Model for Smectic-A Ordering of Parallel Hard Rods

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A fundamental argument for the smectic-A ordering of parallel hard rods is presented, along with a mean-field calculation that agrees well with the main features of numerical simulations of this system. Smectic-A ordering is attributed to more efficient packing of rods compared with nematic ordering. Above a critical volume fraction, the increased entropy per particle in the smectic-A layers more than compensates for the loss of entropy due to the forming of layers.

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Systems of hard particles, interacting only through the excluded-volume effect, have long served as some of the most important models for the understanding of fundamental structural phase transitions in condensed matter. The problem of the melting of a hard-sphere crystal,[1] for example, has been a useful testing ground for theory and computational methods. Likewise, for the understanding of liquid crystals, the system of hard rods has played a fundamental role. Onsager made a major contribution to our understanding of the nematic phase with his simple theory[2] of the isotropic-to-nematic phase transition in the system of hard spherocylinders (cylinders capped with hemispheres). In a recent Letter, Stroobants, Lekkerkerker, and Frenkel (SLF) reported convincing evidence for the appearance of smectic-A order in the system of perfectly parallel hard spherocylinders.[3] Smectic-A order is characterized by a density wave with wave vector along the rod axis and a liquidlike structure perpendicular to the rod axis.[4] In SLF's results, the nematic to smectic-A transition appears to be continuous and occurs at a volume fraction well below that necessary for crystallization. The wavelength of the smectic-A structure found by SLF is slightly longer than the rod length, and, well into the region of smectic-A stability, the ordering is visible as distinct layers of rods. SLF's results, coming from Monte Carlo and molecular-dynamics simulations, serve as experimental data demanding a theoretical explanation. Stimulated by those results, Mulder developed a density-functional calculation[5] which agrees well with SLF's results. In this Letter, we propose a physical model for the appearance of smectic-A order in the parallel–hard-rod system, and present a simple mean-field calculation to demonstrate our model, which is in good agreement with the main features of SLF's computer simulation. This model can be tested by further analysis of the SLF numerical data.

The appearance of ordered phases in systems of hard particles can only be understood via the maximization of the total entropy, because there is no interaction energy among the particles. The development of long-range (or quasi long-range) order intrinsically reduces configurational entropy, but within the ordered structure, excluded-volume effects among neighboring particles are reduced. At high density, the increase in the number of local configurations in an ordered structure outweighs the decrease of entropy due to the appearance of long-range order. Onsager's model for the isotropic-to-nematic transition, for example, argues that translational entropy can be gained in the parallel ordering of hard rods because the excluded volume between neighboring rods is minimized by making them parallel; this outweighs the loss of orientational entropy. Can one find an analogous tradeoff to explain the appearance of smectic-A order? We propose that the appearance of smectic layers is driven by the concurrent decrease in the lateral-packing density of the rods within the layers, which again outweighs the entropy loss involved in the making of layers.

To understand this argument, one must have a clear picture of the excluded-volume effects in the nematic phase. In the nematic phase, neighboring rods overlap one another by random amounts along their axial direction. This tends to create voids adjacent to the ends of each rod, which are accessible only to that rod, and not to its neighbors. Such configurations contain a large excluded volume. In the smectic-A phase, with rods distributed in layers, the random lengthwise overlapping of rods is avoided, and the voids adjacent to the ends of the rods disappear. Although each rod therefore loses some freedom of motion in the axial direction, the volume thereby saved is used to reduce the lateral-packing density in each layer. This transformation of volume that was available only to single rods into volume that is available cooperatively to many neighboring rods is what increases the entropy of the smectic-A phase over that of the nematic phase at high density. Another way to eliminate the voids is to align the rods end-to-end in strings; these strings then tend to pack together in a two-dimensional hexagonal array known as a columnar phase. Indeed, in their recent computer simulations,[6] SLF have found a columnar phase for densities somewhat higher than that of the smectic-A phase.

