

Light intensity dependence of the refractive index of non-dissipative media by a semi-macroscopic approach

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Abstract. By a semi-macroscopic method the following equation is derived:

$$n_{\sigma\tau}^2 - n_0^2 \delta_{\sigma\tau} = \left(\frac{n_0^2 + 2}{3} \right) \{ AI \delta_{\sigma\tau} + B(3I_{\sigma\tau} - I \delta_{\sigma\tau}) \}$$

defining the change in optical permittivity tensor $n_{\sigma\tau}^2$ due to strong light of intensity I . The quantity A describes isotropic changes in $n_{\sigma\tau}$ related with linear and non-linear polarization and opticostriction, whereas B accounts for the optical anisotropy induced in the medium by an intense (e.g. laser) beam. The optical birefringence constant B is discussed in detail statistically for the case of multi-component systems of interacting molecules; it is evaluated numerically for several liquids and compared with the experimental data—the third-order polarizabilities of their molecules are found to be of the order of 10^{-30} e.s.u.

1. Introduction

Recently, Maker *et al.* (1964) and Maker and Terhune (1965) calculated and, using laser techniques, observed light-intensity-induced rotation in several liquids. Simultaneously, Mayer and Gires (1964) and, lately, Paillette (1966) made the first measurement of the optical birefringence induced in various liquids by a strong laser beam. The effect had been predicted theoretically by Buckingham (1956); it represents an extremal case (for optical frequencies) of the Kerr effect produced in liquids by a strong alternating electric field, as considered by Peterlin and Stuart (1943) and Langevin (1910).

These first successful studies provide the basis for the further, systematic investigation not only of optical birefringence but also of various non-linear changes in the light refractive index due to intense optical fields (see e.g. Kielich and Piekara 1959). It is our aim here to propose a general, semi-macroscopic theory of these non-linear effects, with applications to multi-component systems of molecules of arbitrary symmetry interacting with forces of the radial and angular types.

2. General fundamentals of the theory

From electrodynamics and statistical mechanics the general equation

$$(\epsilon - \mathbf{U}) \cdot \mathbf{E}^M = 4\pi \mathbf{P} \quad (1)$$

is derived, relating the electric permittivity tensor ϵ and the vector of electric polarization \mathbf{P} induced in a medium by the electric field of strength \mathbf{E}^M existing therein. \mathbf{U} is the unit tensor of rank 2.

In the general case, when the active electric field \mathbf{E} is not homogeneous, the electric polarization induced in the medium is not only of the dipolar but, moreover, of the quadrupolar, octopolar and still higher types; the polarization vector can be written in the form of the expansion (Kielich 1966 a)

$$\mathbf{P} = \sum_{n=1}^{\infty} (-1)^{n-1} \frac{2^n n!}{(2n)!} \nabla^{n-1} [n-1] \mathbf{P}^{(n)}(\mathbf{r}, t) \quad (2)$$

in a series of tensors of 2^n -pole electric moment densities at position \mathbf{r} and time t :

$$\mathbf{P}^{(n)}(\mathbf{r}, t) = \left\langle \sum_{p=1}^N \mathbf{m}_p^{(n)} \delta(\mathbf{r}_p - \mathbf{r}) \right\rangle. \quad (3)$$

Here, the symbol $\langle \rangle$ stands for appropriately performed statistical averaging, $[n]$ for n -fold contraction of tensors of rank n , whereas ∇ is the derivation operator and $\delta(\mathbf{r}_p - \mathbf{r})$ the Dirac δ function.

In (3), the 2^n -pole electric moment of a microsystem (atom, molecule or ion) at position \mathbf{r}_p is given as follows (Kielich 1965):

$$\mathbf{m}_p^{(n)} = \sum_{\nu} e_{p\nu} r_{p\nu}^n \mathbf{Y}_{p\nu}^{(n)} \quad (4)$$

$e_{p\nu}$ denoting the ν th electric charge of the p th microsystem with radius vector $\mathbf{r}_{p\nu}$, whereas $\mathbf{Y}^{(n)}$ is an n th-order operator having the properties of spherical harmonics.

For a further discussion of equations (1) and (2), one has to establish the explicit relationship between the electric polarization \mathbf{P} and the external electric or magnetic fields inducing it in the medium. For the case of media acted on by strong, time and spatially variable electromagnetic fields, the problem has been discussed quantum-mechanically (Bloembergen 1965, Butcher 1965, Kielich 1965) and phenomenologically (Pershan 1963, Kielich 1966 a). Here, we consider only a non-dissipative isotropic medium under the effect of intense light. However, since it is our aim to derive a theory adapted to dense media, in order to ensure high generality of the results we shall resort to non-linear theory in a semi-macroscopic classical approach (Kielich 1958). This will enable us to avoid specifying a microscopic model at the start, as such a model can present specific features from one case to another.

