A Theory of the Optical and Electrical Properties of Liquids.

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1. Introduction.

Theories of the optical behaviour of liquids generally base themselves on the postulate that the well-known Lorentz formula $(n^2 - 1)/(n^2 + 2)\rho = $ constant correctly expresses the relation between the refractive index and density of a liquid. It has long been known, however, that this formula is at best only an approximation. The quantity $(n^2 - 1)/(n^2 + 2)\rho$ is found experimentally to be not invariable, its deviation from constancy becoming more and more marked as the density is increased. The change in the value of $(n^2 - 1)/(n^2 + 2)\rho$ in passing from the state of vapour to that of a liquid under ordinary conditions, is usually quite appreciable, as might be instanced by the case of benzene, for which Wasastjerna* found for the D-line a molecular refraction of $27 \cdot 20$ in the vapour state, while the corresponding value for the liquid is $26 \cdot 18$, that is, $3 \cdot 8$ per cent. lower. The deviations from the Lorentz formula appear most striking when we use it to compute the change in the refractive index of a liquid produced by alterations of temperature or pressure. Here, again, we might instance the case of benzene, for which the observed value of $dn/dt = -6 \cdot 4 \times 10^{-4}$ per degree Centigrade for the D-line at 20° C., and that of $dn/dp = 5 \cdot 06 \times 10^{-5}$ per atmosphere, while the calculated values are $dn/dt = -7 \cdot 15 \times 10^{-4}$ and $dn/dp = 5 \cdot 66 \times 10^{-5}$. The observed values are thus numerically about 10 per cent. smaller in either case, indicating that $(n^2 - 1)/(n^2 + 2)\rho$ diminishes more and more quickly as the density is increased. An expression of the form $(n^2 - 1)/(n^2 + 2)\rho = a - b\rho^2$, where a and b are positive constants, has been found to represent the refraction of carbon dioxide over a wide range of density more closely than the original Lorentz formula.† It has been deduced theoretically on certain suppositions regarding the magnitude of the polarisation field in liquids, which are, however, somewhat arbitrary in nature.

Considering next the electrical behaviour of liquids, we find that the formula proposed by Debye $(\varepsilon - 1)/(\varepsilon + 2)\rho = A + B/T$ is not adequate to explain

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* 'Soc. Sci. Fenn., Phys.-Math.,' vol. 2, No. 13 (1924).

† Phillips, 'Roy. Soc. Proc.,' A, vol. 97, p. 225 (1920).

the dielectric properties of many known liquids. To illustrate this, we may again consider the case of benzene, whose dielectric constant has been determined over a wide range of temperatures* and pressures.† Since A and B in the formula are essentially positive constants, it follows that $(\varepsilon - 1)/(\varepsilon + 2)\,\rho$ should remain invariable when the liquid is compressed isothermally, and that it should *diminish* with rising temperature. Actually it is found with benzene that the quantity in question falls steadily with increasing pressure and *increases* with rising temperature. A similar apparently anomalous behaviour is shown by many other liquids whose molecules have a negligible electrical polarity. Liquids of marked electrical polarity show a diminution of $(\varepsilon - 1)/(\varepsilon + 2)\,\rho$ with rising temperature as demanded by the formula, but they deviate from it by showing a diminution of the same quantity when isothermally compressed, the latter effect being usually even more marked than for non-polar compounds.‡

It will be clear from the foregoing review that the existing theories of the optical and electrical behaviour of liquids are far from being satisfactory. It is proposed in this paper to put forward a new theory which appears to us competent to offer at least an insight into the whole range of facts referred to. We believe that it is capable of doing more, that is, of actually giving a quantitative explanation of the behaviour of actual liquids for which the necessary data for evaluating the constants appearing in our formulæ are available. In order, however, not to lengthen the paper unduly, we shall confine ourselves to a general discussion, leaving the details for fuller treatment in separate papers.

