

## Gas-liquid coexistence and demixing in systems with highly directional pair potentials

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Recent computer simulation studies strongly indicate that fluids of dipolar hard spheres do not display gas-isotropic liquid coexistence. In this paper we discuss a second example that also exhibits this rather unexpected behavior. This is a simple liquid-crystal model that we explore employing Gibbs ensemble Monte Carlo (GEMC) methods. It is shown that the system has clear gas-nematic liquid coexistence, but that the gas-isotropic liquid coexistence line is completely missing from the phase diagram. We attribute this to the highly directional nature of the attractive potential and argue that similar considerations are likely of relevance in the dipolar hard-sphere case as well. We also use GEMC techniques to investigate demixing in binary mixtures of neutral and dipolar hard spheres. For similar mixtures of neutral and charged hard spheres, it is known that demixing is essentially condensation of the Coulombic fluid weakly influenced by the background of neutral hard spheres. Therefore, given that dipolar hard spheres do not condense, whether or not the present mixtures demix is an interesting question. In fact, demixing is observed and, moreover, the transition temperatures are in reasonable agreement with those predicted by the same integral equation theories that incorrectly predict condensation of the pure dipolar fluid. The critical temperature decreases rapidly with decreasing diameter of the neutral species consistent with the lack of gas-isotropic liquid coexistence for pure dipolar hard spheres. Clearly, for the present model demixing and dipolar condensation are not closely related phenomena as they are in the Coulombic systems. The neutral species appears to reduce the formation of dipolar "chains" or "clusters" that inhibit condensation of the pure dipolar hard-sphere fluid. [S1063-651X(98)00105-6]

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### I. INTRODUCTION

This paper is motivated by recent work on dipolar fluids [1–5]. Computer simulations have shown that fluids of dipolar hard or soft spheres exhibit rather interesting and unexpected phase behavior. Such systems form stable isotropic and ferroelectric fluid phases [1,2] but no gas-isotropic liquid transition is observed [3–5]. Isotropic fluid-ferroelectric fluid coexistence does occur, but the expected gas-isotropic liquid coexistence line appears to be completely missing from the phase diagram. Here we employ the Gibbs ensemble Monte Carlo (GEMC) method [6–9] to further explore the question of gas-liquid coexistence in model fluids characterized by highly directional pair potentials. First we discuss a simple model liquid crystal that also has no gas-isotropic liquid coexistence and second we examine the phase behavior of mixtures of dipolar and neutral hard spheres.

To date, the dipolar hard-sphere fluid is the only model having both attractive and repulsive pair interactions for which a gas-isotropic liquid transition is not observed. In the present paper we give a second example where gas-isotropic liquid coexistence does not appear to occur. This is a simple liquid-crystal model of a type previously considered in computer simulations [10] and theoretical calculations [11]. In the present version, the particles interact via the hard-sphere potential plus a short-range anisotropic term. The model exhibits isotropic-nematic coexistence, but gas-isotropic liquid coexistence is not found. Physically, this unusual phase behavior must arise because the potential is so directional that the dense isotropic liquid cannot achieve an energy low

enough to overcome the entropy of the gas. This is only accomplished by the nematic liquid-crystal phase where orientational order lowers the energy sufficiently to destabilize a dilute disordered gas. Thus one observes only two rather than the expected three fluid phases analogous to the situation for dipolar hard spheres.

Mixtures of dipolar and neutral hard spheres are interesting for several reasons. Integral equation theories [12,13] predict that these systems will demix, but the same theories predict a gas-isotropic liquid condensation for the dipolar hard-sphere fluid [14]. Since the predicted condensation does not occur in the pure fluid case, it is of interest to see if the theories are also qualitatively wrong for the mixture. Further, for mixtures of charged and neutral hard spheres, it has been shown [15,16] that demixing is largely a charged hard-sphere condensation only weakly influenced by the neutral hard-sphere background. Thus one might expect that demixing would not occur for mixtures of neutral and dipolar hard spheres because the pure dipolar hard-sphere system does not condense. Nevertheless, we find that demixing does occur and we investigate the behavior of the critical temperature at fixed pressure as a function of the diameter of the neutral component. This is interesting because as the neutral component decreases in size one must approach the pure dipolar hard-sphere behavior.

