Critical parameters of the restricted primitive model

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The critical parameters for the restricted primitive model of electrolyte solutions were determined from extensive grand canonical Monte Carlo simulations combined with mixed-field finite-size scaling. The fine-lattice discretization method was used for the calculations, with Ewald summation of the long-range coulombic forces. Ising criticality and no pressure mixing were assumed in the finite-size scaling analysis. The critical parameters were obtained as a function of boundary conditions at infinite distance (ε∞), system size L, and lattice discretization parameter ζ. They were found to be sensitive to L for vacuum boundary conditions (ε∞ = 1), but much less so for “tin-foil” boundary conditions (ε∞ = ∞). The critical temperature and density decrease with increasing ζ. These calculations are compared to previous estimates of the critical parameters for this model. Extrapolation of our results to the thermodynamic limit in continuous space (L → ∞ and ζ → ∞) yields T_c* = 0.0489 ± 0.0003, \rho_c* = 0.076 ± 0.003. © 2002 American Institute of Physics. [DOI: 10.1063/1.1435571]

I. INTRODUCTION

The simplest possible model for electrolyte solutions is the restricted primitive model (RPM) consisting of charged hard spheres of equal diameter in a dielectric continuum. Early studies of Stell and co-workers established that the model has a vapor–liquid phase transition. Three recent simulation studies by different groups (referenced from this point on as CLW, YdP, and OP, respectively) are in reasonable agreement with each other with respect to the estimated critical temperature for this transition. However, differences outside of simulation uncertainties remain for the critical density. These studies have also reported a different dependence of the critical parameters on system size, making extrapolation to the thermodynamic limit uncertain. All three groups used variations of the grand canonical Monte Carlo method and have assumed Ising criticality. However, different boundary conditions were utilized in these studies.

The fine-lattice discretization method was introduced in Ref. 5 for ionic and in Ref. 6 for nonionic systems. The essence of the method is to perform calculations on a simple cubic lattice of spacing l less than the particle diameter \( \sigma \), with pre-computed interactions between all lattice sites for computational efficiency. In Ref. 5 ionic models with \( \zeta = \sigma/l = 1 \) or 2 were found to have phase behavior qualitatively different from the continuum model. However, for \( \zeta \geq 3 \) the phase behavior was found to be qualitatively identical; the critical point and coexistence curves matched continuum data within a few percent. Rapid convergence of thermodynamic and structural properties to the continuum limit was also observed for simple nonionic fluids in Ref. 6 for which \( \zeta = 10 \) was found to be indistinguishable from the continuum within statistical uncertainties. However, for ionic fluids, there is presently no systematic study of the effect of the lattice discretization parameter \( \zeta \) on the critical parameters and the finite-size scaling behavior.

The character of criticality in ionic and long-range systems remains a topic of active research.7–10 Valleau and Torrie studied the heat capacity of the RPM near criticality using thermodynamic-scaling methods and report no indication of an Ising-type divergence of the heat capacity. Luijten et al. argue that the observations of Ref. 7 are likely caused by finite-size effects in a system with low critical density in a way that is consistent with Ising criticality. Camp and Patey analyzed the behavior of systems with long-range interactions by mixed-field finite scaling analysis. They comment that for systems for which non-Ising behavior is suspected, inconsistencies are expected to appear in an analysis which uses the Ising limiting distribution. To complicate things even more, Fisher and Orkoulas suggested that the “standard” mixed field finite-size scaling analysis of Wilding and Bruce may be incomplete, with an additional pressure term required in the definition of the order parameter operator. This effect, however, seems to be quite small.

In the present study, we address an outstanding issue of criticality in the RPM concerning the effect of the lattice discretization parameter, \( \zeta \), on the critical parameters. Large system sizes, up to reduced lengths of \( L^* = 22 \) and fine lattices of \( \zeta = 14 \) are included in the analysis and facilitate extrapolation to the thermodynamic limit in the continuum, \( L \rightarrow \infty \) and \( \zeta \rightarrow \infty \). The mixed-field finite scaling ansatz is utilized, with the expectation that any internal discrepancies in the analysis may point to non-Ising criticality.

