STATISTICAL THEORY OF THE ELECTRICAL ANISOTROPY INDUCED IN AN ISOTROPIC MEDIUM BY AN INTENSE LIGHT BEAM

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Synopsis

A semi-macroscopic method is used to show that the nonlinear change in electric permittivity tensor $\varepsilon_{\sigma\tau}$ as induced in an arbitrary dense isotropic medium by a strong optical field of amplitude $\mathscr{E}_0$ is given by

$$\varepsilon_{\sigma\tau} - \varepsilon_{\sigma\tau}^0 = Q_{\mathrm{is}}\,\delta_{\sigma\tau}\mathscr{E}_0^2 + Q_{\mathrm{anis}}(3\mathscr{E}_{0\sigma}\mathscr{E}_{0\tau} - \delta_{\sigma\tau}\mathscr{E}_0^2),$$

where the constant Q_{is} describes isotropic changes in electric permittivity related with nonlinear polarization and opticostriction and Q_{anis} accounts for the optically induced electrical anisotropy. Q_{anis} is proved to consist of four terms, one of which results from third-order electric polarization due to the square of the optical field, whereas the remaining three arise from optical molecular orientation, which depends directly on the temperature. The anisotropy constant Q_{anis} is then discussed in detail statistically for the case of multi-component systems consisting of mutually interacting, isotropically polarizable or electro-optically anisotropic molecules with or without a centre of symmetry. In dense systems the radial and angular interactions of the molecules are accounted for by means of binary and ternary correlation functions. The theory is applied to compressed gas mixtures consisting of nonpolar anisotropic unlike molecules, or molecules with permanent dipole and quadrupole moments.

§ 1. *Introduction.* Even before the coming of lasers, it was known from simple classical calculations that an optical field of very high intensity can affect not only the optical[1]) but also the electric and magnetic[2])[3]) properties of isotropic systems such as gases and liquids. We have in mind nonlinear variations of the electric or magnetic permittivity due to the electric field of a very intense light beam[2])[3]). Since those days, the techniques of constructing high intensity light sources have made enormous progress and the lasers operating at present produce light beams of an intensity that would have seemed inachievable several years ago. At present the detection of the electric nonlinearity induced in an isotropic medium by an intense light beam is only a matter of evolving appropriate ingenious measuring techniques.

In this respect, it may be worth reminding that it was only quite recently that Paillette[4]) used a laser beam to observe and follow quantitatively in several organic liquids the optically induced birefingence predicted theoreti-

cally by Buckingham[1]). It can be hoped that one of these days it will also be possible to observe the electrical anisotropy which can be induced in liquids by an intense laser beam. The investigation of electrical anisotropy, as distinct from that of the absolute nonlinear variations in electric permittivity, would seem more promising in that the former does not depend on various other simultaneously occurring effects such as opticostriction, thermal effects, and so forth. Optically induced electric anisotropy is indeed the inverse of the well-known effect of DC field-induced birefringence i.e. of Kerr's effect. In the Kerr effect, the role of measuring field belongs to a weak light beam, whereas the field which induces birefringence is a DC electric field of high intensity. Inversely, in the effect of electric anisotropy proposed here for measurement, the role of measuring field is played by a weak DC or slowly time-variable electric field, while the field that induces the anisotropy is the oscillating electric field of an intense light beam e.g. from a laser.

Thus, it is now the moment to proceed to a more thorough theoretical investigation of the electrical nonlinearity due to a very strong optical field. The problem has already been dealt with theoretically for not too dense one-component systems only[2][3]). Albeit, these present a degree of generality still insufficient for their providing the possibility of taking into account various factors of a microscopic nature, such as the electric field of molecular multipoles and the nonlinearities induced in the molecules by these fields, etc.

The present paper is aimed at deriving a statistical-molecular theory of optically induced electric anisotropy in multi-component systems on the basis of the existing semi-macroscopic theories of isotropic dielectrics[5]). The theory thus generally formulated can be applied to a wide range of vastly varying special cases beyond the one-component systems discussed previously in some approximation, comprising two-, three-component systems, etc., consisting of atoms or molecules with induced or permanent dipoles, quadrupoles, octopoles, and so forth.

§ 2. *General semi-macroscopic theory.* Let us consider an isotropic medium whose electric permittivity is ε_e and at the centre of which we shall consider a sphere of macroscopic dimensions whose electric permittivity is ε_i and volume V. We suppose that this medium is in a weak uniform electric field of strength $\boldsymbol{E}$, caused by a fixed external charge distribution at a large distance from the medium. The mean macroscopic electric field of strength $\boldsymbol{E}^i$ existing within the sphere is related with the external field $\boldsymbol{E}$ as follows[6]):

$$\boldsymbol{E}^i = \frac{3\varepsilon_e}{\varepsilon_i + 2\varepsilon_e}\,\boldsymbol{E}. \tag{2.1}$$

As long as the electric field strength $\boldsymbol{E}$ is small, the medium undergoes

linear polarization leading to the well-known result[5]). Albeit, we are concerned here with the case when another oscillating electric field $\mathscr{E}$ is acting on the medium. Assume the field E, which will now be termed the measuring field, to be a slowly time-varying electric field, while the additional polarizing field $\mathscr{E}$ is a rapidly varying electric field e.g. the optical field associated with a light beam. The latter will be assumed to be cosine variable $\mathscr{E} = \mathscr{E}_0$ cos ωt, oscillating with the light angular frequency ω excluding, however, frequencies within the range of optical absorption of the substance.

If the intensity of the oscillating electric field $\mathscr{E}$ is very large, the medium becomes anisotropic, characterized by the electric permittivity tensor as measured by the weak electric field E which varies but very slowly with respect to the rapid oscillations of the polarizing field $\mathscr{E}$. In the general case we have

$$\varepsilon_{\sigma\tau} - \delta_{\sigma\tau} = 4\pi \frac{\partial \overline{P_\sigma}^t}{\partial E_\tau^i}, \tag{2.2}$$

where P is the total dipole electric polarization vector of the medium whereas the bar $—^t$ stands for time-averaging over the period with respect to the oscillating field $\mathscr{E}$.

In the case considered here, we have by definition

$$P = \frac{\langle M \rangle_{E,\mathscr{E}}}{V}, \tag{2.3}$$

where $M(\tau, E, \mathscr{E})$ is the total electric dipole moment of the small sphere when its molecules are at configuration τ in the presence of the electric fields E and $\mathscr{E}$, and $\langle \ \rangle_{E,\mathscr{E}}$ is its statistical mean value.

At thermodynamical equilibrium of the system at the temperature T we have in the case of classical statistical mechanics

$$\langle M \rangle_{E,\mathscr{E}} = \frac{\int M(\tau, E, \mathscr{E}) \exp\{-\mathscr{H} \overline{U(\tau, E, \mathscr{E})}^t\} \, d\tau}{\int \exp\{-\mathscr{H} \overline{U(\tau, E, \mathscr{E})}^t\} \, d\tau} \tag{2.4}$$

with $U(\tau, E, \mathscr{E})$ denoting the total potential energy of the system at configuration τ when the electric fields E and $\mathscr{E}$ are present, and with $\mathscr{H} = = 1/kT$.

We assume that the sample of the isotropic medium when acted on by a strong optical field changes its total volume V only, without undergoing a change in shape, and that this change is a quadratic function of the field strength; namely, we have

$$V(\mathscr{E}) = V(0) + \tfrac{1}{2}\left(\frac{\partial^2 V}{\partial \mathscr{E}^2}\right)_0 \mathscr{E}^2 + \dots \tag{2.5}$$

This equation determines the isotropic change in volume of the isotropic

sample due to opticostriction, which in analogy to electrostriction can be expressed as follows[6]:

$$V(\mathscr{E}) - V(0) = -\tfrac{1}{2}\left\{\frac{\partial}{\partial p}\left(\chi^0 V\right)\right\}_T \mathscr{E}^2 = -\frac{V}{2}\left\{\left(\frac{\partial \chi^0}{\partial p}\right)_T - \chi^0 \beta_T\right\} \mathscr{E}^2, \quad (2.6)$$

where χ^0 is the optical susceptibility of the sample,

$$\beta_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$$

its isothermal compressibility, and p — the pressure.

On expanding the right hand side of (2.2) in a power series in $\mathscr{E}$ and using the expressions (2.3) and (2.5) we obtain, to within the second power of the field strength $\mathscr{E}$,

$$\varepsilon_{\sigma\tau} - \varepsilon_{\sigma\tau}^0 = Q_{\sigma\tau}^V + Q_{\sigma\tau}^P, \quad (2.7)$$

where we have introduced the electric permittivity tensor in the absence of the strong optical field

$$\varepsilon_{\sigma\tau}^0 - \delta_{\sigma\tau} = \frac{4\pi}{V}\left\{\frac{\partial}{\partial E_\tau^i}\langle M_\sigma\rangle_E\right\}_0, \quad (2.8)$$

and the following tensors:

$$Q_{\sigma\tau}^V = -\frac{2\pi}{V^2}\left\{\frac{\partial}{\partial E_\tau^i}\langle M_\sigma\rangle_E\right\}_0 \left(\frac{\partial^2 V}{\partial \mathscr{E}^2}\right)_0 \overline{\mathscr{E}^2}^t, \quad (2.9)$$

$$Q_{\sigma\tau}^P = \frac{2\pi}{V}\left\{\frac{\partial^3}{\partial E_\tau^i \partial \mathscr{E}_\nu \partial \mathscr{E}_\rho}\langle M_\sigma\rangle_{E,\,\mathscr{E}}\right\}_0 \overline{\mathscr{E}_\nu \mathscr{E}_\rho}^t \quad (2.10)$$

describing the effects arising from the changes in volume and polarization of the medium respectively, due to the strong optical field.

