

## Theory of Orientational Effects and Related Phenomena in Dielectric Liquids

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Formulas are developed for the molar constants of five non-linear effects of molecular orientation in liquids; namely, the dielectric saturation in electric, magnetic, or optical fields and the electric as well as the magnetic birefringence. No assumption is made concerning the nature of the intermolecular forces, and no special model of molecular interaction is introduced. If the molecules may be considered to possess axial symmetry, four correlation factors  $R_D$ ,  $R_{CM}$ ,  $R_K$ , and  $R_S$  can be derived. These factors appear in the formulas of the molar constants of the Cotton-Mouton and Kerr effects, and of the effect of dielectric saturation in an electric, magnetic, or optical field. The correlation factors have been calculated as functions of  $\theta^{(pp)}$ , the angle between the axes of

symmetry of the  $p$ th and  $q$ th molecules, in the absence of a biasing field. The theory makes it possible to predict the value of the magnetodielectric saturation effect in diamagnetic liquids, as well as the photodielectric saturation, relating these phenomena to magnetic or electric birefringence. Moreover, the meaning of this theory consists in the fact that it gives a quantitative explanation of the inverse saturation effect appearing in some polar liquids and increasing their dielectric constant. Satisfactory results have been obtained by applying this theory to such phenomena as light scattering in liquids or the lowering of the freezing point, in which the orientationally dependent intermolecular forces play an important part.

### 1. INTRODUCTION

**O**RIENTATIONAL nonlinear effects, or phenomena of molecular orientation, are phenomena in which the external electric or magnetic field produces alignment of anisotropic molecules causing a change in electric, magnetic, optical, or other properties of the medium. There are five nonlinear phenomena of molecular orientation which the authors intend to consider in the present paper, namely: (1) dielectric saturation in the electric field or the effect of the electric field on the electric permittivity of the medium, (2) dielectric saturation in the magnetic field, (3) dielectric saturation in the optical field or the effect of an intense light beam on the electric permittivity, (4) electric birefringence or the electro-optical Kerr effect, (5) magnetic birefringence or the Cotton-Mouton effect. In dense gases and liquids these phenomena are influenced by intermolecular forces, among which directional forces causing short-range molecular orientation are of importance. Because of intermolecular forces, such phenomena as the scattering of light or the lowering of the freezing point of solutions are intimately related with the orientational effects.

One of us (A. P.) had previously given a theory of molecular orientational effects in polar liquids and their solutions in nonpolar solvents.<sup>1-7</sup> That theory, however, which was based on the assumption that the directional forces due to the effect of the momentarily nearest molecule play a greater part than other intermolecular forces, had but a restricted field of application. Nevertheless, very good agreement with experimental results had been obtained for nitrobenzene and its solutions in nonpolar solvents,<sup>6,7</sup> and it had been supported by cryoscopic measurements.<sup>8</sup> In particular, the theory yielded a quantitative explanation of the rather peculiar phenomenon of the positive or inverse saturation effect consisting in an increase in the permittivity of polar liquids, when placed in an electric

<sup>1</sup> A. Piekara, *Acta Phys. Polonica* **4**, 53, 73, 163 (1935).

<sup>2</sup> A. Piekara, *Acta Phys. Polonica* **6**, 130, 150 (1937); *Physik. Z.* **38**, 671 (1937).

<sup>3</sup> A. Piekara, *Z. Physik* **108**, 395 (1938).

<sup>4</sup> A. Piekara, *Compt. rend.* **204**, 1106 (1937); **208**, 990, 1150 (1939).

<sup>5</sup> A. Piekara, *Proc. Roy. Soc. (London)* **A172**, 360 (1939).

<sup>6</sup> A. Piekara, *Nature* **159**, 337 (1947).

<sup>7</sup> A. Piekara, *Acta Phys. Polonica* **10**, 37, 107 (1950).

<sup>8</sup> A. Piekara, *Acta Phys. Polonica* **11**, 99 (1951).

field. This effect, first found in nitrobenzene by A. Piekara and B. Piekara<sup>9</sup> in 1936, has been recently observed in a number of other polar liquids (Piekara and Chelkowski<sup>10</sup> and Chelkowski<sup>11</sup>). An earlier theory by Debye<sup>12</sup> in 1935 had failed to explain this phenomenon.

In the subsequent period, papers dealing with the theory of the above-mentioned molecular orientational effects in liquids, and, in particular, with dielectric saturation, were published by various authors (Frenkel,<sup>13</sup> Anselm,<sup>14</sup> Booth,<sup>15</sup> Buckingham<sup>16-18</sup> and Buckingham and Pople<sup>19,20</sup>), none of whom, however, discussed the positive saturation effect. The present authors consider that the aptitude of a theory to provide an explanation of positive saturation in polar liquids constitutes a severe criterion for the reliability of the theory.

Recently, a paper on the theory of dielectric saturation in polar liquids was published by Schellman,<sup>21\*</sup> wherein mention is made of the possibility of explaining the positive saturation effect in polar liquids by that author's theory. However, the scope is restricted merely to the dipolar mechanism of saturation, the anisotropic, anisotropic-dipolar, and both deformational terms not being taken into account. Moreover, the author introduces a specialized model of molecular interaction, whereby the molecules interacting with a given molecule do not interact with each other.

In the present paper the authors propose a theory of the five nonlinear effects of molecular orientation wherein the general formulas expressing the molar constants have been obtained without introducing any specialized interaction model whatsoever and without making assumptions concerning either the nature of the intermolecular forces or the shape of the molecules. Moreover, the nonlinear deformation of molecules in both electric and magnetic fields are taken into account. On the other hand, in the particular case when the molecules are assumed to be conceivable as possessing axial symmetry, the correlation factors  $R_p$ ,  $R_{CM}$ ,  $R_K$ , and  $R_S$  (see subsequent paragraphs) have been calculated.† These formulas apply not only to dipolar but

also to different intermolecular forces, including those of a nonelectrical nature.

Finally, the authors' method is applied to related phenomena, such as light scattering in liquids (Kielich<sup>22</sup>) or the lowering of the freezing point of solutions of polar molecules in nonpolar solvents (Piekara<sup>8</sup>).

## 2. KERR AND COTTON-MOUTON EFFECTS IN POLAR LIQUIDS

Let us consider a volume  $V$  of a liquid dielectric containing  $N$  similar molecules. The relative spatial distribution of the  $N$  molecules is determined by the positional variables  $\mathbf{r} = \{\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N\}$  and the orientational variables  $\omega = \{\omega_1, \omega_2, \dots, \omega_N\}$ . In the case under consideration, the set of positional and orientational variables  $\tau = \tau(\mathbf{r}, \omega)$  is given by the 3  $N$ -Cartesian coordinates  $\mathbf{r}_p = \{X_p, Y_p, Z_p\}$  and the 3  $N$ -Eulerian angles  $\omega_p = \{\delta, \varphi_p, \psi_p\}$ ,  $p = 1, 2, \dots, N$ . The molecules possess a permanent electric dipole moment  $\mathbf{u}$  and anisotropic polarizabilities.

