On Fluctuations of Dielectric Constant in Liquids and Theories of Molecular Scattering of Light.

BY

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I. Introduction.

In two previous papers,[1] the electromagnetic theory of the scattering of light in fluids was dealt with by the present writer from the molecular point of view. Einstein's expression for scattering was derived for liquids composed of isotropic molecules; for liquids composed of anisotropic molecules, it was shown that just as in the case of gases, there would in addition be an unpolarised scattering and expressions for the intensity and polarisation of the scattered light were derived. Gans[2] has, in the meanwhile, developed the phenomenological theory so as to include the case when the transversely scattered light is partially polarised by assuming that the fluctuations of dielectric constant which on Einstein's theory are responsible for the scattering of light, are in general anisotropic, these deviations from isotropy being also responsible for the phenomenon of electric double refraction. Some differences between the expressions for scattering put forward by Gans, by L. V. King[3] and by the present writer have shown the necessity for a re-examination of the question of fluctuations of dielectric constant in a liquid.

[1] K. R. Ramanathan, Proc. Ind. Assoc. for Cult. of Science, Vol. VIII, Part I, pp. 1-22 and Vol. VIII, Part III, pp. 181-198 (1923). These will be referred to in the sequel as papers A and B respectively.

[2] R. Gans, Zeit. für Physik, xvii, p. 353 (1923).

[3] L V. King; Nature, cxi, p. 667 (1923). See also paper B.

Ind. Journ. Phys. 1, 413-436, 1926-27.

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2. *Fluctuations of dielectric constant in a small volume element.*

The relation between the dielectric constant and the molecular density and polarisability which is usually used in deriving the fluctuations of dielectric constant in a liquid, is the Lorentz-Mosotti formula

$$\frac{K-1}{K+2} = \frac{4\pi}{3} nA' \qquad \qquad \text{... (1)}$$

where K is the dielectric constant of the liquid, n is the mean density of the molecules contained in it and A' the average polarisability of the molecules.   By differentiation,

$$dK = \frac{(K-1)\ (K+2)}{3} \left\{ \frac{dn}{n} + \frac{dA'}{A'} \right\} \qquad \text{... (2)}$$

While there is no doubt that the above relation will be perfectly valid if the medium as a whole undergoes the change denoted by dn and dA', the validity is questionable if the particular changes are confined to a very small volume element.   To see this clearly, it is necessary to recollect how the factor $(K+2)/3$ arises.   The total field acting on a molecule within a liquid is obtained as follows.   Consider a long cylindrical cavity described round the molecule, the axis of the cylinder being along the direction of the external field. The length of the cylinder should be very great compared with its radius and the radius, though small in the physical sense, should be many times the diameter of a molecule. The intensity at the molecule will now be Z, that of the external field.   If the cavity is now filled with the molecules that have been removed, an additional intensity will be caused.   The filling can be done in two steps, (1) up to the boundary of a sphere surrounding the molecule, the cylinder being tangential to the sphere and (2) within the sphere. The first of these will cause a field $\frac{4}{3}\pi nM$ at P, where M is the mean induced moment of the molecules outside the sphere.   The molecules within the sphere will cause no

effect at the centre provided they are arranged in cubical order with the central molecule at one of the cube corners or, on the average, when the surrounding molecules can take up continuously-varying positions and orientations as in a liquid. The resultant field will therefore be $Z + \frac{4}{3}\pi n M$ or $Z(K+2)/3$, where K is the dielectric constant of the matter outside the imaginary sphere.

If there is any local deviation of n or M in the region surrounding the molecule, it would cause an additional field whose sign may be positive or negative according to the sign of the deviation and its position with respect to the molecule. Even though the deviation is positive, it would cause a negative field if, for example, it is located in a direction at right angles to the field. When there are many such local deviations of n or M distributed at random round the molecule, the extra addition to the local field need not necessarily be proportioned to the change of $n M$ in a small volume element round the molecule.

In obtaining the intensity of scattering from a finite volume of the liquid, we divide it into *small* volume elements and consider the waves scattered from the parts of each volume element to be coherent. The only restrictions on the size of these volume elements are that their linear dimensions should be small compared with the wave-length and that they should be sufficiently large for the fluctuations of density in one to be independent of those in another. There must be a minimum limit to the size of the volume element of a liquid under definite conditions of pressure and temperature so that the latter condition may be satisfied. This limiting volume is not easy to determine, but some idea about its magnitude can be obtained from the following considerations. Liquid benzene, for example, at $30°C$ has a compressibility of 103×10^{-6} per atmosphere, which is about $1/35$ of that of a perfect gas of the same molecular concentration. Since the mean square of the deviations of density

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in a volume element is proportional to the compressibility and since the fluctuations in a perfect gas are determined by the circumstance that the position of one molecule is uncorrelated with the positions of other molecules, we may take it that the fluctuations of density in a volume element in *liquid benzene* at 30°C. are uncorrelated with those in other volume elements if it contains on the average not less than 35 molecules. If the volume elements are so small as to contain fewer molecules than this and one of them has at a certain instant more than the average density of molecules, then other volume elements in the immediate neighbourhood will have fewer molecules, that is, the correlation between the deviations of density in neighbouring volume elements would be negative. To take another example, liquid CO_2 at 30°C. in equilibrium with its vapour has a compressibility nearly 20 times that of a perfect gas of the same molecular concentration. Here as before, the minimum size of the volume element required to justify the assumption of independence of density-fluctuations will be that it should contain not fewer than 20 molecules, but in neighbouring volume elements of smaller size than this, the fluctuations of concentration will be positively correlated. Except in the immediate neighbourhood of the critical point, we may safely take that the fluctuations of density in different volume elements are independent if they contain not less than 50 molecules.

