Computer simulation of liquid crystals

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SUMMARY

We review recent progress in the computer simulation of liquid crystals, with special emphasis on hard particle models. Surprisingly, the simplest molecular models, taking account only of molecular size and shape, are sufficient to generate a wide variety of liquid crystalline phases, closely analogous to those observed in real life. Thermodynamic stability of different phases is very sensitive to shape, and presumably will also be sensitive to further details of intermolecular interactions as they are incorporated into the model. Realistic atom–atom potential models of liquid crystals are available, but the associated simulations are quite expensive. Thus, while idealized models may be used to study quite general, fundamental properties of mesophases, the modelling of specific liquid crystal systems in a realistic way remains a great challenge. Progress continues to be made on both these fronts.

INTRODUCTION

In this paper we shall describe some of the progress that has been made in recent years in the computer simulation of liquid crystals. Our aim is to offer an overview of the current status of the field and to pick out some specific examples from our own research, to illustrate the way in which computer simulation may be used. We shall not dwell on the technicalities of the Monte Carlo and molecular dynamics methods, preferring instead to concentrate on the molecular modelling aspects, and the science that emerges from such work, but we give references to the methodology where appropriate.

The liquid crystalline state (see Refs. 1 and 2 for an introduction to the subject) is said to be a *mesophase*, intermediate between the familiar solid and liquid phases of matter. The constituent molecules are able to diffuse fairly readily, and viscous flow can occur, just as in a liquid, while at the same time there is long-ranged ordering of the molecular orientations, as in a solid; in some cases, there is also long-range ordering of some of the positional degrees of freedom. Liquid crystals present a substantial challenge to the computer simulator. Firstly, the molecules which are

known to form liquid crystalline phases are quite complicated: some examples are shown in Fig. 1. This makes them expensive to model realistically. Secondly, the interesting phenomena which characterize liquid crystalline behaviour occur over time scales and length scales which are large compared with the familiar molecular units of picoseconds and nanometres. This means that, in some circumstances, lengthy simulations of large systems will be required to obtain properties of interest for comparison with theory and experiment.

This has not deterred computer simulators from taking the first few steps along the road to modelling liquid crystal phases, and recently these efforts have begun to reap rewards. We can classify the simulations conducted to date into four general areas in order of increasing complexity of the molecular models adopted: lattice models; hard nonspherical models; soft nonspherical models; realistic atom–atom potential models. In this review we shall devote most attention to hard nonspherical models, because they have been subject to the most extensive investigation in recent years. In the following section, we use these models to illustrate what a liquid crystal is, and what may be learned from simulations of this kind. Next we describe briefly the progress that has been made using other molecular models, and in the final section we summarize our conclusions.

HARD NONSPHERICAL MODELS

It is well-known that the atomic hard sphere model provides a sound basis for understanding the properties of simple liquids [3]. In broad terms, liquid structure is dominated by the harsh repulsive interactions between atoms as they approach each other closely, and this is simply represented by the infinitely steep hard sphere potential. The effects of long-range attraction, and the softness of the short-range repulsion, can be tackled as perturbations.

One feature of the molecules that form mesophases is that they are highly nonspherical (see Fig. 1). The question naturally arises as to whether or not hard nonspherical bodies such as spherocylinders and spheroids can be used to model molecular fluids, and especially liquid crystals. This would allow us to mimic the basic effects of molecular size and shape. It is not self-evident that this will be enough: molecular shape is just one factor in determining the stability of mesophases,
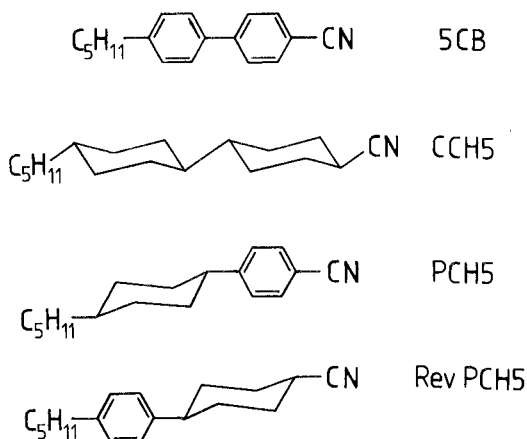

Fig. 1. The structures of four molecules, discussed in the text, which give rise to nematic liquid crystal phases.

and the other factors (electronic charge distribution leading to electrostatic forces, significant polarizability anisotropy, molecular flexibility) are all present in the molecules of interest here (see Fig. 1). Nonetheless, bearing in mind the lessons of hard spheres, a hard convex body seems a good starting point; once we understand it (a little) we can build in the other features in a step-by-step way.

Furthermore, it has been known since the work of Onsager [4] (see also Refs. 1 and 5) that orientational ordering will be seen when the density of a system of needle-like hard bodies, or indeed thin plate-like ones, is increased. Specifically, Onsager considered spherocylinders, i.e. cylinders of length L, diameter D, with hemispherical caps at the ends. He showed that a transition from the isotropic (disordered) fluid phase to a nematic liquid crystal (one in which the molecular axes are aligned, but no other long-range order exists) may be expected at a reduced number density $\rho_{IN} \sim (D/L)\rho_{cp}$, provided that $L \gg D$. Here we are measuring density as a fraction of the close-packed solid density ρ_{cp}, so this transition will occur well below the density ($\rho \sim 0.8\rho_{cp}$) at which the system would be expected to crystallize.

A similar argument applies [5] in the case of hard ellipsoids. These are spheres which have been uniformly elongated, or compressed, in one direction. The system is characterized by the number density and the axial ratio $e = a/b$, where a is the length of the major, or symmetry axis and b the length of the two equivalent minor, perpendicular axes. Values of $e > 1$ correspond to prolate, cigar-shaped ellipsoids, and $e < 1$ to oblate discus-shaped ones; $e = 1$ is the familiar hard-sphere case.
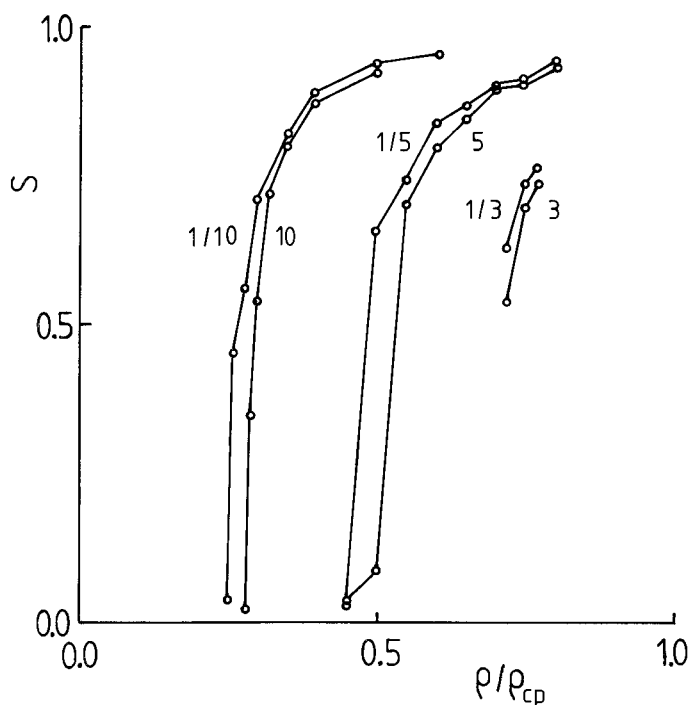

Fig. 2. Order parameter S vs. density (relative to close-packed density) for hard ellipsoids with axial ratio $e = 1/10, 1/5, 1/3, 3, 5, 10$.

