MOLECULAR THEORY OF LIGHT SCATTERING BY MULTI-COMPONENT SYSTEMS

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A molecular theory of light scattering by multi-component systems of optically anisotropic molecules is proposed. General expressions, accounting for the degree of depolarization D of the light scattered, for Rayleigh's ratio S, and for the turbidity h of the medium are derived. These expressions contain the molecular factors F_{is} and F_{anis} of isotropic and anisotropic light scattering, respectively, which are discussed with special reference to multi-component systems of: (*i*) anisotropic molecules with constant polarizability, (*ii*) dipolar molecules with hyperpolarizability, and (*iii*) non-dipolar molecules with quadrupole moments. Formulas are derived relating anisotropic light scattering and the optico-optical birefringence of the medium, and others relating isotropic light scattering to the divergence between the molecular refraction of the substance in the condensed and gaseous states. Applications to one-component systems are given.

1. *Introduction*

Proceeding from ideas of Lord Rayleigh (1899) and Smoluchowski (1908), Einstein (1910) developed a phenomenological theory of light scattering by homogeneous and non-homogeneous liquids consisting of optically isotropic molecules.

According to the Einstein-Smoluchowski theory, light scattering in solutions of liquids is due to local fluctuations of the density and fluctuations of the concentration of the solution. The theory was verified experimentally by Raman and co-workers (1923). The phenomenological theory of light scattering by multi-component systems was further developed by Debye (1947), Kirkwood and Goldberg (1950), Stockmayer (1950), Fürth and Williams (1954), Tatsuo Ooi (1958) and Hill (1959).

The theories of these authors dealt with isotropic light scattering only. In the general case, anisotropic light scattering, resulting from optical anisotropy of the molecules or from anisotropy of the molecular field existing within the medium, should also be accounted for. Thus, within a condensed medium consisting of anisotropic molecules, in addition to radial correlations, angular intermolecular correlations intervene. This latter fact was taken into account by Benoit and Weill (1956,

1958) in computing the optical anisotropy of light scattered by dilute two-component systems of anisotropic molecules.

In the present paper, a general statistical-molecular theory of light scattering by multi-component systems of optically anisotropic and polar molecules is proposed. The fundamental equation of the intensity of the light scattered is derived, containing the molecular factors F_{is} and F_{anis}, which account for isotropic and anisotropic scattering, respectively. The equation is discussed for a number of special cases.

2. The general theory

Let us consider an isotropic medium as represented by a spherical specimen of macroscopic size. We shall consider the molar volume V therein, containing $x_1 N$, $x_2 N$, ... molecules of components 1, 2, ... respectively, with N denoting Avogadro's number, and x_i — the mole fraction of the i-th component. The molar volume is given by

$$V = \frac{1}{\varrho} \sum_i x_i' M_i, \qquad (2.1)$$

wherein summation extends over all the components of the system, M_i denotes the molecular weight of the i-th component, and ϱ — the density of the medium; the sum of all the x_i is unity:

$$\sum_i x_i = 1.$$

The theory of Rayleigh scattering by a system of the kind described, when in normal conditions, can be fully accounted for by the methods of classical electrodynamics and statistical mechanics. Thus, we consider the system in the electric field E of an incident light beam of wavelength λ. The intensity component of the light scattered by the volume V and passing through the analyzing Nicol prism at the point of observation is, quite generally, given by (see, Kielich, 1960):

$$I_n^s = \frac{16 \pi^4}{\lambda_s^4 R_0^2} \langle M_\alpha M_\beta^* n_\alpha n_\beta \rangle_E, \qquad (2.2)$$

wherein R_0 is the distance of the point of observation from the centre of the scattering volume V, n — the unit vector perpendicular to the direction of observation $(R_0 \cdot n = 0)$ and describing the plane of vibrations of the Nicol prism, whilst α and β are summation indexes assuming the values 1, 2, 3; the asterisk denotes the complex-conjugate quantity.

$M = M(\tau, E)$ is the dipole moment induced in volume V by the electric field E of the incident light beam, when the configuration of the system is τ. In the classical treatment, the configurational variables $\tau = \tau(r, \omega)$ are continuous, and account for

the positions (r) and orientations (ω) of all molecules in the system. For a multi-component system, we have

$$M(\tau, E) = \sum_i \sum_{p=1}^{x_i N} m^{(p,i)} e^{i s \cdot r_i^{(p)}} \qquad (2.3)$$

with $m^{(p,i)}$ denoting the electric dipole moment induced by the electric field E of the incident light wave in the p-th molecule of species i, $r_i^{(p)}$ its radius vector, and, for Rayleigh scattering,

$$|s| = |k - k'| = \frac{4\pi}{\lambda} \sin \frac{\vartheta}{2}, \qquad (2.4)$$

k and k' being the wave vectors of the incident and scattered light, respectively, and ϑ — the angle of scattering as subtended by the directions of propagation of the incident and scattered light waves.

The symbol $\langle \ \rangle_E$ in eq. (2.2) denotes the statistical average in the presence of the electric field E of the incident light wave. Let $U(\tau, E)$ denote the total potential energy of the system in the configuration τ and when the external field is E. By classical statistical mechanics, the average statistical value of an arbitrary function of state $\Phi(\tau, E)$ at thermodynamical equilibrium of the system is given by:

$$\langle \Phi \rangle_E = \frac{\int \Phi(\tau, E) e^{-\frac{U(\tau,E)}{kT}} d\tau}{\int e^{-\frac{U(\tau,E)}{kT}} d\tau}, \qquad (2.5)$$

where the integrations with respect to τ are over all configurations of all the molecules of the system, k is Boltzmann's constant, and T — the absolute temperature.

Restricting the problem to linear dependence of $M(\tau, E)$ on the electric field strength E, we have

$$M_\alpha(\tau, E) = \left(\frac{\partial M_\alpha}{\partial E_\gamma}\right)_{E=0} E_\gamma; \qquad (2.6)$$

accordingly, eq. (2.2) assumes the form

$$I_n = \frac{16 \pi^4 I_0}{\lambda^4 R_0^2} \left\langle \frac{\partial M_\alpha}{\partial E_\gamma} \left(\frac{\partial M_\beta}{\partial E_\delta}\right)^* n_\alpha n_\beta e_\gamma e_\delta \right\rangle, \qquad (2.7)$$

where I_0 is the incident light intensity, and e — a unit vector having the direction of the electric field E. Here, the brackets $\langle \ \rangle$ with no index symbolize the average statistical value in the absence of the electric field ($E = 0$):

$$\langle \Phi \rangle = \frac{\int \Phi(\tau, 0) e^{-\frac{U(\tau,0)}{kT}} d\tau}{\int e^{-\frac{U(\tau,0)}{kT}} d\tau}; \qquad (2.8)$$

$U(\tau, 0)$ is the total potential energy of the system when the configuration is τ and $\boldsymbol{E} = 0$.

When the electric field $\boldsymbol{E}$ is absent, the probability for all directions of the unit vectors $\boldsymbol{n}$ and $\boldsymbol{e}$ is the same; thus, the product $n_\alpha n_\beta e_\gamma e_\delta$ of their components can be averaged isotropically, and eq. (2.7) yields

$$I_n = \frac{16\,\pi^4 I_0}{45\,\lambda^4 R_0^2} \{5 \cos^2 \Omega_{en} F_{is}(s) + (\cos^2 \Omega_{en} + 3) F_{anis}'(s)\} \qquad (2.9)$$

with Ω_{en} denoting the angle between the vectors $\boldsymbol{e}$ and $\boldsymbol{n}$. The quantities F_{is} and F_{anis} in eq. (2.9) are of the form

$$F_{is}(s) = \sum_{i,j} \left\langle \delta_{\alpha\beta} \delta_{\gamma\delta} \sum_{p=1}^{x_i N} \sum_{q=1}^{x_j N} \frac{\partial m_\alpha^{(p,i)}}{\partial E_\beta^{(p,i)}} \left(\frac{\partial m_\gamma^{(q,j)}}{\partial E_\delta^{(q,j)}}\right)^* e^{-is \cdot r_{ij}^{(pq)}} \right\rangle, \qquad (2.10)$$

$$F_{anis}(s) = \frac{1}{2} \sum_{i,j} \left\langle (3\,\delta_{\alpha\gamma} \delta_{\beta\delta} - \delta_{\alpha\beta} \delta_{\gamma\delta}) \sum_{p=1}^{x_i N} \sum_{q=1}^{x_j N} \frac{\partial m_\alpha^{(p,i)}}{\partial E_\beta^{(p,i)}} \left(\frac{\partial m_\gamma^{(q,j)}}{\partial E_\delta^{(q,j)}}\right)^* e^{-is \cdot r_{ij}^{(pq)}} \right\rangle, \quad (2.11)$$

and are termed the molecular factors of isotropic and anisotropic light scattering, respectively; $\boldsymbol{r}_{ij}^{(pq)} = \boldsymbol{r}_j^{(q)} - \boldsymbol{r}_i^{(p)}$ is the vector connecting the centres of the p-th and q-th molecules of the i-th and j-th chemical species and $\delta_{\alpha\beta}$ — the substitution tensor (unity if $\alpha = \beta$ and zero when $\alpha \neq \beta$).

Eq. (2.9), together with (2.10) and (2.11), is the fundamental equation of the statistical-molecular theory of light scattering by a multi-component system.

If natural light is used and the light scattered is observed with a Nicol analyzer, we have (see Kielich, 1960):

$$I(\varphi_n, \vartheta) = \frac{16\,\pi^4 I_0}{45\,\lambda^4 R_0^2} \{5(1 - \sin^2 \varphi_n \sin^2 \vartheta) F_{is}(s) + (7 - \sin^2 \varphi_n \sin^2 \vartheta) F_{anis}(s)\},$$
$$(2.12)$$

where φ_n is the azimuth of the unit vector $\boldsymbol{n}$, and ϑ — the angle of scattering.