In this Letter, however, we concentrate on the nematic to smectic-A phase transition. We have described how the appearance of smectic-A order reduces the excluded volume of the nematic phase. It is also useful to look at

the same argument starting from the perfectly ordered smectic-A phase. In the limit of perfect smectic-A order, the distribution function $\rho(z)$ of centers of mass of the rods, as a function of z, the coordinate normal to the smectic layers, is a series of Δ functions, separated by the layer spacing a (equal to the rod length, in the limit of densest packing). Within each layer the rods are packed together as a two-dimensional liquid. As smectic-A order decreases, the layer spacing increases, and $\rho(z)$ broadens in the z direction as rods fluctuate toward the neighboring layers. Any rod that projects into a neighboring layer excludes lateral-packing area for rods in that layer as well as in its original layer. Simultaneously, it creates voids adjacent to its ends as a result of the partially overlapping configuration it has with the neighboring rods in both layers. At high volume fraction, the intrusion of rods from neighboring layers significantly decreases the configurational entropy of each layer; therefore these fluctuations are opposed and the smectic-A phase is stabilized. At lower volume fraction, this effect on lateral-packing entropy is less important, and $\rho(z)$ broadens more in the z direction. Eventually, at a critical volume fraction η_c, $\rho(z)$ becomes uniform along the z direction, and the structure has become nematic.

The argument as stated in the previous paragraph is easily expressed quantitatively. There are three obvious contributions to the entropy changes in going from perfect smectic-A toward nematic order: a term describing directly the changes in long-range order, a term due to the change of packing density within each layer, and a term due to the change in axial freedom of motion of each rod. The first term is easily expressed in terms of $\rho(z)$. The second term requires an expression for the 2D packing density, developed below. The third term is insignificant compared with the others; it is a single-particle entropy rather than a cooperative term, and it changes slowly near the smectic-A to nematic transition. In the following computation we ignore it and other more subtle entropy changes due to correlation effects.

Given $\rho(z)$, the rod length L, the rod radius r and diameter d, the layer spacing a, and the overall volume fraction of rods in the system η, one can calculate the effective packing fraction in a layer, η^{2D}, as

$$\eta^{2D}=L(\pi r^2)^2(a\eta)^{-1}\left[2\int_{-a/2}^{a/2}dz\,\rho(z)\int_{z-L}^{z}dz'\,\rho(z')\left(1-\pi d^2\int_{z'+L}^{z+L}dz''\,\rho(z'')\right)\right.$$
$$\left.+A\int_{-a/2}^{a/2}dz\,\rho(z)\int_{z-L}^{z}dz'\,\rho(z')\int_{z'+L}^{z+L}dz''\,\rho(z'')\right]. \quad (1)$$

The effective 2D density is calculated at each z and averaged over one layer period. For simplicity, no correlations between rods are considered in the η^{2D} calculation. When we consider a plane at z, only those rods whose centers lie within a distance L of the plane can exclude rods with centers at z. The first term above just counts all the single rods, i.e., those rods in this $2L$-thick layer which do not have any rods above or below them in the same layer. The second term accounts for the fact that rods in the upper half of the layer might lie above rods in the lower half of the layer. These pairs of overlapping rods project "clusters" on the plane, having areas ranging from πr^2 to $2\pi r^2$. A is the mean excluded area of a cluster, obtained by an averaging over all cluster configurations: $A=2\pi\int_0^d x\,dx\,S(x)/\pi d^2$. $S(x)$ is the excluded area between a disk due to a single rod and a cluster, in which x is the separation of the axes of the two overlapping rods. When the fraction of clusters in the plane is not large, this is a good approximation. For the perfectly ordered smectic-A phase, Eq. (1) gives $\eta^{2D}=\eta a/L$. If we look at the nematic phase as a limiting case of the smectic-A, with smeared-out layers, Eq. (1) gives $\eta^{2D}=2\eta-1.173\eta^2$.