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Simulations of spherocylinders and ellipsoids were carried out by Vieillard-Baron [6] in the early 1970s, using the Monte Carlo method. Insufficient computer time prevented definite conclusions from being drawn on the question of orientationally ordered phases in three dimensions. In the following years both systems were studied further by Monte Carlo [7–9], but more than a decade elapsed before liquid crystal phases were definitely observed.

For hard ellipsoids, the regions of stability of nematic liquid crystal phases have been established by Monte Carlo simulation for $e = 1/3$, $1/2.75$, 2.75, 3 [10]. For less extreme axial ratios, no nematic phase is seen. One of the striking features of the phase diagram is its near-symmetry under the prolate $\leftrightarrow$ oblate, $e \leftrightarrow 1/e$ transformation. We have recently extended the original study, comparing thermodynamic and dynamical properties of prolate and oblate ellipsoids, and examining more extreme values of e. We carry out molecular dynamics simulations for a few hundred ellipsoids, with periodic boundary conditions applied in the usual way to remove surface effects.
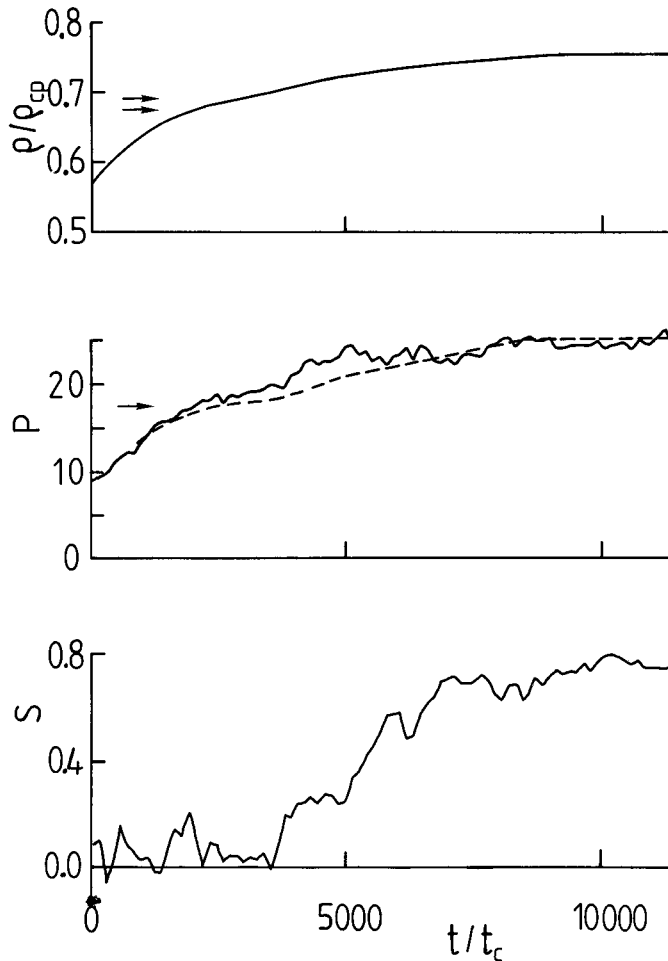

Fig. 3. Time evolution on compressing hard ellipsoid $e = 1/3$ system. Time is measured in units of the single-particle mean time between collisions, t_c. We show density, as a fraction of close-packed density, pressure P in arbitrary reduced units, and the order parameter S.

In this work, the periodic simulation 'box' is in the shape of a truncated octahedron. Further technical details are given elsewhere [11]. In Fig. 2 we show the degree of alignment (the nematic order parameter S) as a function of density for $e = 1/10, 1/5, 1/3, 3, 5, 10$. The similarity between corresponding prolate and oblate systems is apparent but there are also systematic differences: the plate-like systems are slightly more aligned at a given density than the corresponding needle-like ones, and the nematic phase seems to extend to lower densities, so the phase diagram symmetry is not perfect. Exact location of the phase boundaries, by free-energy calculation, has not yet been carried out for $e = 1/10, 1/5, 5, 10$.

We observe *spontaneous* ordering to form the nematic phase on uniformly compressing the isotropic phase through the transition density. It is not necessary to apply an external field. We have made a movie of this process for the case $e = 3$ [12]. In Fig. 3 we plot the time evolution of the density, pressure, and order parameter of the complementary system of oblate ellipsoids with $e = 1/3$. As the system is compressed beyond the limit of thermodynamic stability of the disordered phase, it at first follows a metastable extension of the isotropic liquid equation of state, before jumping over to the nematic branch. In some cases the preferred alignment direction (the *director*) may end up along one of the simulation box symmetry axes; in other cases no special direction is induced by the periodic boundary conditions. Of course, when the existence of a stable nematic phase has been demonstrated, it may be convenient to prepare a system ready-aligned along (say) the z-direction. The extent to which the periodic boundaries influence the properties of the system is thought to be small, but has not been fully investigated.

If we translate the simulation parameters into appropriate molecular units, it turns out that the equilibration runs of Fig. 3 and Ref. 12 correspond very approximately to 0.5–1.0 ns in real time. Production runs, to measure structural and dynamical properties, are up to ten times as long.

We can illustrate the nature of these phases by giving a snapshot of the systems at various densities. In Fig. 4, we show the oblate $e = 1/5$ system in the isotropic phase at $\rho/\rho_{cp} = 0.45$ and in
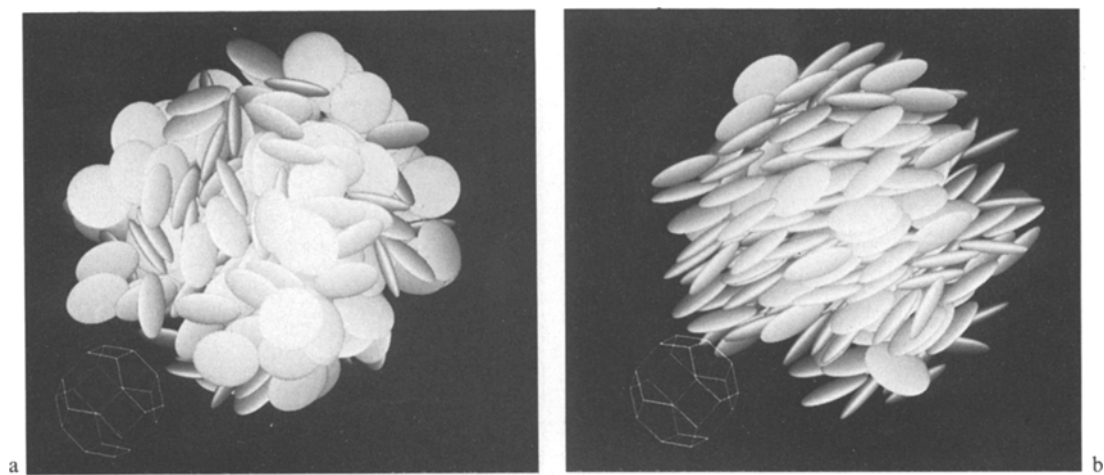

