Island of Vapor-Liquid Coexistence in Dipolar Hard-Core Systems

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Contrary to theoretical expectations, spheres with central point dipoles have recently been shown not to exhibit a vapor-liquid phase transition; instead the system forms chains of dipoles in a nose-to-tail configuration. We study hard spherocylinders with central longitudinal point dipoles, and induce an island of vapor-liquid coexistence by elongating the molecules. As the length of the molecule is increased, a vapor-liquid envelope appears. After further elongation this region diminishes and then disappears; the system now exhibits antiparallel side-by-side chains of dipoles. [S0031-9007(96)00318-3]

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The understanding of phase transitions in a variety of systems has changed dramatically in recent years. Entropy-driven phase transitions are typical examples of this: in keeping with the early predictions of Onsager [1], nematic [2] and smectic [3] liquid crystalline states have been found for systems with purely repulsive interactions; fluid phase separation has been suggested for mixtures of hard spheres of disparate size [4] although this has not been confirmed by computer simulation; phase transitions in solutions of colloids and polymers, reminiscent of a vapor-liquid phase transition, have been reported for model systems with purely repulsive interactions [5]. Novel phase behavior has also been found for systems which possess repulsive and attractive interactions where entropy and enthalpy play competing roles: as the range of the intermolecular attractive interaction is decreased, the usual vapor-liquid envelope is engulfed by a region of fluid-solid phase coexistence, and for systems with a very short attractive range, solid-solid coexistence is found [6]. Of particular current interest is the vapor-liquid transition of hard spheres with Coulombic attractive interactions (the restricted primitive model) [7]. An understanding of the aggregates formed by the charged hard spheres is central to a theoretical description of the system. The formation of chainlike structures by dipolar hard spheres is invoked to explain the lack of a vapor-liquid phase transition in this system [8,9], one of the most surprising recent observations in the light of extensive theoretical predictions to the contrary. Dipolar spheres have also been examined in the context of ferroelectric liquid crystal phases [10], although some of the results seem to be a consequence of the type of boundary conditions that are used. It is in this climate of reborn interest, novel ideas, and controversy in the area of dipolar hard spheres that we undertake our study.

The theoretical approaches examined to date for dipolar hard spheres all predict a region of vapor-liquid coexistence. The possibility of such a transition has been suggested [11] by noting that the Boltzmann weighted orientational average of the dipole-dipole interaction leads to an intermolecular potential with the same form as the van der Waals interaction, which, of course, leads to vapor-liquid coexistence [12]. Perturbation theory (PT) [13], the mean-spherical approximation (MSA) [13,14], and various forms of the hypernetted chain (HNC) integral equation [15] also predict vapor-liquid coexistence for dipolar hard spheres.

The first simulation results for dipolar hard spheres by Ng *et al.* [16] appear to confirm the presence of vapor-liquid coexistence. However, because of the substantial computational requirement, an unusually small system of $N = 32$ particles was simulated using the standard minimum image convention without the special treatment of the long-range interactions, e.g., with the Ewald or reaction field methods. Two recent simulation studies using more sophisticated techniques for the simulation of phase equilibria and the treatment of the long-range interactions have brought these earlier results into question. Caillol [8] has simulated large systems (up to $N = 512$) of dipolar hard spheres with the isothermal-isobaric (*NPT*) [17] and Gibbs ensemble Monte Carlo (GEMC) [18] techniques, treating the long-range interactions with periodic boundaries on a hypersphere. No evidence for a vapor-liquid phase transition was found even at low temperatures. A system size dependence was seen for systems with $N < 512$ which makes the earlier predictions rather suspect. Van Leeuwen and Smit [9] used GEMC with the Ewald technique to examine a model in which the attractive dispersion interactions could be decreased gradually from the Stockmayer fluid (dipolar Lennard-Jones fluid) to the dipolar soft-sphere limit. A vapor-liquid phase transition for the Stockmayer fluid is now well established [19]. However, as the dispersion forces are weakened and the soft-sphere limit is approached, the vapor-liquid envelope disappears to much lower temperatures. The absence of a phase transition is accompanied by the formation of chains of nose-to-tail dipolar spheres; these chain aggregates are not formed in the Stockmayer limit. Presumably the lack of clustering precludes the existence of a vapor-liquid phase transition in dipolar hard spheres, at least for temperatures as low as the ones simulated to date. A fluid phase transition for dipolar soft-sphere systems has been stabilized in the presence of an external electric field [20], although the results are inconclusive as the densities of the two phases are very similar.

