OPTICALLY INDUCED BIREFRINGENCE

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From considerations of classical electrodynamics and statistical mechanics, a general theory of birefringence induced in nondispersive isotropic dense media by a light beam of very high intensity is developed. By a semi-macroscopic method a general equation for the light intensity-dependent refractive index is derived, and the optical birefringence constant B is obtained therefrom. This constant B is proved to consist of two terms, one of which results from the third-order optical polarization due to the strong oscillating electric field, whereas the second term arises from the optical molecular orientation effect which depends directly on the temperature. The birefringence constant B is then discussed in detail for the case of systems consisting of mutually interacting molecules, the latter being isotropically polarizable, or optically anisotropic with a centre of symmetry, or possessing no centre of inversion. Both the radial and angular interactions of the molecules are accounted for by means of binary and ternary correlation functions. The immediate effect on B of the electric fields of the induced and permanent molecular dipoles is also taken into account. Finally, the fundamentals of a statistical theory of the optical birefringence of multi-component systems, with applications to compressed gas mixtures, are proposed.

1. Introduction

The well-known theory of dielectric polarization in a time-dependent electric field

$$\boldsymbol{F} = \boldsymbol{F}_0 \, e^{i\omega t} \tag{1.1}$$

is due to Debye [1], who found that the average moment of a dipole molecule with permanent electric moment μ is

$$\langle \boldsymbol{m} \rangle = \frac{\mu^2 \boldsymbol{F}_0}{3kT} \frac{e^{i\omega t}}{1 + i\omega\tau_1}, \tag{1.2}$$

where

$$\tau_1 = \frac{4\pi r^3 \eta}{kT} \tag{1.3}$$

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is the Debye microscopic relaxation time for a molecular sphere of radius r rotating in a liquid of inner friction constant η. Obviously, for $\omega = 0$ we have the orientational polarization in a static electric field, whereas for very large values of $\omega\tau$, by (1.2), the dipole polarization vanishes.

Peterlin and Stuart [2] extended Debye's relaxation theory to the case of the optical birefringence induced in a substance by a strong oscillating electric field (1.1). In this case we have the following formula:

$$n_{||}-n_{\perp} = \frac{\pi\varrho(n^2+2)^2}{45nkT}\, a\varkappa_a \left\{ 3\alpha\varkappa_\alpha \left[1 + \frac{\cos{(2\omega t-\delta_2)}}{\sqrt{1+4\omega^2\tau_2^2}}\right] + \right.$$
$$\left. + \frac{\mu^2}{kT}\left[\frac{1}{1+\omega^2\tau_1^2} + \frac{\cos{(2\omega t-\delta_3)}}{\sqrt{1+\omega^2\tau_1^2}\sqrt{1+4\omega^2\tau_2^2}}\right]\right\} F_0^2 \tag{1.4}$$

for the difference between the refractive indices in the directions parallel and perpendicular to $\boldsymbol{F}$. In Eq. (1.4), ϱ is the number density of the substance and the quantities $\varkappa_a$ and $\varkappa_\alpha$ determine the anisotropies of optical and electric polarizabilities of the axially-symmetric molecules.

In the case when $\omega = 0$, Eq. (1.4) reduces to the well-known formula

$$n_{||}-n_{\perp} = \frac{2\pi\varrho(n^2+2)^2}{45nkT}\, a\varkappa_a \left\{ 3\alpha\varkappa_\alpha + \frac{\mu^2}{kT}\right\}F^2 \tag{1.5}$$

derived previously by Langevin and Born with a view to explain theoretically the temperature-dependence of the Kerr effect.

If $\omega\tau_1 \to \infty$ and $\omega\tau_2 \to \infty$, formula (1.4) becomes simply

$$n_{||}-n_{\perp} = \frac{\pi\varrho(n^2+2)^2}{15nkT}\, a\varkappa_a\, \alpha\varkappa_\alpha\, F_0^2, \tag{1.6}$$

which is a formula analogous to the one derived by Buckingham [3] for the optical birefringence induced in isotropic media by a light beam of very high intensity (see also Refs [4—6]).

In general, the optical molecular orientational effect of (1.6) is always accompanied by an optical nonlinear deformational effect, which does not depend directly on the temperature. The latter effect consists in the induction of optical anisotropy within the molecule itself and is the counterpart of the nonlinear deformation effect discussed by Voigt and Born in the theory of the Kerr effect. The birefringence due to the effect of nonlinear optical deformation can appear even in inert gases and substances consisting of molecules with spherical symmetry, and is given by the following formula [3,5]:

$$n_{||}-n_{\perp} = \frac{\pi\varrho(n^2+2)^2}{18n}\,(c_{11:11}-c_{11:22})\,F_0^2, \tag{1.7}$$

where $c_{11:11}$ and $c_{11:22}$ are the respective components of the third-order polarizability tensor accounting for the nonlinear change in optical polarizability produced in the molecule by the square of the strong optical field. Clearly, the experimental detection of the optically

induced anisotropy in an isotropic medium would require the use of the oscillating electric field associated with a very intense light beam, *e.g.* from lasers. Recently, optical birefringence has been observed by Gires and Mayer [7] and by Paillette [8] in a number of liquids.

Maker and Terhune [6] calculated the intensity-dependent refractive index variations for the two senses of circular polarization of elliptically polarized incident light and observed this effect in several liquids [9].

In the present paper, we shall first discuss the molecular relaxation theory of optical birefringence in liquids and subsequently derive a semi-macroscopic equation for the refractive index of light in the presence of another light wave of intensity sufficiently great for the dense isotropic medium to undergo nonlinear polarization in its electric field. The general equation is discussed for several special cases of systems of non-interacting or interacting molecules that are spherically symmetrical, or tetrahedrally symmetrical, or axially symmetrical with or without a centre of inverson.

2. Relaxation theory

We shall consider a medium of volume V, macroscopically isotropic in the absence of external forces. Let the medium consisting of N identical molecules be acted on by a local electrical field $\boldsymbol{F}$. The potential energy possessed by a molecule of the medium in the electric field is, to within the second power of $\boldsymbol{F}$,

$$u(\Omega, \boldsymbol{F}) = \mu_\alpha F_\alpha - \frac{1}{2}\alpha_{\alpha\beta}F_\alpha F_\beta, \tag{2.1}$$

where μ_α is the α-component of the electric dipole moment of the molecule and $\alpha_{\alpha\beta}$ — the $\alpha\beta$ component of its electric polarizability tensor; the set of variables Ω describes the orientation of the molecule with respect to the direction of the applied electric field.

The Maxwell-Boltzman distribution function of the molecule with orientation Ω in the presence of the external electric field at thermodynamical equilibrium of the system and at temperature T is given by

$$f(\Omega, \boldsymbol{F}) = \frac{\exp\left\{-\dfrac{u(\Omega, \boldsymbol{F})}{kT}\right\}}{\displaystyle\int \exp\left\{-\dfrac{u(\Omega, \boldsymbol{F})}{kT}\right\} d\Omega}, \tag{2.2}$$

where the integrations are over all molecular directions in a solid angle $d\Omega$.

On expanding the right hand side of (2.2) in a power series in u, we obtain up to the second-order approximation

$$f(\Omega, \boldsymbol{F}) = f(\Omega, 0) + f^{(1)} + f^{(2)} + \dots, \tag{2.3}$$

where $f(\Omega, 0) = \Omega^{-1}$ is the distribution function in the absence of the external field, whereas $f^{(1)}$ and $f^{(2)}$ are the first- and second-order distribution functions in the presence

of the field $\boldsymbol{F}$,

$$f^{(1)}(\Omega, \boldsymbol{F}) = \frac{f(\Omega, 0)}{kT}(\bar{u} - u), \tag{2.4}$$

$$f^{(2)}(\Omega, \boldsymbol{F}) = \frac{f(\Omega, 0)}{2k^2T^2}\{u^2 - \overline{u^2} + 2(\bar{u} - u)\bar{u}\}. \tag{2.5}$$

Here,

$$\overline{u^n} = \int \{u(\Omega, \boldsymbol{F})\}^n f(\Omega, 0)d\Omega \tag{2.6}$$

is the unweighted average evaluated with the zero-order distribution function over all molecular orientations Ω.

With respect to the expressions (2.1) and (2.6) we have

$$\bar{u} = -\frac{1}{2}\alpha\delta_{\alpha\beta}F_\alpha F_\beta,$$

$$\overline{u^2} = \frac{1}{3}\mu^2\delta_{\alpha\beta}F_\alpha F_\beta, \tag{2.7}$$

and the distribution functions (2.4) and (2.5) can be rewritten as follows:

$$f^{(1)}(\Omega, \boldsymbol{F}) = \frac{f(\Omega, 0)}{kT}\left\{\mu_\alpha F_\alpha + \frac{1}{2}(\alpha_{\alpha\beta} - \alpha\delta_{\alpha\beta})F_\alpha F_\beta\right\}, \tag{2.8}$$

$$f^{(2)}(\Omega, \boldsymbol{F}) = \frac{f(\Omega, 0)}{6k^2T^2}(3\mu_\alpha\mu_\beta - \mu^2\delta_{\alpha\beta})F_\alpha F_\beta, \tag{2.9}$$

where $\alpha = \alpha_{\alpha\alpha}/3$ is the mean electric polarizability of the molecule and $\delta_{\alpha\beta}$ — the unit tensor.

If the molecules possess the axial symmetry (the axis of symmetry being the 3-axis) we have

$$\mu_\alpha = \mu k_\alpha, \quad \alpha_{\alpha\beta} = \alpha\delta_{\alpha\beta} + \alpha\varkappa_\alpha(3k_\alpha k_\beta - \delta_{\alpha\beta}), \tag{2.10}$$

where k_α is the α-component of a unit vector along the axis of symmetry of the molecule and the quantities

$$\varkappa_\alpha = \frac{\alpha_{33} - \alpha_{11}}{3\alpha} \tag{2.11}$$

define the anisotropy of electric polarizability of the molecule.

By (2.10), the distribution functions (2.8) and (2.9) assume the following simple form

$$f^{(1)}(\Omega, \boldsymbol{F}) = \frac{f(\Omega, 0)}{kT}\left\{\mu F \cos\vartheta + \frac{1}{2}\alpha\varkappa_\alpha(3\cos^2\vartheta - 1)F^2\right\}, \tag{2.12}$$

$$f^{(2)}(\Omega, \boldsymbol{F}) = \frac{f(\Omega, 0)}{6k^2T^2}(\mu F)^2(3\cos^2\vartheta - 1), \tag{2.13}$$

where ϑ is the angle between the symmetry axis of the molecule and the direction of the electric field $\boldsymbol{F}$.

