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Second-order correlation tensor of Rayleigh light scattered by statistically independent anisotropic microsystems†

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Dealing with the positions and orientations of the molecules as independent stochastic processes, the authors investigate the influence of translational and rotational fluctuations of anisotropically polarizable microsystems on the evolution in time of the second-order intensity correlation tensor of Rayleigh scattered light as well as on its spectral density. The notion of second-order depolarization is introduced and is shown to be a useful quantity for obtaining information on the translational and rotational motions of microsystems and their optical anisotropy.

1. INTRODUCTION

The traditional method of determining the spectral density of scattered-light intensity, $G^{(1)}(\omega)$, by using conventional grid, Fabry–Pérot and similar spectrometers, is adequate for the study of rapid relaxation processes, leading to a relatively large width of the spectral line. It is better adapted to the study of reorientation processes. The obtaining of information concerning the finer details of stochastic translational motions is subject to restriction by the resolving power of the spectrometers.

On the other hand, the intensity correlation spectroscopy technique is now rapidly expanding [1–5]. It measures the evolution in time of the intensity correlation function $G^{(2)}(t)$ of the scattered light and permits the study of ' slow ' processes, i.e. ones slower than the resolving times of the detectors [6–13], such as translational motions of the microsystems.

In some processes, e.g. light-scattering by macromolecules, colloid particles, and assemblages of molecules, the fluctuations in intensity of the scattered light due to reorientation are sufficiently slow to be recorded by the intensity fluctuation spectroscopy method [14, 15]. In the light scattered by anisotropic microsystems or particles, there appears additionally a depolarized component as the result of fluctuations in optical anisotropy of the latter [16], the time-evolution of the fluctuations being defined by the rotational motions of the scatterers.

Thus the two methods are, as it were, complementary when it comes to gaining information on the dynamical structure of the scattering medium.

In this paper we shall be primarily concerned with the second-order intensity

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correlation tensor $G_{ijkl}^{(2)}(t)$ of light, Rayleigh-scattered by a system of N non-interacting, optically anisotropic, rather large scatterers, the positions $\mathbf{r}(t)$ and orientations $\Omega(t)$ of which we consider as independent stochastic processes. This independence leads to a factorization of the probability distribution function into a part dependent on the positional variables and a part dependent on the orientational variables only. On the assumption that the position-dependent distribution function and orientation-dependent function satisfy, respectively, the equation of free translational diffusion and that of free rotational diffusion, we calculate the individual components of the correlation tensor $G_{ijkl}^{(2)}(t)$ and its spectral density $G_{ijkl}^{(2)}(\omega)$.

We, moreover, show that non-gaussian corrections to $G_{ijkl}^{(2)}(t)$ are contributed not only by the mean polarizability of the scatterers [17] but by their polarizability anisotropy as well. These are of the order of N^{-1}, and are negligible if the number of microsystems in the scattering volume is large. They are significant only in the case of a dilute solution (suspension) of macromolecules (particles), when N is not very large.

On neglecting corrections of order N^{-1}, the spectrum $G^{(2)}(\omega)$ is found to contain, in general, three Lorentz lines for the polarized component. The heights of two of them, with line widths defined by rotational diffusion, are proportional, respectively, to the square and the fourth power of the optical anisotropy κ. Since their widths considerably exceed that of the sharp line due solely to translational diffusion, they form the wings of the spectral line. The depolarized component $G^{(2)}(\omega)$ occurs as a single lorentzian, arising from rotational–translational diffusion. Hence, if rotational motion is sufficiently slow, i.e. accessible to recording by intensity correlation spectroscopy, its role has to be taken into account in the interpretation of experimental results.

We also calculate second-order depolarization ratios defined in reference [16]. These should prove convenient parameters in further analyses ; they are to be derived from studies of the second-order correlation tensor.

2. The correlation tensors

We consider the situation when a planar, quasi-monochromatic light wave of circular frequency ω_0, wave vector $\mathbf{k}_0$, polarization state defined in general by the complex versor $\mathbf{e}$, and electric vector of the form

$$\mathbf{E}(\mathbf{r}, t) = E\mathbf{e} \exp\{-i(\omega_0 t - \mathbf{k}_0 \cdot \mathbf{r})\}$$

is incident on a macroscopically isotropic sample, containing N statistically independent microsystems. We restrict our considerations to the electric dipole approximation. Also, the electric field of the incident light wave is assumed to be so weak that the dipole moment induced in each of the particles is a linear function of the field strength, and that multiple scattering, higher-harmonics generation, and higher-order multipole radiation are negligible [18].

In the wave zone, at a distance R from the centre of the scattering volume much larger than the dimensions of the sample, the tensor of first-order electric field correlations $G_{ij}^{(1)}(t)$ of the intensity of Rayleigh-scattered light is given, for a steady-state process, by the formula

$$G_{ij}^{(1)}(t) = k_s^4 R^{-2} \langle M_i(0) M_j^*(t) \rangle. \tag{1}$$

$M_i(t)$ is the ith component of the dipole moment induced in the medium

$$M_i(t) = \sum_{p=1}^{N} m_i^{(p)}(t) \exp(-i\Delta\mathbf{k} \cdot \mathbf{r}_t^{(p)}), \tag{2}$$

where $m_i^{(p)}(t)$ is a component of the dipole moment induced in the pth (anisotropic) particle, having the position $\mathbf{r}_t^{(p)} = \mathbf{r}^{(p)}(t)$ at the moment of time t, and $\Delta\mathbf{k} = \mathbf{k}_s - \mathbf{k}_0$, with $\mathbf{k}_s$ denoting the wave vector of scattered light and k_s its absolute value. For the process under consideration one can write $k_s = k_0$ since the variations in frequency within the spectral line of scattered light are small compared to ω_0.

The symbol $\langle\rangle$ in equation (1) stands for the statistical average over the ensemble of variables defining the positions and orientations of the microsystems and over the states of the electric field of incident light.