II. MODEL AND METHODS

We consider a system of \( 2N \) hard spheres, half of which carry charge \( -q \), and half charge \( +q \). The diameter of all ions is \( \sigma \). The interaction energy between two nonoverlapping ions, \( i \) and \( j \), of charges \( q_i \) and \( q_j \) separated by distance...
$r_{ij}$ is $U_{ij} = q_i q_j / D r_{ij}$, where $D$ represents the dielectric constant of the solvent. Reduced temperature, energy and density are defined via

$$T^* = \frac{k_B T D \sigma}{q^2}, \quad U^* = \frac{k_B D \sigma}{q^2}, \quad \text{and} \quad \rho^* = \frac{2 N \sigma^3}{V}, \quad (1)$$

where $V$ is the system volume. The reduced chemical potential, $\mu^*$, is defined so that at the limit of high temperatures and low densities,

$$\mu^* = 2 T^* \ln \frac{N \sigma^3}{V} \quad \text{for} \quad T^* \to \infty \quad \text{and} \quad \rho^* \to 0. \quad (2)$$

The multiplicative factor of 2 appears because there are two kinetically independent ions per neutral “molecule.”

We used grand canonical Monte Carlo simulations with multihistogram reweighting, following Ref. 16. Insertions and removals were attempted for neutral pairs consisting of a positive and a negative ion. To enhance efficiency, we used a distance-biasing algorithm entailing the Boltzmann factor of the interaction energy of the cluster. The distance-biased simulations were validated against unbiased calculations at high temperatures for which ion association is weaker. The acceptance ratio of the distance-biased insertion–removal steps was $\sim 8\%$ at the critical temperature and density.

Our simulations were performed using the fine-discretization methodology. The main advantage of this approach for systems with Coulombic interactions is that the interactions can be calculated once at the beginning of the simulation. The speedup relative to the continuum calculations is by a factor of up to 100, depending on number of particles. In the present study, the initial Ewald sum was performed with $k_{\text{max}} = 518$ Fourier-space wave vectors and real-space damping parameter $\kappa = 5$. To validate this choice of $k_{\text{max}}$, we performed additional calculations of the energy of typical configurations in small ($L^* = 12$) and large ($L^* = 22$) systems at both low and high densities. We found that the maximum difference between systems with $k_{\text{max}} = 2242$ and $k_{\text{max}} = 518$ was $4 \times 10^{-8}$ in the relative energy, so we felt justified in using the lower number for $k_{\text{max}}$ in the rest of the calculations. The real-space summation was computed only for minimum-image neighbors.

The Ewald summation algorithm requires that the medium externally surrounding the system be specified. Two common choices are conductive ($\epsilon_\infty = \infty$) and vacuum ($\epsilon_\infty = 1$) boundary conditions at infinite distance. We have used both choices in the present study, as one of our aims is to clarify the effect of boundary conditions on the critical parameters.

Critical points were estimated using mixed-field finite-size scaling analysis, under the assumption of Ising-type criticality. An (unnormalized) order parameter was first constructed from the number of particles and energy, $x = (N - s U^*)$, where $s$ is the field mixing parameter. The probability distribution of this operator, $\varphi(x)$, was obtained by multihistogram reweighting of the raw simulation results. The ordering parameter was then normalized to zero mean and unit variance. The resulting distributions were compared to the Ising-class limiting distribution. A downhill simplex optimization method was used to obtain $T_c^*$, $\mu_c^*$ and $s$ so as to minimize the sum of the absolute deviations between observed and Ising-class limiting distribution. Typical results of this procedure are shown in Fig. 1, discussed in the following section.

