

Phase Equilibria of Charge-, Size-, and Shape-Asymmetric Model Electrolytes

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The low-temperature phase behavior of two 2:1 hard-core electrolyte models has been investigated by Monte Carlo simulations. In the first model, both bivalent cations and monovalent anions are spherical, and the charges are located at the ion's centers; in the second model, bivalent cations are modeled as rigid dimers composed of two tangent hard spheres, each carrying a positive charge at the center. It is found that the critical temperature and the critical density are strongly affected by the size asymmetry and the shape of the ions. The results presented in this work provide insights into the behavior of charged colloidal suspensions and polyelectrolytes, where large, symmetric or asymmetric ionic species carrying like charges can attract each other and give rise to thermodynamically unstable conditions.

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Electrolyte solutions are ubiquitous in nature and in numerous industrial processes. Precise knowledge of the thermodynamics and phase behavior of electrolytes is of interest in a wide range of disciplines. Perhaps the simplest representation of electrolyte solutions is provided by the so-called "restricted primitive models," in which monovalent, equal-sized hard spheres interact via a Coulombic potential-energy function. Over the last few years, simulations have gradually provided a coherent picture of the nature and precise location of the critical point of primitive model electrolytes [1–3]. More recently, the phase behavior of size-asymmetric monovalent electrolyte solutions has also been determined [4–6]. An important conclusion of that body of work has been to show that primitive models exhibit a pronounced tendency to form large polymeric structures at low temperatures, a tendency that is exacerbated with increasing size asymmetry between cations and anions. Another important outcome of that work is to learn that available theoretical formalisms are unable to predict the trends observed in simulations, particularly with regards to the decrease of the critical temperature T_c and critical density ρ_c with increasing size asymmetry.

The challenges encountered in the theoretical and numerical study of electrolytes are considerable. For that reason, most of the literature has concentrated on monovalent ions; the arguably more important case of multivalent ions has received much less attention. This work provides a first step towards the study of phase transitions and criticality in multivalent electrolytes. Monte Carlo simulations are conducted to establish the effects of charge asymmetry, size asymmetry, and shape asymmetry on the low-temperature phase behavior of electrolytes.

The elementary model considered in this work consists of charged hard spheres interacting via a Coulombic potential-energy function. Two implementations of this model are considered in this work. In the first of these, both cations and anions are treated as isolated spheres (we refer to this case as the "spherical" model). Cations have diameter σ_+ and carry a positive charge of $+2$; anions have diameter σ_- and carry a negative charge of -1 . To preserve

electroneutrality, the number of negative charges (N_-) is set to be twice that of positive charges (i.e., $N_- = 2N_+$). In order to consider the effects of shape asymmetry, in the second implementation of this model cations are treated as rigid dumbbells consisting of two tangent hard spheres, each having a diameter σ_+ , and each carrying a positive charge of $+1$ (we refer to this case as the "dumbbell" model); note that the charge of a dumbbell molecule is $+2$. Anions are treated as individual spheres of diameter σ_- and negative charge -1 .

Ions are immersed in a dielectric continuum, and they interact via a potential energy function of the form

$$U_{ij} = \begin{cases} +\infty & r_{ij} \leq \sigma_{ij}, \\ \varepsilon z_i z_j \sigma_{\pm} / r_{ij} & r_{ij} > \sigma_{ij}, \end{cases} \quad (1)$$

where r_{ij} is the distance between site i and site j , and σ_{ij} is defined as $\sigma_{ij} = (\sigma_i + \sigma_j)/2$; ε is the unit energy parameter, defined as $\varepsilon = e^2/(4\pi D_0 \sigma_{\pm})$, where e is the charge of the electron, D_0 is the dielectric permeability of vacuum, and $\sigma_{\pm} = (\sigma_+ + \sigma_-)/2$. Note that, for energetic purposes, in the dumbbell system each cation is treated as two (bonded) hard spheres, each having a unit charge.

Following previous simulation work, a size-asymmetry parameter is defined as $x = (\lambda - 1)/(\lambda + 1)$, where $\lambda = \sigma_+/\sigma_-$ [4–6]. Throughout this paper, results are reported in reduced units. The reduced temperature is given by $T^* = k_B T/2\varepsilon$, where k_B is Boltzmann's constant; the reduced density is given by $\rho^* = (N_+ + N_-)/L^{*3}$, where L^* is a dimensionless box size, defined as $L^* = L/\sigma_{\pm}$.

