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# Liquid–vapor criticality in a fluid of charged hard dumbbells

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The vapor–liquid criticality of a fluid of charged hard dumbbells is investigated employing grand canonical Monte Carlo simulations and mixed-field finite-size scaling methods. The reduced critical temperature and density obtained are  $T_c^* = 0.04911 \pm 0.00003$  and  $\rho_c^* = 0.101 \pm 0.003$ , respectively. The critical temperature is very close to that of the restricted primitive model (RPM) for ionic fluids, while the critical density is  $\sim 25\%$  larger than that of the RPM. The “fits” to the Ising ordering operator distribution are good, and are of similar quality to those found for the RPM with systems of comparable size. However, for the finite-size systems simulated, the constant volume heat capacity,  $C_V$ , gives no indication of an Ising-type “divergence” at  $T_c$ . This is analogous to the RPM, and serves to demonstrate that this still puzzling behavior is not restricted to that model. © 2003 American Institute of Physics. [DOI: 10.1063/1.1609192]

## I. INTRODUCTION

The condensation phase transition in Coulombic fluids has been an important topic of investigation in recent years. It has been studied extensively in experimental and theoretical work, as well as with computer simulations. The main source of debate involves the determination of the universality class of the phase transition, which dictates the scaling behavior of various measurable quantities close to the liquid–vapor critical point. As an example, the near-critical temperature dependence of the constant-volume heat capacity,  $C_V$ , along the critical isochore can be described by the equation  $C_V \sim t^{-\alpha}$  as  $t \rightarrow 0$ , where  $\alpha$  is the critical exponent,  $t = |T - T_c|/T_c$ ,  $T$  is the temperature, and  $T_c$  is the critical temperature. Classical or mean-field theories predict  $\alpha = 0$ , while  $\alpha = 0.109 \pm 0.004$  (Ref. 1) if the phase transition belongs to the three-dimensional Ising universality class.

In experimental studies of ionic liquids, signals of both classical and Ising-type criticality have been observed. Some experiments have shown that the vapor–liquid phase transition displays classical critical behavior,<sup>2,3</sup> while more recent work<sup>4–9</sup> tends to indicate that the transition is characterized by a crossover from classical to Ising behavior at values of  $t$  as small as  $10^{-4}$ . These findings are in marked contrast to experimental and theoretical results for nonionic fluids, which typically exhibit classical-to-Ising crossover at  $t \sim 10^{-1}$ .

To some extent, the universality class of a critical point depends on the range of the interactions.<sup>10–12</sup> Using renormalization group (RG) theory, attractive potentials that depend on the pair separation,  $r$ , like  $r^{-n}$  were shown to exhibit classical (mean-field) universality when  $n < 3d/2$ , where  $d$  is the spatial dimension.<sup>11</sup> When  $n > d + 2 - \eta_{SR}$ , where  $\eta_{SR} = 0.0335 \pm 0.0025$  (Ref. 1) is the short-range correlation-length exponent, the criticality is Ising-type. Finally, when  $3d/2 < n < d + 2 - \eta_{SR}$ , the critical exponents take on values which interpolate linearly between the classi-

cal and Ising-type values.<sup>12</sup> These predictions have been tested recently in simulations of lattice<sup>13,14</sup> and fluid<sup>15</sup> models with algebraic interactions.

