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Mixture of hard spherocylinders and spheres in the virial expansion

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A mixture of hard spherocylinders and spheres is studied in a virial expansion. The introduction of spheres into a partially aligned system of spherocylinders induces, via a small two-phase region, a transition to an isotropic phase. The dependence of this transition upon the size of particles is studied.

I. INTRODUCTION

As is well known, the theoretical predictions for pure liquid crystals by the lattice model and the virial expansion[1] are qualitatively similar while quantitatively different. Mixtures of mesomorphic substances have been studied with the lattice model by Peterson, Martire, and Cotter[2] and by Alben.[3] Ågren and Martire[4] recently studied the effect of a nonmesomorphic substance on the nematic-isotropic transition using the lattice model. In this paper we report the results for the same system, but studied in a virial expansion.

II. MODEL

Our system consists of n spherocylinders with diameter D and total length $L+D$ and m spheres with diameter d contained in a volume V. The only forces between the particles are that the particles are impenetrable. Let $f(\Omega)$ be the distribution function for the long axis of the spherocylinders. Following Onsager[5] we can then write down the following expression for the Helmholtz free energy F, truncating after the second virial coefficient,

$$\frac{F}{kT} = -(n+m)\ln(V) + n\ln(n) - n + m\ln(m) - m + \frac{1}{2V}\left\{ n^2 \int d\Omega_1\, d\Omega_2\, \beta(\Omega_1,\Omega_2) f(\Omega_1) f(\Omega_2) + m^2 \tfrac{4}{3}\pi d^3 + 2nm\left[\tfrac{1}{6}\pi(D+d)^3 + \pi\left(\frac{D+d}{2}\right)^2 L\right]\right\} + n\int d\Omega\, f(\Omega)\ln[4\pi f(\Omega)], \qquad (1)$$

where

$$\beta(\Omega_1,\Omega_2) = \tfrac{4}{3}\pi D^3 + 2\pi D^2 L + 2DL^2|\sin\gamma| \qquad (2)$$

is the excluded volume between two spherocylinders pointing in directions Ω and Ω', respectively, and γ is the angle between Ω and Ω'. We make one more simplification, namely, replacing $|\sin\gamma|$ in Eq. (2) by $\sin^2\gamma$. This has very little influence on the results,[1] but simplifies the calculations considerably.

The distribution function $f(\Omega)$ is determined by the condition that the Helmholtz free energy must be stationary with respect to variations of $f(\Omega)$. Using the modified form of Eq. (2), straightforward calculations give

$$f(\Omega) = \zeta \exp[2(n/V)DL^2 S\cos^2\theta], \qquad (3)$$

where S is the order parameter defined through

$$S = \tfrac{1}{2}\int d\Omega\, f(\Omega)(3\cos^2\theta - 1) \qquad (4)$$

and ζ is a normalization factor. It is easily shown that Eqs. (3) and (4) also make the Gibbs free energy stationary. If we had used the exact form of Eq. (2), we would have obtained a nonlinear integral equation for $f(\Omega)$ instead of Eq. (3). Equations (3) and (4) always have the solution $S=0$, $f(\Omega)=1/4\pi$ (an isotropic phase), and this is the only solution for sufficiently low densities and sufficiently short rods. Above some critical density, which depends upon the length of the rods, two new solutions $0<S_1<S_2<1$ appear (an anisotropic phase), where the solution S_1 corresponds to a maximum and the solution S_2 to a minimum in the free energy. At some still higher density $S_1=0$, thus leaving us with only two solutions $S=0$ and $S=S_2$.

III. RESULTS

In systems of hard particles only the ratio of the temperature and pressure appears as an independent variable. Therefore in what follows we will assume that the pressure is held constant and that variations in the temperature-pressure ratio are due to variations in temperature only. In particular, we will be concerned with the reduced temperature $\phi^* = T/T_{N-I}$, where T_{N-I} is the transition temperature for a pure rod system. The effect of the insertion of the spherical solute molecules is to lower the transition temperature. We also find, in addition to the usual nematic and isotropic phases, a small two-phase region. The limits of this two-phase region were determined by equating the chemical potentials of the rods and the spheres, respectively, in the two phases. The transition-temperature depression at the limit between the nematic phase and the two-phase region can be represented by $-\partial\phi^*/\partial x_2$ or $-\partial\phi^*/\partial v_2$, where x_2 is the mole fraction of solute and v_2 the solute volume fraction of the total occupied volume. For small temperature depressions ($\phi^* \gtrsim 0.95$), $-\partial\phi^*/\partial x_2$ and $-\partial\phi^*/\partial v_2$ are nearly independent of ϕ^*. [$\phi^*(x_2)$ at the two-phase boundaries is slightly convex.] They were calculated using a least-squares fit to the concentrations at different ϕ^* (i.e., $\phi^* = 0.990$, 0.980, 0.971, 0.962, 0.952, 0.943, and 0.935). They are displayed in Fig. 1 as a function of d/D for $L/D = 5$ and 10. Qualitatively as well as quantitatively they differ very little from the same curves for the lattice model. In some other respects, too, there are similarities to the lattice model. The order parameter at the transition is virtually independent of solute concentration. The largest variations are from 0.540 for $L/D = 5$ and 0.585 for $L/D = 10$ in the pure rod system to 0.563 and 0.601, respectively, for $\phi^* = 0.935$ and $d/D = 2$. In the lattice model it was found that the extension of the two-phase region, in mole-fraction terms, at a fixed reduced temperature was nearly independent of the size of the solute molecules and could be expressed by the function

$$\Delta x_2 = \kappa(1 - \phi^*). \tag{5}$$

The values of κ are given in Table I. In the lattice model $\kappa = 0.30$ for $L/D = 5$ and 0.47 for $L/D = 10$.