Fig. 4. Oblate hard ellipsoids, with $e = 1/5$, $N = 216$. In this and the following snapshots we indicate the shape and orientation of the simulation box by a line drawing in the corner. For clarity, we only display particles whose centres lie within the basic simulation box, but full periodic boundary conditions are to be understood. (a) $\rho/\rho_{cp} = 0.45$; isotropic liquid. (b) $\rho/\rho_{cp} = 0.55$, nematic liquid crystal.

the nematic phase at $\rho/\rho_{cp} = 0.55$. For obvious reasons the ordered phase is sometimes termed *discotic*. Similar pictures are seen for $e = 1/3$, $1/10$, and in the thin platelet limit $e = 0$ [13].

In Fig. 5, we show isotropic ($\rho/\rho_{cp} = 0.25$) and nematic ($\rho/\rho_{cp} = 0.35$) configurations for the needle-like $e = 10$ system. These illustrate the relatively low densities needed to induce orientational ordering as the Onsager limit is approached. A detailed comparison with Onsager's prediction will have to await the exact determination of the simulation transition densities, by free energy calculations. However, we cannot expect Onsager's theory to be very accurate even for these quite thin needles: it relies on the vanishing of third- and higher-order virial coefficients, and this happens only very slowly as the nonsphericity increases [5].

Some comparisons of simulated properties with experimentally measured ones have been made, although of course quantitative agreement cannot be expected with such a simple model. The initial results are encouraging. The isotropic-nematic transition for hard ellipsoids seems to be weakly first-order [10], in accord with experiment. Nematic precursor fluctuations, the slow collective molecular reorientations that herald the onset of nematic ordering, have been observed [14]. The Frank elastic constants, which measure the 'stiffness' of a liquid crystal as it resists orientational deformations, have been calculated, and they appear to be of the correct order of magnitude [15]. Moreover, the effects of finite system-size appear to be fairly small for the systems studied (up to 500 molecules) [11].

Hard spherocylinders have a somewhat different phase diagram. Frenkel and co-workers have investigated a system of spherocylinders whose symmetry axes are constrained to be perfectly aligned with each other [16], and have extended this work to look at the unconstrained system with full translational and rotational freedom [17]. The pictures in Figs. 6 and 7 show four phases exhibited by unconstrained spherocylinders with $L/D = 3$ and $L/D = 5$. At high densities an ordered solid exists, consisting of layers of aligned molecules, each layer in a hexagonally-packed arrangement. This is shown for $L/D = 3$ in Fig. 6a. As the density is reduced (see Fig. 6c), the molecules become mobile, and the long-range ordering within the layers is lost, as becomes clear from a projection in the z-direction. The layers themselves, however, are preserved and molecular ori-
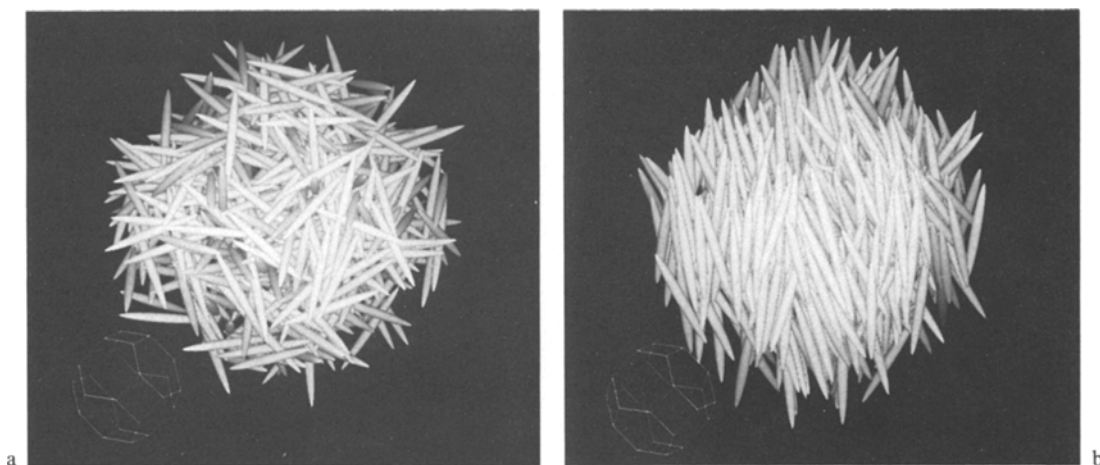

a   b

Fig. 5. Prolate hard ellipsoids, with $e = 10$, $N = 500$. (a) $\rho/\rho_{cp} = 0.25$, isotropic liquid. (b) $\rho/\rho_{cp} = 0.35$, nematic liquid crystal.
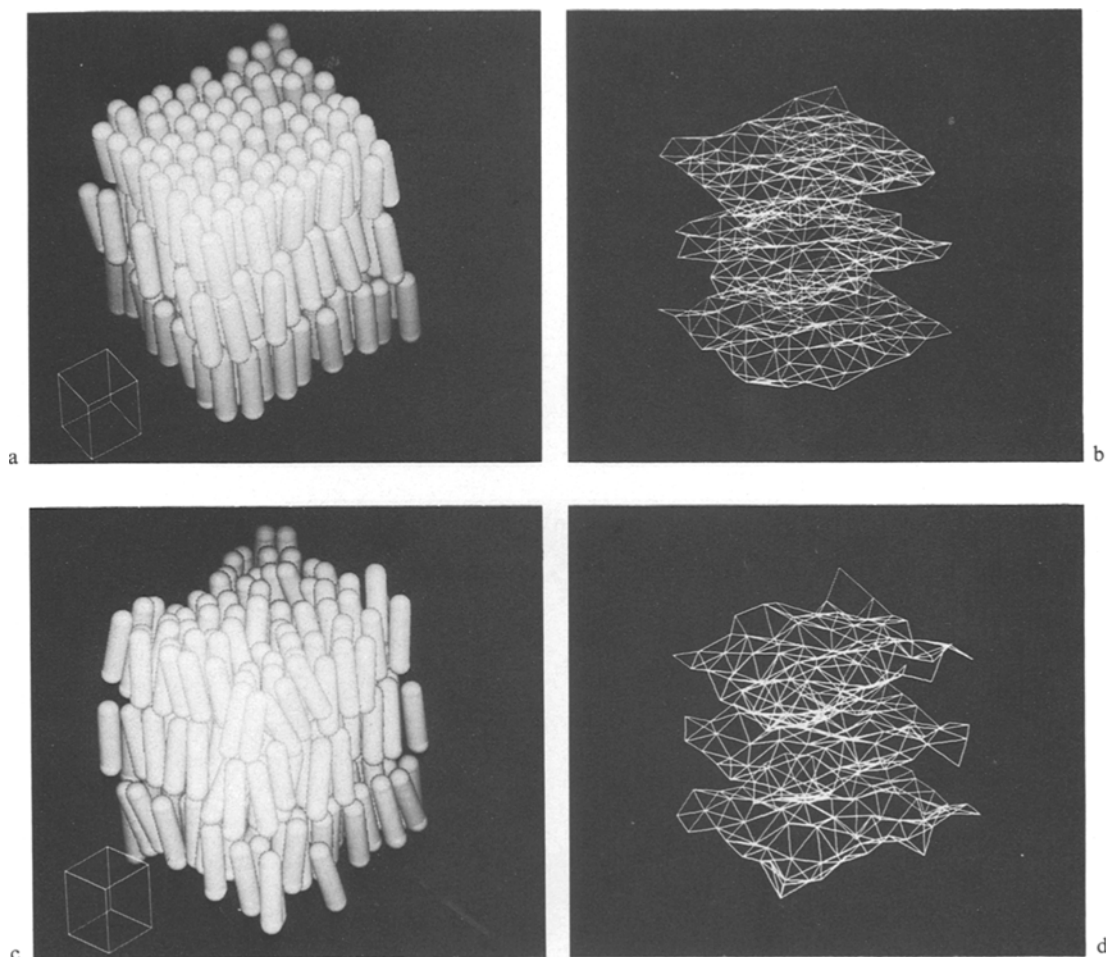
Fig. 6. Spherocylinders with $L/D = 3$, $N = 240$. (a) $\rho/\rho_{cp} = 0.7$, solid. (b) Same as (a), showing nearest-neighbour lines. (c) $\rho/\rho_{cp} = 0.6$, smectic liquid crystal. (d) Same as (b), showing nearest-neighbour lines.