For rigid particles we have

$$m_i^{(p)}(t) = a_{i\alpha}(\Omega_t^{(p)}) E e_\alpha \exp(-i\omega_0 t), \tag{3}$$

on the assumption of equal linear optical polarizability tensor elements $a_{ij}^{(p)} = a_{ij}$ for all the particles. $\Omega_t^{(p)} = \Omega^{(p)}(t)$ defines the orientation of microsystem p at the moment of time t. The variables $\Omega_t^{(p)}$ and $\mathbf{r}_t^{(p)}$, which are stochastic functions of time, determine the phase of the electric field of scattered light, i.e. the spectral intensity distribution, given by the Fourier transform

$$G_{ij}^{(1)}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} G_{ij}^{(1)}(t) \exp(-i\omega t)\, dt. \tag{4}$$

The above quantity is traditionally measured by means of spectrometers. We shall be assuming that $G_{ij}^{(1)}(t) = G_{ij}^{(1)}(-t)$. On the definition (1), t in equation (4) is a shift in time, whereas one should keep in mind that in equation (3) the meaning of t is that of the actual moment of time.

By (1) and with regard to (2) and (3), we obtain for non-interacting microsystems :

$$G_{ij}^{(1)}(t) = N k_s^4 I R^{-2} \langle a_{i\alpha}(\Omega_0) a_{j\beta}^*(\Omega_t) \exp\{i[\omega_0 t + \Delta\mathbf{k} \cdot (\mathbf{r}_t - \mathbf{r}_0)]\}\rangle e_\alpha e_\beta^*. \tag{5}$$

$I = \langle E^2 \rangle$ is the intensity of incident light.

The tensor of second-order intensity correlation $G_{ijkl}^{(2)}(t)$ of the scattered light is, by definition (in the wave zone) :

$$G_{ijkl}^{(2)}(t) = k_s^8 R^{-4} \langle M_i(0) M_j^*(0) M_k(t) M_l^*(t) \rangle, \tag{6}$$

On insertion of (2) it becomes

$$G_{ijkl}^{(2)}(t) = k_s^8 R^{-4} \left\langle \sum_{pqrs}^{N} m_i^{(p)}(0) m_j^{*(q)}(0) m_k^{(r)}(t) m_l^{*(s)}(t) \times \exp\{-i\Delta\mathbf{k} \cdot (\mathbf{r}_0^{(p)} - \mathbf{r}_0^{(q)} + \mathbf{r}_t^{(r)} - \mathbf{r}_t^{(s)})\} \right\rangle. \tag{7}$$

On decomposing this fourfold sum into a simple sum, three twofold sums, and four triple sums we get, on the assumption of non-interacting microsystems whose positions and orientations are mutually independent, only three non-zero components for $p = q = r = s$; $p = q \neq r = s$; and $p = s \neq q = r$.

Standard methods of statistical mechanics now yield

$$G_{ijkl}^{(2)}(t)=Nk_s^8R^{-4}\{\langle m_i(0)m_j^*(0)m_k(t)m_l^*(t)\rangle+(N-1)[\langle m_i(0)m_j^*(0)\rangle \times\langle m_k(t)m_l^*(t)\rangle+\langle m_i(0)m_l^*(t)\exp\{i\Delta\mathbf{k}\,.\,(\mathbf{r}_t-\mathbf{r}_0)\}\rangle\langle m_j^*(0)m_k(t) \times\exp\{-i\Delta\mathbf{k}\,.\,(\mathbf{r}_t-\mathbf{r}_0)\}\rangle]\}. \quad (8)$$

All other components vanish as a result of averaging the factor

$$\exp\{-i\Delta\mathbf{k}\,.\,(\mathbf{r}_t+\mathbf{r}_0)\}$$

over the ensemble of random positions of the molecule with distribution function dependent on $\mathbf{r}_t-\mathbf{r}_0$. In the case of isotropic media this function depends, in fact, on the module $|\mathbf{r}_t-\mathbf{r}_0|$ only.

Since $G_{ij}^{(1)}(t)$ is hermitic, the expression (8) can be re-written briefly as [16]

$$G_{ijkl}^{(2)}(t)=\Gamma\{(1-N^{-1})[G_{ij}^{(1)}(0)G_{kl}^{(1)}(0)+G_{il}^{(1)}(t)G_{jk}^{*(1)}(t)]+S_{ijkl}^{(2)}(t)\}, \quad (9)$$

where the factor $\Gamma\epsilon$ [1, 2] describes the statistical properties of the incident light : $\Gamma=1$ for coherent incident light, $\Gamma=2$ for incoherent light. At $\Gamma=1$, the term $S_{ijkl}^{(2)}(t)$ and the terms in square brackets with the factor N^{-1} define the non-gaussian correction which, for $N\to\infty$, tends to zero. At $1<\Gamma<2$, the tensor $G_{ijkl}^{(2)}(t)$ is non-gaussian even if $N\to\infty$[11].

In particular, in the absence of correlation between the measured intensities, i.e. at $t\to\infty$, the expression (9) has to go over into

$$G_{ijkl}^{(2)}(\infty)=\Gamma G_{ij}^{(1)}(0)G_{kl}^{(1)}(0), \quad (10)$$

where $G_{ij}^{(1)}(0)$ is the tensor of mean integral scattered-light intensity [19]. This will be proved further on.

For $\Gamma=2$, we again get a relation valid for gaussian processes though resulting from fluctuations in intensity of the incident light beam and not from molecular fluctuations.

The tensor $S_{ijkl}^{(2)}(t)$ results from self scattering. By (3), we have

$$S_{ijkl}^{(2)}(t)=Nk_s^8R^{-4}I^2\langle a_{i\alpha}(\Omega_0)a_{j\beta}^*(\Omega_0)a_{k\gamma}(\Omega_t)a_{l\delta}^*(\Omega_t)\rangle e_\alpha e_\beta^* e_\gamma e_\delta^* \quad (11)$$

whence its time-evolution depends on orientational motion only.

The spectral density of $G_{ijkl}^{(2)}(t)$ is given, by analogy to (4), as follows :

$$G_{ijkl}^{(2)}(\omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty}G_{ijkl}^{(2)}(t)\exp(-i\omega t)\,dt. \quad (12)$$

The next section will be devoted to the analysis of equations (9)–(12) from the point of view of the molecular motion model assumed.

