

ANISOTROPIC SCATTERING OF LIGHT BY LIQUID MOLECULAR SOLUTIONS

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(Received June 5, 1973)

A complete molecular-statistical theory of anisotropic light scattering by multi-component systems is proposed. The depolarisation of scattered light is interpreted in terms of an effective optical anisotropy of regions of short-range ordering in the solution. This anisotropy is calculated by molecular-statistical perturbation calculus in the second approximation inclusively. The zero-th approximation accounts for scattering by the optical anisotropy of individual molecules and their angular interactions. In the first approximation, translational-orientational fluctuations intervene. In the second approximation, moreover translational fluctuations and orientational fluctuations are active.

For certain model assumptions, numerical calculations of the various contributions to the effective optical molecular anisotropy are performed to the end yielding very satisfactory agreement with recent measurements of anisotropic light scattering by the binary liquid systems $C_6H_6-CCl_4$ and CS_2-CCl_4 . Investigation of the deviations from additivity in the effective optical anisotropy of the solutions provides highly relevant information bearing on the many-body distribution functions, describing the correlations between the molecules of different species as well as of the same species.

1. Introduction

The method, elaborated at Bordeaux University [1], of separate measurements of anisotropic molecular light scattering, has recently been applied by Bothorel [2] and Deželić *et al.* [3] in studies of depolarized scattered light from molecular solutions in the entire range of concentrations. In this paper, we propose an extension of the existing molecular-statistical theory [4, 5] to account for the above mentioned experimental studies.

Anisotropic light scattering by atomic solutions is currently interpreted in terms of the translational fluctuations introduced by Yvon [6] in the theory of molecular refraction and by Kirkwood [7] in that of molecular polarisation of simple liquids. It will be

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shown here that the optical anisotropy induced in regions of near ordering originates not only in pairwise correlations but also in three- and four-body interactions [8].

In solutions containing anisotropic molecules, besides scattering on angular correlations [9, 10], an important rôle is played by translational-orientational fluctuations [4, 5], especially in cases when the molecules of the solvent are isotropic. Contrary to the earlier belief that such solvents could be considered as neutral, the solvent effect [4, 11] has to be taken into account, in particular when determining the optical anisotropy of asymmetric molecules by the method of infinitely dilute solutions [4]. However, we shall not be taking into consideration the optical activity of molecules the light scattering theory of which has been proposed by Atkins and Barrow [12] as well as Blum and Frisch [13] without molecular correlations, and by Kielich [14] including molecular interactions.

In liquids and dense solutions, one has to deal with an effective molecular anisotropy [4, 5, 9], which we calculate strictly in this paper by molecular-statistical perturbation calculus. The results thus obtained are quite general, and we apply them to various particular cases. On certain model assumptions, we carry out numerical calculations of the successive contributions to anisotropic light scattering. The results of these calculations are found to be in good agreement with experiment for solutions of benzene in CCl_4 as well as of carbon disulphide in CCl_4 .

2. Fundamentals of the theory

We consider a volume V , containing $N = \sum_i N_i$ unlike molecules; N_i is the number of molecules of the i -th species. If neither internal interference nor frequency and spatial dispersion are present, we define the effective optical anisotropy of the many-component system as follows [4, 5]:

$$\Gamma^2 = \frac{3}{2N} \sum_{ij} \left\langle \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \mathbf{D}_{pi} : \mathbf{D}_{qj} \right\rangle, \quad (1)$$

where the symbol $\langle \rangle$ stands for statistical averaging in the presence of molecular correlations.

The deviator of the symmetric optical polarizability tensor A_{pi} of the p -th molecule of the i -th species immersed in the medium is defined by the following equation:

$$\mathbf{D}_{pi} = A_{pi} - \frac{1}{3} U(A_{pi} : U), \quad (2)$$

where U is the unit tensor of rank 2: $U = xx + yy + zz$, x, y, z being unit vectors in the directions of the axes X, Y, Z of Cartesian coordinates; obviously, the trace of the deviator (2) vanishes: $\mathbf{D}_{pi} : U = 0$.

The value of the polarizability tensor A_{pi} depends on the internal state of the molecule, denoted by the lower indices p, i as well as on its configuration with respect to the molecules surrounding it in V . As long as the factors causing a perturbation of the molecular polariz-

ability are not excessively strong, one is justified in applying classical perturbation calculus, which leads to the expansion:

$$A_{pi} = A_{pi}^{(0)} + A_{pi}^{(1)} + A_{pi}^{(2)} + \dots = \sum_{n=0}^{\infty} A_{pi}^{(n)}, \quad (3)$$

where, in the zero-th approximation, the tensor:

$$A_{pi}^{(0)} = a_{pi} \quad (4)$$

defines the optical polarizability of the intrinsically anisotropic molecule in the ground state.

Higher approximations of the expansion (3) are to be derived from various specific processes, such as the translational fluctuations of Yvon [6] and Kirkwood [7], translational-orientational fluctuations [4, 5], and fluctuations of electric molecular fields leading to nonlinear polarizability of the molecules [9, 10].

In the present work, we shall restrict ourselves to the approximations resulting from the Yvon-Kirkwood approach in dipolar treatment, for which the n -th approximation is:

$$A_{pi}^{(n)} = a_{pi} \cdot \left(- \sum_j \sum_{q=1}^{N_j} T_{piqj} \cdot a_{qj} \right)^n, \quad (5)$$

where

$$T_{piqj} = -r_{piqj}^{-5} (3r_{piqj}r_{piqj} - r_{piqj}^2 U) \quad (6)$$

is the tensor of dipole-dipole interaction between the molecules p and q of species i mutually distant by r_{piqj} . The trace of the tensor (6) vanishes, $T : U = 0$.

With regard to the expansion (3), we can re-write the quantity (1) as follows:

$$\Gamma^2 = {}^{(0)}\Gamma^2 + {}^{(1)}\Gamma^2 + {}^{(2)}\Gamma^2 + {}^{(3)}\Gamma^2 + \dots = \sum_{n=0}^{\infty} {}^{(n)}\Gamma^2, \quad (7)$$

where

$${}^{(n)}\Gamma^2 = \frac{3}{2N} \sum_{m=0}^n \sum_{ij} \left\langle \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} D_{pi}^{(m)} : D_{qj}^{(n-m)} \right\rangle \quad (8)$$

is the effective anisotropy of the n -th approximation.

By methods of classical statistical mechanics we obtain:

$$\begin{aligned} & \sum_{i_1 \dots i_n} \left\langle \sum_{p_1=1}^{N_{i_1}} \sum_{p_2=1}^{N_{i_2}} \dots \sum_{p_n=1}^{N_{i_n}} \Phi_1 \Phi_2 \dots \Phi_n \right\rangle = \\ & = \sum_{k=1}^n \sum_{i_1 \dots i_k} x_{i_1} x_{i_2} \dots x_{i_k} \underbrace{Q^k}_{k} \int \dots \int A_k \Phi_1 \Phi_2 \dots \Phi_n g_{i_1 \dots i_k}^{(k)}(\tau_{p_1}, \dots, \tau_{p_k}) d\tau_{p_1} \dots d\tau_{p_k} \quad (9) \end{aligned}$$

with the notation: $x_i = N_i/N$; $\varrho = N/V$ — the number density of molecules; A_k a symmetrizing operator, contracting the product of functions $\Phi_1 \dots \Phi_n$ to a dependence on k

molecules; and $g_{i_1 \dots i_k}^{(k)}(\tau_{p_1}, \dots, \tau_{p_k})$ the correlation function of the k molecules, representing the components $i_1 \dots i_k$ whose configurations are given by the coordinates $\tau_{p_1} \dots \tau_{p_k}$ respectively.

By (9), we re-write the n -th contribution to the effective anisotropy (8) in the following form:

$${}^{(n)}\Gamma^2 = \sum_{k=1}^{n+2} \sum_{i_1 i_2 \dots i_k} x_{i_1} x_{i_2} \dots x_{i_k} {}^{(n)}\Gamma_{i_1 i_2 \dots i_k}^2, \quad (10)$$

with

$${}^{(n)}\Gamma_{i_1}^2 = 0 \quad \text{for} \quad n \geq 1,$$

whereas ${}^{(n)}\Gamma_{i_1 i_2 \dots i_k}^2$ for $k \geq 2$ represents the contributions to the effective anisotropy from k -fold molecular interactions.