entations are still well-ordered perpendicular to the layers: the system is a smectic-A liquid crystal. The layers are most easily seen by drawing lines between the centres of neighbouring spherocylinders, where a 'neighbour' is defined within a distance of about 2 D. This is shown in Figs. 6b and d. At lower densities a nematic liquid crystal should exist, although its range of stability has not yet been determined for this value of L/D, and may be quite narrow. An isotropic liquid is seen as the density is reduced further still. The smectic phase for $L/D = 5$ is illustrated in Fig. 7a for a very large system of 1152 particles. At lower densities the layering disappears, giving a nematic liquid crystal (Fig. 7b) and eventually the orientational order vanishes to give an isotropic liquid (Fig. 7c).

In this work, it was necessary to check the possibility that the apparent smectic layering was an artifact of the periodic boundary conditions used in the simulations. This seems to have been sat-
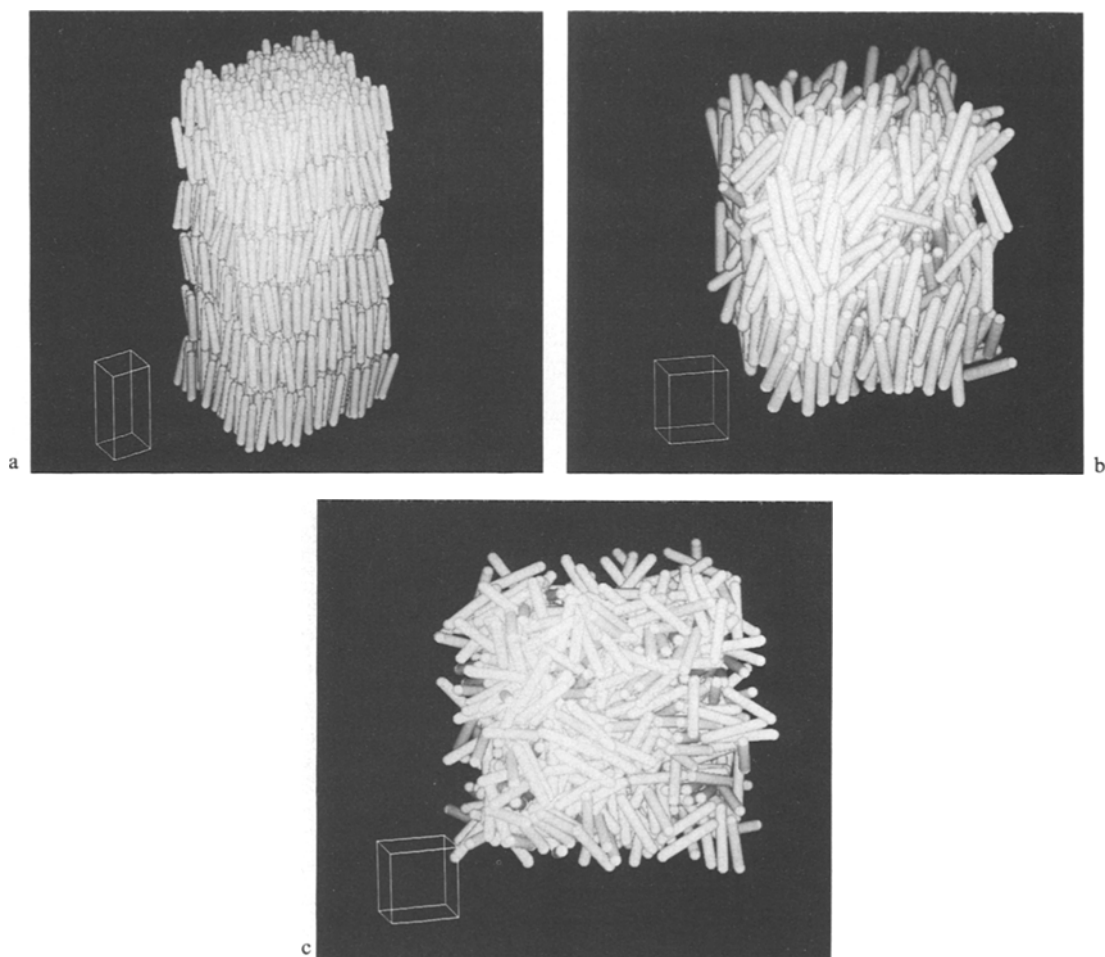
Fig. 7. Spherocylinders with $L/D = 5$. (a) $N = 1152$, $\rho/\rho_{cp} = 0.6$, smectic liquid crystal. (b) $N = 576$, $\rho/\rho_{cp} = 0.5$, nematic liquid crystal showing some smectic precursor fluctuations. (c) $N = 576$, $\rho/\rho_{cp} = 0.4$, isotropic liquid.

isfactorily demonstrated by Frenkel and co-workers, by allowing the simulation box sides to vary in length during the course of the run, and observing (in the aligned spherocylinder case) the interconversion of states with different numbers of layers as the density was changed up and down. It is important to stress that *spontaneous* smectic ordering (rather than ordering set up in the initial conditions) has been seen in this work.

