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INTENSITY CORRELATION TENSOR OF RAYLEIGH LIGHT SCATTERED FROM A SYSTEM OF INTERACTING ANISOTROPIC MOLECULES[+]

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ABSTRACT

The influence of intermolecular interaction on the second-order intensity correlation tensor $C^{(2)}_{ijkl}(t)$ is discussed for light scattered from a system composed of anisotropic, radially and angularly interacting molecules. The expressions derived convey much novel information on the statistical properties of the light scattered and, thus, on the scattering medium. Non-gaussian corrections to $C^{(2)}_{ijkl}(t)$ originate in fluctuations in number density of the molecules, fluctuations of their orientations and, directly, radial-angular correlations of two, three and four distinct molecules.

INTRODUCTION

Correlations in space and time play a very important role in dielectric and optical phenomena since they affect directly the physical quantities measured in dense molecular systems. It has thus become feasible to gain quantitative information concerning the correlations. Dynamical studies of scattered light have disclosed the dynamics of relaxational processes involving not only individual molecules but moreover transitory assemblages of correlated molecules. Increasingly significant is the intensity correlation spectroscopy of scattered light providing information regarding the light statistics (ref. 1). Schaefer and Berne (ref. 2) have shown that fluctuations in number density of statistically independent atoms cause the intensity correlation function $C^{(2)}(t)$ to be non-gaussian. Work by Kozierowski et al (ref. 3) bore on non-gaussian corrections related with fluctuations in orientation of non-interacting anisotropic molecules.

This paper deals with the influence of molecular space-time correla-

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tions in a system with time-variable number density of scatterers on the intensity correlation tensor $C^{(2)}_{ijkl}(t)$ of scattered light. To this aim a radial-angular, time-dependent van Hove function of order 4, defining correlation of four arbitrary molecules, is introduced. Thus, besides binary interactions, ternary and quaternary interactions affect the correlation tensor $C^{(2)}_{ijkl}(t)$ extending our knowledge of multi-molecular interactions in dense media.

THEORETICAL DEVELOPMENT

The intensity correlation tensor of light scattered by a system consisting of $\langle N \rangle$ like anisotropic molecules is defined classically as

$$C^{(2)}_{ijkl}(t) = \left(\frac{\omega_0}{c}\right)^8 \left\langle \overline{M_i^*(0)\; M_j(t)\; M_k(0)\; M_l^*(t)} \right\rangle \qquad (1)$$

where ω_0 is the incident light frequency, $\langle \ldots \rangle$ stands for the mean statistical value, and $\overline{\ldots}$ for averaging over states of the field of the incident wave. In (1), we have introduced the notation

$$M_i(t) = e^{-i\omega_0 t}\; E^o_m \sum_{a=1}^{N} \alpha_{im}(\Omega^t_a)\quad e^{\,i\Delta\vec{k}\cdot\vec{r}} \qquad (2)$$

with: E^o_m the electric field amplitude of the incident wave, $\alpha_{im}(\Omega^t_a)$ the optical polarizability tensor of the a-th molecule, having the orientation Ω^t_a and position $\vec{r}^{\,t}_a$ at the moment of time t, and $\Delta\vec{k}$ the difference in wave vectors of the scattered and incident light waves. On introducing the local number density of molecules (ref. 4) as a function of the time t and configurational variables $\vec{R} = \vec{r}\Omega$ i.e. the positional and orientational variables

$$\rho(\vec{R},t) = \sum_{a=1}^{N} \delta(\vec{R} - \vec{R}^t_a) \qquad (3)$$

we write Eq. (1) in the following form

$$C^{(2)}_{ijkl}(t) = \left(\frac{\omega_0}{c}\right)^8 I^{(2)}_{mnpr} \int\!\!\cdots\!\!\int \left\langle \rho(\vec{R},0)\; \rho(\vec{R}',t)\; \rho(\vec{R}'',0)\; \rho(\vec{R}''',t) \right\rangle \times$$
$$\times\, \alpha^*_{im}(\Omega)\, \alpha_{jn}(\Omega')\, \alpha_{kp}(\Omega'')\, \alpha^*_{lr}(\Omega''')\; \exp\left[-i\Delta\vec{k}\cdot(\vec{r}-\vec{r}\,'-\vec{r}\,''+\vec{r}\,''')\right] \times$$
$$\times\, d\vec{R}\; d\vec{R}'\; d\vec{R}''\; d\vec{R}''' \qquad (4)$$

using the notation $I^{(2)}_{mnpr} = \overline{E^o_m\, E^o_n\, E^o_p\, E^o_r}$.

The microscopic density correlation function occurring in (4) defines radial-angular, time-dependent correlation of order 4 and permits the introduction of a 4-th order radial-angular van Hove function, which we define as follows

$$\left\langle \varrho(\vec{R},0)\,\varrho(\vec{R}',t)\,\varrho(\vec{R}'',0)\,\varrho(\vec{R}''',t)\right\rangle = \left(\frac{\langle\varrho\rangle}{\Omega}\right)^4 G_4\,(\vec{R},\vec{R}',\vec{R}'',\vec{R}''',t) \qquad (5)$$

where $\langle\varrho\rangle = \langle N\rangle / V$. With regard to (3) , a different definition is valid

$$G_4\,(\vec{R},\vec{R}',\vec{R}'',\vec{R}''',t) = \left(\frac{\Omega}{\langle\varrho\rangle}\right)^4 \left\langle \sum_{a=1}^{N}\sum_{b=1}^{N}\sum_{c=1}^{N}\sum_{d=1}^{N} \delta(\vec{R}-\vec{R}_a^o)\,\delta(\vec{R}'-\vec{R}_b^t)\times \right.$$
$$\left. \times\,\delta(\vec{R}''-\vec{R}_c^o)\,\delta(\vec{R}'''-\vec{R}_d^t)\right\rangle \qquad (6)$$

permitting the resolution of the van Hove function into 4 irreducible components: "self" (1-1) ; "binary" (1-2) ; "ternary" (1-2-3) ; and "quaternary" (1-2-3-4) . Thus, $G_4 = G_4^{(1-1)} + G_4^{(1-2)} + G_4^{(1-2-3)} + G_4^{(1-2-3-4)}$.

