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Comment on ''Gas-liquid coexistence and demixing in systems with highly directional pair potentials''

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It is shown that the simulation results of Blair and Patey [Phys. Rev. E **57**, 5682 (1998)] for a model nematic liquid crystal are qualitatively described by mean-field theory. Furthermore, it is pointed out that the absence of (isotropic) liquid-vapor equilibrium appears to be a common feature of a number of model fluids characterized by strongly anisotropic pair potentials. [S1063-651X(99)03201-8]

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In a recent paper Blair and Patey [1] reported a Gibbs ensemble Monte Carlo (GEMC) [2–5] simulation study of a liquid crystal (LC) model characterized by the pair potential [6]

$$u(12)=u_0(12)+u_a(12), \tag{1}$$

where (12) denotes the set of positional and orientational coordinates of molecules 1 and 2, $u_0(12)$ is the interaction between hard spherical cores of diameter σ, and the anisotropic part $u_a(12)$ is given by

$$u_a(12)=-4\lambda\epsilon\left(\frac{\sigma}{r}\right)^6 P_2(\cos\gamma), \tag{2}$$

with r the intermolecular distance, $P_2(x)$ the second Legendre polynomial, and γ the angle between the long axes of the two particles, the strength of their attraction being given by the product $\lambda\epsilon$. They found an isotropic-to-nematic (I-N) transition but, contrary to their expectations, no isotropic liquid-vapor (I-V) coexistence. In what follows I shall argue that this is indeed the behavior to be expected on the basis of the simplest mean-field (MF) theory and that it appears to be common to a number of other systems.

The ''Maier-Saupe'' LC model [7] in question, Eq. (1) with Eq. (2), is in fact a special case of that introduced by Telo da Gama a few years ago [8], viz.,

$$u_{MS}(12)=u_0(12)-A\left(\frac{\sigma}{r}\right)^6-B\left(\frac{\sigma}{r}\right)^6 P_2(\cos\gamma), \tag{3}$$

which in turn can be regarded as a simplification of Luckhurst and Romano's [see [9], Eqs. (2)–(6)]. In subsequent work it was shown that the topology of its phase diagram depends sensitively on the ratio $R=B/A$ of the strengths of the anisotropic and isotropic parts of the intermolecular potential [10]. At small R we find the usual I-V critical point and a N-I-V triple point. As R is increased, the ratio of critical to triple point temperatures decreases until it reaches unity for $R\sim 0.79$. Thus, if $R\gtrsim 0.79$ there is no I-V coexistence, as the amount of isotropic attractive energy present is insufficient to produce condensation at a density lower than that of nematic ordering at a given temperature. The system simulated by Blair and Patey falls into this category, as it corresponds to $R=\infty$. Within MF theory it is straightforward why this should be the case: The only contribution to the free energy density from long-range forces is proportional to η_2^2, where $\eta_2=\langle P_2(\cos\theta)\rangle$ is the nematic order parameter, which therefore vanishes in the I phase [see [8], Eqs. (20) and (21)]. The same conclusion is most likely valid beyond MF theory; see below.

The phase diagram, pressure, and order parameter calculated using the MF theory of [8,10] are compared with simulation in Figs. 1, 2, and 3, respectively. Results are given in terms of the (dimensionless) reduced density $\rho^*=\rho\sigma^3$, temperature $T^*=k_BT/\epsilon$ [11], and pressure $P^*=P\sigma^3/k_BT$. Theory underestimates the width of the I-N coexistence region and predicts too steep slopes for the binodals (which are, however, partially bracketed by simulation data points; see Fig. 1). Consistently, it underestimates the order parameter at the transition and its temperature dependence (Fig. 3).

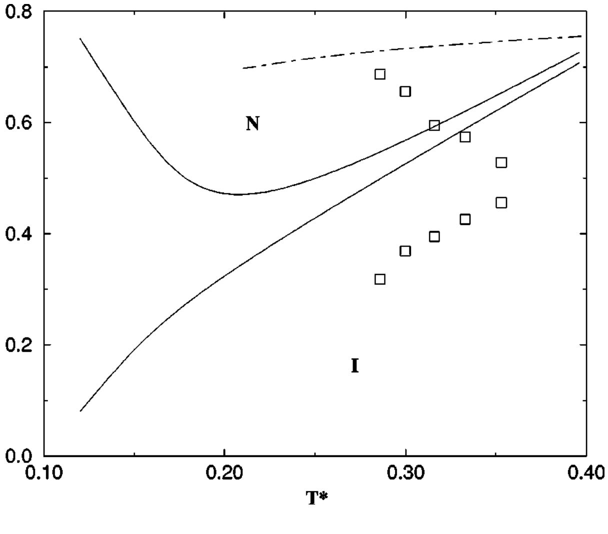

FIG. 1. Phase diagram of the LC model, Eq. (1) with Eq. (2), from MF theory (see [10], Fig. 3) (solid lines) and GEMC simulation [1] (open squares). $\rho^*=\rho\sigma^3$ and $T^*=k_BT/\epsilon$ are the reduced density and reduced temperature, respectively. I, isotropic phase; N, nematic phase. The dot-dashed line is the limit of stability of the N *liquid* phase relative to the N *solid*, obtained from bifurcation analysis [13].