If no Nicol prism is used, eq. (2.12) yields the following expression for the light intensity scattered at the angle ϑ:

$$I(\vartheta) = \frac{8\,\pi^4 I_0}{45\,\lambda^4 R_0^2} \{5(1 + \cos^2 \vartheta) F_{is}(s) + (13 + \cos^2 \vartheta) F_{anis}(s)\}. \qquad (2.13)$$

The degree of depolarization is defined as the ratio of the smallest and largest possible values of the intensity of the light scattered. As $I_{min} = I(90°, \vartheta)$ and $I_{max} = I(0°, \vartheta)$, by eq. (2.12) the general expression for the degree of depolarization of the light scattered at the angle ϑ is obtained in the form

$$D(\vartheta) = \frac{5 \cos^2 \vartheta\, F_{is}(s) + (6 + \cos^2 \vartheta) F_{anis}(s)}{5 F_{is}(s) + 7 F_{anis}(s)}. \qquad (2.14)$$

The light scattering constant, also known as Rayleigh's ratio, is defined as the ratio of the intensity of light scattered by unit volume at angle ϑ, to the incident intensity:

$$S(\vartheta) = \frac{I(\vartheta) R_0^2}{IV}. \tag{2.15}$$

As the incident intensity existing within a medium of refractive index n is related to I_0 by the formula

$$I = \left(\frac{3}{n^2 + 2}\right)^2 I_0, \tag{2.16}$$

the following expression is obtained from (2.15) with respect to eq. (2.13):

$$S(\vartheta) = \frac{8\pi^4 (n^2 + 2)^2}{405 \lambda^4 V} \{5(1 + \cos^2 \vartheta) F_{is}(s) + (13 + \cos^2 \vartheta) F_{anis}(s)\}. \tag{2.17}$$

If the light scattered is observed perpendicularly to the direction of incidence, eqs. (2.14) and (2.17) yield:

$$D = \frac{6 F_{anis}}{5 F_{is} + 7 F_{anis}}, \tag{2.18}$$

$$S = \frac{8\pi^4 (n^2 + 2)^2}{405 \lambda^4 V} (5 F_{is} + 13 F_{anis}). \tag{2.19}$$

Integrating $S(\vartheta)$, as given by eq. (2.17), over the surface of the scattering sphere, the following general expression is obtained for the turbidity:

$$h = \frac{16\pi^5 (n^2 + 2)^2}{405 \lambda^4 V} \int_0^\pi \{5(1 + \cos^2 \vartheta) F_{is}(s) + (13 + \cos^2 \vartheta) F_{anis}(s)\} \sin\vartheta d\vartheta, \tag{2.20}$$

or, in the absence of internal interferences:

$$h = \frac{128\pi^5 (n^2 + 2)^2}{243 \lambda^4 V} (F_{is} + 2 F_{anis}). \tag{2.21}$$

In the subsequent sections, the factors F_{is} and F_{anis} will be discussed for several molecular models.

3. Anisotropic molecules with constant polarizability

In the first approximation, the polarizability of the molecules immersed in the medium may be assumed to remain unaffected by the surroundings, and thus to be that of the isolated molecules. In this case, if the molecules of each species present within the system under consideration are optically anisotropic, we have

$$m_\alpha^{(p,i)} = \alpha_{\alpha\beta}^{(p,i)} E_\beta^{(p,i)}, \tag{3.1}$$

with $\alpha_{\alpha\beta}^{(p,i)}$ denoting the polarizability tensor of the p-th isolated molecule of species i. Hence, the molecular factors (2.10) and (2.11) assume the form

$$F_{\text{is}}(s) = \sum_{i,j} \Big\langle \sum_{q=1}^{x_iN} \sum_{q=1}^{x_jN} \alpha_{\alpha\alpha}^{(p,i)} \alpha_{\beta\beta}^{(q,j)} \cos s \cdot r_{ij}^{(pq)} \Big\rangle, \qquad (3.2)$$

$$F_{\text{anis}}(s) = \tfrac{1}{2} \sum_{i,j} \Big\langle \sum_{p=1}^{x_iN} \sum_{q=1}^{x_jN} (3\,\alpha_{\alpha\beta}^{(p,i)} \alpha_{\alpha\beta}^{(q,j)} - \alpha_{\alpha\alpha}^{(p,i)} \alpha_{\beta\beta}^{(q,j)}) \cos s \cdot r_i^{(pq)} \Big\rangle. \qquad (3.3)$$

Assuming all molecules of one species to possess the same polarizability, and applying the Kirkwood-Buff (1951) method, the molecular factor of isotropic light scattering may be written as follows:

$$F_{\text{is}}(s) = 9\,N \sum_{i,j} \alpha_{(i)}\,\alpha_{(j)} \Big\{ x_i\,\delta_{ij} + x_i\,x_j \int \cos s \cdot r_{ij} \Big[g_{ij}(\tau) - \frac{N}{V} \Big] d\bar\tau \Big\}, \qquad (3.4)$$

with $\alpha_{(i)}$ denoting the mean polarizability of the isolated molecule of species i, and $g_{ij}(\tau)$ — the distribution function of the correlation between the molecules of species i and j; $\Omega^2\,d\bar\tau = d\,r_{ij}\,d\omega_i\,d\omega_j$, where $\Omega = \int d\omega_i$.

The molecular factor of anisotropic light scattering (3.3) will now be represented in a form better adapted to further discussion, namely:

$$F_{\text{anis}}(s) = \tfrac{1}{2} \sum_{i,j} \alpha_{\alpha\beta}^{(i)} \alpha_{\gamma\delta}^{(j)} \Big\langle \sum_{p=1}^{x_iN} \sum_{q=1}^{x_jN} (3\,\omega_{\alpha\gamma}^{(pq;ij)} \omega_{\beta\delta}^{(pq;ij)} - \delta_{\alpha\beta}\,\delta_{\gamma\delta}) \cos s \cdot r_{ij}^{(pq)} \Big\rangle, \qquad (3.5)$$

with $\omega_{\alpha\gamma}^{(pq;ij)}$ denoting the cosine of the angle subtended by the axes of the molecular systems of reference rigidly attached to the p-th and q-th molecules of species i and j, respectively.

For molecules possessing the axial symmetry, this yields

$$F_{\text{anis}}(s) = 9\,N \sum_{i,j} \alpha_{(i)}\,\alpha_{(j)}\,\delta_{\alpha(i)}\,\delta_{\alpha(j)} \Big\{ x_i\,\delta_{ij} +$$

$$+ \frac{1}{2}\,x_i\,x_j \int (3\cos^2\Theta_{ij} - 1) \cos s \cdot r_{ij} \Big[g_{ij}(\tau) - \frac{N}{V} \Big] d\bar\tau \Big\}. \qquad (3.6)$$

Here, Θ_{ij} is the angle between the axes of symmetry of the molecules of species i and j, respectively, and $\delta_{\alpha(i)}$ — the optical anisotropy of the isolated molecule of species i:

$$\delta_{\alpha(i)} = \frac{\alpha_{||}^{(i)} - \alpha_{\perp}^{(i)}}{3\,\alpha_{(i)}} = \frac{\alpha_{||}^{(i)} - \alpha_{\perp}^{(i)}}{\alpha_{||}^{(i)} + 2\,\alpha_{\perp}^{(i)}}, \qquad (3.7)$$

$\alpha_{||}$ and $\alpha_{\perp}$ denoting the polarizabilities parallel and perpendicularly to the symmetry axis of the molecule, respectively.

Eqs. (3.4) and (3.6) can be rewritten as follows:

$$F_{is}(s) = 9 N \sum_{i,j} x_i^{1/2} x_j^{1/2} \alpha_{(i)} \alpha_{(j)} C_{radial}^{(ij)} ,$$ (3.8)

$$F_{anis}(s) = 9 N \sum_{ij} x_i^{1/4} x_j^{1/2} \alpha_{(i)} \alpha_{(j)} \delta_{\alpha(i)} \delta_{\alpha(j)} C_{angular}^{(ij)},$$ (3.9)

with the notation

$$C_{radial}^{(ij)} = x_i^{1/2} x_j^{-1/2} \delta_{ij} + x_i^{1/2} x_j^{1/2} \int \cos \mathbf{s} \cdot \mathbf{r}_{ij} \left[g_{ij}(\tau) - \frac{N}{V} \right] d\bar{\tau},$$ (3.10)

$$C_{angular}^{(ij)} = x_i^{1/2} x_j^{-1/2} \delta_{ij} + \frac{1}{2} x_i^{1/2} x_j^{1/2} \int (3 \cos^2 \Theta_{ij} - 1) \cos \mathbf{s} \cdot \mathbf{r}_{ij} \left[g_{ij}(\tau) - \frac{N}{V} \right] d\bar{\tau},$$ (3.11)

$C_{radial}^{(ij)}$ and $C_{angular}^{(ij)}$ are quantities accounting for the radial and angular intermolecular correlations.

If, in particular, a two-component system is considered, this yields

$$\frac{1}{9N} F_{is}(s) = x_1 \alpha_1^2 \left\{ 1 + x_1 \int \cos \mathbf{s} \cdot \mathbf{r}_{11} \left[g_{11}(\tau) - \frac{N}{V} \right] d\bar{\tau} \right\} +$$

$$+ 2 x_1 x_2 \alpha_{(1)} \alpha_{(2)} \int \cos \mathbf{s} \cdot \mathbf{r}_{12} \left[g_{12}(\tau) - \frac{N}{V} \right] d\bar{\tau} +$$

$$+ x_2 \alpha_{(2)}^2 \left\{ 1 + x_2 \int \cos \mathbf{s} \cdot \mathbf{r}_{22} \left[g_{22}(\tau) - \frac{N}{V} \right] d\bar{\tau} \right\},$$ (3.12)

$$\frac{1}{9N} F_{anis}(s) = x_1 \alpha_{(1)}^2 \delta_{\alpha(1)}^2 \left\{ 1 + \frac{1}{2} x_1 \int (3 \cos^2 \Theta_{11} - 1) \cos \mathbf{s} \cdot \mathbf{r}_{11} \left[g_{11}(\tau) - \frac{N}{V} \right] d\bar{\tau} \right\} +$$

$$+ x_1 x_2 \alpha_{(1)} \alpha_{(2)} \delta_{\alpha(1)} \delta_{\alpha(2)} \int (3 \cos^2 \Theta_{12} - 1) \cos \mathbf{s} \cdot \mathbf{r}_{12} \left[g_{12}(\tau) - \frac{N}{V} \right] d\bar{\tau} +$$

$$+ x_2 \alpha_{(2)}^2 \delta_{\alpha(2)}^2 \left\{ 1 + \frac{1}{2} x_2 \int (3 \cos^2 \Theta_{22} - 1) \cos \mathbf{s} \cdot \mathbf{r}_{22} \left[g_{22}(\tau) - \frac{N}{V} \right] d\bar{\tau} \right\}.$$ (3.13)

Hence, for a dilute two-component solution, and for $\lambda \gg r_{ij}$, the expression given by Benoit and Weill (1956) for the optical anisotropy $\Delta^2 = F_{anis}/F_{is}$ is derived, whereas, for a one-component system, the expression discussed by Benoit and Stockmayer (1956) is obtained (cf. Anselm 1947; Buckingham and Stephen 1957; Kielich 1958).

