

**Large differences in phase behavior of closely related lattice ionic
models**

Athanassios Z. Panagiotopoulos^{1,*}

Institute of Physical Science and Technology and Department of Chemical Engineering,

University of Maryland, College Park, MD 20742-2431

Sanat K. Kumar²

Department of Materials Science and Engineering, Pennsylvania State University, University

Park, PA 16802.

(June 9, 1999)

Abstract

A series of closely related lattice restricted primitive ionic models were studied by grand canonical Monte Carlo simulations. The ratio of ionic diameter to lattice spacing, ξ , was assigned integer values from 1 to 5. Our results for the $\xi = 1$ model provide support for the suggestion of Dickman and Stell that there is a tricritical point involving transitions between a disordered and an antiferromagnetic phase. The $\xi = 2$ model also has an extensive disordered-antiferromagnetic phase coexistence region. For $\xi = 3$ to 5 the phase behavior is similar to that of the continuous-space restricted primitive model, with a region of normal vapor-liquid coexistence at low temperatures. Our findings suggest that there can be large qualitative differences in the phase behavior of closely related lattice models, but that the appropriate continuous-space limit can be approached by fine discretization of the lattice.

Lattice models are frequently used in modeling of fluids even though the physical systems they are meant to represent do not have translational order. The assumption is made that the effect of the lattice structure on the properties of interest is small. This assumption is often justified, for example, in the case of conformational properties of polymers at the limit of long chain lengths. However, in other cases, the effects of the lattice approximation are unknown.

The phase behavior and criticality of the restricted primitive model (RPM) and related models has been the subject of numerous theoretical [3,4] and simulation [7–10] studies. Recent simulation studies [9,10] yield a vapor-liquid critical point at a reduced temperature $T_c = 0.049$ and density $\rho_c = 0.07$ to 0.08 . While there is reasonable agreement between these two most recent studies, there is long history of roaming values for the critical parameters of the continuous-space RPM. An independent confirmation of the validity of the latest estimates is desirable.

The present study focuses on a class of lattice-based RPM models that can systematically approach the continuous-space model by increasing the lattice resolution. The effects of core size and shape on the observed phase transitions of the RPM yield information of -hopefully- general applicability to lattice models with long-range interactions. A secondary goal is to confirm the location of the critical point of the RPM by taking advantage of the greater simulation volumes and sampling times that are possible with lattice models.

The simplest possible lattice RPM model consists of an equal number, N_{\pm} of positive and negative ions on a simple cubic lattice of volume V . Each site has a maximum occupancy of one ion. In the terminology of the present paper, this corresponds to ratio of ionic diameter, σ , to lattice spacing, l , $\xi = \sigma/l = 1$. Coulombic interactions between ions are given by

$U(r) = \pm 1/r$, for like and unlike ions, where r is the distance between the centers of the lattice sites occupied by each ion. The reduced density ρ is defined as $\rho = 2N_{\pm}\sigma^3/V$. This model has been studied by Dickman and Stell [5], who found that there is a first-order transition between a disordered and an antiferromagnetically-ordered phase at temperatures below a tricritical point at $T_c \approx 0.12$. The critical density is $\rho \approx 0.4$. Above T_c , there is a Néel line of second-order transitions between a disordered and an antiferromagnetic phase. Clearly, the behavior of this model does not match at all the behavior of the continuous-space RPM! There is a tricritical (rather than critical) point at more than twice as high a temperature, and there is no vapor-liquid transition.

The key idea in this work is to start from the simple $\xi = 1$ model and systematically refine the spacing lattice so that the model can approach the continuous-space analog to an arbitrary degree. The models for $\xi = 1, 2$ and 3 are schematically illustrated in Fig. 1. A two-dimensional projection is used for simplicity in the figure, even though all our calculations were for three-dimensional systems. For $\xi = 1$, a single lattice site is excluded by each ion. For $\xi = 2$ the total number of excluded sites is 27 (a cube of size $3 \times 3 \times 3$) while for higher ξ the shape of the excluded volume of each ion is no longer a perfect cube. For higher ξ values the excluded volume of each ion takes on an increasingly spherical shape. The number of excluded sites is 93 for $\xi = 3$, 251 for $\xi = 4$ and 485 for $\xi = 5$.

