

MOLECULAR LIGHT SCATTERING IN DENSE MIXTURES*

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Additivity of the scattered light intensity I^S holds only in mixtures of ideal gases, but breaks down in mixtures of real gases or liquids as a result of molecular correlations. Here, by statistical methods, I^S is derived for multi-component systems as a power series in the molar fractions x , the first term (linear in x) describing the additive properties of an ideal mixture and higher terms (nonlinear with regard to x) accounting for deviations from additivity due to various (pairwise, triple *etc.*) molecular correlations. The theory proposed is discussed in detail for certain molecular models taking into consideration the various multipolar interactions.

I. Introduction

Over half a century has elapsed since Rayleigh [1], Smoluchowski [2] and Einstein [3] laid the foundations of the theory of light scattering, and research on this molecular effect is still proceeding intensely. Various monographs of the subject exist [4]–[7]. Interest therein has become greatly enhanced since laser techniques and certain specific properties of laser beams (collimation, coherence, monochromaticity and high intensity) have provided a novel and unfailing instrument of experimental investigation of various optical effects inaccessible to detection by earlier methods of measurement [7].

We restrict considerations in this paper to light scattering in a molecular approach first developed by a number of authors [8]–[11] for the case of so-called isotropic scattering, defined by the Rayleigh ratio (in the direction perpendicular to the non-polarized incident beam)

$$R_{is} = \frac{1}{2} \left(\frac{2\pi}{\lambda} \right)^4 \left(\frac{n^2 + 2}{3} \right)^2 a^2 \rho (1 + G_R), \quad (1)$$

where ρ is the number density of molecules, n the refractive index of the medium, a the mean polarizability of the optically isotropic molecule, and

$$G_R = 4\pi\rho \int_0^\infty \{g_2(r) - 1\} r^2 dr \quad (2)$$

* The present paper is dedicated to the memory of Marian Smoluchowski, born 95 and deceased 50 years ago.

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a parameter related with the radial distribution function $g_2(r)$ of two molecules distant by r . G is linked with the mean square density fluctuation $\Delta\rho$ in a volume V given by Smoluchowski as [2, 12]

$$V\langle(\Delta\rho)^2\rangle = \rho^2 k T \beta_T = \rho(1 + G_R). \quad (3)$$

Thus, investigation of isotropic light scattering provides *i. a.* information on the radial function g_2 . This is particularly true of studies on the angular distribution of scattered X-rays [12]. If the scattering medium presents no molecular correlations, $G_R = 0$ and (1) goes over into the well-known formula of Rayleigh, which provides information concerning ρ or the mean polarizability a .

If the molecules are not isotropic optically, an additional contribution comes from anisotropic scattering, given by [13, 14]:

$$R_{\text{anis}} = \frac{13}{10} \left(\frac{2\pi}{\lambda}\right)^4 \left(\frac{n^2+2}{3}\right)^2 a^2 \kappa_a^2 \rho (1 + J_A) \quad (4)$$

which contains the parameter of optical anisotropy of the molecules [4],

$$\kappa_a = \frac{a_{33} - a_{11}}{3a} \quad (5)$$

and the integral parameter [13]—[15]

$$J_A = \frac{1}{2} \rho \int \int (3 \cos^2 \theta - 1) g_2(r, \omega) dr d\omega \quad (6)$$

accounting for correlation between a pair of anisotropic molecules whose axes of symmetry subtend the angle θ .

The influence of angular molecular correlations on anisotropic light scattering has been discussed by various authors [13]—[18], the parameter (6) accounting for these correlations being accessible to calculation from experimental data [13], [14], [19].

The Rayleigh factor (4) describes anisotropic light scattering by a medium whose molecules have the optical anisotropy (5), which vanishes for $\kappa_a = 0$. However, more exact theories taking into consideration the influence of molecular interactions on optical polarizability show [10], [17] that, in sufficiently condensed atomic fluids also, there can occur anisotropic scattering, which leads to depolarization of the light according to the formula [17], [20]

$$D = \frac{6a^2 J_R}{5(1 + G_R) + 7a^2 J_R} \quad (7)$$

wherein the parameter

$$J_R = 8\pi\rho \int_0^\infty r^{-6} g_2(r) r^2 dr \quad (8)$$

accounts for interaction between the dipole moments induced in the atoms (or isotropic molecules) by radial type microscopic fields. Obviously, as is well-known, isolated atoms or isotropic molecules in the gaseous state do not depolarize scattered light. It is only in condensed media that depolarization occurs as a result of radial correlations given by the para-

meter (8), which appears moreover in molecular refraction [9], [11], [20], [21] and in other molecular effects [22].

When viewed more closely, light scattering can be strongly affected by fluctuations in the anisotropy of the molecular electric field [17], [22]—[24] and by hyperpolarizabilities induced in the atoms or molecules by molecular fields [17], [20]. Finally, the influence on light scattering of various microscopic factors *e. g.* interactions (dispersional, dipolar and quadrupolar, *etc.*) in real gases can be studied by the method of virial coefficients [15], [25]. This latter method, which is apt to yield valuable data on the type and magnitude of the intermolecular forces, has not yet been put to full use.

As seen, the theories stated above in brief involve but the two-molecule (pairwise) correlation function g_2 . Higher approximations of light scattering theory make necessary the appearance of multi-molecule correlation functions. Thus, in double scattering [26] and non-linear light scattering [27] induced in liquids by intense light (*e. g.* from lasers), three-molecule (triple) and four-molecule (quadruple) correlation functions, g_3 and g_4 , appear. Such an extension of the study of light scattering will permit to gain information not only concerning the pairwise function g_2 but moreover on those of multi-molecular correlations which play so great a part in the statistical theory of liquids and highly compressed gases [28], [29].

The thermodynamical theory of light scattering on fluctuations of the concentration in solutions, initiated by Einstein [2], has also undergone development both in the thermodynamical [30]—[32] and molecular [33]—[35] approaches. In this paper, we shall concentrate on developing a general, molecular-statistical theory of light scattering in multi-component systems. It will be shown that Rayleigh's ratio can be represented as an expansion in powers of the molar fractions:

$$R = \sum_i x_i R_i + \sum_{ij} x_i x_j R_{ij} + \sum_{ijk} x_i x_j x_k R_{ijk} + \dots \quad (9)$$

The first term of (9) defines additivity of the Rayleigh ratio whereas the higher ones provide a measure of its deviation from additivity. The coefficients R_i involve only the optical polarizabilities of the isolated molecules. The R_{ij} , R_{ijk} , ... contain moreover the polarizabilities and electric moments; it is most essential that they are linked, respectively, with the pairwise, triple, and multi-molecule correlation functions $g_{ij}^{(2)}$, $g_{ijk}^{(3)}$, ...