Monte Carlo simulations were conducted in the framework of a grand canonical multidimensional parallel tempering formalism, which has been shown to be highly effective for studies of phase transitions in monovalent electrolytes [3,5,6]. Long-range interactions were calculated using the Ewald-sum method with conducting boundary conditions. Following previous work [5,6], the Ewald-sum convergence parameter κ was set at $\kappa = 5/L$;

for this value of κ , approximately 300 k -space wave vectors were necessary for the Fourier-space calculation. The real-space cutoff was set at half the simulation box length. Electric neutrality was maintained by inserting and/or removing ions in pairs (one cation and two anions). Distance-biased sampling techniques were employed to facilitate the insertion or removal of ions [2].

The joint distribution of the number of ions and total potential energy was estimated in the form of histograms at different temperatures and chemical potentials. Histogram reweighting [7,8] and mixed-field finite-size scaling techniques [9,10] were subsequently used to combine these histograms and to locate phase boundaries and the apparent critical parameters for the finite-size systems. The Ising universality class was assumed in the analysis and no attempt was made to determine system-size effects on the critical parameters.

Figures 1 and 2 show the calculated critical temperature and critical density of the two 2:1 systems considered in this work (i.e., the spherical and dumbbell cases), as well as the results of previous work for 1:1 size asymmetric systems [4–6]. Our results are consistent with a prediction by Camp and Patey [12], who placed the critical temperature of symmetric ($x = 0$) 2:1 electrolytes at approximately $T_c^* = 0.05 \pm 0.005$. Our calculated critical temperatures as a function of x are also consistent with recent work by Panagiotopoulos and Fisher, who conducted Monte Carlo simulations of the same model but on a finely discretized lattice to accelerate the computation of interaction energies [13]. There appear to be some minor deviations (less than 10%) in the critical densities, but these could be attributed to truncation, finite sampling, or statistical errors. As mentioned earlier, simulations of

asymmetric electrolytes are particularly challenging; we are encouraged by the fact that different groups have independently arrived at comparable predictions, using completely different methods, thereby lending credence to the validity of the findings presented here and elsewhere [13] concerning the behavior of 2:1 electrolytes.

Just as 1:1 electrolyte systems, 2:1 spherical systems exhibit a maximum in both the critical temperature and the critical density when plotted as a function of size asymmetry. This is in direct contrast to the MSA theory [11], which predicts that both critical temperature and critical density exhibit a *minimum* as a function of size asymmetry. Furthermore, the MSA theory predicts that for equal-size electrolytes ($x = 0$) the critical temperature and density do not depend on charge asymmetry; our results reveal that the critical temperature of equal-size electrolytes decreases with increasing charge asymmetry, and the critical density increases, markedly, with increasing charge asymmetry. Other available theoretical approaches using integral equations [14] predict only slight changes of T_c^* above or below that of the 1:1 system (of at most 2%). In contrast, a field theoretic analysis [15] predicts an increase of T_c^* up to a factor of about 2.8.

The maximum in the critical parameters of 1:1 systems occurs precisely at $x = 0$; the maximum in the critical parameters of 2:1 systems shifts to a positive value of x . In other words, electrolyte systems consisting of large divalent cations surrounded by smaller univalent counterions phase separate more readily (i.e., at higher temperatures) than those consisting of small divalent cations surrounded by large univalent counterions. As in the case of 1:1 electrolytes [6], this can be explained in terms of packing arguments; large divalent cations and small counterions can be organized in more energetically favorable arrangements, thereby leading to stronger effective attractions between like-ion (same charge sign) pairs.

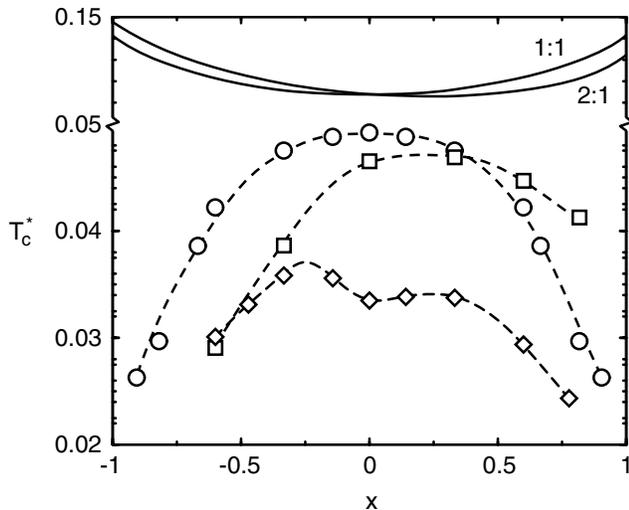


FIG. 1. Critical temperature T_c^* as a function of size asymmetry. Open symbols correspond to simulation results: squares are 2:1 spherical electrolytes; diamonds are 2:1 dumbbell electrolytes; circles are 1:1 spherical electrolytes [3,5]. The solid lines are MSA results [11].