The first three terms of the expansion (7) with regard to (10) for the many-component system assume the form:

$${}^{(0)}\Gamma^2 = \sum_i x_i {}^{(0)}\Gamma_i^2 + \sum_{ij} x_i x_j {}^{(0)}\Gamma_{ij}^2, \quad (11)$$

$${}^{(1)}\Gamma^2 = \sum_{ij} x_i x_j {}^{(1)}\Gamma_{ij}^2 + \sum_{ijk} x_i x_j x_k {}^{(1)}\Gamma_{ijk}^2, \quad (12)$$

$${}^{(2)}\Gamma^2 = \sum_{ij} x_i x_j {}^{(2)}\Gamma_{ij}^2 + \sum_{ijk} x_i x_j x_k {}^{(2)}\Gamma_{ijk}^2 + \sum_{ijkl} x_i x_j x_k x_l {}^{(2)}\Gamma_{ijkl}^2. \quad (13)$$

Eqs (11)–(13) show that, whereas the contribution to effective anisotropy from intrinsic anisotropic properties alone of the molecules of the various components is contained in ${}^{(0)}\Gamma^2$ by way of ${}^{(0)}\Gamma_i^2$, the higher expressions involving ${}^{(n)}\Gamma_{ij}^2$, ${}^{(n)}\Gamma_{ijk}^2$, ${}^{(n)}\Gamma_{ijkl}^2$ describe contributions due respectively to pairwise, triple, and four-molecule interactions between molecules composing the solution irrespective of whether they be molecules of the same or different components. The n -th term of (7) contains contributions from pairwise interactions up to $(n+2)$ -fold interactions.

3. Zero-th approximation of the theory

If the solution in V is free of statistical-fluctuational processes, the effective anisotropy (8) yields in the zero-th approximation:

$${}^{(0)}\Gamma^2 = \frac{3}{2N} \sum_{ij} \left\langle \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \mathbf{D}_{pi}^{(0)} : \mathbf{D}_{qj}^{(0)} \right\rangle, \quad (14)$$

where the deviator of the polarizability tensor of the isolated molecule is:

$$\mathbf{D}_{pi}^{(0)} = \mathbf{a}_{pi} - a_{pi} \mathbf{U}, \quad (15)$$

$\mathbf{a}_{pi} = \mathbf{a}_{pi} : \mathbf{U}/3 = \frac{1}{3}(a_x^{(pi)} + a_y^{(pi)} + a_z^{(pi)})$ denoting the mean optical polarizability of the p -th molecule of species i .

If, in particular, the molecule is isotropically polarizable,

$$\mathbf{a}_{pi} = a_{pi} \mathbf{U}, \quad (16)$$

the deviator of the zero-th approximation (15) vanishes.

The deviator (15) differs from zero only if the molecule is, intrinsically, optically anisotropic. If in particular the molecule presents different polarizabilities in the three directions of its principle axes, Eq. (15) becomes [5]:

$$\mathbf{D}_{pi}^{(0)} = \delta_{pi} \mathbf{Q}_{pi} + \frac{1}{3} \gamma_{pi} \mathbf{S}_{pi}, \quad (15a)$$

where we have introduced the tensors:

$$\mathbf{Q}_{pi} = x_{pi} x_{pi} - y_{pi} y_{pi}, \quad (17)$$

$$\mathbf{S}_{pi} = 3z_{pi} z_{pi} - \mathbf{U}, \quad (18)$$

(having the property of vanishing trace) as well as the optical anisotropies of the isolated molecule of species i :

$$\delta_{pi} = \frac{1}{2} (a_x^{(pi)} - a_y^{(pi)}), \quad \gamma_{pi} = a_z^{(pi)} - (a_x^{(pi)} + a_y^{(pi)})/2. \quad (19)$$

The anisotropy (14) can be represented in the form (11), with:

$${}^{(0)}\Gamma_i^2 = \frac{3}{2} \mathbf{D}_i^{(0)} : \mathbf{D}_i^{(0)} = \frac{3}{2} (\mathbf{a}_i : \mathbf{a}_i - 3a_i^2), \quad (20)$$

$${}^{(0)}\Gamma_{ij}^2 = \frac{3}{2N_i x_j} \left\langle \sum_{p=1}^{N_i} \sum_{\substack{q=1 \\ q \neq p}}^{N_j} \mathbf{D}_{pi}^{(0)} : \mathbf{D}_{qj}^{(0)} \right\rangle. \quad (21)$$

We write the optical anisotropy (20) of the isolated molecule in the well known explicit form:

$${}^{(0)}\Gamma_i^2 = \frac{1}{2} \{ (a_x^{(i)} - a_y^{(i)})^2 + (a_y^{(i)} - a_z^{(i)})^2 + (a_z^{(i)} - a_x^{(i)})^2 \}, \quad (20a)$$

which, for the axially symmetric case ($a_x = a_y \neq a_z$), leads to:

$${}^{(0)}\Gamma_i^2 \equiv \gamma_i^2 = (a_z^{(i)} - a_x^{(i)})^2. \quad (20b)$$

With regard to the form (15a) of the polarizability deviator, we re-write the effective anisotropy (21) due to angular correlations as follows:

$${}^{(0)}\Gamma_{ij}^2 = \delta_i \delta_j J_{ij}^{QQ} + \delta_i \gamma_j J_{ij}^{QS} + \gamma_i \delta_j J_{ij}^{SQ} + \gamma_i \gamma_j J_{ij}^{SS}, \quad (21a)$$

where we have introduced the following angular correlation parameters:

$$J_{ij}^{QQ} = \frac{3}{2x_j} \left\langle \sum_{\substack{q=1 \\ q \neq p}}^{N_j} \mathbf{Q}_{pi} : \mathbf{Q}_{qj} \right\rangle,$$

$$\begin{aligned}
 J_{ij}^{QS} &= \frac{1}{2x_j} \left\langle \sum_{\substack{q=1 \\ q \neq p}}^{N_j} \mathbf{Q}_{pi} : \mathbf{S}_{qj} \right\rangle, \\
 J_{ij}^{SQ} &= \frac{1}{2x_j} \left\langle \sum_{\substack{q=1 \\ q \neq p}}^{N_j} \mathbf{S}_{pi} : \mathbf{Q}_{qj} \right\rangle, \\
 J_{ij}^{SS} &= \frac{1}{6x_j} \left\langle \sum_{\substack{q=1 \\ q \neq p}}^{N_j} \mathbf{S}_{pi} : \mathbf{S}_{qj} \right\rangle.
 \end{aligned} \tag{22}$$

In particular, for axially symmetric molecules, we hence obtain the previous results [4]:

$${}^{(0)}\Gamma_{ij}^2 = \gamma_i \gamma_j J_{ij}^{SS}, \tag{21b}$$

where with regard to (18) the angular correlation parameter is of the form:

$$J_{ij}^{SS} = \frac{1}{2x_j} \left\langle \sum_{\substack{q=1 \\ q \neq p}}^{N_j} \{3(\mathbf{z}_{pi} \cdot \mathbf{z}_{qj})^2 - 1\} \right\rangle. \tag{22a}$$

The above parameter can be expressed anew in terms of binary correlation functions, as follows:

$$J_{ij}^{SS} = \frac{\rho}{2V} \iint (3 \cos^2 \theta_{piqj} - 1) g_{ij}^{(2)}(\tau_{pi}, \tau_{qj}) d\tau_{pi} d\tau_{qj} \tag{22b}$$

with θ_{piqj} denoting the angle between the vectors \mathbf{z}_{pi} and \mathbf{z}_{qj} of the axes of symmetry of two mutually interacting molecules having the configurations τ_{pi} and τ_{qj} .

4. First approximation of the theory

By (8), the effective anisotropy of the first approximation is given by the expression:

$${}^{(1)}\Gamma^2 = \frac{3}{2N} \sum_{ij} \left\langle \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} (\mathbf{D}_{pi}^{(0)} : \mathbf{D}_{qj}^{(1)} + \mathbf{D}_{pi}^{(1)} : \mathbf{D}_{qj}^{(0)}) \right\rangle, \tag{23}$$

where, besides the deviator of the zero-th approximation (15), we have that of the first approximation which, with regard to Eqs (2) and (5), is of the form:

$$\mathbf{D}_{pi}^{(1)} = -\frac{1}{3} \sum_k \sum_{r=1}^{N_k} \{3\mathbf{a}_{pi} \cdot \mathbf{T}_{pirk} \cdot \mathbf{a}_{rk} - U[(\mathbf{a}_{pi} \cdot \mathbf{a}_{rk}) : \mathbf{T}_{pirk}]\}. \tag{24}$$

One readily notes that, in this case too, the intrinsic anisotropy of the molecules owing to which the deviator (15) differs from zero plays an essential rôle. It is feasible to calculate

the anisotropy (23) for the deviators (15) and (24) in general form; however, with the aim of simplifying the final results, we shall restrict our considerations to molecules having the axial symmetry for which the polarizability tensor is of the form:

$$a_{pi} = a_i U + \frac{1}{3} \gamma_i S_{pi} \quad (25)$$

leading to deviators (15) and (24) in the form of:

$$D_{pi}^{(0)} = \frac{1}{3} \gamma_i S_{pi} \quad (15b)$$

$$\begin{aligned} D_{pi}^{(1)} = & -\frac{1}{27} \sum_k \sum_{r=1}^{N_k} \{27a_i a_k T_{pirk} + 3a_i \gamma_k [3(T_{pirk} \cdot S_{rk}) - U(T_{pirk} : S_{rk})] + \\ & + 3\gamma_i a_k [3(S_{pi} \cdot T_{pirk}) - U(S_{pi} : T_{pirk})] + \\ & + \gamma_i \gamma_k [3(S_{pi} \cdot T_{pirk} \cdot S_{rk}) - U(S_{pi} \cdot S_{rk} : T_{pirk})]\}. \end{aligned} \quad (24a)$$

On insertion of (15a) and (24a) in Eq. (23) and on performing a symmetrization operation, we obtain the following effective anisotropy of the first approximation:

$${}^{(1)}\Gamma^2 = \frac{1}{9N} \sum_{ijk} \left\langle \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \sum_{r=1}^{N_k} F_{ijk}^{(pqr)} \right\rangle, \quad (26)$$

where we have introduced the quantity:

$$\begin{aligned} F_{ijk}^{(pqr)} = & -\frac{1}{6} S(pi, qj, rk) \{9\gamma_i a_j a_k S_{pi} : T_{qjrk} + \\ & + 6\gamma_i \gamma_j a_k S_{pi} : (S_{aj} \cdot T_{qjrk}) + \gamma_i \gamma_j \gamma_k S_{pi} : (S_{aj} \cdot T_{qjrk} \cdot S_{rk})\}. \end{aligned} \quad (27)$$

Above, $S(pi, qj, rk)$ is the operator of symmetrization over all 6 permutations of the indices pi, qj, rk .

