MOLECULAR-STATISTICAL THEORY OF QUADRATIC CHANGES IN ELECTRIC PERMITTIVITY TENSOR OF POLAR LIQUID MIXTURES

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Dedicated to Professor Arkadiusz Piekara on the occasion of the 50-th anniversary of his scientific activity

Electric permittivity tensor variations, due to the square of a strong DC electric field, are expressed in terms of tensors dependent on the shape and macroscopic properties of the dielectric and the electric saturation constant S, describing its microscopic structure. A detailed analysis of S is given on models of multi-component systems of, in general, polar molecules, linearly and nonlinearly polarizable both in an external electric field and in the molecular fields of dense media. By statistical methods, S is expanded in powers of the molar fractions. The first, linear term describes the additive properties of an ideal (correlation-less) mixture. The higher terms, nonlinear in powers of the molar fractions, account for divergences from additivity of S due to radial and angular molecular correlations. Effects of spatial molecular redistribution and of electric molecular field fluctuations in regions of short-range order are considered. In mixtures of atoms or simple isotropic molecules, where additivity of S is related with 3-rd order nonlinear distortion only, statistical-fluctuational effects become predominant, causing S to depend on temperature and to diverge from additivity. For polar mixtures, the various temperature-contributions to S not only involve the permanent electric dipoles but also higher electric moments (quadru-, octu-, hexadecapoles). In the light of the present theory, studies of $\Delta\varepsilon(E)$ in judiciously composed two- and three-component solutions will yield novel, highly relevant information on the correlations between polar molecules of the same and different species as well as on their electric multipoles and nonlinear electric polarizabilities.

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1. Introduction

To Langevin [1] is due the statistical-reorientational theory of classical molecular paramagnetism. Debye [2] extended Langevin's results to dielectrics proposing the determination of the electric dipoles from temperature-dependent electric permittivity measurements. The complete theory of electron and dipolar electric polarisation was given by Kroô [3].

Langevin [4], in his interpretation of the temperature-variations of the Kerr constant, showed them to be related to the anisotropic polarizability of molecules, subject to reorientation in the electric field. Born [5] modified the theory to comprise dipolar anisotropically polarizable molecules. Voigt [6], on the basis of Lorentz's electron theory [7], had shown the temperature-independent part of Kerr's constant to arise from nonlinear distortion of molecules proportional to the square of the electric field strength. The idea was subsequently taken up by Born [8], who moreover took into consideration changes in polarizability linear in the field strength (see, also, the monographs [9–12]).

Debye [13], starting from the work of Langevin and Born, extended the dielectric saturation theory of Herweg [14] to dipole molecules with anisotropic linear and nonlinear polarizabilities. Piekara [15] first pointed to the essential rôle, in dielectric saturation, of nonlinear distortion of dipolar molecules like nitrobenzene, and in general of molecules immersed in a strong electric field [16].

Herweg [14] performed the first successful measurements of dielectric saturation in ethyl ether finding, in accordance with the theory of Langevin and Debye, a negative variation in permittivity $\Delta\varepsilon(E)$ quadratically dependent on the electric field strength E. Measurements by Kautzsch [17] in chloroform and chlorobenzene also yielded variations $\Delta\varepsilon(E) < 0$.

Piekara [18–23] proceeded to a systematic experimental and theoretical study of dielectric saturation in dipolar liquids and solutions. In 1936, in co-operation with B. Piekara [18], he discovered the positive dielectric saturation effect in solutions of nitrobenzene. Its theoretical interpretation by Piekara [19, 20] was based on pairs of dipoles, coupled in almost-antiparallel array. Debye's theory [13] did not admit of positive variations in permittivity. The positive saturation effect has since been found on various dipolar solutions [21, 24]. Piekara and Kielich [16, 25] developed a general molecular-statistical theory of dielectric saturation in liquids successfully explaining numerous experimental aspects of the measurements. The body of work bearing on the nonlinear properties of dielectrics is by now comprised in monographs [11, 26–31].

The present paper is aimed at an extension of the molecular-statistical theory of Piekara and Kielich [16, 25] to dielectric saturation in solutions of arbitrarily many components, consisting of atoms and polar molecules. Starting from Kirkwood's semi-macroscopic treatment [32], generalized to the nonlinear case [33], we shall perform a detailed molecular-statistical analysis with applications to some experimentally realistic models. We restrict our calculations to the quadratic field strength dependence of $\Delta\varepsilon(E)$ neglecting higher nonlinearities and including complete dielectric saturation, dealt with in a previous paper [34]. The external electric field E will be assumed as static or sufficiently slowly variable to render the consideration of molecular rotational relaxation processes superfluous [35].

2. Semi-macroscopic theory

In the semi-macroscopic approach, we consider an ellipsoidal sample of macroscopic size, volume V, and electric permittivity ε within an isotropic continuous medium of permittivity ε_0. When an intense electric field E_0 exists in the surrounding medium, the dielectric ellipsoid becomes anisotropic and its anisotropicity is, in general, given by an electric permittivity tensor $\varepsilon_{\sigma\tau}$. Generally, the macroscopic field E existing in the dielectric sample differs from the external field E_0; the two fields are related by the formula:

$$E_{0\sigma} = R_{\sigma\tau}E_\tau, \tag{1}$$

well known from the electrostatics of dielectrics [28] (we apply the summation convention over the twice recurring index $\tau = x, y, z$). The tensor relating E_0 to E is here of the form:

$$R_{\sigma\tau} = \varepsilon_0^{-1}\{\varepsilon_0\delta_{\sigma\tau} + (\varepsilon_{\sigma v} - \varepsilon_0\delta_{\sigma v})L_{v\tau}\}, \tag{2}$$

where $\delta_{\sigma\tau}$ is Kronecker's symmetric unit tensor. $L_{\sigma\tau}$ is a symmetric field depolarisation tensor, dependent on the shape of the dielectric sample, and defined so that its trace shall equal unity, $L_{\sigma\sigma} = L_{xx} + L_{yy} + L_{zz} = 1$.

The principal values are ($\sigma = x, y, z$)

$$L_\sigma = \tfrac{1}{2}\int_0^\infty \frac{r_x r_y r_z ds}{(r_i^2 + s)\left[(r_x^2 + s)(r_y^2 + s)(r_z^2 + s)\right]^{1/2}}, \tag{3}$$

r_x, r_y and r_z denoting the principal semi-axes of the ellipsoid. In particular, for a spherical sample $r_x = r_y = r_z$ and

$$L_{\sigma\tau} = \tfrac{1}{3}\delta_{\sigma\tau} \tag{1a}$$

whence the tensor of Eq. (2) reduces to

$$R_{\sigma\tau} = \frac{\varepsilon_{\sigma\tau} + 2\varepsilon_0\delta_{\sigma\tau}}{3\varepsilon_0}. \tag{2a}$$

If moreover the permittivity of the sample is isotropic, $\varepsilon_{\sigma\tau} = \varepsilon\delta_{\sigma\tau}$, one has the well known relation

$$R_{\sigma\tau} = \left(\frac{\varepsilon + 2\varepsilon_0}{3\varepsilon_0}\right)\delta_{\sigma\tau} = R\delta_{\sigma\tau}. \tag{2b}$$

If the sample is a cylinder, the axis of which is directed along the x-axis, one has $L_x = 0$ and $L_y = L_z = 1/2$. For a circular oblate disc $L_x = L_y = 0$ and $L_z = 1$.

Let us assume the electric field E_0^m whereby we measure the permittivity as so slowly variable that its frequency lies well below Debye dipolar dispersion. Likewise, let the strong field E_0^s inducing changes in permittivity be slowly variable or constant in time. The directions of E_0^m and E_0^s will in general differ, according to the experimental setup.