3. Molecular motions

The ensemble averages, occurring in the preceding expressions, have this meaning :

$$\langle F(\Omega_0,\Omega_t,\mathbf{r}_0,\mathbf{r}_t,t)\rangle=\int F(\Omega_0,\Omega_t,\mathbf{r}_0,\mathbf{r}_t,t)f(\Omega_0,\Omega_t,\mathbf{r}_0,\mathbf{r}_t,t) \times d\Omega_0\,d\Omega_t\,d\mathbf{r}_0\,d\mathbf{r}_t, \quad (13)$$

$f(\Omega_0, \Omega_t, \mathbf{r}_0, \mathbf{r}_t, t)$ is the joint probability density of finding the molecule in the interval $(\Omega_0, \Omega_0 + d\Omega_0)$, $(\mathbf{r}_0, \mathbf{r}_0 + d\mathbf{r}_0)$ at $t=0$ and in $(\Omega_t, \Omega_t + d\Omega_t)$, $(\mathbf{r}_t, \mathbf{r}_t + d\mathbf{r}_t)$ at the moment of time t.

In the absence of interactions, the function $f(\Omega_0, \Omega_t, \mathbf{r}_0, \mathbf{r}_t, t)$ is the product of two functions, the one (f_Ω) dependent only on orientation, and the other (f_r) dependent on position

$$f(\Omega_0, \Omega_t, \mathbf{r}_0, \mathbf{r}_t, t) = f_\Omega(\Omega_0, \Omega_t, t) f_r(\mathbf{r}_0, \mathbf{r}_t, t). \tag{14}$$

(i) *Translational motions*

In order that f_r shall be invariant with respect to the reference system it has to be a function of the difference in positions $\mathbf{r} = \mathbf{r}_t - \mathbf{r}_0$. From physical considerations (isotropicity of the medium) f_r depends on the module $|\mathbf{r}| = r$ only.

In the approximation of free translational diffusion, the probability density distribution function f_r fulfils the equation :

$$\frac{\partial f_r}{\partial t} = D_\mathrm{T} \Delta f_r, \tag{15}$$

where Δ is the Laplace operator, and D_T the translational diffusion coefficient. Its solution is, since the days of Smoluchowski, known to be given by the following expression :

$$f_r = (4\pi D_\mathrm{T} t)^{-3/2} \exp\{-(4D_\mathrm{T} t)^{-1} r^2\}. \tag{16}$$

By (9) and (5), positional averaging is seen to bear on the interference factor $\exp(i\Delta\mathbf{k} \,.\, \mathbf{r})$. On averaging, we obtain

$$g(t) = \langle \exp(i\Delta\mathbf{k} \,.\, \mathbf{r}) \rangle = \exp\{-(\Delta k)^2 D_\mathrm{T} t\}, \tag{17}$$

leading to a Lorentz shape of the spectral line (4) :

$$\Delta k = |\Delta\mathbf{k}| = 2k_0 \sin\frac{\vartheta}{2}, \tag{18}$$

with ϑ the angle between the wave vectors $\mathbf{k}_0$ and $\mathbf{k}_s$, i.e. the scattering angle.

On introducing the notation $\tau_\mathrm{T}^{-1} = (\Delta k)^2 D_\mathrm{T}$ for the translation relaxation time, equation (17) finally becomes :

$$g(t) = \exp(-t/\tau_\mathrm{T}). \tag{19}$$

(ii) *Rotational motions*

When considering the rotational motions of the scatterers, it is convenient to have recourse to the basis of irreducible spherical tensors.

By (14), we write the orientational averages of equations (5) and (11) in the form

$$\langle a_{i\alpha}(\Omega_0) a_{j\beta}^*(\Omega_t) \rangle = \frac{1}{8\pi^2} \int\int a_{i\alpha}(\Omega_0) a_{j\beta}^*(\Omega_t) f_\Omega(\Omega_0, \Omega_t, t)\, d\Omega_0\, d\Omega_t,$$

$$\langle a_{i\alpha}(\Omega_0) a_{j\beta}^*(\Omega_0) a_{k\gamma}(\Omega_t) a_{l\delta}^*(\Omega_t) \rangle = \frac{1}{8\pi^2} \int\int a_{i\alpha}(\Omega_0) a_{j\beta}^*(\Omega_0) a_{k\gamma}(\Omega_t) a_{l\delta}^*(\Omega_t) \times f_\Omega(\Omega_0, \Omega_t, t)\, d\Omega_0\, d\Omega_t. \tag{20}$$

The factor $1/8\pi^2$ ensures conservation of the Wigner functions $D_{MK}{}^J$ in their usual form. We shall leave **e**, the polarization versor of the incident electric light wave vector, in the cartesian reference system, obviously with no loss of generality. Our discussion will be restricted to linear light polarization, so that the cartesian and circular bases can be used just as effectively.

We transform the tensor $a_{i\alpha}(\Omega_0)$ from the laboratory system of reference to the spherical reference system, attached to the principal axes of the scatterer. The transformation, for $a_{i\alpha}(\Omega_0)$ symmetric in the indices i, α, is [20]

$$a_{i\alpha}(\Omega_0)=\sum_{J_1M_1K_1} c_{i\alpha}{}^{J_1M_1}D_{M_1K_1}{}^{J_1}(\Omega_0)\tilde{a}_{K_1}{}^{J_1}, \tag{21}$$

where $c_{i\alpha}{}^{J_1M_1}$ are transformation coefficients leading from laboratory cartesian to laboratory spherical coordinates, and $D_{M_1K_1}{}^{J_1}(\Omega_0)$ are Wigner functions of the Euler angles, describing the orientation in space of the molecular coordinate system with respect to the laboratory system. $\tilde{a}_{K_1}{}^{J_1}$ is the K_1 component of the J_1 rank spherical tensor in molecular coordinates. With regard to the symmetricity of the polarizability tensor and the choice of molecular coordinates for microsystems having axial optical symmetry, $J_1=0$ and 2, whereas $K_1=0$. In the more general case of optically non-symmetric molecules $J_1=0$ and 2 and $K_1=0, \pm 2$.

