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Invited Lecture. Columnar ordering as an excluded-volume effect

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Invited Lecture

Columnar ordering as an excluded-volume effect

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The nature of the possible liquid-crystalline phases that a molecular or colloidal system may exhibit depends sensitively on the shape of the constituent particles. Recent computer simulations on fluids of consisting of non-spherical hard-core molecules suggest that, in order to predict the relative stability of isotropic, nematic, smectic and columnar phases in such very simple model fluids, it is not enough to characterize the molecular shape by an overall length-to-width ratio. New results of computer simulations on a model for disc-like molecules clearly illustrate this point.

1. Introduction

Entropy is often loosely referred to as a measure of the disorder in a system. The second law of thermodynamics expresses the fact that an isolated system tends to maximize its entropy, and hence its 'disorder'. At first sight, it is therefore somewhat surprising to find that this tendency to maximize entropy often appears to act as an *ordering* force. A famous example of such 'entropy-induced' ordering is contained in Onsager's theory of the transition from an isotropic fluid to a nematic liquid crystal [1]. Onsager showed that, at a sufficiently high density, a system of long rod-like molecules will spontaneously form an orientationally ordered phase. Yet, although the entropy associated with the orientational degrees of freedom does indeed *decrease* during this transition, this decrease is more than offset by the *increase* in the translational entropy of the system. The latter increase is a consequence of the fact that the average excluded volume of two rods in an orientationally ordered phase is smaller than in the isotropic phase.

What is more surprising is that it is even possible to have 'entropy-induced' ordering in systems without any orientational degrees of freedom. This was demonstrated in 1957 in the earliest molecular dynamics simulations by Alder and Wainwright [2]. These simulations showed that a system of hard spheres can undergo a first-order phase transition from a liquid to the crystalline solid. Again, entropy is the only driving force for this transition: the system loses 'configurational' entropy by ordering in a regular lattice, but it gains entropy because, at coexistence, the available free volume per molecule is larger in the solid than in the liquid.

It is important to note that the freezing transition of the hard-sphere model is not merely of academic interest. For instance, Kang, Ree and Ree [3] have developed a very successful perturbation scheme to predict the melting behaviour of atomic solids using the hard-sphere model as a reference system.

However, entropic ordering is not limited to the two classes of phase transitions mentioned above. An example of a model where both nematic ordering and freezing are caused by excluded-volume effects is a system consisting of hard ellipsoids of revolution. This model system was studied numerically by Frenkel and Mulder [4]. The shape of hard ellipsoids of revolution is characterized by a single parameter x, the ratio of the length of the major axis ($2a$) to that of the minor axis ($2b$): $x = a/b$. Prior to the simulations reported in [4], the phase behaviour of hard spheroids was only known for a few special values of x: (i) $x = 1$, hard spheres, which freeze at $\frac{2}{3}$ of close packing [5]; (ii) $x \rightarrow \infty$, thin hard needles (i.e. Onsager's model)—this system has a transition to the nematic phase at vanishing volume fraction; (iii) $x \rightarrow 0$, thin hard platelets, which also form a low-density nematic [6]. The simulations of [4] show how the stability of the different phases of hard ellipsoids depend on their length-to-width ratio. Four distinct phases could be identified: the low-density isotropic fluid; an intermediate-density nematic liquid-crystalline phase, which is only stable if the length-to-width ratio of the ellipsoids is larger than 2·5 or less than 0·4; and a high-density orientationally ordered solid phase. In the case of weakly anisometric ellipsoids an orientationally disordered solid phase was also observed.

An obvious question is whether hard-core molecules can only form nematic liquid crystals. For instance, one might wonder if hard ellipsoids of revolution can also form a smectic phase.