Thus, the total electric polarisation of the medium is a function of the two fields, $P(E_0^m, E_0^s)$, and the electric permittivity tensor can be written in the form

$$(\varepsilon_{\sigma\tau} - \varepsilon_0 \delta_{\sigma\tau}) E_\tau^m = 4\pi\varepsilon_0 P_\sigma(E^m, E^s). \tag{4}$$

Since the measuring field E_0^m is weak, it induces but linear polarisation in the medium

$$P_\sigma(E^m, E^s) = \left(\frac{\partial P_\sigma}{\partial E_{0\nu}^m}\right)_{E^m = 0} E_{0\nu}^m, \tag{5}$$

so that by (1) and (4) we have, in the presence of the strong field E_0^s,

$$\varepsilon_{\sigma\tau}(E^s) - \varepsilon_0 \delta_{\sigma\tau} = 4\pi\varepsilon_0 \left\{\frac{\partial P_\sigma(E^m, E^s)}{\partial E_{0\nu}^m}\right\}_{E^m = 0} R_{\nu\tau}^m. \tag{6}$$

The total polarisation of the medium can be resolved into a linear and a nonlinear part

$$P_\sigma(E^m, E^s) = P_\sigma^L(E^m) + P_\sigma^{NL}(E^m, E^s) \tag{7}$$

whence the electric permittivity tensor in the absence of E_0^s is

$$\varepsilon_{\sigma\tau}(0) - \varepsilon_0 \delta_{\sigma\tau} = 4\pi\varepsilon_0 \left\{\frac{\partial P_\sigma^L(E^m)}{\partial E_{0\nu}^m}\right\}_{E^m = 0} R_{\nu\tau}^m. \tag{8}$$

With regard to Eqs (4)–(8) and the relation (1), we obtain the following general relation for the change in electric permittivity tensor induced by the strong electric field

$$\Delta\varepsilon_{\sigma\tau}(E^s) = 4\pi R_{\sigma\varrho}^m R_{\nu\tau}^m \left\{\frac{\partial P_\varrho^{NL}(E^m + E^s)}{\partial E_{0\nu}^m}\right\}_{E^m = 0}. \tag{9}$$

With the aim of calculating the electric polarisation of the medium we have recourse, in conformity with the statistical mechanics of systems at thermodynamical equilibrium, to the definition

$$P_\sigma(E) = \frac{1}{V} \int M_\sigma(\Gamma, E) f(\Gamma, E) d\Gamma, \tag{10}$$

where $E = E^m + E^s$ denotes the total field acting on the medium.

The total electric dipole moment of the medium at configuration Γ and in the presence of the field E is given by the expansion [33]

$$M_\sigma(\Gamma, E) = M_\sigma(\Gamma) + A_{\sigma\tau}(\Gamma) E_{0\tau} + \tfrac{1}{2} B_{\sigma\tau\nu}(\Gamma) E_{0\tau} E_{0\nu} + \tfrac{1}{6} C_{\sigma\tau\nu\varrho}(\Gamma) E_{0\tau} E_{0\nu} E_{0\varrho} + \dots, \tag{11}$$

where $M_\sigma(\Gamma) = M_\sigma(\Gamma, 0)$ is its total dipole moment in the absence of external electric fields. The second-rank tensor $A_{\sigma\tau}(\Gamma)$ defines the linear electric polarizability of the medium; the third-rank tensor $B_{\sigma\tau\nu}(\Gamma)$ defines its first nonlinear polarizability; and the fourth-rank tensor $C_{\sigma\tau\nu\varrho}(\Gamma)$ — its second nonlinear electric polarizability.

The Gibbs distribution function in the external field is

$$f(\Gamma, E) = \frac{\exp\left[-\beta U(\Gamma, E)\right]}{\int \exp\left[-\beta U(\Gamma, E)\right]d\Gamma} \qquad (12)$$

with $\beta^{-1} = kT$. The total potential energy of the system in the presence of the electric field is given, to within the third order, by [33]

$$U(\Gamma, E) = U(\Gamma, 0) - M_\sigma(\Gamma)E_{0\sigma} - \tfrac{1}{2}A_{\sigma\tau}(\Gamma)E_{0\sigma}E_{0\tau} - \tfrac{1}{6}B_{\sigma\tau\nu}(\Gamma)E_{0\sigma}E_{0\tau}E_{0\nu} - \ldots \qquad (13)$$

On expanding the distribution function (12) in powers of βU we obtain by (13), within the same degree of accuracy [16, 28]

$$f(\Gamma, E) = f(\Gamma, 0) + f_1(\Gamma, E) + f_2(\Gamma, E) + f_3(\Gamma, E) + \ldots, \qquad (14)$$

where $f(\Gamma, 0)$ is the non-perturbed distribution function, given by (12) at $E = 0$, whereas the successively higher approximations are of the form

$$f_1(\Gamma, E) = \beta f(\Gamma, 0)\left\{M_\sigma(\Gamma)E_{0\sigma} + \tfrac{1}{2}\Delta A_{\sigma\tau}(\Gamma)E_{0\sigma}E_{0\tau} + \tfrac{1}{6}B_{\sigma\tau\nu}(\Gamma)E_{0\sigma}E_{0\tau}E_{0\nu} + \ldots\right\},$$

$$f_2(\Gamma, E) = \tfrac{1}{2}\beta^2 f(\Gamma, 0)\left\{\Delta M_\sigma(\Gamma)M_\tau(\Gamma)E_{0\sigma}E_{0\tau} + M_\sigma(\Gamma)\Delta A_{\tau\nu}(\Gamma)E_{0\sigma}E_{0\tau}E_{0\nu} + \ldots\right\},$$

$$f_3(\Gamma, E) = \tfrac{1}{6}\beta^3 f(\Gamma, 0)M_\sigma(\Gamma)\left\{M_\tau(\Gamma)M_\nu(\Gamma) - 3\langle M_\tau(\Gamma)M_\nu(\Gamma)\rangle\right\}E_{0\sigma}E_{0\tau}E_{0\nu} + \ldots$$

Above, the symbol $\langle \ \rangle$ stands for statistical averaging with the non-perturbed distribution function $f(\Gamma, 0)$. Also, we have taken into consideration that, for isotropic bodies, $\langle M_\sigma \rangle = 0$ and $\langle B_{\sigma\tau\nu} \rangle = 0$.

On inserting the expansion (11) and (14) into the definition of Eq. (10), we obtain the linear and nonlinear polarisations in the form

$$P_\sigma^L(E_0) = \frac{1}{V}\left(\langle A_{\sigma\tau} \rangle + \beta \langle M_\sigma M_\tau \rangle\right)E_{0\tau}, \qquad (15)$$

$$P_\sigma^{NL}(E_0) = \frac{1}{6V}\left\{\langle C_{\sigma\tau\nu\varrho} \rangle + \beta\left[\langle M_\sigma B_{\tau\nu\varrho} \rangle + 3\langle B_{\sigma\tau\nu}M_\varrho \rangle + 3\langle A_{\sigma\tau}\Delta A_{\nu\varrho} \rangle\right]\right.$$

$$+ 3\beta^2\left[\langle A_{\sigma\tau}\Delta M_\nu M_\varrho \rangle + \langle M_\sigma M_\tau \Delta A_{\nu\varrho} \rangle\right]$$

$$\left. + \beta^3\left[\langle M_\sigma M_\tau M_\nu M_\varrho \rangle - 3\langle M_\sigma M_\tau \rangle \langle M_\nu M_\varrho \rangle\right]\right\}E_{0\tau}E_{0\nu}E_{0\varrho}. \qquad (16)$$

We are now faced with the problem of averaging second- and fourth-rank tensors $T_{\sigma\tau}$ and $T_{\sigma\tau\nu\varrho}$. We begin by transforming them from the laboratory reference system $\sigma = x, y, z$ (attached e.g. to the electric field) to an arbitrary mobile system of reference $\alpha = 1, 2, 3$, attached to a microsystem (an atom or molecule) of the medium. The respective transformations are of the form

$$T_{\sigma\tau} = \mathsf{c}_{\sigma\alpha}\mathsf{c}_{\tau\beta}T_{\alpha\beta}, \qquad T_{\sigma\tau\nu\varrho} = \mathsf{c}_{\sigma\alpha}\mathsf{c}_{\tau\beta}\mathsf{c}_{\nu\gamma}\mathsf{c}_{\varrho\delta}T_{\alpha\beta\gamma\delta}, \qquad (17)$$

where, in the case of Cartesian systems of reference, the transformation coefficients $\mathsf{c}_{\sigma\alpha}$ are cosines of the angles subtended by their axes σ and α. Since in the expansions (15) and (16), all the statistical averages indicated refer to the field-free case, the directional

cosines of Eq. (17) can at the outset be averaged unweightedly over all possible directions of the electric fiedl yielding [36, 37]

$$\langle c_{\sigma\alpha}c_{\tau\beta}\rangle = \tfrac{1}{3}\,\delta_{\sigma\tau}\delta_{\alpha\beta},$$

$$\langle c_{\sigma\alpha}c_{\tau\beta}c_{\nu\gamma}c_{\varrho\delta}\rangle = \frac{1}{30}\begin{pmatrix}\delta_{\sigma\tau} & \delta_{\nu\varrho}\\ \delta_{\sigma\nu} & \delta_{\tau\varrho}\\ \delta_{\sigma\varrho} & \delta_{\tau\nu}\end{pmatrix}\begin{pmatrix}4 & -1 & -1\\ -1 & 4 & -1\\ -1 & -1 & 4\end{pmatrix}\begin{pmatrix}\delta_{\alpha\beta} & \delta_{\gamma\delta}\\ \delta_{\alpha\gamma} & \delta_{\beta\delta}\\ \delta_{\alpha\delta} & \delta_{\beta\gamma}\end{pmatrix}. \tag{18}$$

