

# Computer simulation study of the Rayleigh light scattering in the isotropic phase of PCH5

Sergei Ye. Yakovenko and Anatoli A. Muravski  
*Institute of Applied Physics Problems, Kurchatova 7, Minsk, 220064, Belarus*

Frank Eikelschulte and Alfons Geiger  
*Physical Chemistry, University of Dortmund, D-44221 Dortmund, Germany*

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Configurations of 200 *p-n*-pentyl-(*p*-cyanophenyl)-cyclohexane (PCH5) molecules from molecular dynamics simulations were used to calculate the Rayleigh light scattering spectra of the isotropic phase. The interaction induced contribution is calculated to the first order dipole-induced dipole terms in the point molecular polarizability approximation. The effect of the size of the simulated system is checked from different points of view. Molecular flexibility is explicitly taken into account and comparisons in terms of time correlation functions are performed. In contrast to systems of small-sized molecules no cancellation effect is observed for the interaction induced contribution to the scattered light intensities of this mesogen. Studies of the different contributions induced by the isotropic and the anisotropic part of the molecular polarizability, evidenced the negligibility of the second one and showed the importance of orientational-translational intermolecular correlations for spectra formation in mesogen systems. The problem of comparing anisotropic and isotropic components of Rayleigh spectra is outlined. © 1996 American Institute of Physics. [S0021-9606(96)50336-3]

## I. INTRODUCTION

In the last decade depolarized light scattering became a widely used tool to study not only molecular motions, but also molecular interactions in condensed media. The experimental shapes of various spectra could be explained in terms of interaction induced (II) contributions. This phenomenon was observed in different fluids, from monoatomics<sup>1,2</sup> and homonuclear diatomics<sup>3,4</sup> up to octahedral molecules.<sup>5</sup> The basic theoretical ideas were formulated by different authors.<sup>6-10</sup> The conclusions strongly depend not only on the assumed molecular interactions, but also on a proper description of the spatial correlations between neighboring molecules. It was shown<sup>11</sup> that only with the help of computer simulations of molecular dynamics a correct evaluation of the II phenomena is possible. Thorough verification of the theoretical predictions with experimental data mainly from diatomics and triatomics<sup>8-15</sup> helped to identify the main mechanisms responsible for the experimental spectra. This established interaction induction as a general approach for the interpretation of all kinds of optical molecular spectra: ir, FIR, Rayleigh, Raman, both "allowed" and "forbidden."

The main conclusions of these studies are:

- (i) in most cases the first order dipole-induced dipole (DID) terms correctly describe II contributions;
- (ii) II contributions mainly come through translational fluctuations;
- (iii) II and purely rotational spectra in most cases are hardly separable due to cross correlations and a similar range of relaxation times;
- (iv) strong molecular correlations in molecular fluids lead to a partial cancellation of the contributions origin-

ing from two-, three-, and four-particle interactions and consequently to a reduction of the II contribution compared to gases;

- (v) to treat different kinds of molecular spectra one has to take into consideration interaction of different multipoles (because of symmetry effects).

The successful treatment of small molecules encouraged experimental investigations on larger ones and particularly mesogens.<sup>16,17</sup> The special interest in these substances can be explained easily. The formation of the liquid crystalline phase is strongly controlled by short-range molecular interactions, i.e., by the same parameters which govern II light scattering. To what extent this is true, can be imagined by the fact that the appearance of the mesophase is impossible without the presence of some local disorder; otherwise the substance could immediately form a crystal. On the other hand, the II scattering comes from the breaking of symmetry in the environment. Thus symmetry fluctuations lead to II scattering as well as to the phase transition to the mesophase.

Although studies of II phenomena can evaluate material properties which are relevant for the mesophase formation, the application of this method is not straightforward even for smaller molecules.<sup>18</sup> Moreover, it is not evident that the same mechanisms are causing the spectra of diatomics and mesogens. For example, recently it has been shown<sup>19</sup> that molecular flexibility can play an important role in the case of Raman spectra of mesogens. On the other hand, fluids of di- and triatomics possess properties which are comparable to mesogens. Both systems have similar values of polarizability densities ( $\alpha\rho=0.01-0.1$ ). Despite the differences in molecular structure and size, the ratio of the molecular polarizability anisotropy to its average value also lies in the same range ( $\gamma/\alpha=0.1-0.5$ ). Assuming that the local molecular arrange-

ment in linear triatomic fluids resembles the isotropic phase of mesogens, one can hope to find many II features which are similar in these systems. But due to the dominant influence of the local molecular arrangements on the details of the cancellation effects, a deeper investigation is necessary.

Computer simulations can again be a tool in such studies. The success of realistic molecular dynamics (MD) simulations of nematic liquid crystals<sup>20–22</sup> encouraged relevant studies of even more complex states. Recently, a number of attempts were made to simulate ordering in chiral nematic<sup>23</sup> and smectic C\*<sup>24</sup> phases. Also hydrogen bonded mesophases are under consideration.<sup>25</sup> The simulation of liquid crystals shifted from the use of model ellipsoids<sup>26</sup> to more realistic interactions represented by Lennard-Jones atom–atom potentials. An explicit introduction of molecular flexibility and Coulomb interactions enabled a detailed investigation of local molecular ordering in the nematic and isotropic phases of mesogens<sup>20,22,27,28</sup> and its comparison with experimental results.

We use this tool with the general aim to study interaction induced phenomena. This paper is devoted to Rayleigh scattering in the isotropic phase. We start with the isotropic phase in order to use the existing expressions for scattering intensities. Due to the long-range orientational order, the extension of these formulae to the mesophase is not straightforward. Before doing this one should answer some fundamental questions:

What are the main mechanisms which determine the Rayleigh scattering band shape of mesogens, i.e., is it possible to deduce from it either rotational or II contributions?

Which model can be adopted to describe the band shape formation, or inversely which properties can be neglected? To what extent molecular size, shape, asymmetry, or flexibility are important?

So we organized this paper as follows. In the next section we present the general theoretical background which is conventionally used for the treatment of Rayleigh spectra. We consider in this paper the scattering originating from the polarizability anisotropy fluctuations, so the main attention is paid to the anisotropic light scattering (in the noninteracting fluid this is the only kind which can arise from anisotropy fluctuations). We compare the isotropic scattering at the end of the discussion. In the second section we outline the most important approximations. In the third section we briefly describe the molecular model used and mention some details of the simulation. The discussion of the results in the fourth section is presented in such a way as to answer step by step the questions mentioned before. In the conclusions we outline what is necessary to do in the future.