The answer to this last question is almost certainly 'no'. The reason is the following: smectic phases tend to have a large degree of orientational order. Hence, to a first approximation, we can assume that a smectic consists of perfectly aligned non-spherical molecules. However, a system consisting of hard ellipsoids of revolution with axial ratio a/b, all parallel to the z-axis (say), can be mapped onto the hard-sphere fluid by a simple scaling of all z-coordinates with a factor b/a. Since hard spheres apparently do not form smectics, parallel hard ellipsoids cannot do so either. So, unless the orientational degrees of freedom stabilize the smectic phase (and this seems unlikely), hard ellipsoids of revolution cannot form smectics. The question then arises as to whether smectic phases can be formed by other rigid hard-core models. This is not *a priori* obvious. In fact, to the author's knowledge, most textbooks on liquid crystals do not even seriously consider this possibility.

In order to explore the possibility of smectic order in rigid hard-core systems, we carried out Monte Carlo and molecular dynamics simulations on model systems consisting of parallel spherocylinders with diameter D and length L (i.e. the hemispherical caps were separated by a straight cylindrical segment of length L) [7]. Since the particles in this system are always perfectly aligned, the low-density phase is a 'nematic' fluid. The parallel spherocylinder fluid can be thought of as a model for a fluid of rod-like particles in a strong magnetic field. As mentioned above, we know that the corresponding hard-ellipsoid model will not exhibit smectic order. Simulations were carried out for systems of parallel spherocylinders with L/D ratios of 0·25, 0·5, 1, 2, 3 and 5 and ∞. The well-known case $L/D = 0$ (i.e. hard spheres) was also studied, as a check. System sizes varying from 90 to 1080 particles were studied. For more technical details about the simulations see [8]. The main results can be summarized as follows. For L/D ratios below 0·5, the fluid freezes directly from the nematic phase. However, for $L/D \geqslant 0{\cdot}5$, a thermodynamically stable smectic phase is observed between the nematic and the solid phases. Finally, for the larger L/D values (5 and ∞), there was evidence for the presence of a columnar phase between the smectic and the solid. A schematic 'phase diagram' is shown in figure 1. Snapshots

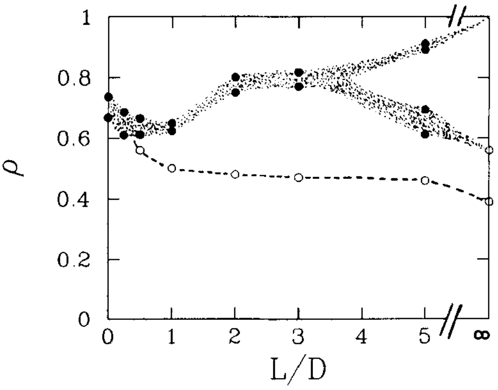

Figure 1. Schematic phase diagram of parallel hard spherocylinders. the abscissa is the length-to-width ratio of the particles L/D, the ordinate the density (divided by the density at regular close packing). Four phases can be identified: (1) The low-density 'nematic' phase; (2) a high-density solid phase; (3) for $L/D \geqslant 0{\cdot}5$, an intermediate-density smectic-A phase; and (4) for $L/D \geqslant 5$, a columnar phase between the smectic and the solid phases. Two-phase regions are indicated by grey areas. The precise nature of the smectic–columnar transition in the limit $L/D \rightarrow \infty$ is not yet clear, since this transition is very sensitive to finite-size effects.

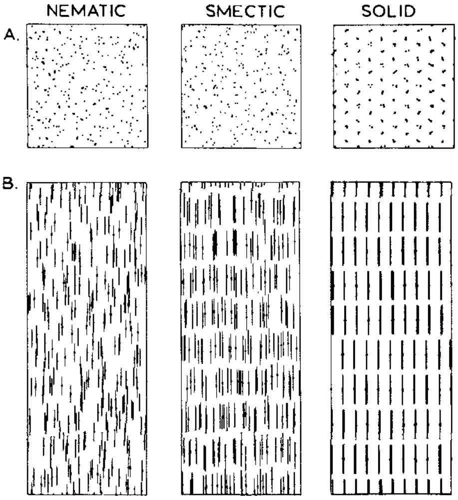

Figure 2. 'Snapshots' of molecular configurations of a system of parallel hard spherocylinders with $L/D = 5$. The density increases from left to right from 24 per cent of regular close packing (nematic phase), to 62 per cent (smectic-A phase), to 89 per cent (crystalline solid phase).

of typical molecular configurations corresponding to the nematic, smectic and solid phases of hard parallel spherocylinders are shown in figure 2.

