

MANY-MOLECULAR CORRELATION-INDUCED ANISOTROPIC LIGHT SCATTERING AND OPTICAL BIREFRINGENCE IN SIMPLE FLUIDS

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By classical statistical perturbation calculus, successive contributions to many-molecular correlation-induced optical anisotropy in simple fluids are calculated taking into account linear dipolar polarizability induced by dipolar and quadrupolar interaction fields, as well as non-linear dipolar polarizabilities due to fluctuating dispersive and octupolar fields. In the approximation of binary correlations (which are sufficient for inducing optical anisotropy) all contributions are positive, whereas three-, and more-molecular correlations can lower or enhance (according to the structure of near order) the anisotropic scattering of light, as confirmed by the latest experiments in liquefied and condensed noble gases.

1. INTRODUCTION

Earlier theoretical work [1-6] has recently stimulated depolarization measurements of light scattering by simple substances in the liquid [7-10] and compressed gaseous state [11,12]. With the aim of providing a satisfactory explanation of the experimental results, an earlier theory [4,6] is extended in this communication to the case of many-molecular radial correlations taking into account not only linear dipole but also quadrupole polarizability as well as non-linear dipole polarizabilities caused by fluctuations of molecular fields in the range of near ordering.

2. FUNDAMENTALS

The effective optical anisotropy accounting for depolarization of light scattered by a medium of N interacting molecules is defined in general as [13]:

$$\Gamma^2(\Delta \mathbf{k}) = (3/2N) \left\langle \sum_{p=1}^N \sum_{q=1}^N \mathbf{D}_p : \mathbf{D}_q^* \times \exp(i \Delta \mathbf{k} \cdot \mathbf{r}_{pq}) \right\rangle, \quad (1)$$

$\Delta \mathbf{k} = \mathbf{k}_d - \mathbf{k}$ denoting the difference between the scattered (\mathbf{k}_d) and incident (\mathbf{k}) wave vectors, $\mathbf{r}_{pq} = \mathbf{r}_q - \mathbf{r}_p$ the vector connecting the centres of scattering molecules at \mathbf{r}_p and \mathbf{r}_q , and $\langle \quad \rangle$

statistical averaging in the presence of molecular correlations.

The deviation tensor \mathbf{D}_p of effective polarizability of molecule p in a dense medium contains, in general, various contributions from fluctuations of molecular fields accessible to calculation by classical perturbation calculus, justifying the expression of eq. (1) in the form:

$$\Gamma^2(\Delta \mathbf{k}) = \Gamma_0^2 + \Gamma_1^2 + \Gamma_2^2 + \Gamma_3^2 + \dots = \sum_{n=0}^{\infty} \Gamma_n^2(\Delta \mathbf{k}), \quad (2)$$

where the optical anisotropy of the n th approximation is:

$$\Gamma_n^2(\Delta \mathbf{k}) = (3/2N) \sum_{m=0}^n \left\langle \sum_{p=1}^N \sum_{q=1}^N \mathbf{D}_p^{(m)} \mathbf{D}_q^{*(n-m)} \times \exp(i \Delta \mathbf{k} \cdot \mathbf{r}_{pq}) \right\rangle. \quad (3)$$

Experimentally, (1) can be determined by measuring the horizontal component H_V of scattered intensity or the depolarization ratio D :

$$H_V = \{6R_{is} D / (6 - 7D)\} I = (\rho k^4 / 15) \{(n^2 + 2)/3\}^2 \Gamma^2(\Delta \mathbf{k}) I, \quad (4)$$

where n is the refractive index of the medium of molecule number density $\rho = N/V$ in scattering volume V , I the incident intensity and R_{is} the isotropic Rayleigh ratio.

In cases when the interference factor ($\Delta \mathbf{k} = 0$)

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in eq. (1) is negligible, the effective anisotropy can also be determined by measuring the molecular Kerr constant due to statistical fluctuational processes [13]:

$$B_m^{SF} = (4\pi \rho / 45 kT) \Gamma^2(0), \quad (5)$$

on neglecting dispersion between the measuring wave and the intense laser beam (or dc electric field) inducing the optical birefringence.

