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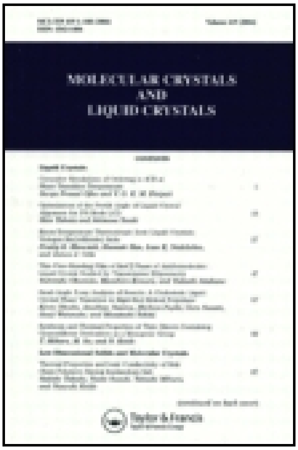

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The First Thousand-Molecule Simulation of a Mesogen at the Fully Atomistic Level

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The First Thousand-Molecule Simulation of a Mesogen at the Fully Atomistic Level

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The first thousand-molecule atomistic simulation of a mesogenic system is described. The simulations involve a study of the mesogen 4-(*trans*-4-n-pentylcyclohexyl) benzonitrile (PCH5) in the isotropic phase, close to the phase transition to a nematic liquid crystal. An all-atom force field is employed to model accurately both internal and external degrees of freedom. Results are presented for the system density and translational diffusion, for molecular structure in the liquid, and for dipole and orientational correlation. While the system size has not reached the thermodynamic limit, most of the calculated properties of the system are in good agreement with experiment and the predictions improve dramatically from simulations of a smaller 125 molecule system.

Keywords: mesogen; atomistic simulation; molecular dynamics; PCH5

1 INTRODUCTION

Computer simulations are an established method for studying the structure and dynamics of liquid crystals. In general, molecular simulations fall in to three main classes: lattice models; off-lattice models often involving single site potentials; and atomistic models. These varied representations involve a trade-off between complexity and computational expense. In lattice models, such as the Lebwohl-Lasher model [1], molecules remain spatially confined and an orientationally dependent pairwise interaction potential is employed, which is cheap to simulate. This allows system sizes of 10^6 particles on contemporary computers [2]. In comparison, off-lattice models such as the Gay-Berne potential [3] are more expensive to simulate, but they provide a mechanism for studying the role

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of shape anisotropy and the anisotropy of attractive interactions in determining phase behaviour. On today's multi-processor parallel machines, 6.5×10^4+ particle simulations are now possible [4], and fast workstations are able to handle over 1000 molecules. Recently, such models have provided a route to the calculation of key material properties such as elastic constants [5], and rotational viscosities [6, 7]. Atomistic models of liquid crystals are more complex [8–16]. They involve potential energy functions on individual atoms and represent intramolecular conformational freedom by force fields of the molecular mechanics type. This generates a huge number of pairwise interactions that must be computed for a single molecular dynamics step or Monte Carlo sweep. Consequently, these models are expensive to simulate and have been limited to small systems sizes < 200 molecules and have been confined mainly to *united atom* models, where carbons and their associated hydrogen atoms are replaced by single united atom sites. Atomistic models have the potential to provide accurate representations of both intermolecular and intramolecular interactions, something which is not possible for single site potentials. They also provide a mechanism to study the influence of molecular flexibility on phase behaviour, which has often been neglected in the past. Intriguingly, they hold also the prospect for future *molecular engineering* applications, whereby a detailed knowledge of molecular interactions can lead to predictions of phase behaviour and the material properties of the phases themselves.

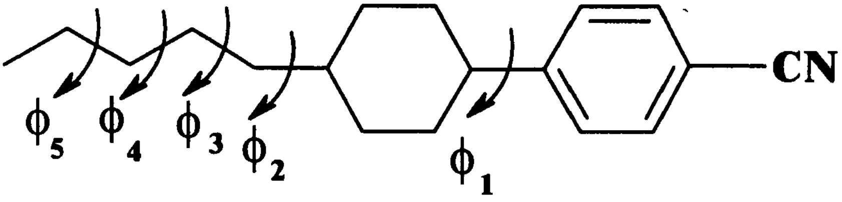

FIGURE 1 The structure of PCH5

In the current study we have attempted a 1000 molecule simulation of the liquid crystal molecule 4-(*trans*-4-n-pentylcyclohexyl)benzonitrile (PCH5 in figure 1) in the isotropic phase close to the transition to a nematic liquid crystal. The simulations employ molecular dynamics methods on a 128 processor parallel supercomputer with a state-of-the-art fully atomistic model, which takes into account each atom in the system. In contrast to the majority of atomistic studies, we have represented fully the long-range contributions to the energy and forces by an Ewald sum. Results are presented for both single molecule and bulk properties of the model system. We show that for detailed models of this type we are