On this basis, one might expect that the Coulombic  $1/r$  interactions in ionic fluids should give rise to classical criticality. However, as has been known since the work of Debye and Hückel, electrostatic screening will decrease the range and alter the functional form of the *effective* interactions. Within the Debye–Hückel (weak-coupling) approximation, the interactions between ions are proportional to  $\exp(-r/\lambda)/r$ , where  $\lambda$  is a density- and temperature-dependent screening length. A potential of this form, with a leading-order term in the Fourier expansion proportional to  $(\lambda q)^2$ , should always lead to Ising-type criticality for any value of  $\lambda > 0$ . On the other hand, it has long been known that the subcritical vapor phase largely consists of strongly aggregated cation–anion pairs<sup>16–21</sup> which introduces the additional effects of dielectric screening, and ion–dipole and dipole–dipole interactions. Note that the leading-order term in the angle-averaged ion–dipole interaction varies like  $1/r^4$ , which would give rise to classical critical behavior if no other interactions were present. Experimental evidence for the existence of ion pairs at subcritical densities and temperatures has been found in recent ionic conductivity measurements.<sup>22,23</sup> From this very brief discussion it is clear that the true situation in ionic fluids is complex, and it is largely for this reason that a reliable Landau–Wilson Hamiltonian has yet to be found which can be used in a RG analysis to determine the universality class once and for all.

In theoretical and simulation work, the primary focus has been on the primitive model (PM) and its derivatives, most commonly the restricted primitive model (RPM). The RPM consists of equal numbers of positively and negatively charged hard spheres, with equal diameter  $\sigma$ , immersed in a continuum with dielectric constant  $\epsilon$ . The pair potential is given by,

$$U_{ij} = \begin{cases} \infty & \text{if } r_{ij} < \sigma, \\ \frac{q_i q_j}{\epsilon r_{ij}} & \text{if } r_{ij} \geq \sigma, \end{cases} \quad (1)$$

where  $q_i = \pm q$  is the charge on ion  $i$ , and  $r_{ij}$  is the distance between ions  $i$  and  $j$ . The properties of the system are most conveniently described in terms of reduced units: the reduced temperature,  $T^* = k_B T \epsilon \sigma / q^2$ , where  $k_B$  is Boltzmann's constant; the reduced density,  $\rho^* = N \sigma^3 / V$ , where  $N$  is total number of ions, and  $V$  is the volume.

Theoretical treatments of the RPM based on either Debye–Hückel (DH) theory<sup>16,24–26</sup> or integral equation theories<sup>27,28</sup> have been studied extensively. For the most part, these theories are all mean-field in nature, and hence will always predict classical criticality, although there is some evidence from integral equation theories to suggest that the asymptotic critical behavior of the RPM should be Ising-type.<sup>29,30</sup>

In recent years, the critical behavior of the RPM has been the subject of extensive computer simulation studies, mainly involving large-scale Monte Carlo (MC) calculations.<sup>31–40</sup> Mixed-field finite-size scaling (MFFSS) analyses of the critical point have yielded very precise values of the critical parameters, and have largely indicated Ising-type critical behavior.<sup>31,33,34,37,38</sup> A subject of current discussion is whether Ising-type criticality can be inferred from simulation measurements of bulk thermodynamic properties such as  $C_V$ . Although an Ising-type divergence in  $C_V$  along the critical isochore is apparent in grand canonical MC (GCMC) simulations reported in Ref. 35, it is absent in canonical ( $NVT$ ) simulations reported in Refs. 32 and 39. In very recent work, it was found that the presence of a peak in  $C_V$  calculated in GCMC simulations does not imply that the criticality is Ising-type, since such a peak is present even for critical points that are known to be classical.<sup>40</sup> It was suggested that this ensemble dependence is an extreme finite-size effect. Finally, it should be pointed out that in Ref. 38, calculations of  $C_V$  from GCMC simulations are not consistent with Ising-type criticality, even though MFFSS analysis yields results which are.

In this paper we concentrate on one particular aspect of ionic criticality, that being the role of ion association. As indicated above, ion association has long been known to affect strongly the properties of the subcritical vapor phase, but it is difficult to describe its extent and effects accurately. In an attempt to isolate the role of ion pairs on the vapor–liquid transition, Shelley and Patey<sup>41</sup> simulated a fluid of so-called charged hard dumbbells (CHDs), each comprising a pair of charged hard spheres—one cation and one anion—fused at contact. The vapor–liquid coexistence curve was found to be very similar to that for the RPM. The conclusion from this work was that ionic condensation (as in the RPM) is likely driven mainly by interactions between ion pairs acting roughly like rigid charged hard dumbbells. Recently, additional evidence supporting this conclusion has been obtained in simulation<sup>42–44</sup> and theoretical<sup>45</sup> studies.