With regard to (17) and (18), Eqs (15) and (16) can be written in the form

$$4\pi P_\sigma^L(E) = \frac{4\pi}{3V}\,(\langle A_{\alpha\alpha}\rangle + \beta\langle M^2\rangle)E_{0\sigma} = 3P_L E_{0\sigma}, \tag{15a}$$

$$4\pi P_\sigma^{NL}(E) = (S_{FR}+S_{ND}+S_{DR}+S_A+S_{AM}+S_M)E_{0\sigma}E_{0\tau}E_{0\tau}$$
$$= S(E_{0\sigma}^m E_{0\tau}^s E_{0\tau}^s + 2E_{0\tau}^m E_{0\sigma}^s E_{0\tau}^s), \tag{16a}$$

where S, the dielectric saturation constant, consists of the following terms:

$$S_{FR} = \frac{2\pi\beta}{9V}\,\langle(\Delta A_{\alpha\alpha}+\beta\Delta M^2)^2\rangle \tag{19}$$

is the term due to fluctuations in reorientation of the induced and permanent dipoles;

$$S_{ND} = \frac{2\pi\beta}{45V}\,\langle C_{\alpha\alpha\beta\beta}+2C_{\alpha\beta\alpha\beta}\rangle \tag{20}$$

is the term accounting for pure, second nonlinear distortion;

$$S_{DR} = \frac{8\pi\beta}{45V}\,\langle M_\alpha(B_{\alpha\beta\beta}+2B_{\beta\alpha\beta})\rangle \tag{21}$$

is the term of first nonlinear distortion and dipolar reorientation;

$$S_A = \frac{4\pi\beta}{45V}\,\langle 3A_{\alpha\beta}A_{\alpha\beta}-A_{\alpha\alpha}A_{\beta\beta}\rangle \tag{22}$$

is that of anisotropic reorientation of the induced dipoles;

$$S_{AM} = \frac{8\pi\beta^2}{45V}\,\langle 3A_{\alpha\beta}M_\alpha M_\beta - A_{\alpha\alpha}M_\beta M_\beta\rangle \tag{23}$$

is that of anisotropic reorientation of the induced and permanent dipoles, and, finally,

$$S_M = -\,\frac{4\pi\beta^3}{45V}\,\langle(M\cdot M)^2\rangle \tag{24}$$

is that of reorientation of the permanent dipoles.

By (15a), the electric permittivity tensor of the medium (8) in the absence of a strong field takes the form

$$\varepsilon_{\sigma\tau}(0) - \varepsilon_0 \delta_{\sigma\tau} = 3\varepsilon_0 P_L R_{\sigma\tau}^m. \tag{25}$$

For a dielectric ellipsoid with isotropic electric permittivity, the tensor (2) is

$$R_{\sigma\tau}^m = \varepsilon_0^{-1}\{\varepsilon_0 + (\varepsilon - \varepsilon_0)L_{\sigma\tau}\}. \tag{2c}$$

Since for an isotropic spherical sample the tensor (2c) goes over into the isotropic tensor (2b), Eq. (25) reduces to its well known form for linear electric polarisation [38]

$$\frac{\varepsilon - \varepsilon_0}{\varepsilon + 2\varepsilon_0} = P_L = \frac{4\pi}{9V}(\langle A_{\alpha\alpha}\rangle + \beta\langle M^2\rangle) \tag{25a}$$

representing a generalisation of the well known Langevin–Debye expression for isotropic dense media.

With regard to (16a), Eq. (9) yields the following general expression for the change in electric permittivity tensor induced by the square of the strong electric field:

$$\Delta\varepsilon_{\sigma\tau}(E^s) = S(R_{\sigma v}^m R_{v\tau}^m R_{\varrho\lambda}^s R_{\varrho\mu}^s + 2R_{\sigma\varrho}^m R_{\varrho\lambda}^s R_{v\tau}^m R_{v\mu}^s)E_\lambda^s E_\mu^s. \tag{26}$$

In particular, if the isotropicity of the tensor $R_{\sigma\tau}$ is assumed in the form given by (2b), Eq. (26) reduces to [39]

$$\Delta\varepsilon_{\sigma\tau}(E^s) = SR^4(\delta_{\sigma\tau}E_v^s E_v^s + 2E_\sigma^s E_\tau^s). \tag{27}$$

Let us now assume a setup with the strong electric field acting along the x-axis. By (27), the changes measured along E_x^s and perpendicularly to E_x^s now are, respectively,

$$\Delta\varepsilon_{xx}(E_x^s) = 3SR^4(E_x^s)^2, \qquad \Delta\varepsilon_{yy}(E_x^s) = SR^4(E_x^s)^2, \tag{27a}$$

their difference amounting to

$$\Delta\varepsilon_{xx}(E_x^s) - \Delta\varepsilon_{yy}(E_x^s) = 2SR^4(E_x^s)^2. \tag{28}$$

Measurements of the anisotropy of changes in electric permittivity present the advantage of not depending on electrostriction [28], provided the latter is isotropic; nor are they denatured by the electro-caloric effect [28].

3. Molecular-statistical analysis in the absence of molecular fields

We now proceed to analyze the contributions (19)–(24) to dielectric saturation by a molecular-statistical treatment. This will permit us to gain insight into the various microscopic mechanisms involved.

We assume quite generally that the volume V of the dielectric contains $N = \sum_i N_i$ microsystems (atoms, molecules, etc.) of different species. N_i is the number of microsystems of the i-th species, and x_i is the molar fraction of the i-th component of the mixture. Obviously, $\sum_i x_i = 1$.

At first, to simplify our considerations, we shall neglect the action of molecular fields; thus, the macroscopic tensors referring to the whole volume of the medium are given additively by the respective microscopic quantities:

$$M_\alpha(\Gamma) = \sum_i \sum_{p=1}^{N_i} m_\alpha^{(i)}(\tau_{pi}), \quad A_{\alpha\beta}(\Gamma) = \sum_i \sum_{p=1}^{N_i} a_{\alpha\beta}^{(i)}(\tau_{pi}), \tag{29}$$

$$B_{\alpha\beta\gamma}(\Gamma) = \sum_i \sum_{p=1}^{N_i} b_{\alpha\beta\gamma}^{(i)}(\tau_{pi}), \quad C_{\alpha\beta\gamma\delta}(\Gamma) = \sum_i \sum_{p=1}^{N_i} c_{\alpha\beta\gamma\delta}^{(i)}(\tau_{pi}), \tag{30}$$

where $m_\alpha^{(i)}(\tau_{pi})$ is the electric dipole moment of molecule p of the i-th species when at the configuration τ_{pi}; and likewise the polarizability tensors $a_{\alpha\beta}^{(i)}(\tau_{pi})$, $b_{\alpha\beta\gamma}^{(i)}(\tau_{pi})$ and $c_{\alpha\beta\gamma\delta}^{(i)}(\tau_{pi})$.

3.1. Fluctuational-reorientation effect

Previous analyses of the experimental results on dielectric saturation did not take into account the fluctuational-reorientational effect, defined by (19). The effect, introduced earlier [39] for pure liquids, now takes the following form with regard to Eq. (29) for many--component systems:

$$S_{FR} = \frac{2\pi\beta}{9V} \left\langle \left\{ \Delta \sum_i \sum_{p=1}^{N_i} a_{\alpha\alpha}^{(i)}(\tau_{pi}) + \beta\Delta \sum_{ij} \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} m_\alpha^{(i)}(\tau_{pi}) m_\alpha^{(j)}(\tau_{qj}) \right\}^2 \right\rangle. \tag{19a}$$

We shall discuss the preceding expression for the case, only, of binary (pairwise) molecular correlations, and molecular parameters $m_\alpha^{(i)}$ and $a_{\alpha\alpha}^{(i)} = 3a_i$ not depending explicitly on the configurational variables τ_{pi}. Eq. (19a) now reduces (omitting angular correlations of permanent dipoles) to the form

$$S_{FR} = \frac{2\pi\beta}{9V} \sum_{ij} (3a_i + \beta m_i^2)(3a_j + \beta m_j^2) \langle \Delta N_i \Delta N_j \rangle. \tag{31}$$

Above, in conformity with Smoluchowski's fluctuation theory [40], the mean value of the product of fluctuations in number of molecules belonging to different species (components) is given as [41]

$$\langle \Delta N_i \Delta N_j \rangle = N(x_i \delta_{ij} + x_i x_j G_{ij}). \tag{32}$$

We have introduced here the radial correlation parameter

$$G_{ij} = \frac{\varrho}{V} \iint \{ g_{ij}^{(2)}(\tau_{pi}, \tau_{qj}) - g_i^{(1)}(\tau_{pi}) g_j^{(1)}(\tau_{qj}) \} d\tau_{pi} d\tau_{qj}, \tag{33}$$

where $\varrho = N/V$ is the number density of molecules, and $g_i^{(1)}(\tau_{pi})$ and $g_{ij}^{(2)}(\tau_{pi}, \tau_{qj})$ are, respectively, the mono-molecular and bi-molecular correlation functions for molecules of species i and j at configurations τ_{pi} and τ_{qj}. By insertion of (32) into (31) we obtain

$$S_{FR} = \sum_i x_i S_{FR}^{(i)} + \sum_{ij} x_i x_j S_{FR}^{(ij)} + \ldots, \tag{34}$$

with:

$$S_{FR}^{(i)} = \frac{2\pi}{9} \beta \varrho (3a_i + \beta m_i^2)^2, \tag{35}$$

$$S_{FR}^{(ij)} = \frac{2\pi}{9} \beta \varrho (3a_i + \beta m_i^2)(3a_j + \beta m_j^2)G_{ij}. \tag{36}$$

The expansion (34) shows that the fluctuation effect is additive in the first approximation. A deviation from additivity arises due to molecular correlations, defined by the parameter (33). Had we taken into account triple and four-molecule correlations when going over from Eq. (19a) to (31), still higher functions of the molar fractions would have appeared in Eq. (34) implying larger deviations from additivity.

