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Molecular organization in liquids consisting of anisometric molecules: Monte Carlo simulations and comparison with theories

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Monte Carlo computer simulations of systems of rigid anisometric molecules with axial ratio $x=3$, 4 and 5 have been performed at densities comparable to those of the mesogenic groups in liquid crystalline materials. The agreement between computer experiments and Flory–Ronca–Irvine theory is quite good. In particular, the nematic–isotropic transition temperatures found in the simulations are within 20 K of those predicted by the theory in all cases examined with $x=3$ and 4, and only slightly higher when $x=5$. Furthermore, the orientational distributions of the molecular long axes with respect to the nematic director are always nearly coincident with those evaluated according to the FRI theory, provided that the order parameter is the same. However, the order parameters at the transition points are smaller than expected on the basis of the theory, and closer to experimental values. Calculations performed by changing the size of the simulated systems prove that the reported results are size independent, while size dependent results are obtained with smaller systems.

1. Introduction

While our understanding of the organization of matter in the gaseous and solid states is based on simple and well defined models (the perfectly disordered ideal gas and the perfectly ordered ideal crystal, respectively), the molecular arrangements in the liquid state cannot be rationalized in terms of a correspondingly simple and general model. In fact, since the molecules are in close contact, the molecular packing and the degree of local disorder in a given liquid are generally dependent on a balance of repulsive and attractive intermolecular forces that are characteristic of the substance, such that each liquid should be considered in principle as a separate case. This is well exemplified by the very existence of substances showing mesomorphic behaviour in the liquid state, where relatively small changes of external conditions may induce dramatic changes of the structure of the mesophase and of its optical properties. It is the extent of these changes, coupled with their rapid reversibility, that makes liquid crystal unique materials for a number of practical applications.

Since molecules are in close contact in liquids, even a small displacement of a molecule may cause a large energy increase due to the intermolecular repulsions, while the energy change associated with the slowly varying attractions is expected to be much smaller [1]. Hence, when strong attractive interactions between specific groups (hydrogen bonds, for instance) are absent, it is reasonable to assume that the role of the slowly varying attractive forces is that of a mean field contributing to establish the overall density of the liquid, while the molecular packing is principally determined by the harsh, nearly hard core repulsive interactions, i.e. by the molecular shape. As a consequence, current theories of the equilibrium structural and thermodynamic properties of liquids are mainly focused on the role of repulsive forces, while attractive forces are ignored or introduced by perturbation theory [1].

For molecules with anisotropic shape, i.e. containing rigid and elongated groups of atoms (mesogenic groups), the balance of packing and orientational entropies may favour, in given conditions, the occurrence of liquid crystalline phases characterized by a partially parallel alignment of the long axes. This simple idea was the basis of the first theoretical treatment of nematic liquids, proposed by Onsager [2] in 1949. Though originally applicable only to unrealistic systems (infinitely long hard rods in very dilute solutions), this treatment proved that liquid crystalline order can be developed on the sole basis of the anisotropy of molecular shape. On the opposite side, Maier and Saupe [3] showed ten years later that liquid crystalline order can also be rationalized in the frame of a theory disregarding the molecular shape and considering each molecule immersed in a mean field due to anisotropic attractions with the surrounding molecules. Being quite simple, this theory soon

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became very popular among scientists working in the field of liquid crystalline materials. However, disregarding molecular shape effects makes the predictive ability of the Maier–Saupe theory rather poor, since liquid crystalline substances having the same nematic–isotropic transition temperature are considered to be totally indistinguishable in this theory, no matter how different they are on a chemical basis. More recently, the two effects (molecular shape and presence of anisotropic attractive forces) have been incorporated into a single molecular theory by Flory and Ronca [4]. This theory, subsequently extended and generalized by Flory and Irvine [5] (FRI theory, see later), is strictly applicable to mixtures of rigid rods of any length and transverse diameter. However, with proper modifications, it has been later utilized for systems with other molecular constitutions, including chains with rod-like sequences at fixed locations, chains with interconvertible rod-like and random-coil sequences in equilibrium, or rods with flexible side chains [6].

One of the problems of all theoretical treatments of liquid crystallinity is that their results can rarely be compared with experiments on a quantitative basis, since even the simplest experimental systems are usually quite far from the idealized systems studied by the theories. In other words, it is not easy to assess the quantitative validity of the many assumptions and approximations constituting the unavoidable frame of these treatments. A second problem is that the behaviour of liquid crystals is often substantially determined by molecular features that cannot be truly incorporated in the available theories, such that the latter are not applicable to these cases even from a qualitative point of view. Both problems can be solved in principle by well devised computer experiments. On one side, results obtained by simulations of the idealized systems studied by a given theory can be directly compared with the predictions of the theory. On the other side, detailed realistic simulations of liquid crystalline systems can serve as a guide for the development of new theories by improving our understanding of the relationships between chemical constitution and properties of these materials.

Several calculations of both kinds have been carried out in the last decade. In particular, simulations of idealized systems have been performed for fluids of hard bodies with various shapes (spherocylinders [7, 8], ellipsoids [9, 10], platelets [11, 12]), and for soft ellipsoids [13–15] modelled by use of the Gay–Berne potential [16]. The main purpose of these calculations was to show that anisotropic phases are stabilized at proper densities in systems of anisometric bodies, and to investigate how the nature (nematic, smectic, columnar, etc.) and degree of order of these phases are influenced by the shape of the model molecules. However, idealized systems that can be directly compared with the predictions of the FRI theory have not been simulated up to now. Also, being limited by the computing power available, studies of this kind have examined relatively small systems, usually consisting of less than 500 molecules [7–15]. This is obviously even more true in the case of realistic simulations, where all atoms and their mutual interactions have to be explicitly taken into account. In fact, simulations of the latter kind are usually confined to systems of 100 molecules or less [17–21], while somewhat larger systems can be studied in semi-realistic simulations, in which parts of the molecules under study are idealized and other parts are explicitly represented at the atomic level [22]. Although the presence of boundaries can be avoided by use of periodicity conditions, the degree of order in the simulated systems is likely to be influenced by the size of the base cell when the system is small and the density is comparable to that of a liquid. Effects of this kind have been discussed in the literature [18], and demonstrated recently by comparing the results obtained for a system of 180 molecules with those for a similar system of 384 molecules [22].

