

Gas-liquid critical parameters of asymmetric models of ionic fluids

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The effects of size and charge asymmetry on the gas-liquid critical parameters of a primitive model (PM) of ionic fluids are studied within the framework of the statistical field theory based on the collective variables method. Recently, this approach has enabled us to obtain the correct trends of the both critical parameters of the equisize charge-asymmetric PM without assuming ionic association. In this paper, we focus on the general case of an asymmetric PM characterized by the two parameters: hard-sphere diameter, $\lambda = \sigma_+ / \sigma_-$, and charge, $z = q_+ / |q_-|$, ratios of the two ionic species. We derive an explicit expression for the chemical potential conjugate to the order parameter which includes the effects of correlations up to the third order. Based on this expression we consider the three versions of PM: a monovalent size-asymmetric PM ($\lambda \neq 1$, $z = 1$), an equisize charge-asymmetric PM ($\lambda = 1$, $z \neq 1$) and a size- and charge-asymmetric PM ($\lambda \neq 1$, $z \neq 1$). Similar to simulations, our theory predicts that the critical temperature and the critical density decrease with the increase in size asymmetry. Regarding the effects of charge asymmetry, we obtain the correct trend of the critical temperature with z , while the trend of the critical density obtained in this approximation is inconsistent with simulations, as well as with our previous results found in the higher-order approximation. We expect that the consideration of the higher-order correlations will lead to the correct trend of the critical density with charge asymmetry.

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I. INTRODUCTION

It is well-known that electrostatic forces determine the properties of various systems: physical as well as chemical or biological. In particular, the Coulomb interactions are of great importance when dealing with ionic fluids. Ionic fluids include molten salts, electrolyte solutions and ionic liquids. In most cases the Coulomb interaction is the dominant interaction and due to its long-range character it can substantially affect the critical properties and the phase behavior of ionic systems. Thus, the investigations dealing with these issues are of fundamental interest and of practical importance.

Over the last fifteen years, both phase diagrams and the critical behavior of the systems with dominant Coulomb interactions have been intensively studied by simulations and theoretical methods. A theoretical model that demonstrates the phase separation driven exclusively by Coulomb forces is a primitive model (PM). In this model, the ionic fluid is described as an electroneutral mixture of charged hard spheres immersed in a structureless dielectric continuum. The simplest version of the two-component PM, its symmetrical version, is called a restricted primitive model (RPM). A gas-liquid phase transition of the RPM is well established. However, over the years the figures for the critical parameters have changed substantially. Now there is a good agreement between the recent simulations performed by different teams. The estimations turn out to be near $T_c^* \approx 0.049$, $\rho_c^* \approx 0.06-0.08$ when the temperature T_c^* and the density ρ_c^* are in standard dimensionless units [1].

As concerns the theory, several theoretical methods have been proposed in which the ion association is explicitly taken into account. The main of them are the generalized Debye-Hückel (GDH) theory and the associated mean spherical approximation [2]. These theories are based on the addition of the chemical association model of Bjerrum [3] or Ebeling and Grigo [4]. The GDH theory (solvated ion-cluster theory

with hard-core term) yields the following estimations for the critical parameters of the RPM: $T_c^* = 0.0557$ and $\rho_c^* = 0.0261$ [5].

More recently, the study of the phase behavior of size- and charge-asymmetric PMs has been started. The key findings from simulation studies of asymmetric models are as follows: the suitably normalized critical temperatures decrease with size and charge asymmetry while the critical densities increase with charge asymmetry but decrease with size asymmetry [6–14]. Comparison of simulated critical parameters and theoretical predictions for asymmetric models has revealed that several established theories, such as the mean spherical approximation (MSA) and the original DH theory are not capable of predicting the trends observed in simulations [15,18]. Moreover, both the original DH theory and the MSA predict no dependence on charge asymmetry in the equisize case. The exception are the theories mentioned above that include the association effects explicitly [5,16,17]. The trends found from the GDH theory for the critical parameters of an equisize ($z:1$) charge-asymmetric PM as a function of charge asymmetry qualitatively agree with simulation data [5]. As regards the size asymmetry, the extensions of the DH theory for monovalent size-asymmetric PMs that describe the charge-unbalanced “border zones” surrounding each ion lead to the trends of the both critical parameters that qualitatively agree with simulation predictions [18]. However, this is true only for modest size asymmetries. More recently, the study of the effects of size and charge asymmetry on the gas-liquid phase separation has been started within the field-theoretical description in [19]. It is found that only some of the effects of the size and charge asymmetry are correctly predicted at the mean-field (MF) level of the theory. For example, the trend of T_c^* with size asymmetry obtained in this approximation is inconsistent with the predictions of simulations. Summarizing, we can state that even the qualitative theoretical understanding of the issue is not quite appropriate.

In this paper we focus on the issue of the effects of charge and size asymmetry on the gas-liquid critical parameters of PMs. To this end, we use the statistical field theory based on the method of collective variables (CVs) (see [20] and the references herein). The approach allows us to derive the exact functional representation of the grand partition function and formulate, on this basis, the perturbation theory. Links between this approach and the other known theories were established recently [21–23]. We also use the method proposed recently [21] for the study of the gas-liquid phase diagram of equisize charge-asymmetric PMs. The method is based on determining the chemical potential conjugate to the order parameter and allows one to take into account the effects of higher-order correlations. Its application to an equisize ($z:1$) charge-asymmetric PM enabled us to obtain the qualitative agreement of the trends of $T_c^*(z)$ and $\rho_c^*(z)$ with simulation findings [21]. The theory also yields the best theoretical quantitative estimates for the critical parameters of the RPM [24]. Here we study the general case of size- and charge-asymmetric PMs.

The layout of the paper is as follows. In Sec. II, starting with the Hamiltonian of a size- and charge-asymmetric PM we sketch out the main points of the CVs based theory. We analyze the Gaussian approximation of the functional of the grand partition function and determine the CV connected with the order parameter for the gas-liquid phase separation. In Sec. III, we study the gas-liquid critical parameters of asymmetric PMs taking into account the correlation effects of higher order. We consider the three versions of PM: an equisize PM with charge asymmetry; a monovalent PM with size asymmetry; a size- and charge-asymmetric PM. We conclude in Sec. IV.

II. COLLECTIVE VARIABLES BASED THEORY FOR ASYMMETRIC PMS

A. Model

We consider a classical two-component system consisting of N_+ hard spheres of diameter σ_+ carrying a charge $q_+=zq$ and N_- hard spheres of diameter σ_- carrying a charge $q_-=-q$. The ions are immersed in a structureless dielectric medium. The system is electrically neutral: $\sum_{\alpha=+,-} q_\alpha \rho_\alpha = 0$ and $\rho_\alpha = N_\alpha/V$ is the number density of the α th species.

The pair interaction potential is assumed to be of the following form:

$$U_{\alpha\beta}(r) = \phi_{\alpha\beta}^{\text{HS}}(r) + \phi_{\alpha\beta}^C(r), \quad (1)$$

where $\phi_{\alpha\beta}^{\text{HS}}(r)$ is the interaction potential between the two additive hard spheres of diameters σ_α and σ_β . We call the two-component hard sphere system a reference system (RS). Thermodynamic and structural properties of RS are assumed to be known. $\phi_{\alpha\beta}^C(r)$ is the Coulomb potential: $\phi_{\alpha\beta}^C(r) = q_\alpha q_\beta \phi^C(r)$, where $\phi^C(r) = 1/(Dr)$, D is the dielectric constant and hereafter we put $D=1$. The model is characterized by the parameters of size and charge asymmetry

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

The fluid is at equilibrium in the grand canonical ensemble. The grand partition function (GPF) of the model (1) can be written as follows:

$$\Xi[\nu_\alpha] = \sum_{N_+ \geq 0} \sum_{N_- \geq 0} \prod_{\alpha=+,-} \frac{\exp(\nu_\alpha N_\alpha)}{N_\alpha!} \times \int (d\Gamma) \exp \left[-\frac{\beta}{2} \sum_{\alpha\beta} \sum_{ij} U_{\alpha\beta}(r_{ij}) \right],$$

where the following notations are used: ν_α is the dimensionless chemical potential, $\nu_\alpha = \beta \mu_\alpha - 3 \ln \Lambda_\alpha$, μ_α is the chemical potential of the α th species, β is the reciprocal temperature, $\Lambda_\alpha^{-1} = (2\pi m_\alpha \beta^{-1}/h^2)^{1/2}$ is the inverse de Broglie thermal wavelength; $(d\Gamma)$ is the element of configurational space of the particles.

