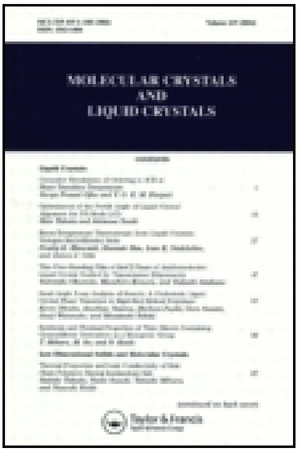

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Short-Time Molecular Orientational Dynamics of PCH5

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Short-Time Molecular Orientational Dynamics of PCH5

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We present results of a molecular dynamics simulation of the liquid crystalline substance *p-n*-pentyl-(*p*'-cyanophenyl)-cyclohexane (PCH5) within a united atom force field approach and analyze in detail the behavior of the orientational autocorrelation functions (CF's). Orientational CF's are calculated for different sections within the molecule in the frame of the nematic director and in the internal frame. Comparison with autocorrelation functions of the torque acting on the molecules and cross-correlation factors have led us to the conclusion that the strong non-exponentiality, observed in the short-time decay of experimentally determined CF's for some mesogens originates from molecule flexibility. Some proposals for model treatments of the internal rotation of mesogen molecules are also specified.

Keywords: Liquid crystals, molecular dynamics simulation

1. INTRODUCTION TO THE SUBJECT OF DISCUSSION

Recently[1] we reported results of a comparative study of PCH5 in the nematic and isotropic phases, using different spectroscopic methods and computer simulations. A fairly good coincidence of experimentally determined microscopic properties with those obained by molecular dynamics simulations (although such a macroscopic feature as the P_2 order parameter had to be scaled based on some models) encouraged us to perform a more detailed analysis of the re-orientational dynamics of mesogen molecules with the help of computer simulations.

In almost all publications devoted to the study of the rotational dynamics of mesogen molecules the diffusional model is adopted as being sufficiently adequate and simple at the same time (one can find this, for example, in pioneering papers[2–5] as well as in recent articles)[6–9]. This model seems to describe fairly well the spectroscopic data obtainedby NMR,[2,3,9] polarized fluorescence[5] and other techniques.[9] The same is true for experimental data obtained by other methods though some discrepancies with the diffusion model predictions which were observed in the high frequency limit of dielectric relaxation spectra,[10] in microwave spectra,[11] or even in time-resolved measurements of the optical Kerr effect[12,13] of liquid crystals could be attributed to collective mode effects.[14] The more surprising is the strong non-exponentially observed in the orientational correlation functions extracted from vibrational spectra[1,15] of different cyano-derivatives and simulations of benzene[16] in a liquid cyrstalline solution, because these data reflect a single molecule process.

A specific feature of vibrational spectra is that one observes the product of the autocorrelation functions of internal vibrational relaxation and of transition polarizability, or dipole moment reorientation. The vibrational autocorrelation function for mesogen molecules normally relaxes within a time interval of about 1–2 ps,[4] while the reorientation time, according to independent experimental estimates,[1,2,5,12,13] is of the order of nanoseconds. Hence, Raman band-shape analysis experiments, being insensitive ot the *overall* reorientation process, are sensitive even to the peculiarities of molecular orientational relaxation in the very beginning. From the point of view of time scales which can be studied by different methods, Raman band-shape analysis and luminescence polarization measurements give complementary information. But if the molecular motion in different time scales is different, then it is difficult to compare their conclusions, because the precision of one of them is very poor in the range of validity of the other one. Probably in the most consistent way this comparison can be made by computer simulations.

Previously,[1,17] it has been reported that in the computer simulation data of one of the mesogen cyano-derivatives, both types of orientational relaxation are observed: non-exponential in the time interval $t < 1$ ps and single-exponential in the time interval $20 < t < 240$ ps. In order to take this into account when interpreting the results of the experiments it is important to understand the nature of this behavior and to build an adequate model. Such a model is especially necessary for the interpretation of NMR and polarized luminescence measurements, because in the mesophase it is impossible to determine all independent parameters. Due to the lowering of the symmetry at the isotropic-mesophase transition their number is strongly increased compared with the isotropic phase and one has to be based on some model considerations. Probably the only method which can provide us with useful information to clarify this behavior is computer simulation. Our present results are obtained for one substance, but the generalization of the conclusions in most cases will be obvious.