This paper describes large scale simulations of the temperature behaviour of model liquids of rigid anisometric molecules. We take a point of view intermediate between those of idealized and realistic simulations. That is, we do not simulate a specific liquid crystalline substance; however, instead of being structureless bodies like spherocylinders or ellipsoids, the molecules modelled in our work possess an internal structure that can be easily modified to explore the effects of constitutional features characteristic of real liquid crystals. Furthermore, the molecules do not interact with each other as hard bodies or through an artificial anisotropic potential, but their interactions are dictated by molecular structure and shape. We have first investigated the behaviour of a few simple base models, to be utilized as a reference in future simulations, and compared the results of our calculations with the predictions of the FRI theory. By simulating systems with various sizes, we also prove that the results described in this paper are size independent, and that size dependent results are obtained at temperatures close to the nematic–isotropic transition point with smaller systems.

2. Theory, models and methods

The model molecules studied in this paper consist of x units rigidly connected in linear sequences by links of length σ. Interactions among non-bonded units are simulated by a truncated and shifted 12–6 Lennard–Jones potential

$$\begin{aligned} &E(r)=\infty && r<r_{\min}\\ &E(r)=\varepsilon[(\sigma/r)^{12}-2(\sigma/r)^{6}+1] && r_{\min}\leqslant r\leqslant\sigma\\ &E(r)=0 && r\geqslant\sigma \end{aligned}$$

Hence, the model molecules can be represented as rigid linear sequences of touching, soft, spherical units of diameter σ (figure 1), the softness of the units being regulated by the value of ε. Models of this kind are well known in polymer science, where semi-flexible long chain molecules are often represented as necklaces of soft isodiametric units [23]. In order to confer on the units a softness comparable with that of real organic substances, we take here $\varepsilon = 416\,\mathrm{J\,mol^{-1}}$, coincident with the literature value for the isodiametric units in polymethylene [23]. The parameter r_{min}, the core diameter of the units, is taken to be $0{\cdot}75\sigma$, unless otherwise indicated.

Anisotropic attractive interactions among spatially adjacent units belonging to different molecules can be easily introduced in our model. However, in order to ensure that the results can be compared with the FRI theory, they are modelled in this work by the same mean field potential present in the theory, of the form $E(\theta) = -(RxT^*/V_{\mathrm{r}})s(3\cos^2\theta - 1)/2$, where V_{r} is the reduced volume (see later), θ is the angle between the molecular long axis and the preferred direction (the z axis in our calculations; see figure 1), $s = (3\langle\cos^2\theta\rangle - 1)/2$ is the overall order parameter and T^* is a characteristic temperature establishing the strength of the mean field.

In each calculation, N molecules were randomly positioned with their long axes parallel to the z direction in a tridimensionally periodic cubic cell of edge $L\,\sigma$, in such a way that non-bonded units could not approach at a distance smaller than r_{min}. The simulated systems have then been equilibrated at various temperatures by Monte Carlo methods using a combination of translations and rigid rotations. At each step, a molecule was selected at random and a new molecular axis was randomly generated such that the angle (ϕ, see figure 1) of the new and old axes was not higher than 10°. The molecule was then repositioned along the new axis with one of the units, selected at random, held fixed in space (figure 1). After each attempt, the resulting configuration was immediately rejected if distances less than r_{min} occurred. Otherwise, the total energy change was evaluated and the new configuration was accepted or rejected according to the outcome of a standard Boltzmann test. In order to check that this sampling scheme is statistically correct, we have performed, at various temperatures, simple calculations for large systems in the absence of repulsive interactions, obtaining in all the cases examined the results theoretically predicted on the basis of the mean field equations. For instance, a system of 6000 molecules with $xT^*/V_{\mathrm{r}} = 933\,\mathrm{K}$ evolved from the initial value $s = 1$ to the equilibrium values $s = 0{\cdot}51$, $s = 0{\cdot}44$ and $s = 0$ when equilibrated at 200, 205 and 210 K, respectively, while a similar system with $xT^*/V_{\mathrm{r}} = 800\,\mathrm{K}$ evolved from $s = 1$ to $s = 0{\cdot}53$, $s = 0{\cdot}45$ and $s = 0$ at 170, 175 and 180 K, respectively. We have also checked that the translational mobility was large enough for adjacent molecules to exchange their position several times in each calculation, even for the systems having the smallest free volume among those studied.

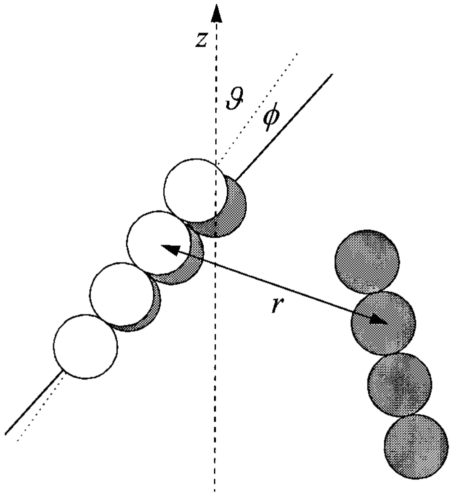

Figure 1. Schematic representation of the model molecules and of the MC transitions utilized for equilibration. In this example, the white units for the molecule on the left correspond to trial positions following an attempted transition in which the first unit has been kept fixed.

