Volume 34, number 3 OPTICS COMMUNICATIONS September 1980

NONLINEAR REFRACTIVE INDEX AND LIGHT SCATTERING DUE TO FLUCTUATIONS OF MOLECULAR MULTIPOLE ELECTRIC FIELDS

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Received 29 May 1980

Statistical fluctuations of multipolar electric molecular fields, leading to variations of isotropic and anisotropic light scattering, are moreover shown to give rise to a temperature-dependent nonlinear refractive index of dense fluids. Some selected models of dipolar and quadrupolar molecules, linearly and nonlinearly polarizable and correlated in binary as well as ternary assemblages, are discussed. The formulae derived for the isotropic and anisotropic scattering constants are applicable to one- and many-component fluids, consisting of atoms and polar molecules, and provide the basis for a deeper interpretation of the latest experimental results.

1. Introduction

According to Yvon [1], statistical translational fluctuations of the dipolar type cause the effective polarizability of an atom in a fluid to be a function of the density as the result of two- and three-body correlations. These variations in the polarizability of atoms are of the nature of an induced optical anisotropy, leading to depolarization of the light scattered by dense atomic fluids. When Yvon's theory is extended to molecules having intrinsic anisotropy, translational-orientational as well as orientational fluctuations have to be taken into consideration considerably affecting the depolarization of scattered light [2,3]. In recent years numerous authors have discussed anew the applicability of the dipolar approximation of the electric molecular field and its utility for the interpretation of the newest experimental observations of scattered light [4,5]. In the case of polar molecules, agreement between the theory and experiment can be enhanced by taking into consideration angular dispersional, electrostatic and inductional interactions in the approximation of binary and ternary correlations [2,3,6]. In atomic gases, as proved by the latest studies [7], it suffices to consider induced anisotropy in the dipole-induced dipole (DID) approximation.

Obviously, beside DID, when studying molecular fluids one has generally to take into consideration the quadrupolar (QIQ) and higher approximations of the molecular electric field giving rise to an additional induced anisotropy of multipolar polarizabilities apparent e.g. as density-dependent molecular refraction or distortional polarization [8–10]. Here, we restrict our considerations to changes in molecular polarizabilities due to long-range electric multipole fields [8], to the exclusion of effects of short-range interactions.

The above discussed fluctuational-statistic processes are apparent moreover as nonlinear changes of refractive index induced in liquids by strong laser light [11–13]. The fact is of great importance for the experimental and theoretical aspects of the two effects in which the stochastic-fluctuational processes taking place in molecular fluids are apparent. We believe that now is the moment to formulate a uniform description of both effects sufficiently general to comprise the various parameters characterizing the electrical properties (intrinsic multipole moments) and optical properties (linear and nonlinear multipolar polarizabilities) of the individual molecules, as well as the parameters characterizing the microstructure of fluids with many-body interactions.

2. The intensity of fluctuationally scattered light

We consider only the integral light scattering due to fluctuations of the electric dipole moment

$$\Delta M(t) = \Delta \mathbf{\Pi}(\omega) \cdot E_0(t) \tag{1}$$

induced by the electric field $E_0(t) = E_0(\omega)\exp(-\mathrm{i}\omega t)$ of a light wave outside the scattering sample, of volume V.

By definition, the fluctuations of the second-rank tensor of linear electric polarizability are given as

$$\Delta\mathbf{\Pi}(\omega) = \mathbf{\Pi}(\omega) - \langle \mathbf{\Pi}(\omega)\rangle\,, \tag{2}$$

where $\langle\ \rangle$ denotes appropriate statistical averaging at zero external fields.

On defining the intensity tensor of light scattered on the fluctuations (1) as

$$I_\mathrm{s} = \tfrac{1}{2}(\omega/c)^4 \langle \Delta M(t)\, \Delta M(t)^* \rangle \tag{3}$$

and neglecting, for simplicity, effects of phase interference and scattering of the antisymmetric type [14], we obtain

$$I_\mathrm{s} = \tfrac{1}{2}(\omega/c)^4 L^{\omega_\mathrm{s}} \{ S_\mathrm{is}^{\omega} E(t)E(t)^* + S_\mathrm{anis}^{\omega}[3U|E(t)|^2 + 3E(t)^*E(t) - 2E(t)E(t)^*] \}\,, \tag{4}$$

where U is the second-rank unit tensor.