In the case of an ideal gas, the radial and angular correlation factors (3.10) and (3.11) reduce to

$$C_{radial}^{(ij)} = x_i^{1/2} x_j^{-1/2} \delta_{ij}, \quad C_{angular}^{(ij)} = x_i^{1/2} x_j^{-1/2} \delta_{ij},$$ (3.14)

and eqs. (3.8) and (3.9) yield

$$_{gas}F_{is} = 9N \sum_i x_i \alpha^2_{(i)} = \sum_i x_i F^{(i)}_{is}, \tag{3.15}$$

$$_{gas}F_{anis} = 9N \sum_i x_i \alpha^2_{(i)} \delta^2_{\alpha(i)} = \sum_i x_i F^{(i)}_{anis}. \tag{3.16}$$

Thus, for an ideal gas, the molecular factors F_{is} and F_{anis} result additively from the factors

$$F^{(i)}_{is} = 9N\alpha^2_{(i)} \quad \text{and} \quad F^{(i)}_{anis} = 9N\alpha^2_{(i)}\delta^2_{\alpha(i)} \tag{3.17}$$

of the components of the multi-component system. This means that the various components of a gaseous system scatter light independently of one another.

4. Molecules with permanent dipole moment and hyperpolarizability

In their theory of the degree of depolarization, Buckingham and Stephen (1957) proved that in the case of a one-component dipolar liquid, the light scattered is largely dependent on the hyperporalizability of the molecules. Here, the method of the foregoing authors will be applied for computing the molecular factors F_{is} and F_{anis} of a multi-component system.

In a condensed medium, the polarizability of a molecule is generally modified by the molecular field of its neighbours. In the case under consideration, the dipole moment induced by the total electric field $(E+F)$ in the p-th polar molecule of species i immersed in the medium is given by the expansion

$$m^{(p,i)}_\alpha = \alpha^{(p,i)}_{\alpha\beta} (E^{(p,i)}_\beta + F^{(p,i)}_\beta) + \tfrac{1}{2} \beta^{(p,i)}_{\alpha\beta\gamma} (E^{(p,i)}_\beta + F^{(p,i)}_\beta)(E^{(p,i)}_\gamma + F^{(p,i)}_\gamma) + ..., \tag{4.1}$$

wherein $\beta^{(p,i)}_{\alpha\beta\gamma}$ is the hyperpolarizability tensor of the p-th molecule of species i, whereas $F^{(p,i)}$ is the molecular field at the centre of molecule p of species i due to the charge distribution of all the others.

Substitution of the expansion (4.1) in eqs. (2.10) and (2.11) yields

$$F_{is}(s) = \sum_{i,j} \langle \sum_{p=1}^{x_i N} \sum_{q=1}^{x_j N} (\alpha^{(i)}_{\alpha\alpha} \alpha^{(j)}_{\beta\beta} + \alpha^{(i)}_{\alpha\alpha} \beta^{(j)}_{\beta\beta\gamma} F^{(j)}_\gamma +$$

$$+ \alpha^{(j)}_{\alpha\alpha} \beta^{(i)}_{\beta\beta\gamma} F^{(i)}_\gamma + ...) \cos s \cdot r^{(pq)}_{ij} \rangle, \tag{4.2}$$

$$F_{anis}(s) = \tfrac{1}{2} \sum_{i,j} \langle \sum_{p=1}^{x_i N} \sum_{q=1}^{x_j N} (\alpha^{(i)}_{\alpha\beta} \alpha^{(j)}_{\gamma\delta} + \alpha^{(i)}_{\alpha\beta} \beta^{(j)}_{\gamma\delta\varepsilon} F^{(j)}_\varepsilon +$$

$$+ \alpha^{(i)}_{\alpha\beta} \beta^{(i)}_{\gamma\delta\varepsilon} F^{(i)}_\varepsilon + ...) (3\, \omega^{(pq;\,ij)}_{\alpha\gamma} \omega^{(pq;\,ij)}_{\beta\delta} - \delta_{\alpha\beta} \delta_{\gamma\delta}) \cos s \cdot r^{(pq)}_{ij} \rangle. \tag{4.3}$$

The terms $\alpha_{\alpha\beta} \dfrac{\partial F_\beta}{\partial E_\alpha}$ have been omitted herein; these are discussed in Appendix A, for the case of a one-component system.

In the Onsager model (1936), the molecular field $\boldsymbol{F}^{(i)}$ appearing in the foregoing expressions is the reaction field in the absence of an external field. The Onsager model was applied by Piekara (1950) to the theory of molecular orientation phenomena in two-component solutions of liquids consisting of anisotropic molecules. In the present case, the reaction field existing at the centre of a molecule of species i, of radius a_i, is given as follows:

$$F_\alpha^{(i)} \equiv R_\alpha^{(i)} = \frac{2\,(\varepsilon - 1)}{2\,\varepsilon + 1}\,\frac{m_\alpha^{(i)}}{a_i^3} = f_i\,m_\alpha^{(i)}, \qquad (4.4)$$

wherein ε is the electric permittivity of the medium as a whole. In the case of dipolar molecules of anisotropic polarizability we have, at $\boldsymbol{E} = 0$,

$$m_\alpha^{(i)} = \mu_\alpha^{(i)} + \alpha_{\alpha\beta}^{(i)}\,F_\beta^{(i)}, \qquad (4.5)$$

and eq. (4.4) yields

$$F_\alpha^{(i)} = \frac{f_i}{1 - f_i\alpha_\alpha^{(i)}}\,\mu_\alpha^{(i)} = \chi_\alpha^{(i)}\,\frac{\mu_\alpha^{(i)}}{\alpha_\alpha^{(i)}}, \qquad (4.6)$$

wherein $\mu_\alpha^{(i)}$ is the component of the permanent electric dipole moment of an isolated molecule of species i and $\alpha_\alpha^{(i)}$ — its polarizability referred to the principal axes. Assuming, according to Onsager,

$$\alpha_{(i)} = \frac{n_i^2 - 1}{n_i^2 + 2}\,a_i^3, \qquad (4.7)$$

the quantity $\chi_\alpha^{(i)}$ in eq. (4.6) can be written as follows:

$$\chi_\alpha^{(i)} = \frac{f_i\alpha_{(i)}}{1 - f_i\alpha_{(i)}\lambda_\alpha^{(i)}} = \frac{2\,(\varepsilon - 1)\,(n_i^2 - 1)}{(2\varepsilon + 1)\,(n_i^2 + 2) - 2\,(\varepsilon - 1)\,(n_i^2 - 1)\,\lambda_\alpha^{(i)}}, \qquad (4.8)$$

where n_i is the refractive index of the i-th component of the system, and $\lambda_\alpha^{(i)} = \alpha_\alpha^{(i)}/\alpha_{(i)}$. For molecules of isotropic polarizability, $\lambda_\alpha^{(i)} = 1$, whence eq. (4.8) reduces to

$$\chi_1^{(i)} = \chi_2^{(i)} = \chi_3^{(i)} = \frac{2\,(\varepsilon - 1)\,(n_i^2 - 1)}{3\,(2\varepsilon + n_i^2)}. \qquad (4.9)$$

By eq. (4.6), with eqs. (4.2) and (4.3), the following result is obtained for molecules whose polarizability has been referred to the principal axes:

$$F_{\mathrm{is}}(s) = \sum_{i,j} \sum_{\alpha,\beta=1}^{3} A_{\alpha\beta}^{(ij)} \Big\langle \sum_{p=1}^{x_i N} \sum_{q=1}^{x_j N} \cos \boldsymbol{s} \cdot \boldsymbol{r}_{ij}^{(pq)} \Big\rangle, \qquad (4.10)$$

$$F_{\mathrm{anis}}(s) = \tfrac{1}{2} \sum_{i,j} \sum_{\alpha,\beta=1}^{3} A_{\alpha\beta}^{(ij)} \Big\langle \sum_{p=1}^{x_i N} \sum_{q=1}^{x_j N} (3\,\omega_{\alpha\beta}^{(pq;ij)}\omega_{\beta\alpha}^{(pq;ij)} - 1) \cos \boldsymbol{s} \cdot \boldsymbol{r}_{ij}^{(pq)} \Big\rangle, \qquad (4.11)$$

with the notation

$$A_{\alpha\beta}^{(ij)\prime} = \alpha_\alpha^{(i)} \alpha_\beta^{(j)} + \sum_{\gamma=1}^{3} \left(\alpha_\alpha^{(i)} \beta_{\beta\beta\gamma}^{(j)} \chi_\gamma^{(j)} \frac{\mu_\gamma^{(j)}}{\alpha_{(j)}} + \alpha_\alpha^{(j)} \beta_{\beta\beta\gamma}^{(i)} \chi_\gamma^{(i)} \frac{\mu_\gamma^{(i)}}{\alpha_{(i)}} \right) + \dots \quad (4.12)$$

For light scattering by molecules possessing the axial symmetry, the foregoing expressions yield

$$F_{is}(s) = 9N \sum_{i,j} x_i^{1/2} x_j^{1/2} \alpha_{(i)}\alpha_{(j)} \left\{ 1 + \chi_{(i)} \frac{\mu_{(i)} \beta_{(i)}}{\alpha_{(i)}^2} + \chi_{(j)} \frac{\mu_{(j)} \beta_{(j)}}{\alpha_{(j)}^2} + \dots \right\} C_{radial}^{(ij)} ,$$
$$(4.13)$$

$$F_{anis}(s) = 9N \sum_{i,j} x_i^{1/2} x_j^{1/2} \alpha_{(i)}\alpha_{(j)} \delta_{\alpha(i)} \delta_{\alpha(j)} \left\{ 1 + \chi_{(i)} \frac{\mu_{(i)} \beta_{(i)} \delta_{\beta(i)}}{\alpha_{(i)}^2 \delta_{\alpha(i)}} + \right.$$
$$\left. + \chi_{(j)} \frac{\mu_{(j)} \beta_{(j)} \delta_{\beta(j)}}{\alpha_{(j)}^2 \delta_{\alpha(j)}} + \dots \right\} C_{angular}^{(ij)} , \quad (4.14)$$

with $\chi_{(i)} = \chi_3^{(i)}$;

$$\delta_{\beta(i)} = \frac{\beta_{||}^{(i)} - \beta_\perp^{(i)}}{3\beta_{(i)}} \quad \text{and} \quad \beta_{(i)} = \frac{1}{3} (\beta_{||}^{(i)} + 2\beta_\perp^{(i)}) \quad (4.15)$$

are the anisotropy and the mean hyperpolarizability of the dipole molecule.