On inspection of Eqs (35) and (36) we see that the fluctuational-reorientational effect can take place both in atomic substances and in ones composed of quasi-spherical molecules with an isotropic electric polarizability $a_i = a_{\alpha\alpha}^{(i)}/3$. The effect is thus of considerable significance in the interpretation of dielectric saturation measurements such as those carried out recently by Davies et al. [42].

In particular, for a one-component liquid we have by (32) the well known Smoluchowski relation for the mean square of the fluctuation in number of molecules

$$\langle (\varDelta N)^2 \rangle = N(1 + G) = N \varrho kT \beta_T, \tag{37}$$

where β_T is the isothermal compressibility coefficient of the medium.

Thus, by (37), for a one-component liquid Eq. (31) takes the form

$$S_{FR} = \frac{2\pi}{9} \varrho^2 \beta_T (3a + \beta m^2)^2, \tag{38}$$

well adapted to direct numerical evaluations [39].

3.2. Nonlinear distortion effects

By insertion of (29) and (30) into Eqs (20) and (21) we obtain

$$S_{ND} = \frac{2\pi}{15V} \sum_i \left\langle \sum_{p=1}^{N_i} c_{\alpha\alpha\beta\beta}^{(i)}(\tau_{pi}) \right\rangle. \tag{20a}$$

$$S_{DR} = \frac{8\pi\beta}{15V} \sum_{ij} \left\langle \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} m_\alpha^{(i)}(\tau_{pi}) b_{\alpha\beta\beta}^{(j)}(\tau_{qj}) \right\rangle. \tag{21a}$$

In the case of pure nonlinear distortion in the absence of molecular redistribution the constant (20a) is additive

$$S_{ND} = \frac{2\pi}{3} \varrho \sum_i x_i c_i = \sum_i x_i S_D^{(i)}, \tag{39}$$

where $c_i = c^{(i)}_{\alpha\alpha\beta\beta}/5$ is the mean value of the second nonlinear polarizability tensor of a molecule of the *i*-th species.

However, the distortional-reorientational constant (21a) is generally not additive. It is given as follows (on resolving the sum into self-correlations for $p = q$ and unlike binary correlations for $p \neq q$)

$$S_{DR} = \sum_i x_i S^{(i)}_{DR} + \sum_{ij} x_i x_j S^{(ij)}_{DR} + \dots, \tag{40}$$

where

$$S^{(i)}_{DR} = \frac{8\pi}{15} \beta \varrho m^{(i)}_\alpha b^{(i)}_{\alpha\beta\beta}, \tag{41}$$

$$S^{(ij)}_{DR} = \frac{4\pi}{15} \beta\varrho\{m^{(i)}_\alpha b^{(j)}_{\beta\gamma\gamma} + m^{(j)}_\beta b^{(i)}_{\alpha\gamma\gamma}\}K^{(ij)}_{\alpha\beta}. \tag{42}$$

We have introduced here the tensor of binary (two-molecule) angular correlations

$$K^{(ij)}_{\alpha\beta} = \frac{\varrho}{V} \iint \cos\theta^{(piqj)}_{\alpha\beta} g^{(2)}_{ij}(\tau_{pi}, \tau_{qj})d\tau_{pi}d\tau_{qj}, \tag{43}$$

where $\theta^{(pi,qj)}_{\alpha\beta}$ is the angle between the axis α of co-ordinates attached to molecule p of species i and the axis β of those attached to molecule q of species j.

In particular, if one assumes the molecules of the two components to be symmetric about their 3-axis, along which the dipole moment $m_3 = m$ is directed, the constants (41) and (42) reduce to

$$S^{(i)}_{DR} = \frac{8\pi\beta}{5kT} m_i b_i, \tag{41a}$$

$$S^{(ij)}_{DR} = \frac{4\pi\varrho}{5kT} (m_i b_j + m_j b_i)K_{ij}, \tag{41b}$$

where $b_i = b_{3\alpha\alpha}/3 = \frac{1}{3}(b_{333} + 2b_{311})$ is the mean value of the first nonlinear polarizability tensor of the axially symmetric molecule of species i, and

$$K_{ij} = \frac{\varrho}{V} \iint \cos\theta_{piqj} g^{(2)}_{ij}(\tau_{pi}, \tau_{qj})d\tau_{pi}d\tau_{qj} \tag{43a}$$

is the form taken by (43) for $\alpha = \beta = 3$.

Eq. (43) goes over into the well known Kirkwood angular correlation parameter for one-component dipolar liquids [32]

$$K = \varrho \int \cos\theta_{pq} g^{(2)}(\tau_{pq})d\tau_{pq}, \tag{43b}$$

discussed earlier by Piekara [43] for almost parallel and antiparallel coupled dipole pairs in linear dielectric polarization.

3.3. Effects of anisotropic molecular reorientation

With regard to (29), the constants (22) and (23) can be written in the following, molecular form

$$S_A = \frac{4\pi\beta}{45V} \sum_{ij} \left\langle \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \{3a_{\alpha\beta}^{(i)}(\tau_{pi})a_{\alpha\beta}^{(j)}(\tau_{qj}) - a_{\alpha\alpha}^{(i)}(\tau_{pi})a_{\beta\beta}^{(i)}(\tau_{qj})\} \right\rangle, \qquad (22a)$$

$$S_{AM} = \frac{8\pi\beta^2}{45V} \sum_{ijk} \left\langle \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \sum_{r=1}^{N_k} \{3a_{\alpha\beta}^{(i)}(\tau_{pi})m_{\alpha}^{(j)}(\tau_{qj})m_{\beta}^{(k)}(\tau_{rk}) \right.$$

$$\left. - a_{\alpha\alpha}^{(i)}(\tau_{pi})m_{\beta}^{(j)}(\tau_{qj})m_{\beta}^{(k)}(\tau_{rk})\} \right\rangle. \qquad (23a)$$

In this approximation the anisotropic reorientation constant (22a) is similar in form to those of Kerr's effect [44] and anisotropic light scattering [45], and can be written as follows

$$S_A = \sum_i x_i S_A^{(i)} + \sum_{ij} x_i x_j S_A^{(ij)} + \dots \qquad (44)$$

with

$$S_A^{(i)} = \frac{4\pi}{45} \beta\varrho(3a_{\alpha\beta}^{(i)}a_{\alpha\beta}^{(i)} - a_{\alpha\alpha}^{(i)}a_{\beta\beta}^{(i)}) = \frac{8\pi}{45} \beta\varrho\kappa_i^2, \qquad (45)$$

The squared molecular electric anisotropy constant defined above assumes the following form in the case of axially-symmetric molecules

$$\kappa_i^2 = \tfrac{1}{2}(3a_{\alpha\beta}^{(i)}a_{\alpha\beta}^{(i)} - a_{\alpha\alpha}^{(i)}a_{\beta\beta}^{(i)}) = (a_{33}^{(i)} - a_{11}^{(i)})^2. \qquad (46)$$

For the sake of simplicity, we write for such molecules the second term of the expansion (44) responsible for the deviation from additivity as follows

$$S_A^{(ij)} = \frac{8\pi}{45} \beta\varrho\kappa_i\kappa_j J_{ij}. \qquad (47)$$

Above, we have introduced the following parameter of binary angular correlations [44]

$$J_{ij} = \frac{\varrho}{2V} \iint (3\cos^2\theta_{piqj} - 1)g_{ij}^{(2)}(\tau_{pi}, \tau_{qj})d\tau_{pi}d\tau_{qj}. \qquad (48)$$

It vanishes in the absence of angular correlation and (44) retains but the first, additive term.