In eq. (4) there appear quantities responsible for the fluctuational-molecular mechanisms of scattering, isotropic as well as anisotropic:

$$S_\mathrm{is}^{\omega} = \tfrac{1}{9}\langle [\Delta\mathbf{\Pi}(\omega) : U]\,[\Delta\mathbf{\Pi}(\omega)^* : U]\rangle\,, \tag{5}$$

$$S_\mathrm{anis}^{\omega} = \tfrac{1}{90}\langle 3\Delta\mathbf{\Pi}(\omega) : \Delta\mathbf{\Pi}(\omega)^* - [\Delta\mathbf{\Pi}(\omega) : U]\,[\Delta\mathbf{\Pi}(\omega)^* : U]\rangle\,. \tag{6}$$

In our semi-macroscopical model, the parameter L^{ω_s} is a result of the difference between the Maxwell electric field $E(t)$, existing within the scattering sample of electric permittivity ϵ, and the field $E_0(t)$ existing in the surrounding medium, of permittivity ϵ_0. In particular, for a spherical sample and for scattered light observed outside the sample, one has:

$$L^{\omega_\mathrm{s}} = (\epsilon_{\omega_\mathrm{s}} + 2\epsilon_0)^2(\epsilon_\omega + 2\epsilon_0)^2/81\epsilon_0^4\,; \tag{4a}$$

where $\epsilon_{\omega_\mathrm{s}}$ and ϵ_ω are the electric permittivities at the scattered light frequency ω_s and incident frequency ω, respectively; usually, $\epsilon_{\omega_\mathrm{s}} = \epsilon_\omega$. Quite generally, the form of L^{ω_s} is dependent on the shape of the sample [9] and the conditions in which the scattered light is observed.

Similarly, scattered light intensities of the magnetic dipole, electric quadrupole, and higher multipole types can be calculated [15].

3. Nonlinear refractive index

When the intense electric field of laser light is incident on the isotropic medium, the electric permittivity undergoes a tensorial variation, given as:

$$\Delta\boldsymbol{\epsilon}(\omega) \cdot E(t) = 4\pi \Delta P(t)\,. \tag{7}$$

The nonlinear change in electric dipole polarization $P(t)$ is caused by a variety of mechanisms [16]; here, we shall consider only the changes due to statistical fluctuations of the dipole moment (1):

$$\Delta P(t) = (1/V)\langle \Delta\mathbf{\Pi}(\omega)\rangle_\mathrm{E} \cdot E_0(t)\,. \tag{8}$$

Here the mean statistical value of fluctuations in the linear polarizability tensor (2) is calculated in the presence of the electric field $\boldsymbol{E}$ by way of the perturbed distribution function

$$f(\tau^N, \boldsymbol{E}) = f(\tau^N)\{1 + (4kT)^{-1}\,\Delta\boldsymbol{\Pi}(\omega):\boldsymbol{E}_0(t)\boldsymbol{E}_0(t)^*\}\,, \tag{9}$$

with: $f(\tau^N)$ the grand canonical distribution function for the ensemble of N molecules having the configuration τ^N at $E = 0$.

By (8) and (9), we obtain finally

$$\Delta\boldsymbol{P}(t) = \frac{L^\omega}{4kTV}\{S_{\mathrm{is}}^\omega \boldsymbol{E}(t)|\boldsymbol{E}(t)|^2 + S_{\mathrm{anis}}^\omega[3\boldsymbol{E}(t)^*\boldsymbol{E}(t)^2 + \boldsymbol{E}(t)|\boldsymbol{E}(t)|^2]\}\,, \tag{10}$$

where the macroscopic parameter L^ω can have the form (4a) for $\epsilon_{\omega_\mathrm{s}} = \epsilon_\omega$ or some other form depending on the conditions of observation and the properties of the sample [9].

Thus we have shown that, on the model assumed, both effects -- that of linear light scattering (4) and that of temperature-dependent nonlinear polarization (10) – originate in the same stochastic fluctuation processes.

Eqs. (10) and (7) permit the calculation of the electric dipole contribution to nonlinear refractive indices $\Delta n \approx (\Delta\epsilon_\omega \Delta\mu_\omega)^{1/2}$ for various states of polarization of the laser beam. The calculation of the magnetic contribution proceeds similarly and can be easily extended to that of higher multipolar contributions, essential in the case of optically active bodies and ones exhibiting spatial dispersion [9].