2. *The Refractivity of Liquids.*

We shall first consider the optical problem, which is relatively simple. In any satisfactory treatment of it we have necessarily to take into account the fact which has been clearly established by recent investigations, namely, that a liquid can be regarded as an optically isotropic medium only when we do not push the analysis of its structure into regions of molecular dimensions. In the first place, it is established by investigations on light-scattering that all known molecules are optically anisotropic, in other words, that they are polarisable to different extents in different directions. From this circumstance it follows that the refractivity of a liquid is really an average effect determined by the contributions of molecules variously orientated relatively to one another

* Isnardi, ' Z. f. Physik,' vol. 9, p. 153 (1922).

† Francke, ' Ann. d. Physik,' vol. 77, p. 159 (1925).

‡ Grenacher, ' Ann. d. Physik,' vol. 77, p. 138 (1925).

and to the field of the incident radiation. Further, it is known from X-ray studies that many actual molecules are highly asymmetric in their geometric form.   In view of this fact we would not be justified in treating the distribution of polarisable matter surrounding any given molecule in a dense fluid as completely symmetrical.   It follows, therefore, that the local field acting on any molecule due to the polarisation of its immediate neighbours, cannot be regarded as independent of the orientation of the molecule in the field.   The study of light-scattering in liquids furnishes striking evidence in support of this idea and indeed enables us in simple cases to actually determine how the polarisation field acting on a molecule varies with its orientation with respect to the incident beam of light.   We shall in what follows proceed to develop the theory of refraction in liquids on the assumption that the molecules are optically anisotropic and that the polarisation field acting on the molecule is a function of its orientation.

Let us choose the optic axes of any given molecule as the axes of a co-ordinate system ξ, η, ζ fixed to it, whose orientations with respect to another system of axes x, y, z fixed in space are given by the Eulerian angles θ, ϕ, ψ. Let b_1, b_2, b_3 be the moments induced in the molecule per unit field (due to a light-wave) *actually* acting on it respectively along its three axes ξ, η, ζ. · When the external field is incident along any one of these axes, say along the ξ-axis, the polarisation field acting on the molecule will, in general, have components also along the η- and ζ-axes. Let p_{11}, p_{12}, p_{13} be the numerical factors which determine the polarisation fields acting along the ξ-, η-, ζ-axes when the external field is incident along the ξ-axis ; and let p_{21}, p_{22}, p_{23} and p_{31}, p_{32}, p_{33} be similar factors when the external field lies along the η- and ζ-axes ; $p_{ik} = p_{ki}$.

Suppose now the field of the incident light-wave, equal to E, say, lies along the z-axis.   Then the moments induced in the molecule under consideration along its three axes are obviously

$$
\left.
\begin{aligned}
b_1 \left[\alpha_1 + \chi \left(p_{11}\alpha_1 + p_{21}\alpha_2 + p_{31}\alpha_3 \right) \right] \text{E} \\
b_2 \left[\alpha_2 + \chi \left(p_{12}\alpha_1 + p_{22}\alpha_2 + p_{32}\alpha_3 \right) \right] \text{E} \\
b_3 \left[\alpha_3 + \chi \left(p_{13}\alpha_1 + p_{23}\alpha_2 + p_{33}\alpha_3 \right) \right] \text{E}
\end{aligned}
\right\}
\tag{1}
$$

and

respectively, where χ is the mean moment induced in unit volume of the fluid by unit field of the incident light-wave ; α_1, α_2, α_3 are the cosines of the angles which the ξ-, η-, ζ-axes make with the direction of the field E, and are given by

$$
\alpha_1 = - \sin \theta \cos \psi ; \quad \alpha_2 = \sin \theta \sin \psi ; \quad \alpha_3 = \cos \theta.
\tag{2}
$$

