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Simulations of phase transitions in ionic systems

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Abstract

A review of recent simulation work in the area of phase transitions in ionic systems is presented. The vapour–liquid transition for the restricted primitive model has been studied extensively in the past decade. The critical temperature is now known to excellent accuracy and the critical density to moderate accuracy. There is also strong simulation-based evidence that the model is in the Ising universality class. Discretized lattice versions of the model are reviewed. Other systems covered are size- and charge-asymmetric electrolytes, colloid–salt mixtures, realistic salt models and charged chains. Areas of future research needs are briefly discussed.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Electrolyte solutions and molten salts are examples of systems with strong Coulombic interactions. There are many other technologically relevant systems for which Coulombic interactions are important, including ionic liquids [1], charge-stabilized colloids and micellar solutions of ionic surfactants. Such systems are encountered in enhanced oil recovery, biochemical separations, energy production operations, electrochemical processes and many other applications. Proteins and nucleic acids carry charges along their backbones and are strongly influenced by the presence of ions in solution. Simple theoretical approaches (such as the standard DLVO theory [2] of interactions between charged surfaces) are increasingly in error in the presence of multivalent ions at biologically relevant concentrations [3]. Counterion valence has been shown experimentally to exert a large influence on the structure and dynamics of highly charged polyelectrolyte solutions [4]. Multivalent salts and charged proteins are potent agents for DNA aggregation and precipitation [5].

Understanding the structure and thermodynamics of such systems is far from complete. Detailed atomistic-level simulations, especially in the presence of explicit solvent, cannot reach the length and time scales accessible using simpler model systems. In addition, it is generally harder to decipher the connections between coarse aspects of the molecular architecture (e.g. ion

valence and size) and macroscopic properties when using atomistic models linked to specific real systems. In recent years, a significant body of simulation work has accumulated on phase transitions in ionic systems, dealing primarily with ‘primitive models’ that contain no explicit solvent. Even for these simplified models, simulations of Coulomb-dominated systems encounter significant sampling difficulties. For a simple 1:1 primitive model electrolyte at conditions near the liquid–vapour critical point, the thermal energy is only 1/20th of the energy of two ions at contact. As a result, the systems are strongly associating and hard to equilibrate. Early simulation work in the area produced results that (in retrospect) turned out to suffer from some inadequate sampling and equilibration problems, even though most of the qualitative features of the observed behaviour were correct.

Partly as a result of the increased availability of consistent simulation data, improved theories of systems dominated by Coulombic interactions have become available in the past few years [6–8]. Unlike earlier theoretical approaches [9, 10], these predict the correct trends with respect to size and valence asymmetries. Recent simulation studies have also contributed towards clarification of the character of ionic criticality, a question of great theoretical importance [11–13] and the subject of multiple experimental investigations (e.g. [14–16]). Recent reviews of theoretical tools for charged systems [17] and ionic criticality [18] are available.

The objective of the present brief review is to summarize simulation work on the phase and critical behaviour of systems dominated by Coulombic interactions. In section 2, work on the well-studied restricted primitive model of ionic solutions is reviewed. Other spherically symmetric ionic systems, including charge- and size-asymmetric primitive models, are the focus of section 3. Section 4 is devoted to charged chains, networks and colloid–salt mixtures. Finally, section 5 touches upon unresolved questions and research needs.

2. The restricted primitive model

The simplest and best studied system dominated by Coulombic interactions is the ‘restricted primitive model’ (RPM) consisting of charged hard spheres of equal diameter, σ , in a uniform continuum of dielectric constant ε . Half of the spheres carry a positive and half a negative charge of identical magnitude, q . The energy of interaction between two particles is

$$U_{ij} = \begin{cases} +\infty & r_{ij} < \sigma \\ \frac{q_i q_j}{4\pi \varepsilon \varepsilon_0 r_{ij}} & r_{ij} \geq \sigma, \end{cases} \quad (1)$$

where r_{ij} is the distance between spheres i and j , q_i and q_j their respective charges and ε_0 the dielectric permittivity of vacuum. It is customary to choose a reduced system of units so that temperature is normalized by the energy of interaction of two ions at contact,

$$T^* = \frac{4\pi \varepsilon \varepsilon_0 \sigma k T}{q^2}, \quad (2)$$

where k is Boltzmann’s constant. The total number density in the system is

$$\rho^* = \frac{N_+ + N_-}{V} \sigma^3, \quad (3)$$

where $N_+ = N_-$ is the number of positive and negative particles and V is the system volume.

