

SEMI-MACROSCOPIC TREATMENT OF THE THEORY OF NON-LINEAR PHENOMENA IN DIELECTRIC LIQUIDS SUBMITTED TO STRONG ELECTRIC AND MAGNETIC FIELDS

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The present paper brings a consistent semi-macroscopic theory of the non-linear effects of molecular orientation produced by strong electric or magnetic fields in condensed media. The deviation from the quadratic effect of dielectric saturation in a strong electric field has been calculated for polar liquids with molecules exhibiting isotropic polarizability (§ 3). Furthermore, general expressions are derived describing the effect of a strong electric or magnetic field on the index of refraction (§ 4) and on the dielectric permittivity (§ 5), and yielding the constants of Kerr and Cotton-Mouton as well as the variation of the dielectric permittivity in electric and magnetic fields. The molecular interpretation of the results yields formulae derived by the molecular method (A. Piekara and S. Kielich).

1. Introduction

J. Herweg (1920), applying the theory of Langevin and Debye (1905, 1912) was the first to calculate successfully the effect of an electric field on the dielectric constant of a dipolar gas. Subsequently, Van Vleck (1932) investigated the effect of electric and magnetic fields on the dielectric constant of paramagnetic gases. A. Piekara (1935 a, b; 1937 b, c), moreover, took into account the electric and magnetic deformation of the molecule in considering the effect of electric and magnetic fields on the dielectric constant of diamagnetic gases. Electric and magnetic deformation of the molecule had been considered by M. Born (1933) in his theory of electro-optical and magneto-optical effects in polar gases. Recently the problem has been taken up by A. D. Buckingham and J. A. Pople (1955, 1956).

In investigating the effect of molecular coupling on the dielectric constant and on the optical refractive index in polar liquids two tendencies may be distinguished as regards the method applied. The first was originated by R. H. Fowler (1935) and P. Debye (1935) and developed in papers by H. Müller (1936), A. Piekara (1937a, 1939, 1950), H. Friedrich (1937) A. Peterlin and H. A. Stuart (1939), A. J. Anselm

(1943) and J. Frenkel (1946), on the basis of a concrete microscopic molecular interaction model and the local field acting upon the molecules. Such a method has recently undergone generalization to cover simultaneously polarization, dielectric saturation in electric and magnetic fields, and the Kerr and Cotton-Mouton effects in polar liquids (Piekara and Kielich, 1957, 1958).

The other tendency is derived from J. Kirkwood's method (1939) and the much more general method of H. Fröhlich (1949), and is based essentially upon the macroscopic model of a sphere (containing N_S mutually interacting molecules) immersed in a definite continuous medium and subjected to the effect of an external electric field. The method was subsequently applied and developed in papers by A. J. Anselm (1944), F. Booth (1951), F. E. Harris and B. J. Alder (1953 a, b), A. D. Buckingham and J. A. Pople (1955, 1956) and J. A. Schellman (1957). Both methods apply classical statistical mechanics for computing the required mean values.

The present paper takes into account simultaneously the effect of electric and magnetic, linear and non-linear deformation and of molecular coupling on the dielectric constant and refractive index in polar liquids while basing on the latter method. From results obtained in this way the author passes to relations obtained according to the former method (Piekara and Kielich, 1957). As was the case in all above-mentioned papers, the system under consideration is assumed to be in a state in which quantum effects are of no importance, thus making the use of classical statistical mechanics legitimate.

2. Fundamental relations

The dielectric permittivity ε of the (homogeneous and isotropic) medium, subjected to the effect of a strong electric field \mathbf{E} and a magnetic field \mathbf{H} forming a given angle Ω with the former, is calculated from the fundamental equation

$$\varepsilon - 1 = \frac{4\pi}{V_S} \frac{\partial \langle \mathbf{M}_S \rangle_{E,H}}{\partial \mathbf{E}} = \frac{4\pi}{V_S} \frac{\partial \langle \mathbf{M}_S \cdot \mathbf{e} \rangle_{E,H}}{\partial E}, \quad (2.1)$$

where \mathbf{M}_S denotes the total electric moment of a macroscopic sphere S of volume V_S , and \mathbf{e} is the unit vector in the direction of the field \mathbf{E} . The statistical mean value $\mathbf{M}_S \cdot \mathbf{e}$ in classical statistical mechanics is given by the expression

$$\langle \mathbf{M}_S \cdot \mathbf{e} \rangle_{E,H} = kT \frac{\partial}{\partial E_S} \ln Z(\tau, E_S, H_S), \quad (2.2)$$

where

$$Z(\tau, E_S, H_S) = \int e^{-\frac{U(\tau, E_S, H_S)}{kT}} d\tau, \quad (2.3)$$

denotes the configurational partition function, k — the Boltzmann constant, T — the absolute temperature, E_S and H_S — the electric and magnetic fields in the presence of the sphere S , respectively. $U(\tau, E_S, H_S)$ denotes the total potential energy of the sphere S in the configuration τ with fields E_S and H_S and $d\tau = dv d\omega$ is the con-

figurational element fixing position (volume element $dv = dx dy dz$) and orientation (orientation element $d\omega = \sin \vartheta d\vartheta d\varphi d\psi$ in Eulerian angles ϑ, φ, ψ). Assuming the macroscopic sphere S contains N_S molecules, we have

$$d\tau = \prod_{q=1}^{N_S} dv_q d\omega_q; \quad dv_q = dx_q dy_q dz_q; \quad d\omega_q = \sin \vartheta_q d\vartheta_q d\varphi_q d\psi_q. \quad (2.3a)$$

The effect of a strong homogeneous electric field \mathbf{E} on the optical refractive index n is calculated similarly:

$$n^2 - 1 = \frac{4\pi}{V_S} \frac{\partial \langle \mathbf{M}_S^0 \rangle_E}{\partial \mathbf{E}^0} = \frac{4\pi}{V_S} \frac{\partial \langle \mathbf{M}_S^0 \cdot \mathbf{e}^0 \rangle_E}{\partial E^0}; \quad (2.4)$$

here, \mathbf{M}_S^0 is the total optical moment of a macroscopic sphere S of volume V_S , \mathbf{e}^0 — the unit vector in the direction of the field \mathbf{E}^0 of the light wave. The mean value $\langle \mathbf{M}_S^0 \cdot \mathbf{e}^0 \rangle_E$ is obtained from the following relation:

$$\langle \mathbf{M}_S^0 \cdot \mathbf{e}^0 \rangle_E = kT \frac{\partial}{\partial E_S^0} \ln Z(\tau, E_S^0, E_S), \quad (2.5)$$

and

$$Z(\tau, E_S^0, E_S) = \int e^{-\frac{U(\tau, E_S^0, E_S)}{kT}} d\tau, \quad (2.6)$$

where the quantities retain their previous meanings. Similar relations hold for the effect of a homogeneous magnetic field \mathbf{H} on the refractive index n : in order to obtain them it is only necessary to substitute the field \mathbf{H} for \mathbf{E} in eqs. (2.4) — (2.6).