### II. PHASE BEHAVIOR OF A SIMPLE LIQUID-CRYSTAL MODEL

Simple axially symmetric liquid-crystal models can be constructed by employing pair potentials of the form [10,11]

TABLE I. GEMC results (512 particles) for isotropic-nematic coexistence for the simple liquid-crystal model with  $\lambda=0.15$ . Boxes I and II are the isotropic and nematic fluids, respectively. The numbers in parentheses are the estimated uncertainties in the last digit(s) given.

$T^*$	$P^*$		$\mu_{res}/kT$		$\langle P_2 \rangle$	
	I	II	I	II	I	II
0.353	1.05(4)	1.06(9)	1.76(7)	1.77(6)	0.13(9)	0.49(10)
0.333	0.93(2)	0.86(5)	1.39(4)	1.39(6)	0.07(5)	0.68(2)
0.316	0.80(2)	0.74(6)	0.99(4)	1.00(9)	0.06(3)	0.74(1)
0.300	0.68(1)	0.67(13)	0.69(5)	0.70(9)	0.04(2)	0.810(8)
0.286	0.53(2)	0.43(27)	0.22(5)	0.21(10)	0.030(9)	0.841(7)

$$u(12) = u_0(r) + u_a(12), \quad (1)$$

where  $u_0(r)$  is a spherically symmetric interaction and  $u_a(12)$  is an anisotropic term. In previous calculations  $u_0(r)$  was usually taken to be the Lennard-Jones (LJ) interaction and the anisotropic potential was defined as

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

where  $P_2(\cos \gamma)$  is the usual second-order Legendre polynomial and  $\gamma$  is the angle between the symmetry axes of the particles (i.e., each particle is embedded with a unit vector

defining a symmetry axis). Also,  $\varepsilon$  and  $\sigma$  are the LJ parameters and  $\lambda$  determines the strength of the anisotropic interaction.

It is known from previous work [10,11] that models of this type exhibit at least isotropic and nematic fluid phases. Here we are interested in investigating gas-liquid coexistence in a model that, as with dipolar hard spheres, has a highly directional pair potential and no dispersion interaction. Therefore, we take  $u_0(r)$  to be the hard-sphere interaction with  $\sigma$  defining the hard-sphere diameter. For fixed  $\lambda$ , a thermodynamic state of this model is completely determined by specifying two parameters, for example, the reduced pressure  $P^* = P\sigma^3/kT$  and the reduced temperature  $T^* = kT/\varepsilon$ , where  $k$  is the Boltzmann constant and  $T$  the absolute temperature. Of course the properties of the hard-core model depend only on the ratio  $T^*/\lambda$  and it is not necessary to specify  $T^*$  and  $\lambda$  independently. However, to be consistent with previous calculations, we set  $\lambda = 0.15$  and vary  $T^*$ .

GEMC calculations [6–9] were performed for this model using 512 particles. *A priori* one would expect to observe three fluid phases for this system (i.e., an isotropic gas, an isotropic liquid, and a nematic liquid). However, only two fluid phases, isotropic and nematic, were observed. Values of  $P^*$ , the reduced residual chemical potential [9]  $\mu_{res}/kT$  and the average second-rank order parameter  $\langle P_2 \rangle$  in each phase are given in Table I. The instantaneous order parameter  $P_2$  was taken to be the largest eigenvalue of the ordering matrix commonly used in liquid-crystal simulations [17]. We see that for all temperatures and pressures one of the coexisting phases is orientationally ordered (i.e.,  $\langle P_2 \rangle$  is nonzero). Also, we note that the pressures and residual chemical potentials in each phase agree within statistical uncertainties.