In order to further explore the influence of ion association on the critical behavior, we have performed extensive GCMC simulations of the near-critical CHD fluid. In this

model, the free-ion interactions are explicitly removed. We determine the critical parameters of CHDs using MFFSS and histogram reweighting techniques.<sup>46–48</sup> We also investigate the behavior of  $C_V$  in the vicinity of the critical point. These calculations provide a comparison with the RPM, and give further insight into the nature of vapor–liquid criticality in that system.

This paper is organized as follows: In Sec. II we summarize the simulation and MFFSS analysis techniques employed in this work. The results are presented in Sec. III, and Sec. IV concludes the paper.

## II. MODEL AND SIMULATION METHODS

GCMC simulations were carried out in cubic simulation cells of side  $L$ , with periodic boundary conditions applied. The long-range Coulomb interactions were evaluated using the Ewald summation method<sup>49</sup> with conducting ( $\epsilon_s = \infty$ ) boundary conditions.

In simulations of the RPM, all of the ions are considered as free particles. In the simulations of CHDs, cation–anion pairs are kept in contact, i.e., at a fixed separation  $\sigma$ . The interaction potential and reduced parameters are the same as for the RPM [Eq. (1)] defined in Sec. I. To facilitate comparisons with the RPM, the total *ion* density will be reported in this work.

In the Monte Carlo simulations, dumbbell moves, insertions, and deletions are selected with equal probabilities. If a dumbbell move is to be attempted, either a translation of the dumbbell center of mass or a rotation about the center of mass is selected with equal probability. The maximum displacements of these moves were set in order to attain acceptance rates ranging between 35% and 65%. For the dumbbell insertions and deletions, an acceptance rate of  $\sim 1\% - 5\%$  was obtained, depending on the density. Such a low acceptance rate meant that very long simulations ( $\sim 3 \times 10^7$  moves per particle after equilibration) were required to obtain a smooth ion-density distribution corresponding to near-critical vapor–liquid coexistence.

In contrast to the RPM no special simulation techniques such as biased particle sampling or cluster moves<sup>50</sup> were necessary in order to obtain good statistics in a reasonable length of time. This can be attributed to the fact that in the dumbbell case, these techniques are already implicit in the model; the dumbbell insertions and deletions can be seen as a limiting case of the biased particle sampling technique with only minimally separated ion pairs considered for insertion or deletion.

*Finite size scaling and histogram reweighting:* We employ the MFFSS technique introduced by Bruce and Wilding.<sup>46–48</sup> The system-size dependent critical parameters are those with which the distribution of an ordering operator,  $\mathcal{M}$ , collapses onto the limiting distribution for the appropriate universality class. For fluids, the ordering operator  $\mathcal{M}$  is often given by,

$$\mathcal{M} = \rho - su, \quad (2)$$

where, in the present case,  $\rho$  is the ion density,  $u = U/V$  is the energy density and  $s$  is a system dependent quantity which determines the degree of mixing between  $\rho$  and  $u$ . This mix-

TABLE I. Summary of GCMC simulation results. The numbers in brackets are the estimated uncertainties in the final digit.

$L/\sigma$	$T_c^*(L)$	$\rho_c^*(L)$	$\beta_c \mu_c^*(L)^a$
10.0	0.04902(5)	0.107(1)	-6.608(7)
13.0	0.04910(5)	0.1050(6)	-6.593(5)
15.0	0.04910(3)	0.1059(3)	-6.589(4)
17.0	0.04907(3)	0.1038(3)	-6.592(4)

<sup>a</sup>The ideal gas contribution to the chemical potential, as well as the internal chemical potential of the dumbbells, are not included.

ing is necessary in order to account for the particle-hole asymmetry present in all continuous space fluid models. It has been suggested that the expression for  $\mathcal{M}$  in Eq. (2) should also contain terms related to the pressure,<sup>51</sup> but these terms are thought to be small in many cases.