3. On the dielectric constant of an isotropically polarizable dense medium in an electric field \mathbf{E}

To begin with, let us assume that the homogeneous electric field \mathbf{E} acting on the system under consideration produces isotropic polarization. This results in the total potential energy of the system in configuration τ and in the presence of the field \mathbf{E} taking the form

$$U(\tau, E_S) = U(\tau, 0) - \mathbf{M}_S \cdot \mathbf{e} E_S - \frac{1}{2} A_S E_S^2, \quad (3.1)$$

where $U(\tau, 0)$ denotes the internal potential energy of the system in the absence of the external field \mathbf{E} (if the sphere S contains N molecules, then $U(\tau, 0) = U_{N_S}$ is the potential energy resulting from interaction of the latter), A_S being the scalar electric polarizability of the sphere S .

Substituting (3.1) in (2.3) we obtain

$$Z(\tau, E_S) = J e^{\frac{A_S E_S^2}{2kT}} \sum_{n=0}^{\infty} \frac{1}{n!} \left(\frac{E_S}{kT} \right)^n \langle (\mathbf{M}_S \cdot \mathbf{e})^n \rangle, \quad (3.2)$$

where

$$\langle (\mathbf{M}_S \cdot \mathbf{e})^n \rangle = \frac{1}{J} \int (\mathbf{M}_S \cdot \mathbf{e})^n e^{-\frac{U(\tau, 0)}{kT}} d\tau, \quad (3.3)$$

and

$$J = \int e^{-\frac{U(\tau, 0)}{kT}} d\tau. \quad (3.4)$$

Relation (3.3) gives the mean statistical value of the n -th power of $(\mathbf{M}_S \cdot \mathbf{e})$ when the field \mathbf{E} is absent, that is, when all orientations of \mathbf{M}_S with respect to \mathbf{e} are equally probable; hence, on averaging and accounting for isotropic conditions, we may write

$$\langle (\mathbf{M}_S \cdot \mathbf{e})^m \rangle = \begin{cases} \frac{1}{2n+1} \langle M_S^{2n} \rangle & \text{for } m = 2n \\ 0 & \text{for } m = 2n + 1 \end{cases}. \quad (3.5)$$

Hence, the configurational partition function (3.2) takes the form

$$Z(\tau, E_S) = J e^{\frac{A_S E_S}{2kT}} \sum_{n=0}^{\infty} \frac{1}{(2n)!(2n+1)} \left(\frac{E_S}{kT}\right)^{2n} \langle M_S^{2n} \rangle, \quad (3.2a)$$

and eq. (2.2) yields

$$\langle \mathbf{M}_S \cdot \mathbf{e} \rangle_E = A_S E_S + \frac{\sum_{n=0}^{\infty} \frac{1}{(2n+1)!(2n+3)} \left(\frac{E_S}{kT}\right)^{2n+1} \langle M_S^{2n+2} \rangle}{\sum_{n=0}^{\infty} \frac{1}{(2n+1)!} \left(\frac{E_S}{kT}\right)^{2n} \langle M_S^{2n} \rangle}. \quad (3.6)$$

With (2.1) and (3.6) we may write the dielectric permittivity as the following general formula:

$$\epsilon - 1 = \frac{4\pi}{V_S} \frac{\partial}{\partial E} \left[\frac{A_S E_S + \sum_{n=0}^{\infty} \frac{1}{(2n+1)!(2n+3)} \left(\frac{E_S}{kT}\right)^{2n+1} \langle M_S^{2n+2} \rangle}{\sum_{n=0}^{\infty} \frac{1}{(2n+1)!} \left(\frac{E_S}{kT}\right)^{2n} \langle M_S^{2n} \rangle} \right]. \quad (3.7)$$

In the case of a weak electric field, eq. (3.7) yields the following formula for the dielectric constant:

$$\epsilon - 1 = \frac{4\pi}{V_S} \left(A_S + \frac{\langle M_S^2 \rangle}{3kT} \right) \left(\frac{\partial E_S}{\partial E} \right)_{E=0}. \quad (3.8)$$

With regard to (3.8), eq. (3.7) yields the following expression for the variation of the dielectric constant determining the effect of dielectric saturation produced within a polar dielectric by a strong DC electric field:

$$\Delta \varepsilon_{sat}^{*e} = -\frac{4\pi}{V_S} \left(\frac{5 \langle M_S^2 \rangle^2 - 3 \langle M_S^4 \rangle}{30 k^3 T^3} - \frac{70 \langle M_S^2 \rangle^3 - 63 \langle M_S^2 \rangle \langle M_S^4 \rangle + 9 \langle M_S^6 \rangle}{1512 k^5 T^5} E_S^2 + \dots \right) E_S^2 d(\varepsilon), \quad (3.9)$$

with

$$d(\varepsilon) = \frac{\partial E_S}{\partial E} \left[1 - \left(\frac{\partial f}{\partial \varepsilon} \right)_{\varepsilon'=\varepsilon} \right]^{-1}, \quad (3.9a)$$

and

$$f(\varepsilon) = \frac{4\pi}{V_S} \left(A_S + \frac{\langle M_S^2 \rangle}{3kT} \right) \left(\frac{\partial E_S}{\partial E} \right)_{E=0}; \quad (3.9b)$$

here, ε' denotes the dielectric constant of the substance in a strong electric field.

Assuming Fröhlich's model (1949) we have

$$\frac{4\pi}{V_S} A_S \left(\frac{\partial E_S}{\partial E} \right)_{E=0} = \varepsilon_\infty - 1; \quad E_S = \frac{3\varepsilon}{2\varepsilon + \varepsilon_\infty} E$$

and eq. (3.8) yields Fröhlich's formula for the static dielectric constant for small field strengths:

$$\varepsilon - \varepsilon_\infty = \frac{4\pi}{V_S} \frac{3\varepsilon}{2\varepsilon + \varepsilon_\infty} \frac{\langle M_S^2 \rangle}{3kT}, \quad (3.10)$$

and eq. (3.9) take the form

$$\Delta \varepsilon_{sat}^{*e} = \frac{4\pi}{V_S} \frac{3\varepsilon^2}{2\varepsilon^2 + \varepsilon_\infty^2} \left(\frac{3\varepsilon}{2\varepsilon + \varepsilon_\infty} \right)^2 \left[\frac{3 \langle M_S^4 \rangle - 5 \langle M_S^2 \rangle^2}{30 k^3 T^3} E^2 + \left(\frac{\varepsilon 3}{2\varepsilon + \varepsilon_\infty} \right)^2 \frac{9 \langle M_S^6 \rangle - 63 \langle M_S^2 \rangle \langle M_S^4 \rangle + 70 \langle M_S^2 \rangle^3}{1512 k^5 T^5} E^4 + \dots \right], \quad (3.11)$$

where ε_∞ is the high frequency dielectric constant of the medium.

