A MOLECULAR THEORY OF LIGHT SCATTERING IN GASES AND LIQUIDS

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The general principles of a statistical-molecular theory of light scattering in an isotropic medium consisting of polar-anisotropic molecules are given.

A general, fundamental equation for the scattered intensity I is derived, containing the molecular factors F_{is} and F_{anis} which account for isotropic and anisotropic light scattering as brought about by the molecules of the medium. The molecular factors F_{is} and F_{anis} are discussed in detail for the case of gases and liquids possessing molecules whose linear dimensions are small with respect to the light wave-length. In such gases and liquids, F_{is} depends on the mean polarizability of the molecule and on the radial intermolecular correlations, whereas F_{anis} depends on the symmetry and anisotropy of polarizability of the molecules and on the orientational intermolecular correlations. From the fundamental equation giving the scattered intensity, general expressions for the optical anisotropy Δ^2 and degree of depolarisation D of the scattered light, and for Rayleigh's ratio S and the extinction coefficient h are derived. For ideal gases, these expressions reduce to the known formulas of Rayleigh-Born-Cabannes. For liquids the molecules of which exhibit the axial symmetry, the expressions obtained for D, S and h differ from those of Cabannes-King-Rocard in the anisotropic term by the angular correlation factor R_{CM}, which also appears in the formulas for the Cotton-Mouton and Kerr constants. For compressed gases the molecular factors F_{is} and F_{anis} are expanded in inverse powers of the volume of the system. The coefficients of the expansion, A_S^{is}, A_S^{anis} and B_S^{is}, B_S^{anis}, termed, respectively, the first and second virial coefficients of isotropic and anisotropic light scattering, are computed for spherical molecules of variable polarizability and for axially symmetrical anisotropic molecules possessing a permanent dipole moment. Moreover, following Buckingham's method, the effect of the internal molecular field and the hyperpolarizability of the molecules on light scattering in liquids is accounted for. Finally, general relations between the quantities D, S and h and formulas relating these quantities and the anisotropic term in Kerr's constant K_{anis} are derived. The relations thus obtained contain no molecular parameters and may serve for checking the theory by experimental results.

1. Introduction

The theory of classical scattering, in which the wave-length of the light is preserved, is due to Lord Rayleigh (1899), who considered a gas of spherical, non-absorbing molecules of linear dimensions small with respect to the wave-length.

Smoluchowski (1908) was the first to prove that light scattering in optically homogeneous media arises from the spontaneous, thermal fluctuations of their density. Einstein (1910), who developed Smoluchowski's ideas, proposed a "phenomenological"

i. e. thermodynamical theory of scattering in liquids whose molecules are spherical[*].
Gans (1923) generalized the Smoluchowski-Einstein theory for anisotropic molecules.

The „molecular" or electronic theory of the scattering of light in gases and liquids possessing optically anisotropic molecules is due to Born (1917, 1933), Cabannes (1921, 1929), King (1923), Rocard (1928) and others.

Investigations by the foregoing authors proved that light scattering by a medium consisting, quite generally, of anisotropic molecules is given by the superposition of the scattering on fluctuations of its density and of the scattering occurring on fluctuations of the optical anisotropy of the molecules. Moreover, Rocard (1928) proved that scattering, especially in the neighbourhood of the critical point, is affected by the fluctuations of the intermolecular field. The foregoing theories assumed molecular interaction between the molecules, spherical or anisotropic, to depend solely on their mutual distances. Clearly this was a weak point of these theories, since both in real gases and in liquids consisting of anisotropic or polar-anisotropic molecules the interaction between the latter is strongly dependent on their mutual orientation. Hence, in addition to radial correlations, a theory of light scattering by condensed media should also account for orientational intermolecular correlations.

Müller (1936) was the first to consider orientational-molecular interaction, using the method of Fowler-Debye, in his theory of scattering in non-polar liquids. Anselm (1947), Benoit and Stockmayer (1956), and Prins and Prins (1956) proposed theories of the degree of depolarisation of light scattered by real gases and liquids, wherein the orientational-molecular interaction is described by Zernike and Prins' (1927) correlation function, as generalized to account for orientation (cf. also Volkensteyn, 1951, and Weill, 1958). Buckingham and Stephen (1957) proposed a general theory of the degree of depolarisation of light scattered by a dense medium; their theory accounts i. a. for scattering on assemblies of spherical molecules and for the effect of hyperpolarizability of the polar molecules.

In a former paper (Kielich, 1958a), the author proposed a generalization of Born's „gas" theory (1933) to liquids; therein, in addition to light scattering on fluctuations of the density and of the anisotropy of polarizability of the molecules, account is taken of scattering arising from the orientational interaction of molecules of arbitrary symmetry. In the present paper a general, statistical-molecular theory of light scattering in an isotropic medium consisting of anisotropic-polar molecules of arbitrary symmetry is proposed.

2. Fundamental Statistical-Molecular Theory of Light Scattering in an Isotropic Medium

We shall be considering an isotropic medium of volume V containing a large number N of identical, optically anisotropic, polar molecules. The origin 0 of the fixed system of reference (X_σ) is located at the centre of the volume. Let molecular

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[*] A molecular theory of light scattering by optically isotropic molecules of a fluid is given by Fixman (1955).

systems of reference $(x_i^{(p)})$, $p = 1, 2, \ldots N$ be rigidly attached to each molecule of the medium. The position and orientation of the molecules in volume V are given by their configurational variables $\tau = \tau\,(r, \omega)$; here, $r = \{r_1, r_2, \ldots r_N\}$ are those determining the position, whereas $\omega = \{\omega_1, \omega_2, \ldots \omega_N\}$ determine the orientation of the molecule.

The probability for a mutual configuration of the molecules in an element $d\tau$ of the configurational space is

$$dP\,(\tau) = f(\tau)\,d\tau,$$

with $f(\tau)$ being the configurational statistical distribution function. By classical statistical mechanics, we assume $f(\tau)$ to be given by Gibbs' canonical distribution function

$$f(\tau) = C\,e^{-\frac{U(\tau)}{kT}}, \tag{2.1}$$

wherein C is the normalisation constant, k — Boltzmann's constant, T — the Kelvin temperature of the system and $U(\tau)$ — its total potential energy.

Electric field of scattered light. Consider a parallel monochromatic light beam of electric field

$$E(t) = E\,e^{-i2\pi\nu t}$$

incident on the volume V of the medium. E denotes the electric field amplitude, ν — the frequency, and t — the time.

Thus, the electric field of the incident light beam at the centre of the p-th molecule of the medium situated at the distance r_p from the origin 0 of the system (X_σ) is of the form

$$E(t)^{(p)} = E\,e^{-i\,(2\pi\nu t\,-\,k\,\cdot\,r_p)}, \tag{2.2}$$

wherein

$$k = \frac{2\pi}{\lambda}\,s_0 = \frac{2\pi\nu}{c}\,s_0,$$

with c and λ denoting the velocity and wave-length of the incident light, respectively; s_0 is the unit vector in the direction of propagation.

The electric field given by (2.2) induces the time dependent dipole moment

$$m'(t)^{(p)} = m'^{(p)}\,e^{-i\,(2\pi\nu t\,-\,k\,\cdot\,r_p)} \tag{2.3}$$

within the p-th molecule of the volume V. Here, $m'^{(p)}$ is the amplitude of the dipole moment of the p-th molecule. By classical electrodynamics, the dipole induced in the molecule radiates electromagnetic waves in all directions. In the present paper, only Rayleigh scattering, i. e. scattered light of the same wavelength λ as that of the incident light will be considered.

At considerable distances from the scattering system, the electric field of the light wave scattered by the p-th molecule of the medium is of the form (cf. Born, 1933)

$$E'\,(t)^{(p)} = -\,\frac{4\pi^2}{\lambda^2\,R_p^3}\,\{R_p \times [R_p \times m'^{(p)}\,e^{-i\left(2\pi\nu t\,-\,k\,\cdot\,r_p\,-\,\frac{2\pi}{\lambda}\,R_p\right)}]\}, \tag{2.4}$$

wherein $R_p = R_0 - r_p$ is the vector directed from the centre of the p-th molecule to the point at which the radiation is observed. The latter point is at the distance R_0 from the origin 0 of the system (X_σ). The distance at which the point of observation is situated is great with respect to the linear dimensions l of the scattering volume and with respect to r_p; thus, the following expansion may be written:

$$R_p = |\boldsymbol{R}_0 - \boldsymbol{r}_p| = R_0 - \boldsymbol{s'} \cdot \boldsymbol{r}_p + |\boldsymbol{r}_p| \left\{ 0 \left(\frac{|\boldsymbol{r}_p|}{R_0} \right) + \ldots \right\}, \qquad (2.5)$$

wherein $\boldsymbol{s'}$ is the unit vector in the direction of the observation vector $\boldsymbol{R}_0 = \boldsymbol{s'} R_0$, thus determining the direction of propagation of the scattered wave.

If $R_0 \gg l \gg r_p$, then R_p may be replaced by R_0 everywhere in eq. (2.4) with the exception of the exponential factor, wherein, with respect to the expansion (2.5), the substitution is $R_p = R_0 - \boldsymbol{s'} \cdot \boldsymbol{r}_p$; this yields

$$\boldsymbol{E'}(t)^{(p)} = - \frac{4\pi^2}{\lambda^2 R_0} e^{-i 2\pi \left(\nu t - \frac{R_0}{\lambda} \right)} \{ \boldsymbol{s'} \times (\boldsymbol{s'} \times \boldsymbol{m'}^{(p)} e^{i(\boldsymbol{k} - \boldsymbol{k'}) \cdot \boldsymbol{r}_p}) \}, \qquad (2.6)$$

with

$$\boldsymbol{k'} = \frac{2\pi}{\lambda} \boldsymbol{s'} = \frac{2\pi \nu}{c} \boldsymbol{s'}$$

denoting the wave vector of the scattered light.

By eq. (2.6), the total electric field resulting from the light wave scattered by all the molecules in volume V at the point of observation is given by

$$\boldsymbol{E'}\left(t + \frac{R_0}{c} \right) = - \frac{4\pi^2}{\lambda^2 R_0} \{ \boldsymbol{s'} \times (\boldsymbol{s'} \times \boldsymbol{M} e^{-i 2\pi \nu t}) \}, \qquad (2.7)$$

wherein

$$\boldsymbol{M} = \sum_{p=1}^{N} \boldsymbol{m'}^{(p)} e^{i(\boldsymbol{k} - \boldsymbol{k'}) \cdot \boldsymbol{r}_p} \qquad (2.8)$$

denotes the amplitude of the total dipole moment induced in the medium of volume V by the electric field of the incident light wave of amplitude $\boldsymbol{E}$.

Intensity of scattered light. We shall now consider the total intensity of the light scattered by the volume V, in order to determine the component thereof transmitted by a Nicol prism analyzer at the point of observation. Let the direction of the vibration transmitted by the nicol be that determined by the unit vector $\boldsymbol{n}$ perpendicular to the vector of observation $\boldsymbol{R}_0 = R_0 \, \boldsymbol{s'}$. Since now $\boldsymbol{s'} \cdot \boldsymbol{n} = 0$, the component of the electric field $\boldsymbol{E'}$ in the direction of the unit vector $\boldsymbol{n}$ is given by:

$$\boldsymbol{E'} \cdot \boldsymbol{n} = \frac{4\pi^2}{\lambda^2 R_0} \boldsymbol{M} \cdot \boldsymbol{n} \, e^{-i 2\pi \nu t}. \qquad (2.9)$$

The intensity of the light scattered by the volume V of an isotropic medium and transmitted by a nicol is defined as follows:

$$I_n \equiv \langle E' \cdot n \, (E' \cdot n)^* \rangle_E \; ; \tag{2.10}$$

herein, the symbol $\langle \quad \rangle_E$ stands for the statistical mean value in the presence of the electric field E of the incident light beam, and the asterisk denotes a complex conjugate. Let $\Phi = \Phi(\tau, E)$ denote an arbitrary state function of the system in the presence of the electric field E; then, with Gibbs' distribution (2.1), the statistical mean value of Φ is determined at thermodynamical equilibrium of the system as follows:

$$\langle \Phi \rangle_E = C \int \int \dots \int \Phi(\tau, E) e^{-\frac{U(\tau, E)}{kT}} \, d\tau_1 \, d\tau_2 \dots d\tau_N; \tag{2.11}$$

here, $U(\tau, E)$ is the total potential energy of the system under consideration in the presence of the electric field E of the incident light wave.

