Phase Transitions in 2:1 and 3:1 Hard-Core Model Electrolytes

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Critical temperatures, $T_c$, densities, $\rho_c$, and coexistence curves for 2:1 and 3:1 hard-core model electrolytes have been found by fine-discretization Monte Carlo simulation. The size ratio of $+1$ and $-1$ ions strongly affects $T_c$ and $\rho_c$; the trends contradict most current theories. Large multivalent ions screened by small monovalent counterions exhibit normal gas-liquid transitions of direct relevance to phase separation in charge-stabilized colloids. Conversely, extrapolation suggests the absence of such transitions for sufficiently small multivalent ions with large monovalent counterions.

A striking result is that both the (appropriately normalized) critical temperatures, densities, and coexistence curves for 2:1 and 3:1 hard-core model electrolytes have been found by fine-discretization Monte Carlo simulation. The size ratio of $+1$ and $-1$ ions strongly affects $T_c$ and $\rho_c$; the trends contradict most current theories. Large multivalent ions screened by small monovalent counterions exhibit normal gas-liquid transitions of direct relevance to phase separation in charge-stabilized colloids. Conversely, extrapolation suggests the absence of such transitions for sufficiently small multivalent ions with large monovalent counterions.

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$$T^* = k_BT_D\sigma_+^2/\kappa q^2$$ and $$\rho^* = N\sigma_+^2/V,$$ where $V$ is the system volume. The reduced chemical potential, $\mu^*$, is defined so that

$$\frac{\mu^*}{(z+1)} \rightarrow T^* \ln \frac{N_0\sigma_+^2}{V} \text{ for } T^* \rightarrow \infty, \rho^* \rightarrow 0. \quad (3)$$

Our simulations were performed using the fine-discretization methodology [10,11]. In the present study, we used a discretization parameter $\zeta = \sigma_+/l = 10$, where $l$ is the simple-cubic lattice spacing. For this relatively high value of $\zeta$, it was found in [5] that the critical parameters of the RPM are well reproduced. There was also agreement between the fine-lattice results of [5] and the continuum calculations of [6] for critical parameters of size-asymmetric 1:1 electrolytes. The main advantage of using the finely discretized lattice approach for systems with Coulombic interactions is that they can be calculated once at the beginning of the simulation. This initial Ewald sum was performed with conducting boundary conditions, 518 Fourier-space wavevectors and real-space damping parameter $\kappa = 5$. The speedup relative to the continuum calculations is by a factor of 100 [10].

We used grand canonical Monte Carlo simulations with multihistogram reweighting [12], following [5]. Insertions and removals were attempted for neutral clusters of $z + 1$ ions. To enhance efficiency, we used a distance-biasing algorithm [13] 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.

Critical points were estimated using mixed-field finite-size scaling methods [14], under the assumption of

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Ising-type criticality. To discern a systematic dependence of critical parameters on valence and size asymmetry, this approach should be satisfactory even though recent results [15] (which indicate that the pressure should also enter the field mixing) cast doubts on its full reliability. The character of criticality in ionic and long-range systems remains a topic of active research [16,17].

Our results for the critical parameters, $T^*_c$, $\mu^*_c$, and $\rho^*_c$ are presented in Table I. The reported parameters are for systems of box length $L^*/\sigma_x = 15$. In our previous work [5], the size dependence of the critical parameters for the RPM was found to be weak for box sizes $L^*/\sigma_x \approx 12$ when conducting boundary conditions were employed. This was confirmed for the multivalent electrolytes with a few test calculations for larger systems; but since our primary goal here is to investigate the dependence of critical parameters on valence and size asymmetry, finite-size effects are of secondary importance.

Figures 1 and 2 portray our results for $T^*_c(\delta; z)$ and $\rho^*_c(\delta; z)$, together with our earlier estimates for 1:1 systems [5]. Consider, first, the dependence on the valence $z$ in the size-symmetric or $\delta = 0$ models. For this special case, Camp and Patey [18] have recently estimated $T^*_c$ (but not $\rho^*_c$) for the 2:1 and 4:1 models by simulation, although with a precision of only 10% and 20%, respectively. The former estimate is consistent with our (better than $\pm 0.8\%$) value; the latter falls nicely in sequence; see Fig. 1. We are also aware of an unpublished independent study by Yan and de Pablo [19] for size-asymmetric 2:1 electrolytes that is broadly consistent with the results of the present work.

