

# A NON-LINEAR THEORY OF THE ELECTRIC PERMITTIVITY AND REFRACTIVITY OF DIELECTRIC LIQUIDS IN ELECTRIC AND MAGNETIC FIELDS

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A consistent molecular theory of the non-linear effects of molecular orientation produced in dielectric gases and liquids by electric and magnetic fields is given by the authors. The molar constant of dielectric polarization  $P_M$ , the Cotton-Mouton constant  $C_M$ , the Kerr constant  $K_M$  and the dielectric saturation constant in an electric field  $S_M^{ee}$  and in a magnetic field,  $S_M^{em}$  have been calculated for gases (§ § 3 and 4) and for liquids (§ § 5 and 6). For liquids with molecules possessing axial symmetry, the correlation factors  $R_P$ ,  $R_{CM}$ ,  $R_K$  and  $R_S$  associated with the five constants determining molecular interaction within the liquid have been obtained. In calculating these factors, no special assumptions concerning the nature of the intermolecular forces were introduced. The factors are given in the form of functions of the angle  $\Theta_{pq}$  between the axes of symmetry of the  $p$ -th and that of the  $q$ -th molecule. In the case of dipole pairwise coupling of the molecules, formulas deduced previously by one of the authors and accounting, among others, for the inversion of the dielectric saturation (§ 7), are obtained. Finally, a relation connecting the variation of the dielectric permittivity in a magnetic field,  $\Delta \epsilon_{sat}^m$ , and the Kerr or Cotton-Mouton constant is derived, and the order of magnitude of  $\Delta \epsilon_{sat}^m$  is evaluated.

## 1. Introduction

The present paper is intended to deal with certain phenomena of molecular orientation in dielectric liquids subjected to the effect of external electric and magnetic fields. We shall consider the following phenomena: dielectric polarization and its saturation in an electric and magnetic field, as well as birefringence in an electric and magnetic field (the Kerr effect and Cotton-Mouton effect, respectively).

The theory of dielectric polarisation, the foundations of which, as applied to rarefied media, i. e. gases, vapours and dilute solutions, is due to Debye (1912) has been generalized for condensed media, i. e. gases under high pressures, concentrated solutions and liquids by a number of authors, and fundamental papers have been published by Debye (1935) and Fowler (1935), Onsager (1936), Kirkwood (1939) and Fröhlich (1949). Debye, as well as Fowler, introduce coupling of the molecule

under consideration with the surrounding medium of a quasi-crystalline type. Denoting the energy of coupling by  $W \cos \Theta$ , wherein  $\Theta$  is the angle between the direction momentarily privileged by quasi-crystalline ordering in the environment of the molecule under consideration within the liquid and that of the dipole, the part of the polarisation due to the dipoles is reduced in the ratio  $R_p: 1$ , the reduction factor  $R_p$  being given, for Debye's model, by the relation

$$R_p = 1 - L^2(y), \quad (1.1)$$

with  $y = \frac{W}{kT}$ ,  $W$  denoting the energy of coupling, and  $L$  — Langevin's function of argument  $y$ .

One of us (Piekara 1938) has shown that, in the case of nitrobenzene, coupling with the momentarily nearest molecule plays a greater part than quasi-crystalline coupling with the medium (Debye-Fowler coupling). If coupling with the momentarily nearest molecule of the same kind tends to produce pairs of almost anti-parallel dipoles, then the following relation is obtained for the reduction factor:

$$R_p = 1 - L(y), \quad (1.2)$$

wherein  $y = \frac{W}{kT}$ , and  $W$  denotes the energy of coupling with the nearest molecule.

This relation has also been proved to be correct by Anzelm (1943). Kirkwood applies a macroscopic method to account for short range interactions, and subsequently the method was brought to a high degree of generality by Fröhlich. According to their theory, the mean polarizability of a molecule  $\langle \alpha^e \rangle$  may be written in the form of the sum of the induced polarizability and the mean orientational polarizability:

$$\langle \alpha^e \rangle = a^e + \frac{\mu \mu^*}{3 kT}, \quad (1.3)$$

wherein  $a^e$  denotes the mean polarizability of a molecule in the condensed-medium system,  $\mu$  — its dipole moment when within the medium, and  $\mu^*$  — the moment induced in a macroscopic sphere by fixing the orientation of one of its molecules. If the short range interactions may be neglected, we have  $\mu^* = \mu$  and the Kirkwood-Fröhlich theory yields results in agreement with that of Onsager. In the case of A. Piekara's model of molecular interaction we have

$$\langle \alpha^e \rangle = a^e + \frac{\mu^2}{3 kT} R_p, \quad (1.4)$$

with  $R_p$  given by (1.2). It is the aim of the present paper to calculate  $R_p$  in general terms with the fewest possible assumptions as to the mechanism of molecular interaction and the nature of the forces.

In the second place, the aim of the present paper consists in calculating the dielectric saturation, both in an electric and in a magnetic field.

It will be remembered that the dielectric saturation in an electric field (simply: dielectric saturation) resulting from Debye's theory (1939) had been calculated for polar gases by Herweg (1920) and subsequently measured in ethyl ether by the same author; his results were corroborated by Kautzsch (1928). The effect is to be observed as a fall in the dielectric permittivity on placing the medium within a strong electric field, the direction of which is parallel to that of the A. C. measuring field. The inverse saturation effect consisting in a rise in the dielectric permittivity was found by A. Piekara and B. Piekara (1936) in pure nitrobenzene. A theoretical explanation of the latter, uncommon phenomenon (Piekara 1937a) has been given on the assumption already presented here, namely, that the most effective of molecular interactions is the coupling between the molecule and its momentarily nearest neighbour. With this assumption the following relation is obtained:

$$\langle \alpha^e \rangle = a^e + \frac{\mu^2}{3kT} R_P + 3 (\Theta_1^{ee} R_{CM} + 2 \Theta_2^{ee} R_K - \Theta_3^{ee} R_S + \dots) F^2, \quad (1.5)$$

wherein the term  $-\Theta_3^{ee} R_S = -\frac{\mu^4}{45 k^3 T^3} R_S$  dominates and accounts for saturation.

Assuming for nitrobenzene, as above, that interaction tends to produce approximately anti-parallel pairs of dipoles, we obtain

$$R_S = 6 \frac{L}{\gamma} - (1 + 5L) \cdot (1 - L). \quad (1.6)$$

According to this formula,  $R_S$  changes its sign, becoming negative for  $\gamma > 1.33$ , thus accounting for the inverse saturation effect increasing the electric permittivity of the liquid for sufficiently strong coupling. Recently, the inverse saturation effect has been found in certain liquids other than nitrobenzene Piekara and Chełkowski 1956, Piekara et al. 1957).

Both theory and experiment prove that the reduction factors, in some cases, may take values larger than unity. Therefore it will be more correct to term them "correlation factors", because their appearance in the expressions giving the molar constants accounts for spatial and directional correlations of the molecules.

Generally, for strongly polar liquids the first two terms within the brackets in (1.5) are small as compared to  $-\Theta_3^{ee} R_S$ . The first of them,  $\Theta_1^{ee} R_{CM}$ , is a purely anisotropic term (cf. § 3 and 6) containing the correlation factor  $R_{CM}$  playing an important part in magnetic birefringence, i. e. appearing in the molar Cotton-Mouton constant. The other, namely  $2 \Theta_2^{ee} R_K$ , is a mixed anisotropic-dipolar term; it contains the correlation factor  $R_K$  appearing in electric birefringence, i. e. in the molar Kerr constant. Besides these and the purely dipolar term  $-\Theta_3^{ee} R_S$ , the bracket in (1.5) contains deformation terms accounting for deformation of the molecule in the electric field. The necessity of taking electric deformation into account when considering dielectric saturation had been previously proved by one of us (Piekara 1937b, 1937c). Subsequently, electric deformation was considered by Buckingham in a number of papers (1956). In the present paper the authors consider both electric and magnetic

deformation with simultaneous existence of molecular interaction in the condensed system.

The theory of dielectric saturation has been the subject of a number of papers, amongst others by Booth (1951) and Schellman<sup>1</sup> (1957). The latter author restricts himself to the purely dipolar term which is definitely calculated on the assumption of a specific interaction model, wherein two molecules being the neighbours of the one under consideration do not interact with one another. In the theory presented in this paper the general formulas for the correlation factors have been obtained without making any special assumptions as to the mechanism of molecular interaction; solely concerning the form of the molecules it has been assumed that they may be considered to be axially symmetric.

Dielectric saturation in a magnetic field has not yet been shown to exist in true liquids<sup>2</sup>. Efforts in this direction by A. Piekara and M. Scherer (Piekara and Scherer 1936, Piekara 1936) resulted only in establishing an upper limit of the effect for several liquids. Investigations are being carried out with modern means. The theory of the effect for paramagnetic gases was given by Van Vleck (1932). The authors' theory of dielectric saturation in a magnetic field covers liquid dielectrics, that is, diamagnetic substances. Deformation of the molecules in the magnetic field and molecular interaction in the dense phase are taken into account. The theory gives insight into the connection existing between the effect of dielectric saturation in a magnetic field and birefringence in an electric and magnetic field and thus makes it possible to predict the effect numerically<sup>3</sup>.

Finally, the two remaining effects to be accounted for by the present theory are: birefringence in an electric field (the electro-optical Kerr effect) and in a magnetic field (the Cotton-Mouton effect). The theory of these effects, based on ideas originating in papers by Cotton, Langevin, Debye and Born (Born 1933), applies to gases. However, on passing from the diluted system, e. g. a solution of nitrobenzene in a non-polar solvent, to the condensed one, i. e. to the pure liquid, the molar Kerr constant is found to diminish abruptly, whereas the molar Cotton-Mouton constant rises to almost twice its previous value (strictly 1.75) (Piekara 1939). One of us has given an explanation of this behaviour of the molar constants based on the above mentioned model of molecular interaction in nitrobenzene (Piekara 1947, 1950, 1951). Here it is the authors' aim to calculate the molar constants of both birefringences, accounting for deformation of the molecules in the electric and magnetic field and molecular interaction in the condensed phase, without introducing any special model. Interesting papers on both effects have been published by Buckingham (1956) and Buckingham and Pople (1956).

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<sup>1</sup> One of us (A. P.) expresses his indebtedness to Dr. Schellman for sending him a typed copy of a paper previous to its publication.

<sup>2</sup> In the case of liquid crystals the effect was discovered by Jeżewski (1924, 1926, 1929) and Kast (1924, 1927).

<sup>3</sup> Cf. Piekara and Kielich (1957); quite recently similar results have been obtained by Buckingham (1957).

An account of some of the results of the authors' theory, not comprising, however, molecular deformation, has been published in "Le Journal de Physique et le Radium" (1957).

## 2. General assumptions of the theory

Let us consider a given volume  $V$  of the dielectric containing  $N$  molecules of the same species, the positions and orientations of which are given by the variables  $\tau = \tau(v, \omega)$ ,  $v$  being the positional variables in Cartesian coordinates  $x, y, z$  and  $\omega$  — the orientational variables in Euler's angles  $\vartheta, \varphi, \psi$ . The molecules of our system possess a permanent electrical dipole moment, and are electrically, magnetically and optically anisotropic.

If the system is subjected to the effect of an external electric field  $\mathbf{E}$ , each molecule undergoes the action of electric forces, besides that of molecular forces. Among the latter we distinguish short range and long range forces. In general, the forces of both kinds are of an extremely complex character.