The anisotropic dipole reorientation constant (23a) is similar to that of the Kerr effect [44], and can be expressed in the form of the expansion (we resolve the triple sum

into parts corresponding to self-correlations $p = q = r$, binary correlations for $p = q \neq r$, $q = r \neq p$, $r = p \neq q$, and triple correlations for $p \neq q \neq r$)

$$S_{AM} = \sum_i x_i S_{AM}^{(i)} + \sum_{ij} x_i x_j S_{AM}^{(ij)} + \sum_{ijk} x_i x_j x_k S_{AM}^{(ijk)} + \dots, \qquad (49)$$

where

$$S_{AM}^{(i)} = \frac{8\pi}{45} \beta^2 \varrho (3 a_{\alpha\beta}^{(i)} m_\alpha^{(i)} m_\beta^{(i)} - a_{\alpha\alpha}^{(i)} m_\beta^{(i)} m_\beta^{(i)}) \qquad (50)$$

describes the additive effect in the absence of molecular correlation.

The higher constants of the expansion (49), for dipole molecules with axial symmetry, are of the form

$$S_{AM}^{(ij)} = \frac{4\pi}{45} \beta^2 \varrho (\kappa_i m_j^2 + m_i^2 \kappa_j) J_{ij}, \qquad (51)$$

$$S_{AM}^{(ijk)} = \frac{8\pi}{45} \beta^2 \varrho \kappa_i m_j m_k J_{ijk}, \qquad (52)$$

where we encounter moreover the parameter of triple angular correlations [44]

$$J_{ijk} = \frac{\varrho^2}{2V} \iiint (3 \cos\theta_{piqj} \cos\theta_{pirk} - \cos\theta_{qjrk}) g_{ijk}^{(3)}(\tau_{pi}, \tau_{qj}, \tau_{rk}) d\tau_{pi} d\tau_{qj} d\tau_{rk}, \qquad (53)$$

where $g_{ijk}^{(3)}(\tau_{pi}, \tau_{qj}, \tau_{rk})$ is the three-molecule correlation function for molecules at configurations $\tau_{pi}, \tau_{qj}, \tau_{rk}$.

The two- and three-molecule angular correlation parameters (48) and (53) occur in the electric field effect of NMR in solutions [46].

3.4. Dipole reorientation effect

Lastly, the dipole reorientation (24) can be written in the form

$$S_M = - \frac{4\pi\beta^3}{45V} \sum_{ijkl} \left\langle \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \sum_{r=1}^{N_k} \sum_{s=1}^{N_l} m_\alpha^{(i)}(\tau_{pi}) m_\alpha^{(j)}(\tau_{qj}) m_\beta^{(k)}(\tau_{rk}) m_\beta^{(l)}(\tau_{sl}) \right\rangle, \qquad (24a)$$

where we resolve the four-fold sum into successive, irreducible contributions, corresponding to self-correlations ($p = q = r = s$), binary correlations (for the 4 possibilities $p = q = = r \neq s$; $q = r = s \neq p$; $r = s = p \neq q$; $s = p = q \neq r$ and 3 possibilities $p = q \neq \neq r = s$; $q = r \neq s = p$; $r = p \neq s = q$), triple correlations (6 possibilities $p = q \neq r \neq s$; $q = r \neq s \neq p$; $r = s \neq p \neq q$; $s = p \neq q \neq r, p = r \neq q \neq s$; $q = s \neq p \neq r$), and four-molecule correlations ($p \neq q \neq r \neq s$). By molecular correlation function methods, this leads to the following expansion for Eq. (24a)

$$S_M = \sum_i x_i S_M^{(i)} + \sum_{ij} x_i x_j S_M^{(ij)} + \sum_{ijk} x_i x_j x_k S_M^{(ijk)} + \sum_{ijkl} x_i x_j x_k x_l S_M^{(ijkl)} + \dots, \qquad (54)$$

where

$$S_M^{(i)} = -\frac{4\pi}{45}\beta^3 \varrho m_i^4, \tag{55}$$

$$S_M^{(ij)} = -\frac{4\pi}{135}\beta^3 \varrho m_i^2 m_j^2 (5G_{ij}+12K_{ij}+4J_{ij}), \tag{56}$$

$$S_M^{(ijk)} = -\frac{8\pi}{135}\beta^3 \varrho m_i^2 m_j m_k (5K_{ijk}+4J_{ijk}), \tag{57}$$

$$S_M^{(ijkl)} = -\frac{4\pi}{45}\beta^3 \varrho m_i m_j m_k m_l K_{ijkl}. \tag{58}$$

Here, besides the molecular correlation parameters (33), (48) and (53), we have the three- and four-molecule ones

$$K_{ijk} = \frac{\varrho^2}{V}\iiint \cos\theta_{qjrk} g_{ijkl}^{(3)}(\tau_{pi}, \tau_{qj}, \tau_{rk}) d\tau_{pi} d\tau_{qj} d\tau_{rk}, \tag{59a}$$

$$K_{ijkl} = \frac{\varrho^3}{V}\iiiint \cos\theta_{piqj}\cos\theta_{rksl} g_{ijkl}^{(4)}(\tau_{pi}, \tau_{qj}, \tau_{rk}, \tau_{sl}) d\tau_{pi} d\tau_{qj} d\tau_{rk} d\tau_{sl}, \tag{59b}$$

$g_{ijkl}^{(4)}$ being the four-molecule correlation function.

Generally, the term proportional to β^3 (i.e. the parts comprised by the fluctuational constant (19) and purely dipolar constant (24)) is discussed jointly. This yields the fluctuational-reorientational constant

$$S'_{FR} = \frac{2\pi\beta}{9V}\langle \Delta A_{\alpha\alpha}\Delta A_{\beta\beta}+2\beta\Delta A_{\alpha\alpha}\Delta M^2\rangle \tag{19b}$$

and dipole reorientation constant [28, 33]

$$S'_M = \frac{2\pi\beta^3}{9V}\langle(\Delta M^2)^2\rangle - \frac{4\pi\beta^3}{45V}\langle M^4\rangle = -\frac{2\pi\beta^3}{45V}\{5\langle M\cdot M\rangle^2 - 3\langle(M\cdot M)^2\rangle\}. \tag{60}$$

Eqs (39)–(60), applied to a one-component system, go over into the expressions derived by Piekara and Kielich [16, 25] for dipole liquids; in the absence of molecular correlation, the latter go over into the results of Debye [13]. The saturation constants in the semi-macroscopic form (19)–(24) are applicable not only to molecular liquids and solutions but also to macromolecular and colloidal systems [28, 47]. They hold, too, for biological systems and liquid crystals, on which highly interesting studies have been reported lately [48, 49].

4. The rôle of molecular fields

4.1. Silberstein's polarizability model

In a dense medium, the electric properties of a molecule undergo modifications by the action of the electric fields of its neighbours. In this way, the permanent electric moments as well as the electric polarizabilities are no longer the same. For the nondipolar molecules of a mixture of real gases, the polarizability variations can be calculated directly by Silberstein's method [50], applied by him to the mutual polarisation of two atoms in a molecule. This, for a molecule consisting of two unlike atoms with polarizabilities a_i and a_j at a large distance r_{ij}, the polarizability along the bond axis and perpendicularly thereto is, according to Silberstein

$$a_{\parallel}(r_{ij}) = \frac{a_i + a_j + 4a_i a_j r_{ij}^{-3}}{1 - 4a_i a_j r_{ij}^{-6}} \ ,$$

$$a_{\perp}(r_{ij}) = \frac{a_i + a_j - 2a_i a_j r_{ij}^{-3}}{1 - a_i a_j r_{ij}^{-6}} \ . \tag{61}$$

The Silberstein model represents a good approximation to the case of two atoms (not bonded in a molecule) and to that of two isotropically polarizable molecules, correlated mutually at a distance r_{ij} (obviously to the exclusion of their collision, for which Eqs (61) cease to hold and have to be generalized [51]). From Eqs (61) we obtain approximately for the mean polarizability and induced anisotropy of two mutually interacting, isotropic molecules

$$a(r_{ij}) = (a_i + a_j)(1 + 2a_i a_j r_{ij}^{-6}) + 4a_i^2 a_j^2 r_{ij}^{-9} - \ldots, \tag{62}$$

$$\kappa(r_{ij}) = 3a_i a_j \{2r_{ij}^{-3} + \tfrac{1}{2}(a_i + a_j)r_{ij}^{-6} + 6a_i a_j r_{ij}^{-9} - \ldots\}. \tag{63}$$

Thus, for atoms and isotropic molecules, the saturation constant (22a) leads on the Silberstein model to the non-additive term of (44) only ($S_A^{(i)} = 0$), and instead of (47) we now have

$$S_A^{(ij)} = \frac{8\pi}{45}\beta\varrho\langle\tfrac{1}{2}\,\kappa^2(r_{ij})\rangle = \frac{16\pi}{5}\beta\varrho a_i^2 a_j^2\{\langle r_{ij}^{-6}\rangle + (a_i + a_j)\langle r_{ij}^{-9}\rangle + \ldots\}, \tag{64}$$

where averaging $\langle\ \rangle$ has to be performed with a correlation function appropriate for the real gas. Silberstein polarizability also affects the fluctuational-reorientation constant (19a), distortional constant (20a), and nonlinear processes in general [52]. The Silberstein model has been extended to linear and unlinear molecules of more than two atoms [12, 28, 53].