In experimental investigations on the Kerr effect, the dielectric medium is acted on simultaneously by the weak measuring field  $\mathbf{E}$  of the light wave and the strong constant electric polarizing field  $\mathbf{E}_0$ . Thus, there will be two local fields acting upon each molecule of the medium, namely, the optical local field  $\mathbf{F}_0$  and the electric local field  $\mathbf{F}_e$ . Each of the local fields consists of an external field and of a field resulting from the polarized molecules of the medium. The latter field depends, in general, on the geometrical configuration of all molecules in the neighborhood of the given one. If the molecules are anisotropic, so is, in principle, the field. For the linear effects, the local field has been strictly accounted for.<sup>23,24</sup> If, instead of the real local field, a mean local field independent of the configuration of the molecules be assumed, the results differ by certain terms, the contribution of which to the polarization is insignificant.<sup>25</sup> The anisotropy of the local field, when taken into account in considering nonlinear effects, causes very great complications of a mathematical nature pertaining—according to the present authors—to relatively unimportant aspects of the mechanism of nonlinear effects in condensed media. Hence, in assuming a local *isotropic* field, the authors introduce a simplification which is not essential to the description of the mechanism of molecular orientational effects in a condensed medium as brought about by strong applied fields. Indeed, the results obtained, e.g., for the effect of dielectric saturation yield an explanation of the positive saturation effect (increasing permittivity) in quantitative agreement with the experimental results.<sup>5-7</sup> The authors conclude that this fact and the consistency in describing other nonlinear effects (those of Kerr and Cotton-Mouton<sup>3,4,7</sup>) justify the assumption of an isotropic local field as an admissible approach to the problem.

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<sup>15</sup> F. Booth, J. Chem. Phys. 19, 391, 1327, 1615 (1951).

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<sup>19</sup> A. D. Buckingham and J. A. Pople, Proc. Phys. Soc. (London) A68, 905 (1955).

<sup>20</sup> A. D. Buckingham and J. A. Pople, Proc. Phys. Soc. (London) B69, 1133 (1956).

<sup>21</sup> J. A. Schellman, J. Chem. Phys. 26, 1225 (1957).

\* One of us (A.P.) expresses his thanks to Dr. Schellman for sending him a typed copy of his paper previous to publication.

† A. Piekara and S. Kielich<sup>26</sup> give some results of this investigation obtained without accounting for higher order deformations of the molecule.

The dipole moment induced in a molecule by the field of the light wave when a strong electric polarizing field is present is, in general, a nonlinear function of the latter. Hence, the optical polarizability of the  $p$ th molecule of the medium is given by the following expression (in tensor notation):

$$\alpha^{(p)} = (a_{ij}^p + b_{ijk}^p \alpha_k^{(p)} F_e + \frac{1}{2} c_{ijkl}^p \alpha_k^{(p)} \alpha_l^{(p)} F_e^2 + \dots) \gamma_i^{(p)} \gamma_j^{(p)}, \quad (2.1)$$

where  $a_{ij}^p$  is the optical polarizability tensor of the  $p$ th molecule in the absence of a biasing electric field,  $b_{ijk}^p$  and  $c_{ijkl}^p$  are the electro-optical deformability tensors determining the direct effect of the biasing electric field on the optical polarizability of the molecule,  $\gamma_i^{(p)}$  and  $\alpha_i^{(p)}$  the directional cosines of the axes of the molecular reference system attached to the  $p$ th molecule with respect to the direction of the local optical field  $\mathbf{F}_o$  and the local electric field  $\mathbf{F}_e$ , respectively, and  $i, j, k, l$  are summation indices taking the values 1, 2, 3.

By classical statistical mechanics, the mean statistical value of the optical polarizability of the  $p$ th molecule as given by Eq. (2.1), for thermodynamic equilibrium of the system subjected to the effect of the electric field  $\mathbf{E}$ , is defined as follows:

$$\langle \alpha^{(p)} \rangle_E = \frac{\int \alpha^{(p)}(\tau, E) \exp[-U(\tau, E)/kT] d\tau}{\int \exp[-U(\tau, E)/kT] d\tau} \quad (2.2)$$

with  $k$  denoting Boltzmann's constant,  $T$  the Kelvin temperature of the system, and

$$d\tau = \prod_{p=1}^N d\tau_p,$$

the configurational space element.

Here, the total potential energy  $U(\tau, E)$  in Eq. (2.2) of the system in the presence of the electric field  $\mathbf{E}$  takes the form

$$U(\tau, E) = U_N - \sum_{p=1}^N \{ \mu_i \alpha_i^{(p)} F_e + \frac{1}{2} a_{ij}^p \alpha_i^{(p)} \alpha_j^{(p)} F_e^2 + \dots \}, \quad (2.3)$$

with  $\mu_i$  denoting the components of the permanent electric dipole moment of the molecule immersed in the medium,  $a_{ij}^p$  being the electric polarizability tensor of the molecule, and  $U_N$  the interaction potential energy of  $N$  molecules. Generally, the potential energy of molecular interaction,  $U_N$ , consists of the Lennard-Jones potential, the energy of the dipolar interaction of the molecules and of the Debye inductive interaction, the London dispersive forces, and of multipole molecular interactions of various other kinds.

Substituting (2.1) and (2.3) in (2.2), expanding in powers of the electric field strength and neglecting

terms of order higher than the second yields

$$\begin{aligned} \langle \alpha^{(p)} \rangle_E &= a_{ij}^p \langle \gamma_i^{(p)} \gamma_j^{(p)} \rangle + \{ b_{ijk}^p \langle \gamma_i^{(p)} \gamma_j^{(p)} \alpha_k^{(p)} \rangle \\ &+ a_{ij}^p \mu_k / kT \langle \langle \sum_{q=1}^N \gamma_i^{(p)} \gamma_j^{(q)} \alpha_k^{(q)} - \langle \gamma_i^{(p)} \gamma_j^{(p)} \rangle \langle \sum_{q=1}^N \alpha_k^{(q)} \rangle \rangle \} F_e \\ &+ \frac{1}{2} c_{ijkl}^p \langle \gamma_i^{(p)} \gamma_j^{(p)} \alpha_k^{(p)} \alpha_l^{(p)} \rangle \\ &+ (2b_{ijk}^p \mu_l / kT) \langle \langle \sum_{q=1}^N \gamma_i^{(p)} \gamma_j^{(p)} \alpha_k^{(p)} \alpha_l^{(q)} \rangle \\ &- \langle \gamma_i^{(p)} \gamma_j^{(p)} \alpha_k^{(p)} \rangle \langle \sum_{q=1}^N \alpha_l^{(q)} \rangle \rangle \\ &+ (a_{ij}^p a_{kl}^p / kT) \langle \langle \sum_{q=1}^N \gamma_i^{(p)} \gamma_j^{(p)} \alpha_k^{(q)} \alpha_l^{(q)} \rangle \\ &- \langle \gamma_i^{(p)} \gamma_j^{(p)} \rangle \langle \sum_{q=1}^N \alpha_k^{(q)} \alpha_l^{(q)} \rangle \rangle \\ &+ (a_{ij}^p \mu_k \mu_l / k^2 T^2) \langle \langle \sum_{q=1}^N \sum_{r=1}^N \gamma_i^{(p)} \gamma_j^{(p)} \alpha_k^{(q)} \alpha_l^{(r)} \rangle \\ &- \langle \gamma_i^{(p)} \gamma_j^{(p)} \rangle \langle \sum_{q=1}^N \sum_{r=1}^N \alpha_k^{(q)} \alpha_l^{(r)} \rangle \rangle \\ &+ 2 \langle \gamma_i^{(p)} \gamma_j^{(p)} \rangle \langle \sum_{q=1}^N \alpha_k^{(q)} \rangle \langle \sum_{r=1}^N \alpha_l^{(r)} \rangle \\ &- 2 \langle \sum_{q=1}^N \gamma_i^{(p)} \gamma_j^{(p)} \alpha_k^{(q)} \rangle \langle \sum_{r=1}^N \alpha_l^{(r)} \rangle \} F_e^2 + \dots, \quad (2.4) \end{aligned}$$

where the symbol  $\langle \Phi \rangle$  denotes the operation of statistical averaging of the quantity  $\Phi$  when the external electric field is absent:

$$\langle \Phi \rangle = \frac{\int \Phi(\tau) \exp[-U_N(\tau)/kT] d\tau}{\int \exp[-U_N(\tau)/kT] d\tau} \quad (2.5)$$

Previous to expanding (2.4), averaging should be effected over all possible orientations of the  $p$ th molecule with respect to the fixed reference system. To do this, express the cosines of the  $q$ th and  $r$ th molecules in terms of those of the  $p$ th by the transformation formulas:

$$\alpha_i^{(q)} = \omega_{qi}^{(pq)} \alpha_i^{(p)}, \quad \alpha_j^{(r)} = \omega_{rj}^{(rp)} \alpha_j^{(p)}, \dots, \quad (2.6)$$

where the transformation coefficients  $\omega_{qi}^{(pq)}$ ,  $\omega_{rj}^{(rp)}$ , ..., the reference systems attached to each molecule being rectangular, are the cosines of the angles between the axes of these systems. Thus, e.g.,  $\omega_{\sigma i}^{(pq)}$  is the cosine of the angle subtended by the  $\sigma$  axis of the molecular system attached to the  $p$ th molecule and the  $i$  axis of that attached to the  $q$ th.

