Orientational order in a liquid crystalline mixture studied by molecular dynamics simulation and NMR

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We have studied the orientational order in a liquid crystalline mixture consisting of benzene and 4-*n*-pentyl-4′-cyanobiphenyl (5CB) employing molecular dynamics simulation and NMR spectroscopy. The temperature-dependent order parameters obtained from the NMR experiments were used to determine the average benzene–5CB and 5CB–5CB interaction parameters. It was found, using mean field theory, that the benzene–5CB interaction is ~45% of that between the solvent particles. This analysis is based on a cascade of approximations. The validity of some of these assumptions was tested in the computer simulation. Various pair correlation functions were also calculated. © *1996 American Institute of Physics.* [S0021-9606(96)50822-6]

I. INTRODUCTION

Liquid crystals are characterized by long-range orientational order. This order originates from the anisotropic nature of the intermolecular interactions. Detailed information about these complex interactions is not directly accessible from experiments. Such knowledge, is, however, essential for the understanding of physical and chemical properties of liquid crystalline systems. Therefore, there is a considerable interest in developing and improving theoretical models for inter- as well as for intramolecular interactions which can be employed in the analysis of experimental data.

Nuclear magnetic resonance (NMR) spectroscopy has proven to be a powerful tool for mesophase studies since it can provide important information about molecular structure, orientational order, and dynamic processes. Furthermore, parameters reflecting various interactions may be extracted. The experimental data set must often, as indicated above, be interpreted using a specific model. A theoretical framework of particular interest is the mean field theory (MFT). Strictly speaking, there is a whole range of MFTs, but they are all based on the assumption that each molecule reorients in the average potential field of all its neighbors. In the pioneering work of Maier and Saupe a simple system of uniaxial, rigid particles was treated.[1] This is clearly only an approximate description of a real liquid crystal since all mesogenic molecules discovered so far exhibit internal motion. The mean field theory was subsequently extended to more general forms in which molecular flexibility was taken into account.[2–5] Due to the strong correlation between orientational order and internal conformational degrees of freedom, the description of flexible molecules in a mesophase is by no means trivial. Mean field theory of liquid crystalline mixtures has also been considered.[6–8]

Molecular dynamics (MD) simulations of liquid crystals using atomic models constitute a challenge in the field of computational chemistry. It is so, not only because the calculations require large computer power, but also due to the chemical complexity of these systems. Several MD simulations of thermotropic liquid crystals using realistic interaction models have been reported.[9–13] Recently, computer simulations of benzene[14] and hexane[15] dissolved in Gay–Berne solvents were performed. The result from an MD simulation relies completely on the physical input, i.e., on the molecular force field parameters and on the specification of the system in terms of temperature, density, etc. The strength of the method is the wealth of information available from the generated trajectories.

In this paper we report MD and NMR investigations of a binary liquid crystalline mixture containing ~8 mol % benzene dissolved in 4-*n*-pentyl-4′-cyanobiphenyl (5CB), see Fig. 1. Neat 5CB forms a nematic phase between 296 and 308 K. The temperature range is convenient for experimental studies, which has made 5CB one of the most investigated mesogenic compounds. The temperature-dependent orientational ordering of both solute and solvent was determined from NMR experiments. The resulting second-rank order parameters are interpreted employing mean field theory to yield average interaction parameters. In the analysis of the MD simulation we focus our attention on the relationship between intermolecular interactions and the molecular organization in the anisotropic phase. In addition, the validity of some of the approximations made in the mean field theory is investigated. The rest of the article is organized in the following way: In Sec. II, experimental and computational details are outlined. Different manifestations of orientational order are presented in Sec. III. Finally, various aspects of molecular pair correlations are discussed in Sec. IV.

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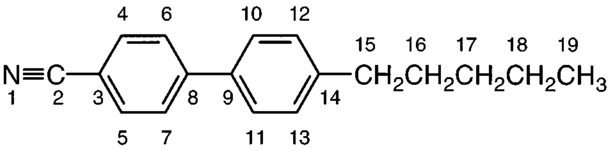

FIG. 1. Chemical structure of 4-*n*-pentyl-4′-cyanobiphenyl (5CB) showing the atomic labeling.

II. EXPERIMENTAL AND COMPUTATIONAL DETAILS

A. NMR experiments

The solute (C_6D_6) and solvent (5CB) compounds were purchased from Merck and used without further purification. The solution was prepared by adding a weighed amount of C_6D_6 into a known quantity of the mesogen, which resulted in a concentration of 7.6 mol %. The width of the biphasic region, where nematic and isotropic phases coexist, is for this mixture ~3 deg. All NMR experiments were performed on a Bruker MSL 200 spectrometer equipped with a standard 10 mm high-resolution probe. The carbon-13 spectra were recorded in a single-pulse experiment combined with modulated proton decoupling as described in Ref. 16. The decoupler field strength corresponded to a frequency of 10.4 kHz, and the recycle delay was 30 s. The ^{13}C peak assignment was taken from the literature.[17,18] Deuterium NMR spectra were acquired employing the quadrupole echo sequence[19] with a 90° pulse length of 7.7 μs. The temperature was controlled using a Bruker B–VT 1000E unit and was calibrated by measuring the ^1H chemical shift difference in ethylene glycol.[20]

