Evidence for Smectic Order in a Fluid of Hard Parallel Spherocylinders

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We present Monte Carlo simulations on systems of parallel spherocylinders with length-to-width ratios L/D between 0.25 and 5. We have determined the solid-liquid coexistence points in these systems by computing the absolute free energy of the solid and fluid phases. In addition we find that for $L/D > 0.5$ a thermodynamically stable smectic phase is formed at densities well below the thermodynamic melting point. The transition from nematic to smectic appears to be continuous. We find no evidence for long-range bond-orientational order in the smectic phase.

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Colloidal solutions of monodisperse rigid rodlike particles are known to exhibit translationally ordered phases[1-5] (solid or smectic) at surprisingly low densities. For example, in a solution of tobacco mosaic virus, layer formation was observed at concentrations as low as 3 wt.%.[2,3] Even with the electrostatic repulsion between the virus particles taken into account this is a puzzlingly low concentration. Computer simulations on hard-core fluids[6,7] suggest solid-liquid coexistence at fluid densities corresponding to $\frac{2}{3}$ or more of the density of closest packing. Smectic ordering has never been observed in numerical simulations of rigid, hard-core model systems. With a few exceptions[8,9] most authors, following the seminal work of McMillan,[10] have attempted to explain the occurrence of smectics in terms of a competition between the loss of translational entropy involved in layer formation and the associated gain in internal energy.

In order to gain a better understanding of the factors that affect the phase changes in systems of rigid rodlike particles, such as the colloidal systems of Refs. 1–5, we have carried out Monte Carlo (MC) simulations on a very simple model sytsem, viz. parallel hard spherocylinders (i.e., cylinders capped at each end by a hemisphere of the same radius). As the particles in this system are always perfectly aligned, the low-density phase is a "nematic" fluid. At high densities the parallel rods can form a close-packed crystalline phase.

The MC simulations were carried out for systems of parallel spherocylinders with the following length-to-width ratios: $L/D = 0.25$, 0.5, 1, 2, 3, and 5 (and, as check, $L/D = 0$). The size of the systems studied varied from 90 to 1080 spherocylinders. Initially, the system was prepared in a regular close-packed lattice [in our case, an fcc lattice distorted along the (111) axis by a factor $(1 + L/D)$]. To study the fluid phase, this initial configuration was expanded to low densities, where it rapidly melted and formed a translationally disordered phase. Higher density points along the fluid isotherm were all generated by compression from a lower-density fluid-state point. All solid-state points were generated by expansion from higher-density solid points.

In order to obtain the equation of state of the fluid, we carried out constant-pressure MC simulations.[11] In the solid phase, we performed constant-stress MC simulations. The latter method was used to ensure that the crystal unit cell could relax to its equilibrium shape. The absolute free energy of the solid was computed by use of the "Einstein crystal" method of Frenkel and Ladd.[12] For the fluid branch we also computed the first five virial coefficients. B_2 is known analytically; B_3 through B_5 were evaluated numerically.[13] A typical example of an isotherm for parallel spherocylinders is shown in Fig. 1.

Knowing the equation of state and the absolute free energy of the fluid and solid, we are now in a position to locate the melting point of the spherocylinder crystal. The pressure and the densities of the coexisting fluid and solid phase for various length-to-width ratios L/D are given in Table I. These coexistence points have been obtained with the assumption that the crystal structure of the solid is an fcc phase distorted along the (111) axis. In fact, we have some evidence that close to melting other crystal phases may be marginally more stable. This is not expected to have a drastic effect on the location of the melting point.