4. Variations in polarizability tensor due to multipolar molecular fields

Previously [15], we developed the quantum-mechanical theory of the linear and nonlinear multipolar polarizabilities of molecules in variable electromagnetic fields, where they possess the semi-classical perturbation hamiltonian

$$H_1^\mathrm{e} = -\sum_{n=1}^{\infty}\frac{1}{(2n-1)!!}\boldsymbol{M}^{(n)}[n]\boldsymbol{E}_0^{(n)} \tag{11}$$

(the symbol $[n]$ denotes n-fold contraction of the product of the two tensors $\boldsymbol{M}^{(n)}$ and $\boldsymbol{E}^{(n)}$ of rank n). In a linear approximation, the 2^m-pole electric moment induced in the isolated molecule at the space-time point $(\boldsymbol{r}, t)$ is [15]

$$\boldsymbol{M}^{(m)}(\boldsymbol{r}, t) = \sum_{n=1}^{\infty}\frac{1}{(2n-1)!!}\,{}^{(m)}\boldsymbol{A}^{(n)}(\omega)[n]\boldsymbol{E}_0^{(n)}(\boldsymbol{r}, t)\,, \tag{12}$$

where the m+n-th rank tensor ${}^{(m)}\boldsymbol{A}_i^{(n)}$ determines the linear polarizability of the 2^m-pole of an ith molecule due to the n-degree electric field $\boldsymbol{E}_0^{(n)}(\boldsymbol{r}, t) = \boldsymbol{\nabla}^{n-1}\boldsymbol{E}_0(\boldsymbol{r}, t)$. The quantum-mechanical frequency-dependence of the tensor, ${}^{(m)}\boldsymbol{A}^{(n)}(\omega)$, is given in ref. [9], where it is split into complex symmetric and antisymmetric parts.

Here, however, we are concerned with the changes in polarizability of an ensemble of N molecules caused by the long-range fields $\boldsymbol{F}^{(n)}(\boldsymbol{r}_i, t)$ produced in the centre of an ith molecule by the polarized electric multipoles of the N–1 surrounding molecules. We have in general [8,9]:

$$\boldsymbol{F}^{(n)}(\boldsymbol{r}_i, t) = \sum_{k\neq i}^{N}\sum_{s=1}^{\infty}\frac{(-1)^s}{(2s-1)!!}\,{}^{(n)}\boldsymbol{G}_{ik}^{(s)}[s]\boldsymbol{M}^{(s)}(\boldsymbol{r}_k, t)\,, \tag{13}$$

where the Green tensor of rank $(n + s)$

$${}^{(n)}\boldsymbol{G}_{ik}^{(s)} = \boldsymbol{\nabla}_i^{n-1}\boldsymbol{\nabla}_k^{s-1}(\boldsymbol{\nabla}_i\,\boldsymbol{\nabla}_k - k^2\boldsymbol{U})r_{ik}^{-1}\,\exp(\mathrm{i}kr_{ik})\,, \tag{13a}$$

describes the (2^n-pole) – (2^s-pole) dynamic interactions between the molecules i and k, separated by a distance r_{ik}.

Hence, in eq. (12), the field $E_0^{(n)}(r, t)$ has to be replaced by the total field $E_0^{(n)}(r, t) + F^{(n)}(r_i, t)$. This leads, for the electric dipole moment induced in the sample by the homogeneous electric field of the light wave, to

$$M(t) = \mathbf{\Pi}(\omega) \cdot E_0(t)\,, \tag{14}$$

where

$$\mathbf{\Pi}(\omega) = \mathbf{\Pi}^{(0)}(\omega) + \mathbf{\Pi}^{(1)}(\omega) + \mathbf{\Pi}^{(2)}(\omega) + \ldots \tag{15}$$

is the tensor of linear dipolar polarization of the medium in the presence of fluctuations of the multipolar electric molecular fields.

In the zeroth approximation we assume no long-range electric molecular field to be present, so that the polarizability tensor of the medium takes the form of the sum:

$$\mathbf{\Pi}^{(0)}(\omega) = \sum_{i=1}^{N} {}^{(1)}A_i^{(1)}(\omega) \tag{16}$$

of polarizability tensors ${}^{(1)}A_i^{(1)}(\omega)$ of the individual molecules.