The electric forces comprise the external field  $\mathbf{E}$  and the field arising from polarized molecules in the system. The field considered to consist of the external electric field  $\mathbf{E}$  and of that arising from remote polarised molecules treated as a continuous medium is termed the local electric field. The latter is generally anisotropic. However, the anisotropy may be considered to recede before the directional interaction of the neighbouring molecules. The local field will be therefore assumed isotropic; on the other hand, the treatment of the more important direct mutual molecular interaction is entirely free of simplification.

The molecular forces are themselves strongly dependent on the distances separating the molecules and on their spatial orientation. The significance of these forces for all effects of molecular orientation in condensed systems, e. g. in liquids, is of importance; in perfect gases or in diluted solutions they may be neglected, if the coupling of dissolved molecules with the solvent is not considerable.

The effect of an external electric field is not restricted to producing polarization of the molecules as given by the tensor of electric polarizability ( $a_{ij}^e$ ); moreover, it gives rise to ulterior non-linear electric deformation defined by deformation tensors of higher orders ( $b_{ijk}^{ee}$ ) and ( $c_{ijkl}^{eee}$ ). Such deformation may consist chiefly in a bending of intramolecular bonds causing changes in the polarizability and in the permanent moment of the molecule. The latter may undergo similar deformations in an external magnetic field. Both the electric and magnetic deformations have been taken into account in the present paper, as well as the intermolecular forces already mentioned.

The mathematical treatment of the theory of the effects of molecular orientation will be brought under two headings: in the first place, gases and highly diluted solutions, in which molecular interaction may be neglected, are considered; in the second — condensed systems, composed of mutually interacting molecules, as solutions or pure liquids.

3. Dielectric polarisation and dielectric saturation of a rarefied diamagnetic medium in an electric and magnetic field

Accordingly, we shall first consider a system of  $N$  molecules, wherein the existence of molecular forces of the mutual interaction of the molecules may be neglected. The system is simultaneously subjected to an external electric field  $\mathbf{E}$  and an external magnetic field  $\mathbf{H}$  making a given angle  $\Omega$ .

The potential energy of a molecule of the system under consideration in the fields  $\mathbf{F}$  and  $\mathbf{H}$  may be expressed by the formula

$$\begin{aligned} u(\tau, F, H) = & - \sum_i \mu_i \alpha_i F - \frac{1}{2} \sum_{ij} a_{ij}^e \alpha_i \alpha_j F^2 - \frac{1}{2} \sum_{ij} a_{ij}^m \beta_i \beta_j H^2 - \\ & - \frac{1}{6} \sum_{ijk} b_{ijk}^{ee} \alpha_i \alpha_j \alpha_k F^3 - \frac{1}{2} \sum_{ijk} b_{i,jk}^{em} \alpha_i \beta_j \beta_k F H^2 - \\ & - \frac{1}{24} \sum_{ijkl} c_{ijkl}^{ee} \alpha_i \alpha_j \alpha_k \alpha_l F^4 - \frac{1}{4} \sum_{ijkl} c_{ij,kl}^{em} \alpha_i \alpha_j \beta_k \beta_l F^2 H^2 + \dots \end{aligned} \quad (3.1)$$

wherein  $\mu_i$  denote the components of the permanent moment of the molecule in the system of reference  $x, y, z$  attached to the molecule ( $i = 1, 2, 3$ ),  $a_{ij}^e$  and  $a_{ij}^m$  — the components of the tensors of electric and magnetic polarisability, respectively,  $b_{ijk}^{ee}$ ,  $c_{ijkl}^{ee}$ ,  $b_{i,jk}^{em}$ ,  $c_{ij,kl}^{em}$  — the components of the tensors of electric and electro-magnetic deformation, and  $\alpha_i, \beta_i$  — the cosines of the angles formed by the directions of the axes  $x, y, z$  with those of the fields  $\mathbf{E}$  and  $\mathbf{H}$ ; the indices take the values  $i, j, k, l = 1, 2, 3$ .

The projection of the total electric moment of the molecule on the direction of the field vector  $\mathbf{E}$  is given by

$$m_E^e = - \frac{d u(\tau, F, H)}{d F},$$

or, with regard to (3.1), by

$$\begin{aligned} m_E^e = & \sum_i \mu_i \alpha_i + \sum_{ij} a_{ij}^e \alpha_i \alpha_j F + \frac{1}{2} \sum_{ijk} b_{ijk}^{ee} \alpha_i \alpha_j \alpha_k F^2 + \frac{1}{2} \sum_{ijk} b_{i,jk}^{em} \alpha_i \beta_j \beta_k H^2 + \\ & + \frac{1}{6} \sum_{ijkl} c_{ijkl}^{ee} \alpha_i \alpha_j \alpha_k \alpha_l F^3 + \frac{1}{2} \sum_{ijkl} c_{ij,kl}^{em} \alpha_i \alpha_j \beta_k \beta_l F H^2 + \dots \end{aligned} \quad (3.2)$$

The statistical mean value of the moment  $m_E^e$  of a gaseous medium is given in classical statistical mechanics by the formula

$$\langle m_E^e \rangle_{E,H} = \frac{\int m_E^e e^{-\frac{u(\tau, F, H)}{kT}} d\tau}{\int e^{-\frac{u(\tau, F, H)}{kT}} d\tau} \quad (3.3)$$

wherein  $d\tau$  denotes the volume element in positional and orientational coordinate space.

Substitution of (3.1) and (3.2) in (3.3), expansion and integration yield (cf. Appendices I and II):

$$\begin{aligned} \langle m_E^e \rangle_{E,H} &= \frac{1}{3} \sum_i \left( a_{ii}^e + \frac{\mu_i^2}{kT} \right) F + \\ &+ (\Theta_1^{em} + \Theta_2^{em} + \Delta_1^{em} + 2\Delta_2^{em}) FH^2 + \\ &+ (\Theta_1^{ee} + 2\Theta_2^{ee} - \Theta_3^{ee} + \Delta_1^{ee} + 4\Delta_2^{ee}) F^3 + \dots \end{aligned} \quad (3.4)$$

with

$$\begin{aligned} \Theta_1^{em} &= \frac{3 \cos^2 \Omega - 1}{90 kT} \sum_{ij} (3a_{ij}^e a_{ij}^m - a_{ii}^e a_{jj}^m), \\ \Theta_2^{em} &= \frac{3 \cos^2 \Omega - 1}{90 k^2 T^2} \sum_{ij} (3a_{ij}^m \mu_i \mu_j - a_{ii}^m \mu_j^2), \\ \Delta_1^{em} &= \frac{1}{30} \sum_{ij} [(3 \cos^2 \Omega - 1) c_{ij,ij}^{em} + (2 - \cos^2 \Omega) c_{ii,jj}^{em}], \\ \Delta_2^{em} &= \frac{1}{30 kT} \sum_{ij} [(3 \cos^2 \Omega - 1) \mu_i b_{j,ij}^{em} + (2 - \cos^2 \Omega) \mu_i b_{i,jj}^{em}], \\ \Theta_1^{ee} &= \frac{1}{45 kT} \sum_{ij} (3a_{ij}^e a_{ij}^e - a_{ii}^e a_{jj}^e), \\ \Theta_2^{ee} &= \frac{1}{45 k^2 T^2} \sum_{ij} (3a_{ij}^e \mu_i \mu_j - a_{ii}^e \mu_j^2), \\ \Theta_3^{ee} &= \frac{1}{45 k^3 T^3} \sum_i \mu_i^2 \mu_j^2, \\ \Delta_1^{ee} &= \frac{1}{90} \sum_{ij} (c_{ii,jj}^{ee} + 2 c_{ij,ij}^{ee}), \\ \Delta_2^{ee} &= \frac{1}{90 kT} \sum_{ij} \mu_i (b_{ij,ij}^{ee} + 2b_{ij,jj}^{ee}), \end{aligned} \quad (3.5)$$

$\Omega$  denoting the angle between the vectors  $\mathbf{E}$  and  $\mathbf{H}$ .

We define the statistical mean value of the electric polarisability of the molecule in the fields  $\mathbf{E}$  and  $\mathbf{H}$  as follows:

$$\langle \alpha^e \rangle_{E,H} \equiv \frac{\partial}{\partial F} \langle m_E^e \rangle_{E,H}. \quad (3.6)$$

In particular, the statistical mean value of the electric polarizability of the molecule, in weak measuring fields and without biasing fields  $\mathbf{E}$  and  $\mathbf{H}$ , is

$$\langle \alpha^e \rangle \equiv \left( \frac{\partial}{\partial F} \langle m_E^e \rangle_{E, H} \right)_{\substack{E=0 \\ H=0}} \quad (3.6a)$$

The molar constant of dielectric polarizability is, by definition,

$$PM \equiv \frac{4\pi}{3} N_A \langle \alpha^e \rangle \quad (3.7)$$

with

$$N_A = N_0 \frac{M}{d}$$

being Avogadro's constant,  $N_0$ —the number of molecules per unit volume of the medium,  $M$ —its molecular weight, and  $d$ —the density of the medium.

With regard to definition (3.6a), eq. (3.4) yields

$$\langle \alpha^e \rangle = \frac{1}{3} \sum_i \left( a_{ii}^e + \frac{\mu_i^2}{kT} \right)$$

whence, with regard to (3.7), the following expression is obtained for the molar constant of dielectric polarizability:

$$PM = \frac{4\pi}{3} N_A \frac{1}{3} \sum_i \left( a_{ii}^e + \frac{\mu_i^2}{kT} \right). \quad (3.8)$$

The molar constant of dielectric saturation in an electric field is defined as follows:

$$S_{ee}^M \equiv \frac{4\pi}{3} N_A \frac{\langle \alpha^e \rangle_{E,0} - \langle \alpha^e \rangle}{F^2}. \quad (3.9)$$

The molar constant of dielectric saturation in a magnetic field is defined similarly:

$$S_{em}^M \equiv \frac{4\pi}{3} N_A \frac{\langle \alpha^e \rangle_{0,H} - \langle \alpha^e \rangle}{H^2}. \quad (3.10)$$

These two definitions, together with eq. (3.4) and definition (3.6), yield

$$S_{ee}^M = 4\pi N_A (\Theta_1^{ee} + 2\Theta_2^{ee} - \Theta_3^{ee} + \Lambda_1^{ee} + 4\Lambda_2^{ee}), \quad (3.11)$$

$$S_{em}^M = \frac{4\pi}{3} N_A (\Theta_1^{em} + \Theta_2^{em} + \Lambda_1^{em} + 2\Lambda_2^{em}). \quad (3.12)$$

If variations arising from electrostriction or magnetostriction are not taken into account, the electric permittivity in strong fields  $\mathbf{E}$  and  $\mathbf{H}$  is given by the general formula

$$\varepsilon(E, H) = 1 + 4\pi N_0 \frac{\partial}{\partial E} \langle m_E^e \rangle_{E, H} \quad (3.13)$$



or, with regard to (3.6), by

$$\varepsilon(E, H) = 1 + 4\pi N_0 \langle \alpha^e \rangle_{E, H} \frac{\partial F}{\partial E}. \quad (3.13a)$$

In particular, with zero field strength, the permittivity is

$$\varepsilon_0 = 1 + 4\pi N_0 \langle \alpha^e \rangle \left( \frac{\partial F}{\partial E} \right)_{\substack{E=0 \\ H=0}}. \quad (3.14)$$

Hence, we obtain the variation of the permittivity arising from the saturation effect resulting from a strong electric field applied:

$$\Delta \varepsilon_{sat}^e = \varepsilon(E, 0) - \varepsilon_0 = 3 \frac{d}{M} S_{ee}^M F^2 \frac{\partial F}{\partial E} \left[ 1 - \left( \frac{\partial f}{\partial \varepsilon} \right)_{\varepsilon=\varepsilon_0} \right]^{-1}. \quad (3.15)$$

On the other hand,  $\Delta \varepsilon_{sat}^m$  resulting from a strong magnetic field is

$$\Delta \varepsilon_{sat}^m = \varepsilon(0, H) - \varepsilon_0 = 3 \frac{d}{M} S_{em}^M H^2 \frac{\partial F}{\partial E} \left[ 1 - \left( \frac{\partial f}{\partial \varepsilon} \right)_{\varepsilon=\varepsilon_0} \right]^{-1}, \quad (3.16)$$

here,  $f$  denotes:

$$f = \frac{4\pi}{3} N_0 \sum_i \left( a_{ii}^e + \frac{\mu_i^2}{kT} \right) \left( \frac{\partial F}{\partial E} \right)_{\substack{E=0 \\ H=0}}. \quad (3.17)$$

It is worth noting that the experimental value of the variation of the permittivity differs from  $\Delta \varepsilon_{sat}^e$ , as it represents a superposition of the latter value and of secondary effects resulting from electrostriction and the electrocaloric effect; both these secondary effects are relatively small and have been calculated elsewhere (cf. Piekara, Chetkowski and Kielich (1957)). The same is true of the effect of the magnetic field on the permittivity.

