DEPOLARIZATION OF SECOND-ORDER INTENSITY CORRELATION TENSOR OF LIGHT SCATTERED BY RANDOM ORIENTATION OF ASYMMETRIC PARTICLES*

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Investigation of second-order intensity correlation tensor elements (SOICT) by depolarization measurement of light scattered on orientational fluctuations of asymmetric particles is shown to yield new information on translational and rotational molecular motions.

The photon statistics of scattered light can be put in relation with the density fluctuations of gaseous and liquid media, Brown motions of particles, and micro-inhomogeneities [1–6]. A recent discussion [7] of the statistical properties of light scattered by N noninteracting isotropic particles shows that the non-Gaussian correction to the intensity autocorrelation function is of order N^{-1} and negligible for $N \to \infty$ but can be significant in dilute macromolecular solutions or colloids, when N is relatively small. However, effects due to orientational fluctuations of anisotropic scattering centres cause a depolarization of the scattered light. These depolarization effects are first calculated here for SOICT.

We consider a system of N statistically independent, anisotropically polarizable microsystems (molecules, assemblages of molecules, macromolecules, colloid particles) of linear dimensions up to $\lambda/20$, in a linear electric dipole approximation, omitting multiharmonic nonlinear scattering or higher multipole radiation [8].

The SOICT of scattered light is now, at unit distance

$$G^{(2)}_{ijkl}(\tau) = k_s^8 \left\langle \sum_{pqrs}^{N} m_i^{(p)}(t)\, m_j^{(q)*}(t)\, m_k^{(r)}(t+\tau)\, m_l^{(s)*}(t+\tau) \right\rangle \tag{1}$$

where $\langle\rangle$ denotes ensemble and time averaging. The electric dipole induced in a microsystem p by the electric field $\boldsymbol{E}(t)$ of the incident wave is

$$m_i^{(p)}(t) = a_{ij}^{(p)}[\Omega_p(t)]\, E_j(t) \exp\{\mathrm{i}\,\Delta\boldsymbol{k}\cdot\boldsymbol{r}_p(t)\}\,. \tag{2}$$

$a_{ij}^{(p)}[\Omega_p(t)]$ is the linear polarizability tensor of the microsystem p, having the position $r_p(t)$ and orientation $\Omega_p(t)$ at the moment of time t in laboratory coordinates xyz, and $\Delta\boldsymbol{k} = \boldsymbol{k}_i - \boldsymbol{k}_s$ with $\boldsymbol{k}_i, \boldsymbol{k}_s$ the propagation vectors of the incident and scattered wave.

Assuming for simplicity the orientations of the microsystems as statistically independent, we can write (1) as

$$G^{(2)}_{ijkl}(\tau) = \Gamma\{S^{(2)}_{ijkl}(\tau) + (1-N^{-1})[S^{(1)}_{ij}(0)\, S^{(1)}_{kl}(0) + G^{(1)}_{il}(\tau)\, G^{(1)*}_{jk}(\tau)]\}, \tag{3}$$

with $\Gamma = 1$ for coherent and $\Gamma = 2$ for incoherent incident light. By (2), we have the first order intensity correlation tensors of self-scattering by isolated microsystems

$$S^{(1)}_{ij}(0) = Nk_s^4 \langle a_{i\alpha}[\Omega(t)]\, a^*_{j\beta}[\Omega(t)]\rangle I_{\alpha\beta}(0), \tag{4}$$

$$G^{(1)}_{il}(\tau) = Nk_s^4 \langle a_{i\alpha}[\Omega(t)]\, a^*_{l\delta}[\Omega(t+\tau)] \exp\{\mathrm{i}\,\Delta\boldsymbol{k}\cdot[\boldsymbol{r}(t) - \boldsymbol{r}(t+\tau)]\}\rangle I_{\alpha\delta}(\tau), \tag{5}$$

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with $I_{\alpha\beta}(\tau) = \langle E_\alpha(t) E^*_\beta(t+\tau)\rangle$ the intensity tensor of incident light. The tensors (4) and (5) are discussed in the theory of integral scattering [9] and in that of spectral scattering [10].