It is worth noting that the regularization of the potential $\phi_{\alpha\beta}^C(r)$ inside the hard core is arbitrary to some extent. For example, different regularizations for the Coulomb potential were considered in [25,26]. Within the framework of the Gaussian approximation of GPF the best estimation for the critical temperature is achieved for the optimized regularization [27] that leads to the optimized random phase approximation (ORPA). However, this approximation does not work properly in the higher orders of the perturbation theory [26]. Here we use the Weeks-Chandler-Andersen (WCA) regularization scheme for $\phi_{\alpha\beta}^C(r)$ [28]

$$\phi_{\alpha\beta}^C(r) = \begin{cases} q_\alpha q_\beta / \sigma_{\alpha\beta}, & r < \sigma_{\alpha\beta} \\ q_\alpha q_\beta / r, & r \geq \sigma_{\alpha\beta}. \end{cases} \quad (2)$$

B. Functional of the GPF of an asymmetric PM: The method of collective variables

Now we use the CVs based theory, developed in [20] for a multicomponent continuous system with short- and long-range interactions in the grand canonical ensemble. As a result, the exact functional representation of the GPF for the PM with the interaction potential (1) can be written in the form

$$\Xi[\nu_\alpha] = \int (d\rho)(d\omega) \exp(-\mathcal{H}[\nu_\alpha; \rho_\alpha, \omega_\alpha]), \quad (3)$$

where the action \mathcal{H} reads as

$$\mathcal{H}[\nu_\alpha; \rho_\alpha, \omega_\alpha] = \frac{\beta}{2V} \sum_{\alpha,\beta} \sum_{\mathbf{k}} \tilde{\phi}_{\alpha\beta}^C(k) \rho_{\mathbf{k},\alpha} \rho_{-\mathbf{k},\beta} - i \sum_{\alpha} \sum_{\mathbf{k}} \omega_{\mathbf{k},\alpha} \rho_{\mathbf{k},\alpha} - \ln \Xi_{\text{HS}}[\bar{\nu}_\alpha - i\omega_\alpha]. \quad (4)$$

Here $\rho_{\mathbf{k},\alpha} = \rho_{\mathbf{k},\alpha}^c - i\rho_{\mathbf{k},\alpha}^s$ is the CV which describes the value of the \mathbf{k} -th fluctuation mode of the number density of the α th species, the indices c and s denote real and imaginary parts of $\rho_{\mathbf{k},\alpha}$. $\omega_{\mathbf{k},\alpha}$ is conjugate to the CV $\rho_{\mathbf{k},\alpha}$ and each of $\rho_{\mathbf{k},\alpha}$ ($\omega_{\mathbf{k},\alpha}$) takes all the real values from $-\infty$ to $+\infty$. $(d\rho)$ and $(d\omega)$ are volume elements of the CV phase space

$$(d\rho) = \prod_{\alpha} d\rho_{0,\alpha} \prod_{\mathbf{k} \neq 0} d\rho_{\mathbf{k},\alpha}^c d\rho_{\mathbf{k},\alpha}^s,$$

$$(d\omega) = \prod_{\alpha} d\omega_{0,\alpha} \prod_{\mathbf{k} \neq 0} d\omega_{\mathbf{k},\alpha}^c d\omega_{\mathbf{k},\alpha}^s,$$

and the product over \mathbf{k} is performed in the upper semispace ($\rho_{-\mathbf{k},\alpha} = \rho_{\mathbf{k},\alpha}^*$, $\omega_{-\mathbf{k},\alpha} = \omega_{\mathbf{k},\alpha}^*$).

$\tilde{\phi}_{\alpha\beta}^C(k)$ is the Fourier transform of the Coulomb potential $\phi_{\alpha\beta}^C(r)$. In the case of the WCA regularization [see Eq. (2)] we obtain for $\beta\tilde{\phi}_{\alpha\beta}^C(k)$

$$\beta\tilde{\phi}_{++}^C(k) = \frac{4\pi z\sigma_{\pm}^3}{T^*(1+\delta)} \frac{\sin[x(1+\delta)]}{x^3}, \quad (5)$$

$$\beta\tilde{\phi}_{--}^C(k) = \frac{4\pi\sigma_{\pm}^3}{T^*z(1-\delta)} \frac{\sin[x(1-\delta)]}{x^3}, \quad (6)$$

$$\beta\tilde{\phi}_{+-}^C(k) = -\frac{4\pi\sigma_{\pm}^3}{T^*} \frac{\sin(x)}{x^3}, \quad (7)$$

where the following notations are introduced:

$$T^* = \frac{k_B T \sigma_{\pm}}{q^2 z}, \quad (8)$$

is the dimensionless temperature,

$$\delta = \frac{\lambda - 1}{\lambda + 1}, \quad (9)$$

and $x = k\sigma_{\pm}$, $\sigma_{\pm} = (\sigma_+ + \sigma_-)/2$.

$\Xi_{\text{HS}}[\bar{\nu}_{\alpha} - i\bar{\omega}_{\alpha}]$ is the GPF of a two-component hard-sphere system with the renormalized chemical potential

$$\bar{\nu}_{\alpha} = \nu_{\alpha} + \frac{\beta}{2V} \sum_{\mathbf{k}} \tilde{\phi}_{\alpha\alpha}^C(k),$$

in the presence of the local field $-i\omega_{\alpha}(r)$.

In order to formulate the perturbation theory we present the CVs in the following form:

$$\rho_{\mathbf{k},\alpha} = \bar{\rho}_{\alpha} \delta_{\mathbf{k}} + \delta\rho_{\mathbf{k},\alpha}, \quad \omega_{\mathbf{k},\alpha} = \bar{\omega}_{\alpha} \delta_{\mathbf{k}} + \delta\omega_{\mathbf{k},\alpha},$$

where the MF values $\bar{\rho}_{\alpha}$ and $\bar{\omega}_{\alpha}$ are the solutions of the saddle-point equations.

Then we present $\ln \Xi_{\text{HS}}[\bar{\nu}_{\alpha} - i\bar{\omega}_{\alpha}]$ in Eq. (4) in the form of the cumulant expansion

$$\begin{aligned} \ln \Xi_{\text{HS}}[\dots] = & \sum_{n \geq 0} \frac{(-i)^n}{n!} \sum_{\alpha_1, \dots, \alpha_n} \sum_{\mathbf{k}_1, \dots, \mathbf{k}_n} \mathfrak{M}_{\alpha_1, \dots, \alpha_n}(\bar{\nu}_{\alpha} \\ & - i\bar{\omega}_{\alpha}; k_1, \dots, k_n) \delta\omega_{\mathbf{k}_1, \alpha_1} \dots \delta\omega_{\mathbf{k}_n, \alpha_n} \\ & \times \delta_{\mathbf{k}_1 + \dots + \mathbf{k}_n}, \end{aligned} \quad (10)$$

with $\mathfrak{M}_{\alpha_1, \dots, \alpha_n}(\bar{\nu}_{\alpha} - i\bar{\omega}_{\alpha}; k_1, \dots, k_n)$ being the n th cumulant defined by

$$\begin{aligned} \mathfrak{M}_{\alpha_1, \dots, \alpha_n}(\bar{\nu}_{\alpha} - i\bar{\omega}_{\alpha}; k_1, \dots, k_n) \\ = \frac{\partial^n \ln \Xi_{\text{HS}}[\dots]}{\partial \delta\omega_{\mathbf{k}_1, \alpha_1} \dots \partial \delta\omega_{\mathbf{k}_n, \alpha_n}} \Big|_{\delta\omega_{\mathbf{k}_i, \alpha_i} = 0}. \end{aligned} \quad (11)$$

The n th cumulant $\mathfrak{M}_{\alpha_1, \dots, \alpha_n}$ coincides with the Fourier transform of the n -partical connected correlation function of the RS [20]. $\delta_{\mathbf{k}_1 + \dots + \mathbf{k}_n}$ is the Kronecker symbol. The n th cumulant depends on both the wave vectors \mathbf{k}_i and the partial chemical potentials $\bar{\nu}_{\alpha} - i\bar{\omega}_{\alpha}$.