Coexisting densities at different temperatures and the nematic-isotropic coexistence line on a  $P^*$  vs  $T^*$  plot are shown in Figs. 1(a) and 1(b), respectively. We emphasize again that the expected gas–isotropic liquid coexistence line is completely missing from Fig. 1(b). We could find no evidence whatsoever for this transition. At the lower temperatures it is possible that the nematic phase found in the simulations might be metastable with respect to the solid. To test for this, fcc lattices were heated under constant pressure until melting and the results obtained are represented by the dashed line in Fig. 1(b). To the left of this line the solid remained either stable (or metastable) with respect to the liquid. To the right of the line the lattice melted to give isotropic or nematic fluid phases. Thus we can be confident

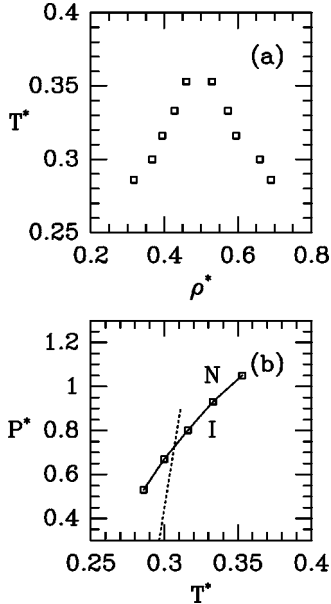


FIG. 1. Gibbs ensemble results giving part of the phase diagram for the simple liquid-crystal model with  $\lambda=0.15$ . The coexisting densities are given in (a). The regions of stability of the isotropic and nematic phases in (b) are denoted by I and N, respectively. To the right of the dashed line in (b) a 108-particle system melts from a fcc lattice; to the left the lattice remains stable or metastable for long simulations. This line was generated by melting the lattice at constant pressure using NPT MC simulations at a variety of pressures.

that for the three highest temperature points the GEMC calculations give the thermodynamically stable coexisting phases.

### III. MIXTURES OF NEUTRAL AND DIPOLAR HARD SPHERES

We consider mixtures consisting of  $N_n$  neutral hard spheres of diameter  $\sigma_n$  and  $N_d$  dipolar hard spheres of diameter  $\sigma_d$ . The total number of particles is  $N=N_n+N_d$  and it is useful to introduce the reduced density  $\rho^*=\rho\sigma_d^3$ , where  $\rho=N/V$  is the total number density, the mole fractions  $x_d=N_d/N$  and  $x_n=N_n/N=1-x_d$ , the reduced diameter  $\sigma_n^*=\sigma_n/\sigma_d$ , and the reduced dipole moment  $\mu^*=\mu/\sqrt{kT}\sigma_d^3$ , where  $k$  is the Boltzmann constant and  $T$  the absolute temperature. Instead of  $\mu^*$ , one could equally define the reduced temperature  $T^*=1/\mu^{*2}$ , but to be consistent with most earlier work, we will describe the system in terms of  $\mu^*$ .

The phase separation was investigated using GEMC simulations [6–9]. This method introduces two simulation boxes, which we label I and II. One then specifies  $N_d$ ,  $N_n$ , and the reduced total volume  $V^*=V/\sigma_d^3$  or, alternatively, the reduced pressure  $P^*=P\sigma_d^3/kT$ . These, along with  $\mu^*$  and  $\sigma_n^*$ , completely characterize the system. Typically, one begins with a uniform mixture in each cell and if the initial state is unstable the system separates into a dipole-rich phase in one box and a neutral-rich phase in the other. The simulation may be carried out in different ways. One method is to exchange both neutral and dipolar particles between boxes I and II. This proved to be a relatively inefficient method because the probability of exchanging dipolar particles becomes prohibitively low as  $\mu^*$  is increased. Another method is to perform particle exchanges for one component (in this case the neutral one) along with identity exchanges. Identity exchanges consist of converting a neutral hard sphere into a dipolar hard sphere in one box while in the same move converting a dipolar hard sphere into a neutral hard sphere in the other. We verified that both methods gave identical results. However, the method using identity exchanges gave better acceptance rates and allowed us to obtain converged results at higher reduced dipole moments.

