

I. Electromagnetic Theory of the Scattering of Light in Fluids.

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I. INTRODUCTION.

The subject of "Molecular Scattering of Light" whose foundations were laid by the late Lord Rayleigh, gained a new significance from the experimental work of Cabannes¹ and the present Lord Rayleigh² on the scattering of light in dust-free gases. Its importance was further increased by Prof. Raman's³ application of Einstein's investigation of critical opalescence to the case of scattering in fluids in general, and his explanation of the blue of the sea as being caused by molecular scattering of light in water. Experimental work by the present author⁴ on the

¹ Cabannes—Ann. Physique, Tome XV, 1920, pp. 1-150.

² Rayleigh—Proc. Roy. Soc. A, 1918, p. 453.

³ C. V. Raman—Proc. Roy. Soc. A, April, 1922, p. 65 and, 'Molecular Diffraction of Light,' Calcutta University Press, 1922.

⁴ K. R. Ramanathan—Proc. Roy. Soc. A., 1922, p. 151.

scattering of light in ether and by Mr. R. Venkateswaran⁵ in normal pentane showed that throughout the range of temperatures from 35°C to the critical point, both in the saturated vapour state and in the liquid state in equilibrium with the vapour, the intensity of scattering in a transverse direction is given by the Einstein-Smoluchowski expression (with a correction for admixture with unpolarised light).

$$I = \frac{\pi^2}{18} \frac{RT\beta}{N\lambda^4 r^2} (\mu^2 - 1)^2 (\mu^2 + 2)^2$$

where I is the intensity of the scattered light from a unit volume at a large distance r from the volume.

R, N are the gas-constant and the number of molecules respectively per gram-molecule

T is the absolute temperature

β is the isothermal compressibility of the medium

μ is its refractive index, and

λ is the wave-length of the incident light.

The above expression was derived by Einstein on the assumption that the scattering of light was caused by the local changes in dielectric displacement consequent upon the local fluctuations of density to which an otherwise uniform medium is subject owing to the thermal movements of its parts. In such a case, the light scattered in a direction transverse to the primary beam should be completely polarised. The same result may be deduced when the individual molecules are regarded as sources of scattered radiation provided that they are supposed to be spherically symmetrical and their restricted freedom of movement is taken into account. Actually, however, the transversely scattered light is in general found to be imperfectly polarised, much more so in a liquid than in its vapour. The imperfect polarisation has been explained

⁵ R. Venkateswaran—Trans. Chem. Soc., 1922, Vol. 121, p. 2655.

by the late Lord Rayleigh,⁶ Born⁷ and Gans⁸ on the assumption of molecular anisotropy. The subject has also been studied by Sir J. J. Thomson⁹ from the point of view of the electron theory. The increase of imperfection of polarisation in the liquid state is remarkable and an explanation of it has been given by Raman on the idea that the scattering in a fluid can be considered to be made up of two parts, a density-scattering and an orientation-scattering of which the former is given by the Einstein-Smoluchowski formula while the latter is proportional to the density of molecules. It is obviously of importance to make an exact investigation of the connection between the state of aggregation of a medium and the quality of the scattered light, especially in view of the fact that it promises to throw light on the nature of the liquid state itself. In the following paper, an attempt is made to develop a general theory of scattering in fluids. In Article 2, the medium is assumed to be continuous as in Einstein's treatment of the subject, but subject to local fluctuations of density depending upon the laws of statistical mechanics. Lorentz's electromagnetic treatment of the scattering of light in gases developed in his book "Les Theories Statistique en Thermodynamique" has been adopted and extended to the general case of a fluid of any compressibility. In Article 3, the subject is treated from the molecular standpoint in the case when the molecules are isotropic and the Einstein-Smoluchowski formula for scattering is deduced. In Article 4, the molecular treatment is extended to the case when the molecules are anisotropic and expressions are deduced for the intensity of the scattered light, its state of polarisation and the co-efficient of extinction in the medium. In

⁶ Rayleigh—Phil. Mag., XXX, 1918, and Scientific Papers, Vol. VI, p. 540.

⁷ Born—Verh. Deutsch. Phys. Gesell., Vol. 19, p. 243, 1917, and Vol. 20, p. 16, 1918.

⁸ Gans—Ann. der Physik—10, 1931.

⁹ Sir J. J. Thomson—Phil. Mag., XL, 1920, p. 393.

Article 5, the results are discussed with reference to experimental data as regards polarisation of the scattered light in liquids and their vapours. Article 6 contains a synopsis of the principal results of the investigation.

2. "CONTINUOUS MEDIUM" THEORY.

Let K_0 be the value of the dielectric constant when there is a uniform distribution of matter and $K_0 + \delta K$ its actual value at a volume element δv .

In any actual fluid, owing to thermal movements, the density at any point undergoes incessant fluctuations and hence the dielectric constant also.

Using Heaviside units, the dielectric displacement $D = K_0 E$ (1) where E is the electric intensity. When the density and consequently the dielectric constant are uniform, there would be no scattering, for the disturbances from different elements of volume would mutually cancel each other, except in the direction of primary propagation.