An entirely different picture results if an oscillating, with frequency ω, electrical field is applied to the medium. In this case

$$\boldsymbol{F}(t) = \boldsymbol{F}_0 \cos \omega t, \tag{2.14}$$

and the distribution function becomes variable with the time t; namely, we have now instead of (2.12) and (2.13)

$$f^{(1)}(\Omega, F_0, t) = \frac{f(\Omega, 0)}{kT} \left\{ A\mu F_0 \cos \vartheta \cos (\omega t - \delta_1) + \right.$$

$$\left. + \frac{1}{4} \ \alpha \varkappa_\alpha F_0^2 (3 \cos^2 \vartheta - 1) [B_1 + B_2 \cos (2\omega t - \delta_2)] \right\}, \tag{2.15}$$

$$f^{(2)}(\Omega, F_0, t) = \frac{f(\Omega, 0)}{12k^2T^2} (\mu F_0)^2 (3 \cos^2 \vartheta - 1) [C_1 + C_2 \cos (2\omega t - \delta_3)]. \tag{2.16}$$

On substitution of the above distribution functions in the following differential equation [1, 2]:

$$\frac{1}{\sin \vartheta} \frac{\partial}{\partial \vartheta} \left(\sin \vartheta \frac{\partial f}{\partial \vartheta} \right) + \frac{1}{kT} \left\{ \frac{\partial u}{\partial \vartheta} \frac{\partial f}{\partial \vartheta} + \frac{1}{\sin \vartheta} \frac{\partial}{\partial \vartheta} \left(\sin \vartheta \frac{\partial u}{\partial \vartheta} \right) f \right\} = \frac{W}{kT} \frac{\partial f}{\partial t}, \tag{2.17}$$

we obtain

$$A = \frac{1}{\sqrt{1 + \omega^2 \tau_1^2}}, \qquad \tau_1 = \frac{W}{2kT},$$

$$B_1 = 1, B_2 = \frac{1}{\sqrt{1 + 4\omega^2 \tau_2^2}}, \qquad \tau_2 = \frac{W}{6kT},$$

$$C_1 = \frac{1}{(1 + \omega^2 \tau_1^2)}, \qquad C_2 = \frac{1}{\sqrt{1 + \omega^2 \tau_1^2} \sqrt{1 + 4\omega^2 \tau_2^2}}, \tag{2.18}$$

where τ_1 and τ_2 are relaxation times and W is a constant measuring the inner friction in a liquid.

We now consider the case when the molecules of the medium are subjected to two electric fields $\boldsymbol{F}'$ and $\boldsymbol{F}$. We assume the electric field strength $\boldsymbol{F}' = \boldsymbol{F}_0' \cos \omega' t$ conveyed by the incident light wave of frequency ω' to be small and assign o it the role of a measuring field, whereas that of the other field $\boldsymbol{F} = \boldsymbol{F}_0 \cos \omega t$ is of very high intensity, sufficient for producing nonlinear polarization of the medium. The dipole moment induced in the molecule by the field $\boldsymbol{F}'$ is given by

$$m_\alpha = a_{\alpha\beta} F_\beta', \tag{2.19}$$

and its component in the direction of the field $\boldsymbol{F}'$ is

$$m_{F'} = \{ a + a\varkappa_a (3 \cos^2 \vartheta' - 1) \} F' \tag{2.20}$$

if the molecule has the axial symmetry and forms the angle ϑ' with $\boldsymbol{F}'$. Here, $a_{\alpha\beta}$ is the optical polarizability tensor of the molecule and

$$\varkappa_a = \frac{a_{33} - a_{11}}{3a} \tag{2.21}$$

its optical anisotropy.

The statistical average of (2.20) at time t in the presence of $\boldsymbol{F}$ is defined as

$$\langle m_{F'} \rangle_F = \int m_{F'} f(\Omega, F_0, t) d\Omega, \tag{2.22}$$

and using the time-dependent distribution functions (2.15) and (2.16) we obtain

$$\langle m_{F'} \rangle_F = aF' + \frac{a\varkappa_a}{30\,kT} (3\cos^2\varphi - 1) \left\{ 3\alpha\varkappa_a \left[1 + \frac{\cos(2\omega t - \delta_2)}{\sqrt{1+4\omega^2\tau_2^2}} \right] + \right.$$
$$\left. + \frac{\mu^2}{kT} \left[\frac{1}{1+\omega^2\tau_1^2} + \frac{\cos(2\omega t - \delta_3)}{\sqrt{1+\omega^2\tau_1^2}\sqrt{1+4\omega^2\tau_2^2}} \right] \right\} F'F_0^2, \tag{2.23}$$

where φ is the angle between the directions of the fields $\boldsymbol{F}'$ and $\boldsymbol{F}$.

Using the fact that the refractive index of a medium with number density $\varrho = N/V$ is given as

$$\frac{n^2-1}{n^2+2} F' = \frac{4\pi}{3} \varrho \langle m_{F'} \rangle_F, \tag{2.24}$$

we obtain by (2.23)

$$\frac{n^2-1}{n^2+2} - \frac{n_0^2-1}{n_0^2+2} = \frac{2\pi\varrho\,a\varkappa_a}{45kT} (3\cos^2\varphi - 1) \left\{ 3\alpha\varkappa_a \left[1 + \frac{\cos(2\omega t - \delta_2)}{\sqrt{1+4\omega^2\tau_2^2}} \right] + \right.$$
$$\left. + \frac{\mu^2}{kT} \left[\frac{1}{1+\omega^2\tau_1^2} + \frac{\cos(2\omega t - \delta_3)}{\sqrt{1+\omega^2\tau_1^2}\sqrt{1+4\omega^2\tau_2^2}} \right] \right\} F_0^2, \tag{2.25}$$

where

$$\frac{n_0^2-1}{n_0^2+2} = \frac{4\pi}{3} \varrho a \tag{2.26}$$

is the well-known Lorentz-Lorenz equation defining the refractive index of the medium.

Eq. (2.25) determines the effect of a strong oscillating electric field on the refractive index of the medium. The fact that n depends on the angle φ means that the isotropic medium has become optically anisotropic under the influence of a strong oscillating electric field and is now characterized by different values of its refractive index for different directions of the wave vector $\boldsymbol{F}'$ with respect to $\boldsymbol{F}$.

It is customary to define the optical anisotropy induced in a medium as the difference $n_{||} - n_{\perp}$ between its refractive indices for incident light with oscillations parallel and perpendicular to the direction of the applied electric field $\boldsymbol{F}$. The values $n_{||}$ and $n_{\perp}$ can be computed directly from Eq. (2.25) by substituting $\varphi = 0°$ and $\varphi = 90°$, respectively. This

yields for the optical birefringence

$$n_{||} - n_{\perp} = \frac{\pi\varrho(n_0^2+2)^2}{45\,kTn_0}\,a\varkappa_a \left\{ 3\alpha\varkappa_\alpha \left[1 + \frac{\cos{(2\omega t - \delta_2)}}{\sqrt{1+4\omega^2\tau_2^2}} \right] + \right.$$

$$\left. + \frac{\mu^2}{kT} \left[\frac{1}{1+\omega^2\tau_1^2} + \frac{\cos{(2\omega t - \delta_3)}}{\sqrt{1+\omega^2\tau_1^2}\sqrt{1+4\omega^2\tau_2^2}} \right] \right\} F_0^2, \tag{2.27}$$

since $n_{||}$ and $n_{\perp}$ differ but little from n_0.

For $\omega = 0$ we have from (2.27) the Langevin-Born formula for the usual Kerr effect

$$n_{||} - n_{\perp} = \frac{2\pi\varrho\,(n_0^2+2)^2}{45kTn_0}\,a\varkappa_\alpha \left(3\alpha\varkappa_\alpha + \frac{\mu^2}{kT} \right) F^2, \tag{2.28}$$

while for very large values of $\omega\tau_1$ and $\omega\tau_2$ Eq. (2.27) reduces to the result derived by Buckingham [3]

$$n_{||} - n_{\perp} = \frac{\pi\varrho(n_0^2+2)^2}{15kTn_0}\,(a\varkappa_a)^2\,F_0^2. \tag{2.29}$$

3. Semi-macroscopic theory

Consider an isotropic medium as represented by a macroscopic spherical specimen of volume V. Let two electromagnetic waves be incident on the volume V, the first with electric vector $\boldsymbol{E}_1 = \boldsymbol{E}_1^0 \cos \omega_1 t$ of low intensity and the second with electric vector $\boldsymbol{E}_2 = \boldsymbol{E}_2^0 \cos \omega_2 t$ of very great intensity. At not too great intensities of the incident light, the dipole moment $\boldsymbol{M}_1$ induced within the volume V can be assumed to be a linear function of the electric field $\boldsymbol{E}_1$, namely its σ component can then be written as follows:

$$M_{1\sigma} = \left(\frac{\partial M_{1\sigma}^{\vec{p}}}{\partial E_{1\tau}} \right)_0 E_{1\tau}. \tag{3.1}$$

In the case considered here we have the following fundamental equation for the refractive index in the presence of a strong electric field $\boldsymbol{E}_2$:

$$\frac{n^2-1}{n^2+2} = \frac{4\pi}{3} \left\langle \overline{\frac{1}{V} \frac{\partial M_{1\sigma}}{\partial E_{1\tau}} e_{1\sigma} e_{1\tau}}^t \right\rangle_{E_2}, \tag{3.2}$$

in which $\boldsymbol{e}_1$ is a unit vector in the direction of $\boldsymbol{E}_1$ and [3,5]

$$\langle \Phi \rangle_{E_2}^{\overline{}t} = \frac{\int \overline{\Phi(\tau, \boldsymbol{E}_2)}^t \exp\left\{ - \overline{\frac{U(\tau, \boldsymbol{E}_2)}{kT}}^t \right\} d\tau}{\int \exp\left\{ - \overline{\frac{U(\tau, \boldsymbol{E}_2)}{kT}}^t \right\} d\tau} \tag{3.3}$$

is the statistical average in the presence of the electric field $\boldsymbol{E}_2$, whereas the symbol $-t$ denotes the time-average over an oscillation period of $\boldsymbol{E}_2$.

The total potential energy of the system at configuration τ in the electric field $\boldsymbol{E}_2$ is given by the expansion

$$U(\tau, \boldsymbol{E}_2) = U(\tau, 0) - M_{2\sigma}^0 E_{2\sigma} - \frac{1}{2} \left(\frac{\partial M_{2\sigma}}{\partial E_{2\tau}} \right)_0 E_{2\sigma} E_{2\tau}, \tag{3.4}$$

where $U(\tau, 0)$ and $\boldsymbol{M}_2^0$ are the potential energy and electric dipole moment of the system at zero electric field.

Similarly we have the following expansion for the differential polarizability tensor of the medium:

$$\left(\frac{\partial M_{1\sigma}}{\partial E_{1\tau}} \right)_{E_2} = \left(\frac{\partial M_{1\sigma}}{\partial E_{1\tau}} \right)_0 + \left(\frac{\partial^2 M_{1\sigma}}{\partial E_{1\tau} \partial E_{2\nu}} \right)_0 E_{2\nu} + \frac{1}{2} \left(\frac{\partial^3 M_{1\sigma}}{\partial E_{1\tau} \partial E_{2\nu} \partial E_{2\varrho}} \right)_0 E_{2\nu} E_{2\varrho} + \ldots \tag{3.5}$$

Performing the time-averaging procedure of Eqs (3.4) and (3.5) we obtain ($\boldsymbol{e}_2$ is a unit vector in the direction of $\boldsymbol{E}_2$)

$$\overline{U(\tau, \boldsymbol{E}_2)}^t = U(\tau, 0) - \frac{1}{4} \left(\frac{\partial M_{2\sigma}}{\partial E_{2\tau}} \right)_0 e_{2\sigma} e_{2\tau} E_{02}^2, \tag{3.6}$$

$$\overline{\left(\frac{\partial M_{1\sigma}}{\partial E_{1\tau}} \right)_{E_2}}^t = \left(\frac{\partial M_{1\sigma}}{\partial E_{1\tau}} \right)_0 + \frac{1}{4} \left(\frac{\partial^3 M_{1\sigma}}{\partial E_{1\tau} \partial E_{2\nu} \partial E_{2\varrho}} \right) e_{2\nu} e_{2\varrho} E_{02}^2, \tag{3.7}$$

since

$$\overline{\boldsymbol{E}_2}^t = 0 \quad \text{and} \quad \overline{E_2^2}^t = \frac{1}{2} E_{02}^2 = \text{light intensity},$$

On substitution of (3.6) and (3.7) in Eq. (3.2) with (3.3), we obtain by expanding in powers of E_{02}

$$\frac{n^2-1}{n^2+2} = \frac{4\pi}{3V} \left\{ \left\langle \frac{\partial M_{1\sigma}}{\partial E_{1\tau}} e_{1\sigma} e_{1\tau} \right\rangle \left[1 - \frac{1}{4V} \left(\frac{\partial^2 V}{\partial E_2^2} \right)_0 E_{02}^2 - \frac{1}{4kT} \left\langle \frac{\partial M_{2\nu}}{\partial E_{2\varrho}} e_{2\nu} e_{2\varrho} \right\rangle E_{02}^2 \right] + \right.$$

$$\left. + \frac{1}{4} \left\langle \left(\frac{\partial^3 M_{1\sigma}}{\partial E_{1\tau} \partial E_{2\nu} \partial E_{2\varrho}} + \frac{1}{kT} \frac{\partial M_{1\sigma}}{\partial E_{1\tau}} \frac{\partial M_{2\nu}}{\partial E_{2\varrho}} \right) e_{1\sigma} e_{1\tau} e_{2\nu} e_{2\varrho} \right\rangle E_{02}^2 \right\}, \tag{3.8}$$

where

$$\langle \Phi \rangle = \frac{\displaystyle\int \Phi(\tau, 0) \exp\left\{ -\frac{U(\tau,0)}{kT} \right\} d\tau}{\displaystyle\int \exp\left\{ -\frac{U(\tau,0)}{kT} \right\} d\tau} \tag{3.9}$$

is the statistical mean value of Φ at zero external fields.

