Gas-liquid coexistence in asymmetric primitive models of ionic fluids

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Introduction

The study of phase diagrams of ionic systems in which the phase separation is mainly driven by electrostatic forces is of great fundamental interest and of practical importance. Electrolyte solutions, molten salts and ionic liquids are examples of systems with strong Coulomb interactions. The simplest representation of the systems dominated by Coulomb interactions is provided by the so-called primitive models (PMs). The interaction potential of a two-component PM can be presented as

$$U_{\alpha\beta}(r) = \phi^{HS}_{\alpha\beta}(r) + \phi^{C}_{\alpha\beta}(r),$$

where $\phi^{HS}_{\alpha\beta}(r)$ is the interaction potential between the two additive hard spheres (HS) of diameters σ_α and σ_β. $\phi^{C}_{\alpha\beta}(r)$ is the Coulomb potential: $\phi^{C}_{\alpha\beta}(r) = q_\alpha q_\beta/(\varepsilon r)$. The model is characterized by the parameters of size and charge asymmetry:

$$\lambda = \frac{\sigma_+}{\sigma_-}, \qquad z = \frac{q_+}{|q_-|}.$$

The purpose of this work is twofold: first, to determine the dependence of the width of the phase diagrams and the slope of the coexistence-curve diameters on size and charge asymmetry; and second, to analyze the shape of the coexistence curves in terms of the critical exponent β.

Theoretical background

A theoretical background for this study is the statistical field theory that exploits the method of collective variables (CVs) [1]. The theory enables us to derive an exact expression for the functional of grand partition function of the model and on this basis to develop the perturbation theory [1]. The well-known approximations for the free energy, in particular Debye-Hückel limiting law and MSA, can be reproduced within the framework of this theory [2].

We study the gas-liquid phase diagrams of asymmetric PMs using the method proposed in [2]. First, we pass from the initial dimensionless chemical potentials ν_+ and ν_- ($\nu_\alpha = \beta\mu_\alpha$) to their linear combinations

$$\nu_1 = \frac{\nu_+ + z\nu_-}{\sqrt{1+z^2}}, \qquad \nu_2 = \frac{z\nu_+ - \nu_-}{\sqrt{1+z^2}}.$$

Chemical potential ν_1 is conjugate to the order parameter for the gas-liquid phase transition ξ_0:

$$\xi_0 = \frac{1}{\sqrt{1+z^2}}\left(\frac{1+z^2}{1+z}\rho_{0,N} + \frac{1-z}{1+z}\rho_{0,Q}\right),$$

CVs $\rho_{0,N} = \delta\rho_{0,+} + \delta\rho_{0,-}$ and $\rho_{0,Q} = z\delta\rho_{0,+} - \delta\rho_{0,-}$ describe long-wavelength fluctuations of the total number density and charge density respectively. ν_2 is conjugate to $\rho_{0,Q}$.

We derived an explicit expression for the chemical potential conjugate to the order parameter which includes the effects of correlations up to the third order [3]:

$$\nu_1 = \nu_1^0 + \frac{\sqrt{1+z^2}}{2V\left[\mathfrak{M}_{++} + 2z\mathfrak{M}_{+-} + z^2\mathfrak{M}_{--}\right]} \sum_{\mathbf{k}} \frac{1}{\det\left[\underline{1} + \Phi_C\mathfrak{M}_2\right]} \times \left(\beta\tilde{\phi}^C_{++}(k)\mathscr{S}_1 + \beta\tilde{\phi}^C_{--}(k)\mathscr{S}_2 + 2\beta\tilde{\phi}^C_{+-}(k)\mathscr{S}_3\right), \qquad (1)$$

$$\mathscr{S}_1 = \mathfrak{M}_{+++} + z\mathfrak{M}_{++-}, \qquad \mathscr{S}_2 = \mathfrak{M}_{+--} + z\mathfrak{M}_{---}, \qquad \mathscr{S}_3 = \mathfrak{M}_{++-} + z\mathfrak{M}_{+--},$$