An extremely fast table lookup algorithm equivalent to an Ewald sum with a large number of Fourier-space wavevectors was developed to compute the infinite-range ionic interactions. The algorithm is analogous to that used by Luitjen [6] for investigating lattice systems with long-range interactions. It involves precomputing the Coulomb interaction between any two sites on the lattice, including all periodic images of the sites to an infinite distance. The

summation is performed with the standard Ewald sum with vacuum boundary conditions, 518 Fourier-space wavevectors and real-space damping parameter $\kappa = 5$. The Ewald sum is only performed *once*, at the beginning of the simulation, and the translationally-invariant contributions stored in an array. A reduced volume of $V = 12^3 = 864$ was used for all the phase diagram calculations, except near the critical points of the $\xi = 3$ to 5 systems, for which volumes of 15^3 , 19^3 and 24^3 were also used. For the maximum system size used in this study, $V = 24^3$ and $\xi = 5$, the number of stored contributions is $24 \times 5^3 = 1.73 \times 10^6$, occupying 13.8 Mb of memory, well within the capacity of modern workstations. The relative acceleration for the lattice calculations versus our earlier off-lattice calculations for the RPM was a factor of at least 100.

Histogram-reweighting grand canonical Monte Carlo techniques [11,12] were used to obtain the phase behavior of the models. Only ion pair additions and removals were attempted. To enhance acceptance of the insertion/removal steps for these strongly interacting coulombic systems, a distance-biasing algorithm [8] was used. We used the Boltzman factor of the interaction energy of a pair at a given separation as the distance-biasing factor.

Our results for the first-order transition curves for the $\xi = 1$ and $\xi = 2$ cases are shown in Fig. 2 as open circles and triangles, respectively. In both cases, coexistence is between a low-density disordered phase and an antiferromagnetically ordered high-density phase. The $\xi = 1$ results are quite similar to those of Dickman and Stell [5], with the exception that our calculations extend nearer to the tricritical point, for which our estimate is $T_c = 0.15 \pm 0.01$, $\rho_c = 0.48 \pm 0.02$. The filled circles and dashed line indicate a preliminary estimate of the Néel line for the $\xi = 1$ model, obtained by locating a peak in the constant-volume heat capacity at three temperatures. The line is nearly vertical, while in the results of Dickman

and Stell the line has a lower slope. Detailed finite-size scaling analysis will be required for resolution of the exact location of the Néel line and will be the subject of subsequent studies by our group.

The $\xi = 2$ model presented special difficulties. The horizontal lines connecting triangles on the low-density side of the figure indicate a range of densities over which hysteresis was observed. A run initiated at low density would remain in an apparently stable disordered low-density state even after 2×10^8 Monte Carlo pair addition/removal steps over a certain range of chemical potentials. On further increase of the chemical potential, it would slowly convert to a nearly-perfect antiferromagnetic high-density state. Conversely, a run started from a high-density ordered state would remain stable over a range of chemical potentials, thus resulting in an extensive hysteresis loop. Hysteresis loops are expected whenever first-order transitions are present. However, for the other cases studied in this paper, we were able to obtain the equilibrium coexistence curves by linking states on opposite sides of the coexistence curve through simulations above a critical (or tricritical in the case $\xi = 1$) point. In the case $\xi = 2$, the critical point occurs at very high densities - our best estimate is $T_c \approx 0.18 \pm 0.01$ and $\rho_c \approx 0.96 \pm 0.03$. We were unable to obtain adequately sampled states at these very high densities for constructing an equilibrium free-energy surface. The first-order transition density, however, is by necessity bounded from above and below by the densities at the extremes of the hysteresis loop shown in Fig. 2. From the figure, it is clear that the $\xi = 2$ model is qualitatively similar to the one for $\xi = 1$, except for a shift of the transition to higher densities. The physical reason for this shift is also clear: For the $\xi = 2$ model, displacement of an ordered structure by a single lattice spacing along any of the principal directions results in a new structure *incommensurate* with the previous one.

This is not the case for the $\xi = 1$ model, for which displacement by one lattice spacing does not change the overall structure, except for interchange of positive and negative ions.

