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Equation of state for parallel hard spherocylinders

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A recent model for positional ordering in systems of monodisperse parallel hard spherocylinders is used to calculate the pressure over the entire range of densities and cylinder axial ratios. Reasonable quantitative agreement with Monte Carlo data is obtained for the full spectrum of nematic, smectic, columnar, and crystalline order. Analytical expressions are also given for the characteristic lengths of the ordering in these phases.

In a recent Letter,[1] we presented an excluded-volume theory for positional ordering in systems of monodisperse hard parallel spherocylinders. The compensation for the loss of positional entropy in some dimensions by the gain in positional entropy in the remaining dimensions is described via a simple intuitive model. The predicted phase sequences are remarkably realistic, although the imposition of stringent positional constraints (see below) forces all transitions to be discontinuous and increases the transition densities. The theoretical phase diagram exhibits the full spectrum of nematic, smectic, columnar, and crystalline behavior found in a recent Monte Carlo (MC) study.[2] A comparison of the two phase diagrams shows good agreement over the full range of densities and cylinder axial ratios.[1] In this report, we extend the above comparison to the equation of state in the various ordering regions. We also discuss possible improvements to our model.

The theory imposes constraints on the particle positions in the ordered dimensions just sufficient to allow maximum positional freedom in the disordered dimensions. Thus particles are not permitted to cross layer boundaries in the smectic phase, hexagonal cylinder boundaries in the columnar phase, or cell boundaries in the crystalline phase. With these constraints, the d disordered dimensions and the $3-d$ ordered dimensions can be modeled separately, and the configurational free energy per particle can be expressed as $f_d^{\text{conf}}=\ln\rho-1+f_d^{\text{fluid}}+f_{3-d}^{\text{cryst}}$, where ρ is the particle number density, f_d^{fluid} represents the nonideality contribution from the d fluid-like dimensions, and f_{3-d}^{cryst} represents the nonideality contribution from the $3-d$ crystal-like dimensions.

f_d^{fluid} is expressed quite accurately in terms of well-known scaled particle theory results for a $(d=3)$-dimensional fluid of spherocylinders (nematic phase),[3] a $(d=2)$-dimensional fluid of disks (smectic phase), and a $(d=1)$-dimensional fluid of lines (columnar phase).[4] Thus

$$f_d^{\text{fluid}}=-\ln(1-v_d)+a_d v_d/(1-v_d)+b_d[v_d/(1-v_d)]^2 ,$$

where v_d, the d-dimensional particle volume fraction in the d fluid dimensions, and the coefficients a_d and b_d, are given in Table I.

An approximation of f_{3-d}^{cryst} is obtained from simple cell theory results for a line in a $(3-d=1)$-dimensional box (smectic phase), a disk in a $(3-d=2)$-dimensional hexagon-shaped box (columnar phase), and a spherocylinder in a $(3-d=3)$-dimensional box in the shape of a hexagonal tube capped by hemidodecahedrons in proportions chosen to minimize f_3^{cryst} (crystalline phase).[5,6] Thus

$$f_{3-d}^{\text{cryst}}=-\delta_{0\text{d}}-(3-d)\ln[(1-v_{3-d}^{*1/(3-d)})] ,$$

where v_{3-d}^*, the reduced $(3-d)$-dimensional particle volume fraction in the $(3-d)$ ordered dimensions, is given in Table I and $\delta_{0\text{d}}$ is the Kronecker delta [contrib-

TABLE I. Theoretical expressions for contributions to the configurational free energy f_d^{conf} (see text) and the reduced pressure P_d^*. Here $y_3=v_3/(1-v_3)$, L and D are the cylinder length and diameter of the particles, respectively, and $\rho_{\text{CP}}=2/[(\sqrt{3}D^3)(L/D+\sqrt{2/3})]$ is the density at close packing.

