FLUCTUATIONS AND RAYLEIGH SCATTERING OF LIGHT IN SYSTEMS WITH ROTATIONAL DEGREES OF FREEDOM

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Equilibrium thermal fluctuations in an isotropic gyrotropic continuous medium with internal rotational degrees of freedom are considered on the basis of the generalized equations of hydrodynamics and the dissipation-fluctuation theorem. It is shown that in contrast to studies in which the gyrotropy of the medium is not taken into account, the fluctuations of the scalar parameters (density, entropy, etc.) are of a nonlocal nature. An expression is obtained in second order of the Kubo theory for that part of the dipole moment which is proportional to the deformation tensors and the applied field, and which is responsible for Rayleigh light scattering. It is concluded from an analysis of the expressions obtained for the intensities of the depolarized scattered-light components that the spectral components I_y^z and I_z^x may not be equal.

1. INTRODUCTION

THE correlation theory of equilibrium thermal fluctuations in an isotropic continuous medium, constructed without account of the rotational degrees of freedom, allows us to describe the character of both the polarized and depolarized components of the scattered light spectrum in liquids.[1-4]. Yet the molecules of the materials studied in experimental researches[5] have translational and rotational degrees of freedom. In a number of researches (see, for example,[6,7]) the depolarization of light in Rayleigh scattering is indeed explained by the translational motion of the molecules. Therefore, in the construction of the theory of Rayleigh light scattering, it is important to take the rotational degrees of freedom into account.

It has been proved statistically[8,9] that a hydrodynamic treatment of systems consisting of nonspherical particles should be based on the equations of the moment theory of a continuous medium.[10] Account of the translational degrees of freedom leads to a number of singularities in its behavior. Thus, two nonsymmetrical tensors of ordinary (Π_{ik}) and moment ($\mathscr{P}_{ik}$) stresses are characteristic in this case, and correspondingly, two deformation tensors (σ_{ik} and γ_{ik}). In a gyrotropic medium, as follows from statistical considerations,[9] this feature also appears in the equilibrium state, as a consequence of the absence of a center of symmetry. For the description of the behavior of the continuous medium, it is necessary to write down the equation for the kinetic moment transfer along with the equation of momentum transfer. In the presence of internal degrees of freedom, these equations are mutually complementary.

In considering fast processes, one can use the equations of generalized hydrodynamics, taking into account the temporal and spatial dispersion which appear in the statistical treatment of a system of nonspherical particles.[9,10] A number of recent researches have demonstrated the applicability of the equations of generalized hydrodynamics up to $\omega \sim 10^{13}$ sec^{-1} and $k \sim 10^8$ cm^{-1}.[12]

2. INITIAL EQUATIONS

The deformed state of an asymmetric continuous medium is described by two deformation tensors:[9,10]

$$\sigma_{ik} = \partial u_i / \partial q_k + \varepsilon_{ikl}\varphi_l, \quad \gamma_{ik} = \partial \varphi_i / \partial q_k, \tag{1}$$

where u_i and φ_i are respectively the vectors of small displacement and small angle of rotation of the particles of the medium, ϵ_{ikl} is the Levi-Civita tensor.

The deformation tensors can be represented in the form of the sums of their traces σ and γ, the nondivergent symmetric $\sigma'^{(s)}_{ik}$ and $\gamma'^{(s)}_{ik}$ and antisymmetric $\sigma^{(a)}_{ik}$ and $\gamma^{(a)}_{ik}$ tensors; the following notation is introduced;

$$\begin{gathered}\pi_{ik}^{(1)} = \gamma\delta_{ik} = (\partial\varphi_l/\partial q_l)\,\delta_{ik}, \quad \pi_{ik}^{(2)} = \sigma\delta_{ik} = (\partial u_l/\partial q_l)\,\delta_{ik}, \\ \pi_{ik}^{(3)} = \gamma_{ik}'^{(s)}, \quad \pi_{ik}^{(4)} = \sigma_{ik}'^{(s)}, \quad \pi_{ik}^{(5)} = \gamma_{ik}^{(a)}, \quad \pi_{ik}^{(6)} = \sigma_{ik}^{(a)}.\end{gathered} \tag{2}$$