#### 4. Refraction and birefringence in electric and magnetic fields in diamagnetic non-condensed media

The component of the total optical moment of the molecule in the direction of the field of the light wave  $\mathbf{E}^o$ , if deformation in the fields  $\mathbf{E}$  and  $\mathbf{H}$  are taken into account, is given by:

$$\begin{aligned} m_{E^o}^o &= \sum_{ij} a_{ij}^o \gamma_i \gamma_j F^o + \sum_{ijk} b_{ijk}^{oe} \gamma_i \gamma_j \alpha_k F^o F + \\ &+ \frac{1}{2} \sum_{ijkl} c_{ijkl}^{oe} \gamma_i \gamma_j \alpha_k \alpha_l F^o F^2 + \frac{1}{2} \sum_{ijkl} c_{ijkl}^{om} \gamma_i \gamma_j \beta_k \beta_l F^o H^2 + \dots \end{aligned} \quad (4.1)$$

wherein  $a_{ij}^o$  denote the components of the tensor of optical polarizability of the molecule,  $b_{ijk}^{oe}$ ,  $c_{ijkl}^{oe}$  and  $c_{ijkl}^{om}$  — the components of the tensors of electrooptical and magnetooptical deformation,  $\gamma_i$  — the cosines of the angles between the field direction  $\mathbf{E}^o$  and the axes  $x, y, z$ .

The optical polarizability of the molecule in the fields  $\mathbf{E}$  and  $\mathbf{H}$  is defined as follows:

$$\alpha^o \equiv \frac{\partial m_{E^o}^o}{\partial F^o} \quad (4.2)$$

The mean statistical value of  $\alpha^o$  is given by:

$$\langle \alpha^o \rangle_{E, H} = \frac{\int \alpha^o e^{-\frac{u(\tau, F, H)}{kT}} d\tau}{\int e^{-\frac{u(\tau, F, H)}{kT}} d\tau} \quad (4.3)$$

wherein  $u(\tau, F, H)$  is the potential energy of the molecule in the fields  $\mathbf{E}$  and  $\mathbf{H}$ , as defined by (3. 1).

By (4.1), (4.2) and (3.1), eq. (4. 3) yields:

$$\begin{aligned} \langle \alpha^o \rangle_{E, H} = & \frac{1}{3} \sum_i a_{ii}^o + (\Theta_1'^{om} + \Delta_1'^{om}) H^2 + \\ & + (\Theta_1'^{oe} + \Theta_2'^{oe} + \Delta_1'^{oe} + 2 \Delta_2'^{oe}) F^2 + \dots \end{aligned} \quad (4.4)$$

with

$$\begin{aligned} \Theta_1'^{om} &= \frac{3 \cos^2 \Omega_H - 1}{90 k T} \sum_{ij} (3 a_{ij}^o a_{ij}^m - a_{ii}^o a_{jj}^m), \\ \Delta_1'^{om} &= \frac{1}{30} \sum_{ij} [(3 \cos^2 \Omega_H - 1) c_{ij,ij}^{om} + (2 - \cos^2 \Omega_H) c_{ii,jj}^{om}], \\ \Theta_1'^{oe} &= \frac{3 \cos^2 \Omega_E - 1}{90 k T} \sum_{ij} (3 a_{ij}^o a_{ij}^e - a_{ii}^o a_{jj}^e), \\ \Theta_2'^{oe} &= \frac{3 \cos^2 \Omega_E - 1}{90 k^2 T^2} \sum_{ij} (3 a_{ij}^o \mu_i \mu_j - a_{ii}^o \mu_j^2), \\ \Delta_1'^{oe} &= \frac{1}{30} \sum_{ij} [3 \cos^2 \Omega_E - 1) c_{ij,ij}^{oe} + (2 - \cos^2 \Omega_E) c_{ii,jj}^{oe}], \\ \Delta_2'^{oe} &= \frac{1}{30 k T} \sum_{ij} [3 \cos^2 \Omega_E - 1) \mu_i b_{ij}^{oe} + (2 - \cos^2 \Omega_E) \mu_i b_{ijj}^{oe}]. \end{aligned} \quad (4.5)$$

Here,  $\Omega_E$  denotes the angle between the light wave vector  $\mathbf{E}^o$  and the vector  $\mathbf{E}$ , and  $\Omega_H$ — that between the vectors  $\mathbf{E}^o$  and  $\mathbf{H}$ .

The molar constant of refraction is defined by the relation

$$R^M \equiv \frac{4\pi}{3} N_A \langle \alpha^o \rangle. \quad (4.6)$$

here,  $\langle \alpha^o \rangle$  is the statistical mean optical polarizability of the molecule when the fields  $\mathbf{E}$  and  $\mathbf{H}$  are absent  $\langle \alpha^o \rangle_{E=0, H=0}$ ; thus, by (4.4) we may write

$$R^M = \frac{4\pi}{3} N_A \frac{1}{3} \sum_i \alpha_{ii}^o. \tag{4.6a}$$

The molar Kerr constant is defined as follows:

$$K^M \equiv \frac{4\pi}{3} N_A \frac{\langle \alpha_{\parallel}^o \rangle_{E,0} - \langle \alpha_{\perp}^o \rangle_{E,0}}{E^2} \tag{4.7}$$

and, similarly, the molar Cotton-Mouton constant:

$$C^M \equiv \frac{4\pi}{3} N_A \frac{\langle \alpha_{\parallel}^o \rangle_{0,H} - \langle \alpha_{\perp}^o \rangle_{0,H}}{H^2}, \tag{4.8}$$

where  $\alpha_{\parallel}^o$  denotes the optical polarizability of the molecule for a light wave field parallel to the vector  $\mathbf{E}$  or  $\mathbf{H}$  (when  $\Omega_E = 0$ , or  $\Omega_H = 0$ ), and  $\alpha_{\perp}^o$  — that for a vector  $\mathbf{E}^o$  perpendicular to  $\mathbf{E}$  or  $\mathbf{H}$  ( $\Omega_E = 90^\circ$ , or  $\Omega_H = 90^\circ$ ).

With (4.4) definitions (4.7) and (4.8) yield

$$K^M = 2\pi N_A (\Theta_1^{oe} + \Theta_2^{oe} + \Delta_1^{oe} + 2\Delta_2^{oe}), \tag{4.9}$$

$$C^M = 2\pi N_A (\Theta_1^{om} + \Delta_1^{om}), \tag{4.10}$$

where

$$\Theta_1^{oe} = \frac{1}{45 kT} \sum_{ij} (3a_{ij}^o a_{ij}^e - a_{ii}^o a_{jj}^e),$$

$$\Theta_2^{oe} = \frac{1}{45 k^2 T^2} \sum_{ij} (3a_{ij}^o \mu_i \mu_j - a_{ii}^o \mu_j^2),$$

$$\Delta_1^{oe} = \frac{1}{45} \sum_{ij} (3c_{ij}^{oe} - c_{ijj}^{oe}),$$

$$\Delta_2^{oe} = \frac{1}{45 kT} \sum_{ij} (3\mu_i b_{ij}^{oe} - \mu_i b_{ijj}^{oe}),$$

$$\Theta_1^{om} = \frac{1}{45 kT} \sum_{ij} (3a_{ij}^o a_{ij}^m - a_{ii}^o a_{jj}^m),$$

$$\Delta_1^{om} = \frac{1}{45} \sum_{ij} (3c_{ij,ij}^{om} - c_{ii,jj}^{om}). \tag{4.11}$$

On the other hand, the molar constants  $K^M$  and  $C^M$  calculated theoretically from eqs. (4.9) and (4.10) should be computed on the basis of experimental results. For

this purpose, the relations defining the usual Kerr constant  $K$  and the usual Cotton-Mouton constant  $C$  are employed:

$$\begin{aligned} K &= \frac{n_{\parallel}(E, 0) - n_{\perp}(E, 0)}{n} \cdot \frac{1}{E^2}, \\ C &= \frac{n_{\parallel}(0, H) - n_{\perp}(0, H)}{n} \cdot \frac{1}{H^2}. \end{aligned} \quad (4.12)$$

The light refraction index is given by the fundamental relation

$$n^2 = 1 + 4\pi N_0 \langle \alpha^o \rangle_{E, H} \frac{\partial F^o}{\partial E^o}. \quad (4.13)$$

The Lorentz formula may be assumed to describe the local field within the light wave:

$$F^o = \frac{n^2 + 2}{3} E^o \quad (4.14)$$

which results in eq. (4.13) yielding the generalized Lorentz-Lorenz formula:

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3} N_0 \langle \alpha^o \rangle_{E, H} \quad (4.15)$$

where

$$\begin{aligned} \langle \alpha^o \rangle_{E, H} &= \frac{1}{3} \sum_i a_{ii}^o + (\Theta_1'^{om} + \Delta_1'^{om}) H^2 + \\ &+ (\Theta_1'^{oe} + \Theta_2'^{oe} + \Delta_1'^{oe} + 2\Delta_2'^{oe}) F^2 + \dots \end{aligned} \quad (4.16)$$

the magnitudes in the brackets being given by (4.5).

The definitions of the molar constants (4.7) and (4.8) and relations (4.12) and (4.15) yield the well-known relations

$$\begin{aligned} K^M &= K \frac{6 n^2}{(n^2 + 2)^2} \frac{M}{d} \left( \frac{E}{F} \right)^2, \\ C^M &= C \frac{6 n^2}{(n^2 + 2)^2} \frac{M}{d} \end{aligned} \quad (4.17)$$

which enable us to compute  $K^M$  and  $C^M$  from experimental data.