The ensuing, detailed discussion of R_{ij} and R_{ijk} is primarily aimed at showing that the role of molecular correlations in light scattering is by no means solely quantitative but in many a case leads to qualitatively new types of scattering, which do not appear if interactions are absent. Particular care will be given to establishing the conditions for the appearance of anisotropic light scattering, the mechanism of which has to remain unexplained in the thermodynamical approach.

2. General fundamentals of the theory

We consider an isotropic medium on which a light wave is incident with electric vector $\mathbf{E} = \mathbf{E}_0 e^{i\omega t}$ oscillating at frequency $\omega = 2\pi c/\lambda$, and define therein a sphere of volume V whose radius is small with respect to λ . Let n and n_0 be the refractive indices within and out-

side the sphere, respectively. The mean macroscopic optical field \mathbf{E}_M existing inside the sphere is now related with \mathbf{E} thus:

$$\mathbf{E}_M = \frac{3n_0^2}{n^2 + 2n_0^2} \mathbf{E}. \quad (10)$$

Since by assumption $V \ll \lambda^3$, we can restrict considerations to light scattering of the dipolar type with electric field in the wave zone distant by R_0 from the centre of the scattering sphere given as [5, 17]

$$\mathbf{E}_{R_0} = \frac{1}{c^2 R_0^3} \{\mathbf{R}_0 \times (\mathbf{R}_0 \times \mathbf{M})\}, \quad (11)$$

where \mathbf{M} is the total dipole moment induced in the sphere by the field \mathbf{E} of the incident wave.

Assuming for generality that V contains $N = \sum_j N_j$ molecules of various species (N_j is the number of those of species j), we can write in a linear approximation

$$\mathbf{M} = \sum_j \sum_{q=1}^{N_j} \mathbf{m}^{(qj)} \exp \{i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{r}_q\}, \quad (12)$$

$\mathbf{m}^{(qj)}$ denoting the electric dipole moment induced in the q -th molecule of species j distant by \mathbf{r}_q from the origin of coordinates; \mathbf{k} and \mathbf{k}' are respectively the wave vectors of the incident and scattered light.

Let us introduce the tensor of scattered light intensity $I_{\sigma\tau}^S$ defined as

$$I_{\sigma\tau}^S = \frac{1}{c^4 V} \langle \overline{\Delta \dot{M}_\sigma \Delta \dot{M}_\tau} \rangle \quad (13)$$

where the symbol $\overline{}$ stands for time-averaging and $\langle \rangle$ for appropriate statistical averaging.

The dipole moment \mathbf{M} is a function of \mathbf{E} , and can be written as the expansion

$$M_\sigma = \left(\frac{\partial M_\sigma}{\partial E_\tau} \right)_0 E_\tau + \frac{1}{2} \left(\frac{\partial^2 M_\sigma}{\partial E_\tau \partial E_\nu} \right)_0 E_\tau E_\nu + \dots, \quad (14)$$

wherein the first term leads to linear and the second and subsequent terms to non-linear [27] light scattering.

In the present paper, we shall discuss linear light scattering only. Moreover, as a simplification, we shall assume intermolecular distances much smaller than λ . By (12) and (14), the tensor (13) now resolves into two parts:

$$I_{\sigma\tau}^S = I_{\sigma\tau}^{\text{is}} + J_{\sigma\tau}^{\text{anis}} \quad (15)$$

the isotropic part being given as

$$I_{\sigma\tau}^{\text{is}} = \left(\frac{\omega}{c} \right)^4 F_{\text{is}}^0 J_{\sigma\tau}^0, \quad (16)$$

and the anisotropic part as

$$I_{\sigma\tau}^{\text{anis}} = \frac{1}{5} \left(\frac{\omega}{c} \right)^4 F_{\text{anis}} (3I^0 \delta_{\sigma\tau} + I_{\sigma\tau}^0). \quad (17)$$

Above, $I_{\sigma\tau}^0 = \overline{E_\sigma E_\tau}$ denotes the incident light intensity tensor, and $I^0 = I_{\nu\nu}^0$ — its trace.

The factors F_{is} and F_{anis} characterize the molecular mechanism of isotropic and anisotropic light scattering, and are defined as¹

$$F_{\text{is}} = \frac{1}{9V} \sum_{ij} \left\langle \Delta \sum_{p=1}^{N_i} \frac{\partial m_\alpha^{(pi)}}{\partial E_\alpha} \Delta \sum_{q=1}^{N_j} \frac{\partial m_\beta^{(jq)}}{\partial E_\beta} \right\rangle, \quad (18)$$

$$F_{\text{anis}} = \frac{1}{18V} \sum_{ij} \left\langle \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \left(3 \frac{\partial m_\alpha^{(pi)}}{\partial E_\beta} \frac{\partial m_\alpha^{(jq)}}{\partial E_\beta} - \frac{\partial m_\beta^{(pi)}}{\partial E_\beta} \frac{\partial m_\beta^{(jq)}}{\partial E_\beta} \right) \right\rangle \quad (19)$$

once we take the differential polarizability tensors $\partial m_\alpha / \partial E_\beta$ to be symmetrical and real, which is the case for optically inactive molecules in bands remote from electronic absorption.

Eqs (16) and (17) are quite general and can be applied for calculating various quantities characterizing the intensity and polarization of scattered light (the Rayleigh ratio R , depolarisation ratio D , turbidity, *etc.*) at well-defined conditions of observation. In particular, for non-polarized incident light propagating along the y -axis and scattered light observed along the x -axis of laboratory coordinates, Eqs (16) and (17) yield

$$I_{yy}^{\text{is}} = 0, I_{zz}^{\text{is}} = \frac{1}{2} \left(\frac{\omega}{c} \right)^4 I^0 F_{\text{is}} \quad (20)$$

$$I_{yy}^{\text{anis}} = \frac{3}{5} \left(\frac{\omega}{c} \right)^4 I^0 F_{\text{anis}}, I_{zz}^{\text{anis}} = \frac{7}{10} \left(\frac{\omega}{c} \right)^4 I^0 F_{\text{anis}}, \quad (21)$$

On defining the Rayleigh ratio as

$$R = \frac{I_{yy}^S + I_{zz}^S}{I_M^0} = \frac{I_{yy}^S + I_{zz}^S}{I^0} \left(\frac{n^2 + 2}{3} \right)^2, \quad (22)$$

where, by (10), I_M^0 denotes the incident light intensity for the interior of the sphere V immersed in vacuum ($n_0 = 1$), we obtain by (20) and (21) the isotropic and anisotropic parts in the form

$$R_{\text{is}} = \frac{1}{2} \left(\frac{\omega}{c} \right)^4 \left(\frac{n^2 + 2}{3} \right)^2 F_{\text{is}}, \quad R_{\text{anis}} = \frac{13}{10} \left(\frac{\omega}{c} \right)^4 \left(\frac{n^2 + 2}{3} \right)^2 F_{\text{anis}} \quad (23)$$

Likewise, Eqs (20) and (21) lead to the following, general expression for the depolarisation ratio:

$$D_u = \frac{I_{yy}^S}{I_{zz}^S} = \frac{6 F_{\text{anis}}}{5 F_{\text{is}} + 7 F_{\text{anis}}} \quad (24)$$

¹ Those of ref. [17] differ by a factor of $9V$.