More recent studies have examined, using the molecular dynamics technique, the time-dependent smectic precursor fluctuations which occur as the nematic-smectic transition is approached from the nematic side. The dynamical technique has also allowed a comparison of diffusion coefficients parallel to the smectic layer planes, corresponding to motion within layers, and in the perpendicular direction, corresponding to inter-layer motion. Further details can be found elsewhere [11]. As in the case of ellipsoids, there are no dramatic, unexpected discrepancies between the properties of hard spherocylinders and those of real liquid crystals.
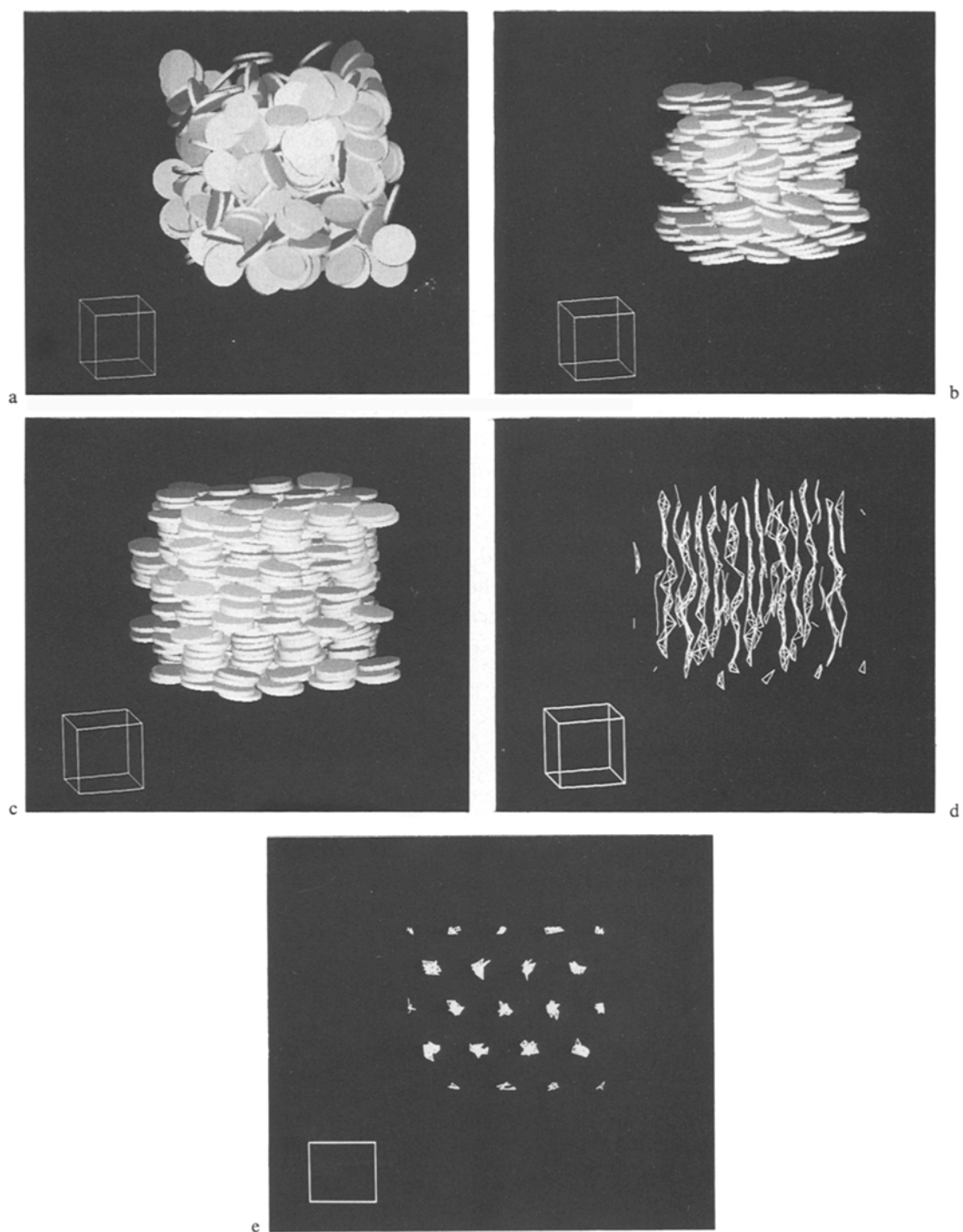
Fig. 8. Cut spheres with $L/D = 0.1$. (a) $N = 256$, $\rho/\rho_{cp} = 0.25$, isotropic liquid. (b) $N = 256$, $\rho/\rho_{cp} = 0.5$, nematic liquid crystal. (c) $N = 512$, $\rho/\rho_{cp} = 0.6$, columnar phase. (d) Same as (c), showing nearest neighbour lines. (e) Same as (d), but viewed from directly above.

Finally, we turn to another hard-particle model: spheres, in which the top and bottom have been cut off, to give a disk-like shape. This model is again defined by a length-to-width ratio L/D, with D being the sphere diameter, and L ($< D$) being the distance between the parallel flat surfaces. These systems have again been studied by Frenkel [18, 19]. Some configurations for $L/D = 0.1$ are shown in Fig. 8. Isotropic and nematic phases are seen (Figs. 8a and b) just as for oblate ellipsoids, but in addition the disks tend to stack up into columns as shown in Fig. 8c. Again, the columnar structure can best be seen by joining nearest neighbours, defined within a distance of roughly 0.5 D (see Figs. 8d and e). The stacks are hexagonally arranged, but with only short-range order within them, thereby distinguishing this *columnar* phase from a solid. There is some evidence for a yet more interesting phase in this system [19]. In Fig. 9 we show a snapshot of a configuration with $L/D = 0.2$. Short-range columnar ordering is apparent, but there is no long-range nematic-like ordering of the axes. However, four-fold orientational ordering, resulting from the packing of short stacks of molecules against each other, with frequent 90° angles, does seem to be long-ranged. The name 'cubatic' has been proposed for this phase, but we should emphasize that its existence is only a tentative suggestion at present.

SOFT NONSPHERICAL MODELS

The next degree of sophistication beyond hard particles is to continue to represent the molecular shape in a simple way, but as a soft rather than a hard body. In addition, long-range attractions between molecules are included. Such potentials are essentially anisotropic versions of the Lennard–Jones potential

$$v(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right]$$

used in atomic simulations. Here ε and σ are energy and length parameters, respectively, while r is the interatomic distance. For such potentials temperature can play a role in determining ther-
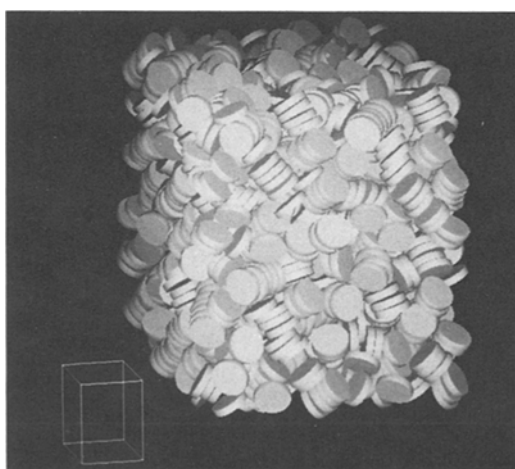

Fig. 9. Cut spheres with $L/D = 0.2$, $N = 1728$, $\rho/\rho_{cp} = 0.625$.

modynamic equilibrium, a feature which is absent in hard-particle models. The simplicity of the potential means that timescales in the ns region are accessible, given current computing resources.