The tensor $S^{(2)}_{ijkl}(\tau)$ results from (1) for self-scattering, when $p = q = r = s$, and is of the form

$$S^{(2)}_{ijkl}(\tau) = N k_s^8 \langle a_{i\alpha}[\Omega(t)]\, a^*_{j\beta}[\Omega(t)]\, a_{k\gamma}[\Omega(t+\tau)]\, a^*_{l\delta}[\Omega(t+\tau)]\rangle \cdot I_{\alpha\beta}(0)\, I_{\gamma\delta}(0). \tag{6}$$

To specify the experimental configuration, we assume the incident wave to propagate along y with electric vector vibrating along x, scattered light observation taking place in the direction z (or generally in the yz plane). The tensor (3) is now independent of the scattering angle and has 8 nonzero elements, 5 of which are mutually independent (for optically inactive microsystems beyond absorption bands). The two principal tensor elements are of the form ($i = x, y$)

$$G^{(2)}_{iiii}(\tau) = \Gamma \{S^{(1)}_{ii}(0)\}^2 \{1 + (1 - N^{-1}) K^{(2)}_{ii}(\tau) - N^{-1}[1 - R^{(2)}_{ii}(\tau)]\}, \tag{7}$$

where we have introduced the autocorrelation functions

$$R^{(2)}_{ii}(\tau) = \frac{N S^{(2)}_{iiii}(\tau)}{\{S^{(1)}_{ii}(0)\}^2}, \qquad K^{(2)}_{ii}(\tau) = \frac{|G^{(1)}_{ii}(\tau)|^2}{\{S^{(1)}_{ii}(0)\}^2}. \tag{8}$$

In the general case the autocorrelation functions (8) are related with translational and rotational relaxation processes. In the particular case of isotropically polarizable microsystems, the tensor (7) has but one nonzero (Rayleigh) component for $i = x$ which goes over into the result of Chen et al. [7] since with regard to (8) we have

$$R^{(2)}_{xx}(\tau) = 1, \qquad K^{(2)}_{xx}(\tau) = |\langle \exp\{i\Delta\boldsymbol{k}\cdot[\boldsymbol{r}(t) - \boldsymbol{r}(t+\tau)]\}\rangle|^2. \tag{8a}$$

In the case of asymmetric microsystems, the polarizability tensor contains an anisotropic part and (7) yields a depolarizing component for $i = y$. Defining the depolarization ratio $D^{(2)}(\tau)$ as $G^{(2)}_{yyyy}(\tau)/G^{(2)}_{xxxx}(\tau)$, we have by (7)

$$D^{(2)}(\tau) = D^2(0)\, \frac{1 + (1 - N^{-1}) K^{(2)}_{yy}(\tau) - N^{-1}[1 - R^{(2)}_{yy}(\tau)]}{1 + (1 - N^{-1}) K^{(2)}_{xx}(\tau) - N^{-1}[1 - R^{(2)}_{xx}(\tau)]}, \tag{9}$$

$D(0) = S^{(1)}_{yy}(0)/S^{(1)}_{xx}(0)$ being the conventional depolarization ratio of scattered light [9].

From (3) we have the following cross components, measured with crossed analyzers of the correlator detectors

$$\begin{aligned} &G^{(2)}_{xxyy}(\tau) + G^{(2)}_{xyyx}(\tau) = G^{(2)}_{yyxx}(\tau) + G^{(2)}_{yxxy}(\tau) \\ &= \Gamma S^{(1)}_{xx}(0) S^{(1)}_{yy}(0) \{1 + (1 - N^{-1}) K^{(2)}_{xy}(\tau) - N^{-1}[1 - R^{(2)}_{xxyy}(\tau) - R^{(2)}_{xyyx}(\tau)]\}, \end{aligned} \tag{10}$$

where the relations: $G^{(2)}_{xxyy}(\tau) = G^{(2)}_{yyxx}(\tau)$ and $G^{(2)}_{xyyx}(\tau) = G^{(2)}_{yxxy}(\tau)$ hold generally.

In (10), we have introduced the correlation functions

$$K^{(2)}_{xy}(\tau) = \frac{G^{(1)}_{xx}(\tau)\, G^{(1)*}_{yy}(\tau)}{S^{(1)}_{xx}(0) S^{(1)}_{yy}(0)}, \qquad R^{(2)}_{xxyy}(\tau) = \frac{N S^{(2)}_{xxyy}(\tau)}{S^{(1)}_{xx}(0) S^{(1)}_{yy}(0)}, \qquad R^{(2)}_{xyyx}(\tau) = \frac{N S^{(2)}_{xyyx}(\tau)}{S^{(1)}_{xx}(0) S^{(1)}_{yy}(0)}. \tag{11}$$

Finally, we still have as possible cross components of the tensor (3)

$$G^{(2)}_{xyxy}(\tau) = G^{(2)}_{yxyx}(\tau) = N^{-1} \Gamma S^{(1)}_{xx}(0) S^{(1)}_{yy}(0) R^{(2)}_{xyyx}(\tau). \tag{12}$$

For brevity, we refrain from giving a complete molecular analysis for the second order correlation functions derived above. We nevertheless hope to have shown that their study in scattered light depolarization measurements can be a source of much new information on the translational and rotational motions of asymmetric microsystems, over and above that provided by the spectral study of first order correlations [10].

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