The distribution function $f_\Omega(\Omega_0, \Omega_t, t)$, expanded in a series in the complete set of Wigner functions, is of the form [20, 21]

$$f_\Omega(\Omega_0, \Omega_t, t)=\sum_{JMM_1K} a_{MM_1}{}^J(t)D_{KM_1}{}^{*J}(\Omega_0)D_{KM}{}^J(\Omega_t). \tag{22}$$

The coefficients $a_{MM_1}{}^J(t)$ are to be calculated, on the assumption that f_Ω fulfils the equation of free rotational diffusion, from

$$\frac{\partial f_\Omega}{\partial t}=-\sum_{i=1,2,3} J_iD_iJ_i{}^*f_\Omega, \tag{23}$$

where D_i are diagonal rotational diffusion tensor elements and J_i angular momentum components. The principal axes of the inertia moment and polarizability tensors are assumed to coincide.

For spherical and symmetric top particles (we shall be applying these approximations throughout) the coefficients $a_{MM_1}{}^J(t)$ are of a very simple form, thus [22] :

$$a_{MM_1}{}^J(t)=\delta_{MM_1}\frac{2J+1}{8\pi^2}\exp(-t/\tau_{JM}). \tag{24}$$

For cylindrical microsystems with axis along the 3-axis of molecular coordinates, the rotational relaxation time τ_{JM} is

$$\tau_{JM}{}^{-1}=J(J+1)D_1+M^2(D_3-D_1). \tag{25}$$

For spherical top particles, $D_3=D_1$.

Applying the well-known orthogonality relations of Wigner functions :

$$\left.\begin{aligned}&\int D_{MK}{}^{*J}(\Omega)D_{M_1K_1}{}^{J_1}(\Omega)\,d\Omega=\frac{8\pi^2}{2J+1}\,\delta_{JJ_1}\delta_{MM_1}\delta_{KK_1}\,,\\&\int D_{MK}{}^{*J}(\Omega)D_{M_1K_1}{}^{J_1}(\Omega)D_{M_2K_2}{}^{J_2}(\Omega)d\Omega=\frac{8\pi^2}{2J+1}\\&\qquad\qquad\times C_{J_1M_1J_2M_2}{}^{JM}C_{J_1K_1J_2K_2}{}^{JK}\end{aligned}\right\} \tag{26}$$

where $C^{JM}{}_{J_1M_1J_2M_2}$ and $C^{JK}{}_{J_1K_1J_2K_2}$ are Clebsch–Gordan coefficients, and on replacing the latter by $3j$ Wigner symbols, we obtain by equations (20), (22) and (24) for mechanically symmetric top and at the same time optically axially symmetric particles :

$$\langle a_{i\alpha}(\Omega_0)a_{j\beta}{}^*(\Omega_t)\rangle = \sum_{JM} \frac{1}{2J+1} c_{i\alpha}{}^{JM} c_{j\beta}{}^{*JM} |\tilde{a}_0{}^J|^2 \exp(-t/\tau_J), \tag{27}$$

$$\langle a_{i\alpha}(\Omega_0)a_{j\beta}{}^*(\Omega_0)a_{k\gamma}(\Omega_t)a_{l\delta}{}^*(\Omega_t)\rangle = \sum_{\substack{J_1J_2J_3J_4J \\ M_1M_2M_3M_4M}} (-1)^{M_2+M_4-M}(2J+1)$$

$$\times c_{i\alpha}{}^{J_1M_1} c_{j\beta}{}^{*J_2M_2} c_{k\gamma}{}^{J_3M_3} c_{l\delta}{}^{*J_4M_4} \tilde{a}_0{}^{J_1} \tilde{a}_0{}^{*J_2} \tilde{a}_0{}^{J_3} \tilde{a}_0{}^{*J_4} \begin{pmatrix} J_1 & J_2 & J \\ 0 & 0 & 0 \end{pmatrix}$$

$$\times \begin{pmatrix} J_1 & J_2 & J \\ M_1 & -M_2 & -M \end{pmatrix} \begin{pmatrix} J_3 & J_4 & J \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} J_3 & J_4 & J \\ M_3 & -M_4 & M \end{pmatrix} \exp\{-t/\tau_J\}, \tag{28}$$

where the parentheses ( ) are $3j$ symbols, and $\tau_J = \tau_{J0}$. With regard to (27) and (25), $G_{ij}{}^{(1)}(t)$ involves one exponential ($J=2$) whence the spectral density $G_{ij}{}^{(1)}(\omega)$ contains one lorentzian, whereas (28) can contain two exponentials ($J=2$ and $J=4$).

In (27) and (28), the case $J=0$ corresponds to isotropic scattering, whereas $J=2$ and additionally in (28) J $=4$ ($J_i=0$ or 2, $i=1$, 2, 3, 4), to anisotropic scattering by fluctuations of orientation, leading to depolarization of the scattered light.

For isotropically polarizable microsystems $J=0$ only in (27)–(28), and we have

$$\left.\begin{aligned} \langle a_{i\alpha}(\Omega_0)a_{j\beta}{}^*(\Omega_t)\rangle &= \tfrac{1}{3}\delta_{i\alpha}\delta_{j\beta}|\tilde{a}_0{}^0|^2, \\ \langle a_{i\alpha}(\Omega_0)a_{j\beta}{}^*(\Omega_0)a_{k\gamma}(\Omega_t)a_{l\delta}{}^*(\Omega_t)\rangle &= \tfrac{1}{9}\delta_{i\alpha}\delta_{j\beta}\delta_{k\gamma}\delta_{l\delta}|\tilde{a}_0{}^0|^4, \end{aligned}\right\} \tag{29}$$

where $\delta_{i\alpha}$ is Kronecker's delta, and $|a_0{}^0|^2 = 3a^2$, with a the mean polarizability. For axially symmetric particles $\tilde{a}_0{}^2$ is given, in the same basis, by

$$|\tilde{a}_0{}^2|^2 = 6a^2\kappa^2, \tag{30}$$

where, as above, a is the mean polarizability, in the present case $a = (a_{33} + 2a_{11})/3$, and $\kappa = (a_{33} - a_{11})/3a$ is its anisotropy.