The total dipole moment M and potential energy U may be expanded in a power series in E and $\mathscr{E}$ and we obtain up to the terms linear in E and quadratic in $\mathscr{E}$:

$$U(\mathbf{r}, E, \mathscr{E}) = U(\mathbf{r}, 0) + \left(\frac{\partial U}{\partial E_\sigma}\right)_0 E_\sigma + \left(\frac{\partial U}{\partial \mathscr{E}_\sigma}\right)_0 \mathscr{E}_\sigma + \left(\frac{\partial^2 U}{\partial E_\sigma \partial \mathscr{E}_\tau}\right)_0 \cdot E_\sigma \mathscr{E}_\tau +$$

$$+ \tfrac{1}{2}\left(\frac{\partial^2 U}{\partial \mathscr{E}_\sigma \partial \mathscr{E}_\tau}\right)_0 \mathscr{E}_\sigma \mathscr{E}_\tau + \tfrac{1}{2}\left(\frac{\partial^3 U}{\partial E_\sigma \partial \mathscr{E}_\tau \partial \mathscr{E}_\nu}\right)_0 E_\sigma \mathscr{E}_\tau \mathscr{E}_\nu + \ldots, \quad (2.11)$$

$$M_\sigma(\mathbf{r}, E, \mathscr{E}) = M_{0\sigma} + \left(\frac{\partial M_\sigma}{\partial E_\tau}\right)_0 E_\tau + \left(\frac{\partial^2 M_\sigma}{\partial E_\tau \partial \mathscr{E}_\nu}\right)_0 E_\tau \mathscr{E}_\nu +$$

$$+ \tfrac{1}{2}\left(\frac{\partial^2 M_\sigma}{\partial \mathscr{E}_\tau \partial \mathscr{E}_\nu}\right)_0 \mathscr{E}_\tau \mathscr{E}_\nu + \tfrac{1}{2}\left(\frac{\partial^3 M_\sigma}{\partial E_\tau \partial \mathscr{E}_\nu \partial \mathscr{E}_\rho}\right)_0 E_\tau \mathscr{E}_\nu \mathscr{E}_\rho + \ldots, \quad (2.12)$$

where $U(\tau, 0)$ and $M_{0\sigma} = M_\sigma(\tau, 0)$ are the potential energy and dipole moment in the absence of electric fields.

By (2.4), (2.11) and (2.12), the expressions (2.8)–(2.10) may be rewritten as follows:

$$\varepsilon^0_{\sigma\tau} - \delta_{\sigma\tau} = \frac{4\pi}{V} \left\{ \left\langle \frac{\partial M_\sigma}{\partial E_\nu} \right\rangle - \mathscr{H} \left\langle M_\sigma \frac{\partial U}{\partial E_\nu} \right\rangle \right\} \left(\frac{\partial E_\nu}{\partial E^i_\tau} \right)_0, \tag{2.13}$$

$$Q^V_{\sigma\tau} = - \frac{1}{2V} (\varepsilon^0_{\sigma\tau} - \delta_{\sigma\tau}) \left(\frac{\partial^2 V}{\partial \mathscr{E}^2} \right)_0 \overline{\mathscr{E}^2}^{\,t}, \tag{2.14}$$

$$Q^P_{\sigma\tau} = \frac{2\pi}{V} \left\{ \left\langle \frac{\partial^3 M_\sigma}{\partial E_\lambda \partial \mathscr{E}_\nu \partial \mathscr{E}_\rho} - \mathscr{H} \left(\frac{\partial^2 M_\sigma}{\partial \mathscr{E}_\nu \partial \mathscr{E}_\rho} \frac{\partial U}{\partial E_\lambda} + \right. \right. \right.$$

$$\left. + M_\sigma \frac{\partial^3 U}{\partial E_\lambda \partial \mathscr{E}_\nu \partial \mathscr{E}_\rho} + \frac{\partial M_\sigma}{\partial E_\lambda} \frac{\partial^2 U}{\partial \mathscr{E}_\nu \partial \mathscr{E}_\rho} \right) + \mathscr{H}^2 M_\sigma \frac{\partial U}{\partial E_\lambda} \frac{\partial^2 U}{\partial \mathscr{E}_\nu \partial \mathscr{E}_\rho} \right\rangle +$$

$$\left. + \mathscr{H} \left\langle \frac{\partial M_\sigma}{\partial E_\lambda} - \mathscr{H} M_\sigma \frac{\partial U}{\partial E_\lambda} \right\rangle \left\langle \frac{\partial^2 U}{\partial \mathscr{E}_\nu \partial \mathscr{E}_\rho} \right\rangle \right\} \left(\frac{\partial E_\lambda}{\partial E^i_\tau} \right)_0 \overline{\mathscr{E}_\nu \mathscr{E}_\rho}^{\,t}, \tag{2.15}$$

where the symbol $\langle \ \rangle$ denotes statistical averaging at zero electric field strength.

On averaging (2.13) and (2.15) over all possible directions of the electric fields, we obtain

$$\varepsilon^0_{\sigma\tau} - \delta_{\sigma\tau} = \frac{4\pi}{3V} \left\langle \frac{\partial M_\alpha}{\partial E_\alpha} - \mathscr{H} M_\alpha \frac{\partial U}{\partial E_\alpha} \right\rangle \left(\frac{\partial E_\sigma}{\partial E^i_\tau} \right)_0, \tag{2.16}$$

$$Q^P_{\sigma\tau} = A \frac{\partial E_\sigma}{\partial E^i_\tau} \overline{\mathscr{E}^2}^{\,t} + B \left(3 \frac{\partial E_\nu}{\partial E^i_\tau} \overline{\mathscr{E}_\sigma \mathscr{E}_\nu}^{\,t} - \frac{\partial E_\sigma}{\partial E^i_\tau} \overline{\mathscr{E}^2}^{\,t} \right), \tag{2.17}$$

where

$$A = \frac{2\pi}{9V} \left\langle \frac{\partial^3 M_\alpha}{\partial E_\alpha \partial \mathscr{E}^2} - \mathscr{H} \left(\frac{\partial^2 M_\alpha}{\partial \mathscr{E}^2} \frac{\partial U}{\partial E_\alpha} + M_\alpha \frac{\partial^3 U}{\partial E_\alpha \partial \mathscr{E}^2} \right) - \right.$$

$$\left. - \mathscr{H} \left(\frac{\partial M_\alpha}{\partial E_\alpha} - \mathscr{H} M_\alpha \frac{\partial U}{\partial E_\alpha} \right) \left(\frac{\partial^2 U}{\partial \mathscr{E}^2} - \left\langle \frac{\partial^2 U}{\partial \mathscr{E}^2} \right\rangle \right) \right\rangle, \tag{2.18}$$

$$B = \frac{\pi}{45V} \chi_{\alpha\beta\gamma\delta} \left\langle \frac{\partial^3 M_\alpha}{\partial E_\beta \partial \mathscr{E}_\gamma \partial \mathscr{E}_\delta} - \mathscr{H} \left(\frac{\partial^2 M_\alpha}{\partial \mathscr{E}_\gamma \partial \mathscr{E}_\delta} \frac{\partial U}{\partial E_\beta} + \right. \right.$$

$$\left. + M_\alpha \frac{\partial^3 U}{\partial E_\beta \partial \mathscr{E}_\gamma \partial \mathscr{E}_\delta} + \frac{\partial M_\alpha}{\partial E_\beta} \frac{\partial^2 U}{\partial \mathscr{E}_\gamma \partial \mathscr{E}_\delta} \right) + \mathscr{H}^2 M_\alpha \frac{\partial U}{\partial E_\beta} \frac{\partial^2 U}{\partial \mathscr{E}_\gamma \partial \mathscr{E}_\delta} \right\rangle, \tag{2.19}$$

with the notation

$$\chi_{\alpha\beta\gamma\delta} = 3\delta_{\alpha\gamma}\delta_{\beta\delta} + 3\delta_{\alpha\delta}\delta_{\beta\gamma} - 2\delta_{\alpha\beta}\delta_{\gamma\delta}. \tag{2.20}$$

The constant A defines nonlinear changes in electric permittivity tensor

of an isotropic nature, whereas B describes the anisotropy induced in the medium by the strong optical field.