In a similar way, Eqs (16) and (17) can serve for deriving expressions for R and D at other conditions [17], also when observation of scattering takes place at an angle ϑ with respect to the direction of incidence, yielding for the isotropic and anisotropic parts of the Rayleigh ratio [17], [36]

$$R_{\text{is}}(\vartheta) = \frac{1}{2} \left(\frac{\omega}{c} \right)^4 \left(\frac{n^2+2}{3} \right)^2 (1 + \cos^2 \vartheta) F_{\text{is}}, \quad (25)$$

$$R_{\text{anis}}(\vartheta) = \frac{1}{10} \left(\frac{\omega}{c} \right)^4 \left(\frac{n^2+2}{3} \right)^2 (13 + \cos^2 \vartheta) F_{\text{anis}}. \quad (26)$$

The general formulas (16) and (17) provide moreover the basis for deriving certain well-known relationships [4, 17, 36] between $R(\vartheta)$ and $D(\vartheta)$, and for proving the validity in this case of Krishnan's reciprocal relations between the various scattered light intensity tensor components for vertically and horizontally polarized light (with respect to the observation scattering plane xy) [27], [36].

3. Discussion of the factors F_{is} and F_{anis}

The subsequent discussion of this theory consists in applications of the molecular factors (18) and (19) to particular situations, rendering the optical properties of the molecules as such, as well as the micro-structure of various substances. We now proceed to consider, one by one, some of the most interesting though simple cases.

3.1. Anisotropic, linearly polarizable molecules.

To begin with, we assume the molecules to polarize linearly only, with polarizability unaffected by interaction, so that the component of the moment induced in the molecule is given by the linear relation

$$m_{\alpha}^{(pi)} = a_{\alpha\beta}^{(pi)} E_{\beta}, \quad (27)$$

where $a_{\alpha\beta}^{(pi)}$ is the optical polarizability tensor component of the p -th molecule of species i in the absence of molecular interactions.

With regard to (27), the molecular factors (18) and (19) become

$$F_{\text{is}} = \frac{1}{V} \sum_{ij} \left\{ \left\langle \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} a_{pi} a_{qj} \right\rangle - \left\langle \sum_{p=1}^{N_i} a_{pi} \right\rangle \left\langle \sum_{q=1}^{N_j} a_{qj} \right\rangle \right\}, \quad (28)$$

$$F_{\text{anis}} = \frac{1}{18V} \sum_{ij} \left\langle \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} (3 a_{\alpha\beta}^{(pi)} a_{\alpha\beta}^{(qj)} - a_{\alpha\alpha}^{(pi)} a_{\beta\beta}^{(qj)}) \right\rangle. \quad (29)$$

By well-known methods of statistical mechanics [28], [29], [37], these can be put in the form

$$F_{\text{is}} = \varrho \sum_{ij} a_i a_j \{x_i \delta_{ij} + x_i x_j G_R^{(ij)}\}, \quad (30)$$

$$F_{\text{anis}} = \frac{\varrho}{18} \sum_{ij} (3 a_{\alpha\beta}^{(i)} a_{\alpha\beta}^{(j)} - a_{\alpha\alpha}^{(i)} a_{\beta\beta}^{(j)}) \{x_i \delta_{ij} + x_i x_j J_A^{(ij)}\}, \quad (31)$$

where the following radial and angular molecular correlation parameters have been introduced:

$$G_R^{(ij)} = \frac{\rho}{V} \iint \{g_{ij}^{(2)}(\tau_p, \tau_q) - g_i^{(1)}(\tau_p)g_j^{(1)}(\tau_q)\} d\tau_p d\tau_q, \quad (32)$$

$$J_A^{(ij)} = \frac{\rho \iint a_{\alpha\beta}^{(i)} a_{\gamma\delta}^{(j)} \{3 \omega_{\alpha\gamma}^{(pq,ij)} \omega_{\beta\delta}^{(pq,ij)} - \delta_{\alpha\beta} \delta_{\gamma\delta}\} g_{ij}^{(2)}(\tau_p, \tau_q) d\tau_p d\tau_q}{V (3 a_{\alpha\beta}^{(i)} a_{\alpha\beta}^{(j)} - a_{\alpha\alpha}^{(i)} a_{\beta\beta}^{(j)})} \quad (33)$$

with $g_i^{(1)}(\tau_p)$ denoting the mono-molecular and $g_{ij}^{(2)}(\tau_p, \tau_q)$ the bi-molecular correlation function for molecules p and q of species i and j , respectively, at configurations τ_p and τ_q ; $\omega_{\alpha\gamma}^{(pq,ij)}$ is the cosine of the angle between axes α and γ of reference systems attached to molecule p of species i and molecule q of species j .

The expressions of Eqs (31) and (33) are valid for any molecular symmetry, whereas they undergo considerable simplification if the scattering molecules are assumed to possess the axial symmetry *e. g.* about their 3-axis:

$$F_{\text{anis}} = \rho \sum_{ij} a_i \kappa_{ai} a_j \kappa_{aj} \{x_i \delta_{ij} + x_i x_j J_A^{(ij)}\} \quad (34)$$

with an axial correlation parameter of the form

$$J_A^{(ij)} = \frac{\rho}{2V} \iint (3 \cos^2 \theta_{pq}^{(ij)} - 1) g_{ij}^{(2)}(\tau_p, \tau_q) d\tau_p d\tau_q \quad (35)$$

and optical anisotropy

$$\kappa_{ai} = (a_{33}^{(i)} - a_{11}^{(i)})/3a_i. \quad (36)$$

Formally, it is also possible to write down Eqs (30) and (31) as follows:

$$F_{\text{is}} = \sum_i x_i F_{\text{is}}^{(i)} + \sum_{ij} x_i x_j F_{\text{is}}^{(ij)} + \dots, \quad (37)$$