At a place where the dielectric constant is $K_0 + \delta K$,

$$D_1 = (K_0 + \delta K) E \quad (2)$$

Here, there is a discontinuity of displacement which could be annulled by introducing a supplementary electric intensity

$$F = - \frac{\delta K}{K_0} E \quad (3)$$

For, then

D_1 would become $(K_0 + \delta K)(E - \frac{\delta K}{K_0} E)$ which is equal to $K_0 E$ if we neglect $(\delta K/K_0)^2$ in comparison with unity. As matters actually are, the scattering is identical with the radiation due to a system of electric intensities $-F$ or $\frac{\delta K}{K_0} E$ at the places where the dielectric constant differs from its mean value K_0 by δK .

Suppose we have a volume element δv at the origin of co-ordinates at which the dielectric constant is $K_0 + \delta K$. When the linear dimensions of the element are small in comparison with the wave-length, the amplitude of the disturbance from the element would be proportional to

$\frac{\delta K}{K_0} E \delta v$ and hence its energy proportional to

$$\left(\frac{\delta K}{K_0}\right)^2 E^2 (\delta v)^2 \quad (4)$$

As a first step, then, we have to calculate the radiation caused by an extraneous periodic intensity acting throughout a volume element δv at a given point in a homogeneous isotropic dielectric. The problem is analogous to that solved by Hertz in the case of the vibrating electric doublet.

Let E represent the electric intensity

H ,, magnetic ,,

D ,, dielectric displacement

and F the extraneous electric intensity acting throughout the element of volume δv ,

We shall take the magnetic permeability of the medium to be unity.

The field equations are

$$\left. \begin{aligned} \text{Curl } H &= \frac{1}{c} \frac{\partial D}{\partial t} \\ \text{Curl } E &= -\frac{1}{c} \frac{\partial H}{\partial t} \end{aligned} \right\} \quad (5)$$

where c is the velocity of light in vacuo

Also $D = K(E + F)$ (6)

$$\left. \begin{aligned} \text{div } H &= 0 \\ \text{div } D &= 0 \end{aligned} \right\} \quad (7)$$

and

Eliminating H from (5) and making use of (6), we get

$$\nabla^2 E - \frac{K}{c^2} \frac{\partial^2 E}{\partial t^2} = \frac{K}{c^2} \frac{\partial^2 F}{\partial t^2} + \text{grad div } E \quad (8)$$

To solve (8), following Lorentz,¹⁰ we shall introduce a new vector A given by

$$\nabla^2 A - \frac{K}{c^2} \frac{\partial^2 A}{\partial t^2} = -F \quad (9)$$

In order that (8) and (9) may simultaneously be true,

$$E = \text{grad div } A - \frac{K}{c^2} \frac{\partial^2 A}{\partial t^2} \quad (10)$$

and

$$H = \frac{K}{c} \frac{\partial}{\partial t} [\text{curl } A] \quad (11)$$

Equation (9) is of a well-known form and its solution is

$$A = \frac{1}{4\pi} \int \frac{1}{r} F \left(t - \frac{r}{v} \right) dv \quad (12)$$

¹⁰ H. A. Lorentz—Les Theories Statistique en Thermodynamique, pp. 42-43.

where the integration is taken over the whole space in which F differs from zero and where $u = \frac{c}{\sqrt{K}}$ is the velocity of electromagnetic waves in the medium, r is the distance from δv of the point at which A is required and $F\left(t - \frac{r}{u}\right)$ is the value of F at time $t - \frac{r}{u}$

When F is a periodic electric intensity $F_0 \cos pt$ in the direction of the z -axis, confined to a single volume element δv at the origin of co-ordinates.

$$F_x = 0, \quad F_y = 0 \quad \text{and} \quad F_z = F_0 \cos pt$$

Hence from (12)

$$A_x = 0, \quad A_y = 0, \quad A_z = \frac{F_0 \delta v}{4\pi r} \cos p \left(t - \frac{r}{u} \right)$$

From (10),

$$E_x = \frac{\partial^2 A_z}{\partial z \partial t^2}, \quad E_y = \frac{\partial^2 A_z}{\partial y \partial z} \quad \text{and} \quad E_z = \frac{\partial^2 A_z}{\partial z^2} - \frac{1}{u^2} \frac{\partial^2 A_z}{\partial t^2}$$

The magnetic intensities, can, if necessary, be easily deduced from (11). For distances from the origin large in comparison with the wave-length,

$\frac{1}{r^2}$ and $\frac{1}{r^3}$ can be neglected in comparison with $\frac{1}{r}$ and hence

$$E_x = -\frac{yz}{r^3} \omega, \quad E_y = -\frac{xz}{r^3} \omega, \quad \text{and} \quad E_z = \left(\frac{1}{r} - \frac{z^2}{r^3} \right) \omega \quad (13)$$

where $\omega = \frac{p^2 F_0 \delta v}{4\pi u^2} \cos p \left(t - \frac{r}{u} \right)$

The intensity of the radiation would be proportional to $E_x^2 + E_y^2 + E_z^2$ which is given by

$$\frac{x^2 + y^2}{r^4} \omega^2 = \frac{\sin^2 \theta}{r^2} \omega^2 \quad (14)$$

where θ is the angle between the direction of the ray and the axis of z (the direction of the applied electric intensity).

In the case of scattering by a single volume element δv ,

$F_0 = -\frac{\delta K}{K_0} E$ and the ratio of $E_x^2 + E_y^2 + E_z^2$ to E^2 the square of the amplitude of the incident wave is given by

$$\frac{\sin^2 \theta}{r^2} \left(\frac{2\pi}{\lambda_1} \right)^4 \left(\frac{\delta K}{K_0} \right)^2 \frac{\delta v^2}{16\pi^2} \quad (15)$$

where $2\pi/\lambda_1$ has been substituted for p/u . λ_1 is the wave-length of the incident vibration in the medium.

