Lattice discretization effects on the critical parameters of model nonpolar and polar fluids

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The effects of the ratio of particle diameter to lattice spacing, $\xi$, on critical parameters for both polar and nonpolar fluids have been examined in detail. Nonpolar systems studied have short range Buckingham exponential-6 interactions, while polar systems have long range Coulombic forces treated with Ewald summation. Monte Carlo simulations in the grand canonical ensemble combined with histogram reweighting and mixed field finite size scaling have been used. Both critical temperature and critical density decrease on increasing $\xi$. The critical temperature scales as $1/\xi^a$ where the exponent was obtained as $a = (6 \pm 2)$ for the nonpolar and $a = (2 \pm 0.5)$ for the polar fluids. The large difference in $a$ values between nonpolar and polar fluids results from a much weaker effect of discretization on the critical parameters of nonpolar fluids. © 2003 American Institute of Physics. [DOI: 10.1063/1.1562613]

I. INTRODUCTION

Lattice models have been used extensively in polymer physics (e.g., the bond fluctuation model\textsuperscript{1,2}), protein,\textsuperscript{3-5} thin film simulations\textsuperscript{6} and for studies of phase transitions and critical phenomena.\textsuperscript{7-9} The greatest advantage of these models is computational efficiency with respect to time and length scales. Through the study of larger systems, finite-size effects near critical points that result from the divergence of the correlation length can be greatly diminished. The fine-lattice discretization method was first introduced in Ref. 10 for ionic systems and in Ref. 11 for nonpolar systems. It is well understood that the structural and thermodynamical properties of fluids approach their continuous counterparts as finer lattice sizes are used. The key concept is schematically presented in Fig. 1. A two dimensional hard-core potential has been used for simplicity, though all our simulations are in three dimensional space and some use soft-core interactions. The cell size and the single particle diameter are represented by $l$ and $\sigma$, respectively. The ratio of $\sigma/l$ is defined as the discretization parameter $\xi$ which controls how closely the lattice system approaches the continuum behavior. As shown in Fig. 1, the number of excluded sites for other particles of the same collision diameter for each specific $\xi$, are all the sites confined in a circle of radius $\sigma$. The positions of particles are allowed to be on a cubic grid with spacing $l$. Simulations of finely discretized lattice models are computationally faster by a factor of 5–100 than the corresponding continuous models due to the use of lookup tables for the interaction energies.\textsuperscript{10-12}

The present study was motivated by recent work of Panagiotopoulos\textsuperscript{13} on a cubic lattice for a simple electrolyte model known as the restricted primitive model (RPM). In Ref. 13, both critical temperature and critical density were found to decrease on increasing the lattice discretization parameter $\xi$. The deviations of the critical parameters from the continuum ($\xi \to \infty$) values were found to scale as $1/\xi^a$. There is at present no theoretical justification for this scaling exponent. As our long-term motivation is to build fine-lattice models reproducing properties of real systems, it is desirable to understand the influence of intermolecular potentials on the approach to the continuum limit. In this work we present this effect for simple monatomic and diatomic nonpolar systems with soft-core short range interactions. We also investigate this effect on more complicated polar systems such as two bead and three bead chains with hard-core interactions.

The outline of this paper is as follows: Section II is devoted to a brief description of computational methods used to obtain the critical parameters. Section III presents the critical temperature and critical density as functions of the discretization lattice parameter for a range of fluids from simple nonpolar to three beads polar chains. Finally, conclusions are given in Sec. IV.

II. SIMULATION METHODS

We used grand canonical Monte Carlo (GCMC) simulations in cubic boxes of dimension $L^3$, under periodic boundary conditions, along with multihistogram reweighting. In GCMC, the temperature, $T$, chemical potential, $\mu$, and volume, $L^3$, are fixed parameters which define the state point being simulated. New microstates were generated by a mixture of 50% replacement and 50% addition/annihilation with standard Metropolis acceptance/rejection criteria.\textsuperscript{14} The acceptance ratio of the unbiased insertion/removal steps was 10% near the critical point. All thermodynamic states of interest are achieved by combining a number of histograms according to the histogram reweighting method of Ferren-
berg and Swendsen.\textsuperscript{15,16} The histogram reweighting is very useful near the critical region, where a single simulation covers a wide range of associated parameter space due to the large fluctuations of energy and number of particles. Finite size scaling concepts of Wilding \textit{et al}.\textsuperscript{17–19} were used for obtaining the critical temperature and critical density. A number of simulations are performed near the critical point and the resulting histograms are combined to obtain self-consistent estimates of the distribution function $P_m^b(N,E)$.