These moments when resolved along the direction of the incident field are together equal to

$$[b_1 (1 + p_{11}\chi) \alpha_1{}^2 + b_2 (1 + p_{22}\chi) \alpha_2{}^2 + b_3 (1 + p_{33}\chi) \alpha_3{}^2$$
$$+ \chi \{p_{12} (b_1 + b_2) \alpha_1\alpha_2 + p_{23} (b_2 + b_3) \alpha_2\alpha_3 + p_{31} (b_3 + b_1)\alpha_3\alpha_1\}] \times E. \quad (3)$$

Now the average values of $\alpha_1{}^2$, $\alpha_2{}^2$ and $\alpha_3{}^2$ taken over all orientations of the molecules with respect to the incident field are equal to $\frac{1}{3}$, while the average values of $\alpha_1\alpha_2$, $\alpha_2\alpha_3$ and $\alpha_3\alpha_1$ vanish. Hence it readily follows that the average moment induced in a molecule in the medium by unit incident field is given by

$$m = \tfrac{1}{3} (b_1' + b_2' + b_3'), \quad (4)$$

where b_1', b_2', b_3' denote the coefficients of $\alpha_1{}^2$, $\alpha_2{}^2$, $\alpha_3{}^2$ respectively in (3) above.
    Further

$$\chi = \nu m = (n^2 - 1)/4\pi, \quad (5)$$

ν being the number of molecules per unit volume and n the refractive index.
    Putting

$$p_{11} = \tfrac{4}{3}\pi + \sigma_1, \quad p_{22} = \tfrac{4}{3}\pi + \sigma_2, \quad p_{33} = \tfrac{4}{3}\pi + \sigma_3,$$

and using relation (5), we obtain from (4)

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3} \, \nu \, \frac{b_1 + b_2 + b_3}{3} + \frac{n^2 - 1}{n^2 + 2} \, \nu \, \frac{b_1\sigma_1 + b_2\sigma_2 + b_3\sigma_3}{3}, \quad (6)$$

which may be written in the form

$$\frac{n^2 - 1}{n^2 + 2} = \nu C + \frac{n^2 - 1}{n^2 + 2} \, \nu \, \Phi, \quad (7)$$

where

$$\Phi = \tfrac{1}{3} (b_1\sigma_1 + b_2\sigma_2 + b_3\sigma_3) \quad (8)$$

and C is a constant characteristic of the molecule. We shall now consider three special cases.

    Case (a):

$$\sigma_1 = \sigma_2 = \sigma_3 = 0,$$

and therefore

$$p_{11} = p_{22} = p_{33} = \tfrac{4}{3}\pi. \quad (9)$$

    We find in this case that equation (7) reduces absolutely to the Lorentz formula.

    The assumption (9) is equivalent to the supposition that the local field acting on the molecule is equal to that at the centre of a spherical cavity excavated around it.

Case (b):

$$\sigma_1 + \sigma_2 + \sigma_3 = 0,$$

and therefore

$$p_{11} + p_{22} + p_{33} = 4\pi. \tag{10}$$

If, in addition, $b_1 = b_2 = b_3$, *i.e.*, if the molecule is optically isotropic, equation (7) again reduces to the Lorentz formula. Equation (10) amounts to assuming that the local field acting on the molecule is equal to that at the centre of an ellipsoidal cavity with three unequal axes,* scooped around the molecule. It may also be interpreted in the sense that the *mean* polarisation field acting on the molecule averaged over all orientations is the same as at the centre of a spherical cavity.

Case (c):

$$\sigma_1 + \sigma_2 + \sigma_3 \neq 0.$$

This is equivalent to the assumption that the mean polarisation field differs from that obtainable at the centre of a spherical cavity around the molecule.

In Case (*a*) we obtain no deviation from the Lorentz formula at all. In Case (*b*) we obtain a deviation provided the molecule is optically anisotropic, and in Case (*c*) we may obtain a deviation from the Lorentz formula even for optically isotropic molecules.