Order	d	a_d	b_d	v_d	v_{3-d}^*	P_d^*
Nematic	3	3	$\frac{3}{2}\frac{1+3L/D+2(L/D)^2}{[1+(3L)/(2D)]^2}$	$[(\pi/6)D^3+(\pi/4)LD^2]\rho$		$y_3+a_3y_3^2+2b_3y_3^3$
Smectic	2	1	0	$(\pi/4)D^2\Delta_s\rho$	$(L+D)/\Delta_s$	$v_3/(1-v_2)^2$
Columnar	1	0	0	$(\sqrt{3}/2)\Delta_c^2(L+D)\rho$	$(D/\Delta_c)^2$	$v_3/(1-v_1)$
Crystalline	0				ρ/ρ_{CP}	$v_3/(1-v_3^{*1/3})$

uting only for crystalline ordering ($d=0$), in which the particles are distinguishable by virtue of being in separate cells]. Notice that f_3^{cryst} represents a straightforward generalization of the self-consistent free volume theory for the freezing of hard spheres.[7]

For $d=1,2$, the characteristic lengths of ordering (i.e., the smectic layer thickness and the columnar tube diameter) couple f_d^{fluid} and f_{3-d}^{cryst}. As the characteristic lengths decrease, v_d and f_d^{fluid} decrease, while v_{3-d}^* and f_{3-d}^{cryst} increase. It is this trade-off that drives positional ordering. The equilibrium values of the characteristic lengths for ordering are those which minimize the total f_d^{conf}. In the smectic phase, the dependence of the layer spacing Δ_s, on the reduced particle density $\rho^*=v_3^*$ and the particle dimensions L and D is given by

$$\Delta_s=[9(L+D)/(8h)]\times[1-2\,\mathrm{sgn}(1-h)\sin(\tfrac{1}{3}\sin^{-1}|1-h|)]\ ,$$

where

$$h=[(27\pi)/(32\sqrt{3})]\gamma v_3^*$$

and

$$\gamma=(L/D+1)/[L/D+\sqrt{(2/3)}]\ .$$

Similarly, the side-to-side diameter of the tube in the columnar phase Δ_c is given by $\Delta_c=D(\gamma v_3^*)^{-1/3}$. Finally, the phase exhibiting the lowest f_d^{conf} is determined to be the globally stable state. The characteristic lengths for ordering, and the predicted phase diagram, are discussed in relation to the MC results in Ref. 1.

The MC study also provides detailed information about the equation of state for hard parallel spherocylinders. It is therefore interesting to compare the MC pressure with the model predictions. Table I compiles the appropriate theoretical expressions for the reduced pressure

$$P_d^*=\beta(v/\rho)P_d=\beta v\rho\partial f_d^{\mathrm{conf}}/\partial\rho\ ,$$

where P_d is the pressure, $\beta=1/k_BT$, and v is the particle volume fraction ($v=v_3$). In Fig. 1 we compare the theoretical predictions with the MC results for the four phase sequences exhibited by the system with increasing cylinder axial ratio, L/D: nematic→crystalline (a), nematic→smectic→crystalline (b), nematic→smectic→columnar→crystalline (c), and nematic→smectic→columnar (d).

The MC pressure data for the low-density nematic fluid branch are in good quantitative agreement with the scaled particle result (Table I) for the entire range of L/D. For small L/D, this merely reflects the well-