Considering in particular the sphere of volume V not as part of the large sample, but in vacuo, we can write

$$M_\alpha = -\frac{\partial U}{\partial E_\alpha}. \tag{2.21}$$

Using, moreover, the fact that in case of a weak electric field the isotropic relation of (2.1) is satisfied (for a dielectric sphere in vacuum we have $\varepsilon_e = 1$ and $\varepsilon_i = \varepsilon_0$), i.e.

$$\frac{\partial E_\sigma}{\partial E_\tau^i} = \frac{\varepsilon_0 + 2}{3} \delta_{\sigma\tau}, \tag{2.22}$$

the tensor $\varepsilon_{\sigma\tau}^0$ reduces to the isotropic tensor $\varepsilon_0\delta_{\sigma\tau}$ with dielectric constant ε_0 given with respect to (2.16) and (2.21) by the well-known result[5)]

$$\frac{\varepsilon_0 - 1}{\varepsilon_0 + 2} = \frac{4\pi}{9V} \left\langle \frac{\partial M_\alpha}{\partial E_\alpha} + \mathscr{H} M_\alpha M_\alpha \right\rangle. \tag{2.23}$$

In the same case, by (2.6), the tensor of (2.14) may be rewritten as follows:

$$Q_{\sigma\tau}^V = \frac{\varepsilon_0 - 1}{16\pi} \left\{ \left(\frac{\partial n^2}{\partial p} \right)_T - (n^2 - 1) \beta_T \right\} \mathscr{E}_0^2 \delta_{\sigma\tau}, \tag{2.24}$$

where n is the refractive index of the medium.

By (2.22), also the tensor of (2.17) can be simplified to the form

$$Q_{\sigma\tau}^P = \frac{\varepsilon_0 + 2}{6} \{ A\delta_{\sigma\tau}\mathscr{E}_0^2 + B(3\mathscr{E}_{0\sigma}\mathscr{E}_{0\tau} - \delta_{\sigma\tau}\mathscr{E}_0^2) \}. \tag{2.25}$$

§ 3. *Anisotropy induced in the medium.* It is customary to define the electric anisotropy induced in a medium by a strong optical field as the difference $\varepsilon_{zz} - \varepsilon_{xx}$ between its electric permittivities measured in the direction of the z and x axes of the laboratory frame. From the expressions (2.7), (2.24) and (2.25) we obtain

$$\varepsilon_{zz} - \varepsilon_{xx} = Q_{zz}^P - Q_{xx}^P = \tfrac{1}{6}(\varepsilon_0 + 2)^2 B(\mathscr{E}_{0z}^2 - \mathscr{E}_{0x}^2), \tag{3.1}$$

where by (2.19) and (2.21) the induced anisotropy constant is now of the form

$$B = \frac{\pi}{45V} \chi_{\alpha\beta\gamma\delta} \left\langle \frac{\partial^3 M_\alpha}{\partial E_\beta \partial \mathscr{E}_\gamma \partial \mathscr{E}_\delta} + \mathscr{H} \left(M_\alpha \frac{\partial^2 M_\beta}{\partial \mathscr{E}_\gamma \partial \mathscr{E}_\delta} + \frac{\partial^2 M_\alpha}{\partial \mathscr{E}_\gamma \partial \mathscr{E}_\delta} M_\beta \right) + \right.$$
$$\left. + \mathscr{H} \left(\frac{\partial M_\alpha}{\partial E_\beta} + \mathscr{H} M_\alpha M_\beta \right) \frac{\partial \tilde{M}_\gamma}{\partial \mathscr{E}_\delta} \right\rangle \tag{3.2}$$

with

$$\tilde{M}_\alpha = -\frac{\partial U}{\partial \mathscr{E}_\alpha} \tag{3.3}$$

denoting the oscillating dipole moment induced in the sphere of volume V by the optical field $\mathscr{E}$.

We see from (3.1) that the anisotropy induced in the isotropic medium is independent of the opticostriction as given by (2.24).

We shall now discuss the anisotropy constant (3.2) quite generally for the case when the sphere of volume V contains $N_1, N_2, \dots N_i, \dots$ molecules of the first, second, $\dots$ and i-th species and its electric dipole moment is given by

$$M = \sum_i \sum_{p=1}^{N_i} m^{(pi)}, \tag{3.4}$$

where $m^{(pi)}$ is the total electric dipole moment of the p-th molecule of species i immersed in the sphere acted upon by the electric fields E and $\mathscr{E}$.

Analogously, we have for the oscillating electric dipole moment

$$\tilde{M} = \sum_j \sum_{q=1}^{N_j} \tilde{m}^{(qj)}. \tag{3.5}$$

On substituting (3.4) and (3.5) in the general eq. (3.2), we have the following expression for the anisotropy constant of a multi-component system:

$$B = \frac{\pi}{45V} \chi_{\alpha\beta\gamma\delta} \left\langle \sum_i \sum_{p=1}^{Ni} \frac{\partial^3 m_\alpha^{(pi)}}{\partial E_\beta \partial \mathscr{E}_\gamma \partial \mathscr{E}_\delta} + \mathscr{H} \sum_{ij} \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \left(m_\alpha^{(pi)} \frac{\partial^2 m_\beta^{(qj)}}{\partial \mathscr{E}_\gamma \partial \mathscr{E}_\delta} + \right.\right.$$

$$\left. + \frac{\partial^2 m_\alpha^{(pi)}}{\partial \mathscr{E}_\gamma \partial \mathscr{E}_\delta} m_\beta^{(qj)} + \frac{\partial m_\alpha^{(pi)}}{\partial E_\beta} \frac{\partial \tilde{m}_\gamma^{(qj)}}{\partial \mathscr{E}_\delta} \right) +$$

$$\left. + \mathscr{H}^2 \sum_{ijk} \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \sum_{r=1}^{N_k} m_\alpha^{(pi)} m_\beta^{(qj)} \frac{\partial \tilde{m}_\gamma^{(rk)}}{\partial \mathscr{E}_\delta} \right\rangle. \tag{3.6}$$

In general, the p-th molecule immersed in the medium is acted on by the effective electric fields $E + F^{(pi)}$ and $\mathscr{E} + \tilde{F}^{(pi)}$, where $F^{(pi)}$ and $\tilde{F}^{(pi)}$ are the molecular fields existing at the centre of the p-th molecule of species i and produced by the remaining molecules of the medium in the presence of the fields E and $\mathscr{E}$. On expanding the moment $m^{(pi)}$ in powers of these effective fields, we obtain for its α-component [7] [8]

$$m_\alpha^{(pi)} = \mu_\alpha^{(pi)} + \tfrac{1}{2}\beta_{\alpha\beta\gamma}^{(pi)}(\mathscr{E}_\beta + \tilde{F}_\beta^{(pi)})(\mathscr{E}_\gamma + \tilde{F}_\gamma^{(pi)}) + \cdots$$

$$+ \{\alpha_{\alpha\beta}^{(pi)} + \tfrac{1}{2}\gamma_{\alpha\beta\gamma\delta}^{(pi)}(\mathscr{E}_\gamma + \tilde{F}_\gamma^{(pi)})(\mathscr{E}_\delta + \tilde{F}_\delta^{(pi)}) + \dots\}(E_\beta + F_\beta^{(pi)}), \tag{3.7}$$

where $\mu_\alpha^{(pi)}$ denotes the α-component of the permanent electric dipole moment of the p-th molecule of species i and $\alpha_{\alpha\beta}^{(pi)}$ – the components of its electrical polarizability tensor. The tensors $\beta_{\alpha\beta\gamma}^{(pi)}$ and $\gamma_{\alpha\beta\gamma\delta}^{(pi)}$ account for the nonlinear

change in the electric dipole moment and polarizability of the p-th molecule of species i due to the strong optical field. These tensors can also be referred to as the second- and third-order polarizability tensors, respectively.

Similarly, we can expand the oscillating dipole moment $\tilde{m}^{(qj)}$ in powers of the optical effective field $\mathscr{E} + \tilde{F}^{(qj)}$,

$$\tilde{m}_\alpha^{(qj)} = a_{\alpha\beta}^{(qj)}(\mathscr{E}_\beta + \tilde{F}_\beta^{(qj)}) + \tfrac{1}{2}b_{\alpha\beta\gamma}^{(qj)}(\mathscr{E}_\beta + \tilde{F}_\beta^{(qj)})(\mathscr{E}_\gamma + \tilde{F}_\gamma^{(qj)}) + ..., \qquad (3.8)$$

where $a_{\alpha\beta}^{(qj)}$ is the optical polarizability tensor of the q-th molecule of species j and $b_{\alpha\beta\gamma}^{(qj)}$ is the tensor of its nonlinear or second-order polarizability due to the strong optical field.