For the case of a gyrotropic isotropic continuous medium with temporal dispersion, linearized relations can now be written down between the stress tensors and entropy on the one hand and the deformation tensors and temperature on the other, and also linearized equations of motion. In the $(\omega, \mathbf{k})$ variables, $(\partial/\partial\tau \to i\omega, \partial/\partial q_k \to ik_k)$ the set of equations has the form

$$\Pi_{ik}(\omega, \mathbf{k}) = \sum_{j=1}^{6} b_j(\omega)\pi_{ik}^{(j)}(\omega, \mathbf{k}) + b_7(\omega)\Theta(\omega, \mathbf{k})\delta_{ik}, \tag{3a}$$

$$\mathscr{P}_{ik}(\omega, \mathbf{k}) = \sum_{j=1}^{6} d_j(\omega)\pi_{ik}^{(j)}(\omega, \mathbf{k}) + d_7(\omega)\Theta(\omega, \mathbf{k})\delta_{ik}, \tag{3b}$$

$$S(\omega, \mathbf{k}) = l_1(\omega)\gamma(\omega, \mathbf{k}) + l_2(\omega)\sigma(\omega, \mathbf{k}) + l_7(\omega)\Theta(\omega, \mathbf{k}); \tag{3c}$$

$$-\rho_0\omega^2 u_i(\omega, \mathbf{k}) = ik_k\Pi_{ik}(\omega, \mathbf{k}) + ik_k\hat{\Pi}_{ik}(\omega, \mathbf{k}), \tag{4a}$$

$$-i_0\omega^2\varphi_i(\omega, \mathbf{k}) = \varepsilon_{inm}\Pi_{mn}(\omega, \mathbf{k}) + ik_k\mathscr{P}_{ik}(\omega, \mathbf{k}) + \varepsilon_{inm}\hat{\Pi}_{mn}(\omega, \mathbf{k}) + ik_k\hat{\mathscr{P}}_{ik}(\omega, \mathbf{k}), \tag{4b}$$

$$i\omega\rho_0 S(\omega, \mathbf{k}) = -k^2\varkappa(\omega)\Theta(\omega, \mathbf{k}) - k^2\varkappa(\omega)\hat{\Theta}(\omega, \mathbf{k}). \tag{4c}$$

Here $\Theta = (T - T_0)/T_0$, T_0, ρ_0 and i_0 are respectively the equilibrium values of the temperature, mass density and moment-of-inertia density of the medium.

We also introduce the external stresses $\hat{\Pi}_{ik}$ and $\hat{\mathscr{P}}_{ik}$ and the external temperature $\hat{\Theta}$; S is the entropy.

Eliminating Π_{ik}, $\mathscr{P}_{ik}$ and Θ, we obtain a set of seven equations in u_i, φ_i and S:

$$-\rho_0\omega^2 u_i = \sum_{j=1}^{6} b_j i k_k \pi_{ik}^{(j)} + \omega k^{-2} k_i b_7' S + i k_k \hat{\Pi}_{ik} - i k_i b_7 \hat{\Theta}, \quad (5a)$$

$$-i_0\omega^2\varphi_i = \sum_{j=5}^{6} b_j \varepsilon_{inm}\pi_{mn}^{(j)} + \sum_{j=1}^{6} d_j i k_k \pi_{ik}^{(j)} + \omega k^{-2} k_i d_7' S + \varepsilon_{inm}\hat{\Pi}_{mn} + i k_k \hat{\mathscr{P}}_{ik} - i k_i d_7 \hat{\Theta}, \quad (5b)$$

$$(i\omega\rho_0 + k^2\varkappa')S - k^2 l_1'\gamma - k^2 l_2'\sigma = -k^2\varkappa\hat{\Theta}, \quad (5c)$$

$$b_7' = \rho_0 b_7 \varkappa^{-1}, \quad d_7' = \rho_0 d_7 \varkappa^{-1}, \quad \varkappa' = \varkappa l_7^{-1}, \quad l_j' = \varkappa l_j l_7^{-1} \quad (j = 1, 2).$$