In order to obtain good statistics, multiple simulations were performed in parallel on a cluster of workstations, using independent initial configurations and random number sequences. A long-period random number generator was used (algorithm ran2 in Ref. 18 with a period of $2.3 \times 10^{18}$). Short initial runs were used to estimate the location of the critical point, followed by longer runs at the estimated critical temperature and chemical potential. A total of $3 \times 10^{10}$ Monte Carlo steps were performed for the largest systems ($L^* = 22$), with proportionally fewer steps for smaller systems. The total computing time required for this study was $\sim 3$ CPU years on 1 GHz Pentium III processors. Maximum memory requirements for $L^* = 22$ and $\zeta = 14$ were $\sim 250$ Mb using 8-byte real numbers (double precision).

### III. RESULTS AND DISCUSSION

Table I summarizes our results for the effective critical parameters of the systems studied. Statistical uncertainties were estimated from 7 to 25 independent runs, depending on...
TABLE I. Critical parameters for the RPM. Statistical uncertainties in parentheses refer to the last decimal place shown.

<table>
<thead>
<tr>
<th>$\varepsilon_*$</th>
<th>$\zeta$</th>
<th>$L^*$</th>
<th>$-\mu^*_c$</th>
<th>$-s$</th>
<th>$100T^*_c$</th>
<th>$100\rho^*_c$</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>12</td>
<td>1.3440(1)</td>
<td>0.75(1)</td>
<td>5.103(9)</td>
<td>7.1(2)</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td></td>
<td>1.3430(1)</td>
<td>0.75(1)</td>
<td>5.022(5)</td>
<td>7.1(1)</td>
</tr>
<tr>
<td></td>
<td>22</td>
<td></td>
<td>1.3426(1)</td>
<td>0.74(1)</td>
<td>4.988(2)</td>
<td>7.4(1)</td>
</tr>
<tr>
<td>$\infty$</td>
<td>10</td>
<td></td>
<td>1.3424(1)</td>
<td>0.74(1)</td>
<td>4.967(3)</td>
<td>7.6(1)</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td></td>
<td>1.3425(2)</td>
<td>0.74(1)</td>
<td>4.963(5)</td>
<td>7.9(2)</td>
</tr>
<tr>
<td></td>
<td>22</td>
<td></td>
<td>1.3421(3)</td>
<td>0.73(1)</td>
<td>4.958(3)</td>
<td>8.0(1)</td>
</tr>
<tr>
<td>5</td>
<td>18</td>
<td></td>
<td>1.3621(1)</td>
<td>0.72(1)</td>
<td>5.065(2)</td>
<td>8.4(1)</td>
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<td>7</td>
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<td>0.72(1)</td>
<td>5.016(2)</td>
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<td>0.73(1)</td>
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<td>8.0(1)</td>
</tr>
<tr>
<td></td>
<td>14</td>
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<td>0.74(1)</td>
<td>4.932(3)</td>
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</tr>
<tr>
<td></td>
<td>22</td>
<td></td>
<td>1.3422(1)</td>
<td>0.73(1)</td>
<td>4.945(2)</td>
<td>8.0(1)</td>
</tr>
</tbody>
</table>

Figure 1 illustrates our results for the critical ordering operator distribution at the estimated critical points for $\zeta=10$, $\varepsilon_*=\infty$ and a range of linear system sizes. Similar results were obtained for the other cases studied. The curves for larger system sizes have been vertically displaced for visual clarity. As seen previously,2–3 there are systematic deviations from the universal Ising-class limiting distribution for small system sizes, esp. for $L^*=12$ and 15, but even for $L^*=18$, at values of the ordering operator $x\ll 1$. The slightly better matching of the data for $L^*=18$ to the Ising distribution in the range $x \equiv 1$ relative to the data for $L^*=22$ is a reflection of better statistical sampling for larger systems. However, it should be pointed out that the systematic deviations from the Ising distribution of the $L^* \approx 18$ data for $x \ll 1$ are not a consequence of inadequate sampling, but a finite-size effect. The low critical density for the RPM results in an insufficient number of particles at low densities for smaller system sizes. The quality of the fit for the larger system sizes in the present study is significantly better than in previous studies (Fig. 3 in CLW2; Fig. 5 in YdP3 and Fig. 7 in OP3). This is a consequence of the much longer simulation runs in the present work.