Since one of the objectives of our work is to compare the results of the simulations with the predictions of the FRI theory, we describe briefly the principal features of this theory. The total partition function for a system of impenetrable rigid rods with anisotropic attractive interactions is considered to be the product of steric, orientational and attractive terms. For a given orientational distribution, the steric term is evaluated as the number of ways of placing the rods on a lattice with no double occupancy of lattice sites. The rigidity of the lattice approximation is reduced by the artifice of breaking rods at a given angle with respect to the nematic director (coinciding with one of the lattice axes) in a number, y, of sub-sequences of equal length parallel to the director. The orientational partition function is then simply written as the number of ways of mixing n_1 rods with disorientation y_1, n_2 rods with disorientation y_2, etc. The third term, related to the anisotropy of molecular polarizability, is evaluated in a mean field approximation (see before). In terms of the FRI theory, the model systems investigated in this work correspond to systems of rigid rods with axial ratio x and reduced volume $V_{\mathrm{r}} = L^3/Nx$. For such systems, the FRI theory predicts that the fraction $f(\theta)\mathrm{d}\theta$ of rigid groups oriented at angle θ with respect to the nematic director be given by

$$f(\theta)\mathrm{d}\theta = f_1^{-1}\sin\theta\exp[-\alpha\sin\theta - \beta\sin^2\theta]\mathrm{d}\theta \quad (1)$$

where f_m is defined in general as

$$f_m = \int_0^{\pi/2} \sin^m\theta \exp[-\alpha\sin\theta - \beta\sin^2\theta]\,\mathrm{d}\theta \qquad (2)$$

such that $\langle\sin\theta\rangle = f_2/f_1$ and $\langle\sin^2\theta\rangle = f_3/f_1$, while

$$\alpha = -\frac{4x}{\pi}\ln\left[1 - \frac{1}{V_r}\left(1 - \frac{4}{\pi}\langle\sin\theta\rangle\right)\right]; \quad \beta = \frac{3}{2}\frac{xsT^*}{V_r T} \qquad (3)$$

The parameters α and β take into account steric effects and attractive anisotropic interactions, respectively. The nematic–isotropic transition temperature, T_{NI}, is obtained under the additional condition that the free energies of the two phases be coincident, leading to

$$\frac{\pi\alpha}{4}(V_r - 1) - \ln f_1 - x\left(1 - \frac{4}{\pi}\langle\sin\theta\rangle\right) - \frac{\beta}{3}(2 - s) = 0 \qquad (4)$$

Parameters of the various systems simulated in this work are listed in table 1. We have selected values of V_r between 1·25 and 1·50, such that the density of mesogenic groups is similar to that in most liquid crystalline substances, in which stable nematic phases are usually obtained when the rigid groups are associated with flexible tails. Also, values of T^* between 250 and 450 K have been properly chosen in the experimentally observed range in order to have nematic–isotropic transition temperatures near to room temperature. Hence, systems with higher axial ratio and smaller reduced volume are characterized by lower values of T^*, such that the relative role of repulsive interactions and mean field anisotropic attractions is strongly different in the various systems studied. Results obtained for system C have been previously published and are included here for completeness [24].

3. Results and discussion

For each of the systems listed in table 1 we have performed several calculations at various temperatures and with various starting points. The calculations performed and their results in terms of the orientational order parameter are summarized in table 2, where s_{in} and s_{fin} are the initial and the final values of the order parameter, respectively. Figure 2 shows the behaviour of the order parameter as a function of Monte Carlo (MC) cycles for system A. A cycle is defined here as a sequence of 10^6 attempted rotations and translations, taking approximately 12′ on an IBM RISC/6000 T250 computer. The behaviour expected for system A on the basis of the FRI theory at temperatures close to the nematic–isotropic transition point is shown in figure 3 in the form of plots of the Helmholtz free energy difference with respect to the isotropic liquid, $\Delta A/NkT$, as a function of the order parameter. At temperatures lower than 307 K, the free energy curves show a minimum corresponding to the isotropic phase and a second minimum in the anisotropic region. The free energies of the two minima are identical at $T_{NI} = 298{\cdot}3$ K, when the isotropic and the anisotropic phases are in equilibrium. For $T < 298{\cdot}3$ K, the anisotropic phase is expected to be stable, while it is expected to be metastable for $298{\cdot}3 < T < 307$ K.

Our first calculation on system A was performed at $T = 290$ K, with the result that the initial configuration with $s = 1$ changed to the isotropic liquid in less than 100 cycles (figure 2). We then utilized the configuration with $s = 0{\cdot}37$, obtained after 40 cycles at 290 K, as the starting point for subsequent calculations at 285 and 280 K. The order parameter rapidly decreased at 285 K, while at 280 K it showed a pronounced increase at first, followed by a clear tendency to stabilize around values in the anisotropic range. This suggests that the nematic–isotropic transition temperature may be higher than 280 K for system A, and shows that our method is capable of simulating both disordering and ordering processes.

We restarted then from the fully aligned initial system and performed a series of calculations at increasing temperatures starting from 270 K. In this case, the order parameter decreased to the value $s = 0{\cdot}58$ in approximately 25 cycles, showing relatively small oscillations around this value for more than 150 subsequent cycles. The final configuration at 270 K was then used as the starting point for calculations at 275 K, with the result that the order parameter rapidly leveled off at $s = 0{\cdot}55$. Analogous procedures led to the plateau values $s = 0{\cdot}49$ at 280 K. As expected, when the final configuration obtained at 280 K was heated to 285 K, the simulated system evolved towards the isotropic liquid.

Table 1. Parameters of the simulated systems.

System	L	N	x	V_r	T^*/K
A	30	6750	3	1·33	450
B	30	4500	4	1·50	350
C	20, 25, 30, 40	1600, 3125, 5400, 12800	4	1·25	250
D	30, 40	4320, 10240	5	1·25	250

Table 2. Summary of calculations.

System A			System B			System C ($L=30$, 40)			System D ($L=40$)		
T/K	s_{in}	s_{fin}	T/K	s_{in}	s_{fin}	T/K	s_{in}	s_{fin}	T/K	s_{in}	s_{fin}
260	0·58	0·63	270	1	0·65	260	0·33	0·68	460	1	0·65
270	1	0·58	280	0·65	0·61	270	0·33	0·65	460	0·38	0·65
270	0·33	0·58	290	0·61	0·56	280	0·33	0·61	480	0·65	0·61
275	0·58	0·55	290	0·33	0·56	290	0·61	0·56	480	0·38	0·61
275	0·33	0·55	295	0·56	0·53	290	0·33	0·56	485	0·38	0·57
280	0·55	0·49	295	0·33	0·53	295	0·56	0·46	490	0·38	$<0{\cdot}17$
280	0·37	0·49	300	1	$\approx 0{\cdot}46$	295	0·33	$<0{\cdot}17$	500	0·61	$<0{\cdot}21$
280	0·33	0·49	300	0·33	$<0{\cdot}14$	300	1	≈ 0			
280	0·27	0·49	310	1	$<0{\cdot}07$						
285	0·49	$<0{\cdot}15$									
285	0·37	$<0{\cdot}18$									
290	1	$<0{\cdot}07$									