With the transformational formulas (2.6) and the definition of the isotropic mean value [(2.5) for  $U_N = 0$ ], the following relations hold for the respective products

of the directional cosines of the  $p$ th,  $\dots$ st $h$  molecules:

$$\begin{aligned} \langle \gamma_i^{(p)} \rangle &= \langle \alpha_i^{(p)} \rangle = \langle \gamma_i^{(p)} \gamma_j^{(p)} \alpha_k^{(p)} \rangle = \dots = 0, \\ \langle \gamma_i^{(p)} \gamma_j^{(p)} \rangle &= \frac{1}{2} \delta_{ij}, \quad \langle \alpha_i^{(p)} \alpha_j^{(p)} \rangle = \frac{1}{2} \omega_{ij}^{(pr)}, \\ \langle \gamma_i^{(p)} \gamma_j^{(p)} \alpha_k^{(p)} \alpha_l^{(p)} \rangle &= \frac{1}{8} [2(2 - \cos^2 \Omega_{oe}) \omega_{ij}^{(pq)} \omega_{kl}^{(pr)} \\ &+ (3 \cos^2 \Omega_{oe} - 1) (\omega_{ik}^{(pr)} \omega_{jl}^{(pq)} + \omega_{il}^{(pq)} \omega_{jk}^{(pr)})], \quad (2.7) \end{aligned}$$

$\delta_{ij}$  being Kronecker's symbol:

$$\delta_{ij} = \begin{cases} 1 & \text{for } i=j \\ 0 & \text{for } i \neq j \end{cases}$$

and  $\Omega_{oe}$  denotes the angle between the vector  $\mathbf{E}$  and the vector  $\mathbf{E}$  of the biasing electric field.

With (2.7) and from  $\omega_{ij}^{(pq)} = \delta_{ij}$  for  $p=q$ , Eq. (2.4) yields a general formula for the mean statistical value of the optical polarizability of the  $p$ th molecule,

$$\begin{aligned} \langle \alpha^{(p)} \rangle_{\mathbf{E}} &= \frac{1}{2} a_{ij}^{(p)} \delta_{ij} + \frac{1}{8} \{ 3(2 - \cos^2 \Omega_{oe}) (c_{ijk}^{(p)} \delta_{ij} \delta_{kl} \\ &+ (2b_{ijk}^{(p)} \mu_l / kT) \langle \sum_{q=1}^N \delta_{ij} \omega_{kl}^{(pq)} \rangle) \\ &+ \frac{1}{2} (3 \cos^2 \Omega_{oe} - 1) [3c_{ijk}^{(p)} (\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}) \\ &+ 6(b_{ijk}^{(p)} \mu_l / kT) \langle \sum_{q=1}^N (\delta_{ik} \omega_{jl}^{(pq)} + \omega_{il}^{(pq)} \delta_{jk}) \rangle \\ &+ (a_{ij}^{(p)} a_{kl}^{(p)} / kT) \langle \sum_{q=1}^N (3\omega_{ik}^{(pq)} \omega_{jl}^{(pq)} \\ &+ 3\omega_{il}^{(pq)} \omega_{jk}^{(pq)} - 2\delta_{ij} \delta_{kl}) \rangle \\ &+ (a_{ij}^{(p)} \mu_k \mu_l / k^2 T^2) \langle \sum_{q=1}^N \sum_{r=1}^N (3\omega_{ik}^{(pq)} \omega_{jl}^{(pr)} \\ &+ 3\omega_{il}^{(pq)} \omega_{jk}^{(pr)} - 2\delta_{ij} \omega_{kl}^{(pr)}) \rangle \} F_e^2. \quad (2.8) \end{aligned}$$

The molar Kerr constant for a liquid is defined as

$$K_M = (4\pi/3)(N_A/F_e^2) (\langle \alpha^{(p)} \rangle_{\mathbf{E}, \Omega_{oe}=0} - \langle \alpha^{(p)} \rangle_{\mathbf{E}, \Omega_{oe}=90^\circ}), \quad (2.9)$$

$N_A$  being Avogadro's number, while  $\langle \alpha^{(p)} \rangle_{\mathbf{E}, \Omega_{oe}=0}$  and  $\langle \alpha^{(p)} \rangle_{\mathbf{E}, \Omega_{oe}=90^\circ}$  denote the values of (2.8) for  $\Omega_{oe}=0$  and  $\Omega_{oe}=90^\circ$ , i.e., for vectors  $\mathbf{E}$  and  $\mathbf{E}$  parallel and perpendicular, respectively.

The molar Kerr constant for a liquid is, in general, computed from Eqs. (2.8) and (2.9); namely, we have

$$\begin{aligned} K_M &= (2\pi N_A/90) \{ 3c_{ijij}^{(p)} + 3c_{ijji}^{(p)} - 2c_{iijj}^{(p)} \\ &+ (2b_{ijk}^{(p)} \mu_l / kT) \langle \sum_{q=1}^N (3\delta_{ik} \omega_{jl}^{(pq)} + 3\omega_{il}^{(pq)} \delta_{jk} \\ &- 2\delta_{ij} \omega_{kl}^{(pq)}) \rangle + (a_{ij}^{(p)} a_{kl}^{(p)} / kT) \langle \sum_{q=1}^N (3\omega_{ik}^{(pq)} \omega_{jl}^{(pq)} \\ &+ 3\omega_{il}^{(pq)} \omega_{jk}^{(pq)} - 2\delta_{ij} \delta_{kl}) \rangle \\ &+ (a_{ij}^{(p)} \mu_k \mu_l / k^2 T^2) \langle \sum_{q=1}^N \sum_{r=1}^N (3\omega_{ik}^{(pq)} \omega_{jl}^{(pr)} \\ &+ 3\omega_{il}^{(pq)} \omega_{jk}^{(pr)} - 2\delta_{ij} \omega_{kl}^{(pr)}) \rangle \}. \quad (2.10) \end{aligned}$$

Similarly, the molar Cotton-Mouton constant of a diamagnetic liquid is

$$\begin{aligned} C_M &= (2\pi N_A/90) \{ 3c_{ij,ij}^{(pm)} + 3c_{ij,ji}^{(pm)} - 2c_{iij,ij}^{(pm)} \\ &+ (a_{ij}^{(p)} a_{kl}^{(m)} / kT) \langle \sum_{q=1}^N (3\omega_{ik}^{(pq)} \omega_{jl}^{(pq)} \\ &+ 3\omega_{il}^{(pq)} \omega_{jk}^{(pq)} - 2\delta_{ij} \delta_{kl}) \rangle \}, \quad (2.11) \end{aligned}$$

here,  $a_{ij}^{(m)}$  is the magnetic polarizability tensor and  $c_{ij,kl}^{(pm)}$  the magneto-optical deformability tensor of the molecule.