The finite-size critical parameters scale with system size,  $L$ , according to the following scaling relations:

$$\delta\mathcal{M} = \sqrt{\langle \mathcal{M}^2 \rangle - \langle \mathcal{M} \rangle^2} \sim L^{-\beta/\nu}, \quad (3)$$

$$T_c(\infty) - T_c(L) \sim L^{-(\theta+1)/\nu}, \quad (4)$$

$$\beta_c \mu_c(\infty) - \beta_c \mu_c(L) \sim L^{-(\theta+1)/\nu}, \quad (5)$$

$$\rho_c(\infty) - \rho_c(L) \sim L^{-(d-1)/\nu}, \quad (6)$$

$$u_c(\infty) - u_c(L) \sim L^{-(d-1)/\nu}. \quad (7)$$

Here,  $\theta$  is Wegner's correction-to-scaling exponent,<sup>52</sup> and  $d$  is the number of dimensions. In this work we shall assume at the outset that the vapor-liquid critical point belongs to the three-dimensional Ising universality class. The various critical exponents are therefore assumed to take the values<sup>53</sup>  $\beta \approx 0.326$ ,  $\nu \approx 0.6294$ , and  $\theta \approx 0.54$ .

For a given system size,  $L$ , the joint distribution function,  $P_L(\rho, u)$ , is measured in GCMC simulations under near-critical conditions. Histogram reweighting techniques are then used to find the values of  $T_c^*(L)$ ,  $\beta_c \mu_c(L)$ , and  $s$  that provide the optimum fit of  $P_L(\mathcal{M})$  to the limiting Ising distribution,  $P_{\text{Ising}}(\mathcal{M})$ . To this end, we compare distributions that are normalized, centered on zero, and with unit variance. From Eq. (3) the relevant independent variable is therefore  $x = a_m^{-1} L^{\beta/\nu} (\mathcal{M} - \langle \mathcal{M} \rangle)$ , where  $a_m^{-1}$  is a system-specific prefactor.  $P_{\text{Ising}}(x)$  is known to a high degree of precision from large-scale simulations of the three-dimensional Ising model.<sup>54</sup>

### III. RESULTS

Simulations were carried out for four systems ranging in size from  $L = 10\sigma$  to  $L = 17\sigma$ . Results for  $T_c^*(L)$ ,  $\rho_c^*(L)$ , and  $\beta_c \mu_c(L)$  are summarized in Table I. It must be noted that the error estimates given in the table (and included in Figs. 2 and 3) are not true statistical uncertainties; many more long Monte Carlo runs would be necessary to obtain a sufficient number of truly independent estimates for a proper statistical analysis at each value of  $L$ , and this is clearly not practical. Rather, the quoted uncertainties represent our "best estimates" of upper and lower bounds, and were obtained by carrying out the analysis on a limited number of different  $P_L(\rho, u)$  data sets. Both the statistical error inherent in the

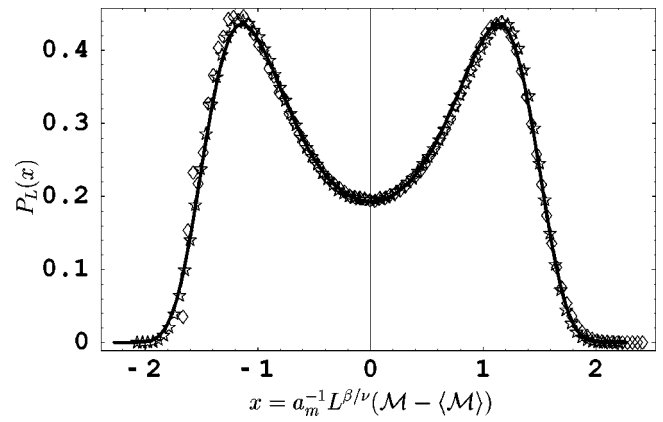


FIG. 1. Matching to the Ising universal order parameter distribution (solid curve) for CHD systems. The diamonds and stars are the results for  $L = 10\sigma$  and  $L = 17\sigma$ , respectively.