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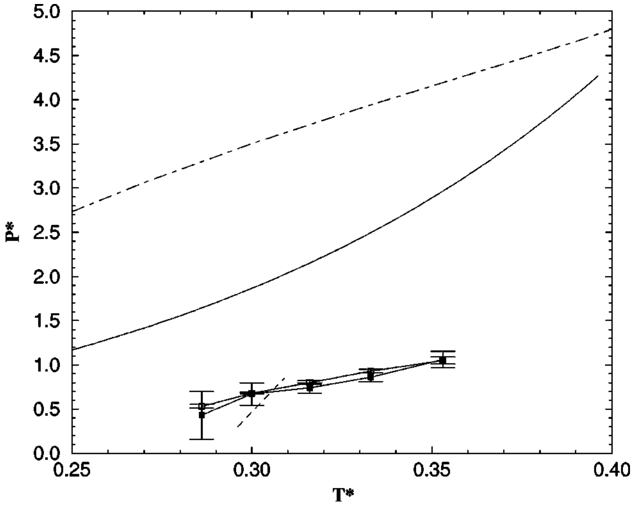

FIG. 2. Pressure at *I*-*N* coexistence for the system in Fig. 1, from MF theory [10] (solid line) and simulation [1] (open squares, *I* phase; filled squares, *N* phase). The short-dashed line is the limit of stability of a fcc solid phase with respect to the liquid [see [1], Fig. 1(b)], whereas the dot-dashed line is, as in Fig. 1, the limit of stability of the *N liquid* phase relative to the *N solid* [13].

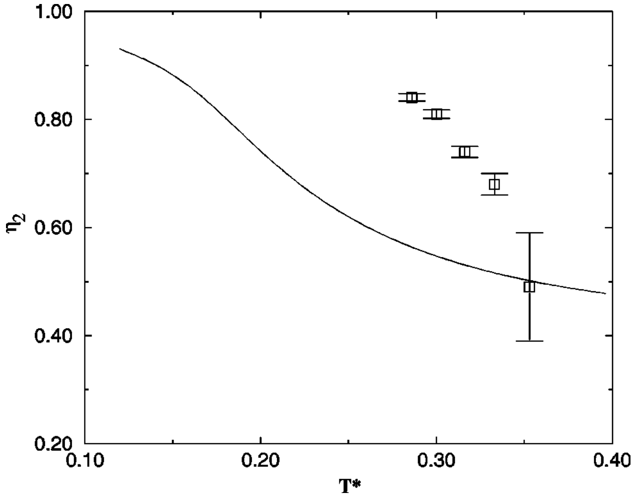

FIG. 3. Order parameter at *I*-*N* coexistence for the system in Fig. 1, from MF theory [10] (solid lines) and simulation (open squares) [1]. Numerical experiment reveals a more strongly ordered *N* phase than is predicted by theory.

Pressures, by contrast, are overestimated by a factor of 2–5 (Fig. 2).

In our earlier papers [8,10] the solid phases that will perforce be present were disregarded [12]. We have since been able to find the limit of stability of the liquid with respect to solid fluctuations, from bifurcation analysis [13]; this is shown as the dot-dashed line in Figs. 1 and 2. It is a different branch of the solid-liquid spinodal from that computed by Blair and Patey (short-dashed line in Fig. 2), but it allows us approximately to locate the freezing transition, which is in poor agreement with simulation.

I conclude by noting that the same phenomenon of the disappearance of the *I*-*V* critical point has been encountered in a number of other model fluids, by both theory and simulation: mixtures of rodlike colloidal particles and (hard-sphere) polymers where the ratio of the diameters of polymer and rod is less than about 0.1 [14], binary mixtures of sufficiently dissimilar thermotropic nematogens [15], very long hard rods in an attractive MF [16,17], the ferromagnetic Heisenberg fluid for $R \sim 0.63-0.71$ [18–22], the Gay-Berne fluid [23,24], and the fluid of hard spherocylinders with generalized square wells if the shape anisotropy parameter exceeds a critical value [17,25]. So it seems to be a general feature of liquid phase behavior whenever there is competition between isotropic and angle-dependent forces rather than an artifact of any particular approximation (which will have only quantitative consequences). Indeed, although a *modified* MF treatment yields a different threshold *R* than the MF for the Heisenberg fluid [21], qualitatively the scenario remains unchanged. Finally, it would be interesting to verify other predictions of the above theories, namely, the occurrence of order-order critical points.

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