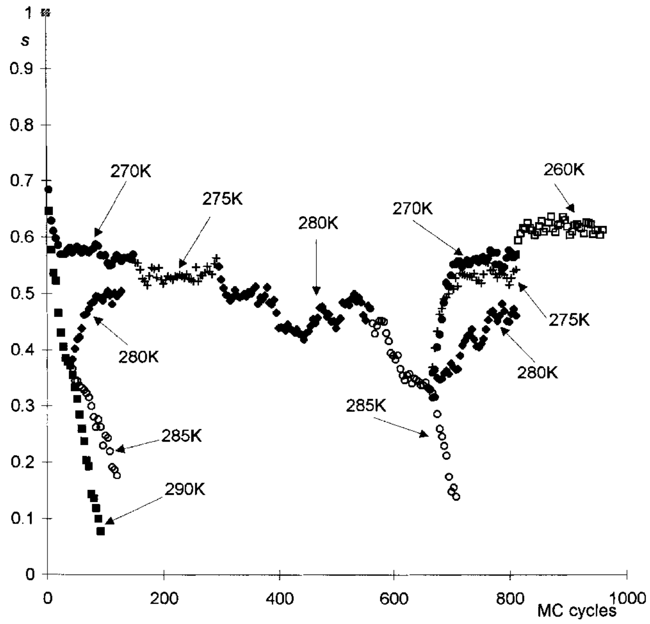

Figure 2. Behaviour of the order parameter, s, as a function of Monte Carlo cycles for system A at various temperatures and with various starting points.

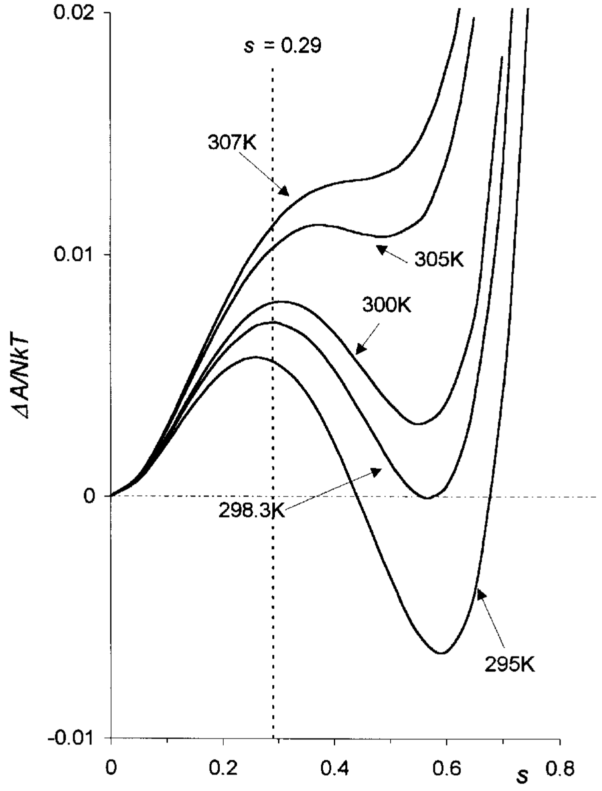

Figure 3. The Helmholtz free energy difference with respect to the isotropic liquid, $\Delta A/NkT$, evaluated according to the FRI theory as a function of the order parameter for system A at temperatures close to the nematic–isotropic transition point (298·3 K).

Figure 3 indicates that the Helmholtz free energy maximum intermediate between the isotropic minimum and the anisotropic minimum is predicted by the FRI theory to be found at $s=0{\cdot}29$ when $T=T_{\mathrm{NI}}$, while it is predicted to be shifted to higher values of s for $T>T_{\mathrm{NI}}$ and to lower values for $T<T_{\mathrm{NI}}$. In other words, according to the theory, a system with order parameter $s=0{\cdot}29$ is expected to evolve towards the isotropic phase at all temperatures higher than T_{NI} and towards the anisotropic phase at all temperatures lower than T_{NI}. We then utilized two configurations obtained at 285 K, one with $s=0{\cdot}27$ and one with $s=0{\cdot}33$, as starting points of two more calculations at 280 K. In both cases the order parameter increased, reaching the plateau value $s=0{\cdot}49$ in about 100 cycles. Although this can be considered as indirect evidence at most, it seems reasonable to assume that the equilibrium value of the order parameter at 280 K is $s=0{\cdot}49$, and that the nematic–isotropic transition temperature for system A is located

between 280 and 285 K. The same configuration with $s=0{\cdot}33$ was also used as the starting point for more calculations at 275 and 270 K. The results, shown in the right part of figure 2, confirm the equilibrium values of s obtained starting from configurations with higher order parameters (0·55 at 275 K and 0·58 at 270 K, respectively). Lastly, the final configuration obtained at 270 K was cooled to 260 K, leading to $s=0{\cdot}63$.

When it is considered that the simulated system is similar, but not identical to the idealized system of rods studied by the FRI theory, and that this theory is based on a lattice treatment, the finding that the transition temperature for system A is only 15 K smaller than that suggested by the theory is pleasantly surprising. Note that the transition temperature predicted for this system on the sole basis of the mean field anisotropic attractions is as low as 223 K (see table 3). Moreover, figure 4 shows that the orientational distribution obtained in our simulations for system A at $T=275$ K is very close to that evaluated according to the FRI theory for the corresponding system of rigid rods, provided that the order parameter is the same. Orientational distributions in good agreement with the FRI theory are also obtained for other values of the order parameter and for other systems with different axial ratio and reduced volume. Our conclusion is that the FRI theory takes quite well into account all the principal factors responsible for the stability of nematic phases in systems of rigid rods and that the artifice of breaking the rods in sub-sequences gives an approximation to the continuum orientational distribution efficiently.