The successive terms of the expansion (15) determine variations of the first, second, ... order due to the action of the multipolar molecular fields (13) in the medium:

$$\mathbf{\Pi}^{(1)}(\omega) = \sum_{i=1}^{N} \sum_{k\neq i}^{N} \sum_{m,n=1}^{\infty} (-1)^n c_{mn}\, {}^{(1)}A_i^{(m)}(\omega)[m]\, {}^{(m)}G_{ik}^{(n)}[n]\, {}^{(n)}A_k^{(1)}(\omega)\,, \tag{17}$$

$$\mathbf{\Pi}^{(2)}(\omega) = \sum_{i=1}^{N} \sum_{k\neq i}^{N} \sum_{l\neq k\neq i}^{N} \sum_{m\ldots u=1}^{\infty} (-1)^{n+u} c_{mnsu}\, {}^{(1)}A_i^{(m)}(\omega)[m]\, {}^{(m)}G_{ik}^{(n)}[n]\, {}^{(n)}A_k^{(s)}(\omega)[s]\, {}^{(s)}G_{kl}^{(u)}[u]\, {}^{(u)}A_l^{(1)}(\omega)\,, \tag{18}$$

where, for brevity, we have denoted the numerical coefficients of the expansion as $c_{m\ldots u} = 1/(2m-1)!! \cdots 1/(2u-1)!!$.

The electric field of the molecules in cooperation with that of the light wave not only cause linear molecular polarizabilities but moreover, in general, nonlinear multipolar polarizabilities [8,9]. On taking this circumstance into account we obtain the following, additional variations of the first and second order, respectively:

$$\mathbf{\Pi}_{\mathrm{NL}}^{(1)}(\omega) = \sum_{i=1}^{N} \sum_{k\neq i}^{N} \sum_{m,n=1}^{\infty} \left\{ (-1)^{(n)} c_{mn}\, {}^{(1)}B_i^{(1+m)}(\omega)[m]\, {}^{(m)}T_{ik}^{(n)}[n] M_k^{(n)}\,, \right. \tag{19}$$

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$$\begin{aligned} \mathbf{\Pi}_{\mathrm{NL}}^{(2)}(\omega) = \sum_{i=1}^{N} \sum_{k\neq i}^{N} \sum_{l\neq k\neq i}^{N} \sum_{m\ldots u=1}^{\infty} c_{mnsu} \{ & (-1)^{n+u}\, {}^{(1)}B_i^{(1+m)}(\omega)[m]\, {}^{(m)}T_{ik}^{(n)}[n]\, {}^{(n)}A_k^{(s)}(\omega)[s]\, {}^{(s)}T_{kl}^{(u)}[u] M_l^{(n)} \\ & + \tfrac{1}{2}(-1)^{s+u}\, {}^{(1)}B_i^{(m+n)}(\omega)\,[m+n]\,[{}^{(m)}T_{ik}^{(s)}[s] M_k^{(s)}\, {}^{(n)}G_{il}^{(u)}[u]\, {}^{(u)}A_l^{(1)}(\omega) \\ & + {}^{(m)}G_{ik}^{(s)}[s]\, {}^{(s)}A_k^{(1)}(\omega)\, {}^{(n)}T_{il}^{(u)}[u] M_l^{(u)}] \}\,, \end{aligned} \tag{20}$$

where the $(1+m+n)$-rank tensor ${}^{(1)}B_i^{(m+n)}$ defines the nonlinear dipole $-\, 2^{m+n}$-pole polarizability of the molecule, ${}^{(m)}T_{ik}^{(n)} = \nabla_i^m \nabla_k^n r_{ik}^{-1}$ is the tensor of electrostatic interactions between the multipolar molecules i and k, whereas $M_k^{(n)}$ is the intrinsic 2^n-pole electric moment of molecule k.

5. Scattering constants for selected models

We exclude from our considerations the zeroth-order contributions $S^{(00)} \sim \langle \Pi^{(0)} \Pi^{(0)} \rangle$ to the scattering constants;

rather, we shall concentrate on the contributions of the types $S^{(02)} \sim \langle \Pi^{(0)}\Pi^{(2)} \rangle$ and $S^{(11)} \sim \langle \Pi^{(1)}\Pi^{(1)} \rangle$ for several selected models.

5.1. Linear dipole–dipole and dipole–quadrupole polarizabilities

Let us consider, in the expansion (17), the first terms containing the tensors of linear dipole–dipole, dipole–quadrupole, and quadrupole–dipole polarizabilities ${}^{(1)}\boldsymbol{A}_i^{(1)}$, ${}^{(1)}\boldsymbol{A}_i^{(2)}$ and ${}^{(2)}\boldsymbol{A}_i^{(1)}$, respectively. We obtain the following contributions to (5) and (6) in the binary correlation approximation:

$$S_{\mathrm{is}}^{(11)} = \tfrac{40}{63} \left\langle \sum_{i=1}^{N} \sum_{j \neq i}^{N} (A_i^2 G_j^{(3,3)} + \tfrac{2}{25} \boldsymbol{D}_i : \boldsymbol{D}_i K_j^{(3,3)}) r_{ij}^{-8} \right\rangle , \tag{21}$$

$$S_{\mathrm{anis}}^{(11)} = \tfrac{8}{105} \left\langle \sum_{i=1}^{N} \sum_{j \neq i}^{N} (A_i^2 P_j^{(3,3)} + \tfrac{73}{90} \boldsymbol{D}_i : \boldsymbol{D}_i R_j^{(3,3)}) r_{ij}^{-8} \right\rangle , \tag{22}$$

with $A_i = {}^{(1)}\boldsymbol{A}_i^{(1)} : \boldsymbol{U}/3$, the mean linear dipole–dipole polarizability, and $\boldsymbol{D}_i = {}^{(1)}\boldsymbol{A}_i^{(1)} - A_i \boldsymbol{U}$, the deviation tensor of linear dipole–dipole polarizability. The molecular parameters $G_j^{(3,3)}, ..., R_j^{(3,3)}$ are in general rather highly complicated combinations of scalar products of the tensors ${}^{(1)}\boldsymbol{A}_j^{(2)}$ and ${}^{(2)}\boldsymbol{A}_j^{(1)}$, and are equal to the product ${}^{(1)}\boldsymbol{A}_j^{(2)} : {}^{(2)}\boldsymbol{A}_j^{(1)}$ on restriction to the symmetric parts ${}^{(1)}\boldsymbol{A}_{\mathrm{s}}^{(2)} = {}^{(2)}\boldsymbol{A}_{\mathrm{s}}^{(1)}$.

Beside the binary correlation contributions (21) and (22), the model under consideration leads, by eqs. (5), (6) and (17), to the following contributions related with ternary molecular correlations:

$$S_{\mathrm{is}}^{(11)} = -\tfrac{4}{567} \left\langle \sum_{i=1}^{N} \sum_{j \neq i}^{N} \sum_{k \neq j \neq i}^{N} A_i G_j^{(3,3)} A_k \, {}^{(1)}\boldsymbol{T}_{ij}^{(2)} : {}^{(2)}\boldsymbol{T}_{jk}^{(1)} \right\rangle , \tag{23}$$

$$S_{\mathrm{anis}}^{(11)} = -\frac{4}{4\underset{7}{\cancel{11}}25} \left\langle \sum_{i=1}^{N} \sum_{j \neq i}^{N} \sum_{k \neq j \neq i}^{N} A_i P_j^{(3,3)} A_k \, {}^{(1)}\boldsymbol{T}_{ij}^{(2)} : {}^{(2)}\boldsymbol{T}_{jk}^{(1)} \right\rangle , \tag{24}$$

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which are independent of dipole polarizability anisotropy $\boldsymbol{D}_i$.

The model moreover leads to contributions, resulting from the second approximation (18), namely for binary correlations

$$S_{\mathrm{is}}^{(02)} = \tfrac{4}{3} \left\langle \sum_{i=1}^{N} \sum_{j \neq i}^{N} A_i^2 ({}^{(1)}\boldsymbol{A}_j^{(2)} : {}^{(2)}\boldsymbol{A}_j^{(1)}) r_{ij}^{-8} \right\rangle , \tag{25}$$

$$S_{\mathrm{anis}}^{(02)} = \tfrac{1}{15} \left\langle \sum_{i=1}^{N} \sum_{j \neq i}^{N} \{A_i [\boldsymbol{D}_j : ({}^{(1)}\boldsymbol{A}_j^{(2)} \underline{:} {}^{(2)}\boldsymbol{A}_j^{(1)})] + \tfrac{1}{105} (\boldsymbol{D}_j : \boldsymbol{D}_j) \underline{W_{\underset{i}{j}}^{(3,3)}} \} r_{ij}^{-8} \right\rangle , \tag{26}$$

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where the symmetric part $W_j^{(3,3)} = {}^{(1)}\boldsymbol{A}_j^{(2)} : {}^{(2)}\boldsymbol{A}_j^{(1)}$.