Thus, the effect of the hyperpolarizability and permanent electric dipoles of the molecules on light scattering by a multi-component system has been accounted for. If, in particular, the scattering medium is a one-component system, the expressions derived by Buckingham and Stephen (1957)[1] are obtained from eqs. (4.13) and (4.14) by neglecting the angular correlations and internal interferences:

$$F_{is} = 9\alpha^2 \frac{N}{V} \left\{ 1 + 2\chi \frac{\mu\beta}{\alpha^2} \right\} RT\beta_T , \quad (4.16)$$

$$F_{anis} = 9\alpha^2 \delta_\alpha^2 N \left\{ 1 + 2\chi \frac{\mu\beta \delta_\beta}{\alpha^2 \delta_\alpha} \right\} , \quad (4.17)$$

with R denoting the gas constant, β_T — the isothermal compressibility coefficient of the medium, and, for $\lambda_3 \approx 1$, χ given by

$$\chi = \frac{2(\varepsilon - 1)(n^2 - 1)}{3(2\varepsilon + n^2)} . \quad (4.18)$$

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[1] Buckingham and Stephen (1957) computed the quantities A and B standing in connection with eqs. (4.16) and (4.17) at

$$F_{is} = \frac{3}{10} NB, \qquad F_{anis} = \frac{3}{2} NA.$$

5. Non-dipolar molecules with quadrupole moments and hyperpolarizability

Let us now consider a multi-component system of non-dipolar molecules with hyperpolarizability. In the present case, the following expansion can be written:

$$m_{\alpha}^{(p,i)} = \{\alpha_{\alpha\beta}^{(p,i)} + \tfrac{1}{6}\gamma_{\alpha\beta\gamma\delta}^{(p,i)}(E_{\gamma}^{(p,i)} + F_{\gamma}^{(p,i)})(E_{\delta}^{(p,i)} + F_{\delta}^{(p,i)}) + ...\} \cdot (E_{\beta}^{(p,i)} + F_{\beta}^{(p,i)}),$$

(5.1)

wherein $\gamma_{\alpha\beta\gamma\delta}^{(p,i)}$ is the hyperpolarizability tensor of the p-th (non-dipolar) molecule of species i.

By eq. (5.1), the molecular factors of isotropic and anisotropic light scattering assume the form

$$F_{\mathrm{is}}(s) = \sum_{i,j} \Big\langle \sum_{p=1}^{x_i N} \sum_{q=1}^{x_j N} \{\alpha_{\alpha\alpha}^{(i)}\alpha_{\beta\beta}^{(j)} + \tfrac{1}{2}\alpha_{\alpha\alpha}^{(i)}\gamma_{\beta\beta\gamma\delta}^{(j)}F_{\gamma}^{(j)}F_{\delta}^{(j)} +$$

(5.2)

$$+ \tfrac{1}{2}\alpha_{\alpha\alpha}^{(j)}\gamma_{\beta\beta\gamma\delta}^{(i)}F_{\gamma}^{(i)}F_{\delta}^{(i)} + ...\}\cos \mathbf{s}\cdot\boldsymbol{r}_{ij}^{(pq)}\Big\rangle,$$

$$F_{\mathrm{anis}}(s) = \tfrac{1}{2}\sum_{i,j} \Big\langle \sum_{p=1}^{x_i N} \sum_{q=1}^{x_j N} \{\alpha_{\alpha\beta}^{(i)}\alpha_{\gamma\delta}^{(j)} + \tfrac{1}{2}\alpha_{\alpha\beta}^{(i)}\gamma_{\gamma\delta\varepsilon\eta}^{(j)}F_{\varepsilon}^{(j)}F_{\eta}^{(j)} +$$

(5.3)

$$+ \tfrac{1}{2}\alpha_{\alpha\beta}^{(j)}\gamma_{\gamma\delta\varepsilon\eta}^{(i)}F_{\varepsilon}^{(i)}F_{\eta}^{(i)} + ...\}(3\,\omega_{\alpha\gamma}^{(pq;ij)}\omega_{\beta\delta}^{(pq;ij)} - \delta_{\alpha\beta}\delta_{\gamma\delta})\cos \mathbf{s}\cdot\boldsymbol{r}_{ij}^{(pq)}\Big\rangle.$$

As previously, the molecular field $\boldsymbol{F}^{i}$ can be replaced by the reaction field of Onsager's model. If, moreover, the molecule possesses an electric quadrupole moment, the reaction field at its centre is given by (see Appendix B)

$$F_{\alpha}^{(i)} = f_i m_{\alpha}^{(i)} + h_i \Theta_{\alpha\beta}^{(i)} r_{i\beta},$$

(5.4)

wherein

$$f_i = \frac{2(\varepsilon - 1)}{2\varepsilon + 1}\frac{1}{a_i^3}, \qquad h_i = \frac{6(\varepsilon - 1)}{3\varepsilon + 2}\frac{1}{a_i^5}.$$

[(5.5)

$\Theta_{\alpha\beta}^{(i)}$ denotes the electric quadrupole moment of a molecule of species i, defined as follows:

$$\Theta_{\alpha\beta}^{(i)} = \tfrac{1}{2}\sum_{n} e_i^{(n)}(3\,r_{i\alpha}^{(n)}r_{i\beta}^{(n)} - r_{in}^2\,\delta_{\alpha\beta}),$$

(5.6)

where $e_i^{(n)}$ is the n-th electric charge of a molecule of species i, and $\boldsymbol{r}_i^{(n)}$ — its radius vector, summation extending over all the charges of the molecule.

The reaction field of a permanent quadrupole induces a dipole moment in a non-polar molecule (the induced quadrupole moment will be neglected):

$$m_{\alpha}^{(i)} = \alpha_{\alpha\beta}^{(i)}F_{\beta}^{(i)}:$$

(5.7)

thus, eq. (5.4) yields

$$F_\alpha^{(i)} = \frac{h_i}{1-f_i\,\alpha_\alpha^{(i)}}\,\Theta_{\alpha\beta}^{(i)}\,r_{i\beta} = \xi_\alpha^{(i)}\,\frac{\Theta_{\alpha\beta}^{(i)}\,r_{i\beta}}{\alpha_{(i)}^{5/3}}\,, \qquad (5.8)$$

wherein

$$\xi_\alpha^{(i)} = \frac{h_i}{f_i}\,\alpha_{(i)}^{2/3}\,\chi_a^{(i)} = 3\left(\frac{2\,\varepsilon+1}{3\,\varepsilon+2}\right)\left(\frac{n_i^2-1}{n_i^2+2}\right)^{2/3}\chi_a^{(i)}\,. \qquad (5.9)$$

With the definition (see Böttcher, 1952)

$$\overline{F_\alpha^{(i)}\,F_\beta^{(i)}} = \frac{N}{V}\int\limits_0^{a_i}\int\limits_0^\pi\int\limits_0^{2\pi} F_\alpha^{(i)}\,F_\beta^{(i}\,r_i^2\,dr_i\,\sin\vartheta_i\,d\vartheta_i\,d\varphi_i$$

and with respect to eq. (5.8), the mean square value of the reaction field is obtained as follows:

$$\overline{F_\alpha^{(i)}\,F_\beta^{(i)}} = \frac{1}{5\,\alpha_{(i)}^{5/3}}\left(\frac{n_i^2+2}{n_i^2-1}\right)^{2/3}\xi_\alpha^{(i)}\,\xi_\beta^{(i)}\,\Theta_{\alpha\gamma}^{(i)}\,\Theta_{\beta\gamma}^{(i)}\,. \qquad (5.10)$$

For molecules having the axial symmetry, this yields

$$\overline{F_\alpha^{(i)}\,F_\alpha^{(i)}} = 9\,\eta^{(i)}\frac{\Theta_{(i)}^2}{\alpha_{(i)}^{5/3}}\,, \qquad (5.11)$$

wherein

$$\eta_{(i)} = \frac{1}{10}\left(\frac{2\,\varepsilon+1}{3\,\varepsilon+2}\right)^2\left(\frac{n_i^2-1}{n_i^2+2}\right)^{2/3}(\chi_1^{(i)2} + 2\chi_3^{(i)2}) \qquad (5.12)$$

and $\Theta_{(i)}$ is the quadrupole moment of the axially symmetric molecule,

$$\Theta_{(i)} = \sum_n e_i^{(n)}\,(z_{in}^2 - x_{in}^2)\,,$$

z_{in} being the distance along the molecular axis of the charge $e_i^{(n)}$ and x_{in} — its distance from the axis.