The quantity in (3.8)

$$\frac{1}{4} \left(\frac{\partial^2 V}{\partial E_2^2} \right)_0 E_{02}^2 = -\frac{V}{8\pi} \left\{ \left(\frac{\partial n_2^2}{\partial p} \right)_T - (n_2^2-1) \beta_T \right\} \overline{E_2^2}^t \tag{3.10}$$

determines the change in volume of the isotropic sample due to the strong optical electric field E_2 (this is an effect analogous to the electrostriction due to a strong DC electric field); p is the pressure and β_T — the isothermal compressibility of the medium.

At zero electric fields, all directions of the unit vectors e_1 and e_2 with respect to the laboratory reference system $(X_\sigma) = (X_1, X_2, X_3)$ have the same probability, so that the products of the components $e_{1\sigma}$ and $e_{2\nu}$ appearing in expansion (3.8) can be averaged over all possible directions of e_1 and e_2 with equal probability, and we obtain finally

$$\frac{n^2-1}{n^2+2} - \frac{n_1^2-1}{n_1^2+2} = \frac{\pi}{135V} \{10\delta_{\sigma\tau}\,\delta_{\nu\varrho} + [3(e_1\cdot e_2)^2 - 1]\chi_{\sigma\tau:\nu\varrho}\} \times$$

$$\times \left\langle \frac{\partial^3 M_{1\sigma}}{\partial E_{1\tau}\,\partial E_{2\nu}\,\partial E_{2\varrho}} + \frac{1}{kT}\frac{\partial M_{1\sigma}}{\partial E_{1\tau}}\frac{\partial M_{2\nu}}{\partial E_{2\varrho}} \right\rangle \overline{E_2^2}^t -$$

$$- \frac{2\pi}{27kTV}\left\langle \frac{\partial M_{1\sigma}}{\partial E_{1\sigma}}\right\rangle \left\{ \left\langle \frac{\partial M_{2\tau}}{\partial E_{2\tau}}\right\rangle - \frac{3kT}{4\pi}\left[\left(\frac{\partial n_2^2}{\partial p}\right)_T - (n_2^2-1)\beta_T \right] \right\} \overline{E_2^2}^t, \qquad (3.11)$$

where

$$\frac{n_1^2-1}{n_1^2+2} = \frac{4\pi}{9V}\left\langle \frac{\partial M_{1\sigma}}{\partial E_{1\sigma}}\right\rangle \qquad (3.12)$$

is the refractive index of the medium at zero external electric field E_2, and

$$\chi_{\sigma\tau:\nu\varrho} = 3\delta_{\sigma\nu}\delta_{\tau\varrho} + 3\delta_{\sigma\varrho}\delta_{\tau\nu} - 2\delta_{\sigma\tau}\delta_{\nu\varrho}. \qquad (3.13)$$

Let us assume the incident measuring electromagnetic wave to propagate in the direction of the Y-axis (x, y and z are unit vectors in the directions of the axes X, Y and Z of the laboratory reference system); computation from (3.11) of the refractive index in the direction of the axes X and Z now leads to the expression

$$n_z - n_x = n_1 B \{(z\cdot e_2)^2 - (x\cdot e_2)^2\} \overline{E_{s2}^2}^t \qquad (3.14)$$

determining the optical birefringence produced in the medium by the applied strong oscillating electric field E_2 related to the mean macroscopic field E_{s2} existing within the sphere by the formula

$$E_{s2} = \frac{3}{n_2^2+2} E_2. \qquad (3.15)$$

In Eq. (3.14) we have introduced the optico-optical birefringence constant B given as follows:

$$B = \frac{\pi}{30V}\left(\frac{n_1^2+2}{3n_1}\right)^2 \left(\frac{n_2^2+2}{3}\right)^2 \times$$

$$\times \chi_{\sigma\tau:\nu\varrho} \left\langle \frac{\partial^3 M_{1\sigma}}{\partial E_{1\tau}\,\partial E_{2\nu}\,\partial E_{2\varrho}} + \frac{1}{kT}\frac{\partial M_{1\sigma}}{\partial E_{1\tau}}\frac{\partial M_{2\nu}}{\partial E_{2\varrho}} \right\rangle. \qquad (3.16)$$

The above equation represents the general form of the optico-optical birefringence constant for an arbitrary isotropic medium.

Eq. (3.14) shows that the value and sign of the optical birefringence depends on the direction of oscillations of the electric vector $\boldsymbol{E}_2$. In particular, the optical birefringence is positive or negative according to whether the vector $\boldsymbol{E}_2$ of a plane polarized electromagnetic wave oscillates in the direction of Z or X. In the case of $\boldsymbol{E}_2$ oscillating parallel to Y, we have $n_z - n_x = 0$ meaning that the refractive index undergoes no nonlinear variation. Also, Eq. (3.14) can be applied in the case when $\boldsymbol{E}_2$ is conveyed by a non-polarized wave; now, however, the factor $g = (\boldsymbol{z} \cdot \boldsymbol{e}_2)^2 - (\boldsymbol{x} \cdot \boldsymbol{e}_2)^2$ has to be averaged over all possible directions of the vector $\boldsymbol{e}_2$ in the plane perpendicular to the direction of propagation of the wave. It should be noted that, if the wave with $\boldsymbol{E}_2$ is nonpolarized and propagates in the direction of Y ($\boldsymbol{E}_2$ oscillating in the XZ-plane at an angle ψ to the plane YZ), birefringence vanishes since $g = \overline{\cos^2 \psi} - \overline{\sin^2 \psi} = 0$. The factor g is equal to $\pm \frac{1}{2}$ according to whether the natural wave $\boldsymbol{E}_2$ propagates in the direction of Z or X.

4. Statistical-molecular theory

The mechanism of optical birefringence can be explained within the framework of the atomic-molecular theory of the structure of the medium. To this effect, the moments $\boldsymbol{M}_1$ and $\boldsymbol{M}_2$ of the macroscopic sphere, as appearing in the general equation (3.16), have to be expressed by means of moments relating to the microscopic properties of the individual atoms or molecules. Thus, let the macroscopic sphere of volume V contain N molecules of one species; we have

$$\boldsymbol{M}_1 = \sum_{p=1}^{N} \boldsymbol{m}_1^{(p)}, \ \boldsymbol{M}_2 = \sum_{q=1}^{N} \boldsymbol{m}_2^{(q)}, \tag{4.1}$$

where $\boldsymbol{m}_1^{(p)}$ and $\boldsymbol{m}_2^{(q)}$ are the electric dipole moments of the p-th and q-th molecule immersed in the medium subjected to the external electric fields $\boldsymbol{E}_1$ and $\boldsymbol{E}_2$.

By (4.1), Eq. (3.16) yields B as expressed by means of molecular parameters, in the form

$$B = \frac{\pi}{30V} \left(\frac{n_1^2 + 2}{3 n_1} \right)^2 \left(\frac{n_2^2 + 2}{3} \right)^2 \chi_{\sigma\tau:\nu\varrho} \left\langle \sum_{p=1}^{N} \frac{\partial^3 m_{1\sigma}^{(p)}}{\partial E_{1\tau} \partial E_{2\nu} \partial E_{2\varrho}} + \right.$$

$$\left. + \frac{1}{kT} \sum_{p=1}^{N} \sum_{q=1}^{N} \frac{\partial m_{1\sigma}^{(p)}}{\partial E_{1\tau}} \frac{\partial m_{2\nu}^{(q)}}{\partial E_{2\varrho}} \right\rangle. \tag{4.2}$$

Neglecting in a first approximation the effect of molecular fields on the optical properties of the molecules, we can express the dipole moment components $m_{1\sigma}^{(p)}$ and $m_{2\nu}^{(q)}$ as follows [10]:

$$m_{1\sigma}^{(p)} = \left\{ a_{\sigma\tau}^{(p)} + b_{\sigma\tau:\nu}^{(p)} E_{2\nu} + \frac{1}{2} c_{\sigma\tau:\nu\varrho}^{(p)} E_{2\nu} E_{2\varrho} + \ldots \right\} E_{1\tau}, \tag{4.3}$$

$$m_{2\nu}^{(q)} = \mu_\nu^{(q)} + \alpha_{\nu\varrho}^{(q)} E_{2\varrho} + \frac{1}{2} \beta_{\nu\varrho\lambda}^{(p)} E_{2\varrho} E_{2\lambda} + \ldots, \tag{4.4}$$

where the tensors $b_{\sigma\tau;\nu}^{(p)}$ and $c_{\sigma\tau;\nu\varrho}^{(p)}$ account for the nonlinear change in the optical polarizability of the p-th molecule due to the strong oscillating electric field $\boldsymbol{E}_2$.