Thus, we deal with a dense medium (isotropic in the absence of external fields) wherein we consider a macroscopic sphere of volume V . We assume a light wave to be incident on the medium with electric field \mathbf{E} of oscillation frequency lying beyond the absorption bands. The field \mathbf{E} induces polarization \mathbf{P} in V and, if \mathbf{E} is sufficiently large, the medium becomes anisotropic and non-linear with optical permittivity tensor (electrical permittivity at optical frequencies) given as

$$n_{\sigma\tau}^2 - \delta_{\sigma\tau} = 4\pi \frac{\partial P_{\sigma}}{\partial E_{\tau}^M} \quad (5)$$

where the indices σ and τ mark the axes X, Y, Z of the laboratory reference system with origin rigidly set at the centre of the sphere.

On restricting further considerations to polarization of the dipolar kind, one can rewrite equation (5) with regard to (2) and (3) as follows:

$$n_{\sigma\tau}^2 - \delta_{\sigma\tau} = 4\pi \left\langle \frac{1}{V} \frac{\partial M_{\sigma}}{\partial E_{\tau}^M} \right\rangle_E. \quad (6)$$

Here, \mathbf{M} denotes the dipole moment induced in the sphere by the electric field, the brackets with index $\langle \rangle_E$ standing for classical statistical averaging in the presence of the field \mathbf{E}

$$\langle \Phi \rangle_E = \int \Phi(\boldsymbol{\tau}, \mathbf{E}) f(\boldsymbol{\tau}, \mathbf{E}) d\boldsymbol{\tau} \quad (7)$$

with the distribution function $f(\boldsymbol{\tau}, \mathbf{E})$ for microsystems at configuration $\boldsymbol{\tau}$ at applied field \mathbf{E} .

In our case, $\mathbf{M}(\boldsymbol{\tau}, \mathbf{E})$ is a non-linear function of E and can be written as the expansion

$$M_\sigma(\boldsymbol{\tau}, \mathbf{E}) = \left(\frac{\partial M_\sigma}{\partial E_\tau} \right)_0 E_\tau + \frac{1}{2} \left(\frac{\partial^2 M_\sigma}{\partial E_\tau \partial E_\nu} \right)_0 E_\tau E_\nu + \frac{1}{6} \left(\frac{\partial^3 M_\sigma}{\partial E_\tau \partial E_\nu \partial E_\rho} \right)_0 E_\tau E_\nu E_\rho + \dots \quad (8)$$

which, when introduced into (6), yields

$$\begin{aligned} n_{\sigma\tau}^2 - \delta_{\sigma\tau} = 4\pi \left\langle \frac{1}{V_E} \left(\left(\frac{\partial M_\sigma}{\partial E_\nu} \right)_0 + \left(\frac{\partial^2 M_\sigma}{\partial E_\nu \partial E_\rho} \right)_0 E_\rho \right. \right. \\ \left. \left. + \frac{1}{2} \left(\frac{\partial^3 M_\sigma}{\partial E_\nu \partial E_\rho \partial E_\lambda} \right)_0 E_\rho E_\lambda + \dots \right) \frac{\partial E_\nu}{\partial E_\tau^M} \right\rangle_E. \end{aligned} \quad (9)$$

It should be kept in mind that, in general, the volume V_E of the sphere is a function of the field strength \mathbf{E} . If for simplicity one assumes the volume of the medium to change isotropically (without change in shape) and quadratically in \mathbf{E} , the following expansion can be written:

$$V_E - V = \frac{1}{2} \left(\frac{\partial^2 V}{\partial E^2} \right)_0 E^2 = -\frac{V}{8\pi} \left\{ \left(\frac{\partial n^2}{\partial p} \right)_T - (n^2 - 1) \beta_T \right\} E^2. \quad (10)$$

Equation (10) defines the effect of electrostriction ($\beta_T = (-1/V)(\partial V/\partial p)_T$ denoting the coefficient of isothermal compressibility, and p the pressure).

In the case when the system is in thermal equilibrium at the temperature T and field \mathbf{E} , according to classical statistical mechanics the distribution function in (7) can be expressed as follows†:

$$f(\boldsymbol{\tau}, \mathbf{E}) = \frac{\exp\{-U(\boldsymbol{\tau}, \mathbf{E})/kT\}}{\int \exp\{-U(\boldsymbol{\tau}, \mathbf{E})/kT\} d\boldsymbol{\tau}}. \quad (11)$$

In the general case the total potential energy of the system in a quadratic approximation can be written as the expansion

$$U(\boldsymbol{\tau}, \mathbf{E}) = U(\boldsymbol{\tau}, 0) + \left(\frac{\partial U}{\partial E_\sigma} \right)_0 E_\sigma + \frac{1}{2} \left(\frac{\partial^2 U}{\partial E_\sigma \partial E_\tau} \right)_0 E_\sigma E_\tau + \dots \quad (12)$$

in which $U(\boldsymbol{\tau}, 0)$ is the potential energy of the non-perturbed system (at $\mathbf{E} = 0$).