$$F_{\text{anis}} = \sum_i x_i F_{\text{anis}}^{(i)} + \sum_{ij} x_i x_j F_{\text{anis}}^{(ij)} + \dots \quad (38)$$

wherein the molecular factors

$$F_{\text{is}}^{(i)} = \rho a_i^2, \quad F_{\text{anis}}^{(i)} = \frac{\rho}{18} (3a_{\alpha\beta}^{(i)} a_{\alpha\beta}^{(i)} - a_{\alpha\alpha}^{(i)} a_{\beta\beta}^{(i)}) \quad (39)$$

define the properties of an ideal mixture of non-interacting molecules, while the expressions

$$F_{\text{is}}^{(ij)} = \rho a_i a_j G_R^{(ij)}, \quad F_{\text{anis}}^{(ij)} = \frac{\rho}{18} (3a_{\alpha\beta}^{(i)} a_{\alpha\beta}^{(j)} - a_{\alpha\alpha}^{(i)} a_{\beta\beta}^{(j)}) J_A^{(ij)} \quad (40)$$

account for those of the real mixture presenting molecular correlations defined by the parameters (32) and (33).

In the absence of molecular correlations $G_R^{(ij)} = 0$ and $J_A^{(ij)} = 0$, whence Eqs (37) and (38) reduce to

$$F_{\text{is}} = \sum_i x_i F_{\text{is}}^{(i)}, \quad F_{\text{anis}} = \sum_i x_i F_{\text{anis}}^{(i)}. \quad (41)$$

which expresses additivity of the molecular factors, amounting to the statement that the molecules of the various components of the ideal mixture scatter light independently. In condensed mixtures, owing to correlations between molecules of the same as well as of different components, the factors F_{is} and F_{anis} are no longer additive quantities.

3.2. Isotropic molecules with effective polarizability

If, in particular, the molecules are isotropically polarizable, we have

$$a_{\alpha\beta}^{(pi)} = a_{pi} \delta_{\alpha\beta} \quad (42)$$

and the anisotropic scattering factor (29) is seen to vanish. Thus, anisotropic molecules of constant polarizability cannot scatter anisotropically. However, the latter conclusion is strictly valid only in the foregoing approximation of the theory *i. e.* if Eq. (27) is postulated. For isotropic molecules, by (42), it reduces to

$$m_{\alpha}^{(pi)} = a_{pi} E_{\alpha}. \quad (43)$$

Now, this relation is strictly correct only when the atom or molecule undergoing polarization in an externally applied electric field is isolated with regard to neighbouring atoms or molecules. Such conditions are ensured only in strongly rarefied gases, where the distances separating the molecules are greatly in excess of their linear dimensions.

In condensed media such as compressed gases or liquids, the atoms or molecules polarize one another by way of their intrinsic microscopic fields, even if no external field is acting on the medium. In the general case, a given molecule is acted on by the externally applied electric field \mathbf{E} and moreover by the molecular field \mathbf{F} due to the charge distribution of the other, polarized molecules of the medium.

We now have to replace Eq. (43) by

$$m_{\alpha}^{(pi)} = a_{pi} (E_{\alpha} + F_{\alpha}^{(pi)}), \quad (44)$$

where the molecular field existing at the centre of molecule p of species i is given in the dipole approximation as [17], [38]

$$F_{\alpha}^{(pi)} = - \sum_j \sum_{q=1}^{N_j} T_{\alpha\beta}^{(pq)} m_{\beta}^{(qj)}, \quad (45)$$

where

$$T_{\alpha\beta}^{(pq)} = -r_{pq}^{-5} (3r_{pq\alpha} r_{pq\beta} - r_{pq}^2 \delta_{\alpha\beta}) \quad (46)$$

is the dipole-dipole type interaction tensor of molecules p and q distant by r_{pq} , vanishing for $p = q$ but non-zero for $p \neq q$.

By Eqs (44) and (45), the method of successive substitutions yields to a^2 :

$$F_{\alpha}^{(pi)} = - \sum_j \sum_{q=1}^{N_j} a_{qj} T_{\alpha\beta}^{(pq)} E_{\beta} + \sum_{jk} \sum_{q=1}^{N_j} \sum_{r=1}^{N_k} a_{qj} a_{rk} T_{\alpha\beta}^{(pq)} T_{\beta\gamma}^{(qr)} E_{\gamma} - \dots \quad (47)$$

It is seen that, on inserting the molecular field (47) into (44), the polarizability a of the isolated molecule relates the dipole moment and field \mathbf{E} inducing it in the first approxima-

tion only. In higher approximations, this polarizability is affected by multipole interactions of the induced dipole-induced dipole type, so that the atom or molecule now presents some effective polarizability.

We shall now consider once more the molecular factors in the form (18) and (19). First, let us discuss F_{anis} , which takes the form

$$F_{\text{anis}} = \frac{1}{18V} \sum_{ij} \left\langle \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} a_{pi} a_{qj} \left\{ 3 \frac{\partial F_{\alpha}^{(pi)}}{\partial E_{\beta}} \frac{\partial F_{\alpha}^{(qj)}}{\partial E_{\beta}} - \frac{\partial F_{\alpha}^{(pi)}}{\partial E_{\alpha}} \frac{\partial F_{\beta}^{(qj)}}{\partial E_{\beta}} \right\} \right\rangle. \quad (48)$$

The foregoing result states that owing to fluctuations of the molecular fields, anisotropic light scattering takes place even when the molecules are isotropically polarizable [10], [17], [20]. With molecular fields of the form (47) and on neglecting terms in higher powers of the polarizability we obtain the result

$$F_{\text{anis}} = \frac{1}{6V} \sum_{ijkl} \left\langle \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \sum_{r=1}^{N_k} \sum_{s=1}^{N_l} a_{pi} a_{qj} a_{rk} a_{sl} T_{\alpha\beta}^{(pr)} T_{\alpha\beta}^{(qs)} \right\rangle, \quad (49)$$

which, by statistical methods, can further be written down in expansion form:

$$F_{\text{anis}} = \sum_{ij} x_i x_j F_{\text{anis}}^{(ij)} + \sum_{ijk} x_i x_j x_k F_{\text{anis}}^{(ijk)} + \dots, \quad (50)$$

where to within ternary molecular correlations we have

$$F_{\text{anis}}^{(ij)} = \varrho a_i^2 a_j^2 J_R^{(ij)}, \quad (51)$$

$$F_{\text{anis}}^{(ijk)} = \varrho a_i a_j^2 a_k J_R^{(ijk)}. \quad (52)$$

Above, we have introduced the following binary and ternary correlations parameters:

$$J_R^{(ij)} = 2 \frac{\varrho}{V} \iint r_{pq}^{-6} g_{ij}^{(2)}(\tau_p, \tau_q) d\tau_p d\tau_q, \quad (53)$$

$$J_R^{(ijk)} = \frac{\varrho^2}{V} \iiint \{3(\mathbf{r}_{pq} \cdot \mathbf{r}_{qr})^2 - r_{pq}^2 r_{qr}^2\} r_{pq}^{-5} r_{qr}^{-5} g_{ijk}^{(3)}(\tau_p, \tau_q, \tau_r) d\tau_p d\tau_q d\tau_r, \quad (54)$$

with the ternary molecular correlation function $g_{ijk}^{(3)}(\tau_p, \tau_q, \tau_r)$.