### 5. The Kerr and Cotton-Mouton effects in a diamagnetic condensed medium

In a condensed medium, in addition to the potential energy of the  $N$  molecules of the system in the field of external forces, the potential energy of molecular inte-

reaction,  $U_N$ , should be taken into account. Thus, the total potential energy of the system of  $N$  molecules under consideration is equal to

$$U' = U(\tau, F, H) + U_N \tag{5.1}$$

where

$$U(\tau, F, H) = \sum_{q=1}^N u(\tau, F, H)^{(q)} \tag{5.1a}$$

is the potential energy of the system of  $N$  molecules in the fields  $\mathbf{F}$  and  $\mathbf{H}$ , and  $u(\tau, F, H)^{(q)}$  — that of the  $q$ -th molecule, defined by a formula analogous to (3.1):

$$\begin{aligned} u(\tau, F, H)^{(q)} = & - \sum_i \mu_i \alpha_i^{(q)} F - \frac{1}{2} \sum_{ij} a_{ij}^e \alpha_i^{(q)} \alpha_j^{(q)} F^2 - \\ & - \frac{1}{2} \sum_{ij} a_{ij}^m \beta_i^{(q)} \beta_j^{(q)} H^2 + \dots \end{aligned} \tag{5.2}$$

$U_N$  is the potential energy of mutual interaction of the  $N$  molecules of the system, accounting for intermolecular forces of any kind, e.g. dipolar, inductive, van der Waals forces, etc.

The optical polarizability  $A^o$  of the system is equal to the sum of the optical polarizabilities of the molecules:

$$A^o = \sum_{q=1}^N \alpha^{o(q)} \tag{5.3}$$

where  $\alpha^{o(q)}$  is the optical polarizability of the  $q$ -th molecule defined, according to (4.1) and (4.2), as follows:

$$\begin{aligned} \alpha^{o(q)} = & \sum_{ij} a_{ij}^o \gamma_i^{(q)} \gamma_j^{(q)} + \sum_{ijk} b_{ijk}^{oe} \gamma_i^{(q)} \gamma_j^{(q)} \alpha_k^{(q)} F + \\ & + \frac{1}{2} \sum_{klji} c_{ijkl}^{oe} \gamma_i^{(q)} \gamma_j^{(q)} \alpha_k^{(q)} \alpha_l^{(q)} F^2 + \frac{1}{2} \sum_{ijkl} c_{ij,kl}^{om} \gamma_i^{(q)} \gamma_j^{(q)} \beta_k^{(q)} \beta_l^{(q)} H^2 + \dots \end{aligned} \tag{5.4}$$

In classical statistical mechanics, the statistical mean value (5.3) for a condensed medium is given by the following expression:

$$\langle A^o \rangle_{E, H}^* = \frac{\int A^o e^{-\frac{U(\tau, F, H) + U_N}{kT}} d\tau}{\int e^{-\frac{U(\tau, F, H) + U_N}{kT}} d\tau} \tag{5.5}$$

with

$$d\tau = \prod_{q=1}^N d\tau_q \tag{5.5a}$$

$d\tau_q = dv_q d\omega_q$  is the configurational element;  $dv_q$ , the volume element of the  $q$ -th molecule is given in the Cartesian coordinates  $x, y, z$ ;  $d\omega_q = \sin \vartheta_q d\vartheta_q d\varphi_q d\psi_q$ , the orientational element given in the Eulerian angles  $\vartheta, \varphi, \psi$ .

On expanding (5.5) in the field strengths  $\mathbf{E}$  and  $\mathbf{H}$  and on dropping all terms containing odd powers of the direction cosines (in isotropic averaging these terms vanish, cf. Appendix II), we have

$$\begin{aligned}
 \langle A^o \rangle_{E,H}^* = & \sum_{ij} a_{ij}^o \left\langle \sum_{q=1}^N \gamma_i^{(q)} \gamma_j^{(q)} \right\rangle \left\{ 1 - \frac{1}{2kT} \sum_{kl} \left[ H^2 a_{kl}^m \left\langle \sum_{r=1}^N \beta_k^{(r)} \beta_l^{(r)} \right\rangle + \right. \right. \\
 & \left. \left. + F^2 \left( a_{kl}^e \left\langle \sum_{r=1}^N \alpha_k^{(r)} \alpha_l^{(r)} \right\rangle + \frac{\mu_k \mu_l}{kT} \left\langle \sum_{r=1}^N \sum_{s=1}^N \alpha_k^{(r)} \alpha_l^{(s)} \right\rangle \right) \right] \right\} + \\
 & + \frac{H^2}{2} \sum_{ijkl} \left( c_{ij,kl}^{om} \left\langle \sum_{q=1}^N \gamma_i^{(q)} \gamma_j^{(q)} \beta_k^{(q)} \beta_l^{(q)} \right\rangle + \frac{a_{ij}^o a_{kl}^m}{kT} \left\langle \sum_{q=1}^N \sum_{r=1}^N \gamma_i^{(q)} \gamma_j^{(q)} \beta_k^{(r)} \beta_l^{(r)} \right\rangle \right) + \\
 & + \frac{F^2}{2} \sum_{ijkl} \left( c_{ijkl}^{oe} \left\langle \sum_{q=1}^N \gamma_i^{(q)} \gamma_j^{(q)} \alpha_k^{(q)} \alpha_l^{(q)} \right\rangle + \frac{a_{ij}^o a_{kl}^e}{kT} \left\langle \sum_{q=1}^N \sum_{r=1}^N \gamma_i^{(q)} \gamma_j^{(q)} \alpha_k^{(r)} \alpha_l^{(r)} \right\rangle \right) + \\
 & + \frac{2b_{ijk}^{eo} \mu_l}{kT} \left\langle \sum_{q=1}^N \sum_{r=1}^N \gamma_i^{(q)} \gamma_j^{(q)} \alpha_k^{(q)} \alpha_l^{(r)} \right\rangle + \frac{a_{ij}^o \mu_k \mu_l}{k^2 T^2} \left\langle \sum_{q=1}^N \sum_{r=1}^N \sum_{s=1}^N \gamma_i^{(q)} \gamma_j^{(q)} \alpha_k^{(r)} \alpha_l^{(s)} \right\rangle + \dots
 \end{aligned} \tag{5.6}$$

( $X_i$ ,  $i = 1, 2, 3$ ) being the system of reference at rest attached to the observer, ( $X_i^{(p)}$ ,  $i = 1, 2, 3$ )—the molecular system attached to the  $p$ -th molecule and ( $X_i^{(q)}$ ,  $i = 1, 2, 3$ )—that attached to the  $q$ -th molecule, we have the relation

$$\alpha_i^{(q)} = \sum_{j=1}^3 \omega_{ij}^{(pq)} \alpha_j^{(p)}, \tag{5.7}$$

where  $\alpha_j^{(p)}$  and  $\alpha_i^{(q)}$  are the cosines of the angles between the direction of the field  $\mathbf{E}$  and the axes of the molecular systems attached to the  $p$ -th and  $q$ -th molecule respectively, and  $\omega_{ij}^{(pq)}$ —the cosines of the angles between the axes of both molecular systems ( $X_j^{(p)}$ ,  $j = 1, 2, 3$ ) and ( $X_i^{(q)}$ ,  $i = 1, 2, 3$ ). Similar relations hold for the remaining direction cosines.

Since the molecules are all of the same kind and in the same conditions, eq. (5.6) may be rewritten (for the principal axes) in the form

$$\langle A^o \rangle_{E,H}^* = N \langle \alpha^o \rangle_{E,H}^* \tag{5.8}$$

where

$$\begin{aligned}
 \langle \alpha^o \rangle_{E,H}^* = & \frac{1}{3} \sum_i a_{ii}^o + (\Theta_1^{*om} + \Delta_1^{*om}) H^2 + \\
 & + (\Theta_1^{*oe} + \Theta_2^{*oe} + \Delta_1^{*oe} + 2 \Delta_2^{*oe}) F^2 + \dots
 \end{aligned} \tag{5.9}$$

with

$$\begin{aligned}
 \Theta_1^{*oe} &= \frac{3 \cos^2 \Omega_H - 1}{90 kT} \sum_{ij} a_{ii}^o a_{jj}^m \left\langle \sum_{q=1}^N (3\omega_{ij}^{(pq)} \omega_{ij}^{(pq)} - 1) \right\rangle, \\
 \Delta_1^{*om} &= \frac{1}{30} \sum_{ij} [(3 \cos^2 \Omega_H - 1) c_{ij,ij}^{om} + (2 - \cos^2 \Omega_H) c_{ii,jj}^{om}], \\
 \Theta_1^{*oe} &= \frac{3 \cos^2 \Omega_E - 1}{90 kT} \sum_{ij} a_{ii}^o a_{jj}^e \left\langle \sum_{q=1}^N (3\omega_{ij}^{(pq)} \omega_{ij}^{(pq)} - 1) \right\rangle, \\
 \Theta_2^{*oe} &= \frac{3 \cos^2 \Omega_E - 1}{90 k^2 T^2} \sum_{ij} a_{ii}^o \mu_j^2 \left\langle \sum_{q=1}^N \sum_{r=1}^N (3\omega_{ij}^{(pq)} \omega_{ij}^{(pr)} - \omega_{jj}^{(qr)}) \right\rangle, \\
 \Delta_1^{*oe} &= \frac{1}{30} \sum_{ij} [(3 \cos^2 \Omega_E - 1) c_{ij,ij}^{oe} + (2 - \cos^2 \Omega_E) c_{ii,jj}^{oe}], \quad (5.10) \\
 \Delta_2^{*oe} &= \frac{1}{30 kT} \sum_{ij} [(3 \cos^2 \Omega_E - 1) \mu_i b_{ij}^{oe} + (2 - \cos^2 \Omega_E) \mu_i b_{ii}^{oe}] \left\langle \sum_{q=1}^N \omega_{ii}^{(pq)} \right\rangle.
 \end{aligned}$$

Hence, as in §4, we calculate the molar Kerr and Cotton-Mouton constants for condensed media:

$$\begin{aligned}
 K^{*M} &= 2\pi N_A (\Theta_1^{*oe} + \Theta_2^{*oe} + \Delta_1^{*oe} + 2\Delta_2^{*oe}), \\
 C^{*M} &= 2\pi N_A (\Theta_1^{*om} + \Delta_1^{*om}), \quad (5.11)
 \end{aligned}$$

with

$$\begin{aligned}
 \Theta_1^{*oe} &= \frac{1}{45 kT} \sum_{ij} a_{ii}^o a_{jj}^e \left\langle \sum_{q=1}^N (3\omega_{ij}^{(pq)} \omega_{ij}^{(pq)} - 1) \right\rangle, \\
 \Theta_2^{*oe} &= \frac{1}{45 k^2 T^2} \sum_{ij} a_{ii}^o \mu_j^2 \left\langle \sum_{q=1}^N \sum_{r=1}^N (3\omega_{ij}^{(pq)} \omega_{ij}^{(pr)} - \omega_{jj}^{(qr)}) \right\rangle, \\
 \Delta_1^{*oe} &= \frac{1}{45} \sum_{ij} (3c_{ij,ij}^{oe} - c_{ii,jj}^{oe}), \\
 \Delta_2^{*oe} &= \frac{1}{45 kT} \sum_{ij} (3\mu_i b_{ij}^{oe} - \mu_i b_{ii}^{oe}) \left\langle \sum_{q=1}^N \omega_{ii}^{(pq)} \right\rangle, \\
 \Theta_1^{*om} &= \frac{1}{45 kT} \sum_{ij} a_{ii}^o a_{jj}^m \left\langle \sum_{q=1}^N (3\omega_{ij}^{(pq)} \omega_{ij}^{(pq)} - 1) \right\rangle, \\
 \Delta_1^{*om} &= \frac{1}{45} \sum_{ij} (3c_{ij,ij}^{om} - c_{ii,jj}^{om}). \quad (5.12)
 \end{aligned}$$