We now proceed to the microscopic interpretation of the result obtained. Assuming the sphere S to contain N_S molecules, we have

$$A_S = \sum_{q=1}^{N_S} a_S^{(q)}, \quad \mathbf{M}_S = \sum_{q=1}^{N_S} \mathbf{m}_S^{(q)}, \quad (3.12)$$

where $a_S^{(q)}$ denotes the electric polarizability of the q -th molecule within the sphere S , and $\mathbf{m}_S^{(q)}$ is its electric moment. As all the molecules are of the same species and as none of them (except for a small number on the surface of the sphere) is in any way

distinguishable from the rest, we may, in determining the position of an arbitrary molecule, write, by (3.12),

$$\langle A_S \rangle = N_S a_S; \langle M_S^{2n+2} \rangle = N_S \mu_S^{2n+2} \left\langle \sum_{q=1}^{N_S} \cos \Theta_{pq} \left(\sum_{r=1}^{N_S} \sum_{s=1}^{N_S} \cos \Theta_{rs} \right)^n \right\rangle, \quad (3.13)$$

here, μ_S is the value of the permanent electric moment of the molecule within the sphere S , and Θ_{pq} is the angle between the electric moments of molecules p and q .

Finally, by (3.13), we may write eqs. (3.7), (3.8) and (3.9) in the form:

$$\varepsilon - 1 = 4\pi \frac{N_S}{V_S} \frac{\partial}{\partial E} \left[a_S E_S + \sum_{n=0}^{\infty} \frac{\mu_S}{(2n+1)!(2n+3)} \left(\frac{\mu_S E_S}{kT} \right)^{2n+1} \left\langle \sum_{q=1}^{N_S} \cos \Theta_{pq} \left(\sum_{r=1}^{N_S} \sum_{s=1}^{N_S} \cos \Theta_{rs} \right)^n \right\rangle \right] + \frac{\sum_{n=0}^{\infty} \frac{1}{(2n+1)!} \left(\frac{\mu_S E_S}{kT} \right)^{2n} \left\langle \left(\sum_{r=1}^{N_S} \sum_{s=1}^{N_S} \cos \Theta_{rs} \right)^n \right\rangle}{\left[\right]}, \quad (3.14)$$

and

$$\varepsilon - 1 = 4\pi \frac{N_S}{V_S} \left(a_S + \frac{\mu_S^2}{3kT} R_P \right) \left(\frac{\partial E_S}{\partial E} \right)_{E=0}, \quad (3.15)$$

$$\Delta \varepsilon_{sat}^{*e} = (\Delta \varepsilon_{sat})_{qd} \left[R_S - \frac{10}{63} \left(\frac{\mu_S E_S}{kT} \right)^2 R_S^{(1)} + \dots \right], \quad (3.16)$$

where

$$(\Delta \varepsilon_{sat})_{qd} = -12 \pi \frac{N_S}{V_S} \frac{\mu_S^4}{45k^3 T^3} d(\varepsilon) E_S^2, \quad (3.17)$$

and

$$R_P = \left\langle \sum_{q=1}^{N_S} \cos \Theta_{pq} \right\rangle, \\ R_S = \frac{1}{2} \left[5 \left\langle \sum_{q=1}^{N_S} \cos \Theta_{pq} \right\rangle \left\langle \sum_{r=1}^{N_S} \sum_{s=1}^{N_S} \cos \Theta_{rs} \right\rangle - 3 \left\langle \sum_{q=1}^{N_S} \sum_{r=1}^{N_S} \sum_{s=1}^{N_S} \cos \Theta_{pq} \cos \Theta_{rs} \right\rangle \right],$$

$$\begin{aligned}
 R_S^{(1)} = \frac{1}{16} & \left[70 \left\langle \sum_{q=1}^{N_S} \cos \theta_{pq} \right\rangle \left\langle \sum_{r=1}^{N_S} \sum_{s=1}^{N_S} \cos \theta_{rs} \right\rangle \left\langle \sum_{t=1}^{N_S} \sum_{u=1}^{N_S} \cos \theta_{tu} \right\rangle - \right. \\
 & - 63 \left\langle \sum_{q=1}^{N_S} \cos \theta_{pq} \right\rangle \left\langle \sum_{r=1}^{N_S} \sum_{s=1}^{N_S} \sum_{t=1}^{N_S} \sum_{u=1}^{N_S} \cos \theta_{rs} \cos \theta_{tu} \right\rangle + \\
 & \left. + 9 \left\langle \sum_{q=1}^{N_S} \sum_{r=1}^{N_S} \sum_{s=1}^{N_S} \sum_{t=1}^{N_S} \sum_{u=1}^{N_S} \cos \theta_{pq} \cos \theta_{rs} \cos \theta_{tu} \right\rangle \right]. \quad (3.18)
 \end{aligned}$$

The relation (3.17) determines the so-called quadratic dielectric saturation effect in a polar substance. The second (and following) terms within the brackets in the general formula (3.16) determine the departure from the quadratic dielectric saturation effect as observed experimentally by Kautzsch (1929). The magnitudes R_p , R_S and $R_S^{(1)}$ account for the interaction of the N_S molecules in the dielectric; we denote them as correlation factors.

For Onsager's (1936) model we obtain

$$\left. \begin{aligned}
 a_S &= \left(\frac{\epsilon_\infty + 2}{3} \right) \left(\frac{2\epsilon + 1}{2\epsilon + \epsilon_\infty} \right) a_0; \quad \mu_S = \left(\frac{\epsilon_\infty + 2}{3} \right) \left(\frac{2\epsilon + 1}{2\epsilon + \epsilon_\infty} \right) \mu_0, \\
 E_S &= \frac{3\epsilon}{2\epsilon + 1} E; \quad d(\epsilon) = \frac{(2\epsilon + \epsilon_\infty)^2}{3(2\epsilon^2 + \epsilon_\infty^2)} \left(\frac{3\epsilon}{2\epsilon + 1} \right)^2,
 \end{aligned} \right\} \quad (3.19)$$

where ϵ_∞ is the high-frequency dielectric constant of the substance, i. e.

$$\frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} = \frac{4\pi N_S}{3 V_S} a_0, \quad (3.20)$$

and a_0 and μ_0 denote the electric polarizability and the permanent electric moment of an isolated molecule. Now eqs. (3.15) — (3.17) take the form:

$$\epsilon - \epsilon_\infty = 4\pi \frac{N_S}{V_S} \frac{3\epsilon}{2\epsilon + \epsilon_\infty} \cdot \left(\frac{\epsilon_\infty + 2}{3} \right)^2 \frac{\mu_0^2}{3kT} R_P, \quad (3.21)$$

and

$$\Delta \epsilon_{sat}^{*e} = (\Delta \epsilon_{sat}^e)_{qd} \left[R_S - \frac{10}{63} \left(\frac{3\epsilon}{2\epsilon + \epsilon_\infty} \right)^2 \left(\frac{\epsilon_\infty + 2}{3} \right)^2 \left(\frac{\mu_0 E}{kT} \right)^2 R_S^{(1)} + \dots \right], \quad (3.22)$$

with

$$(\Delta \epsilon_{sat}^e)_{qd} = -12\pi \frac{N_S}{V_S} \frac{3\epsilon^2}{2\epsilon^2 + \epsilon_\infty^2} \left(\frac{3\epsilon}{2\epsilon + \epsilon_\infty} \right)^2 \left(\frac{\epsilon_\infty + 2}{3} \right)^4 \frac{\mu_0^4}{45 k^3 T^3} E^2. \quad (3.23)$$