Finite-size scaling theory accounts for the asymmetry of fluid phase near the critical point by defining an ordering operator as a combination of number of particles and energy fields:

$$M = N - sE,$$

where $s$ is the field mixing parameter that controls the strength of the coupling between number of particles and energy fields:

$$x = a(L,r).(M - M_c)$$

assumes a universal shape (Ising-type criticality) for the systems with short range interactions. The nonuniversal parameter $a(L,r)$ is chosen to result in unit variance for the $P_L(x)$ distribution, where $r$ is the nonuniversal (system-specific) quantity controlling the degree of field mixing. The distribution is reweighted to find the chemical potential and temperature that result in the best match of the observed data and the universal $P_L(x)$ for the three dimensional Ising distribution. The critical temperature and critical density obtained by this technique are system size dependent and asymptotically vary as $1/L^{2(\theta+1)/\nu}$ and $1/L^{-(1-\alpha)/\nu}$, where $\theta$, $\alpha$ and $\nu$ are Ising universality class exponents. An example of the matching of some of our data to the universal curve is shown in Fig. 2. Additional details of the computational approach can be found in previous publications by our group.\textsuperscript{20–22}

\section*{III. RESULTS AND DISCUSSION}

\subsection*{A. Nonpolar model}

Two variants are considered for the nonpolar model, “monomer” and “dimer” with one and two Buckingham exponential-6 sites, respectively. The exponential-6 potential\textsuperscript{23} (abbreviated as (“Exp-6”’) from this point on) describes the pairwise additive repulsion/dispersion interaction between two nonoverlapping sites $i$ and $j$ as:

\begin{equation}
U_{\text{Exp-6}}(ij) = \begin{cases} 
\frac{6}{\alpha - 6} \exp \left[ -\alpha \frac{r_{ij}}{r_m} - 1 \right] - \frac{\alpha - 6}{\alpha - 6} \left( \frac{r_m}{r_{ij}} \right)^6 & \text{if } r \geq r_{\text{max}} \\
+\infty & \text{if } r < r_{\text{max}}
\end{cases}
\end{equation}
where $\epsilon, r_m$ and $\alpha$ are the model parameters. Parameter $r_m$ is the distance at which the potential has a minimum. The cutoff distance $r_{\text{max}}$ is the smallest positive value for which $du(r)/dr = 0$ and is obtained numerically by iterative solution of Eq. (3). The reason a cutoff distance is required is that at very short distances, the original Exp-6 potential becomes negative. While canonical ensemble Monte Carlo or molecular dynamic simulations never sample the unphysical attractive region, this is not the case on trial insertions in grand canonical simulations. The characteristic size parameter $\sigma$ for this potential is defined as the value of $r$ for which $U(r) = 0$ and is obtained numerically. All quantities are non-dimensionalized by using $\sigma$ and $\epsilon$ as the characteristic length and energy scales for the nonpolar model. For example, $T_\ast$, represents the temperature divided by $\epsilon/k_B$, where $k_B$ is the Boltzmann’s constant; $\rho_\ast$ represents the density multiplied by $\sigma^3$. An $\alpha$ value of 14 has been used for all the models with Exp-6 interactions. At the beginning of the runs the translationally invariant intermolecular potential is stored in an array of dimension $(L/k_\ast)^3$, which accelerated the calculation of the energies during the runs by a factor of 10. In addition to the Exp-6 interactions in the central simulation box, long range corrections according to the method of Theodorou and Suter were applied. To speed up the calculations, all possible orientations for the models studied (except the monomer which only has one possible orientation) are generated at the beginning of the simulation and stored in a “reservoir.” Once the simulation gets started, a random configuration is selected from the reservoir to be added to the system. The number of configurations (NC) for the tethered dimers increases with the degree of lattice discretization. For example, there are 6 distinct configurations for $\zeta = 2$ and 318 for $\zeta = 10$, respectively, for dimer systems restricted to remain at a reduced bond lengths, $l_\ast = L/\sigma$, between 1 and 1.2. However, in order to have the maximum consistency between the systems with different lattice discretization parameters, we selected 6 identical configurations for all the systems with different degrees of discretization.

### Table I. Critical parameters for the “Exp-6 monomer” model. Statistical uncertainties in parentheses refer to the last decimal place shown.