By (9), Eq. (26) can be put in the form (12), where the contribution due to two-body interactions is [4]:

$$\begin{aligned} {}^{(1)}\Gamma_{ij}^2 = & \frac{2}{3} [\gamma_i (3a_j - \gamma_j) (3a_i + \gamma_i - \gamma_j) J_{ij}^{ST} + \gamma_j (3a_i - \gamma_i) (3a_j + \gamma_j - \gamma_i) J_{ij}^{TS}] + \\ & + 2\gamma_i \gamma_j (3a_i + 3a_j + \gamma_i + \gamma_j) K_{ij}, \end{aligned} \quad (28)$$

with the correlation parameters:

$$J_{ij}^{TS} = -\frac{1}{6x_j} \left\langle \sum_{q \neq p}^{N_j} T_{piqj} : S_{aj} \right\rangle, \quad (29)$$

$$K_{ij} = -\frac{1}{18x_j} \left\langle \sum_{q \neq p}^{N_j} (S_{pi} + S_{aj}) : (S_{pi} \cdot T_{piqj} \cdot S_{aj}) \right\rangle. \quad (30)$$

With regard to the definition of the tensors (6) and (18), the above parameters can be expressed in the following form (4):

$$J_{ij}^{ST} = \frac{\rho}{2V} \iint (3 \cos^2 \theta_{pi} - 1) r_{piq}^{-3} g_{ij}^{(2)}(\tau_{pi}, \tau_{qj}) d\tau_{pi} d\tau_{qj}, \quad (29a)$$

$$J_{ij}^{TS} = \frac{\rho}{2V} \iint (3 \cos^2 \theta_{qj} - 1) r_{piq}^{-3} g_{ij}^{(2)}(\tau_{pi}, \tau_{qj}) d\tau_{pi} d\tau_{qj},$$

$$K_{ij} = \frac{\rho}{2V} \iint (3 \cos \theta_{pi} \cos \theta_{qj} - \cos \theta_{piq}) \times \\ \times \cos \theta_{piq} r_{piq}^{-3} g_{ij}^{(2)}(\tau_{pi}, \tau_{qj}) d\tau_{pi} d\tau_{qj}, \quad (30a)$$

rendering apparent the radial and angular dependence (θ_{pi} and θ_{qj} denote the angles between the molecular symmetry axes z_{pi} and z_{qj} and the vector r_{piq}).

It will be noted that, in order that the parameters of pairwise radial-angular correlations (29) and (30) shall be non-zero, correlations of the angular kind have to be present.

The contribution to the effective anisotropy of the first approximation due to three-body interactions is:

$${}^{(1)}\Gamma_{ijk}^2 = \frac{1}{9x_j x_k} \left\langle \sum_{q \neq p}^{N_j} \sum_{\substack{r \neq p \\ r \neq q}}^{N_k} F_{ijk}^{(pqr)} \right\rangle. \quad (31)$$

Likewise to the procedure applied above, by using Eq. (9) one can represent Eq. (31) in the form of (12):

$${}^{(1)}\Gamma_{ijk}^2 = S(p_i, q_j, r_k) \{ \gamma_i a_j a_k J_{ijk} + 2\gamma_i \gamma_j a_k K_{ijk}^{(1)} + \gamma_i \gamma_j \gamma_k K_{ijk}^{(2)} \}, \quad (32)$$

where the following parameters intervene:

$$J_{ijk} = - \frac{1}{6x_j x_k} \left\langle \sum_{q \neq p}^{N_j} \sum_{\substack{q \neq p \\ r \neq q}}^{N_k} S_{pi} : T_{qjrk} \right\rangle, \quad (33)$$

$$K_{ijk}^{(1)} = - \frac{1}{18x_j x_k} \left\langle \sum_{q \neq p}^{N_j} \sum_{\substack{q \neq p \\ r \neq q}}^{N_k} S_{pi} : (S_{qj} \cdot T_{qjrk}) \right\rangle, \quad (34)$$

$$K_{ijk}^{(2)} = - \frac{1}{54x_j x_k} \left\langle \sum_{q \neq p}^{N_j} \sum_{\substack{q \neq p \\ r \neq q}}^{N_k} S_{pi} : (S_{qj} \cdot T_{qjrk} \cdot S_{rk}) \right\rangle, \quad (35)$$

which, with (6), (18) and the symmetrization operators $S(pi, qj, rk)$ acting on the above parameters, go over into:

$$J_{ijk} = \frac{\varrho^2}{2V} \iiint (3 \cos^2 \theta_{pi} - 1) r_{qjrk}^{-3} g_{ijk}^{(3)}(\tau_{pi}, \tau_{qj}, \tau_{rk}) d\tau_{pi} d\tau_{qj} d\tau_{rk}, \quad (33a)$$

$$K_{ijk}^{(1)} = \frac{\varrho^2}{2V} \iiint (3 \cos \theta_{piqj} \cos \theta_{pi} \cos \theta_{qj} - \cos^2 \theta_{piqj} - \cos^2 \theta_{pi} - \cos^2 \theta_{qj} + \frac{2}{3}) r_{qjrk}^{-3} g_{ijk}^{(3)}(\tau_{pi}, \tau_{qj}, \tau_{rk}) d\tau_{pi} d\tau_{qj} d\tau_{rk}, \quad (34a)$$

$$K_{ijk}^{(2)} = \frac{\varrho^2}{2V} \iiint \left\{ \cos \theta_{piqj} \cos \theta_{pirk} (3 \cos \theta_{qj} \cos \theta_{rk} - \cos \theta_{qjrk} - 3 \cos \theta_{piqj} \cos \theta_{pi} \cos \theta_{qj} + \cos^2 \theta_{piqj} + \cos^2 \theta_{rk} - \frac{1}{3}) \right. \\ \left. \times r_{qjrk}^{-3} g_{ijk}^{(3)}(\tau_{pi}, \tau_{qj}, \tau_{rk}) d\tau_{pi} d\tau_{qj} d\tau_{rk}, \quad (35a) \right.$$

θ_{pi} , θ_{qj} , θ_{rk} being the angles between the symmetry axes of molecules z_{pi} , z_{qj} , z_{rk} and the vector r_{qjrk} .

5. Second approximation of the theory

In the second approximation, by (8), we derive the effective anisotropy:

$${}^{(2)}\Gamma^2 = \frac{3}{2N} \sum_{ij} \left\langle \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \{ D_{pi}^{(0)} : D_{qj}^{(2)} + D_{pi}^{(1)} : D_{qj}^{(1)} + D_{pi}^{(2)} : D_{qj}^{(0)} \} \right\rangle. \quad (36)$$

In addition to the deviators (15) and (24), we have here a deviator of the second approximation the form of which, with regard to (2) and (5), is:

$$D_{pi}^{(2)} = \frac{1}{3} \sum_{kl} \sum_{r=1}^{N_k} \sum_{s=1}^{N_l} \{ 3 a_{pi} \cdot T_{pirk} \cdot a_{rk} \cdot T_{rksl} \cdot a_{sl} - U(a_{pi} \cdot a_{sl}) : (T_{pirk} \cdot a_{rk} \cdot T_{rksl}) \}. \quad (37)$$

It is highly significant that, whereas for isotropically polarizable molecules ($\gamma_i = 0$) the deviator (15b) of the zero-th approximation vanishes, the deviator of the first approximation (24a) does not, but assumes the simple form:

$$D_{pi}^{(1)} = - \sum_k \sum_{r=1}^{N_k} a_i a_k T_{pirk}. \quad (24b)$$

In this way, notwithstanding the fact that $D_{pi}^{(0)} = 0$ and owing to the existence of the deviator (24b), the effective anisotropy of the second approximation of the theory is found to differ from zero even in the case of isotropically polarizable molecules:

$${}^{(2)}\Gamma_{is}^2 = \frac{3}{2N} \sum_{ijkl} \left\langle \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \sum_{r=1}^{N_k} \sum_{s=1}^{N_l} a_i a_j a_k a_l T_{pirk} : T_{qjst} \right\rangle. \quad (38)$$