Once more the first moves in this direction took place in the early 1970s, with the development by Berne and Pechukas [20] of the 'Gaussian overlap' model. This was essentially a modified Lennard–Jones form, in which ε and σ were made dependent upon the separation vector and orientations of the two bodies. The model can be thought of as being based on 'soft attractive ellipsoids', in that it has the same symmetry as the hard ellipsoid model. The idea was to fit potentials of this kind to an underlying, more realistic, atomic model of the molecule of interest. It was used in attempts to simulate a nematic liquid crystal [21–23] although subsequent work suggests that this is unstable relative to the isotropic liquid [24]. The original potential also suffered from some unrealistic features, but was improved [25] and the new potential has been used extensively by Luckhurst and co-workers [26].

Adams et al. [24] have demonstrated that, with a suitable choice of parameters, a stable nematic phase can be seen. Subsequent work [26] has shown that the system will form, under appropriate conditions, a smectic-A and then a smectic-B phase, before crystallising. In this work $\sigma_{ee}/\sigma_{ss} = 3$ and $\varepsilon_{ee}/\varepsilon_{ss} = 0.2$, where 'ee' denotes an end-to-end pair configuration and 'ss' denotes a side-by-side arrangement. Thus the molecular shape is elongated, and side-by-side alignment is energetically favoured, as would be expected for real molecules of this kind. The other simulation parameters can be found in the original reference [26]. At high temperatures, an isotropic phase is seen. On cooling from a temperature (in Lennard–Jones scaled units) of $T = 2.5$ to $T = 2.0$, a nematic phase with order parameter $S \approx 0.4$ is formed (see Fig. 10a). (At this modest degree of ordering, it is not easy to spot the molecular alignment by eye. The director is vertical in Fig. 10.) Further cooling to $T = 1.5$ induces a high degree of orientational ordering ($S \approx 0.8$) and also the formation of layers perpendicular to the director (see Fig. 10b). There is no long-range ordering within the layers, however, and so this is a normal smectic-A phase. On reducing the temperature to $T = 1.0$ the orientational ordering increases further ($S \approx 0.9$), and a hexagonal arrangement of molecules within layers sets in. This can be seen from Fig. 10c, but of course is most apparent when looking along the director. For simulations of this size true long-range translational ordering cannot be distinguished from the algebraically-decaying order which characterizes two-dimensional hexatics, but in either case the phase is identifiable as a smectic-B. The observation of molecular diffusion distinguishes this phase from a crystal, which is formed on further lowering the temperature to $T = 0.5$ (Fig. 10d).

Another promising model of this kind is the Kihara potential [27]. Again, a Lennard–Jones form is adopted, but now r is taken as the shortest distance between two convex bodies. If these are simply thin rods, the results is a soft 'Lennard–Jones spherocylinder' model (replacing the Lennard–Jones form by the hard-sphere form would give the usual hard spherocylinders discussed earlier). Simulations of this model have been undertaken [28], but no liquid crystal phases have been reported as yet.

REALISTIC MODELS

It is evident, from the wealth of experimental data available [29] that the stability of the various mesophases found in real life is extremely sensitive to the fine details of intermolecular interactions. Despite an increased understanding of these phases, it is becoming increasingly difficult to
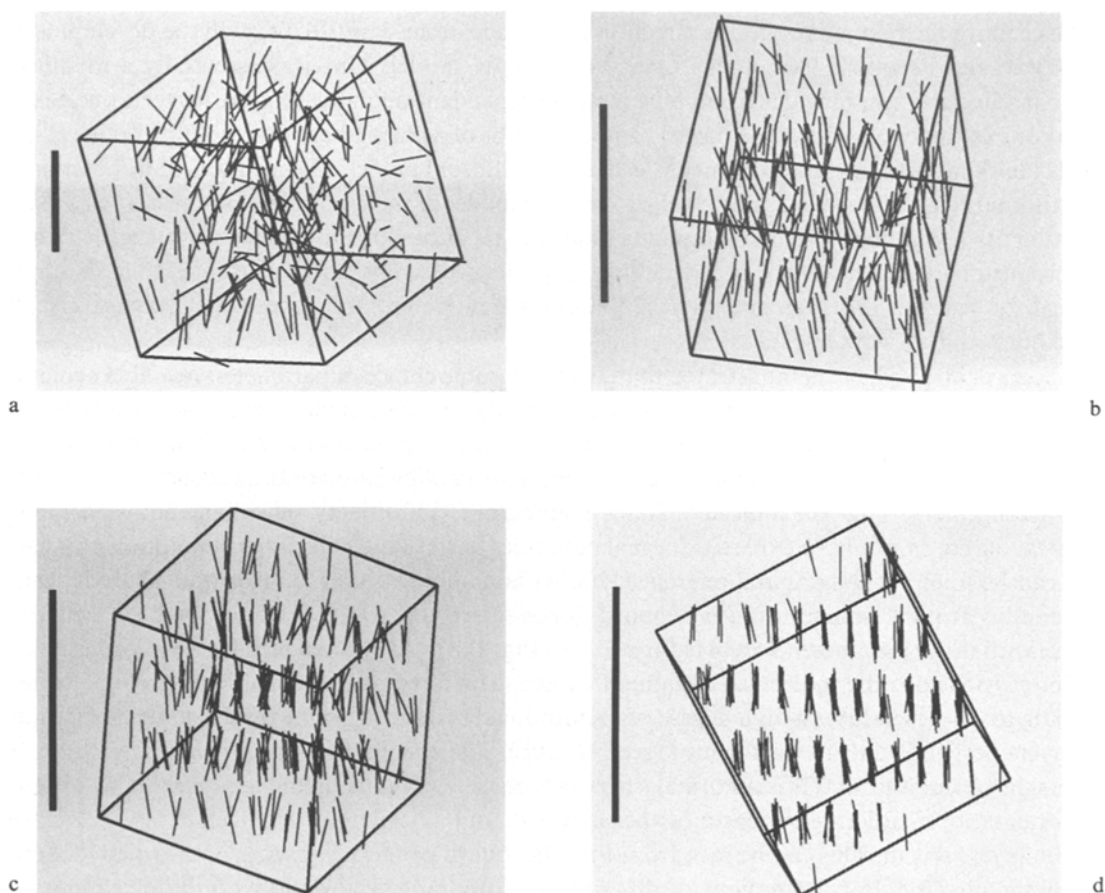
Fig. 10. Gay–Berne ellipsoids with $\sigma_{ee}/\sigma_{ss}=3$, $\varepsilon_{ee}/\varepsilon_{ss}=0.2$, $N=256$. The molecular symmetry axes are represented by line segments, and the cubic simulation box is also shown. This is oriented so as to make the director vertical. The thick vertical line on the left indicates the magnitude of the order parameter: for $S=1$ it would be the same length as the side of the simulation box. (a) $T=2.0$, nematic liquid crystal. (b) $T=1.5$, smectic-A liquid crystal. (c) $T=1.0$, smectic-B liquid crystal. (d) $T=0.5$, crystal.

relate molecular structure to phase behaviour with any degree of certainty [30]. In many cases interesting effects occur. For example, 4-(*trans*-4-n-pentylcyclohexyl)benzonitrile (PCH5) shown in Fig. 1 exhibits a nematic phase between 31 and 55°C [31] but if the rings are reversed to give 4-(*trans*-4-n-pentylphenyl) cyclohexylcarbonitrile (Rev-PCH5) we find that a nematic phase is formed at −25°C [32] only on supercooling from the isotropic liquid. Thus, despite the success achieved in simulating mesophases with relatively simple potentials, in order to understand effects of this type the computer simulator must include detailed aspects of molecular structure in the model.