B. Molecular dynamics simulation

The MD simulation was performed in a rectangular cell containing 110 5CB and 10 benzene molecules yielding a C_6H_6 mol fraction of 8.3%. The simulation was carried out in the nematic phase at 290 K, and the temperature was kept constant (NVT ensemble) by using a weak coupling to an external heat bath.[21] The coupling parameter (36 fs) was chosen to be long compared to the integration step and short compared to the length of the trajectory. The mesogens were modelled using the conventional potential energy function composed of intra- and intermolecular interactions:

$$E_{\text{tot}} = \sum_{\text{angles}} K_\varphi(\varphi-\varphi_0)^2 + \sum_{\text{dihedrals}} \frac{V_n}{2}\left[1-\cos n(\Theta-\gamma)\right] + \sum_{i<j}\left[\left(\frac{A_{ij}}{r_{ij}^{12}}-\frac{B_{ij}}{r_{ij}^{6}}\right)+\frac{q_iq_j}{4\pi\epsilon_0 r_{ij}}\right], \tag{1}$$

where the first two covalent terms represent bond bending and torsional motion. Note that the bond stretching term in Eq. (1) is missing since the SHAKE[22] algorithm was used. The last sum includes nonbonded interactions where the parameters A_{ij}, B_{ij}, and q_i are related to Lennard-Jones and electrostatic energies. The CH, CH_2, and CH_3 groups were treated as single interaction centers (united atoms). Except for the inter-ring and alkyl chain torsional potential, all interaction parameters are identical to those used in our previous simulation of neat 5CB.[12] The torsional parameters in Eq. (1) for the three dihedral angles in the chain were; $V_3=V_4=V_5=8.4$ kJ mol^{-1} and the same phase angle ($\gamma=180°$) was used for all three terms. These values were determined from a conformational and dynamical analysis of the trajectories generated in a set of short simulations of hexane in the isotropic phase. The rotation about the inter-ring bond was in this study modeled using a potential function of the form

$$V(\Theta)=V_2(1-\cos 2\Theta)+V_4\cos 4\Theta, \tag{2}$$

with force constants $V_2=5.85$ and $V_4=5.10$ kJ mol^{-1}. This potential was obtained in an MFT analysis of ^1H NMR data recorded in 4-methoxy-4′-cyanobiphenyl (1-OCB).[23] Except for the absence of partial charges, all interaction parameters describing benzene are identical to those used for the phenyl rings in 5CB. Each solvent molecule consists of 19 sites, while 6 united atoms are used for the solute. The total number of interacting sites in the simulation cell is thus 2150. The rectangular periodic boundary condition, together with minimum image convention and a nonbonded, spherical cutoff of 12.5 Å, were applied on the distances between the atoms. The size of the simulation box was 32.5×32.5×52.0 Å^3 which corresponds to a density of 0.95 g cm^{-3}. The 5CB molecules were initially placed in three layers with the *para* axes oriented parallel to the long axis of the simulation box. In order to prevent a net dipole moment, the vertical orientations of the 5CB molecules were altered. Neglecting the presence of benzene, this initial configuration corresponds to a perfectly ordered smectic A phase. The equations of motion were integrated using the Verlet leap frog algorithm[24] with a time step of 3 fs. This high value was chosen after a careful analysis in which the effect of the integration step on the kinetic and potential energies was investigated. The total length of the simulation was 1.5 ns and a trajectory of 510 ps was used in the final analysis.

A simulation of neat isotropic liquid benzene at 300 K was also performed. The same force field as described above was used with 216 benzene molecules in the cell. The liquid was equilibrated for 100 ps, followed by a 100 ps production run during which trajectory was collected. The shape of the simulation box was cubic with a side length of 31.8 Å, corresponding to the experimental density 0.87 g cm^{-3}. All calculations were carried out on an IBM RISC6000/355 computer using an optimized code written in this laboratory.[25]

III. ORIENTATIONAL ORDER AND AVERAGE INTERMOLECULAR INTERACTIONS

A. Order parameters and MFT analysis of the NMR data

We have studied the orientational order of both the solute and solvent molecules as a function of temperature in the binary mixture described in Sec. II A. Nuclear magnetic resonance spectroscopy is well suited for this kind of investigations since it is possible to obtain the order parameters of both constituent molecules independently. The second-rank

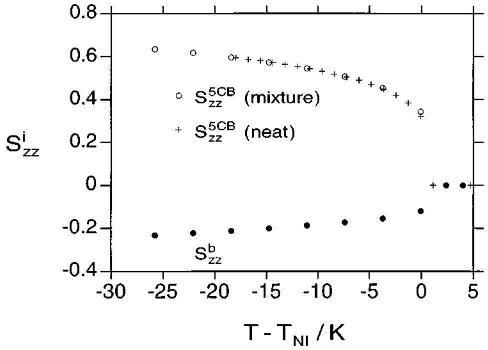

FIG. 2. Variation of S^i_{zz} with the shifted temperature $T-T_{\mathrm{NI}}$. Order parameters of neat 5CB (crosses) are included.

orientational order parameter of benzene-d_6 S^b_{zz} was extracted from the ^{2}H quadrupolar splitting, whereas $S^{5\mathrm{CB}}_{zz}$ was measured by recording the carbon-13 chemical shifts of 5CB.