On substituting (4.3) and (4.4) in Eq. (4.2) we have

$$B = \frac{\pi}{30V}\left(\frac{n_1^2+2}{3n_1}\right)^2\left(\frac{n_2^2+2}{3}\right)^2 \chi_{\sigma\tau;\nu\varrho}\left\langle \sum_{p=1}^{N} c_{\sigma\tau;\nu\varrho}^{(p)} + \frac{1}{kT}\sum_{p=1}^{N}\sum_{q=1}^{N} a_{\sigma\tau}^{(p)}\alpha_{\nu\varrho}^{(q)}\right\rangle. \tag{4.5}$$

For further discussion it is convenient to refer the tensors $a_{\sigma\tau}^{(p)}$ and $c_{\sigma\tau;\nu\varrho}^{(p)}$ (and, similarly, $\alpha_{\nu\varrho}^{(q)}$) to the molecular system $(X_\alpha^{(p)})_{\alpha=1,2,3}$ attached to the centre of the p-th (or, respectively, q-th) molecule of the medium. We shall now carry out the transformation of the tensors $a_{\sigma\tau}^{(p)}, c_{\sigma\tau;\nu\varrho}^{(p)}$ and $\alpha_{\nu\varrho}^{(q)}$ from the laboratory coordinate system (X_σ) to the molecular systems $(X_\alpha^{(p)})$ and $(X_\gamma^{(q)})$ by way of the relations

$$a_{\sigma\tau}^{(p)} = \omega_{\sigma\alpha}^{(p)}\omega_{\tau\beta}^{(p)}a_{\alpha\beta}^{(p)}, \quad \alpha_{\nu\varrho}^{(q)} = \omega_{\nu\gamma}^{(q)}\omega_{\varrho\delta}^{(q)}\alpha_{\gamma\delta}^{(q)}, \quad c_{\sigma\tau;\nu\varrho}^{(p)} = \omega_{\sigma\alpha}^{(p)}\omega_{\tau\beta}^{(p)}\omega_{\nu\gamma}^{(p)}\omega_{\varrho\delta}^{(p)}c_{\alpha\beta;\gamma\delta}^{(p)}, \tag{4.6}$$

where, in the case when the coordinate systems are Cartesian, the transformation coefficients $\omega_{\sigma\alpha}^{(p)}, \ldots, \omega_{\nu\gamma}^{(q)}$ have the meaning of the cosines of the angles subtended by the axes $X_\sigma, \ldots X_\varrho$ of the laboratory system and the axes $X_\alpha^{(p)}, \ldots$ and $X_\gamma^{(q)}, \ldots$ of the respective molecular systems. The directional cosines fulfil the orthonormality conditions

$$\omega_{\sigma\alpha}^{(p)}\omega_{\sigma\gamma}^{(q)} = \begin{cases} \delta_{\alpha\gamma} & \text{for } p=q, \\ \omega_{\alpha\gamma}^{(pq)} & \text{for } p\neq q, \end{cases} \tag{4.7}$$

wherein $\omega_{\alpha\gamma}^{(pq)}$ is the cosine of the angle between the axes $X_\alpha^{(p)}$ and $X_\gamma^{(q)}$ of the molecular systems attached to the p-th and q-th molecules, respectively.

By Eqs (4.6) and (4.7), the following equation is obtained from (4.5) for the constant of optical birefringence:

$$B = \frac{\pi}{30V}\left(\frac{n_1^2+2}{3n_1}\right)^2\left(\frac{n_2^2+2}{3}\right)^2\left\langle \sum_{p=1}^{N}(3c_{\alpha\beta;\alpha\beta}^{(p)}+3c_{\alpha\beta;\beta\alpha}^{(p)}-2c_{\alpha\alpha;\beta\beta}^{(p)}) + \right.$$

$$\left. + \frac{1}{kT}\sum_{p=1}^{N}\sum_{q=1}^{N} a_{\alpha\beta}^{(p)}\alpha_{\gamma\delta}^{(q)}(3\omega_{\alpha\gamma}^{(pq)}\omega_{\beta\delta}^{(pq)}+3\omega_{\alpha\delta}^{(pq)}\omega_{\beta\gamma}^{(pq)}-2\delta_{\alpha\beta}\delta_{\gamma\delta})\right\rangle. \tag{4.8}$$

By classical statistical mechanics methods, Eq. (4.8) can be put in the following form of an expansion in powers of the number density:

$$B = B^{(1)}+\varrho B^{(2)}+\ldots, \tag{4.9}$$

wherein we have for optically inactive substances

$$B^{(1)} = \frac{\pi\varrho}{15V}\left(\frac{n_1^2+2}{3n_1}\right)^2\left(\frac{n_2^2+2}{3}\right)^2 \int \left\{3c_{\alpha\beta;\alpha\beta}^{(p)}-c_{\alpha\alpha;\beta\beta}^{(p)} + \right.$$

$$\left. + \frac{1}{kT}\left(3a_{\alpha\beta}^{(p)}\alpha_{\alpha\beta}^{(p)}-a_{\alpha\alpha}^{(p)}\alpha_{\beta\beta}^{(p)}\right)\right\} g^{(1)}(\tau_p)d\tau_p, \tag{4.10}$$

$$B^{(2)} = \frac{\pi \varrho}{30VkT} \left(\frac{n_1^2+2}{3n_1}\right)^2 \left(\frac{n_2^2+2}{3}\right)^2 \int\int a_{\alpha\beta}^{(p)} \alpha_{\gamma\delta}^{(q)} (3\omega_{\alpha\gamma}^{(pq)} \omega_{\beta\delta}^{(pq)} +$$

$$+ 3\omega_{\alpha\delta}^{(pq)} \omega_{\beta\gamma}^{(pq)} - 2\delta_{\alpha\beta}\delta_{\gamma\delta}) \, g^{(2)}(\tau_p, \tau_q) \, d\tau_p d\tau_q. \tag{4.11}$$

In the preceding expressions $g^{(1)}(\tau_p)$ is the correlation function for a single molecule with configuration τ_p and $g^{(2)}(\tau_p, \tau_q)$ — that for pairs of molecules having the configuration τ_p and τ_q.

If all the molecules present within the volume V are of one kind, $a_{\alpha\beta}^{(p)} = a_{\alpha\beta}^{(q)} = a_{\alpha\beta}$, etc. and if the tensors $\alpha_{\alpha\beta}$, $a_{\alpha\beta}$ and $c_{\alpha\beta:\gamma\delta}$ are independent of the configurational variables and describe only the properties of isolated molecules, Eqs (4.10) and (4.11) may be rewritten as follows:

$$B^{(1)} = \frac{\pi \varrho}{15} \left(\frac{n_1^2+2}{3n_1}\right)^2 \left(\frac{n_2^2+2}{3}\right)^2 \left\{ 3c_{\alpha\beta:\alpha\beta} - c_{\alpha\alpha:\beta\beta} + \frac{1}{kT} \left(3a_{\alpha\beta}\alpha_{\alpha\beta} - a_{\alpha\alpha}\alpha_{\beta\beta}\right) \right\}, \tag{4.12}$$

$$B^{(2)} = \frac{\pi \varrho}{30VkT} \left(\frac{n_1^2+2}{3n_1}\right)^2 \left(\frac{n_2^2+2}{3}\right)^2 a_{\alpha\beta}\alpha_{\gamma\delta} \int\int (3\omega_{\alpha\gamma}^{(pq)} \omega_{\beta\delta}^{(pq)} +$$

$$+ 3\omega_{\alpha\delta}^{(pq)} \omega_{\beta\gamma}^{(pq)} - 2\delta_{\alpha\beta}\delta_{\gamma\delta}) g^{(2)}(\tau_p, \tau_q) \, d\tau_p \, d\tau_q. \tag{4.13}$$

The expressions (4.12) and (4.13) hold for molecules of arbitrary symmetry; we shall now discuss them for certain types of symmetry of the molecules.

Let us begin by considering molecules possessing the symmetry of the point group $D_{4h}(e.g.\ C_4H_8)$, for which the nonvanishing elements of the tensors $\alpha_{\alpha\beta}$, $a_{\alpha\beta}$ and $c_{\alpha\beta,\gamma\delta}$ are given as follows [11]:

$$\alpha_{\alpha\beta} = \alpha_{11}\, \delta_{\alpha\beta} + (\alpha_{33} - \alpha_{11})\, k_\alpha k_\beta, \quad a_{\gamma\delta} = a_{11}\delta_{\gamma\delta} + (a_{33} - a_{11})\, k_\gamma k_\delta,$$

$$c_{\alpha\beta:\gamma\delta} = (c_{11:11} - c_{11:22} - 2c_{12:12})\, (i_\alpha i_\beta i_\gamma i_\delta + j_\alpha j_\beta j_\gamma j_\delta) +$$

$$+ (c_{11:22} - c_{11:33} - c_{33:11} + 2c_{12:12} - 4c_{13:13} + c_{33:33})\, k_\alpha k_\beta k_\gamma k_\delta +$$

$$+ c_{11:22}\, (\delta_{\alpha\beta}\delta_{\gamma\delta} - \delta_{\alpha\beta}k_\gamma k_\delta - k_\alpha k_\beta \delta_{\gamma\delta}) +$$

$$+ c_{12:12}(\delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma}) + c_{11:33}\delta_{\alpha\beta}k_\gamma k_\delta + c_{33:11}k_\alpha k_\beta \delta_{\gamma\delta} +$$

$$+ (c_{13:13} - c_{12:12})(\delta_{\alpha\gamma}k_\beta k_\delta + \delta_{\alpha\delta}k_\beta k_\gamma + k_\alpha k_\gamma \delta_{\beta\delta} + k_\alpha k_\delta \delta_{\beta\gamma}), \tag{4.14}$$

where i, j, k are unit vectors along the axes X_1, X_2, X_3 of the molecular reference system.

With respect to (4.14), Eqs (4.12) and (4.13) now assume the form

$$B^{(1)} = \frac{2\pi \varrho}{15} \left(\frac{n_1^2+2}{3n_1}\right)^2 \left(\frac{n_2^2+2}{3}\right)^2 \left\{ 2c_{11:11} - c_{11:33} - c_{33:12} - c_{11:22} + \right.$$

$$+ 3c_{12:12} + 6c_{13:13} + c_{33:33} + \frac{1}{kT} \left(a_{33} - a_{11}\right) \left(\alpha_{33} - \alpha_{11}\right) \Big\}, \tag{4.15}$$

$$B^{(2)} = \frac{\pi\varrho}{15VkT} \left(\frac{n_1^2 + 2}{3n_1}\right)^2 \left(\frac{n_2^2 + 2}{3}\right)^2 (a_{33} - a_{11})(\alpha_{33} - \alpha_{11}) \times$$

$$\times \iint (3\cos^2\theta_{pq} - 1) \, g^{(2)}(\tau_p, \tau_q) d\tau_p d\tau_q, \tag{4.16}$$

where θ_{pq} denotes the angle between the axis of symmetry of molecule p and that of molecule q.

For molecules of the point groups C_{6h} (e.g. C_6Cl_6) and D_{6h} (e.g. C_6H_6), one has to put in (4.15) $2c_{12:12} = c_{11:11} - c_{11:22}$, whence

$$B^{(1)} = \frac{\pi\varrho}{15} \left(\frac{n_1^2 + 2}{3n_1}\right)^2 \left(\frac{n_2^2 + 2}{3}\right)^2 \Big\{ 7c_{11:11} - 5c_{11:22} - 2c_{11:33} - 2c_{33:11} +$$

$$+ 12c_{13:13} + 2c_{33:33} + \frac{2}{kT}(a_{33} - a_{11})(\alpha_{33} - \alpha_{11})\Big\}. \tag{4.17}$$

This expression is moreover applicable to a great variety of linear molecules belonging to the point group $D_{\infty h}$ (e.g. H_2, CO_2, C_2H_2, and so forth).

In particular, in the case of the point groups T_h and O_h (e.g. for SF_6), we have to put $a_{11} = a_{33}$, $\alpha_{11} = \alpha_{33}$ and $c_{11:11} = c_{33:33}$, $c_{11:22} = c_{11:33} = c_{33:11}$, $c_{12:12} = c_{13:13}$ in Eq. (4.15), which reduces to

$$B^{(1)} = \frac{2\pi\varrho}{5} \left(\frac{n_1^2 + 2}{3n_1}\right)^2 \left(\frac{n_2^2 + 2}{3}\right)^2 (c_{11:11} - c_{11:22} + 3c_{12:12}). \tag{4.18}$$

In the case of spherical symmetry $2c_{12:12} = c_{11:11} - c_{11:22}$ and the above formula becomes simply (for comparison see Refs [3] and [5])

$$B^{(1)} = \pi\varrho \left(\frac{n_1^2 + 2}{3n_1}\right)^2 \left(\frac{n_2^2 + 2}{3}\right)^2 (c_{11:11} - c_{11:22}). \tag{4.19}$$

Eq. (4.19) is the optical counterpart of Voigt's deformational theory of the Kerr effect; namely, a medium consisting of spherical molecules becomes optically birefringent owing to the anisotropy induced in its molecules by the deformational effect of the strong optical field. In gases consisting of atoms or of isotropically polarizable molecules, the optical non-linear deformational effect is the only factor producing optical birefringence. Thus, Eq. (4.19) provides direct information on the nonlinear changes undergone by an atom or spherical molecule under the influence of an intense light beam.