Of course, due to the long-range nature of the dipolar interactions one must employ periodic boundary conditions with Ewald summation methods [17–19]. This requires that the dielectric constant  $\epsilon'$  of a surrounding continuum be specified. This raises a minor question for the present simulation because while  $\epsilon'\approx 1$  would be appropriate for a neutral-rich phase,  $\epsilon'\approx\infty$  would likely be a better choice for a dipole-rich phase. The results reported here were obtained with  $\epsilon'=1$ , but we verified that using  $\epsilon'=\infty$  had little effect on the thermodynamics or observed demixing behavior. Additional tests were performed to ensure that the results obtained were not strongly dependent on the number of particles used. All results reported here were obtained with  $N=500$ . Also, calculations were carried out to verify that the dipole-rich phase had no long-range orientational order at the largest reduced dipole moment considered.

We first attempted to confirm theoretical predictions that a demixing transition does in fact occur. Applying the reference hypernetted-chain (RHNC) approximation, Chen and

TABLE II. Reduced critical dipole moments as a function of reduced pressure for an equal diameter mixture ( $x_n=0.8$ ) of neutral and dipolar hard spheres.  $\rho^*$  is the reduced density of the mixture just before the demixing transition.

$P^*$	$\mu_c^*$	$\rho^*$
5.9	1.8	0.8
3.7	1.9	0.7
2.4	2.0	0.6

Forstmann [13] have determined the absolute stability limits for  $\mu^*=\sqrt{2.5}$  and  $\sigma_n^*=1$  as a function of  $\rho^*$  and mole fraction  $x_n$ . At  $x_n=0.8$ , the system was predicted to demix for all  $\rho^*\geq 0.66$ . Constant volume GEMC calculations were carried out for an equal diameter mixture with  $\rho^*=0.7$  and  $x_n=0.8$ . Starting at  $\mu^*=\sqrt{2.5}\approx 1.6$ , the reduced dipole moment was increased until a demixing transition occurred. At  $\mu^*=1.8$ , the system was clearly mixed and at  $\mu^*=2.0$  it was clearly demixed. At  $\mu^*=1.9$ , the system exhibited very large deviations from the mixed phase and we take this value to be a good estimate of the reduced critical dipole moment,  $\mu_c^*$ . These observations are qualitatively consistent with the RHNC theory, although the theory does appear to underestimate  $\mu_c$ . Chen *et al.* [12] have also reported the absolute stability limits for equal diameter mixtures at  $\rho^*=0.8$  as a function of  $\mu^*$  and  $x_n$ . At  $x_n=0.8$ , they report that the mixture becomes unstable for all  $\mu^*\geq 1.5$ . We also carried out constant volume GEMC calculations at  $\rho^*=0.8$ ,  $x_n=0.8$  and found the reduced critical dipole moment  $\mu_c^*\approx 1.8$ . Again, the theoretical predictions underestimate the critical dipole moment. Some critical dipole moments, pressures, and densities for equal diameter mixtures at  $x_n=0.8$  are summarized in Table II.

We have also used the GEMC method to determine coexistence curves at fixed pressure for different values of  $\sigma_n^*$ . The reduced pressure was fixed at  $P^*=2.0$  and coexistence curves were obtained for  $\sigma_n^*=1.0, 0.9, 0.8$ , and  $0.7$ . Coexistence densities and residual chemical potentials for  $\sigma_n^*=1.0$  are given in Table III. We note that as one might expect the dipole-rich fluid is the denser phase at coexistence. The values of  $\mu_{res,d}$  agree (within the uncertainties) in each phase; however, the uncertainties are rather large. This is due to the difficulty in estimating the chemical potential when the probability of inserting a dipolar hard sphere (real or ghost) becomes extremely small. Reliable converged results could not be obtained in the two-phase region for values of  $\sigma_n^*$  smaller than  $0.7$ . Simulations at  $\sigma_n^*=0.7$  and  $\mu^*=2.5$  were at the limit of our ability to obtain converged results.