Using Eqs. (10) and (11) we can rewrite Eqs. (3) and (4) as follows:

$$\begin{aligned} \Xi[\nu_{\alpha}] = & \Xi_{\text{MF}}[\bar{\nu}_{\alpha} - i\bar{\omega}_{\alpha}] \\ & \times \int (d\delta\rho) \exp \left\{ -\frac{\beta}{2V} \sum_{\alpha, \beta} \sum_{\mathbf{k}} \tilde{\phi}_{\alpha\beta}^C(k) \delta\rho_{\mathbf{k},\alpha} \delta\rho_{-\mathbf{k},\beta} \right. \\ & + i \sum_{\alpha} \sum_{\mathbf{k}} \delta\omega_{\mathbf{k},\alpha} \delta\rho_{\mathbf{k},\alpha} \\ & + \sum_{n \geq 2} \frac{(-i)^n}{n!} \sum_{\alpha_1, \dots, \alpha_n} \sum_{\mathbf{k}_1, \dots, \mathbf{k}_n} \mathfrak{M}_{\alpha_1, \dots, \alpha_n}(\bar{\nu}_{\alpha} \\ & \left. - i\bar{\omega}_{\alpha}; k_1, \dots, k_n) \times \delta\omega_{\mathbf{k}_1, \alpha_1} \dots \delta\omega_{\mathbf{k}_n, \alpha_n} \delta_{\mathbf{k}_1 + \dots + \mathbf{k}_n} \right\}, \end{aligned} \quad (12)$$

where Ξ_{MF} is the GPF of the model in the MF approximation.

(a) *Gaussian approximation.* Now we consider the Gaussian approximation of $\Xi[\nu_{\alpha}]$ setting $\mathfrak{M}_{\alpha_1, \dots, \alpha_n} \equiv 0$ for $n \geq 3$. Then, after integration in Eq. (12) over $\delta\omega_{\mathbf{k},\alpha}$ we obtain

$$\begin{aligned} \Xi_G[\nu_{\alpha}] = & \Xi_{\text{MF}}[\bar{\nu}_{\alpha} - i\bar{\omega}_{\alpha}] \Xi' \\ & \times \int (d\delta\rho) \exp \left\{ -\frac{1}{2} \sum_{\alpha, \beta} \sum_{\mathbf{k}} \tilde{\mathcal{C}}_{\alpha\beta}(k) \delta\rho_{\mathbf{k},\alpha} \delta\rho_{-\mathbf{k},\beta} \right\}, \end{aligned} \quad (13)$$

where $\tilde{\mathcal{C}}_{\alpha\beta}(k)$ is the Fourier transform of the two-particle direct correlation function in the Gaussian approximation

$$\tilde{\mathcal{C}}_{\alpha\beta}(k) = \frac{\beta}{V} \tilde{\phi}_{\alpha\beta}^C(k) + \frac{1}{\sqrt{N_{\alpha} N_{\beta}}} \tilde{\mathcal{C}}_{\alpha\beta}^{\text{HS}}(k). \quad (14)$$

$\tilde{\mathcal{C}}_{\alpha\beta}^{\text{HS}}(k)$ is the Fourier transform of the direct correlation function of a two-component hard-sphere system. It is connected with $\mathfrak{M}_{\alpha\beta}(k)$ by the relation

$$\tilde{\mathcal{C}}_2^{\text{HS}}(k) \mathfrak{M}_2(k) = \mathbf{1}, \quad (15)$$

where $\tilde{\mathcal{C}}_2^{\text{HS}}(k)$ denotes the matrix of elements $\tilde{\mathcal{C}}_{\alpha\beta}^{\text{HS}}(k) / \sqrt{N_{\alpha} N_{\beta}}$ and \mathfrak{M}_2 the matrix of elements $\mathfrak{M}_{\alpha\beta}(k)$. $\mathbf{1}$ is the unit matrix.

It should be noted that $\tilde{\mathcal{C}}_{\alpha\beta}(k)$ is connected to the ordinary direct correlation function $\tilde{c}_{\alpha\beta}(k)$ by [29]

$$\tilde{\mathcal{C}}_{\alpha\beta}(k) = \frac{\delta_{\alpha\beta}}{\langle \rho_{\alpha} \rangle} - \tilde{c}_{\alpha\beta}(k),$$

where $\rho_{\alpha} = \langle N_{\alpha} \rangle / V$.

In order to determine the CV connected with the order parameter, we follow the ideas of [19,30] and introduce independent collective excitations by means of the orthogonal transformation

$$\begin{aligned}\delta\rho_{\mathbf{k},+} &= A(k)\xi_{\mathbf{k},1} + C(k)\xi_{\mathbf{k},2}, \\ \delta\rho_{\mathbf{k},-} &= B(k)\xi_{\mathbf{k},1} + D(k)\xi_{\mathbf{k},2}.\end{aligned}\quad (16)$$

The explicit form of coefficients $A(k)$, $B(k)$, $C(k)$, and $D(k)$ are given in Appendix. As a result, Eq. (13) is rewritten as

$$\begin{aligned}\Xi_G[\nu_\alpha] &= \Xi_{\text{MF}}[\bar{\nu}_\alpha - i\bar{\omega}_\alpha]\Xi' \\ &\times \int (d\xi) \exp\left\{-\frac{1}{2} \sum_{\alpha=1,2} \sum_{\mathbf{k}} \tilde{\varepsilon}_\alpha(k) \xi_{\mathbf{k},\alpha} \xi_{-\mathbf{k},\alpha}\right\},\end{aligned}\quad (17)$$

where eigenvalues $\tilde{\varepsilon}_1(k)$ and $\tilde{\varepsilon}_2(k)$ are found to be

$$\begin{aligned}\tilde{\varepsilon}_{1,2}(k) &= \frac{1}{2}(\tilde{C}_{++}(k) + \tilde{C}_{--}(k) \pm \{[\tilde{C}_{++}(k) - \tilde{C}_{--}(k)]^2 \\ &+ 4\tilde{C}_{+-}^2(k)\}^{1/2}).\end{aligned}\quad (18)$$

Here we are interested in the gas-liquid critical point. Thus, we are now in a position to study Eqs. (16) and (18) in the long-wavelength limit. In this case Eq. (16) has the form

$$\begin{aligned}\delta\rho_{0,+} &= \frac{z}{\sqrt{1+z^2}}\xi_{0,1} + \frac{1}{\sqrt{1+z^2}}\xi_{0,2}, \\ \delta\rho_{0,-} &= -\frac{1}{\sqrt{1+z^2}}\xi_{0,1} + \frac{z}{\sqrt{1+z^2}}\xi_{0,2},\end{aligned}\quad (19)$$

which in turn leads to the relations

$$\begin{aligned}\xi_{0,1} &= \frac{1}{\sqrt{1+z^2}}(z\delta\rho_{0,+} - \delta\rho_{0,-}), \\ \xi_{0,2} &= \frac{1}{\sqrt{1+z^2}}(\delta\rho_{0,+} + z\delta\rho_{0,-}).\end{aligned}\quad (20)$$