For a C_6D_6 molecule undergoing fast reorientation about its C_6 axis the quadrupolar splitting $\Delta\nu$ is given by

$$\Delta\nu=\tfrac{3}{4}q_{\mathrm{CD}}S^b_{zz}, \qquad (3)$$

where $q_{\mathrm{CD}}=183$ kHz is the static quadrupolar coupling constant. To obtain Eq. (3), the director is assumed to orient along the external magnetic field. The sign of S^b_{zz} cannot be determined from the ^{2}H NMR spectrum since only the absolute value of the quadrupolar splitting is observed. However, if the liquid crystalline solvent consists of rodlike particles it is known that the normal of a disklike solute molecule orients perpendicular to the director.[26] In the following we will therefore assume that S^b_{zz} is negative. This assumption will be verified in the next section.

The orientational ordering of the nematic solvent was studied at different temperatures by means of ^{13}C chemical shift measurements. It is in general difficult to extract the order parameters from the chemical shifts σ_{LC} observed in a mesophase. The reason for this is that the magnitude and orientation of the shift tensor components in some molecular-fixed reference frame must be known. Fortunately, it has been shown for 5CB that there exists a simple semi-empirical correlation between the ^{13}C chemical shifts and the order parameter according to[27,28]

$$\Delta\sigma=aS^{5\mathrm{CB}}_{zz}+b, \qquad (4)$$

where $\Delta\sigma=\sigma_{\mathrm{LC}}-\sigma_{\mathrm{iso}}$. The empirical constants a and b are different for each nonequivalent carbon in the molecule and are tabulated in Ref. 27. All ring carbons except C6[27] were used for calculating an average value of $S^{5\mathrm{CB}}_{zz}$ at each experimental temperature. For a flexible molecule like 5CB, all order parameters will depend on the molecular conformation. The quantity $S^{5\mathrm{CB}}_{zz}$ does consequently not describe the orientational order of the entire solvent molecule, but refers to the local ordering of the *para* axis in the core fragment.

The temperature dependence of S^b_{zz} and $S^{5\mathrm{CB}}_{zz}$ is shown in Fig. 2. For comparison, the order parameters of neat 5CB are included. These were obtained from ^{13}C chemical shift data exactly as described above, and no significant difference in temperature dependence between the two samples is observed. The higher ordering of the solvent molecules as compared to the solutes is clearly seen. Note that the limiting orientational order parameters in a perfectly aligned system composed of disks and rods differ by a factor of $-1/2$. Due to supercooling effects, the nematic range for the liquid crystalline mixture is apparently broader than for neat 5CB. The clearing point of the mixture was observed at ~297 K which agrees with the value of ~298 K reported previously for this system.[29]

It is interesting to analyze the temperature dependence of the order parameters using simple mean field theory. In order to do so, the solvent molecules will be treated as rigid, axially symmetric objects which allow us to use the $S^{5\mathrm{CB}}_{zz}$ values in Fig. 2 as unique molecular order parameters. This assumption is clearly not strictly valid, but has proven to be a reasonable approximation for 5CB.[30] We will further discuss this approximation in the following sections. According to Maier–Saupe theory for binary mixtures of cylindrically symmetric molecules, the potential of mean torque $U^i(\theta)$ may be written as[6]

$$U^i(\theta)=-\epsilon^i\tfrac{1}{2}(3\cos^2\theta-1), \qquad (5)$$

where θ is the angle between the molecular symmetry axis and the nematic director, and i denotes the two molecular species. The interaction parameter ϵ^i determines the strength of the anisotropic ordering potential. The second-rank order parameter can be expressed in terms of the potential of mean torque by the relation

$$S^i_{zz}=(Q^i)^{-1}\int\tfrac{1}{2}(3\cos^2\theta-1)\times\exp\{-U^i(\theta)/RT\}\sin\theta\,d\theta, \qquad (6)$$

where Q^i is the orientational partition function

$$Q^i=\int\exp\{-U^i(\theta)/RT\}\sin\theta\,d\theta. \qquad (7)$$

From the measured values of S^b_{zz} and $S^{5\mathrm{CB}}_{zz}$ we can calculate ϵ^b and $\epsilon^{5\mathrm{CB}}$ using Eqs. (5) and (6). The interaction parameters are functions of the order in the system[6]

$$\epsilon^b=x_b\overline{u^{bb}}S^b_{zz}+(1-x_b)\overline{u^{b5\mathrm{CB}}}S^{5\mathrm{CB}}_{zz}, \qquad (8)$$

$$\epsilon^{5\mathrm{CB}}=x_b\overline{u^{b5\mathrm{CB}}}S^b_{zz}+(1-x_b)\overline{u^{5\mathrm{CB}5\mathrm{CB}}}S^{5\mathrm{CB}}_{zz}, \qquad (9)$$

where $\overline{u^{ij}}$ are average values of the pair potentials over the intermolecular separations, and x_b is the mole fraction of benzene. The $\overline{u^{ij}}$ values measure the anisotropic interaction strengths between molecules of species i and j. In order to proceed with the analysis we have to make some additional assumptions [Eqs. (8) and (9) contain three unknown parameters]. Two different cases will be compared. *First case*: For an infinitely dilute solution ($x_b\approx 0$) Eqs. (8) and (9) reduce to

$$\epsilon^b=\overline{u^{b5\mathrm{CB}}}S^{5\mathrm{CB}}_{zz} \qquad (10)$$

and

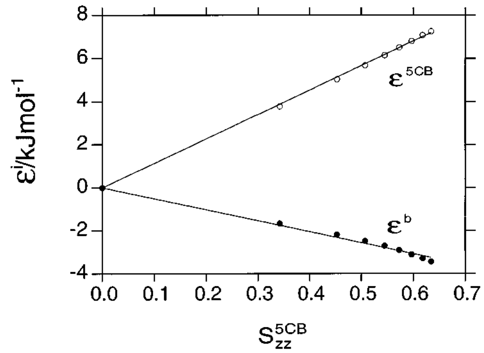

FIG. 3. The strength parameter ϵ^i as a function of the solvent order parameter.