3. *The Dielectric Constant of Liquids.*

For the corresponding electrical problem we choose the principal axes of electrostatic polarisability of the molecule as its ξ-, η-, ζ-axes. When an electrostatic field E is incident in the medium along the z-axis, the actual fields acting on the molecule along its axes are given by

$$
\left.
\begin{aligned}
E_1 &= [\alpha_1 + \chi_e\,(q_{11}\alpha_1 + q_{21}\alpha_2 + q_{31}\alpha_3)]\,E \\
E_2 &= [\alpha_2 + \chi_e\,(q_{12}\alpha_1 + q_{22}\alpha_2 + q_{32}\alpha_3)]\,E \\
E_3 &= [\alpha_3 + \chi_e\,(q_{13}\alpha_1 + q_{23}\alpha_2 + q_{33}\alpha_3)]\,E
\end{aligned}
\right\}, \tag{11}
$$

and

where χ_e is the mean electrostatic moment produced in unit volume of the medium per unit incident field; and the q's denote the constants of the static polarisation fields acting on the molecule, analogous to the p's in the optical problem. If μ_1, μ_2, μ_3 be the components of the permanent electric moment μ of the molecule resolved along the ξ-, η-, ζ-axes and a_1, a_2, a_3 the moments induced in it by unit field acting along these axes, the contribution from the

* See Routh, ' Analytical Statics,' vol. 2, p. 100.

molecule under consideration to the moment along the direction of the incident field is given by

$$L = [a_1 (1 + q_{11}\chi_e) \alpha_1{}^2 + a_2 (1 + q_{22}\chi_e) \alpha_2{}^2 + a_3 (1 + q_{33}\chi_e) \alpha_3{}^2$$
$$+ \{q_{12} (a_1 + a_2) \alpha_1\alpha_2 + q_{23} (a_2 + a_3) \alpha_2\alpha_3 + q_{31} (a_3 + a_1) \alpha_3\alpha_1\}\chi_e] \times E$$
$$+ \mu_1\alpha_1 + \mu_2\alpha_2 + \mu_3\alpha_3. \tag{12}$$

The potential energy of the molecule in the field due to the existence of the permanent moment in it, is given by

$$u = - (\mu_1 E_1 + \mu_2 E_2 + \mu_3 E_3)$$
$$= - (M_1\alpha_1 + M_2\alpha_2 + M_3\alpha_3) E, \tag{13}$$

where

$$M_1 = \mu_1 + \chi_e (q_{11}\mu_1 + q_{21}\mu_2 + q_{31}\mu_3) \left. \right\}$$
$$M_2 = \mu_2 + \chi_e (q_{12}\mu_1 + q_{22}\mu_2 + q_{32}\mu_3) \left. \right\} . \tag{14}$$
$$M_3 = \mu_3 + \chi_e (q_{13}\mu_1 + q_{23}\mu_2 + q_{33}\mu_3) \left. \right\}$$

By Boltzmann's theorem the number of molecules per unit volume whose orientations in the field correspond to the range $\sin \theta\, d\theta\, d\phi\, d\psi$ is equal to

$$c\, e^{-u/kT} \sin \theta\, d\theta\, d\phi\, d\psi, \tag{15}$$

where c is a constant which can be evaluated from the obvious relation

$$c \int_{\theta = 0}^{\theta = \pi} \int_{\phi = 0}^{\phi = 2\pi} \int_{\psi = 0}^{\psi = 2\pi} e^{-u/kT} \sin \theta\, d\theta\, d\phi\, d\psi = \nu, \tag{16}$$

the total number of molecules per unit volume.

The average contribution from a molecule in the medium to the moment along the field

$$= \frac{\iiint e^{-u/kT} L \sin \theta\, d\theta\, d\phi\, d\psi}{\iiint e^{-u/kT} \sin \theta\, d\theta\, d\phi\, d\psi} = m_e E \text{ (say)}, \tag{17}$$

the limits of integration being the same as in (16), and neglecting terms involving E^2 and higher powers of E.   On actual evaluation of the integrals in (17) we obtain

$$m_e = \frac{a_1 (1 + q_{11}\chi_e) + a_2 (1 + q_{22}\chi_e) + a_3 (1 + q_{33}\chi_e)}{3}$$
$$+ \frac{1}{3kT} (M_1\mu_1 + M_2\mu_2 + M_3\mu_3). \tag{18}$$

Further,

$$\chi_e = \nu m_e = \frac{\varepsilon - 1}{4\pi}, \tag{19}$$

where ε is the dielectric constant.