4.2. Molecular field fluctuations

At sufficiently high densities, the electric moments of molecules in regions of short--range order give rise to intense molecular fields F. Such fields exist even if no external field is present, and modify the electric properties of the microsystems composing the

dense medium causing i.a. a lowering of their intrinsic symmetry. Namely, one can replace Eq. (29) in a first approximation by

$$M_\alpha(\Gamma) = \sum_i \sum_{p=1}^{N_i} \{m_\alpha^{(i)}(\tau_{pi}) + a_{\alpha\beta}^{(i)}(\tau_{pi})F_\beta(\tau_{pi}) + ...\}, \tag{65}$$

showing that the total dipole moment of the medium is non-zero even if the molecules are not dipolar ($m = 0$), since now

$$M_\alpha(\Gamma) = \sum_i \sum_{p=1}^{N_i} a_{\alpha\beta}^{(i)}(\tau_{pi})F_\beta(\tau_{pi}) + ... \tag{65a}$$

By analogy to the expansion (65) one can write [54]:

$$B_{\alpha\beta\gamma}(\Gamma) = \sum_j \sum_{q=1}^{N_j} \{b_{\alpha\beta\gamma}^{(j)}(\tau_{qj}) + c_{\alpha\beta\gamma\delta}^{(j)}(\tau_{qj})F_\delta(\tau_{qj}) + ...\} \tag{66}$$

whence, for centrosymmetric molecules ($b_{\alpha\beta\gamma} = 0$),

$$B_{\alpha\beta\gamma}(\Gamma) = \sum_j \sum_{q=1}^{N_j} c_{\alpha\beta\gamma\delta}^{(j)}(\tau_{qj})F_\delta(\tau_{qj}) + ... \tag{66a}$$

In the previously discussed approximation in the absence of a molecular field the saturation constant (21a) was non-zero for dipolar molecules only. We shall now show that in the presence of molecular fields, when the expansions (65a) and (66a) are valid, the constant (21) takes the form

$$S_{DR} = \frac{8\pi\beta}{15V} \sum_{ij} \left\langle \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} a_{\alpha\gamma}^{(i)}(\tau_{pi})c_{\alpha\beta\beta\delta}^{(j)}(\tau_{qj})F_\gamma(\tau_{pi})F_\delta(\tau_{qj}) \right\rangle \tag{67}$$

and, in general, differs from zero as the result of fluctuations of the molecular fields.

Neglecting in (67), for simplicity, the anisotropy of linear and nonlinear polarizability, we have

$$S_{DR} = \frac{8\pi\beta}{15V} \sum_{ij} a_i c_j \left\langle \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} F_{pi} \cdot F_{qj} \right\rangle . \tag{67a}$$

We note that in this particular case the distortional-reorientational constant is a function of the mean value of the squared molecular field, as it is in the case of second-harmonic cooperative light scattering by centrosymmetric molecules [55].

The electric field existing at the centre of the p-th molecule of species i due to the presence of the electric moments of its neighbours is

$$F_{pi} = \sum_k \sum_{r=1}^{N_k} F_{pirk}, \tag{68}$$

and (67a) is seen to contain the following contribution from binary correlations

$$S_{DR}^{(ij)} = \frac{4\pi}{15} \beta \varrho (a_i c_j + c_i a_j) \langle F_{ij}^2 \rangle, \tag{69}$$

where

$$\langle F_{ij}^2 \rangle = \frac{\varrho}{2V} \iint (F_{piqj} \cdot F_{piqj} + F_{piqj} \cdot F_{qjpi} + F_{qjpi} \cdot F_{piqj}$$

$$+ F_{qjpi} \cdot F_{qjpi}) g_{ij}^{(2)}(\tau_{pi}, \tau_{qj}) d\tau_{pi} d\tau_{qj}. \tag{70}$$

In Eq. (70), F_{piqj} is the field induced at the centre of the p-th molecule of species i by the electric moments of the q-th molecule of species j. In fact, for quadrupolar axially-symmetric molecules one has [28]

$$F_{piqj} = \tfrac{3}{2} \Theta_j \{[5(r_{piqj}k_{qj})^2 - r_{piqj}^2]r_{piqj} - 2r_{piqj}^2(r_{piqj} \cdot k_{qj})k_{qj}\} r_{piqj}^{-7}, \tag{71}$$

whence, in the absence of angular correlation, Eq. (70) takes the form

$$\langle F_{ij}^2 \rangle = \tfrac{3}{2} (\Theta_i^2 + \Theta_j^2) \langle r_{ij}^{-8} \rangle, \tag{70a}$$

where Θ_i is the electric quadrupole moment of a molecule of the species i, and where we have introduced the radial average

$$\langle r_{ij}^{-n} \rangle = 4\pi \varrho \int r_{piqj}^{-n+2} g_{ij}^{(2)}(r_{piqj}) dr_{piqj}. \tag{72}$$

Eq. (69) is valid for octahedrally-symmetric molecules also (e.g. SF_6), for which the lowest non-zero moment is a hexadecapole Φ. In this case, the mean squared molecular electric field (70) is

$$\langle F_{ij}^2 \rangle = \tfrac{120}{7} (\Phi_i^2 + \Phi_j^2) \langle r_{ij}^{-12} \rangle. \tag{70b}$$

The preceding simple examples prove the importance of molecular field fluctuations in regions of short-range order. Owing to these fluctuations, the constant (21) plays a highly significant rôle, not only in dipolar substances but also in non-dipolar ones composed of molecules possessing even electric moments (a quadrupole, hexadecapole, etc.). The same discussion applies to the influence of molecular field fluctuations on the other saturation constants (19), (22), (23), and especially on the dipolar constant (24), which can lead to a strongly temperature-dependent behaviour in non-dipolar substances [28].

4.3. Spatial molecular redistribution

Yvon [56] and Kirkwood [57] proposed a theory of the electric permittivity of non--polar liquids taking into account translational fluctuations, related to interaction of induced molecular dipoles. The Yvon–Kirkwood theory has since been extended by Brown [58] and many others (see Refs [28, 30]). Kielich showed that two, or three isotropic molecules, interacting mutually by way of induced electric dipoles, form anisotropic assemblages which undergo reorientation in an intense field leading to electro-optical and magneto-optical birefringence [59] as well as optical-optical birefringence induced

by intense light [60]. Subsequently, Helwarth [61] described the mechanism as spatial molecular redistribution and showed it to play an important part in self-focussing of laser light in simple liquids. Interactions between induced atomic and molecular dipoles are highly relevant to higher optical nonlinearities, as shown by Kielich and Woźniak [62]. Their importance in the effect of picosecond pulses on matter is obvious from recent results of Piekara [63].

In the presence of the molecular redistribution effect, the linear polarizability tensor of the medium can be written in the form of the expansion

$$A_{\alpha\beta}(\Gamma) = A_{\alpha\beta}^{(0)}(\Gamma) + A_{\alpha\beta}^{(1)}(\Gamma) + A_{\alpha\beta}^{(2)}(\Gamma) + \ldots, \tag{73}$$

the first term of which is given, in the absence of translational fluctuations, by (29). For isotropic molecules and interactions of the dipole-dipole kind, the successive terms of (73) resulting by perturbations of the first, second and higher order are of the form [64]

$$A_{\alpha\beta}^{(1)}(\Gamma) = -\sum_{ij} \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} a_i(\tau_p) T_{\alpha\beta}^{(piqj)} a_j(\tau_q), \tag{73a}$$

$$A_{\alpha\beta}^{(2)}(\Gamma) = \sum_{ijk} \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \sum_{r=1}^{N_k} a_i(\tau_p) T_{\alpha\gamma}^{(pirk)} a_k(\tau_r) T_{\gamma\beta}^{(rkqj)} a_j(\tau_q) \tag{73b}$$

where

$$T_{\alpha\beta}^{(piqj)} = -r_{piqj}^{-5}(3r_\alpha^{piqj} r_\beta^{piqj} - r_{piqj}^2 \delta_{\alpha\beta}) \tag{74}$$

is the tensor of dipole-dipole interaction between molecules p and q of the species i and j mutually distant by r_{piqj}.