Substituting (2.9) in (2.10), the fundamental equation for I_n may be written as follows in tensor notation:

$$I_n = \frac{1}{R_0^2} \left(\frac{2\pi}{\lambda} \right)^4 \langle M_\sigma M_\tau n_\sigma n_\tau \rangle, \tag{2.12}$$

the summation indices σ, τ assuming the values 1, 2, 3.

At not too great intensities of the incident light, the dipole moment M induced within the volume V may be assumed to be a linear function of the electric field E. The dipole moment may then be written as follows:

$$M_\sigma(\tau, E) = A_{\sigma\tau} E_\tau = A_{\sigma\tau} e_\tau E, \tag{2.13}$$

wherein

$$A_{\sigma\tau} = \left(\frac{\partial M_\sigma}{\partial E_\tau} \right)_{E=0} \tag{2.14}$$

is the tensor of the optical polarizability of the medium of volume V, and e is the unit vector in the direction of the electric field, $E = e \, E$.

By (2.13), eq. (2.12) yields for a spherical scattering sample of volume V in vacuum

$$I_n = \frac{I_0}{R_0^2} \left(\frac{2\pi}{\lambda} \right)^4 \left(\frac{n^2 + 2}{3} \right)^2 \langle A_{\sigma\tau} A_{\nu\varrho}^* n_\sigma e_\tau n_\nu e_\varrho \rangle, \tag{2.15}$$

wherein $I_0 = \left(\dfrac{3}{n^2 + 2} \right)^2 EE^*$ is the incident light intensity within the spherical sample of refractive index n; the symbol $\langle \; \rangle$ without lower indice denotes the statistical mean value in the absence of an electric field ($E = 0$):

$$\langle \Phi \rangle = C \int \int \dots \int \Phi(\tau) e^{-\frac{U(\tau)}{kT}} \, d\tau_1 \, d\tau_2 \dots d\tau_N. \tag{2.16}$$

Since the unit vectors n and e satisfy the relations

$$e_\sigma n_\sigma = \cos \Omega_{en} , \quad e_\sigma e_\sigma = n_\sigma n_\sigma = 1,$$

averageing over all possible directions of $\boldsymbol{n}$ and $\boldsymbol{e}$ with respect to the fixed system of reference (X_σ) yields

$$\overline{n_\sigma e_\tau n_\nu e_\varrho} = \frac{1}{30} \{(3 \cos^2 \Omega_{en} - 1)(\delta_{\sigma\tau}\delta_{\nu\varrho} + \delta_{\sigma\varrho}\delta_{\nu\tau}) + 2(2 - \cos^2 \Omega_{en})\delta_{\sigma\nu}\delta_{\tau\varrho}\}, \quad (2.17)$$

with Ω_{en} denoting the angle subtended by the unit vectors $\boldsymbol{e}$ and $\boldsymbol{n}$, and $\delta_{\sigma\tau}$ being Kronecker's symbol:

$$\delta_{\sigma\tau} = \begin{cases} 1 \text{ for } \sigma = \tau \\ 0 \text{ for } \sigma \neq \tau \end{cases}.$$

The optical polarizability tensor $A_{\sigma\tau}$ being Hermitian, $A_{\sigma\tau} = A_{\tau\sigma}^*$, and with respect to (2.17), eq. (2.15) yields the following general, fundamental equation for the intensity of the light scattered by an isotropic medium:

$$I_n = Q \{5 \cos^2 \Omega_{en} F_{is} + (3 + \cos^2 \Omega_{en}) F_{anis}\}, \quad (2.18)$$

wherein

$$F_{is} = \langle \delta_{\sigma\tau} \delta_{\nu\varrho} A_{\sigma\tau} A_{\nu\varrho}^* \rangle, \quad (2.19)$$

$$F_{anis} = \tfrac{1}{2} \langle (3\delta_{\sigma\nu} \delta_{\tau\varrho} - \delta_{\sigma\tau} \delta_{\nu\varrho}) A_{\sigma\tau} A_{\nu\varrho}^* \rangle, \quad (2.20)$$

with

$$Q = \frac{I_0}{45R_0^2} \left(\frac{2\pi}{\lambda}\right)^4 \left(\frac{n^2 + 2}{3}\right)^2. \quad (2.21)$$

The quantities F_{is} and F_{anis} will be termed the molecular factors of *isotropic* and *anisotropic* light scattering, respectively. With (2.8) and (2.14), F_{is} and F_{anis} may by rewritten in general form involving molecular parameters

$$F_{is}(s) = \left\langle \delta_{\sigma\tau} \delta_{\nu\varrho} \sum_{pq} \frac{\partial m_\sigma'^{(p)}}{\partial E_\tau^{(p)}} \left(\frac{\partial m_\nu'^{(q)}}{\partial E_\varrho^{(q)}}\right)^* e^{-i\boldsymbol{s} \cdot \boldsymbol{r}_{pq}} \right\rangle, \quad (2.22)$$

$$F_{anis}(s) = \frac{1}{2} \left\langle (3\delta_{\sigma\nu} \delta_{\tau\varrho} - \delta_{\sigma\tau} \delta_{\nu\varrho}) \sum_{pq} \frac{\partial m_\sigma'^{(p)}}{\partial E_\tau^{(p)}} \left(\frac{\partial m_\nu'^{(q)}}{\partial E_\varrho^{(q)}}\right)^* e^{-i\boldsymbol{s} \cdot \boldsymbol{r}_{pq}} \right\rangle, \quad (2.23)$$

wherein the quantity

$$\boldsymbol{s} \cdot \boldsymbol{r}_{pq} = (\boldsymbol{k} - \boldsymbol{k}') \cdot \boldsymbol{r}_{pq} \quad (2.24)$$

determines the difference in phase between the light scattered by the p-th and q-th molecules of the medium, with $\boldsymbol{r}_{pq} = \boldsymbol{r}_q - \boldsymbol{r}_p$ being the vector connecting their centres, and

$$\boldsymbol{s} = \boldsymbol{k} - \boldsymbol{k}' = \frac{2\pi}{\lambda} (\boldsymbol{s}_0 - \boldsymbol{s}'). \quad (2.25)$$

The polarizability tensor of a molecule immersed in the medium. As a first approximation, it may be assumed that within a moderately condensed medium the di-

pole moment is induced in the molecule only by the electric field $\boldsymbol{E}$ of the incident light wave. If the medium is a condensed one, however, an internal field $\boldsymbol{F}^{(p)}$ due to the charge distribution of all the other $N-1$ molecules and superimposing its effect on that of the field $\boldsymbol{E}^{(p)}$ appears and acts on the p-th molecule. The dipole moment induced in a molecule immersed within the condensed medium is given by (see Buckingham and Stephen 1957)

$$m_\sigma^{'(p)} = \alpha_{\sigma\alpha}^{(p)} (E_\alpha^{(p)} + F_\alpha^{(p)}) + \tfrac{1}{2} \beta_{\sigma\alpha\beta}^{(p)} (E_\alpha^{(p)} + F_\alpha^{(p)}) (E_\beta^{(p)} + F_\beta^{(p)}) + \tfrac{1}{6} \gamma_{\sigma\alpha\beta\gamma}^{(p)} (E_\alpha^{(p)} +$$

$$+ F_\alpha^{(p)}) (E_\beta^{(p)} + F_\beta^{(p)}) (E_\gamma^{(p)} + F_\gamma^{(p)}) + \dots \qquad (2.26)$$

where $\alpha_{\sigma\alpha}^{(p)}$ is the polarizability tensor, and $\beta_{\sigma\alpha\beta}^{(p)}$, $\gamma_{\sigma\alpha\beta\gamma}^{(p)}$ are the hyperpolarizability tensors describing the field dependence of the polarizability. These tensors are symmetric in all suffixes and have been discussed by Buckingham and Pople (1955 a).

The field $F_\alpha^{(p)}$ may be computed by Kirkwood's method (1936). Namely, if the medium consists of anisotropic-polar molecules, and considering only dipolar interactions, we have

$$F_\alpha^{(p)} = - \sum_{q=1}^{N} T_{\alpha\beta}^{(pq)} (\mu_\beta^{(q)} + m_\beta^{'(q)}) , \qquad (2.27)$$

wherein $\mu_\beta^{(q)}$ is the permanent electric dipole moment of the isolated molecule, and the tensor of dipolar interactions is given as follows:

$$T_{\alpha\beta}^{pq} = \frac{1}{r_{pq}^5} (r_{pq}^2 \delta_{\alpha\beta} - 3 r_{pq\alpha} r_{pq\beta}); \qquad (2.28)$$

the latter assumes non-zero values for $p \neq q$ and is zero for $p = q$.

From eqs. (2.26) and (2.27), the following formula is obtained for the field $F_\alpha^{(p)}$ at the centre of the p-th molecule of the medium:

$$F_\alpha^{(p)} = F_{o\alpha}^{(p)} - \sum_q T_{\alpha\beta}^{(pq)} \alpha_{\beta\gamma}^{(q)} E_\gamma^{(q)} + \sum_{qr} T_{\alpha\beta}^{(pq)} \alpha_{\beta\gamma}^{(q)} T_{\gamma\delta}^{(qr)} \alpha_{\delta\varepsilon}^{(r)} E_\varepsilon^{(r)} -$$

$$- \sum_{qrs} T_{\alpha\beta}^{(pq)} \alpha_{\beta\gamma}^{(q)} T_{\gamma\delta}^{(qr)} \alpha_{\delta\varepsilon}^{(r)} T_{\varepsilon\eta}^{(rs)} \alpha_{\eta\lambda}^{(s)} E_\lambda^{(s)} + \qquad (2.29)$$

$$+ \sum_{qrst} T_{\alpha\beta}^{(pq)} \alpha_{\beta\gamma}^{(q)} T_{\gamma\delta}^{(qr)} \alpha_{\delta\varepsilon}^{(r)} T_{\varepsilon\eta}^{(rs)} \alpha_{\eta\lambda}^{(s)} T_{\lambda\mu}^{(st)} \alpha_{\mu\varrho}^{(t)} E_\varrho^{(t)} - \dots$$

with $F_{o\alpha}^{(p)}$ denoting the intermolecular field existing at the centre of the p-th molecule immersed in the medium when the electric field $\boldsymbol{E}$ of the incident light wave is absent ($\boldsymbol{E} = 0$). The field $F_{o\alpha}^{(p)}$ is given quite generally as follows:

$$F_{o\alpha}^{(p)} = - \sum_{q=1}^{N} T_{\alpha\beta}^{(pq)} m_{o\beta}^{(q)}, \qquad (2.30)$$

wherein

$$m_{o\beta}^{(q)} = \mu_\beta^{(q)} + \alpha_{\beta\gamma}^{(q)} F_{0\gamma}^{(q)} + \dots \qquad (2.31)$$

is the total dipole moment of the molecule immersed in the medium at $\boldsymbol{E} = 0$, or explicitly:

$$F_{o\alpha}^{(p)} = -\sum_q T_{\alpha\beta}^{(pq)} \mu_\beta^{(q)} + \sum_{qr} T_{\alpha\beta}^{(pq)} \alpha_{\beta\gamma}^{(q)} T_{\gamma\delta}^{(qr)} \mu_\delta^{(r)} - $$
$$- \sum_{qrs} T_{\alpha\beta}^{(pq)} \alpha_{\beta\gamma}^{(q)} T_{\gamma\delta}^{(qr)} \alpha_{\delta\varepsilon}^{(r)} T_{\varepsilon\eta}^{(rs)} \mu_\eta^{(s)} + \dots \qquad (2.23)$$