Formulas (2.10) and (2.11) determining both the molar Kerr and Cotton-Mouton constants are valid for arbitrary symmetry of molecules of the system. In the special case of molecules possessing axial symmetry, Eqs. (2.10) and (2.11) yield

$$K_M = 2\pi N_A (\Delta_1^{oe} + 2\Delta_2^{oe} R_P + \Theta_1^{oe} R_{CM} + \Theta_2^{oe} R_K), \quad (2.12)$$

$$C_M = 2\pi N_A (\Delta_1^{om} + \Theta_1^{om} R_{CM}), \quad (2.13)$$

here

$$\begin{aligned} \Delta_1^{oe} &= 2c_{ijij}^{(p)oe} / 45, \\ \Delta_2^{oe} &= 2\mu b_{ijk}^{(p)oe} / 45kT, \\ \Theta_1^{oe} &= (2/45kT) (a_{33}^{(p)oe} - a_{11}^{(p)oe}) (a_{33}^{(p)oe} - a_{11}^{(p)oe}), \\ \Theta_2^{oe} &= (2\mu^2/45k^2 T^2) (a_{33}^{(p)oe} - a_{11}^{(p)oe}), \\ \Delta_1^{om} &= \frac{1}{45} (3c_{ij,ij}^{(p)om} - c_{iij,ij}^{(p)om}), \\ \Theta_1^{om} &= (2/45kT) (a_{33}^{(p)om} - a_{11}^{(p)om}) (a_{33}^{(p)om} - a_{11}^{(p)om}). \quad (2.15) \end{aligned}$$

A discussion of the tensors  $b_{ijk}^{(p)oe}$ ,  $c_{ijk}^{(p)oe}$ , and  $c_{ij,kl}^{(pm)}$  for axial and spherical symmetry of the molecules has been given by various authors, see, e.g., Buckingham and Pople.<sup>19,20</sup>

The quantities  $R_P$ ,  $R_{CM}$ , and  $R_K$  appearing in Eqs. (2.12) and (2.13), and termed correlation factors are

$$R_P = \langle \sum_{q=1}^N \cos \Theta^{(pq)} \rangle, \quad (2.16)$$

$$R_{CM} = \frac{1}{2} \langle \sum_{q=1}^N (3 \cos^2 \Theta^{(pq)} - 1) \rangle, \quad (2.17)$$

$$R_K = \frac{1}{2} \langle \sum_{q=1}^N \sum_{r=1}^N (3 \cos \Theta^{(pq)} \cos \Theta^{(pr)} - \cos \Theta^{(qr)}) \rangle, \quad (2.18)$$

with  $\Theta^{(pq)}$  denoting the angle between the axes of symmetry of the  $p$ th and  $q$ th molecules.

The correlation factors account for the interaction of the molecules, their values depending on the con-

figuration of the latter and on the potential energy  $U_N$  of molecular interaction.

If the deformational terms are neglected, the Kerr and Cotton-Mouton molar constants as defined by Eqs. (2.12) and (2.13) take the form obtained in an earlier paper.<sup>25</sup>

The following relationships exist between the molar constants  $K_M$  and  $C_M$ , on the one hand, and the experimentally measured constants  $K$  and  $C$ , on the other (assuming a Lorentz<sup>26</sup> local field for that of the light wave):

$$K_M = K[6n^2/(n^2+2)^2](M/d)(E/F_e)^2, \quad (2.19)$$

$$C_M = C[6n^2/(n^2+2)^2](M/d)(H/F_m)^2, \quad (2.20)$$

where  $d$  denotes the density,  $M$  the molecular weight, and  $n$  the optical refractive index of the substance,  $E$  and  $H$  the external electric and magnetic fields,  $F_e$  being the electric local field (to be calculated, e.g., by a method similar to that of Onsager,<sup>27</sup> adapted to anisotropic molecules<sup>7,28</sup>) and  $F_m$  the local magnetic field  $F_m \cong H$ .

### 3. DIELECTRIC SATURATION OF LIQUIDS IN ELECTRIC, MAGNETIC, OR OPTICAL FIELDS

The method described in Sec. 2 may be used with slight modifications for computing the dielectric saturation or change in the dielectric permittivity caused by an external polarizing field. This method, for the case of molecules possessing axial symmetry, was described in earlier papers<sup>28,29</sup> by the present authors. The polarizing field may be electric or magnetic, or else the electric field of an electromagnetic wave of frequency exceeding that of Debye dispersion, which will be termed the "optical field." Thus, according to the polarizing field used, we shall be dealing with three distinct saturation effects. The molar constants, defined as follows, have been calculated for these effects. The molar constant of dielectric saturation in an electric field is

$$S_M^{ee} = (4\pi/3)(N_A/F_e^2) \{ (\partial/\partial F_e) \langle m_E \rangle_E - [(\partial/\partial F_e) \langle m_E \rangle_E]_{E=0} \}, \quad (3.1)$$

here  $m_E$  is the component of the total electric moment of the molecule in the direction of the electric field vector  $\mathbf{E}$ . The method of computing the quantity  $\langle m_E \rangle_E$  is similar to the one used for computing the

mean optical polarizability, given in Sec. 2. For the remaining effects, the molar constants  $S_M^{em}$  and  $S_M^{eo}$  are defined by analogy, and the mean electric moment  $\langle m_E \rangle_E$  and  $\langle m_E \rangle_{E, \mu, i}$  in the presence of the biasing magnetic and optical fields, respectively, are to be computed as in Sec. 2.

The molar dielectric saturation constant for the electric biasing field is

$$\begin{aligned} S_M^{ee} = & (2\pi N_A/45) \{ c_{ijj}^{ee} + c_{ijj}^{eo} + c_{ijj}^{oe} \\ & + (4\mu_i b_{ijk}^{ee}/kT) \langle \sum_{q=1}^N (\omega_{ij}^{(pq)} \delta_{kl} + \omega_{ik}^{(pq)} \delta_{jl} + \omega_{il}^{(pq)} \delta_{jk}) \rangle \\ & + (a_{ij}^e a_{kl}^e/kT) \langle \sum_{q=1}^N (3\omega_{ik}^{(pq)} \omega_{jl}^{(pq)} \\ & + 3\omega_{il}^{(pq)} \omega_{jk}^{(pq)} - 2\delta_{ij} \delta_{kl}) \rangle \\ & + (2a_{ij}^e \mu_k \mu_l/k^2 T^2) \langle \sum_{q=1}^N \sum_{r=1}^N (3\omega_{ik}^{(pq)} \omega_{jl}^{(rq)} \\ & + 3\omega_{il}^{(pq)} \omega_{jk}^{(rq)} - 2\delta_{ij} \delta_{kl}^{(qr)}) \rangle \\ & + (\mu_i \mu_j \mu_k \mu_l/k^2 T^3) \{ 3 \langle \sum_{q=1}^N \sum_{r=1}^N \sum_{s=1}^N \omega_{ij}^{(pq)} \omega_{kl}^{(rs)} \rangle \\ & - 5 \langle \sum_{q=1}^N \omega_{ij}^{(pq)} \rangle \langle \sum_{r=1}^N \sum_{s=1}^N \omega_{kl}^{(rs)} \rangle \} \}, \quad (3.2) \end{aligned}$$

where  $\mu_i$  and  $a_{ij}^e$  denote the permanent electric dipole moment and the tensor of electric polarizability of the molecule, respectively, and  $b_{ijk}^{ee}$ ,  $c_{ijj}^{ee}$  the tensors of the electro-electric deformability of the molecule.