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now able to achieve good agreement with experimentally measured properties. The structure of this paper is as follows. The model used is described in section 2, results are presented in section 3 and we draw some conclusions in section 4 and make some general comments on the use of atomistic studies of this type in the modelling of liquid crystal systems.

2 COMPUTATIONAL

PCH5 molecules are represented by a harmonic force field of the form

$$E_{total} = \sum_{\text{angle}} K_\theta(\theta - \theta_{eq})^2 + \sum_{\text{dihedral}} \left(\sum_{m=1}^{3} \frac{V_m}{2}[1 + cos(m\phi - \delta_m)] \right) + \sum_{i<j} \left(\frac{q_i \cdot q_j}{Dr_{ij}} + \frac{A_{ij}}{r_{ij}^{12}} - \frac{C_{ij}}{r_{ij}^{6}} \right) f_{ij}, (1)$$

where θ and θ_{eq} are the actual and equilibrium bond angles, ϕ and δ_m are dihedral and phase angles, and K_θ, V_m are force constants representing bond bending and torsional motion respectively. The nonbonded energy between atoms i and j at a distance r_{ij} is represented by a Coulomb plus Lennard-Jones potential, where A_{ij} and C_{ij} can be expressed in terms of the well depth and collision parameters, ϵ_{ij} and σ_{ij} respectively: $A_{ij} = 4\epsilon_{ij}\sigma_{ij}^{12}$, $C_{ij} = 4\epsilon_{ij}\sigma_{ij}^{6}$. ($f_{ij} = 0.5$ for 1,4 12:6 non-bonded terms, $f_{ij}= 0.125$ for 1,4 electrostatic terms and $f_{ij} = 1$ for all other non-bonded interactions.) In the current work we constrain bonds at their equilibrium values and use the OPLS-AA *all-atom force field* of Jorgensen and co-workers [17–19] for the parameters in equation 1. OPLS-AA treats each atom individually in the simulation. While this leads to considerable computational expense in comparison to a *united atom* model, such a force field allows a better representation of the charge distribution in the molecule. In particular, the separation of partial charge in a phenyl ring (δ^- on carbons and δ^+ on hydrogens) allows for the representation of the quadrupole moment that arises in this group [20].

The molecular dynamics simulations were carried out using the parallel simulation program, DL_POLY [21] (version 2.12). The leap frog algorithm was employed to solve the equations of motion using a time step of 2 fs. The long range electrostatic interactions were handled by a Ewald sum with the convergence parameter set at 0.48 Å^{-1} and 6 k-vectors were used for each of the directions (x, y, z) in the periodic box. The short-range 12:6 Lennard-Jones interactions were truncated at 9 Å and a long range correction for $r \rightarrow \infty$ was applied for this potential.

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The preparation of a cubic system of 125 molecules has been already discussed in our previous work [22]. In brief, we started from a *bcc* lattice of randomly orientated molecules at low density and applied random translations. The system was then brought to the approximate experimental density using a Berendsen thermostat and barostat at a pressure of 10^5 Pa, and equilibrated with a Nosé-Hoover thermostat of relaxation time 1 ps and a Hoover barostat of relaxation time 4 ps. The calculations were undertaken at 343 K (15 K above the isotropic/nematic transition temperature for PCH5). Full equilibration took approximately 200 ps and thereafter the system was simulated for a further 600 ps. In the current work, the final configuration from the 125 molecule system was doubled-up in each direction and was equilibrated for a further 500 ps. Most system quantities equilibrated rapidly within 200 ps. However, longer range quantities, such as $g_1(r)$ (see section 3) required 350 ps for the positive peak at half the box length (caused by the coordinate doubling procedure) to decay to zero. Final results were calculated over a further 250 ps production run. The 1000 molecule simulations were undertaken using 128 processors of a Cray T3E at the Edinburgh Parallel Computer Centre and required a total of 128 × 128 CPU hours.