On the basis of the results obtained for system A, we utilized the same base cell to investigate the effects of changing the parameters of the model (x, V_r and T^*). System B consists of molecules with axial ratio $x=4$ and reduced volume $V_r=1{\cdot}50$. The effects of increasing x with respect to system A are compensated only in part by the reduced value of V_r. We then selected a lower value of T^* (i.e. $T^*=350$ K), in order to have the nematic–isotropic transition temperature predicted by the FRI theory close to room temperature. When $x=4$, $V_r=1{\cdot}50$ and $T^*=350$ K, the transition is predicted by the FRI theory to take place at 293 K. Starting from the fully aligned initial system, our first calculation (aimed at obtaining the isotropic liquid) was then performed at 300 K. However, after a rapid initial drop to $s=0{\cdot}5$ in about 30 cycles, the subsequent decrease of the order parameter was extremely slow, with s still of the order of 0·46 after 100 cycles (figure 5). We restarted then at 310 K, obtaining the isotropic phase quite rapidly. A configuration with $s=0{\cdot}33$ obtained at 310 K was then used as the starting point for calculations at 300, 295 and 290 K. At the higher temperature, the system evolved to the isotropic liquid, while at 295 and 290 K, the order parameter increased at first and then levelled off at $s=0{\cdot}53$ and $s=0{\cdot}56$, respectively. The same order parameters were obtained at these two temperatures starting from more ordered configurations. It is reasonable to conclude that the nematic–isotropic transition temperature is located for system B between 295 and 300 K, while the very slowly decreasing value of s observed at 300 K, when starting from $s=1$, may be indicative of a metastable anisotropic phase. Hence, the value of T_{NI} found for system B differs about 5 K from that predicted by the FRI theory. Considering that all parameters have been changed with respect to system A, this confirms that the agreement between theory and computer simulations is extremely good. The results of other calculations performed for system B at temperatures lower than 310 K are listed in table 2.

With a reduced volume equal to 1·25, system C is characterized by a greater relative role of the intermolecular repulsive interactions with respect to the mean field anisotropic attractions than in system B. The results obtained for system C, already published [24], are summarized in table 2. The FRI theory indicates the nematic–isotropic transition temperature at 281 K, while the simulated system shows the transition at between 290 and 295 K, the agreement between FRI theory and simulations being again very good.

We have shown in the case of system C that the behaviour of the simulated systems can be influenced by the size of the base cell utilized in the simulations, especially at temperatures close to the transition point. In fact, we have performed exactly the same calculations for a system of 5400 molecules in a base cell with $L=30$ and for a much larger system of 12 800 molecules in a base cell with $L=40$, the behaviour of these two systems being practically coincident at all temperatures and with all starting points. This indicates that a base cell with $L=30$ is large enough for system C to give size independent results. Among the others, system C shows a stable anisotropic phase with $s=0{\cdot}56$ at 290 K and a metastable anisotropic phase with $s\approx 0{\cdot}45$ at 295 K. The first phase is obtained both on heating at 290 K systems that have been equilibrated at lower temperatures and on cooling at 290 K systems with $s=0{\cdot}33$ obtained at

Table 3. Comparison of transition data predicted by theories and obtained in the simulations (T in K).

	MS		FRI		sim	
System	T_{NI}	s_{NI}	T_{NI}	s_{NI}	T_{NI}	s_{NI}
A	223	0·43	298	0·57	280–285	$<0{\cdot}49$
B	205	0·43	293	0·59	295–300	$<0{\cdot}53$
C	176	0·43	281	0·65	290–295	$<0{\cdot}56$
D	220	0·43	425	0·71	485–490	$<0{\cdot}57$

