

# XI. Electromagnetic Theory of the Scattering of Light in Fluids—Paper B.

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## INTRODUCTION.

In a previous paper,<sup>1</sup> the author has worked out a theory of the scattering of light in fluids both for the case when the medium is composed of isotropic molecules and when it is composed of simple anisotropic molecules with random orientation. Since writing the above, there have appeared articles of great interest by Dr. Cabannes<sup>2 3</sup> and Prof. L. V. King<sup>4</sup> dealing with the same subject. Some of the arguments and conclusions of these investigators appear to me to be open to question, and in order to clear up the matter, it seems desirable to set forth in somewhat greater detail certain parts of my aforesaid paper. Moreover, it has been pointed out to me by Prof. Raman that there is an error in my investigation of the case of anisotropic molecules which makes it necessary to revise some of the calculations given there. It is proposed in the first part of this paper to discuss the case of anisotropic molecules more fully with the necessary corrections put in and compare the theoretical results with experimental data, and in the second and third parts to review and discuss the theories put forward by Cabannes and King.

<sup>1</sup> Proc. Ind. Assoc. for the Cultivation of Science, Vol. VIII, pp. 1-22. We shall refer to this paper in the sequel as Paper A.

<sup>2</sup> Journal de Physique ; Ser. VI, Tome III, pp. 429-442 (1922).

<sup>3</sup> Comptes Rendus ; Tome 175, p. 875.

<sup>4</sup> Nature, May 19, 1923.

*I. Scattering by a Fluid composed of Anisotropic Molecules.*

It was shown in Paper A that when a fluid medium of any density is composed of isotropic molecules, the intensity of scattering in any direction is given by the Einstein-Smoluchowski formula when in addition to the external field we take into account the polarisation field due to the neighbouring molecules. If the external field be parallel to  $O_z$  and of intensity  $Z$ , then the resultant field is also parallel to  $O_z$  and is of intensity  $Z(K_0+2)/3$ ,  $K_0$  itself being given by the well-known relation

$$\frac{K_0-1}{K_0+2} = \frac{4\pi}{3} n_0 A.$$

Even when the molecules are anisotropic, the resultant field is still given by  $Z(K_0+2)/3$  provided the molecules are oriented at random. In this case, however,  $K_0$  is given by

$$\frac{K_0-1}{K_0+2} = \frac{4\pi}{3} n_0 \left( \frac{A+B+C}{3} \right)^2$$

To get the intensity of light scattered in any direction from a unit of volume, we have to add together the contributions from all the molecules contained in it, due regard being paid to the phases of the waves scattered. In the case of isotropic molecules, the induced moments are all parallel to the external field and the direction of vibration in the scattered light is parallel to that in the incident. With anisotropic molecules, however, the directions of the induced moments are fixed in each molecule and the scattered light has in general also vibrations perpendicular to those in the incident light. In a medium composed of anisotropic molecules, the scattering can be supposed to arise out of two causes, one arising from the density fluctuations such as is contemplated in Einstein's theory and the other from the random character of the orientations of the anisotropic molecules.

<sup>1</sup> The notation of Paper A is used.

We may divide the volume of fluid illuminated by the incident light into a large number of equal elementary volumes  $\delta v$ , the linear dimensions of each of which are small compared with the wave-length of light in the medium, but yet so large compared with the size of a molecule that the fluctuations of density in one element may be independent of those in the neighbouring elements. Let us consider one of these elements with its centre at  $O$ . In order to get the intensity at any instant of the light scattered from  $\delta v$ , we have to square the algebraical sum of the components of the electric vector from the different molecules, and to get the average intensity over a finite interval of time, we have to calculate the average value of this quantity in a large number of independent trials in each of which the closeness of packing of the molecules and their orientations are re-distributed according to the principles of statistical mechanics. If the incident light be plane-polarised with the electric vector  $Z$  parallel to  $OZ$  and the direction of propagation be  $Ox$ , then at a point  $P$  on the  $y$ -axis distant  $r$  from  $O$ , the  $x$ -component of the electric vector due to scattering from a molecule at  $O$  is given by

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

where

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

and  $\theta, \phi, \psi$  are the Eulerian angles defining the orientation of the principal axes of the molecule.