Solution of the set of equations (5) allows us to obtain the connection between the generalized coordinates σ_{ik}, γ_{ik} and S, and the external forces $\hat{\Pi}_{ik}$, $\hat{\mathscr{P}}_{ik}$ and $\hat{\Theta}$, i.e., the matrix of the generalized susceptibility, and then, by using the dissipation-fluctuation theorem (DFT) (see, for example,[13]), to compute the fluctuations of the generalized coordinates. However, direct solution in the general form of the set (5) relative to u_i, φ_i and S is very cumbersome. It is much simpler to obtain the solution if we first write the equations for the irreducible parts of the deformation tensors.

3. FLUCTUATIONS OF THE SCALAR AND TENSOR PARAMETERS

To obtain equations in the scalar parameters, we multiply (5a) and (5b) by ik and sum over the index i. Equation (5a) has already been written relative to the scalar parameters. Solving this set and representing the tensors $\hat{\Pi}_{ik}$ and $\hat{\mathscr{P}}_{ik}$ by their irreducible parts, similar to (2), we obtain the corresponding part of the generalized susceptibility matrix.

Without writing out the cumbersome expressions, we shall set down as an example the result for the spatial density correlator ($\sigma = \delta\rho/\rho$):

$$\frac{1}{\rho^2}\langle\delta\rho(0,0)\,\delta\rho(0,\mathbf{r})\rangle = \frac{k_B T a^2 d_{n0}}{2b_{60}\,b_{g0}}\left\{\delta(\mathbf{r}) - \frac{a^2 - 2b_{60}/d_{n0}}{4\pi r}e^{-ar}\right\}, \quad (6)$$

$$a^2 = 2b_{60}b_{g0} / (b_{g0}d_{\ 0} - b_{n0}d_{n0}), \quad \alpha_r = \alpha_2 + {}^2/_3\alpha_4, \quad \alpha_n = \alpha_1 + {}^2/_3\alpha_3 \quad (\alpha = b,\ d).$$

The index 0 denotes the limiting low frequency values of the coefficients. To obtain (6), we used one of the theorems given in[1] (it was assumed that the frequency dependence of the coefficients could be represented in the form of the sum

$$\sum_m i\omega\tau_m n_m/(1 + i\omega\tau_m)).$$

Calculation of the integrated (over space) intensity of the density fluctuations leads to the usual result if we assume that $b_{20} = K_0$ and $b_{40} = 2\mu_0$, K_0 and μ_0 being the low-frequency moduli of the bulk and shear viscosities, respectively.

Statistical considerations show[9] that the tensor of moment stresses is different from zero in a gyrotropic medium, because of the absence of a center of symmetry, and that the tensor of ordinary stresses is nonsymmetric even in the equilibrium state. In this case, the low-frequency modulus $b_{60} \neq 0$ and, consequently, $a \neq 0$. This also leads to an nonlocal character for the density correlation. The quantity a determines the scale of the spatial inhomogeneity brought about by the presence of the gyrotropic character of the medium. Making use of measurement data of[14], which were obtained in liquid crystals, we estimate the order of magnitude of a. According to[14] $d_{n0} \sim 10^{-6}$ dyn. Taking $b_{60} \sim 10^8$ dyn/cm^2 (such an order of magnitude follows from statistical estimates[15]), we find $a \sim \sqrt{b_{60}/d_{n0}} \sim 10^7$ cm^{-1}. The correlations $\langle\gamma(0,0)\gamma(0,\mathbf{r})\rangle$ and $\langle\delta S(0,0)\delta(0,\mathbf{r})\rangle$ have a similar character, and the integrated intensity of the entropy fluctuations $\langle(\delta S)^2\rangle$ is seen to be the same as without account of the rotational degrees of freedom, and $\langle\gamma^2\rangle = 0$.

For a nongyrotropic medium, $b_{60} = 0$, $d_{g0} = 0$, $b_{n0} = 0$ and the fluctuations of the given quantities are local.