Our results for $\xi = 3, 4$ and 5 are shown in Fig. 3, together with previous calculations for the continuous-space RPM [10]. Critical points for the lattice RPM models were estimated from finite-size scaling [14] assuming that the systems belong to the Ising universality class. In all cases, our results for the matching of the critical distribution to the universal curve and for the system-size dependence of the critical parameters are highly consistent with the hypothesis of Ising criticality. The use of larger system sizes than in previous continuous-space studies provides a more stringent test of this assumption. Extrapolated critical points for infinite system size and the subcritical vapor-liquid coexistence curves are shown on Fig. 3. Clearly, the behavior of the lattice RPM models for the finely discretized lattices is quite similar to the continuous-space RPM. Already at $\xi = 4$, the difference in the critical temperature is less than 5 % and the critical density is higher by an amount less than the combined simulation uncertainties. While no significant change in the phase coexistence curve or critical point was observed between $\xi = 4$ and $\xi = 5$, this is likely to be an effect of the relatively small value of our maximum ξ . At very high ξ values the "lattice" and continuous-space RPM models are identical by construction.

The solid-liquid coexistence of the continuous-space restricted primitive model has been studied by Smit *et al.* [13]. Liquid-solid phase coexistence was observed above the triple point located at approximately $T=0.025$. The low-density solid phase formed has a body-centered cubic structure. Using these results for guidance, we expect that the $\xi = 3, 4$ and 5 models will exhibit a transitions to an ordered (solid) phase over the temperature range of Fig. 2 at sufficiently high densities. These liquid-solid transitions can be considered a

natural continuation of the order-disorder transitions observed for $\xi = 1$ and 2, now shifted to even lower temperatures. In essence, the absence of liquid-vapor transitions for the $\xi = 1$ and 2 cases is simply a manifestation of the tendency of the low- ξ models to solidify before forming a "proper" liquid. This situation has been seen previously in models with extremely short-range interactions [15] but also in lattice models with weak long-range interactions [16], but not, to the best of our knowledge in systems with strong long-range interactions.

In summary, we have computed the phase diagrams of a series of related lattice restricted primitive models. For the coarsely discretized models, order-disorder transitions occur at sufficiently high temperatures to obstruct the normal vapor-liquid critical point. The phase behavior of finely discretized models approaches that of the continuous-space analog quite rapidly. However, even finely discretized lattice models retain a large computational advantage over their continuous-space counterparts. This opens up the possibility of detailed studies of phase and aggregation behavior of ionic solutions by simulation.

Funding for this research was provided by the Department of Energy [DE-FG02-98ER14858]. We thank Michael Fisher and Gerassimos Orkoulas for helpful discussions and comments on the manuscript and George Stell for extensive correspondence and for providing reprints and copies of manuscripts prior to publication.

REFERENCES

- [1] e-mail address: thanos@ipst.umd.edu.
- [2] e-mail address: kumar@plmsc.psu.edu.
- [3] G. Stell, K. C. Wu and B. Larsen, Phys. Rev. Lett. **37**, 1369 (1976); Y. Zhou, S. Yeh and G. Stell, J. Chem. Phys. **102**, 5785 (1995);
- [4] M. E. Fisher and Y. Levin, Y., Phys. Rev. Lett. **71**, 3826 (1993); B. J. Lee and M. E. Fisher, Phys. Rev. Lett. **76**, 2906 (1996); D. M. Zuckerman, M. E. Fisher and B. P. Lee, Phys. Rev. E **56**, 6569 (1997).
- [5] G. Stell, chapter in *New Approaches to Problems in Liquid State Theory*, C. Caccamo, J.-P. Hansen and G. Stell (eds.), NATO ASI Series, Kluwer Academic Publishers, Dordrecht (1999). Figure 2 provides Monte Carlo results of Dickman and Stell for the $\xi=1$ model studied here.
- [6] E. Luijten and K. Binder, Phys. Rev. E **58**, R4060 (1998).
- [7] Valleau, J.P., J. Chem. Phys. **95**, 584 (1991).
- [8] G. Orkoulas and A.Z. Panagiotopoulos, J. Chem. Phys. **101**, 1452 (1994).
- [9] J. M. Caillol, D. Levesque and J. J. Weis, Phys. Rev. Lett. **77**, 4039 (1996); J. Chem. Phys. **107**, 1565 (1997).
- [10] G. Orkoulas and A. Z. Panagiotopoulos, J. Chem. Phys. **110**, 1581 (1999).
- [11] Ferrenberg, A.M.; Swendsen, R.H., Phys. Rev. Lett. **61**, 2635 (1988).
- [12] Ferrenberg, A.M. and R.H. Swendsen, Phys. Rev. Lett. **63**, 1195 (1989).