From all the molecules contained in  $\delta v$  the value is

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

Since  $\delta v$  contains a large number of molecules with their orientations at random,  $\sum M_x$  would in general be small,

since positive and negative values of  $M_x$  are equally probable. But it is also possible the values of  $M_x$  are all positive or all negative, or that the sum of all the positive values is just equal to the sum of all the negative values. These are extreme cases; at any trial, there would in general be a slight excess of the sum of all the positive values over the negative and *vice versa*. Thus, although in a large number of trials,  $\sum M_x$  would be zero,  $(\sum M_x)^2$  would not be. As the late Lord Rayleigh<sup>1</sup> has shown, when the value of  $M_x$  is as often positive as negative,

$$(\overline{\sum M_x})^2 = n \overline{M_x^2} \delta v$$

where  $n \delta v$  is the number of molecules contained in  $\delta v$ . The average expectation of  $X^2$  from  $\delta v$  is thus

$$\begin{aligned} \overline{X^2} &= \frac{p^2}{c^2 r^2} \cdot \overline{M_x^2} \cdot n \delta v \\ &= \frac{p^2}{c^2 r^2} Z^2 \left( \frac{k+2}{3} \right)^2 f n \delta v \end{aligned}$$

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

When we take the average effect over a finite volume  $V$ ,

$$\overline{X^2} = \frac{p^2}{c^2 r^2} Z^2 \left( \frac{k_0+2}{3} \right)^2 f n_0 V. \quad \dots (1)$$

The  $z$ -component of the electric vector at P in the wave scattered from a molecule at O is<sup>2</sup>

$$\frac{p^2}{c^2 r} M_x = \frac{p^2}{c^2 r} \cdot Z \left( \frac{k+2}{3} \right) L_s$$

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

<sup>1</sup> Theory of Sound, Vol. I, p. 36.

<sup>2</sup> In paper A, the square of this expression multiplied by  $n^2 \delta v^2$  was taken to represent the intensity of the light scattered from all the molecules contained in  $\delta v$ . This is erroneous, since a part of  $L_s$ , namely that arising from the anisotropy of the molecule varies from molecule to molecule.

and  $k$  is the value appropriate to the density in  $\delta v$ . The value of  $L_3$  averaged over all orientations is  $(A+B+C)/3$  and the above expression can be written

$$\frac{p^3}{c^2 r^2} \cdot Z \left( \frac{k+2}{3} \right) \left[ \frac{A+B+C}{3} + \left( L_3 - \frac{A+B+C}{3} \right) \right]$$

The square of the  $z$ -component of the electric vector from all the molecules contained in  $\delta v$  is therefore

$$\frac{p^4}{c^4 r^2} \cdot Z^2 \left( \frac{k+2}{3} \right)^2 \left[ \left( \frac{A+B+C}{3} \right)^2 n^2 \delta v^2 + \left\{ \overline{\left( L_3 - \frac{A+B+C}{3} \right)^2} \right\} + 2 \left\{ \overline{\left( L_3 - \frac{A+B+C}{3} \right) \left( \frac{A+B+C}{3} \right)} \right\} \right]$$

The third term is zero when averaged over all orientations. In the second term,  $L_3 - \frac{A+B+C}{3}$  varies from molecule to molecule and may either be positive or negative, the average value over a large number of molecules with all possible orientations being zero. In such a case

$$\left[ \overline{\left( L_3 - \frac{A+B+C}{3} \right)^2} \right] = n \delta v \left[ \overline{L_3^2} + \left( \frac{A+B+C}{3} \right)^2 - 2 \overline{L_3} \left( \frac{A+B+C}{3} \right) \right] = n \delta v \cdot \frac{4}{3} f$$

because

$$\overline{L_3^2} = \frac{1}{15} (3A^2 + 3B^2 + 3C^2 + 2AB + 2BC + 2CA)$$

and

$$\overline{L_3} = (A+B+C)/3.$$

The first term varies from one volume element to another owing to the fluctuations of density and the attendant fluctuations of dielectric constant, and as in the case of isotropic molecules (Sec. 3 of paper A), the expectation of the square of the  $z$ -component in the light scattered from  $\delta v$  arising out of this cause is

$$\frac{p^4}{c^2 r^2} Z^2 \left( \frac{k_0+2}{3} \right)^2 \left( \frac{A+B+C}{3} \right)^2 \frac{RT\beta}{N} n_0^2 \delta v$$