The coexistence curves are plotted in Fig. 2. From the figure we see that the neutral-rich phase remains a very dilute solution of dipolar hard spheres in neutral hard spheres as  $\sigma_n^*$  decreases. In the dipole-rich phase, the mole fraction of neutral hard spheres (at fixed  $\mu^*$ ) increases significantly as  $\sigma_n^*$  is reduced from 1 to 0.9, but then varies only slightly as  $\sigma_n^*$  is further reduced to 0.8 and 0.7. Estimated values of  $\mu_c^*$  as a function of  $\sigma_n^*$  are given in Table IV. We note that  $\mu_c^*$

TABLE III. Some coexistence results ( $N=500$ ) for equal diameter mixtures of neutral and dipolar hard spheres at  $P^*=2.0$ . Boxes I and II are the dipole-rich and neutral-rich phases, respectively.  $\mu_{res,n}$  and  $\mu_{res,d}$  are the residual chemical potentials of the neutral and dipolar hard spheres. The numbers in parentheses are the estimated uncertainties in the last digit(s) given.

$\mu^*$	$\rho^*$		$\mu_{res,n}/kT$		$\mu_{res,d}/kT$	
	I	II	I	II	I	II
2.1	0.662(6)	0.546(7)	3.83(11)	3.84(11)	-1.05(30)	-1.25(45)
2.2	0.685(3)	0.546(6)	3.86(8)	3.86(9)	-0.92(39)	-1.36(10)
2.3	0.697(9)	0.546(8)	3.86(15)	3.86(14)	-2.15(70)	-1.94(44)
2.4	0.719(6)	0.543(5)	3.81(10)	3.81(9)	-1.70(76)	-1.90(13)

increases in an apparently linear fashion with decreasing  $\sigma_n^*$ . It is possible to show [20] that in the  $\sigma_n^*=0$  limit any apparent demixing must come from condensation of the dipolar hard-sphere component. A *very bold* linear extrapolation suggests the  $\mu_c^* \approx 3$  in the limit  $\sigma_n^* \rightarrow 0$ . This is a relatively large value of  $\mu^*$  (or low temperature) and it is possible that the dipole-rich phase becomes orientationally ordered before this limit is reached, thus cutting off the gas-isotropic liquid transition. One might well have gas-ferroelectric liquid coexistence in the pure dipolar system, but convergence problems make this possibility extremely difficult to explore with GEMC simulations.

#### IV. SUMMARY AND CONCLUSIONS

Previous computer simulation studies [3–5] strongly indicate that gas-isotropic liquid coexistence does not exist for dipolar hard-sphere fluids. In this paper we give a second example of this rather surprising behavior. We discuss a simple liquid-crystal model that exhibits gas-nematic liquid coexistence, but the expected gas-isotropic liquid coexistence branch is completely missing from the phase diagram. This behavior is clearly related to the fact that the attractive part of the pair potential is highly directional. This means that the energy of the system cannot be greatly reduced by condensation to a denser *isotropic* fluid phase. Increasing the number of near neighbors a particle has does not lead to a significant energetic advantage if it can only interact favor-

ably with a few of them. Indeed, for the present model it is only in the nematic phase that the energy of the liquid can achieve energies low enough to drive condensation. The dipolar potential is also highly directional and we would expect similar considerations to apply. However, for the present model we do not observe the “chains” or “clusters” that appear to help stabilize the dipolar hard sphere “gas.”

