

Theory of Ordered Phases in a System of Parallel Hard Spherocylinders

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Recent Monte Carlo studies have demonstrated the existence of positionally ordered phases in systems of monodisperse, parallel hard spherocylinders. We present an excluded-volume theory of this system which utilizes a scaled-particle treatment of dimensions possessing full translational freedom combined with a simple cell model for positionally ordered dimensions. The calculated phase diagram is in excellent qualitative agreement with the Monte Carlo results, exhibiting regions of nematic, smectic, columnar, and crystalline stability.

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Explanations for the order exhibited by liquid crystals have usually followed two main schools of thought. Onsager originally demonstrated that excluded volume alone is sufficient to induce the orientational ordering of anisotropic hard particles.¹ On the other hand, Maier and Saupe have emphasized long-range anisotropic interactions as the basis of nematic alignment.² The latter interactions have also been used to explain the existence of smectic order.³ However, Monte Carlo experiments have shown that excluded volume alone is sufficient to induce positional order, as found for the freezing of hard spheres,⁴ the freezing of hard ellipsoids,⁵ the smectic, columnar, and crystalline ordering of parallel hard spherocylinders,⁶ and the smectic ordering of orientationally unconstrained hard spherocylinders.⁷ In addition, density-functional calculations have confirmed the smectic phase in the spherocylinder systems.⁸⁻¹⁰ Such complex phase behavior of hard-particle systems is at first quite surprising. However, Wen and Meyer have pointed out that the entropic losses inherent in smectic ordering are more than compensated by the concomitant reduction in the excluded volume.⁸ This type of argument can also be applied to the columnar and crystalline phases.

In this Letter, we present a theory for parallel hard spherocylinders using a scaled-particle calculation to treat dimensions possessing full translational freedom, combined with a simple cell model to describe the positionally ordered dimensions. This approach yields a phase diagram remarkably similar to that obtained from Monte Carlo calculations.⁶ This includes stable columnar and crystalline ordering which has not been described by density-functional theory. Our predicted smectic layer spacing at the nematic-smectic crossover is almost identical to that reported in the Monte Carlo study. The single significant limitation to our model is that all transitions are required to be discontinuous. As a consequence, the second-order nematic-smectic transition demonstrated by the Monte Carlo study is here found to be first order.

We consider a closed system of volume V containing N parallel hard spherocylinders of diameter D and cylinder length L (particle volume $b_0 = \pi D^3/6 + \pi D^2 L/4$). When the axial ratio $L/D = 0$ this reduces to a hard-sphere system. The series of possible positionally ordered phases in the parallel hard-rod system (smectic, columnar, crystalline) can be generated by a sequential reduction in the degrees of full translational freedom available to the system. Such restrictions on the system's translational freedom impose severe entropic losses, making the stability of such ordered phases seem unlikely. However, these entropic losses can be compensated for by a reduction in the excluded volume between particles in the ordered phase and the interplay of these two effects determines the phase behavior of the system.

In this model, the periodicity of the density in the positionally ordered phases is approximated by restricting the particles in the positionally ordered dimensions to discrete compartments. We also require that these compartments accommodate no more than one particle in the ordered dimension. Thus for a smectic phase, particles may take any position within a layer, but may not double up in the layer or penetrate an adjacent layer. For a columnar phase, particles may take any position within a tube, but may not pass each other along the tube or penetrate an adjacent tube. And for a crystalline phase, particles may take any position within a cell, but may not share the cell with another particle or penetrate an adjacent cell. Compartmentalizing the particles in this fashion allows us to separate the contributions of the ordered and disordered dimensions to the free energy and to use simple rules for the statistics of placing the centers of the particles in these different dimensions. In the 3D ordered dimensions, each particle is alone in a (3D) dimensional box and the center of the particle has a well defined set of allowed positions that keep the particle within the box. In the d disordered dimensions, the positions of the centers of the particles are constrained only by excluded-volume interactions between the particles and the behavior is that of a d -dimensional fluid of d -

dimensional hard particles. In the three disordered dimensions of a nematic phase, parallel spherocylinders behave as a three-dimensional fluid of spherocylinders with a pair excluded volume $V_{ex} = 2\pi D^3(2/3 + L/D)$. Analogously, in the two disordered dimensions of a smectic phase, parallel spherocylinders behave as a two-dimensional fluid of hard disks of diameter D with a pair excluded area $A_{ex} = \pi D^2$. Similarly, in the one disordered dimension of a columnar phase, parallel spherocylinders behave as a one-dimensional fluid of hard rods of length $L + D$ with a pair excluded length $L_{ex} = 2(L + D)$.