<table>
<thead>
<tr>
<th>$L_\ast$</th>
<th>$\zeta$</th>
<th>$-\mu_\ast$</th>
<th>$-s$</th>
<th>$T_\ast$</th>
<th>$\rho_\ast$</th>
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<td>4.149(2)</td>
<td>0.01(2)</td>
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<td>1.301(5)</td>
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<tr>
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<td>3.488(4)</td>
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<td>1.272(3)</td>
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<tr>
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<td>0.01(1)</td>
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<td>15</td>
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<table>
<thead>
<tr>
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<th>$\zeta$</th>
<th>$-\mu_\ast$</th>
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<tr>
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### Table II. Critical parameters for the “Exp-6 dimer” model. Statistical uncertainties in parentheses refer to the last decimal place shown.

We summarize our results for the critical temperature and critical density for specific lattice discretization parameters in Tables I and II. Statistical uncertainties were estimated from independent runs at identical conditions with different random number seeds (algorithm ran2 in Ref. 25) and are reported in parentheses in units of the last decimal point. All the nonpolar models with short range interactions show excellent matching to Ising-type criticality. The very small values of the field mixing parameter, $s$, confirm the symmetry of the nonpolar systems. Figures 3 and 4 show the dependence of the effective reduced critical temperature, $T_\ast$, on the inverse lattice discretization parameter for monomer and dimer models, respectively. The best fit was obtained by having $1/\zeta$ scaled to the 6th and 7th power, respectively. Power-law least squares fitting taking into account the statistical uncertainties was used to obtain the best exponent. The points for $\zeta < 5$ do not follow the trend of higher values of $\zeta$ and were excluded from the extrapolation. Statistical uncertainties for the critical temperatures are comparable to symbol size. As shown in Table I, the critical temperatures and critical densities for values of $\zeta = 10$ and $\zeta = 15$ fall within each other’s statistical uncertainties for the monomer model with $L_\ast = 7$. These results and the high value of the

![Figure 3](image-url)

FIG. 3. Reduced critical temperature, $T_\ast$, as a function of $1/\zeta$ for the “Exp-6 monomer” model with $L_\ast = 7$ (filled square), $L_\ast = 10$ (filled star) and $L_\ast = 12$ (filled circle). The dashed line shows the power-law least squares fitting to the data.
have diameters of 2 as "trimer." For this model, the center bead and side beads model that we are investigating is a three-bead chain denoted of the models is presented in Fig. 5.

The critical densities decrease on increasing $\zeta$ values for both monomer and dimer models. No specific trend has been observed for the critical densities with different values of $\zeta$ for the two nonpolar models studied, partly as a result of the higher statistical uncertainties associated with the calculation for the two nonpolar models studied, partly as a result of the same orientations as for the Exp-6 dimer model, but in this case all the possible orientations are used.

The Coulombic interaction between two charged sites $i$ and $j$ is defined as:

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

where $q_i$ and $q_j$ are charges of sites $i$ and $j$ that are separated by distance $r_{ij}$ and $D$ represents the dielectric constant of the structureless medium. $\sigma$ is the hard-core diameter for the monatomic model. For both models, reduced temperature and density are defined via $T^* = k T / \sigma^2$ and $\rho^* = N \sigma^3 / L^3$ where $N$ represents the total number of beads existing in the system. For the unlike collision diameter we used

$$\sigma_{ij} = (\sigma_{ii} + \sigma_{jj}) / 2.$$  

The Ewald summation was applied for polar systems with 518 Fourier-space wave vectors, $k = 5$ real-space damping parameter and conductive boundary condition at infinite distance, $e_r = \infty$. The translationally invariant intermolecular potential is stored in an array of size $(L^2 / \zeta^2)$, which accelerated the calculation of the energies by a factor of 100. For the dumbbell case study, the reservoir structural configurations have the same orientations as for the Exp-6 dimer model, but in this case all the possible orientations are used. In the first set of simulations ("fixed charge") each of the beads carry a unit of charge. In the second set of simulations ("fixed dipole"), all configurations have identical molecular dipole moments, so the charges on each bead vary somewhat. The structural parameters in the two sets of simulations are shown in Table III. Figure 6 shows the dependence of the effective reduced critical temperature, $T^*_c$, on the inverse lattice discretization parameter squared, $1 / \zeta^2$, for both sets of data. It is shown that the critical temperature values follow almost the same trend as for the restricted primitive model, except that some moderate odd–even effect can be observed. We postulate that the distinct number of configurations enforced by fine lattice structure for models with different values of $\zeta$ are responsible for this feature. Critical densities decrease on increasing $\zeta$ values with no particular trend. Comparable values for the critical temperature and critical density are available from Ref. 26 for $\zeta = 10$ with 318 configurations and reduced bond length, $l^* = l / \sigma$, of 1–1.2.