Now, the amplitude of the scattered waves from each volume element will be proportional to the number of molecules contained in it without any regard to how they are distributed inside, and to the average field at the molecules. The value of the latter depends on the dielectric constant outside the imaginary sphere described round it. Even if we take the sphere so small that its radius is only three times the average distance between two molecules, it will contain more than 110 molecules and hence the fluctuations of density inside the sphere will have very little correlation with those

outside. The volume of polarised matter responsible for the extra local field at the molecules of a volume element is thus not only larger than the volume element itself, but the fluctuations of density in it are independent of those in the element. Hence, the fluctuations of local field at the molecules of a volume element will be uncorrelated with those of density in the element. Thus, in equation (1), which may also be written in the form

$$K-1=\left(\frac{K+2}{3}\right)4\pi n A',$$

the K's on the two sides of the equation are not identical; while the K on the left hand side changes with the fluctuations of density in the volume element, the K on the right hand side does not. If the latter be treated as constant,

$$dK=(K-1)\left\{\frac{dn}{n}+\frac{dA'}{A'}\right\} \qquad \dots \ (3)$$

It has been tacitly assumed in the above that the fluctuations of local field caused by the variations of molecular polarisability are altogether negligible. When a liquid is not subjected to electric or magnetic fields, the latter arise mainly from the varying orientations of anisotropic molecules. If we assume that the orientations of different molecules are uncorrelated with each other, the mean deviation of polarisability in a small volume element will also be uncorrelated with the average local field at the molecules since it depends mainly on the polarisation of the surrounding medium beyond the bounds of the volume element.

3. Molecular theory of scattering.

We may thus consider equation (3) as more correctly representing the relation between the deviations in dielectric constant, molecular concentration and molecular polarisability than equation (2). It was shown in paper A that in

a medium composed of isotropic molecules, the electric intensity at a distant point P due to scattering from δv is

$$\frac{p^2}{c^2 d} \sin \theta' \, \delta v. \, Mn$$

where $p/2\pi$ is the frequency of the incident radiation, c is the velocity of light in vacuo, θ' the angle between the scattered wave and the direction of the electric vector in the incident radiation, M the moment induced in a molecule and n the density of molecules contained in the volume element. Subtracting the part common to all volume elements which would destroy each other by interference, the excess electric intensity in the scattered wave will be

$$\frac{p^2}{c^2 d} \sin \theta' (Mn - M_0 n_0) \delta v$$

where M_0 and n_0 are the mean values of the moment and density respectively.

It was assumed in paper A that M is the moment appropriate to density n, but since as we have seen, its value is not appreciably affected by the fluctuations of density, M can be equated to M_0 and the above expression will reduce to

$$\frac{p^2}{c^2 d} \sin \theta' M_0 \delta n. \delta v \qquad \qquad \ldots \ (4)$$

and the square of the electric intensity at P due to scattering from δv will be

$$\frac{p^4}{c^4 d^2} \sin^2 \theta' \frac{(K_0 - 1)^2}{16 \pi^2} Z^2 \frac{\delta n^2}{n_0^2} . \, \delta v^2$$

The mean value of this quantity is

$$\overline{E^2} = \frac{p^4 \sin^2 \theta'}{c^4 d^2} \frac{(K_0 - 1)^2}{16 \pi^2} Z^2 \frac{\overline{\delta n^2}}{n_0^2} \delta v^2$$

$$= \frac{\pi^2 RT \beta}{N \lambda^4} (K_0 - 1)^2 \frac{\sin^2 \theta'}{d^2} . \, \delta v \qquad \qquad \ldots \ (5)$$

When the incident light is unpolarised, the intensity of the transversely scattered light from a finite volume V is

$$I = \frac{I_0 V}{d^2} \; \frac{\pi^2 RT\beta}{2N\lambda^4}(K_0 - 1)^2 \qquad \qquad \dots \quad (6)$$

where J_0 is the intensity of the incident light. This differs from the expression given in paper A by the suppression of the factor $(K_0 + 2)^2/9.$[1]

Turning now to the case of a liquid composed of anisotropic molecules, the Z component of the electric intensity in the light scattered from δv at P is, as shown in page 184 of paper B

$$\frac{p^2}{c^2 d} Z \left(\frac{K+2}{3} \right) L_3 n \delta v \qquad \qquad \dots \quad (7)$$

where

$$L_3 = C \cos^2\theta + B \sin^2\theta \sin^2\phi + A \sin^2\theta \cos^2\phi$$

A, B and C being the polarisabilities of each molecule along three principal directions and θ, ϕ, ψ being the Eulerian angles defining the directions of the molecular axes with respect to the co-ordinate axes. The above can be written

$$\frac{p^2}{c^2 d} Z\left(\frac{K+2}{3} \right) \left\{ \frac{A+B+C}{3} + \left(L_3 - \frac{A+B+C}{3} \right) \right\} n\delta v \quad \dots \quad (7a)$$

$$= \frac{p^2}{c^2 d} Z \left(\frac{K+2}{3} \right) \left\{ \frac{A+B+C}{3} n_0 \delta v + \frac{A+B+C}{3} \delta n \delta v \right.$$

$$\left. + \left(L_3 - \frac{A+B+C}{3} n dv \right) \right\} \qquad \qquad \dots \quad 7(b)$$

in which $n_0 + \delta n$ is substituted for n.

[1] M. Born in his paper on Scattering in Phys. Zeit. Nr. 1/4 p. 16 (1918) and L. V. King in his letter to Nature (cxi, p. 667, 1923) have both omitted this factor, but without giving reasons.