† Clearly, the system subjected to the effect of the oscillating field $E(t)$ is not at thermal equilibrium, and the distribution function should be determined (e.g. from the appropriate kinetic equation). The solution of a problem of this kind for the general case is beset with considerable difficulties and can be obtained for special cases (see e.g. Debye 1929, Peterlin and Stuart 1943, Lebowitz and Résibois 1965, Kielich 1966 b). These kinetic solutions, in the extremal case $\omega = 0$ and $\omega \rightarrow \infty$, allow us to conclude that, in the case of a non-dissipative medium, a state of thermal quasi-equilibrium can be assumed to set in some time after switching on the perturbation, thus justifying the use (with sufficient accuracy) of the distribution function in the form of (11) with a time-independent part of the potential energy, or with a time-averaged potential energy (see Pershan 1963).

However, in the optical case when the electric field is of the form

$$\mathbf{E}(t) = \frac{1}{2}(\mathbf{E}_0 e^{i\omega t} + \mathbf{E}_0^* e^{-i\omega t}) \quad (13)$$

in order to satisfy the conditions of applicability of the distribution function (11) to systems at thermal equilibrium we have to take into consideration to the right of (12) only the time-independent part†

$$U(\boldsymbol{\tau}, I) = U(\boldsymbol{\tau}, 0) + \frac{1}{2} \left(\frac{\partial^2 U}{\partial E_\sigma \partial E_\tau} \right)_0 I_{\sigma\tau}. \quad (14)$$

Here, we have introduced the intensity tensor of incident light

$$I_{\sigma\tau} = \frac{1}{2} E_\sigma E_\tau^*. \quad (15)$$

By (10) and (11) with (14), equation (9) can be brought to the form‡

$$n_{\sigma\tau}^2 - n_{0\sigma\tau}^2 = A \left(\frac{\partial E_\sigma}{\partial E_\tau^M} \right)_0 I + B \left\{ 3 \left(\frac{\partial E_\nu}{\partial E_\tau^M} \right)_0 I_{\sigma\nu} - \left(\frac{\partial E_\sigma}{\partial E_\tau^M} \right)_0 I \right\} \quad (16)$$

where

$$n_{0\sigma\tau}^2 - \delta_{\sigma\tau} = \frac{4\pi}{3V} \left\langle \frac{\partial M_\alpha}{\partial E_\alpha} \right\rangle \left(\frac{\partial E_\sigma}{\partial E_\tau^M} \right)_0 \quad (17)$$

is the refractive index independent of the light intensity I , the symbol $\langle \rangle$ standing for statistical averaging with the non-perturbed distribution function

$$f(\boldsymbol{\tau}, 0) = \frac{\exp\{-U(\boldsymbol{\tau}, 0)/kT\}}{\int \exp\{-U(\boldsymbol{\tau}, 0)/kT\} d\boldsymbol{\tau}}. \quad (18)$$

The constant A in equation (16) accounts for isotropic changes in refractive index due to intense light of intensity I :

$$A = \frac{2\pi}{9V} \left\{ \left\langle \frac{\partial^3 M_\alpha}{\partial E_\alpha \partial E^2} \right\rangle - \frac{3}{V} \left\langle \frac{\partial M_\alpha}{\partial E_\alpha} \right\rangle \left(\frac{\partial^2 V}{\partial E^2} \right)_0 - \frac{1}{kT} \left(\left\langle \frac{\partial M_\alpha}{\partial E_\alpha} \frac{\partial^2 U}{\partial E^2} \right\rangle - \left\langle \frac{\partial M_\alpha}{\partial E_\alpha} \right\rangle \left\langle \frac{\partial^2 U}{\partial E^2} \right\rangle \right) \right\} \quad (19)$$

which, as we see, is related with opticostriction (electrostriction at optical frequencies, as defined by (10)).

† Obviously, the result of equation (14) can be derived by taking the time average of (12) over an oscillation period such that the polarizability ellipsoids of microsystems shall be able to follow the field. The time-averaging procedure makes the terms with periodic factors $\exp(\pm i\omega t)$, $\exp(\pm i2\omega t)$, ... vanish. Such statistical averaging with time-averaged potential energy has been applied by Buckingham (1956) in his theory of optical birefringence (see also Kielich and Piekara 1959, Pershan 1963).

‡ Since, as already stated, we are interested in the variations of the refractive index for a loss-free medium, using (13) we can separate the time-independent (relevant here) part in the right-hand term of the expansions (9) and (10) and reject the remaining part dependent on the time by way of the periodic factors $\exp(\pm i\omega t)$, $\exp(\pm i2\omega t)$, etc. We then carry out statistical averaging with the distribution function (11) with time-averaged potential energy (14); in the case of an isotropic medium it is convenient first to perform averaging over all possible directions of the electric field with regard to the axes of the laboratory reference system.