Monte Carlo method, and errors associated with the "fit" to  $P_{\text{Ising}}(\mathcal{M})$  contribute to the total estimated error.

In Fig. 1 we show the optimum critical ordering operator distributions,  $P_L(x)$ , for the smallest ( $L = 10\sigma$ ) and largest ( $L = 17\sigma$ ) CHD systems, along with the limiting distribution,  $P_{\text{Ising}}(x)$ , for the three-dimensional Ising model.<sup>54</sup> For the  $L = 10\sigma$  case we have tuned values of  $T_c^*$ ,  $\beta_c \mu_c$ , and  $s$  to ensure that the minima at  $x = 0$  in the simulated and limiting distributions coincide. The agreement between  $P_L(x)$  and  $P_{\text{Ising}}(x)$  with  $L = 10\sigma$  is quite good. The simulation results for  $L = 17\sigma$  collapse onto the limiting distribution almost perfectly, with only minor deviations in the regions of the maxima at  $|x| \approx 1.2$ .

In Fig. 2 we plot the apparent critical temperature,  $T_c^*(L)$ , as a function of  $L^{-(\theta+1)/\nu}$ , in accordance with Eq. (4). We see from the figure and from Table I that the variation of  $T_c^*(L)$  with  $L$  is *very small*. Given this, and taking note of the error estimates, it is apparent that attempting to extrapolate to  $L^{-(\theta+1)/\nu} = 0$  is a rather dubious procedure. Nevertheless, employing a weighted least squares fit (including all four points) we obtain an estimate for the bulk critical

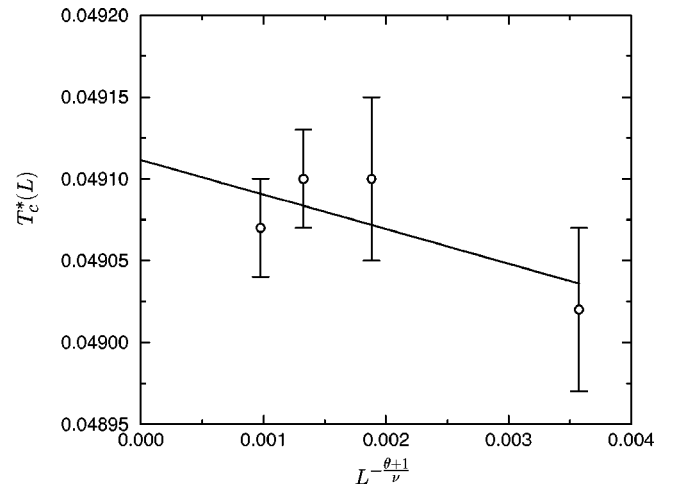


FIG. 2. Extrapolation of the critical temperature for CHD systems to the limit  $L^{-(\theta+1)/\nu} \rightarrow 0$ . The solid line is the least squares fit to the four data points.