When the induced polarization is neglected, ϵ_∞ being taken equal to 1, eqs. (3.21) and (3.22) reduce to

$$\epsilon - 1 = 4\pi \frac{N_S}{V_S} \frac{3\epsilon}{2\epsilon + 1} \frac{\mu_0^2}{3kT} R_P, \quad (3.24)$$

and

$$\Delta \varepsilon_{sat}^{*e} = 3 (\Delta \varepsilon_{sat}^e)'_{qd} \left[R_S - \frac{10}{63} \left(\frac{3\varepsilon}{2\varepsilon + 1} \right)^2 \left(\frac{\mu_0 E}{kT} \right)^2 R_S^{(1)} + \dots \right], \quad (3.25)$$

where

$$(\Delta \varepsilon_{sat}^e)'_{qd} = -4\pi \frac{N_S}{V_S} \frac{3\varepsilon^2}{2\varepsilon^2 + 1} \left(\frac{3\varepsilon}{2\varepsilon + 1} \right)^2 \frac{\mu_0^4}{45 k^3 T^3} E^2, \quad (3.26)$$

a formula first derived by Van Vleck (1937).

In the formulas derived previously, the correlation factors R_P , R_S , $R_S^{(1)}$ given in general terms by eq. (3.18) remain to be calculated in special cases:

(i) In extremely dilute systems we may assume zero interaction ($U_N = 0$); then

$$R_P = R_S = R_S^{(1)} = 1 \quad (3.27)$$

and eqs. (3.15) — (3.25) hold for polar gases. In this case eqs. (3.21) and (3.24) yield the well-known Onsager formula (1936) for the static dielectric constant of a polar substance.

(ii) Concentration is considerable, yet at a given moment the molecules interact pairwise only, each molecule having no more than one neighbour in its nearest vicinity. Thus, our system is a set of momentary pairs. In this case eqs. (3.18) assume the form:

$$\begin{aligned} R_P &= 1 + \langle \cos \Theta_{12} \rangle, \\ R_S &= 1 - 3 \left(\langle \cos^2 \Theta_{12} \rangle - \frac{1}{3} \right) + (4 + 5 \langle \cos \Theta_{12} \rangle) \langle \cos \Theta_{12} \rangle, \\ R_S^{(1)} &= 1 - 9 \left(\langle \cos^2 \Theta_{12} \rangle - \frac{1}{3} \right) + 3(4 + 7 \langle \cos \Theta_{12} \rangle) \langle \cos \Theta_{12} \rangle + \\ &+ \frac{1}{4} (70 \langle \cos \Theta_{12} \rangle^3 - 63 \langle \cos \Theta_{12} \rangle \langle \cos^2 \Theta_{12} \rangle + 9 \langle \cos^3 \Theta_{12} \rangle). \end{aligned} \quad (3.28)$$

Thus, our problem reduces to that of computing integrals of the following type:

$$\langle \cos^n \Theta_{12} \rangle = \frac{\int \cos^n \Theta_{12} e^{-\frac{U_2}{kT}} d\tau_1 d\tau_2}{\int e^{-\frac{U_2}{kT}} d\tau_1 d\tau_2}, \quad (3.29)$$

where the interaction energy of a pair of molecules is of the form

$$\begin{aligned} U_2 &= U(r) - \frac{\mu_0^2}{r^3} (3 \cos \Theta_1 \cos \Theta_2 - \cos \Theta_{12}) - \\ &- \frac{a_0 \mu_0^2}{2r^6} (3 \cos^2 \Theta_1 + 3 \cos^2 \Theta_2 + 2), \end{aligned} \quad (3.29a)$$

and the cosine of the angle formed by the dipole axes of the two neighbouring molecules is given by

$$\cos \Theta_{12} = \cos \Theta_1 \cos \Theta_2 + \sin \Theta_1 \sin \Theta_2 \cos (\varphi_2 - \varphi_1), \quad (3.29b)$$

Θ_1 and Θ_2 being the angles between the direction of the axis \mathbf{r} joining the centers of dipoles 1 and 2 and the axes of both dipoles, respectively, $\varphi = \varphi_2 - \varphi_1$ being the azimuth.

Because of the involved nature of U_2 , integrals (3.29) can be computed only approximately (viz. F. E. Harris and B. J. Alder, 1953b, and also A. D. Buckingham and J. A. Pople, 1955, 1956).

In computing (3.29) we apply A. Piekara's method (1937, 1939, 1950) consisting in the assumption of a specialized interaction model resulting in a simplification of eqs. (3.29 a, b) and hence facilitating computation of (3.29). According to A. Piekara, with regard to its chemical structure a molecule may form either a nearly parallel or nearly antiparallel momentary pair with its next neighbour; thus, when the dipoles tend towards a parallel array one may assume $\Theta_1 = 0$, $\Theta_2 = \Theta$ (the angle between two dipoles), which yields $\cos \Theta_{12} = \cos \Theta$ and the dipole-dipole interaction energy is

$$U_2 = W_0 - W \cos \Theta \quad (3.30)$$

with $W = 2 \frac{\mu^2}{r^3}$ (the permanent dipole-induced dipole interaction is neglected).

On the other hand, in the case of nearly antiparallel coupling we put $\Theta_1 = \Theta_2 = 90^\circ$, $\varphi = 180^\circ - \Theta$ ($180^\circ - \Theta$ being the angle between two dipoles) and the dipole-dipole interaction energy is given by the same expression (3.30) with a different value of W and with $\cos \Theta_{12} = -\cos \Theta$.

For both cases we have

$$\langle \cos^n \Theta_{12} \rangle = (\pm 1)^n L_n(y), \quad (3.31)$$

where

$$L_n(y) = \frac{\int_0^\pi \cos^n \Theta e^{y \cos \Theta} \sin \Theta d\Theta}{\int_0^\pi e^{y \cos \Theta} \sin \Theta d\Theta}. \quad (3.32)$$

$L_n(y)$ denote functions introduced by A. Piekara (1939b), which are expressed in terms of the Langevin function $L(y)$, with $y = \frac{W}{kT}$ denoting the coupling energy of the molecular dipoles in kT units. In general, integration of (3.32) yields

$$L_n(y) = \sum_{k=0}^n \frac{n!}{(n-k)!} \left(-\frac{1}{y}\right)^k \left[\frac{e^y + (-1)^{n-k-1} e^{-y}}{e^y - e^{-y}} \right] \quad (3.32a)$$

whence

$$\begin{aligned}
 L_0 &= 1, L_1 = L(y) = \coth y - \frac{1}{y}, \\
 L_2 &= 1 - 2 \frac{L}{y}, L_3 = L - \frac{2}{y} \left(1 - 3 \frac{L}{y} \right), \\
 L_4 &= 1 - 4 \frac{L}{y} + \frac{8}{y^2} \left(1 - 3 \frac{L}{y} \right); \dots
 \end{aligned} \tag{3.32b}$$