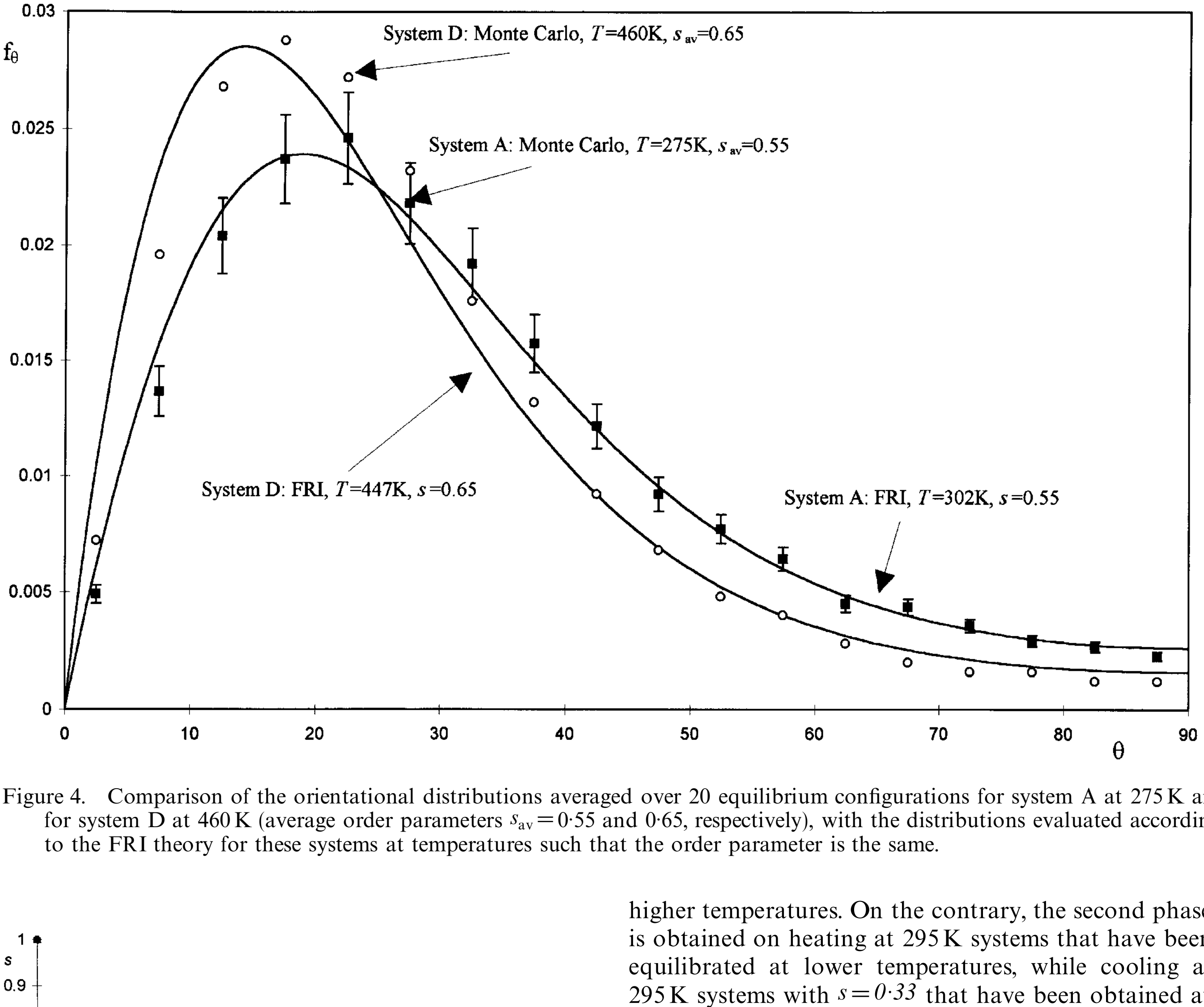

Figure 4. Comparison of the orientational distributions averaged over 20 equilibrium configurations for system A at 275 K and for system D at 460 K (average order parameters $s_{av} = 0{\cdot}55$ and 0·65, respectively), with the distributions evaluated according to the FRI theory for these systems at temperatures such that the order parameter is the same.

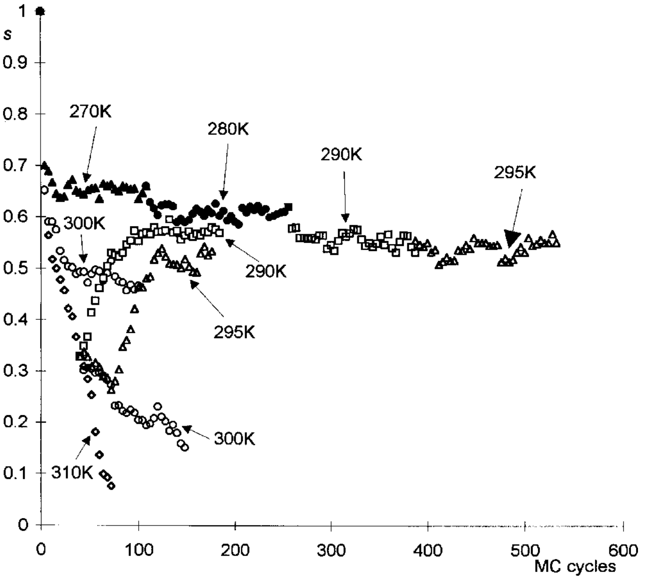

Figure 5. Behaviour of the order parameter, s, as a function of Monte Carlo cycles for system B at various temperatures and with various starting points.

higher temperatures. On the contrary, the second phase is obtained on heating at 295 K systems that have been equilibrated at lower temperatures, while cooling at 295 K systems with $s = 0{\cdot}33$ that have been obtained at higher temperatures gives the isotropic liquid [24].

When the same calculations were attempted for a smaller system of 3125 molecules in a base cell with $L = 25$, the results were identical to those of the larger systems at 300 K and at all temperatures far from the transition point. However, a configuration with $s = 0{\cdot}33$ obtained at 300 K evolved in this case toward the isotropic phase when cooled at 290 K, instead of giving the stable anisotropic phase with $s = 0{\cdot}56$ found for the larger systems. In other words, the phase with $s = 0{\cdot}56$ is found to be metastable when $L = 25$, indicating that the results obtained for system C at temperatures close to the transition point depend on the exact value of L when $L < 30$. We have also performed calculations on a smaller system of 1600 molecules in a base cell with $L = 20$. To our surprise, these calculations gave erratic results. In fact, we utilized in this case the same configuration with $s = 0{\cdot}33$ obtained at 300 K for several equilibrations at 290 K, changing only the value of the random seed. We obtained the isotropic phase in some cases and the nematic phase with $s=0{\cdot}56$ in others. Anyway, when the latter phase was obtained, heating at 295 K gave the isotropic liquid instead of the metastable phase with $s\approx 0{\cdot}45$ found for the larger systems. These findings can be interpreted as arising from the superposition of two different effects, both related to the size of the base cell. On the one hand, the dependence of the free energy on the order parameter is likely modified in small systems by the artificially imposed periodicity. Calculations at temperatures close to the transition point are obviously more sensitive to these changes. On the other hand, small systems near the transition point can be subject to relatively large random fluctuations of the order parameter that may condition the subsequent evolution of the system. There is little doubt that effects of this kind should be taken into account when simulating small systems of mesogenic molecules at liquid densities. However, their importance is possibly exaggerated in our calculations by the mean field approximation utilized to model the presence of anisotropic attractive interactions. This approximation, introduced in the present work in order to make the simulation results comparable to the predictions of the FRI theory, can be easily removed.

We have also performed calculations with $x=5$, maintaining the values of V_{r} and T^* utilized in system C (1·25 and 250 K, respectively). The FRI theory predicts for this new system (system D) the nematic–isotropic transition at 425 K. However, a few preliminary calculations very soon indicated that the behaviour of the simulated system is quite far from that indicated by the theory and depends on the size of the base cell when $L<40$. In particular, when the fully aligned configuration with $L=40$ was equilibrated at 460 K (see figure 6 and table 2), the order parameter changed from 1 to 0·65 in 16 cycles and remained fluctuating around this value for more than 80 cycles. When the final configuration with $s=0{\cdot}65$ was equilibrated at 480 K, the order parameter first decreased and then leveled off at around 0·61. The isotropic phase was only obtained at 500 K. Calculations analogous to those shown in figure 3 show that, according to the FRI theory, the free energy maximum intermediate between the isotropic minimum and the anisotropic minimum is located for system D at $s=0{\cdot}38$. We then used a configuration with $s=0{\cdot}38$ obtained at 500 K as the starting point for new calculations at 460 and 480 K. In both calculations, the order parameter increased, the final results being identical to those previously obtained at the same temperatures. An increase of the order parameter was also observed in a similar calculation performed at 485 K, the order parameter fluctuating around a plateau value of 0·57. On the contrary, when the same starting configuration was used at 490 K, the order parameter decreased, suggesting that the nematic–isotropic transition temperature is between 485 and 490 K.