By (2.26), the polarizability tensor of the p-th molecule immersed in the condensed medium is given as follows:

$$\left(\frac{\partial m_\sigma'^{(p)}}{\partial E_\chi^{(p)}}\right)_{E=0} = \left\{\alpha_{\sigma\alpha}^{(p)} + \beta_{\sigma\alpha\beta}^{(p)} F_{o\beta}^{(p)} + \frac{1}{2}\gamma_{\sigma\alpha\beta\gamma}^{(p)} F_{o\beta}^{(p)} F_{o\gamma}^{(p)} + \dots\right\}\left\{\delta_{\alpha\chi} + \frac{\partial F_\alpha^{(p)}}{\partial E_\chi^{(p)}}\right\}_{E=0}, \quad (2.33)$$

or, with respect to the expansion (2.29), explicitly:

$$\left(\frac{\partial m_\sigma'^{(p)}}{\partial E_\chi^{(p)}}\right)_{E=0} = \alpha_{\sigma\chi}^{(p)} - \sum_q \alpha_{\sigma\alpha}^{(p)} T_{\alpha\beta}^{(pq)} \alpha_{\beta\chi}^{(q)} e^{i\boldsymbol{k}\cdot\boldsymbol{r}_{pq}} + $$
$$+ \sum_{qr} \alpha_{\sigma\alpha}^{(p)} T_{\alpha\beta}^{(pq)} \alpha_{\beta\gamma}^{(q)} T_{\gamma\delta}^{(qr)} \alpha_{\delta\chi}^{(r)} e^{i\boldsymbol{k}\cdot\boldsymbol{r}_{pr}} - \sum_{qrs} \alpha_{\sigma\alpha}^{(p)} T_{\alpha\beta}^{(pq)} \alpha_{\beta\gamma}^{(q)} T_{\gamma\delta}^{(qr)} \alpha_{\delta\varepsilon}^{(r)} T_{\varepsilon\eta}^{(rs)} \alpha_{\eta\chi}^{(s)} e^{i\boldsymbol{k}\cdot\boldsymbol{r}_{ps}} + $$
$$+ \sum_{qrst} \alpha_{\sigma\alpha}^{(p)} T_{\alpha\beta}^{(pq)} \alpha_{\beta\gamma}^{(q)} T_{\gamma\delta}^{(qr)} \alpha_{\delta\varepsilon}^{(r)} T_{\varepsilon\eta}^{(rs)} \alpha_{\eta\lambda}^{(s)} T_{\lambda\mu}^{(st)} \alpha_{\mu\chi}^{(t)} e^{i\boldsymbol{k}\cdot\boldsymbol{r}_{pt}} - \dots \qquad (2.34)$$

The foregoing expansion shows the polarizability tensor of a molecule immersed in a condensed medium to be constant in the first approximation only; generally, however, this tensor is a function of the intermolecular field.

Potential energy of molecular interaction within the medium. From the definition of eq. (2.16), in order to compute effectively the molecular factors $F_{is}(s)$ and $F_{anis}(s)$ given by (2.22) and (2.23), respectively, the potential energy $U(\tau)$ of the mutual interaction existing between the N molecules immersed in the medium of volume V should be known. The energy $U(\tau)$ is dependent, in general, on the structure of the molecules and on the thermodynamical state of the medium, and, in principle, consists of two terms

$$U(\tau) = U^{(1)}(\boldsymbol{r}) + U^{(2)}(\boldsymbol{r},\omega), \qquad (2.35)$$

$U^1(\boldsymbol{r})$ denoting the potential energy inherent in *radial* interaction of the molecules only, and $U^2(\boldsymbol{r},\omega)$ denoting that due to *radial-orientational* interaction.

For $U^{(1)}(\boldsymbol{r})$, the Lennard-Jones potential (1924) is usually applied (cf. Pople, 1954), of the form

$$U^{(1)}(r) = 4\varepsilon^*\left\{\left(\frac{r_0}{r}\right)^{12} - \left(\frac{r_0}{r}\right)^6\right\}, \qquad (2.36)$$

wherein the first term represents the repulsive energies and the second — the attractive. The quantity ε^* represents the negative value of the lowest potential energy, r is the intermolecular distance and r_0 — the value of r at which the attractive and repulsive energies exactly balance.

It is customary to include in $U^{(2)}(\mathbf{r}, \omega)$ the energy of the Keesom dipole-dipole interaction, as well as those of the Debye-Falkenhagen permanent dipole-induced dipole interaction, the London anisotropic-dispersive interaction and, finally, the multipole molecular interactions. For anisotropic-dipolar molecules, by (2.32), Barker's expression (1953) in tensor notation is obtained for $U^{(2)}(\mathbf{r}, \omega)$:

$$U^{(2)}(\mathbf{r}, \omega) = \tfrac{1}{2} \sum_{pq} \mu_\alpha^{(p)} T_{\alpha\beta}^{(pq)} \mu_\beta^{(q)} - \tfrac{1}{2} \sum_{pqr} \mu_\alpha^{(p)} T_{\alpha\beta}^{(pr)} \alpha_{\beta\gamma}^{(r)} T_{\gamma\delta}^{(rq)} \mu_\delta^{(q)} +$$
$$+ \tfrac{1}{2} \sum_{pqrs} \mu_\alpha^{(p)} T_{\alpha\beta}^{(ps)} \alpha_{\beta\gamma}^{(s)} T_{\gamma\delta}^{(sr)} \alpha_{\delta\varepsilon}^{(r)} T_{\varepsilon\eta}^{(rq)} \mu_\eta^{(q)} - \ldots ; \qquad (2.37)$$

herein, the consecutive terms determine interaction within assemblies of two (pq), three (pqr), four $(pqrs)$, ... of the N molecules present within the volume V of the medium.

The fundamental equation (2.18) containing the factors $F_{\text{is}}(s)$ and $F_{\text{anis}}(s)$ as determined by (2.22) and (2.23), together with the polarizability tensor of the molecule as given by (2.33) and the potential energy of molecular interaction (2.35) jointly determine the general form of the statistical-molecular theory of light scattering by an isotropic medium of an arbitrary nature.

3. Light Scattering in Gases and Liquids.

Factors F_{is} and F_{anis} for molecules exhibiting constant polarizability. If the medium is but a moderately condensed one, the effect of the intermolecular field on the polarizability tensor of the molecule may be neglected in the expansion of eq. (2.34), and the expressions (2.22) and (2.23) may be written in the first approximation as follows:

$$F_{\text{is}}(s) = \left\langle \delta_{\sigma\tau} \delta_{\nu\varrho} \sum_{pq} \alpha_{\sigma\tau}^{(p)} \alpha_{\nu\varrho}^{(q)\star} e^{-i\mathbf{s}\cdot\mathbf{r}_{pq}} \right\rangle, \qquad (3.1)$$

$$F_{\text{anis}}(s) = \tfrac{1}{2} \left\langle (3\,\delta_{\sigma\nu} \delta_{\tau\varrho} - \delta_{\sigma\tau} \delta_{\nu\varrho}) \sum_{pq} \alpha_{\sigma\tau}^{(p)} \alpha_{\nu\varrho}^{(q)\star} e^{-i\mathbf{s}\cdot\mathbf{r}_{pq}} \right\rangle. \qquad (3.2)$$

For further discussion it is convenient to refer the tensor $\alpha_{\sigma\tau}^{(p)}$ (and, similarly, $\alpha_{\nu\varrho}^{(q)}$) to the molecular system $(x_i^{(p)})_{i=1,2,3}$ attached to the p-th (or, respectively, q-th) molecule of the medium. Thus, we have the following transformation formulas:

$$\alpha_{\sigma\tau}^{(p)} = \omega_{\sigma i}^{(p)} \omega_{\tau j}^{(p)} \alpha_{ij}^{(p)}, \quad \alpha_{\nu\varrho}^{(q)} = \omega_{\nu k}^{(q)} \omega_{\varrho l}^{(q)} \alpha_{kl}^{(q)} ; \qquad (3.3)$$

in the case under consideration, the fixed $(X_\sigma)_{\sigma=1,2,3}$ and molecular $(x_i^{(p)})_{i=1,2,3}$ systems being rectangular ones, the transformation coefficients $\omega_{\sigma i}^{(p)}, \ldots \omega_{\varrho l}^{(q)}$ have the meaning of the cosines of the angles subtended by the axes of these systems. The cosines satisfy the general relationship

$$\delta_{\sigma\nu} \omega_{\sigma i}^{(p)} \omega_{\nu k}^{(q)} = \omega_{\sigma i}^{(p)} \omega_{\sigma k}^{(q)} = \begin{cases} \delta_{ik} & \text{for } p = q, \\ \omega_{ik}^{(pq)} & \text{for } p \neq q, \end{cases} \qquad (3.4)$$

$\omega_{ik}^{(pq)}$ denoting the cosine of the angle subtended by the i-th and k-th axes of the systems $(x_i^{(p)})$ and $(x_k^{(q)})$ attached to the p-th and q-th molecules, respectively.

The tensor $\alpha_{ij}^{(p)}$ determines the constant polarizability of the isolated molecule, i. e. the polarizability independent of intermolecular fields. In optically inactive substances and throughout spectral ranges widely remote from those in which absorption appears, the tensor $\alpha_{ij}^{(p)}$ is symmetrical and real.

If all the scattering molecules present within the volume V are of one kind $\alpha_{ij}^{(p)} = \alpha_{ij}^{(q)} = \alpha_{ij}$, then, by (3.3) and (3.4), eqs. (3.1) and (3.2) may be rewritten as follows:

$$F_{\text{is}}(s) = \left\langle \alpha_{ii}\,\alpha_{jj} \sum_{pq} \frac{\sin sr_{pq}}{sr_{pq}} \right\rangle, \tag{3.5}$$

$$F_{\text{anis}}(s) = \frac{1}{2} \left\langle \alpha_{ij}\alpha_{kl} \sum_{pq} (3\omega_{ik}^{(pq)}\,\omega_{jl}^{(pq)} - \delta_{ij}\,\delta_{kl}) \frac{\sin sr_{pq}}{sr_{pq}} \right\rangle, \tag{3.6}$$

wherein

$$s = \frac{2\pi}{\lambda}\,|\mathbf{s_0} - \mathbf{s'}| = \frac{4\pi}{\lambda}\,\sin\frac{\vartheta}{2}\,; \tag{3.7}$$

ϑ denotes the angle between the direction of propagation $\mathbf{s_0}$ of the incident wave and that of the scattered wave $\mathbf{s'}$, and is termed the angle of scattering.

Isotropic light scattering. With the radial correlation function $g(r)$ introduced into the theory of X-ray scattering by Zernike and Prins (1927), eq. (3.5) yields

$$F_{\text{is}}(s) = \alpha_{ii}\,\alpha_{jj}\,N \left\{ 1 + 4\pi \int \frac{\sin sr}{sr} \left[g(r) - \frac{N}{V} \right] r^2\, dr \right\}, \tag{3.8}$$

wherein $g(r)\,4\pi\,r^2\,dr$ is the probability for the presence of a molecule within the volume element $4\pi\,r^2\,dr$ at a distance r from the molecule whose position is fixed.

If the linear dimensions of the scattering molecules are small as compared to the light wave-length λ, we have[1]

$$\frac{\sin sr}{sr} = 1 - \frac{1}{6}\,(sr)^2 + \ldots \simeq 1, \quad \text{for } \lambda \gg r, \tag{3.9}$$

and eq. (3.8) may now be written as follows:

$$F_{\text{is}} = 9\,\alpha^2\,N \left\{ 1 + 4\pi \int_0^\infty \left[g(r) - \frac{N}{V} \right] r^2\, dr \right\}, \tag{3.10}$$

with

$$\alpha = \frac{1}{3}\,\alpha_{ii} = \frac{1}{3}\,(\alpha_{11} + \alpha_{22} + \alpha_{33}) \tag{3.11}$$

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[1] For values of r that are not small as compared with λ, a quantity similar to the factor F_{is} has been discussed in a paper by Fürth and Williams (1954).

denoting the mean polarizability of the isolated molecule. It is seen that F_{is} depends on the mean polarizability of the molecules α and on a quantity determining the *radial* intermolecular correlations (see, Zernike and Prins 1927):

$$\gamma_R = 1 + 4\pi \int_0^\infty \left[g(r) - \frac{N}{V} \right] r^2 \, dr = \frac{N}{V} kT\beta_T, \qquad (3.12)$$

wherein

$$\beta_T = - \frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T \qquad (3.13)$$

is the isothermal compressibility coefficient of the medium.

Smoluchowski (1908) and Einstein (1910) showed that the quantity γ_R accounts for the light scattering resulting from spontaneous density fluctuations in the medium. As both α and γ_R are isotropic quantities, F_{is} determines *isotropic* scattering only.