Defining the 2D number density $\rho^{2D}=\eta^{2D}/\pi r^2$, we can now calculate the two terms discussed above in the free energy F of the smectic-A phase, or of the nematic phase as a limiting case:

$$\beta F=\int d^3r\,\rho(\mathbf{r})[\ln(\Lambda^3\rho(\mathbf{r}))-1]+NS\sum_{n=0}B_{n+2}(\rho^{2D})^{n+2}/(n+1). \quad (2)$$

In this expression, $\beta=1/k_BT$, $\Lambda=h/(2\pi mk_BT)^{1/2}$, the thermodynamic wavelength, and N and S are the number and the area of smectic layers in the system, respectively. B_{n+2} are the virial coefficients for a 2D system of hard disks.[7] The first term in F is the long-range-order term, representing the entropy involved in making $\rho(z)$ nonuniform, i.e., in the forming of layers. The second term is the excess entropy of a 2D-liquid layer of density ρ^{2D}.

Using the free-energy expression in Eq. (2), we explored the parameter space for smectic-A structures described by $\rho(z)$ equal to the sum of a constant term plus Gaussian peaks of inverse width b and layer spacing a,

$$\rho(z)=(\eta/\pi r^2L)\{(1-\alpha)+(\alpha ab/\sqrt{\pi})\textstyle\sum_n\exp[-(z-na)^2b^2]\}. \quad (3)$$

For each value of η, we calculated the difference between the free energies of the nematic phase and the lowest-free-energy smectic-A structure.

We found the nematic to smectic-A phase transition at $\eta_c^*=0.202$, in which η^* is η divided by the close-packed

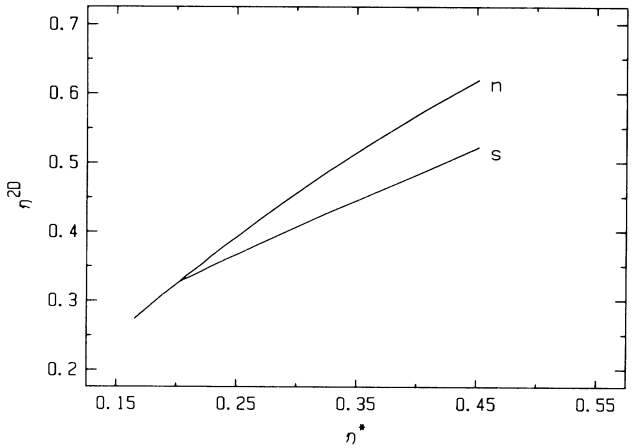

FIG. 1. The effective 2D packing fraction in the nematic (n) and smectic-A (s) phases vs $\eta^* = \eta/\eta_{cl}$, in which η_{cl} is the close-packed volume fraction of parallel cylinders.

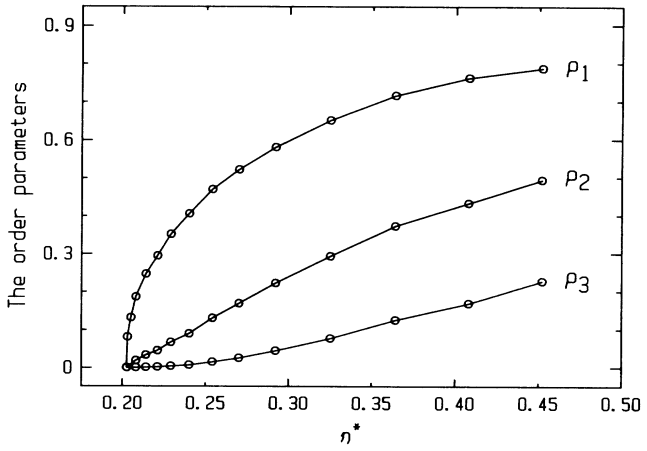

FIG. 2. The amplitudes of the first three Fourier components (ρ_1, ρ_2, and ρ_3) of $\rho(z)$ vs η^*.