3 RESULTS AND DISCUSSION

3.1 Density and diffusion coefficient

The calculated density ρ from the simulation at 343 K is 928.94 ± 1.94 kg m^{-3}, compared to the experimental density of 926 kg m^{-3}. The percentage error of 0.3% is excellent, and points to the accuracy of the force field in providing a good description of the intermolecular forces. The diffusion coefficient for the centre of mass (r_i) has been calculated from the Einstein relation

$$D = \frac{1}{6t}\langle|\mathbf{r}_i(t) - \mathbf{r}_i(t_0)|^2\rangle. \tag{2}$$

A value of $1.089 \times 10^{-10} \pm 0.142 \times 10^{-10}$ m^2s^{-1} was obtained from equation 2. There are no experimental measurements for the translational diffusion of PCH5 at this temperature. However, an experimental value of 1.0×10^{-10} m^2s^{-1} is available at 333 K.* Consequently, the results indicate that the simulation appears to be reproducing a translational diffusion coefficient of the correct order of magnitude. We stress however that equation 2 is valid only in the long time limit, and it is importance to test such results over longer simulation runs, where

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* This value is reported as a private communication in reference [14].

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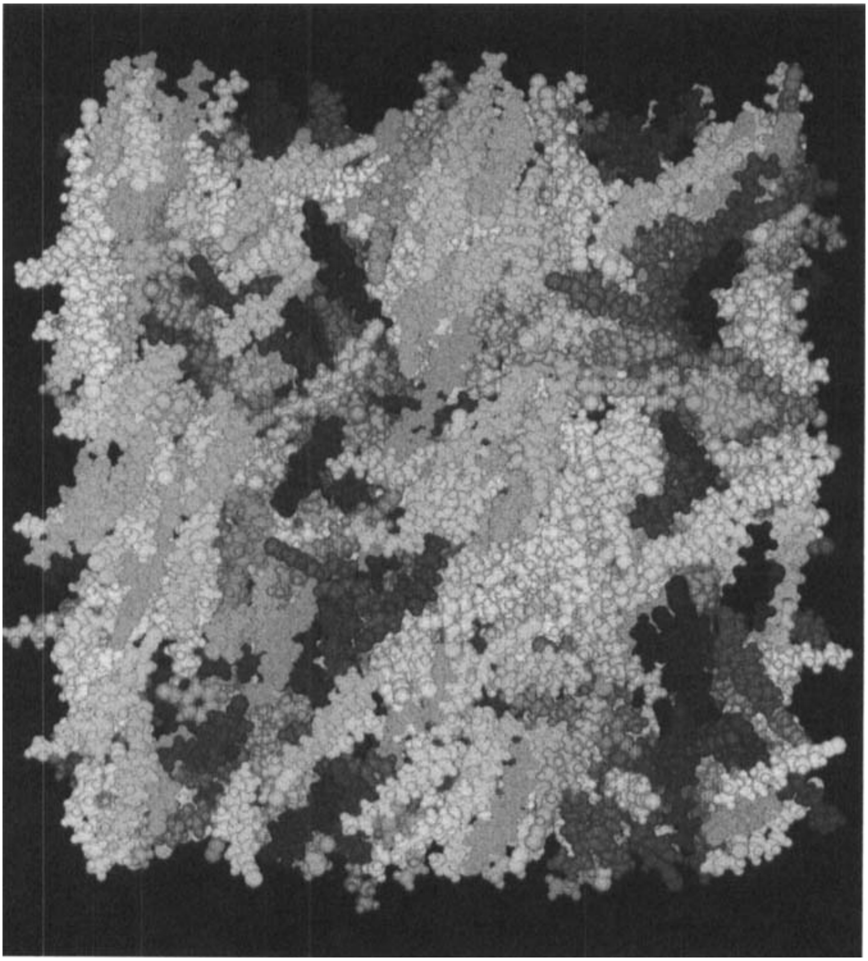