- [13] Smit, B.; Esselink, K.; Frenkel, D., *Molec. Phys.* **87**, 159 (1996).
- [14] A.D. Bruce and N. B. Wilding, *Phys. Rev. Lett.* **68**, 193 (1992); N. B. Wilding and A. D. Bruce, *J. Phys.: Condens. Matter* **4**, 3087 (1992).
- [15] P. R. ten Wolde and D. Frenkel, *Science* **277**, 1975 (1997).
- [16] G. Stell, H. Narang and C. K. Hall, *Rhys. Rev. Lett.* **28**, 292 (1972); C. K. Hall and G. Stell, *Phys. Rev. A* **7**, 1679 (1973).

FIGURES

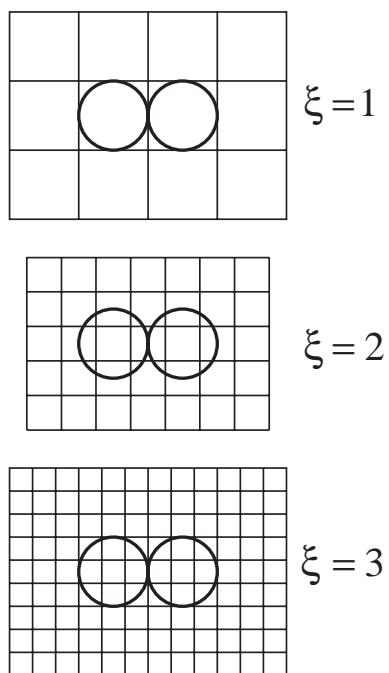


FIG. 1. Schematic diagram (in two dimensions) of the $\xi = 1, 2$ and 3 models. All models studied were in three dimensions. Two ions at contact are represented for each case.