Combining the contributions from the ordered and the disordered dimensions, the configurational free energy for a phase with d disordered dimensions can be expressed as

$$F^{\text{config}} = F_d^{\text{fluid}} + F_{3D}^{\text{cryst}}. \quad (1)$$

F_{3D}^{cryst} is simply related to the number of positions Γ_{3D} accessible to a given particle in the (3D) ordered dimensions according to the standard statistical formulation $\beta F_{3D}/N = -\ln \Gamma_{3D}$ where $\beta = 1/k_B T$. For the smectic phase, particles of length $L + D$ are restricted to close-packed layers of thickness Δ_s , where $\Delta_s > L + D$ to accommodate the particle and $\Delta_s \lesssim 2(L + D)$ so the particles cannot double up in the layer. Thus $\Gamma_1 = \Delta_s - (L + D)$. For the columnar phase, particles of a circular cross section with diameter D are restricted to close-packed hexagonal tubes of width Δ_c (cross-sectional area $\sqrt{3}\Delta_c^2/2$), where $\Delta_c > D$ to accommodate the particles and $\Delta_c \lesssim 2D$ so particles cannot pass each other along the tube. Thus $\Gamma_2 = \sqrt{3}(\Delta_c - D)^2/2$. For the crystalline phase, the cell represents a hexagonal tube of width Δ_x and length Θ_x , capped by hemi-dodecahedrons [cell volume $\Delta_x^2(\sqrt{2}\Delta_x + \sqrt{3}\Theta_x)/2$]. Since the cells are close packed, the volume of a single cell must be V/N and

$$\Gamma_3 = (\Delta_x - D)^2[\sqrt{2}(\Delta_x - D) + \sqrt{3}(\Theta_x - L)]/2,$$

where $\Theta_x = (2V - \sqrt{2}N\Delta_x^3)/\sqrt{3}N\Delta_x^2$. Notice that for spheres ($L/D = 0$) the cell becomes a dodecahedron, and the theory is identical to the self-consistent free volume

theory.¹¹ Notice also that this single-occupancy cell theory is governed by the shape of the Wigner-Seitz cell in the close-packing limit and therefore does not distinguish between fcc and hcp packing. The above expressions for Γ_{3D} are summarized in Table I.

F_d^{fluid} also depends on the characteristic lengths Δ_s , Δ_c , and Δ_x , and the joint optimization of F^{config} [Eq. (1)] relative to these lengths provides the coupling between the ordered and disordered dimensions. Good expressions for F_d^{fluid} can be obtained with scaled-particle theory. The central quantity of scaled-particle theory is the reversible work W_d associated with insertion of an appropriately scaled particle into a d -dimensional fluid system.¹² For a nematic phase, a spherocylinder of scaled diameter αD and scaled cylinder length λL is inserted into a three-dimensional fluid of parallel spherocylinders of cylinder length L and diameter D . For a smectic phase, a disk of scaled diameter αD is inserted into a two-dimensional fluid of disks of diameter D . And for a columnar phase, a rod of scaled length $\lambda(L + D)$ is inserted into a one-dimensional fluid of rods of length $L + D$. The work function is related to the probability P_d of successful insertion according to $\beta W_d = -\ln P_d$. In the limit of a vanishingly small scaled particle ($\alpha, \lambda \rightarrow 0$), only two-body interactions are involved. P_d can then be expressed exactly in terms of the pair excluded volume (V_{ex}) and total volume (V_{tot}) for the bulk nematic, the pair excluded area (A_{ex}) and total area ($A_{tot} = V/\Delta_s$) for the smectic layer, and the pair excluded length (L_{ex}) and total length [$L_{tot} = V/(\sqrt{3}\Delta_c^2/2)$] for the columnar tube. The results are shown in Table I. At the other extreme of a macroscopically large scaled particle ($\alpha, \lambda \rightarrow \infty$), the work function can also be expressed exactly in terms of a d -dimensional hydrostatic pressure Π_d resisting the formation of a macroscopic cavity in the d -dimensional fluid. The premise of scaled-particle theory is that interpolation between these two exact limits (via an expansion of the work function in terms of the scaling parameters α, λ) provides valid results for the case of $\alpha, \lambda = 1$.