## II. THEORETICAL BACKGROUND

Formulas for the description of light scattering from a fluctuating atomic medium were derived in their present form in Ref. 29 and extended to the case of molecular fluids in Ref. 8. In the point dipole approximation for isotropic fluids of nonpolar point polarizable molecules a factorization of the scattered intensity into a local field contribution and

the power spectrum of the microscopic fluctuating polarizability was justified. The explicit expression for the scattered intensity at distance  $R$  from the scattering volume can be written as a Fourier transform of the microscopic polarizability correlation function<sup>8</sup>

$$I_{\alpha}(\mathbf{k}', \omega') = I_{\beta}(\mathbf{k}, \omega) \frac{n(\omega')}{n(\omega)} \left[ \frac{\varepsilon(\mathbf{k}', \omega') + 2}{3} \right]^2 \times \left[ \frac{\varepsilon(\mathbf{k}, \omega) + 2}{3} \right]^2 \frac{\omega'^4}{16\pi^2 R^2 c^2} \frac{1}{2\pi} \times \int_{-\infty}^{\infty} \exp(i\omega' t) dt \langle \delta\Pi_{\alpha\beta}(\mathbf{k}', 0) \delta\Pi_{\alpha\beta}(\mathbf{k}', t) \rangle, \quad (1)$$

where  $\mathbf{k}$ ,  $\mathbf{k}'$ ,  $\omega$ , and  $\omega'$  are the wave vectors and the frequencies of the incident and the scattered light waves, respectively.  $n$  and  $\varepsilon$  are the refractive index and the dielectric susceptibility of the fluid.  $\delta$  denotes fluctuation of the variable. Indices  $\alpha$  and  $\beta$  show the polarization direction of the light wave and angular brackets denote time and system averaging. In  $(r, t)$  representation the expression for the fluctuating polarizability tensor of an assembly of  $N$  (nonspherical) molecules is

$$\Pi(r, t) = \frac{1}{N} \sum_{i=1}^N \alpha_i + \frac{1}{N} \sum_{i=1}^N \sum_{j \neq i}^N \alpha_i T(r_{ij}) \alpha_j \equiv A + \Delta A, \quad (2)$$

where  $\alpha_i$  is the intrinsic polarizability tensor of a single molecule,  $N$  is their number.  $A$  and  $\Delta A$ , defined by this equation, are the intrinsic and II parts of the microscopic polarizability density (in the rest of the paper the capital  $\Delta$  denotes the II part).  $T(r_{ij})$  is the dipole interaction tensor

$$T(r_{ij}) = \frac{1}{r_{ij}^3} \left[ 3 \frac{r_{ij} r_{ij}}{r_{ij}^2} - 1 \right]. \quad (3)$$

In Eq. (2) the interaction induced polarizability is calculated only in the lowest DID approximation, so that the higher order DID terms

$$\sum_{i=1}^N \sum_{j \neq i}^N \sum_{k \neq j}^N \alpha_i T(r_{ij}) \alpha_j T(r_{jk}) \alpha_k, \quad (4)$$

as well as the contribution of higher order induced multipoles (permanent multipoles do not contribute to the Rayleigh scattering) are neglected. To discuss symmetry properties of the polarizability tensor  $\Pi$  it is more appropriate to decompose it not as it is shown in Eq. (2), but into the zero and the second rank parts<sup>8</sup>

$$\Pi = \Pi^{(0)} + \Pi^{(2)} \equiv \bar{\Pi} I + \Pi^{(2)}, \quad (5)$$

where  $\Pi^{(2)}$  is a traceless tensor. In the following we use similar decomposition for other tensors. Here, as in the following, the superscripts in parentheses denote the rank of the tensor. Anisotropic scattering is caused by the fluctuations of the second rank polarizability  $\Pi^{(2)}$  (fluctuations of the first term give rise to the isotropic scattering), so the product of the  $\alpha\beta$  components in Eq. (1) should be replaced by the contraction of the second rank polarizability tensors

$$\langle \delta\Pi^{(2)}(0); \delta\Pi^{(2)}(t) \rangle. \quad (6)$$

In the case of high symmetry of the molecular environment, the second term in Eq. (2) vanishes after summation over all molecules (the Lorentz field of the molecules which are inside the Lorentz cavity is zero if the symmetry is at least tetrahedral). Then the only effect of the medium on the scattered light intensity (as compared to the gas phase value) is through the Lorentz local field factor and fluctuations of the intrinsic polarizability  $A$  occur due to the rotation of single molecules. In contrast, when the local surrounding of the molecules is not symmetric ( $T$  is a second rank traceless tensor) then the light scattering is no longer of purely rotational origin, and the local molecular interactions contribute to the scattered intensity. Certainly, these molecular interactions modify also the refractive index.<sup>29</sup> To keep the Lorentz-Lorentz equation unchanged an effective polarizability of the molecule in the medium is introduced,<sup>8</sup> i.e., the molecular polarizability of a nonfluctuating medium with the same dielectric constant  $\epsilon$ . This effective polarizability is certainly different from the gas phase value.

In a similar manner as for the Lorentz-Lorentz equation, the effect of molecular interactions on the scattered intensity can be analyzed in terms of the effective polarizability. As seen from definition (2), the collective variable  $\Pi$  and also its induced part  $\Delta A$  depend explicitly on the polarizabilities of all molecules. For this reason we may expect that the  $\Pi$  contribution to the polarizability  $\Pi$  will be strongly correlated with the collective intrinsic polarizability  $A$ . So  $\Pi$  can be separated into a part that is correlated with  $A$ , using the projection operator

$$PA = \langle A : \Delta A \rangle \langle A : A \rangle^{-1} A, \quad (7)$$

and an uncorrelated remainder

$$\Delta\Pi = \Delta A - PA. \quad (8)$$

The projection  $PA$  of the total collective polarizability has the same time dependence as the intrinsic collective polarizability  $A$  (they are correlated by definition) and it can be naturally added to  $A$  leading to the renormalization of the gas phase polarizability. The uncorrelated part  $\Delta\Pi$  will not contribute to the polarizability, or Lorentz-Lorentz equation, since  $\langle \Delta\Pi : A \rangle = 0$  (for equal times) by definition, but this purely collision induced polarizability will contribute to collision induced scattering. With these definitions formulas (1) for the anisotropic light scattering can be rewritten as

$$I(\omega) = K \int_{-\infty}^{\infty} \exp(i\omega t) dt \left[ (1+P)^2 \langle A^{(2)}(0); A^{(2)}(t) \rangle + (1+P) \langle \langle A^{(2)}(0); \Delta\Pi^{(2)}(t) \rangle + \langle \Delta\Pi^{(2)}(0); A^{(2)}(t) \rangle + \langle \Delta\Pi^{(2)}(0); \Delta\Pi^{(2)}(t) \rangle \right]. \quad (9)$$