By (3.31) and (3.32b), eq. (3.28) may be rewritten as follows:

$$\begin{aligned}
 R_p &= 1 \pm L, \\
 R_S &= 1 - 2 \left(1 - 3 \frac{L}{y} \right) + (5L \pm 4)L, \\
 R_S^{(1)} &= 1 - 6 \left(1 - 3 \frac{L}{y} \right) + 3(7L \pm 4)L + \\
 &\pm \frac{1}{2} \left[35L^3 + 9 \left(7 \frac{L}{y} - 3 \right) L + \frac{9}{y} \left(3 \frac{L}{y} - 1 \right) \right].
 \end{aligned} \tag{3.33}$$

Thus, we have determined A. Piekara's correlation factors (1937a, 1939b, 1950): R_p is the factor corresponding to dielectric polarisation and R_S —that corresponding to dielectric saturation. In the above expressions, the upper signs refer to nearly parallel coupling, whereas the lower ones correspond to the case of nearly antiparallel coupling. A. Piekara has shown that the correlation factors R_p and R_S account well for experimental data: this is especially important in the case of the factor R_S , which changes its sign when the interaction energy of a pair of almost antiparallel dipoles assumes a critical value, thus accounting theoretically for the positive dielectric saturation effect resulting from experiment.

4. On the refractive index of a dense medium subjected to deformation in an electric or magnetic field

A material medium undergoing the effect of a light wave \mathbf{E}^o and that of a strong electric field \mathbf{E} forming the angle Ω_E with the vector \mathbf{E}^o is subjected to electro-optical deformation (apart from mechanical deformations). The total potential energy of the system in the state described above may be expressed (in tensor notation) as follows:

$$\begin{aligned}
 U(\tau, E_S^o, E_S) &= U(\tau, 0) - M_\sigma E_\sigma - \frac{1}{2!} (A_{\sigma\tau}^o E_\sigma^o E_\tau^o + A_{\sigma\tau}^e E_\sigma E_\tau) + \\
 &- \frac{1}{3!} (B_{\sigma\tau\nu}^{oo} E_\sigma^o E_\tau^o E_\nu^o + 3 B_{\sigma\tau\nu}^{oe} E_\sigma^o E_\tau^o E_\nu + \dots) + \\
 &- \frac{1}{4!} (C_{\sigma\tau\nu\varrho}^{oo} E_\sigma^o E_\tau^o E_\nu^o E_\varrho^o + 6 C_{\sigma\tau\nu\varrho}^{oe} E_\sigma^o E_\tau^o E_\nu E_\varrho + \dots) + \dots,
 \end{aligned} \tag{4.1}$$

where $U(\tau, 0)$ denotes the internal potential energy of the system, M_σ — the electric moment of the macroscopic sphere S , $A_{\sigma\tau}^e$ and $A_{\sigma\tau}^o$ — the respective electric and optical polarizability tensors of the sphere S , $B_{\sigma\tau\nu}^{oe}$ and $C_{\sigma\tau\nu\rho}^{oe}$ — the tensors of electro-optical non-linear deformation of the sphere S ; the summation indices take the values 1, 2, 3. M_σ , $A_{\sigma\tau}^e$, $A_{\sigma\tau}^o$, $B_{\sigma\tau\nu}^{oe}$ and $C_{\sigma\tau\nu\rho}^{oe}$ are tensors symmetrical in all indices.

On substituting (4.1) in (2.6), expanding in powers of E_S^0 and E_S and isotropically averaging, we obtain

$$\begin{aligned} Z(\tau, E_s^o, E_s) = & J \left\langle 1 + \frac{\delta_{\sigma\tau}}{3! kT} \left[\left(A_{\sigma\tau}^e + \frac{M_\sigma M_\tau}{kT} \right) E_s^2 + A_{\sigma\tau}^o E_s^{o2} \right] + \right. \\ & + \frac{1}{5! kT} [2(2 - \cos^2 \Omega_E) \delta_{\sigma\tau} \delta_{\nu\rho} + (3 \cos^2 \Omega_E - 1) (\delta_{\sigma\tau} \delta_{\nu\rho} + \delta_{\sigma\rho} \delta_{\tau\nu})] \times \\ & \left. \times \left[C_{\sigma\tau\nu\rho}^{oe} + \frac{1}{kT} \left(A_{\sigma\tau}^o A_{\nu\rho}^e + 2B_{\sigma\tau\nu}^{oe} M_\rho + \frac{A_{\sigma\tau}^o M_\nu M_\rho}{kT} \right) \right] E_S^{o2} E_S^2 + \dots \right\rangle, \end{aligned} \quad (4.2)$$

where

$$\delta_{\sigma\tau} = \begin{cases} 1 & \text{for } \sigma = \tau \\ 0 & \text{for } \sigma \neq \tau \end{cases} \quad (4.3)$$

By (4.2), eqs. (2.5) and (2.4) yield the general formula for the optical refractive index of a dense medium:

$$\begin{aligned} n^2 - 1 = & \frac{4\pi}{V_S} \frac{\partial E_S^o}{\partial E^o} \left\{ \frac{1}{3} \langle A_{\sigma\sigma}^o \rangle \left(1 - \frac{E_S^2}{3! kT} \langle A_{\tau\tau}^e + \frac{1}{kT} M_\tau M_\tau \rangle \right) + \right. \\ & + \frac{4E_S^2}{5!} \left\langle (2 - \cos^2 \Omega_E) \left[C_{\sigma\sigma\tau\tau}^{oe} + \frac{1}{kT} \left(2B_{\sigma\sigma\tau}^{oe} M_\tau + A_{\sigma\sigma}^e A_{\tau\tau}^o + \frac{A_{\sigma\sigma}^o M_\tau M_\tau}{kT} \right) \right] + \right. \\ & \left. \left. + (3 \cos^2 \Omega_E - 1) \left[C_{\sigma\sigma\sigma\tau}^{oe} + \frac{1}{kT} \left(2B_{\sigma\sigma\sigma}^{oe} M_\tau + A_{\sigma\sigma}^e A_{\sigma\tau}^o + \frac{A_{\sigma\sigma}^o M_\sigma M_\tau}{kT} \right) \right] \right\rangle + \dots \right\}. \end{aligned} \quad (4.4)$$

Similarly, a formula accounting for the effect of a magnetic field on the refractive index may be obtained; in particular, for a diamagnetic dense medium we have:

$$\begin{aligned} n^2 - 1 = & \frac{4\pi}{V_S} \frac{\partial E_S^o}{\partial E^o} \left\{ \frac{1}{3} \langle A_{\sigma\sigma}^o \rangle \left(1 - \frac{H_S^2}{3! kT} \langle A_{\tau\tau}^m \rangle \right) + \right. \\ & + \frac{4H_S^2}{5!} \left\langle (2 - \cos^2 \Omega_H) \left(C_{\sigma\sigma,\tau\tau}^{om} + \frac{A_{\sigma\sigma}^m A_{\tau\tau}^o}{kT} \right) + \right. \\ & \left. \left. + (3 \cos^2 \Omega_H - 1) \left(C_{\sigma\tau,\sigma\tau}^{om} + \frac{A_{\sigma\tau}^m A_{\sigma\tau}^o}{kT} \right) \right\rangle + \dots \right\}, \end{aligned} \quad (4.5)$$

where $A_{\sigma\tau}^m$ is the diamagnetic polarizability tensor of a diamagnetic sphere S , and $C_{\sigma\tau,\nu\rho}^{om}$ is that of the magneto-optical non-linear deformation of the latter;

Ω_H denotes the angle formed by the light wave vector \mathbf{E}^o and the magnetic field vector \mathbf{H} . The tensor $C_{\sigma\tau,\nu\varrho}^{om}$ will be symmetrical in the separate pairs of indices σ, τ and ν, ϱ .