For molecules possessing axial symmetry, expressions (5.11) and (5.12) take the form:

$$\begin{aligned} K^{*M} &= 2\pi N_A (\Theta_1^{oe} R_{CM} + \Theta_2^{oe} R_K + \Delta_1^{oe} + 2\Delta_2^{oe} R_P), \\ C^{*M} &= 2\pi N_A (\Theta_1^{om} R_{CM} + \Delta_1^{om}), \end{aligned} \quad (5.13)$$

where the terms:

$$\begin{aligned} \Theta_1^{oe} &= \frac{2}{45 kT} (a_{33}^o - a_{11}^o) (a_{33}^e - a_{11}^e), \\ \Theta_2^{oe} &= \frac{2}{45 k^2 T^2} (a_{33}^o - a_{11}^o) \mu^2, \\ \Delta_1^{oe} &= \frac{2}{45} \left[ c_{3333}^{oe} + \frac{4}{3} (3c_{1133}^{oe} + 2c_{1111}^{oe}) \right], \\ \Delta_2^{oe} &= \frac{2}{45 kT} (b_{333}^{oe} + 2b_{113}^{oe}) \mu, \\ \Theta_1^{om} &= \frac{2}{45 kT} (a_{33}^o - a_{11}^o) (a_{33}^m - a_{11}^m), \\ \Delta_1^{om} &= \frac{2}{45} [c_{33,33}^{om} + 2c_{11,11}^{om} + (3c_{12,12}^{om} - c_{11,22}^{om}) + 2(3c_{13,13}^{om} - c_{11,33}^{om})], \end{aligned} \quad (5.14)$$

are accompanied by the following correlation factors:

$$\begin{aligned} R_P &= \left\langle \sum_{q=1}^N \cos \Theta_{2q} \right\rangle, \\ R_{CM} &= \frac{1}{2} \left\langle \sum_{q=1}^N (3 \cos^2 \Theta_{pq} - 1) \right\rangle, \\ R_K &= \frac{1}{2} \left\langle \sum_{q=1}^N \sum_{r=1}^N (3 \cos \Theta_{pq} \cos \Theta_{pr} - \cos \Theta_{qr}) \right\rangle, \end{aligned} \quad (5.15)$$

$\Theta_{pq}$  denoting the angle between the axes of symmetry of the  $p$ -th molecule and that of the  $q$ -th.

Here, too, relations analogous to (4.17) are valid, namely:

$$\begin{aligned} K^{*M} &= K^* \frac{6n^2}{(n^2 + 2)^2} \frac{M}{d} \left( \frac{E}{F} \right)^2, \\ C^{*M} &= C^* \frac{6n^2}{(n^2 + 2)^2} \frac{M}{d}, \end{aligned} \quad (5.16)$$

where  $K^*$  and  $C^*$  are the usual Kerr and Cotton-Mouton constants for condensed media (e. g. for liquids).



6. Dielectric polarization and dielectric saturation of condensed media in the electric and magnetic field

The component of the electric moment of the system of  $N$  molecules under consideration in the direction of the vector  $\mathbf{E}$  is the sum of the components of the electric moments of the molecules:

$$M_E^e = \sum_{q=1}^N m_E^{e(q)} ; \tag{6.1}$$

here,  $m_E^{e(q)}$  denotes the component of the electric moment of the  $q$ -th molecule of the system as defined by the formula similar to (3.2)

$$\begin{aligned} m_E^{e(q)} = & \sum_i \mu_i \alpha_i^{(q)} + \sum_{ij} a_{ij}^e \alpha_i^{(q)} \alpha_j^{(q)} F + \frac{1}{2} \sum_{ijk} b_{ijk}^{ee} \alpha_i^{(q)} \alpha_j^{(q)} \alpha_k^{(q)} F^2 + \\ & + \frac{1}{2} \sum_{ijk} b_{ijk}^{em} \alpha_i^{(q)} \beta_j^{(q)} \beta_k^{(q)} H^2 + \\ & + \frac{1}{6} \sum_{ijkl} c_{ijkl}^{ee} \alpha_i^{(q)} \alpha_j^{(q)} \alpha_k^{(q)} \alpha_l^{(q)} F^3 + \frac{1}{2} \sum_{ijkl} c_{ijkl}^{em} \alpha_i^{(q)} \alpha_j^{(q)} \beta_k^{(q)} \beta_l^{(q)} FH^2 + \dots \end{aligned} \tag{6.1a}$$

In classical statistical mechanics the statistical mean value  $M_E^e$  for a condensed medium is given by

$$\langle M_E^e \rangle_{E,H}^* = \frac{\int M_E^e e^{-\frac{U(\tau, F, H) + U_N}{kT}} d\tau}{\int e^{-\frac{U(\tau, F, H) + U_N}{kT}} d\tau} . \tag{6.2}$$

Substituting herein the expressions (5.1) and (6.1), we obtain as in §5:

$$\begin{aligned} \langle M_E^e \rangle_{E,H}^* = & (A^{*e} + \Theta^{*e}) F + (\Theta_1^{*em} + \Theta_2^{*em} + \Delta_1^{*em} + 2\Delta_2^{*em}) F H^2 + \\ & + (\Theta_1^{*ee} + 2\Theta_2^{*ee} - \Theta_3^{*ee} + \Delta_1^{*ee} + 4\Delta_2^{*ee}) F^3 + \dots \end{aligned} \tag{6.3}$$

With

$$\begin{aligned} A^{*e} = & \sum_{ij} a_{ij}^e \left\langle \sum_{q=1}^N \alpha_i^{(q)} \alpha_j^{(q)} \right\rangle, \\ \Theta^{*e} = & \frac{1}{kT} \sum_{ij} \mu_j \mu_j \left\langle \sum_{q=1}^N \sum_{r=1}^N \alpha_i^{(q)} \alpha_j^{(r)} \right\rangle, \\ \Theta_1^{*em} = & \frac{1}{2kT} \sum_{ijkl} a_{ij}^e a_{kl}^m \left( \left\langle \sum_{q=1}^N \sum_{r=1}^N \alpha_i^{(q)} \alpha_j^{(q)} \beta_k^{(r)} \beta_l^{(r)} \right\rangle - \right. \\ & \left. - \left\langle \sum_{q=1}^N \alpha_i^{(q)} \alpha_j^{(q)} \right\rangle \left\langle \sum_{r=1}^N \beta_k^{(r)} \beta_l^{(r)} \right\rangle \right), \end{aligned}$$

$$\begin{aligned}
\Theta_2^{*em} &= \frac{1}{2k^2T^2} \sum_{ijkl} \mu_i \mu_j a_{kl}^m \left( \left\langle \sum_{q=1}^N \sum_{r=1}^N \sum_{s=1}^N \alpha_i^{(q)} \alpha_j^{(r)} \beta_k^{(s)} \beta_l^{(s)} \right\rangle - \right. \\
&\quad \left. - \left\langle \sum_{q=1}^N \sum_{r=1}^N \alpha_i^{(q)} \alpha_j^{(r)} \right\rangle \left\langle \sum_{s=1}^N \beta_k^{(s)} \beta_l^{(s)} \right\rangle \right), \\
\Delta_1^{*em} &= \frac{1}{2} \sum_{ijkl} c_{ijkl}^{em} \left\langle \sum_{q=1}^N \alpha_i^{(q)} \alpha_j^{(q)} \beta_k^{(q)} \beta_l^{(q)} \right\rangle, \\
\Delta_2^{*em} &= \frac{1}{2kT} \sum_{ijkl} \mu_i b_{j,kl}^{em} \left\langle \sum_{q=1}^N \sum_{r=1}^N \alpha_i^{(q)} \alpha_j^{(r)} \beta_k^{(r)} \beta_l^{(r)} \right\rangle, \\
\Theta_1^{*ee} &= \frac{1}{2kT} \sum_{ijkl} a_{ij}^e a_{kl}^e \left( \left\langle \sum_{q=1}^N \sum_{r=1}^N \alpha_i^{(q)} \alpha_j^{(q)} \alpha_k^{(r)} \alpha_l^{(r)} \right\rangle - \right. \\
&\quad \left. - \left\langle \sum_{q=1}^N \alpha_i^{(q)} \alpha_j^{(q)} \right\rangle \left\langle \sum_{r=1}^N \alpha_k^{(r)} \alpha_l^{(r)} \right\rangle \right), \\
\Theta_2^{*ee} &= \frac{1}{2k^2T^2} \sum_{ijkl} a_{ij}^e \mu_k \mu_l \left( \left\langle \sum_{q=1}^N \sum_{r=1}^N \sum_{s=1}^N \alpha_i^{(q)} \alpha_j^{(q)} \alpha_k^{(r)} \alpha_l^{(s)} \right\rangle - \right. \\
&\quad \left. - \left\langle \sum_{q=1}^N \alpha_i^{(q)} \alpha_j^{(q)} \right\rangle \left\langle \sum_{r=1}^N \sum_{s=1}^N \alpha_k^{(r)} \alpha_l^{(s)} \right\rangle \right), \\
\Theta_3^{*ee} &= \frac{1}{6k^3T^3} \sum_{ijkl} \mu_i \mu_j \mu_k \mu_l \left( 3 \left\langle \sum_{q=1}^N \sum_{r=1}^N \alpha_i^{(q)} \alpha_j^{(r)} \right\rangle \left\langle \sum_{s=1}^N \sum_{t=1}^N \alpha_k^{(s)} \alpha_l^{(t)} \right\rangle - \right. \\
&\quad \left. - \left\langle \sum_{q=1}^N \sum_{r=1}^N \sum_{s=1}^N \sum_{t=1}^N \alpha_i^{(q)} \alpha_j^{(r)} \alpha_k^{(s)} \alpha_l^{(t)} \right\rangle \right), \\
\Delta_1^{*ee} &= \frac{1}{6} \sum_{ijkl} c_{ijkl}^{ee} \left\langle \sum_{q=1}^N \alpha_i^{(q)} \alpha_j^{(q)} \alpha_k^{(q)} \alpha_l^{(q)} \right\rangle, \\
\Delta_2^{*ee} &= \frac{1}{6kT} \sum_{ijkl} \mu_i b_{jkl}^{ee} \left\langle \sum_{q=1}^N \sum_{r=1}^N \alpha_i^{(q)} \alpha_j^{(r)} \alpha_k^{(r)} \alpha_l^{(r)} \right\rangle, \tag{6.4}
\end{aligned}$$