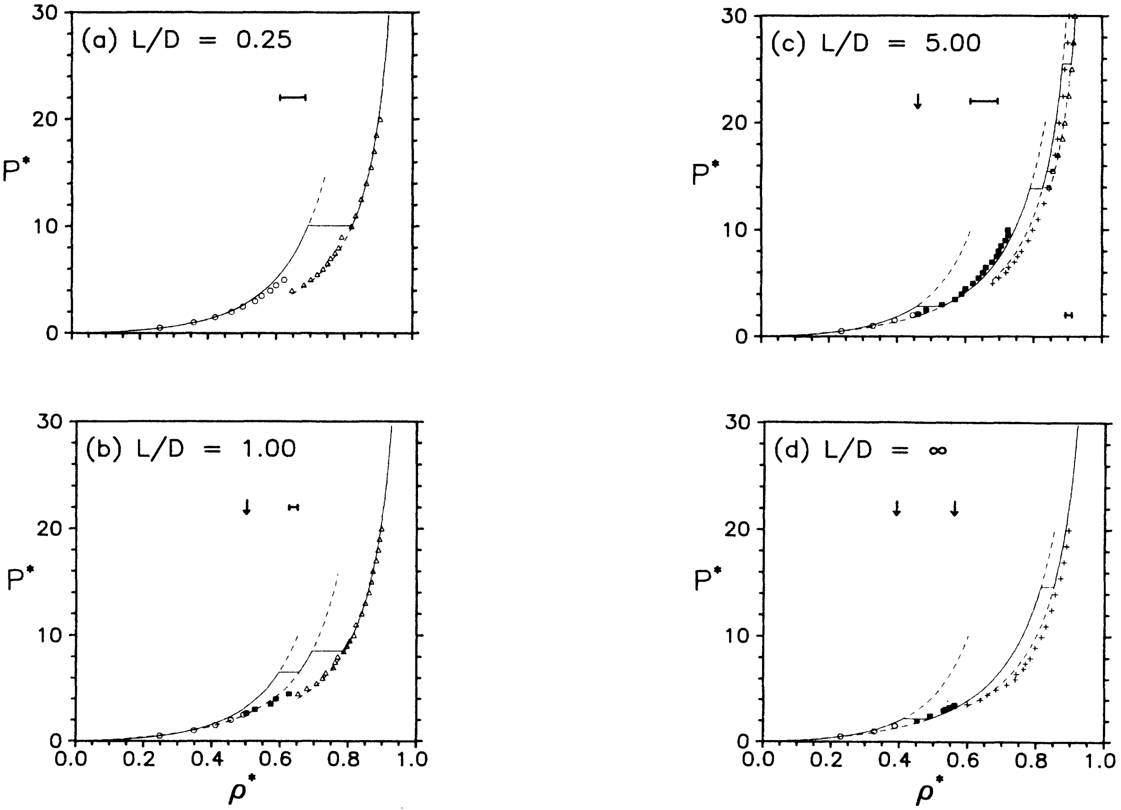

FIG. 1. Comparison of the theoretical equation of state (solid line) with the MC data of Ref. 2 for $L/D=0.25$ (a), 1.0 (b), 5.0 (c), and ∞ (d). $P^*(=P_d^*)$ is the reduced pressure and $\rho^*=\rho/\rho_{\mathrm{CP}}$ is the reduced density. Plateaus indicate theoretically predicted phase coexistence. Dashed lines represent the extensions of the respective theoretical pressure equations. The symbols indicate MC results for the nematic fluid branch (○), smectic ordering (■), columnar (+), and solid branch (△). Bars indicate MC phase coexistence, and arrows show the location of MC continuous transitions.

known accuracy of the scaled particle equation of state for hard spheres, which is equivalent to the Percus-Yevick expression obtained via the compressibility equation (e.g., Refs. 4 and 8). Thus, while the second virial coefficient is exact for all L/D, for $L/D=0.25$ (a), the third, fourth, and fifth virial coefficients exceed the numerical results (cf. Table III in Ref. 2) by only $<0.01\%$, 4%, and 12%, respectively. As the particle asymmetry increases, these deviations gradually become more pronounced, i.e., 0.6%, 9%, and 30% for $L/D=1$ (b); 2%, 21%, and 86% for $L/D=5$ (c); and 3%, 29%, and 136% for $L/D=\infty$ (d). These increased deviations arise from the too weak L/D dependence of the scaled particle pressure (e.g., $1 \geq b_3 \geq \frac{8}{9}$). Compared to the generalized Carnahan-Starling equation,[9] which for parallel particles lacks L/D dependence in its virial coefficients, scaled particle theory performs slightly better for large L/D and is somewhat less accurate for small L/D.

