Gas-liquid critical point in model ionic fluids with charge and size asymmetry

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The phase and critical behaviour of ionic fluids has long been a topic of great interest. A lot of efforts have been made to obtain the phase diagrams and calculate the locus of the gas-liquid (GL) critical point even for the simplest model of ionic fluids, the so-called restricted primitive model, in which monovalent equi-sized hard spheres interact via the Coulomb potential. The studies of the effects of asymmetry on the GL phase diagram of the size- and charge-asymmetric primitive models (PM) have been recently started using both the computer simulations and theoretical methods. Comparison of simulated critical parameters and theoretical predictions has revealed that several established theories, such as the mean spherical approximation are unable to predict the trends observed in simulations, particularly with regards to the decrease of the critical temperature and critical density with increasing size asymmetry [1,2].

We develop the theoretical approach to the study of the GL phase behaviour of the size- and charge-asymmetric PM. The model is characterized by the two parameters: diameter-, $\lambda = \sigma_+/\sigma_-$ and charge, $z = q_+/|q_-|$, ratios of the two ionic species. The approach allows us to derive the exact functional representation of the grand partition function and formulate, on this basis, the perturbation theory. First, we perform the stability analysis in the Gaussian approximation. This leads us to the trends for the critical parameters consistent with [3]. Then, we study the GL critical point of the PM taking into account the correlation effects of higher order. We calculate binodal curves and critical parameters as functions of λ and z and compare our results with those obtained by the theory and computer simulations.

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