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Liquid-vapor coexistence in fluids of dipolar hard dumbbells and spherocylinders

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Fluids of dipolar hard spheres are thought to have rather unusual phase behavior in that liquid-vapor equilibrium has not been observed in computer simulations. Recently, McGrother and Jackson [Phys. Rev. Lett. **76**, 4183 (1996)] have reported Gibbs ensemble Monte Carlo (GEMC) results for dipolar hard spherocylinders. At the reduced temperature $T^*=0.12$ they report liquid-vapor coexistence for aspect ratios $L/D \gtrsim 0.19$, but no coexistence was found for smaller values. In the present paper we investigate the phase behavior of dipolar hard dumbbells and dipolar hard spherocylinders using both GEMC and grand canonical Monte Carlo methods. For both models at the same reduced temperature we find liquid-vapor coexistence for aspect ratios as low as 0.1. For aspect ratios $\lesssim 0.1$, the strong dipolar interactions create severe sampling problems and reliable results cannot be obtained. This is particularly true for the GEMC method and possibly accounts for the disagreement we find with the earlier simulations. [S1063-651X(99)08502-5]

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I. INTRODUCTION

Computer simulations have shown that fluids of dipolar spheres have rather unusual and interesting phase behavior [1–5]. For example, such models form both isotropic and ferroelectric fluid phases [1,2]. However, for dipolar hard (or soft) spheres, where dispersion interactions are absent and the only attractive interactions are due to the dipole-dipole potential, no liquid-vapor coexistence has been found [3–5]. Thus, rather than the three fluid phases one would expect (i.e., vapor, isotropic liquid, ferroelectric liquid), only two have been observed.

In recent simulations, McGrother and Jackson [6] have examined liquid-vapor coexistence in fluids of dipolar hard spherocylinders of varying aspect ratio L/D. Since the dipoles are embedded at the center of the spherocylinders and are directed along the long axis, in the limit $L=0$ these particles become dipolar hard spheres. Employing Gibbs ensemble Monte Carlo (GEMC) calculations these authors report liquid-vapor coexistence for certain values of L/D. More precisely, for a fixed temperature and dipole moment they find an ''island'' of liquid-vapor coexistence. For example, for the reduced temperature $T^*=kTD^3/\mu^2=0.12$ (μ is the dipole moment, k the Boltzmann constant, and T the absolute temperature), they find liquid-vapor coexistence for aspect ratios between ~ 0.19 and ~ 0.28, but only a single fluid phase for values of L/D smaller or larger than these limits. McGrother and Jackson conclude that their calculations confirm that dipolar hard spheres ($L=0$) do not have liquid-vapor coexistence, at least for temperatures as low as $T^*=0.1$.

The work discussed in the present paper was begun as a study of dipolar hard dumbbells, which are of interest for various reasons [7]. This model is similar to dipolar hard spherocyclinders in that dipolar hard spheres are recovered at zero aspect ratio. Further, for small aspect ratios we would expect the phase behavior of this model to closely resemble that of the dipolar hard spherocylinders. However, employing both GEMC [8] and grand canonical Monte Carlo (GCMC) [9] methods, we observed coexistence behavior, which differed from that reported by McGrother and Jackson [6]. Also, we were unable to completely reproduce their results for dipolar hard spherocylinders. In particular, at $T^*=0.12$ we agree with McGrother and Jackson for larger aspect ratios, but we find evidence of liquid-vapor coexistence for aspect ratios as low as 0.1, which disagrees with their observations. We argue that the discrepancies between our results and those of McGrother and Jackson arise because the

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TABLE I. GEMC coexistence results for dipolar hard dumbbells and spherocylinders. N is the number of particles, U is the average configurational energy, and μ_g and μ_l are the chemical potentials of the gas and liquid phases, respectively. The packing fraction is $\eta = \rho V_{\mathrm{HC}}$, where V_{HC} is the particle volume.