Of course, a model system consisting of *parallel* spherocylinders is rather unphysical. It is therefore of considerable interest to know if a system of freely rotating hard-core molecules can form a smectic phase. This question is of some practical interest, in view of the recent experimental evidence that smectic ordering may take place in concentrated solutions of rod-like DNA molecules [9]. We therefore carried out molecular dynamics and Monte Carlo simulations on a system of freely rotating spherocylinders with a length-to-width ratio $L/D = 5$. The number of spherocylinders in a periodic box was chosen to be 576. This number of particles was needed to guarantee that a given particle would only interact with the nearest periodic image of any other particle. The initial configuration was instantaneously expanded to 20 per cent of the density of regular close packing. Subsequently, a constant-volume Monte Carlo simulation was carried out during which the original lattice rapidly melted while the distribution of molecular orientations became isotropic. After that, the system was compressed step-by-step to higher densities with density steps of 5 per cent of the density at regular close packing. At each density the system was equilibrated again. At low densities (35 per cent of close packing, and less), equilibration was always achieved in 20 000 trial moves per particle. Close to phase transitions, it was in general necessary to equilibrate for much longer. For the higher densities, where spontaneous ordering occurred, equilibration was achieved by alternating molecular dynamics simulations and (constant-stress) MC simulations. After equilibration, MC and MD production runs were carried out.

At low densities the nematic order parameter S is always, within the statistical accuracy of the simulations, equal to zero. At 45 per cent of close packing S fluctuates strongly: its average value is equal to 0·3. This is a typical value for a nematic order parameter at the transition to the isotropic phase. As the density is increased even more, the nematic order parameter S grows from 0·3 at 45 per cent of close packing to more than 0·9 at 60·4 per cent of close packing. Although the fact that we observe spontaneous nematic ordering is gratifying, it is not really surprising. The more interesting question is whether the smectic ordering that is observed in parallel spherocylinders is preserved in spherocylinder fluid with full orientational freedom.

Upon further compression of a well equilibrated and annealed nematic phase, an increase was noted in the amplitude of one-dimensional density fluctuations along the nematic director. As the density increased, the amplitude of these fluctuations grew, as did their decay times. At 60 per cent of close packing the system developed a static one-dimensional density modulation. However, no translational ordering was observed in the directions perpendicular to the director. This is the hallmark of a smectic-A liquid-crystalline phase. Although the fact that the latter phase formed spontaneously on compression indicates that it is stable with respect to both the isotropic and the nematic phases, its thermodynamic stability with respect to the crystalline state had to be established. This requires calculation of the free energy of both the solid and the liquid phase. Such calculations (reported in [10]) show that the smectic phase of hard spherocylinders with $L/D = 5$ is indeed thermodynamically stable. Figure 3 shows a typical snapshot of the smectic-A phase of a system of hard spherocylinders with $L/D = 5$.

There are nevertheless several qualitative differences between the phase diagrams of parallel and freely rotating spherocylinders. First of all, the freely rotating spherocylinders must always have an orientationally disordered low-density phase. In contrast, the parallel spherocylinder fluid remains (by construction) a nematic, even in the dilute-gas phase. More interesting for the present discussion is the observation that, whereas parallel spherocylinders with $L/D = 5$ appear to form a columnar phase, freely rotating spherocylinders with the same L/D ratio apparently do not. There is in fact a good reason for this difference in behaviour. To see this, we should look more closely at the 'scaling' behaviour of long parallel spherocylinders with length-to-width ratio L/D. Let us assume that the particles are aligned parallel to