Introducing CVs $\rho_{0,N} = \delta\rho_{0,+} + \delta\rho_{0,-}$ and $\rho_{0,Q} = z\delta\rho_{0,+} - \delta\rho_{0,-}$ that describe long-wavelength fluctuations of the total number density and charge density, respectively, we can rewrite Eq. (20) in the form

$$\begin{aligned}\xi_{0,1} &= \frac{1}{\sqrt{1+z^2}}\rho_{0,Q}, \\ \xi_{0,2} &= \frac{1}{\sqrt{1+z^2}}\left(\frac{1+z^2}{1+z}\rho_{0,N} + \frac{1-z}{1+z}\rho_{0,Q}\right).\end{aligned}\quad (21)$$

As is seen, CV $\xi_{0,1}$ describes fluctuations of the charge density. In the general case $z \neq 1$, $\xi_{0,2}$ is a linear combination of CVs $\rho_{0,N}$ and $\rho_{0,Q}$ with the z -dependent coefficients. At $z = 1$, CV $\xi_{0,2}$ describes solely fluctuations of the total number density. Thus, we suggest that CV $\xi_{0,2}$ is connected with the order parameter of the gas-liquid critical point.

At $k=0$ one finds that

$$\tilde{\varepsilon}_1(k=0) = \infty, \quad (22)$$

$$\begin{aligned}\tilde{\varepsilon}_2(k=0) &= \frac{1+z}{1+z^2} \left(-\frac{4\pi\rho^*z\delta^2}{3T^*(1+z)} + \tilde{c}_{++}^{\text{HS}}(0) + 2\sqrt{z}\tilde{c}_{+-}^{\text{HS}}(0) \right. \\ &\quad \left. + z\tilde{c}_{--}^{\text{HS}}(0) \right),\end{aligned}\quad (23)$$

where T^* and δ are given by Eqs. (8) and (9) and $\rho^* = \rho\sigma_\pm^3$ is a reduced total number density.

Equation (22) leads to

$$\tilde{G}_{QQ}(k=0) = 0, \quad (24)$$

where $\tilde{G}_{QQ}(k=0)$ is the Fourier transformation of the charge-charge connected correlation function; Eq. (24) reflects the fact that the first moment Stillinger-Lovett rule is satisfied in the Gaussian approximation.

At $\delta=0$, $\tilde{\varepsilon}_2(k=0)$ reduces to the form

$$\tilde{\varepsilon}_2(\delta=0; k=0) = \frac{(1+z)^2}{1+z^2} \frac{1}{S_2(0)},$$

where $S_2(0)$ is the two-particle structure factor of a one-component hard-sphere system at $k=0$. In the Percus-Yevick (PY) approximation [29]

$$S_2(0) = \frac{(1-\eta)^4}{(1+2\eta)^2}, \quad (25)$$

where $\eta = \frac{\pi}{6}\rho\sigma^3$ is the packing fraction. It is worth noting that $\tilde{\varepsilon}_2(\delta=0; k=0)$ takes only positive values. It suggests that in the size-symmetric case no phase separation between two uniform phases can be found at the Gaussian level of the description.

Equation $\tilde{\varepsilon}_2(\delta \neq 0; k=0) = 0$ leads to the gas-liquid spinodal curve in the Gaussian approximation

$$T_s^* = \frac{4\pi\rho^*\delta^2}{3(1+z)} [\tilde{c}_{++}^{\text{HS}}(0)/z + 2\tilde{c}_{+-}^{\text{HS}}(0)/\sqrt{z} + \tilde{c}_{--}^{\text{HS}}(0)]^{-1}. \quad (26)$$

Eqs. (19)–(26) are analogous to those obtained in [19] but for another type of the regularization of the Coulomb potential inside the hard core. The trends of the critical parameters calculated from the maximum point of spinodal (26) are consistent with the corresponding trends found in [19]: at the fixed z the critical temperature T_c^* is a convex down function of δ while the critical density $\rho^*(\delta)$ is a convex up in δ ; both T_c^* and ρ^* increase at a given $\delta > 0$ and decrease at a given $\delta < 0$ when z increases. Therefore, only some of the trends are correctly predicted within the framework of this approximation. In order to properly describe the effects of size and charge asymmetry on the critical parameters one should take into account the terms of the higher order than the second order in the functional Hamiltonian (12). We consider this task below.

III. CRITICAL PARAMETERS OF ASYMMETRIC PMS: BEYOND THE GAUSSIAN APPROXIMATION

In order to study the gas-liquid critical points of asymmetric PMs we use the method proposed in [21]. First we pass

from the initial chemical potentials ν_+ and ν_- to their linear combinations

$$\nu_1 = \frac{z\nu_+ - \nu_-}{\sqrt{1+z^2}}, \quad \nu_2 = \frac{\nu_+ + z\nu_-}{\sqrt{1+z^2}}. \quad (27)$$

Chemical potentials ν_1 and ν_2 are conjugate to CVs $\xi_{0,1}$ and $\xi_{0,2}$, respectively. Since we suggest that CV $\xi_{0,2}$ is connected with the order parameter, ν_2 appears to be of special interest in our study.

Following the ideas of [21] we start with the logarithm of GPF in the Gaussian approximation (28)

$$\ln \Xi_G[\nu_\alpha] = \ln \Xi_{\text{HS}}[\bar{\nu}_\alpha] - \frac{1}{2} \sum_{\mathbf{k}} \ln \det[1 + \Phi_C \mathfrak{M}_2], \quad (28)$$

where Φ_C and \mathfrak{M}_2 are matrices of elements $\beta\tilde{\phi}_{\alpha\beta}^C(k)$ and $\mathfrak{M}_{\alpha\beta}(\bar{\nu}_\alpha; k)$, respectively.

We approximate cumulants $\mathfrak{M}_{\alpha\beta}(k)$ by their values in the long-wavelength limit putting $\mathfrak{M}_{\alpha\beta}(k) = \mathfrak{M}_{\alpha\beta}(k=0) = \mathfrak{M}_{\alpha\beta}$. If it is remembered that $\ln \Xi_{\text{HS}}$ and $\mathfrak{M}_{\alpha_1\alpha_2\dots\alpha_n}$ are functions of the full chemical potentials we can present ν_1 and ν_2 as

$$\nu_1 = \nu_1^0 + \lambda^0 \Delta \nu_1, \quad \nu_2 = \nu_2^0 + \lambda^0 \Delta \nu_2,$$

with ν_1^0 and ν_2^0 being the MF values of ν_1 and ν_2 , respectively, and $\Delta \nu_1$ and $\Delta \nu_2$ being the solutions of the equations

$$\frac{\partial \ln \Xi_G(\nu_1, \nu_2)}{\partial \Delta \nu_1} = 0, \quad (29)$$

$$\frac{\partial \ln \Xi_G(\nu_1, \nu_2)}{\partial \Delta \nu_2} = \lambda^0 (\langle N_+ \rangle_{\text{HS}} + z \langle N_- \rangle_{\text{HS}}). \quad (30)$$

We self-consistently solve Eqs. (29) and (30) for the relevant chemical potential $\Delta \nu_2$ by means of successive approximations keeping terms of a certain order in parameter λ^0 [21]. To this end, we expand Eq. (28) in powers of $\Delta \nu_1$ and $\Delta \nu_2$

$$\ln \Xi_G(\nu_1, \nu_2) = \sum_{n=0}^{\infty} \sum_{i_n \geq 0} C_n^{i_n} \frac{\mathcal{M}_n^{(i_n)}(\nu_1^0, \nu_2^0)}{n!} \Delta \nu_1^{n-i_n} \Delta \nu_2^{i_n}, \quad (31)$$

where

$$\mathcal{M}_n^{(i_n)}(\nu_1^0, \nu_2^0) = \left. \frac{\partial^n \ln \Xi_G(\nu_1, \nu_2)}{\partial \Delta \nu_1^{n-i_n} \partial \Delta \nu_2^{i_n}} \right|_{\Delta \nu_1=0, \Delta \nu_2=0}.$$