$$\epsilon^{5CB}=\overline{u^{5CB5CB}}S_{zz}^{5CB}. \tag{11}$$

By plotting ϵ^b and ϵ^{5CB} versus the solvent order parameter (cf. Fig. 3) one obtains the following average interaction parameters; $\overline{u^{b5CB}}=-5.1$ kJ mol^{-1} and $\overline{u^{5CB5CB}}=11.3$ kJ mol^{-1}. The same value of $\overline{u^{5CB5CB}}$ was found in a previous MFT analysis of quadrupolar splittings obtained in neat ^{2}H-labeled 5CB.[31] There however, the measurements were performed at a constant volume ($V_m=0.243$ dm^3 mol^{-1}). The opposite signs of $\overline{u^{b5CB}}$ and $\overline{u^{5CB5CB}}$ reflect the perpendicular orientation of the benzene molecules with respect to the liquid crystalline director (i.e., that $S_{zz}^b<0$), and should not be interpreted in terms of attractive/repulsive interactions. This simple mean field analysis indicates that the benzene–5CB interaction is ~45% of that between the 5CB molecules. *Second case*: Another approach, which avoids the assumption about infinite dilution, is to invoke the geometric mean rule[6]

$$\overline{u^{b5CB}}=-(\overline{u^{bb}}\,\overline{u^{5CB5CB}})^{1/2}. \tag{12}$$

The negative sign comes from the fact that the mixture is composed of disk-like and rod-like particles. If this expression is inserted in Eqs. (8) and (9) one finds that

$$-\frac{\epsilon^b}{(\overline{u^{bb}})^{1/2}}=\frac{\epsilon^{5CB}}{(\overline{u^{5CB5CB}})^{1/2}} \tag{13}$$

or

$$\frac{\epsilon^b}{\epsilon^{5CB}}=-\left(\frac{\overline{u^{bb}}}{\overline{u^{5CB5CB}}}\right)^{1/2}=\frac{\overline{u^{b5CB}}}{\overline{u^{5CB5CB}}}. \tag{14}$$

Equation (14) predicts that the ratio between ϵ^b and ϵ^{5CB} should be constant for all compositions and temperatures. This rather surprising result has also been pointed out by others.[26] Moreover, it is interesting to note that both the above cases give identical result [cf. Eqs. (10), (11), and (14)].

It must be emphasized that the calculations of $\overline{u^{ij}}$ are based on several approximations. In addition to the ones already mentioned, it is assumed that[6] (i) the distribution of intermolecular vectors is spherically symmetric, and (ii) it is allowed to truncate the potential of mean torque after the second-rank term. These assumptions can, at least partly, be tested by the MD simulation discussed in the following sections. Another problem is that the NMR experiments are performed at constant pressure, while the Maier–Saupe theory refers to a constant volume situation. This issue has been addressed by several authors[31,32] and it is well established that molecular ordering is both temperature and volume dependent. The extent and precise form of the volume dependence is however not yet fully understood.

B. Order parameters and distribution functions from the MD simulation

The first step in the analysis of the MD trajectories is to define a molecular-fixed frame M. Computer simulations provide a unique possibility to evaluate the effect of different definitions of the molecular frame. For a flexible molecule, the most convenient choice of M is that corresponding to the principal axis system of the moment of inertia tensor $\mathbf{I}$. This frame is determined for every molecule at each time step, and the z axis corresponds to the smallest eigenvalue of $\mathbf{I}$. On the other hand, the z axis relevant for the experimental 5CB order parameters discussed in Sec. III A, coincides with the *para* axis of the biphenyl fragment. In our previous MD study of 5CB, several liquid crystalline properties were calculated using these two definitions, and it was found that they essentially produced identical results.[12] This observation was confirmed in the present simulation and we will therefore use the inertial frame definition of the molecular coordinate system. The unique z axis of a benzene molecule coincides with the sixfold symmetry axis.

The next problem is to find the director frame of the mesophase. In a computer simulation the instantaneous orientation of the director $\mathbf{n}$ can be determined from a general Cartesian ordering matrix $\mathbf{Q_{zz}}$.[33] Assuming that only the solvent molecules determine the orientation of $\mathbf{n}$, the elements of $\mathbf{Q_{zz}}$ may be written

$$Q_{zz}^{\alpha\beta}=\frac{1}{N}\sum_{j=1}^{N}\frac{1}{2}\,(3\cos\theta_{z\alpha}^{j}\cos\theta_{z\beta}^{j}-\delta_{\alpha\beta}), \tag{15}$$

where N is the number of solvent particles, and $\theta_{z\alpha}^j$ is the angle between the long molecular axis z and an axis α fixed in the simulation box. The diagonalization of $\mathbf{Q_{zz}}$ gives three eigenvalues, and the nematic director is the eigenvector associated with the largest eigenvalue. In practice, the director never deviated more than 9° from the long axis of the simulation cell.