3. LINEAR DIPOLE POLARIZABILITY APPROXIMATION

In zeroth approximation (in the absence of fluctuating molecular fields and Jansen-Mazur effect [14]) the deviation tensor \mathbf{D}_p is non-zero only for intrinsically anisotropic molecules. Here, we are concerned with atomic substances or ones consisting of isotropically polarizable molecules for which neither a zeroth approximation deviation tensor nor anisotropy Γ_0^2 exist. In such substances, deviation \mathbf{D}_p is non-zero only in the presence of statistical fluctuations of the molecular fields \mathbf{F} which perturb the isotropic polarizability [14]. Linear approximation of the dipole polarizability a_p of the molecules yields:

$$\mathbf{D}_p^L = a_p \left[(\partial \mathbf{F}_p / \partial \mathbf{E}) - \frac{1}{3} \mathbf{u} \{ (\partial \mathbf{F}_p / \partial \mathbf{E}) : \mathbf{u} \} \right], \quad (6)$$

where \mathbf{F}_p is the time- and space-fluctuating electric field due to the distribution of $N-1$ molecular charges surrounding molecule p in the medium polarized by the electric field \mathbf{E} of the light wave; \mathbf{u} is Kronecker's unit tensor.

By (6), the anisotropy (1) becomes, in linear approximation,

$$\Gamma_L^2(\Delta \mathbf{k}) = \frac{1}{2N} \left\langle \sum_{p=1}^N \sum_{q=1}^N a_p a_q \left\{ 3 \left(\frac{\partial \mathbf{F}_p}{\partial \mathbf{E}} \right) : \left(\frac{\partial \mathbf{F}_q}{\partial \mathbf{E}} \right)^* - \left(\frac{\partial \mathbf{F}_p}{\partial \mathbf{E}} : \mathbf{u} \right) \left(\frac{\partial \mathbf{F}_q}{\partial \mathbf{E}} : \mathbf{u} \right)^* \right\} \exp(i \Delta \mathbf{k} \cdot \mathbf{r}_{pq}) \right\rangle. \quad (7)$$

Eq. (7) expresses generally the optical anisotropy induced in simple fluids by fluctuations of molecular fields in the near order region [4].

(i) *Molecular field of dipole interactions.* In Kirkwood-Yvon approximation, we have:

$$\left(\frac{\partial \mathbf{F}_p}{\partial \mathbf{E}} \right)_{\text{dip}} = - \sum_{s=1}^N \mathbf{T}_{ps} a_s + \sum_{s=1}^N \sum_{t=1}^N \mathbf{T}_{ps} \cdot \mathbf{T}_{st} a_s a_t - \dots, \quad (8)$$

where [3]

$$\mathbf{T}_{ps} = - (\nabla \nabla + k^2 \mathbf{u}) \exp(i \mathbf{k} \cdot \mathbf{r}_{ps}) / r_{ps} \quad (8a)$$

is the interaction tensor between induced dipoles of molecules p and s . ∇ is the spatial derivative operator.

Eqs. (7) and (8) lead to the non-zero induced anisotropies of second-, third-, ... order approximations:

$$\Gamma_2^2 = (3a^4 / 2N) \left\langle \sum_{pqrs}^N \mathbf{T}_{pr} : \mathbf{T}_{qs} \right\rangle, \quad (9)$$

$$\Gamma_3^2 = - (3a^5 / 2N) \left\langle \sum_{pqrst}^N \{ \mathbf{T}_{pr} : (\mathbf{T}_{qs} \cdot \mathbf{T}_{st}) + \mathbf{T}_{qr} : (\mathbf{T}_{ps} \cdot \mathbf{T}_{st}) \} \right\rangle \quad (10)$$

(in the absence of spatial dispersion, $\mathbf{k} = 0$). By well-known classical statistical many-molecular correlation (9) and (10) become:

$$\Gamma_2^2 = 9a^4 \{ J_R^{(2,2)} + 2J_R^{(2,3)} + \dots \}, \quad (9a)$$

$$\Gamma_3^2 = 18a^5 \{ J_R^{(3,2)} + 2J_R^{(3,3)} + \dots \}, \quad (10a)$$

where we have introduced the radial correlation parameters

$$J_R^{(2,2)} = (2\rho/V) \iint r_{pq}^{-6} g^{(2)}(r_p, r_q) dr_p dr_q, \quad (11a)$$

$$J_R^{(2,3)} = (\rho^2/V) \iiint \{ 3(\mathbf{r}_{pq} \cdot \mathbf{r}_{qs})^2 - r_{pq}^2 r_{qs}^2 \} \times r_{pq}^{-5} r_{qs}^{-5} g^{(3)}(r_p, r_q, r_s) dr_p dr_q dr_s, \dots \quad (11b)$$

$$J_R^{(3,2)} = (2\rho/V) \iint r_{pq}^{-9} g^{(2)}(r_p, r_q) dr_p dr_q, \quad (12a)$$