Of the three terms in the last expression, the first is constant for every equal volume element and the third varies from molecule to molecule. When finite volume elements are considered, the first term cancels by interference, the second is summed by adding together the squares of the electric vector from the different volume elements and the third by adding together the squares of the electric vector from the different molecules. The last term is the one introduced owing to the anisotropy of the molecules. If the K in $(K+2)/3$ is taken to be the mean dielectric constant of the liquid, it can easily be shown that the total value of Z'^2 from a volume V is

$$\overline{Z'^2} = \frac{p^4}{c^4 d^2} Z^2 \left(\frac{K_0+2}{3}\right)^2 n_0 V \left\{ \left(\frac{A+B+C}{3}\right)^2 \frac{RT\beta n_0}{N} + \frac{4}{3}f \right\}$$

where

$$f = \tfrac{1}{15}(A^2 + B^2 + C^2 - AB - BC - CA)$$

As was shown in paper B (equation 1)

$$\overline{X'^2} = \frac{p^4}{c^4 d^2} Z^2 \left(\frac{K_0+2}{3}\right)^2 f n_0 V$$

Hence

$$\frac{\overline{X'^2}}{\overline{Z'^2}} = \frac{f}{\left(\dfrac{A+B+C}{3}\right)^2 \dfrac{RT\beta n_0}{N} + \dfrac{4}{3}f}$$

If the incident light is unpolarised, the ratio of the weak component to the strong in the transversely scattered light is

$$r = \frac{2f}{\left(\dfrac{A+B+C}{3}\right)^2 \dfrac{RT\beta n_0}{N} + \dfrac{4}{3}}$$

$$= \frac{6\delta}{\dfrac{5RT\beta n_0}{N} + 7\delta} \qquad \qquad \dots \ (8)$$

where
$$\delta = (A^2 + B^2 + C^2 - AB - BC - CA)/(A+B+C^2)$$

And the intensity of the light scattered in the transverse direction expressed in terms of r is

$$\frac{I_0 V}{d^2} \frac{RT\beta}{2N\lambda^4} (K_0 - 1)^2 \frac{6(1+r)}{6-7r} . \qquad \dots (9)$$

The value of the co-efficient of attenuation can easily be shown to be

$$h = \frac{8\pi^3}{3} \frac{RT\beta}{N\lambda^4} (K_0 - 1)^2 + \frac{8\pi^3}{3n_0\lambda^4} (K_0 - 1)^2 \, 2\delta$$

$$= \frac{8\pi^3}{3n_0\lambda^4} (K_0 - 1)^2 \left\{ \frac{RT\beta n_0}{N} + 2\delta \right\} \qquad \dots (10)$$

4. Gans's theory of scattering.

Lord Rayleigh's expression for the scattering of light by a particle whose linear dimensions are small in comparison with the wave-length, when its dielectric constant differs by only a small amount from that of the surrounding medium, takes the form[1]

$$\frac{I}{I_0} = \frac{\pi^2 \wedge^2}{2\lambda^4 d^2} (\delta v)^2 \, (1 + \cos^2\chi) \qquad \dots (11)$$

where $\wedge$ is the deviation in dielectric constant of the particle, χ is the angle between the incident and scattered beams, and δv is the volume of the particle. When we substitute for $\wedge^2$ the mean value of the square of the fluctuations of dielectric constant taking place in a volume element δv of a pure liquid and assume that these are solely caused by the fluctuations of density, we have

$$\overline{\wedge^2} = \left(\frac{\delta K}{\delta \rho} \right) \overline{\delta \rho^2}$$

$$= \left(\frac{\delta K}{\delta \rho} \right)^2 \frac{RT\beta}{N\delta v} \rho^2$$

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[1] Lord Rayleigh. Scientific papers, Vol. i, p. 526.

and equation (11) becomes

$$\frac{I}{I_0} = \frac{\pi^2 RT\beta}{2N\lambda^4 d^2}\ \rho^2 \left(\frac{\delta K}{\delta\rho}\right)^2 \delta v\ (1 + \cos^2\chi) \qquad \dots (12)$$

which can easily be seen to be identical with Einstein's expression.

If now we consider the deviations of dielectric constant of a volume element δv to be anisotropic, the intensity of scattering will be increased and the transversely scattered light will also appear partially polarised. Let $\wedge_1, \wedge_2, \wedge_3$ be the deviations of optical dielectric constant of a volume element δv along three principal directions of anisotropy and let $\wedge_1 = \wedge + \lambda_1,\ \wedge_2 = \wedge + \lambda_2,\ \wedge_3 = \wedge + \lambda_3,\ \bar{\lambda}_1 + \bar{\lambda}_2 + \bar{\lambda}_3$ being equal to zero. Then $\wedge$ is the purely isotropic part of the deviations and $\lambda_1, \lambda_2, \lambda_3$ the purely anisotropic part. $\overline{\wedge^2}$ is identified with the $(\delta K/\delta\rho)^2\ \delta\rho^2$ of Einstein's theory. Gans showed that the imperfection of polarisation of the scattered light in a direction at right angles to the incident unpolarised beam, which is measured by the ratio of the intensity of the weak component that of the strong is given by

$$r = \frac{(\overline{\wedge_1^2} + \overline{\wedge_2^2} + \overline{\wedge_3^2}) - 2(\overline{\wedge_1\wedge_2} + \overline{\wedge_2\wedge_3} + \overline{\wedge_3\wedge_1})}{4(\overline{\wedge_1^2} + \overline{\wedge_2^2} + \overline{\wedge_3^2}) + (\overline{\wedge_1\wedge_2} + \overline{\wedge_2\wedge_3} + \overline{\wedge_3\wedge_1})}$$