The first nontrivial approximation corresponding to $\Delta \nu_1=0$ yields the following expression for $\Delta \nu_2$

$$\Delta \nu_2 = \frac{\sqrt{1+z^2}}{2V[\mathfrak{M}_{++} + 2z\mathfrak{M}_{+-} + z^2\mathfrak{M}_{--}]} \sum_{\mathbf{k}} \frac{1}{\det[1 + \Phi_C \mathfrak{M}_2]} (\beta\tilde{\phi}_{++}^C(k) \mathcal{S}_1 + \beta\tilde{\phi}_{--}^C(k) \mathcal{S}_2 + 2\beta\tilde{\phi}_{+-}^C(k) \mathcal{S}_3), \quad (32)$$

where

$$\mathcal{S}_1 = \mathfrak{M}_{+++} + z\mathfrak{M}_{++-}, \quad \mathcal{S}_2 = \mathfrak{M}_{+--} + z\mathfrak{M}_{-}, \quad \mathcal{S}_3 = \mathfrak{M}_{+-} + z\mathfrak{M}_{+--}. \quad (33)$$

Apart from $\mathfrak{M}_{\alpha_1\alpha_2}$, formulas (32) and (33) include the third-order cumulants $\mathfrak{M}_{\alpha_1\alpha_2\alpha_3}$ or equivalently the third order connected correlation functions of the RS.

Finally, we can write the full chemical potential ν_2 in the form

$$\nu_2 = \nu_2^{\text{HS}} + \nu_2^{\text{S}} + \Delta \nu_2, \quad (34)$$

where

$$\nu_2^{\text{HS}} = \frac{\nu_+^{\text{HS}} + z\nu_-^{\text{HS}}}{\sqrt{1+z^2}}, \quad (35)$$

with ν_+^{HS} (ν_-^{HS}) being the hard-sphere chemical potential of the α th species and ν_2^{S} being the combination of the self-energy parts of chemical potentials ν_+ and ν_-

$$\nu_2^{\text{S}} = - \frac{1}{2V\sqrt{1+z^2}} \sum_{\mathbf{k}} [\beta\tilde{\phi}_{++}^C(k) + z\beta\tilde{\phi}_{--}^C(k)]. \quad (36)$$

Now some comments are in order:

(i) Here we consider the two-component hard-sphere system as a RS. In this case the analytical expressions for second order cumulants $\mathfrak{M}_{\alpha_1\alpha_2}$ can be obtained in the PY approximation using the Lebowitz' solution [31,32]. The corresponding formulas for $\mathfrak{M}_{\alpha_1\alpha_2}(k=0)$ are given in Appendix.

(ii) In order to derive the expressions for the third-order cumulants one can use the recurrent relation

$$\mathfrak{M}_{\alpha_1\alpha_2\dots\alpha_n} = \mathfrak{M}_{\alpha_1\alpha_2\dots\alpha_n}(0, \dots) = \frac{\partial \mathfrak{M}_{\alpha_1\alpha_2\dots\alpha_{n-1}}(0, \dots)}{\partial \nu_{\alpha_n}^0}, \quad (37)$$

where $\nu_{\alpha_i}^0$ is the MF value of chemical potential ν_{α_i} which due to the electroneutrality condition coincides with the hard-sphere chemical potential of the α_i th species.

Formulas (32)–(36) will be used for the study of the gas-liquid phase equilibria in asymmetric PMs. Below we consider some particular cases.

TABLE I. Critical parameters $T_c^* = k_B T \sigma_{\pm} / q^2$ and $\rho_c^* = \rho_c \sigma_{\pm}^3$ of the monovalent PM for different values of λ .

λ	T_c^*	$10^2 \rho_c^*$
1.0	0.0848	0.907
0.75	0.0831	0.816
0.5	0.0786	0.637
0.25	0.0709	0.433
0.1	0.0586	0.195

A. Monovalent PMs with size asymmetry

First we consider a monovalent PM with size asymmetry corresponding to $z=1$ and $\lambda \neq 1$. Because of symmetry with respect to the exchange of + and - ions, only $\lambda < 1$ (or $\lambda > 1$) need be considered in this case.

We put $z=1$ in Eqs. (32)–(36) and consider the PY approximation for the thermodynamic and structural functions of the two-component hard sphere system [31,32]. For cumulants $\mathfrak{M}_{\alpha_1 \alpha_2}$ and $\mathfrak{M}_{\alpha_1 \alpha_2 \alpha_3}$ we use formulas (43)–(58) from Appendix. The Fourier transforms of the interaction potentials are given by Eqs. (5)–(7).

The explicit expressions for ν_2^{HS} and ν_2^{S} are obtained using the results of Ref. [32] supplemented by the electroneutrality condition. They are given in Appendix.

Based on the expressions (32)–(36) (at $z=1$) supplemented by the Maxwell construction we calculate the coexistence curves and the corresponding critical parameters for different values of λ . Estimates of the critical point values of T_c^* and ρ_c^* are given by their values for which the maxima and minima of the van der Waals loops coalesce. The estimated values of the critical parameters are presented in Table I.

Figures 1 and 2 demonstrate the effects of size asymmetry on the critical parameters of the monovalent PM. In Fig. 1 the critical temperature T_c^* depending on λ is shown by the solid circles for λ ranging from 0.1 to 1. As is seen, a quali-

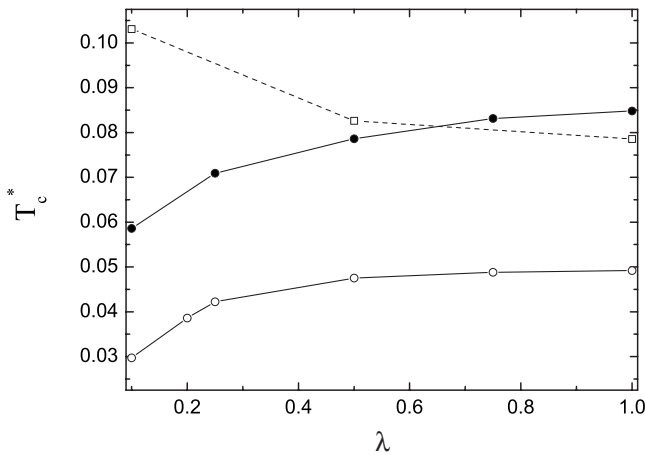


FIG. 1. Critical temperature T_c^* of the monovalent PM as a function of size asymmetry. Open circles correspond to the results of simulations [9]; open squares are MSA results via the energy route [15] and solid circles correspond to the results of the CV based theory.

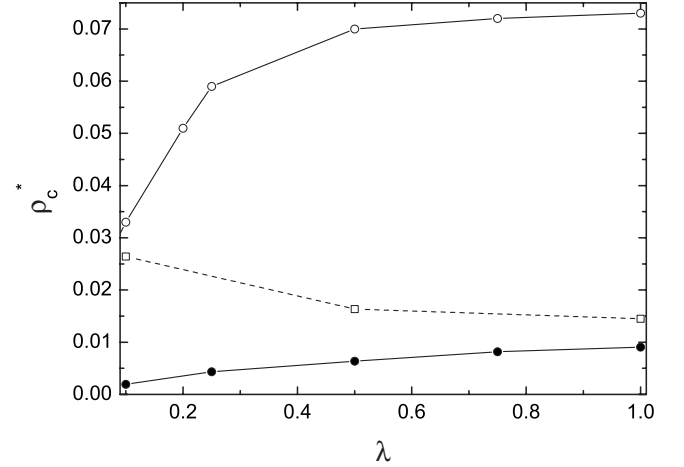


FIG. 2. Critical density ρ_c^* of the monovalent PM as a function of size asymmetry. The meaning of the symbols is the same as in Fig. 1.

tative agreement with the simulation data shown by the open circles is obtained. The results obtained in the MSA are shown by the open squares. In Fig. 2 the dependence of the critical density ρ_c^* on λ is shown. Similar to the computer simulation findings our results indicate a decrease in the critical density with the increase in λ but the figures obtained in this approximation turn out to be too small.