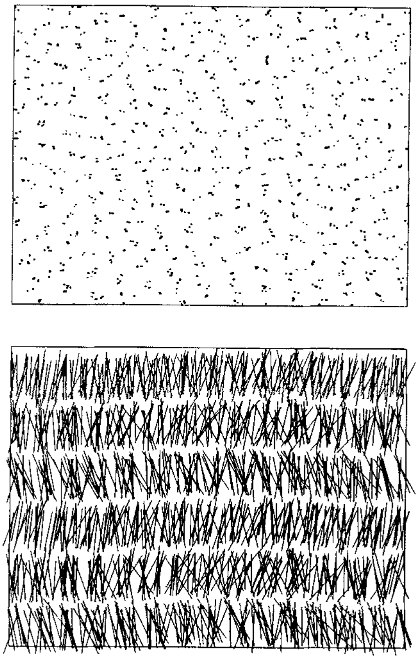

Figure 3. ‘Snapshot’ of a molecular configuration of 1152 freely rotating hard spherocylinders with $L/D = 5$ at a density of 62·5 per cent of regular close packing. The bottom part of the figure shows a side view of the system. Smectic layering can clearly be recognized. The top half of the figure shows a view along the nematic director. Although this part of the snapshot shows appreciable local ordering, there is no long-range translational order in the smectic planes. Nor is there any evidence for long-range bond-order (see [11]).

the z-xis. If we scale all z-coordinates with a factor D/L then the shape of the spherocylinder changes. Instead of a cylinder of length L and diameter D with hemispherical caps, we now have a cylinder of length 1, with flattened (oblate hemispheroidal) caps. The axial ratio of the ellipsoidal caps is L/D. In the limit of large L/D the caps become flat, and the spherocylinders have transformed into capless cylinders. Note, however, that this scale transformation has no effect on the statistical-mechanical equilibrium properties of the model system. Hence we may take the point of view that a system of long parallel spherocylinders is in fact a model for a system of short capless cylinders. And, seen in this light, it is not surprising that such a model exhibits a columnar phase.

Now consider what happens if we allow the molecules in our model to rotate. In this case it *does* make a difference whether we are considering long spherocylinders or short capless ‘platelets’. Any small rotation of a long axis of the spherocylinder away from the z-direction will destroy the mapping from spherocylinder to platelet. So, if we are interested in the effect of orientational freedom on a system of parallel spherocylinders with a given L/D ratio, it is not sufficient to study only freely rotating spherocylinders with the same L/D ratio. We should also consider the effect of free rotation on the flat plate-like particles that are equivalent to these spherocylinders, only when aligned.

The present paper reports the first results of recent simulations on a system of freely rotating plate-like molecules with variable length-to-width ratio.

2. The cut-sphere model

Let us first put the problem posed in the previous section in a broader perspective: we wish to study the phase behaviour of the oblate counterpart of a spherocylinder, for a range of length-to-width ratios. Unfortunately, the choice of the oblate equivalent of a spherocylinder is not unambiguous, as it is for ellipsoids. The shape that is usually referred to as 'oblate spherocylinder' is best described as a 'spheroplatelet'. Loosely speaking, a spheroplatelet is a convex body that can be generated by moving the centre of a sphere with diameter L over the surface of a circular disc with diameter D (note that a spherocylinder is obtained by moving a sphere with diameter D along a line segment with length L). The low-density behaviour of this 'spheroplatelet' fluid has been studied numerically by Wojcik and Gubbins [12]. Unfortunately, the spheroplatelet is not a particularly attractive model to use in numerical simulations, because the test for overlap between two such particles involves the evaluation of the distance of closest approach of two circular discs. And the latter calculation may require an iterative search. Although this, in itself, is no problem, it is often preferable to have an overlap criterion that only involves tests that can be evaluated analytically in a fixed number of steps.

A second model that might be considered is the capless cylinder with length L and diameter D. This model has two drawbacks—one aesthetic, the other numerical. The aesthetic drawback is that there is no L/D ratio for which this model reduces to a sphere (this would constitute a natural separation between 'prolate' and 'oblate'). The numerical drawback is much the same as for the spheroplatelet, only worse. One simulation of elongated ($L/D = 4{\cdot}44$) right cylinders has been reported by Duro *et al.* [14], who used a simpler, but approximate, overlap criterion.