Anisotropic light scattering. If the scattering molecules are small in terms of the light wave-length, then, with respect to (3.9), eq. (3.6) yields

$$F_{anis} = \tfrac{1}{2} \alpha_{ij} \alpha_{kl} \left\langle \sum_{pq} \left(3\omega_{ik}^{(pq)} \omega_{jl}^{(pq)} - \delta_{ij} \delta_{kl} \right) \right\rangle . \qquad (3.14)$$

It is seen that the factor F_{anis} depends on the anisotropy of the molecules as determined by the polarizability tensor α_{ij}, and on the angular intermolecular correlations determined in general by the statistical distribution of the directions of the molecular axes.

If the axes of the molecular systems coincide with the principal axes of the respective molecules, eq. (3.14) may be rewritten in the form

$$F_{anis} = \tfrac{1}{2} \sum_{ij} \alpha_i \alpha_j \left\langle \sum_{pq} (3 \cos^2 \Theta_{ij}^{(pq)} - 1) \right\rangle , \qquad (3.15)$$

with $\Theta_{ij}^{(pq)}$ denoting the angle between the i-th and j-th principal axes of the p-th and q-th molecules, respectively, and α_i — the polarizability tensor referred to the principal axes of the molecule.

If the molecules possess the axial symmetry, the axis of symmetry being the 3-axis, then $\alpha_1 = \alpha_2 \neq \alpha_3$, and (3.15) yields

$$F_{anis} = \tfrac{1}{2} (\alpha_3 - \alpha_1)^2 \left\langle \sum_{pq} (3 \cos^2 \Theta^{(pq)} - 1) \right\rangle , \qquad (3.16)$$

$\Theta^{(pq)}$ denoting the angle between the axes of symmetry of the p-th and q-th molecules, and α_3, α_1 — the polarizabilities of the molecule in the two principal directions parallel and perpendicular to its axis of symmetry.

If, in particular, the molecules exhibit the spherical symmetry, $\alpha_3 = \alpha_1$ and, by eq. (3.16), $F_{anis} = 0$. This means that F_{anis} determines the *anisotropic* light scattering only. The latter arises chiefly from the anisotropy of the molecules and from the angular intermolecular correlations.

Light scattering in ideal gases. In ideal gases, the molecules are mutually independent and may assume all possible configurations within the volume V. Since now $\exp\left\{-\dfrac{U(\tau)}{kT}\right\} = 1$, the statistical mean value $\langle \ \rangle$ of eq. (2.16) reduces to the isotropical average. As shown by Smoluchowski (1908), the density fluctuations in an ideal gas yield $\gamma_R = 1$, so that eq. (3.10) assumes the form

$$_{\text{gas}}F_{\text{is}} = 9\,\alpha^2\,N. \tag{3.17}$$

The factor F_{anis} as determined by eq. (3.14) may now be expanded as follows:

$$_{\text{gas}}F_{\text{anis}} = \tfrac{1}{2}\,\alpha_{ij}\,\alpha_{kl}\,N\,\Big\{3\,\delta_{ik}\,\delta_{jl} - \delta_{ij}\,\delta_{kl} + \sum_{q \neq p}(\overline{3\omega_{ik}^{(pq)}\,\omega_{jl}^{(pq)}} - \delta_{ij}\,\delta_{kl})\Big\}; \tag{3.18}$$

with respect to

$$\overline{\omega_{ik}^{(pq)}\,\omega_{jl}^{(pq)}} = \tfrac{1}{3}\,\delta_{ij}\,\delta_{kl}, \ \text{for } p \neq q, \tag{3.19}$$

we finally obtain

$$_{\text{gas}}F_{\text{anis}} = \tfrac{1}{2}\,(3\,\alpha_{ij}\,\alpha_{ij} - \alpha_{ii}\,\alpha_{jj})\,N. \tag{3.20}$$

In ideal gases, the anisotropic scattering depends only on the anisotropy of the isolated molecules, whereas isotropic scattering depends on their mean polarizability.

Factor accounting for angular intermolecular correlations. Eq. (3.16) may be written as follows:

$$F_{\text{anis}} = (\alpha_3 - \alpha_1)^2\,NR_{CM}; \tag{3.21}$$

the quantity

$$R_{CM} = \frac{1}{2N}\left\langle \sum_{pq}(3\cos^2\Theta^{(pq)} - 1)\right\rangle \tag{3.22}$$

appearing therein is termed *angular intermolecular correlation factor*, if the molecules possess the axial symmetry. A factor R_{CM} of the same form also appears in the theory of molecular orientational effects (cf. Buckingham 1955, and Piekara and Kielich 1957, 1958). For an ideal gas $U(\tau) = 0$, and eq. (3.22) yields:

$$R_{CM} = 1 + \tfrac{1}{2}\sum_{q \neq p}(3\,\overline{\cos^2\Theta^{(pq)}} - 1) = 1. \tag{3.23}$$

The correlation factor (3.22) accounts for the angular interaction of the molecules entering molecular assemblies which coalesce and disappear continually within the medium; such assemblies present a momentary axis of maximum polarizability arising statistically from the effect of ordering of the molecular axes. From the foregoing formulas it is seen that in an assembly of mutually „coupled" molecules light scattering differs from that resulting from free molecules, for which $R_{CM} = 1$.

For instance, for the case of molecules entering aggregates of two, R_{CM} as first computed by Piekara (1939, 1950) is given by

$$R_{CM} = 2 - 3\frac{L}{y}, \tag{3.24}$$

wherein $L = L(y)$ is the well-known Langevin function and $y = \dfrac{W}{kT}$ — the energy of dipole coupling in kT units. This refers to nitrobenzene, for which R_{CM} as calculated according to eq. (3.14) for the Cotton-Mouton effect (hence the indices CM) fits well with the experimental data. It is of interest that R_{CM} for $y \neq 0$ is always larger than unity.

Anselm (1947), and Benoit and Stockmayer (1956) introduced the correlation function $g(r, \omega)$ into the theory of the degree of depolarisation of scattered light; this function has the properties of the radial distribution function $g(r)$ of Zernike and Prins (1927) as generalized for orientational correlations of the molecules. With the function $g(r, \omega)$, the correlation factor (3.22) takes the form

$$R_{CM} = 1 + 2\pi \int\limits_{r} \int\limits_{\omega} (3 \cos^2 \Theta - 1) \left[g(r, \omega) - \frac{N}{4\pi V} \right] r^2 \, dr \, d\omega, \quad (3.25)$$

wherein Θ is the angle subtended by the axis of symmetry of a given molecule and that of an arbitrary one at distance r.

4. Optical Anisotropy and Degree of Depolarisation of Scattered Light

Optical anisotropy. The ratio of F_{anis} and F_{is} which determine, respectively, anisotropic and isotropic light scattering, i. e.

$$\Delta^2 \equiv \frac{F_{\text{anis}}}{F_{\text{is}}}, \quad (4.1)$$

yields a measure of the optical anisotropy of the scattering medium.

Substituting herein the expressions of eqs. (3.10) and (3.14), we have

$$\Delta^2 = \frac{\alpha_{ij} \, \alpha_{kl} \left\langle \sum\limits_{pq} (3\omega_{ik}^{(pq)} \, \omega_{jl}^{(pq)} - \delta_{ij} \, \delta_{kl}) \right\rangle}{2\alpha_{ii} \, \alpha_{jj} \, N \left\{ 1 + 4\pi \int\limits_{0}^{\infty} \left[g(r) - \dfrac{N}{V} \right] r^2 \, dr \right\}}; \quad (4.2)$$

this is an expression yielding a measure of the optical anisotropy of a liquid consisting of molecules of arbitrary symmetry.

Hence, for ideal gases, we have $_{\text{gas}}\Delta^2 = \delta_\alpha^2$, wherein δ_α is the optical anisotropy of an isolated molecule

$$\delta_\alpha^2 = \frac{3\alpha_{ij} \, \alpha_{ij} - \alpha_{ii} \, \alpha_{jj}}{2\alpha_{ii} \, \alpha_{jj}}, \quad (4.3)$$

or, if the polarizability tensor be referred to the principal axes of the molecule,

$$\delta_\alpha^2 = \frac{(\alpha_1 - \alpha_2)^2 + (\alpha_2 - \alpha_3)^2 + (\alpha_3 - \alpha_1)^2}{2(\alpha_1 + \alpha_2 + \alpha_3)^2}. \quad (4.4)$$

For molecules having the axial symmetry the foregoing expression reduces to

$$\delta_\alpha^2 = \left(\frac{\alpha_3 - \alpha_1}{\alpha_3 + 2\alpha_1}\right)^2 = \left(\frac{\alpha_3 - \alpha_1}{3\alpha}\right)^2; \tag{4.5}$$

clearly, for spherically symmetrical molecules $\delta_\alpha = 0$.

In condensed gases and liquids whose molecules have the axial symmetry, eq. (4.1) yields, with respect to (3.10) and (3.21):

$$\Delta^2 = \delta_\alpha^2 \frac{R_{CM}}{\gamma_R}; \tag{4.6}$$

this means that the optical anisotropy of condensed gases and liquids depends on that of the isolated molecule, δ_α, and on the ratio of the orientational (R_{CM}) and radial ($\gamma_\varkappa$) correlations.

Introducing R_{CM} from (3.25) into eq. (4.6), we obtain the Benoit-Stockmayer (1956) formula:

$$\Delta^2 = \frac{\delta_\alpha^2 V}{Nk\,T\beta_T}\left\{1 + 2\pi \int\limits_r \int\limits_\omega (3\cos^2\Theta - 1)\left[g\,(r,\,\omega) - \frac{N}{4\pi V}\right] r^2\,dr\,d\omega\right\}; \tag{4.7}$$

the latter has since been generalized by Benoit and Weill (1956) and by Weill (1958) for dilute solutions of liquids.

Depolarisation ratio of scattered light. In a medium exhibiting anisotropic scattering ($F_{anis} \neq 0$), the light scattered undergoes depolarisation. The degree of depolarisation is usually defined as the ratio of the lowest (I_{min}) and highest (I_{max}) possible values of the scattered intensity (see, Born 1933):

$$D \equiv \frac{I_{min}}{I_{max}}, \tag{4.8}$$

I_{min} and I_{max} being computed from the fundamental equation (2.18).

If the light beam incident on the scattering medium is not polarized and if the light scattered is observed with a Nicol prism, we have

$$\cos\Omega_{en} = \cos\varphi_e \cos\varphi_n + \sin\varphi_e \sin\varphi_n \cos\vartheta; \tag{4.9}$$

the angles φ_e, φ_n and ϑ are explained in Fig. 1. In the case under consideration, the fundamental equation (2.18) should be averaged over all directions of the electric vector $\boldsymbol{E}$ in the plane perpendicular to the propagation direction of the incident wave, i. e. to the vector $\boldsymbol{S}_o$. This is equivalent to averageing over φ_e from 0 to 2π:

$$I\,(\varphi_n,\,\vartheta) = 2 \cdot \frac{1}{2\pi}\int\limits_0^{2\pi} I_n\,d\,\varphi_e, \tag{4.10}$$

which yields, by (4.9),

$$I\,(\varphi_n,\,\vartheta) = Q\,\{5\,(1 - \sin^2\varphi_n \sin^2\vartheta)\,F_{is}\,(s) + (7 - \sin^2\varphi_n \sin^2\vartheta)\,F_{anis}\,(s)\}. \tag{4.11}$$

When the nicol is rotated, the scattered intensity transmitted attains its maximum value with the former transmitting vibrations parallel to the plane of the incident light vector $\boldsymbol{E}$ only, i. e. at $\varphi_n = 0$. The minimum scattered intensity is observed when the nicol is set so as to transmit vibrations perpendicular to the plane of $\boldsymbol{E}$, i. e. at
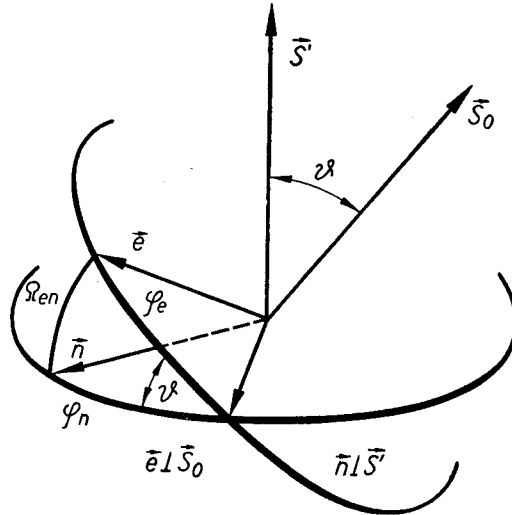

Fig. 1. Space arrangement of the unit vectors $\vec{s_0}$ and $\vec{s}$ in the direction of the incident and scattered light beams, and of unit electric vectors $\vec{e}$ and $\vec{n}$ in either light beam, respectively.