The volume fraction of the total volume occupied by rods at the transition varies by less than 1.5%, being 0.633 for $L/D = 5$ and 0.307 for $L/D = 10$ in a pure rod system, when d/D and ϕ^* are varied, which is also found in the lattice model.

IV. DISCUSSION

The agreement between the theory and experiments, which is fairly good, is discussed elsewhere.[4]

The main point we want to stress is the behavior of the lattice model and the virial expansion with respect to the solute. Although the relative density changes at the transition differ by up to a factor of 2, the density changes are in both cases almost (less than 5% variation) independent of the solute concentration. The degree of order in the two models is quite different, but the variation with added solute is the same. To compare $d\phi^*/dx_2$ and $d\phi^*/dv_2$ from the virial expansion with those from the lattice model is less trivial, however. The problem is that because of the different shapes of the particles in the two models there is no obvious way to relate exactly their sizes. But if we compare directly the values of Fig. 1 for $L = 5$ we see that $d\phi^*/dx_2$ is 23% greater in the lattice model for $d/D = 1.0$ and 54% at $d/D = 2.0$. For $L = 10$ the same variation is from 23% to 37%. In view of the above-mentioned difficulties we think this is a reasonable agreement, and one could certainly improve upon it by playing around a little with the sizes.

Thus the interesting conclusion to be drawn from the comparison between the lattice model and the virial expansion is that the responses of the two models to the introduction of a solute are mostly

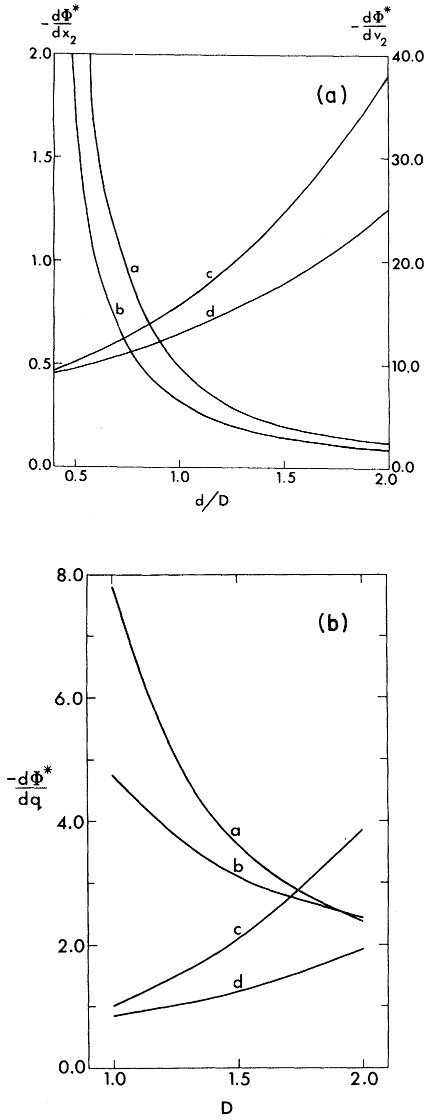

FIG. 1. (a) $-\partial\phi^*/\partial v_2$ and $-\partial\phi^*/\partial x_2$ at the nematic–two-phase boundary for the virial expansion as a function of solute size. Curve a: $\partial\phi^*/\partial v_2$, $L = 10$; curve b: $\partial\phi^*/\partial v_2$, $L = 5$; curve c: $\partial\phi^*/\partial x_2$, $L = 5$; curve d: $\partial\phi^*/\partial x_2$, $L = 10$. (b) Same as for (a) but for the lattice model (from Ref. 4, where L is the length-to-breadth ratio of the rods and D is ratio of the cube side to the breadth of the rod).

TABLE I. Coefficient for the extension of the two-phase region for different solute and solvent sizes.

	κ	
d/D	$L/D=5$	$L/D=10$
0.4	0.316	0.370
0.6	0.330	0.382
0.8	0.343	0.392
1.0	0.354	0.403
1.2	0.365	0.413
1.4	0.373	0.423
1.6	0.382	0.432
1.8	0.389	0.441
2.0	0.400	0.450

very similar and always much closer than the results for the pure rod systems, which often show great quantitative differences due to the use of discrete orientations in the first case and a continuous range of orientations in the second. Or, expressed differently, if A_{1m} and A_{ve} is a property of the system at the phase transition (e.g., the order parameter) calculated in the lattice model and the virial expansion, respectively, then A_{1m} and A_{ve} can differ considerably, but derivates of the type $\partial A_{1m}/\partial x_2$ and $\partial A_{ve}/\partial x_2$ are nearly equal.

The similar predictions of the lattice model and the virial expansion can be contrasted with those made by Humphries, James, and Luckhurst,[6] who studied the same system using a mean field treatment of the Maier-Saupe type. They, of course, also obtained the same constancy of the order parameter at the transition, but, on the other hand, they predict $d\phi^*/dx_2=-1$ for all solvents and solutes. This and other aspects of their theory are discussed more extensively elsewhere.[2]

With the relatively high densities, $\rho=0.633$ at the transition for $L/D=5$ and 0.307 for $L/D=10$, a virial expansion that only retains the second virial coefficient is of course questionable. We think that it is, however, justified by its close agreement with both experiments and the lattice model. The latter is perhaps not so surprising since both describe systems of hard rods in a mean field approximation.

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