Here,  $K$  substitutes for all preintegral factors from formula (1). The purpose of this conversion is only to separate contributions of the  $\Pi$  and intrinsic polarizabilities in the integral intensity of the scattered light. But certainly, as seen, from Eq. (9), cross correlations between them change the shape of the spectra. The drawback of such an approach is that cross

correlations between  $A$  and  $\Delta A$ , which can be of self-interest, are hidden and therefore it will not be specially mentioned until we retain the unprojected  $\Pi$  and analyze the intrinsic (purely rotational, subscript  $r$ ), interaction induced (subscript  $i$ ) scattering and cross correlation between them (subscript  $x$ ) according to the definition

$$I(\omega) = K \int_{-\infty}^{\infty} \exp(i\omega t) dt \left[ \langle A^{(2)}(0); A^{(2)}(t) \rangle + \langle \langle A^{(2)}(0); \Delta A^{(2)}(t) \rangle + \langle \Delta A^{(2)}(0); A^{(2)}(t) \rangle + \langle \Delta A^{(2)}(0); \Delta A^{(2)}(t) \rangle \right] \\ = K \int_{-\infty}^{\infty} \exp(i\omega t) dt \left[ \langle A^{(2)}; A^{(2)} \rangle C_r(t) + 2 \langle A^{(2)}; \Delta A^{(2)} \rangle C_x(t) + \langle \Delta A^{(2)}; \Delta A^{(2)} \rangle C_i(t) \right],$$

where  $C(t)$  are the normalized correlation functions, defined by the last equality.

### III. MOLECULAR DYNAMICS SIMULATIONS

We have chosen PCH5 for our studies as a typical mesogen, having a nematic phase in the range 302 to 327 K. For the simulation, the molecules were built up from 18 fragments ("pseudoatoms")  $\text{CH}_n$  ( $n=0,1,2,3$ ) and the nitrogen atom. The total interaction energy for a system of such molecules has the form

$$V_{\text{total}} = \sum_{\theta} \frac{1}{2} k_{\theta} (\theta - \theta_0)^2 + \sum_{\xi} \frac{1}{2} k_{\xi} (\xi - \xi_0)^2 + \sum_n \frac{1}{2} k_{\phi_n} [1 + \cos(n\phi - \delta)] + \sum_{i < j} \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{r_{ij}} + \sum_{i < j} \frac{A_{ij}}{r_{ij}^{12}} - \frac{B_{ij}}{r_{ij}^6}. \quad (11)$$

Here,  $k_{\theta}$ ,  $k_{\xi}$ , and  $k_{\phi}$  are force constants for valence angles, improper dihedrals, and torsions (bond lengths were kept constant),  $r_{ij}$  is the distance between sites  $i$  and  $j$ ,  $q_i$  are partial charges,  $A_{ij}$ ,  $B_{ij}$  are the Lennard-Jones parameters. The summation is over all sites within the cutoff of 1.2 nm (only Coulomb and Lennard-Jones terms are taken for interactions between different molecules and the cutoff is effective only between neutral charge groups). The intra- and intermolecular interaction parameters are taken from the general simulation program GROMOS,<sup>30</sup> which was used for the molecular dynamics calculations. Details of the simulation procedure, as well as parameters used, can be found elsewhere.<sup>31</sup> For the determination of partial charges a geometry optimization on the Hartree-Fock level using GAUSSIAN 92<sup>32</sup> was done with the 3-21G\* basis set. The quantum mechanically calculated electrostatic potential was fitted by the classical Coulomb potential arising from the point charges at the sites of the heavy atoms and these charges were used in the simulations. An isotropic system of 200 molecules was simulated in a box with periodic boundary conditions at constant pressure of 1 atm and temperature of 330 K, just above

TABLE I. Principle values of the bond polarizabilities (Ref. 34) and the whole PCH5 molecule in Å<sup>3</sup>. Experimental values are recalculated from Ref. 35 in axial symmetry approximation.

Bond or fragment	$\alpha_1$	$\alpha_2$	$\alpha_3$
C-H	0.65	0.65	0.65
C-C	0.97	0.26	0.26
C-C≡N	4.03	1.54	1.54
C <sub>6</sub> H <sub>6</sub>	11.15	11.15	7.44
C <sub>6</sub> H <sub>5</sub> C≡N	16.27	11.34	8.30
PCH5 (av)	36.8	28.1	27.9
PCH5 (exp)	42.7	28.2	28.2

the nematic to isotropic phase transition of the real substance. The equilibration run was 130 ps and the production run was 900 ps. The detailed properties of the system will be published separately.<sup>33</sup>

## IV. RESULTS AND DISCUSSION

### A. Molecular polarizability

The polarizabilities of the PCH5 molecules were built up from anisotropic bond polarizabilities in the additivity approximation. The principal values of the bond polarizabilities were taken from Ref. 34 and are summarized in Table I. Because of strong conjugation in the benzonitrile fragment, it is seen from the table (rows 3 to 5) that the additivity approximation fails to describe its polarizability correctly. Therefore, it was treated as a whole. The polarizability values for the whole molecule given in the table are averages over the molecular conformations of the whole simulation runs. It is seen that the experimental average values and the polarizability anisotropy are somewhat higher than those obtained from the additive scheme. The reason for this is not clear. Nevertheless, we did not renormalize calculated values to fit the experimental ones because the errors due to these deviations are smaller than possible errors due to nonsufficient averaging.

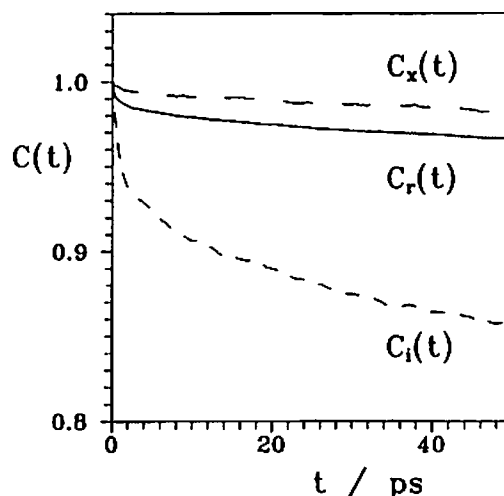


FIG. 1. Normalized time correlation functions [as defined by Eq. (10)] for the isotropic system of 200 PCH5 molecules at 330 K.  $C_r(t)$ —pure rotational CF,  $C_i(t)$ —CF of the interaction induced contribution,  $C_x(t)$ —cross-correlation functions.