By analogy, the molar electric saturation constant of a diamagnetic liquid in a magnetic field is:

$$\begin{aligned} S_M^{em} = & (2\pi N_A/135) \{ 3(2 - \cos^2 \Omega_{em}) \times \\ & [c_{ijj}^{em} + (2\mu_i b_{ijk}^{em}/kT) \langle \sum_{q=1}^N \omega_{ij}^{(pq)} \delta_{kl} \rangle \\ & + \frac{1}{2} (3 \cos^2 \Omega_{em} - 1) [3c_{ijj}^{em} + 3c_{ijj}^{em}] \\ & + (6\mu_i b_{ijk}^{em}/kT) \langle \sum_{q=1}^N (\omega_{ik}^{(pq)} \delta_{jl} + \omega_{il}^{(pq)} \delta_{jk}) \rangle \\ & + (a_{ij}^e a_{kl}^m/kT) \langle \sum_{q=1}^N (3\omega_{ik}^{(pq)} \omega_{jl}^{(pq)} \\ & + 3\omega_{il}^{(pq)} \omega_{jk}^{(pq)} - 2\delta_{ij} \delta_{kl}) \rangle \\ & + (a_{ij}^m \mu_k \mu_l/k^2 T^2) \langle \sum_{q=1}^N \sum_{r=1}^N (3\omega_{ik}^{(pq)} \omega_{jl}^{(rq)} \\ & + 3\omega_{il}^{(pq)} \omega_{jk}^{(rq)} - 2\delta_{ij} \delta_{kl}^{(qr)}) \rangle \} \}, \quad (3.3) \end{aligned}$$

<sup>25</sup> A. Piekara and S. Kielich, J. phys. radium **18**, 490 (1957).

<sup>26</sup> H. A. Lorentz, *The Theory of Electrons* (B. G. Teubner, Leipzig, 1909).

<sup>27</sup> L. Onsager, J. Am. Chem. Soc. **58**, 1486 (1936).

<sup>28</sup> A. Piekara and S. Kielich, Acta Phys. Polonica **18**, 209 (1958).

<sup>29</sup> S. Kielich, Acta Phys. Polonica **18**, 239 (1958).

and the molar electric saturation constant for the optical biasing field:

$$\begin{aligned}
 S_M^{eo} = & (2\pi N_A/135) \{ 3(2 - \cos^2\Omega_{eo}) [c_{ijj}^{eo} \\
 & + (2\mu_i b_{jki}^{eo}/kT) \langle \sum_{q=1}^N \omega_{ij}^{(pq)} \delta_{kl} \rangle] \\
 & + \frac{1}{2} (3 \cos^2\Omega_{eo} - 1) [3c_{ijj}^{eo} + 3c_{ijj}^{eo} \\
 & + (6\mu_i b_{jki}^{eo}/kT) \langle \sum_{q=1}^N (\omega_{ik}^{(pq)} \delta_{jl} + \omega_{il}^{(pq)} \delta_{jk}) \rangle \\
 & + (a_{ij}^{eo} a_{kl}^{eo}/kT) \langle \sum_{q=1}^N (3\omega_{ik}^{(pq)} \omega_{il}^{(pq)} \\
 & + 3\omega_{il}^{(pq)} \omega_{jk}^{(pq)} - 2\delta_{ij} \delta_{kl}) \rangle \\
 & + (a_{ij}^{eo} \mu_i \mu_j / k^2 T^2) \langle \sum_{q=1}^N \sum_{r=1}^N (3\omega_{ik}^{(pq)} \omega_{jl}^{(pr)} \\
 & + 3\omega_{il}^{(pq)} \omega_{jk}^{(pr)} - 2\delta_{ij} \delta_{kl}^{(qr)}) \rangle \} \}, \quad (3.4)
 \end{aligned}$$

with  $b_{ijk}^{em}$ ,  $c_{ijk}^{em}$  denoting the tensors of the magneto-electric deformability, and  $b_{ijk}^{eo}$ ,  $c_{ijk}^{eo}$  tensors of the optical-electric deformability of the molecule, and  $\Omega_{em}$ ,  $\Omega_{eo}$  the angles between the vector of the measuring electric field  $\mathbf{E}$  and those of the polarizing magnetic  $\mathbf{H}$  and optical  $\boldsymbol{\varepsilon}$  fields, respectively.

The equations (3.2)–(3.4) are quite general, while if the molecules possess axial symmetry, they yield:

$$\begin{aligned}
 S_M^{ee} = & 4\pi N_A (\Delta_1^{ee} + 4\Delta_2^{ee} R_P + \Theta_1^{ee} R_{CM} \\
 & + 2\Theta_2^{ee} R_K - \Theta_3^{ee} R_B), \quad (3.5)
 \end{aligned}$$

$$\begin{aligned}
 S_M^{em} = & (4\pi N_A/3) (\Delta_1^{em} + 2\Delta_2^{em} R_P + \Theta_1^{em} R_{CM} + \Theta_2^{em} R_K), \\
 & (3.6)
 \end{aligned}$$

$$\begin{aligned}
 S_M^{eo} = & (4\pi N_A/3) (\Delta_1^{eo} + 2\Delta_2^{eo} R_P + \Theta_1^{eo} R_{CM} + \Theta_2^{eo} R_K). \\
 & (3.7)
 \end{aligned}$$

Here, the following symbols have been introduced:

$$\begin{aligned}
 \Delta_1^{ee} = & \frac{1}{30} c_{ijj}^{eo}, \\
 \Delta_2^{ee} = & \mu b_{3ii}^{eo}/30kT, \\
 \Theta_1^{ee} = & (2/45kT) (a_{33}^{eo} - a_{11}^{eo})^2, \\
 \Theta_2^{ee} = & (2\mu^2/45k^2T^2) (a_{33}^{eo} - a_{11}^{eo}), \\
 \Theta_3^{ee} = & \mu^4/45k^2T^3, \\
 \Delta_1^{em} = & \frac{1}{30} [(3 \cos^2\Omega_{em} - 1) c_{ijj}^{em} + (2 - \cos^2\Omega_{em}) c_{ijj}^{em}], \\
 \Delta_2^{em} = & (\mu/30kT) [(3 \cos^2\Omega_{em} - 1) b_{3ii}^{em} \\
 & + (2 - \cos^2\Omega_{em}) b_{3ii}^{em}], \quad (3.8)
 \end{aligned}$$

$$\Delta_1^{em} = \frac{3 \cos^2\Omega_{em} - 1}{45kT} (a_{33}^{em} - a_{11}^{em}) (a_{33}^{em} - a_{11}^{em}),$$

$$\Delta_2^{em} = \frac{3 \cos^2\Omega_{em} - 1}{45k^2T^2} (a_{33}^{em} - a_{11}^{em}) \mu^2,$$

$$\Delta_1^{eo} = \frac{1}{30} (1 + 2 \cos^2\Omega_{eo}) c_{ijj}^{eo},$$

$$\Delta_2^{eo} = \frac{1}{30} (1 + 2 \cos^2\Omega_{eo}) \mu b_{3ii}^{eo}/kT,$$

$$\Theta_1^{eo} = \frac{3 \cos^2\Omega_{eo} - 1}{45kT} (a_{33}^{eo} - a_{11}^{eo}) (a_{33}^{eo} - a_{11}^{eo}),$$

$$\Theta_2^{eo} = \frac{3 \cos^2\Omega_{eo} - 1}{45k^2T^2} (a_{33}^{eo} - a_{11}^{eo}) \mu^2. \quad (3.10)$$

The correlation factors  $R_P$ ,  $R_{CM}$ , and  $R_K$  are defined by Eqs. (2.15) to (2.18), while  $R_B$ , the correlation factor appearing in the dipolar term of the dielectric saturation, is of the form

$$\begin{aligned}
 R_B = & \frac{1}{2} (5 \langle \sum_{q=1}^N \cos\Theta^{(pq)} \rangle \langle \sum_{r=1}^N \sum_{s=1}^N \cos\Theta^{(rs)} \rangle \\
 & - 3 \langle \sum_{q=1}^N \sum_{r=1}^N \sum_{s=1}^N \cos\Theta^{(pq)} \cos\Theta^{(rs)} \rangle); \quad (3.11)
 \end{aligned}$$

here,  $\Theta^{(pq)}$  is the angle between the axes of symmetry of the  $p$ th and  $q$ th molecules.