With respect to eq. (5.11), eqs. (5.2) and (5.3) assume the form

$$F_{is}(s) = 9\,N\sum_{i,j} x_i^{1/2}\,x_j^{1/2}\,\alpha_{(i)}\alpha_{(j)}\left\{1 + \frac{5}{2}\,\eta_{(i)}\frac{\gamma_{(i)}\Theta_{(i)}^2}{\alpha_{(i)}^{11/3}} + \right.$$
$$\left. + \frac{5}{2}\,\eta_{(j)}\frac{\gamma_{(j)}\Theta_{(j)}^2}{\alpha_{(j)}^{11/3}} + ...\right\}C_{\text{radial}}^{(i,j)}\,, \qquad (5.13)$$

$$F_{\text{anis}}(s) = 9\,N\sum_{i,j} x_i^{1/2}\,x_j^{1/2}\,\alpha_{(i)}\alpha_{(j)}\,\delta_{\alpha(i)}\,\delta_{a(j)}\left\{1 + \frac{7}{4}\,\eta_{(i)}\frac{\gamma_{(i)}\delta_{\gamma(i)}\Theta_{(i)}^2}{\alpha_{i(i)}^{11/3}\,\delta_{\alpha(i)}} + \right.$$
$$\left. + \frac{7}{4}\,\eta_{(j)}\frac{\gamma_{(j)}\delta_{\gamma(j)}\Theta_{(j)}^2}{\alpha_{(j)}^{11/3}\,\delta_{\alpha(j)}} + ...\right\}C_{\text{angular}}^{(ij)}\,, \qquad (5.14)$$

which holds for axially symmetric molecules. Here, the quantities

$$\delta_{\gamma(i)} = \frac{\gamma_{||}^{(i)} - \gamma_{\perp}^{(i)}}{3\,\gamma_{(i)}}, \qquad \gamma_{(i)} = \frac{1}{3}\,(\gamma_{||}^{(i)} + 2\,\gamma_{\perp}^{(i)}), \tag{5.15}$$

have been introduced, being the anisotropy of hyperpolarizability of the quadrupole molecule and its mean hyperpolarizability, respectively.

Thus, the effect of the hyperpolarizability and of the permanent quadrupole moments of the molecules on light scattering has been computed.

In the case of a one-component system, and neglecting the internal interferences, we have, by eqs. (5.13) and (5.14),

$$F_{is} = 9\,\alpha^2\,\frac{N}{V}\left\{1 + 5\,\eta\,\frac{\gamma\Theta^2}{\alpha^{11/3}} + \ldots\right\}RT\beta_T, \tag{5.16}$$

$$F_{anis} = 9\,\alpha^2\,\delta_\alpha^2\,N\left\{1 + \frac{7}{2}\,\eta\,\frac{\gamma\delta_\gamma\Theta^2}{\alpha^{11/3}\delta_\alpha} + \ldots\right\}C_{angular}, \tag{5.17}$$

where

$$\eta = \frac{1}{10}\left(\frac{2\,\varepsilon+1}{3\,\varepsilon+2}\right)^2\left(\frac{n^2-1}{n^2+2}\right)^{2/3}(\chi_1^2 + 2\,\chi_3^2), \tag{5.18}$$

and

$$C_{angular} = 1 + \frac{1}{2}\int(3\cos^2\Theta - 1)\left[g(\tau) - \frac{N}{V}\right]d\bar\tau. \tag{5.19}$$

is the angular correlation factor (cf. Anselm 1947, Benoit and Stockmayer 1956, Kielich 1960).

6. Relation between anisotropic light scattering and the effect of optico-optical birefringence in an isotropic medium

From the discussion of sections 3—5, the molecular factors of isotropic and anisotropic light scattering are seen generally to contain certain molecular constants accounting for the electro-optical properties of isolated molecules, such as the polarizability α, hyperpolarizabilities β and γ, and permanent dipole μ or quadrupole Θ moment. The factor F_{is} is, moreover, dependent on the radial intermolecular correlations, whereas F_{anis} depends on the angular intermolecular correlations. For the greater part, the values of these molecular parameters are not known, and so the factors F_{is} and F_{anis} are more conveniently expressed by quantities that are accessible to measurement.

Eq. (2.18) defining the degree of depolarization can be used for eliminating the factor F_{is} from eq. (2.19), which is that of the scattering constant; this yields

$$S = \frac{8\pi^4\,(n^2+2)^2}{81\,\lambda^4\,V}\,\frac{6+6\,D}{5\,D}\,F_{anis}. \tag{6.1}$$

In considering light scattering by a multi-component system, it is convenient to introduce the molecular light scattering constant S_m:

$$S_m^i = \frac{9V}{(n^2+2)^2} S;$$ (6.2)

by eq. (6.1), the latter may be rewritten as follows:

$$S_m^i = \frac{8\pi^4}{9\lambda^4} \frac{6+6D}{5D} F_{\text{anis}}.$$ (6.3)

A relation between anisotropic light scattering on the one hand, and the optical birefringence arising in an isotropic medium from the effect of a very intense light beam on the other, will now be derived. This latter effect was theoretically predicted by Buckingham (1956) and, as far as the present author is aware, has not been experimentally detected as yet. Generalizing Buckingham's theory for multi-component systems, the molecular constant of optico-optical birefringence is obtained in the form

$$B_m^0 = \frac{2\pi}{45}(3\delta_{\alpha\gamma}\delta_{\beta\delta} - \delta_{\alpha\beta}\delta_{\gamma\delta})\left\{\sum_i \left\langle \sum_{p=1}^{x_iN} \frac{\partial^3 m_\alpha^{(p,i)}}{\partial E_\beta \partial E_\gamma \partial E_\delta} \right\rangle + \right.$$

$$\left. + \frac{1}{kT}\sum_{i,j}\left\langle \sum_{p=1}^{x_iN}\sum_{q=1}^{x_jN} \frac{\partial m_\alpha^{(p,i)}}{\partial E_\beta}\frac{\partial m_\gamma^{(q,j)}}{\partial E_\delta}\right\rangle \right\}.$$ (6.4)

In deriving this expression it had been assumed that the frequency of the weak measuring light beam is identical with, or differs but little from that of the intense light beam giving rise to the optical birefringence of the medium. In this case, the molecular constant B_m^0 and the constant measured

$$B^0 = \frac{n_{||} - n_\perp}{n} \frac{1}{\widetilde{E^2}}$$ (6.5)

are related as follows:

$$B_m^0 = \frac{54 n^2}{(n^2+2)^4} VB^0,$$ (6.6)

with $\widetilde{E^2}$ denoting the time mean square of E.

In particular, neglecting the effect of the molecular field, the dipole moment induced in the p-th molecule of species i by the electric field $\boldsymbol{E}$ of the light wave can be expressed by the expansion (cf. Buckingham and Pople, 1955)

$$m_\alpha^{(p,i)} = \alpha_{\alpha\beta}^{(p,i)} E_\beta + \tfrac{1}{2}\beta_{\alpha\beta\gamma}^{(p,i)} E_\beta E_\gamma + \tfrac{1}{6}\gamma_{\alpha\beta\gamma\delta}^{(p,i)} E_\beta E_\gamma E_\delta + \ldots;$$ (6.7)

by eq. (6.4), this yields

$$B_m^0 = \frac{2\pi N}{45}\left\{2\sum_i x_i \gamma_{\alpha\alpha\beta\beta}^{(i)} + \frac{1}{kT}\sum_{i,j} x_i \alpha_{\alpha\beta}^{(i)}\alpha_{\gamma\delta}^{(j)}\left\langle \sum_{q=1}^{x_jN}(3\omega_{\alpha\gamma}^{(1q;ij)}\omega_{\beta\delta}^{(1q;ij)} - \delta_{\alpha\beta}\delta_{\gamma\delta})\right\rangle\right\}.$$

(6.8)

Neglecting herein the term accounting for the hyperpolarizability γ, the following expression is obtained for molecules presenting the axial symmetry:

$$B_m^0 = \frac{4\pi N}{5\,kT} \sum_{i,j} \alpha_{(i)}\,\alpha_{(j)}\,\delta_{\alpha(i)}\,\delta_{\alpha(j)}\,\{x_i\,\delta_{ij}{}' +$$

$$+ \tfrac{1}{2}\,x_i\,x_j \int (3\cos^2\Theta_{ij} - 1)\,g_{ij}(\tau)\,d\tau\}; \tag{6.9}$$

for a one-component system, the latter expression becomes identical with the one derived by Buckingham (1956)[2].

In the case of scattering molecules whose linear dimensions are small as compared to the light wavelength λ, the molecular factor of anisotropic light scattering as given by eq. (2.11) assumes the form

$$F_{\text{anis}} = \frac{1}{2}\,(3\,\delta_{\alpha\gamma}\,\delta_{\beta\delta} - \delta_{\alpha\beta}\,\delta_{\gamma\delta}) \sum_{i,j} \left\langle \sum_{p=1}^{x_iN} \sum_{q=1}^{x_jN} \frac{\partial m_\alpha^{(p,i)}}{\partial E_\beta}\frac{\partial m_\gamma^{(q,j)}}{\partial E_\delta} \right\rangle. \tag{6.10}$$

If, on the other hand, the first term relating to the hyperpolarizability of the molecules be omitted in the general expression (6.4) for B_m^0, we have, by eq. (6.10).

$$F_{\text{anis}} = \frac{45\,kT}{4\,\pi}\,B_m^0. \tag{6.11}$$

Eq. (6.11) relates the molecular factor of anisotropic light scattering and the molecular constant of optico-optical birefringence, and holds for an isotropic medium of arbitrary density.

With respect to eq. (6.11), the molecular constant of light scattering (6.3) is now given by

$$S_m = \frac{12\pi^3}{\lambda^4}\,kT\frac{1+D}{D}\,B_m^0. \tag{6.12}$$

By eqs. (6.2) and (6.6), the latter relation can now be expressed in constants that are accessible to measurement:

$$S = \frac{72\pi^3\,n^2\,kT(1+D)}{\lambda^4\,(n^2+2)^2\,D}\,B^0. \tag{6.13}$$

The foregoing relations contain no molecular quantities explicitly, and hence can be conveniently subjected to direct experimental checking. If the values of S and D are known experimentally, eq. (6.13) yields that of the optico-optical birefringence constant B^0. On the other hand, for non-polar substances, B^0 can be expressed by Kerr's constant K:

$$B^0 = \frac{(n^2-1)\,(n^2+2)}{(\varepsilon-1)\,(\varepsilon+2)}\,K. \tag{6.14}$$

[2]) The quantity L computed by Buckingham (1956) differs from B_m^0 by the factor 1/9, i. e. $B_m^0 = 9L$.