L/D	T^*	N	cycles	η_g	μ_g	η_l	μ_l	$(U/NkT)_g$	$(U/NkT)_l$
					Dumbbells				
0.20	0.111	400	177000	0.005 ± 0.002	-0.82	0.24 ± 0.02	-0.70	-6.7	-10.1
0.20	0.120	400	130000	0.014 ± 0.003	-0.78	0.21 ± 0.03	-0.92	-6.7	-8.5
0.20	0.122	400	135000	0.012 ± 0.005	-0.82	0.19 ± 0.04	-0.80	-6.3	-8.4
0.20	0.125	400	300000	0.012 ± 0.005	-0.75	0.18 ± 0.04	-0.75	-5.8	-7.9
0.26	0.100	400	105000	0.007 ± 0.002	-0.74	0.27 ± 0.02	-0.92	-6.9	-10.4
0.26	0.111	400	108000	0.010 ± 0.003	-0.72	0.20 ± 0.02	-0.88	-5.2	-8.4
0.26	0.120	400	108000	0.022 ± 0.004	-0.74	0.14 ± 0.03	-0.70	-4.9	-6.9
0.50	0.075	364	90000	0.007 ± 0.002	-0.57	0.29 ± 0.01	-0.54	-6.3	-10.3
0.50	0.085	364	50000	0.017 ± 0.004	-0.53	0.22 ± 0.02	-0.53	-4.9	-8.0
0.50	0.089	364	90000	0.019 ± 0.005	-0.54	0.22 ± 0.03	-0.52	-4.4	-6.9
0.75	0.060	364	130000	0.023 ± 0.006	-0.48	0.27 ± 0.03	-0.41	-8.7	-11.3
0.75	0.065	364	110000	0.028 ± 0.006	-0.46	0.21 ± 0.03	-0.45	-7.7	-9.4
0.75	0.068	364	70000	0.032 ± 0.006	-0.43	0.20 ± 0.03	-0.43	-6.8	-8.5
0.75	0.070	364	80000	0.035 ± 0.008	-0.43	0.16 ± 0.03	-0.43	-6.1	-7.9
					Spherocylinders				
0.10 [a]	0.12	512	260000	0.02 ± 0.01	-0.91	0.13 ± 0.01	-0.98	-11.1	-11.4
0.15 [b]	0.12	512	386000	0.003 ± 0.0015	-0.86	0.20 ± 0.02	-1.01	-5.2	-9.9
0.18 [c]	0.12	512	306000	0.0025 ± 0.001	-0.81	0.18 ± 0.015	-0.98	-4.6	-9.0
0.20 [d]	0.12	512	500000	0.004 ± 0.001	-0.78	0.17 ± 0.02	-1.01	-4.8	-8.4
0.24 [e]	0.12	512	300000	0.014 ± 0.014	-0.76	0.16 ± 0.01	-0.88	-4.5	-7.5

[a] Initial conditions $N_1=256, \eta_1=0.036, N_2=256, \eta_2=0.090$.

[b] Initial conditions $N_1=256, \eta_1=0.032, N_2=256, \eta_2=0.096$.

[c] Initial conditions from last configuration of run at $L/D=0.20, N_1=122, \eta_1=0.0047, N_2=390, \eta_2=0.1634$.

[d] Initial conditions $N_1=256, \eta_1=0.010, N_2=256, \eta_2=0.102$.

[e] Initial conditions $N_1=256, \eta_1=0.093, N_2=256, \eta_2=0.093$.

Monte Carlo sampling becomes extremely poor for small aspect ratios [10]. Reliable GEMC and GCMC calculations appear to be all but impossible for dipolar hard spheres at temperatures and densities where condensation might be expected to occur. The problem is particularly severe for the GEMC method because head-to-tail association of the dipolar particles greatly restricts volume fluctuations and renders the method very unreliable at low temperatures. If one is unaware that the method is failing, incorrect conclusions about the phase behavior at low aspect ratios may be drawn. Our experience suggests that better simulation methods may be necessary before any final conclusion can be reached about whether or not liquid-vapor coexistence exists for dipolar hard spheres.