The preceding expression can be written explicitly in the form (13), as follows:

$${}^{(2)}\Gamma_{ij}^2 = 9a_i^2 a_j^2 J_{ij}^R, \quad (39)$$

$${}^{(2)}\Gamma_{is^4}^2 = 3S(p_i, q_j, r_k) a_i a_j^2 a_k J_{ijk}^R, \quad (40)$$

$${}^{(2)}\Gamma_{is^4}^2 = \frac{1}{8} S(p_i, q_j, r_k, s_l) a_i a_j a_k a_l J_{ijkl}^R, \quad (41)$$

where the integral parameters due successively to two-body, three-body and four-body interaction are of the form:

$$J_{ij}^R = \frac{1}{3x_j} \left\langle \sum_{q \neq p}^{N_j} T_{piqj} : T_{piqj} \right\rangle = 2 \frac{\rho}{V} \iint r_{piqj}^{-6} g_{ij}^{(2)}(\tau_{pi}, \tau_{qj}) d\tau_{pi} d\tau_{qj} \quad (42)$$

$$J_{ijk}^R = \frac{\rho^2}{V} \iiint [3(r_{piqj} \cdot r_{qjrk})^2 - r_{piqj}^2 r_{qjrk}^2] r_{piqj}^{-5} r_{qjrk}^{-5} g_{ijk}^{(3)}(\tau_{pi}, \tau_{qj}, \tau_{rk}) d\tau_{pi} d\tau_{qj} d\tau_{rk}, \quad (43)$$

$$J_{ijkl}^R = \frac{\rho^3}{2V} \iiint T_{pirk} : T_{qjst} g_{ijkl}^{(4)}(\tau_{pi}, \tau_{qj}, \tau_{rk}, \tau_{sl}) d\tau_{pi} d\tau_{qj} d\tau_{rk} d\tau_{sl}. \quad (44)$$

When dealing with intrinsically anisotropic molecules, all three deviators (15b), (24a) and (37) have to be inserted in Eq. (36). This leads, on symmetrization, to:

$${}^{(2)}\Gamma^2 = {}^{(2)}\Gamma_{is}^2 + \frac{1}{162N} \sum_{ijkl} \left\langle \sum_{pqrs}^{N_i \dots N_k} F_{ijkl}^{(pqrs)} \right\rangle, \quad (45)$$

where the first term is given by (38). In the second term, we have introduced the following function:

$$\begin{aligned} F_{ijkl}^{(pqrs)} = & \frac{1}{24} S(pi, qj, rk, sl) \{ 162\gamma_i a_j a_k a_l [S_{pi} : (T_{qjrk} \cdot T_{rksl}) + \\ & + 2(S_{pi} \cdot T_{piqj}) : T_{rksl}] + 18\gamma_i \gamma_j a_k a_l [6S_{pi} : (S_{qj} \cdot T_{qjrk} \cdot T_{rksl}) + \\ & + 3S_{pi} : (T_{qjrk} \cdot S_{rk} \cdot T_{rksl}) + 3(S_{pi} \cdot T_{piqj} \cdot S_{qj}) : T_{rksl} + 6(S_{pi} \cdot T_{pirk}) : (S_{qj} \cdot T_{qjst}) - \\ & - 2(S_{pi} : T_{pirk}) (S_{qj} : T_{qjst})] + 6\gamma_i \gamma_j \gamma_k a_l [6S_{pi} : (S_{qj} \cdot T_{qjrk} \cdot S_{rk} \cdot T_{rksl}) + \\ & + 3S_{pi} : (S_{qj} \cdot T_{qjst} \cdot T_{slrk} \cdot S_{rk}) + 6(S_{pi} \cdot T_{piqj} \cdot S_{qj}) : (S_{rk} \cdot T_{rksl}) - \\ & - 2(S_{pi} \cdot S_{qj} : T_{piqj}) (S_{rk} : T_{rksl})] + \gamma_i \gamma_j \gamma_k \gamma_l [6S_{pi} : (S_{qj} \cdot T_{qjrk} \cdot S_{rk} \cdot T_{rksl} \cdot S_{sl}) + \\ & + 3(S_{pi} \cdot T_{pirk} \cdot S_{rk}) : (S_{qj} \cdot T_{qjst} \cdot S_{sl}) - (S_{pi} \cdot S_{rk} : T_{pirk}) (S_{qj} \cdot S_{sl} : T_{qjst})] \}. \quad (46) \end{aligned}$$

6. Discussion of some particular cases

In this paper, our discussion will bear more closely on the two-component system. On symmetrization of ${}^{(0)}\Gamma_{i_1 \dots i_k}^2$ with regard to the order of all indices (to take into account the physical properties of the interactions), the expansions (11)–(13) now become:

$${}^{(0)}\Gamma^2 = x_1 {}^{(0)}\Gamma_1^2 + x_2 {}^{(0)}\Gamma_2^2 + x_1^2 {}^{(0)}\Gamma_{11}^2 + 2x_1 x_2 {}^{(0)}\Gamma_{21}^2 + x_2^2 {}^{(0)}\Gamma_{22}^2, \quad (47)$$

$$\begin{aligned} {}^{(1)}\Gamma^2 = & x_1^2 {}^{(1)}\Gamma_{11}^2 + 2x_1 x_2 {}^{(1)}\Gamma_{21}^2 + x_1^3 {}^{(1)}\Gamma_{111}^2 + 3x_1^2 x_2 {}^{(1)}\Gamma_{211}^2 + \\ & + 3x_1 x_2^2 {}^{(1)}\Gamma_{221}^2 + x_2^3 {}^{(1)}\Gamma_{222}^2, \end{aligned} \quad (48)$$

$$\begin{aligned} {}^{(2)}\Gamma^2 = & x_1^2 {}^{(2)}\Gamma_{11}^2 + 2x_1 x_2 {}^{(2)}\Gamma_{21}^2 + x_2^2 {}^{(2)}\Gamma_{22}^2 + x_1^3 {}^{(2)}\Gamma_{111}^2 + \\ & + 3x_1^2 x_2 {}^{(2)}\Gamma_{211}^2 + 3x_1 x_2^2 {}^{(2)}\Gamma_{211}^2 + x_2^3 {}^{(2)}\Gamma_{222}^2 + x_1^4 {}^{(2)}\Gamma_{1111}^2 + \\ & + 4x_1^3 x_2 {}^{(2)}\Gamma_{2111}^2 + 6x_1^2 x_2^2 {}^{(2)}\Gamma_{2211}^2 + 4x_1 x_2^3 {}^{(2)}\Gamma_{2221}^2 + x_2^4 {}^{(2)}\Gamma_{2222}^2. \end{aligned} \quad (49)$$

In addition to contributions due to anisotropy of linear polarizability of the isolated molecules of the components unperturbed by interaction (${}^{(0)}\Gamma_1^2$, ${}^{(0)}\Gamma_2^2$), Eqs (47)–(49) now contain explicitly the effect of interactions between like molecules of each of the components (${}^{(0)}\Gamma_{11}^2$, ${}^{(1)}\Gamma_{11}^2$, ${}^{(0)}\Gamma_{22}^2$ etc.) as well as between unlike molecules of different components (${}^{(0)}\Gamma_{21}^2$, ${}^{(1)}\Gamma_{21}^2$, ${}^{(2)}\Gamma_{21}^2$ etc.).

a. Solution with a low concentration of one component

Let us assume component 2 as present at very low concentration ($x_2 \rightarrow 0$). This amounts to considering solutions in which the molecules of component 2 are surrounded by molecules of component 1 and in which the probability of an interaction between the molecules of component 2 is very small ($N_2/N \rightarrow 0$).