$$J_R^{(3,3)} = (\rho^2/2V) \iiint \{ [9(\mathbf{r}_{pq} \cdot \mathbf{r}_{qs})(\mathbf{r}_{qs} \cdot \mathbf{r}_{sp})(\mathbf{r}_{sp} \cdot \mathbf{r}_{pq}) - 3r_{pq}^2(\mathbf{r}_{qs} \cdot \mathbf{r}_{sp})^2 - 3r_{qs}^2(\mathbf{r}_{sp} \cdot \mathbf{r}_{pq})^2 - 3r_{sp}^2(\mathbf{r}_{pq} \cdot \mathbf{r}_{qs})^2 + 2r_{pq}^2 r_{qs}^2 r_{sp}^2] r_{pq}^{-5} r_{qs}^{-5} r_{sp}^{-5} + 2 [3(\mathbf{r}_{pq} \cdot \mathbf{r}_{qs})^2 - r_{pq}^2 r_{qs}^2] r_{pq}^{-8} r_{qs}^{-5} + [3(\mathbf{r}_{pq} \cdot \mathbf{r}_{sp})^2 - r_{pq}^2 r_{sp}^2] r_{pq}^{-5} r_{sp}^{-8} \} \times g^{(3)}(r_p, r_q, r_s) dr_p dr_q dr_s, \quad (12b)$$

$g^{(2)}(r_p, r_q)$ is the binary correlation function of molecules at \mathbf{r}_p and \mathbf{r}_q and $g^{(3)}(r_p, r_q, r_s)$ the ternary correlation function of 3 molecules at $\mathbf{r}_p, \mathbf{r}_q$ and \mathbf{r}_s .

The radial parameters (11a) and (12a) in two-molecule correlation approximation are always

positive; the most important role belongs to $J_R^{(2,2)}$ of the second approximation (calculated previously by this author [4,6] as twice larger than in ref. [2]), which is sufficiently for inducing optical anisotropy. The contributions from three-molecular and higher correlations are positive or negative according to the structure of near ordering. In the case of asymmetric structure, when at least two of the vectors r_{pq}, r_{qs}, r_{sp} are almost parallel, the parameters (11b) and (12b) are positive, raising the value of induced anisotropy. In that of quasi-symmetric structure (equilateral triangle, the vectors r_{pq}, r_{qs}, r_{sp} subtending angles of 60° , or two of them mutually perpendicular), the ternary correlation parameters (11b) and (12b) are negative, lowering the induced anisotropy.

(ii) *Molecular field of quadrupole interaction.* This field is of the form [15]:

$$\left(\frac{\partial F_p}{\partial E}\right)_{\text{quadr}} = -\frac{1}{3} \sum_{s=1}^N \sum_{t=1}^N (\nabla \mathbf{T}_{ps}) : (\nabla \mathbf{T}_{st}) q_s a t + \dots, \quad (13)$$

yielding the contribution:

$$Q \Gamma_3^2(0) = (a^4 q / 2N) \left\langle \sum_{pqrst} \{ \mathbf{T}_{pr} : (\nabla \mathbf{T}_{qs} : \nabla \mathbf{T}_{st}) + \mathbf{T}_{qr} : (\nabla \mathbf{T}_{ps} : \nabla \mathbf{T}_{st}) \} \right\rangle \quad (14)$$

to the third approximation of the anisotropy; q_s is the quadrupole polarizability induced in molecule s by the gradient of the field of neighbouring molecules.

The quadrupole contribution (14) can be expressed as:

$$Q \Gamma_3^2(0) = 36 a^4 q \{ Q_R^{(3,2)} + Q_R^{(3,3)} + \dots \}, \quad (14a)$$

where the radial correlation parameters are:

$$Q_R^{(3,2)} = (4\rho/V) \iint r_{pq}^{-11} g^{(2)}(r_p, r_q) dr_p dr_q, \quad (15a)$$

$$\begin{aligned} Q_R^{(3,3)} &= -(\rho^2/2V) \iiint \{ [75(r_{pq} \cdot r_{qs})(r_{qs} \cdot r_{sp})^2 (r_{sp} \cdot r_{pq}) \\ &- 30r_{sp}^2 (r_{sp} \cdot r_{qs})(r_{qs} \cdot r_{pq})^2 \\ &- 30r_{qs}^2 (r_{qs} \cdot r_{sp})(r_{sp} \cdot r_{pq})^2 \\ &- 25r_{pq}^2 (r_{qs} \cdot r_{sp})^3 - 3r_{qs}^2 r_{sp}^2 (r_{pq} \cdot r_{qs})(r_{sp} \cdot r_{pq}) \} \end{aligned}$$