Our aim, in analogy to §5, consists in calculating the above expressions as functions of the angles subtended by the systems of reference attached to the various molecules of the medium (whereas all the angles  $\alpha$  and  $\beta$  are related to the vectors  $\mathbf{E}$  and  $\mathbf{H}$ ). This aim has been achieved without introducing any assumptions

whatsoever as to the nature of the intermolecular forces and without recourse to any special model of molecular interaction; we have, however, assumed that the molecules may be considered to possess rotational symmetry (an outline of the calculations is to be found in Appendix III). Denoting by  $\Theta_{mn}$  the angle between the axes of symmetry of the  $m$ -th and  $n$ -th molecules, we have:

$$\langle M_E^e \rangle_{E,H}^* = N \langle m_E^e \rangle_{E,H}^* \quad (6.5)$$

where

$$\begin{aligned} \langle m_E^e \rangle_{E,H}^* &= \left( a^e + \frac{\mu^2}{3 kT} R_P \right) F + \\ &+ (\Theta_1'^{em} R_{CM} + \Theta_2'^{em} R_K + \Delta_1'^{em} + 2\Delta_2'^{em} R_P) FH^2 + \\ &+ (\Theta_1^{ee} R_{CM} + 2\Theta_2^{ee} R_K - \Theta_3^{ee} R_S + \Delta_1^{ee} + 4\Delta_2^{ee} R_P) F^3 + \dots \end{aligned} \quad (6.6)$$

with

$$\begin{aligned} \Theta_1'^{em} &= \frac{3 \cos^2 \Omega - 1}{45 kT} (a_{33}^e - a_{11}^e) (a_{33}^m - a_{11}^m), \\ \Theta_2'^{em} &= \frac{3 \cos^2 \Omega - 1}{45 k^2 T^2} (a_{33}^m - a_{11}^m) \mu^2, \\ \Delta_2'^{em} &= \frac{1}{30} [(1 + 2 \cos^2 \Omega) (c_{33,33}^{em} + 2c_{11,11}^{em}) + 2(3 \cos^2 \Omega - 1) (c_{12,12}^{em} + 2c_{13,13}^{em}) + \\ &+ 2(2 - \cos^2 \Omega) (c_{11,22}^{em} + 2c_{11,33}^{em})], \\ \Delta_2^{em} &= \frac{\mu}{15 kT} [(1 + 2 \cos^2 \Omega) b_{3,33}^{em} + 2(3 \cos^2 \Omega - 1) b_{1,13}^{em} + 2(2 - \cos^2 \Omega) b_{3,11}^{em}], \\ \Theta_1^{ee} &= \frac{2}{45 kT} (a_{33}^e - a_{11}^e)^2, \\ \Theta_2^{ee} &= \frac{2}{45 k^2 T^2} (a_{33}^e - a_{11}^e) \mu^2, \\ \Theta_3^{ee} &= \frac{\mu^4}{45 k^3 T^3}, \\ \Delta_1^{ee} &= \frac{1}{90} (3c_{3333}^{ee} + 12c_{1133}^{ee} + 8c_{1111}^{ee}), \\ \Delta_2^{ee} &= \frac{\mu}{30 kT} (b_{333}^{ee} + 2b_{113}^{ee}). \end{aligned} \quad (6.7)$$

The correlation factors  $R_P$ ,  $R_{CM}$  and  $R_K$  are given by eqs. (5.15), and

$$R_S = \frac{1}{2} \left( 5 \left\langle \sum_{q=1}^N \cos \Theta_{pq} \right\rangle \left\langle \sum_{r=1}^N \sum_{s=1}^N \cos \Theta_{rs} \right\rangle - 3 \left\langle \sum_{q=1}^N \sum_{r=1}^N \sum_{s=1}^N \cos \Theta_{pq} \cos \Theta_{rs} \right\rangle \right). \quad (6.8)$$

As was the case in § 3, we employ (6.6) to calculate the molar constant of polarization of the condensed medium:

$$P^{*M} = \frac{4\pi}{3} N_A \left( a^e + \frac{\mu^2}{3kT} R_P \right), \quad (6.9)$$

the molar constant of dielectric saturation in the electric field

$$S_{ee}^{*M} = 4\pi N_A (\Theta_1^{ee} R_{CM} + 2 \Theta_2^{ee} R_K - \Theta_3^{ee} R_S + \Delta_1^{ee} + 4 \Delta_2^{ee} R_P) \quad (6.10)$$

and the molar constant of dielectric saturation in the magnetic field

$$S_{em}^{*M} = \frac{4\pi}{3} N_A (\Theta_1^{em} R_{CM} + \Theta_2^{em} R_K + \Delta_1^{em} + 2\Delta_2^{em} R_P). \quad (6.11)$$

Similarly are obtained: the permittivity in a weak electric field

$$\varepsilon_0^* = 1 + 4\pi N_0 \left( a^e + \frac{\mu^2}{3kT} R_P \right) \left( \frac{\partial F}{\partial E} \right)_{E=0} \quad (6.12)$$

the variation of the permittivity in a strong electric field

$$\Delta \varepsilon_{sat}^{*e} = 3 \frac{d}{M} S_{ee}^{*M} F^2 \frac{\partial F}{\partial E} \left[ 1 - \left( \frac{\partial f}{\partial \varepsilon} \right)_{\varepsilon=\varepsilon_0} \right]^{-1} \quad (6.13)$$

and the variation of the permittivity in a strong magnetic field

$$\Delta \varepsilon_{sat}^{*m} = 3 \frac{d}{M} S_{em}^{*M} H^2 \frac{\partial F}{\partial E} \left[ 1 - \left( \frac{\partial f}{\partial \varepsilon} \right)_{\varepsilon=\varepsilon_0} \right]^{-1} \quad (6.14)$$

where

$$f = 4\pi N_0 \left( a^e + \frac{\mu^2}{3kT} R_P \right) \left( \frac{\partial F}{\partial E} \right)_{E=0} \quad (6.15)$$

### 7. The calculation of the correlation factors in some special cases

It was seen in § 5 and 6 that all five effects due to molecular orientation in condensed dielectrics are described by four correlation factors, which account for the mutual interaction of the molecules, namely:

$$\begin{aligned} R_P &= \left\langle \sum_{q=1}^N \cos \Theta_{pq} \right\rangle, \\ R_{CM} &= \frac{1}{2} \left\langle \sum_{q=1}^N (3 \cos^2 \Theta_{pq} - 1) \right\rangle, \\ R_K &= \frac{1}{2} \left\langle \sum_{q=1}^N \sum_{r=1}^N (3 \cos \Theta_{pq} \cos \Theta_{pr} - \cos \Theta_{qr}) \right\rangle, \\ R_S &= \frac{1}{2} \left( 5 \left\langle \sum_{q=1}^N \cos \Theta_{pq} \right\rangle \left\langle \sum_{r=1}^N \sum_{s=1}^N \cos \Theta_{rs} \right\rangle - 3 \left\langle \sum_{q=1}^N \sum_{r=1}^N \sum_{s=1}^N \cos \Theta_{pq} \cos \Theta_{rs} \right\rangle \right) \end{aligned} \quad (7.1)$$

where

$$\langle X(\Theta) \rangle = \frac{\int X(\Theta) e^{-\frac{U_N}{kT}} d\tau}{\int e^{-\frac{U_N}{kT}} d\tau}. \quad (7.2)$$

In order to calculate the set of correlation factors (7.1), it is necessary to make specific assumptions concerning the form of the molecules and the nature of the forces with which they interact. This complex problem is greatly facilitated if an adequate simplified model of the mutual interaction of the molecules of the system under consideration is adopted.

The most simple, trivial case is, of course, that of  $U_N = 0$ ; then

$$R_P = R_{CM} = R_K = R_S = 1, \quad (7.3)$$

and the formulas obtained in § 5 and 6 become identical with those of § 3 and 4 for a non-condensed medium, as, for instance, a gas or dilute solution, if the coupling with the solvent is to be neglected.

Another simple case is that of a system consisting of molecules interacting only in pairs, each molecule interacting significantly with one nearest neighbour only. In this case  $N = 2$  and the set of correlation factors (7.1) takes the form

$$\begin{aligned} R_P &= 1 + \langle \cos \Theta_{12} \rangle, \\ R_{CM} &= 1 + \frac{3}{2} \left( \langle \cos^2 \Theta_{12} \rangle - \frac{1}{3} \right), \\ R_K &= 1 + \frac{3}{2} \left( \langle \cos^2 \Theta_{12} \rangle - \frac{1}{3} \right) + 2 \langle \cos \Theta_{12} \rangle, \\ R_S &= 1 - 3 \left( \langle \cos^2 \Theta_{12} \rangle - \frac{1}{3} \right) + (4 + 5 \langle \cos \Theta_{12} \rangle) \langle \cos \Theta_{12} \rangle, \end{aligned} \quad (7.4)$$

with

$$\langle \cos^n \Theta_{12} \rangle = \frac{\int \cos^n \Theta_{12} e^{-\frac{U_2}{kT}} d\tau_1 d\tau_2}{\int e^{-\frac{U_2}{kT}} d\tau_1 d\tau_2} \quad (7.5)$$

$n$  being an integer. In the above formulas  $\Theta_{12}$  is the angle between the axes of symmetry of the two molecules, and  $U_2$  denotes the potential energy of their mutual interaction.

The exact expression giving the potential energy of mutual interaction of a pair of molecules is of a rather intricate nature, and thus it is possible to compute the magnitudes in (7.4) and (7.5) only approximately for small values of the energy of pairwise interaction — an assumption considerably diminishing the range of applications.

A model given formerly by one of us (A. Piekara 1937 a, 1938, 1939 a, 1947, 1950, 1951) involving dipolar interaction of two neighboring molecules, is free of this restriction. In this case the interaction energy is that of two dipoles:

$$U_N = U_2 = -\frac{\mu^2}{r^3} (3 \cos \Theta_1 \cos \Theta_2 - \cos \Theta_{12}) \quad (7.6)$$

with

$$\cos \Theta_{12} = \cos \Theta_1 \cos \Theta_2 + \sin \Theta_1 \sin \Theta_2 \cos \varphi, \quad (7.7)$$

$\Theta_1$  and  $\Theta_2$  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,  $\varphi$  being the azimuth.

When the dipoles tend to a parallel array one may put  $\Theta_1 = 0$ ,  $\Theta_2 = \Theta$  (the angle between two dipoles) and one obtains  $\cos \Theta_{12} = \cos \Theta$  and

$$U_2 = -W \cos \Theta \quad (7.8)$$

with  $W = 2 \frac{\mu^2}{r^3}$ . On the other hand, in the case of nearly anti-parallel coupling we put  $\Theta_1 = \Theta_2 = 90^\circ$ ,  $\varphi = 180^\circ - \Theta$  ( $180^\circ - \Theta$  being the angle between two dipoles) and the interaction energy is given by the same expression (7.8) with a different value of  $W$  and with  $\cos \Theta_{12} = -\cos \Theta$ .

For both cases we have

$$\langle \cos^n \Theta_{12} \rangle = (\pm 1)^n L_n(y), \quad (7.9)$$

where

$$L_n(y) = \frac{\int_0^\pi \cos^n \Theta e^{y \cos \Theta} \sin \Theta d\Theta}{\int_0^\pi e^{y \cos \Theta} \sin \Theta d\Theta} \quad (7.10)$$

is a function previously calculated (viz. Piekara 1939a).

By (7.9), eqs. (7.4) yield the following correlation factors for pairwise coupling:

$$\begin{aligned} R_P &= 1 \pm L, \\ R_{CM} &= 1 + \left(1 - 3 \frac{L}{y}\right), \\ R_K &= 1 + \left(1 - 3 \frac{L}{y}\right) \pm 2L, \\ R_S &= 1 - 2 \left(1 - 3 \frac{L}{y}\right) + (5L \pm 4)L. \end{aligned} \quad (7.11)$$

In the above expressions, the upper signs refer to nearly parallel coupling, whereas the lower ones correspond to the case of nearly anti-parallel coupling.