4. The geometry of the effect, and the depolarization ratios

Light, incident along the z'-axis of laboratory coordinates $x'y'z'$, is linearly polarized along x'. Scattered-light observation is performed along the z-axis of coordinates xyz at an angle ϑ to z' in the yz-plane, which coincides with $y'z'$. This choice of the polarization state considerably simplifies equations (27) and (28) without loss of information concerning the molecular motions, since now the principal components of (27) and (28) do not depend on the scattering angle ϑ. Dependence on ϑ is restricted to the last term of (9) by way of the translational factor (18) and (19).

From (9) we have in general eight non-zero components, five of which are mutually independent :

$$\left.\begin{aligned} G_{yyyy}{}^{(2)}(t) &= \Gamma\{G_{yy}{}^{(1)}(0)\}^2\{1+K_{yy}{}^{(2)}(t)-N^{-1}[1+K_{yy}{}^{(2)}(t)-R_{yyyy}{}^{(2)}(t)]\}, \\ G_{xxxx}{}^{(2)}(t) &= \Gamma\{G_{xx}{}^{(1)}(0)^2\}\{1+K_{xx}{}^{(2)}(t)-N^{-1}[1+K_{xx}{}^{(2)}(t)-R_{xxxx}{}^{(2)}(t)]\}, \end{aligned}\right\} \tag{31}$$

and

$$\begin{aligned} G_{xxyy}{}^{(2)}(t)+G_{xyyx}{}^{(2)}(t) &= G_{yyxx}{}^{(2)}(t)+G_{yxxy}{}^{(2)}(t) = \Gamma G_{xx}{}^{(1)}(0)G_{yy}{}^{(1)}(0) \\ &\quad \times\{1+K_{xy}{}^{(2)}(t)-N^{-1}[1+K_{xy}{}^{(2)}(t)-R_{xxyy}{}^{(2)}(t)-R_{xyyx}{}^{(2)}(t)]\}, \end{aligned} \tag{32}$$

measured at crossed analysers, or accessible to determination from the relation

$$G_{xxyy}{}^{(2)}(t)+G_{xyyx}{}^{(2)}(t) = \tfrac{1}{2}\{G_{\mathrm{tot}}{}^{(2)}(t)-G_{xxxx}{}^{(2)}(t)-G_{yyyy}{}^{(2)}(t)\}, \tag{33}$$

where $G_{\mathrm{tot}}{}^{(2)}(t)$ is the autocorrelation function for the total light intensity scattered into a given direction.

The other two components :

$$G_{xyxy}{}^{(2)}(t) = G_{yxyx}{}^{(2)}(t) = N^{-1}\Gamma G_{xx}{}^{(1)}(0)G_{yy}{}^{(1)}(0)R_{xyyx}{}^{(2)}(t), \tag{34}$$

have to be measured in a more highly ingenious manner with regard to their smallness and, moreover, their form (cf. equation (6), the disposition of the coupling symbols).

Above, we have introduced the notation

$$\begin{aligned} &K_{ii}{}^{(2)}(t) = \frac{|G_{ii}{}^{(1)}(t)|^2}{\{G_{ii}{}^{(1)}(0)\}^2}, \quad R_{iiii}{}^{(2)}(t) = \frac{NS_{iiii}{}^{(2)}(t)}{\{G_{ii}{}^{(1)}(0)\}^2}, \quad i = x \text{ or } y, \\ &R_{xxyy}{}^{(2)}(t) = R_{yyxx}{}^{(2)}(t) = \frac{NS_{xxyy}{}^{(2)}(t)}{G_{xx}{}^{(1)}(0)G_{yy}{}^{(1)}(0)}, \\ &R_{xyyx}{}^{(2)}(t) = R_{yxxy}{}^{(2)}(t) = R_{xyxy}{}^{(2)}(t) = R_{yxyx}{}^{(2)}(t) = \frac{NS_{xyyx}{}^{(2)}(t)}{G_{xx}{}^{(1)}(0)G_{yy}{}^{(1)}(0)}. \end{aligned} \tag{35}$$

We now proceed to the depolarization ratios of second order [16] :

$$D_1{}^{(2)}(t) = \frac{G_{yyyy}{}^{(2)}(t)}{G_{xxxx}{}^{(2)}(t)} = D^2\,\frac{1+K_{yy}{}^{(2)}(t)-N^{-1}[1+K_{yy}{}^{(2)}(t)-R_{yyyy}{}^{(2)}(t)]}{1+K_{xx}{}^{(2)}(t)-N^{-1}[1+K_{xx}{}^{(2)}(t)-R_{xxxx}{}^{(2)}(t)]}, \tag{36}$$

$$\begin{aligned} D_2{}^{(2)}(t) &= \frac{G_{xxyy}{}^{(2)}(t)+G_{xyyx}{}^{(2)}(t)}{G_{xxxx}{}^{(2)}(t)} \\ &= D\,\frac{1+K_{xy}{}^{(2)}(t)-N^{-1}[1+K_{xy}{}^{(2)}(t)-R_{xxyy}{}^{(2)}(t)-R_{xyyx}{}^{(2)}(t)]}{1+K_{xx}{}^{(2)}(t)-N^{-1}[1+K_{xx}{}^{(2)}(t)-R_{xxxx}{}^{(2)}(t)]}, \end{aligned} \tag{37}$$

$$\begin{aligned} D_3{}^{(2)}(t) &= \frac{G_{yyyy}{}^{(2)}(t)}{G_{xxyy}{}^{(2)}(t)+G_{xyyx}{}^{(2)}(t)} \\ &= D\,\frac{1+K_{yy}{}^{(2)}(t)-N^{-1}[1+K_{yy}{}^{(2)}(t)-R_{yyyy}{}^{(2)}(t)]}{1+K_{xy}{}^{(2)}(t)-N^{-1}[1+K_{xy}{}^{(2)}(t)-R_{xxyy}{}^{(2)}(t)-R_{xyyx}{}^{(2)}(t)]}, \end{aligned} \tag{38}$$