The molecular fields appearing in the expansions (3.7) and (3.8) are defined in the dipole approximation as follows:

$$F_\alpha^{(pi)} = - \sum_j \sum_{\substack{q=1 \\ q \neq p}}^{N_j} T_{\alpha\beta}^{(pq)} m_\beta^{(qj)}, \qquad (3.9)$$

$$\tilde{F}_\alpha^{(pi)} = - \sum_j \sum_{\substack{q=1 \\ q \neq p}}^{N_j} T_{\alpha\beta}^{(pq)} \tilde{m}_\beta^{(qj)}, \qquad (3.10)$$

wherein the tensor

$$T_{\alpha\beta}^{(pq)} = -r_{pq}^{-5}(3r_{pq\alpha}r_{pq\beta} - r_{pq}^2\delta_{\alpha\beta}) \qquad (3.11)$$

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

From (3.7)–(3.10) we have in linear approximation in E and $\mathscr{E}$

$$F_\alpha^{(pi)} = F_{0\alpha}^{(pi)} - \sum_j \sum_{\substack{q=1 \\ q \neq p}}^{N_j} T_{\alpha\beta}^{(pq)} \alpha_{\beta\gamma}^{(qj)} E_\gamma +$$
$$+ \sum_{jk} \sum_{\substack{q=1 \\ q \neq p}}^{N_j} \sum_{\substack{r=1 \\ r \neq q}}^{N_k} T_{\alpha\beta}^{(pq)} \alpha_{\beta\gamma}^{(qj)} T_{\gamma\delta}^{(qr)} \alpha_{\delta\varepsilon}^{(rk)} E_\varepsilon - ..., \qquad (3.12)$$

$$\tilde{F}_\alpha^{(pi)} = -\sum_j \sum_{\substack{q=1 \\ q \neq p}}^{N_j} T_{\alpha\beta}^{(pq)} a_{\beta\gamma}^{(qj)} \mathscr{E}_\gamma + \sum_{jk} \sum_{\substack{q=1 \\ q \neq p}}^{N_j} \sum_{\substack{r=1 \\ r \neq q}}^{N_k} T_{\alpha\beta}^{(pq)} a_{\beta\gamma}^{(qj)} T_{\gamma\delta}^{(qr)} a_{\delta\varepsilon}^{(rk)} \mathscr{E}_\varepsilon - ..., \qquad (3.13)$$

wherein in (3.12)

$$F_{0\alpha}^{(pi)} = - \sum_j \sum_{\substack{q=1 \\ q \neq p}}^{N_j} T_{\alpha\beta}^{(pq)} \mu_\beta^{(qj)} + \sum_{jk} \sum_{\substack{q=1 \\ q \neq p}}^{N_j} \sum_{\substack{r=1 \\ r \neq q}}^{N_k} T_{\alpha\beta}^{(pq)} \alpha_{\beta\gamma}^{(qj)} T_{\gamma\delta}^{(qr)} \mu_\delta^{(rk)} - ... \qquad (3.14)$$

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

In the case now under consideration, the configurational variables τ of the system form a set of variables $\tau^N = \tau^{N_1}\tau^{N_2} ... \tau^{N_i}, ...$ describing the configuration of all $N = \sum_i N_i$ molecules present therein. For convenience we introduce the probability $P^{(n)}(\tau^n)\, d\tau^n$ of finding a selected group of n

molecules in the elementary configurational volume $d\tau^n$ centered about the point τ^n, independently of the configurations of the remaining $(N - n)$ molecules of the system. Since the probability densities $P^{(n)}$ are of the form

$$P^{(n)}(\tau^n) = \frac{\int \ldots \int\limits_{(N-n)} \exp\{-\mathcal{H}U(\tau^N)\}\, d\tau^{N-n}}{\int \ldots \int\limits_{(N)} \exp\{-\mathcal{H}U(\tau^N)\}\, d\tau^N} \tag{3.15}$$

the statistical average operation denoted by the brackets $\langle\ \rangle$ in eq. (3.2) or (3.6) can now be defined thus:

$$\langle \Phi \rangle = \int \ldots \int\limits_{(n)} \Phi(\tau^N)\, P^{(n)}(\tau^n)\, d\tau^n. \tag{3.16}$$

Since the probabilities of (3.15) are related with the correlation functions $g^{(n)}$ of the n molecules as follows[9]:

$$\rho^n g^{(n)}(\tau^n) = \frac{N!}{(N-n)!}\, P^{(n)}(\tau^n), \tag{3.17}$$

we have in the case of multi-component systems

$$\rho x_i g_i^{(1)}(\tau_p) = N_i P_i^{(1)}(\tau_p),$$

$$\rho^2 x_i x_j g_{ij}^{(2)}(\tau_p, \tau_q) = N_i(N_j - \delta_{ij})\, P_{ij}^{(2)}(\tau_p, \tau_q), \tag{3.18}$$

$$\rho^3 x_i x_j x_k g_{ijk}^{(3)}(\tau_p, \tau_q, \tau_r) = N_i(N_j - \delta_{ij})(N_k - \delta_{ik} - \delta_{jk})\, P_{ijk}^{(3)}(\tau_p, \tau_q, \tau_r), \ldots,$$

where $\rho = N/V$ is the mean number density of molecules of the medium and $x_i = N_i/N$ is the mole fraction of the i-th component of the system. In the foregoing expression $g_i^{(1)}(\tau_p)$ is the ordinary correlation function for single molecules p of species i, $g_{ij}^{(2)}(\tau_p, \tau_q)$ is the binary correlation function for pairs of molecules p and q of species i and j, and $g_{ijk}^{(3)}(\tau_p, \tau_q, \tau_r)$ is the ternary correlation function for triples of molecules p, q and r of species i, j and k, respectively.

Neglecting in the first step the effect of molecular fields we obtain from (3.6) by expansions (3.7) and (3.8):

$$B = \frac{\pi}{45V}\, \chi_{\alpha\beta\gamma\delta} \Big\langle \sum_i \sum_{p=1}^{N_i} \gamma_{\alpha\beta\gamma\delta}^{(pi)} + \mathcal{H} \sum_{ij} \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} (\mu_\alpha^{(pi)} \beta_{\beta\gamma\delta}^{(qj)} +$$

$$+ \beta_{\alpha\gamma\delta}^{(pi)} \mu_\beta^{(qj)} + \alpha_{\alpha\beta}^{(pi)} a_{\gamma\delta}^{(qj)}) + \mathcal{H}^2 \sum_{ijk} \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \sum_{r=1}^{N_k} \mu_\alpha^{(pi)} \mu_\beta^{(qj)} a_{\gamma\delta}^{(rk)} \Big\rangle. \tag{3.19}$$

By (3.16) and (3.18), (3.19) can be expressed formally as follows:

$$B = \sum_i x_i B_i^{(1)} + \sum_{ij} x_i x_j B_{ij}^{(2)} + \sum_{ijk} x_i x_j x_k B_{ijk}^{(3)} + \ldots, \tag{3.20}$$

wherein

$$B_i^{(1)} = \frac{\pi\rho}{45V} \chi_{\alpha\beta\gamma\delta} \int \{\gamma_{\alpha\beta\gamma\delta}^{(pi)} + \mathscr{H}(\mu_\alpha^{(pi)}\beta_{\beta\gamma\delta}^{(pi)} + \beta_{\alpha\gamma\delta}^{(pi)}\mu_\beta^{(pi)} +$$

$$+ \alpha_{\alpha\beta}^{(pi)}a_{\gamma\delta}^{(pi)}) + \mathscr{H}^2\mu_\alpha^{(pi)}\mu_\beta^{(pi)}a_{\gamma\delta}^{(pi)}\} g_i^{(1)}(\boldsymbol{\tau}_p) \, \mathrm{d}\boldsymbol{\tau}_p, \qquad (3.21)$$

$$B_{ij}^{(2)} = \frac{\pi\rho^2}{45V} \mathscr{H}\chi_{\alpha\beta\gamma\delta} \int \int \{\mu_\alpha^{(pi)}\beta_{\beta\gamma\delta}^{(qj)} + \beta_{\alpha\gamma\delta}^{(pi)}\mu_\beta^{(qj)} +$$

$$+ \alpha_{\alpha\beta}^{(pi)}a_{\gamma\delta}^{(qj)} + \mathscr{H}(\mu_\alpha^{(pi)}\mu_\beta^{(pi)}a_{\gamma\delta}^{(qj)} + \mu_\alpha^{(pi)}\mu_\beta^{(qj)}a_{\gamma\delta}^{(pi)} +$$

$$+ \mu_\alpha^{(pi)}\mu_\beta^{(qj)}a_{\gamma\delta}^{(qj)})\} g_{ij}^{(2)}(\boldsymbol{\tau}_p, \boldsymbol{\tau}_q) \, \mathrm{d}\boldsymbol{\tau}_p \, \mathrm{d}\boldsymbol{\tau}_q, \qquad (3.22)$$

$$B_{ijk}^{(3)} = \frac{\pi\rho^3}{45V} \mathscr{H}^2\chi_{\alpha\beta\gamma\delta} \int \int \int \mu_\alpha^{(pi)}\mu_\beta^{(qj)}a_{\gamma\delta}^{(rk)} g_{ijk}^{(3)}(\boldsymbol{\tau}_p, \boldsymbol{\tau}_q, \boldsymbol{\tau}_r) \, \mathrm{d}\boldsymbol{\tau}_p \, \mathrm{d}\boldsymbol{\tau}_q \, \mathrm{d}\boldsymbol{\tau}_r. \quad (3.23)$$

In general, the configurational variables $\boldsymbol{\tau}_p$ comprise the variables $\boldsymbol{r}_p$ and $\boldsymbol{\omega}_p$ determining the position and orientation of the p-th molecule, respectively. Thus, the integral

$$\int \mathrm{d}\boldsymbol{\tau}_p = \int_V \mathrm{d}\boldsymbol{r}_p \int_\Omega \mathrm{d}\boldsymbol{\omega}_p = V\Omega$$

extends over all possible configurations of the p-th molecule.