Using this relation and putting

$$q_{11} = \tfrac{4}{3}\pi + s_1, \quad q_{22} = \tfrac{4}{3}\pi + s_2, \quad q_{33} = \tfrac{4}{3}\pi + s_3,$$

we obtain from (18)

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi}{3} \nu \left(\frac{a_1 + a_2 + a_3}{3} + \frac{\mu^2}{3kT} \right) + \frac{\varepsilon - 1}{\varepsilon + 2} \nu \left\{ \frac{a_1 s_1 + a_2 s_2 + a_3 s_3}{3} \right.$$

$$\left. + \frac{1}{3kT} \left(\Sigma \mu_i^2 s_i + 2\Sigma \mu_i \mu_k q_{ik} \right) \right\}$$

$$= \frac{4\pi}{3} \nu \left(\frac{a_1 + a_2 + a_3}{3} + \frac{\mu^2}{3kT} \right) + \frac{\varepsilon - 1}{\varepsilon + 2} \nu \left(\Psi + \frac{1}{3kT} \Theta \right), \tag{20}$$

where

$$\Psi = \tfrac{1}{3} \left(a_1 s_1 + a_2 s_2 + a_3 s_3 \right) \tag{21}$$

and.

$$\Theta = \mu_1^2 s_1 + \mu_2^2 s_2 + \mu_3^2 s_3 + 2 \left(\mu_1 \mu_2 q_{12} + \mu_2 \mu_3 q_{23} + \mu_3 \mu_1 q_{31} \right). \tag{22}$$

The second term in (20) containing Ψ and Θ appears as an addition to the first term which is identical with Debye's expression. We may rewrite (20) in the form

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \nu \left(\frac{4\pi}{3} \frac{a_1 + a_2 + a_3}{3} + \frac{\varepsilon - 1}{\varepsilon + 2} \Psi \right) + \frac{\nu}{3kT} \left(\frac{4\pi}{3} \mu^2 + \frac{\varepsilon - 1}{\varepsilon + 2} \Theta \right). \tag{23}$$

The first term on the right-hand side of (23) has a form similar to the expression for refractivity obtained in the preceding section and does not explicitly involve the temperature. The second term, on the other hand, is inversely proportional to the absolute temperature.

4. *Discussion of the Theory.*

Our formulæ offer a natural explanation why with increase of density the Lorentz refraction-constant usually diminishes. Equation (7) runs

$$\frac{n^2 - 1}{n^2 + 2} = \nu C + \nu \frac{n^2 - 1}{n^2 + 2} \Phi,$$

where

$$\Phi = \tfrac{1}{3} \left(b_1 \sigma_1 + b_2 \sigma_2 + b_3 \sigma_3 \right).$$

The expression for the dielectric constant of non-polar liquids is very similar,

see equation (23) above, and the following remarks may be regarded as applying equally well in respect of the same.

The constants b_1, b_2, b_3 represent the polarisabilities of the molecule along its optic axes and are therefore essentially positive. We shall, for the present at any rate, be justified in making the simplifying assumption, see equation (10) above, that $p_{11} + p_{22} + p_{33} = 4\pi$, in other words, that the polarisation field acting on the molecule *when averaged over all its orientations* is the same as at the centre of a spherical cavity. We have, then, $\sigma_1 + \sigma_2 + \sigma_3 = 0$, and it follows that σ_1, σ_2, σ_3 cannot all have the same sign.