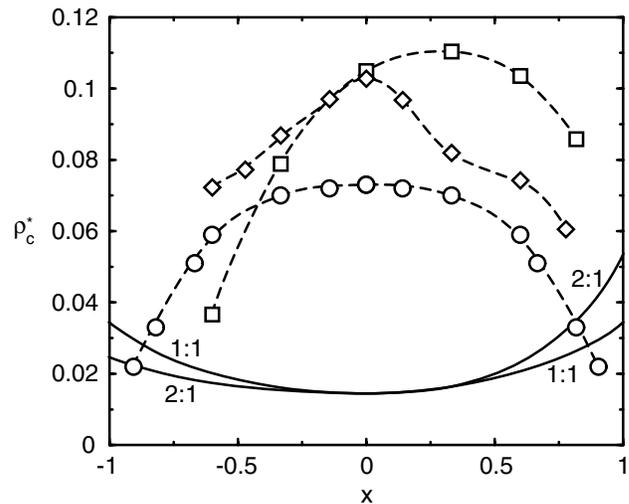


FIG. 2. Critical density ρ_c^* as a function of size asymmetry. The meaning of the symbols is the same as in Fig. 1.

Figure 3 shows the energy change associated with bringing together two or three infinitely separated colinear neutral ion triplets to form a tight minimum-energy cluster. The ground-state configuration and the concomitant energy change depend strongly on the size asymmetry. For two ion triplets, the largest energy drop is achieved in the range $x = [-0.21; 0.44]$; for three ion triplets, this range changes to $x = [0; 0.5]$. In general, the energy drop on the $x < 0$ side is smaller than that on the $x > 0$ side. These energetically favorable arrangements dominate the behavior of electrolytes at low temperatures, and in fact the general features of Fig. 3 follow closely the trends observed in the critical temperature curve (the open squares in Fig. 1). Also note that the energy change is negative over the entire range of size asymmetry, indicating that neutral ion complexes are favored and are effectively attracted to each other.

Figures 4 show radial distribution functions for the 2:1 spherical system with $x = 0.6$ and with $x = -0.6$, at approximately the same density ($\rho^* \approx 0.02$) and at a temperature slightly below the critical ($T^* \approx 0.97T_c^*$). In addition to trivial cation-anion peaks, both systems exhibit clear like-ion peaks at $r \approx 1.3$, and broad peaks in the range $r = [1.5; 3.0]$. Furthermore, except at distances close to contact, the distribution functions for all three pairs are larger than unity, indicating that even ions carrying a

charge of the same sign are effectively *attracted* to each other. Inspection of the distribution functions of the two systems shows that the system with $x = 0.6$ (large divalent cations) exhibits a higher cation-cation first peak and a more pronounced second peak than that of the other system with $x = -0.6$ (small divalent cations). Also note that the actual temperature of the $x = 0.6$ system is higher than that of the $x = -0.6$ system (the $x = 0.6$ system has a higher critical temperature than the $x = -0.6$ system), thereby reinforcing our view that the larger-cation systems exhibit stronger effective, counterion mediated attractions between like ions.

The phase behavior of dumbbell systems exhibits a number of additional, surprising features. The critical temperature for charged dumbbells is much lower than for spherical 2:1 systems. In the $x > 0$ range, T_c^* has the same general shape as in the spherical system, but for $x < 0$ a second, higher maximum appears near $x = -0.25$. The origin of this surprising second maximum can be traced