In particular, if the system presents no interaction between the molecules, the correlation functions (3.18) reduce to

$$\Omega g_i^{(1)}(\boldsymbol{\tau}_p) = \Omega^2 g_{ij}^{(2)}(\boldsymbol{\tau}_p, \boldsymbol{\tau}_q) = \Omega^3 g_{ijk}^{(3)}(\boldsymbol{\tau}_p, \boldsymbol{\tau}_q, \boldsymbol{\tau}_r) = \dots = 1. \qquad (3.24)$$

It is readily verified that this condition always implies the vanishing of the constants $B_{ij}^{(2)}$ and $B_{ijk}^{(3)}$ as given by eqs. (3.22) and (3.23), so that (3.20) reduces to

$$B = \sum_i x_i B_i^{(1)}, \qquad (3.25)$$

where (3.21) can now be expressed as follows:

$$B_i^{(1)} = \frac{2\pi\rho}{45} \{3\gamma_{\alpha\beta\alpha\beta}^{(i)} - \gamma_{\alpha\alpha\beta\beta}^{(i)} + 2\mathscr{H}(3\mu_\alpha^{(i)}\beta_{\beta\alpha\beta}^{(i)} - \mu_\alpha^{(i)}\beta_{\alpha\beta\beta}^{(i)}) +$$

$$+ \mathscr{H}(3\alpha_{\alpha\beta}^{(i)}a_{\alpha\beta}^{(i)} - \alpha_{\alpha\alpha}^{(i)}a_{\beta\beta}^{(i)}) + \mathscr{H}^2(3\mu_\alpha^{(i)}\mu_\beta^{(i)}a_{\alpha\beta}^{(i)} - \mu_\alpha^{(i)}\mu_\alpha^{(i)}a_{\beta\beta}^{(i)})\}. \quad (3.26)$$

Here we have assumed for simplicity that the tensors $\alpha_{\alpha\beta}$ and $a_{\alpha\beta}$ are symmetric in the suffixes α and β, the tensor $\beta_{\alpha\beta\gamma}$ is symmetric in the suffixes β and γ and the tensor $\gamma_{\alpha\beta\gamma\delta}$ – in the separate pairs of α, β and γ, δ (this assumption is satisfied strictly in the case of optically inactive substances and throughout spectral ranges widely remote from those in which absorption appears).

Since $B_i^{(1)}$ as given by (3.26) does not depend on the concentration of the system, eq. (3.25) expresses the additivity of B. Hence B is seen to be a strictly additive quantity only in the case of a mixture of ideal components,

i.e. only if molecular interaction is absent. On dropping the index i, eq. (3.26) becomes analogous to the one derived previously[3]) for systems of molecules of one species.

Dense multi-component systems such as mixtures of real gases, or liquid mixtures, exhibit a deviation from additivity determined in the expansion of (3.20) by terms in the second or third power of the molar fractions. The coefficients $B_{ij}^{(2)}$ and $B_{ijk}^{(3)}$ of these terms depend respectively on the two-molecule and three-molecule correlation functions and in the absence of molecular fields in the system are given by the expressions (3.22) and (3.23).

§ 4. *Application of the theory to special cases.* The expressions (3.19)–(3.26) hold for systems of molecules of arbitrary symmetry and we shall discuss them for certain types of molecular symmetry.

Let us begin by considering systems of molecules possessing a centre of inversion, for which all elements of the tensors μ_α and $\beta_{\alpha\beta\gamma}$ vanish and the expressions (3.21)–(3.26) yield:

$$B_i^{(1)} = \frac{2\pi\rho}{45} \{3\gamma_{\alpha\beta\alpha\beta}^{(i)} - \gamma_{\alpha\alpha\beta\beta}^{(i)} + \mathscr{H}(3\alpha_{\alpha\beta}^{(i)}a_{\alpha\beta}^{(i)} - \alpha_{\alpha\alpha}^{(i)}a_{\beta\beta}^{(i)})\}, \qquad (4.1)$$

$$B_{ij}^{(2)} = \frac{\pi\rho^2}{90V} \mathscr{H}\chi_{\alpha\beta\gamma\delta} \int \int \{\alpha_{\alpha\beta}^{(pi)}a_{\gamma\delta}^{(qj)} + \alpha_{\alpha\beta}^{(qj)}a_{\gamma\delta}^{(pi)}\} g_{ij}^{(2)}(\tau_p, \tau_q) \, \mathrm{d}\tau_p \, \mathrm{d}\tau_q. \qquad (4.2)$$

The first term in (4.1), $3\gamma_{\alpha\beta\alpha\beta}^{(i)} - \gamma_{\alpha\alpha\beta\beta}^{(i)}$, accounts for the temperature-independent effect of optical nonlinear deformation of the molecules due to the strong optical field, whereas the second temperature-dependent term $\mathscr{H}(3\alpha_{\alpha\beta}^{(i)}a_{\alpha\beta}^{(i)} - \alpha_{\alpha\alpha}^{(i)}a_{\beta\beta}^{(i)})$ – for the effect of optical molecular orientation in substances presenting no molecular interactions. The constant (4.2) determines the influence of molecular correlations on the effect of optical molecular orientation.

For molecules possessing the symmetry of the point groups C_{6h} and D_{6h}, as well as $D_{\infty h}$, the expressions (4.1) and (4.2) yield the result:

$$B_i^{(1)} = \frac{2\pi\rho}{45} \{7\gamma_{1111}^{(i)} - 5\gamma_{1122}^{(i)} - 2\gamma_{1133}^{(i)} - 2\gamma_{3311}^{(i)} + 12\gamma_{1313}^{(i)} +$$
$$+ 2\gamma_{3333}^{(i)} + 18\mathscr{H}\alpha_i\kappa_{\alpha i}a_i\kappa_{ai}\}, \qquad (4.3)$$

$$B_{ij}^{(2)} = \frac{2\pi}{5} \rho\mathscr{H}(\alpha_i\kappa_{\alpha i}a_j\kappa_{aj} + a_i\kappa_{ai}\alpha_j\kappa_{\alpha j}) \mathscr{J}_{ij}^{(2)}, \qquad (4.4)$$

where the quantities

$$\kappa_{\alpha i} = \frac{\alpha_{33}^{(i)} - \alpha_{11}^{(i)}}{\alpha_{33}^{(i)} + 2\alpha_{11}^{(i)}}, \quad \kappa_{ai} = \frac{a_{33}^{(i)} - a_{11}^{(i)}}{a_{33}^{(i)} + 2a_{11}^{(i)}} \qquad (4.5)$$

determine the anisotropies of the electrical and optical polarizabilities of the isolated molecule of species i.

In (4.4), the following integral parameter is introduced:

$$\mathscr{J}_{ij}^{(2)} = \frac{\rho}{2V} \int \int (3\cos^2\theta_{pq} - 1)\, g_{ij}^{(2)}(\boldsymbol{\tau}_p, \boldsymbol{\tau}_q)\, \mathrm{d}\boldsymbol{\tau}_p\, \mathrm{d}\boldsymbol{\tau}_q \qquad (4.6)$$

accounting for the angular correlations between molecules p and q, whose axes of symmetry form the angle θ_{pq}.

In the case of spherical symmetry, we have to put $\kappa_\alpha = \kappa_a = 0$ and $\gamma_{1111} = \gamma_{3333}$, $2\gamma_{1313} = \gamma_{3333} - \gamma_{1133}$, $\gamma_{1122} = \gamma_{1133} = \gamma_{3311}$ in equations (4.3) and (4.4), which now reduce to[3]

$$B_i^{(1)} = \frac{2\pi}{3}\,\rho(\gamma_{3333}^{(i)} - \gamma_{1133}^{(i)}), \quad B_{ij}^{(2)} = 0. \qquad (4.7)$$

Hence we find that electric anisotropy can also arise in a medium consisting of atoms or spherical molecules as a result of the non-linear anisotropy induced in them by the square of a strong optical field. Moreover, as it was to be expected, in substances of isotropically polarizable molecules the effect of optical molecular orientation does not appear.