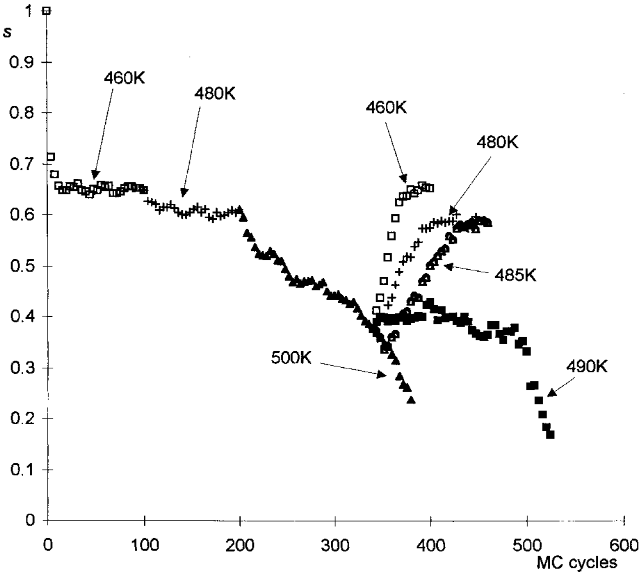

Figure 6. Behaviour of the order parameter, s, as a function of Monte Carlo cycles for system D at various temperatures and with various starting points.

In the case of system D with $L=30$, we performed consecutive calculations with a temperature increase of 10 K, starting from 460 K. We obtained plateau values of s at 0·65, 0·63 and 0·61 for $T=460$, 470 and 480 K, respectively, in good agreement with those obtained when $L=40$. However, when a configuration with $s=0{\cdot}61$ was heated to 490 K, the order parameter reached the plateau value 0·57. When the final configuration obtained at 490 K was heated to 500 K, s decreased to 0·49 in about 80 cycles and kept fluctuating around 0·49 *for more than 400 subsequent cycles*. This confirms that the artificially imposed periodicity influences the results of the simulations, unless L is larger than a limiting value characteristic of each system. Our results indicate that this limiting value, L^*, is between 25 and 30 for system C and greater than 30 for system D. On the other hand, one expects L^* to decrease with decreasing x and increasing V_{r}, such that a base cell with $L=30$ was certainly adequate for the simulation of systems A and B.

Although we cannot prove that $L^*<40$ for system D, the fact that the results obtained at 460 and 480 K are coincident in the two calculations with $L=30$ and $L=40$ indicates a transition temperature for this system much higher than the value (425 K) predicted by the FRI theory. This is consistent with the observation that the transition temperature for system A is lower than indicated by the theory, while those for systems B and

C are higher, suggesting a trend that should be investigated by performing more calculations. Anyway, the FRI theory behaves quite well in this respect for x between 3 and 4, V_r between 1·25 and 1·5 and T^* between 250 and 450 K, that is in a range of values comparable with those found in most low molecular weight liquid crystals. Figure 4 indicates that this is also true for the orientational distribution around the z axis. For each system investigated, including system C, the orientational distribution found in the Monte Carlo simulations is always close to that calculated according to the FRI theory for the same system at a temperature such that the order parameter is the same.

The temperature dependence of the order parameter in the proximity of the transition point is shown in figure 7 for all simulated systems. Dotted curves refer to the behaviour evaluated for systems A and D according to the FRI theory; the curve for system C (not shown) is intermediate, while the curve for system B is very close to that for system A. The full curve represents the universal behaviour expected on the basis of the Maier–Saupe theory. Transition data predicted by the theories and obtained in our simulations are listed in table 3 (T_{NI}(MS) are the transition temperatures evaluated for the various systems on the sole basis of the anisotropic attractive interactions). Although the uncertainty on the exact location of the data points in figure 7 is quite high (presumable error bars are shown in a few cases), the order parameters obtained in the simulations are seen to be much smaller than those predicted by the FRI theory. For instance, s_{NI} is calculated according to the theory to be 0·65 for system C, while it is as small as 0·56 in the nematic phase obtained in our simulations at 290 K. In other words, the theory seems to overestimate the degree of order in nematic systems at the transition point with respect to our simulations.

4. Conclusions

We have utilized the Monte Carlo method to obtain computer models of systems of rigid molecules with axial ratio 3, 4 and 5 at densities comparable with the density of the mesogenic groups in liquid crystalline substances. Our calculations differ from those reported in the recent literature because: (i) the model molecules can be easily modified to include features characteristic of real liquid crystals, such as a partial flexibility, the presence of flexible end tails, the presence of side groups, etc.; (ii) the simulated systems are such that the results