5.2. Linear dipole–dipole and quadrupole–quadrupole polarizabilities

We now take the next term of (18) containing the linear quadrupole–quadrupole polarizability ${}^{(2)}\boldsymbol{A}_i^{(2)}$. For binary correlations, we obtain:

$$S_{\mathrm{is}}^{(02)} = \tfrac{4}{3} \left\langle \sum_{i=1}^{N} \sum_{j \neq i}^{N} A_i (A_i^2 + \tfrac{1}{3} \boldsymbol{D}_i : \boldsymbol{D}_i)(\boldsymbol{U}_{13} : {}^{(2)}\boldsymbol{A}_j^{(2)} : \boldsymbol{U}_{24}) r_{ij}^{-8} \right\rangle , \tag{27}$$

$$S_{\text{anis}}^{(02)} = \tfrac{2}{105}\left\langle \sum_{i=1}^{N}\sum_{j\neq i}^{N} \{(A_i^2 + \tfrac{1}{30}\boldsymbol{D}_i : \boldsymbol{D}_i)(\boldsymbol{D}_j : {}^{(2)}A_j^{(2)} : \boldsymbol{U}_{24}) + \tfrac{7}{6}[\boldsymbol{D}_i : (\boldsymbol{D}_i \cdot \boldsymbol{D}_i) + 2A_i(\boldsymbol{D}_i : \boldsymbol{D}_i)](\boldsymbol{U}_{13} : {}^{(2)}A_j^{(2)} : \boldsymbol{U}_{24})\} r_{ij}^{-8} \right\rangle , \tag{28}$$

and for ternary correlations:

$$S_{\text{is}}^{(02)} = -\tfrac{1}{45}\left\langle \sum_{i=1}^{N}\sum_{j\neq i}^{N}\sum_{k\neq j\neq i}^{N} A_i^2(\boldsymbol{U}_{13} : {}^{(2)}A_j^{(2)} : \boldsymbol{U}_{24}) A_k \, {}^{(1)}\boldsymbol{T}_{ij}^{(2)} : {}^{(2)}\boldsymbol{T}_{jk}^{(1)} \right\rangle , \tag{29}$$

$$S_{\text{anis}}^{(02)} = -\tfrac{1}{4725}\left\langle \sum_{i=1}^{N}\sum_{j\neq 1}^{N}\sum_{k\neq j\neq i}^{N} \{A_i(\boldsymbol{D}_j : {}^{(2)}A_j^{(2)} : \boldsymbol{U}_{24}) + \tfrac{7}{3}(\boldsymbol{D}_i : \boldsymbol{D}_i)(\boldsymbol{U}_{13} : {}^{(2)}A_j^{(2)} : \boldsymbol{U}_{24})\} A_k \, {}^{(1)}\boldsymbol{T}_{ij}^{(2)} : {}^{(2)}\boldsymbol{T}_{jk}^{(1)} \right\rangle . \tag{30}$$

5.3. *Dipolar nonlinearly polarizable molecules*

For molecules with an intrinsic dipole moment $\boldsymbol{M}_i^{(1)}$ and polarizable nonlinearly, the first approximation of (19) leads to previously calculated results [3]; however, the second approximation of (18) yields the following contributions for binary correlations:

$$S_{\text{is}}^{(02)} = \tfrac{2}{3}\left\langle \sum_{i=1}^{N}\sum_{j\neq i}^{N} A_i(A_i + A_j)(\boldsymbol{U} : {}^{(1)}\boldsymbol{B}_j^{(2)} \cdot \boldsymbol{M}_j^{(1)}) r_{ij}^{-6} \right\rangle , \tag{31}$$

$$S_{\text{anis}}^{(02)} = \tfrac{1}{15}\left\langle \sum_{i=1}^{N}\sum_{j\neq i}^{N} \{A_i(\boldsymbol{D}_j : {}^{(1)}\boldsymbol{B}_j^{(2)} \cdot \boldsymbol{M}_j^{(1)}) + \tfrac{1}{225}(\boldsymbol{D}_i : \boldsymbol{D}_i)(\boldsymbol{U} : {}^{(1)}\boldsymbol{B}_j^{(2)} \cdot \boldsymbol{M}_j^{(1)})\} r_{ij}^{-6} \right\rangle . \tag{32}$$

The parameter $\boldsymbol{U}^{(1)} : \boldsymbol{B}_j^{(2)} \cdot \boldsymbol{M}_j^{(1)}$ intervenes in the theory of DC field-induced second-harmonic light generation [17,18] permitting the determination of the value of the nonlinear dipole–dipole polarizability tensor ${}^{(1)}\boldsymbol{B}_j^{(1+1)} \equiv {}^{(1)}\boldsymbol{B}_j^{(2)}$. The new contributions (31) and (32) first calculated here are of interest as containing the first power of the tensor ${}^{(1)}\boldsymbol{B}^{(2)}$ and not its square, as it is the case for the $S^{(11)}$ approximation (cf. [2,3]).