7. Relation between light scattering and molecular refraction

From eqs. (2.18) and (2.19), we have the following relation:

$$S = \frac{8\pi^4 (n^2 + 2)^2}{81\lambda^4 V} \frac{6 + 6D}{6 - 7D} F_{is},$$
(7.1)

wherein $(6+6D)/(6-7D)$ is the Cabannes factor (1929). In the foregoing relation, the factor F_{is} is the only quantity to contain molecular parameters. It will now be proved that the molecular factor of isotropic light scattering F_{is} can be expressed in terms of the molecular refraction of the medium

$$R_m = \frac{n^2 - 1}{n^2 + 2} V.$$
(7.2)

For a multi-component condensed system, the molecular theory yields the following general expression for R_m:

$$R_m = \frac{4\pi}{9} N \sum_i x_i \left\langle \frac{\partial m_\alpha^{(i)}}{\partial E_\alpha} \right\rangle.$$
(7.3)

Hence, with the models discussed in sections 4 and 5, the following relations are derived for dipole molecules:

$$R_m = \frac{4\pi}{3} N \sum_i x_i \left\{ \alpha_{(i)} + \chi_{(i)} \frac{\mu_{(i)} \beta_{(i)}}{\alpha_{(i)}} + ... \right\},$$
(7.4)

and, for quadrupole molecules:

$$R_m = \frac{4\pi}{3} N \sum_i x_i \left\{ \alpha_{(i)} + \frac{5}{2} \eta_{(i)} \frac{\gamma_{(i)} \Theta_{(i)}^2}{\alpha_{(i)}^{8/3}} + ... \right\}.$$
(7.5)

From these relations it is seen that the molecular refraction of a condensed system and the factor of isotropic light scattering given by eq. (4.13) or (5.13) are expressed in terms of the same molecular quantities.

Now, restricting the problem, for simplicity, to that of a one-component system, we obtain by eqs. (7.4) and (7.5)

$$\frac{R_m - {}_{gas}R_m}{{}_{gas}R_m} = \chi \frac{\mu \beta}{\alpha^2},$$
(7.6)

$$\frac{R_m - {}_{gas}R_m}{{}_{gas}R_m} = \frac{5}{2} \eta \frac{\gamma \Theta^2}{\alpha^{11/3}},$$
(7.7)

wherein

$$_{gas}R_m = \frac{4\pi}{3} N \alpha$$
(7.8)

denotes the molecular refraction of an ideal gas.

The foregoing expression together with the factor F_{is} as given by eq. (4.16) or (5.16) yield the required relationship:

$$F_{is} = \frac{81}{16\,\pi^2} \left\{ 1 + 2 \left(\frac{R_m - {}_{gas}R_m}{{}_{gas}R_m} \right) \right\} {}_{gas}R_m^2 \frac{RT\beta_T}{NV}, \qquad (7.9)$$

which holds for either of the models under consideration.

By eq. (7.9), the scattering constant of eq (7.1) can be represented by the following formula:

$$S = \frac{\pi^2 (n^2 + 2)^2}{2\lambda^4 NV^2} \frac{6 + 6D}{6 - 7D} \left\{ 1 + 2 \left(\frac{R_m - {}_{gas}R_m}{{}_{gas}R_m} \right) \right\} {}_{gas}R_m^2 RT\beta_T, \qquad (7.10)$$

which contains no molecular quantities explicitly.

Similarly, by eq. (7.9) and the relation between F_{anis} and the anisotropic term in Kerr's constant,

$$F_{anis} = \frac{1215\, n^2 (n^2 - 1)\, kTV}{2\,\pi\,(\varepsilon - 1)\,(\varepsilon + 2)\,(n^2 + 2)^3} K_{anis}, \qquad (7.11)$$

we have, with respect to eq. (2.18):

$$\frac{\beta_T\,D}{6 - 7D} \left\{ 1 + 2 \left(\frac{R_m - {}_{gas}R_m}{{}_{gas}R_m} \right) \right\} = \frac{24\pi\, n^2\,(n^2 - 1)\,V^2\,K_{anis}}{(\varepsilon - 1)(\varepsilon + 2)(n^2 + 2)^3 {}_{gas}R_m^2}. \qquad (7.12)$$

The term $(R_m - {}_{gas}R_m)/{}_{gas}R_m$ in the latter equation accounts for the effect of the molecular field on light scattering by a condensed medium. More exactly, terms of the type of $\dfrac{\partial F_\alpha}{\partial E_\beta}$, ..., accounting for the anisotropy of the molecular field, have been neglected in the computation of F_{is} and F_{anis} in sections 4 and 5. In the first approximation, identical terms will appear in the expression for the molecular refraction R_m. Divergences will arise only in higher order approximations, but, as these additional contributions are extremely small, they may well be neglected. Hence, the expressions of (7.10) and (7.12) still remain valid if the effect of anisotropy of the molecular field on light scattering is taken into account. In the present case, however, the following term due to anisotropy of the molecular field should be added to the expressions of eqs. (7.6) and (7.7), which account for the difference between the molecular refraction of a substance and that of the perfect gas:

$$\left(\frac{R_m - {}_{gas}R_m}{{}_{gas}\,R_m} \right)_{anis} = \frac{1}{3\,\alpha} \left\langle \alpha_{\alpha\beta} \frac{\partial F_\alpha}{\partial E_\beta} \right\rangle = \frac{1}{3} \sum_{\alpha=1}^{3} \lambda_\alpha\,\psi_\alpha, \qquad (7.13)$$

wherein, for Onsager's model, we have (see Appendix A)

$$\psi_\alpha = \frac{2\,(n^2 - 1)^2\,(\lambda_\alpha - 1)}{(2\,n^2 + 1)\,(n^2 + 2) - 2\,(n^2 - 1)^2\,\lambda_\alpha}. \qquad (7.14)$$

For isotropically polarizable molecules $\lambda_\alpha = \alpha_\alpha/\alpha = 1$, and so the contribution resulting from anisotropy of the molecular field vanishes, i. e. $\psi_\alpha = 0$.

Neglecting fluctuations of the molecular field and fluctuations of its anisotropy, we have

$$R_m = {}_{gas}R_m = \frac{n^2 - 1}{n^2 + 2} V : \tag{7.15}$$

hence, eq. (7.10) yields the well-known Cabannes-King-Rocard formula (see Cabannes, 1929):

$$S = \frac{\pi^2 (n^2 - 1)^2}{2\lambda^4 N} \frac{6 + 6D}{6 - 7D} RT\beta_T , \tag{7.16}$$

whereas eq. (7.12) reduces to Gans' (1923) relation:

$$\frac{\beta_T D}{6 - 7D} = \frac{24\pi n^2 K_{anis}}{(n^2 - 1)(\varepsilon - 1)(n^2 + 2)(\varepsilon + 2)} . \tag{7.17}$$

In considering a condensed medium consisting of spherical molecules, eq. (7.9) should be replaced by

$$F_{is} = 9 \alpha^2 N \left\{ \frac{RT\beta_T}{V} + 2 \left(\frac{R_m - {}_{gas}R_m}{{}_{gas}R_m} \right) \right\}, \tag{7.18}$$

herein, we have approximately (cf. Buckingham and Stephen, 1957)

$$\frac{R_m - {}_{gas}R_m}{{}_{gas}R_m} = \frac{1}{3} \left\langle \frac{\partial F_\alpha^s}{\partial E_\alpha} \right\rangle = 2 \alpha^2 \int r^{-6} g(r) \, d\mathbf{r} + \dots , \tag{7.19}$$

$g(r)$ being the radial distribution function.

Buckingham and Stephen (1957) proved that, in the case under consideration, the factor of anisotropic light scattering can also be approximated by the quantity of eq. (7.19):

$$F_{anis}{}^r = \frac{9}{2} \alpha^2 N \left(\frac{R_m - {}_{gas}R_m}{{}_{gas}R_m} \right). \tag{7.20}$$

By substituting (7.18) and (7.20) in eqs. (2.18) and (2.19), the degree of depolarization[3])

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[3]) Eq. (7.21) for the degree of depolarization D differs from Buckingham and Stephen's (1957) formula by the larger numerical coefficient (27 as against 7) of the second term in the denominator. The difference arises from the fact that Buckingham and Stephen neglected the effect of the molecular field on isotropic light scattering. If the term due to fluctuations of the molecular field is numerically negligible with respect to the one accounting for fluctuations of the density, i.e. if $\frac{R_m - {}_{gas}R_m}{{}_{gas}R_m} << \frac{RT\beta_T}{V}$, eq. (7.21) reduces to

$$D = \frac{3}{5} \left(\frac{R_m - {}_{gas}R_m}{{}_{gas}R_m} \right) \frac{V}{RT\beta_T} = \frac{6 \alpha^2 V}{5 RT\beta_T} \int r^{-6} g(r) \, dr.$$

and Rayleigh's ratio are obtained as follows:

$$D = \frac{6\left(\frac{R_m - {}_{gas}R_m}{{}_{gas}R_m}\right)}{10\,\frac{RT\beta_T}{V} + 27\left(\frac{R_m - {}_{gas}R_m}{{}_{gas}R_m}\right)}, \qquad (7.21)$$

$$S = \frac{\pi^2\,(n^2+2)^2}{20\,\lambda^4\,NV}\left\{10\,\frac{RT\beta_T}{V} + 33\left(\frac{R_m - {}_{gas}R_m}{{}_{gas}R_m}\right)\right\}\,{}_{gas}R_m^2 \qquad (7.22)$$

The foregoing expressions hold for condensed substances consisting of spherical molecules. For the ideal gas, $D = 0$, whereas eq. (7.22) reduces to Rayleigh's (1899) well-known formula

$$S = \frac{\pi^2\,(n^2-1)^2}{2\,\lambda^4\,N}\,V = \frac{2\,\pi^2\,(n-1)^2}{\lambda^4\,N}\,V. \qquad (7.23)$$

Finally, as Kerr's constant for a condensed medium of spherical molecules is given by

$$K = \frac{\pi\,(n^2+2)^2\,(\varepsilon+2)^2\,N}{1215\,n^2\,V}\left\{10\,\gamma + \frac{81\,{}_{gas}P_m^2}{16\,\pi^2\,N^2\,kT}\left(\frac{R_m - {}_{gas}R_m}{{}_{gas}R_m}\right)\right\}, \qquad (7.24)$$

we have, by eq. (7.21),

$$K = \frac{2\,\pi\,(n^2+2)^2\,(\varepsilon+2)^2\,N}{243\,n^2\,V}\left\{\gamma + \frac{27\,{}_{gas}P_m^2\,\beta_T\,D}{16\,\pi^2\,NV\,(2-9\,D)}\right\}, \qquad (7.25)$$

wherein ${}_{gas}P_m = 4\pi/3\ N\alpha_e$ denotes the molecular electric polarisation of a gas consisting of spherical molecules of polarizability α_e.