On neglecting deformational terms, the molar constants (3.5) and (3.6) reduce to those obtained previously.<sup>25</sup>

Experimental investigations on electric saturation in an electric field deal with the variation of the dielectric permittivity given by the difference between the dielectric permittivity  $\epsilon$  measured in a strong electric field and  $\epsilon_0$  measured in a weak field:  $\Delta\epsilon = \epsilon - \epsilon_0$ .

The variation of the dielectric permittivity resulting from the effect of dielectric saturation in a strong electric field is obtained in the form

$$\Delta\epsilon_{\text{sat}}^{ee} = 3(d/M) S_M^{ee} [1 - (\partial f/\partial \epsilon)]^{-1} \epsilon_0 (\partial F_e/\partial F) F_e^2, \quad (3.12)$$

and the respective quantities resulting from the effect of a strong magnetic or optical field are:

$$\Delta\epsilon_{\text{sat}}^{em} = 3(d/M) S_M^{em} [1 - (\partial f/\partial \epsilon)]^{-1} \epsilon_0 (\partial F_e/\partial F) F_m^2, \quad (3.13)$$

$$\Delta\epsilon_{\text{sat}}^{eo} = 3(d/M) S_M^{eo} [1 - (\partial f/\partial \epsilon)]^{-1} \epsilon_0 (\partial F_e/\partial F) \langle F_o^2 \rangle, \quad (3.14)$$

with

$$f = (4\pi/3) (N/V) [a_{ii}^{eo} + (\mu_i \mu_j / kT) \langle \sum_{q=1}^N \omega_{ij}^{(pq)} \rangle] \partial F_e / \partial F, \quad (3.15)$$

here,  $S_M^{ee}$ ,  $S_M^{em}$  and  $S_M^{eo}$  are defined by Eqs. (3.2) to (3.4) or (3.5) to (3.7),  $\langle F_o^2 \rangle$  denoting the time mean square of  $F_o$ .

It is noteworthy that the value of  $\Delta\epsilon^e$ , the variation of the permittivity in a strong electric field as obtained by measurement, in reality results from the superposition of  $\Delta\epsilon_{\text{rot}}^e$  and of two by-effects arising from electrostriction and from the electrocaloric effect.<sup>30</sup>

The foregoing formulas are valid for dielectric dense media: condensed gases and liquids. The theory of magnetodielectric saturation in paramagnetic gases was given by Van Vleck<sup>31</sup> and that for diamagnetic gases by one of the present authors.<sup>1</sup> Essentially the same result for  $\Delta\epsilon_{\text{rot}}^m$  was derived by Buckingham<sup>18</sup> for diamagnetic liquids.

Dielectric saturation in a magnetic field, i.e., the effect of a magnetic field on the permittivity of a liquid, has as yet not been observed in pure liquids. Attempts in this direction by Piekara and Schärer<sup>32</sup> succeeded in establishing an upper limit of the effect only. Notwithstanding the very considerable difficulties, investigations are being continued in this laboratory by modern methods.

The quantity  $\Delta\epsilon^e$  accounting for the effect of the field of a light wave on the dielectric permittivity has not been experimentally observed so far. Buckingham calculated the effect on the refractive index.<sup>33</sup>

Thus, both effects,  $\Delta\epsilon^m$  and  $\Delta\epsilon^e$ , still await to be detected experimentally.

The present theory makes it possible to compute the variation of the permittivity in a magnetic or optical field from the experimental value of Kerr's constant of a liquid. Namely, on neglecting deformational terms in Eqs. (2.12), (3.6), and (3.7), with regard to (2.19), Eqs. (3.13) and (3.14) yield

$$\Delta\epsilon_{\text{rot}}^m = (3 \cos^2 \Omega_m - 1) [6n^2 / (n^2 + 2)^2] (\kappa_m / \kappa_e) K h(\epsilon) H^2, \quad (3.16)$$

$$\Delta\epsilon_{\text{rot}}^e = (3 \cos^2 \Omega_m - 1) (n^2 / 3) K h(\epsilon) \mathcal{E}_0^2, \quad (3.17)$$

where

$$h(\epsilon) = [1 - (\partial f / \partial \epsilon)]^{-1} \lim_{\epsilon_0 \rightarrow 0} \partial F_c / \partial E (E / F_c)^2, \quad (3.18)$$

and

$$\kappa_0 = a_{33}^m - a_{11}^m; \quad \kappa_m = a_{33}^m - a_{11}^m, \quad (3.19)$$

$K$  being Kerr's constant for a liquid, and  $\mathcal{E}_0$  the amplitude of the light vector  $\mathcal{E}$ .

For nitrobenzene at 20°C we have the following

values:

$$\begin{aligned} \epsilon &= 34.3, & \epsilon_{\infty} &\cong n^2 = 2.5, \\ \kappa_0 &= 7.3 \cdot 10^{-24}, & \kappa_m &= 1.3 \cdot 10^{-28}, \\ K &= 1.3 \cdot 10^{-9}. \end{aligned} \quad (3.20)$$

With the Lorentz<sup>26</sup> local field, we have

$$\begin{aligned} \mu &= \mu_0, & \alpha' &= \frac{1}{3} a_{11}^e = \alpha_0^e, \\ F_c &= [(\epsilon + 2) / 3] E, & h(\epsilon) &= 1, \end{aligned} \quad (3.21)$$

(here,  $\mu_0$  and  $\alpha_0^e$  denote the permanent electric moment and the mean electric polarizability of an isolated molecule, respectively) and Eqs. (3.16), (3.17), and (3.20) yield

$$\begin{aligned} \Delta\epsilon_{\text{rot}}^m &= 1.8 (3 \cos^2 \Omega_m - 1) \times 10^{-14} H^2, \\ \Delta\epsilon_{\text{rot}}^e &= 1.2 (3 \cos^2 \Omega_m - 1) \times 10^{-9} \mathcal{E}_0^2. \end{aligned} \quad (3.22)$$

On the other hand, for Onsager's<sup>27</sup> local field, neglecting the anisotropy, we obtain

$$\begin{aligned} \mu &= [(\epsilon_{\infty} + 2) / 3] [(2\epsilon + 1) / (2\epsilon + \epsilon_{\infty})] \mu_0, \\ \alpha' &= [(\epsilon_{\infty} + 2) / 3] [(2\epsilon + 1) / (2\epsilon + \epsilon_{\infty})] \alpha_0^e, \\ F_c &= [3\epsilon / (2\epsilon + 1)] E, \\ h(\epsilon) &= (2\epsilon + \epsilon_{\infty})^2 / 3(2\epsilon^2 + \epsilon_{\infty}^2), \end{aligned} \quad (3.23)$$

(where  $\epsilon_{\infty}$  is the high-frequency dielectric constant of the substance) and the results are

$$\begin{aligned} \Delta\epsilon_{\text{rot}}^m &= 1.3 (3 \cos^2 \Omega_m - 1) \times 10^{-14} H^2, \\ \Delta\epsilon_{\text{rot}}^e &= 0.8 (3 \cos^2 \Omega_m - 1) \times 10^{-9} \mathcal{E}_0^2. \end{aligned} \quad (3.24)$$

The value of  $(\Delta\epsilon_{\text{rot}}^m)_{\text{rot}}^m$  as computed from (3.22) and (3.24) for nitrobenzene at  $H = 40 \text{ k}\phi\epsilon$ , amounts to  $(\Delta\epsilon_{\text{rot}}^m)_{\text{rot}}^m = 6.10^{-6}$  if a local Lorentz field be assumed, whereas the assumption of the Onsager field yields  $(\Delta\epsilon_{\text{rot}}^m)_{\text{rot}}^m = 4.10^{-6}$ . Those values differ to some extent from those previously given (5.10<sup>-6</sup> and 3.10<sup>-6</sup>, respectively<sup>29</sup>) because of different experimental data used.