With the sphere S containing N_S molecules of the same species, we may write

$$\begin{aligned} M_\sigma &= \sum_{q=1}^{N_S} \mu_\sigma^{(q)}, & A_{\sigma\tau} &= \sum_{q=1}^{N_S} a_{\sigma\tau}^{(q)}, \\ B_{\sigma\tau\nu} &= \sum_{q=1}^{N_S} b_{\sigma\tau\nu}^{(q)}, & C_{\sigma\tau\nu\varrho} &= \sum_{q=1}^{N_S} c_{\sigma\tau\nu\varrho}^{(q)} \end{aligned} \quad (4.6)$$

here, $\mu_\sigma^{(q)}$, $a_{\sigma\tau}^{(q)}$, $b_{\sigma\tau\nu}^{(q)}$ and $c_{\sigma\tau\nu\varrho}^{(q)}$ are the respective tensors referring to the q -th molecule within the macroscopic sphere S .

Let us attach a molecular coordinate system (X_i , $i = 1, 2, 3$) to each molecule within the sphere S , and let us transform the tensor components (4.6) from the external (X_σ , $\sigma = 1, 2, 3$) to the molecular system according to the transformation formula

$$T_{\sigma\tau\nu\varrho} = \sum_{ijkl} \omega_{\sigma i} \omega_{\tau j} \omega_{\nu k} \omega_{\varrho l} T'_{ijkl}, \quad (4.7)$$

with the assumption that the systems (X_σ) and (X_i) are rectangular, $\omega_{\sigma i}$, $\omega_{\tau j}$, ... representing the cosines of the angles formed by the axes X_σ and X_i . By (4.6) and (4.7) and proceeding as in the case of eq. (3.13), we may rewrite (4.4) and (4.5) as follows (assuming the axes of the molecular system attached to the molecule coincide with the principle axes of the latter):

$$\begin{aligned} \frac{n^2 - 1}{n^2 + 2} &= \frac{4\pi N_S}{3 V_S} \left\{ \frac{1}{3} \sum_i a_{ii}^o + \frac{1}{30} \sum_{ij} \left[(3 \cos^2 \Omega_E - 1) \left(c_{ijij}^{oe} + \frac{2b_{ijij}^{oe} \mu_j}{kT} \left\langle \sum_{q=1}^{N_S} \omega_{ij}^{(pq)} \right\rangle + \right. \right. \right. \\ &+ \frac{2a_{ii}^o a_{jj}^o}{3 kT} \left\langle \sum_{q=1}^{N_S} (3\omega_{ij}^{(pq)} \omega_{ij}^{(pq)} - 1) \right\rangle + \frac{2a_{ii}^o \mu_j^2}{3 k^2 T^2} \left\langle \sum_{q=1}^{N_S} \sum_{r=1}^{N_S} (3\omega_{ij}^{(pq)} \omega_{ij}^{(pr)} - \omega_{ij}^{(qr)}) \right\rangle \left. \left. \left. \right) + \right. \right. \\ &\left. \left. + (2 - \cos^2 \Omega_E) \left(c_{ijij}^{oe} + \frac{2b_{ijij}^{oe} \mu_j}{kT} \left\langle \sum_{q=1}^{N_S} \omega_{ij}^{(pq)} \right\rangle \right) \right] E_S^2 + \dots \right\}, \end{aligned} \quad (4.8)$$

and

$$\begin{aligned} \frac{n^2 - 1}{n^2 + 2} &= \frac{4\pi N_S}{3 V_S} \left\{ \frac{1}{3} \sum_i a_{ii}^o + \frac{1}{30} \sum_{ij} \left[(2 - \cos^2 \Omega_H) c_{ii,jj}^{om} + \right. \right. \\ &\left. \left. + (3 \cos^2 \Omega_H - 1) \left(c_{ij,ij}^{om} + \frac{2a_{ii}^o a_{jj}^o}{3 kT} \left\langle \sum_{q=1}^{N_S} (3\omega_{ij}^{(pq)} \omega_{ij}^{(pq)} - 1) \right\rangle \right) \right] H_S^2 + \dots \right\}, \end{aligned} \quad (4.9)$$

where $\omega_{ij}^{(pq)}$ is the cosine of the angle formed by axes $X_i^{(p)}$ (of the system attached to the p -th molecule) and axes $X_j^{(q)}$ (of that attached to the q -th molecule).

On effecting the transition from (4.4) and (4.5) to (4.8) and (4.9) we had assumed a Lorentz field as appropriate for the light wave E_S^0 within the sphere S , i. e.

$$E_S^0 = \frac{n^2 + 2}{3} E^0.$$

The Kerr constant is defined as

$$K^* = \frac{n_{\parallel} - n_{\perp}}{n} \frac{1}{E^2} = \frac{(n^2 + 2)^2}{6n^2} \left(\frac{n_{\parallel}^2 - 1}{n_{\parallel}^2 + 2} - \frac{n_{\perp}^2 - 1}{n_{\perp}^2 + 2} \right) \frac{1}{E^2}, \quad (4.10)$$

where n_{\parallel} and n_{\perp} are the optical refractive indices for a light wave field \mathbf{E}^0 parallel and perpendicular to the electric vector \mathbf{E} .