Applying Racah algebra, approximating rotational and translational molecular motions by free /axially symmetric/ rotation and translational diffusion, and postulating a Poisson distribution for the number density of molecules /at zero interaction/, we obtain

$$C^{(2)}_{ijkl}(t) = {}_{\mathrm{self}}C^{(2)}_{ijkl}(t) + \left(\frac{\omega_0}{c}\right)^8 I^{(2)}_{mnpr}\left(\frac{\langle\varrho\rangle}{\Omega}\right)^4 \int\!\cdots\!\int \alpha^*_{im}(\Omega)\,\alpha_{jn}(\Omega')\,\times$$
$$\times\,\alpha_{kp}(\Omega'')\,\alpha^*_{lr}(\Omega''')\,\exp\left[-i\Delta\vec{k}\cdot(\vec{r}-\vec{r}'-\vec{r}''+\vec{r}''')\right]\left\{G_4^{(1-2)}(\vec{R},\vec{R}',\vec{R}'',\vec{R}''',t)\right.$$
$$+\,G_4^{(1-2-3)}(\vec{R},\vec{R}',\vec{R}'',\vec{R}''',t) + G_4^{(1-2-3-4)}(\vec{R},\vec{R}',\vec{R}'',\vec{R}''',t)$$
$$\left.-\,F\,(\vec{R},\vec{R}',\vec{R}'',\vec{R}''',t)\right\} d\vec{R}\,d\vec{R}'\,d\vec{R}''\,d\vec{R}''' \qquad (7)$$

with $F\,(\vec{R},\vec{R}',\vec{R}'',\vec{R}''',t)$ having the meaning of a normalisation factor. In the limit of non-interacting molecules, the preceding expression reduces to a value of ${}_{\mathrm{self}}C^{(2)}_{ijkl}(t)$ (ref. 3) .

On omission of angular correlations i.e. on transition from a molecular to an atomic system of reference Eq.(7) simplifies to the scalar form (ref. 5)

$$C^{(2)}(t) = \left(\frac{\omega_0}{c}\right)^8 I^{(2)}\left\{\langle N\rangle^2\left[1 + e^{-2(\Delta k)^2 Dt}\right] + \langle\Delta N(0)\,\Delta N(t)\rangle\right.$$
$$+\,\langle\varrho\rangle^4\int\!\cdots\!\int\left[G_4^{(1-2)}(\vec{r},\vec{r}',\vec{r}'',\vec{r}''',t) + G_4^{(1-2-3)}(\vec{r},\vec{r}',\vec{r}'',\vec{r}''',t) + G_4^{(1-2-3-4)}\times\right.$$
$$\left.\left.\times\,(\vec{r},\vec{r}',\vec{r}'',\vec{r}''',t) - F(\vec{r},t)\right]\exp\left[-i\Delta\vec{k}\cdot(\vec{r}-\vec{r}'-\vec{r}''+\vec{r}''')\right] d\vec{r}\,d\vec{r}'\,d\vec{r}''\,d\vec{r}'''\right\} \qquad (8)$$

/D is the translational diffusion coefficient and $\langle \Delta N(0)\Delta N(t)\rangle$ the fluctuation correlation function of the number of atoms/ which, if further simplified /by omission of atomic correlations/, reduces to the well known Schaefer-Berne formula (ref. 2)

$$C^{(2)}(t) = \left(\frac{\omega_0}{c}\right)^8 I^{(2)}\left\{\langle N\rangle^2\left[1 + e^{-2(\Delta k)^2 Dt}\right] + \langle \Delta N(0)\Delta N(t)\rangle\right\} \quad (9)$$

DISCUSSION

The results obtained by us contain more extensive information regarding the scattering medium than those of Schaefer and Berne (ref. 2) or Kozierowski et al (ref. 3), since they concern space-time molecular correlations as well. Quite generally, light scattered by molecular systems is non-gaussian due to fluctuations in number density of the molecules (9), radial binary, ternary and quaternary correlations (8), fluctuations in orientation (ref. 3), as well as angular-radial correlations between 2,3 and 4 molecules (7). Accordingly, the method of intensity correlation functions is a source of information regarding molecular interactions up to order 4 inclusively. Now usual spectroscopic technique, bearing on the intensity spectrum of scattered light provides information on binary interactions only. The expressions derived by us permit finer analyses of the molecular interactions involving selected model approximations. For simplicity, we have neglected in (2) all contributions from molecular electric fields, spatial dispersion, and nonlinear molecular polarizabilities. These, if taken into account, lead to the appearance in (4) of additional contributions due to translational fluctuations /spatial redistribution/ and translational-orientational fluctuations. The respective calculations can be carried out similarly as in the usual molecular-statistical theory of light scattering (refs 6,7) .

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