In order to determine the remaining part of the generalized susceptibility matrix, we multiply Eqs. (5a) and (5b) by ik_j. In the two resultant equations, there will be four combinations of the unknows under study: ik_ju_i, $ik_j\varphi_i$, $k_j\epsilon_{ikl}k_ku_l$ and $k_j\epsilon_{ikl}k_k\varphi_l$. To obtain a closed set of equations, these two equations must be multiplied by $k_m\epsilon_{nji}$, contracted with respect to the indices j and i and the indices relabeled.

We call attention to the fact that the complete dispersion equation describing the possible wave processes in a gyrotropic isotropic continuous medium divides into two independent equations for the scalar parameters

$$\Delta_{um\,\mathrm{gyr}} = \begin{vmatrix} -i_0\omega^2 + 2b_6 + k^2 d_n & k^2 d_r & -i\omega d_7' \\ k^2 b_n & -\rho_0\omega^2 + k^2 b_r & -i\omega b_7' \\ -k_2 l_1' & -k^2 l_2' & i\omega\rho_0 + k^2\varkappa' \end{vmatrix} = 0 \quad (7)$$

and the tensor parameters

$$\Delta_{\mathrm{gyr}} = \begin{vmatrix} \Delta_\rho & b_6 & 0 & {}^1/_2 k^2(b_3 + b_5) \\ k^2 b_6 & \Delta_i & {}^1/_2 k^2(d_4 + d_6) & k^2(b_5 + d_6) \\ 0 & {}^1/_2 k^2(b_3 + b_5) & \Delta_\rho & k^2 b_6 \\ {}^1/_2 k^2(d_4 + d_6) & b_5 + d_6 & b_6 & \Delta_i \end{vmatrix} = 0,$$

$$\Delta_\rho = -\rho_0\omega^2 + {}^1/_2 k^2(b_4 + b_6), \quad \Delta_i = -i_0\omega^2 + 2b_6 + {}^1/_2 k^2(d_3 + d_5). \quad (8)$$

However, (8) no longer divides into two identical equations (which, in the usual medium, correspond to shear waves of mutually perpendicular polarizations) and, consequently, the gyrotropic character of the medium becomes degenerate. In addition, Eqs. (7) and (8) show that a significantly larger number of waves is propagated in the media under consideration, for corresponding conditions, than in ordinary continuous media. The conditions for appearance and the form of the possible acoustic waves were considered previously for a homogeneous, isotropic, nongyrotropic asymmetric medium by a method that is different than the one used here.[15] In this case, $l_1 = 0$, $d_2 = d_4 = d_6 = d_7 = 0$, $b_1 = b_3 = b_5 = 0$, so that $\Delta_{\mathrm{nongyr}} = (\Delta_i\Delta_\rho - k^2 b_6^2)^2$ and the presence of a symmetry center leads to twofold degeneracy.

4. FEATURES OF THE DEPOLARIZATION OF SCATTERED LIGHT DUE TO THE ACCOUNT OF ROTATIONAL DEGREES OF FREEDOM

Let us consider a system of nonspherical polarized particles that may possess a constant dipole moment.

In the theory of Rayleigh scattering, it is important to calculate the part of the dipole moment that is proportional to the applied field **E** and the deformation tensors σ_{ik} and γ_{ik}. For this purpose, we use the theory of nonlinear reactions of Kubo, which takes second order perturbation theory into account[16].

The initial expression for the mean value of the change in the dynamical quantity $B(t)$ has the form

$$\Delta B = \int_{-\infty}^{t} dt_1 \int_{-\infty}^{t_1} dt_2\, \mathrm{Sp}\,\{[\Delta H(t_1)[\Delta H(t_2)\rho]]B(t)\}. \tag{9}$$

in second order perturbation theory.