FIGURE 2 Snapshot from an equilibrated configuration of 1000 PCH5 molecules in an isotropic phase. Individual molecules are colour coded according to their orientation with red, green and blue colours representing mutually orthogonal directions (See Color Plate VI at the back of this issue)

molecules would be able to diffuse over longer distances. A comparison with previous simulation work for atomistic nematic liquid crystals, summarized in references [23, 24], is informative. In the past, united atom force fields have lead often to errors in the simulated density of around 5%. Many previous molecular dynamics simulations have tended to over-estimate diffusion coefficients by over an order of magnitude.

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3.2 Molecular structure

A snapshot from the equilibrated system is shown in figure 2. It is evident from the picture that considerable conformational freedom is present in the liquid phase. To investigate this, we have calculated the dihedral angle distributions $S(\phi)$ for the five key dihedrals shown in figure 1 that influence strongly the molecular structure of the molecule. As expected for ϕ_1, we see a two-fold peak in the dihedral angle distribution. The two peaks corresponds to the phenyl ring lying in the symmetry plane of the cyclohexane ring as shown in figure 3: a conformation which, by symmetry, is two-fold degenerate. Assuming Boltzmann statistics, we have calculated barrier heights from the effective torsional potential, $\upsilon(\phi)$, obtained from

$$S(\phi) = C \exp\left(\frac{-v(\phi)}{k_B T}\right). \qquad (3)$$

The mean barrier height for ϕ_1 in the liquid phase at 343 K is 15 kJ mol^{-1}. This is comparable to a typical *gauche-trans* barrier in a chain dihedral (≈16 kJ mol^{-1}). Consequently, even in the liquid phase, there is considerable freedom for the phenyl ring to rotate relative to the rest of the molecule. For the ring-chain dihedral angle, ϕ_2, the minimum energy conformation is also doubly degenerate and corresponds to the chain lying at an angle to the symmetry plane of the cyclohexane ring. This is well-known and was seen in earlier studies of both PCH5 and the closely related molecule CCH5 [9]. Such conformations are also seen as the minimum energy arrangements in gas phase molecular mechanics calculations with most standard force fields (for example MM2 and MM3 [23]) and in the crystal phase of CCH5 [25].

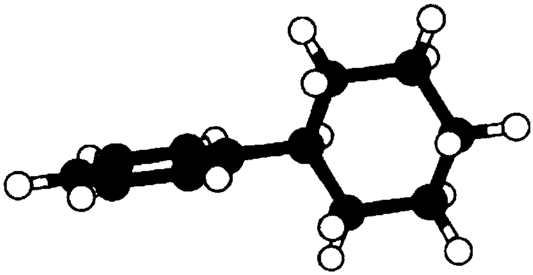

FIGURE 3 The lowest energy conformation for the inter-ring dihedral angle in PCH5

In the nematic phase several studies have indicated that there is a strong coupling between internal molecular structure and the orientational order of mole-

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cules [9, 10, 26], particularly with respect to dihedral angles in alkyl chains. For example, in the molecule CCH5 [9], the conformational preference exhibited by the dihedral angles ϕ_3, ϕ_4, ϕ_5, is *ttt*, *tgt*, *ttg*, *gtt*. *tgt* is more favoured than either of the other *gauche* arrangements, because in this conformation the molecule is able to adopt a more linear shape, which aids packing in the nematic phase. It is an interesting question as to whether the same preference is shown in the isotropic liquid close to the phase transition where molecules are known to form transient orientationally ordered clusters. In the current study, there is already evidence for local orientational alignment (see section 3.3), but the distribution functions for ϕ_3, ϕ_4, ϕ_5 in figure 4(c-e) show no evidence that $S(\phi)$ is influenced by this. Integrating and normalizing the curves in figure 4(c-e) yields trans/gauche populations (table I). The relative preference for *trans* conformations goes as $\phi_3 > \phi_4 > \phi_5$. However, the differences between these three dihedrals are small and arise simply from a greater steric hindrance for gauche conformations the closer one is to the cyclohexane ring. The conformational preference in the isotropic liquid is therefore closer to the gas phase, than to the nematic.