where D is the usual depolarization ratio :

$$D = G_{yy}{}^{(1)}(0) : G_{xx}{}^{(1)}(0). \tag{39}$$

From (36) and (37) we directly derive the simple relation between depolarization ratios :

$$D_1^{(2)}(t) = D_2^{(2)}(t) D_3^{(2)}(t), \tag{40}$$

and, on combining equations (33) and (37) and (38) :

$$D_2^{(2)}(t) = \tfrac{1}{2} \left\{ \frac{G_{\text{tot}}^{(2)}(t)}{G_{xxxx}^{(2)}(t)} - D_1^{(2)}(t) - 1 \right\}, \tag{41}$$

$$D_3^{(2)}(t) = 2 \left\{ \frac{G_{\text{tot}}^{(2)}(t)}{G_{yyyy}^{(2)}(t)} - \frac{1}{D_1^{(2)}(t)} - 1 \right\}^{-1}. \tag{42}$$

Experimental studies of the relationships (40)–(42) can serve as a means of checking the light-scattering model proposed here. Studies of the depolarization ratios (36)–(38) will be most useful in determining the value (and sign) of the optical anisotropy of scatterers, as well as relaxation times. The depolarization ratios, defined as quotients of correlation tensor components, are no longer dependent on the constants of the measuring device.

Equations (5) and (35), with (19), (27), (28) and (30), yield for symmetric top particles [21]

$$\left.\begin{aligned} G_{yy}^{(1)}(t) &= \tfrac{3}{5} N k_s^4 I R^{-2} a^2 \kappa^2 \exp(-t/\tau_2) g(t), \\ G_{xx}^{(1)}(t) &= N k_s^4 I R^{-2} a^2 g(t) + \tfrac{4}{3} G_{yy}^{(1)}(t), \end{aligned}\right\} \tag{43}$$

and

$$\left.\begin{aligned} K_{yy}^{(2)}(t) &= \exp(-t/\tau_3) g^2(t), \\ K_{xy}^{(2)}(t) &= \frac{5 \exp(-t/\tau_2) + 4\kappa^2 \exp(-t/\tau_3)}{5 + 4\kappa^2} g^2(t), \\ K_{xx}^{(2)}(t) &= \frac{25 + 40\kappa^2 \exp(-t/\tau_2) + 16\kappa^4 \exp(-t/\tau_3)}{(5 + 4\kappa^2)^2} g^2(t), \end{aligned}\right\} \tag{44}$$

where, on the model of rotational diffusion, $2\tau_3 = \tau_2$ is the relaxation time given by (25) for $J = 3$. It is noteworthy that the relaxation time τ_3 of equations (44) occurs as well in the spectral theories of non-linear second-harmonic light scattering [22] and hyper-Raman scattering in liquids [23].

Moreover :

$$\left.\begin{aligned} R_{yyyy}^{(2)}(t) &= 1 + \tfrac{4}{49}[5 \exp(-t/\tau_2) + 9 \exp(-t/\tau_4)], \\ R_{xxyy}^{(2)}(t) &= 1 + \frac{4\kappa}{49} \frac{5(7 + 2\kappa) \exp(-t/\tau_2) - 24\kappa \exp(-t/\tau_4)}{5 + 4\kappa^2}, \\ R_{xyyx}^{(2)}(t) &= \tfrac{5}{49} \frac{(7 + 2\kappa)^2 \exp(-t/\tau_2) + 24\kappa^2 \exp(-t/\tau_4)}{5 + 4\kappa^2}, \\ R_{xxxx}^{(2)}(t) &= 1 + \frac{16\kappa^2}{49} \frac{5(7 + 2\kappa)^2 \exp(-t/\tau_2) + 36\kappa^2 \exp(-t/\tau_4)}{(5 + 4\kappa^2)^2}. \end{aligned}\right\} \tag{45}$$

By (9) and with regard to the form of equations (43)–(45), one has the possibility of determining the sign of the optical anisotropy of microsystems provided the non-gaussian corrections are measurable.

The relaxation times τ_2 and τ_4 intervene, too, in third-harmonic light scattering by liquids [24].

5. Discussion

In particular, equations (43)–(45) yield in the limit :

(i) Of $t=0$

$$\left.\begin{aligned} G_{yy}^{(1)}(0) &= \tfrac{3}{5}Nk_s^4IR^{-2}a^2\kappa^2, \\ G_{xx}^{(1)}(0) &= \tfrac{1}{5}Nk_s^4IR^{-2}a^2(5+4\kappa^2), \end{aligned}\right\} \tag{46}$$

$$K_{yy}^{(2)}(0)=K_{xy}^{(2)}(0)=K_{xx}^{(2)}(0)=1, \tag{47}$$

$$\left.\begin{aligned} &R_{yyyy}^{(2)}(0)=\tfrac{15}{7}\,; \quad R_{xxyy}^{(2)}(0)=R_{xyyx}^{(2)}(0)=1+\frac{4\kappa}{7}\,\frac{5-2\kappa}{5+4\kappa^2}, \\ &R_{xxxx}^{(2)}(0)=1+\frac{16\kappa^2}{7}\,\frac{35+20\kappa+8\kappa^2}{(5+4\kappa^2)^2}. \end{aligned}\right\} \tag{48}$$

(ii) For $t\to\infty$, i.e. for a shift in time much in excess of both the translational and rotational relaxation times :

$$K_{yy}^{(2)}(\infty)=K_{xy}^{(2)}\infty)=K_{xx}^{(2)}(\infty)=0, \tag{49}$$

$$R_{yyyy}^{(2)}(\infty)=R_{xxyy}^{(2)}(\infty)=R_{xxxx}^{(2)}(\infty)=1, \quad R_{xyyx}^{(2)}(\infty)=0. \tag{50}$$

(iii) If the resolving time of the detectors exceeds the rotational relaxation times, i.e. if the fluctuations in scattered-light intensity due to rotation of the microsystems are too rapid for recording (as is the case for small molecules) equations (43)–(45) approximate to the form :

$$K_{yy}^{(2)}(t)=K_{xy}^{(2)}(t)=0, \quad K_{xx}^{(2)}(t)=\frac{25}{(5+4\kappa^2)^2}\,g^2(t), \tag{51}$$

and the tensor components $R^{(2)}(t)$, as dependent on rotational relaxation times only, fall sub (ii) and are thus given by the expressions (50).