The radial correlation parameters (53) and (54) occur moreover in the theories of molecular refraction [21] as well as magnetic [22] and optical [39] birefringence of atomic fluids.

The expansion (50) fails to contain the additive term $\sum_i x_i F_{\text{anis}}^{(i)}$, since by what has been said, isolated atoms or isotropic molecules fail to produce anisotropic light scattering. In the condensed medium, as a result of interaction between induced molecular moments, anisotropic scattering appears. Indeed, such a medium will present binary or ternary assemblages of atoms or molecules coupled more or less strongly by radial forces. As long as they hold together, such assemblages behave like optically anisotropic elements on which light can undergo anisotropic scattering. This slight anisotropic scattering suffices for light depolarization to appear.

Similarly, one can calculate additional contributions to the isotropic scattering factor which, in the second and third approximations, will involve the correlation parameters (53) and (54).

3.3. Nonlinearly polarizable atoms

Although we consider but linear scattering due to a weak light beam, one would be wrong in concluding that the atoms or molecules of dense media reveal linear polarization only, as is the case in rarefied gases. Indeed, within dense media there exist molecular fields \mathbf{F}_0 whose strength is quite considerable as compared with that of the weak light beam \mathbf{E} and which can induce not only linear but moreover nonlinear polarization in the atoms or molecules. One now has to push further the expansion of Eq. (44), yielding for atoms immersed in a dense medium the tensor of differential polarizability

$$\frac{\partial m_{\alpha}^{(pi)}}{\partial E_{\beta}} = a_{pi} \delta_{\alpha\beta} + \frac{1}{6} c_{pi} (\delta_{\alpha\beta} F_{0\gamma}^{(pi)} F_{0\gamma}^{(pi)} + 2 F_{0\alpha}^{(pi)} F_{0\beta}^{(pi)}) + \frac{3}{4} q_{pi} F_{0\alpha\beta}^{(pi)} + \dots, \quad (55)$$

where, in addition to the atom's mean linear polarizability a_{pi} , we encounter its mean nonlinear polarizability c_{pi} induced by the square of the molecular field $F_{0\alpha}^{(pi)}$ and mean quadrupolar polarizability q_{pi} induced by the molecular field gradient $F_{0\alpha\beta}^{(pi)}$.

Insertion of (55) into the anisotropic factor (19) shows it to be in general non-zero, amounting to

$$F_{\text{anis}} = \frac{1}{162V} \sum_{ij} \left\{ c_i c_j \left\langle \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} [3(F_{0\alpha}^{(pi)} F_{0\beta}^{(pi)}) (F_{0\alpha}^{(qj)} F_{0\beta}^{(qj)}) - (F_{0\alpha}^{(pi)} F_{0\alpha}^{(pi)})(F_{0\beta}^{(qj)} F_{0\beta}^{(qj)})] \right\rangle + \frac{243}{16} q_i q_j \left\langle \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} F_{\alpha\beta}^{(pi)} F_{\alpha\beta}^{(qj)} \right\rangle \right\}. \quad (56)$$

Hence, nonlinearity in the dipolar polarizability of atoms on the one hand and quadrupolar polarizability on the other give rise to anisotropic light scattering at $\mathbf{E} = 0$ due to fluctuations of the molecular fields.

Assuming for the sake of simplicity that two atoms interact with dispersive London forces, we get [40]

$$a_i F_{0\alpha}^{(pi)} F_{0\beta}^{(pi)} = a_j F_{0\alpha}^{(qj)} F_{0\beta}^{(qj)} = \frac{\hbar}{4} \frac{v_i v_j}{v_i + v_j} a_i a_j r_{pq}^{-8} (3r_{pq} \alpha_{pq\beta} + r_{pq}^2 \delta_{\alpha\beta}), \quad (57)$$

$\hbar v_i$ and $\hbar v_j$ being characteristic energies of the species i and j respectively.

Omitting in (56) the term related with quadrupolar polarizabilities and taking into account the fields (57) one obtains the anisotropic scattering factor for pairwise atomic interactions in the form

$$F_{\text{anis}}^{(ij)} = \frac{\varrho}{72} (a_i^2 c_j^2 + 2a_i a_j c_i c_j + c_i^2 a_j^2) \left(\frac{\hbar v_i \hbar v_j}{v_i + v_j} \right)^2 R_{12}^{(ij)}, \quad (58)$$

where the radial correlation parameter $R_{12}^{(ij)}$ is given by

$$R_n^{(ij)} = \varrho \int r_{pq}^{-n} g_{ij}^{(2)}(r_{pq}) dr_{pq} \quad (59)$$

for an exponent of $n = 12$.

3.4. Tetrahedral, nonlinearly polarizable molecules.

In the case of tetrahedral molecules (*e.g.* CH₄), the differential polarizability tensor expansion contains a term linear in the molecular field:

$$\frac{\partial m_{\alpha}^{(pi)}}{\partial E_{\beta}} = a_{pi} \delta_{\alpha\beta} + b_{\alpha\beta\gamma}^{(pi)} F_{0\gamma}^{(pi)} + \dots, \quad (60)$$

which involves the tensor $b_{\alpha\beta\gamma}^{(pi)}$ having non-zero components $b_{123} \equiv b$ and describing the change in polarizability of the molecule due to the field $\mathbf{F}_0^{(pi)}$.

Insertion of (60) into (19) yields in the relevant approximation the following result:

$$F_{\text{anis}} = \frac{1}{6V} \sum_{ij} \left\langle \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} b_{\alpha\beta\gamma}^{(pi)} b_{\alpha\beta\delta}^{(qj)} F_{0\gamma}^{(pi)} F_{0\delta}^{(qj)} \right\rangle, \quad (61)$$

whence, in general, mutually interacting tetrahedral molecules are also seen to scatter light anisotropically.