(13)

and the intensity in the same direction from a volume δv by

$$\frac{I}{I_0} = \frac{\pi^2 \overline{\wedge^2}}{2\lambda^4 d^2}\ (\delta v)^2\ \frac{6 + 6r}{6 - 7r} \qquad \dots (14)$$

This differs from the expression on the right-hand side of (11) (with $\chi = \pi/2$) by the introduction of the factor

$6(1+r)/(6-7r)$. The co-efficient of attenuation was obtained by Gans to be

$$h = \frac{8\pi^3}{3\lambda^4} \quad \frac{\overline{\wedge_1{}^2} + \overline{\wedge_2{}^2} + \overline{\wedge_3{}^2}}{3} \, \delta v$$

$$= \frac{8\pi^3}{3\lambda^4}\left(\overline{\wedge^2} + \frac{\overline{\lambda_1{}^2} + \overline{\lambda_2{}^2} + \overline{\lambda_3{}^2}}{3}\right) \delta v \qquad \dots (15)$$

Gans next connects the anisotropic part of the fluctuations of dielectric constant with the Kerr constant of electric double refraction somewhat on the same lines as in Langevin's work connecting molecular anisotropy with electric double refraction. It may be useful to give a summary of Gans's treatment. If anisotropic fluctuations of dielectric constant occur in a liquid, there will also be similar fluctuations of electrostatic dielectric constant. In an isotropic liquid, the fluctuations will be in random directions, but when an electrostatic field is put on, the directions will no longer be random, but there will be a tendency for the largest of the three principal dielectric constants to set themselves along the direction of the field, so that when a beam of light is passed through the medium perpendicular to the field, the velocities of the components parallel and perpendicular to it will be unequal, that is, the medium will become doubly refracting. If $\wedge_1{}^\circ$, $\wedge_2{}^\circ$, $\wedge_3{}^\circ$ be the three principal deviations of electrostatic dielectric constant of a volume element and they make angles whose cosines are γ_1, γ_2 and γ_3 with the applied electrostatic field E_0 (parallel to OZ), then the difference of potential energy of the volume element from that of an isotropic volume element containing the same mass but having the mean dielectric constant of the liquid is

$$-\frac{E_0{}^2}{8\pi}\, \delta v(\wedge_1{}^\circ\gamma_1{}^2 + \wedge_2{}^\circ\gamma_2{}^2 + \wedge_3{}^\circ\gamma_3{}^2) \qquad \dots (16)$$

By Boltzmann's theorem, the probability that one of the principal axes of a volume element has its direction between

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θ and $\theta + d\theta$, ϕ and $\phi + d\phi$, and ψ and $\psi + d\psi$, where θ is the angle between the direction of the field and the axis under consideration and ϕ and ψ have their usual significance, is

$$_e Q(\wedge_1{}^0\gamma_1{}^2 + \wedge_2{}^0\gamma_2{}^2 + \wedge_3{}^0\gamma_3{}^2) \quad \sin\theta \, d\theta \, d\phi \, d\psi$$

where

$$Q = E_0{}^2 N \, \delta v / 8\pi RT$$

By the usual method of obtaining mean values

$$\overline{\gamma_1{}^2} = \frac{\iiint \gamma_1{}^2 e^{Q(\wedge_1{}^0\gamma_1{}^2 + \wedge_2{}^0\gamma_2{}^2 + \wedge_3\gamma_3{}^2)} \sin\theta \, d\theta \, d\phi \, d\psi}{\iiint e^{Q(\wedge_1{}^0\gamma_1{}^2 + \wedge_2{}^0\gamma_2{}^2 + \wedge_3{}^0\gamma_3{}^2)} \sin\theta \, d\theta \, d\phi \, d\psi}$$

Reducing, we get

$$\overline{\gamma_1{}^2} = \frac{1}{3} + \frac{2Q}{15}\left(\wedge_1{}^0 - \frac{\wedge_1{}^0 + \wedge_2{}^0 + \wedge_3{}^0}{3} \right)$$

$$\overline{\gamma_2{}^2} = \frac{1}{3} + \frac{2Q}{15}\left(\wedge_2{}^0 - \frac{\wedge_1{}^0 + \wedge_2{}^0 + \wedge_3{}^0}{3} \right)$$

and

$$\overline{\gamma_3{}^2} = \frac{1}{3} + \frac{2Q}{15}\left(\wedge_3{}^0 - \frac{\wedge_1{}^0 + \wedge_2{}^0 + \wedge_3{}^0}{3} \right) \quad \cdots \quad (17)$$

Gans takes the change of dielectric constant of the medium as a whole in the direction of the Z-axis to be the average change of dielectric constant of the volume elements composing it, in that direction. Thus

$$K_z - K_0 = \overline{(\wedge_1 \, \gamma_1{}^2 + \wedge_2 \, \gamma_2{}^2 + \wedge_3 \, \gamma_3{}^2)} \quad \cdots \quad (18)$$

Substituting the value for $\overline{\gamma_1{}^2}, \overline{\gamma_2{}^2}, \overline{\gamma_3{}^2}$ and remembering that $\overline{\wedge_1} + \overline{\wedge_2} + \overline{\wedge_3} = 0$,

$$K_z - K_0 = \frac{2Q}{15}\left\{ \overline{(\wedge_1{}^0\wedge_1 + \wedge_2{}^0\wedge_2 + \wedge_3{}^0\wedge_3)} \right.$$

$$\left. - \frac{\overline{(\wedge_1{}^0 + \wedge_2{}^0 + \wedge_3{}^0)} \; \overline{(\wedge_1 + \wedge_2 + \wedge_3)}}{3} \right\} \quad (19)$$