In the case of molecules without a centre of inversion, not all elements of the tensors μ_α and $\beta_{\alpha\beta\gamma}$ vanish and the full expressions of (3.19)–(3.23) must be taken into account. For simplicity, we apply these expressions to the particularly interesting case of axially-symmetric dipolar molecules for which we obtain

$$B_i^{(1)} = \frac{4\pi\rho}{45}\,\{5\gamma_i + 6\mathscr{H}\beta_{i\kappa\beta i}\mu_i + 3\mathscr{H}a_{i\kappa a i}(3\alpha_{i\kappa\alpha i} + \mathscr{H}\mu_i^2)\}, \qquad (4.8)$$

$$B_{ij}^{(2)} = \frac{2\pi\rho}{15}\,\mathscr{H}\{2[\beta_{i\kappa\beta i}\mu_j + \mu_i\beta_{j\kappa\beta j} + \mathscr{H}\mu_i\mu_j(a_{i\kappa a i} + a_{j\kappa a j})]\,\mathscr{J}_{ij}^{(1)} +$$

$$+ [(3\alpha_{i\kappa\alpha i} + \mathscr{H}\mu_i^2)\,a_{j\kappa a j} + a_{i\kappa a i}(3\alpha_{j\kappa\alpha j} + \mathscr{H}\mu_j^2)]\,\mathscr{J}_{ij}^{(2)}\}, \quad (4.9)$$

$$B_{ijk}^{(3)} = \frac{4\pi}{15}\,\rho\mathscr{H}^2\mu_i\mu_j a_{k\kappa a k}\,\mathscr{J}_{ijk}^{(3)}, \qquad (4.10)$$

where besides the parameter $\mathscr{J}_{ij}^{(2)}$ given by (4.6) we have the two additional parameters

$$\mathscr{J}_{ij}^{(1)} = \frac{\rho}{V} \int \int \cos\theta_{pq} g_{ij}^{(2)}(\boldsymbol{\tau}_p, \boldsymbol{\tau}_q)\, \mathrm{d}\boldsymbol{\tau}_p\, \mathrm{d}\boldsymbol{\tau}_q, \qquad (4.11)$$

$$\mathscr{J}_{ijk}^{(3)} = \frac{\rho^2}{2V} \int \int \int (3\cos\theta_{pr}\cos\theta_{qr} - \cos\theta_{pq})\, g_{ijk}^{(3)}(\boldsymbol{\tau}_p, \boldsymbol{\tau}_q, \boldsymbol{\tau}_r)\, \mathrm{d}\boldsymbol{\tau}_p\, \mathrm{d}\boldsymbol{\tau}_q\, \mathrm{d}\boldsymbol{\tau}_r, \tag{4.12}$$

which describe the angular correlations between axially-symmetric dipolar molecules.

Let us now consider the situation when the molecular electric fields existing in the medium are so strong that the dipole moments of molecules undergo a change and become dependent on the intermolecular distances. At first we shall restrict the problem to the case of isotropically and linearly polarizable molecules, for which we have from the general equation (3.6) with regard to the linear terms of expansion (3.7) and (3.8)

$$B = \frac{2\pi\mathscr{H}}{45V} \left\{ \left\langle \sum_{ij} \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \alpha_{pi} a_{qj} \left(3 \frac{\partial F_\alpha^{(pi)}}{\partial E_\beta} \frac{\partial \tilde{F}_\alpha^{(qj)}}{\partial \mathscr{E}_\beta} - \frac{\partial F_\alpha^{(pi)}}{\partial E_\alpha} \frac{\partial \tilde{F}_\beta^{(qj)}}{\partial \mathscr{E}_\beta} \right) \right\rangle + \right.$$

$$\left. + \mathscr{H} \left\langle \sum_{ijk} \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \sum_{r=1}^{N_k} \alpha_{pi}\alpha_{qj}a_{rk} \left(3 F_{0\alpha}^{(pi)}F_{0\beta}^{(qj)} \frac{\partial \tilde{F}_\alpha^{(rk)}}{\partial \mathscr{E}_\beta} - F_{0\alpha}^{(pi)}F_{0\alpha}^{(qj)} \frac{\partial \tilde{F}_\beta^{(rk)}}{\partial \mathscr{E}_\beta} \right) \right\rangle \right\}, \quad (4.13)$$

where α_{pi} and a_{pi} are the electric and optical isotropic polarizabilities of molecule p of species i. In this case we have by (3.12) and (3.13)

$$\frac{\partial F_\alpha^{(pi)}}{\partial E_\beta} = - \sum_j \sum_{\substack{q=1 \\ q\neq p}}^{N_j} \alpha_{qj} T_{\alpha\beta}^{(pq)} + \sum_{ij} \sum_{\substack{q=1 \\ q\neq p}}^{N_j} \sum_{\substack{r=1 \\ r\neq q}}^{N_k} \alpha_{qj}\alpha_{rk} T_{\alpha\gamma}^{(pq)}T_{\gamma\beta}^{(qr)} - \dots, \quad (4.14)$$

$$\frac{\partial \tilde{F}_\alpha^{(pi)}}{\partial \mathscr{E}_\beta} = - \sum_j \sum_{\substack{q=1 \\ q\neq p}}^{N_j} a_{qj} T_{\alpha\beta}^{(pq)} + \sum_{ij} \sum_{\substack{q=1 \\ q\neq p}}^{N_j} \sum_{\substack{r=1 \\ r\neq q}}^{N_k} a_{qj}a_{rk} T_{\alpha\gamma}^{(pq)}T_{\gamma\beta}^{(qr)} - \dots \quad (4.15)$$

Using the fact that for atoms in the absence of London dispersional forces $F_{0\alpha}^{(pi)} = 0$ and (4.13) yields by (4.14) and (4.15) with the accuracy of $\alpha^2 a^2$:

$$B = -\frac{2\pi\mathscr{H}}{15V} \sum_{ijkl} \left\langle \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \sum_{\substack{r=1 \\ r\neq p}}^{N_k} \sum_{\substack{s=1 \\ s\neq q}}^{N_l} \alpha_{pi}a_{qj}\alpha_{rk}a_{sl} T_{\alpha\beta}^{(pr)}T_{\alpha\beta}^{(qs)} \right\rangle. \quad (4.16)$$

Our subsequent calculations will be restricted to terms which, ultimately, can be expressed by means of bi-molecular correlation functions, and (4.16) leads to the simple result

$$B = \sum_{ij} x_i x_j B_{ij}^{(2)}, \quad (4.17)$$

where

$$B_{ij}^{(2)} = \frac{2\pi}{5} \rho\mathscr{H} (\alpha_i a_j + a_i\alpha_j)^2 R_{ij}^{(6)} \quad (4.18)$$

with the integral parameter for $n = 6$

$$R_{ij}^{(n)} = \frac{\rho}{V} \int \int r_{pq}^{-n} g_{ij}^{(2)}(\mathbf{r}_p, \mathbf{r}_q) \, d\mathbf{r}_p \, d\mathbf{r}_q \quad (4.19)$$

describing the radial correlations of atoms (or spherical molecules).

The result of eqs. (4.13) or its special case of (4.16) or (4.18) signifies that, even in fluids consisting of linearly and isotropically polarizable molecules,

owing to interaction between induced dipolar moments, anisotropy of the molecular orientational kind can appear in the medium.

We will now discuss the second term in (4.13) depending on $\mathscr{H}^2$, which is nonzero when the system consists of isotropically polarizable molecules having permanent dipole, quadrupole, octopole, etc. moments. Namely, by (4.15) we obtain from (4.13) in the approximation of pairwise correlations again (4.17) with a new contribution to (4.18)

$$F_0 B_{ij}^{(2)} = -\frac{2\pi\mathscr{H}^2}{15V} \Big\langle \sum_{p=1}^{N_i} \sum_{\substack{q=1 \\ q \neq p}}^{N_j} a_{pi} a_{qj} \{ \alpha_{pi}^2 F_{0\alpha}^{(pi)}(qj) F_{0\beta}^{(pi)}(qj) +$$
$$+ \alpha_{qj}^2 F_{0\alpha}^{(qj)}(pi) F_{0\beta}^{(qj)}(pi) \} T_{\alpha\beta}^{(pq)} \Big\rangle, \qquad (4.20)$$

where $F_0^{(pi)}(qj)$ is the electric field at the centre of the p-th molecule of species i due to the permanent electric moments of the q-th molecule of species j and in general is given by [10]

$$F_{0\alpha}^{(pi)}(qj) = -T_{\alpha\beta}^{(pq)} \mu_\beta^{(qj)} + \tfrac{1}{3} T_{\alpha\beta\gamma}^{(pq)} \Theta_{\beta\gamma}^{(qj)} - \frac{1}{15} T_{\alpha\beta\gamma\delta}^{(pq)} \Omega_{\beta\gamma\delta}^{(qj)} + \dots \qquad (4.21)$$

Here, the tensors of the dipole, quadrupole, octopole etc. moments of a molecule are defined, respectively, as

$$\mu_\alpha = \sum_\nu e_\nu r_\nu_\alpha, \qquad (4.22)$$

$$\Theta_{\alpha\beta} = \tfrac{1}{2} \sum_\nu e_\nu (3r_{\nu\alpha} r_{\nu\beta} - r_\nu^2 \delta_{\alpha\beta}), \qquad (4.23)$$

$$\Omega_{\alpha\beta\gamma} = \tfrac{1}{2} \sum_\nu e_\nu \{ 5r_{\nu\alpha} r_{\nu\beta} r_{\nu\gamma} - r_\nu^2 (r_{\nu\alpha} \delta_{\beta\gamma} + r_{\nu\beta} \delta_{\gamma\alpha} + r_{\nu\gamma} \delta_{\alpha\beta}) \}, \qquad (4.24)$$

where e_ν is the ν-th electric charge of a molecule and $\mathbf{r}_\nu$ its radius vector. The tensor of dipole-dipole interaction is given by (3.11), whereas the tensors of dipole-quadrupole and dipole-octopole interactions as

$$T_{\alpha\beta\gamma}^{(pq)} = 3r_{pq}^{-7} \{ 5r_{pq\alpha} r_{pq\beta} r_{pq\gamma} - r_{pq}^2 (r_{pq\alpha} \delta_{\beta\gamma} + r_{pq\beta} \delta_{\gamma\alpha} + r_{pq\gamma} \delta_{\alpha\beta}) \}, \qquad (4.25)$$

$$T_{\alpha\beta\gamma\delta}^{(pq)} = -3r_{pq}^{-9} \{ 35r_{pq\alpha} r_{pq\beta} r_{pq\gamma} r_{pq\delta} - 5r_{pq}^2 (r_{pq\alpha} r_{pq\beta} \delta_{\gamma\delta} +$$
$$+ r_{pq\alpha} r_{pq\gamma} \delta_{\beta\delta} + r_{pq\alpha} r_{pq\delta} \delta_{\gamma\beta} + r_{pq\beta} r_{pq\gamma} \delta_{\alpha\delta} + r_{pq\beta} r_{pq\delta} \delta_{\alpha\gamma} +$$
$$+ r_{pq\gamma} r_{pq\delta} \delta_{\alpha\beta}) + r_{pq}^4 (\delta_{\alpha\beta} \delta_{\gamma\delta} + \delta_{\alpha\gamma} \delta_{\beta\delta} + \delta_{\alpha\delta} \delta_{\beta\gamma}) \}. \qquad (4.26)$$