We have now seen that dispersion forces stabilize a vapor-liquid phase transition in systems of dipolar spheres. In this contribution we induce a vapor-liquid phase transition in hard-core dipolar systems by making the molecules nonspherical, without invoking any additional attractive interactions. A model which is frequently used to describe nonspherical molecules is the hard spherocylinder (HSC), a cylinder of length L with a hemispherical cap of diameter D on each end, and is thus characterized by the aspect ratio L/D. We study a HSC with a central longitudinal point dipole characterized by the dipole moment μ [see Fig. 1(a)]; the limit of the dipolar hard sphere is recovered when $L/D = 0$. The pair interaction is given by

$$u(12) = \begin{cases} +\infty, & \text{if the hard cores overlap}, \\ -(\mu^2/r_{12}^3)[3(\hat{\mu}_1 \cdot \hat{\mathbf{r}}_{12})(\hat{\mu}_2 \cdot \hat{\mathbf{r}}_{12}) - \hat{\mu}_1 \cdot \hat{\mu}_2] & \text{otherwise}, \end{cases} \tag{1}$$

where $\hat{\mu}_i$ is the unit vector denoting the orientation of the dipole of molecule i, $\hat{\mathbf{r}}_{12}$ is the unit vector denoting the orientation of the intermolecular vector $\mathbf{r}_{12}$, and r_{12} is its magnitude. The scaled temperature, intermolecular pair potential energy, and packing fraction are defined as $T^* = kTD^3/\mu^2$, $u^* = uD^3/\mu^2$, and $\eta = v_{\mathrm{HSC}}N/V$, where v_{HSC} is the volume of the HSC. We present the results of both canonical (*NVT*) [21] and GEMC simulations of dipolar HSCs treating the long-range interactions with a spherical reaction field and a tinfoil boundary condition (infinite dielectric) [22]. The reaction field approach has been shown to be very satisfactory for the simulation of vapor-liquid equilibria of polar systems [23]; we checked a limited number of state points with the more computationally intensive Ewald approach and found no significant differences.

The phase behavior of the dipolar HSC system turns out to be very sensitive to the aspect ratio of the molecules. An examination of the dipole-dipole intermolecular potential for the nose-to-tail and antiparallel side-by-side configurations [see Fig. 1(b)] provides a rationale for these differences; the maximum strengths of the pair potential for these two orientations at hard-core contact are $u^* = -2$ and -1, respectively. At first we studied the dipolar hard-sphere limit ($L/D = 0$) for a state point well within the vapor-liquid phase envelope predicted by the various theories, and as expected it was not possible to

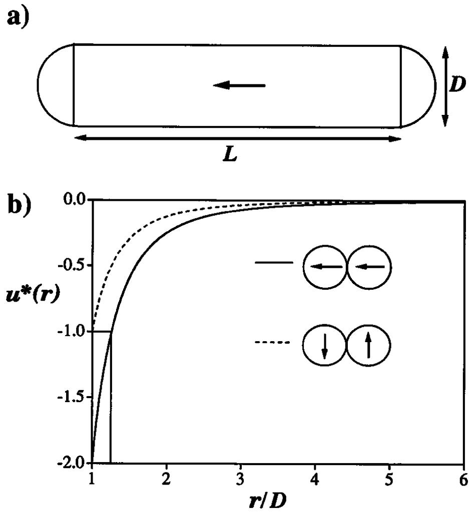

FIG. 1. (a) Dipolar hard spherocylinder. (b) The dipole-dipole pair potential for the nose-to-tail (continuous curve) and antiparallel side-by-side (dashed curve) geometries.