Vorontsov-Velyaminov *et al* [19, 20] were the first to propose that the RPM has a liquid–vapour transition and critical point, using constant-pressure Monte Carlo simulations; they obtained $T_c \approx 0.095$ and $\rho_c \approx 0.17$. Stell *et al* [21] used equation of state data from simulations and theoretical approximations of the free energy to obtain $T_c \approx 0.085$ and $\rho_c \approx 0.01$. While

Table 1. Recent results for the critical parameters of the RPM.

Ref.	T_c^*	ρ_c^*
[37]	$0.049\,33 \pm 0.000\,05$	0.075 ± 0.001
[31]	$0.049\,17 \pm 0.000\,02$	0.080 ± 0.005
[32]	$0.049\,0 \pm 0.0003$	0.070 ± 0.005
[33]	$0.049\,2 \pm 0.0003$	0.062 ± 0.005
[34]	$0.048\,9 \pm 0.0003$	0.076 ± 0.003

the estimated values of the critical parameters differ significantly from ‘modern’ values given in table 1, these early studies established firmly that the system has a low-temperature transition.

Several years after these first studies, the present author published an estimate of the critical point of $T_c = 0.056$ and $\rho_c = 0.04$ using Gibbs ensemble Monte Carlo [22] with single-ion transfers. Orkoulas and Panagiotopoulos [23] also used the Gibbs ensemble and introduced biased pair transfers used by subsequent investigations—they obtained $T_c = 0.053$ and $\rho_c = 0.025$. It should be noted that it is now known that the Gibbs ensemble is not well suited for high precision phase coexistence calculations in the immediate vicinity of critical points [24]. Clearly, significant uncertainties remained as to the location of the critical point of the RPM as late as ten years ago.

A methodological advance in calculations of critical points of fluids that do not have particle–hole symmetry was the mixed-field finite-size scaling approach of Bruce and Wilding [25, 26]. The method is based on matching results for the scaled order parameter probability distribution to the universal curve appropriate for the universality class of the system under study. For bulk fluids, the appropriate scaling variable is a linear combination of density and energy, assuming that there is no pressure mixing in the scaling fields [27]. This method has been used by most simulation studies of the vapour–liquid critical point of the RPM in the past decade. The method works well in combination with the grand canonical histogram reweighting approach of Ferrenberg and Swendsen [28] that allows extrapolation of results from a simulation run to a range of chemical potentials and temperatures in its vicinity.

The critical parameters of the RPM were obtained using the Bruce–Wilding approach by Caillol *et al* [29–31] in hyperspherical boundary conditions and Orkoulas and Panagiotopoulos [32] in standard cubic boundary conditions. Yan and de Pablo [33] used it in combination with hyper-parallel tempering Monte Carlo that allows for multiple replicas of the simulation at different conditions of temperature and chemical potential. Panagiotopoulos [34] obtained the critical parameters of the continuum RPM by extrapolating results on the finely discretized lattice analogue to the RPM to infinitely fine discretization.

The Bruce–Wilding approach used in these studies of RPM criticality *assumes* that the system is in the three-dimensional Ising universality class. At most, one may claim consistency with Ising critical behaviour. An unbiased finite-size extrapolation method using the grand canonical ensemble [35] was applied to a discretized version of the RPM by Luijten *et al* [36]. Kim and Fisher [37] examined the discretization dependence of the critical behaviour and extrapolated to the continuum limit. The unequivocal conclusion from these two studies was that the RPM is in the three-dimensional Ising universality class, as also argued on theoretical grounds [38]. Some earlier studies of the heat capacity in the canonical (NVT) ensemble [39, 40] did not observe a peak near the critical point and interpreted this as an indication of non-Ising behaviour. However, these observations were later shown to be due to the suppression of density fluctuations in the canonical ensemble [41].