The second constant B in equation (16) accounts for anisotropic changes in the tensor $n_{\sigma\tau}^2$, and is given as follows:

$$B = \frac{\pi}{45V} (3\delta_{\alpha\gamma}\delta_{\beta\delta} + 3\delta_{\alpha\delta}\delta_{\beta\gamma} - 2\delta_{\alpha\beta}\delta_{\gamma\delta}) \left\langle \frac{\partial^3 M_\alpha}{\partial E_\beta \partial E_\gamma \partial E_\delta} - \frac{1}{kT} \frac{\partial M_\alpha}{\partial E_\beta} \frac{\partial^2 U}{\partial E_\gamma \partial E_\delta} \right\rangle. \quad (20)$$

With sufficient accuracy, the relationship between the field \mathbf{E}^M and \mathbf{E} can be assumed to be linear and vectorial; for a sphere in vacuum, it is of the form

$$\mathbf{E}^M = \frac{3}{n_0^2 + 2} \mathbf{E} \quad (21)$$

so that equations (16) and (17) can be written in the simpler form

$$n_{\sigma\tau}^2 - n_0^2 \delta_{\sigma\tau} = \left(\frac{n_0^2 + 2}{3} \right) \{ AI \delta_{\sigma\tau} + B(3I_{\sigma\tau} - I \delta_{\sigma\tau}) \} \quad (22)$$

$$\frac{n_0^2 - 1}{n_0^2 + 2} = \frac{4\pi}{9V} \left\langle \frac{\partial M_\alpha}{\partial E_\beta} \right\rangle. \quad (23)$$

The generalized Lorentz-Lorenz equation (23) has been discussed in an earlier paper (Kielich 1962 a) for multi-component systems, and will not be given further consideration here. But we shall discuss equation (22), and particularly the birefringence constant (20) appearing therein, in more detail. This constant can now be expressed in the form

$$B = \frac{\pi}{45V} (3\delta_{\alpha\gamma}\delta_{\beta\delta} + 3\delta_{\alpha\delta}\delta_{\beta\gamma} - 2\delta_{\alpha\beta}\delta_{\gamma\delta}) \left\langle \frac{\partial^3 M_\alpha}{\partial E_\beta \partial E_\gamma \partial E_\delta} + \frac{1}{kT} \frac{\partial M_\alpha}{\partial E_\beta} \frac{\partial M_\gamma}{\partial E_\delta} \right\rangle \quad (24)$$

since the dipole moment induced in a sphere in vacuum is defined as

$$M_\alpha = - \frac{\partial U}{\partial E_\alpha}. \quad (25)$$

In the case when the incident light beam propagates along the Y axis, equation (22) yields for the optical permittivity tensor components

$$\left. \begin{aligned} n_{xx}^2 - n_0^2 &= \left(\frac{n_0^2 + 2}{3} \right) \{ (A - B)I + 3BI_{xx} \} \\ n_{yy}^2 - n_0^2 &= \left(\frac{n_0^2 + 2}{3} \right) (A - B)I \\ n_{zz}^2 - n_0^2 &= \left(\frac{n_0^2 + 2}{3} \right) \{ (A - B)I + 3BI_{zz} \} \end{aligned} \right\} \quad (26)$$

$$\left. \begin{aligned} n_{xz}^2 &= 3 \left(\frac{n_0^2 + 2}{3} \right) BI_{xz} \\ n_{zx}^2 &= 3 \left(\frac{n_0^2 + 2}{3} \right) BI_{zx} \\ n_{xy}^2 &= n_{yx}^2 = n_{yz}^2 = n_{zy}^2 = 0 \end{aligned} \right\} \quad (27)$$

By the diagonal components (26), the optical birefringence induced in the medium by the intense beam of intensity $I = I_{xx} + I_{yy}$ is

$$n_{zz}^2 - n_{xx}^2 = 3 \left(\frac{n_0^2 + 2}{3} \right)^2 B(I_{zz} - I_{xx}). \quad (28)$$

In particular from equation (28) a non-polarized light beam propagating along the Y axis is seen to induce no birefringence, since $I_{xx} = I_{zz} = \frac{1}{2}I$ and thus $n_{zz}^2 - n_{xx}^2 = 0$.

For the case of incident elliptically polarized light, the non-diagonal components (27) yield

$$n_R^2 - n_L^2 = 3i \left(\frac{n_0^2 + 2}{3} \right) B(I_R - I_L) \quad (29)$$

for the difference in refractive indices between the circularly polarized light waves of opposite rotation, of intensities I_R and I_L respectively. Equation (29) defines in general form the rotation of the plane of polarization as induced by intense light, as first studied theoretically and experimentally by Maker and Terhune (1965) and Maker *et al.* (1964).

It is thus seen from equation (26) that the absolute changes in refractive index measured in the X , Y or Z direction are related not only with the induced optical anisotropy B but moreover, in general, with the changes in volume of the medium due to the effect of the strong optical field, i.e. with the opticostriction implicit in the constant A . On the other hand, from equations (28) and (29) we see that the differential changes in refractive index are related only with the anisotropy induced in the medium, as defined by the constant B . Hence, measuring the absolute non-linear changes in refractive index in a given substance and, independently, its optical anisotropy, we can use equations (26)–(29) to determine numerically the constant A , thus determining its opticostriction.

3. Optical birefringence in multi-component systems

We shall now discuss the semi-macroscopic theory proposed in the preceding section with relation to the microscopic structure of the medium involving molecular interactions of the radial and angular kinds.

In the microscopic picture, the dipole moment \mathbf{M} of the volume V containing $N = \sum_i N_i$ microsystems of various species is

$$\mathbf{M} = \sum_i \sum_{p=1}^{N_i} \mathbf{m}^{(pi)} \quad (30)$$

where $\mathbf{m}^{(pi)}$ is the dipole moment of the p th microsystem of species i .