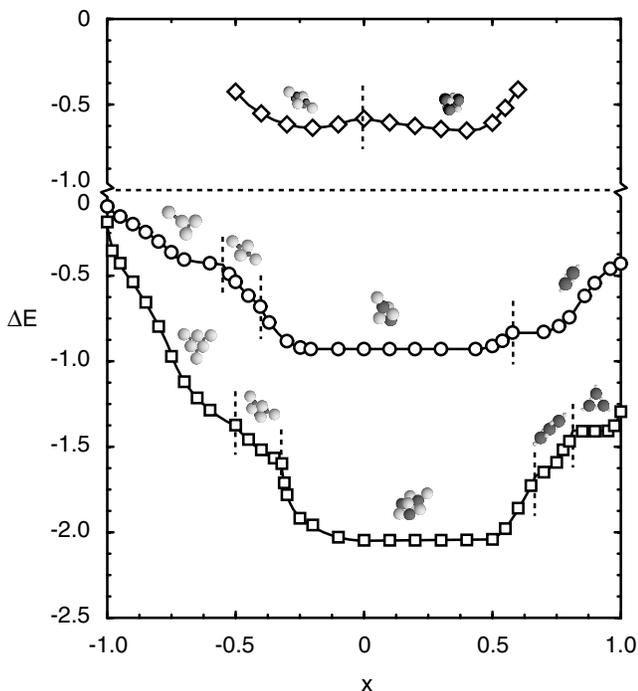


FIG. 3. Ground-state energy of ion clusters. Circles and squares correspond to two-triplet and three-triplet spherical clusters, respectively; diamonds are for two-triplet dumbbell clusters. Regions of size asymmetry having distinct ground-state configurations are separated by dashed lines; these configurations are depicted above the curves.

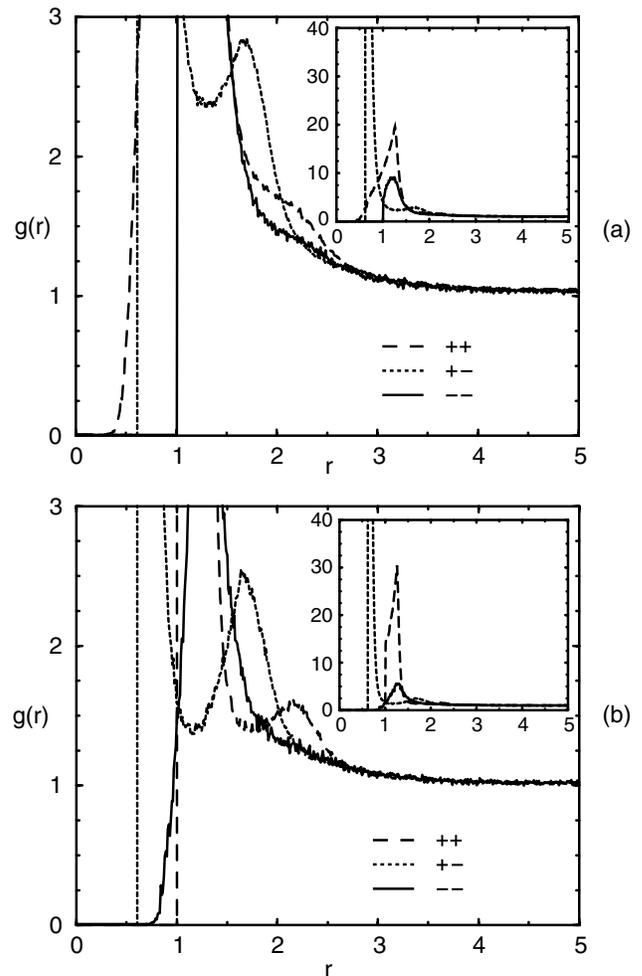


FIG. 4. Radial distribution functions $g(r)$ for 2:1 spherical electrolytes: (a) $x = -0.6$, $T^* = 0.028$, and $\rho^* = 0.02$; (b) $x = 0.6$, $T^* = 0.044$, and $\rho^* = 0.02$. The insets provide an expanded-scale view of the first two peaks of these functions.

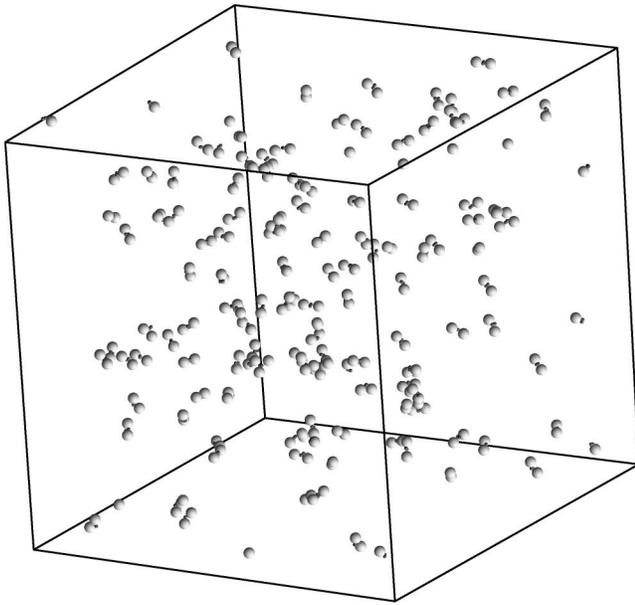


FIG. 5. Typical instantaneous configuration of a 2:1 dumbbell electrolyte ($x = -0.6$, $T^* = 0.06$, $\rho^* = 0.02$).