In the present paper yet another geometry is used to model plate-like molecules, namely the 'cut sphere'. The cut sphere is obtained as follows: consider a sphere with diameter D. Now remove those parts of the sphere that are more than $\frac{1}{2}L$ above, or below, the equatorial plane. What remains is a cheese-like object with flat caps and spherical rims (see figure 4). This model has the pleasant feature that the test for overlap involves a finite number of analytical evaluations. Moreover, in the limit $L/D = 1$, the cut sphere reduces to a hard sphere. A disadvantage of the cut sphere

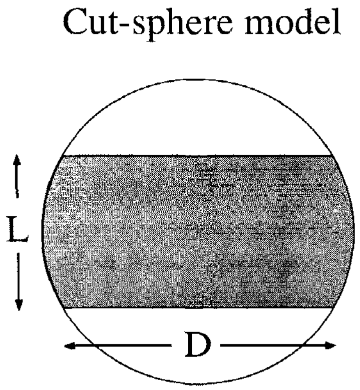
Cut-sphere model

Figure 4. Side view of a cut sphere with diameter D and thickness L. the cut sphere is shown in grey. To clarify the definition of the cut sphere, the contour of the original sphere has been indicated in this figure. In the limit $L/D = 1$ the cut sphere reduces to an ordinary sphere. For $L/D \to 0$, the cut sphere becomes a cylindrical platelet.

is that, unlike the spherocylinder and the spheroplatelet, it is not the product of two simpler geometrical objects.

The cut sphere is a hard convex body. Using the standard techniques applicable to such objects (see e.g. [14]), the second virial coefficient of cut spheres can be evaluated for arbitrary L/D ratios:

$$B_2 = \tfrac{1}{6}\pi D^3[\cos\theta_M\,(1 + \tfrac{1}{2}\sin^2\theta_M) + 3(\cos\theta_M + \tfrac{1}{2}\theta_M\sin\theta_M)(\cos\theta_M + \tfrac{1}{2}\sin^2\theta_M)], \tag{1}$$

where $\theta_M \equiv \arccos(L/D)$.

At high densities, cut spheres can be stacked in a regular close-packed lattice. The volume fraction at regular close-packing is: $\eta_{cp} = \tfrac{1}{6}\pi[3 - (L/D)^2]^{1/2}$. Note that for $L/D = 1$ (hard spheres), this reduces to the well-known hard-sphere result $\eta_{cp} = \pi/\sqrt{18}$. For $L/D \to 0$ (flat cylindrical platelets), we obtain the two-dimensional hard-disc value $\eta_{cp} = \pi/\sqrt{12}$.

To carry out the actual numerical test for overlap between two cut spheres, we must distinguish between different 'collision' geometries, viz rim–rim, cap–cap and cap–rim, where 'rim' denotes the spherical rim of the cut sphere and 'cap' the flat caps. All three types of test can be expressed in terms of explicit functions of the particle coordinates. In order to test if the overlap criteria work correctly, two tests were carried out. In one, the second virial coefficient was evaluated numerically by Monte Carlo sampling, and compared with the analytical expression (1). This test was satisfied to within the statistical accuracy of the numerical integration (for instance, for $L/D = 0{\cdot}2$, the MC result is $B_2^{MC} = 1{\cdot}0846 \pm 0{\cdot}0022$, while the exact result is $B_2 = 1{\cdot}08521 \cdots$). In the other test, the numerical overlap criterion was used to generate a configuration of non-overlapping cut spheres by Monte Carlo sampling. Next, test points were generated randomly on the surface of the cut spheres. A check was then made to see if any of these test points was contained in more than one cut sphere (this would imply hard-core overlap). This involves a completely different (and very simple, though not very efficient) test. No such overlap was ever detected. However, if the system was set up with an artificially generated overlap, the latter was detected simultaneously by both methods.