TABLE I Percentage of trans conformations in chain dihedrals

dihedral	%
ϕ_3	88.2
ϕ_4	81.7
ϕ_5	78.8

3.3 Dipole and orientational correlation

The distance dependence of the dipole and orientational correlation in PCH5 can be examined by plotting the distance dependent correlation functions

$$g_l(r) = \langle P_l \cos(\theta_{ij}) \rangle_{\text{shell}}, l = 1, 2; \quad (4)$$

where $\langle\rangle_{\text{shell}}$ indicates an ensemble average over molecules j in a spherical shell of width dr at a distance r between the molecules i and j. In figures 5 and 6 we plot these functions for $l = 1$ and $l = 2$ respectively, and compare the results for 1000 and 125 molecules. The negative peak at ≈ 4 Å in $g_1(r)$ can be attributed to the pairwise anti-parallel association of PCH5 molecules that is believed to occur in both the liquid and nematic liquid crystalline phases. This phenomena was studied in detail in reference [22] where individual transient pair configurations were identified that arose from quadrupolar interactions. The 1000 molecule plot allows $g_1(r)$ to be calculated for longer distances (×2), and this shows conclusively that the dipole correlation is truly short range. In both the 125 and 1000 molecule system a small positive peak is seen at ≈ 7.5 Å. This can be attributed to transient clustering of molecules in the isotropic phase. The nearest neighbour molecules prefer anti-parallel dipole alignment, but because of this, the next nearest neighbours in a transient cluster prefer a parallel dipole alignment.

