z+\zeta)\, dxdydz = \iiint\limits_{-\infty}^{+\infty} f\,(xyz)\, dndydz$$

or

$$G = \frac{F}{1-F} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

Multiplying (6) by $\cos Cz$ and again integrating, we get

$$G_c - \iiint\limits_{-\infty}^{+\infty} g(\xi\eta\zeta)\, d\xi d\eta d\zeta \iiint\limits_{-\infty}^{+\infty} \{\cos C\,(z+\zeta) \cos C\zeta + \sin C\,(z+\zeta) \sin C\zeta\}$$

$$f\,(x+\xi, y+\eta, z+\zeta)\, dxdydz = F_c.$$

The integral with the sines disappears because f and g are even functions; we find

$$G_c = \frac{F_c}{1-F_c} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

In order to apply the results obtained and to test them experimentally, one might try to deduce f from molecular theory. This would at best be possible under very simplifying suppositions and even then only an approximation can be obtained. Therefore we will take another way. As remarked in § 1, the exact value of $\overline{\nu^2}$ for *very great volumes* was already known. In our notation we have

$$\overline{\nu^2}\,V = -\frac{RT}{N}\,\frac{a^2}{v\,\dfrac{dp}{dv}}$$

where N is the number of AVOGRADO, v the molecular volume.

According to formula (4) we have

$$\overline{\nu^2}\,V = a\,(1+G) = \frac{a}{1-F}.$$

Putting these results equal, we get

$$1 - F = -\frac{v^2}{RT}\,\frac{dp}{dv}.$$

In the critical point $F = 1$.[1]

The formula of opalescence first arrived at by KEESOM and EINSTEIN

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[1] There appears to exist a closer correspondence between the given statistic-mechanical method and the method using general considerations of probability, than perhaps might be expected. The elements of the discriminant (which is an infinite determinant in the former) agree with the function f in the latter. The former finds from this the value of $\overline{\nu_\sigma\,\nu_\tau}$ as the quotient of a minor with that discriminant, the latter deduces this value from an integral-equation. In the critical point the discriminant vanishes, corresponding to this the FREDHOLM determinant of the integral-equation is likewise zero. That this is the case when $F = 1$, appears by more closely studying the equation

$$g(\xi\eta\zeta) - \lambda\int g(\xi\eta\zeta)\,f(x+\xi,\,y+\eta,\,z+\zeta)\,d\xi\,d\eta\,d\zeta = 0$$

which only permits appropriate solutions if $\lambda = \frac{1}{F}$, (i. e. this is the only proper value). For $F = 1$ this is therefore the case with the equation (6) without second member.

From the formula (15) it will be seen that form. (6) can be solved by a FOURIER integral. Putting

$$\iiint_{-\infty}^{+\infty} \cos mx \cos ny \cos lz\, f(xyz)\,dx\,dy\,dz = \varphi\,(m,n,l)$$

we have

$$g\,(xyz) = \frac{1}{8\pi^3}\iiint_{-\infty}^{+\infty} \frac{\varphi(m,n,l)}{1-\varphi(m,n,l)} \cos mx \cos ny \cos lz\; dm\,dn\,dl.$$

$$\frac{I_{\text{Op.}}}{I}=\frac{2\pi^2 V}{D^2}\frac{RT}{N}\frac{\mu v\left(\frac{d\mu}{dv}\right)^2}{-\frac{dp}{dv}}\lambda^{-4}\sin^2\psi . \quad . \quad . \quad . \quad . \qquad (16)$$

in which represent

D distance of observation

μ index of refraction,

ψ angle of electric force in incident light with direction of observation,

will likewise be found by using in (13) the value found for F instead of F_c. The exact formula then will result by multiplying by the factor $\frac{1+G_c}{1+G}=\frac{1-F}{1-F_c}$.

Developing the cosine in F_c we find

$$F - F_c = \frac{C^2}{2}\iiint\limits_{-\infty}^{+\infty} z^2 f(xyz)\, dxdydz .$$

Representing this integral by ε^2 and introducing the value of C, we get

$$F - F_c = 4\pi^2 (1+\cos\varphi)\left(\frac{\varepsilon}{\mu\lambda}\right)^2 .$$

The formula of opalescence then will be:

$$\frac{I_{\text{Op.}}}{I}=\frac{2\pi^2\frac{V}{D^2}\frac{RT}{N}v\mu\left(\frac{d\mu}{dv}\right)^2\lambda^{-4}\sin^2\psi}{-\frac{dp}{dv}+4\pi^2\frac{RT}{v^2}(1+\cos\varphi)\left(\frac{\varepsilon}{\mu\lambda}\right)^2} . \quad . \quad . \quad . \qquad (17)$$

In the critical point itself it therefore is

$$\frac{I_{\text{Op.}}}{I}=\frac{V}{D^2}\frac{v^3\mu^3\left(\frac{d\mu}{dv}\right)^2\sin^2\psi}{N\varepsilon^2(1+\cos\varphi)}\lambda^{-2} . \quad . \quad . \quad . \quad . \qquad (18)^{1)}$$

The greater exactness of form. (17) as compared with (16) is confirmed by the measurements of one of us (Z.). According to these measurements, which however bear upon a mixture of liquids the

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1) According to this formula the proportionality of the opalescence to λ^{-4}, which holds for higher temperatures, changes continuously in the immediate neigbourhood of the critical point, into proportionality with λ^{-2}. This *real* "getting whiter" of the opalescence should not be confused with the *apparent* changing of colour which is always observed much farther from the critical point. The latter indeed is only a result of the method of observation, as is clearly proved by the measurements of one of us (cf. **Zernike** thesis).

reciprocal value of a quantity proportional to the opalescence changes linearly with the difference of temperature $T-T_k$, but by extrapolation does not vanish for $T=T_k$, but for $T-T_k=0{,}^{\circ}012$. When therefore for this value of $T-T_k$ the denominator of (17) is equal to zero, we can find from this, using VAN DER WAALS' equation, an estimation for ε/λ. The calculation yields:

$$\frac{\varepsilon}{\lambda}=0{,}0022 \text{ or } \varepsilon=1{,}2.10^{-7}\,cm.$$

The quantity ε is a measure for the size of the sphere of attraction. For

$$\varepsilon^2=\frac{1}{3}\iiint_{-\infty}^{+\infty}\varrho^2 f(xyz)\,dxdydz$$

(ϱ distance to origin) whereas in the critical point

$$\iiint_{-\infty}^{+\infty} f(xyz)\,dx\,dy\,dz=1.$$

If f were constant within a sphere with radius R, then ε^2 would be $^1/_5\,R^2$, and the above estimation would give

$$R=2{,}7\,.\,10^{-7}\,cm.$$

SUMMARY.

1. The known formulae of critical opalescence give an infinite value at the critical point. Efforts to escape from this difficulty have furnished formulae for the deviations of density with a dependence upon the volume, at variance with the assumed mutual independence of the elements of volume.

2. In order to obtain formulae applicable in the critical point, it is found necessary to take into account the mutual influence of the elements of volume, it being shown that near the critical point this influence is sensible for distances large in comparison with the radius of the sphere of attraction.

3. Two functions are introduced, one relating to the direct interaction of molecules, the other to the mutual influence of two elements of volume. An integral equation gives the relation between the two functions.

4. Corrected values are found for the mean deviations, and in the formula of opalescence a correction is introduced. The latter depends upon the sphere of attraction which can thus be calculated from observations.

5. Further it is shown that the same results may be arrived at by taking into account the mutual influence of the elements of volume in the deductions of statistical mechanics.

Groningen, Sept. 1914.