# Critical Behavior of the Restricted Primitive Model

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Monte Carlo simulations of the critical region of the restricted primitive model are reported. Using mixed-field finite size scaling analysis we show that the critical behavior is compatible with Ising-like behavior. The critical temperature is estimated to be 0.0487 ± 0.0001 and the critical density 0.065 ± 0.002. [S0031-9007(96)01559-1]

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A number of recent investigations of the liquid-liquid phase transition of ionic solutions have shown that the critical behavior displayed by these fluids is, in some cases, classical (mean-field-like) up to reduced temperatures $t = |T - T_c|/T_c \approx 10^{-4}$ or less [1–3], while in others it is Ising-like [4–7], or there may be crossover from mean-field to Ising criticality [8]. In systems where the critical exponents which describe the singular part of the physical properties appear to be classical over the whole range of measurement (in practice, systems of large sized ions in solvents of low dielectric constant) phase separation is commonly believed to be primarily caused by the long ranged Coulomb interactions. For these systems it is also found, using corresponding states arguments, that the critical parameters are close to those predicted for the restricted primitive model (RPM) [7–9]. The RPM consists of equally sized charged hard spheres of diameter $\sigma$, one half carrying charges $+q$, the other half charges $-q$, in a uniform dielectric continuum (of dielectric constant $\epsilon$). The interaction between ions is given by

$$u_{ij}(r)/kT = \begin{cases} +\infty, & r \le \sigma\,, \\ \dfrac{q_i q_j}{\epsilon kT\sigma}\,\dfrac{\sigma}{r}, & r > \sigma\,, \end{cases} \tag{1}$$

where $T$ is the temperature and $k$ Boltzmann's constant. It is convenient to define a reduced coupling strength $w = q^2/\epsilon kT\sigma$ and a reduced temperature $T^* = 1/w$.

From computer simulations [10–14] and theory [15–17] it is now well established that the RPM presents gas-liquid coexistence at low temperatures with critical temperature $T_c^*$ in the range 0.050–0.056 and critical density $\rho_c^*$ in the range 0.023–0.040. However, its critical behavior is not yet known with certainty. Theoretical analysis [15,18] suggests that it is of the Ising type, while experiment in the Coulombic fluids appears rather to be compatible with mean-field behavior (except maybe very close to the critical point [8]). In this Letter we address the question by using Monte Carlo (MC) simulations in conjunction with finite size scaling (fss) arguments. The simulations are performed in the grand canonical ensemble (GCE) [19] and the fss approach used is that developed by Bruce and Wilding [20,21] to account for the lack of "particle-hole" symmetry in fluid systems. This reduced symmetry in fluids manifests in a mixed character of the relevant scaling fields [22]. In our case they are linear combinations of the deviations of the reduced coupling strength $w$ and the chemical potential (divided by $kT$) $\mu$ from their critical values $\tau = w - w_c + s(\mu - \mu_c)$ and $h = \mu - \mu_c + r(w_c - w)$ where the system-specific parameters $s$ and $r$ determine the degree of field mixing. Associated with the relevant scaling fields $\tau$ and $h$ are two conjugate operators $\mathcal{E}$ and $\mathcal{M}$ satisfying

$$\langle\mathcal{E}\rangle = \frac{1}{V}\frac{\delta}{\delta\tau}\ln\Xi, \quad \langle\mathcal{M}\rangle = \frac{1}{V}\frac{\delta}{\delta h}\ln\Xi\,, \tag{2}$$

where $\Xi$ is the grand canonical partition function and $V$ the volume of the system. $\mathcal{E}$ and $\mathcal{M}$ are linear combinations of the reduced energy ($u = U/kTV\sigma^3$) and number ($\rho = N/V\sigma^3$) densities

$$\mathcal{E} = \frac{1}{1 - sr}(u - r\rho), \quad \mathcal{M} = \frac{1}{1 - sr}(\rho - su)\,. \tag{3}$$