The change in the Hamiltonian upon application to the system of a small deformation was determined in[11] and, with account of the electric field, takes the form

$$\Delta H(t) = \Pi_{ik}{}^{+}\sigma_{ik} + \mathscr{P}_{ik}{}^{+}\gamma_{ik} - P_i{}^{+}\mathscr{G}_i. \tag{10}$$

Here P_i^{+}, Π_{ik}^{+}, $\mathscr{P}_{ik}^{+}$ are the operators of the dipole moment and the fluxes of momentum and kinetic moment. $\mathscr{G}_i$ is the field of the macroscopic elliptical cavity expressed in terms of the external field E_i and the principal values of the tensor of dielectric permittivity at the frequency ω.[17]

We select as an averaged quantity the dipole moment operator P_i^{+} and use the expression for the increase of the Hamiltonian (10). For the sought part of the dipole moment, we obtain in correspondence with (9)

$$\begin{aligned}\Delta P_n(t) = &-\int_0^{\infty} d\tau \int_0^{\infty} \mathrm{Sp}\,\{[\Pi_{ik}{}^{+}(s)[P_r{}^{+}(0)\rho]]P_n{}^{+}(\tau+s)\}\sigma_{ik}(t\\ &-\tau)\mathscr{G}_r(t-\tau-s)\,ds - \int_0^{\infty} d\tau \int_0^{\infty} \mathrm{Sp}\,\{[P_r{}^{+}(s)[\Pi_{ik}{}^{+}(0)\rho]]P_n{}^{+}(\tau\\ &+s)\}\mathscr{G}_r(t-\tau)\sigma_{ik}(t-\tau-s)\,ds - \int_0^{\infty} d\tau \int_0^{\infty} \mathrm{Sp}\,\{[\mathscr{P}_{ik}{}^{+}(s)\\ &\times[P_r{}^{+}(0)\rho]]P_n{}^{+}(\tau+s)\}\gamma_{ik}(t-\tau)\mathscr{G}_r(t-\tau-s)\,ds\\ &-\int_0^{\infty} d\tau \int_0^{\infty} \mathrm{Sp}\,\{[P_r{}^{+}(s)[\mathscr{P}_{ik}{}^{+}(0)\rho]]P_n{}^{+}(\tau+s)\}\mathscr{G}_r(t-\tau)\gamma_{ik}(t-\tau-s)\,ds\end{aligned} \tag{11}$$

Here ρ is the equilibrium distribution function $[\ldots]$ are the Poisson brackets, the operator Sp means integration over phase space (the classical case) or summation over the quantum states.

We limit ourselves to the consideration of a nongyrotropic medium. Then the terms in the last equation that contain the second deformation tensor fall out. Assuming the deformation and the field to be periodic in time, $\sigma_{ik} \sim \exp(i\omega t)$, $\gamma_{ik} \sim \exp(i\omega t)$, $\mathscr{G}_r \sim \exp(i\omega_1 t)$, we rewrite the expression for the polarization in the form

$$\begin{aligned}\Delta P_n(\omega_1+\omega) = -\int_0 e^{-i(\omega_1+\omega)\tau}\Big\{&\int_0 e^{-i\omega_1 s}\,\mathrm{Sp}([\Pi_{ik}{}^{+}(s)[P_r{}^{+}(0)\rho]]P_n{}^{+}(\tau+s))\,ds\\ &+\int_0 e^{-i\omega s}\,\mathrm{Sp}([P_r{}^{+}(s)[\Pi_{ik}{}^{+}(0)\rho]]P_n{}^{+}(\tau+s))\,ds\Big\}d\tau\,\sigma_{ik}(\omega)\mathscr{G}_r(\omega_1).\end{aligned} \tag{12}$$

In the problem of Rayleigh scattering, the frequency of the incident light $\omega_1 \sim 10^{15}\ \mathrm{sec}^{-1}$ and is, on the one hand, much greater than the frequencies $\sim 10^{11}$–10^{13} sec^{-1} that are typical of translational and rotational motions of the molecules, and on the other hand, the absorption of light at these frequencies (far from molecular absorption bands) is extremely small. These considerations permit us to eliminate the frequency ω_1 in the integral term, so that we obtain the expression

$$\Delta P_n(\omega_1+\omega) = a_{nrik}(\omega)\sigma_{ik}(\omega,\mathbf{k})E_r(\omega_1). \tag{13}$$

In the general case, the tensor a_{nrik} depends on the frequency of the incident light, ω_1.