Similarly, evaluating $\overline{a_1^2}$, $\overline{a_2^2}$ $\overline{a_3^2}$ where a_1, a_2, a_3 are the angles made by the directions of Λ_1^0, Λ_2^0, Λ_3^0 with OX he gets

$$\overline{a_1^2} = \frac{1}{3} - \frac{Q}{15}\left(\Lambda_1^0 - \frac{\Lambda_1^0 + \Lambda_2^0 + \Lambda_3^0}{3} \right)$$

with similar expressions for $\overline{a_2^2}$ and $\overline{a_3^2}$.

$$K_z - K_0 = \Lambda_1 \overline{a_1^0} + \Lambda_2 \overline{a_2^2} + \Lambda_3 \overline{a_3^3}$$

$$= -\frac{Q}{15}\left(\overline{\Lambda_1^0 \Lambda_1} + \overline{\Lambda_2^0 \Lambda_2} + \overline{\Lambda_3^0 \Lambda_3} \right.$$

$$\left. - \frac{\overline{(\Lambda_1^0 + \Lambda_2^0 + \Lambda_3^0)(\Lambda_1 + \Lambda_2 + \Lambda_3)}}{3} \right) \quad \ldots \text{ (20)}$$

If we write ν_z and ν_x for the refractive indices for vibrations parallel and perpendicular to the field (ν_z^2 being equal to K_z) etc., and ν for the mean refractive index,

$$\frac{\nu_z - \nu_x}{E_0^2} = \frac{N\delta v}{80n\nu RT}\left\{ \overline{\Lambda_1^0 \Lambda_1} + \overline{\Lambda_2^0 \Lambda_2} + \overline{\Lambda_3^0 \Lambda_3} \right.$$

$$\left. - \frac{\overline{(\Lambda_1^0 + \Lambda_2^0 + \Lambda_3^0)(\Lambda_1 + \Lambda_2 + \Lambda_3)}}{3} \right. \quad \ldots \text{ (21)}$$

Assuming that

$$\frac{\Lambda_1^0}{\Lambda_1} = \frac{\Lambda_2^0}{\Lambda_2} = \frac{\Lambda_3^0}{\Lambda_3} = \frac{(\epsilon-1)(\epsilon+2)}{(\nu^2-1)(\nu^2+2)} \quad \ldots \text{ (22)}$$

where ϵ is the electrostatic dielectric constant, equation (21) becomes

$$\frac{\nu_z - \nu_x}{E_0^2} = \frac{N\delta v}{80\pi\nu RT} \frac{(\epsilon-1)(\epsilon+2)}{(\nu^2-1)(\nu^2+2)}\left\{ \overline{\Lambda_1^2} + \overline{\Lambda_2^2} + \overline{\Lambda_3^2} - \frac{\overline{(\Lambda_1 + \Lambda_2 + \Lambda_3)^2}}{3} \right\}$$

$$= \frac{N\delta v}{80\pi\nu RT} \frac{(\epsilon-1)(\epsilon+2)}{(\nu^2-1)(\nu^2+2)}\left(\overline{\lambda_1^2} + \overline{\lambda_2^2} + \overline{\lambda_3^2} \right)$$

Since the Kerr constant

$$B^1 = (\nu_z - \nu_x)/\lambda E_0^2$$

$$\overline{\lambda_1^2} + \overline{\lambda_2^2} + \overline{\lambda_3^2} = \frac{80\pi\nu RT\lambda B^1 (\nu^2 - 1)(\nu^2 + 2)}{N\delta v(\epsilon - 1)(\epsilon + 2)} \qquad \ldots \quad (23)$$

Substituting this value in (15) and writing

$$\overline{\Lambda^2} = \frac{(\nu^2 - 1)^2(\nu^2 + 2)^2}{9} \quad \frac{RT\beta}{N\delta v}$$

Gans obtains the co-efficient of attenuation to be

$$h = \frac{8\pi^3}{3} \frac{RT}{N\lambda^4} \left\{ \frac{\beta(\nu^2 - 1)^2(\nu^2 + 2)^2}{9} + \frac{80\pi\nu\lambda B^1}{3} \frac{(\nu^2 - 1)(\nu^2 + 2)}{(\epsilon - 1)(\epsilon + 2)} \right\} \ldots \quad (24)$$

5. *Discussion of Gans's theory.*

The quantity

$$\overline{\lambda_1^2} + \overline{\lambda_2^2} + \overline{\lambda_3^2}$$

which is determined in (23) differs, however, in an important way from the same expression in (15). Gans's assumption in (22) that

$$\Lambda_1^0/\Lambda_1 \text{ etc,} = \frac{(\epsilon - 1)(\epsilon + 2)}{(\nu^2 - 1)(\nu^2 + 2)}$$

is equivalent to assuming

$$\lambda_1^0/\lambda_1, \text{ etc.} = (\epsilon - 1)(\epsilon + 2)/(\nu^2 - 1)(\nu^2 + 2),$$

as can easily be seen by reducing (21) in terms of Λ^0, Λ and λ_1^0, λ_1, etc. In a liquid under ordinary conditions, the aniso-tropic fluctuations of dielectric constant of different volume elements (even when they are very small and contain only a few molecules) are entirely uncorrelated with each other, but when the liquid is placed in an electrostatic field, the axis of largest dielectric constant in each volume element tends to place itself parallel to the field. The resulting change in

dielectric constant is conditioned not only by the turning of the anisotropic volume elements, but also by the change in local field produced by such *general* turning. The potential energy of an anisotropic volume element when the medium is placed in an electrostatic field E_0 is written by Gans to be

$$-\frac{E_0{}^2}{8\pi} (\Lambda_1{}^0\gamma_1{}^2 + \Lambda_2{}^0\gamma_2{}^2 + \Lambda_3{}^0\gamma_3{}^2)\delta v, \qquad \ldots (25)$$