We are now in a position of defining the molecular ordering matrix $\mathbf{S}$, whose principal values are given by

$$S_{aa}=\langle\tfrac{1}{2}(3\cos^2\theta_a-1)\rangle, \tag{16}$$

where the angular bracket indicates an ensemble average, and θ_a is the angle between $\mathbf{n}$ and the molecular-fixed principal axis $a(a=x,y,z)$. Since $\mathbf{S}$ is traceless, it is sufficient to specify two of the three diagonal elements. The time developments of the various order parameters are shown in Fig. 4. The trajectory was divided into 15 ps intervals, and each point corresponds to an average within the interval. We see that the orientational ordering is constant during the simula-

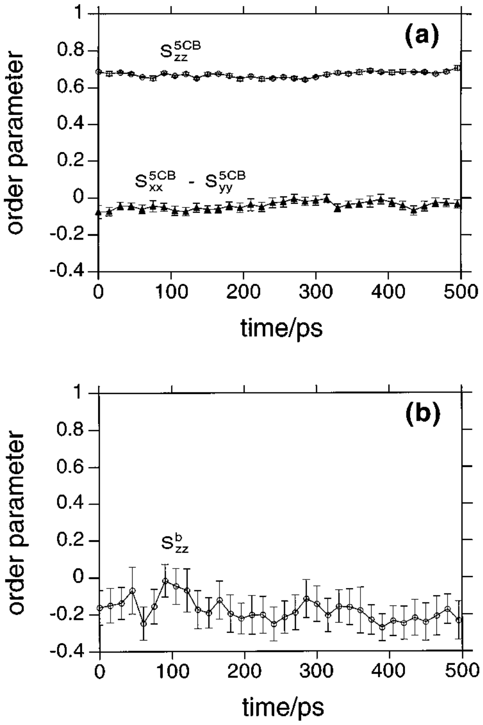

FIG. 4. The time dependence of the second-rank order parameters for (a) 5CB and (b) benzene. Each point represents an average of a 15 ps interval and the error bars indicate one standard deviation.

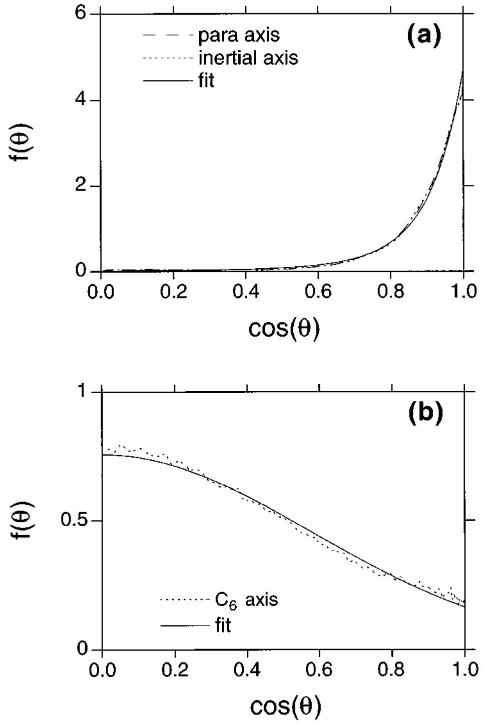

FIG. 5. The singlet orientational distribution functions describing (a) the inertial and *para* axes of 5CB and (b) the C_6 axis of benzene. Fitted distributions are also shown (see the text).

tion which indicates that the system is in equilibrium. The poor statistics of the solute order parameter [cf. Fig. 4(b)] is due to the small number of benzene molecules in the simulation cell. It is nevertheless clear that the solutes prefer to orient perpendicular to the director. The averaged (over the trajectory of 510 ps) order parameters can be compared with the NMR results discussed in the previous section. The temperature in the simulation (290 K) is ~8 deg below the clearing point of the real mixture.[29] The experimental order parameters S_{zz}^{i} at this shifted temperature are 0.52 and -0.18 for 5CB and benzene, respectively. The corresponding values obtained from the simulation are 0.66 ± 0.17 and -0.17 ± 0.20. The agreement can be regarded as satisfactory, especially keeping in mind all approximations introduced in an MD simulation of a liquid crystal. In particular, the force field used in the simulation is not calibrated with respect to the real transition temperatures of the mixture. The density of the simulated system is another source of uncertainty. A careful adjustment of the density could improve the agreement between the simulation and experiment. However, given the approximate nature of the force field and the unknown phase diagram associated with this potential energy function, no such adjustments were attempted. We estimate the difference in density between the real and simulated mixture to be no more than a few percent.

From the simulation we find the ratio $|(S_{xx}-S_{yy})/S_{zz}|$ to be 0.06 for 5CB, which is somewhat lower than values observed in NMR investigations of neat 5CB.[34–36]

So far, we have expressed the molecular ordering in terms of the second-rank S_{aa}^{i} parameters. The most complete description of the order is however provided by the singlet orientational distribution function f.[37] For an axially symmetric molecule in a nematic phase, f will only depend on the angle θ between the unique molecular axis and the director. The knowledge of the distribution function enables access to the statistical average of any observable in the mesophase. A computer simulation offers a unique opportunity to obtain $f(\theta)$ directly. In Fig. 5 the distribution functions for 5CB and benzene are shown. The distribution of the *para* axis of 5CB (defined by a unit vector between carbon atoms 3 and 14) is also included. As indicated above, the inertial frame and *para* axes exhibit essentially identical distributions. We have once again treated the mesogen as a uniaxial particle. The distribution function describing the solvent peaks, as expected, at 0° while the solute function has a maximum at 90°.