It should be noted that the RPM limit turns out to be a special case. When $z=\lambda=1$ expression (32) reduces to the form that corresponds to the random phase approximation (RPA) [21].

B. Equisize PMs with charge asymmetry

Another particular case is an equisize PM with charge asymmetry corresponding to $\lambda=1$ and $z \neq 1$. At $\lambda=1$ ($\delta=0$) the expression

$$\beta \tilde{\phi}_{++}^C(k) S_1 + \beta \tilde{\phi}_{--}^C(k) S_2 + 2\beta \tilde{\phi}_{+-}^C(k) S_3,$$

entering Eq. (32) reduces to the form [see Eqs. (5)–(7), (32), and (33) and the formulas in Appendix]:

$$-\frac{\sin(x)}{T^* x^3} [(1-z)^2 - (1+z^2) S_2(0)], \quad (38)$$

where the dimensionless temperature T^* is given by Eq. (8) under condition $\sigma_{\pm} = \sigma$. $S_2(0)$ is given by Eq. (25).

As a result, Eqs. (32)–(36) read as

$$\Delta \nu_2 = \frac{1+z}{\sqrt{1+z^2}} \frac{i_1}{\pi} \left(1 - \frac{(1-z^3)(1-z)}{z(1-z)^2 + (1+z^2)^2 S_2(0)} \right), \quad (39)$$

$$\nu_2^{\text{HS}} = \frac{(1+z)}{\sqrt{1+z^2}} \nu_2^{\text{HS}}, \quad \nu_2^{\text{S}} = -\frac{1+z}{\sqrt{1+z^2}} \frac{1}{2T^*}, \quad (40)$$

where i_1 under conditions (2) is reduced to the form

$$i_1 = \frac{1}{T^*} \int_0^{\infty} dx \frac{x^2 \sin(x)}{x^3 + \kappa^{*2} \sin(x)}, \quad (41)$$

$\kappa^* = \kappa_D \sigma$, κ_D is the Debye number.

TABLE II. Critical parameters of the equisize PM with charge asymmetry for different values of λ .

z	T_c^*	$10^2 \rho_c^*$
1	0.0848	0.907
2	0.0640	0.720
3	0.0469	0.549

In the PY approximation ν^{HS} is as follows

$$\nu^{\text{HS}} = \ln(\eta) + \ln(1 - \eta) + \frac{z}{1+z} \ln(z) - \ln(1+z) + \frac{\eta(14 - 13\eta + 5\eta^2)}{2(1-\eta)^3}.$$

Taking into account only the first term in Eq. (39) we arrive at the expression for the chemical potential ν_2 in the RPA. As is seen from Eq. (41), $\Delta\nu_2$ does not include the factor of charge asymmetry explicitly in this case. The second term is the correction to the RPA resulting from the consideration of the higher-order correlation effects, namely the third order. It should be noted that Eq. (39) is obtained in the approximation which is different from that considered in [21] (our notation $\Delta\nu_2$ corresponds to $\Delta\nu_N$ in [21]). In particular, the corresponding formula in [21] (Eq. (31) in [21]) includes the third and fourth order cumulants.

Putting $z=1$ in Eqs. (39)–(41) we arrive at the chemical potential of the RPM in the RPA

$$\nu_2 = \sqrt{2} \left(\nu^{\text{HS}} - \frac{1}{2T^*} + \frac{i_1}{\pi} \right), \quad (42)$$

which reflects the fact of a special symmetry of this model. In order to go beyond the RPA, the higher-order correlations should be taken into account as it was done in [24].

Based on Eqs. (39)–(41) we calculate the coexistence curves and the corresponding critical parameters for different values of z . The values of the critical parameters T_c^* and ρ_c^* for different z are shown in Table II.

Figures 3 and 4 show trends of $T_c^*(z)$ and $\rho_c^*(z)$ obtained from Eqs. (39)–(41), together with simulation data [6,14]. The results of [21] are added for comparison. It should be noted that the Carnahan-Starling approximation for the hard-sphere system was used in [21]. The critical parameters of the RPM obtained within the framework of this theory but in the higher-order approximation are shown by the solid squares ($T_c^*=0.0503$, $\rho_c^*=0.042$) [24].

As in [21], the trend of $T_c^*(z)$ obtained from Eqs. (39)–(41) qualitatively agrees with simulation findings. Moreover, now the numerical values of T_c are much closer to the simulation data than those found previously. On the other hand, the trend of $\rho_c^*(z)$ found from Eqs. (39)–(41) is inconsistent with the simulations. It follows from [21] that the correlation effects of the higher order than the third order should be taken into account in order to get the correct trend of the critical density.

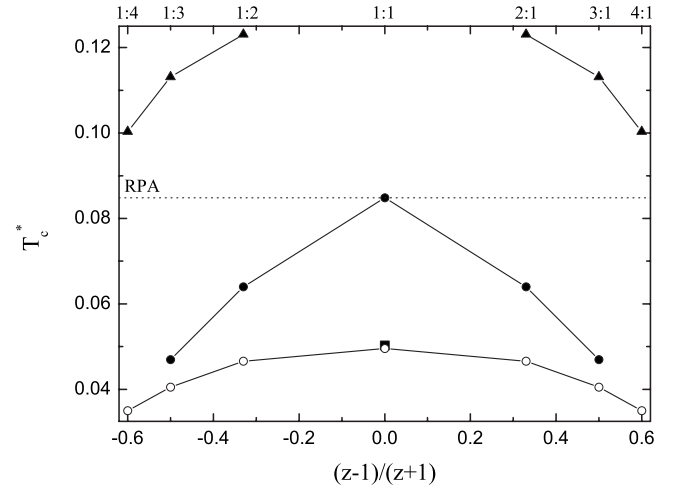


FIG. 3. Dependence of the critical temperature on charge asymmetry for equisize PMs. Solid symbols correspond to the results of the CV based theory: circles are the results based on Eqs. (39)–(41), triangles are the results from [21] and \blacksquare is for RPM [24]. Open circles are the results of simulations: $z=1$ [12], $z=2-3$ [14], and $z=4$ [6]. The dotted line is the result from the RPA.

C. PMs with size and charge asymmetry

Now we use formulas (32)–(36) for the study of the size- and charge-asymmetric PMs with $z=2$ and $\lambda \neq 1$. As before, in order to calculate the coexistence curves and the corresponding critical parameters at different values of λ we apply the Maxwell construction. Our results for the critical parameters T_c^* and ρ_c^* are given in Table III. As is seen, both the critical temperature and the critical density decrease with the increase in size asymmetry.

The dependence of the critical parameters on the size asymmetry is shown graphically in Figs. 5 and 6, respectively, along with the results of simulations [10]. In general, the trends of T_c^* and ρ_c^* with δ are consistent with the simulation findings: 2:1 systems exhibit a maximum in both the critical temperature and the critical density when plotted as a function of size asymmetry. Similar to simulations, our re-

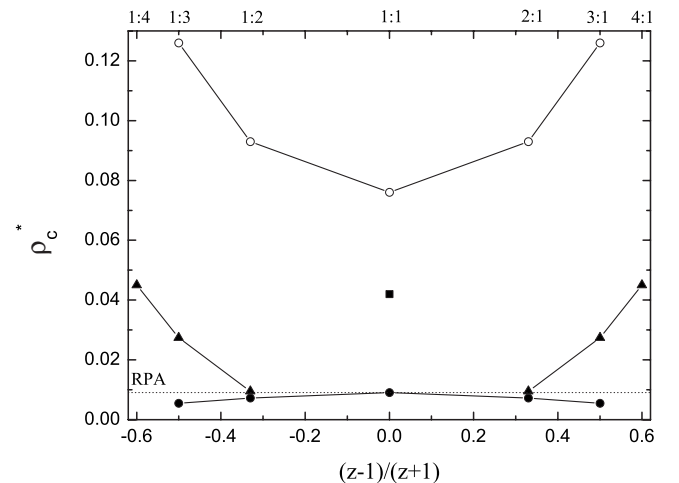


FIG. 4. Dependence of the critical density $\rho^* = \rho\sigma^3$ on charge asymmetry. The meaning of the symbols is the same as in Fig. 4.