The total value of  $\overline{Z^2}$  from a volume  $V$  is therefore

$$\overline{Z^2} = \frac{p^4}{c^4 r^2} Z^2 \left( \frac{k_0 + 2}{3} \right)^2 n_0 V \left[ \left( \frac{A+B+C}{3} \right)^2 \gamma + \frac{4}{3} f \right] \quad \dots (2)$$

where

$$\gamma = \frac{RT\beta}{N} n_0 \left( \frac{k_0 + 2}{3} \right)^2$$

The ratio of the weak component to the strong in the light scattered along  $Oy$  is

$$\frac{\overline{X^2}}{\overline{Z^2}} = \frac{f}{\gamma \left( \frac{A+B+C}{3} \right)^2 + \frac{4}{3} f}$$

When the incident light is unpolarised, the ratio is

$$r = \frac{2f}{\gamma \left( \frac{A+B+C}{3} \right)^2 + \frac{7}{3} f} \quad \dots (3)$$

When the substance is in the form of a vapour so rare as to obey Boyle's law, this becomes

$$\frac{2f}{\left( \frac{A+B+C}{3} \right)^2 + \frac{7}{3} f}$$

Denoting this by  $r_1$  and substituting the values of  $\frac{A+B+C}{3}$  and  $f$  in terms of the constants of the medium,<sup>1</sup> the above becomes

$$r = \frac{6r_1}{\gamma(6-7r_1) + 7r_1} \quad \text{or} \quad \frac{\gamma r}{6-7r} = \frac{r_1}{6-7r_1} \quad \dots (4)$$

The intensity of the transversely scattered light from a volume  $V$  at a distance  $r$  large compared with the linear dimensions of  $V$  is

$$\begin{aligned} & \frac{p^4}{c^4 r^2} Z^2 \left( \frac{k_0 + 2}{3} \right)^2 n_0 V \cdot \left\{ \left( \frac{A+B+C}{3} \right)^2 \gamma + \frac{13}{3} f \right\} \\ &= \frac{Z^2}{r^2} \left\{ \frac{\pi^2 RT\beta}{9 N \lambda^4} (k_0 - 1)^2 (k_0 + 2)^2 + \frac{\pi^2}{n_0 \lambda^4} (k_0 - 1)^2 \frac{13r_1}{6-7r_1} \right\} V. \end{aligned}$$

<sup>1</sup> Page 17 of Paper A.

Substituting  $r_1$  by  $r$  and introducing  $I_0$  the intensity of the incident unpolarised light, this becomes

$$\frac{I_0 V}{r^2} \left\{ \frac{\pi^2 RT\beta}{18N\lambda^4} (k_0 - 1)^2 (k_0 + 2)^2 \left( \frac{6 + 6r}{6 - 7r} \right) \right\} \dots (5)$$

— the same expression as was first proposed by Prof. Raman<sup>1</sup> from general considerations to represent the scattering of light in liquids.

In a direction making an angle  $\chi$  with the incident light, the intensity is easily seen to be

$$\frac{I_0 V}{r^2} \left[ \frac{\pi^2 RT\beta}{18N\lambda^4} (k_0 - 1)^2 (k_0 + 2)^2 \cdot \left\{ \frac{6 - 6r}{6 - 7r} (1 + \cos^2 \chi) + \frac{12r}{6 - 7r} \right\} \right] \dots (6)$$

and the coefficient of extinction becomes

$$\frac{8\pi^3}{27} \cdot \frac{RT\beta}{N\lambda^4} (k_0 - 1)^2 (k_0 + 2)^2 \left\{ \frac{6 + 3r}{6 - 7r} \right\}.$$

#### *Comparison with Experiment.*

Prof. Raman and Mr. Seshagiri Rao<sup>2</sup> have compared the experimental values of the intensity of light transversely scattered by a number of liquids at the ordinary temperature with the values calculated according to (5), and shown that there is satisfactory agreement between the two except in the case of carbon disulphide which shows a very large depolarisation. In table I are included these values and also the values obtained by Messrs. Martin<sup>3</sup> and Lehrman. To reduce the two sets of values to the same standard, the intensities of scattering for ether have been assumed to be the same.