The potential of mean torque and $f^{i}(\theta)$ are related to each other according to

$$f^{i}(\theta)=(Q^{i})^{-1}\exp[-U^{i}(\theta)/RT], \tag{17}$$

where Q^{i} is defined in Eq. (7). If the second-rank truncated form of $U^{i}(\theta)$ is employed [cf. Eqs. (5), (10), and (11)] we can fit the curves in Fig. 5 to Eq. (17), and obtain the interaction parameters $\overline{u^{b5CB}}$ and $\overline{u^{5CB5CB}}$. This nonlinear fitting procedure gave $\overline{u^{5CB5CB}}=13.2$ kJ mol^{-1} and $\overline{u^{b5CB}} = -3.7$ kJ mol^{-1}. As can be seen in Fig. 5, the agreement between fitted and computed (from the trajectory) distributions is almost perfect. In addition, the parameters derived from the

TABLE I. Intermolecular interactions calculated in the computer simulation (kJ mol^{-1}).

Type of interaction	5CB–5CB	5CB–benzene	Benzene–benzene
Lennard-Jones	−96.1±0.8	−5.4±0.2	−0.1±0.1
Electrostatic	−0.6±0.1	⋯	⋯

fitting are close to those determined experimentally ($\overline{u}^{5\mathrm{CB}5\mathrm{CB}}=11.3$ and $\overline{u}^{b5\mathrm{CB}} = -5.1$ kJ mol^{-1}) in the previous section.

In order to quantify how well the fitted distribution functions describe the real MD distributions, we have calculated the order parameters using Eq. (6) and the fitted values of $\overline{u}^{5\mathrm{CB}5\mathrm{CB}}$ and $\overline{u}^{b5\mathrm{CB}}$. The following result was obtained; $S_{zz}^{5\mathrm{CB}} = 0.68$ and $S_{zz}^{b}=-0.17$ which clearly agree with the average values in Fig. 4. Additional consistency tests were performed by calculating order parameters of higher rank. The averages of the fourth-rank Legendre polynomial, $\langle P_4^i \rangle$, were found to be 0.32 and 0.02 for 5CB and benzene, respectively. The corresponding values computed directly from the trajectory were 0.31 and 0.03. We may therefore conclude that the second-rank truncated potential of mean torque provides a reasonable description of true distribution functions.

C. Interaction energies in the MD simulation

Average pair interaction energies calculated in the MD simulation are given in Table I. All contributions have been normalized by the total number of molecules in the simulation box. Electrostatic interactions involving benzene are absent, because there are no partial charges on the solute molecules. Clearly, the Coulombic energies between the solvent molecules are of limited significance. The importance of electrostatic interactions in nematic phases have previously been investigated in MD simulations.[9,10] It was found that the effect of the corresponding forces on orientational order is weak, whereas the dynamic properties (translational and rotational diffusion) are affected by the choice of charge distribution.

Before closing this section we want to comment on another aspect of molecular interactions. In order to ensure that the MD simulation is performed on a system in equilibrium, various contributions to the total kinetic energy have been analyzed. Details of such considerations have been presented elsewhere,[12] and below only the important conclusions are summarized. According to the equipartition theorem, the translational and rotational energies should be equal, and indeed we found the ratio $E_{\mathrm{tr}}/E_{\mathrm{rot}}=0.98$. The total number of internal degrees of freedom, N_{intra}, for the entire system is 3470 (31 in 5CB and 6 in C_6H_6) compared to $N_{\mathrm{rot}}=N_{\mathrm{tr}}=360$ where N_{rot} and N_{tr} are the numbers of degrees of freedom for rotational and translational motions, respectively. The ratio $N_{\mathrm{intra}}/N_{\mathrm{tr}}=9.7$ and the simulated energy ratio $E_{\mathrm{intra}}/E_{\mathrm{tr}}=10.1$ are in good agreement. We may therefore conclude that the system is at equilibrium during the trajectory sampling.

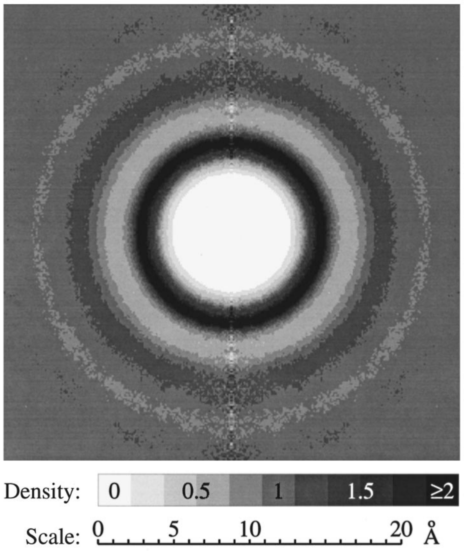

FIG. 6. The cylindrical distribution function in neat liquid benzene.