II. MODEL AND SIMULATION RESULTS

The hard dumbbell model we consider consists of two spheres of diameter D with a distance L separating their centers. Hard spherocylinders consist of a cylinder of length L with hemispherical caps of diameter D at each end. In both cases, point dipoles are placed at the particle centers and are directed along the long axis. Thus the pair potentials $u(12)$ are of the form

$$u(12)=u_{\mathrm{HC}}(12)-\frac{\mu^2}{r^3}[3(\hat{\boldsymbol{\mu}}_1\cdot\hat{\mathbf{r}})(\hat{\boldsymbol{\mu}}_2\cdot\hat{\mathbf{r}})-\hat{\boldsymbol{\mu}}_1\cdot\hat{\boldsymbol{\mu}}_2] \quad , \quad (1)$$

where $u_{\mathrm{HC}}(12)$ is the hard-core interaction, μ is the dipole moment, $\hat{\boldsymbol{\mu}}_i$ is a unit vector along the dipole of particle i, $\hat{\mathbf{r}}$ is a unit vector associated with the interparticle vector $\mathbf{r}$ and $r=|\mathbf{r}|$. A thermodynamic state of a system of dipolar hard dumbbells or spherocylinders can be completely determined by specifying the reduced temperature $T^*=kTD^3/\mu^2$ and the packing fraction $\eta=\rho V_{\mathrm{HC}}$, where $\rho=N/V$ is the number density and V_{HC} is the volume of a hard dumbbell ($V_{HD}=(\pi D^3/6)[1+(3/2)(L/D)-(1/2)(L/D)^3]$) or spherocylinder ($V_{HSC}=(\pi D^3/6)[1+(3/2)(L/D)]$).

The GEMC and GCMC calculations were carried out in the conventional manner [8,9]. Periodic boundary conditions were applied and the Ewald summation method [11] was employed to take account of the long-range dipolar interactions. The dielectric constant of the surrounding continuum was taken to be infinity. GEMC results for both dipolar hard dumbbells and dipolar hard spherocylinders are given in Table I. Some simulation details are also included. Note that n GEMC cycles consisted of $nN/2$ trial translational plus rotational moves, $nN/2$ trial box exchange moves (N is the total number of particles in the simulation) and n volume changes. We remark that in the GEMC simulations the number of particles in the gas box is generally small and different from the number in the liquid box. This could influence the quantitative results [12], but here we are only attempting to get the correct qualitative picture.

GCMC calculations were carried out only for dipolar hard dumbbells. These employed a cubical cell and each GCMC

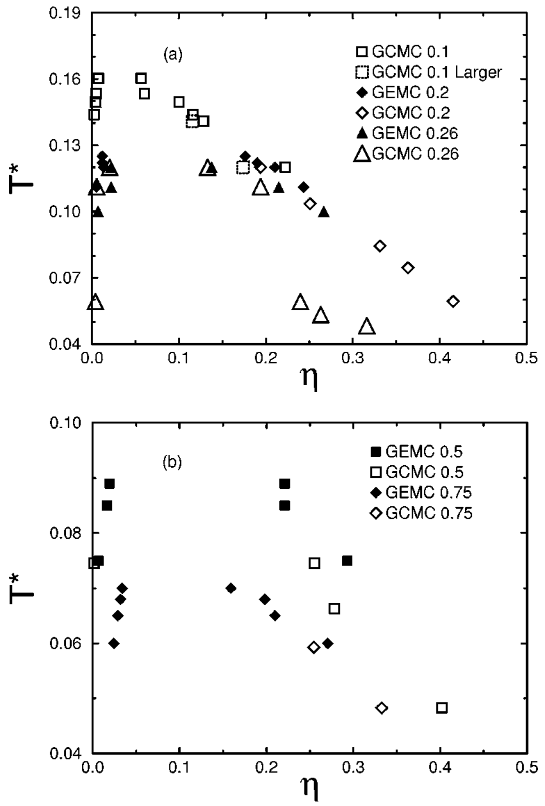

FIG. 1. Liquid-vapor coexistence points for dipolar hard dumbbells as determined by GEMC and GCMC simulations. Results for L/D values up to 0.26 are shown in (a) and for $L/D=0.5$ and 0.75 in (b). For $L/D=0.1$, GCMC points are shown for $N=155$ and $N=289$ at $T^*=0.12$ and for $N=90$ and $N=192$ at $T^*=0.14$. Note that GCMC vapor densities were not obtained for all temperatures and aspect ratios.