On insertion of the expansion (73) into the saturation constant (22) one obtains in a satisfactory approximation

$$S_A = \frac{4\pi\beta}{15V} \sum_{ijkl} \left\langle \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \sum_{r=1}^{N_k} \sum_{s=1}^{N_l} a_i(\tau_p) a_j(\tau_q) a_k(\tau_r) a_l(\tau_s) T_{pirk} : T_{qjsl} \right\rangle, \tag{75}$$

which can be re-written in the form

$$S_A = \sum_{ij} x_i x_j S_A^{(ij)} + \sum_{ijk} x_i x_j x_k S_A^{(ijk)} + \sum_{ijkl} x_i x_j x_k x_l S_A^{(ijkl)}. \tag{76}$$

Hence (as one would expect) in the case of isotropic molecules no additive term occurs in the absence of correlation; this was directly obvious from Eq. (45), since for molecules without intrinsic anisotropy ($\kappa_i = 0$), $S_A^{(i)} = 0$. Many-body correlations of atoms or isotropic molecules cause successive nonadditivities in (76). In the approximation of binary correlation and taking into account constructive interference [59, 66] one has

$$S_A^{(ij)} = \frac{16\pi}{5} \beta\varrho a_i^2 a_j^2 \langle r_{ij}^{-6} \rangle. \tag{77}$$

In the approximation applied, this result is the counterpart of that (64) derived on the Silberstein model.

For ternary correlations one has by (75)

$$S_A^{(ijk)} = \frac{8\pi}{5}\beta\varrho(a_i a_j^2 a_k \langle r_{ij}^{-3} r_{jk}^{-3}\rangle + 2a_i^2 a_j a_k \langle r_{ik}^{-3} r_{ij}^{-3}\rangle$$

$$+ a_i a_j a_k^2 \langle r_{ik}^{-3} r_{kj}^{-3}\rangle), \tag{78}$$

involving the ternary radial correlation parameter

$$\langle r_{ij}^{-3} r_{jk}^{-3}\rangle = \frac{\varrho^2}{2V}\iiint \{3(\mathbf{r}_{piqj}\cdot\mathbf{r}_{qjrk})^2 - r_{piqj}^2 r_{qjrk}^2\}$$

$$r_{piqj}^{-5} r_{qjrk}^{-5} g_{ijk}^{(3)}(\mathbf{r}_{pi}, \mathbf{r}_{qj}, \mathbf{r}_{rk}) d\mathbf{r}_{pi} d\mathbf{r}_{qj} d\mathbf{r}_{rk}. \tag{79}$$

The last term of the expansion (76) accounts for quaternary radial correlations, and is of the form

$$S_A^{(ijkl)} = \frac{8\pi}{5}\beta\varrho a_i a_j a_k a_l \langle r_{ik}^{-3} r_{jl}^{-3}\rangle, \tag{80}$$

with

$$\langle r_{ik}^{-3} r_{jl}^{-3}\rangle = \frac{\varrho^3}{6V}\iiiint \mathbf{T}_{pirk}:\mathbf{T}_{qjsl}g_{ijkl}^{(4)}(\mathbf{r}_{pi}, \mathbf{r}_{qj}, \mathbf{r}_{rk}, \mathbf{r}_{sl}) d\mathbf{r}_{pi} d\mathbf{r}_{qj} d\mathbf{r}_{rk} d\mathbf{r}_{sl}; \tag{81}$$

$g_{ijkl}^{(4)}$ being the four-molecule correlation function.

Likewise, an analysis of molecular distribution can be performed for intrinsically electrically anisotropic molecules [45, 61, 62]. The results, in this case, are rather complicated and we refrain from adducing them in this paper.

It is a noteworthy feature of the redistribution mechanism that, with regard to the definition of Eq. (72), the binary radial correlation parameter $\langle r_{ij}^{-6}\rangle$ intervening in Eq. (77) is positive for the model of rigid spheres at minimal distance d_{ij}, when [28]

$$\langle r_{ij}^{-n}\rangle = \frac{4\pi\varrho}{n-3} d_{ij}^{n-3}. \tag{72a}$$

On the contrary, the triple radial correlation parameter (79) is in general negative for realistic models [28, 65] thus lowering the induced electric anisotropy of the assemblage of molecules.

4.4. Redistributions and fluctuations of molecular fields

We still have to calculate the effect of linear molecular redistribution on the constant (23); the latter, for non-dipolar isotropically polarizable molecules, is by (65a) and (73a) in a satisfactory approximation

$$S_{AM} = -\frac{8\pi\beta^2}{15V}\sum_{ijkl} a_i a_j a_k a_l \left\langle \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \sum_{r=1}^{N_k} \sum_{s=1}^{N_l} \mathbf{T}_{piqj}:(\mathbf{F}_{rk}\mathbf{F}_{sl})\right\rangle. \tag{82}$$

Thus the constant (82) owing to translational fluctuations and molecular field fluctuations also is non-zero for non-dipolar, isotropically polarizable molecules. Methods of statistical mechanics lead to an expansion of (82) similar to that of (76) with no additive term since, by (50), $S_{AM}^{(i)}$ vanishes in the absence of correlation in the case of non-dipolar molecules and ones with no electric polarizability anisotropy.

The expression (82) is approximately applicable to quadrupole molecules, whose polarizability anisotropy can·be neglected. Binary radial correlations now lead to

$$S_{AM}^{(ij)} = \frac{32\pi}{25} \beta^2 \varrho a_i a_j (a_i^2 \Theta_j^2 + \Theta_i^2 a_j^2) \langle r_{ij}^{-11} \rangle. \tag{83}$$

Tetrahedrally symmetric molecules (e.g. CCl_4) have no linear polarizability anisotropy, but present an octupole moment Ω; in this case Eq. (82), in the approximation of binary radial correlations, leads to

$$S_{AM}^{(ij)} = \frac{128\pi}{35} \beta^2 \varrho a_i a_j (a_i^2 \Omega_j^2 + \Omega_i^2 a_j^2) \langle r_{ij}^{-13} \rangle. \tag{84}$$

The discussion of the constant S_{AM} proceeds similarly for dipole molecules, for which in the absence of molecular fields one has Eqs (49)–(52). If, however, the dipoles are polarizable, their spatial redistribution makes it necessary to consider further contributions; in the binary approximation, we obtain by (82)

$$S_A^{(ij)} = \frac{16\pi}{15} \beta^2 \varrho a_i a_j (a_i^2 m_j^2 + m_i^2 a_j^2) \langle r_{ij}^{-9} \rangle, \tag{85}$$

where, obviously, anisotropy of polarizability has been neglected.

It is equally feasible to discuss along similar lines the effect of molecular redistribution with respect to other molecular models including anisotropic linear and nonlinear polarizabilities as well as translational-orientational fluctuations [60, 45, 67].

In Section 4.2, with regard to the expansion (65), we assumed the molecular electric field to polarize the molecules but linearly. In fact, the molecular fields largely exceed in strength the externally applied DC electric field. For this reason, it is indispensable to consider nonlinear polarisations, induced in the molecular systems by the fields F and leading apart from (65) to

$$M_\alpha^{NL}(\Gamma) = \sum_i \sum_{p=1}^{N_i} \{ \tfrac{1}{2} b_{\alpha\beta\gamma}^{(i)}(\tau_{pi}) F_\beta(\tau_{pi}) F_\gamma(\tau_{pi}) + \tfrac{1}{6} c_{\alpha\beta\gamma\delta}^{(i)}(\tau_{pi}) F_\beta(\tau_{pi}) F_\gamma(\tau_{pi}) F_\delta(\tau_{pi}) + \ldots \}. \tag{86}$$

Clearly, the effect of nonlinear molecular polarizability due to fluctuating electric fields has a bearing on the linear polarizability tensor also

$$A_{\alpha\beta}^{NL}(\Gamma) = \sum_i \sum_{p=1}^{N_i} \{ b_{\alpha\beta\gamma}^{(i)}(\tau_{pi}) F_\gamma(\tau_{pi}) + \tfrac{1}{2} c_{\alpha\beta\gamma\delta}^{(i)}(\tau_{pi}) F_\gamma(\tau_{pi}) F_\delta(\tau_{pi}) + \ldots \}. \tag{87}$$

When taken into account in the analysis of the saturation constants (21)–(24), the expansions (65), (73), (86) nad (87) lead to new coupling mechanisms between molecular redistribution and molecular field fluctuations and hence to nonadditivities in S.

5. Discussion and conclusions

The above proposed theory states that the dielectric saturation constant S of a multi-component system takes the form of the following expansion in a power series of the molar fractions

$$S = \sum_i x_i S_i + \sum_{ij} x_i x_j S_{ij} + \sum_{ijk} x_i x_j x_k S_{ijk} + \sum_{ijkl} x_i x_j x_k x_l S_{ijkl} + \dots . \tag{88}$$

In the absence of intermolecular interaction S reduces to the first term of (88), and thus is an additive property. The investigation of such perfect mixtures (perfect, or rarefied gases) permits to determine the electric properties of the individual molecules.