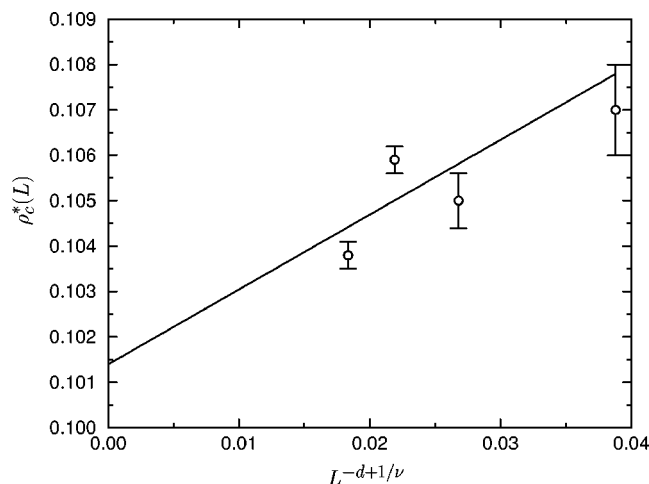


FIG. 3. Extrapolation of the critical density for CHD systems to the limit  $L^{-(d-1/\nu)} \rightarrow 0$ . The solid line is the least squares fit to the four data points.

temperature of the CHD fluid of  $T_c^* = 0.04911 \pm 0.00003$ . We note that simply averaging the values obtained for the three largest systems (which are indistinguishable within the error estimates) gives  $T_c^* = 0.04909 \pm 0.00004$ , which is close to the extrapolated value. In Fig. 3 we show the apparent critical ion density,  $\rho_c^*(L)$ , as a function of  $L^{-(d-1/\nu)}$ , in accordance with Eq. (6). Our estimate of the bulk critical ion density, again obtained with a least squares fit, is  $\rho_c^* = 0.101 \pm 0.003$ . Similarly, we obtain an estimate for the bulk critical excess chemical potential of  $\beta_c \mu_c = -6.583 \pm 0.004$ , using Eq. (5). We note that these values of  $T_c^*$  and  $\rho_c^*$  are in good agreement with those obtained by employing Monte Carlo calculations on a finely discretized lattice.<sup>42,44</sup> For comparison, the best current determinations for the critical parameters of the RPM are  $T_c^* = 0.04917 \pm 0.00002$  and  $\rho_c^* = 0.080 \pm 0.005$ .<sup>38</sup> Therefore, the effects of constraining cation–anion pairs at contact on the critical parameters are quite small; the critical temperature is decreased by  $\sim 0.1\%$ , and the critical ion density is increased by  $\sim 25\%$ .

For the  $L = 17\sigma$  case, we have also obtained the canonical heat capacity,  $C_V$ , and  $C_V/Nk_B$  is plotted as a function of  $T^*$  in Fig. 4. The figure shows results obtained from the

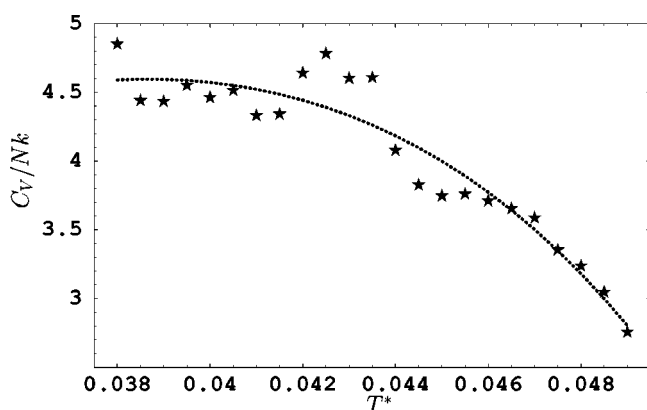


FIG. 4. The canonical heat capacity per ion for the CHD system with  $L = 17\sigma$ . The stars are the values given by the usual fluctuation formula, and the dotted curve is obtained by fitting the energy with a [5,5] Padé approximant.

standard  $NVT$  fluctuation formula, and those obtained by differentiating a fit to the energy using the [5,5] Padé approximant,

$$\frac{\sum_{k=0}^5 a_k x^k}{1 + \sum_{l=1}^5 b_l x^l}, \quad (8)$$

where  $x = \sqrt{T^*}$ . Although a function of this type cannot be used to describe a true Ising-type divergence in the heat capacity, it is adequate to fit the rounded-off peaks in  $C_V$  measured in finite-size simulations. We note that both estimates of  $C_V$  are similar, and display no significant features in the vicinity of  $T_c^*$ . The small “peaks” in the results from the fluctuation formula do not occur in the Padé fit and are not statistically significant. This  $C_V$  behavior is consistent with earlier observations for the RPM,<sup>32,38–40</sup> and demonstrates again that at least for systems of this type and size, the canonical heat capacity provides no indication of Ising-type behavior.