### B. Brief comparison with small linear molecules

Molecular point polarizability tensors were calculated as described above for each molecule at each step of the simulation run and were used for evaluation of the correlation functions (CFs) determined by Eqs. (2), (5), and (10) and presented in Fig. 1. Even for these normalized functions a qualitative difference for the case of small-size molecules is obvious. Due to much larger molecular dimensions, these CFs relax orders of magnitude slower, and one can expect that almost all intensity of the scattered light is concentrated in the central component. In fact, relaxation times of the order of nanoseconds (which can be roughly estimated from these curves) imply Rayleigh bandwidths of about 0.01 cm<sup>-1</sup>. Also, in contrast to systems of small molecules, two distinct regions are well seen in all CFs. The fast relaxing part (picosecond or subpicosecond relaxation time) redistrib-

TABLE II. Interaction induced and cross-correlation contributions to the anisotropic [Eq. (16)] and isotropic [Eq. (19)] Rayleigh scattering intensities of simulated PCH5 separated into two-, three-, and four-body terms in units of  $(2/3)\gamma^2$ . The last column displays the contribution arising only from the isotropic part of the molecular polarizability [Eq. (17)]. The accuracy, estimated from averages for four parts of the production run is about 10%. The precision estimated from the simulation runs with a smaller number of molecules is about 10%. The third part of the table are the data estimated from the plots of Ref. 3 for N<sub>2</sub> at  $\rho^* = 2.54$  (in these plots the single particle CF is normalized to 1, similar to our case).

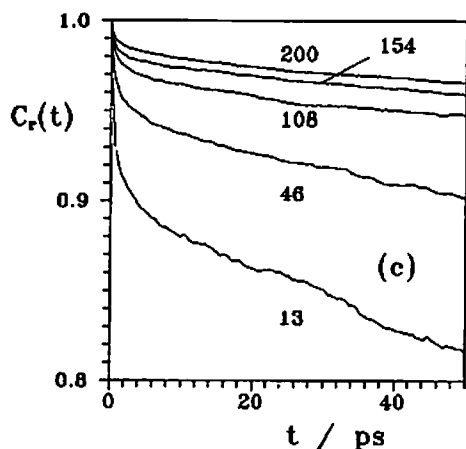
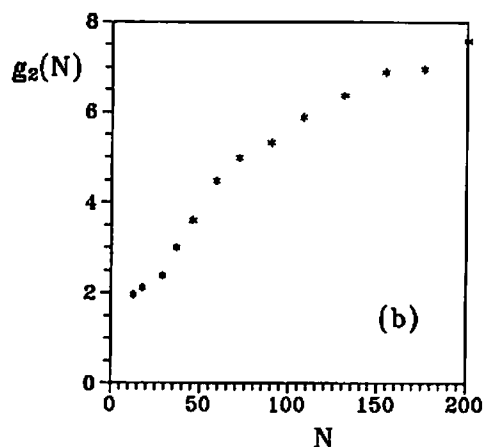
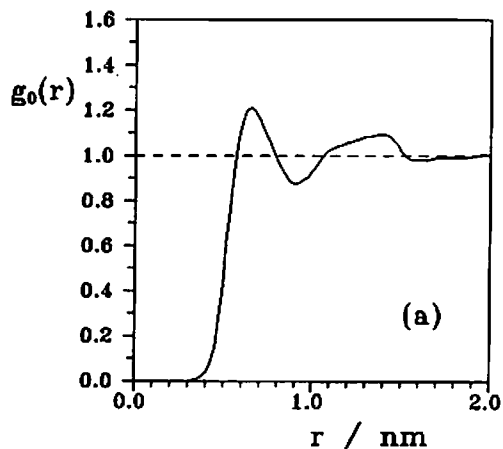
Kind of contribution	2b	3b	4b	All	$\alpha^{(0)}$
PCH5 Anisotropic scattering					
$\langle A^{(2)}(0):A^{(2)}(0) \rangle$				7.57	
$\langle A^{(2)}(0):\Delta A^{(2)}(0) \rangle$	-0.79	-7.53	-	-8.32	-7.06
$\langle \Delta A^{(2)}(0):\Delta A^{(2)}(0) \rangle$	5.20	-1.15	13.03	17.08	14.31
PCH5 Isotropic scattering					
$\langle \Delta A^{(0)}(0):\Delta A^{(0)}(0) \rangle$	0.011	0.029	0.055	0.095	-
N <sub>2</sub> Anisotropic scattering <sup>a</sup>					
$\langle A^{(2)}(0):\Delta A^{(2)}(0) \rangle$	-0.27	0.07	-	-0.20	
$\langle \Delta A^{(2)}(0):\Delta A^{(2)}(0) \rangle$	0.56	-0.86	0.36	0.06	

<sup>a</sup>Evaluated from Fig. 5 of Ref. 3.

utes about 5% to 10% of the II and 2% of the pure rotational contribution to the high-frequency wings. This must give rise to a shoulder in the Rayleigh line at frequency shifts of about  $100 \text{ cm}^{-1}$ , as observed in diatomics.

### C. Test of reliability

The difference between mesogens and small molecules is even more striking if one compares the correlation factors



(zero-time equilibrium averages) presented in Table II. The normalized mean-square fluctuation of the polarizability, i.e., the conventional  $g_2$  factor

$$\frac{\langle A^{(2)}:A^{(2)} \rangle}{(2/3)\gamma^2} = g_2 = \left\langle \frac{1}{N} \sum_{i=1}^N \sum_{j=1}^N P_2(\cos \Theta_{ij}) \right\rangle, \quad (12)$$