With the existing modern measuring techniques it would be possible to detect both  $\Delta\epsilon^m$  and  $\Delta\epsilon^e$  by using magnetic fields about 40 k $\phi\epsilon$  or by using powerful light flashes of energy flux of the order of 10<sup>6</sup> watts cm<sup>-2</sup>.

#### 4. COMPUTATION OF CORRELATION FACTORS FOR A SPECIAL MODEL

The interaction of the molecules of a liquid, which is of importance in the effects of molecular orientation as discussed in Secs. 2 and 3, is accounted for by the four correlation factors  $R_p$ ,  $R_{CM}$ ,  $R_K$ , and  $R_N$  defined by Eqs. (2.16) to (2.18) and (3.11), respectively.

<sup>30</sup> Piekara, Chelkowski, and Kielich, *Z. physik. Chem.* **206**, 375 (1957).

<sup>31</sup> J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, London, 1932).

<sup>32</sup> A. Piekara and M. Schärer, *Compt. rend.* **202**, 1159 (1936).

<sup>33</sup> A. D. Buckingham, *Proc. Phys. Soc. (London)* **B69**, 344 (1956).

The correlation factors may be expressed as follows:

$$R_p = 1 + \left\langle \sum_{q \neq p}^{(q)} \cos \Theta^{(pq)} \right\rangle, \quad (4.1)$$

$$R_{CM} = 1 + \frac{3}{2} \left\langle \sum_{q \neq p}^{(q)} (\cos^2 \Theta^{(pq)} - \frac{1}{3}) \right\rangle, \quad (4.2)$$

$$R_K = 1 + \frac{3}{2} \left\langle \sum_{q \neq p}^{(q)} \sum_{r \neq p}^{(r)} (\cos \Theta^{(pq)} \cos \Theta^{(pr)} - \frac{1}{3} \cos \Theta^{(qr)}) \right. \\ \left. + 2 \left\langle \sum_{q \neq p}^{(q)} \cos \Theta^{(pq)} \right\rangle \right\rangle, \quad (4.3)$$

$$R_S = 1 - 3 \left\langle \sum_{q \neq p}^{(q)} \sum_{r \neq p}^{(r)} (\cos \Theta^{(pq)} \cos \Theta^{(pr)} - \frac{1}{3} \cos \Theta^{(qr)}) \right. \\ \left. + \frac{3}{2} \left\langle \sum_{q \neq p}^{(q)} \cos \Theta^{(pq)} \left( 2 - \sum_{r \neq p}^{(r)} \sum_{s \neq p}^{(s)} \cos \Theta^{(rs)} \right) \right\rangle \right. \\ \left. + \frac{5}{2} \left\langle \sum_{q \neq p}^{(q)} \cos \Theta^{(pq)} \right\rangle \left\langle 2 \sum_{r \neq p}^{(r)} \cos \Theta^{(pr)} \right. \right. \\ \left. \left. + \sum_{r \neq p}^{(r)} \sum_{s \neq p}^{(s)} \cos \Theta^{(rs)} \right\rangle \right\rangle, \quad (4.4)$$

where all  $\sum$ 's should be extended to all indices  $q, r, s = 1, 2, \dots, N$ , except  $q = p, r = p, s = p$ .

It will be seen from Eqs. (4.1) to (4.4) that if the energy of molecular interaction  $U_N = 0$ , the statistical mean values  $\langle \Phi \rangle$  defined by Eq. (2.5) become identical with the isotropic mean values, and, because of  $\langle \cos \Theta \rangle = 0$ ,  $\langle \cos^2 \Theta \rangle = \frac{1}{3}$ , we have

$$R_p = R_{CM} = R_K = R_S = 1. \quad (4.5)$$

Thus, the formulas obtained in Secs. 2 and 3 hold for rarefied gases.

To compute the correlation factors numerically for liquids, it is necessary to make assumptions as to the shape of the molecules and the nature of the forces with which they interact. This problem is, in general, a very involved one, and we shall proceed to consider an important particular case of dipole pairwise coupling of the molecules.

Namely, assuming a very simple model for this kind of interaction (see A. Piekara<sup>4,5,7</sup>), Eqs. (4.1) to (4.4) yield the correlation factors previously computed,<sup>2-7</sup> namely:

$$R_p = 1 \pm L,$$

$$R_{CM} = 1 + (1 - 3L/y),$$

$$R_K = 1 + (1 - 3L/y) \pm 2L,$$

$$R_S = 1 - 2(1 - 3L/y) + (5L \pm 4)L, \quad (4.6)$$

wherein  $L = L(y)$  is the well-known Langevin function, and  $y = W/kT$ , the energy of dipole coupling of a pair of molecules in  $kT$  units.

The upper sign applies to pairs of molecules tending toward almost parallel mutual orientation, while the lower sign in the formulas holds for molecules tending toward almost antiparallel array. In this last case  $R_S$  changes the sign for  $y \geq 1.33$  and thus the inverse saturation effect appears in formulas (3.5) and (3.12), because the term  $-O_2^* R_S$  predominates in polar liquids.<sup>2,5,7</sup>

The correlation factor  $R_p$  for polarization as defined by (4.1) was obtained by Kirkwood<sup>24</sup> (see also Fröhlich's monograph<sup>25</sup>) and computed numerically some time ago for pairwise molecular interaction by Harris and Adler,<sup>26</sup> Harris<sup>23</sup> and Buckingham and Pople.<sup>24</sup>

## 5. MOLECULAR LIGHT SCATTERING IN LIQUIDS

If the effect of molecular interaction be taken into account in considering light scattering in liquids and neglecting the fluctuation of the local field, the  $\mathbf{s}$  component of the intensity of the light scattered is obtained in the form<sup>22</sup>:

$$I_s = I_o (2\pi/\lambda)^4 (N_o V/r^2) [(n^2 + 2)/3]^2 \\ \{ (\cos^2 \Omega_{os}/9) \gamma a_{ij}^o a_{jj}^o + [(\cos^2 \Omega_{os} + 3)/90] a_{ij}^o a_{kl}^o \times \\ \left\langle \sum_{q=1}^N (3\omega_{ik}^{(pq)} \omega_{jl}^{(pq)} - \delta_{ij} \delta_{kl}) \right\rangle \}, \quad (5.1)$$

where  $I_o$  is the intensity of the incident beam,  $\lambda$  the wavelength *in vacuo*,  $\mathbf{r}$  the distance to the point of observation,  $\Omega_{os}$  the angle subtended by the electric vector of the incident light wave  $\boldsymbol{\xi}$  and the vector  $\mathbf{s}$ , ( $\mathbf{s}$  denotes the unit vector perpendicular to  $\mathbf{r}$  and determining the position of the analyzer) and  $\gamma = \beta N_o kT$ , as first computed by Smoluchowski<sup>27</sup> and Einstein,<sup>28</sup> with  $\beta$  denoting the isothermal compressibility of the substance:  $\beta = -1/V(\partial V/\partial P)_T$ . For an ideal gas  $\gamma = 1$ .