If

$$\left. \begin{array}{c} b_1 > b_2 > b_3 \\ \\ \sigma_1 < \sigma_2 < \sigma_3 \end{array} \right\}, \tag{24}$$

and

it is easily shown that the value of Φ, that is, of $\frac{1}{3}(b_1\sigma_1 + b_2\sigma_2 + b_3\sigma_3)$ is necessarily negative. In other words, provided the condition stated in (24) is satisfied, the value of $(n^2 - 1)/(n^2 + 2)$ would necessarily have a smaller value than that given by the Lorentz formula.

The condition stated in (24) has a physical significance, namely, that the direction in the molecule corresponding to maximum polarisability is that along which the field due to its neighbours has a minimum value, and vice versa. That this condition would be satisfied in most cases seems highly probable. If we can regard the chemical molecule as roughly equivalent to an ellipsoidal particle of polarisable matter, its longest axis would be the one of maximum polarisability and its shortest axis that of minimum polarisability. If we consider a liquid composed of such molecules, it is obvious that the centre of a second molecule could approach that of the first most closely in the direction of the shortest axis, and least closely in the direction of its longest axis. The polarisation field due to its neighbours would be the sum of the fields due to the individual molecules occupying various positions with respect to it. If we consider a particular molecule in such position that the line joining the centres of the two molecules is parallel to the external field, its influence would appear as an addition to the field ; while if the joining line is perpendicular to the field, its influence would be equivalent to a diminution of the external field. These effects would conspire to diminish the aggregate polarisation field acting on the molecule when the external field is along its longest dimension, and to increase it when the field is along its shortest dimension, in comparison with the case of spherical molecules. This is precisely the result which is required to satisfy the condition stated in (24) above.

It must, however, be remembered that the preceding argument is based on the assumption that the optical anisotropy of the molecule is determined by its geometric shape. The origin of the optical anisotropy of molecules as evidenced in observations on light-scattering has been the subject of discussion in recent papers.* It is found that pronounced asymmetry of geometric form does not necessarily mean pronounced optical anisotropy, the latter being determined by the chemical nature and arrangement of the atoms in the molecule. Nevertheless, the order of the geometric dimensions of a molecule in different directions is usually also the order of its optical polarisabilities along those directions. It must not be forgotten, however, that there may be exceptions to this rule.†

Returning now to formula (7), we may, since the second term on the right is much smaller than the first, write it in the form

$$\frac{n^2 - 1}{n^2 + 2} = \nu C \left(1 + \nu \Phi\right), \tag{25}$$

from which it is seen that apart from any possible variation of Φ with density or temperature, the correction to the Lorentz formula increases in importance with increasing density. There is *prima facie* reason to believe that Φ must itself increase numerically with increasing density of the fluid. To realise this, we recall the argument set out above regarding the relation between the geometric form of the molecule and the polarisation field acting on it. In the gaseous condition, or even in a dense vapour, there would ordinarily be almost complete freedom of orientation for the molecules. Further, the fraction of the time during which a molecule is in actual collision with a neighbour is a small part of the whole, and hence, in determining the polarisation field, we would not be sensibly in error in ignoring the non-spherical shape of the molecule altogether. It is only when the density becomes comparable with that of a liquid that a molecule is almost continually in collision with one or other of its neighbours, and that in evaluating the polarisation field we cannot ignore the restrictions imposed by the geometric form of the molecules on their relative positions and orientations. These considerations indicate a progressive change in the *character* of the polarisation field acting on a molecule as the density increases. At low densities, the field acting on a molecule would be appreciably the same as

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* See K. R. Ramanathan, ' Roy. Soc. Proc.,' A, vol. 107, p. 684 (1924) ; vol. 110, p. 123 (1926). Also T. H. Havelock, ' Phil. Mag.,' vol. 3, pp. 158, 433 (1927).