Since in gases and their mixtures the $\Delta\varepsilon$ effect is small and not measurable by available methods [28], experimental work is directed towards liquids and liquid solutions, where the effects are considerable [68, 69] and at present measurable in non-dipolar solvents [42]. By (88), however, the saturation constant S of dense mixtures is additive in a first approximation only, so that the study of deviations from additivity in S automatically yields information regarding the nature and magnitude of the intermolecular forces as well as the microscopic structure of the solution. The gaining of these novel data is made easier owing to the circumstance that expansions like (88) hold, as well, for the constants characterizing a variety of other effects, namely linear molecular polarization [38], molecular refraction [70], light scattering [41, 45], the Cotton–Mouton effect [59], Kerr effect [44] and optically induced Kerr effect [60], DC electric field-induced second-harmonic generation [54], and double-photon scattering [55, 71]. The molecular-statistical mechanisms of these effects recur in the contributions (19)–(24) to S. Hence as was first noted by Piekara [19, 20], a complete analysis of dielectric saturation can be given only insofar as results on related dielectric, electro- and magneto-optical, and other effects are available. It is to be regretted that since the publication of Piekara's paper [20] no such complete experimental and theoretical analysis of nonlinear effects in liquids and solutions has appeared. The numerous existing studies are mostly restricted in scope (see the review article [28]). Lately, Mrs Danielewicz–Ferchmin [72] has given a more thorough analysis of dielectric saturation measurements in solutions of alcohols based on ideas of Piekara [23].

Within the treatment applied throughout this paper the saturation constant S, in accordance with the expansion (88), depends on the molar fractions directly and explicitly and, implicitly, by way of the multi-molecular correlation functions $g_{ij}^{(2)}$, $g_{ijk}^{(3)}$, ..., defined in the statistical mechanics of fluids as functions of density [73]. If the form of the functions expressing the dependence of the g's on the density, and hence on the molar fractions, is available, the expansion (88) can be put in a form such that the expansion coefficients no longer depend explicitly on the concentration of the solution. This can be done with ease e.g. for a two-component system in which $x = x_2$ is the molar fraction of the solute

and $1-x = x_1$ that of the solvent, leading to [28]

$$S(x) = \sum_{n=0} Q_n x^n = Q_0 + Q_1 x^1 + Q_2 x^2 + Q_3 x^3 + \dots, \qquad (89)$$

where the coefficients

$$Q_n = \frac{1}{n!} \left\{ \frac{\partial^n S(x)}{\partial x^n} \right\}_{x=0} \qquad (90)$$

can be measured directly in experiment and, on the other hand, calculated theoretically from the statistical expansion (88). The analysis follows a path similar to that proposed earlier for the Kerr effect in liquid solutions [44].

Namely, we have by (88)–(90) for the successive coefficients

$$Q_0 = (f_0)_{x=0},$$

$$Q_1 = \left(\frac{\partial f_0}{\partial x} + f_1 \right)_{x=0},$$

$$Q_2 = \left(\tfrac{1}{2} \frac{\partial^2 f_0}{\partial x^2} + \frac{\partial f_1}{\partial x} + f_2 \right)_{x=0},$$

$$Q_3 = \left(\tfrac{1}{6} \frac{\partial^3 f_0}{\partial x^3} + \tfrac{1}{2} \frac{\partial^2 f_1}{\partial x^2} + \frac{\partial f_2}{\partial x} + f_3 \right)_{x=0}, \qquad (91)$$

where we have introduced functions, dependent on x by way of molecular correlation functions

$$f_0 = S_1 + S_{11} + S_{111} + S_{1111} + \dots,$$

$$f_1 = S_2 - S_1 + 2(S_{12} - S_{11}) + 3(S_{112} - S_{111}) + 4(S_{1112} - S_{1111}) + \dots$$

$$f_2 = S_{11} - 2S_{12} + S_{22} + 3(S_{111} - 2S_{112} + S_{122}) + 6(S_{1111} - 2S_{1112} + S_{1122}) + \dots$$

$$f_3 = S_{222} - 2S_{122} + 3S_{112} - S_{1111} + 4S_{1222} - 4(S_{1122} + 4S_{1112} - S_{1111}) + \dots \qquad (92)$$

Above, we assume the non-additive constants $S_{ij}, S_{ijk} \dots$ of Eq. (88) to be symmetric in the indices $i, j, k \dots$

Since Q_0 is related with the properties of the solvent only, it is convenient to consider the variation in saturation constant

$$\Delta S(x) = \frac{S(x) - Q_0}{x} = \sum_{n=1}^{\infty} Q_n x^{n-1} = Q_1 + Q_2 x + Q_3 x^2 + Q_4 x^3 + \dots \qquad (93)$$

characterizing the solution apart from the solvent.

To describe the nonlinear electric properties of the solute molecules, we apply the method of infinite dilution, whe Eq. (93) becomes, in the limit

$$\Delta S_\infty = \lim_{x \to 0} \left\{ \frac{S(x) - Q_0}{x} \right\} = Q_1. \tag{94}$$

As apparent from (91) and (92), the quantity Q_1 is now a function of the properties of the isolated molecules of the solute (S_2) modified by the influence of the solvent $(S_1, S_{11}, ...)$ leading to effects measurable by existing technique [42]. This is so because in the highly dilute case the rare molecules of the solute are separated from one another by the very numerous solvent molecules, with which they are free to interact $(S_{12}, S_{112}, ...)$. Eq. (94) thus provides essential information regarding the interaction between a solute molecule and the solvent molecules surrounding it.

When experiment reveals a linear deviation from additivity (the case of moderately concentrated solutions) one has to consider the coefficient Q_2, dependent on binary correlations between molecules of the solute (S_{22}) as well as on two- and multi-molecular solute-solvent interactions $(S_{12}, S_{112}, S_{122}, ...)$. At still higher concentrations the variables (93) depend on x quadratically, and Q_3 accounts for triple correlations between molecules of the solvent (S_{222}). The higher functions of x in Eq. (93) account for correlations of 4 and more molecules of the solute.

Numerical computations of the contributions to S obviously depend on the availability of the electric parameters of the molecules — their permanent multipoles [28] and induced linear [11, 12] and nonlinear dipoles, available from theoretical calculations [74] and from experimental studies on gases [75] (cf. [28]). As we have said, besides direct angular correlations of anisotropic molecules a decisive role in dense media belongs to fluctuations of electrical fields (68) induced generally by molecular multipoles [38]

$$F_{piqj} = \sum_{n=1}^{\infty} \frac{(-1)^n}{(2n-1)!!} \, {}^{(1)}T_{piqj}^{(n)}[n] M_{qj}^{(n)}. \tag{95}$$

Here, M_{qj}^n is the electric 2^n-pole moment of the q-th molecule of species j, and ${}^{(1)}T_{piqj}^{(n)} = -\nabla^{n+1}(r_{piqj}^{-1})$ is the two-molecule interaction tensor. As already shown, the constant (69) and others contain the mean square of the molecular field (70) which, by (91), is of the general form [76]

$$\langle F_{piqj} \cdot F_{piqj} \rangle = \sum_{n=1}^{\infty} \frac{(n+1)!}{(2n-1)!!} \, M_j^{(n)}[n] M_j^{(n)} \langle r_{piqj}^{-2n+2} \rangle. \tag{96}$$

The foregoing expression is directly applicable to polar molecules of all kinds, since the tensorial elements of molecular multipole moments up to $n = 4$ inclusively are now available for all molecular symmetries [77].

In the general case, the statistical averages in Eqs (19)–(24) have to be taken with the dispersional, inductional and electrostatic potential energy of intermolecular interaction given by [76]

$$V(\Gamma) = -\tfrac{1}{2} \sum_{ij} \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \sum_{n=0} \sum_{m=0} \frac{(-1)^n}{(2n-1)!!(2m-1)!!}$$

$$M_{pi}^{(n)}[n]^{(n)}T_{piqj}^{(m)}[m]M_{qj}^{(m)} + \dots \tag{97}$$

Applying statistical perturbation calculus [28], it is thus possible to calculate further temperature-dependent contributions to the constants (19)–(24) as done previously with regard to dielectric molecular polarisation [38].

Studies of the constants S_{ij}, S_{ijk}, ... of the expansion (88) will yield direct information regarding the multi-molecular correlation function, including superposition principles of the Kirkwood type [73]. Multi-molecular functions intervene but indirectly in linear phenomena; nonlinear effects in dense media depend, however, on multiple correlations in a manner making them accessible to determination by direct, experimental measurement *versus* concentration and its temperature-variations.

The formulae (26) and (27) for the quadratic change in electric permittivity tensor in conjunction with the constants (19)–(24) are of so high a grade of generality as to be applicable to solutions of synthetic and biological macromolecules, and liquid crystals. These plastic crystalline bodies, the electric field behaviour of which has in the past been studied by Jeżewski [71] and Mięsowicz [79], are of interest in dielectric saturation studies, as proved by the latest work of Krupkowski and Vieth [49], and have recently become the object of widely ranging studies and applications [80].

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