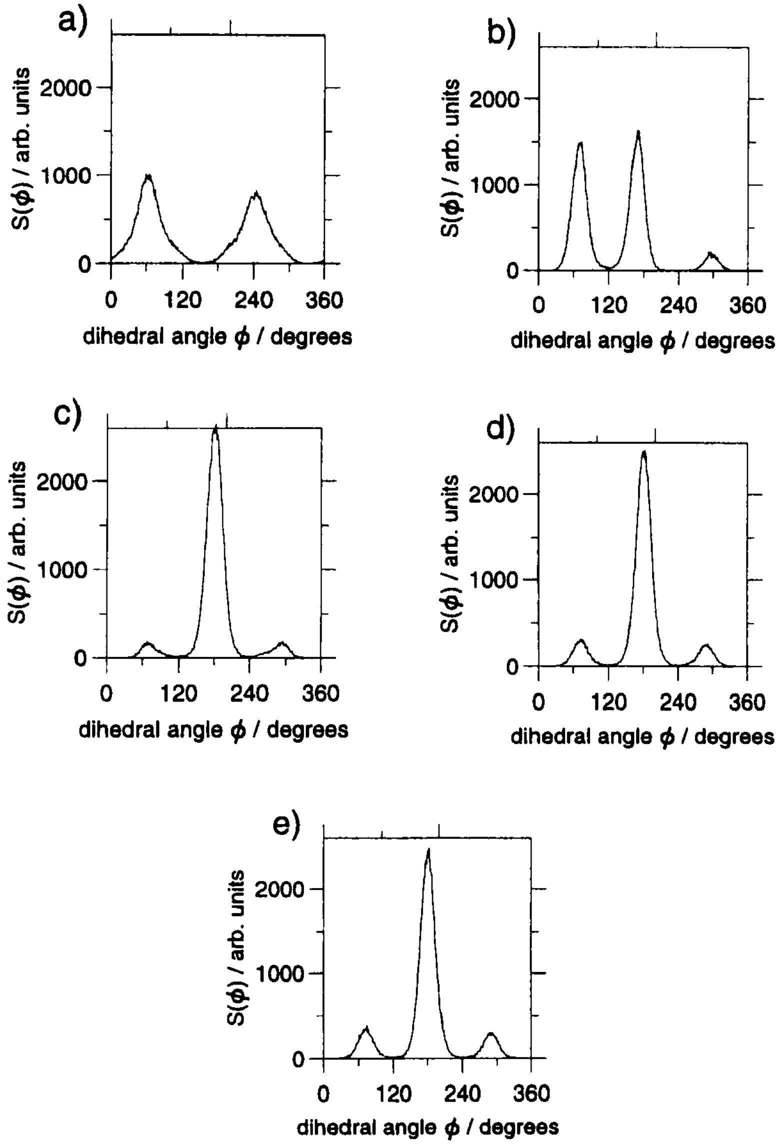

FIGURE 4 Dihedral angle distributions for the five dihedral angles of PCH5 shown in figure 1. a) ϕ_1, b) ϕ_2, c) ϕ_3, d) ϕ_4, e) ϕ_5

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The $g_2(r)$ results in figure 6 are informative. For the 1000 molecule system, it is noted that $g_2(r)$ does not decay completely to zero within half the simulation box, showing that orientational correlation is present in the isotropic phase over large length-scales. This is consistent with the formation of clusters of molecules in the isotropic phase for a temperature close to the phase transition (the experimental phase transition for PCH5 occurs at 328 K). However, it is also evident that even for 1000 molecules, the simulations are a long way from the thermodynamic limit. We therefore expect some system sizes effect errors arising from the fact that the length-scales are insufficient to allow $g_2(r)$ to decay to zero.

The Kirkwood correlation factor g_1 can be calculated using the following expression

$$g_1 = 1 + \frac{1}{N}\left\langle \sum_{i}^{N} \sum_{j \neq i}^{N} \cos\theta_{ij} \right\rangle, \tag{5}$$

where $\langle\rangle$ indicates an ensemble average. For PCH5 a value of 0.886 ± 0.015 is obtained. Again, this value is in good agreement with experiment which gives a value of $g_1 = 0.88$ and a considerable improvement over the value of $g_1 = 0.66$ that was obtained from the 125 molecule simulations. Similarly a value of g_2 can be obtained from

$$g_2 = 1 + \frac{1}{N}\left\langle \sum_{i}^{N} \sum_{j \neq i}^{N} \frac{3}{2}\cos^2\theta_{ij} - \frac{1}{2} \right\rangle. \tag{6}$$

No experimental g_2 values are available for PCH5 and in general g_2 are difficult to obtain experimentally, though in principle they should be available from light scattering data. The calculated value of g_2 is 12.9 ± 0.1. This is consistent with data obtained from single site potentials in the isotropic phase close to a phase transition [27]. We note that this value is considerably higher than that obtained from simulations of 125 molecules: $g_2 = 3.63$. We attribute the difference in these two results to system size effects. These are particularly significant for g_2 because the 125 system was too small to detect orientational correlation over the large distances shown in figure 6.

4 CONCLUSIONS

We have carried out the first 1000 molecule simulation of a fully atomistic model of a mesogen. The results from this study are promising. We have obtained good agreement with key experimental quantities such as the system density, the diffusion coefficient and the value of the Kirkwood correlation factor, g_1. The results