IV. PAIR CORRELATION FUNCTIONS AND PHASE STRUCTURE

Molecular organization in isotropic liquids as well as in anisotropic systems is conveniently examined using pair correlation functions. The most general form of this function, expressed in the laboratory frame L, is $g(\mathbf{r}_1,\boldsymbol{\Omega}_1,\mathbf{r}_2,\boldsymbol{\Omega}_2)$. This pair distribution represents the probability of finding particle 1 at position $\mathbf{r}_1$ with orientation $\boldsymbol{\Omega}_1$, when particle 2 is at $\mathbf{r}_2$ with orientation $\boldsymbol{\Omega}_2$. $\boldsymbol{\Omega}_i$ is a set of Euler angles specifying the orientation of particle i with respect to the laboratory axis system. By invoking the cylindrical symmetry of the nematic phase, and treating the molecules as uniaxial objects, the number of degrees of freedom is reduced by six. Further simplification of g is achieved by using the relative values $\mathbf{r}_{12}$ and $\boldsymbol{\Omega}_{12}$, together with an average procedure over all molecular orientations. The result is a function which only depends on two variables; Z and $D=(X^2+Y^2)^{1/2}$. Thus, a cylindrical distribution function (CDF) is obtained. The quantity $g(Z,D)$ gives the probability of finding a molecule at (Z,D) relative a molecule chosen as origin. We calculate the intermolecular vector distributions in the director frame, i.e., Z is a distance along $\mathbf{n}$ while D is a distance perpendicular to $\mathbf{n}$. Computational details of CDFs are given in Ref. 38.

The CDF for isotropic liquid benzene is shown in Fig. 6. The vertical axis of the picture coincides with one of the three equivalent box axes. The white area corresponds to an orientational average of excluded volumes of the central molecule. As expected for an isotropic system, the distribution of neighboring molecules is spherically symmetric, demonstrating that $g(Z,D)$ reduces to $g(R)$ (the radial distribution function) in a simple liquid. The positions of the first maximum and minimum are at 5.7 and 7.7 Å which agree with values found in a previous Monte Carlo (MC) simulation of benzene in which a different interaction potential was used.[39] At larger intermolecular distances the distri-

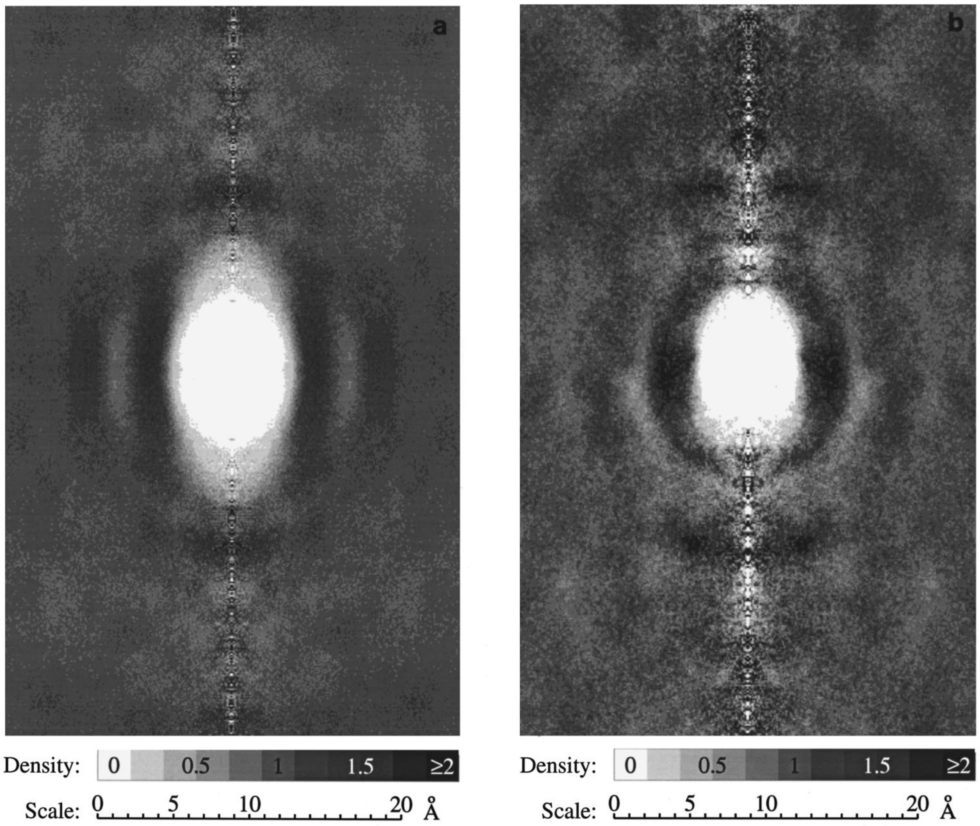

FIG. 7. The cylindrical distribution functions in the nematic mixture: (a) 5CB–5CB and (b) 5CB–benzene.

bution approaches unity. The central line in Fig. 6 is an artefact due to the small volume of cylindrical segments close to the *Z* axis. Consequently, a small number of events is registered and a noisy region is observed.