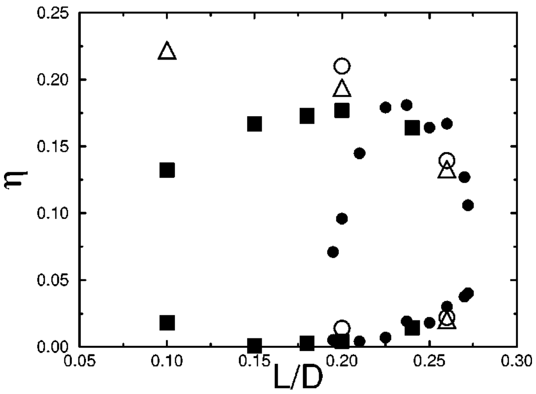

FIG. 2. Coexisting densities for dipolar hard dumbbells and dipolar hard spherocylinders as a function of the aspect ratio for $T^*=0.12$. The open circles and open triangles are, respectively, GEMC and GCMC results for dipolar dumbbells. The solid squares are the present GEMC results for dipolar spherocylinders and the solid circles are the previous results of McGrother and Jackson [6]. Note that GCMC vapor densities were not obtained for $L/D=0.20$ and 0.10.

cycle consisted of $\sim N$ translational plus rotational moves, $\sim 4N$ particle insertions, and $\sim N/2$ particle deletions (a correction was applied for this bias). The location of the phase transition (signaled by an abrupt change in density) was first roughly determined by scanning the chemical potential up or down depending on whether the starting point was a vapor or a liquid. Then several much longer runs (typically 20 000 cycles) at fixed chemical potential in the vicinity of the transition were used to refine our estimate of the transition density. Scanning the chemical potential in GCMC simulations is a good way to detect the existence of phase transitions. However, the method does not necessarily locate the coexisting densities. In practice, there is always some hysteresis observed for upward and downward scans, and, while the ''apparent transition'' must surely occur at a density somewhere between the spinodal and coexistence values, the results determined by this method should not be regarded as a precise determination of the coexistence curve. In the GCMC calculations the number of particles present at the transition varied quite widely for the different systems and state parameters. Typically, 100–200 particles were present on the liquid side. For the $L/D=0.1$ case, where the sampling was most difficult, two test runs approximately doubling the sample volume were performed and the results are included in Fig. 1(a). We note that the apparent transition occurs at somewhat lower densities for the larger systems but that the qualitative behavior is unchanged. In GCMC calculations we might expect the liquid to remain metastable at lower densities for larger systems and this could be the main contribution to the observed system size dependence. On the gas side, the densities are low and often far fewer particles were present. Thus, the gas densities must be regarded as very uncertain. Also, due to these difficulties, we only attempted to obtain gas densities for some aspect ratios at the more elevated temperatures using the GCMC method. Thus, some gas densities are ''missing'' from the GCMC results plotted in Figs. 1 and 2.