2. SIMULATIONS

Simulation data for PCH5 were obtained by the molecular dynamics method with 50 and 100 molecules in a box with periodic boundary conditions using the general simulation programme GROMOS.[18] For the simulation, the molecules were divided into 18 fragments ('pseudoatoms') CH_n ($n = 0, 1, 2, 3$) and the nitrogen atom, the intra- and intermolecular interaction parameters being taken from GROMOS, except the charges of the cyano-fragment, which have been taken to be ± 0.5e as delivered by CHARMM.[19] The details of the simulation data can be found in.[17] The isotropic and nematic phases were simulated at the same temperature 333 K just above the liquid crystalline nematic phase, so at least one of the phases was metastable, but no drift of the order parameters towards the phase transition was observed. This is an obvious indication of the smallness of the simulation box for treating macroscopic properties, but as it has been shown in[1] this exerts an only minor effect on the local properties and even the correct values of various order parameters can be obtained from the simulation data after re-scaling.

3. RESULTS AND DISCUSSION

Keeping in mind our main goal – to explain experimentally observed data – we did not treat the PCH5 molecule as an unstructured rigid rotor. In different experiments different parts of the molecules are observed. In luminescence experiments[5] the main contribution comes from the rigid π-bonded core. Raman studies[1] were performed for the cyano fragment. In NMR[3] different atoms can be studied depending on isotopic substitution. Therefore, orientational autocorrelation functions for different molecular fragments have been derived for both phases from the simulation data, as it is shown in Figure 1. We reduce the number of CF's without imposing a molecular symmetry (this could not be done without additional assumptions for such flexible units as in our simulations). Nevertheless the obvious axial symmetry of a vector connecting any two atoms and the axial symmetry of the simulated system have been accounted for. In order to enable comparison between different phases and for different fragments we represent the autocorrelation functions in the form[2]

$$C_{Lm}(t)=\frac{\langle D^{L}_{m0}[\Omega(0)]\,D^{L*}_{m0}[\Omega(t)]\rangle-|\langle D^{L}_{m0}[\Omega(0)]\rangle|^{2}}{\langle|D^{L}_{m0}[\Omega(0)]|^{2}\rangle-|\langle D^{L}_{m0}[\Omega(0)]\rangle|^{2}}, \qquad (1)$$

where D^{L}_{m0} $(\Omega(t))$ – are Wigner rotation functions of the set of Euler angles determining the orientation of the molecule fixed coordinate system at time t in the pricipal axes frame of the order parameter tensor of the simulated system. In the isotropic phase

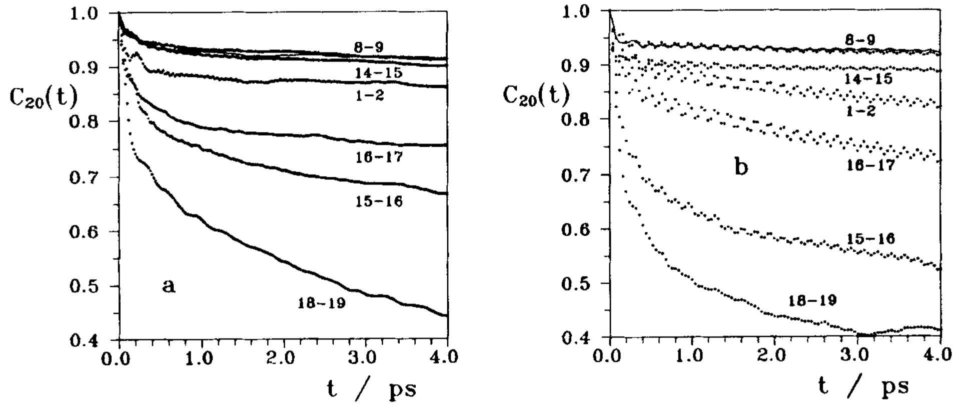

FIGURE 1 Orientational autocorrelation functions for different bonds (they are marked by the numbers of atoms in the Figure) of PCH5 molecule in the (a) isotropic and (b) nematic phases. The CF for the 4–5 bond is represented by the solid line.