Following Cotter,¹³ we expand the scaled-particle work functions as follows:

TABLE I. Statistical expressions for the d positionally disordered and (3D) positionally ordered dimensions of a system of parallel hard spherocylinders in four possible phases.

| Phase | d | $\lim_{\alpha, \lambda \rightarrow 0} (P_d)$ | Γ_{3D} |
|----------|-----|--|---|
| Nematic | 3 | $1 - NV_{ex}/V_{tot} = 1 - \rho[\frac{1}{6}\pi D^3(1 + \alpha)^3 + \frac{1}{4}\pi D^2 L(1 + \alpha)^2(1 + \lambda)]$ | |
| Smectic | 2 | $1 - NA_{ex}/A_{tot} = 1 - \rho\Delta_s[\frac{1}{4}\pi D^2(1 + \alpha)^2]$ | $\Delta_s - (L + D)$ |
| Columnar | 1 | $1 - NL_{ex}/L_{tot} = 1 - \rho(\sqrt{3}\Delta_c^2/2)[(L + D)(1 + \lambda)]$ | $\sqrt{3}(\Delta_c - D)^2/2$ |
| Crystal | 0 | | $(\Delta_x - D)^2[(\sqrt{2}/2)(\Delta_x - D) + (\sqrt{3}/2)(\Theta_x - L)]$ |

$$\beta W_c^{\text{nematic}}(\alpha, \lambda) = c_{00}^n + c_{10}^n \alpha + c_{01}^n \lambda + c_{11}^n \alpha \lambda + c_{20}^n \alpha^2 + \left(\frac{1}{4} \pi D^2 L\right) (\beta \Pi_3) \alpha^2 \lambda + \left(\frac{1}{6} \pi D^3\right) (\beta \Pi_3) \alpha^3, \quad (2a)$$

$$\beta W_2^{\text{smectic}}(\alpha) = c_{00}^s + c_{10}^s \alpha + \left(\frac{1}{4} \pi D^2\right) (\beta \Pi_2) \alpha^2, \quad (2b)$$

$$\beta W_1^{\text{columnar}}(\lambda) = c_{00}^c + (L + D) (\beta \Pi_1) \lambda, \quad (2c)$$

where $\Pi_2 = \Pi_3 \Delta_s$ and $\Pi_1 = \Pi_3 \sqrt{3} \Delta_c^2 / 2$. Using the fact that the expressions for P_d of Table I are exact for $\alpha, \lambda = 0$, the coefficients in these expansions are taken as

$$c_{mn} = (1/m!n!) \partial^{m+n} (-\ln P_d) / \partial \alpha^m \partial \lambda^n \Big|_{\alpha, \lambda = 0}.$$

The interpolated d -dimensional work function, $\beta W_d(\alpha, \lambda = 1)$, and the d -dimensional number density, ρ_d , directly give the Gibbs free energy $\beta G_d^{\text{fluid}}/N = \ln \rho_d + \beta W_d/N$. Integrating the Gibbs-Duhem relation to obtain an expression for the pressure Π_d , we finally obtain the configurational Helmholtz free energy for the d -dimensional fluid

$$\beta F_d^{\text{fluid}}/N = \beta G_d^{\text{fluid}}/N - \beta \Pi_d / \rho_d.$$

For a given particle volume fraction, $v_p = Nb_0/V$, and spherocylinder axial ratio, L/D , the total free energy [Eq. (1)] for each phase is minimized to obtain the optimal characteristic lengths (Δ_s , Δ_c , and Δ_x) in the ordered dimensions. The phase exhibiting the lowest free energy is then determined to be the globally stable solution. The crossover from one stable phase to another is accompanied by a discontinuous change in the pressure [$\beta \Pi_3 = -(\partial \beta F / \partial V)_{N, T}$] and chemical potential [$\beta \mu = (\partial \beta F / \partial N)_{V, T}$], characteristic of a first-order phase transition. The thermodynamic phase boundaries are computed by simultaneously matching the pressure and chemical potential between the coexisting phases. The results of this calculation are shown in Fig. 1.

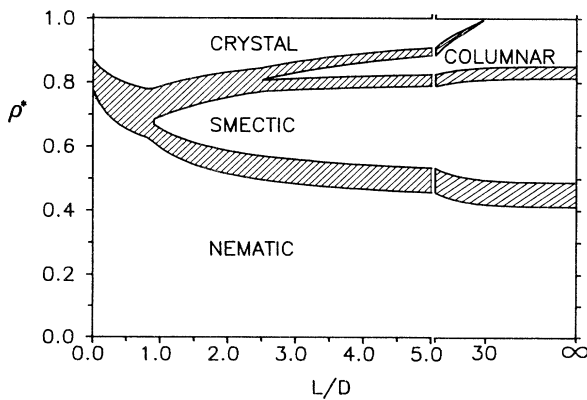


FIG. 1. Phase diagram of the parallel-hard-spherocylinder system as a function of spherocylinder axial ratio (L/D) and the reduced particle number density [$\rho^* = v_p/v_{cp}$, where $v_{cp} = (\pi\sqrt{3}/6)(L/D + \frac{2}{3})/(L/D + \sqrt{2}/3)$ is the spherocylinder close-packing fraction]. Shaded areas denote regions of phase coexistence.