TABLE III. Critical parameters of the (2:1) PM for different values of δ [$\delta=(\lambda-1)/(\lambda+1)$].

δ	T_c^*	$10^2 \rho_c^*$
-0.67	0.054	0.319
-0.5	0.0587	0.458
-0.33	0.0614	0.545
-0.2	0.0630	0.619
0	0.0640	0.720
0.2	0.0611	0.616
0.33	0.0583	0.528
0.5	0.0553	0.461
0.67	0.0529	0.436

sults (especially the critical temperature) reveal a pronounced sensitivity to δ . However, both the critical temperature and the critical density found from Eqs. (32)–(36) demonstrate maxima at $\delta=0$ ($\lambda=1$) while the corresponding maxima obtained by simulations are shifted towards nonzero values of δ ($\delta>0$). Interestingly, $\rho_c^*(\delta)$ demonstrates the general shape similar to that obtained for the dumbbell system. As before, our values of the critical density are more than an order of magnitude lower than those found in the simulations [10].

IV. CONCLUSIONS

In this paper, we have studied the effects of size and charge asymmetry on the gas-liquid critical parameters of two-component PMs using the CV based theory. The theory allows one to take into consideration the effects of higher-order correlations. On the other hand, the well-known approximations for the free energy, in particular the Debye-Hückel limiting law and ORPA, can be reproduced within the framework of this theory. Recently, this approach has been used for the study of the effects of charge asymmetry

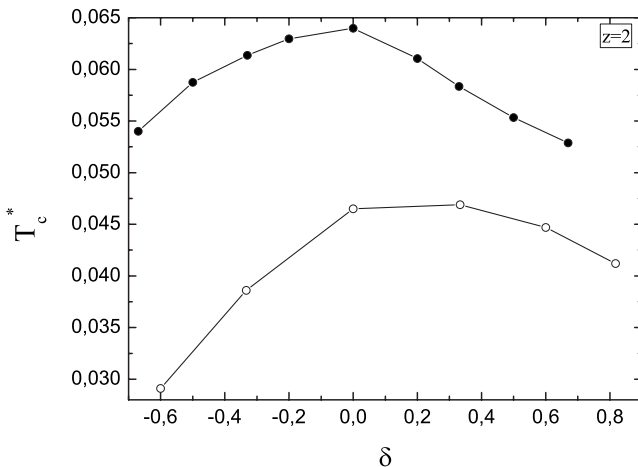


FIG. 5. Critical temperature of the (2:1) PM as a function of size asymmetry. Solid circles correspond to the results of the CV based theory; open circles are the results of simulations [10].

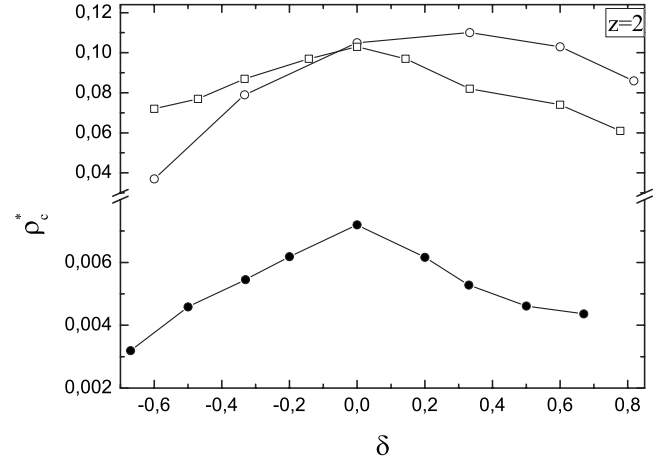


FIG. 6. Critical density of the (2:1) PM as a function of size asymmetry. Solid circles are the results of the CV based theory. Open symbols correspond to the results of simulations [10]: circles are spherical electrolytes; squares are dumbbell electrolytes.

on the critical parameters of equisize charge-asymmetric PMs. It allowed us to calculate, without additional assumptions (such as the presence of the dipoles or the higher-order clusters, for example), the trends of both the critical temperature and the critical density with charge asymmetry that qualitatively agree with Monte Carlo simulation results [21].

First, we have studied the Gaussian approximation of the functional Hamiltonian of the asymmetric PM. The stability analysis has led us to the trends for the critical parameters consistent with those obtained in [19]. As was shown in [19], only some of the effects of size and charge asymmetry can be reproduced correctly at this level of consideration. Then, we study the critical parameters of size- and charge-asymmetric PMs taking into account the higher-order correlation effects. Following the procedure described in [21] we have derived in the first nontrivial approximation an explicit expression for the chemical potential conjugate to the order parameter. It includes the third-order correlation functions of the reference system. Then, this expression was used to study the three versions of PM: an equisize PM with charge asymmetry; a monovalent PM with size asymmetry; a size- and charge-asymmetric PM.

In conclusion, within the framework of the same approximation we have obtained the trends of the critical temperature and the critical density with size asymmetry that qualitatively agree with the Monte Carlo simulation findings: both T_c^* and ρ_c^* decrease with increasing size asymmetry at the fixed z . As regards the charge asymmetry, the present approximation for the relevant chemical potential yields a correct trend of the critical temperature with z and improves the numerical values of T_c^* when compared with our previous findings. Unlike the results of [21], this approximation leads to the opposite trend of the critical density with charge asymmetry although the variation in ρ_c^* with z is small. We expect that the consideration of the correlation effects of higher order will enable us to correct the trends of the critical density with charge asymmetry as well as to improve the numerical values of the critical parameters. This issue will be considered elsewhere.

APPENDIX

1. Explicit expressions for the coefficients $A(k)$, $B(k)$, $C(k)$, and $D(k)$

$$A(k) = \frac{1}{\sqrt{1 + \alpha_1^2}}, \quad B(k) = \frac{\alpha_1}{\sqrt{1 + \alpha_1^2}},$$

$$C(k) = \frac{1}{\sqrt{1 + \alpha_2^2}}, \quad D(k) = \frac{\alpha_2}{\sqrt{1 + \alpha_2^2}},$$

where

$$\alpha_{1,2} = \frac{\tilde{c}_{--}(k) - \tilde{c}_{++}(k) \pm \sqrt{[\tilde{c}_{++}(k) - \tilde{c}_{--}(k)]^2 + 4\tilde{c}_{+-}(k)^2}}{2\tilde{c}_{+-}(k)}.$$

2. Expressions for $\mathfrak{M}_{\alpha_1\alpha_2}(0)$ and $\mathfrak{M}_{\alpha_1\alpha_2\alpha_3}(0,0)$ in the PY approximation