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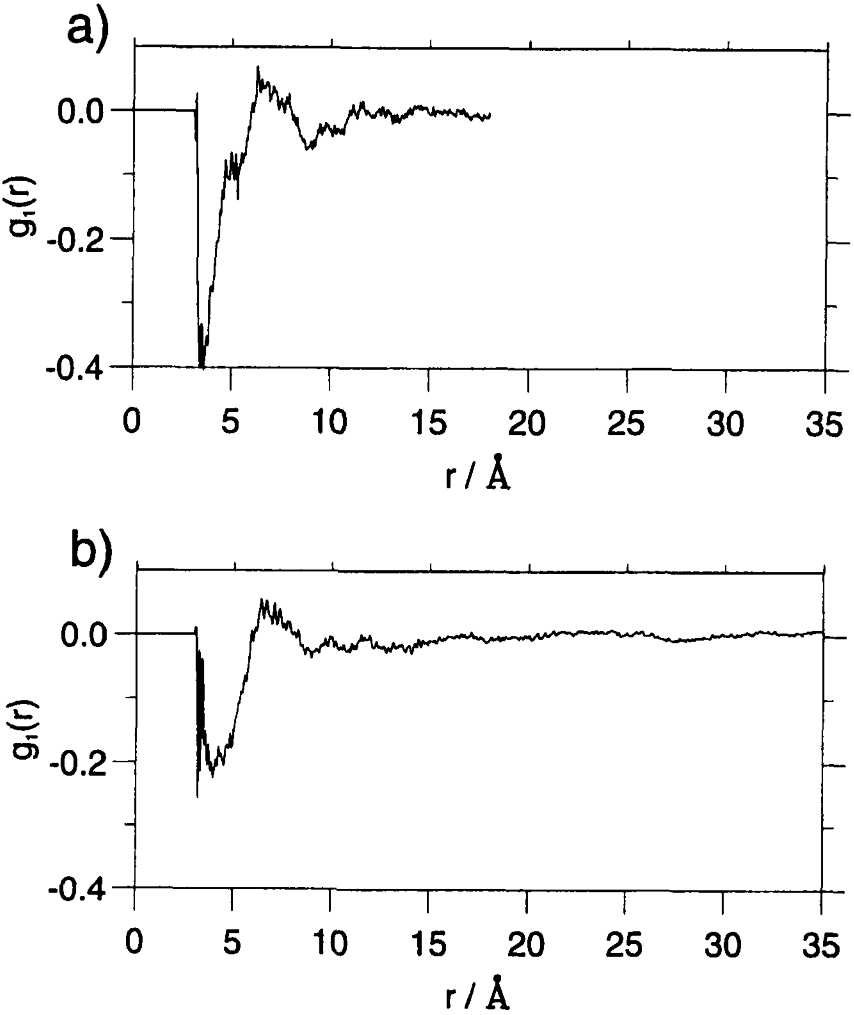

FIGURE 5 $g_1(r)$ in the isotropic phase for PCH5. a) 125 molecules, b) 1000 molecules. (r is measured as the distance between carbon atoms in the 4 position on the phenyl ring.)

provide strong evidence that the model we use provides an accurate representation of the intermolecular forces in PCH5, including the long-range electrostatic forces.

In the light of this work, it is interesting to reassess the prospects of using atomistic simulations in molecular engineering applications for liquid crystals. The success of such studies depends on three factors: accuracy of force field, system size dependence, and time-scale. We address each of these factors below.