$\varphi_n = 90°$. Thus, by the definition of eq. (4.8) and with respect to (4.11), a general expression for the degree of depolarisation of light scattered by an isotropic medium is obtained as follows:

$$D(\vartheta) = \frac{5 \cos^2 \vartheta \, F_{is}(s) + (6 + \cos^2 \vartheta) \, F_{anis}(s)}{5 \, F_{is}(s) + 7 \, F_{anis}(s)}, \qquad (4.12)$$

When observation of the light scattered is carried out at an angle of 90° with respect to the direction of incidence and if the scattering medium satisfies the condition of eq. (3.9), the following relation is obtained for $\vartheta = 90°$:

$$D(90°) \equiv D = \frac{6 \, F_{anis}}{5 \, F_{is} + 7 \, F_{anis}}. \qquad (4.13)$$

The degree of depolarisation D thus defined is related to

$$D' = \frac{3 \, F_{anis}}{5 \, F_{is} + 4 \, F_{anis}}, \qquad (4.14)$$

the degree of depolarisation for plane polarized incident light, by the formula

$$D = \frac{2D'}{1 + D'}. \qquad (4.15)$$

The formula (4.13) (or (4.14)) together with expressions (2.22) and (2.23) is identical with the one derived by Buckingham and Stephen (1957) in their theory of the degree of depolarisation of light scattered by a dense medium.

Degree of depolarisation in some special cases. Substituting F_{is} and F_{anis}, as given by (3.10) and (3.14), in the general expression (4.13), an expression for the degree of depolarisation of light in condensed gases and liquids possessing molecules of arbitrary symmetry is obtained (Kielich 1958a, Piekara and Kielich 1958):

$$D = \frac{6\,\alpha_{ij}\,\alpha_{kl}\left\langle \sum_{pq}(3\,\omega_{ik}^{(pq)}\,\omega_{jl}^{(pq)} - \delta_{ij}\,\delta_{kl})\right\rangle}{10\,\alpha_{ii}\,\alpha_{jj}\,N\gamma_R + 7\,\alpha_{ij}\,\alpha_{kl}\left\langle \sum_{pq}(3\,\omega_{ik}^{(pq)}\,\omega_{jl}^{(pq)} - \delta_{ij}\,\delta_{kl})\right\rangle}. \tag{4.16}$$

For substances whose molecules exhibit the axial symmetry, (4.16) reduces to

$$D = \frac{6\,\delta_\alpha^2\,R_{CM}}{5\,\gamma_R + 7\,\delta_\alpha^2\,R_{CM}}, \tag{4.17}$$

where $\delta_\alpha = (\alpha_3 - \alpha_1)\,/\,3\alpha$, and R_{CM} is given by (3.22). If the angular correlation factor R_{CM} is given by (3.25), the eq. (4.17) is identical with the result obtained by Anselm (1947), and Benöit and Stockmayer (1956).

For an ideal gas, (4.16) yields the Gans-Cabannes formula:

$$_{gas}D = \frac{6\,(3\,\alpha_{ij}\,\alpha_{ij} - \alpha_{ii}\,\alpha_{jj})}{10\,\alpha_{ii}\,\alpha_{jj} + 7\,(3\,\alpha_{ij}\,\alpha_{ij} - \alpha_{ii}\,\alpha_{jj})} = \frac{6\,\delta_\alpha^2}{5 + 7\,\delta_\alpha^2}. \tag{4.18}$$

For a substance whose molecules possess the spherical symmetry, $\delta_\alpha = 0$, and the degree of depolarisation assumes the value zero, which means that in such a medium light undergoes no depolarization.

5. Rayleigh's Ratio and Coefficient of Extinction

Rayleigh's ratio. With an incident beam of natural light, and if observation is carried out without a nicol, eq. (4.11) should, additionally, be averaged over all values of φ_n from 0 to 2π, thus

$$I(\vartheta) = \frac{1}{2\pi}\int_0^{2\pi} I(\varphi_n, \vartheta)\,d\varphi_n\;; \tag{5.1}$$

hence, with respect to (4.11),

$$I(\vartheta) = \tfrac{1}{2}\,Q\,\{5\,(1 + \cos^2\vartheta)\,F_{is}(s) + (13 + \cos^2\vartheta)\,F_{anis}(s)\}. \tag{5.2}$$

The scattering constant, also known as Rayleigh's ratio, is defined as follows:

$$S(\vartheta) \equiv \frac{I(\vartheta)}{I_0}\,\frac{R_0^2}{V}\;; \tag{5.3}$$

by (5.2), the following general expression for Rayleigh's ratio is obtained

$$S(\vartheta) = \frac{1}{90V} \left(\frac{2\pi}{\lambda}\right)^4 \left(\frac{n^2+2}{3}\right)^2 \{5(1+\cos^2\vartheta) F_{is}(s) + (13+\cos^2\vartheta) F_{anis}(s)\}. \quad (5.4)$$

If observation is at an angle of 90° with respect to the direction of incidence ($\vartheta = 90°$) and if eq. (3.9) is satisfied, the foregoing expression reduces to

$$S(90°) \equiv S = \frac{1}{90V} \left(\frac{2\pi}{\lambda}\right)^4 \left(\frac{n^2+2}{3}\right)^2 (5 F_{is} + 13 F_{anis}). \quad (5.5)$$

Extinction coefficient. In passing through the medium, the intensity of the light beam diminishes as a result of scattering (the effect of absorption is neglected here). On emerging from a layer of thickness l, the intensity is given by the well-know Lambert law

$$I_l = I_0 e^{-hl}, \quad (5.6)$$

wherein h is a coefficient dependent on the properties of the medium and on the light wave-length λ, and determines the weakening of a beam of intensity I_0 resulting from scattering. By definition (see, Cabannes 1929),

$$h = \int_0^{2\pi} \int_0^{\pi} S(\vartheta) \sin\vartheta \, d\vartheta \, d\varphi, \quad (5.7)$$

i. e. by (5.4), a general expression for the coefficient of extinction (turbidity) is hence derived:

$$h = \frac{\pi}{45V} \left(\frac{2\pi}{\lambda}\right)^4 \left(\frac{n^2+2}{3}\right)^2 \int_0^{\pi} \{5(1+\cos^2\vartheta) F_{is}(s) + (13 + $$
$$ + \cos^2\vartheta) F_{anis}(s)\} \sin\vartheta d\vartheta, \quad (5.8)$$

wherein $F_{is}(s)$ and $F_{anis}(s)$ are given by eqs. (2.22) and (2.23).

In particular, for small molecules, i. e. if the condition of eq. (3.9) is satisfied, the foregoing equation yields

$$h = \frac{8\pi}{27V} \left(\frac{2\pi}{\lambda}\right)^4 \left(\frac{n^2+2}{3}\right)^2 (F_{is} + 2 F_{anis}). \quad (5.9)$$

S and h for special cases. Substituting F_{is} and F_{anis} from eqs. (3.10) and (3.14) in eqs. (5.5) and (5.9), the following expression is obtained for real gases and liquids consisting of molecules of arbitrary symmetry:

$$S = \frac{1}{18} \left(\frac{2\pi}{\lambda}\right)^4 \left(\frac{n^2+2}{3}\right)^2 \frac{N}{V} \alpha_{ij} \alpha_{kl} \left\{ \delta_{ij} \delta_{kl} \left[1 + 4\pi \int_0^{\infty} \left(g - \frac{N}{V}\right) r^2 dr \right] + \right.$$
$$\left. + \frac{13}{10N} \left\langle \sum_{pq} (3\omega_{ik}^{(pq)} \omega_{jl}^{(pq)} - \delta_{ij}\delta_{kl}) \right\rangle \right\}, \quad (5.10)$$

$$h = \frac{8\pi}{27} \left(\frac{2\pi}{\lambda}\right)^4 \left(\frac{n^2 + 2}{3}\right)^2 \frac{N}{V} \, \alpha_{ij} \, \alpha_{kl} \left\{ \delta_{ij} \, \delta_{kl} \left[1 + 4\pi \int\limits_0^\infty \left(g - \frac{N}{V} \right) r^2 \, dr \right] + \right.$$

$$\left. + \frac{1}{N} \left\langle \sum_{pq} (3 \, \omega_{ik}^{(pq)} \, \omega_{jl}^{(pq)} - \delta_{ij} \, \delta_{kl}) \right\rangle \right\}. \tag{5.11}$$

If the tensor of optical polarizability be referred to the principal ¦axes of the molecule, these equations yield:

$$S = \frac{1}{18} \left(\frac{2\pi}{\lambda}\right)^4 \left(\frac{n^2 + 2}{3}\right)^2 \frac{N}{V} \sum_{i,j=1}^3 \alpha_i \, \alpha_j \left\{ \gamma_R + \frac{13}{10N} \left\langle \sum_{pq} (3 \cos^2 \Theta_{ij}^{(pq)} - 1), \right\rangle \right\}, \tag{5.12}$$

$$h = \frac{8\pi}{27} \left(\frac{2\pi}{\lambda}\right)^4 \left(\frac{n^2 + 2}{3}\right)^2 \frac{N}{V} \sum_{i,j=1}^3 \alpha_i \, \alpha_j \left\{ \gamma_R + \frac{1}{N} \left\langle \sum_{pq} (3 \cos^2 \Theta_{ij}^{(pq)} - 1) \right\rangle \right\}. \tag{5.13}$$

With the Lorentz-Lorenz formula

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3} \frac{N}{V} \, \alpha, \tag{5.14}$$

and for molecules having the axial symmetry, eqs. (5.12) and (5.13) reduce to

$$S = \frac{\pi^2 (n^2 - 1)^2 V}{2 \lambda^4 N} \left(\gamma_R + \frac{13}{5} \delta_\alpha^2 \, R_{CM} \right), \tag{5.15}$$

$$h = \frac{8\pi^3 (n^2 - 1)^2 V}{3\lambda^4 N} \left(\gamma_R + 2 \delta_\alpha^2 \, R_{CM} \right), \tag{5.16}$$

wherein δ_α is the optical anisotropy of an axially symmetric molecule. The formulas derived differ from the analogous King-Rocard formulas by the orientational correlation factor R_{CM} in the term accounting for anisotropy. For spherically symmetrical molecules, $\delta_\alpha = 0$, and eqs. (5.15) and (5.16) assume the form of the Einstein-Smoluchowski-Rocard formulas for liquids consisting of spherical molecules:

$$S = \frac{\pi^2 (n^2 - 1)^2}{2\lambda^4} \, kT \beta_T, \qquad h = \frac{8\pi^3 (n^2 - 1)^2}{3\lambda^4} \, kT \beta_T. \tag{5.17}$$

For an ideal gas, by (4.3) and with the Lorentz-Lorenz equation, eqs. (5.10) and (5.11) yield the Born-Cabannes formulas:

$$_{gas}S = \frac{\pi^2 (n^2 - 1)^2 V}{2\lambda^4 N} \left(1 + \frac{13}{5} \delta_\alpha^2 \right), \tag{5.18}$$

$$_{gas}h = \frac{8\pi^3 (n^2 - 1)^2 V}{3\lambda^4 N} (1 + 2\delta_\alpha^2). \tag{5.19}$$

For an ideal gas consisting of spherical molecules the Born-Cabannes formulas reduce to the well-known formulas given by Rayleigh:

$$_{\text{gas}}S = \frac{2\pi^2 (n-1)^2 V}{\lambda^4 N}, \qquad _{\text{gas}}h = \frac{32\pi^3 (n-1)^2 V}{3\lambda^4 N}. \tag{5.20}$$

6. Second Virial Coefficients for Light Scattering in Compressed Gases

General form of virial coefficients. Virial coefficients have been computed by Harris and Alder (1953) and by Buckingham and Pople (1955) in the theory of electric polarisation, and by Buckingham (1955) in that of Kerr's effect. The virial coefficients for light scattering in compressed gases will now be computed by the method of the latter authors. For this, the molecular factors $F_{\text{is}}(s)$ and $F_{\text{anis}}(s)$ given by eqs. (2.22) and (2.23) are expanded in powers of $1/V$:

$$F_{\text{is}}(s) = A_S^{\text{is}} + \frac{B_S^{\text{is}}}{V} + \frac{C_S^{\text{is}}}{V^2} + \dots, \tag{6.1}$$

$$F_{\text{anis}}(s) = A_S^{\text{anis}} + \frac{B_S^{\text{anis}}}{V} + \frac{C_S^{\text{anis}}}{V^2} + \dots; \tag{6.2}$$

the coefficients A_S^{is}, A_S^{anis}, B_S^{is}, B_S^{anis}, C_S^{is}, C_S^{anis}, ... are termed the first, second, third, ... virial coefficient of isotropic (F_{is}) and anisotropic (F_{anis}) light scattering, respectively.