#### IV. CONCLUSIONS

We have investigated the vapor–liquid critical point in the CHD fluid using GCMC simulations together with mixed-field finite-size scaling and histogram reweighting techniques. Our estimates of the critical temperature and ion density are  $T_c^* = 0.04911 \pm 0.00003$  and  $\rho_c^* = 0.101 \pm 0.003$ . These results for the critical parameters of CHDs are comparable to the critical parameters of the RPM. The CHD critical temperature is almost exactly equal to that of the RPM, while the CHD critical ionic density is  $\sim 25\%$  larger than that of the RPM. We attribute this difference in  $\rho_c^*$  to the dumbbells having a smaller “size,” and hence dipole moment, than that of aggregated ion pairs in the RPM.

As for the question of the universality class of CHDs, there seems to be little difference between the results of the current study and those found for the ionic RPM. The fit of  $P_L(x)$  to the limiting Ising distribution is very good, except with the smallest system sizes. This finite-size effect is pronounced in the CHD and RPM systems because the critical density is so low, and hence the portion of  $P_L(x)$  at large negative values of  $x$  is determined from vapor-phase configurations containing a very small number of ion pairs. In other systems, such as Lennard-Jones fluids, the fit to  $P_{\text{Ising}}(x)$  is affected to a much lesser extent because the critical density is roughly three times larger, and the MFSS analysis unambiguously indicates Ising-type criticality.<sup>55</sup>

In PM electrolytes the low-density effects are important enough to make an absolute determination of the universality class through the fit to  $P_{\text{Ising}}(x)$  impossible without the examination of very large systems ( $L \sim 30$  and above). We note that recent GCMC studies of criticality in the RPM on large systems up to  $L = 34$  still show no deviation from Ising behavior in the matching of  $P_L(x)$  to  $P_{\text{Ising}}(x)$ .<sup>37,38</sup> Our overall conclusion at this point is that CHDs do not display a deviation from Ising behavior any greater or less than that of the RPM. There may still be qualitative differences, but an absolute determination of the universality class seems impractical using MFSS techniques. That being said, it may be feasible to change the model to allow a smaller difference

between the gas and liquid densities, but without making the nature of the interactions too different from the RPM.

A still puzzling aspect of RPM criticality is the behavior of the constant volume heat capacity,  $C_V$ , which should diverge if the system is Ising-type. This has been investigated<sup>32,39</sup> using canonical MC simulations, and no sign of a finite-size “divergence” was seen. Reference 35 reports clear “divergences” observed in GCMC simulations, whereas the large-scale GCMC simulations reported in Ref. 38 show  $C_V$  to exhibit non-Ising behavior. Our very recent work on this question<sup>40</sup> shows that the contradiction between the results in Refs. 32 and 35 could be due to a pronounced ensemble dependence of energy and density fluctuations, which should, presumably, disappear with large enough system sizes.

The present calculations indicate that the situation for the CHD fluid is very similar to that for the RPM; our  $C_V$  results for  $L=17\sigma$  show no sign of Ising-type behavior at  $T_c$ . To further explore this question, we are currently carrying out extensive simulations to determine the system-size dependence of  $C_V$  for a fluid characterized by a short-range potential that decays as  $r^{-6}$ . Our preliminary results for this model do show indications of the expected Ising-type behavior for systems comparable in size to those used in studies of the RPM and CHDs. This suggests that it is the long-range nature of the interactions in the RPM and CHD fluids that, at least for systems of a size suitable for simulation, suppresses the Ising-type “divergence” of  $C_V$  near the critical point.

## ACKNOWLEDGMENT

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