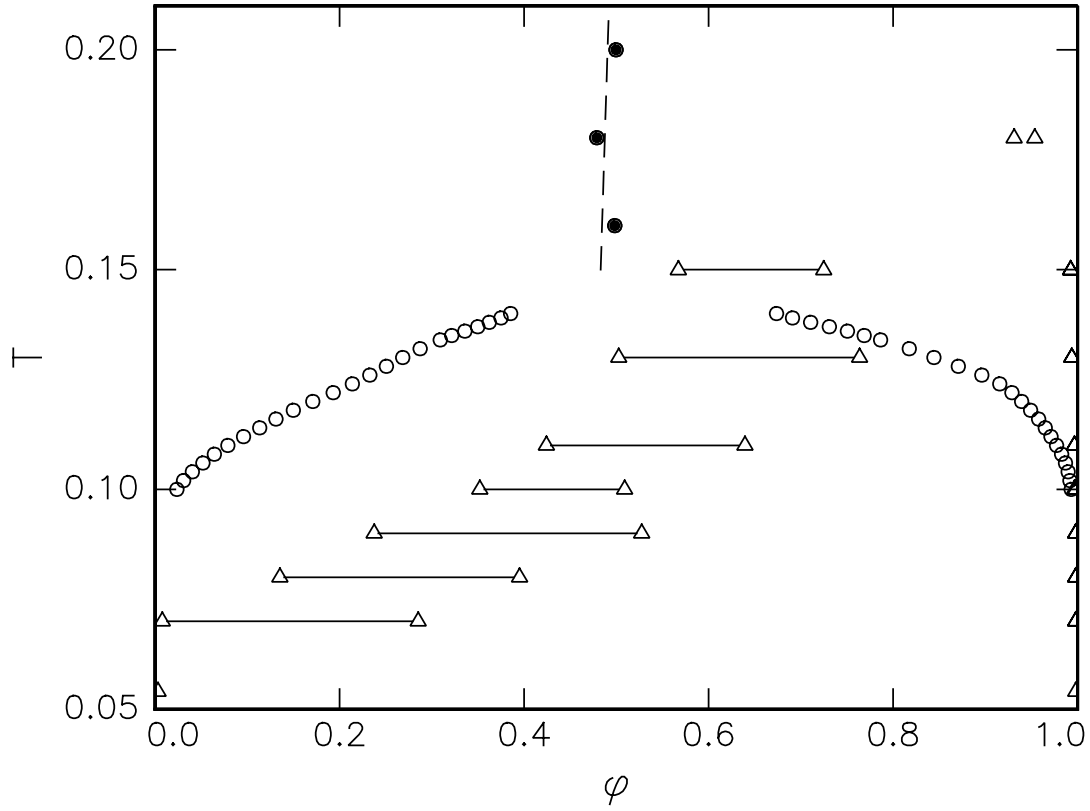


FIG. 2. Phase behavior of the $\xi = 1$ and $\xi = 2$ models. Open circles are for the first-order transition for $\xi = 1$, filled circles and dashed line are for the Néel line for $\xi = 1$. Open triangles are for the first-order transition for $\xi = 2$, with continuous line segments indicating the hysteresis region.

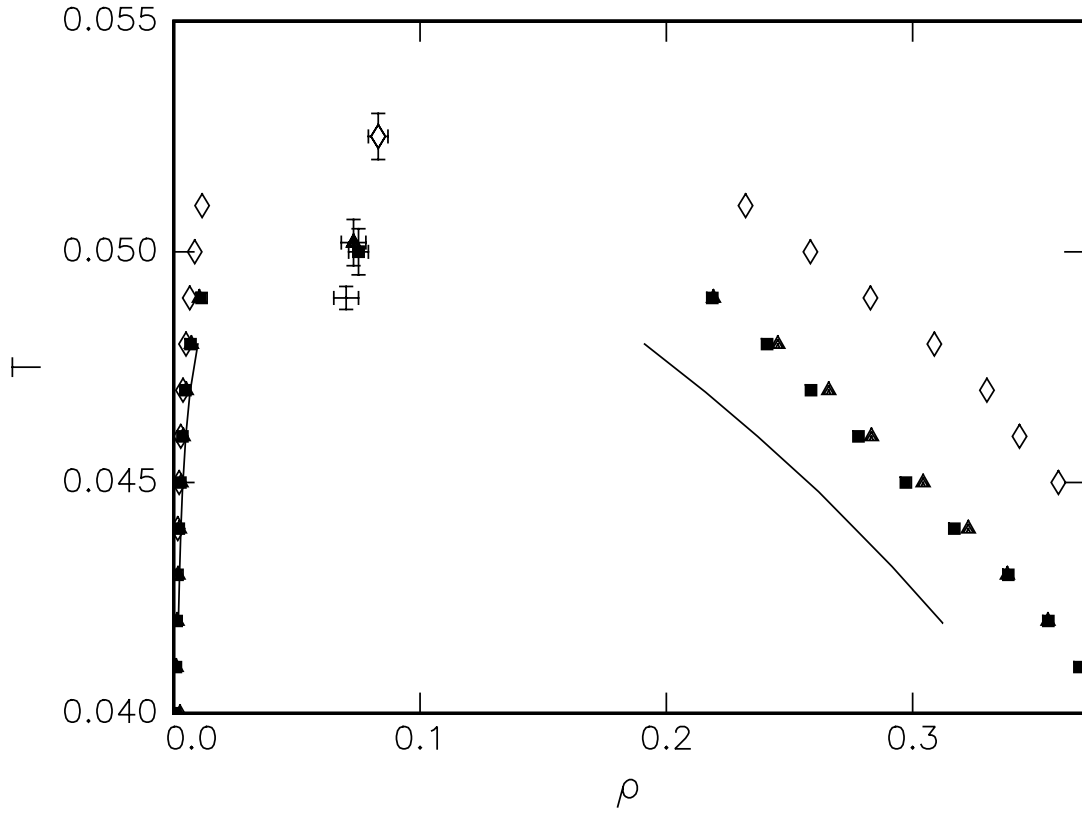


FIG. 3. Phase behavior of the $\xi = 3, 4$ and 5 models (diamonds, filled squares and filled triangles, respectively) and the continuous-space RPM (line).