For a nonpolarized incident beam, the degree of depolarization of the light scattered in the liquid is given by

$$D_n = \frac{2I_{s, \Omega_{os} = 90^\circ}}{I_{s, \Omega_{os} = 90^\circ} + I_{s, \Omega_{os} = 0}}, \quad (5.2)$$

and by (5.1), we have

$$D_n = \frac{6a_{ij}^o a_{kl}^o \left\langle \sum_{q=1}^N (3\omega_{ik}^{(pq)} \omega_{jl}^{(pq)} - \delta_{ij} \delta_{kl}) \right\rangle}{10\gamma a_{ij}^o a_{jj}^o + 7a_{ij}^o a_{kl}^o \left\langle \sum_{q=1}^N (3\omega_{ik}^{(pq)} \omega_{jl}^{(pq)} - \delta_{ij} \delta_{kl}) \right\rangle}. \quad (5.3)$$

The constant of light scattering (Rayleigh's constant) is defined as

$$R = (I_{\perp}/I_o) (r^2/V); \quad (5.4)$$

here  $I_{\perp}$  is the total intensity of the light scattered by the volume  $V$  of the liquid in the direction perpendicular to that of the incident beam of natural light, to be

<sup>24</sup> J. Kirkwood, *J. Chem. Phys.* **7**, 911 (1939).

<sup>25</sup> H. Fröhlich, *Theory of Dielectrics* (Oxford University Press, London, 1949).

<sup>26</sup> F. E. Harris and B. J. Adler, *J. Chem. Phys.* **21**, 1031, 1351 (1953).

<sup>27</sup> M. Smoluchowski, *Ann. Physik* **25**, 205 (1908).

<sup>28</sup> A. Einstein, *Ann. Physik* **33**, 1275 (1910).



computed from Eq. (5.1) (see Born<sup>39</sup>). Thus, we have

$$R = N_0/2(2\pi/\lambda)^4 [(n^2+2)/9]^2 \{ \gamma a_{ii}'' a_{ij}'' + \frac{1}{5} \sum_{\mu \neq i}^3 a_{ij}'' a_{\mu l}'' \langle \sum_{\nu=1}^3 (3\omega_{ik}^{(\mu\nu)} \omega_{jl}^{(\mu\nu)} - \delta_{ij} \delta_{kl}) \rangle \}. \quad (5.5)$$

Hence, assuming the molecules to possess axial symmetry, we have

$$D_n = (6\delta_0^2 R_{CM}) / (5\gamma + 7\delta_0^2 R_{CM}), \quad (5.6)$$

and

$$R = [\pi^2(n^2-1)^2/2\lambda^4 N_0] (\gamma + \frac{1}{5} \delta_0^2 R_{CM}), \quad (5.7)$$

with

$$\delta_0 = (a_{33}'' - a_{11}'') / (a_{33}'' + 2a_{11}'') \quad (5.8)$$

denoting the quantity known as the optical anisotropy of the molecule, and  $R_{CM}$  the correlation factor defined by (4.2).

If the molecular interaction be neglected, the foregoing formulas take the form of those of Born for perfect gases.<sup>39,40</sup>

By (5.6), Eq. (5.7) giving the scattering constant  $R$  becomes identical with the Cabannes-Rocard formula,<sup>40</sup>

$$R = [\pi^2(n^2-1)^2/(2\lambda^4 N_0)] \gamma (6+6D_n)/(6-7D_n), \quad (5.9)$$

with  $R_{CM}$  involved in  $D_n$ .

From the Cabannes-Rocard formula (5.9), the scattering constant  $R$  of a liquid may be computed if the degree of depolarization  $D_n$  is known experimentally for the latter.

The scattering constant  $R$  may, however, be computed from Eq. (5.7) if the value of the correlation factor  $R_{CM}$  is known. The theoretical computation of the correlation factor  $R_{CM}$  is, in general, an involved problem; its value may be determined, though, from the molar Kerr and Cotton-Mouton constants. Thus, by (2.12) and (2.13) we have for nonpolar liquids, on neglecting small deformational terms:

$$K_M = 2\pi N_A G_1'' R_{CM}, \quad (5.10)$$

$$C_M = 2\pi N_A G_1'' R_{CM}. \quad (5.11)$$

The constants  $K_M$  and  $C_M$  being known [as computed by (2.19) and (2.20) from experimental data], the correlation factor  $R_{CM}$  may be computed from the above relations and, ultimately, the scattering constant  $R$  for a given liquid is obtained from (5.7).

Recently, much importance has been attached to measuring the scattering constant  $R$  of benzene, which plays a great part in determining molecular weights by Debye's method. However, the results of those measurements are not consistent, as those of Carr and Zimm,<sup>41</sup> and other authors yield "high" values of the

constant  $R$  of benzene:  $R = 48.10^{-6} \text{ cm}^{-1}$  (at  $T = 298^\circ \text{K}$ ,  $\lambda = 4360 \text{ \AA}$ ), whereas those of Cabannes,<sup>40</sup> Harrard,<sup>42</sup> and others yield "low" values amounting to  $R = 28.10^{-6} \text{ cm}^{-1}$ .

Computing the scattering constant  $R$  by the Cabannes-Rocard formula (5.9) from the experimental degree of depolarization  $D_n$  of benzene, we have  $R = 27.10^{-6} \text{ cm}^{-1}$ .

On the other hand, for benzene, measurements of the Cotton-Mouton constant yield the correlation factor  $R_{CM} = 0.62$ , whereas measurements of Kerr's constant result in a value of  $R_{CM} = 0.57$ . Inserted in Eq. (5.7), the two values yield  $R = 30.10^{-6} \text{ cm}^{-1}$  and  $R = 28.5 \cdot 10^{-6} \text{ cm}^{-1}$ , respectively, which should indeed be considered to represent a rather good degree of agreement between theoretical and "low" experimental values.

## 6. LOWERING OF THE FREEZING POINT OF LIQUIDS

Surely, the effect of the lowering of the freezing point of liquids is no molecular orientational effect; however, directionally dependent molecular interaction plays an important part therein.

Let  $\Delta T_{id}$  denote the lowering of the freezing point of an ideal solution, and  $\Delta T$  that of the solution under consideration; then the quantity

$$j = (\Delta T_{id} - \Delta T) / \Delta T_{id} \quad (6.1)$$

measures the deviation of the solution from the state of an ideal solution, which, in turn, is a certain measure of the molecular interaction existing between the molecules of the solute. Let  $m$  denote the molar concentration; the curve  $j = j(m)$  may be traced experimentally.

Theoretical considerations<sup>43,8</sup> yield  $j$  in the form

$$j = \frac{1}{2} (N/V) J, \quad (6.2)$$

where  $J$  is the multiple integral

$$J = \int [\exp(-U_N/kT) - 1] d\tau \quad (6.3)$$

extending over the sphere of action of radius  $R$ , and  $U_N$  is the energy of molecular interaction.

For pairwise dipole coupling<sup>8</sup> in sufficiently dilute solutions, the integral (6.3) takes the form

$$J = 4\pi \int_{\tau_0}^R [(r^3/a) \sinh(a/r^3) - 1] r^2 dr \quad (6.4)$$

with  $a = \mu^2/kT$ , and  $\tau_0$  denoting the smallest distance between the coupled dipoles.

The present theory has been checked for some dilute solutions of polar substances in benzene. The tangents  $(dj/dm)_{m=0}$  to the curve  $j(m)$ , as computed theoretically from (6.2) and (6.4), were generally found to be in good agreement with the experimental curves.<sup>8</sup>

<sup>39</sup> M. Born, *Optik* (Verlag Julius Springer, Berlin, 1933).

<sup>40</sup> J. Cabannes, *La diffusion de la lumière* (Hermann et Cie, Paris, 1929).

<sup>41</sup> C. J. Carr and B. H. Zimm, *J. Chem. Phys.* **18**, 1616 (1950) (quoted from reference 42).

<sup>42</sup> M. Harrard, *Ann. phys.* **8**, 646 (1953).

<sup>43</sup> R. M. Fuoss, *J. Am. Soc.* **56**, 1027 (1934).