If the molecules of both components are anisotropically polarizable, Eqs (20b) and (47)–(49) with $x_2 = x$ ($x_1 = 1 - x$) yield:

$$\begin{aligned} \left(\frac{\partial \Gamma^2}{\partial x} \right)_{x \rightarrow 0} = & \gamma_2^2 - \gamma_1^2 + \left\{ \frac{\partial}{\partial x} ({}^{(0)}\Gamma_{11}^2 + {}^{(1)}\Gamma_{11}^2 + {}^{(1)}\Gamma_{111}^2 + \right. \\ & + {}^{(2)}\Gamma_{11}^2 + {}^{(2)}\Gamma_{111}^2 + {}^{(2)}\Gamma_{1111}^2 + \dots) + 2[({}^{(0)}\Gamma_{21}^2 + {}^{(1)}\Gamma_{21}^2 + {}^{(2)}\Gamma_{21}^2 + \dots) - \\ & - ({}^{(0)}\Gamma_{11}^2 + {}^{(1)}\Gamma_{11}^2 + {}^{(2)}\Gamma_{11}^2 + \dots)] + 3[({}^{(1)}\Gamma_{211}^2 + {}^{(2)}\Gamma_{211}^2 + \dots) - \\ & \left. - ({}^{(1)}\Gamma_{111}^2 + {}^{(2)}\Gamma_{111}^2 + \dots)] + 4[{}^{(2)}\Gamma_{2111}^2 - {}^{(2)}\Gamma_{1111}^2 + \dots] \right\}_{x \rightarrow 0}. \end{aligned} \quad (50)$$

b. Solution consisting of isotropically and anisotropically polarizable molecules

In our further considerations, we shall be dealing with a special class of binary solutions, namely ones in which the molecules of component 1 are isotropically polarizable (e.g. CCl_4 , for which $\gamma_1 = 0$) whereas those of component 2 are anisotropically polarizable (e.g. CS_2 , C_6H_6 , for which $\gamma_2 \neq 0$). We shall consider a component 2 with molecules having

the axial symmetry and thus obeying Eq. (20b). For the solution described above ($\gamma_1 = 0$, $\gamma_2 \neq 0$), Eqs (20b), (21b), (28) and (32) lead to:

$${}^{(0)}\Gamma_1^2 = {}^{(0)}\Gamma_{11}^2 = {}^{(0)}\Gamma_{21}^2 = {}^{(1)}\Gamma_{11}^2 = {}^{(1)}\Gamma_{111}^2 = 0 \quad (51)$$

since the ${}^{(1)}\Gamma_{11}^2$, ${}^{(1)}\Gamma_{111}^2$ vanish owing to the circumstance that translational fluctuations are inoperative unless $n \geq 2$ (there can be no radial-angular interaction between isotropic molecules). The radial correlation parameters, which determine the contribution to effective anisotropy from the component with isotropically polarizable molecules alone, depend on powers $n \geq 2$ of the interaction tensor T .

For the case under consideration, we have:

$${}^{(0)}\Gamma^2 = x_2 {}^{(0)}\Gamma_2^2 + x_2^2 {}^{(0)}\Gamma_{22}^2, \quad (52)$$

$${}^{(1)}\Gamma^2 = 2x_1x_2 {}^{(1)}\Gamma_{21}^2 + x_2^2 {}^{(1)}\Gamma_{22}^2 + 3x_1^2x_2 {}^{(1)}\Gamma_{211}^2 + 3x_1x_2^2 {}^{(1)}\Gamma_{221}^2 + x_2^3 {}^{(1)}\Gamma_{222}^2. \quad (53)$$

Eq. (50), for very small x_2 , becomes:

$$\begin{aligned} \left(\frac{\partial \Gamma^2}{\partial x} \right)_{x \rightarrow 0} = & \gamma_2^2 + \left\{ \frac{\partial}{\partial x} ({}^{(2)}\Gamma_{11}^2 + {}^{(2)}\Gamma_{111}^2 + {}^{(2)}\Gamma_{1111}^2 + \right. \\ & + 2({}^{(1)}\Gamma_{21}^2 + {}^{(2)}\Gamma_{21}^2 - {}^{(2)}\Gamma_{11}^2) + 3({}^{(1)}\Gamma_{211}^2 + {}^{(2)}\Gamma_{211}^2 - {}^{(2)}\Gamma_{111}^2 + \\ & \left. + 4({}^{(2)}\Gamma_{2111}^2 - {}^{(2)}\Gamma_{1111}^2) \right\}_{x \rightarrow 0}. \end{aligned} \quad (54)$$

Calculated by methods of classical mechanics and statistical physics, the expressions in (54) describing the interactions between the molecules in solution have the following form, resulting from considerations of previous Sections of this paper:

$${}^{(1)}\Gamma_{21}^2 = 2a_1\gamma_2(3a_2 + \gamma_2)^{(3,1)}J_{21}^{RA}, \quad (55)$$

$${}^{(1)}\Gamma_{211}^2 = 2a_1^2\gamma_2 {}^{(3)}J_{211}^{RA}, \quad (56)$$

$${}^{(2)}\Gamma_{11}^2 = 9a_1^4J_{11}^R, \quad (57)$$

$$\begin{aligned} {}^{(2)}\Gamma_{21}^2 = & [9a_1^2a_2^2 + \frac{4}{3}a_1^2\gamma_2^2 + 2a_1\gamma_2^2(a_2 + \frac{1}{6}\gamma_2)]J_{21}^R + \\ & + a_1\gamma_2[2\gamma_2^2 + 2a_1(6a_2 - \gamma_2) + (3a_2 - \gamma_2)(a_1 + a_2 + \gamma_2)]^{(6,1)}J_{21}^{RA} + 4a_1^2\gamma_2^{(6,2)}J_{21}^{RA}, \end{aligned} \quad (58)$$

$${}^{(2)}\Gamma_{111}^2 = 18a_1^4J_{1111}^R, \quad (59)$$

$$\begin{aligned} {}^{(2)}\Gamma_{211}^2 = & \frac{1}{6}S(q_1, r_1)a_1^2\{(3a_2 - \gamma_2)[6(2a_1 - \gamma_2)J_{211}^R + \\ & + (6a_2 - \gamma_2)J_{121}^R + 5\gamma_2J_{211}^{RA} + 2\gamma_2[(6a_1 + 3a_2 - \gamma_2)J_{121}^{RA} + 3a_1 {}^{(6)}J_{211}^{RA}]\}, \end{aligned} \quad (60)$$

$${}^{(2)}\Gamma_{1111}^2 = 9a_1^4J_{11111}^R, \quad (61)$$

$${}^{(2)}\Gamma_{2111}^2 = \frac{1}{6}S(q_1, r_1, s_1)a_1^3[(3a_2 - \gamma_2)J_{2111}^R + \frac{3}{2}\gamma_2J_{2111}^{RA}], \quad (62)$$

where the parameters J_{ij}^R , J_{ijk}^R , J_{ijkl}^R are given respectively by Eqs (42)–(44) and the others are defined as follows:

$${}^{(n,m)}J_{21}^{RA} = \frac{\varrho}{2V} \iint [(3 \cos^2 \theta_{p_2}^{(p_2q_1)} - 1)^m + c_m] r_{p_2q_1}^{-n} g_{12}^{(2)}(\tau_{p_2}, \tau_{q_1}) d\tau_{p_2} d\tau_{q_1}, \quad (63)$$

$${}^{(n)}J_{211}^{RA} = \frac{\varrho^2}{2V} \iiint (3 \cos^2 \theta_{p_2}^{(q_1r_1)} - 1) r_{q_1r_1}^{-n} g_{211}^{(3)}(\tau_{p_2}, \tau_{q_1}, \tau_{r_1}) d\tau_{p_2} d\tau_{q_1} d\tau_{r_1}, \quad (64)$$

$$J_{211}^{RA} = \frac{\varrho^2}{V} \iiint (9 \cos \theta_{p_2}^{(p_2q_1)} \cos \theta_{p_2}^{(p_2r_1)} \cos \theta_{(p_2q_1)}^{(p_2r_1)} - 3 \cos^2 \theta_{p_2}^{(p_2q_1)} - 3 \cos^2 \theta_{p_2}^{(p_2r_1)} + 1) r_{p_2q_1}^{-3} r_{p_2r_1}^{-3} g_{211}^{(3)}(\tau_{p_2}, \tau_{q_1}, \tau_{r_1}) d\tau_{p_2} d\tau_{q_1} d\tau_{r_1}, \quad (65)$$

$$J_{121}^{RA} = \frac{\varrho^2}{V} \iiint (9 \cos \theta_{p_2}^{(p_2q_1)} \cos \theta_{p_2}^{(q_1r_1)} \cos \theta_{(p_2q_1)}^{(q_1r_1)} - 3 \cos^2 \theta_{p_2}^{(p_2q_1)} - 3 \cos^2 \theta_{p_2}^{(q_1r_1)} + 1) r_{p_2q_1}^{-3} r_{q_1r_1}^{-3} g_{211}^{(3)}(\tau_{p_2}, \tau_{q_1}, \tau_{r_1}) d\tau_{p_2} d\tau_{q_1} d\tau_{r_1}, \quad (66)$$

$$J_{2111}^{RA} = \frac{\varrho^3}{2V} \iiint [9 \cos \theta_{p_2}^{(r_1s_1)} (2 \cos \theta_{p_2}^{(p_2q_1)} \cos \theta_{(p_2q_1)}^{(s_1r_1)} r_{p_2q_1}^{-3} + \cos \theta_{p_2}^{(q_1r_1)} \cos \theta_{(q_1r_1)}^{(r_1s_1)} r_{q_1r_1}^{-3}) - 3(2 \cos^2 \theta_{p_2}^{(p_2q_1)} r_{p_2q_1}^{-3} + \cos^2 \theta_{p_2}^{(q_1r_1)} r_{q_1r_1}^{-3}) - 3 \cos^2 \theta_{p_2}^{(r_1s_1)} (2r_{p_2q_1}^{-3} + r_{q_1r_1}^{-3}) - 3 \cos^2 \theta_{(q_1r_1)}^{(r_1s_1)} r_{q_1r_1}^{-3} + 2(r_{p_2q_1}^{-3} + r_{q_1r_1}^{-3})] \times r_{r_1s_1}^{-3} g_{2111}^{(4)}(\tau_{p_2}, \tau_{q_1}, \tau_{r_1}, \tau_{s_1}) d\tau_{p_2} d\tau_{q_1} d\tau_{r_1} d\tau_{s_1}, \quad (67)$$

with $\theta_{p_i}^{(q_jr_k)}$ — the angle between the symmetry axis of molecule p of component i (axis z_{p_i}) and the radius connecting molecules q and r of components j and k , and $\theta_{(p_iq)}^{(r_ksi)}$ — the angle between the radius connecting molecule p of component i and molecule q of component j and the radius connecting molecule r of component k and molecule s of component l .