3. Monte Carlo simulations

Monte Carlo simulations were carried out on a system of cut spheres with $L/D = 0{\cdot}1$, over a range of densities between dilute gas and crystalline solid. Most simulations where performed on a system consisting of 256 cut spheres, except for some of the higher density runs, where a larger number of particles ($N = 576$) was employed. In all cases periodic boundary conditions were used: for the low-density systems the simulation box was cubic. For the crystalline phases the box was orthorhombic, but otherwise free to adjust to any changes in the shape of the crystalline unit cell. To study the behaviour of the fluid phase, the system was initially expanded from a regular close-packed lattice to a low density (10 per cent of regular close packing), at which density the system rapidly melted to form an isotropic fluid. The system was thereupon slowly recompressed to higher densities. Each compression step was followed by an equilibration run. The length of the compression plus equilibration run was 15 000 trial moves per particle. It was followed by a production run of another 10 000 trial moves per particle. The magnitude of the Monte Carlo trial move was chosen such that the average acceptance probability of trial moves was

Figure 5.

Figure 6.

Figure 7.

around 20 per cent. During the production run, several radial and angular correlation functions (see below) were measured, and, in addition, the nematic order parameter and the pressure were monitored. The latter quantity was measured using the method of Eppenga and Frenkel [5]. In every case the final, equilibrated configuration of one compression step was used as the starting configuration for the next. Typically, the change in density on compression was 0·025, in reduced units. At a reduced density of 0·35 (i.e. at 35 per cent of regular close packing), it was observed that the system spontaneously ordered to form a nematic phase. However, the director of this nematic phase was not aligned with any edge of the cubic simulation box. The system was thereupon *prepared* in a well-equilibrated, pre-aligned nematic state at the same density ($\varrho = 0{\cdot}35$). When the latter nematic was expanded to $\varrho = 0{\cdot}325$, the nematic order was found to disappear spontaneously. The subsequent compression runs were started from the pre-aligned nematic at $\varrho = 0{\cdot}35$. Finally, a series of runs was started from the crystalline state. In these simulations subsequent state points were generated by expansion, followed by equilibration.

4. Results

In order to illustrate the structural changes that take place in the cut-sphere fluid as the density is increased, figure 5, 6 and 7 show snapshots of typical equilibrated configurations obtained at a reduced density $\varrho = 0{\cdot}3$ (figure 5), $\varrho = 0{\cdot}35$ (figure 6) and $\varrho = 0{\cdot}525$ (figure 7). The configuration in figure 5 corresponds to an isotropic phase. Indeed, at this density, the nematic order parameter fluctuates around 0, and orientational correlation functions $g_l(r) \equiv \langle P_l(\mathbf{u}(0) \cdot \mathbf{u}(r))\rangle$ for $l = 2$ and 4, decay to zero essentially within one molecular diameter. At $\varrho = 0{\cdot}35$ the system is in a nematic phase, as can be clearly seen from figure 6. The snapshot shows that there still is an appreciable amount of orientational disorder in the system. Nevertheless, the orientational order parameter $S \equiv \langle P_2(\cos\theta)\rangle$ has an average value of $0{\cdot}73 \pm 0{\cdot}02$. As was mentioned above, a slight expansion of the system to a reduced density $\varrho = 0{\cdot}325$ results in the disappearance of the nematic order. It seems likely that the density

Figure 5. Snapshot of an instantaneous configuration of a system of 256 cut spheres at a reduced density $\varrho = 0{\cdot}30$. At this density the system is in the isotropic phase. For the sake of clarity, the cut spheres are represented by infinitely thin discs with a diameter that is about 50 per cent of the true diameter. The orange and blue colouring distinguish the 'top' and 'bottom' of the platelets. As the model itself does not distinguish between top and bottom, this colouring makes it possible to see if there is any residual alignment in the system.

Figure 6. Snapshot of an instantaneous configuration of a system of 256 cut spheres at a reduced density $\varrho = 0{\cdot}35$. This system was *prepared* in a nematic phase and left to relax for 50 000 trial moves per particle. However, the order parameter was already stable at a value of $S = 0{\cdot}73(2)$ at a run of half this length. The present snapshot shows a 'top' view of the system, along the nematic director. Note that most platelets are approximately perpendicular to the director, and very few have lost their original alignment (for the meaning of the colouring, see figure 5).