### 8. The relationship between $\Delta \varepsilon_{sat}^{*m}$ and the Kerr and Cotton-Mouton constants

The variation of the permittivity resulting from the effect of a magnetic field and the usual Kerr constant, for a condensed medium, are given by the following formulas:

$$\Delta \varepsilon_{sat}^{*m} = 3 \frac{d}{M} S_{em}^{*M} H^2 \frac{\partial F}{\partial E} \left[ 1 - \left( \frac{\partial f}{\partial \varepsilon} \right)_{\varepsilon=\varepsilon_0} \right]^{-1}, \quad (8.1)$$

$$K^* = \frac{d}{M} K^{*M} \frac{(n^2 + 2)^2}{6n^2} \left( \frac{F}{E} \right)^2. \quad (8.2)$$

On omitting the deformational terms of higher order, the molar constants  $S_{em}^{*M}$  and  $K^{*M}$ , in the case of axial symmetric molecules, assume the form (viz. (6.11) and (5.13)):

$$S_{em}^{*M} = \frac{4\pi}{135 kT} N_A (3 \cos^2 \Omega - 1) \delta^m \left( \delta^e R_{CM} + \frac{\mu^2}{kT} R_K \right), \quad (8.3)$$

$$K^{*M} = \frac{4\pi}{45 kT} N_A \delta^o \left( \delta^e R_{CM} + \frac{\mu^2}{kT} R_K \right) \quad (8.4)$$

wherein  $\delta^m$ ,  $\delta^e$  and  $\delta^o$  denote the magnetic, electrical and optical anisotropies respectively:

$$\delta^m = a_{33}^m - a_{11}^m, \quad \delta^e = a_{33}^e - a_{11}^e, \quad \delta^o = a_{33}^o - a_{11}^o. \quad (8.5)$$

The above equations yield the relations

$$S_{em}^{*M} = \frac{3 \cos^2 \Omega - 1}{3} K^{*M} \frac{\delta^m}{\delta^o} \quad (8.6)$$

and

$$\Delta \varepsilon_{sat}^{*m} = (3 \cos^2 \Omega - 1) \frac{6n^2}{(n^2 + 2)^2} K^* \frac{\delta^m}{\delta^o} h(\varepsilon) H^2, \quad (8.7)$$

with

$$h(\varepsilon) = \left[ 1 - \left( \frac{\partial f}{\partial \varepsilon} \right)_{\varepsilon=\varepsilon_0} \right]^{-1} \left( \frac{E}{F} \right)^2 \frac{\partial F}{\partial E} \quad (8.7a)$$

and

$$f(\varepsilon) = 4\pi N_0 \left( a^e + \frac{\mu^2}{3 kT} R_P \right) \left( \frac{\partial F}{\partial E} \right)_{E=0} \quad (8.7b)$$

The magnetic anisotropy  $\delta^m$  appearing in (8.7) may be determined from the Cotton-Mouton constant, which, if the deformational term  $\Delta_1^{om}$  is omitted, has the form

$$C^{*M} = \frac{4\pi}{45 kT} N_A \delta^o \delta^m R_{CM}. \quad (8.8)$$

For non-polar substances, it is more convenient to express the relationship (8.7) by means of the Cotton-Mouton constant. From (8.3) with  $\mu = 0$  and (8.8) we have immediately

$$S_{em}^{*M} = \frac{3 \cos^2 \Omega - 1}{3} \frac{\partial^\epsilon}{\partial \sigma} C^{*M} \quad (8.9)$$

which, together with (8.1) and (4.17) yields

$$\Delta \varepsilon_{sat}^{*m} = (3 \cos^2 \Omega - 1) \frac{6n^2}{(n^2 + 2)^2} C^* \frac{\partial^\epsilon}{\partial \sigma} h'(\varepsilon) H^2 \quad (8.10)$$

with

$$h'(\varepsilon) = \left[ 1 - \left( \frac{\partial f'}{\partial \varepsilon} \right)_{\varepsilon=\varepsilon_0} \right]^{-1} \frac{\partial F}{\partial E}, \quad (8.10a)$$

$$f'(\varepsilon) = 4\pi N_0 a^\varepsilon \left( \frac{\partial F}{\partial E} \right)_{E=0}. \quad (8.10b)$$

In relationships (8.7) and (8.10) it is necessary to specialize the type of local field acting on the molecule.

For the Lorentz field we have

$$\mu_i = \mu_{oi}, \quad a_{ii}^e = a_{oi}^e, \quad F = \frac{\varepsilon + 2}{3} E, \quad (8.11)$$

where  $\mu_{oi}$  and  $a_{oi}^e$  are the values of the components of the permanent moment and electric polarizability of the isolated molecule, respectively.

For the Onsager field we have

$$\mu_i = s_i \mu_{oi}, \quad a_{ii}^e = s_i a_{oi}^e, \quad F = \frac{3\varepsilon}{2\varepsilon + 1} E \quad (8.12)$$

with

$$s_i = \frac{(2\varepsilon + 1)(\varepsilon_\infty + 2)}{(2\varepsilon + 1)(\varepsilon_\infty + 2) - 2(\varepsilon - 1)(\varepsilon_\infty - 1)\lambda_i} \quad \text{and} \quad \lambda_i = \frac{a_{oi}^e}{\frac{1}{3}(a_{o1}^e + a_{o2}^e + a_{o3}^e)} \quad (8.13)$$

In the case of isotropic molecules, the degree of anisotropy of the polarizability of the molecule  $\lambda_i = 1$ , resulting in

$$s_i = s = \left( \frac{\varepsilon_\infty + 2}{3} \right) \left( \frac{2\varepsilon + 1}{2\varepsilon + \varepsilon_\infty} \right). \quad (8.13a)$$

Hence, for the Lorentz field we have  $h(\varepsilon) = 1$ , whereas for the Onsager field (on neglecting anisotropy)

$$h(\varepsilon) = \frac{(2\varepsilon + \varepsilon_\infty)^2}{3(2\varepsilon^2 + \varepsilon_\infty^2)}. \quad (8.14)$$



Thus, in the case of polar substances eq. (8.7) may be written for the Lorentz field as follows:

$$\Delta \varepsilon_{sat}^{*m} = (3 \cos^2 \Omega - 1) \frac{6 n^2}{(n^2 + 2)^2} K^* \frac{\delta^m}{\delta^o} H^2 \quad (8.15)$$

and, for the Onsager field:

$$\Delta \varepsilon_{sat}^{*m} = (3 \cos^2 \Omega - 1) \frac{6n^2}{(n^2 + 2)^2} \frac{(2\varepsilon + \varepsilon_\infty)^2}{3(2\varepsilon^2 + \varepsilon_\infty^2)} K^* \frac{\delta^m}{\delta^o} H^2. \quad (8.16)$$

In the case of non-polar substances, eq. (8.11) assumes the form

$$\Delta \varepsilon_{sat}^{*m} = (3 \cos^2 \Omega - 1) \frac{6n^2}{(n^2 + 2)^2} \left( \frac{\varepsilon + 2}{3} \right)^2 C^* \frac{\delta^e}{\delta^o} H^2 \quad (8.17)$$

for both types of local field.

The ratio of the electrical and optical anisotropies may be evaluated from the relationship

$$\frac{\delta^e}{\delta^o} = \frac{\varepsilon - 1}{n^2 - 1}. \quad (8.18)$$

The evaluation of  $\Delta \varepsilon_{sat}^{*m}$  for nitrobenzene in a field of  $H = 40$  kOe yields

$$\Delta \varepsilon_{sat}^{*m} = 6 \times 10^{-5}$$

for the Lorentz field, and

$$\Delta \varepsilon_{sat}^{*m} = 4 \times 10^{-5}$$

for the Onsager field. These values differ to some extent from those previously given ( $5 \cdot 10^{-5}$  and  $3 \cdot 10^{-5}$  respectively, see Piekara and Kielich 1957) because of different experimental data used.

### Appendix I

#### *Expansion of the statistical mean value of an arbitrary function $\Phi$*

In classical statistical mechanics, the statistical mean value of an arbitrary function  $\Phi$  describing the state of a system of molecules and not depending on their kinetic energy is given by the following expression:

$$\langle \Phi \rangle_F^* = \frac{\int \Phi e^{-\frac{U_F + U_N}{kT}} d\tau}{\int e^{-\frac{U_F + U_N}{kT}} d\tau}, \quad (I.1)$$

where  $U_F$  denotes the potential energy of the system in the field of external forces  $F$ ,  $U_N$  — the energy of mutual interaction of the  $N$  molecules of the system, and  $d\tau = \prod_{q=1}^N d\tau_q$  — the volume element of configurational space.

Expanding the exponential functions in power series, eq. (I.1) may be rewritten in the form

$$\langle \Phi \rangle_F^* = \frac{\sum_{n=0}^{\infty} \left(-\frac{1}{kT}\right)^n \frac{1}{n!} \langle \Phi U_F^n \rangle}{\sum_{n=0}^{\infty} \left(-\frac{1}{kT}\right)^n \frac{1}{n!} \langle U_F^n \rangle} \quad (\text{I.2})$$

with

$$\langle X \rangle_{F=0} \equiv \langle X \rangle = \frac{\int X e^{-\frac{U_N}{kT}} d\tau}{\int e^{-\frac{U_N}{kT}} d\tau} \quad (\text{I.3})$$

From (I.2) we obtain, with the desired approximation

$$\begin{aligned} \langle \Phi \rangle_F^* &= \langle \Phi \rangle + \left(-\frac{1}{kT}\right) (\langle \Phi U_F \rangle - \langle \Phi \rangle \langle U_F \rangle) + \\ &+ \frac{1}{2!} \left(-\frac{1}{kT}\right)^2 [\langle \Phi U_F^2 \rangle - 2 \langle \Phi U_F \rangle \langle U_F \rangle + \langle \Phi \rangle (2 \langle U_F \rangle^2 - \langle U_F^2 \rangle)] + \\ &+ \frac{1}{3!} \left(-\frac{1}{kT}\right)^3 [\langle \Phi U_F^3 \rangle - 3 \langle \Phi U_F^2 \rangle \langle U_F \rangle + 3 \langle \Phi U_F \rangle (2 \langle U_F \rangle^2 - \langle U_F^2 \rangle) - \\ &- \langle \Phi \rangle (6 \langle U_F \rangle^3 - 6 \langle U_F \rangle \langle U_F^2 \rangle + \langle U_F^3 \rangle)] + \dots \end{aligned} \quad (\text{I.4})$$

## Appendix II

### Calculation of the geometrical mean values of the direction cosines

If the direction cosines are given in terms of the Eulerian angles  $\vartheta, \varphi, \psi$ , then isotropically averaging we have:

$$\overline{\alpha_i \alpha_i} = \frac{1}{3} \delta_{ij}, \text{ with } \delta_{ij} = \begin{cases} 1, & \text{for } i = j, \\ 0, & \text{for } i \neq j; \end{cases} \quad (\text{II.1})$$

$$\overline{\alpha_i \alpha_j \alpha_k \alpha_l} = \frac{1}{15} (\delta_{ij} \delta_{kl} + \delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}); \quad (\text{II.2})$$

$$\overline{\alpha_i \alpha_j \beta_k \beta_l} = \frac{1}{30} [2(2 - \cos^2 \Omega) \delta_{ij} \delta_{kl} + (3 \cos^2 \Omega - 1) (\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk})]; \quad (\text{II.3})$$

$$\overline{\alpha_i} = \overline{\alpha_i \alpha_j} = \overline{\alpha_k} = \overline{\alpha_i \beta_j \beta_k} = \dots = 0; \quad (\text{II.4})$$

Similarly, we have:

$$\overline{\cos^m \vartheta} = \begin{cases} \frac{1}{2n+1}, & \text{for } m = 2n, \\ 0, & \text{for } m = 2n+1. \end{cases} \quad (\text{II.5})$$

## Appendix III

Calculation of the correlation factors in the functions  $\Theta_{mn}$  (the angles between the axes of the  $m$ -th and  $n$ -th molecules)