5.4. *Quadrupolar nonlinearly polarizable molecules*

For molecules having an intrinsic quadrupole moment $\boldsymbol{M}_j^{(2)}$ and the nonlinear dipole–quadrupole polarizability ${}^{(1)}\boldsymbol{B}_j^{(3)} \equiv {}^{(1)}\boldsymbol{B}_j^{(1+2)}$, eqs. (5), (6) and (20) lead, in the binary correlation approximation, to:

$$S_{\text{is}}^{(02)} = \tfrac{2}{3}\left\langle \sum_{i=1}^{N}\sum_{j\neq i}^{N} \{A_i(A_i + A_j)(\boldsymbol{U} : {}^{(1)}\boldsymbol{B}_j^{(3)} : \boldsymbol{M}_j^{(2)})\} r_{ij}^{-8} \right\rangle , \tag{33}$$

$$S_{\text{anis}}^{(02)} = \tfrac{1}{15}\left\langle \sum_{i=1}^{N}\sum_{j\neq i}^{N} \{A_i(\boldsymbol{D}_j : {}^{(1)}\boldsymbol{B}_j^{(3)} : \boldsymbol{M}_j^{(2)}) + \tfrac{1}{315}(\boldsymbol{D}_i : \boldsymbol{D}_i)(3\boldsymbol{U}_{13} : {}^{(1)}\boldsymbol{B}_j^{(3)} - \boldsymbol{U}_{12} : {}^{(1)}\boldsymbol{B}_j^{(3)}) : \boldsymbol{M}_j^{(2)}\} r_{ij}^{-8} \right\rangle . \tag{34}$$

These formulae provide an indirect method for the determination of the sign of the quadrupole moment $\boldsymbol{M}_j^{(2)}$. The first-order approximation of (19) leads, for binary correlations, to

$$S_{\text{is}}^{(11)} = \tfrac{56}{405}\left\langle \sum_{i=1}^{N}\sum_{j\neq i}^{N} \{(\boldsymbol{U} : {}^{(1)}\boldsymbol{B}_i^{(3)}) : (\boldsymbol{U} : {}^{(1)}\boldsymbol{B}_i^{(3)})(\boldsymbol{M}_j^{(2)} : \boldsymbol{M}_j^{(2)}) + (\boldsymbol{U} : {}^{(1)}\boldsymbol{B}_i^{(3)} : \boldsymbol{M}_i^{(2)})(\boldsymbol{U} : {}^{(1)}\boldsymbol{B}_j^{(3)} : \boldsymbol{M}_j^{(2)})\} r_{ij}^{-10} \right\rangle , \tag{35}$$

$$S^{(11)}_{\text{anis}} = \tfrac{28}{2025}\Big\langle \sum_{i=1}^{N}\sum_{j\neq 1}^{N} \{[3\,{}^{(1)}\boldsymbol{B}_i^{(3)} :: {}^{(1)}\boldsymbol{B}_i^{(3)} - (\boldsymbol{U} : {}^{(1)}\boldsymbol{B}_i^{(3)}) : (\boldsymbol{U} : {}^{(1)}\boldsymbol{B}_i^{(3)})](\boldsymbol{M}_j^{(2)} : \boldsymbol{M}_j^{(2)})$$

$$+ \tfrac{8}{49}[(3\boldsymbol{U}_{13} : {}^{(1)}\boldsymbol{B}_i^{(3)} - \boldsymbol{U}_{12} : \underline{{}^{(1)}\boldsymbol{B}_i^{(3)}) : \boldsymbol{M}_i^{(2)}}]\,[(3\boldsymbol{U}_{13} : {}^{(1)}\boldsymbol{B}_j^{(3)} - \boldsymbol{U}_{12} : {}^{(1)}\boldsymbol{B}_j^{(3)}) : \boldsymbol{M}_j^{(2)}]\}\, r_{ij}^{-10} \Big\rangle . \tag{36}$$