Let us now consider the scattering produced by the accidental deviations of density in an extended volume. Let us take the X-axis to be the direction of the primary beam. The density deviations would change both in magnitude as well as in position in a perfectly arbitrary manner and there would be no co-ordination of phase between the vibrations scattered by the various elements. As a consequence, over any finite time-interval, the energies and not the amplitudes of the scattered radiations from the different elements of volume would be additive. If $\delta\rho$ denotes the deviation of density from its uniform value ρ_0 in a volume element δv then we can easily show¹¹ by applying Boltzmann's principle of entropy-probability that the mean square of deviation of density is given by

$$\overline{(\delta\rho)^2} = \frac{RT\beta}{N\delta v} \rho_0^2 \quad (16)$$

The relation between density and dielectric constant is given by Lorentz's equation

$$\begin{aligned} \frac{K_0 - 1}{(K_0 + 2)} \rho_0 &= \text{constant.} \\ \text{Hence } \frac{\partial K}{\partial \rho} &= \frac{(K_0 - 1)(K_0 + 2)}{3\rho_0} \\ &\text{and} \\ \delta K &= \frac{\partial K}{\partial \rho} \delta \rho \\ \overline{\delta K^2} &= \frac{(K_0 - 1)^2 (K_0 + 2)^2}{9\rho_0^2} \overline{\delta \rho^2} \\ &= \frac{(K_0 - 1)^2 (K_0 + 2)^2}{9} \frac{RT\beta}{N\delta v} \end{aligned}$$

Substituting in (15) $\overline{\delta K^2}$ for δK^2 we get for the ratio of the average intensity of the scattered radiation to that of the incident

$$\frac{\pi^2}{9} \frac{RT\beta}{NK^2\lambda_1^4} (K_0 - 1)^2 (K_0 + 2)^2 \frac{\sin^2\theta}{r^2} \delta v$$

and since the radiations from different volume elements are additive

$$\frac{\pi^2}{9} \frac{RT\beta}{N\lambda^4} (K_0 - 1)^2 (K_0 + 2)^2 \frac{\sin^2\theta}{r^2} \text{ per unit volume} \quad (17)$$

¹¹ Einstein—Ann. der Physik, Vol. 1910, p. 1275, also C. V. Raman and K. B. Ramanathan—Phil. Mag., Jan. 1923.

where λ is the wave-length of the incident vibration in vacuo. The radiation in the direction of the z axis is zero and is a maximum in the xy plane.

When the incident light is unpolarised, the ratio of the intensity of the light scattered in a transverse direction to the intensity of the incident beam is given by

$$\frac{\pi^2}{18} \frac{RT\beta}{N\lambda^4} (K_0 - 1)^2 (K_0 + 2)^2 \frac{1}{r^3}$$

In a direction making an angle ϕ with the incident beam, this becomes

$$\frac{\pi^2}{18} \frac{RT\beta}{N\lambda^4} (K_0 - 1)^2 (K_0 + 2)^2 \left\{ \frac{1 + \cos^2 \phi}{r^2} \right\} \quad (18)$$

To get the extinction co-efficient, we have only to find the total scattering from a stratum of thickness dx and unit area of cross-section. Integrating (18) over the surface of a sphere of radius r , the ratio of the energy scattered by such a stratum to the incident energy is given by

$$\frac{dI}{I_0} = \frac{8\pi^3}{27} \frac{RT\beta}{N\lambda^4} (K_0 - 1)^2 (K_0 + 2)^2 dx$$

$$\therefore I = I_0 e^{-hx}$$

$$\text{where } h = \frac{8\pi^3}{27} \frac{RT\beta}{N\lambda^4} (K_0 - 1)^2 (K_0 + 2)^2$$

We might substitute μ^2 for K_0 in the above expressions where μ is the refractive index of the medium for the particular frequency.

3. Scattering by Isotropic Molecules.

Considering the problem from a molecular standpoint, the effect of an incident electromagnetic wave on the molecules of a medium is to produce a displacement of the electrons in the molecules which is equivalent to creating an oscillating electric doublet in each molecule

with a period the same as that of the wave. When the molecules are isotropic, the axes of the doublets coincide in direction with that of electric intensity, but when they are anisotropic, the displacements of the electrons are not in general in that direction, but the effect may approximately be taken to be equivalent to creating three doublets with their axes along three principal directions in each molecule. The field to which any molecule is subject is the resultant of that due to the incident wave and that due to the polarisation of the neighbouring molecules. The latter is taken account of in Lorentz's well known treatment of dispersion in homogeneous, isotropic media. In the case of a gas at atmospheric pressure, its effect is negligible. The treatments of the scattering of light by isotropic molecules by the late Lord Rayleigh, Natanson, Sir J. J. Thomson and others do not take into account the influence of the surrounding molecules. Einstein's treatment of the subject does consider the effect due to the polarisation of the surrounding dielectric, but the treatment is non-molecular, and the results apply only to the case of a medium composed of isotropic molecules. With a view to extension to the case when the molecules are anisotropic, a molecular treatment of the problem is given below, taking into account the effect of the neighbouring molecules.