On substituting (30) into equation (24), we get the optical birefringence constant of the multi-component systems in molecular form

$$B = \frac{\pi}{45V} (3\delta_{\alpha\gamma}\delta_{\beta\delta} + 3\delta_{\alpha\delta}\delta_{\beta\gamma} - 2\delta_{\alpha\beta}\delta_{\gamma\delta}) \left\{ \sum_i \left\langle \sum_{p=1}^{N_i} \frac{\partial^3 m_\alpha^{(pi)}}{\partial E_\beta \partial E_\gamma \partial E_\delta} \right\rangle + \frac{1}{kT} \sum_{ij} \left\langle \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \frac{\partial m_\alpha^{(pi)}}{\partial E_\beta} \frac{\partial m_\gamma^{(qj)}}{\partial E_\delta} \right\rangle \right\}. \quad (31)$$

In a condensed medium, the polarizability of a microsystem is generally modified by the molecular field \mathbf{F} of its neighbours, and the dipole moment $\mathbf{m}^{(pi)}$ induced in the p th microsystem by the total field $\mathbf{E} + \mathbf{F}^{(pi)}$ is given by the expansion (Kielich 1960, 1963)

$$m_\alpha^{(pi)} = \left\{ a_{\alpha\beta}^{(pi)} + \frac{1}{2} b_{\alpha\beta\gamma}^{(pi)} (E_\gamma + F_\gamma^{(pi)}) + \frac{1}{6} c_{\alpha\beta\gamma\delta}^{(pi)} (E_\gamma + F_\gamma^{(pi)}) (E_\delta + F_\delta^{(pi)}) + \dots \right\} (E_\beta + F_\beta^{(pi)}) \quad (32)$$

wherein the tensor $a_{\alpha\beta}^{(p i)}$ defines the linear, i.e. first-order, electric polarizability of the p th microsystem of species i , whereas the tensors $b_{\alpha\beta\gamma}^{(p i)}$ and $c_{\alpha\beta\gamma\delta}^{(p i)}$ define its non-linear polarizabilities of the second and third order, respectively, as being due to the strong optical field \mathbf{E} .

In certain cases, in a first approximation, we can neglect the molecular fields in the expansion (32) and the birefringence constant (31) becomes

$$B = \frac{\pi}{45V} \left\{ \sum_i \left\langle \sum_{p=1}^{N_i} (3c_{\alpha\beta\alpha\beta}^{(p i)} + 3c_{\alpha\beta\beta\alpha}^{(p i)} - 2c_{\alpha\alpha\beta\beta}^{(p i)}) \right\rangle + \frac{1}{kT} \sum_{ij} \left\langle \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} (3a_{\alpha\beta}^{(p i)} a_{\alpha\beta}^{(q j)} + 3a_{\alpha\beta}^{(p i)} a_{\beta\alpha}^{(q j)} - 2a_{\alpha\alpha}^{(p i)} a_{\beta\beta}^{(q j)}) \right\rangle \right\}. \quad (33)$$

By methods of classical mechanics, the birefringence constant (33) can be written formally as the following expansion in a power series in the molar fractions $x_i = N_i/N$:

$$B = \sum_i x_i B_i + \sum_{ij} x_i x_j B_{ij} + \dots \quad (34)$$

where we have

$$B_i = \frac{\pi\rho}{45} \left\{ 3c_{\alpha\beta\alpha\beta}^{(i)} + 3c_{\alpha\beta\beta\alpha}^{(i)} - 2c_{\alpha\alpha\beta\beta}^{(i)} + \frac{1}{kT} (3a_{\alpha\beta}^{(i)} a_{\alpha\beta}^{(i)} + 3a_{\alpha\beta}^{(i)} a_{\beta\alpha}^{(i)} - 2a_{\alpha\alpha}^{(i)} a_{\beta\beta}^{(i)}) \right\} \quad (35)$$

$$B_{ij} = \frac{\pi\rho^2}{45VkT} \iint \left\{ 3a_{\alpha\beta}^{(p i)} a_{\alpha\beta}^{(q j)} + 3a_{\alpha\beta}^{(p i)} a_{\beta\alpha}^{(q j)} - 2a_{\alpha\alpha}^{(p i)} a_{\beta\beta}^{(q j)} \right\} g_{ij}^{(2)}(\boldsymbol{\tau}_p, \boldsymbol{\tau}_q) d\boldsymbol{\tau}_p d\boldsymbol{\tau}_q \quad (36)$$

$\rho = N/V$ being the number density, and $g_{ij}^{(2)}(\boldsymbol{\tau}_p, \boldsymbol{\tau}_q)$ a binary correlation function for pairs of microsystems p and q of species i and j having the configurations $\boldsymbol{\tau}_p$ and $\boldsymbol{\tau}_q$.

The first term in (35) accounts for the temperature-independent effect of optical non-linear deformation of the microsystems due to the strong optical field, whereas the second, temperature-dependent term accounts for the effect of optical molecular orientation in substances presenting no molecular interaction. The constant (36) determines the influence of molecular correlations on the effect of optical molecular orientation.