which for normal diatomics does not exceed 1.2,<sup>8</sup> for our system of mesogen molecules is larger than 7 [ $\gamma$  is defined by Eq. (14)]. Therefore, the question of reliability of the results is quite natural. Considering translational disorder, our simulations are rather representative: The radial distribution function is 1 within computational uncertainty at distances greater than 1.5 nm [see Fig. 2(a)], whereas the fluctuating rectangular box dimensions exceeded 3.0, 4.5, and 7 nm during the whole simulation run. Also, the radial distribution functions do not show any peculiar behavior at the cutoff distance (in our simulations the interaction cutoff was 1.2 nm). But anisotropic light scattering is determined by orientational fluctuations. Orientational correlations must not be necessarily spherical (in the molecular frame even the average has no spherical symmetry), and therefore we studied the dependence of  $g_2$ , not as a function of radius, but as a function of the number of particles involved in the summation. Thus we use parts of the whole system by constructing boxes similar to the simulation one of increasing size around the center of the simulation box and calculate the properties of interest as a function of the number of particles. As seen from Figs. 2(b) and 2(c), for molecules larger than 100 in the set of rotational correlation functions and the  $g_2$  factors start to converge. But until the borders of our system meet, the convergence is not complete. It should be mentioned, that our value of the  $g_2$  factor, while seeming to be very big, is comparable to the experimental data for analogous systems, obtained from light scattering.<sup>17</sup> However, a detailed comparison is not possible, mainly because the results in Ref. 17 are obtained only for solutions at other temperatures and for slightly different molecules. From the simulations of model mesogens<sup>36</sup> one can conclude, that convergence can be achieved for several hundreds of molecules. Therefore, only relative comparison of the results for our system is possible, but the absolute values still require a more accurate determination.

The interaction induced contribution (as well as the cross-correlation term) depends also on the distance between the interacting particles as seen from formula (3). Contrary to the multiparticle polarizability, the II contribution decreases with  $r^3$  and therefore its convergence is much better, as seen from Fig. 3. Only  $C_i(t)$  are represented in Fig. 3, because for  $C_r(t)$  the convergence is quite similar. The distance dependence of the II CFs was studied by summation over all molecules  $j$  in formula (2), separated from the central one not more than  $r_{\text{int}}$ , and the averaging was carried over all molecules in the box, so that the correlation factors in Fig. 3(a) can be compared with the limiting value in Fig. 2(b). It is evident that the dependence of the correlation factors has no specific features in the region of the interaction cutoff distance used in our simulation (1.2 nm). Probably, polar inter-

FIG. 2. Center of mass radial pair distribution function for the isotropic system of 200 PCH5 molecules at 330 K (a). Dependence of the  $g_2$  factor (b) and the pure rotational correlation function (c) on the number of molecules involved in the averaging [represented by numbers in (c)].

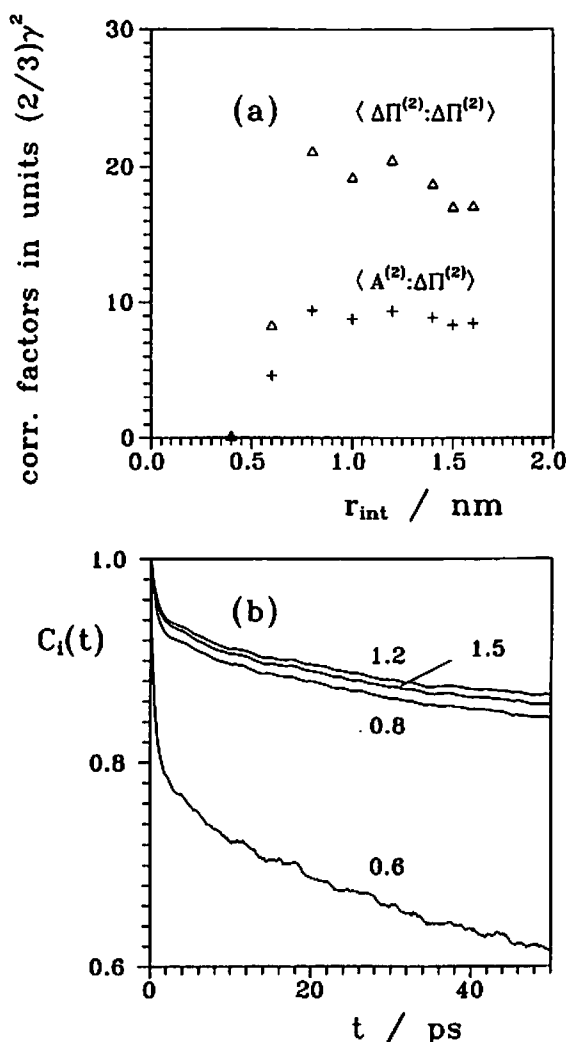


FIG. 3. The dependence of the correlation factors (a) [in units of  $(2/3)\gamma^2$ ] and time correlation functions (b) on the radius of integration of the II contribution [indicated in (b) by the values in nanometers].

actions do not change considerably the second rank  $N$ -particle distribution function which is responsible for II contributions. It is also seen, that the molecules separated more than by 1.5 nm do not change the first order DID term. That is one of the reasons why we believe that relative values of the pure rotational and interaction induced contributions are determined in our study rather correctly. Some comments on the statistical reliability can be found in the Appendix.

#### D. Effect of flexibility

Molecular flexibility plays an important role in liquid crystals contrary to the case of small linear molecules. Only the bond lengths were fixed in our simulations so that conformational changes of all molecular fragments can influence the molecular polarizability. During the simulation run fluctuations of about  $\pm 8\%$  and  $\pm 3\%$  were observed for the transversal and longitudinal polarizability components, respectively. This means that fluctuations of polarizability an-

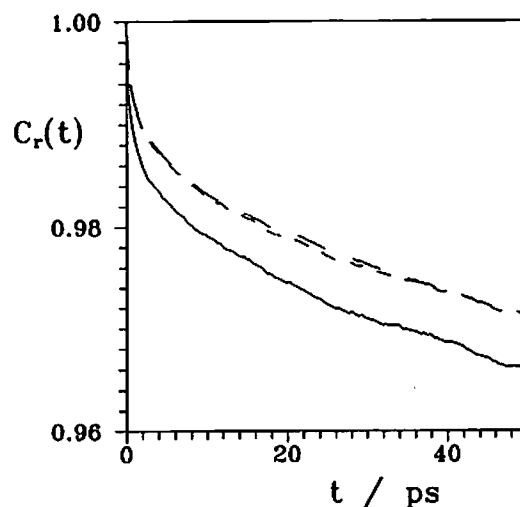


FIG. 4. Pure rotational correlation functions  $\langle A^{(2)}(0) : A^{(2)}(t) \rangle$ , normalized to 1 at  $t=0$ , where  $A^{(2)} = \sum_{i=1}^N \alpha_i^{(2)}$ —solid curve;  $A^{(2)} = \sum_{i=1}^N \Delta \alpha_i Q_i$ —short dashes;  $A^{(2)} = (2/3) \Delta \alpha \sum_{i=1}^N Q_i$ —long dashes.