Consider a plane polarised wave travelling in the direction Ox . Let Z be the electric intensity in the wave parallel to Oz and proportional to $\cos pt$. Under the influence of the wave, each molecule becomes equivalent to a doublet with its axis parallel to Oz . Let A be the moment induced in a molecule when it is placed in a field of unit intensity. If the medium be of uniform density and if n_0 denotes the number of molecules per unit volume and M_0 the electric moment of each doublet,

the actual intensity at any point O in the medium is given by

$$Z + \frac{4\pi}{3} n_o M_o$$

and

$$\begin{aligned} M_o &= A \left(Z + \frac{4\pi}{3} n_o M_o \right) \\ &= AZ / \left(1 - \frac{4\pi}{3} n_o A \right) \end{aligned} \quad (19)$$

Now K_o the square of the refractive index of the medium for waves of frequency $p/2\pi$ is given by

$$\frac{K_o - 1}{K_o + 2} = \frac{4\pi}{3} n_o A \quad (20)$$

and hence

$$M_o = AZ \frac{(K_o + 2)}{3} \quad (21)$$

A vibrating electric doublet radiates out energy. According to Hertz's well known solution, the electric intensity at time t at a point r distant (great in comparison with λ) from the doublet is

$$\frac{p^2 M_o \sin \theta}{c^2 r} \quad \text{at time } t - \frac{r}{c} \quad (22)$$

where c is the velocity of light in vacuo, θ is the angle between Oz and the direction of the ray and $M_o \left(t - \frac{r}{c} \right)$ stands for the value of the moment at time $t - \frac{r}{c}$.

When the molecules of the medium are uniformly distributed and we consider the effect due to a volume whose dimensions are large compared with λ , it vanishes in all directions except in the direction of primary propagation where the secondary waves from the different molecules in the wave-front combine with the original wave and give rise to a plane wave moving with an altered velocity. In any actual fluid medium, however, owing to the thermal movements of the molecules, and the consequent fluctuations of density at any point, there

is a finite radiation of energy in all directions. If n_0 represents the average number of molecules per unit volume in a volume element δv and $\overline{\delta n^2}$ the mean square of the deviations of that number, then as before

$$\frac{\overline{\delta n^2}}{n_0^2} = \frac{RT\beta}{N\delta v} \quad (23)$$

Consider a volume element δv at O small in comparison with a cubic wave-length, but large compared to the dimensions of a molecule. Let n be the number of molecules per unit volume in δv and let n be equal to $n_0 + \delta n$. The electric intensity at P due to scattering by the molecules contained in δv would be given by

$$\frac{p^2}{c^2 r} \sin \theta \delta v (Mn - Mn_0) \quad (24)$$

where M is the electrical moment appropriate to the density n . When we are considering the average effect over finite intervals of time, the distinction between M and $M(t - \frac{r}{c})$ may be dropped. Now

$$= \frac{p^2}{c^2 r} \sin \theta \left[(M_0 + \delta M)(n_0 + \delta n) - M_0 n_0 \right] \delta v \quad (24)$$

$$= \frac{p^2}{c^2 r} \sin \theta (M_0 \delta n + n_0 \delta M) \delta v \quad (25)$$

Now, differentiating (19) and applying (20)

$$\delta M = \frac{(K_0 - 1)(K_0 + 2)}{9} AZ \frac{\delta n}{n_0}$$

$$\begin{aligned} \therefore n_0 \delta M + M_0 \delta n &= \left(\frac{K_0 + 2}{3} \right)^2 AZ \delta n \\ &= \frac{(K_0 - 1)(K_0 + 2)}{12\pi} Z \frac{\delta n}{n_0} \end{aligned} \quad (26)$$

Let us consider the effect due to (25). If E is the electric intensity at P due to radiation from δv , the energy is proportional to E^2 . It is thus

$$\begin{aligned} &\frac{p^4 \sin^2 \theta}{c^4 r^2} (M_0 \delta n + n_0 \delta M)^2 \delta v^2 \\ &= \frac{p^4 \sin^2 \theta}{c^4 r^2} \frac{(K_0 - 1)^2 (K_0 + 2)^2}{144\pi^2} Z^2 \frac{\delta n^2}{n_0^2} \delta v^2 \end{aligned}$$

Since δn varies from instant to instant according to the laws of chance the average expectation of E^2 over a sufficiently long interval of time is

$$\overline{E^2} = \frac{p^4 \sin^2 \theta}{c^4 r^2} \frac{(K_o - 1)^2 (K_o + 2)^2}{144 \pi^2} Z^2 \frac{\overline{\delta n^2}}{n_o^2} \delta v^2$$

By (23),

$$\overline{E^2} = \frac{p^4 \sin^2 \theta}{c^4 r^2} \frac{(K_o - 1)^2 (K_o + 2)^2}{144 \pi^2} Z^2 \frac{RT\beta}{N} \delta v$$

When we consider the effect due to a volume v whose dimensions are large in comparison with λ , the ratio of the square of the electric vector in the scattered radiation to that in the incident is

$$\begin{aligned} \frac{\overline{E^2}}{Z^2} &= \frac{p^4 \sin^2 \theta}{c^4 r^2} \frac{(K_o - 1)^2 (K_o + 2)^2}{144 \pi^2} \frac{RT\beta}{N} v. \\ &= \frac{\pi^2}{9} \frac{RT\beta}{N\lambda^4} (K_o - 1)^2 (K_o + 2)^2 v. \frac{\sin^2 \theta}{r^2} \end{aligned}$$

where λ is the wave-length of the light in vacuo.