In the case of multi-component systems consisting of non-interacting microsystems $B_{ij} = 0$ and (34) becomes

$$B = \sum_i x_i B_i \quad (37)$$

expressing additivity of the optical birefringence constant.

The second and higher terms of (34) responsible for the deviations from additivity of B result from interaction between unlike molecules in a dense medium.

For microsystems possessing the symmetry of the point group D_{4h} expressions (35) and (36) yield

$$B_i = \frac{4\pi\rho}{45} \left\{ c_{3333}^{(i)} + 2c_{1111}^{(i)} - c_{1122}^{(i)} - c_{1133}^{(i)} - c_{3311}^{(i)} + 3c_{1212}^{(i)} + 6c_{1313}^{(i)} + \frac{1}{kT} (a_{33}^{(i)} - a_{11}^{(i)})^2 \right\} \quad (38)$$

$$B_{ij} = \frac{4\pi\rho}{45kT} (a_{33}^{(i)} - a_{11}^{(i)})(a_{33}^{(j)} - a_{11}^{(j)}) J_{ij}^A \quad (39)$$

where (Kielich 1963)

$$J_{ij}^A = \frac{\rho}{2V} \iint (3 \cos^2 \theta_{pq} - 1) g_{ij}^{(2)}(\boldsymbol{\tau}_p, \boldsymbol{\tau}_q) d\boldsymbol{\tau}_p d\boldsymbol{\tau}_q \quad (40)$$

is an integral parameter determining pairwise molecular correlations of the angular kind.

On putting in (38) $2c_{1212}^{(i)} = c_{1111}^{(i)} - c_{1122}^{(i)}$ we have an expression that holds for microsystems of the point groups C_{6h} and D_{6h} as well as $D_{\infty h}$.

In particular, in the case of the point groups T_h and O_h , we have $a_{11}^{(i)} = a_{33}^{(i)} = a_i$ and $c_{1111}^{(i)} = c_{3333}^{(i)}$, $c_{1122}^{(i)} = c_{1133}^{(i)} = c_{3311}^{(i)}$, $c_{1212}^{(i)} = c_{1313}^{(i)}$, whence equations (38) and (39) reduce to

$$B_i = \frac{4\pi}{15} \rho (3c_{1313}^{(i)} + c_{3333}^{(i)} - c_{1133}^{(i)}), \quad B_{ij} = 0 \quad (41)$$

which for the special case of spherical symmetry becomes simply

$$B_i = \frac{2\pi}{3} \rho (c_{3333}^{(i)} - c_{1133}^{(i)}) = \frac{4\pi}{3} \rho c_{1313}^{(i)} \quad (42)$$

since in this case $2c_{1313}^{(i)} = c_{3333}^{(i)} - c_{1133}^{(i)}$. Hence, as was expected, in a medium of microsystems with high symmetry the effect of optical molecular orientation does not appear, but only non-linear optical deformation.

We shall now take into account the effect of the molecular field on the orientational part of the birefringence constant given in a general form in (31). The field in the expansion (32) can be expressed as follows, with interactions of the dipole type:

$$F_\alpha^{(pi)} = - \sum_j \sum_{\substack{q=1 \\ q \neq p}}^{N_j} T_{\alpha\beta}^{(pq)} (\mu_\beta^{(qj)} + m_\beta^{(qj)}) \quad (43)$$

$\mu_\beta^{(qj)}$ denoting the β component of the permanent electric dipole moment of the q th microsystem of species j ;

$$T_{\alpha\beta}^{(pq)} = -r_{pq}^{-5} (3r_{pq\alpha} r_{pq\beta} - r_{pq}^2 \delta_{\alpha\beta}) \quad (44)$$

is the tensor characterizing dipole-dipole interaction between microsystems p and q distant by r_{pq} .

For simplicity, we restrict further calculations to linearly and isotropically polarizable microsystems for which we obtain from (31) and (32)

$$B = \frac{2\pi}{45VkT} \sum_{ij} \left\langle \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} a_{pi} a_{qj} \left(3 \frac{\partial F_\alpha^{(pi)}}{\partial E_\beta} \frac{\partial F_\alpha^{(qj)}}{\partial E_\beta} - \frac{\partial F_\alpha^{(pi)}}{\partial E_\alpha} \frac{\partial F_\beta^{(qj)}}{\partial E_\beta} \right) \right\rangle \quad (45)$$

which by (43) can be expressed as

$$B = \sum_{ij} x_i x_j B_{ij} + \sum_{ijk} x_i x_j x_k B_{ijk} + \dots \quad (46)$$

with the pairwise correlation constant

$$B_{ij} = \frac{4\pi\rho}{5kT} a_i^2 a_j^2 J_{ij}^R. \quad (47)$$

Here, we have introduced the integral parameter (Kielich 1960, 1962 b)

$$J_{ij}^R = 2 \frac{\rho}{V} \iint r_{pq}^{-6} g_{ij}^{(2)}(\mathbf{r}_p, \mathbf{r}_q) d\mathbf{r}_p d\mathbf{r}_q \quad (48)$$

defining radial correlations of isotropically polarizable microsystems of linear mean polarizability a_i .