In the general case the first term in Eq. (4.12), $3c_{\alpha\beta:\alpha\beta} - c_{\alpha\alpha:\beta\beta}$, accounts for the temperature-independent effect of optical nonlinear molecular deformation, whereas the second temperature-dependent term, $(3a_{\alpha\beta}\alpha_{\alpha\beta} - a_{\alpha\alpha}\alpha_{\beta\beta})(kT)^{-1}$, for the effect of optical molecular orientation analogous to that discussed by Langevin for explaining the temperature-dependence for the Kerr effect. The birefringence constant (4.12) contains the respective molecular parameters determining the linear and nonlinear optical properties of the isolated molecules of an ideal medium presenting no molecular interactions. The constant (4.13) determines the influence of the angular intermolecular correlations on the effect of optical molecular orientation. In the case of strongly anisotropic molecules the effect of nonlinear deforma-

tion can be neglected with respect to that of molecular orientation. If moreover the axes of the molecular reference systems coincide with the principal axes of the respective molecules, Eqs (4.12) and (4.13) may be rewritten in the form

$$B^{(1)} = \frac{\pi \varrho}{15kT} \left(\frac{n_1^2+2}{3n_1} \right)^2 \left(\frac{n_2^2+2}{3} \right)^2 \Big\{ (a_1-a_2)\,(\alpha_1-\alpha_2) +$$

$$+ (a_2-a_3)\,(\alpha_2-\alpha_3) + (a_3-a_1)\,(\alpha_3-\alpha_1) \Big\}, \tag{4.20}$$

$$B^{(2)} = \frac{\pi \varrho}{15VkT} \left(\frac{n_1^2+2}{3n_1} \right)^2 \left(\frac{n_2^2+2}{3} \right)^2 \sum_{s,t=1}^{3} a_s \alpha_t \int\int (3\cos^2\theta_{st}^{(pq)}-1) g^{(2)}(\tau_p,\tau_q)\, d\tau_p d\tau_q, \tag{4.21}$$

wherein $\theta_{st}^{(pq)}$ is the angle between the principal axes s and t of molecules p and q with polarizabilities a and α_t along these axes.

For molecules presenting the axial symmetry, Eqs (4.20) and (4.21) reduce to (see also Refs [3, 4, 5])

$$B^{(1)} = \frac{6\pi \varrho}{5kT} \left(\frac{n_1^2+2}{3n_1} \right)^2 \left(\frac{n_2^2+2}{3} \right)^2 a \varkappa_a \alpha \varkappa_\alpha, \tag{4.22}$$

$$B^{(2)} = \frac{1}{2V} B^{(1)} \int\int (3\cos^2\theta_{pq}-1)\, g^{(2)}(\tau_p,\tau_q) d\tau_p d\tau_q = \varrho^{-1} B^{(1)} J_A^{(1)}, \tag{4.23}$$

where [10]

$$J_A^{(1)} = \frac{\varrho}{2V} \int\int (3\cos^2\theta_{pq}-1) g^{(2)}(\tau_p,\tau_q) d\tau_p d\tau_q \tag{4.24}$$

is an integral parameter accounting for the angular correlations of the axially symmetric molecules.

5. The effect of the molecular electric fields on B

We shall now compute the additional contributions to the optical birefringence constant resulting from the existence of molecular electric fields in a dense medium.

In general, a molecule immersed in the dense medium is acted on by the local electric fields E_1+F_1 and E_2+F_2, in which F_1 and F_2 are the additional molecular fields due to all other N-1 molecules in the presence of applied fields E_1 and E_2. For simplicity we assume the incident light wavelength to be considerably larger than the linear dimensions of the molecules and intermolecular distances. In this case the Eqs (4.3) and (4.4) should be replaced by the following ones [12]:

$$m_{1\sigma}^{(p)} = \Big\{ a_{\sigma\tau}^{(p)} + b_{\sigma\tau;\nu}^{(p)}(E_{2\nu}+F_{2\nu}^{(p)}) + \frac{1}{2} c_{\sigma\tau;\nu\varrho}^{(p)}(E_{2\nu}+F_{2\nu}^{(p)})\,(E_{2\varrho}+F_{2\varrho}^{(p)}) + \ldots \Big\}(E_{1\tau}+F_{1\tau}^{(p)}), \tag{5.1}$$

$$m_{2\nu}^{(q)} = \mu_\nu^{(q)} + \alpha_{\nu\varrho}^{(q)}(E_{2\varrho}+F_{2\varrho}^{(q)}) + \frac{1}{2} \beta_{\nu\varrho\lambda}^{(q)}(E_{2\varrho}+F_{2\varrho}^{(q)})\,(E_{2\lambda}+F_{2\lambda}^{(q)}) + \ldots, \tag{5.2}$$

where the molecular electric fields are defined to within dipole interaction as follows:

$$F_{1\sigma}^{(p)} = - \sum_{\substack{q=1 \\ q \neq p}}^{N} T_{\sigma\tau}^{(pq)} m_{1\tau}^{(q)}, \; F_{2\sigma}^{(p)} = - \sum_{\substack{q=1 \\ q \neq p}}^{N} T_{\sigma\tau}^{(pq)} m_{2\tau}^{(q)}, \tag{5.3}$$

where the tensor

$$T_{\sigma\tau}^{(pq)} = -r_{pq}^{-5}(3r_{pq\sigma}r_{pq\tau} - r_{pq}^{2}\delta_{\sigma\tau}) \tag{5.4}$$

accounts for the interactions of the dipolar type between molecules p and q separated by a distance r_{pq}.

From Eqs (5.1)—(5.3), we have approximately

$$F_{1\sigma}^{(p)} = - \sum_{\substack{q=1 \\ q \neq p}}^{N} T_{\sigma\tau}^{(pq)} a_{\tau\nu}^{(q)} E_{1\nu} + \sum_{\substack{q=1 \\ q \neq p}}^{N} \sum_{\substack{r=1 \\ r \neq q}}^{N} T_{\sigma\tau}^{(pq)} a_{\tau\nu}^{(q)} T_{\nu\varrho}^{(qr)} a_{\varrho\lambda}^{(r)} E_{1\lambda} + ..., \tag{5.5}$$

$$F_{2\sigma}^{(p)} = F_{0\sigma}^{(p)} - \sum_{\substack{q=1 \\ q \neq p}}^{N} T_{\sigma\tau}^{(pq)} \alpha_{\tau\nu}^{(q)} E_{2\nu} + \sum_{\substack{q=1 \\ q \neq p}}^{N} \sum_{\substack{r=1 \\ r \neq q}}^{N} T_{\sigma\tau}^{(pq)} \alpha_{\tau\nu}^{(q)} T_{\nu\varrho}^{(qr)} \alpha_{\varrho\lambda}^{(r)} E_{2\lambda} + ..., \tag{5.6}$$

wherein

$$F_{0\sigma}^{(p)} = - \sum_{\substack{q=1 \\ q \neq p}}^{N} T_{\sigma\tau}^{(pq)} \mu_{\tau}^{(q)} + \sum_{\substack{q=1 \\ q \neq p}}^{N} \sum_{\substack{r=1 \\ r \neq q}}^{N} T_{\sigma\tau}^{(pq)} \alpha_{\tau\nu}^{(q)} T_{\nu\varrho}^{(qr)} \mu_{\varrho}^{(r)} - ... \tag{5.7}$$

is the molecular electric field strength at the centre of the p-th molecule in the absence of external electric fields.

In a first step we shall restrict the problem to the case of isotropically polarizable molecules. On substituting the expansions (5.1) and (5.2) in the general Equation (4.2), and using the fact that by (4.14)

$$\alpha_{\alpha\beta} = \alpha\delta_{\alpha\beta}, \; a_{\alpha\beta} = a\delta_{\alpha\beta},$$

$$c_{\alpha\beta:\gamma\delta} = c_{11:22}\,\delta_{\alpha\beta}\delta_{\gamma\delta} + \tfrac{1}{2}\,(c_{11:11} - c_{11:22})\,(\delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma}), \tag{5.8}$$

we have

$$B = \frac{\pi}{15V}\left(\frac{n_1^2+2}{3n_1}\right)^2\left(\frac{n_2^2+2}{3}\right)^2\left\{5\left\langle \sum_{p=1}^{N}(c_{11:11}^{(p)} - c_{11:22}^{(p)})\left(3 + \frac{\partial F_{1\sigma}^{(p)}}{\partial E_{1\sigma}} + 2\frac{\partial F_{2\sigma}^{(p)}}{\partial E_{2\sigma}} + ...\right)\right\rangle \right. +$$

$$+ \left. \frac{1}{kT}\left\langle \sum_{p=1}^{N}\sum_{q=1}^{N} a^{(p)}\alpha^{(q)}\left(3\frac{\partial F_{1\sigma}^{(p)}}{\partial E_{1\tau}}\frac{\partial F_{2\sigma}^{(q)}}{\partial E_{2\tau}} - \frac{\partial F_{1\sigma}^{(p)}}{\partial E_{1\sigma}}\frac{\partial F_{2\tau}^{(q)}}{\partial E_{2\tau}}\right)\right\rangle \right\}. \tag{5.9}$$

In the case of isotropically polarizable molecules, Eqs (5.5) and (5.6) yield

$$\frac{\partial F_{1\sigma}^{(p)}}{\partial E_{1\chi}} = - \sum_{\substack{r=1 \\ r \neq p}}^{N} a^{(r)} T_{\sigma\chi}^{(pr)} + \sum_{\substack{r=1 \\ r \neq p}}^{N} \sum_{\substack{s=1 \\ s \neq r}}^{N} a^{(r)} a^{(s)} T_{\sigma\tau}^{(pr)} T_{\tau\chi}^{(rs)} - ..., \tag{5.10}$$

$$\frac{\partial F_{2\sigma}^{(q)}}{\partial E_{2\chi}} = - \sum_{\substack{r=1 \\ r \neq q}}^{N} \alpha^{(r)} T_{\sigma\chi}^{(qr)} + \sum_{\substack{r=1 \\ r \neq q}}^{N} \sum_{\substack{s=1 \\ s \neq r}}^{N} \alpha^{(r)} \alpha^{(s)} T_{\sigma\tau}^{(qr)} T_{\tau\chi}^{(rs)} - \ldots, \tag{5.11}$$

whence Eq. (5.9) goes over into

$$B = \frac{\pi}{5V} \left(\frac{n_1^2 + 2}{3n_1}\right)^2 \left(\frac{n_2^2 + 2}{3}\right)^2 \left\{ 5 \left\langle \sum_{p=1}^{N} (c_{11:11}^{(p)} - c_{11:22}^{(p)}) [1 + O(\alpha^2)] \right\rangle + \right.$$

$$\left. + \frac{1}{kT} \left\langle \sum_{p=1}^{N} \sum_{q=1}^{N} \sum_{\substack{r=1 \\ r \neq p}}^{N} \sum_{\substack{s=1 \\ s \neq r}}^{N} a^{(p)} \alpha^{(q)} a^{(r)} \alpha^{(s)} T_{\sigma\tau}^{(pr)} T_{\sigma\tau}^{(qs)} + \ldots \right\rangle \right\}. \tag{5.12}$$

By statistical methods Eq. (5.12) is rewritten as follows:

$$B = B^{(1)} + \varrho B^{(2)} + \varrho^2 B^{(3)} + \ldots, \tag{5.13}$$

wherein $B^{(1)}$ is again given by (4.19), whereas

$$B^{(2)} = \pi \left(\frac{n_1^2 + 2}{3n_1}\right)^2 \left(\frac{n_2^2 + 2}{3}\right)^2 \left\{ (c_{11:11} - c_{11:22}) O(\alpha^2) + \frac{6a^2\alpha^2}{5kT} J_R^{(1)} \right\}, \tag{5.14}$$

$$B^{(3)} = \pi \left(\frac{n_1^2 + 2}{3n_1}\right)^2 \left(\frac{n_2^2 + 2}{3}\right)^2 \left\{ (c_{11:11} - c_{11:22}) O(\alpha^2) + \frac{12 a^2\alpha^2}{5kT} J_R^{(2)} \right\}. \tag{5.15}$$

In the foregoing expressions we have introduced the following radial correlations integral parameters:

$$J_R^{(1)} = 2 \frac{\varrho}{V} \int \int r_{pq}^{-6} g^{(2)} (\tau_p, \tau_q) \, d\tau_p d\tau_q = 2\varrho \int r_{pq}^{-6} g(r_{pq}) \, d\mathbf{r}_{pq}, \tag{5.16}$$

$$J_R^{(2)} = \frac{\varrho}{3V} \int \int \int T_{\sigma\tau}^{(pq)} T_{\sigma\tau}^{(qr)} g^{(3)} (\tau_p, \tau_q, \tau_r) \, d\tau_p \, d\tau_q \, d\tau_r \tag{5.17}$$

describing the pairs and triples molecular correlations, respectively.