For an isotropic, nongyrotropic, continuous medium, the latter expression can be represented in the form

$$\begin{aligned}\Delta P_i(\omega_1+\omega) = [&a_2(\omega)\sigma(\omega,\mathbf{k})\delta_{ik} + a_4(\omega)\sigma_{ik}{}'^{(s)}(\omega,\mathbf{k})\\ &+a_6(\omega)\sigma_{ik}^{(a)}(\omega,\mathbf{k})]E_k(\omega_1).\end{aligned} \tag{14}$$

The expression in the square brackets represents the change in the dielectric permittivity tensor $\epsilon_{ik}(\omega, \mathbf{k})$ due to fluctuations of the deformation tensor, and can be used for calculation of the scattered-light spectrum.

Using the method of the nonequilibrium statistical operator,[16] a term that is proportional to the change in temperature can be obtained in the expression for ΔP_i. This allows us to take into account the light scattering due to the temperature fluctuations.

The set of equations of generalized hydrodynamics with account of the rotational degrees of freedom, which is established on the basis of the present research, was obtained by the strict methods of nonequilibrium statistical mechanics. The equations contain a dispersion which is the consequence of the contraction of the description in the transition from Liouiville's equation, which gives a complete description of the system. The form of the dispersion is determined by explicit statistical expressions for the kinetic coefficients. In contrast with this, it is necessary in the use of the equations of relaxation hydrodynamics, for guaranteeing the dispersion in the equations of motion, to introduce additional internal relaxing parameters, the physical interpretation of which is not clear.

In what follows, we consider the scattering due only to fluctuations of the deformation tensor.

For the calculation of the spectral density of the $(\omega, \mathbf{k})$ amplitudes of the dielectric permittivity $\langle \epsilon_{ik}\epsilon_{lm}^{*}\rangle$ only correlations of the first deformation tensor are required. Therefore, we write down the solution of Eq. (5) which contains only terms containing $\hat{\Pi}_{ik}$:

$$\sigma(\omega,\mathbf{k}) = \frac{i\omega\rho_0 + k^2\varkappa'}{\Delta_{um}}\left[k^2\left(-\frac{1}{3}\hat{\Pi}\right) + \overline{k_jk_i}(-\hat{\Pi}_{ij}{}'^{(s)})\right] + \ldots, \tag{15a}$$

$$\begin{aligned}\sigma_{ij}{}'^{(s)}(\omega,\mathbf{k}) = &\frac{i\omega\rho_0 + k^2\varkappa'}{\Delta_{um}}\overline{k_jk_i}\left(-\frac{1}{3}\hat{\Pi}\right) + \frac{\Delta_i - 2b_6}{\Delta}\overline{s_{ji}a_{kl}}(-\hat{\Pi}_{lk}^{(a)})\\ &+\left[\frac{\Delta_i}{\Delta}\left(\overline{s_{ji}s_{kl}} - \frac{1}{k^2}k_jk_ik_kk_l\right) + \frac{i\omega\rho_0 + k^2\varkappa'}{k^2\Delta_{um}}\overline{k_jk_i}\,\overline{k_kk_l}\right](-\hat{\Pi}_{lk}{}'^{(s)})\end{aligned} \tag{15b}$$

$$\begin{aligned}\sigma_{ij}^{(a)}(\omega,\mathbf{k}) = &\frac{\Delta_i - 2b_6}{\Delta}\overline{a_{ji}s_{kl}}(-\hat{\Pi}_{lk}{}'^{(s)}) + \left[\frac{\Delta_i - 4b_6}{\Delta}\overline{a_{ji}a_{kl}}\right.\\ &\left.+\frac{\Delta_\rho}{\Delta}(\delta_{jk}\delta_{il} - \delta_{jl}\delta_{ik}) + \left(\frac{\Delta_\rho}{\Delta} - \frac{1}{\Delta_i'}\right)\frac{1}{k^2}k_m\varepsilon_{mij}k_n\varepsilon_{nkl}\right](-\hat{\Pi}_{lk}^{(a)})\end{aligned} \tag{15c}$$