If, for a given substance, Kerr's constant K and the degree of depolarisation D are known experimentally, eq. (7.25) yields the mean hyperpolarizability γ of a spherical molecule.

8. Discussion and conclusions

The formulas derived previously will now be applied to the aim of computing the hyperpolarizability of the carbon disulphide molecule. In the present case, we have the following numerical data: at $t = 20°C$, $n = 1.636$, $\varepsilon = 2.26$, $\beta_T = 92 \times 10^{-12}$ CGS, $D = 0.62$ (Weill, 1958), and $K = 12.1 \times 10^{-12}$ e. s. u. (Stuart and Volkmann, 1933); by eq. (7.12), this yields

$$\frac{R_m - {}_{gas}R_m}{{}_{gas}R_m} = 0.097.$$

By comparison with eqs. (7.) and (7.13) we have

$$\frac{1}{3}\sum_{\alpha=1}^{3}\lambda_\alpha\,\psi_\alpha + \frac{5}{2}\,\eta\,\frac{\gamma\,\Theta^2}{\alpha^{11/3}} = 0.097,$$

and hence, for $\alpha = 8.77 \times 10^{-24}$ cm^3 and the value of $\eta = 0.007$ as computed by eq. (5.18) and $\frac{1}{3} \sum_{\alpha=1}^{3} \lambda_\alpha \psi_\alpha = 0.084$, we obtain

$$\gamma \Theta^2 = 20.8 \times 10^{-86}.$$

On the other hand, the quadrupole moment of the CS_2 molecule can be computed numerically from the Debye formula (1920) for the constant a in the Van der Waals equation:

$$a = \frac{6\pi}{5} N^2 \frac{\alpha \Theta^2}{d^5},$$

wherein d is the diameter of the molecule. Since, for CS_2, $a = 11.3 \times 10^{12}$ dyne cm^4 and $d = 3.86$ Å, Debye's formula yields

$$\Theta = 28 \times 10^{-26} \text{ e. s. u.}$$

With the quadrupole moment as computed above, the mean hyperpolarizability of the CS_2 molecule is

$$\gamma = 2.6 \times 10^{-36} \text{ e. s. u.}$$

Measurements by Blaker, Badger and Gilman (1949) of the constant of light scattering in CS_2 yield a value of $S = 151 \times 10^{-6}$ cm^{-1}, ($\lambda = 4358$ Å, $t = 25°C$); thus, by eq. (7.10), we have

$$\frac{R_m - {}_{gas}R_m}{{}_{gas}R_m} = 0.265.$$

On the other hand, with eqs. (7.7), (7.13) and the numerical values used above, this yields $\gamma = 36.5 \times 10^{-36}$, a value almost 14 times larger than that previously computed from eq. (7.12).

The quadrupole moment of the CS_2 molecule as evaluated above is certainly exaggerated. If a value of $\Theta = 6 \times 10^{-26}$ e. s. u. is assumed in place of $\Theta = 28 \times 10^{-26}$ e. s. u., eq. (7.12) yields $\gamma = 56.5 \times 10^{-36}$ e. s. u. (instead of 2.6×10^{-36} e. s. u.), which is a value not far remote from that of $\gamma = 54.4 \times 10^{-36}$ e. s. u. computed by Buckingham and Raab (1957) from Kerr's constant.

For CCl_4 at $t = 20°C$, we have $\beta = 105 \times 10^{-12}$ cgs, $\alpha = 10.5 \times 10^{-24}$ cm^3, $n = 1.461$, $\varepsilon = 2.24$, $D = 0.06$ (Krishnan, 1925), $K = 31.4 \times 10^{-14}$ e. s. u. (Stuart and Volkmann, 1933); hence, eq. (7.25) yields a value of $\gamma = 4.7 \times 10^{-36}$ e. s. u. for the mean hyperpolarizability of the CCl_4 molecule. Buckingham and Pople (1955) computed the mean hyperpolarizability of the CH_4 molecule from the molecular Kerr constant of the gas, obtaining a value of $\gamma = 2.6 \times 10^{36}$ e. s. u.

From the discussion of the foregoing examples it is seen that parallel theoretical and experimental investigation of light scattering in liquids can lead to the numerical evaluation of the hyperpolarizability of the molecules or of their quadrupole moments. The foregoing molecular theory of light scattering proves that investigation of light

scattering in multi-component systems can provide equally interesting information on the electro-optical properties of molecules of various kinds and on the nature of the forces with which they interact.

It results from the present paper that, in a multi-component system, in addition to light scattering on fluctuactions of the density and concentration and on those of the anisotropy and orientation of the molecules, an essential part is played by light scattering on fluctuations of the anisotropy of the molecular field and by scattering related to higher order effects such as hyperpolarizability of the dipoles or polarizability of the molecular quadrupoles.

Acknowledgments

Appendix A. The Effect of Molecular Field Anisotropy on Light Scattering in Liquids

The terms omitted in the computations of sections 4 and 5 and relating to anisotropy of the molecular field will now be considered. The expansion of eq. (4.1) or (5.1), if higher order terms are neglected, yields

$$\frac{\partial m_\alpha^{(p,i)}}{\partial E_\chi} = \alpha_{\alpha\chi}^{(p,i)} + \alpha_{\alpha\beta}^{(p,i)}\frac{\partial F_\beta^{(p,i)}}{\partial E_\chi} + ..., \tag{A.1}$$

whence eqs. (2.10) and (2.11) assume the form

$$F_{is}(s) = \sum_{i,j} \left\langle \sum_{p=1}^{x_iN} \sum_{q=1}^{x_jN} \left\{ \alpha_{\alpha\alpha}^{(i)}\alpha_{\beta\beta}^{(j)} + \alpha_{\alpha\alpha}^{(i)}\alpha_{\beta\gamma}^{(j)}\frac{\partial F_\gamma^{(j)}}{\partial E_\beta^{(j)}} + \alpha_{\beta\beta}^{(j)}\alpha_{\alpha\gamma}^{(i)}\frac{\partial F_\gamma^{(i)}}{\partial E_\alpha^{(i)}} \right. \right.$$

$$\left. \left. + \alpha_{\alpha\gamma}^{(i)}\alpha_{\beta\delta}^{(j)}\frac{\partial F_\gamma^{(i)}}{\partial E_\alpha^{(i)}}\frac{\partial F_\delta^{(j)}}{\partial E_\beta^{(j)}} + ... \right\} \cos \boldsymbol{s}\cdot\boldsymbol{r}_{ij}^{(pq)} \right\rangle, \tag{A.2}$$

$$F_{anis}(s) = \frac{1}{2}\sum_{i,j} \left\langle \sum_{p=1}^{x_iN} \sum_{q=1}^{x_jN} \left\{ \alpha_{\alpha\beta}^{(i)}\alpha_{\gamma\delta}^{(j)} + \alpha_{\alpha\beta}^{(i)}\alpha_{\gamma\varepsilon}^{(j)}\frac{\partial F_\varepsilon^{(j)}}{\partial E_\gamma^{(j)}} + \alpha_{\gamma\delta}^{(j)}\alpha_{\alpha\varepsilon}^{(i)}\frac{\partial F_\varepsilon^{(i)}}{\partial E_\beta^{(i)}} \right. \right.$$

$$\left. \left. + \alpha_{\alpha\varepsilon}^{(i)}\alpha_{\gamma\eta}^{(j)}\frac{\partial F_\varepsilon^{(i)}}{\partial E_\beta^{(i)}}\frac{\partial F_\eta^{(j)}}{\partial E_\delta^{(j)}} + ... \right\} (3\,\omega_{\alpha\gamma}^{(pq;ij)}\omega_{\beta\delta}^{(pq;ij)} - \delta_{\alpha\beta}\,\delta_{\gamma\delta})\cos\boldsymbol{s}\cdot\boldsymbol{r}_{ij}^{(pq)} \right\rangle.$$

The quantities $\dfrac{\partial F_\alpha^{(i)}}{\partial E_\beta^{(i)}}$ herein account for the anisotropy of the molecular field and are readily computed from Onsager's (1936) model. Namely, we have

$$F_\alpha^{(i)} = \psi_\alpha^{(i)} E_\alpha^{(i)}, \tag{A.3}$$

wherein

$$\psi_\alpha^{(i)} = \frac{9\, n^2\, (n_i^2 + 2) - (n^2 + 2)\, [(2\, n^2 + 1)\, (n_i^2 + 2) - 2\, (n^2 - 1)\, (n_i^2 - 1)\, \lambda_\alpha^{(i)}]}{(n^2 + 2)\, [(2\, n^2 + 1)\, (n_i^2 + 2) - 2\, (n^2 - 1)\, (n_i^2 - 1)\, \lambda_\alpha^{(i)}]}$$

(A.4)

is the parameter of the molecular field anisotropy. For a one-component system $n_i = n$, and eq. (A.4) reduces to (7.14), whilst eq. (A.3) yields the expression (7.13) for molecular refraction.