Theoretically, both the original DH theory (see [4]) and the MSA [7] predict no dependence on $z$ in the equisize ($\delta = 0$) case, yielding $T^*_c = 0.063, 0.086$ and $\rho^*_c = 0.005, 0.040$, respectively. (The MSA predictions for general $\delta$ are included in the figures.) Sabir et al. [20] also studied the modified Poisson-Boltzmann and symmetric Poisson-Boltzmann approximate integral equations for 1:1, 2:1, and 3:1 models. The former theory predicts an increase in $T^*_c$ of about 1% in going from 1:1 to either 2:1 or 3:1 electrolytes, the latter yields decreases of about 1% and 3%, respectively. On the other hand, Netz and Orland

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**Table I.** Dependence of critical parameters on size asymmetry for (a) 2:1 and (b) 3:1 electrolytes. The 1σ statistical uncertainties in parentheses refer to the last decimal place quoted.

<table>
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<tr>
<th>$\delta$</th>
<th>$T^*_c \times 10^2$</th>
<th>$-\mu^*_c$</th>
<th>$\rho^*_c \times 10^2$</th>
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<td>-0.6</td>
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<td>1.8740(2)</td>
<td>5.1(1)</td>
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<td>-0.5</td>
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<td>1.9067(4)</td>
<td>6.0(2)</td>
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<td>7.5(1)</td>
</tr>
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<td>1.9925(2)</td>
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<td>9.3(3)</td>
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<td>4.10(3)</td>
<td>2.628(2)</td>
<td>11.5(4)</td>
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**FIG. 1.** Critical temperature, $T^*_c$, as a function of size and charge asymmetry. Simulation results are shown as symbols connected by dashes for visual clarity. 1:1 data are from [5], 2:1 and 3:1 from the present study, and 4:1 from [18]. Continuous lines are for the MSA, from [7].

**FIG. 2.** Critical density, $\rho^*_c$, as a function of size and charge asymmetry. Symbols and lines are as for Fig. 1.
[21] have presented a cutoff field theoretic analysis which predicts large increases in \(T_c\), by factors of 2.88 and 4.32 as \(z\) goes from 1 to 3, while \(\rho_c(z)\) falls to about 41% and 55% of \(\rho_c^*(1) = 0.042\).

By contrast, our simulations reveal a rapid decrease in \(T_c^*\), by 5% and 17%, while \(\rho_c^*\) increases by about 20% and 65%, respectively. It turns out, nonetheless, that this behavior is quite closely mirrored by an extension of the Fisher-Levin [4] DH-based theory that explicitly considers association into solvated charged dimers as well as into trimers, for the 2:1 model, and also tetramers for the 3:1 case [22].

On varying the size asymmetry, \(\delta\), our results for \(T_c^*(\delta;z)\) and \(\rho_c^*(\delta;z)\) in 1:1 systems exhibit a maximum at \(\delta = 0\) [5,6]. The MSA displays the opposite behavior. For multivalent electrolytes, both maxima move to larger values of \(\delta\) while remaining together, within the precision of our simulations, as evidenced by the near constancy at fixed \(z\) of the reduced inverse Debye length, \(\kappa_c^* \approx (\rho_c^*/T_c^*)^{1/2}\), implied by our data. The underlying physical mechanism is undoubtedly related to the optimal packing of smaller counterions around the large multivalent ions (\(\delta > 0\)). On the simplest picture the maximal critical density would then be expected when a compact neutral cluster of one cation and \(z\) anions has minimal volume \(\propto (\sigma_+^3 + z\sigma_-^3)\). For 2:1 and 3:1 systems this yields the values \(\delta_{\text{max}}(2) = 0.172\) and \(\delta_{\text{max}}(3) = 0.268\). In fact, however, minimizing the overall cluster area \(\propto (\sigma_+^3 + z\sigma_-^3)\)—which may serve to allow for inter-cluster interactions—yields \(\delta_{\text{max}}(z) = (z - 1)/(z + 1)\), which represents our data fairly well. As is clear from the figures, the MSA fails badly to represent the variation with \(\delta\) and \(z\).