$$\begin{aligned} &+ 21r_{pq}^2 r_{qs}^2 r_{sp}^2 (r_{sp} \cdot r_{qs}) r_{pq}^{-5} r_{ps}^{-7} r_{sp}^{-7} \\ &+ 8 [5(r_{pq} \cdot r_{sp})^2 - 3r_{pq}^2 r_{sp}^2] (r_{pq} \cdot r_{sp}) r_{pq}^{-10} r_{sp}^{-7} \\ &- 4 [3(r_{pq} \cdot r_{qs})^2 - r_{pq}^2 r_{qs}^2] r_{pq}^{-5} r_{qs}^{-10} \} \\ &\times g^{(3)}(r_p, r_q, r_s) dr_p dr_q dr_s. \quad (15b) \end{aligned}$$

Here, too, the binary correlation parameter is always positive. That of ternary correlations, (15b), deserves especial attention since its sign depends on the structure of near neighbourhood.

4. NON-LINEAR DIPOLE POLARIZABILITY APPROXIMATION

In very dense media, molecular fields F^0 exist even in the absence of an external field E causing a non-linear third-order polarizability c_p^0 of the atoms which contributes additionally the amount

$$D_p^{\text{NL}} = \frac{1}{3} c_p^0 \left\{ F_p^0 F_p^0 - \frac{1}{3} \mathbf{u} (F_p^0 F_p^0) \right\}, \quad (16)$$

to the deviation tensor. Hence, by (1), (6) and (16) we have in third approximation the cross contribution:

$$\Gamma_{\text{NL}3}^{\text{Q}}(0) = (ac/2N) \left\langle \sum_{p=1}^N \sum_{q=1}^N \left\{ \left(\frac{\partial F_p}{\partial E}\right) : F_q^0 F_q^0 + F_p^0 F_p^0 : \left(\frac{\partial F_q}{\partial E}\right) \right\} \right\rangle \quad (17)$$

(in the absence of spatial dispersion). Since the electric field of two-atom dispersive interaction yields [16]:

$$F_p^0 F_p^0 = F_q^0 F_q^0 = \frac{1}{8} h\nu a (3r_{pq} r_{pq} + r_{pq}^2 \mathbf{u}) r_{pq}^{-8} \quad (18)$$

we have, by (17)

$$\Gamma_{\text{NL}3}^2 = \frac{3}{4} a^3 ch\nu \{ J_R^{(3,2)} + \dots \}, \quad (17a)$$

$h\nu$ being a characteristic dispersive energy of the atom.

In the case of isotropically polarizable molecules without a centre of symmetry (e.g. $\text{CH}_4, \text{CCl}_4$), having non-linear second-order polarizability b , we obtain additionally the contributions:

$$\Gamma_{\text{NL}}^2(0) = \frac{9}{4} ab^2 h\nu J_R^{(2,2)} + \frac{144}{7} b^2 \Omega^2 G_R^{(2,2)} + \dots \quad (19)$$

induced by the dipole-dispersional and molecular octupole fields [6,18], where

$$G_R^{(2,2)} = (2\rho/V) \iint r_{pq}^{-10} g^{(2)}(r_p, r_q) dr_p dr_q, \quad (20)$$

where Ω is the electric octupole moment of the tetrahedral molecule.

All binary, ternary and higher correlation parameters - and consequently the various contributions to Γ^2 - can be calculated numerically on the assumption of Kirkwood's rigid sphere model or a Lennard-Jones potential [17,18]. For liquefied argon ($T = 85^\circ\text{K}$), the contribution of (10a) to the anisotropy (9a) amounts to 30%, whereas the non-linear contribution (17a) attains about 6%. In CCl_4 (at 300°K), (10a) contributes 40% to the anisotropy, whereas the non-linear contributions (17a) and (19) amount to 10%. This shows that in general it is by no means sufficient to calculate the induced anisotropy to within second dipole approximation (9a). In fact, the higher approximations have also to be taken into account.

Thus, in atomic substances and ones consisting of molecules without intrinsic linear anisotropy, the optical anisotropy induced by fluctuations of binary regroupings will increase or decrease under the influence of multiple regroupings in the region of near order. In general, with growing density, the structure of near order becomes increasingly symmetrical and, from our theoretical formulas, the optical anisotropy induced by the correlations has to decrease. This conclusion is confirmed by the latest measurements of the depolarized light scattered by liquefied [7-9] and highly compressed [11,12] noble gases.

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