Closer inspection of Fig. 1 (the isotherm for $L/D = 5$) reveals that the equation of state of the fluid phase appears to change slope at a density well below melting. In an attempt to understand the cause of this

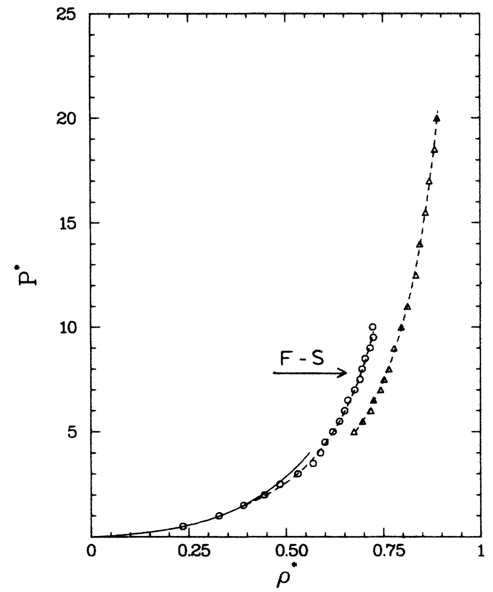

FIG. 1. Isotherm for a system of hard parallel spherocylinders with $L/D=5$. Open circles, fluid branch; open triangles, solid branch; solid line, five-term virial series; dashed lines, fits through the MC data. The arrow indicates the location of the fluid-to-solid transition.

TABLE I. Densities ρ_F^* and ρ_S^*, pressure P_{FS}^*, and chemical potential μ_{FS}^* of the coexisting fluid (F) and solid (S) phases for various length-to-width ratios L/D. The reduced density $\rho^*=\rho/\rho_{cp}$ where ρ_{cp} is the density of closest packing, $P^*=Pv_0/kT$ where v_0 is the molecular volume, and $\mu^*=\mu/kT$.

L/D	ρ_F^*	ρ_S^*	P_{FS}^*	μ_{FS}^*
0.25	0.610	0.685	4.75	12.97
0.50	0.612	0.665	4.58	12.17
1.00	0.624	0.650	4.50	11.41
2.00	0.751	0.802	9.99	19.36
3.00	0.771	0.818	11.22	20.57
5.00	0.693	0.759	7.83	15.09

effect we studied the behavior of the distribution functions $g_\perp(x,y)$ and $g_\parallel(z)$. Here $g_\parallel(z)$ is the pair distribution function in the direction along the particle axes, while $g_\perp(x,y)$ is the corresponding transverse distribution function. To our surprise we found that, whereas $g_\perp(x,y)$ is "liquidlike" throughout the fluid branch, $g_\parallel(z)$ starts exhibiting strong periodic oscillations at densities well below melting. We checked that this behavior did not occur for hard spheres nor for the system with the smallest value for L/D studied ($L/D=0.25$). The effect did not show any tendency of becoming less pronounced with increasing system size (up to 1080 particles). Nor did it disappear when we performed constant-stress simulation on the fluid, to relax possible transverse stresses (for which, incidentally, we found no evidence).

The effect immediately suggests some kind of smectic ordering. This is further corroborated by snapshots of the positions of the particles at different densities presented in Fig. 2. However, before drawing definite conclusions, we should rule out the possibility that we are looking at an incompletely melted solid. There are two good reasons to assume that this is not the case. First of all, all fluid configurations were obtained by our (slowly) compressing a completely disordered low-density phase. More importantly, the numbers of "layers" formed in the fluid is, in general, not the same as in the solid. Typically we start with nine close-packed layers in the crystal, whereas the number of layers in the fluid varies from eleven at low densities to nine at high densities, in such a manner that the layer spacing is approximately constant.

The longitudinal structure factor $S(k_z)$ develops pronounced peaks at $k_z=n(2\pi/d)$, where d is the interlayer spacing. In scattering experiments on real thermotropic smectics, the (001) Bragg reflection is usually much stronger than the higher-order ones. This behavior is not reproduced by our hard-core smectics. Typical ratios between the intensities of the (001) and (002) reflections are of the order of 5 to 10. The value of d was found to depend little, if at all, on density. It does depend strongly on L—actually $d \cong 1.4L$.

In order to obtain additional data on the nature of the ordering in the fluid phase, we carried out molecular-dynamics simulations on the same system. In these simulations we computed the transverse and longitudinal (with respect to the particle axes) diffusion coefficients and the intermediate scattering function $F(k_z,t)$, where k_z is the longitudinal component of the wave vector.

At low densities we find that $D_\parallel$ is larger than $D_\perp$ (the more so for the larger L/D ratios). At higher densities, the longitudinal diffusion coefficient decreases more rapidly than the transverse, and in the "smectic" phase the in-plane diffusion is slightly larger than the interplane diffusion. Most importantly, both diffusion constants are typically "liquidlike"; there is no evidence for partial crystallization at these densities.