Making use of (6.4), we may write for axial symmetric molecules:

$$\begin{aligned}
 A^{*e} &= N \left[ \frac{2a_{11}^e + a_{33}^e}{3} + (a_{33}^e - a_{11}^e) \left\langle \cos^2 \vartheta_p^e - \frac{1}{3} \right\rangle \right], \\
 \Theta^{*e} &= N \frac{\mu^2}{kT} \left\langle \sum_{q=1}^N \cos \vartheta_p^e \cos \vartheta_q^e \right\rangle, \\
 \Theta_1^{*em} &= N \frac{(a_{33}^e - a_{11}^e)(a_{33}^m - a_{11}^m)}{2kT} \left( \left\langle \sum_{q=1}^N \cos^2 \vartheta_p^e \cos^2 \vartheta_q^m \right\rangle - \right. \\
 &\quad \left. - \langle \cos^2 \vartheta_p^e \rangle \left\langle \sum_{q=1}^N \cos^2 \vartheta_q^m \right\rangle \right), \\
 \Theta_2^{*em} &= N \frac{(a_{33}^m - a_{11}^m) \mu^2}{2k^2 T^2} \left( \left\langle \sum_{q=1}^N \sum_{r=1}^N \cos^2 \vartheta_p^m \cos \vartheta_q^e \cos \vartheta_r^e \right\rangle - \right. \\
 &\quad \left. - \langle \cos^2 \vartheta_p^m \rangle \left\langle \sum_{q=1}^N \sum_{r=1}^N \cos \vartheta_q^e \cos \vartheta_r^e \right\rangle \right), \\
 \Theta_1^{*ee} &= N \frac{(a_{33}^e - a_{11}^e)^2}{2kT} \left( \left\langle \sum_{q=1}^N \cos^2 \vartheta_p^e \cos^2 \vartheta_q^e \right\rangle - \langle \cos^2 \vartheta_p^e \rangle \left\langle \sum_{q=1}^N \cos^2 \vartheta_q^e \right\rangle \right), \\
 \Theta_2^{*ee} &= N \frac{(a_{33}^e - a_{11}^e) \mu^2}{2k^2 T^2} \left( \left\langle \sum_{q=1}^N \sum_{r=1}^N \cos^2 \vartheta_p^e \cos \vartheta_q^e \cos \vartheta_r^e \right\rangle - \right. \\
 &\quad \left. - \langle \cos^2 \vartheta_p^e \rangle \left\langle \sum_{q=1}^N \sum_{r=1}^N \cos \vartheta_q^e \cos \vartheta_r^e \right\rangle \right), \\
 \Theta_3^{*ee} &= N \frac{\mu^4}{6k^3 T^3} \left( 3 \left\langle \sum_{q=1}^N \cos \vartheta_p^e \cos \vartheta_q^e \right\rangle \left\langle \sum_{r=1}^N \sum_{s=1}^N \cos \vartheta_r^e \cos \vartheta_s^e \right\rangle - \right. \\
 &\quad \left. - \left\langle \sum_{q=1}^N \sum_{r=1}^N \sum_{s=1}^N \cos \vartheta_p^e \cos \vartheta_q^e \cos \vartheta_r^e \cos \vartheta_s^e \right\rangle \right), \tag{III.1}
 \end{aligned}$$

where  $\vartheta_p^e$  denotes the angle between the axis of symmetry of the  $p$ -th molecule and the direction of the electric field  $\mathbf{E}$ , and  $\vartheta_p^m$  — that formed with the direction of the

magnetic field  $\mathbf{H}$ ; similarly we write  $\vartheta_q^e$ ,  $\vartheta_q^m$ , etc. From the spherical triangle in Fig. 1 we have

$$\cos \vartheta_p^m = \cos \vartheta_p^e \cos \Omega + \sin \vartheta_p^e \sin \Omega \cos \varphi, \quad (\text{III.2})$$

$\Omega$  denoting the angle between the vector  $\mathbf{E}$  and  $\mathbf{H}$ . In order to calculate the isotropic mean values of the magnitudes (III.1), it is necessary to obtain relations between the cosine of  $\vartheta_p^e$  (the position of the  $p$ -th molecule being fixed) and the field  $\mathbf{E}$ , on the one hand, and the cosines of the angles  $\vartheta_q^e$ ,  $\vartheta_r^e$  and  $\vartheta_s^e$  between the  $q$ -th,  $r$ -th and  $s$ -th molecules and the field  $\mathbf{E}$ , on the other hand. From Fig. 2 we have the following relations:

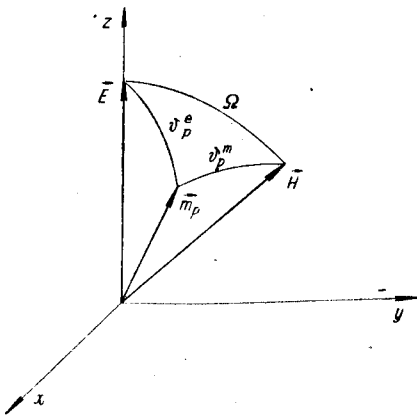


Fig. 1

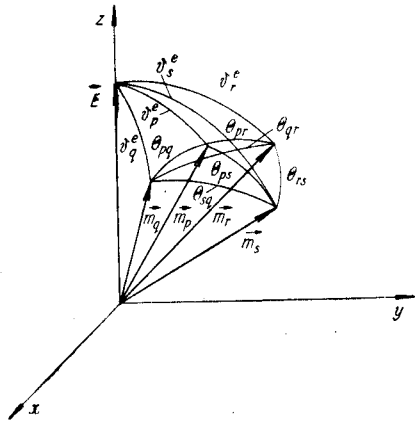


Fig. 2

$$\begin{aligned} \cos \vartheta_q^e &= \cos \vartheta_p^e \cos \Theta_{pq} + \sin \vartheta_p^e \sin \Theta_{pq} \cos \varphi_{pq}, \\ \cos \vartheta_r^e &= \cos \vartheta_p^e \cos \Theta_{pr} + \sin \vartheta_p^e \sin \Theta_{pr} \cos \varphi_{pr}, \\ \cos \vartheta_s^e &= \cos \vartheta_p^e \cos \Theta_{ps} + \sin \vartheta_p^e \sin \Theta_{ps} \cos \varphi_{ps}. \end{aligned} \quad (\text{III.3})$$

and

$$\begin{aligned} \cos \Theta_{qr} &= \cos \Theta_{pq} \cos \Theta_{pr} + \sin \Theta_{pq} \sin \Theta_{pr} \cos \varphi_{qr}, \\ \cos \Theta_{rs} &= \cos \Theta_{pr} \cos \Theta_{ps} + \sin \Theta_{pr} \sin \Theta_{ps} \cos \varphi_{rs}, \\ \cos \Theta_{sq} &= \cos \Theta_{ps} \cos \Theta_{pq} + \sin \Theta_{ps} \sin \Theta_{pq} \cos \varphi_{sq}. \end{aligned} \quad (\text{III.4})$$

By (II.5) and (III. 2, 3, 4), and on averaging, we have

$$\overline{\cos \vartheta_p^e \cos \vartheta_q^e} = \frac{1}{3} \cos \Theta_{pq}, \quad \overline{\cos^2 \vartheta_p^e} = \overline{\cos^2 \vartheta_p^m} = \frac{1}{3},$$

$$\overline{\cos^2 \vartheta_p^e \cos^2 \vartheta_q^e} = \frac{1}{15} (1 + 2 \cos^2 \Theta_{pq}),$$

$$\overline{\cos^2 \vartheta_p^e \cos \vartheta_q^e \cos \vartheta_r^e} = \frac{1}{15} (\cos \Theta_{qr} + 2 \cos \Theta_{pq} \cos \Theta_{pr}),$$

$$\overline{\cos \vartheta_p^e \cos \vartheta_q^e \cos \vartheta_r^e \cos \vartheta_s^e} = \frac{1}{15} (\cos \Theta_{pq} \cos \Theta_{rs} + \cos \Theta_{pr} \cos \Theta_{qs} + \cos \Theta_{ps} \cos \Theta_{qr}),$$

$$\overline{\cos^2 \vartheta_p^e \cos^2 \vartheta_q^m} = \frac{1}{15} [(3 \cos^2 \Omega - 1) \cos^2 \Theta_{pq} + (2 - \cos^2 \Omega)],$$

(III.5)

$$\overline{\cos^2 \vartheta_p^m \cos \vartheta_q^e \cos \vartheta_r^e} = \frac{1}{15} [(3 \cos^2 \Omega - 1) \cos \Theta_{pq} \cos \Theta_{pr} + (2 - \cos^2 \Omega) \cos \Theta_{qr}]$$

Accordingly, the expressions (III.1) now take the form

$$A^* = N \frac{2 a_{11}^e + a_{33}^e}{3},$$

$$\Theta^{*e} = N \frac{\mu^2}{3kT} R_P,$$

$$\Theta_1^{*em} = N \frac{(a_{33}^e - a_{11}^e)(a_{33}^m - a_{11}^m)}{45 k T} (3 \cos^2 \Omega - 1) R_{CM},$$

$$\Theta_2^{*em} = N \frac{(a_{33}^m - a_{11}^m) \mu^2}{45 k^2 T^2} (3 \cos^2 \Omega - 1) R_K,$$

$$\Theta_1^{*ee} = N \frac{2(a_{33}^e - a_{11}^e)^2}{45 k T} R_{CM},$$

$$\Theta_2^{*ee} = N \frac{2(a_{33}^e - a_{11}^e) \mu^2}{45 k^2 T^2} R_K,$$

$$\Theta_3^{*ee} = N \frac{\mu^4}{45 k^3 T^3} R_S,$$

where the correlation factors  $R_P$ ,  $R_{CM}$ ,  $R_K$  and  $R_S$  are given by (5.15) and (6.8)

#### КРАТКОЕ СОДЕРЖАНИЕ

А. Пекара и С. Келих. *Нелинейная теория электрической проницаемости и рефракции диэлектрических жидкостей в электрических и магнитных полях.*

Авторами дается общая молекулярная теория нелинейных молекулярно-ориентировочных эффектов вызываемых в газах и диэлектрических жидкостях приложением электрических и магнитных полей. Вычисляются молярные постоянные: диэлектрической поляризации  $P_M$ , Коттона—Мутона  $S_M$ , Керра  $K_M$ , и диэлектрической насыщенности в электрическом  $S_M^{ee}$  и в магнитном поле  $S_M^{em}$  для газов (§ 3 и 4) и жидкостей (§ 5 и 6). Для жидкостей, молекулы которых обладают аксиальной симметрией, авторы вычислили факторы корреляции  $R_P$ ,  $R_{CM}$ ,  $R_K$ , и  $R_S$  относящиеся к этим константам и определяющие взаимодействие молекул

в жидкости. В выводе факторов корреляции не сделано каких бы то ни было специальных положений относительно природы сил действующих между молекулами. Факторы корреляции выражаются функциями угла  $\Theta_{pq}$  между осью симметрии  $p$ -той и  $q$ -той молекул. Для случая взаимодействия приводящего к образованию пар диполей получаются формулы доказанные раньше одним из авторов. которыми учитывается, между прочим, инверсия диэлектрической насыщенности (§ 7). Наконец, приводится соотношение между изменением диэлектрической проницаемости в магнитном поле и постоянной Керра или Коттона—Мутона, и дается оценка порядка величины  $\Delta \epsilon_{sat}^m$ .

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