5.5. *Dipolar–quadrupolar molecules*

The preceding expressions were derived by averaging the many-body radial correlation distribution function. Generally, averaging should be performed with the grand canonical statistical ensemble

$$f(\tau^N) = Q_N \exp[-(U_{\text{R}}^{\text{N}} + U_{\text{A}}^{\text{N}})/kT] , \tag{37}$$

where, in addition to the potential energy of radial interaction of the molecules U_{R}^{N}, we have the energy U_{A}^{N} dependent on the angular configurations of the N multipolar molecules. Usually, electrostatic multipole interactions, defined as [8]:

$$U_{\text{A}}^{\text{el}}(\tau^N) = -\tfrac{1}{2}\sum_{i=1}^{N}\sum_{j\neq i}^{N}\sum_{m,n=1}^{\infty} (-1)^n c_{mn} \boldsymbol{M}_i^{(m)}[m]\,{}^{(m)}\boldsymbol{T}_{ij}^{(n)}[n]\boldsymbol{M}_j^{(n)} \tag{38}$$

play the predominant role. Assuming here, as an example, dipole–quadrupole type interactions only, we obtain with regard to (5), (6) and (17):

$$S^{(01)(1)}_{\text{is}} = -\frac{1}{15kT}\Big\langle \sum_{i=1}^{N}\sum_{j\neq i}^{N} (A_i + A_j)(\boldsymbol{D}_i : \boldsymbol{M}_i^{(2)})[\boldsymbol{U} : ({}^{(1)}\boldsymbol{A}_j^{(2)} + {}^{(2)}\boldsymbol{A}_j^{(1)}) \cdot \boldsymbol{M}_j^{(1)}]\, r_{ij}^{-8} \Big\rangle , \tag{39}$$

$$S^{(01)(1)}_{\text{anis}} = -\frac{1}{75kT}\Big\langle \sum_{i=1}^{N}\sum_{j\neq i}^{N} \{\boldsymbol{D}_i : ({}^{(1)}\boldsymbol{A}_i^{(1)} \cdot \boldsymbol{M}_i^{(2)})[\boldsymbol{U} : ({}^{(1)}\boldsymbol{A}_j^{(2)} + {}^{(2)}\boldsymbol{A}_j^{(1)}) \cdot \boldsymbol{M}_j^{(1)}]$$

$$+ [\boldsymbol{D}_i : ({}^{(1)}\boldsymbol{A}_i^{(2)} + {}^{(2)}\boldsymbol{A}_i^{(1)}) \cdot \boldsymbol{M}_i^{(1)}](\boldsymbol{D}_j : \boldsymbol{M}_j^{(2)})\}\, r_{ij}^{-8} \Big\rangle . \tag{40}$$

The contributions (39) and (40) attract our attention because they involve the first power of the tensors ${}^{(1)}\boldsymbol{A}_i^{(2)}$ and ${}^{(2)}\boldsymbol{A}_i^{(1)}$. Likewise, had we taken the first term of (19) and (38) for $m = n = 1$, we would have arrived at the previously calculated [2] additional contribution, linearly dependent on ${}^{(1)}\boldsymbol{B}_i^{(2)}$ and proportional to r_{ij}^{-6}/kT, to the constants (31) and (32).

6. Conclusions

The expressions (21)–(40) derived above for the constants of isotropic and anisotropic light scattering, though rather complicated from the mathematical point of view, take a simple form when applied to molecules having well defined properties of symmetry (a centre, or an axis) for which the intrinsic electric multipoles and multipole polarizability tensor present one, or two independent components. Since the numerical values of these molecular parameters are available [16,17,19], we obtain those of the various contributions to the scattering constants (5) and (6) by calculating the radial binary and ternary averages $\langle r_{ij}^{-2n}\rangle$ and $\langle r_{ij}^{-n} r_{jk}^{-n}\rangle$. One is easily convinced that these contributions are, in fact, highly essential – especially the cross-contributions of the type $S^{(01)} = S^{(10)}$ and $S^{(02)} = S^{(20)}$ hitherto not considered in the literature. Certain of these contributions can be positive or negative, depending on the electrical structure of the molecule and the model of the three-body molecular correlations. Obviously, it was by no means our aim to calculate all the contributions to (5) and (6) derivable from the linear (17) and (18) and nonlinear ((19) and (20)) multipole polarizabilities but solely to point to the vast possibilities offered by our theory in application to one-component – and, even more so – many-component fluids [3]. The temperature-dependent measurements of the nonlinear refractive index carried out by Lalanne et al. [12] and, lately, by Ho and Alfano [13] prove that the contributions obtained when averaging in (5) and (6) with (37) and an appropriately chosen tensorial molecular interaction energy U_A^N (cf. [3,8,19]) are essential.

Our molecular-statistical theory of integral light scattering is well adapted for extension to spectral distributions, as has been done by Knast [14] for the contribution $S^{(0,0)}$ and, recently, by Bancewicz [21] for $S^{(01)}$.

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