For linearly polarized molecules, $c_{11:11} - c_{11:22} = 0$, and Eqs. (5.14) and (5.15) reduce to

$$B^{(2)} = \frac{6\pi a^2\alpha^2}{5kT} \left(\frac{n_1^2 + 2}{3n_1}\right)^2 \left(\frac{n_2^2 + 2}{3}\right)^2 J_R^{(1)}, \tag{5.18}$$

$$B^{(3)} = 2B^{(2)} \frac{J_R^{(2)}}{J_R^{(1)}}. \tag{5.19}$$

The foregoing result is equivalent to the statement that, in a dense medium of atoms or spherical molecules, radial correlations of the molecules can lead to optical birefringence even in the absence of a nonlinear molecular deformation effect.

Since the optical birefringence does not involve direct orientation of the permanent electric dipoles in the high frequency oscillating field as in the case of a DC electric field (Kerr effect), Eq. (4.12) extends to dipolar gases also. In certain cases Eq. (4.13) also can be applied to dipolar liquids. However, in dipolar fluids whose molecules possess large dipolar

moments, a strong molecular electric field (5.7) generally exists, which can affect the shape of the optical birefringence noticeably. In this case by (4.2) (5.1) and (5.2) the following equation holds:

$$B = \frac{\pi}{30V} \left(\frac{n_1^2+2}{3n_1}\right)^2 \left(\frac{n_2^2+2}{3}\right)^2 \chi_{\sigma\tau:\nu\varrho} \left\langle \sum_{p=1}^{N} (c_{\sigma\tau:\nu\varrho}^{(p)} + ...) + \right.$$

$$\left. + \frac{1}{kT} \sum_{p=1}^{N} \sum_{q=1}^{N} (a_{\sigma\tau}^{(p)} \alpha_{\nu\varrho}^{(q)} + a_{\sigma\tau}^{(p)} \beta_{\nu\varrho:\lambda}^{(q)} F_{0\lambda}^{(q)} + b_{\sigma\tau:\lambda}^{(p)} \alpha_{\nu\varrho}^{(q)} F_{0\lambda}^{(p)} + ...) \right\rangle. \tag{5.20}$$

We shall now proceed to a discussion of the foregoing for the case of dipolar molecules having the axial symmetry and for which we have by the transformational formulas (4.6):

$$a_{\sigma\tau} = a\delta_{\sigma\tau} - a\varkappa_a(3k_\sigma k_\tau - \delta_{\sigma\tau}),$$

$$b_{\sigma\tau:\nu} = b\delta_{\sigma\tau}k_\nu + b\varkappa_b(3k_\sigma k_\tau - \delta_{\sigma\tau}) k_\nu, \text{ ect.}, \tag{5.21}$$

wherein the quantities

$$\varkappa_b = \frac{b_{33:3} - b_{11:3}}{3b}, \qquad b = \frac{1}{3}(b_{33:3} + 2b_{11:3}) \tag{5.22}$$

provide a measure of the anisotropy of first-order nonlinear polarizability and its mean polarizability.

By (5.7) and (5.21) we obtain from (5.20) for $B^{(2)}$, instead of (4.23),

$$B^{(2)} = \varrho^{-1} B^{(1)} \left\{ J_A^{(1)} + \mu \left(\frac{b\varkappa_b}{\alpha\varkappa_a} + \frac{\beta\varkappa_\beta}{a\varkappa_a}\right) J_A^{(2)} \right\}, \tag{5.23}$$

wherein $B^{(1)}$ is given by (4.22), $J_A^{(1)}$ by (4.24) and $J_A^{(2)}$ by the following formula:

$$J_A^{(2)} = \frac{\varrho}{2V} \int \int (3\cos^2\theta_{pq}+1)(3\cos\theta_p \cos\theta_q - \cos\theta_{pq}) r_{pq}^{-3} g^{(2)}(\tau_p,\tau_q) d\tau_p d\tau_q. \tag{5.24}$$

Eq. (5.23) as given above is not adapted to numerical evaluations, as not all molecular and correlation parameters appearing therein are known. This obstacle is circumvented by means e.g. of the Onsager model replacing the molecular electric fields (5.5) and (5.6) by a mean local field [12].

On neglecting short range angular correlations we obtain from Eq. (4.2) (the temperature-independent term is now omitted)

$$B = \frac{\pi\varrho}{30 kT} \left(\frac{n_1^2+2}{3n_1}\right)^2 \left(\frac{n^2+2}{3}\right)^2 \chi_{\sigma\tau:\nu\varrho} \left(\frac{\partial \overline{m}_{1\sigma}}{\partial E_{1\tau}}\right)_0 \left(\frac{\partial \overline{m}_{2\nu}}{\partial E_{2\varrho}}\right)_0, \tag{5.25}$$

where by the expressions (5.1) and (5.2) we have

$$\left(\frac{\partial \overline{m}_{1\sigma}}{\partial E_{1\chi}}\right)_0 = \{a_{\sigma\tau} + b_{\sigma\tau:\nu} \overline{F}_{0\nu} + ...\} \left\{\delta_{\tau\chi} + \frac{\partial \overline{F}_{1\tau}}{\partial E_{1\chi}}\right\}_0, \tag{5.26}$$

$$\left(\frac{\partial \overline{m}_{2\nu}}{\partial E_{2\chi}}\right)_0 = \{\alpha_{\nu\varrho} + \beta_{\nu\varrho:\lambda} \overline{F}_{0\lambda} + ...\} \left\{\delta_{\varrho\chi} + \frac{\partial \overline{F}_{2\varrho}}{\partial E_{2\chi}}\right\}_0. \tag{5.27}$$

Here, with respect to the Onsager-Scholte model [13], the anisotropies of the molecular electric fields are given by

$$\frac{\partial \overline{F}_{1\sigma}}{\partial E_{1\tau}} = \delta_{\sigma\tau} (\psi_{1\tau}-1), \quad \frac{\partial \overline{F}_{2\sigma}}{\partial E_{2\tau}} = \delta_{\sigma\tau} (\psi_{2\tau}-1), \tag{5.28}$$

with $(h = 1,2)$

$$\psi_{h\tau} = \frac{\left(\dfrac{3n_h^2}{n_h^2+2}\right)}{\{n_h^2+(1-n_h^2)\,A_\tau\}\,(1-f_{h\tau}\,\alpha_{h\tau})} . \tag{5.29}$$

The reaction field parameter $f_{h\tau}$ for an ellipsoidal cavity of semi-axes $r_x,\,r_y,\,r_z$, situated in a medium of refractive index n_h is given by

$$f_{h\tau} = \frac{3A_\tau\,(1-A_\tau)\,(n_h^2-1)}{r_x r_y r_z\,\{n_h^2+(1-n_h^2)A_\tau\}}, \tag{5.30}$$

where the structural factors are $(\tau = x, y, z)$

$$A_\tau = \frac{1}{2}\,r_x r_y r_z \int\limits_0^\infty \frac{dS}{(r_\tau^2+S)\,\{(r_x^2+S)\,(r_y^2+S)\,(r_z^2+S)\}} . \tag{5.31}$$

Analogously the mean molecular electric field in the absence of external fields (reaction field) is

$$\overline{F}_{0\sigma} = \frac{f_{0\sigma}\,\mu_\sigma}{1-f_{0\sigma}\,\alpha_\sigma} , \tag{5.32}$$

with

$$f_{0\sigma} = \frac{3A_\sigma\,(1-A_\sigma)\,(\varepsilon-1)}{r_x r_y r_z\,\{\varepsilon+(1-\varepsilon)\,A_\sigma\}}, \tag{5.33}$$

where ε is the electric permittivity of the medium.

On substituting in Eq. (5.25) the expansions (5.26) and (5.27) we obtain

$$B = \frac{\pi\varrho}{15kT}\left(\frac{n_1^2+2}{3n_1}\right)^2 \left(\frac{n_2^2+2}{3}\right)^2 \{(a_1^*-a_2^*)\,(\alpha_1^*-\alpha_2^*) +$$

$$+ (a_2^*-a_3^*)\,(\alpha_2^*-\alpha_3^*) + (a_3^*-a_1^*)\,(\alpha_3^*-\alpha_1^*)\}, \tag{5.34}$$

where we have denoted

$$a_\sigma^* = \psi_{1\sigma}\left\{a_\sigma + \frac{b_{\sigma:\tau} f_{0\tau}\,\mu_\tau}{1-f_{0\tau}\alpha_\tau} +\dots\right\}, \tag{5.35}$$

$$\alpha_\sigma^* = \psi_{2\sigma}\left\{\alpha_\sigma + \frac{\beta_{\sigma:\tau} f_{0\tau}\,\mu_\tau}{1-f_{0\tau}\alpha_\tau} +\dots\right\}. \tag{5.36}$$

6. Optical birefringence of multi-component systems

Since the general Eq. (3.16) is valid for an arbitrary isotropic medium, it can also be applied to a multi-component system. Assuming $N = \sum_i N_i$ molecules of different species (N_i is the number of molecules of species i) to be present within the sphere of volume V, Eq. (4.1) has to be replaced by

$$M_1 = \sum_i \sum_{p=1}^{N_i} m_1^{(pi)}, \qquad M_2 = \sum_j \sum_{q=1}^{N_j} m_2^{(qj)}, \tag{6.1}$$

where $m_1^{(pi)}$ and $m_2^{(qj)}$ are the dipole moments, respectively, of the p-th molecule belonging to species i and of the q-th molecule of species j.