The result of equation (45) or its special case (47) signifies that, even in fluids consisting of linearly and isotropically polarizable microsystems, owing to interaction

between induced dipolar moments, birefringence of the orientational kind can appear in the medium. Clearly, we have in mind an effect of orientation of assemblages consisting of atoms or spherical molecules coupled by way of radial forces. We have seen (equations (41) and (42)) that in a medium of non-interacting atoms or spherical molecules only birefringence due to non-linear deformation can arise, since the isolated atoms and spherical molecules do not undergo orientation in an electric field. However, as seen from equations (47) and (48), it suffices that the medium be sufficiently dense to give rise to pairwise radially coupled assemblages, and the latter will behave at a given instant like anisotropic elements which become oriented by the electric field. This leads to weak birefringence of the medium dependent rather strongly on the temperature.

Similarly, equation (31) can be used for calculating the effect of molecular fields on the birefringence of liquids consisting of molecules that are dipolar, quadrupolar, and so forth.

4. Comparison of the theory and experimental data

We shall now attempt a numerical confrontation of the theory with the experimental results of Paillette (1966). To this aim, we resort to the definition of the experimental optical birefringence

$$n_{zz} - n_{xx} = \lambda B_{\lambda} (I_{zz}^M - I_{xx}^M) \quad (49)$$

where λ is the light wavelength and $I^M = \{3/(n_0^2 + 2)\}^2 I$ —the light intensity within the medium.

Considering that n_{zz} and n_{xx} differ only slightly from n_0 , we can write

$$n_{zz}^2 - n_{xx}^2 = 2n_0(n_{zz} - n_{xx})$$

and a comparison of equations (28) and (49) yields the relation

$$B_{\lambda} = \frac{3}{2n\lambda} \left(\frac{n_0^2 + 2}{3} \right)^4 B. \quad (50)$$

Let us first consider liquids of isotropically polarizable molecules for which, by (42) and (47), the part describing the effect of non-linear deformation is

$$B^{\text{def}} = \frac{2\pi}{3} \rho (c_{3333} - c_{1133}) \quad (51)$$

and that of the effect of radial molecular orientation

$$B^{\text{or}} = \frac{4\pi\rho}{5kT} a^4 J_R \quad (52)$$

wherein the radial correlation parameter J_R given by (48) without indices i and j can be determined experimentally from the following formula for the degree of depolarization of scattered light (Kielich 1962 b):

$$D = \frac{6a^2 J_R}{5\rho kT\beta_T + 7a^2 J_R}. \quad (53)$$

For liquid CCl_4 we have the following data at $t = 20^\circ\text{C}$ (Kielich 1962 b):

$$\begin{aligned} a &= 10.5 \times 10^{-24} \text{ cm}^3, & \rho &= 6.23 \times 10^{21} \text{ cm}^{-3} \\ \beta_T &= 90.5 \times 10^{-12} \text{ c.g.s.}, & D &= 0.056. \end{aligned}$$

Consequently, expressions (52) and (53) yield $B^{\text{or}} = 4.9 \times 10^{-14}$ e.s.u. With $\lambda = 4880 \text{ \AA}$, we obtain $n = 1.457$ and equation (50) yields $B_{\lambda}^{\text{or}} = 3.7 \times 10^{-9}$ e.s.u. so that the conclusion is that the contribution from non-linear deformation not taken into account in our calculations amounts to $B^{\text{def}} = 1.4 \times 10^{-9}$ e.s.u., i.e. approximately 28% of the experimental value 5.1×10^{-9} e.s.u. Thus by applying expressions (50) and (51) we obtain for the optical anisotropy induced in the CCl_4 molecule by intense light a value of $c_{3333} - c_{1133} = 1.43 \times 10^{-36}$ e.s.u., whose order of magnitude is in accordance with the anisotropy determined from Kerr's effect amounting to (Kielich 1962 b)

$$4.34 \times 10^{-36} \text{ e.s.u.}$$

For one-component systems consisting of axially symmetric molecules, one has by (38) and (39)

$$B^{\text{def}} = \frac{4\pi\rho}{45} (c_{3333} + 2c_{1111} - c_{1122} - c_{1133} - c_{3311} + 3c_{1212} + 6c_{1313}) \quad (54)$$

$$B^{\text{or}} = \frac{4\pi\rho}{5kT} a^2 \kappa^2 (1 + J_A) \quad (55)$$

where $\kappa = (a_{33} - a_{11})/3a$ is the optical anisotropy parameter of the molecule. The unknown parameter of angular correlations J_A , given by equation (40) without indices i and j , can be eliminated from (55) by resorting to the formula for the depolarization ratio (Kielich 1960):

$$D = \frac{6\kappa^2(1 + J_A)}{5\rho kT\beta_T + 7\kappa^2(1 + J_A)} \quad (56)$$

and one obtains the relation

$$B^{\text{or}} = 4\pi\rho^2 a^2 \frac{\beta_T D}{6 - 7D}. \quad (57)$$

This relation is readily shown to hold for linearly polarizable molecules of arbitrary symmetry.