Taking the square of the field (4.21) and performing unweighted averaging over all orientations of the molecules, we obtain

$$\overline{F_{0\alpha}^{(pi)} F_{0\beta}^{(pi)}} = \tfrac{1}{3} \mu_{qj}^2 T_{\alpha\gamma}^{(pq)} T_{\beta\gamma}^{(pq)} + \tfrac{1}{45} T_{\alpha\gamma\delta}^{(pq)} T_{\beta\gamma\delta}^{(pq)} \Theta_{\varepsilon\eta}^{(qj)} \Theta_{\varepsilon\eta}^{(qj)} +$$
$$+ \tfrac{1}{4725} T_{\alpha\gamma\delta\varepsilon}^{(pq)} T_{\beta\gamma\delta\varepsilon}^{(pq)} \Omega_{\eta\lambda\mu}^{(qj)} \Omega_{\eta\lambda\mu}^{(qj)} + \dots \qquad (4.28)$$

and finally:

$$\overline{F_{0\alpha}^{(pi)} F_{0\beta}^{(pi)}} T_{\alpha\beta}^{(pq)} = -2\mu_{qj}^2 r_{pq}^{-9} - \tfrac{8}{5} \Theta_{\alpha\beta}^{(qj)} \Theta_{\alpha\beta}^{(qj)} r_{pq}^{-11} - \tfrac{8}{21} \Omega_{\alpha\beta\gamma}^{(qj)} \Omega_{\alpha\beta\gamma}^{(qj)} r_{pq}^{-13} - \dots \qquad (4.29)$$

By (4.29), we obtain immediately from (4.20) for dipolar molecules

$$\mu B_{ij}^{(2)} = \frac{4\pi\rho}{15} \, \mathscr{H}^2 a_i a_j (\alpha_i^2 \mu_j^2 + \mu_i^2 \alpha_j^2) \, R_{ij}^{(9)}, \tag{4.30}$$

for quadrupolar molecules with axial symmetry

$$_\Theta B_{ij}^{(2)} = \frac{8\pi\rho}{25} \, \mathscr{H}^2 a_i a_j (\alpha_i^2 \Theta_j^2 + \Theta_i^2 \alpha_j^2) \, R_{ij}^{(11)}, \tag{4.31}$$

and finally, for octopolar molecules possessing the tetrahedral symmetry

$$_\Omega B_{ij}^{(2)} = \frac{32\pi\rho}{105} \, \mathscr{H}^2 a_i a_j (\alpha_i^2 \Omega_j^2 + \Omega_i^2 \alpha_j^2) \, R_{ij}^{(13)}, \tag{4.32}$$

where the radial correlations parameters $R_{ij}^{(9)}$, $R_{ij}^{(11)}$ and $R_{ij}^{(13)}$ are given by (4.19) for $n = 9$, $n = 11$, and $n = 13$, respectively.

§ 5. *Correlation parameters for compressed gas mixtures.* The pair angular correlation parameters given by (4.6) and (4.11) will now be applied to not excessively compressed gas mixtures i.e. to ones admitting of a binary correlation function $g_{ij}^{(2)}$ in the form[9]

$$\Omega^2 g_{ij}^{(2)}(\boldsymbol{\tau}_p, \boldsymbol{\tau}_q) = \exp\{-\mathscr{H} u_{ij}(\boldsymbol{\tau}_p, \boldsymbol{\tau}_q)\}\{1 + O(\rho)\}, \tag{5.1}$$

where $u_{ij}(\boldsymbol{\tau}_p, \boldsymbol{\tau}_q)$ is the total potential energy of interactions between molecules p and q of species i and j.

Obviously, in the special case of noninteracting molecules, when (3.24) holds, all angular correlation parameters vanish.

In many cases it is convenient to resolve the total potential energy $u_{ij}(\boldsymbol{\tau}_p, \boldsymbol{\tau}_q)$, which in general is a function of the position $\boldsymbol{r}_p$, $\boldsymbol{r}_q$ and orientation $\boldsymbol{\omega}_p$, $\boldsymbol{\omega}_q$ of the molecules, into a term $u_{ij}(\boldsymbol{r}_{pq})$ due to interaction of the central type and dependent only on the distance $\boldsymbol{r}_{pq}$ between two molecules p and q, and one $v_{ij}(\boldsymbol{r}_{pq}, \boldsymbol{\omega}_p, \boldsymbol{\omega}_q)$ due to interactions of noncentral type and depending both on $\boldsymbol{r}_{pq}$ and the orientational variables $\boldsymbol{\omega}_p$ and $\boldsymbol{\omega}_q$. Strictly, the latter, v_{ij}, is the potential energy of interaction between permanent or induced electric multipoles of molecules that cannot be dealt with as rigid spheres. Obviously, such interaction will in general be of a tensorial nature, leading to a mathematically highly involved form of the energy. E.g. the potential energy due to electrostatic interaction between permanent moments of two molecules is to within the dipole-octopole interaction[10]:

$$v_{ij}(\boldsymbol{r}_{pq}, \boldsymbol{\omega}_p, \boldsymbol{\omega}_q)_{\text{el}} = \mu_\alpha^{(pi)} T_{\alpha\beta}^{(pq)} \mu_\beta^{(qj)} - \tfrac{1}{3}(\mu_\alpha^{(pi)}\Theta_{\beta\gamma}^{(qj)} - \Theta_{\alpha\beta}^{(pi)}\mu_\gamma^{(qj)}) \, T_{\alpha\beta\gamma}^{(pq)} +$$

$$+ \tfrac{1}{45}(3\mu_\alpha^{(pi)}\Omega_{\beta\gamma\delta}^{(qj)} - 5\Theta_{\alpha\beta}^{(pi)}\Theta_{\gamma\delta}^{(qj)} + 3\Omega_{\alpha\beta\gamma}^{(pi)}\mu_\delta^{(qj)}) \, T_{\alpha\beta\gamma\delta}^{(pq)} - \ldots \tag{5.2}$$

Still more highly complicated expressions result for the case of the potential energy due to molecular interaction of the inductional type; to

within the induced dipolar approximation, the latter amounts to

$$v_{ij}(\boldsymbol{r}_{pq}, \boldsymbol{\omega}_p, \boldsymbol{\omega}_q)_{\text{ind}} = -\tfrac{1}{2}\{\alpha_{\alpha\beta}^{(pi)}F_{0\alpha}^{(pi)}F_{0\beta}^{(pi)} + \alpha_{\alpha\beta}^{(qj)}F_{0\alpha}^{(qj)}F_{0\beta}^{(qj)}\}, \qquad (5.3)$$

wherein the electric molecular field is given by (4.21).

Naturally, in these circumstances there can be no question of calculating the parameters (4.6) and (4.11) with (5.1) strictly, and we have to recur to approximations. Satisfactory success is achieved by treating the noncentral part of v_{ij} as a small perturbation to the central energy $u_{ij}(\boldsymbol{r}_{pq})$, as this allows to replace the exact expression (5.1) by the following approximation:

$$\Omega^2 g_{ij}^{(2)}(\boldsymbol{\tau}_p, \boldsymbol{\tau}_q) = g_{ij}^{(2)}(\boldsymbol{r}_p, \boldsymbol{r}_q) \sum_{n=0}^{\infty} \frac{(-\mathscr{H})^n}{n!} \{v_{ij}(\boldsymbol{r}_{pq}, \boldsymbol{\omega}_p, \boldsymbol{\omega}_q)\}^n. \qquad (5.4)$$

a) Anisotropic nonpolar molecules. We shall take into account axially-symmetric nonpolar molecules interacting with anisotropic-dispersive forces leading to the potential energy in the form[10])

$$v_{ij}(\boldsymbol{r}_{pq}, \boldsymbol{\omega}_p, \boldsymbol{\omega}_q)_{\text{disp}} = \frac{3}{4}\frac{h\nu_i h\nu_j}{h\nu_i + h\nu_j}\,\alpha_i\alpha_j\{\kappa_{\alpha i} + \kappa_{\alpha j} - 3\kappa_{\alpha i}(1 - \kappa_{\alpha j})\cos^2\theta_p -$$

$$- 3\kappa_{\alpha j}(1 - \kappa_{\alpha i})\cos^2\theta_q - 3\kappa_{\alpha i}\kappa_{\alpha j}(3\cos\theta_p\cos\theta_q - \cos\theta_{pq})^2\}\,r_{pq}^{-6}, \qquad (5.5)$$

where $h\nu_i$ and $h\nu_j$ are characteristic energies of two interacting molecules of species i and j.