A sensitive method to observe precursors to smectic ordering is to look at the behavior of the relaxation time of the longitudinal intermediate scattering function $F(k_z,t)$ at a value of k_z corresponding to the first peak. We have plotted the relaxation rate (i.e., the inverse relaxation time) of $F(k_z,t)$ as a function of density, for $L/D=0.5$, in Fig. 3. At low densities we note that the relaxation rate increases with increasing density. Then, quite suddenly, it starts to drop precipitously and becomes effectively zero at a reduced density of 0.56. The point where the relaxation rate of the

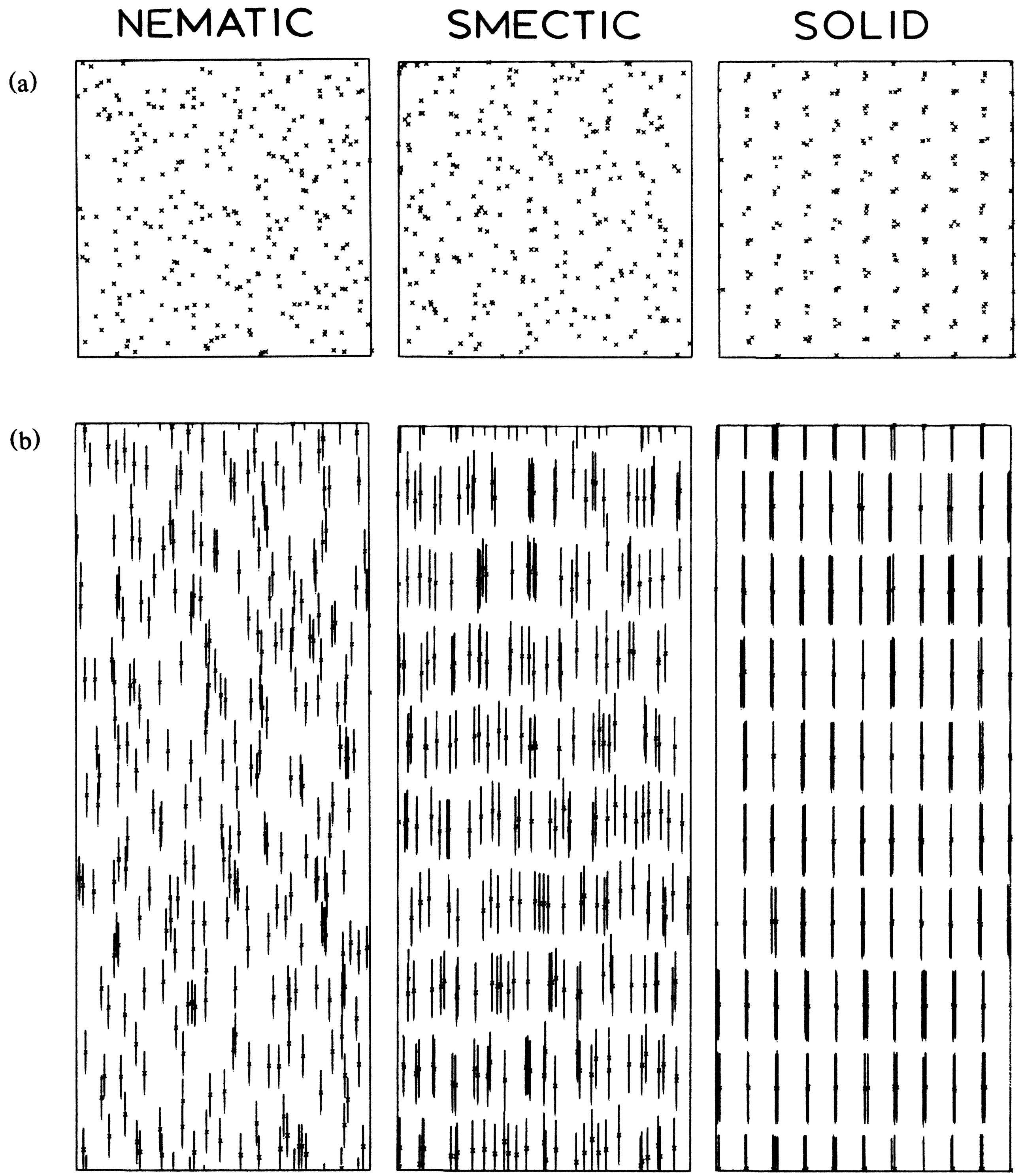

FIG. 2. Snapshots of the positions of the particles at typical densities in the nematic phase ($\rho^* = 0.24$), smectic phase ($\rho^* = 0.62$), and solid phase ($\rho^* = 0.89$), for the case $L/D = 5$. (a) Top view perpendicular to the particle axes. (b) Side view along the particle axes.

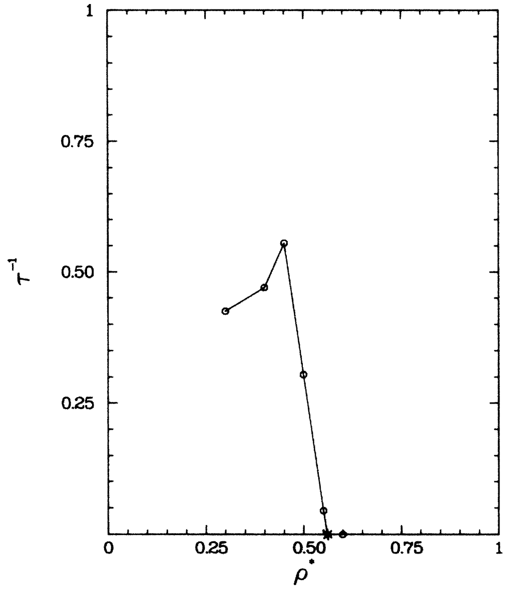

FIG. 3. Inverse relaxation time τ^{-1} of the longitudinal intermediate scattering function $F(k_z,t)$ as a function of density, for $L/D=0.5$. A black star indicates the density where the system undergoes a nematic-to-smectic phase transition.

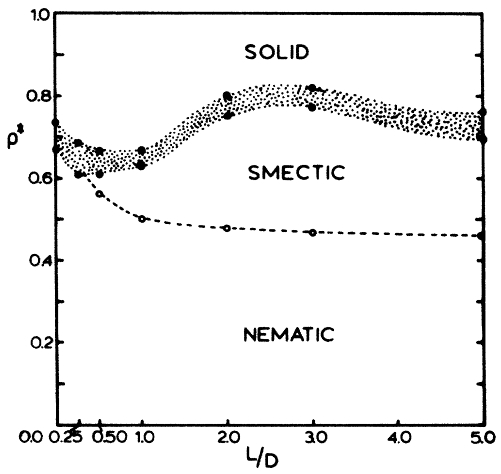

FIG. 4. Phase behavior of hard parallel spherocylinders as a function of the length-to-width ratio L/D. The shaded area corresponds to the fluid-solid two-phase region. Black circles, densities of the coexisting fluid and solid phase; open circles, densities where smectic ordering sets in; dashed line, nematic-smectic phase boundary.

$F(k_z,t)$ vanishes is a reasonable estimate for the density where smectic ordering sets in. In Fig. 4 we have indicated the estimated densities for the transition to the smectic phase for various length-to-width ratios. Inspection shows that for $L/D > 0.5$ the transition density depends only weakly on the L/D ratio. For $L/D=0.5$ the transition to the smectic phase moves to higher densities, and for $L/D=0.25$ we have not been able to find precursor effects to smectic ordering at all.

Summarizing, we conclude that we have found evidence for the occurrence of a thermodynamically stable smectic phase in fluids of parallel spherocylinders with $L/D > 0.5$ for densities well below the fluid-solid transition. The transition to the smectic phase is not associated with an observable change in the density, but is preceded by strong pretransitional fluctuations. Hence we tentatively identify the transition as being continuous. The order in the smectic layers is liquidlike. Moreover, we have looked for possible bond-orientational order, but not found any. This suggests that the phase we are observing is a simple smectic *A*.

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