4. *Scattering by Anisotropic Molecules.*

Let $O'\xi$, $O'\eta$, $O'\zeta$ denote the three principal directions in a molecule whose centre is O' .

Let A , B , C be the moments induced in the molecule when placed in a field of unit intensity parallel to $O'\xi$, $O'\eta$, $O'\zeta$ respectively.

As before, let Oz be the direction of the incident polarised plane wave and Z the electric intensity along Oz . In a medium composed of isotropic molecules the axis of the induced doublet in each molecule would be parallel to Z ; there would be no component along Oz or Oy . In a medium composed of anisotropic molecules, however, there would, in general, be components both along the x and the y axes. But when the axes of the molecules are oriented *at random* the components of the induced moments along the x and y directions would be as much positive as negative and hence the polarisation fields parallel to the x and y axis

which may be taken as $\frac{4}{3}\pi n_o \overline{M}_x$ and $\frac{4}{3}\pi n_o \overline{M}_y$ respectively would

vanish. We would however still have $\frac{4}{3}\pi n_o \overline{M}_z$ because M_z can have

only positive values. The effect of the polarisation of the surrounding

molecules is then to produce an additional field of $\frac{4}{3}\pi n_o \bar{M}_z$. The resultant electric field at a point in the medium is therefore

$$Z + \frac{4}{3}\pi n_o \bar{M}_z \quad (27)$$

To calculate \bar{M}_z , we note that if the molecules are oriented at random,

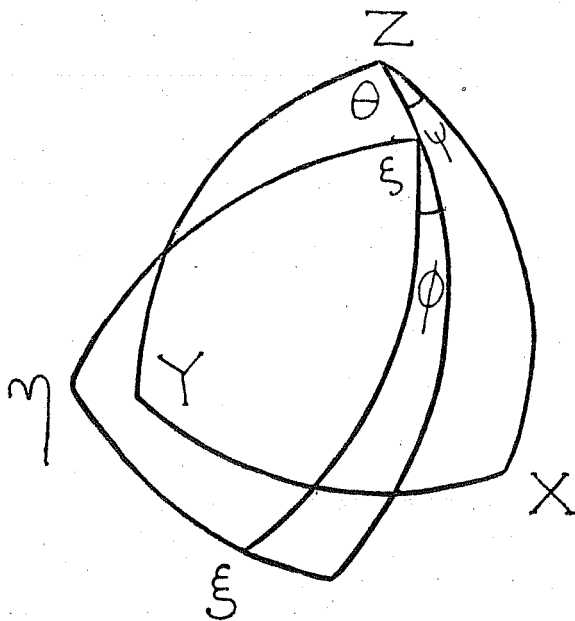
$$\begin{aligned} \bar{M}_z &= \frac{A+B+C}{3} \left[Z + \frac{4}{3}\pi n_o \bar{M}_z \right] \\ &= \frac{A+B+C}{3} Z \cdot \frac{K_o+2}{3} \end{aligned}$$

and

$$\frac{K_o-1}{K_o+2} = \frac{4\pi n_o}{3} \left[\frac{A+B+C}{3} \right] \quad (28)$$

Consider a molecule, the direction of whose principal axes is defined by the Eulerian angles θ, ϕ, ψ .¹

In figure 1, x, y, z represent the points where $O'x, O'y, O'z$ cut a sphere of unit radius, and ξ, η, ζ the points where the axes of the molecule cut the same sphere.



The moments induced in the molecule parallel to $O'\xi, O'\eta, O'\zeta$ are

$$\begin{aligned} &-AZ \left(\frac{K_o+2}{3} \right) \sin \theta \cos \phi \\ &BZ \left(\frac{K_o+2}{3} \right) \sin \theta \sin \phi \\ &CZ \left(\frac{K_o+2}{3} \right) \cos \theta \end{aligned} \quad (29)$$

¹ Lord Rayleigh and Sir J. J. Thomson, *loc. cit.*

When these are resolved along Ox , Oy , Oz the components are

$$M_x = Z \left(\frac{K_o + 2}{3} \right) \left[\sin \theta \cos \theta \cos \psi (C - A \cos^2 \phi - B \sin^2 \phi) \right. \\ \left. + (A - B) \sin \theta \sin \psi \sin \phi \cos \phi \right]$$

$$M_y = Z \left(\frac{K_o + 2}{3} \right) \left[\sin \theta \cos \theta \sin \psi (C - A \cos^2 \phi - B \sin^2 \phi) \right. \\ \left. + (A - B) \sin \theta \cos \psi \sin \phi \cos \phi \right]$$

$$M_z = Z \left(\frac{K_o + 2}{3} \right) \left[C \cos^2 \theta + B \sin^2 \theta \sin^2 \phi + A \sin^2 \theta \cos^2 \phi \right] \quad (30)$$

which, for shortness, we may write

$$Z \left(\frac{K_o + 2}{3} \right) L_1, \quad Z \left(\frac{K_o + 2}{3} \right) L_2, \quad Z \left(\frac{K_o + 2}{3} \right) L_3$$

The mean value of M_x and M_y taken over all orientations is zero, while that of M_z is $Z \left(\frac{K_o + 2}{3} \right) \left(\frac{A+B+C}{3} \right)$. At a point on the y -axis distant r from O , the square of the x -component of the electric intensity due to scattering from a molecule at O is

$$\frac{p^4}{c^4 r^2} M_x^2$$

and from the molecules contained in a volume element δv the average expectation of X'^2 is

$$\overline{X'^2} = \frac{p^4}{c^4 r^2} \overline{M_x^2} n \delta v$$

Since M_x has positive and negative values equally often at random,

$\overline{X'^2}$ is proportional to the number of molecules.