Let us first assume that the tetrahedral molecules interact with dispersive forces of the type (57); considering pairwise correlations only, Eq. (61) yields

$$F_{\text{anis}}^{(ij)} = \frac{1}{2} \varrho \left(\frac{h\nu_i \nu_j}{\nu_i + \nu_j} \right) (a_i b_j^2 + b_i^2 a_j) R_6^{(ij)}, \quad (62)$$

where the radial correlation parameter $R_6^{(ij)}$ is given by Eq. (59) for $n = 6$.

On the other hand, tetrahedral molecules are known to possess an octupole moment [37]

$$\Omega \equiv \Omega_{123} = \frac{5}{2} \sum_n e_n x_n y_n z_n, \quad (63)$$

e_n being the n -th electric charge of the molecule.

The electric field due to octupole moments of molecules is of the general form [41]

$$F_{0\alpha}^{(pi)} = -\frac{1}{15} \sum_j \sum_{q=1}^{N_j} T_{\alpha\beta\gamma\delta}^{(pq)} \Omega_{\beta\gamma\delta}^{(qj)}, \quad (64)$$

where $\Omega_{\alpha\beta\gamma}$ is the octupole moment tensor, and $T_{\alpha\beta\gamma\delta}^{(pq)} = -\nabla_{\alpha} \nabla_{\beta} \nabla_{\gamma} \nabla_{\delta} (1/r_{pq})$ that of dipole-octupole (or quadrupole-quadrupole) interaction.

Substitution of the field (64) into Eq. (61), in the tetrahedral case, yields

$$F_{\text{anis}}^{(ij)} = \frac{8\varrho}{35} (7b_i^2 \Omega_j^2 + 6b_i b_j \Omega_i \Omega_j + 7\Omega_i^2 b_j^2) R_{10}^{(ij)}. \quad (65)$$

3.5. Anisotropic, nonlinearly polarizable molecules.

For anisotropic molecules of arbitrary symmetry, the differential polarizability tensor is given by the expansion [34]

$$\frac{\partial m_{\alpha}^{(pi)}}{\partial E_x} = \left\{ a_{\alpha\beta}^{(pi)} + b_{\alpha\beta\gamma}^{(pi)} F_{0\gamma}^{(pi)} + \frac{1}{2} c_{\alpha\beta\gamma\delta}^{(pi)} F_{0\gamma}^{(pi)} F_{0\delta}^{(pi)} + \right. \\ \left. + \frac{1}{3} g_{\alpha\beta\gamma\delta}^{(pi)} F_{0\gamma\delta}^{(pi)} + \dots \right\} \left\{ \delta_{\beta x} + \frac{\partial F_{\beta}^{(pi)}}{\partial E_x} \right\}, \quad (66)$$

$b_{\alpha\beta\gamma}$ and $c_{\alpha\beta\gamma\delta}$ denoting the dipolar nonlinear polarizability tensors, and $g_{\alpha\beta\gamma\delta}$ the quadrupole polarizability tensor.

The molecular field \mathbf{F} is now of a more general form than that of Eq. (45); to within quadrupole type interaction, we have namely [40], [41]

$$F_{\alpha}^{(pi)} = - \sum_j \sum_{q=1}^{N_j} T_{\alpha\beta}^{(pq)} (\mu_{\beta}^{(qi)} + m_{\beta}^{(qi)}) + \frac{1}{3} \sum_j \sum_{q=1}^{N_j} T_{\alpha\beta\gamma}^{(pq)} (\Theta_{\beta\gamma}^{(qi)} + Q_{\beta\gamma}^{(qi)}) - \dots, \quad (67)$$

μ_{α} and m_{α} being respectively the permanent and induced dipole moment of the molecule, and $\Theta_{\alpha\beta}$, $Q_{\alpha\beta}$ the tensor of its permanent and induced quadrupole moments.

One notes that in the present, general case the problem of effectively calculating the molecular factors F_{is} and F_{anis} becomes highly complicated, the more so as we now have also to take into consideration the energy U of intermolecular interaction inherent in the statistical mean values marked in (18) and (19):

$$\langle X \rangle = \frac{\int X(\tau) \exp \left\{ -\frac{U(\tau)}{kT} \right\} d\tau}{\int \exp \left\{ -\frac{U(\tau)}{kT} \right\} d\tau}. \quad (68)$$

The energy $U(\tau)$ is a function of the positional variables \mathbf{r} and orientational variables ω of the molecules, and comprises contributions from central interaction U_{centr} , electrostatic interaction U_{el} , inductive interaction U_{ind} , and dispersive interaction U_{disp} :

$$U(\tau) = U_{\text{centr}} + U_{\text{el}} + U_{\text{ind}} + U_{\text{disp}}. \quad (69)$$

With the exception of central interaction energy, which depends on the variables \mathbf{r} only, all the other energies are moreover in general dependent on the orientational variables ω .

With accuracy up to quadrupole-quadrupole interaction, the energy of electrostatic interaction is of the form [37], [41]

$$U_{\text{el}} = \frac{1}{2} \sum_{ij} \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \left\{ \mu_{\alpha}^{(pi)} T_{\alpha\beta}^{(pq)} \mu_{\beta}^{(qi)} - \right. \\ \left. - \frac{1}{3} (\mu_{\alpha}^{(pi)} \Theta_{\beta\gamma}^{(qi)} - \Theta_{\alpha\beta}^{(pi)} \mu_{\gamma}^{(qi)}) T_{\alpha\beta\gamma}^{(pq)} - \frac{1}{9} \Theta_{\alpha\beta}^{(pi)} T_{\alpha\beta\gamma\delta}^{(pq)} \Theta_{\gamma\delta}^{(qi)} - \dots \right\}, \quad (70)$$

whereas that of inductational interaction relating to the same approximation (omitting the quadrupolar polarizabilities) is [37]

$$\begin{aligned}
 U_{\text{ind}} = & -\frac{1}{2} \sum_{ijk} \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \sum_{r=1}^{N_k} \left\{ \mu_{\alpha}^{(pi)} T_{\alpha\beta}^{(pr)} \alpha_{\beta\gamma}^{(rk)} T_{\gamma\delta}^{(rq)} \mu_{\delta}^{(qj)} - \right. \\
 & -\frac{1}{3} (\mu_{\alpha}^{(pi)} T_{\alpha\beta}^{(pr)} \alpha_{\beta\gamma}^{(rk)} T_{\gamma\delta\epsilon}^{(rq)} \Theta_{\delta\epsilon}^{(qj)} - \Theta_{\alpha\beta}^{(pi)} T_{\alpha\beta\gamma}^{(pr)} \alpha_{\gamma\delta}^{(rk)} T_{\delta\epsilon}^{(rq)} \mu_{\epsilon}^{(qj)}) - \\
 & \left. -\frac{1}{9} \Theta_{\alpha\beta}^{(pi)} T_{\alpha\beta\gamma}^{(pr)} \alpha_{\gamma\delta}^{(rk)} T_{\delta\epsilon\eta}^{(rq)} \Theta_{\epsilon\eta}^{(qj)} - \dots \right\}, \quad (71)
 \end{aligned}$$

$\alpha_{\alpha\beta}^{(rk)}$ being the electric polarizability tensor of molecule r belonging to species k ; the interaction tensors $T_{\alpha\beta\gamma}$, $T_{\alpha\beta\gamma\delta}$ and electric multipole moment tensors $\Theta_{\alpha\beta}$, $\Omega_{\alpha\beta\gamma}$ are to be found *e.g.* in refs [40], [42].