$C_{20}(t) + 2C_{21}(t) + 2C_{22}(t)$ equals to $\langle D_{00}(\delta\Omega(t))\rangle$, where $\delta\Omega(t)$ is the variation of the set of Euler angles due to molecular rotation. For a more correct averaging of the simulation data, in practice the denominator in (1) has been taken in the form

$$[\langle|D^L_{m0}[\Omega(0)]|^2 - |\langle D^L_{m0}[\Omega(0)]\rangle|^2\rangle\langle|D^L_{m0}[\Omega(t)]|^2 - |\langle D^L_{m0}[\Omega(t)]\rangle|^2\rangle]^{1/2} \qquad (2)$$

This eliminated the systematic errors due to long time fluctuations of the orientational ordering of the simulated system to which the slowly decaying correlation functions are very sensitive. The sufficiency of the averaging and the reproducibility of the data can be seen from Figure 2, where autocorrelation functions are represented by taking various amounts of molecular trajectories for averaging.

The infinite time value for all of these functions in the nematic phase is zero and does not depend on the static orientational ordering of different fragments. Nevertheless the short time orientational relaxation rate differs for different fragments, indicating the effect of molecular flexibility. The common feature for all these CF's is a non-exponential decay at the short-time limit. It is well observed even for the orientational relaxation of the rigid molecular core and is increasing for more flexible fragments.

To test the origin of this short-time decay we fitted it with a parabola in the interval 0–0.1 ps and estimated from this the apparent moment of inertia[20] of the PCH5 molecule. The values $13 \pm 2\ 10^{-46}\,\mathrm{kg\,m^2}$ and $27 \pm 9\ 10^{-46}\,\mathrm{kgm^2}$ thus obtained for the isotropic and nematic phases are much smaller than $8.4\ 10^{-44}\,\mathrm{kgm^2}$ – an average directly obtained for the short molecular axis from the simulation configurations. The fact that even at intervals < 0.1 ps we do not observe free rotation of the whole molecule is supported by the calculation of the autocorrelation function of the torque, acting on the molecule (see Fig. 3). Both, the absolute value and the projections relax during this time interval.

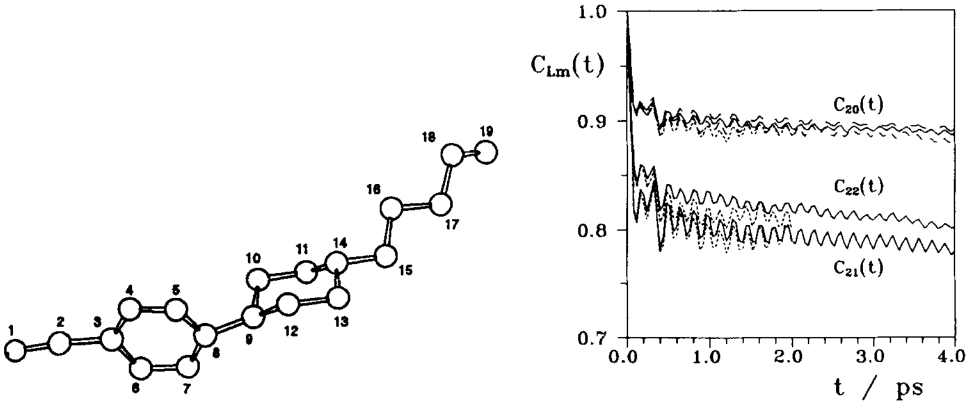

FIGURE 2 Orientational autocorrelation functions of various symmetry for cyano-bond of the PCH5 in the nematic phase. The data were obtained after averaging over different numbers of molecular trajectories using different time origins: solid line – 50000 (the curve 1–2 in Fig. 1b), long dashed line – 25000, short dashed line – 10000, dot line – 5000 molecular trajectories.

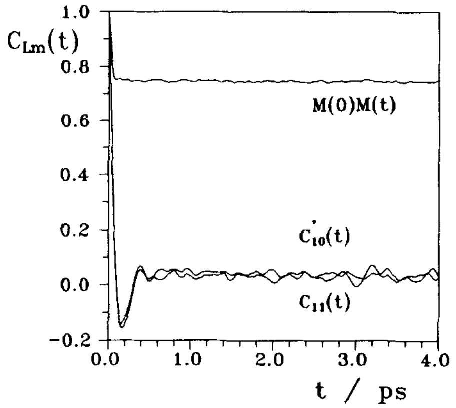

FIGURE 3 Autocorrelation functions of the absolute value of the torque, acting on the PCH5 molecule and its projections along the director ($C_{10}(t)$) and perpendicular to it ($C_{11}(t)$).