Here the following notation is used:

$$\Delta_{um} = (-\rho_0\omega^2 + k^2b_r)(i\omega\rho_0 + k^2\varkappa') - i\omega k^2 l_2{}'b_7{}',$$

$$\overline{k_jk_i} = k_jk_i - {}^1/_3k^2\delta_{ji},$$

$$\Delta = \Delta_i\Delta_\rho - k^2b_6{}^2, \qquad \Delta_i{}' = -i_0\omega^2 + 2b_6 + k^2d_{\text{н}},$$

$$\overline{s_{ji}\,{}^{s_{kl}}_{a_{kl}}} = \frac{1}{4}(k_jk_k\delta_{il} \pm k_jk_l\delta_{ik} + k_ik_k\delta_{jl} \pm k_ik_l\delta_{jk}),$$
$$\overline{a_{ji}\,{}^{s_{kl}}_{a_{kl}}} = \frac{1}{4}(k_jk_k\delta_{il} \pm k_jk_l\delta_{ik} - k_ik_k\delta_{jl} \mp k_ik_l\delta_{jk}). \qquad (16)$$

For the intensity of the scattered light, in correspondence with (14) we find, for $i \neq j$,

$$I_j^i = (2\pi)^3\langle\varepsilon_{ji}\varepsilon_{ji}^*\rangle = (2\pi)^3[a_4a_4^*\langle\sigma_{ji}^{\prime(s)}\sigma_{ji}^{\prime(s)*}\rangle + a_6a_6^*\langle\sigma_{ji}^{(a)}\sigma_{ji}^{(a)*}\rangle \qquad (17)$$
$$+ a_4a_6^*\langle\sigma_{ji}^{\prime(s)}\sigma_{ji}^{(a)*}\rangle + a_4^*a_6\langle\sigma_{ji}^{\prime(s)*}\sigma_{ji}^{(a)}\rangle].$$

We shall investigate the components I_y^z and I_z^x in scattering at the angle $\theta = \pi/2$ (the upper index denotes the polarization of the incident light propagating along the y axis, the lower, scattered light observed along the x axis). In this case, $k_1 = -k_2 = k/\sqrt{2}$ and $k_3 = 0$, while the correlators have the form

$$\langle\sigma_{23}^{\prime(s)}\sigma_{23}^{\prime(s)*}\rangle = \langle\sigma_{31}^{\prime(s)}\sigma_{31}^{\prime(s)*}\rangle = -\frac{k_BT}{(2\pi)^4\omega}\frac{1}{4}k^2\,\mathrm{Im}\frac{\Delta_i}{\Delta}, \qquad (18a)$$
$$\langle\sigma_{23}^{(a)}\sigma_{23}^{(a)*}\rangle = \langle\sigma_{31}^{(a)}\sigma_{31}^{(a)*}\rangle = -\frac{k_BT}{(2\pi)^4\omega}\,\mathrm{Im}\left[\frac{1}{4}k^2\frac{\Delta_i - 2b_6}{\Delta}\right.$$
$$\left. + \frac{\Delta_\rho - {}^1\!/_2k^2b_6}{\Delta} + \frac{1}{\Delta_i'}\right], \qquad (18b)$$

$$\langle\sigma_{23}^{\prime(s)}\sigma_{23}^{(a)*}\rangle = \langle\sigma_{23}^{\prime(s)*}\sigma_{23}^{(a)}\rangle = -\langle\sigma_{31}^{\prime(s)}\sigma_{31}^{(a)*}\rangle = -\langle\sigma_{31}^{\prime(s)*}\sigma_{31}^{(a)}\rangle$$
$$= \frac{k_BT}{(2\pi)^4\omega}\frac{1}{4}k^2\,\mathrm{Im}\frac{\Delta_i - 2b_6}{\Delta}. \qquad (18c)$$