Averaged over all orientations of molecules

$$\overline{X'^2} = \frac{p^4}{c^4 r^2} Z^2 \left(\frac{K_o + 2}{3} \right)^2 \frac{1}{15} (A^2 + B^2 + C^2 - AB - BC - CA) n_o \delta v \\ = \frac{p^4}{c^4 r^2} Z^2 \left(\frac{K_o + 2}{3} \right)^2 f n_o \delta v$$

where

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

and from a volume V

$$\overline{X^2} = \frac{p^4}{c^4 r^2} Z^2 \left(\frac{K_0 + 2}{3} \right)^2 f n_0 V \quad (31)$$

In the case of the Z -component, we note that it can have only values of the same sign as Z . Hence from a *small* volume element δv , the amplitudes of the electric forces are additive. The Z -component of the electric force due to a single molecule at O is given by

$$\frac{p^2}{c^2 r} M_z$$

and from the $n\delta v$ molecules contained in the volume element δv

$$\begin{aligned} Z^1 &= \frac{p^2}{c^2 r} M_z n \delta v \\ &= \frac{p^2}{c^2 r} (\overline{M}_z + \delta M_z) (n_0 + \delta n) \delta v \\ &= \frac{p^2}{c^2 r} (\overline{M}_z n_0 + \overline{M}_z \delta n + n_0 \delta \overline{M}_z) \delta v \end{aligned}$$

The amplitude due to the first term cancels when the effect is taken over a finite volume and as in the case of isotropic molecules, we are left with the second and third terms

$$\begin{aligned} \therefore Z^{1^2} &= \frac{p^4}{c^4 r^2} (\overline{M}_z \delta n + n_0 \delta \overline{M}_z)^2 \delta v^2 \\ &= \frac{p^4}{c^4 r^2} Z^2 \left(\frac{K_0 + 2}{3} \right)^4 \overline{L_3^2} \delta v^2 \overline{\delta n^2} \end{aligned}$$

as in (26).

The mean value of L_3^2 taken over all orientations is

$$g = \frac{1}{15} (3A^2 + 3B^2 + 3C^2 + 2AB + 2BC + 2CA)$$

$$\therefore \overline{Z^{1^2}} = \frac{p^4}{c^4 r^2} Z^2 \left(\frac{K_0 + 2}{3} \right)^4 \overline{\delta n^2} \delta v^2 \cdot g$$

and by (23)

$$= \frac{p^4}{c^4 r^2} Z^2 \left(\frac{K_0 + 2}{3} \right)^4 \frac{RT\beta}{N} \delta v. n_0^2 \cdot g$$

and from a volume V, the same quantity

$$= \frac{p^4}{c^4 r^2} Z^2 \left(\frac{K_0 + 2}{3} \right)^4 \frac{RT\beta}{N} n_0^2 g V \quad (32)$$

and

$$\frac{\overline{X^{1/2}}}{\overline{Z^{1/2}}} = \left(\frac{K_0 + 2}{3} \right)^2 \frac{f}{N} \frac{RT\beta}{n_0 g} = \frac{f}{\gamma g} \quad (33)$$

where

$$\gamma = \left(\frac{K_0 + 2}{3} \right)^2 \frac{RT\beta}{N} n_0. \quad (34)$$

When the incident light is unpolarised, the ratio of the weak component to the strong in a direction perpendicular to the incident beam is

$$\frac{2f}{f + \gamma g} \quad (35)$$

For a gas at ordinary pressure obeying Boyle's law, this becomes

$$\frac{2f}{f + g} \quad (36)$$

in accordance with Rayleigh's result.

The total intensity of the scattered light from a unit volume in a direction perpendicular to the incident beam is

$$\frac{p^4}{c^4 r^2} Z^2 \left(\frac{K_0 + 2}{3} \right)^2 \{3fn_0 + \gamma gn_0\} \quad (37)$$

To connect g and f with experimentally determinable quantities, we note that

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

$$g = \frac{1}{15}(3A^2 + 3B^2 + 3C^2 + 2AB + 2BC + 2CA)$$

$$\therefore g - \frac{4}{3}f = \frac{1}{3}(A + B + C)^2$$

$$= \frac{9}{16\pi^2 n_0^2} \frac{(K_0 - 1)^2}{(K_0 + 2)^2} \quad (38)$$

and from (36) in the case of rare vapour for which Boyle's law holds good, the ratio of the weak component to the strong in the transversely scattered light is

$$r_1 = \frac{2f}{f+g} \quad \therefore f = \frac{3r_1(g - \frac{4}{3}f)}{6 - 7r_1} \quad (39)$$