Let us first consider the general expressions of § 4 for the case (iii). Equations (31)–(33) now become

$$\left.\begin{aligned} &G_{yyyy}^{(2)}(t)=\tfrac{9}{25}\Gamma N^2k_s^8I^2R^{-4}a^4\kappa^4, \\ &G_{xxyy}^{(2)}(t)+G_{xyyx}^{(2)}(t)=\tfrac{3}{25}\Gamma N^2k_s^8I^2R^{-4}a^4\kappa^2(5+4\kappa^2), \\ &G_{xxxx}^{(2)}(t)=\Gamma N^2k_s^8I^2R^{-4}a^4\left(\frac{(5+4\kappa^2)^2}{25}+(1-N^{-1})g^2(t)\right), \end{aligned}\right\} \tag{52}$$

and (34) yields $G_{xyxy}^{(2)}=G_{yxyx}^{(2)}(t)=0$. It is immediately obvious from (52) that the depolarized strictly anisotropic component and the cross components are time-independent and present the case of uncorrelated intensities. Hence the conclusion that, in order that there shall be any correlation altogether in this case, it is necessary that the system shall present sufficiently slow rotational molecular motion.

The time-evolution of the polarized component is obviously determined by the translational molecular motions alone, but its distribution at $\Gamma=1$ is not gaussian even if $N\to\infty$. By (12), (17), (19), its spectral density is

$$G_{xxxx}{}^{(2)}(\omega)=\Gamma N^2 k_s{}^8 I^2 R^{-4} a^4 \times\left\{\frac{(5+4\kappa^2)^2}{25}\,\delta(\omega)+(1-N^{-1})\pi^{-1}\frac{2(\Delta k)^2 D_T}{\omega^2+4(\Delta k)^4 D_T{}^2}\right\}, \tag{53}$$

with Δk given by (18). The first term describes a time-constant part, usually filtered away in measurements. The second term represents a Lorentz line, centred at $\omega=0$ and of a half-width $\Delta\omega=4\tau_T{}^{-1}=4(\Delta k)^2 D_T$ twice that of $G_{xx}{}^{(1)}(\omega)$. Our result is thus in conformity with the theorem of the convolution of two Lorentz-lines of the same width.

With (52), the depolarization ratios (36)–(38) defined by us take the form

$$\left.\begin{aligned} &D_1{}^{(2)}(t)=D,^2\ D_3{}^{(2)}(t)=D,\\ &D_2{}^{(2)}(t)=D\,\frac{(5+4\kappa^2)^2}{(5+4\kappa^2)^2+25(1-N^{-1})g^2(t)},\end{aligned}\right\} \tag{54}$$

where $D=3\kappa^2/(5+4\kappa^2)$.

On making the limiting transition $t\to\infty(g(\infty)=0)$ thus fulfilling the condition (ii), we get by (52)–(54) a result coinciding with (10), i.e. corresponding to an absence of correlation. It should, however, be stated clearly that equations (52)–(54) should not be applied for symmetrically disposed detectors ($t=0$), since at the outset we neglected the factors related to fast orientational motions.

In the general case, when both kinds of motion are recorded, the final formulae for the time-evolution of intensity correlation are of a more highly complicated form and can be derived directly from the definitions (31)–(34) and (36)–(38). We restrict ourselves to adducing the spectral densities for the components

$$\left.\begin{aligned} G_{yyyy}{}^{(2)}(\omega)&=\tfrac{9}{25}\Gamma N^2 k_s{}^8 I^2 R^{-4} a^4\kappa^4\{\delta(\omega)+L_1(\omega)-N^{-1}[L_1(\omega)\\ &\qquad -\tfrac{4}{49}(5L_4(\omega)+9L_5(\omega))]\},\\ G_{xxyy}{}^{(2)}(\omega)+G_{xyyx}{}^{(2)}(\omega)&=\tfrac{3}{25}\Gamma N^2 k_s{}^8 I^2 R^{-4} a^4\kappa^2\{(5+4\kappa^2)\delta(\omega)\\ &\quad +5L_2(\omega)+4\kappa^2 L_1(\omega)-N^{-1}[5L_2(\omega)+4\kappa^2 L_1(\omega)-\tfrac{1}{49}(5(7+2\kappa)\\ &\qquad \times(7+6\kappa)L_4(\omega)+24\kappa^2 L_5(\omega))]\},\\ G_{xxxx}{}^{(2)}(\omega)&=\tfrac{1}{25}\Gamma N^2 k_s{}^8 I^2 R^{-4} a^4\Big\{(5+4\kappa^2)^2\delta(\omega)+25L_3(\omega)+40\kappa^2 L_2(\omega)\\ &\quad +16\kappa^4 L_1(\omega)-N^{-1}\Big[25L_3(\omega)+40\kappa^2 L_2(\omega)+16\kappa^4 L_1(\omega)-\frac{16\kappa^2}{49}\\ &\qquad \times(5(7+2\kappa)^2 L_4(\omega)+36\kappa^2 L_5(\omega))\Big]\Big\}.\end{aligned}\right\} \tag{55}$$

Above, for brevity, $L_1(\omega)-L_5(\omega)$ denote the following Lorentz line-shape functions :

$$\left.\begin{aligned} L_1(\omega)&=\frac{1}{\pi}\frac{12D_1+2(\Delta k)^2D_T}{\omega^2+4[6D_1+(\Delta k)^2D_T]^2},\\ L_2(\omega)&=\frac{1}{\pi}\frac{6D_1+2(\Delta k)^2D_T}{\omega^2+4[3D_1+(\Delta k)^2D_T]^2},\end{aligned}\right\} \tag{56}$$

dependent on both the rotational (D_1) and translational (D_T) diffusion coefficients :

$$L_3(\omega)=\frac{1}{\pi}\frac{2(\Delta k)^2D_T}{\omega^2+4(\Delta k)^4D_T{}^2}, \tag{57}$$

dependent only on translational motion, and

$$\left.\begin{aligned} L_4(\omega)&=\frac{1}{\pi}\frac{6D_1}{\omega^2+36D_1{}^2}\\ L_5(\omega)&=\frac{1}{\pi}\frac{20D_1}{\omega^2+400D_1{}^2},\end{aligned}\right\} \tag{58}$$

dependent on rotational motions only.