Figure 7. Snapshot of an instantaneous configuration of a system of 256 cut spheres at a reduced density $\varrho = 0{\cdot}525$. This system was slowly compressed from the nematic phase and left to relax for 50 000 trial moves per particle. The present snapshot shows a 'top' view of the system, along the nematic director. Note that most platelets are organized in somewhat buckled columns. For the meaning of the colouring, see figure 5.

$\varrho = 0{\cdot}325$ is quite close to the isotropic–nematic transition point, because the decay of the initial nematic order proceeds very slowly (from $S = 0{\cdot}7$ to $S = 0{\cdot}25$ requires more than 610^6 trial moves). Further stepwise compression of the nematic phase (in steps $\Delta\varrho = 0{\cdot}025$) results in an increase of the overall orientational order, and, in addition, increasing local ordering is observed in the fluid. As the system is compressed to a reduced density of $\varrho = 0{\cdot}45$, there is an increasingly clear tendency of the system towards local columnar ordering. The 'nucleation' of a columnar phase is greatly facilitated by allowing the shape of the periodic box to fluctuate. In fact, if the cubic box is allowed to become orthorhombic, the pressure of the system is found to drop rapidly, and 'nucleation' of a hexagonal columnar phase is observed. Figure 7 shows a snapshot of such a spontaneously nucleated columnar phase. On closer inspection, it turns out that the nucleated columnar structure contains some defects.

In order to prepare a defect free columnar phase, a series of simulations were performed in which the system was expanded from the crystalline phase. As it turns out, true crystalline order already disappears at quite high densities ($\varrho > 0{\cdot}75$). This can, for instance, be seen by direct inspection of a snapshot of the molecular configuration at a reduced density of $\varrho = 0{\cdot}65$ (figure 8). This figure shows that, although the molecules are arranged in a regular hexagonal array of columns, there is considerable disorder inside these columns. A more quantitative measure for the absence of long-range positional ordering in the direction of the column axis is provided by the 'longitudinal' density correlation function $g_{\parallel}(r) \equiv \langle \varrho(0)\varrho(r)\rangle / \langle \varrho \rangle^2$, where r measures the displacement along the nematic director. In a true crystalline solid this correlation function would have a long-range oscillatory modulation, due to the periodicity of the lattice. As can be seen in figure 9, no such behaviour is observed in the cut-sphere

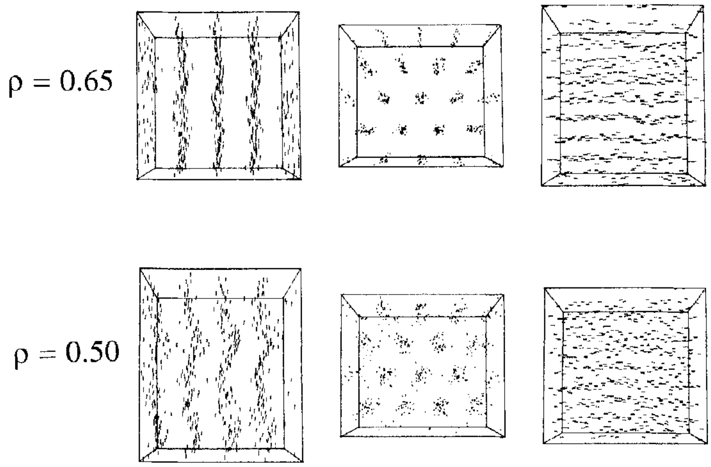

Figure 8. Top: snapshot of an instantaneous configuration of a system of 576 cut spheres at a reduced density $\varrho = 0{\cdot}65$. This system was started in a crystalline configuration and left to relax for 20 000 trial moves per particle. The figure shows a view from three mutually perpendicular directions ('x, y, z'). The left-most and right-most pictures provide a side view of the columnar structure. These two pictures show that there is considerable disorder in the columns. The middle picture represents a 'top' view. It shows the hexagonal columnar lattice. In order to provide a better view of the columnar structure, the cut spheres are represented by line-segments of length L along the molecular symmetry axis. Bottom: as in the top half of the figure, but for a system of cut spheres at a reduced density $\varrho = 0{\cdot}50$. This system was slowly expanded from a columnar configuration at $\varrho = 0{\cdot}65$ and left to relax for 20 000 trial moves per particle. Note that the hexagonal columnar lattice has become quite diffuse.