A central role in the subsequent fss analysis plays the joint distribution function $p_L(\mathcal{M},\mathcal{E})$ for the operators $\mathcal{M}$ and $\mathcal{E}$. The characteristic length $L$ of the system being defined as $L = V^{1/3}$, the limiting $L \to \infty$ behavior of $p_L(\mathcal{M},\mathcal{E})$ at criticality $(h = 0, \tau = 0)$ has been assumed, following Bruce and Wilding [21], to be of the form

$$p_L(\mathcal{M},\mathcal{E}) \simeq \Lambda_{\mathcal{M}}^+ \Lambda_{\mathcal{E}}^+ \tilde{p}^*_{\mathcal{M},\mathcal{E}}(\Lambda_{\mathcal{M}}^+ \delta\mathcal{M}, \Lambda_{\mathcal{E}}^+ \delta\mathcal{E})\,, \tag{4}$$

where $\Lambda_{\mathcal{E}} = a_{\mathcal{E}} L^{1/\nu}$, $\Lambda_{\mathcal{M}} = a_{\mathcal{M}} L^{d-\beta/\nu}$, $\Lambda_{\mathcal{M}}\Lambda_{\mathcal{M}}^+ = \Lambda_{\mathcal{E}}\Lambda_{\mathcal{E}}^+ = L^d$, and $\delta\mathcal{M} = \mathcal{M} - \langle\mathcal{M}\rangle_c$, $\delta\mathcal{E} = \mathcal{E} - \langle\mathcal{E}\rangle_c$ and the averages are at criticality. Given an appropriate choice of the nonuniversal scale factors $a_{\mathcal{M}}$

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and $a_{\mathcal{E}}, \tilde{p}_{\mathcal{M},\mathcal{E}}$ is a function which depends only on the universality class of the system.

In order to determine the critical behavior of the RPM we will follow the same strategy as adopted by Wilding [23] to demonstrate that the critical behavior of the Lennard-Jones system is of the 3D Ising type. Specifically, as $\tilde{p}^*_{\mathcal{M},\mathcal{E}}(x,y)$ is known from MC simulations [24], we shall show that our MC results for the distribution functions $p_L(\mathcal{M}) = \int d\mathcal{E}\, p_L(\mathcal{M},\mathcal{E})$ and $p_L(\mathcal{E}) = \int d\mathcal{M}\, p_L(\mathcal{M},\mathcal{E})$ of the RPM match the universal fixed point functions $\tilde{p}^*_{\mathcal{M}}(x) = \int dy\, \tilde{p}^*_{\mathcal{M},\mathcal{E}}(x,y)$ and $\tilde{p}^*_{\mathcal{E}}(y) = \int dx\, \tilde{p}^*_{\mathcal{M},\mathcal{E}}(x,y)$ of the Ising model.

The MC simulations were performed by confining the system of charged hard spheres to the surface of a four-dimensional hypersphere [25]. Previous work on the RPM has shown [13,14] that the hypersphere boundary conditions (bc) give thermodynamic and structural properties identical to those obtained with the more familiar Ewald bc where the basic simulation cell is replicated periodically in space [19]. The advantage of using hypersphere bc is a reduction of computer time by a factor of 3–4 compared to the Ewald method for system sizes of a few hundred ions. We followed the method proposed in Refs. [13,14,26]. The MC sampling in the GCE was made in cycles, each cycle comprising displacement trial moves, as well as insertion and deletion moves of charged hard spheres. For the latter moves a biased scheme similar to the one proposed by Orkoulas and Panagiotopoulos [12] adapted to the present hypersphere bc was used. In the gas phase where clustering of the ions is important [14] ion-pair translation/rotation moves were combined with moves which displace and rotate clusters as a whole [13,14]. Each cycle comprised approximately 250 trial moves; at each MC step a random choice was made as to which type of move would be made. The pair $(\rho, u)$ was recorded every cycle in a wide range of temperatures and chemical potentials around the critical parameters and from these data histograms for the joint distribution of energy and number density $p_L(\rho, u)$ were constructed. Each histogram comprised of the order of $5 \times 10^6$ entries. In order to estimate finite size effects five volumes $V/\sigma^3 = 1500$, 2500, 3500, 5000, and 10 000 were investigated.