This figure is remarkably similar to the phase diagram constructed from the extensive Monte Carlo (MC) study of Ref. 6. Regions of nematic, smectic, columnar, and crystalline stability all occur in very good correspondence with the MC phase diagram. The smectic layer spacing at the nematic-smectic free-energy crossover, shown in Fig. 2, is found to be in excellent quantitative agreement with the MC results (i.e., as good as or better than that obtained with density-functional theory¹⁰). At the smectic-columnar transition, the scaled smectic layer spacing and scaled columnar tube width are found to be essentially independent of spherocylinder axial ratio with values $\Delta_s/(L+D) = 1.04$ and $\Delta_c/D = 1.06$, respectively.

Detailed comparisons can be made between the features of our phase diagram and the MC phase diagram. For the hard-sphere system ($L/D = 0$), we find a first-order freezing transition at $\rho^* = 0.78 \rightarrow 0.87$ (MC result: $\rho^* = 0.67 \rightarrow 0.73$). A stable smectic phase is first seen for $L/D = 0.9$ at $\rho^* = 0.68$ (MC result: $0.25 < L/D < 0.50$, $\rho^* \approx 0.60$). A stable columnar phase, intervening between the smectic and crystalline phases, first occurs for $L/D = 2.5$ at $\rho^* = 0.81$ (MC result: $3.0 < L/D < 5.0$, $\rho^* \approx 0.80$). The columnar-crystalline transition moves to higher ρ^* with increasing L/D until the crystalline phase disappears completely at $L/D \approx 30$ (MC result: crystalline phase disappears in the range $5 < L/D \leq \infty$). In the limit of $L/D \rightarrow \infty$, the nematic-smectic transition occurs at $\rho^* = 0.41 \rightarrow 0.49$ with a smectic layer spacing of $\Delta_s = 1.27L$ at the crossover (MC result: $\rho^* = 0.39$, $\Delta_s = 1.27L$) and the smectic-columnar transition occurs at $\rho^* = 0.82 \rightarrow 0.85$ (MC result: $\rho^* = 0.56$). This comparison demonstrates a fair quantitative agreement between our theory and the MC study.

Differences between the present results and the MC

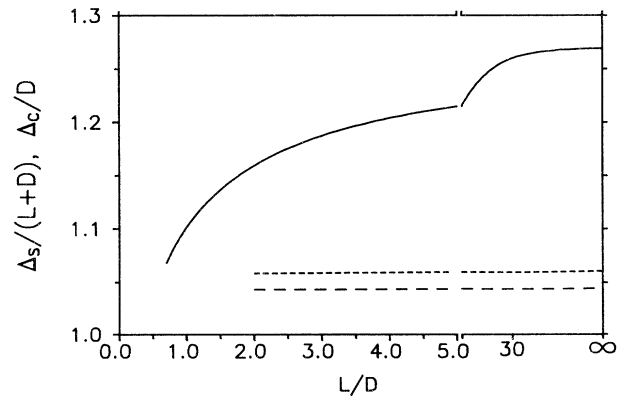


FIG. 2. Scaled smectic layer spacing [$\Delta_s/(L+D)$] at the nematic-smectic (—) and smectic-columnar (---) crossovers, and scaled columnar tube width (Δ_c/D) at the smectic-columnar crossover (···) as a function of spherocylinder axial ratio (L/D).

results can be attributed to the severity of the positional ordering imposed by our model. Our strict compartmentalization of particles in the ordered dimensions is known to underestimate the free volume which, in turn, would be expected to shift transitions to higher densities. Strict compartmentalization also exaggerates discontinuities at the transitions. Thus, it is not surprising that our calculated transitions are systematically shifted to somewhat higher ρ^* than are found in the MC study and that the second-order nematic-smectic transition found in the MC study is predicted to be first order in our model.

The above phase behavior depends on the assumed packing arrangements of the columnar and crystalline phases. We have considered other possible geometries (e.g., cubic versus hexagonal) but, not surprisingly, we find that they lead to less stable states.

Scaled-particle theory is known to be exact in one dimension and has been shown to be good, even for high fluid densities, for disks in two dimensions and spheres in three dimensions.¹² We find that replacing the scaled-particle theory with cruder excluded-volume theories (Alben,¹⁴ Herzfeld¹⁵) leads to very poor results.

We conclude that scaled-particle theory seems to provide a good description of the fluid dimensions while straightforward statistics seem to provide a good approximation of the entropy remaining in the positionally ordered dimensions. This approach may prove useful in describing positionally ordered phases in more complex liquid-crystalline systems.

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