The first virial coefficients are defined as follows:

$$A_S^{\text{is}} = \lim_{V\to\infty} F_{\text{is}}(s), \qquad A_S^{\text{anis}} = \lim_{V\to\infty} F_{\text{anis}}(s); \tag{6.3}$$

by (2.22) and (2.23) we have

$$A_S^{\text{is}} = 9\alpha^2 N, \qquad A_S^{\text{anis}} = 9\alpha^2 \delta_\alpha^2 N, \tag{6.4}$$

wherein α is the mean polarizability of the isolated molecule, and δ_α denotes its anisotropy as given in general form by eq. (4.3). Comparison with eqs. (3.17) and (3.20) shows that the first virial coefficients A_S^{is} and A_S^{anis} account for light scattering by free molecules ("gas molecules").

By definition, the second virial coefficients are given by

$$B_S^{\text{is}} = \lim_{V\to\infty} \{[F_{\text{is}}(s) - A_S^{\text{is}}] \, V\}, \tag{6.5}$$

$$B_S^{\text{anis}} = \lim_{V\to\infty} \{[F_{\text{anis}}(s) - A_S^{\text{anis}}] \, V\}; \tag{6.6}$$

by (2.22), (2.23) and (6.4), they may be written in the following general form:

$$B_S^{\text{is}} = \lim_{V \to \infty} \left\{ \left\langle \delta_{\sigma\tau} \delta_{\nu\varrho} \sum_{pq} \frac{\partial m_\sigma^{'(p)}}{\partial E_\tau^{(p)}} \left(\frac{\partial m_\nu^{'(q)}}{\partial E_\varrho^{(q)}} \right)^* e^{-i\mathbf{s}\cdot\mathbf{r}_{pq}} - 9\alpha^2 N \right\rangle V \right\}, \quad (6.7)$$

$$B_S^{\text{anis}} = \lim_{V \to \infty} \left\{ \left\langle \frac{1}{2}(3\delta_{\sigma\nu}\delta_{\tau\varrho} - \delta_{\sigma\tau}\delta_{\nu\varrho}) \sum_{pq} \frac{\partial m_\sigma^{'(p)}}{\partial E_\tau^{(p)}} \left(\frac{\partial m_\nu^{'(q)}}{\partial E_\varrho^{(q)}} \right)^* e^{-i\mathbf{s}\cdot\mathbf{r}_{pq}} - 9\alpha^2 \delta_\alpha^2 N \right\rangle V \right\}. \quad (6.8)$$

As the second virial coefficients contain only contributions accounting for the inter-action of molecules in pairs, eqs. (6.7) and (6.8) may be rewritten as follows

$$B_S^{\text{is}} = \frac{4\pi N^2}{\Omega} \int_r \int_\omega \left\{ \frac{\partial m_\sigma^{'(1)}}{\partial E_\sigma^{(1)}} \left(\frac{\partial m_\tau^{'(1)}}{\partial E_\tau^{(1)}} + \frac{\partial m_\tau^{'(2)}}{\partial E_\tau^{(2)}} \right)^* - 9\alpha^2 \right\} e^{-\frac{U_{12}}{kT}} r^2 \, dr \, d\omega, \quad (6.9)$$

$$B_S^{\text{anis}} = \frac{2\pi N^2}{\Omega} \int_r \int_\omega \left\{ (3\delta_{\sigma\nu}\delta_{\tau\varrho} - \delta_{\sigma\tau}\delta_{\nu\varrho}) \frac{\partial m_\sigma^{'(1)}}{\partial E_\tau^{(1)}} \left(\frac{\partial m_\nu^{'(1)}}{\partial E_\varrho^{(1)}} + \frac{\partial m_\nu^{'(2)}}{\partial E_\varrho^{(2)}} \right)^* - \right.$$
$$\left. - 18\alpha^2 \delta^2 \right\} e^{-\frac{U_{12}}{kT}} r^2 \, dr \, d\omega, \quad (6.10)$$

wherein $m_\sigma^{'(1)}$, $m_\nu^{'(2)}$ are the dipole moments of molecules 1 and 2, U_{12} is the potential energy of interaction between a pair of molecules, and $\Omega = \int_\omega d\omega$ is the integral over all angular coordinates.

Spherically symmetric molecules. For simplification, assume the scattering molecules to have spherical symmetry. Then, by (6.4), the first virial coefficients are

$$A_S^{\text{is}} = 9\alpha^2 N, \qquad A_S^{\text{anis}} = 0, \quad (6.11)$$

i. e., the first virial coefficient of anisotropic scattering vanishes.

To compute the second virial coefficients, the expansion (2.34), which accounts for the effect of the intermolecular field on the polarizability of a molecule immersed in a condensed medium, will be applied. Since for spherically symmetrical molecules the tensor α_{ij} reduces to the isotropic tensor $\alpha_{ij} = \alpha \delta_{ij}$, and with respect to expansion (2.34) and condition (3.9), eqs. (6.9) and (6. 10) yield

$$B_S^{\text{is}} = 36\pi\alpha^2 N^2 \int_r \left\{ 1 + 8\frac{\alpha^2}{r^6} + 8\frac{\alpha^3}{r^9} + 32\frac{\alpha^4}{r^{12}} + \dots \right\} e^{-\frac{U(r)}{kT}} r^2 \, dr, \quad (6.12)$$

$$B_S^{\text{anis}} = 72\pi\alpha^2 N^2 \int_r \left\{ \frac{\alpha^2}{r^6} + 2\frac{\alpha^3}{r^9} + 7\frac{\alpha^4}{r^{12}} + \dots \right\} e^{-\frac{U(r)}{kT}} r^2 \, dr. \quad (6.13)$$

Pople (1954), assuming $U(r)$ in the form of the Lennard-Jones potential (2.36), proved that

$$\int_0^\infty r^{-n} e^{-\frac{U(r)}{kT}} r^2 \, dr = \frac{r_0^{3-n}}{12} y^{-4} H_n(y), \quad (6.14)$$

wherein

$$H_n(y) = y^{\frac{27-n}{6}} \sum_{m=0}^{\infty} \Gamma \left(\frac{6m+n-3}{12} \right) \frac{y^m}{m!}, \qquad (6.15)$$

with $y = 2 \left(\frac{\varepsilon^*}{kT} \right)^{\frac{1}{2}}$. The functions $H_n(y)$ have been discussed and their values tabulated by Buckingham and Pople (1955 b).

With eq. (6.14), we obtain finally from (6.12) and (6.13)

$$B_S^{\text{is}} = 9\alpha^2 NV(\gamma_R - 1) + \frac{24\pi \alpha^4 N^2}{r_0^3 y^4} \left\{ H_6(y) + \frac{\alpha}{r_0^3} H_9(y) + 4 \frac{\alpha^2}{r_0^6} H_{12}(y) + \cdots \right\}, \quad (6.16)$$

$$B_S^{\text{anis}} = \frac{6\pi \alpha^4 N^2}{r_0^3 y^4} \left\{ H_6(y) + 2 \frac{\alpha}{r_0^3} H_9(y) + 7 \frac{\alpha^2}{r_0^6} H_{12}(y) + \cdots \right\}, \qquad (6.17)$$

wherein γ_R is defined in analogy with (3.12).

Thus, in compressed gases consisting of spherical molecules, $A_S^{\text{is}} \neq 0$, $B_S^{\text{is}} \neq 0$ and $A_S^{\text{anis}} = 0$, whilst $B_S^{\text{anis}} \neq 0$. This means that free spherical molecules give rise to isotropic light scattering in a medium. However, in compressed gases, intermolecular forces cause the spherical molecules to form assemblies, which represent anisotropic scattering centres for the incident light beam. It is seen from eq. (6.17) that even the presence of assemblies consisting of no more that two spherical molecules is sufficient for the medium to exhibit additional, anisotropic scattering. Hence, on passing through such a medium, light may undergo depolarization.

Axial symmetrical molecules with dipole moment. If the anisotropic molecules possess the axial symmetry, then, neglecting all terms in the higher powers of the tensor α_{ij} in expansion (2.34), we may write, by (6.9) and (6.10)

$$B_S^{\text{is}} = \frac{36\pi \alpha^2 N^2}{\Omega} \int_r \int_\omega e^{-\frac{U_{12}}{kT}} r^2 \, dr \, d\omega, \qquad (6.18)$$

$$B_S^{\text{anis}} = \frac{18\pi \alpha^2 \delta_\alpha^2 N^2}{\Omega} \int_r \int_\omega (3\cos^2 \Theta^{(12)} - 1) e^{-\frac{U_{12}}{kT}} r^2 \, dr \, d\omega, \qquad (6.19)$$

wherein $\Theta^{(12)}$ is the angle subtended by the axes of symmetry of molecules 1 and 2.

Combining eqs. (2.36) and (2.37), the following expression is obtained for the potential energy of interaction of two dipole molecules (the permanent dipole-induced dipole interaction is neglected):

$$U_{12} = 4\varepsilon^* \left\{ \left(\frac{r_0}{r} \right)^{12} - \left(\frac{r_0}{r} \right)^6 \right\} - \frac{\mu^2}{r^3} (3\cos \Theta^{(1)} \cos \Theta^{(2)} - \cos \Theta^{(12)}), \quad (6.20)$$

with $\cos \Theta^{(12)} = \cos \Theta^{(1)} \cos \Theta^{(2)} + \sin \Theta^{(1)} \sin \Theta^{(2)} \cos(\varphi_2 - \varphi_1)$, wherein the angles $\Theta^{(12)}, \Theta^{(1)}, \ldots \varphi_2$ are explained in Fig. 2.

Substituting (6.20) in (6.18) and (6.19) we obtain, by (6.14),

$$B_S^{is} = 9\alpha^2 NV(\gamma_R - 1) + \frac{\pi \alpha^2 r_0^3 x^2 N^2}{16} \left\{ H_6(y) + \frac{3x^2 y^4}{400} H_{12}(y) + ... \right\}, \quad (6.21)$$
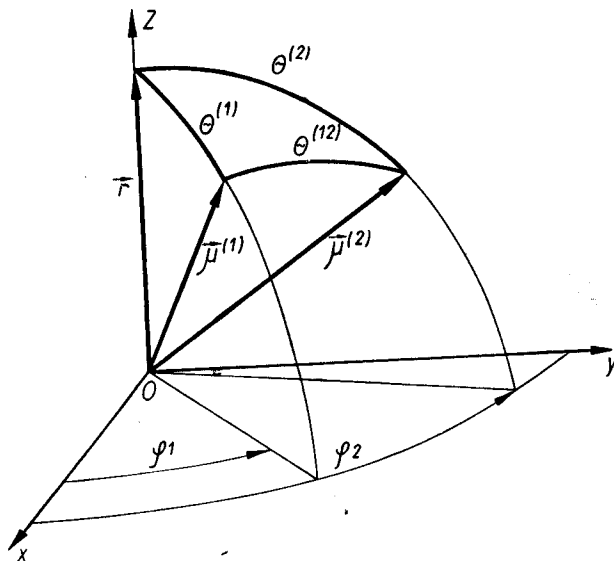

Fig. 2. Angles determining the mutual orientation of two dipoles $\vec{\mu}^{(1)}$ and $\vec{\mu}^{(2)}$ in the fixed system of reference (x, y, z)

$$B_S^{anis} = \frac{\pi \alpha^2 \delta_\alpha^2 r_0^3 x^2 N^2}{400} \left\{ H_6(y) + \frac{3x^2 y^4}{196} H_{12}(y) + ... \right\}, \quad (6.22)$$

wherein $x = \dfrac{\mu^2}{\varepsilon^* r_0^3}$.