This may also be written

$$-\frac{E_0{}^2\delta v}{8\pi} \left\{ \Lambda^0 + (\lambda_1{}^0\gamma_1{}^2 + \lambda_2{}^0\gamma_2{}^2 + \lambda_3{}^0\gamma_3{}^2) \right\} \qquad \ldots (26)$$

Now, $\lambda_1{}^0\gamma_1{}^2 + \lambda_2{}^0\gamma_2{}^2 + \lambda_3{}^0\gamma_3{}^2$ is the anisotropic deviation in dielectric constant in the direction of the field if the change due to the field is confined to the particular volume element so that the local polarisation field is not affected. But since a correlated change of dielectric constant is suffered by every volume element, the actual anisotropic deviation in dielectric constant will be

$$\left(\frac{\epsilon+2}{3} \right)(\lambda_1{}^0\gamma_1{}^2 + \lambda_2{}^0\gamma_2 + \lambda_3{}^0\gamma_3{}^2)$$

[compare equations (2) and (3)] and the second term in expression (26) for the potential energy will become

$$-\frac{E_0{}^2\delta v}{8\pi} \left\{ \frac{\epsilon+2}{3} \right\} (\lambda_1{}^0\gamma_1{}^2 + \lambda_2{}^0\gamma_2{}^2 + \lambda_3{}^0\gamma_3{}^2) \qquad \ldots (27)$$

This term alone is of importance in determining electric double refraction. $\overline{\gamma_1^2}$ will therefore become equal to

$$\frac{1}{3} + \frac{2Q}{15} \left(\frac{\epsilon+2}{3} \right) \left(\lambda_1{}^0 - \frac{\lambda_1{}^0 + \lambda_2{}^0 + \lambda_3{}^0}{3} \right)$$

and $\overline{\gamma_2^2}$ and $\overline{\gamma_3^2}$ will also get similarly altered.

Expression (18) will also get changed to

$$K_z - K_0 = \left(\frac{\nu^2 + 2}{3}\right)\left(\overline{\lambda_1 \gamma_1{}^2 + \lambda_2 \gamma_2{}^2 + \lambda_3 \gamma_3{}^2}\right)$$

$\overline{\lambda_1} + \overline{\lambda_2} + \overline{\lambda_3}$ being equal to zero.

Therefore,

$$\frac{K_z - K_x}{E_0{}^2} = \frac{N\delta v}{40\pi RT}\left(\frac{\epsilon + 2}{3}\right)\left(\frac{\nu^2 + 2}{3}\right)\frac{\lambda_1{}^0}{\lambda_1} \cdot \left\{\overline{\lambda_1{}^2} + \overline{\lambda_2{}^2} + \overline{\lambda_3{}^2}\right.$$

$$\left. - \frac{\overline{(\lambda_1 + \lambda_2 + \lambda_3)^2}}{3}\right\} \qquad \ldots (28)$$

If the average field acting on the molecules of a small volume element in the absence of an electrostatic field is unaffected by the anisotropic fluctuations of dielectric constant and if we assume that the directions of the principal electrostatic and optical polarisabilities in each molecule are the same and their magnitudes are proportional to each other,

$$\frac{\lambda_1{}^0}{\lambda_1} = \frac{\epsilon - 1}{\nu^2 - 1}$$

and

$$\frac{\nu_z - \nu_x}{E_0{}^2} = \frac{N\delta v}{80\pi\nu RT}\frac{\epsilon - 1}{\nu^2 - 1} \cdot \frac{\epsilon + 2}{3} \cdot \frac{\nu^2 + 2}{3} \cdot \left(\overline{\lambda_1{}^2} + \overline{\lambda_2{}^2} + \overline{\lambda_3{}^2}\right)$$

$$= \frac{N\delta v}{80\pi\nu RT}\frac{(\epsilon - 1)(\epsilon + 2)}{(\nu^2 - 1)(\nu^2 + 2)}\left(\frac{\nu^2 + 2}{3}\right)^2\left(\overline{\lambda_1{}^2} + \overline{\lambda_2{}^2} + \overline{\lambda_3{}^2}\right)$$

$$\therefore \left(\overline{\lambda_1{}^2} + \overline{\lambda_2{}^2} + \overline{\lambda_3{}^2}\right) = \frac{80\pi\nu RT}{N\delta v}\frac{\lambda B^1}{(\epsilon - 1)}\frac{(\nu^2 - 1)(\nu^2 + 2)}{(\epsilon + 2)} \cdot \frac{9}{(\nu^2 + 2)^2} \qquad (29)$$

If at the same time for reasons discussed in section I, we take

$$\overline{\lambda_1{}^2} = \frac{(\nu^2 - 1)^2 RT\beta}{N\delta v},$$

Gans's expression (24) for h will get transformed into

$$h = \frac{8\pi^3}{3} \frac{RT}{N\lambda^4} l \cdot \left\{ \beta(\nu^2-1)^2 \frac{80\pi\nu\lambda B^1}{(\nu^2+2)} \cdot \frac{(\nu_2-1).3}{(\epsilon-1)(\epsilon+2)} \right\} \quad \ldots \quad (30)$$

6. Anisotropic fluctuations of dielectric constant in terms of molecular constants.

It can easily be seen that anisotropic fluctuations of dielectric constants of small volume elements are a necessary consequence of the anisotropy of the individual molecules. Consider a small volume element of an isotropic liquid composed of anisotropic molecules. Since the molecular axes are by hypothesis oriented at random, the number of molecules pointing in directions included within any small solid angle will not, in general, be exactly the same as the number pointing in directions included within another equal solid angle pointing in some other direction. Thence will arise a residual anisotropy of the volume element whose magnitude and direction will vary from instant to instant. The smaller the number of molecules, the greater will be the fluctuations from isotropy.