While not conclusive, the good matching of our data to the limiting Ising-class distribution is consistent with Ising-type criticality for this model. Since no pressure mixing contributions were included in the analysis, any such contributions are likely to be small. These observations are particularly encouraging in light of the recent results of Ref. 8 that found that for a model with long-range interactions, it became increasingly difficult to match the ordering parameter distributions to the Ising-class distributions for larger system sizes.

Figure 2 shows the dependence of the effective reduced critical temperature, $T^*_c$, and density, $\rho^*_c$, on the inverse lattice discretization parameter squared, $1/\zeta^2$, for $\varepsilon_*=\infty$ and a fixed linear system size, $L^*=18$. Both critical temperature and critical density decrease with increasing $\zeta$, but it is not clear a priori what the appropriate scaling exponent should be. The points for $\zeta=5$ do not follow the trend of higher $\zeta$ and were excluded from the extrapolation. The best linear fit for the three largest $\zeta$ values was obtained with $1/\zeta^2$. At this point, there is no theoretical justification for this choice of scaling exponent. By extrapolating to $\zeta \to \infty$ we obtain that for this particular system size and boundary condition, the magnitude of the finite-$\zeta$ lattice discretization effect is $\delta T^*_c(\zeta,L^*)=T^*_c(\infty,18)-T^*_c(10,18)=-0.0005(1)$ and $\delta \rho^*_c(\zeta,L^*)=\rho^*_c(\infty,18)-\rho^*_c(10,18)=-0.03(1)$. Statistical uncertainty estimates do not include the uncertainty in the
The critical parameter extrapolation is sensitive to the value of this scaling exponent.

Figure 3 illustrates the dependence of the effective reduced critical temperature, $T^*_c$, on the scaling variable $(L^*)^{-(\theta+1)/\nu}$ for the systems with $\xi=10$ (filled points), along with previously reported results in the continuum (open points,2-4). We used values appropriate for the Ising universality class for the correction-to-scaling exponent, $\theta=0.52$, and for the correlation length exponent, $\nu=0.630$, both from Ref. 19. The points for the largest three system sizes fall on approximately straight lines, but the dependence of the effective critical temperature on system size is quite different for $\epsilon_n=\infty$ (filled circles) and $\epsilon_n=1$ (filled triangles). The dashed lines through our points are drawn with a common intercept to facilitate extrapolations to $L^*\rightarrow\infty$. The common intercept is estimated as $T^*_c(\xi=10;L\rightarrow\infty) = 0.0494(2)$. This uncertainty estimate does not include contributions from uncertainties in the critical exponents. By subtracting the finite-$\xi$ lattice discretization effect discussed in the previous paragraph (assuming that the effect is independent of $L^*$) we arrive at an estimate of $T^*_c(\xi\rightarrow\infty;L\rightarrow\infty) = 0.0489(3)$. This estimate is indicated by the arrow in Fig. 3 and is in good agreement with the results of YdP and CLW.

The previous simulation study from our group (OP; open triangles) was performed with $\epsilon_n=1$ and explored relatively small systems. The points from OP are parallel, but below, results for $\epsilon_n=1$ in the present study. The difference between the present study and OP is somewhat less than would be expected on the basis of finite-$\xi$ effect illustrated in Fig. 2. Results from CLW (open squares) also follow a line parallel to the results for $\epsilon_n=1$ of the present study. The results are displaced from our present results by amounts matching the finite-$\xi$ lattice discretization effect illustrated in Fig. 2. Results from YdP (open circles) are also parallel and below the results for $\epsilon_n=\infty$ of the present study, displaced by an amount roughly equal to the finite-$\xi$ lattice discretization effect. From the good agreement of our present results corrected for finite-$\xi$ effects with the calculations of CLW and YdP we conclude that the critical temperature of the continuum-space RPM in the thermodynamic limit is now established quite accurately.