The calculation of the factors (18), (19) with Eqs (66)—(71) is thus seen to involve very great complications, and is feasible only if appropriate simplifying assumptions are made. Usually, all non-central interaction energies, $U_p = U_{\text{el}} + U_{\text{ind}} + U_{\text{disp}}$, can be dealt with as a small perturbation to U_{centr} , and the averaging procedure of Eq. (68) can be replaced by the approximation

$$\begin{aligned}
 \langle X \rangle = & \langle X \rangle_0 - \frac{1}{kT} (\langle XU_p \rangle_0 - \langle X \rangle_0 \langle U_p \rangle_0) + \\
 & + \frac{1}{2k^2 T^2} [\langle XU_p^2 \rangle_0 - \langle X \rangle_0 \langle U_p^2 \rangle_0 - 2(\langle XU_p \rangle_0 - \langle X \rangle_0 \langle U_p \rangle_0) \langle U_p \rangle_0] - \dots, \quad (72)
 \end{aligned}$$

where $\langle \rangle_0$ symbolizes statistical averaging with non-perturbated central interaction energy.

When the expressions (66)—(72) are applied in calculating the anisotropic factor (19), one obtains for pairwise correlations of axially-symmetric molecules the following contributions to F_{anis} which result one by one from permanent dipole-induced (first-order) dipole interaction

$$\begin{aligned}
 \mu_{-\alpha} F_{\text{anis}}^{(ij)} = & \frac{\varrho}{25kT} a_i \kappa_{ai} a_j \kappa_{aj} \{ (\alpha_i \kappa_{ai} \mu_j^2 + \mu_i^2 \alpha_j \kappa_{aj}) R_6^{(ij)} + \\
 & + \frac{4\mu_i^2 \mu_j^2}{49k^2 T^2} [\alpha_i (7 + 11\kappa_{ai}) \mu_j^2 + \mu_i^2 \alpha_j (7 + 11\kappa_{aj})] R_{12}^{(ij)} + \dots \} \quad (73)
 \end{aligned}$$

from permanent dipole-permanent dipole interaction

$$\mu_{-\mu} F_{\text{anis}}^{(ij)} = \frac{\varrho \mu_i^2 \mu_j^2}{75k^2 T^2} a_i \kappa_{ai} a_j \kappa_{aj} \left\{ R_6^{(ij)} + \frac{12\mu_i^2 \mu_j^2}{49k^2 T^2} R_{12}^{(ij)} + \frac{13\mu_i^4 \mu_j^4}{441k^4 T^4} R_{18}^{(ij)} + \dots \right\}, \quad (74)$$

and from permanent dipole-induced (second-order) dipole interaction

$$\begin{aligned}
 \mu_{-b} F_{\text{anis}}^{(ij)} = & \frac{2\varrho \mu_i \mu_j}{75kT} \left\{ [\mu_i a_i \kappa_{ai} b_j (1 + 25 \kappa_{bj}) + b_i (1 + 25 \kappa_{bi}) \mu_j a_j \kappa_{aj}] R_6^{(ij)} + \right. \\
 & \left. + \frac{6\mu_i^2 \mu_j^2}{49k^2 T^2} [\mu_i a_i \kappa_{ai} b_j (2 + 51 \kappa_{bj}) + b_i (2 + 51 \kappa_{bi}) \mu_j a_j \kappa_{aj}] R_{12}^{(ij)} + \dots \right\}, \quad (75)
 \end{aligned}$$

wherein

$$\varkappa_{bi} = (b_{333}^{(i)} - b_{113}^{(i)})/3b_i \quad \text{and} \quad b_i = (b_{333}^{(i)} + 2b_{113}^{(i)})/3 \quad (76)$$

stand for the anisotropy and mean value of the second-order polarizability.

Similar calculations for quadrupolar, axially-symmetric molecules yield successively the following interactional contributions to $F_{\text{anis}}^{(ij)}$:

permanent quadrupole-induced dipole

$$\Theta_{-\alpha} F_{\text{anis}}^{(ij)} = \frac{3\varrho}{35kT} a_i \varkappa_{ai} a_j \varkappa_{aj} (\alpha_i \varkappa_{ai} \Theta_j^2 + \Theta_i^2 \alpha_j \varkappa_{aj}) R_8^{(ij)}, \quad (77)$$

permanent quadrupole-permanent quadrupole

$$\Theta - \Theta F_{\text{anis}}^{(ij)} = \frac{4\varrho}{35k^2T^2} a_i \varkappa_{ai} a_j \varkappa_{aj} \Theta_i^2 \Theta_j^2 R_{10}^{(ij)}, \quad (78)$$

and permanent quadrupole-induced (third-order) dipole

$$\Theta_{-c} F_{\text{anis}}^{(ij)} = \frac{\varrho}{84} \left\{ a_i \varkappa_{ai} (20 \Theta_i^2 c_j + 49 c_j \varkappa_{ci} \Theta_j^2) + (20 c_i \Theta_j^2 + 49 \Theta_j^2 c_j \varkappa_{cj}) a_j \varkappa_{aj} \right\} R_8^{(ij)}, \quad (79)$$

where we have used the molecular parameters

$$\varkappa_{ci} = (c_{333}^{(i)} - c_{111}^{(i)})/3c_i \quad \text{and} \quad c_i = (c_{333}^{(i)} + 2c_{111}^{(i)})/3 \quad (80)$$

defining the anisotropy and mean value of the third-order dipolar polarizability.

Analogous calculations, which are of a somewhat lesser degree of complication, can be carried out for the factor of isotropic scattering (18).