The constant occurring in Eq. (63) amounts to:

$$c_m = - (3 \cos^2 \theta_p - 1)^m, \quad (68)$$

which denotes a quantity isotropically averaged over all possible directions. In Eq. (68), we have: $c_1 = 0$, $c_2 = -4/5$. As apparent from Eqs (55)–(67), the effective optical anisotropy of a solution of two components with respectively isotropically and anisotropically polarizable molecules depends on the following factors: the “pure” anisotropy of the isolated molecule of component 2 (γ_2^2), as well as the intermolecular radial interactions (parameters J^R) and radial-angular interactions (parameters J^{RA}) due to fluctuations of the molecular fields. Hence, not only redistribution through radial interactions (radial configuration) is effective, but moreover an essential rôle belongs to the mutual configuration of the molecules with respect to the privileged symmetry axis of one of them (the z -axis).

c. Effective optical anisotropy of a two-component solution consisting of isotropic molecules

For a two-component solution both components of which have isotropically polarizable molecules ($\gamma_1 = \gamma_2 = 0$), Eqs (55)–(62) assume the following form:

$${}^{(1)}\Gamma_{21}^2 = {}^{(1)}\Gamma_{211}^2 = 0, \quad (69)$$

$${}^{(2)}\Gamma_{11}^2 = 9a_1^4 J_{11}^R, \quad (70)$$

$${}^{(2)}\Gamma_{21}^2 = 9a_1^2 a_2^2 J_{21}^{R\ddagger}, \quad (71)$$

$${}^{(2)}\Gamma_{211}^2 = 3S(q_1, r_1) a_1^2 a_2 [2a_1 J_{211}^R + a_2 J_{121}^R], \quad (72)$$

$${}^{(2)}\Gamma_{1111}^2 = 9a_1^4 J_{1111}^R, \quad (73)$$

$${}^{(2)}\Gamma_{2111}^2 = \frac{1}{2} S(q_1, r_1, s_1) a_2 a_1^3 J_{2111}^R. \quad (74)$$

Thus, such systems can exhibit an effective optical anisotropy due solely to Yvon-Kirkwood translational fluctuations (expressed in terms of radial interaction parameters).

7. Numerical calculations

We now proceed to a closer analysis and numerical calculations of some two-component solutions, consisting of a component 1 with isotropically polarizable molecules and a component 2 with anisotropically polarizable ones. As "1" we consider carbon tetrachloride, whereas for "2" we take benzene and carbon disulphide: the former is characterized by a negative anisotropy ($\gamma_2 < 0$) and the latter by a positive anisotropy ($\gamma_2 > 0$). Our numerical calculations are restricted to two-molecule interactions. Accordingly, the effective anisotropy is numerically given, quite generally, by the expression:

$$\Gamma^2 = x_2 \gamma_2^2 + x_1^2 \Gamma_{11}^2 + 2x_1 x_2 \Gamma_{21}^2 + x_2^2 \Gamma_{22}^2, \quad (75)$$

where

$$\Gamma_{11}^2 = {}^{(2)}\Gamma_{11}^2,$$

$$\Gamma_{21}^2 = {}^{(1)}\Gamma_{21}^2 + {}^{(2)}\Gamma_{21}^2,$$

$$\Gamma_{22}^2 = {}^{(0)}\Gamma_{22}^2 + {}^{(1)}\Gamma_{22}^2 + {}^{(2)}\Gamma_{22}^2.$$

The quantities ${}^{(2)}\Gamma_{11}^2$, ${}^{(1)}\Gamma_{21}^2$, ${}^{(2)}\Gamma_{21}^2$, ${}^{(0)}\Gamma_{22}^2$, and ${}^{(1)}\Gamma_{22}^2$ are given by Eqs (57), (55), (59), (21) and (28). The expressions derived from Eq. (45) for ${}^{(2)}\Gamma_{22}^2$ are highly involved and will not be adduced explicitly in this paper, but will be dealt with separately. They depend on the radial correlation parameter (42) as well as on certain radial-angular parameters.

In practice, the calculation of the effective anisotropy reduces to the numerical computation of the interaction parameters. The two-molecule correlation functions occurring in these parameters can be expressed quite generally as follows [9, 21]:

$$g_{ij}^{(2)}(\tau_{pi}, \tau_{qj}) = \Omega^{-2} g_{ij}(r_{piqj}) \exp \{-V_{piqj}/kT\}, \quad (76)$$

where $g_{ij}(r_{piqj})$ is the radial correlation function, whereas $V_{piqj}(r_{piqj}, \omega_{pi}, \omega_{qj})$ is the energy of non-central two-body interactions [5, 15] ($\Omega = \int d\omega_p = \int d\omega_q$). Since the lowest multipole moment of the CCl_4 molecule is an octupole (which we may as well omit in our calculations), the interaction energy V_{11} between two molecules of component 1 coincides with the dispersive energy, $V_{11}(r_{p1p1}, \omega_p, \omega_q) = V_{11}^{\text{disp}}$. The molecules of component 2, C_6H_6 and CS_2 , have quadrupole moments. Hence the energy of interaction V_{21} between molecules of "2" and "1" consists of the energy of dispersive interaction and that of interaction between the dipole moment induced in molecule "1" and the quadrupole moment of molecule "2" ($V_{12} = V_{12}^{\text{disp}} + V_{12}^{\alpha-\theta}$). Finally, the energy of interaction between molecules of component 2, V_{22} , consists of the energy of dispersive interaction, that of interaction between the induced dipole moment and the quadrupole moment, and that of interaction between the two quadrupole moments ($V_{22} = V_{22}^{\text{disp}} + V_{22}^{\alpha-\theta} + V_{22}^{\theta-\theta}$). On expanding the exponential function in (76), we can express the angular-radial correlation parameters in terms of radial correlation parameters:

$$\langle r_{piqj}^{-n} \rangle = 4\pi \rho \int_0^\infty r_{piqj}^{-n+2} g(r_{piqj}) dr_{piqj}. \quad (77)$$

For example, the parameters describing radial interactions between molecules of component 1 and with molecules of component 2 (J_{11}^R, J_{12}^R), occurring in Eqs (57) and (58), are given as follows:

$$J_{11}^R = 2 \langle r_{p1q1}^{-6} \rangle, \quad (78)$$

$$J_{21}^R = 2 \langle r_{p1q2}^{-6} \rangle, \quad (79)$$

whereas the parameters of angular-radial interaction between molecules of the two components (${}^{(3,1)}J_{21}^{RA}, {}^{(6,1)}J_{21}^{RA}, {}^{(6,2)}J_{21}^{RA}$), written explicitly so as to render apparent the dispersive and induced dipole-quadrupole interactions, are of the form:

$${}^{(3,1)}J_{21}^{RA \text{ disp}} = C_1 (\langle r_{p1q2}^{-9} \rangle + \frac{5}{7} C_1 \langle r_{p1q2}^{-15} \rangle), \quad (80)$$

$${}^{(6,1)}J_{21}^{RA \text{ disp}} = C_1 (\langle r_{p1q2}^{-12} \rangle + \frac{5}{7} C_1 \langle r_{p1q2}^{-18} \rangle), \quad (81)$$

$${}^{(6,2)}J_{21}^{RA \text{ disp}} = \frac{4}{7} C_1 (\langle r_{p1q2}^{-12} \rangle + 2C_1 \langle r_{p1q2}^{-18} \rangle), \quad (82)$$

$${}^{(3,1)}J_{21}^{RA\alpha-\theta} = C_2 (\langle r_{p1q2}^{-11} \rangle + \frac{5.5}{8} C_1 \langle r_{p1q2}^{-17} \rangle + \frac{7.0}{9.9} C_2 \langle r_{p1q2}^{-19} \rangle), \quad (83)$$

$${}^{(6,1)}J_{21}^{RA\alpha-\theta} = C_2 (\langle r_{p1q2}^{-14} \rangle + \frac{5.5}{8} C_1 \langle r_{p1q2}^{-20} \rangle + \frac{7.0}{9.9} C_2 \langle r_{p1q2}^{-22} \rangle), \quad (84)$$

$${}^{(6,2)}J_{21}^{RA\alpha-\theta} = C_2 (\langle r_{p1q2}^{-14} \rangle + \frac{13.1}{2.2} C_1 \langle r_{p1q2}^{-20} \rangle + \frac{7.21}{10.4} C_2 \langle r_{p1q2}^{-22} \rangle), \quad (85)$$

where:

$$C_1 = \frac{1}{10} \frac{h\nu_1\nu_2}{\nu_1 + \nu_2} \frac{a_1\gamma_2}{kT}, \quad (86)$$

$$C_2 = \frac{12}{35} a_1 \frac{\Theta_2^2}{kT}. \quad (87)$$

The parameters of interaction between molecules of the component 2 are calculated similarly.