On substituting (6.1) in the general Eq. (3.16), we have the following expression for the optical birefringence constant of a multi-component system:

$$B = \frac{3}{2V} \left(\frac{n_1^2 + 2}{3n_1} \right)^2 \left(\frac{n_2^2 + 2}{3} \right)^2 B_m, \tag{6.2}$$

where for further convenience we have introduced the molecular constant of optical birefringence [12]

$$B_m = \frac{\pi}{45} \chi_{\sigma\tau:\nu\varrho} \left\langle \sum_i \sum_{p=1}^{N_i} \frac{\partial^3 m_{1\sigma}^{(pi)}}{\partial E_{1\tau} \partial E_{2\nu} \partial E_{2\varrho}} + \right.$$
$$\left. + \frac{1}{kT} \sum_{ij} \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \frac{\partial m_{1\sigma}^{(pi)}}{\partial E_{1\tau}} \frac{\partial m_{2\nu}^{(qj)}}{\partial E_{2\varrho}} \right\rangle. \tag{6.3}$$

In the present case, the expressions (4.3) and (4.4) remain valid provided the index i or j is added everywhere beside p or q, so that we now obtain from (6.3)

$$B_m = \frac{\pi}{45} \chi_{\sigma\tau:\nu\varrho} \left\langle \sum_i \sum_{p=1}^{N_i} c_{\sigma\tau:\nu\varrho}^{(pi)} + \frac{1}{kT} \sum_{ij} \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} a_{\sigma\tau}^{(pi)} \alpha_{\nu\varrho}^{(qj)} \right\rangle. \tag{6.4}$$

By analogy to the expansion (4.9), we now have

$$B_m = \sum_i x_{im} B_i^{(1)} + \varrho \sum_{ij} x_i x_{jm} B_{ij}^{(2)} + \dots, \tag{6.5}$$

wherein [12]

$$_m B_i = \frac{2\pi N}{45} \left\{ 3c_{\alpha\beta:\alpha\beta}^{(i)} - c_{\alpha\alpha:\beta\beta}^{(i)} + \frac{1}{kT} \left(3a_{\alpha\beta}^{(i)} \alpha_{\alpha\beta}^{(i)} - a_{\alpha\alpha}^{(i)} \alpha_{\beta\beta}^{(i)} \right) \right\}, \tag{6.6}$$

$$_m B_{ij}^{(2)} = \frac{\pi\varrho}{90kT} \left(a_{\alpha\beta}^{(i)} \alpha_{\gamma\delta}^{(j)} + a_{\alpha\beta}^{(j)} \alpha_{\gamma\delta}^{(i)} \right) \int\int \left\{ 3\omega_{\alpha\gamma}^{(pq,\,ij)} \omega_{\beta\delta}^{(pq,\,ij)} + 3\omega_{\alpha\delta}^{(pq,\,ij)} \omega_{\beta\gamma}^{(pq,\,ij)} - \right.$$
$$\left. - 2\delta_{\alpha\beta} \delta_{\gamma\delta} \right\} g_{ij}^{(2)}(\tau_p, \tau_q) \, d\tau_p d\tau_q, \tag{6.7}$$

with x_i denoting the molar fraction of the i-th component of the system; obviously, $\sum_i x_i = 1$.

In particular, if the system presents no interaction between the molecules, the latter assume all possible configurations in volume V with equal probability, $i.\ e.$ the pairs correlation $g_{ij}^{(2)}\,(\tau_p,\,\tau_q) \to 1$ and the expansion (6.5) reduces to

$$B_m = \sum_i x_{im} B_i^{(1)},$$

since in this case $_m B_{ij}^{(2)} = 0$.

Hence B_m is seen to be a strictly additive quantity only for the case of a mixture of perfect gases. In dense multi-component systems, as a result of correlations between the molecules of a given component or between those of different components of the system, the constant $_m B_{ij}^{(2)}$ is non-zero, and B_m does not fulfil the additivity rule.

The expression (6.7) will now be applied to not excessively condensed gaseous systems $i.e.$ to ones admitting of the binary correlation function $g_{ij}^{(2)}$ in the form

$$g_{ij}^{(2)}\,(\tau_p,\,\tau_q) = \varOmega^{-2}\exp\left\{-\frac{u_{ij}(r_{pq},\,\omega_p,\,\omega_q)}{kT}\right\}, \tag{6.8}$$

in accordance with classical statistical mechanics, with $u_{ij}\,(r_{pq},\,\omega_p,\,\omega_q)$ denoting the total potential energy of interactions between molecules p and q of species i and j, distant from one another by r_{pq} and having the orientations ω_p and ω_q, respectively.

With regard to (6.8), the molecular constant (6.7) can be expressed as

$$_m B_{ij}^{(2)} = \frac{\pi N}{90\,kT\varOmega^2}\iiint \chi_{\alpha\beta:\gamma\delta}\,(a_{\alpha\beta}^{(pi)}\alpha_{\gamma\delta}^{(qj)} + a_{\alpha\beta}^{(qj)}\alpha_{\gamma\delta}^{(pi)})\times$$

$$\times\exp\left\{-\frac{u_{ij}(r_{pq},\,\omega_p,\,\omega_q)}{kT}\right\}d\boldsymbol{r}_{pq}\,d\omega_p\,d\omega_q. \tag{6.9}$$

Anisotropic molecules. The expression (6.9) will be discussed first for the case of non-polar molecules for which the total potential interaction energy has the following form [14, 15]:

$$u_{ij}(r_{pq},\,\omega_p,\,\omega_q) = u_{ij}\,(r_{pq}) - \frac{1}{4}\left(\frac{h\nu_i\,h\nu_j}{h\nu_i + h\nu_j}\right)\{\alpha_{\alpha\beta}^{(pi)}\alpha_{\gamma\delta}^{(qj)} - \alpha_i\alpha_j\,\delta_{\alpha\beta}\,\delta_{\gamma\delta}\}\,T_{\alpha\gamma}^{(pq)}T_{\beta\delta}^{(pq)}, \tag{6.10}$$

where $u_{ij}(r_{pq})$ is the potential energy of central interaction of two molecules and the second term determines the potential energy resulting from London's anisotropic dispersion forces with characteristic energies $h\nu_i$ and $h\nu_j$ of the two interacting molecules of species i and j.

If we consider the anisotropic dispersive energy in Eq. (6.10) as a perturbation to $u_{ij}(r_{pq})$, we obtain from (6.9) on integration over all possible orientations of the axially-symmetric molecules

$$_m B_{ij}^{(2)} = \frac{3\pi N}{125k^2T^2}\left(\frac{h\nu_i h\nu_j}{h\nu_i + h\nu_j}\right)(a_i\varkappa_{ai}\alpha_j\varkappa_{aj} + \alpha_i\varkappa_{ai}a_j\varkappa_{aj})\,\alpha_i\varkappa_{ai}\alpha_j\varkappa_{aj}\left\{\langle r_{ij}^{-6}\rangle_R + \right.$$

$$\left. + \frac{3\,\alpha_i\alpha_j}{98\,kT}\left(\frac{h\nu_i\,h\nu_j}{h\nu_i + h\nu_j}\right)[49 - 14(\varkappa_{ai} + \varkappa_{aj}) + 38\,\varkappa_{ai}\varkappa_{aj}]\,\langle r_{ij}^{-12}\rangle_R + \ldots\right\}, \tag{6.11}$$

where we have introduced the radial mean values

$$\langle r_{ij}^{-n}\rangle_R = \int r_{pq}^{-n} \exp\left\{-\frac{u_{ij}(r_{pq})}{kT}\right\} d\boldsymbol{r}_{pq}. \tag{6.12}$$

Dipole molecules. The total potential energy of mutual interaction between two dipolar molecules is given by [14]

$$u_{ij} = u_{ij}(r_{pq}) + \mu_\alpha^{(pi)} T_{\alpha\beta}^{(pq)} \mu_\beta^{(qj)} - \frac{1}{2}\left(\alpha_{\alpha\beta}^{(pi)}\mu_\gamma^{(qj)}\mu_\delta^{(qj)} + \alpha_{\alpha\beta}^{(qj)}\mu_\gamma^{(pi)}\mu_\delta^{(pi)}\right) T_{\alpha\gamma}^{(pq)}T_{\beta\delta}^{(pq)} - \dots \tag{6.13}$$

Besides $u_{ij}(r_{pq})$, herein are included terms representing dipole-dipole and dipole-induced dipole interactions. Thus we obtain by inserting (6.13) into (6.9)

$$_mB_{ij}^{(2)} = \frac{2\pi\mu_i^2\mu_j^2 N}{375\,k^3T^3}\left(a_i\varkappa_{ai}\alpha_j\varkappa_{aj} + \alpha_i\varkappa_{ai}a_j\varkappa_{aj}\right)\left\{\langle r_{ij}^{-6}\rangle_R + \right.$$

$$+ \frac{12\,\mu_i^2\,\mu_j^2}{49\,k^2\,T^2}\langle r_{ij}^{-12}\rangle_R + \frac{13\,\mu_i^4\,\mu_j^4}{441k^4T^4}\langle r_{ij}^{-18}\rangle_R + \dots\right\} +$$

$$+ \frac{2\pi N}{125\,k^2T^2}\left(a_i\varkappa_{ai}\alpha_j\varkappa_{aj} + \alpha_i\varkappa_{ai}a_j\varkappa_{aj}\right)\left\{\left(\alpha_i\varkappa_{ai}\mu_j^2 + \mu_i^2\alpha_j\varkappa_{aj}\right)\langle r_{ij}^{-6}\rangle_R + \right.$$

$$+ \frac{4\mu_i^2\mu_j^2}{49\,k^2T^2}\left[\alpha_i(7+11\varkappa_{ai})\mu_j^2 + \mu_i^2\alpha_j(7+11\varkappa_{aj})\right]\langle r_{ij}^{-12}\rangle_R + \dots\right\}. \tag{6.14}$$

Quadrupole molecules. Let us now calculate $_mB_{ij}^{(2)}$ for the case of an imperfect gas mixture with molecules having a permanent quadrupole moment defined by the tensor

$$\Theta_{\alpha\beta}^{(pi)} = \frac{1}{2}\sum_n e_{pi}^{(n)}(3r_{pn\alpha}r_{pn\beta} - r_{pn}^2\delta_{\alpha\beta}), \tag{6.15}$$

where $e_{pi}^{(n)}$ denotes the n-th electric charge of the p-th molecule of species i and $\boldsymbol{r}_{pn}$ — its radius vector.

The potential energy of mutual interaction of two anisotropically polarizable quadrupole molecules is given by [14]

$$u_{ij} = u_{ij}(r_{pq}) - \frac{1}{9}\Theta_{\alpha\beta}^{(pi)} T_{\alpha\beta\gamma}^{(pq)}\Theta_{\gamma\delta}^{(qj)} - \frac{1}{18}\left(\alpha_{\alpha\beta}^{(pi)}\Theta_{\gamma\delta}^{(qj)}\Theta_{\varepsilon\eta}^{(qj)} + \alpha_{\alpha\beta}^{(qj)}\Theta_{\gamma\delta}^{(pi)}\Theta_{\varepsilon\eta}^{(pi)}\right) T_{\alpha\gamma\delta}^{(pq)}T_{\beta\varepsilon\eta}^{(pq)}, \tag{6.16}$$

where the tensors

$$T_{\alpha\beta\gamma}^{(pq)} = 3r_{pq}^{-7}\left\{5r_{pq\alpha}r_{pq\beta}r_{pq\gamma} - r_{pq}^2(r_{pq\alpha}\delta_{\beta\gamma} + r_{pq\beta}\delta_{\gamma\alpha} + r_{pq\gamma}\delta_{\alpha\beta})\right\},$$

$$T_{\alpha\beta\gamma\delta}^{(pq)} = -3r_{pq}^{-9}\left\{35r_{pq\alpha}r_{pq\beta}r_{pq\gamma}r_{pq\delta} - 5r_{pq}^2\left(r_{pq\alpha}r_{pq\beta}\delta_{\gamma\delta} + \right.\right.$$

$$+ r_{pq\alpha}r_{pq\gamma}\delta_{\beta\delta} + r_{pq\alpha}r_{pq\delta}\delta_{\beta\gamma} + r_{pq\beta}r_{pq\gamma}\delta_{\alpha\delta} + r_{pq\beta}r_{pq\delta}\delta_{\alpha\gamma} +$$

$$+ r_{pq\gamma}r_{pq\delta}\delta_{\alpha\beta}) + r_{pq}^4(\delta_{\alpha\beta}\delta_{\gamma\delta} + \delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma})\right\} \tag{6.17}$$

describe the dipole-quadrupole and quadrupole-quadrupole interactions, respectively.