We have also considered mixtures of dipolar and neutral hard spheres. It is shown that this system undergoes demixing into two fluid phases as predicted by integral equation theories [12,13]. The critical reduced dipole moments given by the theory are somewhat low, but the qualitative predictions are correct. This contrasts with the situation for the pure dipolar hard-sphere fluid where the gas-isotropic liquid coexistence predicted by the same theories is never in fact observed. This behavior also differs from that of mixtures of charged and neutral hard spheres, where demixing can be viewed essentially as condensation of the Coulombic fluid weakly perturbed by the neutral hard-sphere background. This is obviously not the case for the mixtures considered here. Furthermore, it was found that at constant pressure the coexistence curves are strongly dependent on the diameter of the neutral species. The critical reduced dipole moment increases (the critical temperature decreases) as  $\sigma_n^*$  decreases. However, unfortunately, the dipolar interactions become too strong for reliable coexistence curves to be obtained for values of  $\sigma_n^* < 0.7$ . In the limit  $\sigma_n^* = 0$ , any apparent demixing must come from condensation of the dipolar species. Obviously, extrapolating to this limit using points for  $\sigma_n^* \geq 0.7$  is a highly dubious procedure. Nevertheless, we note that linear extrapolation gives a critical dipole moment of  $\sim 3$  at  $\sigma_n^* = 0$ . This value is sufficiently large to suggest that ferroelectric order might develop in the dipole-rich phase as  $\sigma_n^*$  approaches zero. Thus it is possible that gas-ferroelectric liquid coexistence exists for dipolar hard-sphere fluids. This would be similar to the gas-nematic coexistence found for the simple liquid-crystal model, but the reduced dipole mo-

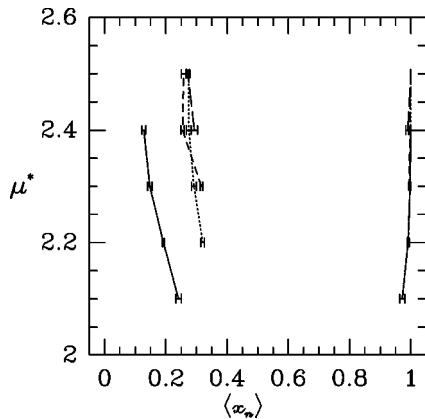


FIG. 2. Coexistence curves for mixtures of neutral and dipolar hard spheres at  $P^*=2.0$ . The solid, dotted, short-dashed, and long-dashed curves are for  $\sigma_n^*=1.0, 0.9, 0.8,$  and  $0.7$ , respectively. The horizontal bars on the data points indicate the estimated uncertainties in the coexisting mole fractions.

TABLE IV. Reduced critical dipole moments as a function of the  $\sigma_n^*$  at  $P^*=2.0$ .

$\sigma_n^*$	$\mu_c^*$
1.0	2.0
0.9	2.1
0.8	2.2
0.7	2.3

ments required are too large for this to be tested directly using GEMC calculations.

It is interesting to ask why the neutral species is so important here or, in other words, why demixing and dipolar condensation are so unrelated for this system. As least a partial answer seems to be that the neutral species inhibits the formation of dipolar "chains" that appear to prevent condensation in computer simulations of pure dipolar hard-sphere fluids. As the diameter of the neutral species is de-

creased, this effect is diminished and the critical reduced dipole moments increase.

#### ACKNOWLEDGMENT

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- [20] At first sight one might think that the correct limit is  $\sigma_{nd} = (\sigma_n + \sigma_d)/2 = 0$  or, equivalently,  $\sigma_n^* = -1$ , since in this limit the neutral component is strictly an ideal gas that can penetrate the dipolar hard spheres. However, a careful analysis shows that in the thermodynamic limit any demixing observed for  $\sigma_n^* \leq 0$  can come only from condensation of the dipolar hard spheres and that in this region the critical reduced dipole moment would be unaffected by the presence of the neutral particles.