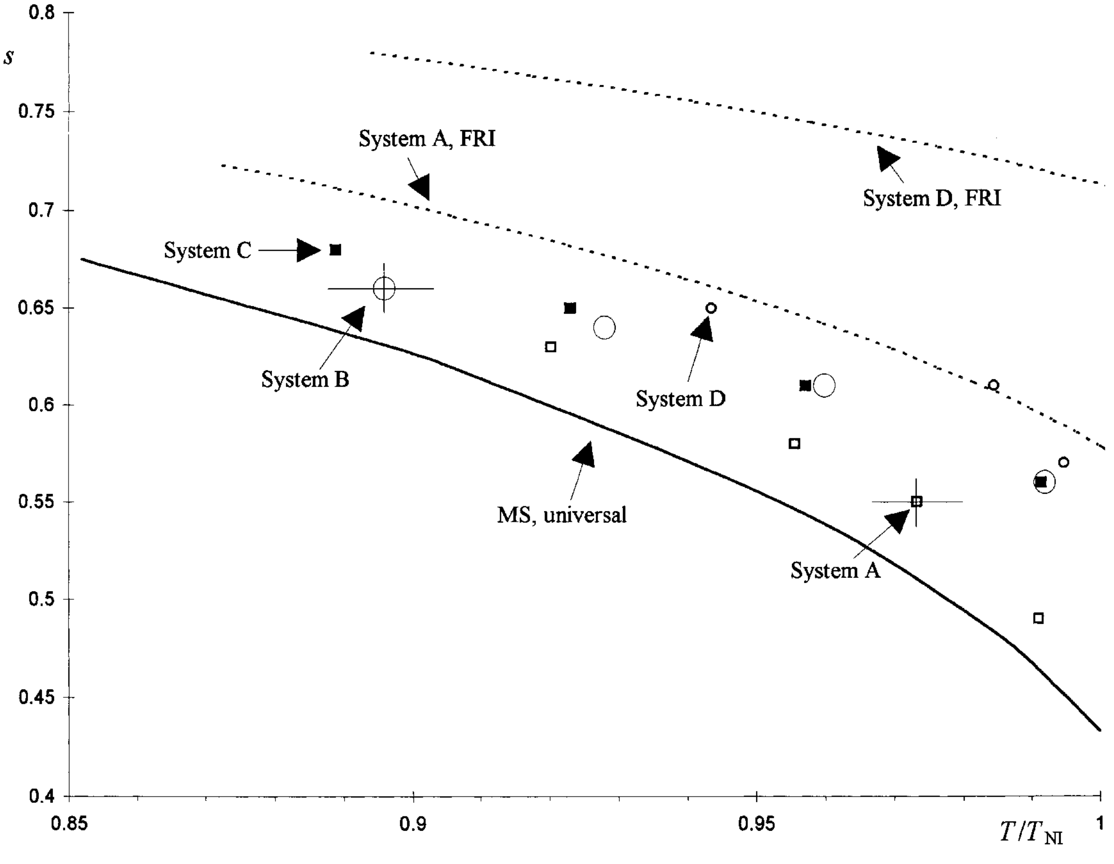

Figure 7. The order parameter of the various systems studied as a function of T/T_{NI}.

can be directly compared with the predictions of the FRI theory; (iii) we prove that our results do not depend on the size of the base cell utilized in the simulations.

Considering that the FRI theory is based on a lattice and that the simulated molecules are not exactly coincident with those studied by the theory, the results of our calculations are in remarkably good agreement with this theory, especially for systems with T_{NI} close to room temperature. In fact, for the three systems with axial ratio 3 and 4 and with values of V_{r} and T^* chosen such that $T_{\mathrm{NI}} \approx 300\,\mathrm{K}$ (systems A, B and C), the nematic–isotropic transition temperatures found in the simulations differ only a few degrees from those indicated by the theory. Also, the orientational distributions of the molecular long axes with respect to the nematic director obtained in our simulations for all systems and all temperatures are in good agreement with those evaluated according to the FRI theory, provided that the order parameter is the same. Differences between theory and simulations are found only with respect to the degree of order in the nematic phases, in the sense that the simulated systems are less ordered than indicated by the theory. This relatively minor discrepancy can be partly attributed to a residual rigidity of the lattice constituting the basis of the theoretical treatment, and partly to the fact that the simulated molecules interact in our calculations through a more realistic Lennard–Jones potential, instead of being sequences of impenetrable lattice units. On the other hand, the order parameters at the transition points predicted by the FRI theory are higher than the values 0·3–0·4 typically observed for low molecular weight liquid crystals. This has been attributed to the neglect of local fluctuations in the mean field approach and to the perfect rigidity assumed in the theory for the model molecules [6]. Since both the mean field and perfectly rigid molecules have been included in our simulations, it appears that the effects of these two approximations may be less important than suspected.

The results reported in this paper refer in all cases to calculations performed for systems with $L \geqslant L^*$, L^* being the minimum value of L such that the simulation results are size independent. We have shown that $25 < L^* \leqslant 30$ for system C, and $L^* > 30$ for system D. It seems then very reasonable to assume that $L^* \leqslant 30$ for systems A and B, owing to the fact that both these systems are less dense than system C and the axial ratio in system A is smaller. The necessity of modelling such large systems in order to achieve size independency of the simulation results is possibly a consequence of the mean field approximation, adopted in this paper to make the results comparable with the predictions of the FRI theory. Since this approximation can be easily removed by explicitly evaluating orientation dependent attractive interactions as a function of the distance of separation of the interacting units, it will be quite interesting to compare the size dependency of the behaviour of mean field and non-mean field systems. We have also performed calculations with various values of $r_{\min}$, indicating that the behaviour of the simulated systems depends strongly on how the intermolecular repulsions are handled. For instance, the fully ordered initial configuration generated for system B gave the isotropic liquid when equilibrated at 310 K with $r_{\min} = 0{\cdot}75$, while a nematic phase with $s = 0{\cdot}56$ was obtained with $r_{\min} = 0{\cdot}85$. A similar calculation for system C (1600 molecules, $L = 20$) produced at 300 K an ordered phase with $s = 0{\cdot}62$ for $r_{\min} = 0{\cdot}85$, instead of the isotropic phase obtained for $r_{\min} = 0{\cdot}75$. This result was mentioned in [24] without reporting the value of $r_{\min}$, since the importance of this parameter was unknown at the time. Our calculations suggest then that results obtained for hard bodies may not be immediately transferable to systems of molecules interacting with realistic potentials. Lastly, we have checked that the Fourier transform of the distribution of the various units along the z axis does not show evidence of long range positional order for all the systems studied. This is not surprising, since it was the purpose of this work to investigate the behaviour of the simulated systems at temperatures close to the nematic–isotropic transition points. It is obviously possible that the model could exhibit more structured phases at lower temperatures and/or higher densities.

At variance with fixed shape bodies like spherocylinders or ellipsoids, the model molecules simulated in our computer experiments can be easily modified to study the effects of simple constitutional changes. For instance, the intramolecular positional and orientational correlations between mesogenic groups and end tails can be investigated by simulating systems at a liquid density in which the orientation of the terminal units is unrestricted or restricted only in part. Though quite long, due to the small free volume, calculations of this kind are nowadays feasible even for large systems like those studied in the present work. Similar models in which flexible or semi-flexible units are linked to the mesogenic groups as side chains can be utilized to study the experimentally observed strong effects [25] of lateral substituents on the thermal stability of anisotropic phases. Several other molecular features characteristic of liquid crystalline materials can be easily introduced, such as a small amount of flexibility of the mesogenic groups or a slightly bent fixed shape. Finally, we are studying modifications of our methods allowing us to investigate the behaviour of oligomers with mesogenic groups in the main chain or in the side chains.

Note added in proof

After our paper was accepted, we became aware of the work of M. Yoshida and H. Toriumi (1995, *Mol.*

Cryst Liq. Cryst., **262,** 525), simulating systems of model molecules constituted by four aligned LJ centres. Their results suggest that anisotropic phases may be stable even in the absence of explicit anisotropic attractive interactions, provided that the density is much higher than those examined in our work.

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