Since the values of a , β_T and D are known for quite a number of substances (cf. the Landolt-Börnstein tables) we can easily compare the values of B calculated from expressions (50) and (57) with the experimental values of Paillette (1966). The results are assembled in the table. It is seen that, save for acetone and benzene where the values of B_{λ}^{or} , calculated on the assumption of a molecular orientational effect only, are in excess of the experimental data, the theoretical values are smaller by 20% on the average. This difference ought probably to be ascribed to the contributions from the effect of non-linear deformation, which can be calculated from equation (54) or a formula simplified as follows:

$$B^{\text{def}} = \frac{4\pi}{9} \rho c \quad (58)$$

which holds on the assumption that the tensor $c_{\alpha\beta\gamma\delta}$ is entirely symmetric, when $c = (3c_{\alpha\beta\alpha\beta} - c_{\alpha\alpha\beta\beta})/10 \simeq c_{\alpha\alpha\beta\beta}/5$ denotes the mean third-order polarizability.

In the case of CS_2 , if one considers that the difference between the experimental value of 418×10^{-9} e.s.u. and the theoretical value 344×10^{-9} e.s.u., calculated on taking into account only the effect of molecular orientation, is due to the effect of non-linear deformation, i.e. $B_{\lambda}^{\text{def}} = 74 \times 10^{-9}$ e.s.u., expressions (50) and (48) yield $c = 50.1 \times 10^{-36}$ e.s.u. This latter value is in good agreement with that of

Calculated and experimental values of the optical birefringence constant for $\lambda = 4880 \text{ \AA}$ at $t = 20^\circ \text{C}$

Liquid	$\rho \times 10^{-21}$ (cm^{-6})	$\beta_T \times 10^{12}$ (c.g.s.)	n	$a \times 10^{24}$ (cm^3)	$D \times 10^2$	$B^{\text{or}} \times 10^{14}$ (e.s.u.)	$B_{\lambda}^{\text{or}} \times 10^9$ (e.s.u.)	$B_{\lambda}^{\text{exper}} \times 10^{11}$ (e.s.u.)
carbon disulphide CS_2	9.99	92.0	1.613	8.74	62	329.0	344.0	418.0
acetone $\text{C}_3\text{H}_6\text{O}$	8.21	123.4	1.356	6.33	20.8	19.1	11.2	7.3
chloroform CHCl_3	7.51	87.1	1.446	8.23	20.0	17.4	12.8	16.5
benzene C_6H_6	6.78	93.2	1.494	10.32	42	78.7	63.0	40.0
cyclohexane C_6H_{12}	5.58	112.0	1.440	10.87	5.8	4.7	3.4	4.1
toluene $\text{C}_6\text{H}_5\text{CH}_3$	5.66	88.4	1.497	12.20	48	94.7	75.8	93.0
nitrobenzene $\text{C}_6\text{H}_5\text{NO}_2$	5.89	49.0	1.553	12.92	70.9	248.6	225.4	290.0
water H_2O	33.62	46.0	1.334	1.59	10.8	3.5	2.1	2.9

† All values of $B_{\lambda}^{\text{exper}}$ are from Paillette (1966).

54.4×10^{-36} e.s.u., determined by Buckingham and Raab (1957) from Kerr's effect and 56.5×10^{-36} e.s.u. determined from molecular light scattering (Kielich 1960).

Similarly, one can calculate the mean third-order non-linear polarizabilities for the other molecules, obtaining $c = 4.8 \times 10^{-36}$ e.s.u. for CHCl_3 , $c = 1.2 \times 10^{-36}$ e.s.u. for C_6H_{12} , $c = 27.2 \times 10^{-36}$ e.s.u. for $\text{C}_6\text{H}_5\text{CH}_3$ and $c = 85.0 \times 10^{-36}$ e.s.u. for $\text{C}_6\text{H}_5\text{NO}_2$. These would seem to be quite reasonable values.

From this comparison of the theoretically assessed values of B and the experimental data it can be concluded that, although the essential role in the effect of optical birefringence belongs to molecular orientation, the contributions related with the effect of non-linear deformation are not to be neglected, as they amount on average to about 20% of the experimental value. It would be of great interest to carry out measurements of the dependence of optical birefringence on temperature, as this would permit us to resolve the two effects with more precision.

Along similar lines, one can make a comparison of equation (29) and the experimental results of Maker *et al.* (1964). It would seem useful to continue experimental work on the effects considered above, particularly on their dispersion and absorption†—processes not considered theoretically in this paper—and to link them with self-trapping of optical beams due to non-linear increases in refractive index as well as with the stimulated Raman effect in liquids (see Chiao *et al.* 1964, Garmire *et al.* 1966, Lallemand and Bloembergen 1965, Bloembergen and Lallemand 1966, Kelley 1965, Shen 1966 and the papers cited therein).

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† Recently, the author has received from Dr. P. R. Longaker the preprint of a paper written in co-operation with Dr. M. M. Litvak and presented at the American Physical Society meeting on January 29, 1966, discussing attempts at measuring changes in the refractive index of absorbing media induced by a pulsed laser beam.