back to the ground-state energy of two-triplet clusters, which exhibits two distinct minima (Fig. 3). Overall, the ground-state energy of dumbbell clusters (about -0.65 at the minimum) is higher than that of spherical clusters (about -0.93 at the minimum), which explains the lower values of T_c^* in dumbbell systems. The behavior of the critical density of dumbbells is also markedly different from that observed in spherical systems. A maximum in ρ_c^* occurs for size-symmetric electrolytes ($x = 0$), and it decreases quite rapidly when the system becomes size asymmetric. This decrease slows down when x reaches 0.3, where a shoulder can be seen on the positive side of x (Fig. 2). These results raise questions as to how longer, multication “rods” (e.g., 3:1, 4:1, etc.) or polyelectrolytes behave; does the coexistence region disappear? We are currently pursuing phase-equilibria simulations to that end.

Figure 5 shows a typical instantaneous configuration of a dumbbell electrolyte system with $x = -0.6$ at $T^* = 0.06$ and $\rho^* = 0.02$. As expected, almost every cation is associated with two anions, forming a tight, electrically neutral triplet. Unlike 1:1 electrolytes, which tend to form large, linear clusters of several dozen ionic pairs, the charge asymmetry of 2:1 systems gives rise to the formation of more complex multi-ion structures having a branched topology. These branched structures are observed in the spherical (Fig. 3) and dumbbell systems.

The critical parameters of spherical, 2:1 electrolytes have now been determined as a function of size asymmetry. The overall trends observed for the critical temperature

and density are at odds with available theoretical predictions regarding the low-temperature phase behavior of electrolytes. Results for shape-asymmetric, dumbbell 2:1 electrolytes reveal additional, unforeseen features which have not been considered theoretically. In particular, the critical temperatures are substantially lower than for spherical systems, and two maxima arise in T_c^* , at around $x = -0.25$ and at around $x = 0.3$. These results could be of importance in the study of colloidal suspensions and polyelectrolytes. In general, colloidal entities are not spherical and their charge is distributed throughout the particle. Polyelectrolytes, on the other hand, are often modeled as charged rods. While the dumbbells considered here can at best be regarded as colloids or small polyelectrolytes in some highly limiting situations, they do provide interesting preliminary insights into how phase transitions are likely to evolve as we move towards more general, realistic cases.

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- [1] J. W. J. M. Caillol and D. Levesque, *J. Chem. Phys.* **107**, 1565 (1997).
- [2] F. O. Orkoulas and A. Z. Panagiotopoulos, *J. Chem. Phys.* **110**, 1581 (1999).
- [3] Q. L. Yan and J. J. de Pablo, *J. Chem. Phys.* **111**, 9509 (1999).
- [4] J. M. Romero-Enrique, G. Orkoulas, A. Z. Panagiotopoulos, and M. E. Fisher, *Phys. Rev. Lett.* **85**, 4558 (2000).
- [5] Q. L. Yan and J. J. de Pablo, *Phys. Rev. Lett.* **86**, 2054 (2001).
- [6] Q. L. Yan and J. J. de Pablo, *J. Chem. Phys.* **114**, 1727 (2001).
- [7] A. M. Ferrenberg and R. H. Swendsen, *Phys. Rev. Lett.* **61**, 2635 (1988).
- [8] A. M. Ferrenberg and R. H. Swendsen, *Phys. Rev. Lett.* **63**, 1195 (1989).
- [9] A. D. Bruce and N. B. Wilding, *Phys. Rev. Lett.* **68**, 193 (1992).
- [10] N. B. Wilding and A. D. Bruce, *J. Phys. Condens. Matter* **4**, 3087 (1992).
- [11] E. González-Tovar, *Mol. Phys.* **97**, 1203 (1999).
- [12] J. P. Camp and G. N. Patey, *J. Chem. Phys.* **111**, 9000 (1999).
- [13] A. Z. Panagiotopoulos and M. E. Fisher, *Phys. Rev. Lett.* **88**, 045701 (2002).
- [14] A. K. Sabir, L. B. Bhuiyan, and C. W. Outhwaite, *Molec. Phys.* **93**, 405 (1998).
- [15] R. R. Netz and H. Orland, *Europhys. Lett.* **45**, 726 (1999).