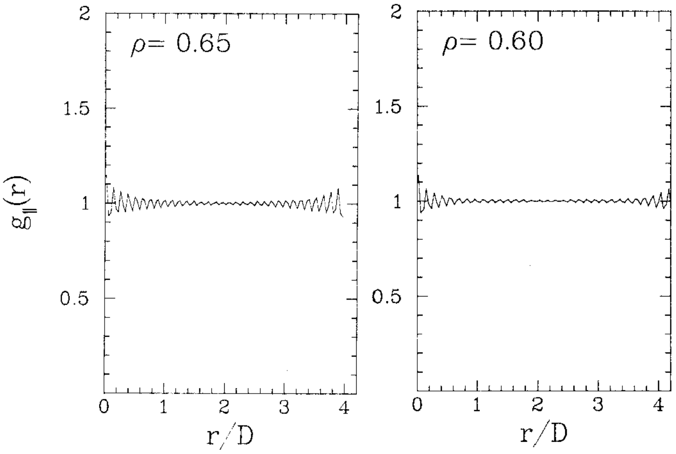

Figure 9. Density–density correlation function $g_{\|}(r)$, where r is the distance along the nematic director. Two densities are shown: ϱ = 0·65 (for a snapshot, see figure 8), and ϱ = 0·60. In a crystalline phase the amplitude of the oscillations in $g_{\|}(r)$ would decay to a finite level as $r \rightarrow \infty$. In contrast, in a columnar phase these oscillations are expected to decay to zero. In the present figure they decay to a value close to zero within a few 'lattice spacings'. The oscillations grow again for large values of r. This is simply a consequence of the periodic boundary conditions.

system at a reduced density ϱ = 0·65. Rather, the oscillatory decay over 4–5 lattice spacings. The range of the oscillations in $g_{\|}(r)$ is a measure of the distance over which positional correlations in the column direction persist. As can be seen in figure 9, this range is even shorter for ϱ = 0·60.

Expanding the initially crystalline system even more, we see that the columnar ordering becomes increasingly diffuse (see figure 8). At a reduced density of ϱ = 0·45 it has all but disappeared. At that density the pressure of the expanded columnar system has become equal to that of the compressed nematic. The present evidence (hysteresis, 'nucleation') strongly suggests that the transition from the nematic to to columnar phase is first-order. However, at this stage we have not yet completed the calculation of the thermodynamic coexistence line.

5. Conclusions

The results reported in this paper provide the first (numerical) example that excluded-volume effects alone can induce columnar ordering in a system of freely translating and rotating plate-like molecules. No special attractions are needed to make the disc-like molecules stack in columns. Of course, this does not imply that specific attractions, or, for that matter, the effect of molecular flexibility, are unimportant for the formation of such liquid-crystalline phases. On the contrary, these factors are of as crucial an importance for the stability of discotics as they are for nematics and smectics. However, excluded-volume effects are all that is needed in order to understand why discotics form in the first place. Note, however, that the packing effects that determine whether or not a particular model will form a discotic are quite subtle: cut spheres do become discotic, oblate ellipsoids do not. Similarly, prolate spherocylinders may form a smectic, unlike ellipsoids with the same overall length-to-width ratio. Finally, it even appears that the formation of something as 'simple' as a nematic depends not just on the overall aspect ratio of a molecule: oblate ellipsoids form a nematic for all axial ratios below 0·4 [4]. In contrast, preliminary results for other cut-sphere model systems [15] seem to indicate that cut spheres that are twice as oblate ($L/D = 0{\cdot}2$) still do not form a nematic.

Although the hard-core models that have been discussed here are very simple, they give rise to a surprisingly rich variety of possible ordering phenomena. Of course, real mesogens are neither hard rods nor platelets. Nevertheless, it is the author's opinion that if we can gain a better understanding of the relation between the phase diagram of hard-core molecules and their molecular shape, then we should be in a better position to understand, and predict, the phase behaviour of real liquid crystals.

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