<sup>1</sup> "Molecular Diffraction of Light," p. 58, and C. V. Raman and K. Seshagiri Rao, *Phil. Mag.*, March 1923.

<sup>2</sup> *Phil. Mag.*, March 1923.

<sup>3</sup> *Journ. Phys. Chemistry*, Vol. 26, pp. 75-88 (1922).

Table I.—Intensity of transversely scattered light in liquids.

The intensities are expressed in terms of that of the polarised scattering of air at N. T. P.

Liquid.	Temp. °C.	$r = \frac{\text{Weak Component}}{\text{Strong Component}}$ (per cent.)			Intensity (calculated).	Intensity (observed)	Author.
		R & R	M & L	Adopted			
Water ...	30°	12.5		11.0	159	165	R & R <sup>1</sup>
			6.7			165	M & L <sup>2</sup>
Ether ...	30°	8.3		9.0	930	860	R & R
			10.0			860	M & L (assumed)
Methyl Alcohol ...	30°	15.1		11.0	512	495	R & R
			7.1			462	M & L
Ethyl Alcohol ...	30°	13.0		10.0	608	620	R & R
			7.8			485	M & L
<i>n</i> -Propyl alcohol	18°	...	8.5	8.5	546	630	M & L
Iso-butyl Alcohol	18°	...	3.5	8.5	610	679	M & L
Iso-amyl Alcohol	...	...	9.0	9.0	595	722	M & L
<i>n</i> -Hexane ...	...	...	10	10	835	969	M & L
Cyclo-hexane ...	...	...	8	8	816	750	M & L
			...	...		...	...
Benzene ...	30°	39.8		48.0	3,600	3,135	R & R
			45.5			2,477	M & L
Toluene ...	30°	40.0		49.0	4,170	2,970	R & R
			49.0			2,804	M & L
Chloro-benzene ...	...	...	54	...	...	3,535	M & L
CS <sub>2</sub> ...	30°	70		71.0	23,000	16,000	R & R
			71.0			10,850	M & L

<sup>1</sup> R. & R.; C. V. Raman and K. S. Rao.

<sup>2</sup> M. & L.; W. H. Martin and S. Lehrman.



The last four liquids which have a large depolarisation show a scattering power lower than that calculated.

In table II, the polarisation of the transversely scattered light in a number of liquids is calculated from the corresponding values in their vapours according to (4) and the results compared with experiment.

Table II.

Substance.	Weak Component Strong Component (per cent.)		
	Vapour.	Liquid at 30°C (calculated).	Liquid at 30°C (observed).
Ether ... ..	3.0	26.7	9.0
Benzene ... ..	6.5	50.4	48
CS <sub>2</sub> ... ..	12.0	52	72
CHCl <sub>3</sub> ... ..	3.0	26	15
CCl <sub>4</sub> ... ..	3.1	37	11

Except in the the case of benzene, the calculated values show no agreement with the observed ones. With carbon disulphide, the observed value is higher than the calculated, while with the others, it is lower. This disagreement between observation and theory seems to show that the molecules in a liquid are not oriented at random. We should, however, still have expected the observed intensities to agree with the calculated, provided we make use of the *observed* values of the imperfection of polarisation. Although there is a good agreement for liquids showing a moderate depolarisation, it is no longer so for liquids showing strong depolarisation. It is remarkable that for these liquids, the observed intensities are *smaller* than the calculated ones.