volume fraction of parallel rods (0.907). In the parallel hard-spherocylinder system, SLF found $\eta_c^* \approx 0.45$. Results from further Monte Carlo simulations in the system of hard rods without hemispherical caps[6] give $\eta_c^* \approx 0.36$. The 2D packing fraction as a function of η^* is plotted in Fig. 1. Near the transition it is much less than the minimum density for 2D crystallization[8] (about 0.76), and so our calculation is consistent with fluid layers and smectic-A ordering. The transition is second order, in agreement with SLF's opinion. The first three smectic-A order parameters ρ_{1-3}, being the amplitudes of the first three Fourier components of $\rho(z)$, are plotted in Fig. 2. As expected, near the transition, $\rho_1 \propto (\eta - \eta_c)^{1/2}$, and $\rho_n \propto \rho_1^n$. The ratio of ρ_1 to ρ_2 is similar to that found by SLF. The equilibrium layer spacing is $1.28L$ at the transition, decreasing linearly to $1.2L$ at $\eta^* = 0.4$. This agrees very well with SLF's results, and with the value $a \approx 1.27L$ at the transition found in the computer simulation in the capless hard-rod system.[6] The inverse Gaussian width b increases from 2.3 at the phase transition to 6.0 at $\eta^* = 0.4$, representing the formation of well-defined layers, as found by SLF. We calculated the pressure difference between the smectic-A and nematic phases. The results, in Fig. 3, compare well with the data of SLF. Our model does not contain any dependence on the length-to-diameter ratio of the rods. Once they are anisotropic enough for the interpenetration concept to be meaningful, our argument should apply. SLF also find almost no dependence of the phase transition on the length-to-diameter ratio of the rods, for spherocylinders above a minimal length.

The calculation in this paper is presented mainly for demonstrating our model; for this reason it has been kept at the simplest level. Fluctuations have a strong effect on the nature of the nematic to smectic-A transition. Their contribution is not included in our mean-field calculation. The discrepancy between the value of η_c^* in our calculation and the measured value in the computer simulation may be explained by the simplicity of our η^{2D} calculation. Our η^{2D} expression does not include correlations between rods which probably leads to somewhat more efficient packing in the nematic phase, and therefore a lower η^{2D} than we have estimated. This lower 2D density would favor the nematic phase in our free-energy expression, shifting η_c^* to a higher value. Still, the fact that this simple calculation predicts many features of the observed phase transition suggests that it contains the correct physics.

A real test of our basic idea can be made by our examining the lateral and end-to-end packing of rods in the nematic phase in SLF's data, looking for voids adjacent to the ends of the rods that disappear in the smectic-A phase. One should be able to determine the effective

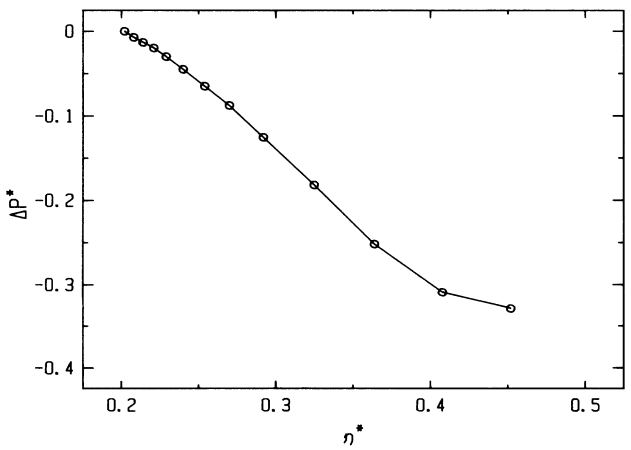

FIG. 3. The scaled pressure difference $\Delta P^* = \beta\pi r^2 L \Delta P$ between the smectic-A and nematic phases as a function of η^*.

value of η^{2D} as a function of density in the nematic phase, and extrapolate it into the region of smectic-A stability, where one should find a lower value of η^{2D} for the smectic-A phase.

The appearance of smectic ordering is very sensitive to the shape of the particles, a fact that is explained by our model. For example, if one applies our argument to the system of parallel prolate ellipsoids, smectic ordering is not favored. Because of their tapered shape, ellipsoids in the nematic phase, that partially overlap lengthwise, create only small voids and have a smaller 2D excluded area than they would in a perfectly ordered smectic-A phase, in which they interact at their points of maximum cross section. In contrast, a pair of cylinders have an excluded area that is independent of the degree of lengthwise overlap. A preliminary calculation of our model for ellipsoids predicts no stable smectic phase, in agreement with numerical simulations.[9] This shape sensitivity probably also explains the lower value of η_c^* found in the simulations for uncapped cylinders, compared with spherocylinders. We discuss this topic and the relative stability of smectic-A and smectic-C order in another publication.

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