Coexistence T^* vs η plots for dipolar hard dumbbells with aspect ratios ranging from 0.1 to 0.75 are shown in Fig. 1. For $L/D=0.2$, 0.26, 0.5, and 0.75, results obtained using both GEMC and GCMC methods are shown, although both methods have not been applied for all values of T^*. For $L/D=0.1$, the GEMC method (starting with equal densities in each box) did not achieve phase separation for $T^*=0.14$ and 0.12 and calculations at lower temperatures were not attempted. We believe that the GEMC method is less reliable than the GCMC method at small aspect ratios and this is discussed in detail below. We note that for aspect ratios between 0.2 and 0.75, the GEMC and GCMC results are in fair agreement and indicate that the critical temperature decreases with increasing aspect ratio. Some of the discrepancy between the GEMC and GCMC results likely reflects sampling problems, which become severe as the aspect ratio is reduced. It should also be kept in mind that the GEMC method gives, at least in principle, the coexistence curve whereas this is not necessarily true of the GCMC method as applied here. In GCMC calculations the liquid or vapor state may remain metastable as one scans the chemical potential, and it is possible that the GCMC results more closely follow the spinodal rather than the coexistence curve. This could account for some of the difference between the GEMC and GCMC results at temperatures significantly below the critical temperature.

In order to compare with the earlier results of McGrother and Jackson [6], in Fig. 2 we have plotted the coexisting densities as a function of L/D for $T^*=0.12$ [this is comparable with Fig. 4(b) of [6])]. Both GEMC and GCMC results are given for dipolar hard dumbbells and GEMC results are plotted for dipolar hard spherocylinders. The results of McGrother and Jackson are also included. Considering first the spherocylinder case, we note that at $L/D=0.24$ our results agree (within combined uncertainties, $\sim\pm0.03$) with those of McGrother and Jackson. However, at $L/D=0.2$ there is a serious discrepancy in the densities of the liquid phase. Furthermore, for aspect ratios $\lesssim 0.19$, McGrother and Jackson report no phase separation whatsoever, whereas we observe phase separation for L/D values as small as 0.1. At $L/D=0.1$ our GEMC results also appear to be tending towards a ''closed loop'' with the phase transition disappearing for smaller values of L/D. However, as discussed below, for small aspect ratios the sampling is very poor and the GEMC method is unreliable. In all likelihood, the large and significant discrepancies between our results and those of McGrother and Jackson for $L/D\lesssim 0.20$ arise because as the aspect ratio is reduced, the sampling becomes so poor that it very difficult to achieve anything close to converged equilibrium states [10].

For dipolar hard dumbbells, the GCMC and GEMC results are in good agreement for $L/D\geqslant 0.20$ and also lie quite close to the dipolar hard spherocylinder curve as we would expect because the models are physically similar for small aspect ratios. For $L/D=0.1$ the GCMC calculations indicate phase separation [see Fig. 1(a)] in an apparently smooth continuation of the results for higher aspect ratios. However, starting with equal densities in each box (see discussion below), the GEMC method did not achieve phase separation even after very long runs (800 000 cycles). For dipolar hard dumbbells GEMC calculations were not carried out for aspect ratios between 0.1 and 0.2. For aspect ratios smaller than 0.1, the GCMC sampling was not good enough to produce reliable results, but it is possible that coexistence does exist for aspect ratios all the way down to the dipolar hard-sphere limit. If this were true, assuming a smooth extrapolation, one would expect a reduced critical temperature of ~ 0.18 and a very low critical density for dipolar hard spheres. However, current Monte Carlo methods may not be capable of producing reliable results for the phase behavior of dipolar hard spheres in the relevant region of temperature and density.

We now discuss the sampling problems in more detail. Both the GEMC and GCMC methods require moves that involve particle insertions and deletions. If the aspect ratio is sufficiently small, then at low temperatures and densities the dipolar particles tend to ''associate'' into ''chains.'' This tendency may well be artificially enhanced by the periodic boundary conditions applied in the simulations. In any case, the dipole-dipole interactions within these chains are very strong and as the temperature or aspect ratio is lowered, the probability of achieving successful deletion or insertion moves becomes very small. It is this problem alone, which eventually kills the GCMC method for small aspect ratios and low temperatures. In the GEMC case this problem is even more severe because a deletion and an insertion must be achieved simultaneously, hence lowering the probability of a successful move still further.