In dense liquids ($\rho\sigma^3 = 1.31$ for CCl_4 , 1.03 for C_6H_6 , 0.90 for CS_2), the decisive rôle in defining the structure of the liquid belongs to repulsive forces. The function $g(r_{ij})$ of Eq. (77) can now be represented as follows [16]:

$$g(r_{ij}) = y_0(r_{ij}) \exp \left\{ -\frac{u_0(r_{ij})}{kT} \right\}, \quad (88)$$

where:

$$u_0(r_{ij}) = 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \varepsilon_{ij} \quad \text{for } r_{ij} < 2^{1/6}\sigma_{ij}, \quad (89)$$

$$u_0(r_{ij}) = 0 \quad \text{for } r_{ij} \geq 2^{1/6}\sigma_{ij}.$$

In our numerical calculations we have assumed, for $y_0(r_{ij})$:

$$y_0(r_{ij}) = 0 \quad r_{ij} < \sigma_{ij} \text{ and } r_{ij} > 2^{1/6}\sigma_{ij}$$

$$y_0(r_{ij}) = 1 \quad \sigma_{ij} < r_{ij} < 2^{1/6}\sigma_{ij}. \quad (90)$$

In Eqs (88)–(90), the parameters $\langle r^{-n} \rangle$ have the form:

$$\langle r_{ij}^{-n} \rangle = \frac{4\pi\rho}{\rho^{\beta\varepsilon_{ij}}\sigma_{ij}^{n-3}} \sum_{m=0}^{\infty} \sum_{k=0}^m \frac{(-1)^{k+2} \binom{m}{k} (4\beta\varepsilon_{ij})^m}{m! [n+3(2m+2k-1)]} \left(1 - 2^{-\frac{[n+3(2m+2k-1)]}{6}} \right) \quad (91)$$

with $\beta = (kT)^{-1}$. Here, and in all angular, radial and angular-radial parameters, ρ stands for the number density of molecules *i.e.* the number of molecules per unit volume which is a function of the concentration. Denoting the concentration of component 2 by x ($x = x_2$, $x_1 = 1 - x$), we can express ρ in terms of the concentrations of the pure components:

$$\rho = \frac{\rho_1\rho_2}{\rho_2 - x(\rho_2 - \rho_1)}. \quad (92)$$

The parameters σ_{ij} and ε_{ij} of the Lennard-Jones potential for two unlike molecules can be expressed in terms of the parameters for molecules of each species by way of the following empirical relation [17, 18]:

$$\sigma_{ij} = \frac{1}{2} (\sigma_i + \sigma_j),$$

$$\varepsilon_{ij} = \sqrt{\varepsilon_i\varepsilon_j}. \quad (93)$$

TABLE I

Liquid	$\rho \times 10^{-21}$ [cm ⁻³]	$a_x \times 10^{24}$ [cm ³]	$a_y \times 10^{24}$ [cm ³]	$a_z \times 10^{24}$ [cm ³]	$a \times 10^{24}$ [cm ³]	$\gamma \times 10^{24}$ [cm ³]	$\sigma \times 10^8$ [cm] [17]	ε/k [°K] [17]	$\Theta \times 10^{26}$ [esu]
CCl_4	6.21	10.5	10.5	10.5	10.5	0	5.947	322.7	0
C_6H_6	6.74	12.31	12.31	6.35	10.32	-5.96	5.349	412.3	12 [19]
CS_2	9.94	5.54	5.54	15.14	8.74	9.60	4.483	467	9 [20]

TABLE II

Calculated contributions from each of the components of the system $\text{CCl}_4-\text{C}_6\text{H}_6$ to the effective optical anisotropy Γ^2 and theoretically calculated anisotropic scattered intensity H_v for the wavelength $\lambda = 546 \text{ m}\mu$ at 25°C throughout the entire range of concentrations

x_2	$\rho \times 10^{-21}$ [cm^{-3}]	n^* $\lambda = 546 \text{ m}\mu$	$x_2 \gamma_2^2 \times 10^{48}$ [cm^6]	$x_1^2 \Gamma_{11}^2 \times 10^{48}$ [cm^6]	$2x_1 x_2 \Gamma_{12}^2 \times 10^{48}$ [cm^6]	$x_2^2 \Gamma_{22}^2 \times 10^{48}$ [cm^6]	$\Gamma^2 \times 10^{48}$ [cm^6]	$H_v^{\text{theor}} \times 10^6$ [cm^{-1}]
0.00	6.21	1.4596	0	5.45	0	0	5.45	0.75
0.02	6.22	1.4604	0.71	5.24	0.28	-0.001	6.23	0.86
0.04	6.23	1.4612	1.42	5.04	0.56	-0.005	7.02	0.97
0.06	6.24	1.4621	2.13	4.84	0.82	-0.01	7.78	1.08
0.08	6.25	1.4629	2.84	4.65	1.07	-0.02	8.54	1.19
0.1	6.26	1.4638	3.55	4.45	1.32	-0.03	9.29	1.29
0.2	6.31	1.4680	7.10	3.55	2.36	-0.12	12.89	1.82
0.3	6.36	1.4722	10.66	2.73	3.12	-0.27	16.24	2.33
0.4	6.41	1.4764	14.21	2.03	3.59	-0.48	19.35	2.81
0.5	6.46	1.4807	17.76	1.42	3.77	-0.76	22.19	3.27
0.6	6.52	1.4849	21.31	0.92	3.65	-1.11	24.77	3.70
0.7	6.57	1.4892	24.86	0.52	3.22	-1.52	27.08	4.10
0.8	6.63	1.4934	28.42	0.23	2.48	-2.01	29.12	4.48
0.9	6.68	1.4977	31.97	0.06	1.40	-2.56	30.87	4.81
1.0	6.74	1.5019	35.52	0	0	-3.19	32.33	5.12

* calculated from Ref. [3].

TABLE III

Calculated contributions from each of the components of the system CCl_4-CS_2 to the effective optical anisotropy Γ^2 and theoretically calculated anisotropic scattered intensity H_v for the wavelength $\lambda = 546 \text{ m}\mu$ at 25°C throughout the entire range of concentrations

x_2	$\rho \times 10^{-21}$ [cm^{-3}]	n^* $\lambda = 546 \text{ m}\mu$	$x_2 \gamma_2^2 \times 10^{48}$ [cm^6]	$x_1^2 \Gamma_{11}^2 \times 10^{48}$ [cm^6]	$2x_1 x_2 \Gamma_{12}^2 \times 10^{48}$ [cm^6]	$x_2^2 \Gamma_{22}^2 \times 10^{48}$ [cm^6]	$\Gamma^2 \times 10^{48}$ [cm^6]	$H_v^{\text{theor}} \times 10^6$ [cm^{-1}]
0.00	6.21	1.4610	0	5.45	0	0	5.45	0.75
0.02	6.26	0.4623	1.84	5.27	0.42	0.01	7.54	1.05
0.04	6.30	1.4639	3.69	5.10	0.83	0.03	9.65	1.35
0.06	6.35	1.4654	5.53	4.92	1.23	0.08	11.76	1.66
0.08	6.40	1.4671	7.37	4.76	1.62	0.14	13.89	1.99
0.1	6.45	1.4687	9.22	4.58	1.99	0.22	16.01	2.31
0.2	6.71	1.4786	18.43	3.77	3.69	0.91	26.80	4.08
0.3	7.00	1.4904	27.65	3.01	5.05	2.14	37.85	6.12
0.4	7.31	1.5040	36.84	2.31	6.00	3.97	49.12	8.46
0.5	7.64	1.5203	46.08	1.67	6.55	6.48	60.78	11.19
0.6	8.01	1.5383	55.30	1.12	6.60	9.27	72.74	14.40
0.7	8.42	1.5583	64.51	0.66	6.07	14.01	85.25	18.24
0.8	8.87	1.5805	73.73	0.31	4.87	19.28	98.19	22.84
0.9	9.38	1.6046	82.94	0.08	2.90	25.80	111.72	28.43
1.0	9.94	1.6308	92.16	0	0	33.75	125.91	35.22

* calculated from Ref. [3].