Following Wilding [23], the chemical potential realizing coexistence at fixed temperature is obtained from the requirement that the ordering distribution $p_L(\mathcal{M})$ is symmetric in $\mathcal{M} - \langle\mathcal{M}\rangle$. However, as the ordering operator $\mathcal{M}$ contains the unknown mixing parameter $s$, this symmetry condition can be satisfied only by adjusting both $\mu$ and $s$. Towards this end we advantageously used (multiple) histogram reweighting [27]. This technique enables one to determine $p_L(\rho, u)$ for any state $(\mu, T)$ knowing the histogram(s) $p_L(\rho, u)$ at one (or several) nearby state(s) $(\mu', T')$. It proves therefore sufficient to determine $p_L(\rho, u)$ for a series of states close to the coexistence curve [we considered several temperatures in the range 0.048–0.051; these states are easily identified from the double peak structure of the density distribution function $p_L(\rho) = \int du\, p_L(\rho, u)$] and to tune $\mu$ and $s$ (at fixed $T$) within the reweighting scheme of $p_L(\rho, u)$ to achieve symmetry of $p_L(\mathcal{M})$. In our simulations a symmetric $p_L(\mathcal{M})$ could be obtained for volumes $V/\sigma^3 \geq 5000$. At the smaller volumes the number of particles present in the system is too small to allow an adequate sampling of the gas phase. In particular, no formation of appreciable size clusters is possible. At these volumes symmetrization could be achieved only in an approximate way due to a too rapid decrease of $p_L(\mathcal{M})$ at small $\mathcal{M}$ (corresponding to small $\rho$ values) (cf. Fig. 1).

The final step will be to determine the critical behavior and the critical parameters. If $T^*_c$ and $\mu^*_c$ were known with great precision, the critical exponent ratio $\beta/\nu$ could, in principle, be determined from the collapse of $p_L(\mathcal{M})$, when expressed in terms of the scaling variable $x = a_{\mathcal{M}}^{-1} L^{\beta/\nu}(\mathcal{M} - \mathcal{M}_c)$, for different system sizes. Similarly, the ratio $1/\nu$ could be obtained from the collapse of $p_L(\mathcal{E})$, when expressed in terms of the scaling variable $y = a_{\mathcal{E}}^{-1} L^{d-1/\nu}(\mathcal{E} - \mathcal{E}_c)$. In the absence of a precise knowledge of the critical parameters we assumed the RPM to be of the Ising universality class and showing that $p_L(\mathcal{M})$ and $p_L(\mathcal{E})$ will collapse on the corresponding Ising fixed point functions. More explicitly, for a given volume, $T$, $\mu$ and $s$ were adjusted so that $p_L(\mathcal{M})$ matches the fixed point function $\tilde{p}^*_{\mathcal{M}}(x)$ corresponding to the Ising universality class. As simulation results for the latter [24] were not available to us we relied on the theoretical approximation given by Hilfer [28], using equation of state exponent $\delta = 4.8$, which reproduces the simulation results quite accurately (cf. Ref. [28]). In fact, because of the lack of complete symmetry for the