isotropy amount to about  $\pm 25\%$ . And these are probably underestimates, because we attribute a constant polarizability tensor to the benzonitrile fragment, which mostly contributes to the polarizability anisotropy. As we do not want to oversimplify our considerations, our formulas differ from those used for linear rigid molecules. We do not use an axially symmetric tensor

$$\frac{2}{3} Q_{\alpha\beta} = u_{\alpha} u_{\beta} - \frac{1}{3} \delta_{\alpha\beta} \quad (13)$$

to describe molecular orientations. We define our collective orientational variable as the second rank part of the intrinsic polarizability  $A = A^{(0)} + A^{(2)}$  [see formula (2)] divided by  $(2/3)\gamma^2$ , where

$$\gamma = [(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{xx} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{yy})^2]^{1/2} l^2 \quad (14)$$

should be distinguished from

$$\Delta \alpha = \alpha_{zz} - (\alpha_{xx} + \alpha_{yy})/2 \quad (15)$$

due to the lack of molecular axial symmetry. The effect of such a simplification for our particular mesogen system can be seen in Fig. 4. It is obvious that fluctuations of the molecular biaxiality make the collective orientational variable to relax substantially faster than the axially symmetric analog, because the spinning motion also contributes in the former case. The computation of the two dashed curves differs only in the sense that in one case fluctuations of the polarizability anisotropy value  $\Delta \alpha$  are accounted for. The CF defined by the third formula is normally used in papers devoted to small linear molecules. Therefore, we believe that our consideration is slightly more general than usually used and this generalization is really necessary in the mesogen case.

#### E. $N$ -body terms expansion

From Figs. 3(a) and 2(b) (see also Table II) it is seen that molecular interactions play a much more important role in

the light scattering by mesogenic substances as compared to small molecules. For dense diatomic fluids the ratio  $\langle A:\Delta A \rangle / \langle A:A \rangle$  is about 0.1–0.2 and the pure II contribution is even smaller:  $\langle \Delta A:\Delta A \rangle / \langle A:A \rangle$  is only a few percent.<sup>3,4</sup> In the isotropic phase of mesogens the situation is strikingly different. Probably very strong orientational correlations not only drastically increase  $g_2$ , but also change the balance of the interaction terms with different number of molecules. It is clear from formula (2) that II CFs can be split into two-body, three-body, and four-body terms

$$\langle A^{(2)}(0):\Delta A^{(2)}(t) \rangle_{2b} = \frac{1}{N} \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \alpha_i^{(2)} : [\alpha_j T(r_{ij}) \alpha_j]^{(2)} \right\rangle,$$

$$\langle A^{(2)}(0):\Delta A^{(2)}(t) \rangle_{3b} = \frac{1}{N} \left\langle \sum_{i=1}^N \sum_{k \neq i}^N \sum_{j \neq i, j \neq k}^N \alpha_i^{(2)} : [\alpha_k T(r_{kj}) \alpha_j]^{(2)} \right\rangle,$$

$$\langle \Delta A^{(2)}(0):\Delta A^{(2)}(t) \rangle_{2b} = \frac{1}{N} \left\langle \sum_{i=1}^N \sum_{j \neq i}^N [\alpha_i T(r_{ij}) \alpha_j]^{(2)} : [\alpha_i T(r_{ij}) \alpha_j]^{(2)} \right\rangle,$$

$$\langle \Delta A^{(2)}(0):\Delta A^{(2)}(t) \rangle_{3b} = \frac{1}{N} \left\langle \sum_{i=1}^N \sum_{k \neq i}^N \sum_{j \neq i, j \neq k}^N [\alpha_i T(r_{ij}) \alpha_j]^{(2)} : [\alpha_i T(r_{ik}) \alpha_k]^{(2)} \right\rangle,$$

$$\langle \Delta A^{(2)}(0):\Delta A^{(2)}(t) \rangle_{4b} = \frac{1}{N} \left\langle \sum_{i=1}^N \sum_{k \neq i}^N \sum_{j \neq i, j \neq k}^N \sum_{n \neq i, n \neq k, n \neq j}^N [\alpha_i T(r_{ij}) \alpha_j]^{(2)} : [\alpha_k T(r_{kn}) \alpha_n]^{(2)} \right\rangle.$$

Comparing the data from Table II with those available in the literature on small linear molecules,<sup>3,9</sup> one can follow the changes resulting from the increase of the molecular anisotropy and intermolecular orientational correlations (because other properties, such as polarizability anisotropy for liquid crystals are not larger than for diatomics). The two-particle term increases in PCH5 compared to N<sub>2</sub> almost by the same extent as the pure rotational contribution does.<sup>3</sup> So this cannot increase the II contribution compared to the rotational one. The four-particle term, while being increased several times relative to the two-particle term, still has the same order of magnitude, but the most drastic changes can be observed for three-particle contributions. Due to the orientational, or orientation-position correlations (based only on these data it is impossible to distinguish these contributions) the three-body term in the cross-correlation function  $\langle \Delta A:A \rangle$  of the mesogen increases by 2 orders of magnitude. The absolute value of this term in the II intensity  $\langle \Delta A:\Delta A \rangle$  nearly does not change, but if compared with other II terms, its relative contribution changes more than 1 order of mag-

nitude. The result is that the cancellation effect discussed in Refs. 3, 9, and 14 is no longer observed for liquid crystals (column "all").

## F. Symmetry components expansion

To clarify the reason for the observed removal of the balance between two-, three-, and four-body terms, we separated the II and cross-correlation functions into contributions originating from interacting sites of different symmetry. It is seen from the last column of Table II that mainly the isotropic parts

$$\begin{aligned} \langle A:\Delta A^{(0,0)} \rangle &= \frac{1}{N} \left\langle \sum_{i=1}^N \sum_{k=1}^N \sum_{j \neq k}^N \alpha_i^{(2)} : \alpha_k^{(0)} T(r_{kj}) \alpha_j^{(0)} \right\rangle, \\ \langle \Delta A^{(0,0)}:\Delta A^{(0,0)} \rangle &= \frac{1}{N} \left\langle \sum_{i=1}^N \sum_{k=1}^N \sum_{j \neq i}^N \sum_{n \neq k}^N \alpha_i^{(0)} T(r_{ij}) \right. \\ &\quad \left. \times \alpha_j^{(0)} : \alpha_k^{(0)} T(r_{kn}) \alpha_n^{(0)} \right\rangle \end{aligned} \quad (17)$$

contribute to both, the II and cross-correlation terms. The rest (within a precision of approximately 2%) comes from