The molecular data used in the computations are listed in Table I. Tables II and III contain the theoretically calculated values of effective optical anisotropies respectively for the solutions $C_6H_6-CCl_4$ and CS_2-CCl_4 at $25^\circ C$ in the entire range of concen-

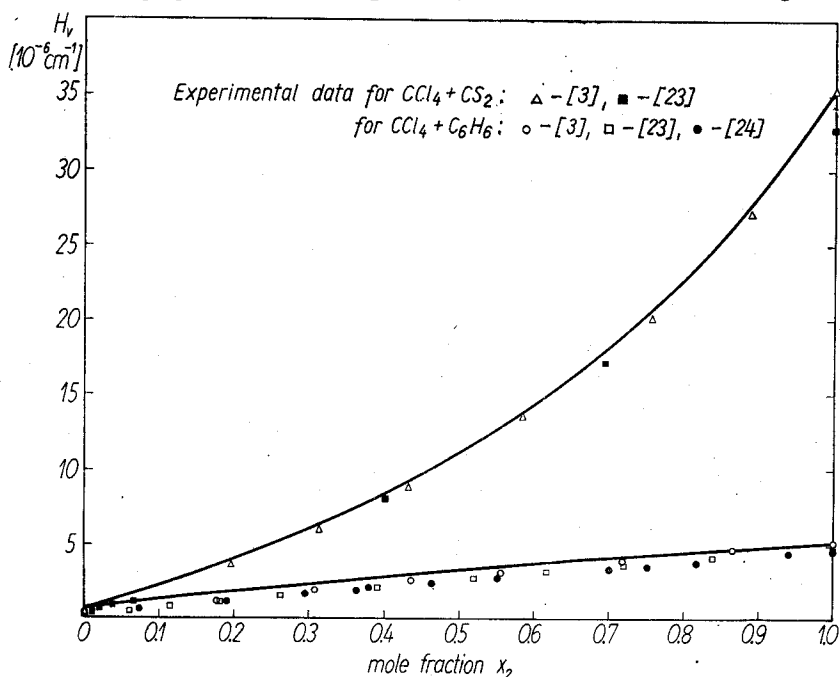


Fig. 1. Intensity of the anisotropic scattered component vs. the molar fraction x_2 . The present theoretical results are plotted as continuous curves (upper curve — $CCl_4 + CS_2$ solution; lower curve — $CCl_4 + C_6H_6$ solution)

trations. Also, by resorting to the relation between the anisotropic component of scattered light intensity H_v and the effective anisotropy [5, 9, 21]:

$$H_v = \frac{16\pi^4}{15\lambda^4} \left(\frac{n^2 + 2}{3} \right)^2 e\Gamma^2 \quad (94)$$

we have calculated the theoretical values of H_v for the wavelength $\lambda = 5460 \text{ \AA}$ and plotted them against recent experimental results [3, 23, 24] in Fig. 1.

8. Conclusions

The present paper contains a theoretical analysis of the molecular mechanisms, a discussion of the intermolecular interactions, and numerical calculations for the anisotropic component of scattered light for two, selected binary solutions ($C_6H_6-CCl_4$; CCl_4-CS_2). Satisfactory agreement with experiment is thought to be achieved. The subsisting divergences between the theoretical and experimental results are due, among others, to the fact that the present numerical calculations are restricted to pairwise molecular interactions, though we give general expressions for the contribution to the effective optical anisotropy from three- and four-molecule interactions also. These expressions

will be the subject of further analysis. The per cent deviation of the theoretical results from the experimental data is the largest in pure CCl_4 (although small in absolute value); this can be taken as corroborating our supposition that multi-molecular interactions, which are particularly high in isotropically polarizable molecules, play an important rôle.

Our numerical calculations point to a decisive rôle of repulsive forces, as implied by the Lennard-Jones potential, in the formation of the internal structure of dense liquids, for which $\rho\sigma^3 \geq 0.65$ (in addition to noncentral forces due to the electric and optical properties of the molecules, like dispersional and multipole interactions, *etc.*). This, in our calculations, is apparent by way of the potential of Eq. (89). It was our assumption that, beyond the range of action of the forces of repulsion between two molecules, the latter cease to interact with one another, as they become involved in much stronger repulsive interaction with other molecules. The radial correlation parameters $\langle r^{-n} \rangle$, calculated here for this model, yield results in satisfactory agreement with experiment.

Our calculations point to non-additivity of the effective anisotropy of solutions. Tables II and III show how the contributions to the effective optical anisotropy from interaction between molecules of the same species and of different species vary in the entire range of concentrations. A calculation for a solvent consisting of isotropic molecules (CCl_4) points to the rôle of interactions between its molecules and those of the solute. The contribution to effective optical anisotropy from interactions between unlike molecules is non-negligible even if one of the two species consists of isotropic molecules. Significantly, this contribution varies with concentration, up to a maximal value of 20% of the effective optical anisotropy in $\text{CCl}_4\text{—C}_6\text{H}_6$ at $x_2 = 0.3$, and up to 13% of the total in $\text{CCl}_4\text{—CS}_2$ at $x_2 = 0.4$.

Interaction between anisotropically polarizable molecules (in our case, between like ones, thus C_6H_6 , and CS_2) leads to the emergence of some near range ordering; the probability of a given structure depends on their optical and geometrical properties. This last problem, however, requires a separate analysis, which will be given in another paper.

We moreover hope to extend the molecular mechanisms proposed above to the case of gases under high pressure [22].

The present work was intended in the honour of the Centenary of Marian Smoluchowski (28.V.1872–5.XI.1917), to whom is due the basis of the molecular fluctuational theory of light scattering.

The authors wish to thank the Physics Committee of the III Department of the Polish Academy of Sciences for sponsoring this investigation.

APPENDIX

On insertion of (25) into (37), we obtain the following second-approximation deviator for axially symmetric molecules:

$$D_{pi}^{(2)} = \frac{1}{81} \sum_{kl} \sum_{r=1}^{N_k} \sum_{s=1}^{N_l} \{27a_i a_k a_l [3T_{pirk} \cdot T_{rksl} - U(T_{pirk} : T_{rksl})] + \\ + 9a_i a_k \gamma_l [3T_{pirk} \cdot T_{rksl} \cdot S_{sl} - U(T_{pirk} \cdot T_{rksl}) : S_{sl}] +$$

$$\begin{aligned}
& +9a_i\gamma_k a_i [3T_{pirk} \cdot S_{rk} \cdot T_{rksl} - U(T_{pirk} \cdot T_{rksl}) : S_{rk}] + \\
& +9\gamma_i a_k a_i [3S_{pi} \cdot T_{pirk} \cdot T_{rksl} - U(T_{pirk} \cdot T_{rksl}) : S_{pi}] + \\
& +3a_i\gamma_k\gamma_l [3T_{pirk} \cdot S_{rk} \cdot T_{rksl} \cdot S_{sl} - U(T_{pirk} \cdot S_{rk} \cdot T_{rksl}) : S_{sl}] + \\
& +3\gamma_i\gamma_k a_i [3S_{pi} \cdot T_{pirk} \cdot S_{rk} \cdot T_{rksl} - U(T_{pirk} \cdot S_{rk} \cdot T_{rksl}) : S_{pi}] + \\
& +3\gamma_i a_k\gamma_l [3S_{pi} \cdot T_{pirk} \cdot T_{rksl} \cdot S_{sl} - U(S_{pi} \cdot S_{sl}) : (T_{pirk} \cdot T_{rksl})] + \\
& +\gamma_i\gamma_k\gamma_l [3S_{pi} \cdot T_{pirk} \cdot S_{rk} \cdot T_{rksl} \cdot S_{sl} - U(S_{pi} \cdot S_{sl}) : (T_{pirk} \cdot S_{rk} \cdot T_{rksl})] \}. \quad (A1)
\end{aligned}$$

This deviator, inserted with the deviators (15b) and (24a) into Eq. (36), leads to the result given by formula (45).

When decomposing the expression (27) into contributions from two-molecule and three-molecule correlations, it is convenient to use the following relations (we resort to the definition of the tensor (18)):

$$S_{pi} : T_{qjrk} = 3(z_{pi} \cdot T_{qjrk} \cdot z_{pi}), \quad (A2)$$

$$S_{pi} : (S_{qj} \cdot T_{qjrk}) = 9(z_{pi} \cdot z_{qj}) (z_{pi} \cdot T_{qjrk} \cdot z_{qj}) - (S_{pi} + S_{qj}) : T_{qjrk}, \quad (A3)$$

$$\begin{aligned}
& S_{pi} : (S_{qj} \cdot T_{qjrk} \cdot S_{rk}) = 27(z_{pi} \cdot z_{qj}) (z_{rk} \cdot z_{pi}) (z_{qj} \cdot T_{qjrk} \cdot z_{rk}) - \\
& - S_{pi} : (S_{qj} \cdot T_{qjrk}) - S_{qj} : (T_{qjrk} \cdot S_{rk}) - (S_{pi} \cdot T_{qjrk}) : S_{rk} - (S_{pi} + S_{qj} + S_{rk}) : T_{qjrk}. \quad (A4)
\end{aligned}$$

On putting $p_i = q_j$ in (A3) and (A4), we get the following identities for pairs:

$$S_{pi} : (S_{pi} \cdot T_{pirk}) = S_{pi} : T_{pirk}, \quad (A3a)$$

$$S_{pi} : (S_{pi} \cdot T_{pirk} \cdot S_{rk}) = S_{pi} : (T_{pirk} \cdot S_{rk}) + 2T_{pirk} : S_{rk}. \quad (A4a)$$

Similar relations can also be derived for products of the tensors occurring in (46).

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