At this point, without carrying out the calculation of the spectra of the scattered light intensities to their conclusion, we can make a judgment as to the various components I_y^z and I_z^x, namely,

$$I_z^x - I_y^z = -\frac{k_BT}{4\pi\omega}k^2(a_4a_6^* + a_4^*a_6)\,\mathrm{Im}\frac{\Delta_i - 2b_6}{\Delta}. \qquad (19)$$

It is seen from (17) and (19) that the indicated asymmetry is the consequence of the correlation connection between the fluctuations of the symmetric and antisymmetric components of the deformation tensor. Although the dielectric permittivity tensor ϵ_{ik} in not Hermitian in the general case (see[18], Par. 81), nevertheless, the equation $I_y^z = I_z^x$ in [1-4] is satisfied by virtue of their symmetry.

Account of rotational degrees of freedom leads to asymmetry of the deformation and dielectric permittivity tensors. The antisymmetric part of the deformation tensor corresponds to the vector $\frac{1}{2}\,\mathrm{curl}\,\mathbf{u} - \boldsymbol{\varphi}$, which describes the rotation of the particles relative to the accompanying set of coordinates. Just this quantity can account for the appearance of the antisymmetric component of the dielectric permittivity tensor; because the rotary motion of the liquid as a whole, which is described by the vector $\frac{1}{2}\,\mathrm{curl}\,\mathbf{u}$, cannot lead to additional light scattering.[18] The equations of motion (4) in turn guarantee the correlation dependence between the fluctuations of the symmetric and antisymmetric components of the deformation tensor (or, in other words, between the translational and orientational degrees of freedom), which also leads to a disruption of the reversibility principle.[19]

The problem of the detailed investigation of the spectral composition of the scattered light has not been put forward in this work. Nevertheless, by using the statistical estimates, made earlier,[15] of the coefficients entering into (18) and (19), one can indicate the parts of the spectrum where the features associated with the non-symmetry of the dielectric permittivity tensor can stand out to the strongest possible degree.

According to[15] for carbon bisulfide, $b_{200} \sim b_{400} \sim 10^9$ dyn/cm^2, $b_{600} \sim 10^8$ dyn/cm^2, $d_{100} \sim d_{300} \sim d_{500} \sim 10^{-7}$ dyn. Then, keeping it in mind that $i_0 \approx 10^{-16}$ g/cm, $\rho_0 \sim 1$ g/cm^3, $k \sim 10^5$ cm^{-1}, for the portion of the spectrum $\omega \ll 10^{12}$ sec^{-1}, we get $\Delta_i \approx 2b_6$, $\Delta \approx 2b_6(-\rho_0\omega^2 + \frac{1}{2}k^2b_4)$.

Consequently, for the portion of the spectrum considered, the scattering by the symmetric part of the deformation tensor, which is determined by the quantity (see (18a)) $\Delta_i/\Delta = (-\rho_0\omega^2 = \frac{1}{2}k^2b_4)^{-1}$, is the same as in the case in which the rotational degrees of freedom are generally not taken into account ($b_4 = 2\mu$). The difference between I_y^x and I_Z^x will naturally be insignificant here in view of the strong inequality $\Delta_i - 2b_6 \ll \Delta_i$. In the range of frequencies $\omega \gtrsim 10^{12}$ sec^{-1}, the inertia term $i_0\omega^2$ begins to play an important role in Δ_i, which can lead to an increase in the difference $I_Z^x - I_y^z$.

The case of carbon bisulfide, which is considered here as an example, can scarcely be a convenient object for the discovery of the effect of the rotational degrees of freedom on the Rayleigh light scattering, in view of the smallness of i_0 and the other coefficients. Naturally, for materials consisting of large molecules and characterized by a strong noncentral interparticle interaction, the situation is quite different. Unfortunately, statistical methods do not at the present time allow us to make estimates of these quantities for more complicated systems, and the experimental data are few.

The discovery of singularities in the scattering of light would be an experimental confirmation of the importance of consideration of moment stresses in liquids and would reveal the possibilities of the experimental investigation of additional viscoelastic characteristics of the medium.

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