† From some observations by Mr. I. Ramakrishna Rao in the authors' laboratory, on light-scattering in formic and acetic acid vapours, it appears that these form such exceptions. The available data on refractivity appear also to indicate an *increase* of the Lorentz constant of refractivity with increasing density.

if it were placed at the centre of a spherical cavity excavated around it, and would be independent of its orientation. At higher densities, the non-spherical shape of the molecule would begin to influence the results. A detailed treatment of the problem on the basis of the kinetic theory would be complicated by the circumstance that the molecules are themselves optically anisotropic and that therefore the mutual influence of two molecules depends both on their relative position and their relative orientation. Ignoring this difficulty, however, we may make the simplifying assumption that the surrounding molecules can be regarded as equivalent to a distribution of polarisable matter which is of uniform density and symmetrical except in a small region surrounding the given molecule. With increasing density, this small region and its lack of symmetry become of greater importance, until finally, when a density as great as that of the amorphous solid is reached, we shall not be much in error in regarding the molecule as practically embedded in a cavity having its own shape, the dependence of the polarisation field on the orientation of the molecule relatively to the external field then reaching its maximum value. We thus arrive at the general conclusion that the value of Φ increases numerically with increasing density, beginning with zero at low densities and reaching a limiting value at densities as high as those of the amorphous solid. The correction $\nu\Phi$ appearing in our modified form of the Lorentz formula must therefore increase at a greater rate than in proportion to the density, during a greater part of its course.

A clearer view of the whole subject may be obtained in the following way : In section 2, we obtained the expression (equation (4))

$$m = \tfrac{1}{3}(b_1' + b_2' + b_3'),$$

where

$$b_1' = b_1[1 + \chi\,(\tfrac{4}{3}\pi + \sigma_1)],$$

etc., etc., for the average moment induced in a molecule per unit external field. In a rarefied medium we have

$$m = \tfrac{1}{3}(b_1 + b_2 + b_3).$$

The ratios $b_1 : b_2 : b_3$ are a measure of the optical anisotropy of the molecule in the state of vapour. In the dense fluid the ratios $b_1' : b_2' : b_3'$ similarly indicate the optical anisotropy of the molecule as effectively modified by the influence of its neighbours. The preceding discussion shows that the result of such influence is to diminish these ratios and make them approach more nearly to unity, in other words, to diminish the effective optical anisotropy of the molecule, and that a diminution in refractivity is a necessary consequence of the same effect.

Independent evidence that the effect of increasing density is to cause an apparent diminution in the optical and electrical anisotropies of the molecule, is furnished by studies of the electrical birefringence of liquids, and by the study of the depolarisation of the light scattered by liquids at different temperatures. The authors have developed a theory of electric birefringence in liquids, and a theory of light-scattering in liquids, based on ideas very similar to those underlying the present paper, and find strong support for these theories in the experimental evidence available. The theory of light-scattering in liquids indicates that it is possible in simple cases to evaluate the quantities appearing in the formulæ of the present paper and thus offer a quantitative test of the proposed theory of refraction and dielectric behaviour. Very encouraging results have already been obtained in this direction, but to enter into these details would be foreign to the scope of this paper.

5. *Summary.*

A review of the experimental evidence shows that the existing theories of the refractivity and dielectric behaviour of liquids are inadequate to explain all that is known concerning the changes of these properties with density and temperature. A new theory is accordingly developed in this paper, which is based on the idea that the molecules of the fluid are optically and electrically anisotropic, and that, in addition, the polarisation field, acting on a molecule in a dense fluid, varies with its orientation relatively to the external field. The theory offers an immediate explanation why in general an *increased* density causes a *diminished* molecular refractivity as calculated from the Lorentz formula. It is shown that these changes in refractivity and dielectric constant are closely related to a change in the effective optical or electrical anisotropy of the molecules produced by the influence of its immediate neighbours. Similar ideas have been adopted in theories of electric birefringence and of light-scattering in liquids developed by the authors, which have found strong experimental support, and with the aid of which the anisotropic constants appearing in the formulæ of the present paper can be evaluated.