Table 1 shows a summary of recent results for the critical parameters of the RPM. There is generally good agreement between simulations that used different boundary conditions and

sampling algorithms. The critical temperature has relatively small uncertainties; the two most recent estimates [37, 31] disagree by more than their combined error bars but the difference is only 0.3% of the value of T_c^* . The other simulations listed in the table (with more generous error bars) overlap these two. This difference may be due to the use of the Bruce–Wilding approach in [31] versus an unbiased extrapolation with no assumption of universality class in [37]. The situation for the critical density is less satisfactory, with large relative uncertainties and several differences outside the combined simulation uncertainties. Kim and Fisher [27] suggested that the use of the Bruce–Wilding method with no pressure mixing could lead to unreliable estimates of the critical density, but is not likely to result in major errors in the critical temperature. Clearly, the precise determination of the critical density for the RPM remains a topic for future work.

It has already been mentioned that several recent studies used a discretized version of the RPM. In this approach, calculations are performed on a simple cubic lattice of spacing l less than the particle diameter σ , with pre-computed interactions between all lattice sites for computational efficiency [42, 43]. Parameter $\zeta = \sigma/l$ controls how closely the model approximates continuous space. For $\zeta = 1$, the lattice-discretized RPM has a tricritical point and an order–disorder transition, as first observed by Dickman and Stell [44]. The lattice RPM model with $\zeta = 2$ was also found [42] to have phase behaviour qualitatively different from the continuum model. However, for $\zeta \geq 3$ the phase behaviour is qualitatively identical to the continuum; critical point and coexistence curves match continuum data within a few per cent. Lattice discretization effects have been subsequently analysed in detail using theoretical approaches [45–47] and simulations [34, 37]. Phase diagrams of the $\zeta = 1$ model with additional anisotropic interactions [48] and nearest-neighbour repulsions and attractions [49, 50] are also available.

In addition to the liquid–vapour transition, the RPM has several possible solid phases. Simulations of fluid–solid and solid–solid equilibria for the RPM were performed by Smit *et al* [51] and Vega *et al* [52], who identified a liquid–bcc transition at low temperatures and a liquid–fcc one at high temperatures. Bresme *et al* [53] identified additional order–disorder transitions and triple points.

Finally, closely related to the RPM are systems of charged hard dumbbells or tethered dimers, since there is strong ion pairing in the (untethered) RPM at its critical temperature. For the contact tethered dimer of equal-size opposite charges, the critical temperature is almost the same as for the unconstrained RPM, but the critical density is significantly higher: $T_c^* = 0.04911 \pm 0.00003$, $\rho_c^* = 0.101 \pm 0.003$ [54]. Tethered-ion systems of varying tether length were studied in [55]. Interestingly, as the tether length approaches infinity, care must be exercised to prevent an ‘entropy catastrophe’ and obtain a proper thermodynamic limit. The dependence of the critical parameters on tether length was found to be smooth but non-monotonic.

3. Generalized primitive models and ionic salts

For the RPM model discussed in the previous section all ions have the same size and absolute charge and only interact through Coulombic forces and hard-sphere repulsions. This section summarizes simulation studies of ionic systems for which these constraints have been relaxed.

Phase diagrams of size-asymmetric electrolytes were obtained by Romero-Enrique *et al* [56] using a fine-lattice discretization approach and by Yan and de Pablo [57, 58] using a multidimensional parallel tempering algorithm. The key finding from these studies was that the critical temperature and critical density are at a maximum for the size-symmetric case and then drop off as the size asymmetry increases. This is in contrast to predictions of commonly

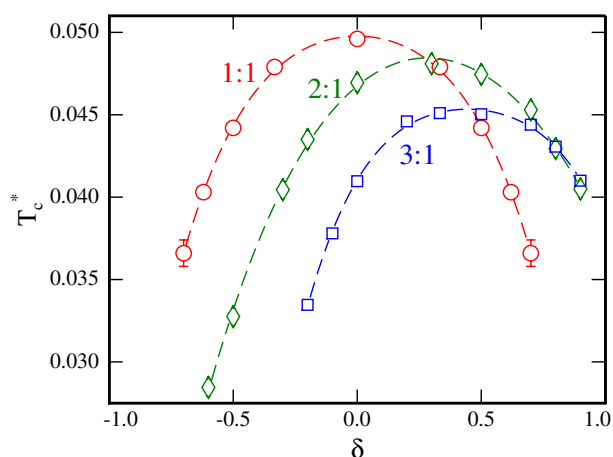


Figure 1. Reduced critical temperature versus size asymmetry parameter $\delta = \frac{\sigma_+ - \sigma_-}{\sigma_+ + \sigma_-}$. Data are from [56, 59].