$$\begin{aligned} \langle A:\Delta A^{(2,0)} \rangle &= \frac{1}{N} \left\langle \sum_{i=1}^N \sum_{k=1}^N \sum_{j \neq k}^N \alpha_i^{(2)} : \alpha_k^{(2)} T(r_{kj}) \alpha_j^{(0)} \right\rangle, \\ \langle \Delta A^{(2,0)}:\Delta A^{(0,0)} \rangle &= \frac{1}{N} \left\langle \sum_{i=1}^N \sum_{k=1}^N \sum_{j \neq i}^N \sum_{n \neq k}^N \alpha_i^{(2)} T(r_{ij}) \right. \\ &\quad \left. \times \alpha_j^{(0)} : \alpha_k^{(0)} T(r_{kn}) \alpha_n^{(0)} \right\rangle, \end{aligned} \quad (18)$$

and their permutations. Now it becomes clear, why in spite of the noticeable decrease in the molecular polarizability anisotropy (as compared to triatomics), the II contribution for liquid crystals strongly increases. An extremely high local anisotropy in the distribution of molecules around the central one, which is caused not only by the hard core repulsions, but also by molecular association,<sup>16,17</sup> distinguishes mesogen systems from the systems of small-size molecules. Therefore, Rayleigh scattering spectroscopy can become a key in investigation of specifics of the molecular arrangement in the low-temperature mesogen phases.

## G. Renormalization of the II contributions

In many papers on II phenomena in light scattering by small-size molecules,<sup>4,8–13</sup> another definition of the pure rotational and the II part is adopted, the one described by formula (9). If we apply this definition, the difference between the small-size molecules and the mesogen becomes even more evident (see Fig. 5). In our case the cancellation effect is observed not in the interaction induced, but in the rotational part [ $(1+P)^2$  is about 0.01]. Strong intermolecular correlations suppress the fluctuations of the polarizability density which arise from single molecule rotation. As a result, the effective polarizability anisotropy is strongly decreased and the pure rotational part of the intensity becomes even

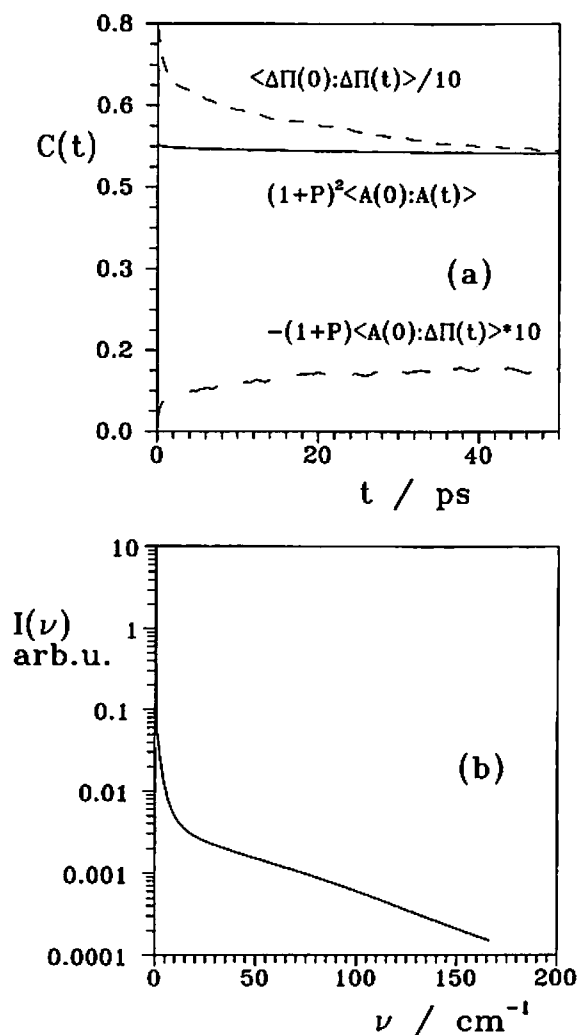


FIG. 5. Correlation functions (a) and the spectrum of the anisotropic light scattering (b) for the isotropic system of 200 PCH5 molecules at 330 K.  $(1+P)^2 \langle A^{(2)}(0) : A^{(2)}(t) \rangle$ —pure rotational CF,  $\langle \Delta \Pi^{(2)}(0) : \Delta \Pi^{(2)}(t) \rangle$ —CF of the interaction induced contribution,  $(1+P) \langle A^{(2)}(0) : \Delta \Pi^{(2)}(t) \rangle + \langle \Delta \Pi^{(2)} : A^{(2)}(t) \rangle$ —their cross-correlation CF, as defined by Eqs. (7)–(9) in units of  $(2/3)\gamma^2$ . The spectrum has been calculated by exponential extension of the CF.

smaller than the anisotropic light scattering by similar molecules, which are uncorrelated and noninteracting. The relaxation times of the pure rotational and the II contributions also seem to be different: The first one relaxes no faster than within several nanoseconds, while the relaxation time of the second one does not exceed 500 ps. Although to make more definite conclusions, more lengthy simulations are necessary, from the experimental point of view such long relaxation times probably will be hardly distinguishable from the bandwidth measurements.

It is not possible to estimate the relaxation time of the cross-correlation contribution, because during the time available to us the corresponding CF has no decreasing tendency. In any case our simulations predict that pure rotation must contribute about 10% to the central line and even much less in the high-frequency wing. Together with the cross-

correlation terms they do not change the intensity in the region of the frequency shift of  $100 \text{ cm}^{-1}$  by more than about 1% [the curve corresponding to the II intensity is indistinguishable from the total scattered intensity in Fig. 5(b)].