For the trimer case study, similar to the dumbbells, the reduced bond lengths ($l^* = l / \sigma$) between the center bead and the side beads are restricted to 1–1.2. The angle between the two center-side bonds was fixed to 180°. The center bead carries positive charge while the side beads carry negative charges. The charge of the center bead is always twice as large as that of the side beads. No intramolecular interaction

![FIG. 5. Schematic illustration of two polar models considered in this work. (a) The "dumbbell" model; (b) the "trimer" model.](image)
has been considered within the beads of a single molecule. All the configurations have the same quadrupole moments by having different charges assigned to either of the beads. The odd–even effect has to do with the distinct number of configurations for models with different \( z \) values. The narrow range of variations for the critical densities preclude us from being able to make a precise judgement about the effect of the lattice discretization parameter on this set of data. The good matching of our data to the Ising-class is an indication but not a proof of Ising-type criticality for the polar models studied.

**C. Polar+Exp-6 model**

The effect of lattice discretization parameter, \( z \), has been considered for this model, in which the potential contains both short- and long-range parts described in previous sections. The short range interactions influence the charge ordering in such a way that the critical temperature is approximately the same as for the dimer model. This model consists of a two bead chain with one Exp-6 site on each bead and a unit positive and a unit negative charge on each bead as well. All the configurations have reduced bond length between 1 and 1.2. As for the nonpolar systems only six identical configurations are used to have consistency between the different systems. Figure 7 shows the dependence of the effective reduced critical temperature, \( T_c^\star \), on the inverse lattice discretization parameter to the ninth, \( 1/\zeta^9 \), for this model. We interpret the slightly larger value of the exponent compared to the exponents obtained for nonpolar models as due to the fact that this model encompasses both short- and long-range interactions.

**IV. CONCLUSIONS**

In this work, we have addressed the issue of how to estimate the effect of the lattice discretization parameter, \( \zeta \), on critical parameters of fluids. Specifically, we have considered the Exp-6 soft-core model for nonpolar fluids. The data suggest that deviations of the critical temperatures scale as \( 1/\zeta^{2\pm1} \) and \( 1/\zeta^{2\pm2} \) for monomer and dimer models respectively. The same effect of \( z \) on critical temperatures for both Exp-6 model of this study and Lennard-Jones model of Panagiotopoulos in Ref. 11 can be observed for values of \( \zeta \).
Deviations of the critical temperatures are stronger by a factor of 5 for polar models (dipolar dumbbells) compared to the nonpolar fluids and scale as $1/\zeta^{2.0.5}$. The exponent found in the present study for polar fluids is essentially identical to the exponent found for the restricted primitive ionic model.\textsuperscript{13} The strong similarities found by Romero-Enrique \textit{et al.}\textsuperscript{28} between true ionic fluids and corresponding “tethered dimer” fluids are likely to be responsible for the agreement between the exponents for ionic and polar models.

For the model with both Coulombic and Exp-6 interactions, the critical temperatures scale as $1/\zeta^{2.0.5}$ for different integer values of $\zeta$. Within the narrow range of critical densities for different values of the discretization parameter, no particular trend has been dominant for the various models studied. The critical density values decrease as the $\zeta$ values increase for all the fluids considered in this paper, except the trimer model. The computational cost to estimate precisely the location of the critical density is prohibitively high with the methods of the present work.

Based on these observations, the lattice discretization parameter effect is more pronounced for polar fluids than the nonpolar fluids. This is contrary to the intuitive idea that the presence of the lattice influences primarily short range structures. However, the dipole–dipole interactions are dominant forces in the polar fluids (dumbbell model) as found by Romero-Enrique \textit{et al.}\textsuperscript{28} It is possible that the dipole interactions among the neutral clusters at close contact coupled with existing long range forces are sensitive to the degree of lattice discretization. For the quadrupolar interactions (trimer model) the sensitivity is much less. In the nonpolar fluids on the other hand, the interactions are purely driven by homogeneous short range contacts, which are influenced by the lattice discretization to a minor extent. The concept of the repulsive part of the intermolecular potential being responsible for these effects is open to further theoretical investigation.

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