The quantity under the brackets in (37) can be written

$$fn_0(3 + \frac{4}{3}\gamma) + (g - \frac{4}{3}f)n_0\gamma$$

By (39), this reduces to

$$n_0(g - \frac{4}{3}f) \left\{ \gamma + \frac{r_1(9 + 4\gamma)}{6 - 7r_1} \right\}$$

and (37) becomes

$$\frac{p^2}{c^2 r^2} Z^2 \left(\frac{K_0 + 2}{3} \right)^2 n_0(g - \frac{4}{3}f) \left\{ \gamma + \frac{r_1(9 + 4\gamma)}{6 - 7r_1} \right\}$$

substituting the values of γ and $g - \frac{4}{3}f$ it reduces to

$$\frac{\pi^2 RT\beta}{9N\lambda^4} \frac{Z^2}{r^2} (K_0 - 1)^2 (K_0 + 2)^2 + \frac{Z^2}{r^2} \frac{\pi^2}{n_0\lambda^4} (K_0 - 1)^2 \frac{r_1(9 + 4\gamma)}{6 - 7r_1}$$

Since the square of the electric intensity in the incident unpolarised light is $Y^2 + Z^2 = 2Z^2 = I_0$ say, this becomes

$$\frac{I_0}{r^2} \left\{ \frac{\pi^2}{18} \frac{RT\beta}{N\lambda^4} (K_0 - 1)^2 (K_0 + 2)^2 + \frac{\pi^2}{2n_0\lambda^4} (K_0 - 1)^2 \frac{r_1(9 + 4\gamma)}{6 - 7r_1} \right\} \quad (40)$$

When $A=B=C$, that is, when the molecules are isotropic, $f=0$ and the expression reduces to the Einstein Smoluchowski formula

$$\frac{I_0}{r^2} \frac{\pi^2}{18} \frac{RT\beta}{N\lambda^4} (K_0-1)^2 (K_0+2)^2$$

In the case of a vapour obeying Boyle's law, the expression becomes

$$\frac{I_0}{r^2} \frac{\pi^2}{2n_0\lambda^4} (K_0-1)^2 \left\{ 1 + \frac{13r_1}{6-7r_1} \right\}$$

The quantity outside the square brackets is the Rayleigh expression for scattering in gases obeying Boyle's law and the multiplying factor is the same as that introduced by Cabannes.

To obtain the co-efficient of extinction, we shall first find an expression for the total radiation from a unit volume when the incident light is polarised with its electric vector along the z axis. The squares of the components of the electric intensity in the light scattered from unit volume, in directions perpendicular to Ox , Oy , Oz are (31) and (32)

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

and

$$\begin{aligned} Z'^2 &= \frac{p^4}{c^4 r^2} Z^2 \left(\frac{K_0+2}{3} \right)^4 \frac{RT\beta}{N} n_0^2 g \\ &= \frac{p^4}{c^4 r^2} Z^2 \left(\frac{K_0+2}{3} \right)^2 \gamma g n_0. \end{aligned}$$

This can be looked upon as a mixture of unpolarised light equal to $\frac{p^4}{c^4 r^2} Z^2 \left(\frac{K_0+2}{3} \right)^2 2f n_0$ and of polarised light

equal to $\frac{\rho^4}{c^4 r^2} Z^2 \left(\frac{K_0 + 2}{3} \right)^2 n_0 (\gamma g - f)$ with the vibrations parallel to the z -axis. Integrating over the surface of a sphere of radius r , the total radiation becomes

$$\begin{aligned} & \frac{\rho^4}{c^4} Z^2 \left(\frac{K_0 + 2}{3} \right)^2 n_0 \left[8\pi f + \frac{8\pi}{3} (\gamma g - f) \right] \\ &= \frac{128\pi^5}{3\lambda^4} Z^2 \left(\frac{K_0 + 2}{3} \right)^2 n_0 (2f + \gamma g) \end{aligned}$$

Putting in the values of f , g and γ , this becomes

$$Z^2 \left\{ \frac{8\pi^3}{27} \frac{RT\beta}{N\lambda^4} (K_0 - 1)^2 (K_0 + 2)^2 + \frac{8\pi^3}{3n_0\lambda^4} (K_0 - 1)^2 \frac{6r_1}{6 - 7r_1} \right. \\ \left. \left(1 + \frac{2\gamma}{3} \right) \right\}$$

and the fraction of the incident radiation scattered is

$$\begin{aligned} & \frac{8\pi^3}{27} \frac{RT\beta}{N\lambda^4} (K_0 - 1)^2 (K_0 + 2)^2 + \frac{8\pi^3}{3} \cdot \frac{(K_0 - 1)^2}{n_0\lambda^4} \frac{6r_1}{6 - 7r_1} \\ & \left(1 + \frac{2}{3} \gamma \right) \quad \dots \quad (41) \end{aligned}$$

Even if the incident light is unpolarised, the same expression holds good. For a gas obeying Boyle's law, this reduces to

$$\frac{8\pi^3}{3} \frac{(K_0 - 1)^2}{n_0\lambda^4} \left\{ \frac{6 + 3r_1}{6 - 7r_1} \right\} \quad \dots \quad \dots \quad (42)$$

We can easily see that with unpolarised light, since the intensity of the light scattered along the y and z -axis is each

$$\frac{\rho^4}{c^4 r^2} Z^2 \left(\frac{K_0 + 2}{3} \right)^2 n_0 (3f + \gamma g)$$

and that along the x -axis is

$$\frac{p^2}{e^2 r^2} Z^2 \left(\frac{K_0 + 2}{3} \right)^2 n_0 (2f + 2\gamma g)$$

the distribution of intensity is given by

$$\frac{8\pi^4}{\lambda^4} \cdot \frac{I_0}{r^2} \left(\frac{K_0 + 2}{3} \right)^2 n_0 \{ (3f + \gamma g) + (\gamma g - f) \cos^2 \phi \}$$

where ϕ is the angle between the directions of the incident and scattered beams.