The virial coefficient B_S^{anis} is related as follows to the second Kerr constant virial coefficient B_K as computed for the case under consideration by Buckingham (1955):

$$B_K = \frac{4\pi}{405 \, kT} \frac{a \, \delta_a}{\alpha \, \delta_\alpha} B_S^{anis}, \quad (6.23)$$

wherein

$$\delta_a = \frac{a_3 - a_1}{3a} \quad (6.24)$$

is the electrical anisotropy of an axially symmetric molecule, and $a = \frac{1}{3}(a_3 + 2a_1)$ — its mean polarizability in a static electric field*).

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*) A detailed discussion of B_S^{is} and B_S^{anis} for other molecular models will be given in a subsequent paper by the author.

7. Effect of the Molecular Field and Hyperpolarizability of the Molecules on Light Scattering in Liquids

In a condensed medium, light scattering depends also on the molecular field and on the hyperpolarizability of the molecules (see Buckingham and Stephen 1957). In the present case, when computing the molecular factors F_{is} and F_{anis}, the tensor of the polarizability of the molecules, as given by the expansion (2.33), should be applied. The expressions of (2.22) and (2.23) may be written as follows:

$$F_{is}(s) = \left\langle \delta_{\sigma\tau} \delta_{\nu\varrho} \sum_{pq} (\alpha^{(p)}_{\sigma\tau} \alpha^{(q)}_{\nu\varrho} + V^{(pq)}_{\sigma\tau\nu\varrho}) \cos s \cdot r_{pq} \right\rangle, \qquad (7.1)$$

$$F_{anis}(s) = \frac{1}{2} \left\langle (3\delta_{\sigma\nu} \delta_{\tau\varrho} - \delta_{\sigma\tau} \delta_{\nu\varrho}) \sum_{pq} (\alpha^{(p)}_{\sigma\tau} \alpha^{(q)}_{\nu\varrho} + V^{(pq)}_{\sigma\tau\nu\varrho}) \cos s \cdot r_{pq} \right\rangle, \quad (7.2)$$

wherein the tensor

$$\begin{aligned}
V^{(pq)}_{\sigma\tau\nu\varrho} &= \alpha^{(p)}_{\sigma\tau} \beta^{(q)}_{\nu\varrho\gamma} F^{(q)}_{0\gamma} + \alpha^{(q)}_{\nu\varrho} \beta^{(p)}_{\sigma\tau\gamma} F^{(p)}_{0\gamma} + \beta^{(p)}_{\sigma\tau\gamma} \beta^{(q)}_{\nu\varrho\delta} F^{(p)}_{0\gamma} F^{(q)}_{0\delta} + \\
&+ \tfrac{1}{2} \alpha^{(p)}_{\sigma\tau} \gamma^{(q)}_{\nu\varrho\gamma\delta} F^{(q)}_{0\gamma} F^{(q)}_{0\delta} + \tfrac{1}{2} \alpha^{(q)}_{\nu\varrho} \gamma^{(p)}_{\sigma\tau\gamma\delta} F^{(p)}_{0\gamma} F^{(p)}_{0\delta} + \dots \\
&+ (\alpha^{(p)}_{\sigma\alpha} \alpha^{(q)}_{\nu\beta} + \dots) \left(\frac{\partial F^{(p)}_\alpha}{\partial E^{(p)}_\tau} \delta_{\beta\varrho} + \delta_{\alpha\tau} \frac{\partial F^{(q)}_\beta}{\partial E^{(q)}_\varrho} + \frac{\partial F^{(p)}_\alpha}{\partial E^{(p)}_\tau} \frac{\partial F^{(q)}_\beta}{\partial E^{(q)}_\varrho} \right)
\end{aligned} \qquad (7.3)$$

determines the effect of the internal molecular field and hyperpolarizability of the molecules on light scattering in a condensed medium.

Light scattering on assemblies of spherical molecules. In order to obtain insight into the part played by the internal molecular field in the scattering of light, it will be assumed for the sake of simplicity that the condensed medium consists of assemblies of spherical molecules. Thus, $\mu_i = \beta_{ijk} = 0$ and $\alpha_{ij}, \gamma_{ijkl}$ reduce to the isotropic tensors given by

$$\alpha_{ij} = \alpha_{ij}, \quad \gamma_{ijkl} = \tfrac{1}{3} \gamma(\delta_{ij}\delta_{kl} + \delta_{ik}\delta_{jl} + \delta_{il}\delta_{kj}), \qquad (7.4)$$

and the foregoing expressions yield, quite generally:

$$\begin{aligned}
F_{is}(s) = \Big\langle \sum_{pq} \Big\{ \alpha^2 \Big(9 &+ 3 \frac{\partial F^{(p)}_\alpha}{\partial E^{(p)}_\alpha} + 3 \frac{\partial F^{(q)}_\beta}{\partial E^{(q)}_\beta} + \frac{\partial F^{(p)}_\alpha}{\partial E^{(p)}_\alpha} \frac{\partial F^{(q)}_\beta}{\partial E^{(q)}_\beta} \Big) + \\
&+ \frac{5}{2} \alpha\gamma \ (F^{(p)}_{o\alpha} F^{(p)}_{o\alpha} + F^{(q)}_{o\beta} F^{(q)}_{o\beta}) + \dots \Big\} \cos s \cdot r_{pq} \Big\rangle,
\end{aligned} \qquad (7.5)$$

$$F_{anis}(s) = \frac{1}{2} \left\langle \sum_{pq} \left\{ \alpha^2 \left(3 \frac{\partial F^{(p)}_\alpha}{\partial E^{(p)}_\beta} \frac{\partial F^{(q)}_\alpha}{\partial E^{(q)}_\beta} - \frac{\partial F^{(p)}_\alpha}{\partial E^{(p)}_\alpha} \frac{\partial F^{(q)}_\beta}{\partial E^{(q)}_\beta} \right) + \dots \right\} \cos s \cdot r_{pq} \right\rangle. \quad (7.6)$$

If $\lambda \gg r$, the foregoing relations yield a general expression for the optical anisotropy Δ^2 of a condensed medium consisting of spherical molecules:

$$\Delta^2 = \frac{\left\langle \sum_{pq} \left(3 \frac{\partial F_\alpha^{(p)}}{\partial E_\beta^{(p)}} \frac{\partial F_\alpha^{(q)}}{\partial E_\beta^{(q)}} - \frac{\partial F_\alpha^{(p)}}{\partial E_\alpha^{(p)}} \frac{\partial F_\beta^{(q)}}{\partial E_\beta^{(q)}} \right) \right\rangle}{2 \left\langle \sum_{pq} \left(9 + 3 \frac{\partial F_\alpha^{(p)}}{\partial E_\alpha^{(p)}} + 3 \frac{\partial F_\beta^{(q)}}{\partial E_\beta^{(q)}} + \frac{\partial F_\alpha^{(p)}}{\partial E_\alpha^{(p)}} \frac{\partial F_\beta^{(q)}}{\partial E_\beta^{(q)}} \right) \right\rangle} . \tag{7.7}$$

Hence, it is clearly seen that the optical anisotropy of such a medium arises from *fluctuations of the molecular field*. If the internal molecular field $F_\alpha^{(p)}$ is here assumed to be given by the expansion (2.29), which, in the case of spherical molecules, takes the form

$$F_\alpha^{(p)} = F_{o\alpha}^{(p)} - \alpha \sum_r T_{\alpha\beta}^{(pr)} E_\beta^{(r)} + \alpha^2 \sum_{rs} T_{\alpha\beta}^{(pr)} T_{\beta\gamma}^{(rs)} E_\gamma^{(s)} - \ldots, \tag{7.8}$$

then eq. (7.7) reduces to

$$\Delta^2 = \frac{\alpha^2 \left\langle \sum_{pqrs} T_{\alpha\beta}^{(pr)} T_{\alpha\beta}^{(qs)} \right\rangle}{6N\gamma_R + 2\alpha^2 \left\langle \sum_{pqrs} (T_{\alpha\beta}^{(pr)} T_{\alpha\beta}^{(rs)} + T_{\alpha\beta}^{(qr)} T_{\alpha\beta}^{(rs)}) \right\rangle} . \tag{7.9}$$

This yields, by approximation,

$$\Delta^2 = \frac{\alpha^2 V}{6N k T \beta_T} \left\langle \sum_{qrs} T_{\alpha\beta}^{(pr)} T_{\alpha\beta}^{(qs)} \right\rangle = \frac{4\pi \alpha^2 V}{k T \beta_T} \int_0^\infty r^{-4} g(r) \, dr. \tag{7.10}$$

As $F_{\text{anis}} \neq 0$, the light scattered on assemblies of spherical molecules undergeos depolarisation ($D \neq 0$). Buckingham and Stephen (1957) showed that, in the case under consideration, the degree of depolarisation D may be expressed by the difference between the molecular refraction of the fluid (R_M) and that of the perfect gas ($_{\text{gas}}R_M$).

Polar liquids. Buckingham and Stephen, in the theory proposed by them (1957), proved the value of the degree of depolarization D in polar liquids to be strongly dependent on the hyperpolarizability of the molecules.

If an isolated molecule possesses an axis of symmetry, and if this is the 3-axis, then the following components of the tensors μ_i, α_{ij} and β_{ijk} have non-zero values:

$$\mu_3 \equiv \mu, \, \alpha_{11} = \alpha_{22} \equiv \alpha_1 \neq \alpha_{33} \equiv \alpha_3, \, \beta_{113} = \beta_{223} \equiv \beta_{13} \neq \beta_{333} \equiv \beta_{33}. \tag{7.11}$$

As a first approximation, expressions (7.1) and (7.2) may be reduced to the form

$$F_{\text{is}}(s) = \left\langle \sum_{pq} \{(\alpha_3 + 2\alpha_1) + (\beta_{33} + 2\beta_{13}) F_{03}\}^2 \frac{\sin sr_{pq}}{sr_{pq}} \right\rangle, \tag{7.12}$$

$$F_{\text{anis}}(s) = \frac{1}{2} \left\langle \sum_{pq} \{(\alpha_3 - \alpha_1) + (\beta_{33} - \beta_{13}) F_{03}\}^2 (3 \cos^2 \Theta^{(pq)} - 1) \frac{\sin sr_{pq}}{sr_{pq}} \right\rangle. \tag{7.13}$$

Buckingham and Stephen (1957) showed that, in the case of Onsager's model (1936),

$$F_{03} = \frac{2\,(\varepsilon - 1)\,(n^2 - 1)}{3\,(2\varepsilon + n^2)} \cdot \frac{\mu}{\alpha}, \qquad (7.14)$$

wherein ε is the static dielectric constant of the medium. Thus, for small scattering molecules, eqs. (7.12) and (7.13) reduce to

$$F_{\mathrm{is}} = 9\alpha^2 \left\{ 1 + \frac{2\,(\varepsilon - 1)\,(n^2 - 1)}{3\,(2\varepsilon + n^2)}\,\frac{\mu\beta}{\alpha^2} \right\}^2 N\gamma_R, \qquad (7.15)$$

$$F_{\mathrm{anis}} = 9\alpha^2 \left\{ 1 + \frac{2\,(\varepsilon - 1)\,(n^2 - 1)}{3\,(2\varepsilon + n^2)}\,\frac{\mu\beta\,\delta_\beta}{\alpha^2\,\delta_\alpha} \right\}^2 \delta_\alpha^2 N R_{CM}, \qquad (7.16)$$

$$\beta = \frac{1}{3}\,(\beta_{33} + 2\beta_{13}), \qquad \delta_\beta = \frac{\beta_{33} - \beta_{13}}{3\beta}, \qquad (7.17)$$

with β denoting the mean hyperpolarizability of the isolated dipolar molecule, and δ_β yielding a measure of the anisotropy of its hyperpolarizability.