To do this techniques may be borrowed from the modelling of proteins and nucleic acids. The assignment of soft Lennard–Jones potentials to each atom in the system provides a complicated

intermolecular potential which models the detailed shape anisotropy of real molecules [33], yet is simple to program. Such a potential can account for both changes in excluded volume and polarizability between different molecules, by the use of different nonbonded parameters for each atom type. Dipolar interactions may also be included in the model. Typically these are represented by partial electronic charges on each atom which interact via a Coulomb potential (though in many thermotropic liquid crystals charge interactions are small compared to dispersive and steric effects [33]). It is common practice to use a *united atom* force field which replaces hydrogens attached to non-electronegative atoms by single united atoms. This approach greatly reduces the total number of atoms in the system with a consequent reduction in computer time. The intermolecular parameters can be derived by a variety of techniques [34].

Use has been made of these potentials in a series of molecular mechanics calculations on pairs of rigid mesogens. The calculations produced a series of minimum energy configurations for two molecules and examination of dimer energies and geometries, provided a semi-quantitative way of studying the relationship between molecular structure and intermolecular interactions. Despite the simplicity of the calculations, results have been encouraging. Calculations on 4-n-pentyl-4'-cyanobiphenyl (5CB) and *trans*-4-(*trans*-4-n-pentyl-cyclohexyl)-cyclohexylcarbonitrile (CCH5) (see Fig. 1) accurately modelled the relative strengths of anti-parallel/parallel dipole-dipole correlation seen experimentally [35], and studies of apolar angular correlation provided new insights into the role played by anisotropic dispersive forces in the stability of liquid crystalline phases [33]. Studies of larger clusters of molecules using modern molecular dynamics techniques provides the means of going beyond the two-particle model, thereby allowing the study of longer-range effects.

In practice however the modelling of molecules as rigid groups of atoms is a major simplification. In reality molecular structure is rapidly changing, leading to large changes in intermolecular interactions. It is desirable therefore to allow for some flexibility within a molecule. Traditionally this may be done by assigning a system of forces to each internal degree of freedom within the molecule. Potential functions are assigned to each bond stretch, bend, torsion, etc., in a standard way. Use can be made of the excellent parameterizations of molecular mechanics force fields such as MM2 [36], AMBER [37], and CHARMM [38], to model internal structure. In the molecular mechanics formulation the incorporation of molecular flexibility causes a severe problem by the introduction of many more potential energy minima. These complicate the potential energy surface to such a degree that it is difficult to obtain any useful information from the results [39]. In molecular dynamics however, we are interested in time-averaged phenomena, so the extra energy terms only have an adverse effect on the complexity of the program and the amount of computer time required. The equations of motion can be solved as usual in a step-by-step manner using standard finite-difference methods [40]. The time step in such simulations is typically of order 1–2 fs, much smaller than that used in the simulations of simple atomic systems, and is governed by the speed of the fastest motion in the system. Invariably this turns out to be the bond stretching motion. However, this may be excluded from the system by the use of constraint algorithms such as SHAKE [41] and RATTLE [42] which keep bonds rigid, thereby allowing longer time steps.

Although the prescription is simple, the simulations are so expensive that, to our knowledge, only one simulation of this kind has been attempted [43]. This work was an attempt to examine the specific effects of the charge distribution around the molecular framework on the stability of the nematic phase of 5CB. A system of 64 molecules was simulated for a total time of 60 ps. Although the simulation run lengths were limited by the available computer time, and clear evidence

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of problems with equilibration emerged from them, they pointed the way to the possibilities of success as computer power steadily improved.

Our current work in this area seeks to understand how subtle changes in molecular structure or temperature can lead to large changes in liquid crystal phase behaviour. Consequently, we are engaged in the simulation of a number of small thermotropic liquid crystal molecules. Figure 11 shows a snapshot from a system of 64 molecules of CCH5, simulated using the molecular dynamics module of AMBER [37]. The calculation employs a united atom force field and a 1 fs time step. On the Bristol University IBM 3090 with vector facility, each step takes about 1 second, so runs of a few ps are routine, but the ns regime is not easily accessible. This work is at an early stage, and we have not yet observed nematic ordering.

LATTICE MODELS

We turn now to rather more idealized models, based more on the spin systems of statistical physics than on molecular considerations. The system is taken to be a set of classical spin vectors, located on the sites of a cubic lattice, with nearest neighbour interactions.

$$v(\theta) = \varepsilon \left(\frac{3}{2} \cos^2 \theta - \frac{1}{2} \right)$$

θ being the angle between the vectors and ε an energy parameter. The spins should not be taken to represent individual molecules in a liquid crystal, as is evident from the imposed lattice structure and the crude form of the potential. Rather, each site represents a small region of the liquid, with the spin denoting the locally-averaged nematic ordering within that region. The interaction has the correct symmetry to describe, at the lowest order, the effect of one part of the liquid on another.

The model was proposed by Maier and Saupe [44] and solved within the mean field approxima-
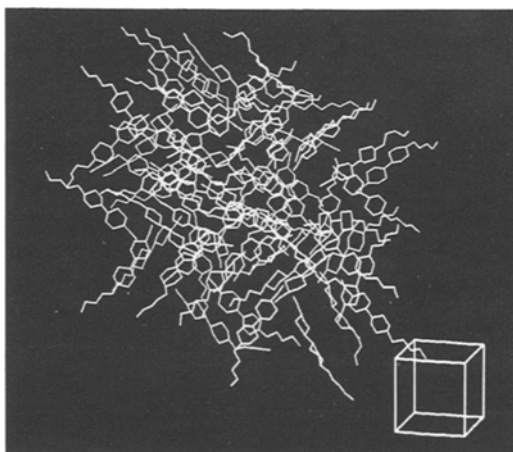

Fig. 11. A configuration of CCH5. For clarity, only the main chain bonds are shown.

tion, where a strongly first-order transition is predicted between nematic and isotropic states. Monte Carlo simulations of this model, by Lebwohl and Lasher [45] and later by Luckhurst and Simpson [46] and Fabbri and Zannoni [47] have eventually shown that the transition is really weakly first-order, and hence rather akin to that seen experimentally. Mean-field theory, therefore, is not a good guide for these systems. Recently, both simulation [48] and theoretical arguments [49] have addressed the possibility of extrapolating from systems of high dimensionality, where mean-field theory is accurate, to the real world of three dimensions.