For axial ratios exceeding 0.25 the MC calculation exhibits a continuous nematic-to-smectic transition in the range $0.6 \gtrsim \rho^* \gtrsim 0.4$ with increasing axial ratio. Figures 1(b)–1(d) illustrate the pronounced difference between the nematic and smectic pressures predicted by the theory. This lends additional support to our intuitive approach, since the latter provides a good fit to the smectic MC results for all L/D and all densities, except in the immediate vicinity of the transition. At sufficiently high densities, the spherocylinders freeze into a hexagonally packed crystalline solid, except at large L/D ($\gtrsim 30$), where the columnar mesophase is stable even at close packing.[1,2] The theoretical pressure equation for the solid is again in good overall agreement with the corresponding MC results. It is worth mentioning, that the asymptotic pressure, i.e., the leading term in the high density expansion,

$$P_0^* = 3[v_3/(1-v_3^*)][1-\tfrac{1}{3}(1-v_3^*)+O((1-v_3^*)^2)] ,$$

already represents a reasonable fit to the MC solid branch (with deviations $\lesssim 10\%$ for all L/D values studied in Ref. 2). Unfortunately, the scatter in the MC data does not permit a sufficiently precise determination of expansion coefficients. The expression $P_0^* = Dv_3/(1-v_3^*)$, where D is the space dimension, has previously been shown to be exact in the high-density limit for finite hard disk and hard sphere systems (cf. Ref. 10). Finally, for the columnar case [cf. $L/D=5$ (c) and $L/D=\infty$ (d)] the agreement between our theory and the MC results is still fair, but poorer than in the other comparisons.

Although the theoretical pressure curves for each phase show good agreement with the MC results, the transitions occur at somewhat higher densities than in the MC simulation. Consequently, the theoretically predicted transition pressures are also exaggerated. As discussed previously,[1] this is not surprising considering the strict positional constraints imposed by the simple cell model that was used to separate the degrees of freedom of the ordered and disordered dimensions. However, the close correspondence between the theoretical pressure and the MC results for each phase indicates that the model provides a reasonable description of the variation of the free energy with density, and that the excess free energy due to the strict positional constraints is only weakly density dependent.

Clearly, it would be desirable to relax the positional constraints in the model. Although the separation of the ordered and disordered degrees of freedom would no longer be rigorous, this separation may still be adopted as a physically reasonable approximation. We can then consider whether the model can be improved introducing generalized expressions for f_d^{fluid} and f_{3-d}^{cryst} based on other fluid and cell theories. For instance, slightly more accurate expressions for f_d^{fluid} can be obtained via suitable expansions, e.g., multiterm virial or y expansions and Padé approximations. However, our preliminary calculations show that an improved f_d^{fluid} has little effect on the above results. It is more important to improve on the expression for f_{3-d}^{cryst}, i.e., the corresponding free volume. For simpler systems, i.e., spheres in three dimensions and disks in two dimensions, it is well known that the Lennard-Jones-Devonshire theory or the correlated cell model yield not only a good description of the variation of the free volume, but also describe the free volume itself quite well. These theories, therefore, yield better coexistence densities and somewhat improved equations of state for spheres and disks than the simple cell model.[10] For our system, the adaptation of the correlated cell model for f_{3-d}^{cryst} seems most promising, although it requires a rather complicated free volume geometry to account for local correlations near the melting transition.[11,12]

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[6] There is no *a priori* way of choosing the symmetries in the constrained dimensions of the solid and columnar phases. However, the hexagonal symmetries used here agree with the MC result and prove to be stable against other types of ordering, e.g., simple cubic symmetry.

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