To treat more carefully the effect of molecular flexibility, we also calculated the orientational autocorrelation functions for different fragments in the internal molecular frame (the frame of the benzene ring has been taken for this as the most slowly reorienting in the external frame). Two regions are also well distinguished in all internal CF's (for example, for the bond 16–17, as is shown in Figure 4). The long-time decay looks like diffusion with correlation times of the order of hundreds of picoseconds, but the short-time decay looks more like originating from librational motions. When calculating the internal correlation functions, we supposed cylindrical symmetry of the molecule and hence $C_{Lm}(t)$ with $m \neq 0$ correspond to twist motions around the long molecular axis. It is evident from Figure 4 that this twisting motion strongly

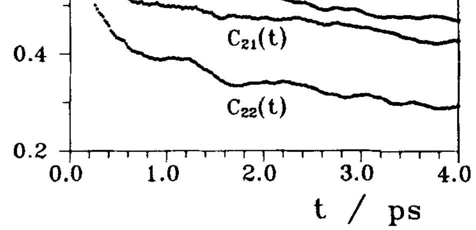

FIGURE 4 Orientational autocorrelation functions of different symmetry for the 16–17 bond in the emolecular fixed frame (dots) and in the external frame (solid line, identical to 16–17 curve in Fig. 1a).

TABLE 1

Correlation factors g_{Lm} between 1–2 and other bonds within the PCH5 molecule; formula (3)

The bond	g_{11}
8–9	0.00964
14–15	0.00652
16–17	0.00387
18–19	0.00323

randomizes the molecular conformation within half of a picosecond. This, certainly, does not mean the absolute randomization of the orientation of the relevant molecular fragment (see, for example, CF in the external frame represented by the solid line in Figure 4). But probably this process also governs the short time behavior of the orientational CF's in the external frame.

One can get some insight into this process by studying cross-correlations between the deviations of different bonds from their average orientation in the internal frame:

$$g_{Lm} = \langle [D^L_{m0}(\Omega_1) - \langle D^L_{m0}(\Omega_1)\rangle][D^{L*}_{m0}(\Omega_2) - \langle D^{L*}_{m0}(\Omega_2)\rangle]\rangle. \tag{3}$$

From Table it is obvious that internal molecular motion is sufficiently intercorrelated. The positive value of g_{11} indicates the formation of an S-shaped molecule. For example, a value of 0.005 corresponds to deviations of the lateral bonds from their average orientation of 4° (if one supposes total correlation between the fragments with orientation Ω_1 and Ω_2). That is a rather high value, keeping in mind that the mean-square deviation of the cyano-bond from its average orientation is about 10°. This correlation between the conformation of fragments placed in opposite ends of the molecule can be explained by a strong interaction of the cyano-fragment with surrounding due to the reorientation of the whole molecule caused by changes in the conformation of the alkyl chain.

To interpret experimental data, different models of molecular orientational relaxation are applied: small-step diffusion models,[2,21] J-diffusion[22] and other models. But the results of the present simulations show that good agreement with experimental data cannot be obtained without accounting for molecular flexibility. Such a model has been developed[8,23] and some improvement has been achieved. But in this model conformational relaxation is treated in the mean-field potential and also has exponential decay, thus unfortunately important features are missing. In liquid crystals molecular interactions due to thermal agitation substantially disturb intramolecular motions which therefore show non-exponential behavior.

4. CONCLUSIONS

From the data obtained with the help of computer simulations it is clear that in the short-time scale molecular orientational relaxation is strongly influenced by the molecular flexibility. This is true not only for conformationally flexible parts of the molecule, but for the rigid core as well: after conformational changes the whole molecule has to fit its cage. At this time its orientational relaxation is no longer diffusional in nature. The contribution of this short-time process in the total orientational relaxation is not negligibly small (at least 10% for both isotropic and nematic phases, as can be estimated from the Figures). This fact has to be taken into account when one attempts to interpret experimental data on orientational relaxation.

Acknowledgements

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