By inserting (6.16) into (6.9) and assuming that the quadrupole molecules are axially-symmetric, we have

$$_mB_{ij}^{(2)} = \frac{6\pi N}{175\,k^2T^2}\,(a_i\varkappa_{ai}\alpha_j\varkappa_{aj} + \alpha_i\varkappa_{ai}a_j\varkappa_{aj})\Big\{(\alpha_i\varkappa_{ai}\Theta_j^2 + \Theta_i^2\alpha_j\varkappa_{aj})\,\langle r_{ij}^{-8}\rangle_R +$$

$$+ \frac{4\Theta_i^2\,\Theta_j^2}{3kT}\,\langle r_{ij}^{-10}\rangle_R - \frac{2\Theta_i\Theta_j}{7kT}\,[\alpha_i(7+2\varkappa_{ai})\Theta_j^2 + \Theta_i^2\alpha_j(7+2\varkappa_{aj})]\langle r_{ij}^{-13}\rangle_R + \dots\Big\}, \quad (6.18)$$

where $\Theta_i = \Theta_{33}^{(i)} = -2\,\Theta_{11}^{(i)} = -2\Theta_{22}^{(i)}$ is the quadrupole moment of the axially symmetric molecule of species i.

In order to be able to test numerically the foregoing expression for $_mB_{ij}^{(2)}$, we have to know the values of the radial averages (6.12). To compute the latter, one has to assume the following form of the central energy:

$$u_{ij}(r_{pq}) = 4\varepsilon_{ij}\left\{\left(\frac{\sigma_{ij}}{r_{pq}}\right)^s - \left(\frac{\sigma_{ij}}{r_{pq}}\right)^t\right\}, \quad (6.19)$$

and we obtain from (6.12) by the Lennard-Jones method [15]

$$\langle r_{ij}^{-n}\rangle = \frac{4\pi\sigma_{ij}^{3-n}}{sy_{ij}^4}\,H_n^{s-t}(y_{ij}), \quad (6.20)$$

wherein ε_{ij} and σ_{ij} are the central force parameters having the dimensions of an energy and length, and

$$H_n^{s-t}(y_{ij}) = y_{ij}^{2(2s+3-n)/s}\sum_{m=0}^{\infty}\frac{1}{m!}\,y_{ij}^{2m(s-t)/s}\,\Gamma\left(\frac{tm+n-3}{s}\right), \quad (6.21)$$

with $y_{ij} = 2\,(\varepsilon_{ij}/kT)^{1/2}$. For $s = 12$ and $t = 6$ the functions (6.21) reduce to those introduced by Pople [16].

In cases when the values of the molecular parameters ε_{ij} and σ_{ij} are known, we can use Eq. (6.20) for evaluating $_mB_{ij}^{(2)}$ numerically; obviously, according to the system dealt with, one will have to assume such values of the molecular dipole or quadrupole moment as to achieve satisfactory agreement with the experimental values available for the second optical birefringence constant virial coefficient. In this way we can obtain information concerning the values of the multipole electric moments of molecules.

7. Discussion and conclusions

In the case of an atomic gas or of one consisting of isotropically polarizable non-interacting molecules, optical birefringence is due only to the third-order polarization and is determined by Eqs (3.14) and (4.19). In the condensed state, however, this effect appears with a temperature-dependent effect resulting from interaction between induced dipoles of atoms or spherical molecules. This latter effect is determined in a first approximation by the parameter of pairwise radial correlations $J_R^{(1)}$ given by Eq. (5.16). The constant of optical

birefringence, by Eqs (4.9), (4.19) and (5.14), has the form (on neglecting three-fold and higher correlations)

$$B = \pi \varrho \left(\frac{n_1^2+2}{3n_1}\right)^2 \left(\frac{n_2^2+2}{3}\right)^2 \left\{(c_{11\,:\,11} - c_{11\,:\,22})\,[1+0(\alpha^2)] + \frac{6a^2\alpha^2}{5kT}\,J_R^{(1)}\right\}. \qquad (7.1)$$

An identical parameter $J_R^{(1)}$ appears in the molecular theory of light scattering (see *e.g.* Ref. [12]), namely, in the formulas for the degree of depolarization of scattered light

$$D = \frac{6a^2 J_R^{(1)}}{5\varrho kT\beta_T(1+\ldots) + 7a^2 J_R^{(1)}}, \qquad (7.2)$$

and the Rayleigh ratio

$$R = \frac{\pi^2(n^2-1)^2}{10\lambda^4\varrho}\{5\varrho kT\beta_T(1+\ldots) + 13\,a^2 J_R^{(1)}\}. \qquad (7.3)$$

The optical birefringence of a substance whose molecules are optically anisotropic depends almost entirely on the effect of optical molecular orientation intimately related with angular correlations of the molecules. In the special case of axially symmetric molecules and in the first approximation of the theory, the angular correlations are described by the single integral parameter $J_A^{(1)}$ given by Eq. (4.24). For liquids whose molecules are strongly anisotropic and linearly polarizing, the effect with third-order polarizability can be neglected and we have by Eqs (4.9), (4.22) and (4.23)

$$B = \frac{6\pi\varrho}{5kT}\left(\frac{n_1^2+2}{3n_1}\right)^2 \left(\frac{n_2^2+2}{3}\right)^2 a\varkappa_a\,\alpha\varkappa_\alpha(1+J_A^{(1)}). \qquad (7,4)$$

The angular parameter $J_A^{(1)}$ appears also *e.g.* in the following formulas for the depolarization and Rayleigh ratios [12]:

$$D = \frac{6\varkappa_a^2(1+J_A^{(1)})}{5\varrho kT\beta_T + 7\varkappa_a^2(1+J_A^{(1)})}, \qquad (7.5)$$

$$R = \frac{\pi^2(n^2-1)^2}{10\lambda^4\varrho}\{5\varrho kT\beta_T + 13\varkappa_a^2(1+J_A^{(1)})\}. \qquad (7.6)$$

From Eqs (7.4) and (7.5) we have the relation (assuming $a\varkappa_a = \alpha\varkappa_\alpha$, $n_1 = n_2 = n$)

$$B = \left(\frac{n^2-1}{4\pi}\right)^2 \left(\frac{n^2+2}{3n}\right)^2 \frac{6\pi\beta_T D}{6-7D} \qquad (7.7)$$

permitting to compute the optical birefringence constant B of a liquid if the depolarization ratio D for it is known experimentally.

In very condensed media, the optical birefringence constant B depends not only on the optical properties of the isolated molecules but is moreover dependent on their electric properties, *e.g.* on their permanent electric dipole or quadrupole moments. The electric properties of the molecules affect the optical birefringence of the liquid indirectly, both through the correlation functions involving the potential energy of molecular interaction, and through

the internal electric fields of the permanent molecular dipoles or quadrupoles and the nonlinear polarizations induced in the molecules by these fields in the absence of external fields.

The theory of the optical birefringence of multi-component systems presents in general a high degree of complication, as involving not only correlations between molecules belonging to the same species but also correlations between molecules of the different components of the system. The molecular constant B_m of optical birefringence behaves additively in the case of a mixture of perfect gases only. In dense systems such as e.g. compressed gas mixtures or liquid mixtures, owing to intermolecular correlations, the constant B_m fails to fulfil the condition of additivity. Molecular light scattering and the Kerr effect in multi-component systems is similarly dependent on the intermolecular correlations (see e.g. Refs [10] and [12]).

From the foregoing statistical molecular theory of optical birefringence and its discussion, it is clear that the constant B of dense isotropic media can depend quite generally on a considerable number of factors of a microscopic nature. The part played by each of these factors can generally be said to be different, and depends in principle on the species and structure of the molecules and on the interaction between them. Investigation of the optical birefringence in the gaseous state is a source of data on the optical properties of the isolated molecules (the linear and nonlinear optical polarizabilities and their anisotropy). In dense systems, the data thus obtained concerning the molecular correlation functions may well be of decisive importance in the statistical theory of liquids with spherical or anisotropic molecules.

In concluding, it should be stressed that the molecular optical birefringence constant of a multi-component system can be expanded in a power series in the mole fraction,

$$B_m = \sum_i x_i B_m^{(i)} + \varrho \sum_{ij} x_i x_j B_m^{(ij)} + \varrho^2 \sum_{ijk} x_i x_j x_k B_m^{(ijk)} + \dots, \tag{7.8}$$

where the first term represents the additivity rule, while the subsequent terms account for deviations therefrom. The constants $B_m^{(ij)}$ and $B_m^{(ijk)}$ are non-zero only for systems in which interactions occur both between molecules of the same species and between those of various components in dense systems. The expressions obtained here for $B_m^{(ij)}$ allow to state that investigation of deviations of B_m from additivity can be a source i.a. of information concerning the permanent and induced electric multiples of molecules of various species as well as on the nature and magnitude of the forces with which they interact in dense mixtures.

In this investigation, we have not as yet considered explicitly the dependence of optical birefringence on the frequency of oscillation of light beams. The problem has already been discussed in part elsewhere [17] and will be dealt with in detail in a subsequent paper on the basis of the previously evolved quantum-mechanical formalism of mutual interaction of molecular systems and intense electromagnetic fields [18].

REFERENCES

[1] P. Debye, *Polar Molecules*, Dover Publications, Inc. New York 1945.
[2] A. Peterlin, and H. Stuart, *Hand. u. Jahrbuch d. Chem. Physik*, **8**, 26 (1943), (quoted from the monograph of Volkenshteyn, M., *Molekularnaya Optika*, Moskva 1951).

[3] A. D. Buckingham, *Proc. Phys. Soc.* (London) B **69,** 344 (1956).

[4] A. Piekara and S. Kielich, *J. Chem. Phys.*, **29,** 1297 (1958); *Third Conference on Quantum Electronics*, Paris, Vol. II. p. 1603 (1963).

[5] S. Kielich, and A. Piekara, *Acta Phys. Polon.*, **18,** 439 (1959).

[6] P. D., Maker and R. W. Terhune, *Phys. Rev.*, **137,** A 80 (1965).

[7] G. Mayer, and F. Gires *CRAS*, **258,** 2039 (1964).

[8] M. Paillette, *CRAS*, **262,** 264 (1966).

[9] P. D., Maker, R. W. Terhune and C. M. Savage, *Phys. Rev. Letters*, **12,** 507 (1964).

[10] S. Kielich, *Molecular Physics*, **6,** 49 (1963).

[11] S. Kielich, *Acta Phys. Polon.*. **26,** 135 (1964).

[12] S. Kielich, *Acta Phys. Polon.*, **19,** 149, 573 (1960).

[13] Rao Narayana, D.A.A.S., *Trans. Farad. Soc.*, **54,** 954 (1958).

[14] S. Kielich, *Acta Phys. Polon.*, **22,** 65 (1962); **25,** 39 (1964).

[15] S. Kielich, *Physica*, **31,** 444 (1965).

[16] J. A. Pople, *Proc. Roy. Soc.*, A **221,** 508 (1954); A. D. Buckingham and J. A. Pople, *Trans. Faraday Soc.*, **51,** 1173 (1955).

[17] S. Kielich, *Bull. Acad. Polon. Sci. Sér. Sci. Math. Astron. Phys.* **11,** 201 (1963); *Acta Phys. Polon.*, **28,** 913 (1965).

[18] S. Kielich, *Proc. Phys. Soc.*, **86,** 709 (1965); *Acta Phys. Polon.*, **29,** 875 (1966).