In addition to this problem, which occurs for both simulation methods, the GEMC method has an additional serious sampling problem also associated with the dipolar association or chaining. In the GEMC method, moves that involve changing the volume of both simulation cells while maintaining the total volume fixed are necessary in order to achieve mechanical equilibrium. The formation of associated species greatly restricts the volume fluctuations. Physically, this is not difficult to understand. Particle association introduces a very short length scale into the system and from a simulation viewpoint, it behaves as though it were much denser than it actually is. In practice, we find that even dipolar pairing greatly reduces the probability of successful volume contractions. It is this additional sampling problem coupled with the requirement for simultaneous insertions and deletions that greatly restricts the usefulness of the GEMC method for these systems.

From a practical standpoint, sampling problems in the GEMC method become evident mainly because the results obtained begin to depend strongly on the initial conditions. Moreover, to confuse matters still further, even for very long simulation runs, apparent ''convergence'' to different states can be observed. As an example, in Fig. 3 we have plotted the densities in each cell as a function of the number of Monte Carlo cycles for the same system begun with different initial conditions. The run shown in Fig. 3(a) was begun with the same number of particles in each cell. We see that for $\sim$200 000 cycles the system does very little and one could easily conclude that no phase change occurs at these state parameters. However, at $\sim$200 000 cycles the system achieves a clear phase separation, the densities appear to rapidly equilibrate, and then remain essentially unchanged as the run is extended to nearly 600 000 cycles. However, this too is misleading. Figure 3(b) shows another run for the same system begun with unequal numbers of particles in each cell. We see that as this run converges, the vapor phase obtained is significantly less dense than that achieved in Fig. 3(a). We could give additional examples but this is sufficient to demonstrate that there are serious sampling problems with the GEMC method for small aspect ratios and low temperatures. Furthermore, as evidenced by Fig. 3(a), it would not be difficult to be ''fooled'' into incorrect conclusions by apparent convergence when in fact the GEMC method has not found the true equilibrium states.

III. SUMMARY AND CONCLUSIONS

In this paper we have investigated the liquid-vapor phase behavior of fluids of dipolar hard dumbbells and dipolar hard spherocylinders. Employing both GEMC and GCMC methods we report liquid-vapor coexistence for aspect ratios ranging between 0.1 and 0.75. It is observed that the critical temperature drops as the aspect ratio is increased.

In contrast with earlier GEMC calculations of McGrother and Jackson [6] for dipolar hard spherocylinders, at $T^*=0.12$ we find evidence for liquid-vapor coexistence for aspect ratios as small as 0.1. At this reduced temperature, McGrother and Jackson found no liquid-vapor coexistence for $L/D\lesssim 0.19$. Our results agree with those of McGrother and Jackson for larger aspect ratios but not for the smaller values. We believe that the disagreement between our calculations and those of McGrother and Jackson is due to the fact that the GEMC sampling becomes very poor for small aspect ratios at the temperatures and densities where condensation occurs. The results obtained are unreliable and one can be