From (4.8) and (4.10) we obtain the following expression for the Kerr constant of a dense medium:

$$\begin{aligned} K^* = & \frac{\pi}{15} \frac{N_S}{V_S} \left(\frac{n^2 + 2}{3n} \right)^2 \left(\frac{E_S}{E} \right)^2 \sum_{ij} \left[3c_{ijij}^{oe} - c_{ijij}^{oe} + \right. \\ & + \frac{2\mu_i}{kT} (3b_{jj}^{oe} - b_{ijij}^{oe}) \left\langle \sum_{q=1}^{N_S} \omega_{ii}^{(pq)} \right\rangle + \frac{a_{ii}^e a_{jj}^o}{kT} \left\langle \sum_{q=1}^{N_S} (3\omega_{ij}^{(pq)} \omega_{ij}^{(pq)} - 1) \right\rangle + \\ & \left. + \frac{a_{ii}^o \mu_j^2}{k^2 T^2} \left\langle \sum_{q=1}^{N_S} \sum_{r=1}^{N_S} (3\omega_{ij}^{(pq)} \omega_{ij}^{(pr)} - \omega_{jj}^{(qr)}) \right\rangle \right]. \quad (4.11) \end{aligned}$$

Analogously to the Kerr constant, we shall define a Cotton-Mouton constant by

$$C^* = \frac{n_{\parallel} - n_{\perp}}{n} \frac{1}{H^2} = \frac{(n^2 + 2)^2}{6n^2} \left(\frac{n_{\parallel}^2 - 1}{n_{\parallel}^2 + 2} - \frac{n_{\perp}^2 - 1}{n_{\perp}^2 + 2} \right) \frac{1}{H^2}$$

and eq. (4.9) yields the Cotton-Mouton constant of a dense medium:

$$\begin{aligned} C^* = & \frac{\pi}{15} \frac{N_S}{V_S} \left(\frac{n^2 + 2}{3n} \right)^2 \left(\frac{H_S}{H} \right)^2 \sum_{ij} \left(3c_{ij,ij}^{om} - c_{ii,jj}^{om} + \right. \\ & \left. + \frac{a_{ii}^m a_{jj}^o}{kT} \left\langle \sum_{q=1}^{N_S} (3\omega_{ij}^{(pq)} \omega_{ij}^{(pq)} - 1) \right\rangle \right). \quad (4.12) \end{aligned}$$

Neglecting deformation terms, we obtain from (4.11) and (4.12) the following relations holding for molecules presenting axial symmetry:

$$K^* = 3\pi \frac{N_S}{V_S} \left(\frac{n^2 + 2}{3n} \right)^2 \left(\frac{E_S}{E} \right)^2 (\Theta_1^{oe} R_{CM} + \Theta_2^{oe} R_K),$$

and

$$C^* = 3\pi \frac{N_S}{V_S} \left(\frac{n^2 + 2}{3n} \right)^2 \left(\frac{H_S}{H} \right)^2 \Theta_1^{om} R_{CM}, \quad (4.13)$$

where

$$\begin{aligned}\Theta_1^{oe} &= \frac{2}{45 kT} (a_{33}^e - a_{11}^e) (a_{33}^o - a_{11}^o); \quad \Theta_2^{oe} = \frac{2}{45 k^2 T^2} (a_{33}^o - a_{11}^o) \mu_S^2, \\ \Theta_1^{om} &= \frac{2}{45 kT} (a_{33}^m - a_{11}^m) (a_{33}^o - a_{11}^o),\end{aligned}\quad (4.14)$$

and the correlation factors:

$$\begin{aligned}R_{CM} &= \frac{1}{2} \left\langle \sum_{q=1}^{N_S} (3 \cos^2 \Theta_{pq} - 1) \right\rangle \\ R_K &= \frac{1}{2} \left\langle \sum_{q=1}^{N_S} \sum_{r=1}^{N_S} (3 \cos \Theta_{pq} \cos \Theta_{pr} - \cos \Theta_{qr}) \right\rangle\end{aligned}\quad (4.15)$$

with Θ_{pq} representing the angle formed by the axis of symmetry of molecule p and that of molecule q .

On assuming A. Piekara's model discussed in §3, eqs. (4.15) yield

$$\begin{aligned}R_{CM} &= 1 + \frac{3}{2} \left(\langle \cos^2 \Theta_{12} \rangle - \frac{1}{3} \right) = 1 + \left(1 - 3 \frac{L}{y} \right), \\ R_K &= 1 + \frac{3}{2} \left(\langle \cos^2 \Theta_{12} \rangle - \frac{1}{3} \right) + 2 \langle \cos \Theta_{12} \rangle = 1 + \left(1 - 3 \frac{L}{y} \right) \pm 2L\end{aligned}\quad (4.16)$$

which are A. Piekara's (1939, 1950) correlation factors appearing in the Kerr and Cotton-Mouton effect theory.

5. On the dielectric constant of a diamagnetic dense medium deformable in electric and magnetic fields

The total potential energy of a system subject to the effect of a strong electric \mathbf{E} and magnetic field \mathbf{H} forming the angle Ω is (apart from mechanical deformations):

$$\begin{aligned}U(\tau, E_S, H_S) &= U(\tau, 0) - M_\sigma E_\sigma - \frac{1}{2!} (A_{\sigma\tau}^e E_\sigma E_\tau + A_{\sigma\tau}^m H_\sigma H_\tau) - \\ &\quad - \frac{1}{3!} (B_{\sigma\tau\nu}^{ee} E_\sigma E_\tau E_\nu + 3 B_{\sigma,\tau\nu}^{em} E_\sigma H_\tau H_\nu + \dots) - \\ &\quad - \frac{1}{4!} (C_{\sigma\tau\nu\varrho}^{ee} E_\sigma E_\tau E_\nu E_\varrho + 6 C_{\sigma\tau,\nu\varrho}^{em} E_\sigma E_\tau H_\nu H_\varrho + \dots) + \dots,\end{aligned}\quad (5.1)$$

where $U(\tau, 0)$ represents the internal potential energy of the system, M_σ — the electric moment of the macroscopic sphere S , $A_{\sigma\tau}^e$ and $A_{\sigma\tau}^m$ — the tensors of the electric and diamagnetic polarizability of the macroscopic sphere S respectively, $B_{\sigma\tau\nu}^{ee}$, $C_{\sigma\tau\nu\varrho}^{ee}$ —

the electric non linear deformation tensors of the macroscopic sphere S and, finally, $B_{\sigma, \tau \nu}^{em}$ and $C_{\sigma \tau, \nu \rho}^{em}$ — the electro-magnetic non linear deformation tensor. M_{σ} , $A_{\sigma \tau}^e$, $A_{\sigma \tau}^m$, $B_{\sigma \tau}^{ee}$ and $C_{\sigma \tau \nu \rho}^{ee}$ are tensors symmetrical in all indices, $B_{\sigma, \tau \nu}^{em}$ is symmetrical in τ and ν , whilst $C_{\sigma \tau, \nu \rho}^{em}$ is symmetrical in the separate pairs σ, τ and ν, ρ . As above, (5.1) and (2.3) yield

$$\begin{aligned} Z(\tau, E_S, H_S) = & J \left\langle 1 + \frac{\delta_{\sigma \tau}}{3! kT} \left[\left(A_{\sigma \tau}^e + \frac{M_{\sigma} M_{\tau}}{kT} \right) E_S^2 + A_{\sigma \tau}^m H_S^2 \right] + \right. \\ & + \frac{1}{3 \cdot 5! kT} (\delta_{\sigma \tau} \delta_{\nu \rho} + \delta_{\sigma \nu} \delta_{\tau \rho} + \delta_{\sigma \rho} \delta_{\tau \nu}) \left[C_{\sigma \tau \nu \rho}^{ee} + \frac{1}{kT} (3A_{\sigma \tau}^e A_{\nu \rho}^e + 4M_{\sigma} B_{\tau \nu \rho}^{ee}) + \right. \\ & + \frac{M_{\sigma} M_{\tau}}{k^2 T^2} \left(6A_{\nu \rho}^e + \frac{M_{\nu} M_{\rho}}{kT} \right) \left. \right] E_S^4 + \frac{1}{5! kT} [2(2 - \cos^2 \Omega) \delta_{\sigma \tau} \delta_{\nu \rho} + \\ & + (3 \cos^2 \Omega - 1) (\delta_{\sigma \nu} \delta_{\tau \rho} + \delta_{\sigma \rho} \delta_{\tau \nu})] \times \left[C_{\sigma \tau, \nu \rho}^{em} + \frac{1}{kT} (A_{\sigma \tau}^e A_{\nu \rho}^m + 2M_{\sigma} B_{\tau \nu \rho}^{em}) + \right. \\ & \left. + \frac{M_{\sigma} M_{\tau} A_{\nu \rho}^m}{k^2 T^2} \right] E_S^2 H_S^2 + \dots \left. \right\rangle. \end{aligned} \quad (5.2)$$