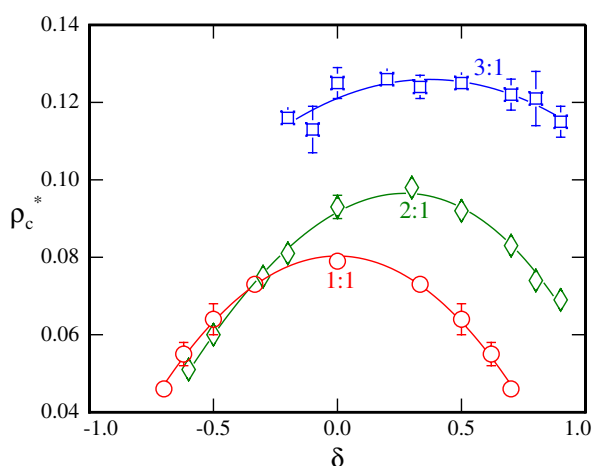


Figure 2. Reduced critical density versus size asymmetry parameter $\delta = \frac{\sigma_+ - \sigma_-}{\sigma_+ + \sigma_-}$. Data are from [56, 59].

used theories for ionic fluids [9, 10]. Newer theories have been developed [6–8] that predict the correct trends of the critical parameters with size asymmetry.

Multivalent electrolytes have been studied much less than monovalent ones, despite their importance in micellar, colloidal and biological systems. Detailed studies of 2:1 and 3:1 electrolytes for a broad range of size ratios were performed by Panagiotopoulos and Fisher [59] and Yan and de Pablo [60]. The main finding from these studies is that the critical temperature and density show a maximum for multivalent ions of increasing size as the valency is increased, as illustrated in figures 1 and 2. Reference [59] suggested that for small multivalent ions with large monovalent counterions (for small values of δ in figures 1 and 2) the vapour–liquid phase transition is likely to disappear because of the formation of an open network.

Reščič and Linse [61] have investigated the critical parameters for a 10:1 electrolyte at the point counterion limit using thermodynamic scaling Monte Carlo. Linse [62, 63] suggested

a scaling law for the critical temperature of systems with charge ratios up to 80:1, also at the point counterion limit. A study of charge-asymmetric electrolytes with charge ratios up to 10:1 was performed in [64], using reservoir grand canonical simulations. Some discrepancies were observed between the results of this study and the scaling law of Linse that remain to be resolved. However, it is clear from these studies that salt-free colloidal systems phase separate through effective like-ion attractions at sufficiently high couplings, as also seen experimentally ([65, 66]—but reference [67] suggests an alternative explanation). This issue has been the topic of several theoretical [68–70] studies.

Realistic intermolecular potentials for ionic systems include soft repulsions and dispersion forces in addition to the Coulombic interactions [71]. Simulation studies of phase transitions for realistic salt model salts have been performed by Guissani and Guillot for NaCl [72] and NH_4Cl [73]. Thermodynamic integration methods were used to obtain the melting point for the Fumi–Tosi model of NaCl [74] in good agreement to experimental data. Studies of charged Yukawa systems are also available [75–77].

4. Charged chains and ionic mixtures

Polyelectrolytes and polyampholytes are polymers that contain charged groups along their linear backbones. They can be found naturally in the form of proteins and nucleic acids, or they can be made synthetically. They are involved in industrial processes such as waste water treatment or oil recovery and are found in many consumer products. An important natural polyelectrolyte is DNA, the main carrier of genetic information. It is well known that multivalent ions induce attractions between DNA strands mediated by strong correlation effects [5]. Experiments have shown precipitation and subsequent redissolution of DNA with addition of polyamine salts [78].

There have been relatively few studies of phase transitions in charged chains. Orkoulas *et al* [79] studied fully charged lattice chains of chain lengths up to 24 beads, along with monomeric counterions. The critical density was found to be approximately independent of chain length, in sharp contrast to homopolymers, for which the critical density approaches zero as the chain length increases. Cheong and Panagiotopoulos [80] studied polyampholyte lattice chains with both charged and uncharged beads and determined that the critical parameters are sensitive functions of the charge sequence, as illustrated in figure 3. Phase transitions in polyelectrolyte networks with explicit counterions were observed by Yan and de Pablo [81].