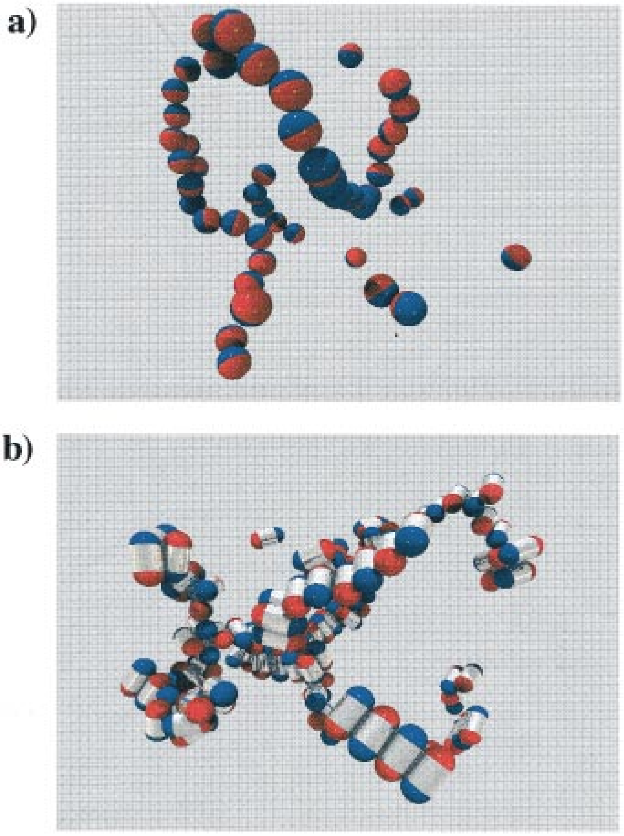

FIG. 2 (color). Snapshots of typical configurations from an *NVT* Monte Carlo simulation of (a) dipolar hard spheres and (b) dipolar HSC molecules with $L/D = 1$, both for the state point with $T^* = 0.05$ and $\eta = 0.05$. The two ends of the dipoles are denoted by the red and blue hemispheres, and the cylindrical core is shown white.

stabilize vapor-liquid coexistence. The two subsystems in the GEMC simulations do not exhibit a tendency for phase separation. A snapshot of a configuration obtained during an *NVT* simulation of the dipolar hard spheres is shown in Fig. 2(a). The formation of nose-to-tail chains of dipoles is clearly visible for this state point, and can easily be understood in terms of the large nose-to-tail interaction. To avoid this nose-to-tail chain formation the effect of the side-by-side interaction is increased by elongating the molecule to an aspect ratio of $L/D = 1$. As can be seen from Fig. 1(b) the maximum intermolecular potential for the antiparallel geometry ($u^* = -1$) is now stronger than that for the nose-to-tail geometry ($u^* = -1/4$). The system is now seen to form antiparallel side-by-side chains of dipoles and no indication of vapor-liquid phase separation is seen [see Fig. 2(b)]. This is not surprising due to the relative strengths of the two extreme orientations. To observe clustering of the dipolar molecules we then examine the system with $L/D = 1/4$ where the maximum strengths of the interactions for the two geometries are now both $u^* = -1$. It is gratifying to find vapor-liquid phase separation into a low-density gas phase [Fig. 3(a)] and a high-density liquid phase [Fig. 3(b)] in which clustering is seen. The GEMC results for the vapor-liquid phase envelope of the dipolar HSC system with $L/D = 1/4$ are shown in Fig. 4(a). Data for two system sizes of $N = 512$ and 1728 are reported, and indicate only a small system size dependence. The critical point for this system was estimated as $T^* = 0.124$ and $\eta = 0.076$ by assuming a universal critical exponent ($\beta = 0.33$) and a law of rectilinear diameters (e.g., see [24]). For most systems it is usual to assume universal critical scaling without invoking any extension to scaling such as that proposed by Wegner [25]. In our case, however, the use of a universal exponent and one extension to scaling term (see [26]) slightly improves the fit to the simulation data, with a corresponding critical point of $T^* = 0.125$ and $\eta = 0.051$. It should be noted that the question of universal critical behavior in purely dipolar systems is still unresolved, and that an unusual critical behavior for dipolar spheres was suggested by van Leeuwen and Smit [9]. We did not, however, find the need to use