All the lorentzians of equations (55) are centred at $\omega=0$.

The simplest in form is thus the anisotropic component $G_{yyyy}{}^{(2)}(\omega)$. It consists in general of four lorentzians ; and the part proportional to N^2, which is predominant, involves $L_1(\omega)$ alone. The half-width $\Delta\omega=24D_1+4(\Delta k)^2D_T$ is twice that of $G_{yy}{}^{(1)}(\omega)$.

Within the cross component, the part proportional to N^2 includes two lorentzians resulting from rotational–translational motions, the broader one $L_1(\omega)$ involving the fourth power of the optical anisotropy κ, and the narrower one, $L_2(\omega)$, its square. Hence the conclusion that, if κ is small, the lorentzian $L_2(\omega)$ predominates. In the inverse case, both lorentzians have to be taken into consideration when analysing experimental data.

The polarized component (omitting corrections of order N^{-1}) contains three lorentzians. A sharp line, due to translational motions solely, is given by $L_3(\omega)$. The other two lorentzians, $L_2(\omega)$ at κ^2 and $L_1(\omega)$ at κ^4, of considerably larger half-width, form the wings of the spectral line. In the case of small anisotropy κ, the contribution from $L_1(\omega)$ can be regarded as a background (as was the case for the cross component). The preceding interpretation, though based on the simplest of models, appears to suit Lallemand's experimental results for glycerol [15] exhibiting two lorentzians. In our discussion we have omitted the term of the type $\delta(\omega)$ which, as already mentioned, is usually blocked in measurements. Correction terms of order N^{-1} still contain several Lorentz lines, but are so small that the lines will be discernible against the background in particular cases only.

In the case of scattered-light modulation by extremely rapid rotation processes and hence inaccessible to recording by the detectors, corresponding in equations (56) and (58) to the limiting transition $D_1\to\infty$, the expressions (55) go over into (52) and (53).

In the limit of $t=0$, on integrating (55) over ω or from (31), (32) and (46)–(48), we obtain the following mean integral values of second-order correlation tensor components :

$$\left.\begin{aligned}
G_{yyyy}{}^{(2)}(0) &= \tfrac{9}{25}\Gamma N^2 k_s{}^8 I^2 R^{-4} a^4 \kappa^4 \left\{2+\frac{1}{7N}\right\},\\
G_{xxyy}{}^{(2)}(0)+G_{xyyx}{}^{(2)}(0) &= \tfrac{3}{25}\Gamma N^2 k_s{}^8 I^2 R^{-4} a^4 \kappa^2 (5+4\kappa^2)\left\{2+\frac{8\kappa}{7N}\frac{5-2\kappa}{5+4\kappa^2}\right\},\\
G_{xxxx}{}^{(2)}(0) &= \tfrac{1}{25}\Gamma N^2 k_s{}^8 I^2 R^{-4} a^4 (5+4\kappa^2)^2\\
&\quad\times\left\{2+N^{-1}\left[1-\frac{16\kappa^2}{7}\frac{35+20\kappa+8\kappa^2}{(5+4\kappa^2)^2}\right]\right\},
\end{aligned}\right\} \tag{59}$$

whereas, on omitting corrections in N^{-1}, the depolarization ratios reduce to

$$D_1{}^{(2)}(0)=D^2, \quad D_2{}^{(2)}(0)=D_3{}^{(2)}(0)=D. \tag{60}$$

For isotropically polarizable microsystems we obtain from (55) with $\kappa=0$, i.e. on neglecting rotational effects related with optical anisotropy, but a single non-zero polarized component with a spectral distribution defined by translational diffusion (57) :

$$G_{xxxx}{}^{(2)}(\omega)=\Gamma N^2 k_s{}^8 I^2 R^{-4} a^4 \left\{\delta(\omega)+(1-N^{-1})\pi^{-1}\frac{2(\Delta k)^2 D_T}{\omega^2+4(\Delta k)^4 D_T{}^2}\right\}, \tag{61}$$

in agreement with reference [3].

6. Conclusions

We have proposed a general formalism, permitting one to calculate the time-dependence of the intensity correlation tensor $G^{(2)}(t)$ and the corresponding spectral density $G^{(2)}(\omega)$ of light scattered by N non-interacting, anisotropically polarizable microsystems. Experimentally, the case is that of, e.g., a dilute solution. With regard to the translational and orientational motions of the microsystems, we assume the free diffusion model ; especially in the case of dilute solutions of relatively large microsystems, this assumption is justified, and can be used in the spectral theory of second-order correlation tensor. On this model, we derive strictly results valid for anisotropically polarizable, electrically and mechanically axially symmetrical microsystems. Within this framework, we neglect interaction between the microsystems and between the latter and the solvent molecules, though this by no means negates the influence they may exert on the $G^{(2)}(\omega)$ spectrum and the second-order depolarization ratios. If interactions are present, the rotational and translational motions have to be dealt with as statistically dependent [25]. Moreover, in general, the translational diffusion coefficient has to be taken as anisotropic in the calculations, though the experiment of Schaefer *et al.* [26] on light scattering by Tobacco Mosaic Virus has led to a zero value of this anisotropy. We nonetheless are convinced that even the present, very simple approach can prove useful in the interpretation of experimental results.

Surely, more information concerning the motions of the microsystems is to be derived from $G^{(2)}(\omega)$ studies of light scattered in situations where rotational motion is modulated by a slowly variable electric field. Studies of this kind are now under way.

It would also be most interesting to compare the rotation relaxation times τ_{JM}, determined from light-scattering spectra, and the corresponding relaxation times inherent in non-linear electro-optical phenomena [27].

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