ν_1^0 is the mean-field part of the chemical potential, $\tilde{\phi}^C_{\alpha\beta}(k)$ is the Fourier transform of the Coulomb potential $\phi^C_{\alpha\beta}(r)$. The nth cumulant $\mathfrak{M}_{\alpha_1\ldots\alpha_n}$ coincides with the Fourier transform of the n-particle connected correlation function of the two-component HS system [1]. Φ_C and $\mathfrak{M}_2$ are matrices of elements $\beta\tilde{\phi}^C_{\alpha\beta}(k)$ and $\mathfrak{M}_{\alpha\beta}(k)$, respectively. Apart from $\mathfrak{M}_{\alpha_1\alpha_2}$, Eq. (1) includes the third order cumulants.

Based on Eq. (1) supplemented by the Maxwell construction we calculated the coexistence data and the corresponding critical parameters: critical temperature T_c^* ($T^* = k_BT\varepsilon\sigma_\pm/|q_\alpha q_\beta|$) and critical density ρ_c^* ($\rho^* = \rho\sigma_\pm^3$).

In order to determine the asymptotic shape of the coexistence curve we apply the scaling law that uses the leading amplitude term of the Wegner expansion

$$\frac{\rho_l - \rho_g}{2\rho_c} \simeq B|\tau^*|^\beta, \qquad \tau^* = |T - T_c|/T_c \to 0_-.$$

We assume the rectilinear law for the diameter of the coexistence curve

$$\frac{\rho_l + \rho_g}{2\rho_c} = 1 + A|\tau^*|.$$

Results

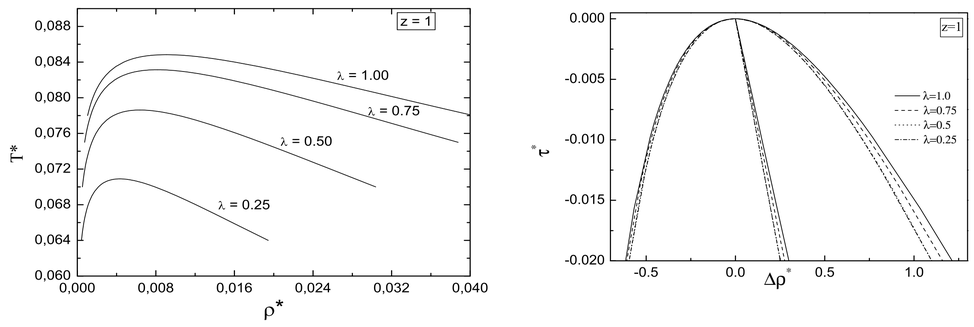

Figure 1: *Phase diagrams for* 1:1 *PMs with different* λ *in the* (T^*, ρ^*)*-plane (left) and in the* $(\tau^*,\Delta\rho^*)$*-plane (right),* $\tau^* = |T - T_c|/T_c$, $\Delta\rho^* = (\rho - \rho_c)/\rho_c$.