By (5.2), eqs. (2.1) and (2.2) yield the dielectric permittivity of a dense medium in general form:

$$\begin{aligned} \epsilon - 1 = & \frac{4\pi}{V_S} \frac{\partial E_S}{\partial E} \left\{ \frac{1}{3} \left\langle A_{\sigma \sigma}^e + \right. \right. \\ & + \frac{M_{\sigma} M_{\sigma}}{kT} \left. \right\rangle \left(1 - \frac{1}{3! kT} \left\langle A_{\tau \tau}^m H_S^2 + 3 \left(A_{\tau \tau}^e + \frac{M_{\tau} M_{\tau}}{kT} \right) E_S^2 \right\rangle \right) + \\ & + \frac{4E_S^2}{5!} \left\langle C_{\sigma \sigma \tau \tau}^{ee} + 2C_{\sigma \tau \sigma \tau}^{ee} + \frac{1}{kT} [4M_{\sigma}^e (B_{\sigma \tau \tau}^{ee} + 2B_{\tau \sigma \tau}) + 3(A_{\sigma \sigma}^e A_{\tau \tau}^e + 2A_{\sigma \tau}^e A_{\sigma \tau}^e)] + \right. \\ & + \frac{3}{k^2 T^2} \left(2A_{\sigma \sigma}^e M_{\tau} M_{\tau} + 4A_{\sigma \tau}^e M_{\sigma} M_{\tau} + \frac{1}{kT} M_{\sigma} M_{\tau} M_{\sigma} M_{\tau} \right) \left. \right\rangle + \\ & + \frac{4H_S^2}{5!} \left\langle (2 - \cos^2 \Omega) \left[C_{\sigma \sigma, \tau \tau}^{em} + \frac{2}{kT} M_{\sigma} B_{\sigma, \tau \tau}^{em} + \frac{A_{\sigma \sigma}^m}{kT} \left(A_{\tau \tau}^e + \frac{M_{\tau} M_{\tau}}{kT} \right) \right] + \right. \\ & \left. + (3 \cos^2 \Omega - 1) \left[C_{\sigma \tau, \sigma \tau}^{em} + \frac{2}{kT} M_{\sigma} B_{\tau, \sigma \tau}^{em} + \frac{A_{\sigma \tau}^m}{kT} \left(A_{\sigma \tau}^e + \frac{M_{\sigma} M_{\tau}}{kT} \right) \right] \right\rangle + \dots \left. \right\}. \end{aligned} \quad (5.3)$$

Neglecting the deformation terms with polar molecules presenting axial symmetry (5.3) yields

$$\begin{aligned} \epsilon - 1 = & 4\pi \frac{N_S}{V_S} \frac{\partial E_S}{\partial E} \left[a_S + \frac{\mu_S^2}{3kT} R_P + \frac{3 \cos^2 \Omega - 1}{2} (\Theta_1^{em} R_{CM} + \Theta_2^{em} R_K) H_S^2 + \right. \\ & \left. + (\Theta_1^{ee} R_{CM} + 2\Theta_2^{ee} R_K - \Theta_3^{ee} R_S) E_S^2 \right], \end{aligned} \quad (5.4)$$

where

$$\begin{aligned} \Theta_1^{em} &= \frac{2}{45 k T} (a_{33}^e - a_{11}^e) (a_{33}^m - a_{11}^m); \Theta_2^{em} = \frac{2}{45 k^2 T^2} (a_{33}^m - a_{11}^m) \mu_s^2, \\ \Theta_1^{ee} &= \frac{2}{45 k T} (a_{33}^e - a_{11}^e)^2; \Theta_2^{ee} = \frac{2}{45 k^2 T^2} (a_{33}^e - a_{11}^e) \mu_s^2; \Theta_3^{ee} = \frac{\mu_s^4}{45 k^3 T^3}, \end{aligned} \quad (5.4a)$$

and $a_s = \frac{1}{3} (2 a_{11}^e + a_{33}^e)$ represents the mean electric polarizability of a molecule within the sphere S , the correlation factors R_{CM} and R_K being given by (4.15) and R_P and R_S by (3.18).

For the variation of the dielectric constant in a strong electric field, eq. (5.4) yields

$$\Delta \varepsilon_{sat}^{*e} = 12\pi \frac{N_S}{V_S} (\Theta_1^{ee} R_{CM} + 2\Theta_2^{ee} R_K - \Theta_3^{ee} R_S) d(\varepsilon) E_S^2, \quad (5.5)$$

where $d(\varepsilon)$ is defined by eq. (3.9a).

Similarly, for the variation of the dielectric constant in a strong magnetic field, eq. (5.4) yields:

$$\Delta \varepsilon_{sat}^{*m} = 2\pi \frac{N_S}{V_S} (3 \cos^2 \Omega - 1) (\Theta_1^{em} R_{CM} + \Theta_2^{em} R_K) d(\varepsilon) H_S^2. \quad (5.6)$$

The microscopic method yields identical results for the correlation factors R_P , R_{CM} , R_K and R_S (A. Piekara and S. Kielich, 1957, 1958).

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КРАТКОЕ СОДЕРЖАНИЕ

С. Келих. Семимакроскопическое представление теории нелинейных явлений в диэлектрических жидкостях подвергнутых сильным электрическим и магнитным полям.

Автором построена общая полу-макроскопическая теория нелинейных эффектов молекулярной ориентации, вызываемых в жидкостях сильными электрическими и магнитными полями. Автор дает вычисление отклонения от квадратического эффекта диэлектрического насыщения в сильном электрическом поле для полярных жидкостей с изотропно поляризуемыми молекулами (§ 3). Затем дается вывод общих выражений определяющих влияние сильных электрических и магнитных полей на показатель преломления (§ 4) и диэлектрическую проницаемость (§ 5); основываясь на этих выражениях, автор вычисляет постоянные Керра и Коттона—Мутона, а также изменение диэлектрической проницаемости в электрическом и магнитном поле. Молекулярная интерпретация этих результатов приводит к формулам полученным раньше молекулярным методом (см. А. Пекара и С. Келих).

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