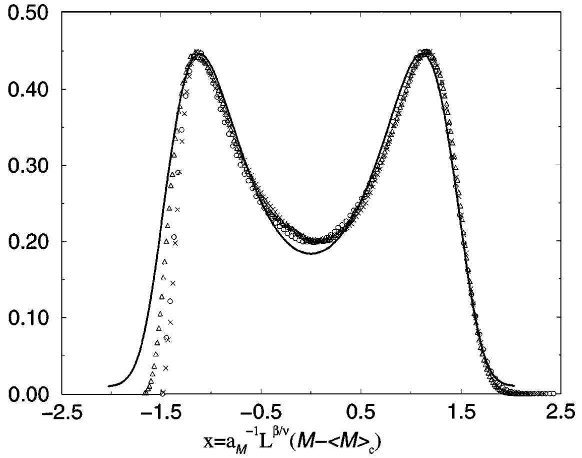

FIG. 1. Collapse of the ordering operator distribution function $p_L(\mathcal{M})$ on the universal fixed point ordering operator distribution $\tilde{p}^*_{\mathcal{M}}(x)$ for $V/\sigma^3 = 2500$, $T^*_c(L) = 0.0498$ (circles), $V/\sigma^3 = 3500$, $T^*_c(L) = 0.04955$ (crosses), and $V/\sigma^3 = 5000$, $T^*_c(L) = 0.04922$ (triangles). The universal distribution $\tilde{p}^*_{\mathcal{M}}(x)$ (solid line) is the theoretical approximation given by Hilfer [28]. The scaling variable is $a_{\mathcal{M}}^{-1} L^{\beta/\nu}(\mathcal{M} - \mathcal{M}_c)$. The nonuniversal scale factor $a_{\mathcal{M}}^{-1}$ is chosen so that the distributions have unit variance.

small system sizes, only the $x > 0$ part of $\tilde{p}^*_{\mathcal{M}}(x)$ has been matched. It was verified that by applying the same procedure to the larger volumes, the result is identical to that obtained by matching $\tilde{p}^*_{\mathcal{M}}(x)$ for all values of $x$. The matching is realized by normalizing to unity $\tilde{p}^*_{\mathcal{M}}(x)$ and its variance in both the MC results and Hilfer's theoretical approximation in the domain of $x$ values where MC data are available ($x \leq 2.3$). These conditions fix the nonuniversal scale factor $a^{-1}_{\mathcal{M}}$ [23].

The collapse of $p_L(\mathcal{M})$ on $\tilde{p}^*_{\mathcal{M}}(x)$ is shown in Fig. 1 for the volumes $V/\sigma^3 = 2500$, 3500, and 5000. The mismatch in the negative wing of the curve is due, as explained above, to inadequate sampling of the low density configurations for small volumes. By increasing the system size this error diminishes with concomitant improvement of the symmetrization. The mixing parameter $s$ for volume 5000 is $-1.47$; it depends slightly on system size. As Eq. (4) does not include corrections to scaling the critical parameters determined by matching $\tilde{p}^*_{\mathcal{M}}(x)$ turn out to be size dependent. The apparent critical temperatures are $T^*_c(L) = 0.0503$, 0.0498, 0.04955, 0.04922, and 0.04905 at the volumes $V/\sigma^3 = 1500$, 2500, 3500, 5000, and 10 000, respectively. The true critical temperature $T^*_c$ was inferred from the scaling relation [23]

$$T^*_c(\infty) - T^*_c(L) \propto L^{-(\theta+1)/\nu}, \tag{5}$$

where for the Ising system $\theta \simeq 0.54$ [29] and $\nu = 0.629$ [30]. $T^*_c(L)$ as a function of $L^{-(\theta+1)/\nu}$ is shown in Fig. 2. Linear least square extrapolation yields the infinite volume critical temperature $T^*_c = 0.0487 \pm 0.0001$. The corresponding critical chemical potential is estimated to be $\mu^*_c = -13.733 \pm 0.001$.

The statistical error on a histogram computed in a run of $10^6$ cycles is estimated to be $\approx 10\%$, that on a (multiple) reweighted histogram calculated with the set of runs performed at given $V$ of the order of 1%–2%. This uncertainty induces an error of 0.00005 on the values of $T_c(L)$ obtained by matching the universal distribution function.

The collapse of the energy operator distribution function $p_L(\mathcal{E})$ on the limiting fixed point function $\tilde{p}^*_{\mathcal{E}}(y)$ is shown in Fig. 3. The data are expressed in terms of the scaling variable $y = a^{-1}_{\mathcal{E}} L^{d-1/\nu}(\mathcal{E} - \mathcal{E}_c)$. Again the theoretical approximation of Hilfer [28] has been used for $\tilde{p}^*_{\mathcal{E}}(y)$. The field mixing parameter $r$ is estimated to be $-0.622$ for the volume 5000. This value is in good agreement with the value $-0.62$ of $d\langle\mu\rangle/dw$ at $T^*_c$.