When the values of f , g and γ are substituted this becomes

$$\begin{aligned} & \frac{I_0}{r^2} \left[\frac{\pi^2 RT\beta}{18 N\lambda^4} \cdot (K_0 - 1)^2 (K_0 + 2)^2 (1 + \cos^2 \phi) \right. \\ & \left. + \frac{\pi^2}{2} \cdot \frac{(K_0 - 1)^2}{n_0 \lambda^4} \cdot \frac{r_1}{6 - 7r_1} \{ (9 + 4\gamma) + (4\gamma - 3) \cos^2 \phi \} \right] \\ & = \frac{I_0}{r^2} \left[\frac{\pi^2 RT\beta}{18 N\lambda^4} \cdot (K_0 - 1)^2 (K_0 + 2)^2 (1 + \cos^2 \phi) \right. \\ & \left. + \frac{\pi^2}{2} \cdot \frac{(K_0 - 1)^2}{n_0 \lambda^4} \cdot \frac{r_1}{6 - 7r_1} (4\gamma - 3)(1 + \cos^2 \phi) \right. \\ & \left. + 12 \cdot \frac{\pi^2}{2} \cdot \frac{(K_0 - 1)^2}{n_0 \lambda^4} \cdot \frac{r_1}{6 - 7r_1} \right] \end{aligned}$$

5. Comparison with Experiment.

We shall calculate the imperfection of polarisation of the transversely scattered light in a number of liquids from (35) and (36) from the corresponding values for their vapours, and compare the results with the values obtained experimentally. For this, we shall use the data

obtained by Rayleigh¹ and by Raman and Seshagiri Rao.² The following table summarises the results.

Substance.	$\frac{\text{WEAK COMPONENT}}{\text{STRONG COMPONENT}}$ (per cent).		
	Vapour.	Liquid at 3 °c (Calc.).	Liquid at 30°c (obs.).
Ether	1.7	20	8.8
Benzene	6.5	75	39.8
CS ₂	12.0	75	70
CHCl ₃	3.0	31	15
CCl ₄	3.1	49	11

The calculated values are uniformly too high. This seems to show that the *hypothesis of random orientations of molecules in liquids, which we have assumed in the development of the theory does not hold good.*

6. Synopsis.

1. An electromagnetic theory of the scattering of light in fluids has been worked out without assuming a molecular structure on the basis of Lorentz's treatment of the scattering of light in gases and the Einstein-Smoluchowski formula for scattering derived.

2. The same result is shown to follow if the fluid medium be supposed to be composed of isotropic molecules.

3. The treatment is extended to the case when the molecules are anisotropic in which case it is shown that if the orientations of the molecules are entirely at random, the transversely scattered light is imperfectly polarised, the ratio of the weak component to the strong being

¹ Rayleigh: Proc. Roy Soc. A, loc cit.

² C V. Raman and K. Seshagiri Rao: Phil. Mag vol. 45, 1923, p. 625 and "Molecular Diffraction of Light"

given by

$$r_1 = \frac{2f}{f + \gamma g}$$

where $\gamma = \left(\frac{K_0 + 2}{3} \right)^2 \frac{RT\beta}{N} n_0$ and f and g are constants for the molecule. The intensity of the light scattered in a direction making an angle ϕ with the incident beam is shown to be

$$\begin{aligned} \frac{I_0}{r^2} \left[\frac{\pi^2}{18} \frac{RT\beta}{N\lambda^4} (K_0 - 1)^2 (K_0 + 2)^2 (1 + \cos^2 \phi) \right. \\ \left. + \frac{\pi^2}{2} \cdot \frac{(K_0 - 1)^2}{n_0 \lambda^4} \cdot \frac{r_1}{6 - 7r_1} \right. \\ \left. + 12 \cdot \frac{\pi^2}{2} \frac{(K_0 - 1)^2}{n_0 \lambda^4} \cdot \frac{r_1}{6 - 7r_1} \right] \end{aligned}$$

The expression reduces to the appropriate forms when the medium consists of isotropic molecules and when the medium is a vapour obeying Boyle's law.

The co-efficient of extinction is shown to be

$$\frac{8\pi^3}{27} \frac{RT\beta}{N\lambda^4} \cdot (K_0 - 1)^2 (K_0 + 2)^2 + \frac{8\pi^3}{3} \frac{(K_0 - 1)^2}{n_0 \lambda^4} \frac{6r_1}{6 - 7r_1} \left(1 + \frac{2}{3} \gamma \right)$$

For a vapour obeying Boyle's law, this becomes

$$\frac{8\pi^3}{3} \frac{(K_0 - 1)^2}{n_0 \lambda^4} \frac{6 + 3r_1}{6 - 7r_1}$$

4. The observed values of the imperfection of polarisation in liquids are compared with the calculated values and the former are found to be much too small. This seems to indicate that the assumption of random orientation of molecules in liquids is not valid.

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