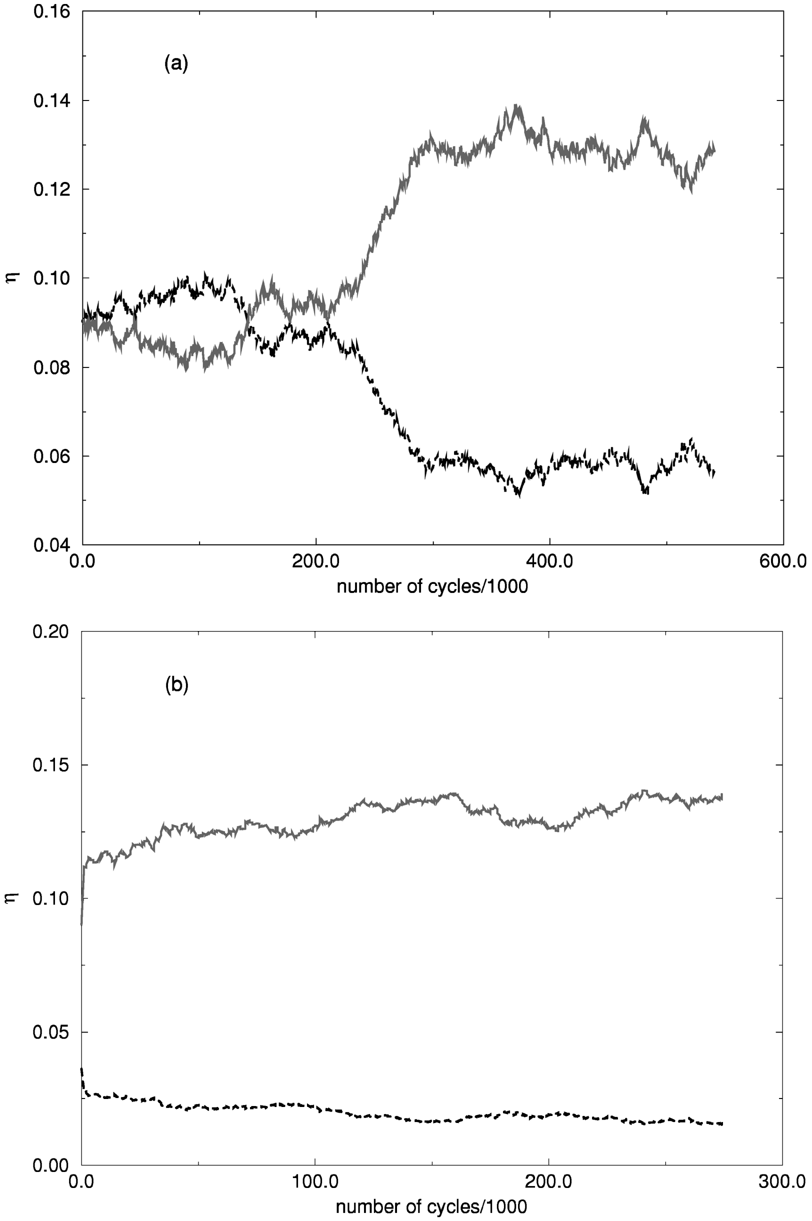

FIG. 3. Instantaneous densities for dipolar hard spherocylinders at $L/D=0.10$ and $T^*=0.12$ from GEMC simulations with different initial conditions. The initial conditions are (a) $N_1=256, \eta_1=0.090, N_2=256, \eta_2=0.090$; (b) $N_1=256, \eta_1=0.036, N_2=256, \eta_2=0.090$.

easily mislead into incorrect conclusions by apparent convergence even though true equilibrium has not been reached.

The origin of the convergence problems lies with the tendency of dipolar particles with small aspect ratio to associate into chainlike structures at low temperatures and densities. These chains are energetically very stable and their presence greatly reduces the probability of successful insertion and deletion moves in both the GEMC and GCMC methods, but the problem is more severe in the GEMC method where insertions and deletions must be carried out simultaneously. It is the insertion-deletion problem alone that limits the GCMC method. However, for the GEMC method there is an additional serious problem in that the presence of associated dipolar species greatly reduces the probability of successful moves involving volume contractions. This clearly generates sampling problems and acts to prevent the large volume fluctuations necessary for phase separation.

The severity of the GEMC sampling problems for these dipolar systems does not appear to have been fully appreciated in earlier work [3,6], and it is possible that a liquid-vapor transition has not been observed for dipolar hard (or soft) spheres simply because the sampling is extremely poor. Our calculations suggest that the possibility of liquid-vapor coexistence for dipolar hard spheres should be left open, at least until the question is further explored with more reliable sampling methods.

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[10] In their simulations McGrother and Jackson [6] used reaction field boundary conditions, whereas we employed Ewald summation methods to take account of the long-range dipolar forces. However, because we agree with McGrother and Jackson for larger aspect ratios (where the sampling problems are much less severe), we do not believe that the different boundary conditions account for the discrepancies observed.

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