## H. Isotropic scattering

In a similar way, as has been done for anisotropic scattering, the formula for the isotropic part can be derived. Inserting  $\Pi^{(0)}$  in Eq. (1) because of

$$\delta \Pi^{(0)} = \Delta A^{(0)} - \langle \Delta A \rangle^{(0)},$$

one has

$$\begin{aligned} I(\omega) &= K \int_{-\infty}^{\infty} \exp(i\omega t) dt [\langle \Delta \Pi^{(0)}(0) : \Delta \Pi^{(0)}(t) \rangle] \\ &\equiv K \int_{-\infty}^{\infty} \exp(i\omega t) dt (\Delta \Pi^{(0)} : \Delta \Pi^{(0)}) C_i(t). \end{aligned} \quad (19)$$

It should be noticed that here we do not consider density fluctuations, whose contribution in mesogen liquids is negligible in comparison with anisotropy fluctuations. Due to this reason the term  $\langle A^{(0)} : A^{(0)} \rangle$  is absent. For zero-rank tensors the projection simply means averaging, because  $\bar{\alpha}$  is constant, i.e.,

$$\Delta \Pi^{(0)} = \Pi^{(0)} - P^{(0)} A^{(0)} = \Delta A^{(0)} - \langle \Delta A \rangle^{(0)}, \quad (20)$$

where the average II polarizability does not vanish. In general,  $\langle \Delta A \rangle^{(0)}$ , similarly to  $A^{(0)}$ , can fluctuate with density fluctuations, and thus it changes the gas phase value of the polarizability, but does not contribute to the scattering by anisotropy fluctuations. Another consequence of Eq. (20) is that the cross-correlation term also contributes only to the change of the gas phase polarizability and therefore for isotropic scattering the analogs of formulas (9) and (10) coincide. The correlation function of the pure II terms, which is the only contributor to the isotropic scattering by the anisotropy fluctuations, is represented in Fig. 6.

Contrary to anisotropic scattering, where the molecules must not necessarily possess polarizability anisotropy, the isotropic scattering in the DID approximation can arise only if at least one of the polarizabilities in Eq. (2) is anisotropic [because  $T(r_{ij})$  is traceless]

$$\begin{aligned} \Delta A^{(0)} &= \sum_{i=1}^N \sum_{j \neq i}^N (\alpha_i^{(0)} T(r_{ij}) \alpha_j^{(2)})^{(0)} + (\alpha_i^{(2)} T(r_{ij}) \alpha_j^{(0)})^{(0)} \\ &\quad + (\alpha_i^{(2)} T(r_{ij}) \alpha_j^{(2)})^{(0)}. \end{aligned} \quad (21)$$

For mesogens the polarizability anisotropy is usually smaller than the average value and hence the isotropic II component should be smaller than the anisotropic one. Due to this same reason even the third term can be neglected: The first two terms give 90% of the intensity for PCH5 and they almost precisely reproduce the time dependence of the II correlation function (see Fig. 6).

It should be noticed that it is impossible to compare isotropic and anisotropic components for our system correctly. As a matter of fact, it is seen from Fig. 1 that during



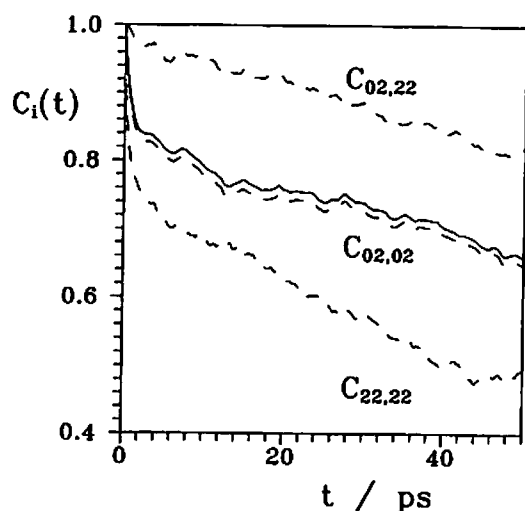


FIG. 6. Normalized correlation functions of the interaction induced contribution to the isotropic Rayleigh scattering.  $\langle \Delta \Pi^{(0)}(0) : \Delta \Pi^{(0)}(t) \rangle$  is represented by the solid curve. The dashed curves are its components  $C_{\mu q,rs}(t) = \langle (\alpha_i^{(\mu)} T(r_{ij}) \alpha_j^{(q)})^{(0)} : (\alpha_i^{(r)} T(r_{km}) \alpha_m^{(s)})^{(0)} \rangle$ . The summation over the repeated indices is implied [see Eq. (21)].

the simulation run our system does not relax completely (at least not all the components). During computations of the isotropic CF we subtract these nonrelaxed contributions, because we can not distinguish them from the average. So the values for the isotropic scattering in Table II are certainly underestimated.

The fact that the smallness of the isotropic II intensity does not result from the cancellation effect is supported by computations of the two-, three-, and four-body contributions with formulas (16). As it is clear from Table II, the features observed for anisotropic scattering governs also the isotropic components.

## V. CONCLUSIONS

Molecular dynamics simulations of the typical mesogen system PCH5 showed the importance of the interaction induced contribution to depolarized Rayleigh scattering in the isotropic phase. The calculations were done only to the first order dipole-induced-dipole approximation, taking into account biaxiality and fluctuations of the molecular polarizability. They provided evidence of the absence of cancellation effects in a mesogen system due to strong orientational-translational correlations of neighboring molecules. While the pure rotational and II contributions occurred to be non-separable in time or frequency domains, it is seen that their contributions to the central line and to the high-frequency shoulders are quite different and this can be a check point for experimental verification.

There is no direct evidence for the sufficiency of the first order DID approximation for mesogens. One can mention some arguments based on fast convergence of the II contributions as a function of the distance between interacting sites. This and the relative negligibility of the molecular anisotropy effect to the II term can be a simplifying factor in

more rigorous considerations. The point-polarizability approximation is even more difficult to justify. The distance between the interacting sites in mesogen molecules can be much smaller than the molecular length. But the application of a more correct treatment, such as atom-point or bond-point polarizability is not straightforward, because it implies a new definition of the molecular polarizability to be adopted. And any such model will require a new parameterization, different from the well verified additivity approximation.

In general, mesogen systems can be much more useful and interesting in studying II phenomena than small linear molecules.

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## APPENDIX

In spite of a rather long production run and relatively big system dimensions, we still had problems with statistical scattering of the results. This was one of the reasons why we took the conjunction  $\langle \Delta A : A \rangle$  rather than one of the components. Averaging over five components of these second rank tensors and in both directions in time considerably decreased statistical errors. Because of this reason and because of the time reversibility requirements we present only a sum

$$\langle \langle A^{(2)}(0) : \Delta A^{(2)}(t) \rangle + \langle \Delta A^{(2)}(0) : A^{(2)}(t) \rangle \rangle / 2$$

rather than separate CFs.

It should be noted that, in general,

$$\sum_{j \neq i}^N \alpha_i T(r_{ij}) \alpha_j$$

is not a symmetric tensor. Only when being summed over all the molecules in the box, i.e., when there are both,  $\Delta \alpha_{ij}$  and  $\Delta \alpha_{ji}$ , which are transpose of each other, does it become symmetric. Due to this reason we varied the number of the molecules under consideration starting from the center of the box rather than applied toroidal boundary conditions<sup>37</sup> to study the size dependence of the mean-square fluctuations.

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