Restricting the problem, for simplicity, to the case of a one-component system, and neglecting short range angular correlations, we have, by eq. (A.3),

$$F_{is} = 9\, \alpha^2 \left\{ 1 + \frac{2}{3} \sum_{\alpha=1}^{3} \lambda_\alpha\, \psi_\alpha + \frac{1}{9} \sum_{\alpha,\beta=1}^{3} \lambda_\alpha\, \lambda_\beta\, \psi_\alpha\, \psi_\beta \right\} \frac{N}{V}\, RT\beta_T,$$

$$F_{anis} = \frac{\alpha^2}{2} \left\{ 3 \sum_{\alpha=1}^{3} \lambda_\alpha^2 - \sum_{\alpha,\beta=1}^{3} \lambda_\alpha\, \lambda_\beta + 2 \left(3 \sum_{\alpha=1}^{3} \lambda_\alpha^2\, \psi_\alpha - \sum_{\alpha,\beta=1}^{3} \lambda_\alpha\, \lambda_\beta\, \psi_\beta \right) + \right.$$

$$\left. + 3 \sum_{\alpha=1}^{3} \lambda_\alpha^2\, \psi_\alpha^2 - \sum_{\alpha,\beta=1}^{3} \lambda_\alpha\, \lambda_\beta\, \psi_\alpha\, \psi_\beta \right\} N,$$

(A.5)

wherein ψ_α is given by eq. (7.14).

For molecules possessing the axial symmetry, the foregoing expressions reduce to

$$F_{is} = 9\alpha^2 \left\{ 1 + \frac{1}{3}\, (\lambda_{||}\, \psi_{||} + 2\lambda_\perp \psi_\perp) \right\}^2 \frac{N}{V}\, RT\beta_T,$$

$$F_{anis} = 9\alpha^2\, \delta_\alpha^2 \left\{ 1 + \left(\frac{\lambda_{||}\, \psi_{||} - \lambda_\perp\, \psi_\perp}{\lambda_{||} - \lambda_\perp} \right) \right\}^2 N,$$

(A.6)

with $\lambda_{||} = \lambda_3$, $\lambda_\perp = \lambda_1 = \lambda_2$ and $\psi_{||} = \psi_3$, $\psi_\perp = \psi_1 = \psi_2$.

The effect of fluctuations of the molecular field anisotropy on isotropic light scattering (F_{is}) in benzene amounts to no more than 3 %; the respective figure for CS_2 attains, however, 18 %. Fluctuations of the molecular field anisotropy yield a far greater contribution to anisotropic light scattering (F_{anis}), one amounting to e. g. 28 % in benzene, and to as much as 87 % in CS_2.

Appendix B. On the Effect of the Molecular Polarizability Due to the Reaction Field Gradient on Light Scattering

The author is indebted to Dr A. D. Buckingham for kindly directing his attention to the necessity, in the computations of Section 5, of accounting for the dipole moment induced in the molecule by the gradient of the reaction field (cf. eq. (5.4)). This involves the term containing the tensor $B_{\alpha\beta:\gamma\delta}$ intervening in the effect of optical

birefringence induced in the medium by the gradient of a constant external electric field, as computed recently by Buckingham (1959).

For simplicity, only a one-component medium will be considered. With Buckingham's (1959) general expression for the total dipole moment, $m_\alpha^{(r)}$ the total differential polarizability of the molecule is obtained in the form

$$\left(\frac{m\partial_\alpha^{(p)}}{\partial E_\chi}\right)_{E=0} = \left\{\alpha_{\alpha\beta}^{(p)} + \beta_{\alpha\beta\gamma}^{(p)} F_\gamma^{(p)} + \frac{1}{2} \gamma_{\alpha\beta\gamma\delta}^{(p)} F_\gamma^{(p)} F_\delta^{(p)} + \right.$$
$$\left. + \frac{1}{3} B_{\alpha\beta:\gamma\delta}^{(p)} F_{\gamma\delta}^{(p)} + ...\right\} \left(\delta_{\beta\chi} + \frac{\partial F_\beta^{(p)}}{\partial E_\chi}\right)_{E=0}. \tag{B.1}$$

The tensor $B_{\alpha\beta:\gamma\delta}$ is symmetrical in the pairs of indices $\alpha\beta$ and $\gamma\delta$, and accounts for the additional polarization of the molecule as induced by the field gradient $F_{\alpha\beta}^{(p)} = \partial F_\alpha^{(p)}/\partial r_\beta$. A discussion of the relations between the components of the tensors in eq. (B.1), for molecules having the spherical or axial symmetry, is to be found in the paper by Buckingham (1959).

Substituting the expansion of eq. (B.1) in eqs. (2.10) and (2.11), and neglecting short range angular correlations, the following expressions for non-dipolar molecules are obtained:

$$F_{is} = \left\{\alpha_{\alpha\alpha}\alpha_{\beta\beta} + \alpha_{\alpha\alpha}\gamma_{\beta\beta\gamma\delta}\overline{F_\gamma F_\delta} + \frac{2}{3}\alpha_{\alpha\alpha}B_{\beta\beta:\gamma\delta}\overline{F}_{\gamma\delta} + ...\right\}\frac{N}{V} RT\beta_T,$$

$$F_{anis} = \tfrac{1}{2}\left\{3\alpha_{\alpha\beta}\alpha_{\alpha\beta} - \alpha_{\alpha\alpha}\alpha_{\beta\beta} + (3\alpha_{\alpha\beta}\gamma_{\alpha\beta\delta} - \alpha_{\alpha\alpha}\gamma_{\beta\beta\gamma\delta})\overline{F_\gamma F_\delta} + \right. \tag{B.2}$$
$$\left. + \tfrac{2}{3}(3\alpha_{\alpha\beta}B_{\alpha\beta:\gamma\delta} - \alpha_{\alpha\alpha}B_{\beta\beta:\gamma\delta})\overline{F}_{\gamma\delta} + ...\right\} N.$$

For molecules whose axis of symmetry is in the direction of the 3-axis, the foregoing expressions reduce to

$$F_{is} = 3\alpha\left\{3\alpha + (\gamma_{33\alpha\beta} + 2\gamma_{11\alpha\beta})\overline{F_\alpha F_\beta} + ...\right\}\frac{N}{V} RT\beta_T,$$

$$F_{anis} = (\alpha_{||} - \alpha_\perp)\left\{\alpha_{||} - \alpha_\perp + (\gamma_{33\alpha\beta} - \gamma_{11\alpha\beta})\overline{F_\alpha F_\beta} + \right.$$
$$\left. + \tfrac{2}{3}(B_{33:\alpha\beta} - B_{11:\alpha\beta})\overline{F}_{\alpha\beta} + ...\right\} N. \tag{B.3}$$

The former is identical with the one derived by Buckingham and Stephen (1957), whilst the latter one differs therefrom by an additional term containing the tensor $B_{\alpha\beta:\gamma\delta}$.

The field F_α and field gradient $F_{\alpha\beta}$ are computed with respect to Onsager's (1936) model:

$$F_\alpha = R_\alpha + R_{\alpha\beta} r_\beta + ... \tag{B.4}$$

wherein (cf. Onsager, 1936)

$$R_\alpha = \frac{2(\varepsilon - 1)}{2\varepsilon + 1}\frac{m_\alpha}{a^3} = f m_\alpha \tag{B.5}$$

is the reaction field, and (cf. Buckingham, 1959)

$$R_{\alpha\beta} = \frac{6\,(\varepsilon - 1)}{3\,\varepsilon + 2}\,\frac{\Theta_{\alpha\beta}}{a^5} = h\,\Theta_{\alpha\beta} \qquad (B.6)$$

is the reaction field gradient inside a spherical cavity of radius a in a continuous medium of electric permittivity ε due to a dipole and a quadrupole of, moments m_α and $\Theta_{\alpha\beta}$ at the center.

Neglecting the quadrupole induced, eq. (B.4) yields, for anisotropically polarized polar molecules,

$$F_\alpha = \frac{f}{1 - f\alpha\,\lambda_\alpha}\,\mu_\alpha + \frac{h}{1 - f\alpha\,\lambda_\alpha}\,\Theta_{\alpha\beta}\,r_\beta, \qquad (B.7)$$

whence

$$F_{\alpha\beta} = \frac{\partial F_\alpha}{\partial r_\beta} = \frac{h}{1 - f\alpha\,\lambda_\alpha}\,\Theta_{\alpha\beta}. \qquad (B.8)$$

Substituting the foregoing in eqs. (B.3) yields finally

$$F_{\text{is}} = 9\,\alpha^2\left\{1 + 5\,\eta\,\frac{\gamma\Theta^2}{\alpha^{11/3}}\right\}\frac{N}{V}\,RT\beta_T, \qquad (B.9)$$

$$F_{\text{anis}} = 9\,\alpha^2\,\delta_\alpha^2\left\{1 + \frac{7}{2}\,\eta\,\frac{\gamma\delta_\gamma\,\Theta^2}{\alpha^{11/3}\,\delta_\alpha} + \frac{1}{2}\,\xi\,\frac{B\Theta}{\alpha^{8/3}\,\delta_\alpha}\right\}N, \qquad (B.10)$$

where η is given by (5.18) and:

$$\xi = \frac{1}{3}\,(\xi_1 + 2\,\xi_3) = \left(\frac{2\,\varepsilon + 1}{3\,\varepsilon + 2}\right)\left(\frac{n^2 - 1}{n^2 + 2}\right)^{3/2}(\chi_1 + 2\,\chi_3). \qquad (B.11)$$

Until the numerical values of the quantities $3\,\gamma\delta_\gamma = \gamma_{||} - \gamma_\perp$ and $B = B_{33:33}$ are known it is difficult to say which of the terms in eq. (B.10) plays the greater part. It seems reasonable that both are of the same order of magnitude.

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Note added in proof.

1. An account of the flucuation theory of isotropic scattering in binary fluid mixtures and of its application to critical opalescence is to be found in the following papers: Pearson, F. J. and Rushbrooke, G. S., *Proc. Roy. Soc.* [Edinburgh]. A **64**, 305 (1957); and Pearson, F. J., *Proc. Phys. Soc.* **75**, 633 (1960), which became available to the author thanks to the kindness of Dr. F.J. Pearson after the present had been handed in for printing. The foregoing papers contain i.a.a detailed discussion of the equation for I(s), as analogous to eq. (2.13), for the case when F_{is} is given by (3.12) and $F_{anis} = 0$.

2. The computations leading from the general formulas (5.2) and (5.3) to eqs. (5.13) and (5.14) were carried out on certain simplifying assumptions not explicitly stated. These will be discussed in a separate supplementary note, wherein, moreover, the factors F_{is} and F_{anis} will be derived without these assumptions.