The effective reduced critical density, $\rho^*_c$, is plotted as a function of the scaling variable $(L^*)^{-(1-\alpha)/\nu}$ (with $\alpha=0.1091^{19}$) in Fig. 4. Statistical uncertainties are noticeably greater for the critical density than for the critical temperature. Drawing straight lines with a common intercept through our results for $\epsilon_n=\infty$ and $\epsilon_n=1$ is a bit more problematic. Extrapolation was done jointly for six data points corresponding to the larger system sizes for the two boundary conditions. It should be noted here that the error bars of the points for $\epsilon_n=\infty$ (circles) and $\epsilon_n=1$ (triangles) were calculated from an identical number of runs of the same length. The greater uncertainties for vacuum boundary conditions must, therefore, be a reflection of inherently greater density fluctuations. The common extrapolation of the data in Fig. 4, results in the estimate $\rho^*_c(\xi=10;L\rightarrow\infty) = 0.079(2)$. By assuming once more that the finite-$\xi$ lattice discretization effect is independent of $L^*$, we obtain an estimate of $\rho^*_c(\xi\rightarrow\infty;L\rightarrow\infty) = 0.076(3)$, indicated by the arrow in Fig. 4.

Comparison of the critical density with previous studies is complicated by the large statistical uncertainties and scatter in the data. Comparison of statistical uncertainties across different studies should be performed with caution, as it is not clear that they have been computed in the same fashion. In particular, YdP report larger uncertainties than other studies, even though the internal scatter of their data is much less than would be expected based on these uncertainties. OP and CLW do not report estimates for the statistical uncertainties of the critical densities. The results of OP are over a limited range of $L^*$ and cannot be reliably extrapolated to $L^*\rightarrow\infty$. The results of YdP have a much stronger dependence on $L^*$ than either our present study or CLW. At this point, there does not seem to be a convincing explanation for these apparent discrepancies. Determination of the critical density from finite-size scaling is quite sensitive to the quality of the underlying histogram data. Given the quality of the fits observed for higher $L^*$ in Fig. 1, we are inclined to recommend the values resulting from the common extrapolation of our data, corrected for lattice discretization effects.

IV. CONCLUSIONS

In summary, we have demonstrated that excellent agreement is obtained between the Ising-class universal limiting distribution of the ordering operator in the RPM for sufficiently large systems. No pressure mixing is necessary in the finite-size scaling analysis. The effective critical temperature and density depend weakly on system size for $\epsilon_n=\infty$, but much more strongly for $\epsilon_n=1$. There have been suggestions in the literature that the “correct” boundary condition for Ewald summation at infinite distance in ionic systems is $\epsilon_n=\infty$.20 On one hand, it is shown in the present study that the use of $\epsilon_n=1$ does not lead to “incorrect” results, in the sense that the extrapolated values as $L\rightarrow\infty$ match those of $\epsilon_n=\infty$. On the other hand, it is definitely desirable to reduce
Both critical temperature and critical density decrease on increasing the lattice discretization parameter $\xi$. Data from the present study suggest that the deviations of the critical parameters scale as $1/\xi^2$, but there is at present no theoretical justification for this relationship. The extrapolated properties for the continuum limit, $\xi \rightarrow \infty$, are sensitive to the choice of scaling exponent. The difference between critical parameters for $\xi = 10$ and $\xi \rightarrow \infty$ was found to be $\approx 1\%$ for the temperature and $\approx 4\%$ for the density.

A recently developed methodology\textsuperscript{21} allows for unambiguous determination of the universality class in asymmetric fluids but requires significantly greater computational effort than the Wilding and Bruce finite-size scaling analysis we used here. In an independent study,\textsuperscript{10} the methods of Ref. 21 have been extended to study the universality class of the finely discretized RPM model with $\xi = 5$. The work of Ref. 10 finds strong evidence for Ising universality class. Agreement between the present results and those of Ref. 10 is quite satisfactory with respect to the critical temperature, but less so for the critical density. From Ref. 21, it is established that our present analysis method is likely to slightly overestimate the true critical density for asymmetric systems. However, the computational cost of Ref. 10 is significantly higher than that of the present study and as a consequence, that study was restricted to a single, relatively low, value of $\xi$.

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