Real charged chain or colloidal systems almost always have varying amounts of salt or other ionic species. Simulations of phase transitions in charged colloidal (macroion) systems with added salt have been performed by Hynninen *et al* [82]. The critical parameters were determined for macroion to counterion charge asymmetries of 2:1, 3:1 and 10:1. This study found that binary electrolyte mixtures are type I mixtures, with the two components mixing continuously. A typical configuration from the 10:1 system near the mixture critical point for salt mole fraction of 48% is shown in figure 4. Large voids and clusters are apparent—these may be related to similar observations in recent simulations using effective potentials [83] and to earlier experiments [66] that have generated significant controversy [67].

5. Possible future directions

Simulations of phase transitions of ionic systems over the past decade have greatly expanded the range of systems for which quantitative results are available. This is primarily due to the development of sophisticated Monte Carlo sampling and simulation data analysis algorithms.

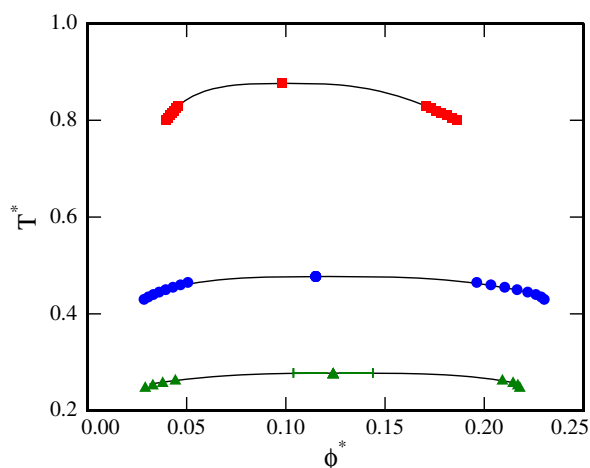


Figure 3. Phase diagrams of fully charged chains of length 16 on a simple cubic lattice (data from [80]). The sequences from top to bottom are P_8N_8 , $P_4N_4P_4N_4$ and $PN_2P_3NPN_3P_2NPN$, where P and N are positive and negative charges.

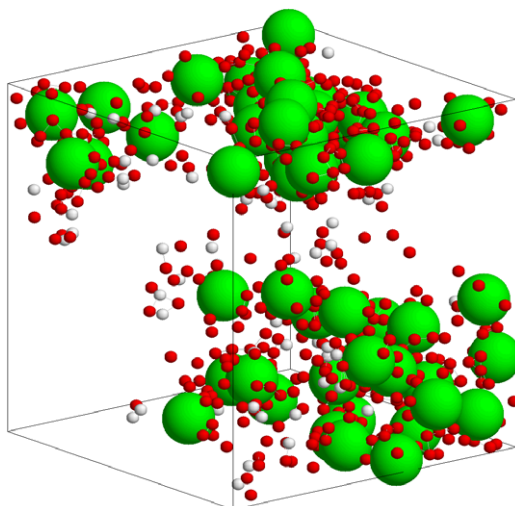


Figure 4. Snapshot of a colloid–salt mixture near a critical point for phase demixing. Large spheres are macroions with charge $+10q$, white small spheres are coions with charge $+q$ and dark (red) small spheres counterions with charge $-q$ (data from [82]).

For vapour–liquid transitions, critical temperatures of simple models such as the RPM are now known to fractional accuracies of 10^{-3} or better. Critical densities are known with much less accuracy—improving the methods for their determination is a priority area for future research.

Another major limitation of current approaches is their inability to deal with extremely large charge asymmetries. There are few results for phase transitions in systems with charge asymmetries significantly above 10:1. Novel sampling methods are needed for significantly expanding the range of charge asymmetries that can be successfully simulated and for resolving remaining questions on the scaling behaviour of critical parameters for large charge asymmetries.

In recent years, methods to calculate electrostatic interactions have emerged [84] that promise to be considerably faster than conventional Ewald summation. It would be interesting to see if such methods can be used to speed up ionic phase transition simulations. It would also be of interest to incorporate dielectric contrast between particles and surrounding solvent in the simulations—at the moment such calculations are prohibitively expensive. Faster simulation algorithms may also facilitate calculations in ‘non-primitive’ systems that take into account explicitly the molecular character of solvents in which most real ionic systems exist.

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