Thin films of liquid crystal have been studied by Monte Carlo simulation using this model [50, 51] in an effort to examine liquid crystal surface characteristics. A fixed number of layers are simulated, with periodic boundary conditions in two directions, but with free surfaces at the top and bottom. The surface regions tend to be less well-ordered than the interior. Interest has focused on the shift of the transition temperature which occurs as a result of the presence of the surfaces, on the way this scales with the number of layers in the system, and on the possibility that the first-order character may disappear with decreasing film thickness.

In Fig. 12 we show the order parameter in each layer for a 10-layer and a 32-layer system, at several temperatures. The disordered surface layer penetrates into the system as the transition temperature is approached. There is great interest in comparing the measured extent of this penetration with theoretical predictions. Moreover, when the free surfaces are replaced by walls which exert a local orienting field there is the possibility of observing 'wetting' of the walls by orientationally ordered or disordered phases [52]. Theoretical studies (M. Telo da Gama and P. Tarazona, private communication) indicate that the phase diagram becomes very rich in these circumstances. These surface phase transitions are currently areas of study, and of great technological relevance, despite the crude model which has to be adopted.

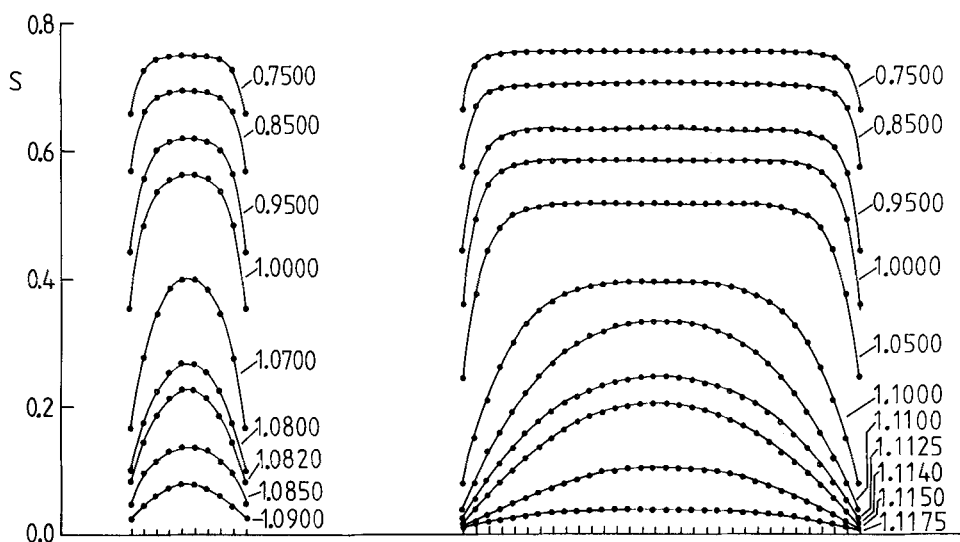The precise location of the transition temperature, and the study of equilibration and wetting

Fig. 12. Order parameter in each layer for various temperatures in the Lebwohl–Lasher model. We show the 10-layer system, for which $T_{IN} = 1.0830$, and the 32-layer system, for which $T_{IN} = 1.1145$.

phenomena, require extremely long simulation runs. These would be impossible for a realistic model with current computer resources. Very roughly, we can identify one Monte Carlo sweep or one molecular dynamics timestep for a simple model like this as representing about 1 ps. Total run lengths equivalent to about 1 μs are used to see the effects discussed here.

DISCUSSION AND CONCLUSIONS

All of the models described above bear some relation to the molecules known to form liquid crystals. While fairly realistic atom–atom models remain too expensive to simulate for long periods with current computer resources, we shall be forced to continue with the more idealized ones. Indeed, these simple models are of interest to the physicist, if not the chemist, in their own right.

Investigations on hard bodies have been more fruitful than perhaps we expected initially. They have shown that a highly nonspherical molecular shape alone is sufficient to produce a stable liquid crystal phase, and that indeed the thermodynamics is quite sensitive to shape. Encouraging signs have emerged from the few comparisons with real systems that have been made thus far. Of course, many factors contribute to these properties in real systems, and any agreement obtained with experiment may be fortuitous. Moreover, the stability of mesophases is clearly sensitive to the precise details of the shape, as has been seen already, and exactly how this can be related to a real 'soft' molecule is unclear.

It is possible that the anisotropy of the long-range forces cannot be neglected. Even the simple Lebwohl–Lasher lattice model has the correct phase transition properties, and this might be taken to justify the original ideas of Maier and Saupe, that the long-ranged, smoothly-varying, interactions between 'swarms' of molecules are the crucial factor in determining the stability of mesophases. However, it seems unlikely that a model based on this alone, or incorporating spherical rather than anisotropic cores, will constitute a realistic representation of liquid crystals.

None of the simulations to date have shed light on the importance of flexible head–tail interactions in determining the relative stability of isotropic, nematic, smectic and solid phases. In this re-
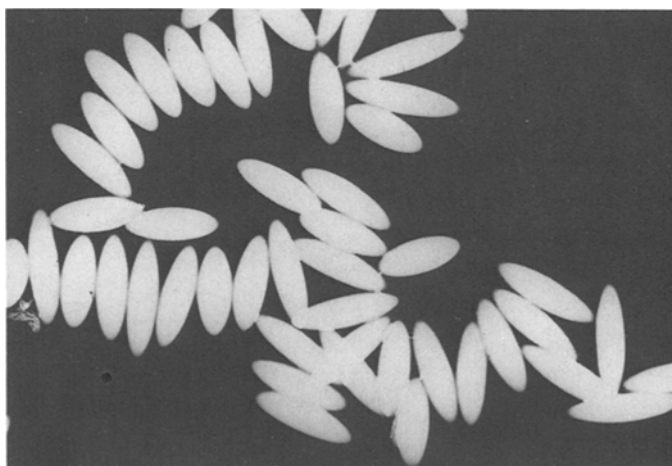

Fig. 13. A transmission electron micrograph of ellipsoidal polystyrene latex particles. For further details see Ref. 54.

spect, the next important step may be the further development of models based on soft nonspherical bodies, and perhaps with molecular flexibility incorporated in a controlled way.

Even if these models are too crude to describe real molecules, we can compare with other experimental systems. Colloids of spherical latex particles, the interactions between which are 'tunable' by varying the ionic strength of the solvent, have already provided a rich field of study. In suitable circumstances, direct comparison with the hard sphere model is appropriate [53]. It is now possible to prepare ellipsoidal latex particles of linear dimensions roughly in the range 0.1–10 μm, with specified axial ratio $1.1 \le e \le 10$ [54]. A typical configuration (obtained from a transmission electron micrograph) is shown in Fig. 13. This particular sample is quasi-two-dimensional, and the particles have aggregated together, but uniform three-dimensional suspensions can be prepared and are amenable to investigation by a variety of techniques. These ellipsoidal lattices should provide direct test-beds of both hard- and soft-ellipsoidal potentials.

Ultimately, we will want to simulate specific experimental liquid crystal systems in a realistic way. Currently, to allow for proper equilibration and production runs, this requires of the order of 50–500 hours of supercomputer time for a single state point. Thus, studies of this kind are just about feasible with current technology, and will become much more common in the next few years.

ACKNOWLEDGEMENTS

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