The 5CB–5CB and 5CB–benzene CDFs are displayed in Figs. 7(a) and 7(b), respectively. The vertical axes coincide with the director. The two maxima on either side of the central molecule in Fig. 7(a) reveal the tendency of the 5CB molecules to form a side-by-side arrangement. In contrast to the liquid benzene distribution in Fig. 6, the average excluded volume of the central 5CB molecule is no longer spherical. This is due to the orientational order with respect to the director. Note that none of the distribution functions exhibits true spherical symmetry. This is in accordance with MC[40] and MD[41] investigations of Gay–Berne liquid crystals in which anisotropic intermolecular vector distributions were observed. The orientation dependence of the pair correlation function is indeed important. In particular when discussed in conjunction with mean field theory. A very important assumption made in many molecular field theories is that the intermolecular vectors are spherically distributed.[42,43] This approximation is clearly not strictly valid, and constitutes therefore an additional source of uncertainty in an MFT analysis of experimental data. As discussed by Emerson *et al.*,[41] the deviations from spherical symmetry are probably correlated with electrostatic energy contributions to the potential of mean torque.

We conclude this section by considering the pair correlation along different directions in the liquid crystal. This function gives the probability of finding a molecule with a displacement along a certain direction from another molecule chosen as origin.[40] The pair correlations between the solvent molecules along the director are shown in Fig. 8(a). During the first picosecond of the simulation, the liquid crystal corresponds to a smectic phase with a layer separation of 17.4 Å. The flat distribution, which is an average over the production run, demonstrates clearly that the layered structure is absent in the nematic mesophase. Pair correlations orthogonal to the director were also calculated (not shown), and were found to be essentially flat. The corresponding pair correlations between the benzene molecules are shown in Fig. 8(b). In the beginning of the MD simulation the solutes are arranged in a layer-like structure. No such behavior is observed during the production run. It is however obvious that the benzene molecules are not uniformly distributed along the director. The reason for this partial aggregation is not yet clear to us, but may be a statistical artefact or an effect of the employed force field.

V. CONCLUSIONS

The objective of this article has been to study orientational order in a binary liquid crystalline mixture consisting of benzene and 5CB. This investigation was performed by means of NMR spectroscopy and MD simulation. Temperature-dependent order parameters of both solute and

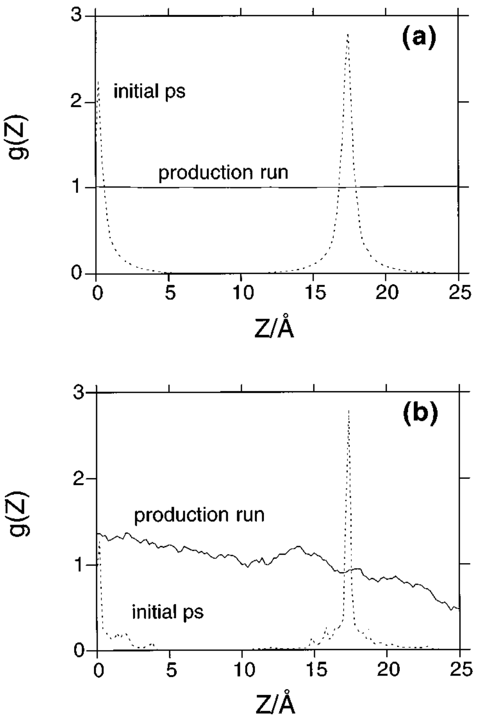

FIG. 8. The pair correlation functions between (a) 5CB and (b) benzene molecules along the director. The figure shows both averages over the first picosecond of the MD simulation (dashed lines), and averages over the 510 ps production run (solid lines). Note that the functions describing the first picosecond have not been normalized.

solvent were extracted from the NMR spectra. A simple mean field analysis of S_{zz}^{b} and $S_{zz}^{5\mathrm{CB}}$ yielded values of the average interaction parameters. It was found that the benzene–5CB interaction is ~45% of that between the solvent particles. The particular molecular field theory employed here is based on several simplifying approximations. For example, it is assumed that the distribution of intermolecular vectors is spherically symmetric and that the potential of mean torque is dominated by the second-rank term. Furthermore, the solvent molecules were treated as uniaxial, rigid rods.

The results from a molecular dynamics simulation are strongly dependent on the force field used in the computation. It is therefore important to compare calculated quantities with experimental results obtained from, e.g., NMR measurements. We found a reasonable agreement between experimental and simulated values of the orientational order parameters. Furthermore, the system was well equilibrated during trajectory sampling.

Computer simulations offer unique possibilities to test many of the assumptions introduced in mean field theories. The main conclusions of the MD investigation may be summarized as follows: (i) the second-rank truncated form of the potential of mean torque is quite capable of predicting correct orientational distribution functions (cf. Fig. 5), (ii) the distribution of intermolecular vectors exhibit small but significant deviations from spherical symmetry (cf. Fig. 7), and (iii) the electrostatic interactions in this system are small compared to the Lennard-Jones terms. Moreover, the average interaction parameters derived from the MFT analysis of the experimental data set and from the simulated trajectory agree fairly well to each other. Yet another important result was that the orientational distribution functions of the 5CB *para* axis, and of the long axis defined by the moment of inertia tensor were essentially equivalent. This is of practical importance in NMR studies of similar mesogens, since we usually measure the molecular order of a fixed vector in the molecule (e.g., the *para* axis), and not of the whole molecule.

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wrong. Note also that this paper contains a few additional errata; the sign in Eq. (5) should be +, not −, and the carbon labeling in Fig. 1 is erroneous (1 and 1′ should be connected to each other).

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