We have already seen that in a small volume element of of an isotropic liquid under normal conditions

$$\delta K = (K_0-1)\left(\frac{\delta n}{n} + \frac{\delta A'}{A'} \right)$$

$$\therefore \quad \overline{\delta K^2} = (K_0-1)^2 \left\{ \frac{\overline{\delta n^2}}{n^2} + \frac{\overline{\delta A'^2}}{A'^2} \right\} \quad \ldots \quad (31)$$

where it is assumed that δn and $\delta A'$ are independent of each other. The first term of the above equation can be identified with $\overline{\Lambda^2}$ and the second with

$$(\overline{\lambda_1^2} + \overline{\lambda_2^2} + \overline{\lambda_3^2})/3.$$

It suffices now to evaluate

$$\overline{\delta A'^2}/A'^2.$$

When a unit field parallel to the axis of Z is applied to the medium, the mean value of the square of the sum of the induced moments of the molecules is [See $7(a)$ and $7(b)$ above]

$$\overline{\left\{\frac{A+B+C}{3}\right\}^2 n^2 \delta v^2} + \overline{\Sigma\left\{L_3 - \frac{A+B+C}{3}\right\}^2}$$

$$=\left(\frac{A+B+C}{3}\right)^2 n_0^2 \delta v^2 + \overline{\left(\frac{A+B+C}{3}\right)^2 \delta n^2 \delta v^2} + n_0 \delta v \cdot \tfrac{4}{3}f$$

Of these, only the last term contributes to $\delta A'^2$. The mean value of the squares of the moments induced parallel to the X and Y axis will each be

$$n_0 \delta v \cdot f. \qquad\qquad \text{(Paper B, Eq, 1)}$$

$$\therefore\quad \overline{\delta A'^2} = \frac{n_0 \delta v \cdot (\tfrac{4}{3}f + 2f)}{n_0^2 \delta v^2} = \tfrac{10}{3}f \Big/ n_0 \delta v. \qquad\qquad \dots \text{(32)}$$

and

$$\frac{\overline{\lambda_1^2} + \overline{\lambda_2^2} + \overline{\lambda_3^2}}{3} = (K_0 - 1)^2 \frac{\tfrac{10}{3} \cdot \tfrac{1}{15}(A^2 + B^2 + C^2 - AB - BC - CA)}{\left(\dfrac{A+B+C}{3}\right)^2 n_0 \delta v}$$

$$= \frac{2(K_0 - 1)^2(A^2 + B^2 + C^2 - AB - BC - CA)}{(A + B + C)^2 n_0 \delta v}$$

$$= \frac{2(K_0 - 1)^2 \delta}{n_0 \delta v} = \frac{2(\nu^2 - 1)^2 \delta}{n_0 \delta v} \qquad\qquad \dots \text{(33)}$$

Identifying this $\overline{\lambda_1^2} + \overline{\lambda_2^2} + \overline{\lambda_3^2}$ derived from *a priori* considerations with the same quantity expressed in terms of the Kerr constant in (29), we can express B' in terms of δ

$$B' = \frac{(v^2-1)(v^2+2)(\epsilon-1)(\epsilon+2)N\delta}{120\pi RTn_0 v\lambda} \qquad \text{... (34)}$$

on the assumption that the principal axes of dielectric and optical constants are parallel and proportional to each other. This is the same expression as is obtained on Langevin's theory of electrical double refraction.[1]

In terms of molecular constants,

$$h = \frac{8\pi}{3\lambda^4} \left\{ \overline{\wedge^2} + \frac{\overline{\lambda_1^2} + \overline{\lambda_2^2} + \overline{\lambda_3^2}}{3} \right\} \delta v$$

$$= \frac{8\pi}{3n_0\lambda^4} \left\{ \frac{RT\beta n_0}{N} + 2\delta \right\} (K_0-1)^2 \qquad \text{... (35)}$$

which is identical with (10).

The expression for the intensity in a transverse direction also becomes the same as (9).

7. Comparison of phenomenological and molecular theories.

We see from the above that both the phenomenological and molecular theories lead exactly to the same result, and this is what is to be expected. Strictly, the phenomenological theory itself is partly molecular, since in developing it, we have to use the Lorentz formula of refraction which is based on molecular considerations. As regards the theory of

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[1] P. Debye, Handbuch der Radiologie, Band VI, p. 768. Also K. S. Krishnan, Proc. Ind. Assoc. Cult. of Science, Vol. IX, Part IV, p. 251.

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electric double refraction, the advantage lies with the molecular way of treatment. It is more direct and simple and is capable of extension to the case when the molecules possess a permanent electric moment.[1] And since we know for a certainty from the partial polarisation of the transversely scattered light in gases and vapours that molecules are in general optically anisotropic, there is nothing to be gained by avoiding that assumption and preferring instead the assumption of anisotropic dielectric constants of small elements of volume.

In a recent paper, Mr. K. S. Krishnan[2] has compared the available experimental data on light-scattering in liquids with different formulæ that have been proposed from time to time and shown that so far as comparative values of intensities are concerned, relation (9) is in better agreement with experiment than the formulæ involving $(K+2)^2/9$ as a factor. As regards absolute measurements, the data are not decisive, but it is hoped that results of critical measurements of intensity in a few selected liquids will soon be available to decide the question. Measurements near the critical temperature are not of much help in this respect, as the values of $(K+2)^2/9$ in that region generally differ very little from unity.