In this case, by (5.4) and (5.5) the parameter (4.11) vanishes, whereas (4.6) is given by

$$_{\text{disp}}\mathscr{J}_{ij}^{(2)} = \frac{3\mathscr{H}}{50}\frac{h\nu_i h\nu_j}{h\nu_i + h\nu_j}\,\alpha_i\kappa_{\alpha i}\alpha_j\kappa_{\alpha j}\left\{R_{ij}^{(6)} +\right.$$

$$\left. + \frac{3\mathscr{H}}{98}\frac{h\nu_i h\nu_j}{h\nu_i + h\nu_j}[49 - 14(\kappa_{\alpha i} + \kappa_{\alpha j}) + 38\kappa_{\alpha i}\kappa_{\alpha j}]R_{ij}^{(12)} + ...\right\}. \qquad (5.6)$$

b) Anisotropic dipolar molecules. The noncentral potential energy of mutual interaction of two dipolar molecules is [10])

$$v_{ij}(\boldsymbol{r}_{pq}, \boldsymbol{\omega}_p, \boldsymbol{\omega}_q) = -\mu_i\mu_j(3\cos\theta_p\cos\theta_q - \cos\theta_{pq})\,r_{pq}^{-3} -$$

$$- \tfrac{1}{2}\{\alpha_i(1 - \kappa_{\alpha i})\mu_j^2(3\cos^2\theta_q + 1) + \alpha_j(1 - \kappa_{\alpha j})\mu_i^2(3\cos^2\theta_p + 1) +$$

$$+ 3(\alpha_i\kappa_{\alpha i}\mu_j^2 + \mu_i^2\alpha_j\kappa_{\alpha j})(3\cos\theta_p\cos\theta_q - \cos\theta_{pq})^2\}\,r_{pq}^{-6} - ..., \qquad (5.7)$$

and we obtain from (4.6), (4.11) and (5.4) on integration over all possible orientations of the molecules

$$\mathscr{J}_{ij}^{(1)} = \frac{2\mathscr{H}^3}{75}\,\mu_i^3\mu_j^3\left\{R_{ij}^{(9)} + \frac{8\mathscr{H}^2}{49}\,\mu_i^2\mu_j^2 R_{ij}^{(15)} + \frac{5\mathscr{H}^4}{441}\,\mu_i^4\mu_j^4 R_{ij}^{(21)} + ...\right\} +$$

$$+ \frac{4\mathscr{H}^2}{15}\,\mu_i\mu_j(\alpha_i\mu_j^2 + \mu_i^2\alpha_j)\left\{R_{ij}^{(9)} + \frac{12\mathscr{H}^2}{35}\,\mu_i^2\mu_j^2 R_{ij}^{(15)} + ...\right\}, \qquad (5.8)$$

$$\mathcal{J}_{ij}^{(2)} = \frac{\mathcal{H}^2}{75}\,\mu_i^2\mu_j^2\left\{R_{ij}^{(6)} + \frac{12\mathcal{H}^2}{49}\,\mu_i^2\mu_j^2 R_{ij}^{(12)} + \frac{13\mathcal{H}^4}{441}\,\mu_i^4\mu_j^4 R_{ij}^{(18)} + \dots\right\} +$$

$$+ \frac{\mathcal{H}}{25}\left\{(\alpha_i\kappa_{\alpha i}\mu_j^2 + \mu_i^2\alpha_j\kappa_{\alpha j})\,R_{ij}^{(6)} + \frac{4\mathcal{H}^2}{49}\,\mu_i^2\mu_j^2[\alpha_i(7 + 11\kappa_{\alpha i})\,\mu_j^2 + \right.$$

$$\left. + \mu_i^2\alpha_j(7 + 11\kappa_{\alpha j})]\,R_{ij}^{(12)} + \dots\right\}. \tag{5.9}$$

c) Anisotropic quadrupolar molecules. In the case of anisotropic molecules which, though not dipolar, possess a permanent quadrupole moment, we have[10]

$$v_{ij}(\boldsymbol{r}_{pq}, \omega_p, \omega_q) = \tfrac{3}{4}\Theta_i\Theta_j\{1 - 5(\cos^2\theta_p + 3\cos^2\theta_p\cos^2\theta_q + \cos^2\theta_q) +$$

$$+ 2(5\cos\theta_p\cos\theta_q - \cos\theta_{pq})^2\}r_{pq}^{-5} - \tfrac{9}{8}\{\alpha_i(1-\kappa_{\alpha i})\,\Theta_j^2(1 - 2\cos^2\theta_q + 5\cos^4\theta_q) +$$

$$+ \alpha_j(1 - \kappa_{\alpha j})\,\Theta_i^2(1 - 2\cos^2\theta_p + 5\cos^4\theta_p) + 3\alpha_i\kappa_{\alpha i}\Theta_j^2(5\cos\theta_p\cos^2\theta_q -$$

$$- 2\cos\theta_{pq}\cos\theta_q - \cos\theta_p)^2 + 3\alpha_j\kappa_{\alpha j}\Theta_i^2(5\cos^2\theta_p\cos\theta_q - 2\cos\theta_{pq}\cos\theta_p -$$

$$- \cos\theta_q)^2\}\,r_{pq}^{-8} - \dots, \tag{5.10}$$

and the parameter (4.11) vanishes, whereas (4.6) can be expressed as

$$\mathcal{J}_{ij}^{(2)} = \frac{\mathcal{H}}{35}\left\{3(\alpha_i\kappa_{\alpha i}\Theta_j^2 + \Theta_i^2\alpha_j\kappa_{\alpha j})\,R_{ij}^{(8)} + 4\mathcal{H}\Theta_i^2\Theta_j^2 R_{ij}^{(10)} - \right.$$

$$\left. - \frac{6\mathcal{H}}{7}\,\Theta_i\Theta_j[\alpha_i(7 + 2\kappa_{\alpha i})\,\Theta_j^2 + \Theta_i^2\alpha_j(7 + 2\kappa_{\alpha j})]\,R_{ij}^{(13)} + \dots\right\}. \tag{5.11}$$

In order to be able to test numerically the foregoing expressions for $\mathcal{J}_{ij}^{(1)}$ and $\mathcal{J}_{ij}^{(2)}$, we have to know the values of the radial parameters (4.19). To compute the latter, one has to assume some form of the central force potential appearing in the Boltzmann factor of the radial correlation

$$g_{ij}^{(2)}(\boldsymbol{r}_p, \boldsymbol{r}_q) = \exp\{-\mathcal{H}u_{ij}(\boldsymbol{r}_{pq})\}\{1 + O(\rho)\}. \tag{5.12}$$

With (5.12) and the Lennard-Jones method, we can express the radial parameters (4.19) in terms of the well-known central forces parameters and appropriate functions[11].

§ 6. *Conclusions.* As we have just seen, a theory of the nonlinear variations in electric permittivity due to a strong optical field can be derived in general by classical semimacroscopic methods. This nonlinear variation is composed of two parts, the one characterizing the isotropic properties of the medium, whereas the second, described by the constant B, accounts for the electrical anisotropy induced in the medium by the electric field of the intense light beam. We have derived a general equation for the anisotropy constant (eq. 3.2) which is discussed for multi-component systems consisting of atoms and molecules without or with permanent moments. From the statistical-

molecular discussion of the constant B it is clear that the electrical anisotropy induced in the isotropic medium can depend quite generally on a considerable number of factors of a microscopic nature. The part played by each of these can be said to be different, and is dependent in principle on the species and structure of the atoms or molecules and on the interaction between them.

The anisotropy constant B behaves additively in the case of a mixture of perfect gases only. Thus, investigations of the electro-optical anisotropy in the gaseous state is a source of valuable information concerning linear and nonlinear electric and optical properties of the isolated, like or unlike molecules. In particular, in the case of an atomic gas or of one consisting of isotropically polarizable molecules, electrical anisotropy is due to the temperature-independent nonlinear optical effect alone. If the molecules are anisotropic, besides the nonlinear deformation effect, an optical orientational effect exists, which depends directly on the temperature.

In dense multi-component systems (e.g. real mixtures or solutions of liquids) owing to intermolecular correlations, the anisotropy constant B fails to fulfil the condition of additivity. In the special case of axially symmetric dipolar molecules, the temperature-dependent terms of the constant B include the angular correlation parameters (4.6), (4.11) and (4.12). Identical correlation parameters appear in certain related phenomena, e.g. the parameter (4.6) in molecular light scattering[12]) and magnetic birefringence[7]), the parameter (4.11) in electric polarization[3)8]) and the parameter (4.12) in electric birefringence[8]). Consequently, investigation on the deviations of B from additivity can provide direct information on the nature of the intermolecular forces acting between the molecules of different components, and on the structure of the multi-component system considered. Obviously, a theory thus generally formulated is, in its explicit form, apt to present obstacles of a mathematical nature; this, however, is compensated by its wide range of applicability to various special cases, of which only some – and we might well say the simplest – have been discussed in some detail in this paper.

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