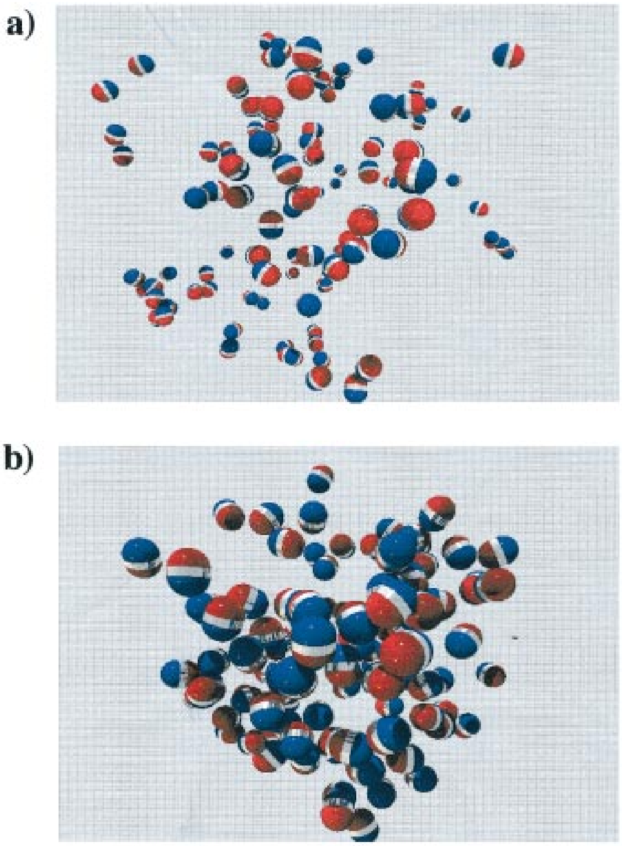

FIG. 3 (color). Snapshot of typical configurations of the (a) vapor and (b) liquid phases from a GEMC simulation of dipolar HSC molecules with $L/D = 1/4$ for $T^* = 0.12$ and a total density of $\eta = 0.05$.

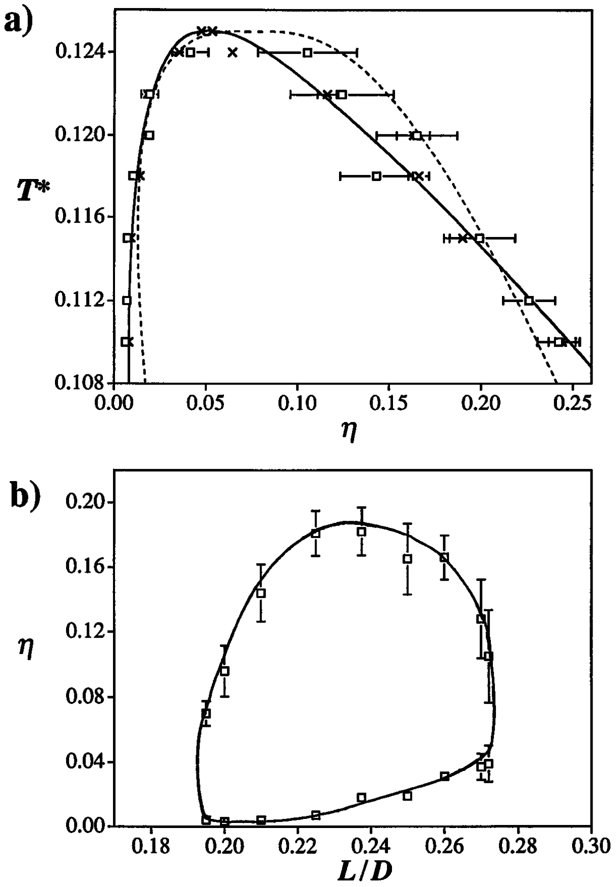

FIG. 4. (a) The vapor-liquid coexistence curve for the dipolar HSC with $L/D = 1/4$ obtained from GEMC simulations. The data points represent the simulation results for total system sizes of $N = 512$ (squares) and 1728 (crosses), and the dashed and continuous curves represent the fits obtained with the usual scaling arguments and with one Wegner term, respectively. (b) The effect of the aspect ratio on the densities of the coexisting vapor and liquid phases for a fixed temperature of $T^* = 0.12$.

a nonuniversal critical exponent. The values of the critical temperature and density are unusually low; the former is much lower than the theoretical results for dipolar hard spheres. It is now apparent that the dipolar HSC system exhibits a vapor-liquid phase transition between the aspect ratios of $L/D = 0$ and 1. The effect of varying the aspect ratio on the densities of the coexisting phases at a fixed temperature is shown in Fig. 4(b). An island of the vapor-liquid coexistence is found between $L/D \sim 0.19$ and ~ 0.28. Shelley and Patey [27] have shown that a dipolar diatomic hard-sphere system exhibits vapor-liquid coexistence [27]. This is rather surprising as the molecular aspect ratio $(L/D = 1)$ lies outside the island of coexistence found for the HSC system.

We thus confirm that dipolar hard spheres do not exhibit a vapor-liquid phase transition, at least for temperatures as low as $T^* = 0.1$, due to the formation of chains of nose-to-tail dipoles. At these low temperatures and densities the vapor-liquid transition may be inside a region of fluid-solid coexistence. We show that it is also possible to induce an island of vapor-liquid coexistence in dipolar HSC molecules by elongating the hard core. For the longer elongations the system forms chains of side-by-side dipoles in an antiparallel configuration, precluding the clustering that is necessary for vapor-liquid coexistence. In practice we expect that the presence of dispersion forces will be the major feature in stabilizing a vapor-liquid transition of real dipolar systems.

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