Mr. Krishnan has utilized the data about polarisation to calculate the values of δ which gives a measure of the optical anisotropy of the molecule and compared them with the values calculated from the Kerr constant of electric double refraction according to (34). Here again, he finds that values of δ given by the revised expressions are in better agreement with the values calculated from the Kerr constant. It may be mentioned that liquids containing polar molecules are excluded from consideration.

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[1] C. V. Raman and K. S. Krishnan, Nature, Vol. 118, p. 302, 1926 ; also same authors Phil. Mag., Vol. 3, pp. 713-723 and pp. 724-735, April 1927.

[2] K. S. Krishnan, *loc. cit.*

8. Binary Liquid Mixtures.

The arguments discussed in Sections 1 and 2 should also be applicable to the fluctuations of concentration in a binary liquid mixture. In a detailed paper[1] on the "Opalescence of binary liquid mixtures," Dr. J. C. K. Rav has obtained the following expression for the intensity of the transversely scattered light from a volume V

$$\frac{p^4 Z^2}{c^4 d^2} V \left\{ \frac{13}{3} \left(\frac{K+2}{3} \right)^2 (f_1 n_1 + f_2 n_2) + \frac{(K-1)^2 (K+2)^2}{144 \pi^2} \cdot \frac{RT\beta}{N} \right.$$

$$\left. + \frac{1}{16\pi^2} \cdot \frac{M_2}{Nm_1} \frac{(\partial K / \partial k)^2}{\partial \log p_2 / \partial k} \right\} \qquad \dots \text{(36)}$$

(See equation 41 on p. 45) where f_1, f_2 are the values of f which is equal to

$$\tfrac{1}{15}(A^2 + B^2 + C^2 - AB - BC - CA)$$

for the first and second components respectively, n_1, n_2 are the numbers of molecules of the two components per unit of volume, M_2 is the molecular weight in the gaseous phase and p_2 the partial vapour pressure, of the second component, m_1 and m_2 are the masses of the first and second components in unit volume of the mixture and k is the fraction m_2/m_1. The factor $(K+2)^2/9$ in the second term is introduced in the same manner as in the previous treatments of liquids with isotropic

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[1] J. C. K. Rav. Proc. Ind. Assoc. for Cult. of Science, Vol. IX, Part I, p. 19 (1924).

molecules, that is, assuming that the local field in a small volume element changes with the changes of density in the element. According to section 2, this factor should be omitted.

$\partial K/\partial k$ in the third term is obtained by measuring the tangent at desired points from a graph showing the variation of K with k. These values are appropriate to the case where similar changes of concentration occur throughout the liquid. When the deviations of concentration from normal in different volume elements are uncorrelated with each other, the changes of dielectric constant in them will be due solely to these changes of concentration and the local field will remain unaffected. The values of $\partial K/\partial k$ which we should adopt are therefore not those obtaining when similar changes of concentration occur throughout the liquid, but these values divided by a factor $(K+2)/3$. Making these changes, expression (36) will become

$$\frac{p^4 Z^2}{c^4 d^2} \, V \left\{ \frac{13}{3} \frac{(K+2)^2}{9} (f_1 n_1 + f_2 n_2) + \frac{(K-1)^2}{16\pi^2} \frac{RT\beta}{N} \right.$$

$$\left. + \frac{1}{16\pi^2} \frac{M_2 (\partial K/\partial k)^2}{N m_1 \partial \log p_2/\partial k} \frac{9}{(K+2)^2} \right\} \qquad \dots \ (37)$$

and equation (40) of Dr. Rav's paper for the depolarisation of the transversely scattered light will be changed to

$$\frac{\dfrac{2(K+2)^2}{9} (f_1 n_1 + f_2 n_2)}{\dfrac{7}{3}\left(\dfrac{K+2}{3}\right)^2 (f_1 n_1 + f_2 n_2) + \dfrac{(K-1)^2}{16\pi^2} \dfrac{RT\beta}{N} + \dfrac{9}{16\pi^2 (K+2)^2} \dfrac{M_2 (\partial K/\partial k)^2}{N m_1 \partial \log p_2/\partial k}}$$

The available experimental data are not sufficiently accurate to decide whether these or Dr. Rav's expressions better represent the facts.

9. Summary.

In this paper, the question of fluctuations of dielectric constant of a small volume element of a liquid is discussed with reference to the theories of molecular scattering of light. Reasons are given for concluding that the fluctuations of dielectric constant responsible for scattering cannot be determined by differentiating Lorentz's relation between dielectric constant and density but that the factor $(K+2)/3$ must be omitted from the expression for δK. Revised expressions for the intensity and polarisation of the scattered light are given in terms of the molecular theory.

Gans's phenomenological method of treatment is outlined and discussed and the assumptions underlying it pointed out. If the omission of the $(K+2)/3$ factor of the expression for δK be accepted, Gans's theory and molecular theory lead to identical results.

It is shewn that if the molecules of a liquid are anisotropic, small volume elements must necessarily possess accidental deviations from isotropy; the relation between them, the constants of molecular anisotropy and the Kerr constant of electric double refraction is worked out.

Mr. Krishnan has shown that results of experiments are favourable to the omission of the factor $(\nu^2+2)^2/9$.

It is pointed out that similar arguments should hold in the case of binary liquid mixtures and that the fluctuations of concentration accidentally occurring in such a mixture cannot be assumed to be identical with the changes of

dielectric constant with concentration obtained from experiments on liquids in mass. Revised expressions for scattering are given.

I wish to express my thanks to Prof. C. V. Raman for his kind interest in the work.