In Fig. 3 we present the critical points and phase-coexistence envelopes for \(z:1\) systems of size asymmetries corresponding to the \((T_c, \rho_c)\) maxima. It is remarkable that the liquid sides of these coexistence curves practically coincide independently of the valence. This seems again to reflect some optimal packing condition. By contrast, vapor densities are far lower for higher valence, presumably representing a preponderance of neutral clusters of \((z + 1)\) ions.

For systems with \(\delta < 0\), the strong repulsions between large, like anions predominantly yield weakly interacting open clusters near criticality. For 1:1 electrolytes these clusters tend to approximate linear chains [5], while for \(z > 1\) a branched topology is favored as seen in the typical configuration for the 3:1 system with \(\delta = -0.2\) shown in Fig. 4 for \(T\) just above \(T_c\). A parabolic fit of our data for \(\delta \leq 0.2\) indicates that \(T_c^*(\delta;z = 3)\) vanishes at \(\delta_0(3) = -0.67(9)\). Even a simple linear extrapolation of the data (which are clearly curving downwards) for \(\delta < 0\), suggests that \(T_c^*\) becomes very small, even zero, when \(\delta \rightarrow -1\), the point-cation limit. The trends with valence clearly indicate that \(\delta_0(z)\) increases with \(z\). These facts lead us to speculate that a system of multivalent point cations with finite-size monovalent anions may not have a vapor-liquid transition when \(z\) exceeds some \(z_c \approx 3\).

On the other hand, when \(\delta \rightarrow 1\) the critical parameters seem to approach well-defined limits for all \(z \geq 1\). For \(z = 2\) or 3 our data indicate \(T_c^* = 0.037\). This is near the estimate of [23] \(T_c^* = 0.038\) for a 10:1 macroion/point counterion (\(\delta = 1\)) system. The critical density at this limit increases with \(z\), also consistent with [23]. The existence of a critical point for \(\delta \rightarrow 1\) is significant for the question of phase separation in charge-stabilized colloids. Linse [24] has also studied a range of charge asymmetries (10 \(\leq z \leq 80\)) and concluded that the critical temperature decreases with \(z\). Clearly, further work is needed to reliably quantify this transition.

To exhibit explicitly the effective attractions between like pairs of ions [25] in the critical region, we present, in Fig. 5, the radial distribution functions, \(g(r^*)\), for reduced separations \(r^* = r/\sigma_c\), for the 3:1 system with \(\delta = -0.2\) at a density \(\rho = \rho_c/4\) and temperature \(T = 1.04T_c\). As expected, \(g(r^*)\) for unlike ions (dotted line)
becomes very large close to contact, \( r^* \lesssim 1 \), with a smaller, second peak around \( r^* = 2.4 \). However, there is also a large and broad anion-anion peak in \( g(r^*) \) (solid line) spanning the range \( r^* \approx 1.2-2.0 \) with a broad secondary peak centered at \( r^* \approx 3.0 \) and a sharp cation-cation peak in \( g(r^*) \) at \( r^* = 2.0 \). At this density the correlations then decay monotonically and fairly rapidly; but on the high density, fluid side oscillatory behavior sets in quite soon. An interesting quantity to compute in future studies would be the anion-averaged cation-cation pair potential that gives rise to the observed correlation functions. Such a potential is likely to include regions of strong attraction between like-charge multivalent ions.

In conclusion, we have obtained by simulation precise estimates of critical parameters and coexistence curves for size-asymmetric 2:1 and 3:1 hard-core primitive model electrolytes (significantly extending previous studies of size-asymmetry for 1:1 systems [5,6]). Except for recent Debye-Hückel based treatments [9,22], the observed trends of \( T_c \) and \( \rho_c \) with valence and size disparity contradict most available theories. Extrapolation raises the possibility that sufficiently small multivalent \( (z > z_c \gtrsim 3) \) ions with large counterions \( (\sigma_-/\sigma_+ \gtrsim 10) \) may exhibit no vapor-liquid phase transitions. By contrast, criticality in the point-charge limit of small counterions screening large multivalent ions seems well defined implying that phase separation “caused” by effective like-ion attractions in charge-stabilized colloidal systems should be a generic feature (although detectable, in reality, only at sufficiently low temperatures or for counterions of sufficiently large valence [25]).

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