Substituting (7.15) and (7.16) with $R_{CM} = 1$ in eq. (4.13), the Buckingham-Stephen formula for the degree of depolarization in polar liquids is obtained:

$$D = \frac{6\left\{1 + \dfrac{4\,(\varepsilon - 1)\,(n^2 - 1)}{3\,(2\varepsilon + n^2)} \cdot \dfrac{\mu\beta\,\delta_\beta}{\alpha^2\,\delta_\alpha}\right\}\delta_\alpha^2}{5\left\{1 + \dfrac{4\,(\varepsilon - 1)\,(n^2 - 1)}{3\,(2\varepsilon + n^2)}\,\dfrac{\mu\beta}{\alpha^2}\right\}\gamma_R + 7\left\{1 + \dfrac{4\,(\varepsilon - 1)\,(n^2 - 1)}{3\,(2\varepsilon + n^2)}\,\dfrac{\mu\beta\,\delta_\beta}{\alpha^2\,\delta_\alpha}\right\}\delta_\alpha^2}. \qquad (7.18)$$

Similarly, by (5.5), the following formula for Rayleigh's ratio is obtained:

$$S = \frac{\pi^2\,(n^2 - 1)^2\,V}{2\,\lambda^4\,N}\left\{\left[1 + \frac{4\,(\varepsilon - 1)\,(n^2 - 1)}{3\,(2\varepsilon + n^2)}\,\frac{\mu\beta}{\alpha^2}\right]\gamma_R + \right.$$

$$\left. + \frac{13}{5}\left[1 + \frac{4\,(\varepsilon - 1)\,(n^2 - 1)}{3\,(2\varepsilon + n^2)}\,\frac{\mu\beta\,\delta_\beta}{\alpha^2\,\delta_\alpha}\right]\delta_\alpha^2\right\}. \qquad (7.19)$$

These are formulas which, if the quantities D and S are known from experimental data, yield the value of the hyperpolarizability of the isolated molecule.

8. General Relations

From the theory, as discussed in detail in §§ 3 to 7, it is seen that, in order to compute the quantities D, S and h for a given condensed substance, the quantities accounting for the radial and angular intermolecular correlations should be known,

in addition to those describing the properties of the isolated molecules. Since, for a given substance, it may well be the case that not all the molecular parameters are known simultaneously, it is convenient to compute the quantities D, S and h from relations containing only such quantities as are accessible to experimental determination.

Relations between D, S and h. Eqs. (4.1) and (4.12) yield

$$\frac{F_{\text{anis}}(s)}{F_{\text{is}}(s)} = \Delta^2(\vartheta) = \frac{5\{D(\vartheta) - \cos^2\vartheta\}}{6 - 7D(\vartheta) + \cos^2\vartheta},\tag{8.1}$$

a relation whose left hand side coincides with the theoretical definition of the optical anisotropy of the medium, and whose right hand side makes it possible to compute Δ^2 directly from experimental data on the degree of depolarisation of the light scattered.

By (8.1), eq. (5.4) determining $S(\vartheta)$ may be rewritten in the form

$$S(\vartheta) = \frac{1}{18V}\left(\frac{2\pi}{\lambda}\right)^4\left(\frac{n^2+2}{3}\right)^2\frac{\{6 + 6D(\vartheta)\}\sin^2\vartheta}{6 - 7D(\vartheta) + \cos^2\vartheta}F_{\text{is}}(s),\tag{8.2}$$

$$S(\vartheta) = \frac{1}{18V}\left(\frac{2\pi}{\lambda}\right)^4\left(\frac{n^2+2}{3}\right)^2\frac{\{6 + 6D(\vartheta)\}\sin^2\vartheta}{5\{D(\vartheta) - \cos^2\vartheta\}}F_{\text{anis}}(s),\tag{8.3}$$

wherein $F_{\text{is}}(s)$ and $F_{\text{anis}}(s)$ are given by (2.22) and (2.23), and ϑ is the angle of scattering.

If observation is perpendicular to the incident beam ($\vartheta = 90°$), eqs. (8.1) — (8.3) yield, for scattering molecules of small dimensions,

$$\frac{F_{\text{anis}}}{F_{\text{is}}} = \Delta^2 = \frac{5D}{6 - 7D},\tag{8.4}$$

$$S = \frac{1}{18V}\left(\frac{2\pi}{\lambda}\right)^4\left(\frac{n^2+2}{3}\right)^2\frac{6 + 6D}{6 - 7D}F_{\text{is}},\tag{8.5}$$

$$S = \frac{1}{18V}\left(\frac{2\pi}{\lambda}\right)^4\left(\frac{n^2+2}{3}\right)^2\frac{6 + 6D}{5D}F_{\text{anis}}.\tag{8.6}$$

Under identical conditions, by eq. (5.9) and with respect to (8.4), the extinction coefficient is obtained as follows:

$$h = \frac{8\pi}{27V}\left(\frac{2\pi}{\lambda}\right)^4\left(\frac{n^2+2}{3}\right)^2\frac{6 + 3D}{6 - 7D}F_{\text{is}},\tag{8.7}$$

$$h = \frac{8\pi}{27V}\left(\frac{2\pi}{\lambda}\right)^4\left(\frac{n^2+2}{3}\right)^2\frac{6 + 3D}{5D}F_{\text{anis}}.\tag{8.8}$$

Finally, the foregoing expressions yield the general relations:

$$D(\vartheta) = D\left(1 + \frac{1-D}{D}\cos^2\vartheta\right),$$ (8.9)

$$S(\vartheta) = S\left(1 + \frac{1-D}{1+D}\cos^2\vartheta\right),$$ (8.10)

$$h = \frac{8\pi}{3}S\frac{2+D}{1+D},$$ (8.11)

which hold for a medium of arbitrary density consisting of scattering molecules of small dimensions. Analogous relations were derived by Cabannes (1929) for light scattering on isolated molecules.

If the intermolecular field existing within the condensed medium be neglected, the molecular factor F_{is} of isotropic scattering may be expressed by experimentally known quantities. Namely, with respect to the Lorentz-Lorenz equation (5.14), eq. (3.10) yields

$$F_{is} = \frac{81}{16\pi^2}\left(\frac{n^2-1}{n^2+2}\right)^2 V\,kT\,\beta_T.$$ (8.12)

Substituting the foregoing expressions in eqs. (8.5) and (8.7), we obtain the Cabannes-King-Rocard formulas

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

(8.13)

$$h = \frac{8\pi^3(n^2-1)^2}{3\lambda^4}\frac{6+3D}{6-7D}kT\,\beta_T,$$

which contain no molecular parameters and may be checked experimentally.

Anisotropic light scattering and Kerr effect. The molecular factor F_{anis} accounting for anisotropic scattering may be expressed by the anisotropic term in Kerr's constant. By a general relation,

$$F_{anis} = \frac{1215\,n^2(n^2-1)\,kTV}{2\pi(\varepsilon-1)(\varepsilon+2)(n^2+2)^3}K_{anis},$$ (8.14)

wherein ε denotes the electric permittivity of the medium. The anisotropic term in Kerr's constant is, in general, given by the following expression (cf. Kielich 1958b):

$$K_{anis} = \frac{\pi(n^2+2)^2(\varepsilon+2)^2}{1215\,n^2\,kTV}\left\langle(3\delta_{\sigma\nu}\delta_{\tau\varrho}-\delta_{\sigma\tau}\delta_{\nu\varrho})\sum_{pq}\frac{\partial m_\sigma'^{(p)}}{\partial E_\tau}\frac{\partial m_\nu^{(q)}}{\partial E_{o\varrho}}\right\rangle$$ (8.15)

with $m_\sigma'^{(p)}$ denoting the dipole moment induced in the molecule by the variable electric field $\boldsymbol{E}$ of the light wave, and $m_\nu^{(q)}$ — the total dipole moment of the q-th molecule in the presence of the static electric field $\boldsymbol{E_0}$ inducing optical birefringence in the medium.

For molecules possessing constant polarizability, eq. (8.15) yields

$$K_{anis} = \frac{\pi(n^2 + 2)^2 (\varepsilon + 2)^2 \alpha_{ij} a_{kl}}{1215 \, n^2 \, kTV} \left\langle \sum_{pq} (3\omega_{ik}^{(pq)} \, \omega_{jl}^{(pq)} - \delta_{ij} \, \delta_{kl}) \right\rangle \quad (8.16)$$

wherein a_{ij} is the electric polarizability tensor of the isolated molecule. In particular, if the molecules have the axial symmetry, eq. (8.16) reduces to

$$K_{anis} = \frac{(n^2 - 1) (\varepsilon - 1) (n^2 + 2) (\varepsilon + 2) \, V}{120\pi \, n^2 \, kTN} \, \delta_\alpha \, \delta_a \, R_{CM}, \quad (8.17)$$

with R_{CM} denoting the correlation factor given by (3.22).

For the case of a condensed medium consisting of spherical molecules, the general expression (8.15) yields

$$K_{anis} = \frac{\pi \, (n^2 + 2)^2 (\varepsilon + 2)^2 \, \alpha \, a}{1215 \, n^2 \, kTV} \left\langle \sum_{pq} \left(3 \frac{\partial F_\alpha^{(p)}}{\partial E_\beta} \frac{\partial F_\alpha^{(q)}}{\partial E_{o\beta}} - \frac{\partial F_\alpha^{(p)}}{\partial E_\alpha} \frac{\partial F_\beta^{(q)}}{\partial E_{o\beta}} \right) \right\rangle, \quad (8.18)$$

or, as a first approximation:

$$K_{anis} = \frac{\pi \, (n^2 + 2)^2 (\varepsilon + 2)^2 \, \alpha^2 \, a^2}{405 \, n^2 \, kTV} \left\langle \sum_{pqrs} T_{\alpha\beta}^{(pr)} \, T_{\alpha\beta}^{(qs)} \right\rangle. \quad (8.19)$$

The quantities D, S, h, and Kerr's constant K_{anis}. Substituting eq. (8.14) in (8.6) and (8.8), we obtain the general expressions

$$S = \frac{72\pi^3 \, n^2 \, (n^2 - 1) \, kT}{\lambda^4 \, (\varepsilon - 1) \, (\varepsilon + 2) \, (n^2 + 2)} \, (1 + D^{-1}) \, K_{anis}, \quad (8.20)$$

$$h = \frac{192\pi^4 \, n^2 \, (n^2 - 1) \, kT}{\lambda^4 \, (\varepsilon - 1) \, (\varepsilon + 2) \, (n^2 + 2)} \, (1 + 2D^{-1}) \, K_{anis}, \quad (8.21)$$

which contain experimentally accessible quantities only, and hold for condensed media consisting of molecules of arbitrary symmetry.

Combining expression (8.4) and eqs. (8.12) and (8.14), we have

$$\frac{5D}{6 - 7D} = \frac{120\pi \, n^2}{(n^2 - 1) \, (\varepsilon - 1) \, (n^2 + 2) \, (\varepsilon + 2)} \, \frac{K_{anis}}{\beta_T}; \quad (8.22)$$

hence, Gans' formula (1923) is obtained:

$$K_{anis} = \frac{(n^2 - 1) \, (\varepsilon - 1) \, (n^2 + 2) \, (\varepsilon + 2)}{24\pi \, n^2} \cdot \frac{\beta_T \, D}{6 - 7D}, \quad (8.23)$$

which yields a relation between Kerr's constant and the degree of depolarisation of the light scattered.

Substituting F_{is} and F_{anis} as given by (8.12) and (8.14) in eqs. (5.5) and (5.9), we have

$$S = \frac{\pi^2 (n^2 - 1)^2}{2\lambda^4} \, kT \left\{ \beta_T + \frac{312\pi \, n^2 \, K_{anis}}{(n^2 - 1) \, (\varepsilon - 1) \, (n^2 + 2) \, (\varepsilon + 2)} \right\}, \qquad (8.24)$$

$$h = \frac{8\pi^3 (n^2 - 1)^2}{3\lambda^4} \, kT \left\{ \beta_T + \frac{240\pi \, n^2 \, K_{anis}}{(n^2 - 1) \, (\varepsilon - 1) \, (n^2 + 2) \, (\varepsilon + 2)} \right\}. \qquad (8.25)$$

Conclusions. The quantities D, S and h accounting for light scattering in an isotropic medium are given (§§ 4—7) in terms of various molecular parameters inaccessible to experiment; on the other hand, the same quantities are related mutually and with Kerr's constant, thus yielding the basis for comparing the theoretically predicted results and those obtained experimentally. Thus, a study of light scattering may serve not only to determine the shape and properties of the isolated molecules, but also to obtain valuable data on the nature of the molecular interaction existing in a condensed medium.

The author wishes to express his sincere thanks to Professor Dr A. Piekara for his valuable advice and for his helpful interest throughout the present investigation. The author is greatly indebted to Dr A. D. Buckingham for his stimulating discussions of some of the problems under consideration.

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