An apparent critical density $\rho^*_c(L)$ was obtained from $\int d\rho\, \rho\, p_L(\rho)$ calculated at $T^*_c(L)$ and $\mu^*_c(L)$. Its shift from the infinite volume value is expected to vary as [23,24]

$$\rho^*_c(L) - \rho^*_c(\infty) \propto L^{-(d-1/\nu)}. \tag{6}$$

From linear least square extrapolation of $\rho^*_c(L)$ [0.1090, 0.0961, 0.0928, 0.884, 0.0835 with increasing volume], we find the infinite volume critical density $\rho^*_c = 0.065 \pm 0.002$. The critical density is higher than previous estimates. The larger value of $\rho^*_c$ results from the present fss analysis which implies that histograms for $p_L(\rho)$ with two peaks of equal height or weight obtained for temperatures close to but larger than the estimate $T_c(L)$ do not correspond to a gas-liquid phase equilibrium contrary to what was assumed in the Gibbs ensemble simulations [12,13].

Using the mixed field fss theory developed by Bruce and Wilding [20,21] we show that $p_L(\rho, u)$ of the RPM computed by GCE simulation can be mapped onto the joint distribution of critical scaling operators appropriate to the Ising fixed point where from it seems legitimate to conclude that the RPM belongs to the Ising universality class. We stress that we have assumed that the shape of $\tilde{p}^*$ [cf. Eq. (4)], corresponding to periodic boundary

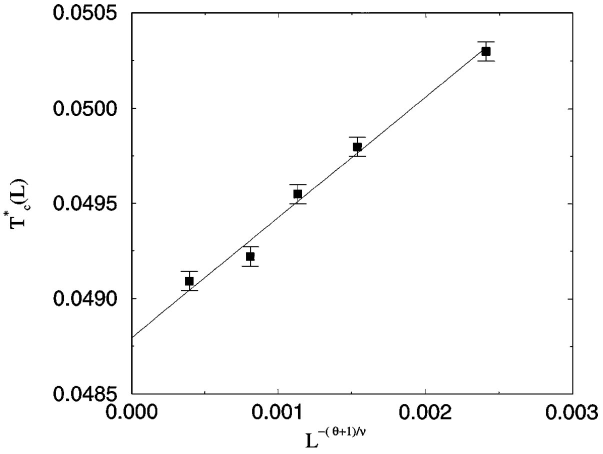

FIG. 2. The apparent critical temperature $T^*_c(L)$ as a function of $L^{-(\theta+1)/\nu}$, with $\theta = 0.54$ and $\nu = 0.629$. Extrapolation of the least squares fit gives the infinite volume temperature estimate $T^*_c = 0.04868$.

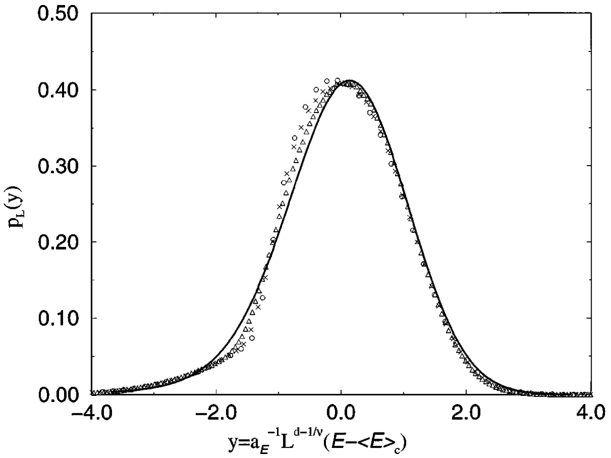

FIG. 3. Collapse of the energy operator distribution function $p_L(\mathcal{E})$ on the universal fixed point ordering operator distribution $\tilde{p}^*_{\mathcal{E}}(y)$ (symbols as in Fig. 1). The universal distribution $\tilde{p}^*_{\mathcal{E}}(y)$ (solid line) is the theoretical approximation given by Hilfer [28]. The scaling variable is $a^{-1}_{\mathcal{E}} L^{d-1/\nu}(\mathcal{E} - \mathcal{E}_c)$. The nonuniversal scale factor $a^{-1}_{\mathcal{E}}$ is chosen so that the distributions have unit variance.

conditions is appropriate for the hypersphere boundary conditions as well. A full account of the present study will be given elsewhere.

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