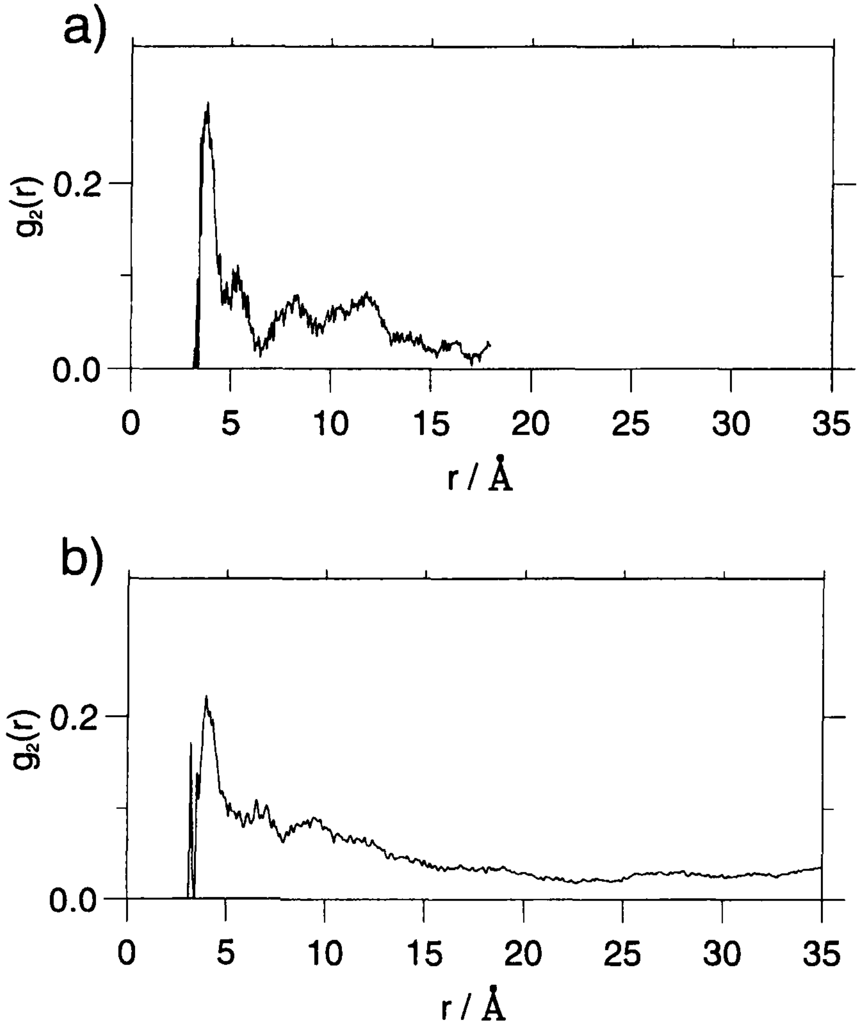

FIGURE 6 $g_2(r)$ in the isotropic phase for PCH5. a) 125 molecules, b) 1000 molecules. (r is measured as the distance between carbon atoms in the 4 position on the phenyl ring.)

Until recently many standard force fields were unable to simulate the properties of molecular fluids. However, the new generation of force fields [17–19], with intermolecular potential functions that have been formulated to predict the densities and heats of vapourization for simple liquids, have changed this situation. In addition, high level *ab initio* quantum calculations are now possible for single liquid crystal molecules in the gas phase [20, 28]. These calculations can

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supply accurate intramolecular force field data for angles and dihedrals. Already, these force fields have been shown to give good results for the thermodynamic properties of key liquid crystal fragment molecules [20], and the balance of evidence points to the fact that, for the properties of fluids, force field parameters (including intermolecular potential functions) are transferable between molecules with similar functional groups. The current study adds weight to the supposition that force fields are approaching the level where a good representation of mesogenic interactions is now possible.

The system size dependence of results is an interesting problem, which was partially addressed in the current study. The system studied was large enough for $g_1(r)$ to decay to zero. However, the orientational correlation was found to extend to longer length-scales, and $g_2(r)$ did not completely decay to zero within our simulation box. In a nematic liquid crystal phase, experience with single site potentials indicates that good results are possible for a few thousand molecules for state points not too close to a phase transition. However, in the isotropic/nematic pretransitional region, small domains of orientationally ordered molecules form and grow as the phase transition is approached (as seen in the current work). These pretransitional effects are dependent on the proximity to the hypothetical second order phase transition temperature, which is never reached, but can be deduced from light scattering studies [29]. In practice for temperature of 20 degrees or more above T_{NI}, g_2 values are expected to be fairly small and so simulations of a few thousand molecules would be expected to yield reasonably good results for the liquid phase, without system size dependency. However, a major problem would still arise in the prediction of phase transition temperatures. Simulations of single site potentials point to considerable hysteresis associated with cooling or heating a system through weakly first order liquid crystalline phase transitions. For lattice models these problems can be overcome by applying histogram re-weighting techniques and finite scaling methods to study the phase transition [30]. Computational expense means that it is not yet feasible to apply such methods to atomistic models.

A recent publication [15] has described the first atomistic simulation study where a liquid crystal phase was grown from a completely isotropic fluid. This process required approximately 10 ns to accomplish. Further atomistic work points to the fact that less than 1 ns of simulation time is required to go from one equilibrated state point in a nematic phase to a second nematic state point with a different order parameter. In terms of 1000 molecules of PCH5, 10 ns scales to 71 × 128 CPU days on a Cray T3E. While this presently represents a huge expenditure of computational power, the continued development of faster cheaper processors will make such studies accessible in the near future.

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