Using the Lebowitz' solution of the PY equation [31] for a hard sphere system one can obtain the explicit expressions for the Fourier transforms of Ornstein-Zernike (OZ) direct correlation functions $\tilde{c}_{\alpha\beta}^{\text{HS}}(k)$. In the long-wavelength limit they are of the form [33]

$$\rho_+ \tilde{c}_{++}^{\text{HS}}(0) = -2\eta_+(4a_+ + 3\beta_+ + 2\gamma_+), \quad (\text{A1})$$

$$\rho_- \tilde{c}_{--}^{\text{HS}}(0) = -2\eta_-(4a_- + 3\beta_- + 2\gamma_+ \lambda^{-3}), \quad (\text{A2})$$

$$\begin{aligned} \sqrt{\rho_+ \rho_-} \tilde{c}_{+-}^{\text{HS}}(0) = & -\frac{1}{5!} \{A + B[10\beta_{+-}(4\tilde{a} + 3) + 6\gamma_{+-}(5\tilde{a} + 4) \\ & + 4\gamma_+(6\tilde{a} + 5)]\}, \end{aligned} \quad (\text{A3})$$

where the following notations are introduced

$$\eta = \eta_+ + \eta_-, \quad \eta_+ = \frac{x_+ \eta \lambda^3}{x_- + x_+ \lambda^3}, \quad \eta_- = \frac{x_- \eta}{x_- + x_+ \lambda^3}, \quad (\text{A4})$$

$$\tilde{a} = \frac{1 - \lambda}{2\lambda}, \quad h = \eta \frac{\sqrt{x_+ x_-}}{x_- + x_+ \lambda^3}, \quad x_i = \frac{\rho_i}{\rho}, \quad (\text{A5})$$

$$\begin{aligned} a_+ = & \frac{1}{(1 - \eta)^4} \{1 - \eta^3 + (\eta_+ + \lambda^3 \eta_-)[\eta^2 + 4(1 + \eta)] - 3\eta_-(1 \\ & - \lambda)^2 \{[1 + \eta_+ + \lambda(1 + \eta_-)](1 - \eta + 3\eta_+) + \eta_+(1 - \eta)\}\}, \end{aligned} \quad (\text{A6})$$

$$\begin{aligned} a_- = & \frac{1}{\lambda^3(1 - \eta)^4} \{\lambda^3(1 - \eta^3) + (\eta_+ + \lambda^3 \eta_-)[\eta^2 + 4(1 + \eta)] \\ & - 3\eta_+(1 - \lambda)^2 \{[1 + \eta_+ + \lambda(1 + \eta_-)](1 - \eta + 3\eta_-) \\ & + \lambda \eta_-(1 - \eta)\}\}, \end{aligned}$$

$$\beta_+ = -6 \left[\eta_+ g_{++}^2 + \frac{1}{4} \eta_-(1 + \lambda)^2 \lambda g_{+-}^2 \right],$$

$$\beta_- = -6 \left[\eta_- g_{--}^2 + \frac{1}{4} \eta_+ \lambda^{-3} (1 + \lambda)^2 g_{+-}^2 \right], \quad (\text{A7})$$

$$\beta_{+-} = -3\lambda(1 - \lambda)(\lambda^{-2} \eta_+ g_{++} + \eta_- g_{--}) g_{+-},$$

$$\gamma_+ = \frac{1}{2} (\eta_+ a_+ + \lambda^3 \eta_- a_-), \quad (\text{A8})$$

$$\gamma_- = \frac{\gamma_+}{\lambda^3}, \quad \gamma_{+-} = 2\gamma_+ \frac{1 - \lambda}{\lambda},$$

$$g_{++} = \frac{1}{(1 - \eta)^2} \left[1 + \frac{\eta}{2} + \frac{3}{2} \eta_- (\lambda - 1) \right],$$

$$g_{--} = \frac{1}{(1 - \eta)^2} \left[1 + \frac{\eta}{2} + \frac{3}{2} \eta_+ (\lambda^{-1} - 1) \right], \quad (\text{A9})$$

$$g_{+-} = \frac{1}{(1 - \eta)^2} \left[1 + \frac{3\eta(1 - \lambda)}{4(1 + \lambda)} (\eta_+ - \eta_-) \right]. \quad (\text{A10})$$

$$A = \frac{5a_+(1 + \lambda)^3 B}{\lambda^3}, \quad B = 4! \sqrt{\lambda^3 \eta_+ \eta_-}. \quad (\text{A11})$$

The expressions for $S_{\alpha\beta}(k) = \mathfrak{M}_{\alpha\beta}(k) / \sqrt{N_\alpha N_\beta}$ can be found from the OZ equations

$$S_{++}(k) = \frac{1 - \rho_- \tilde{c}_{--}^{\text{HS}}(k)}{[1 - \rho_+ \tilde{c}_{++}^{\text{HS}}(k)][1 - \rho_- \tilde{c}_{--}^{\text{HS}}(k)] - \rho_+ \rho_- [\tilde{c}_{+-}^{\text{HS}}(k)]^2}, \quad (\text{A12})$$

$$S_{--}(k) = \frac{1 - \rho_+ \tilde{c}_{++}^{\text{HS}}(k)}{[1 - \rho_+ \tilde{c}_{++}^{\text{HS}}(k)][1 - \rho_- \tilde{c}_{--}^{\text{HS}}(k)] - \rho_+ \rho_- [\tilde{c}_{+-}^{\text{HS}}(k)]^2}, \quad (\text{A13})$$

$$S_{+-}(k) = \frac{\sqrt{\rho_+ \rho_-} \tilde{c}_{+-}^{\text{HS}}(k)}{[1 - \rho_+ \tilde{c}_{++}^{\text{HS}}(k)][1 - \rho_- \tilde{c}_{--}^{\text{HS}}(k)] - \rho_+ \rho_- [\tilde{c}_{+-}^{\text{HS}}(k)]^2}. \quad (\text{A14})$$

Equations (A3)–(A14) should be supplemented by the electroneutrality condition.

The explicit expressions for $S_{+++}(0,0) = \mathfrak{M}_{+++}(0,0) / N_+$ and $S_{++-}(0,0) = \mathfrak{M}_{++-}(0,0) / N_+$ can be obtained from the relations

$$\begin{aligned} S_{+++}(0,0) = & S_{++}(0) \left[S_{++}(0) + \eta_+ \left(\frac{\partial S_{++}(0)}{\partial \eta_+} \right)_{\eta_-} \right] \\ & + \eta_- \sqrt{\frac{x_+}{x_-}} S_{+-}(0) \left(\frac{\partial S_{++}(0)}{\partial \eta_-} \right)_{\eta_+}, \end{aligned} \quad (\text{A15})$$

$$\begin{aligned} S_{++-}(0,0) = & \sqrt{\frac{x_-}{x_+}} \left[S_{++}(0) + \eta_+ \left(\frac{\partial S_{++}(0)}{\partial \eta_+} \right)_{\eta_-} \right] \\ & + \eta_- S_{--}(0) \left(\frac{\partial S_{++}(0)}{\partial \eta_-} \right)_{\eta_+}. \end{aligned} \quad (\text{A16})$$

The expressions for $\mathfrak{M}_{---}(0,0)$ and $\mathfrak{M}_{+-+}(0,0)$ can be ob-

tained replacing indices “+” by indices “-” and vice versa.
Final formulas should be supplemented by the electroneutrality condition.

3. Explicit expressions for ν_2^S and ν_2^{HS}

We obtain for ν_2^S

$$\nu_2^S = \frac{(1+\lambda)(z+\lambda)}{4T^*\lambda\sqrt{1+z^2}}.$$

In the PY approximation ν_2^{HS} has the form

$$\nu_2^{\text{HS}} = \frac{1+z}{\sqrt{1+z^2}} \left[\ln \eta + \ln(1-\eta) + \frac{z}{1+z} \ln(z) - \ln(z+\lambda^3) \right. \\ \left. + \frac{\eta(1+\eta+\eta^2)}{(1-\eta)^3} - \frac{3\eta}{2(1+z)(1-\eta)^3(z+\lambda^3)^2} [2z\eta(1-\lambda)^2((1+\lambda)(z+\lambda^3) + \eta\lambda(z+\lambda^2)) - 4(z+\lambda)(z+\lambda^2)(z+\lambda^3)(1-\eta)^2 - 3\eta(z+\lambda^2)^3(1-\eta)] \right].$$

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