*Dependence of the polarisation of the scattered light on wave-length.*

The question whether there is any change in the polarisation of the scattered light when the wave-length is altered is one of considerable interest. Experiments with ordinary gases in the visible region of the spectrum do not show any effect : but by reason of their greater depolarisation, liquids may show the effect, which would, however, depend not only on the anisotropy of the molecule, but also on the dispersive power of the substance. Equation (4) shows that even when  $\nu_1$  remains constant,  $\nu$  would change with the wave-length, the value decreasing with decreasing wave-length, and if  $\nu_1$  increases with decreasing wave-length (as we might expect it to do for theoretical reasons), the two would act in opposite ways. Previous work in the laboratory of the Indian Association with dust-free carbon disulphide and benzene had failed to show any change of the imperfection of polarisation with wave-length. Cabannes in his recent paper has obtained an effect with carbon disulphide, getting 66 per cent. with red light and 80 per cent. with blue. The experiments have been repeated by the author with the following liquids repeatedly distilled in vacuo, carbon disulphide, benzene, toluene, ethyl ether, ethyl alcohol and water ; none of them show a distinct change of  $\nu$  with wave-length. Strong sunlight was used for illuminating the liquids and colour filters for transmitting definite regions of the spectrum—cuprammonium for the blue and Wratten filters for the green and the red. With carbon disulphide, the imperfection was found to be 72 per cent. for white light and practically the same with the different colour filters. At any rate, the values lie between 70 and 75 per cent. The value for benzene was 48 per cent., for toluene 50 per cent. and for ether 9 per cent. In the case of alcohol and water, a difference between the

values has been previously recorded<sup>1</sup> when different colour filters are introduced in the path of the incident light, but a closer examination shows that this is not the effect sought for, but is due to the presence of a trace of fluorescence. This is made quite evident when the colour filters are transferred from the path of the incident beam to that of the scattered. The following tables give the values of the depolarisation.

Table III.—Ethyl Alcohol.

	$\frac{\text{Weak Component}}{\text{Strong Component}}$ (per cent.)		
	Red.	Green.	Blue.
Filter in incident beam ...	8.0	7.7	15.0
Filter in scattered beam ...	11.2	10.2	10.5

The value with no filter was 10.2 per cent.

Table IV.—Water.

(Repeatedly distilled in vacuo in pyrex glass bulb.)

	$\frac{\text{Weak Component}}{\text{Strong Component}}$ (per cent.)		
	Red.	Green.	Blue.
Filter in incident beam ...	10.0	10.0	17.5
Filter in scattered beam ...	10.2	10.8	11.0

<sup>1</sup> C. V. Raman, 'Molecular Diffraction of Light,' p 55; see also C. V. Raman and K. Seshagiri Rao, Phil. Mag., March, 1923.

The value with no filter was 10·8 per cent. The origin of the fluorescence has not yet been definitely ascertained. The alcohol used was the purest obtainable and it was distilled by cooling the condensing bulb with ice, keeping the other bulb slightly above the room temperature. As for the water, a specimen which had already been distilled over alkaline permanganate was used in the distillation bulbs (made of pyrex glass) and the distillations in vacuo were carried out very slowly. In spite of many re-distillations, the effect remained practically undiminished.

## II. Cabannes's Theory.

The theory of scattering developed by Cabannes, though in some respects similar to the above, yet differs from it in certain fundamental points. In calculating the effect due to the neighbouring molecules, Cabannes follows the usual method (following Lorentz) of describing a sphere of radius  $R$  (small in comparison with the wave-length, but large compared with the linear dimensions of a molecule) about  $O$ , and considering the field at  $O$  to be made up with two parts, (1) the external field plus the field due to the molecules outside the sphere and (2) the field due to the polarisation of the molecules within the sphere. Lorentz and Rayleigh have shown that for a cubical arrangement of isotropic molecules, (2) is zero. Cabannes considers that although in a sufficiently long time, the components  $X_1, Y_1, Z_1$  of this field may cancel, they would at any instant, owing to the irregularities in the distribution of molecules, differ from zero, and the quantities  $\overline{X_1^2}, \overline{Y_1^2}, \overline{Z_1^2}$  would be finite. To calculate these mean values, he takes the mean square of the components  $\overline{X_1^2}, \overline{Y_1^2}, \overline{Z_1^2}$  produced by a single molecule situated in all positions on the surface of a sphere of radius  $r$  and in all possible orientations and then sums up the effect for all the molecules contained between two spheres of radii  $d$  and  $R$  where  $d$  is the shortest possible distance between the centres of two neighbouring

molecules. On making the necessary calculations with the implicit assumption that each molecule scatters independently, he arrives at a formula for the imperfection of polarisation of the transversely scattered light from which it appears that even when the molecules of a medium are isotropic, there would be an imperfection of polarisation which would disappear when the density is very small, but which would increase with increasing density. He also obtains a relation between imperfection of polarisation in a liquid and its vapour in terms of the refractivity of the substance and the smallest possible distance between two molecules in the liquid state.