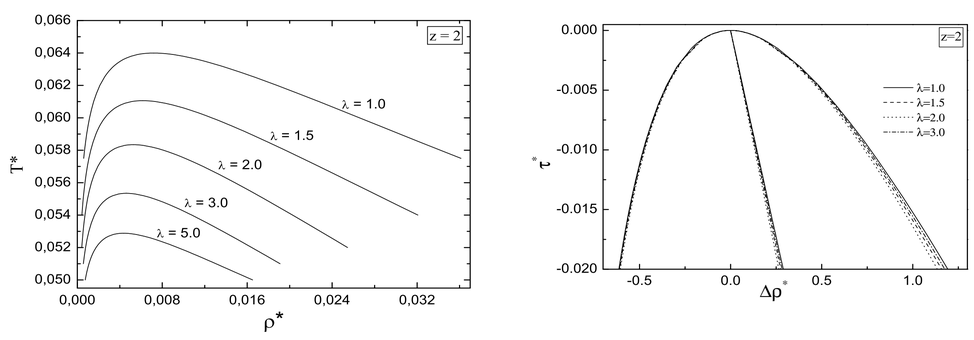

Figure 2: *Same as in Fig. 1 for* 2:1 *PMs.*

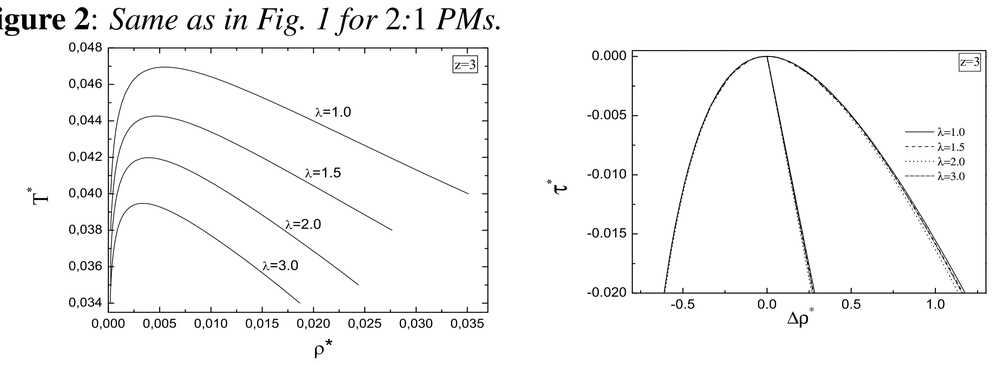

Figure 3: *Same as in Fig. 1 for* 3:1 *PMs.*

Tables: *Critical temperature* T_c^**, critical density* ρ_c^**, slope of the coexistence-curve diameter A, amplitude of the coexistence curve B and critical exponent* β *for* 2:1 *(left) and* 3:1 *(right) PMs at different values of* λ*;* $|\tau^*| < 0.01$.

λ	$10^2T_c^*$	$10^3\rho_c^*$	A	B	β
0.33	5.87	4.58	12.67	5.87	0.501
0.5	6.14	5.45	12.38	5.85	0.502
0.67	6.30	6.19	12.67	5.78	0.498
1	6.40	7.20	14.42	6.26	0.502
1.5	6.11	6.16	13.72	6.03	0.499
2	5.83	5.28	13.25	5.96	0.499
3	5.53	4.61	14.07	6.21	0.502

λ	$10^2T_c^*$	$10^3\rho_c^*$	A	B	β
0.2	4.41	3.80	13.02	5.63	0.489
0.5	4.66	4.67	12.42	5.87	0.503
0.75	4.71	5.11	12.56	6.0	0.504
1	4.70	5.49	14.08	6.18	0.502
1.5	4.43	4.65	13.85	6.15	0.501
2	4.20	3.92	13.31	6.01	0.5
3	3.95	3.35	13.72	6.01	0.497

Summary

- We propose the theory for the study of effects of charge and size asymmetry on the gas-liquid critical point of ionic PMs. The theory allows one to take into account the higher order fluctuation corrections.
- Within the framework of the same approximation we obtain the trends of T_c^* and ρ_c^* with size asymmetry that qualitatively agree with Monte Carlo findings.
- Using the corresponding-state variables we analyze a dependence of the critical amplitude of the coexistence curve and the slope of the coexistence-curve diameter on the ion size ratio at a fixed valence. It is shown that the both characteristics take maximum values in the equisize case and demonstrate a nonmonotonous behavior with λ at $z \geq 2$. Besides, the critical amplitude depends on λ very weakly.
- The approximation considered predicts the mean-field critical behavior for PMs.

References

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[3] O.V. Patsahan and T.M. Patsahan, Phys. Rev. E, **8**1, 031110 (2010).