4. Applications to mixtures of real gases

For moderately compressed gases, the binary and ternary correlation functions can be written as [28], [37]

$$\begin{aligned} \Omega^2 g_{ij}^2(\tau_p, \tau_q) &= \exp \left[-\frac{u_{ij}(\tau_p, \tau_q)}{kT} \right] \left\{ 1 + \varrho \sum_k x_k \int \left[\exp \left(-\frac{u_{ik}(\tau_p, \tau_r)}{kT} \right) - 1 \right] \times \right. \\ &\quad \left. \times \left[\exp \left(-\frac{u_{kj}(\tau_r, \tau_q)}{kT} \right) - 1 \right] d\tau_r + O(\varrho^2) \right\}, \end{aligned} \quad (81)$$

$$\Omega^3 g_{ijk}^{(3)}(\tau_p, \tau_q, \tau_r) = \exp \left[-\frac{u_{ijk}(\tau_p, \tau_q, \tau_r)}{kT} \right] \{ 1 + O(\varrho) \}, \quad (82)$$

where u_{ij} and u_{ijk} are the total potential interaction energies for two or three molecules, respectively; $\Omega = \int d\omega$.

By (81) and (82), the factors $F^{(ij)}$ and $F^{(ijk)}$ can in general be certain functions of the molar fractions. However, if pairwise interaction alone is considered, $F_{\text{is}}^{(ij)}$ and $F_{\text{anis}}^{(ij)}$

will not depend explicitly on the latter. In this approximation, it is convenient to separate a radial part $g_{ij}^{(2)}(r_{pq})$ from the binary correlation function, as follows:

$$\Omega^2 g_{ij}^{(2)}(\tau_p, \tau_q) = g_{ij}^{(2)}(r_{pq}) \exp \left[- \frac{v_{ij}(r_{pq}, \omega_p, \omega_q)}{kT} \right] \quad (83)$$

with $v_{ij}(r_{pq}, \omega_p, \omega_q)$ the noncentral potential energy of interaction between two molecules having orientations ω_p and ω_q .

Using the approximation of Eq. (83), one can effectively compute the correlation parameters (32) and (33) for various molecular models. Indeed, the parameter (32) can now be expressed directly by means of the second virial coefficient of the equation of state for gases:

$$B_{ij} = - \frac{1}{2} V G_R^{(ij)} = - \frac{N}{2\Omega^2} \int \int \int \left\{ \exp \left[- \frac{u_{ij}(r_{pq}, \omega_p, \omega_q)}{kT} \right] - 1 \right\} d\mathbf{r}_{pq} d\omega_p d\omega_q \quad (84)$$

which has been discussed in full for various models of noncentral forces [42].

With regard to the approximation (83), the angular correlation parameter (35) can be written as

$$J_A^{(ij)} = \frac{1}{2} \rho \int \int \int g_{ij}^{(2)}(r_{pq}) (3 \cos^2 \theta_{pq}^{(ij)} - 1) \exp \left[- \frac{v_{ij}(r_{pq}, \omega_p, \omega_q)}{kT} \right] d\mathbf{r}_{pq} d\omega_p d\omega_q \quad (85)$$

a form well-adapted to direct computations for appropriately chosen models.

In particular, in the case of molecules that are anisotropic and non-polar, the only noncentral interaction energy is that due to anisotropy of dispersive forces. This can be put in the form [40]

$$\begin{aligned} v_{ij}^{\text{disp}} = & \frac{3}{4} \frac{h\nu_i\nu_j}{\nu_i + \nu_j} \alpha_i \alpha_j \{ \kappa_{ai} + \kappa_{aj} - 3\kappa_{ai}(1 - \kappa_{aj}) \cos^2 \theta_p - \\ & - 3\kappa_{aj}(1 - \kappa_{ai}) \cos^2 \theta_q - 3\kappa_{ai}\kappa_{aj} (3 \cos \theta_p \cos \theta_q - \cos \theta_{pq})^2 \} r_{pq}^{-6}. \end{aligned} \quad (86)$$

On inserting (86) into Eq. (85), one gets with an accuracy up to the second approximation of perturbation calculus

$$\begin{aligned} J_A^{(ij)} = & \frac{3}{50 kT} \left(\frac{h\nu_i\nu_j}{\nu_i + \nu_j} \right) \alpha_i \kappa_{ai} \alpha_j \kappa_{aj} \left\{ R_6^{(ij)} + \right. \\ & \left. + \frac{3}{98 kT} \left(\frac{h\nu_i\nu_j}{\nu_i + \nu_j} \right) [49 - 14 (\kappa_{ai} + \kappa_{aj}) + 38\kappa_{ai}\kappa_{aj}] R_{12}^{(ij)} + \dots \right\}. \end{aligned} \quad (87)$$

The above expression still contains radial parameters given by (59) which can be calculated if the form of $g_{ij}^{(2)}(r_{pq})$ is known explicitly. In cases when

$$g_{ij}^{(2)}(r_{pq}) = \exp \left\{ -y_{ij}^2 \left[\left(\frac{\sigma_{ij}}{r_{pq}} \right)^s - \left(\frac{\sigma_{ij}}{r_{pq}} \right)^t \right] \right\}, \quad (88)$$

one derives from (59) by the Lennard-Jones method [42]

$$R_n^{(ij)} = \frac{4\pi Q \sigma_{ij}^{3-n}}{s y_{ij}^A} H_n^{s-t}(y_{ij}), \quad (89)$$

wherein

$$H_n^{s-t}(y_{ij}) = y_{ij}^{2(2s+3-n)/s} \sum_{m=0}^n \frac{1}{m!} y_{ij}^{2m(s-t)/s} \Gamma\left(\frac{tm+n-3}{s}\right) \quad (90)$$

are functions discussed for $s = 12$ and $t = 6$ by Pople [43] and for $s = 18$ and $t = 6$ as well as $s = 28$ and $t = 7$ by Saxena and Joshi [44]; ε_{ij} and σ_{ij} are central forces parameters having the dimensions of an energy and length, respectively; $y_{ij} = 2(\varepsilon_{ij}/kT)^{1/2}$.

Eq. (89) permits to calculate numerically not only the correlation parameter (87), but moreover the other expressions (58), (62), (65) and (73)—(79) containing the radial correlation parameters $R_n^{(ij)}$. Since most parameters such as ε_{ij} , σ_{ij} , α_i , κ_i , μ_i , Θ_i etc. are known for a large variety of molecules, evaluations of the various contributions to the factors F_{is} and F_{anis} can be made and point to a rather essential role of noncentral interactions, particularly nonlinear polarizability [25]. It is to be regretted that as yet there are no measurements on light scattering by compressed gases and their mixtures. Once light scattering measurements in real gases become feasible, it will be possible to determine the values of molecular multipoles and to compare them with the values obtained by other methods [42], [45].

In recent years, a number of papers [46]—[50] have been published on the experimental study of light scattering in various liquid solutions. A discussion of their results with the present theory will be given separately.

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