In adding the effects of the different molecules, Cabannes adds the squares of the electric intensities, thus assuming independence of phase between the radiations scattered by the different molecules—an assumption obviously invalid. The calculation of  $\overline{X_1^2}$ ,  $\overline{Y_1^2}$ ,  $\overline{Z_1^2}$  also seems to be in error. It is true that in the case of a liquid, when we go down to the individual molecule, the actual field to which it is subject would vary from molecule to molecule, being in part dependent on the positions and orientations of the neighbouring molecules. The residual effect may be looked upon as due to the fluctuations from the cubical arrangement, and the exact magnitude of the fluctuations is not easy to calculate, but the scattering due to this cause may be expected to be small. For, consider a doublet at P with its axis parallel to OX. The electric intensity due to this will diminish as  $\frac{1}{r^3}$  so that beyond a distance of a few molecular diameters from P, the intensity will be negligible. The space surrounding the doublet can be divided into two regions such that the  $x$  component of the flux of intensity in one is positive while that in the other is negative. These two regions *always accompany each other* and since the volume over which the intensity due to the doublet is sensible is small compared with a wave-length cube, we have to add together the electric intensities

of the scattered waves from the different molecules in this small volume. This sum will be of the second order of small quantities unless there is great asymmetry of distribution round P. The same remarks hold for the  $y$  and  $z$  components. Cabannes's method of calculation is tantamount to assuming that the positions of the molecules are perfectly random.

In his second paper, Cabannes has adapted Einstein's result to the general case of an isotropic fluid composed of anisotropic molecules by multiplying Einstein's expression for scattering by a factor derived from his own previous investigation. In view of the objections set forth above, this result also cannot be considered as acceptable.

Comparing Cabannes's theoretical results with experiment, it is not true that liquids have always a larger imperfection of polarisation than their vapours at low densities. As the temperature of liquid is raised, the imperfection of polarisation gets smaller and smaller and may reach a value much lower than that for the rare vapour. Experiments on benzene by the author<sup>1</sup> and by Martin and Lehrman<sup>2</sup> and on carbon dioxide by Raman and the author<sup>3</sup> furnish numerous instances of this. In the case of saturated vapour, an increase of density is accompanied by a diminution of the imperfection of polarisation.

Cabannes has deduced the smallest possible distance between the centres of two molecules in a liquid from the depolarizations in the liquid and vapour states. The values obtained are *much too small*. For, example, in benzene, the smallest distance is calculated to be 2.2 A. U, while the average distance<sup>4</sup> calculated from the density of the liquid on the hypothesis of a close packing of spherical molecules is 7.4 A. U.

<sup>1</sup> Physical Review, 21, p. 564 (1923).

<sup>2</sup> Journ. Phys. Chemistry, June 1923, pp. 558-564.

<sup>3</sup> In course of publication.

<sup>4</sup> Jeans, Dynamical Theory of Gases.

### III. King's Theory.

Prof. King's extension of the theory of scattering to media composed of *complex anisotropic* molecules is of considerable interest. With regard to scattering by liquids, he considers that equally probable orientations of complex anisotropic molecules would result in the transversely scattered light being completely polarised. As we have seen in Part I, this is not true. The incompleteness of polarisation of the scattered light cannot, therefore, serve as a basis for the conclusion that liquids have a fine-grained crystalline structure.

In deriving his formula for the intensity of the scattered light in a direction  $\theta$  with the incident beam, *viz.*,

$$\frac{r^2 I_{\theta}}{V I} = \frac{1}{2} \frac{\pi^2}{\lambda^4} (\mu^2 - 1)^2 \cdot \frac{6(1+\rho)}{6-7\rho} \cdot \frac{RT\alpha}{N} \left\{ 1 + \frac{1-\rho}{1+\rho} \cos^2 \theta \right\},$$

King has apparently neglected to take into account the fluctuations of the polarisation field consequent upon the fluctuations of density. His formula therefore does not reduce to Einstein's in the case when the transversely scattered light is completely polarised. Again, it is not clear why King has used  $\alpha$ , the adiabatic compressibility instead of the isothermal compressibility. The compressibility is introduced in finding the work done in changing the actual density at some volume element to the mean density under the condition of ideal thermodynamic equilibrium. Einstein's investigation<sup>1</sup> makes it quite clear that this work must be reckoned isothermally.

#### Conclusion.

Although the phenomena of molecular scattering do not furnish any definite evidence for the view that liquids possess a crystalline structure, the change of polarisation of a substance from vapour to liquid seems to show that we cannot

<sup>1</sup> Ann. der Physik, 33, 1275 (1910), see p. 1281.

assume that the molecules have random orientations. As was suggested by Prof. Raman in a letter to Nature,<sup>1</sup> there may be temporary groupings of molecules in a liquid having a higher degree of symmetry than the individual molecule. As already mentioned, with many liquids although the calculated values of the imperfection of polarisation are larger than the observed, the calculated intensities agree with the observed values: this can be explained by the assumption of such loose molecular groupings as Prof. Raman has suggested. The presence of these would not appreciably affect the refractivity and so long as their linear dimensions are small compared with a wave-length, they would play the same part as the same number of single molecules oriented at random, with the difference that the anisotropic scattering would be altered.

### *Summary.*

1. The theory of scattering by a fluid medium composed of anisotropic molecules in random orientation developed in a previous paper is revised and new expressions for the intensity and polarisation of the scattered light and for the coefficient of extinction derived.

With incident light unpolarised, the intensity of scattering in a direction making an angle  $\chi$  with the incident beam is

$$\frac{I_0 V}{r^2} \left[ \frac{\pi^2 RT \beta}{18N \lambda^4} (k_0 - 1)^2 (k_0 + 2)^2 \left\{ \frac{6 - 6r}{6 - 7r} (1 + \cos^2 \chi) + \frac{12r}{6 - 7r} \right\} \right],$$

the polarisation of the transversely scattered light is

$$r = \frac{2f}{\gamma \left( \frac{A + B + C}{3} \right)^2 + \frac{7}{3} f}$$

<sup>1</sup> Nature, March 31, 1923. See also Sir W. H. Bragg's note on the above,



and the coefficient of extinction

$$\frac{8\pi^3}{27} \frac{RT\beta}{N\lambda^2} (k_0 - 1)^2 (k_0 + 2)^2 \left\{ \frac{6 + 3r}{6 - 7r} \right\}$$

2. The theoretical results are compared with experiment. While there is good agreement between the observed and calculated values of the intensity of scattering for liquids having molecules of moderate anisotropy, there is a marked disagreement in the case of liquids with strongly anisotropic molecules.

The values of the imperfection of polarisation of liquids calculated from the corresponding vapour values show considerable deviation from the experimental values.

3. A reported change in the imperfection of polarisation of the transversely scattered light in carbon disulphide when the wave-length of the incident light is altered is not confirmed.

Some other liquids have also been examined and the effect has not been found in any of them. Incidentally, it is shown that a change previously observed in the imperfection of polarisation with water and alcohol is due to the presence of a trace of fluorescence.

4. An analysis is made of two recent papers by Cabannes on the theory of molecular scattering of light in fluids and it is shown that the assumption of independence of scattering by different molecules implicitly made therein and his calculation of the effect of local fields are not valid and that his theoretical conclusions are in disagreement with experiment.

5. Some critical remarks are offered about King's theory of scattering in liquids. It is pointed out that his assumption of a crystalline structure in liquids is unnecessary to account for the imperfection of polarisation of the transversely scattered light in liquids. Criticisms are also made regarding his formula for scattering.

The presence of loose molecular groupings having a higher degree of symmetry than the individual molecule would explain the observed low value of the imperfection of polarisation of the scattered light in many liquids.

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