Vapor-liquid phase behavior of a size-asymmetric model of ionic fluids confined in a disordered matrix: The collective-variables-based approach

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We develop a theory based on the method of collective variables to study the vapor-liquid equilibrium of asymmetric ionic fluids confined in a disordered porous matrix. The approach allows us to formulate the perturbation theory using an extension of the scaled particle theory for a description of a reference system presented as a two-component hard-sphere fluid confined in a hard-sphere matrix. Treating an ionic fluid as a size- and charge-asymmetric primitive model (PM) we derive an explicit expression for the relevant chemical potential of a confined ionic system which takes into account the third-order correlations between ions. Using this expression, the phase diagrams for a size-asymmetric PM are calculated for different matrix porosities as well as for different sizes of matrix and fluid particles. It is observed that general trends of the coexistence curves with the matrix porosity are similar to those of simple fluids under disordered confinement, i.e., the coexistence region gets narrower with a decrease of porosity and, simultaneously, the reduced critical temperature T_c^* and the critical density $\rho_{i,c}^*$ become lower. At the same time, our results suggest that an increase in size asymmetry of oppositely charged ions considerably affects the vapor-liquid diagrams leading to a faster decrease of T_c^* and $\rho_{i,c}^*$ and even to a disappearance of the phase transition, especially for the case of small matrix particles.

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I. INTRODUCTION

Ionic liquids confined in mesoporous matrices attract a significant attention because of their specific physicochemical properties and find widespread application in many areas of modern science and technologies ranging from electrochemistry to biology and medicine. In particular, such systems are considered as very promising candidates for new types of electrolytes in fuel cells, supercapacitors, solar cells, and batteries. Ionic liquids confined in nanoporous materials are used in catalysis, sensing and biosensing, gas capture and separation. Having a high surface area and a large pore volume the biocompatible porous materials are used for a drug delivery, and ionic liquid encapsulated together with bioactive molecules can be utilized for controlled release of the latter. Ionic liquids are also considered as efficient porogenic agents used to tune a porous structure (porosity, pore surface area) during formation of confining material. In the literature one can find a number of excellent reviews devoted to ionic liquids confined in different porous geometries; in particular, special attention has been paid to disordered mesoporous materials [1–3].

One of the interesting phenomena related to liquids in confinements, which have been a subject of intensive investigations for the last decades, is the vapor-liquid phase-transition behavior [4–6]. It has been shown that a porous medium strongly affects the phase diagram of a guest liquid. In particular, the phase behavior of liquids in a confined geometry is considerably altered relative to their unconfined (bulk) state. A distinguished feature of the phase diagrams of such systems as compared with the bulk case is a lowering of both the critical temperature and the critical density and a narrowing of the coexistence region. A review of experimental and theoretical efforts in the field is also given in Refs. [5–7]. However, despite much efforts being devoted to theoretical studies of these systems, most of them have been related to studies of simple liquids or ionic liquids in simple geometries like a single slit or cylindrical pore [8–11]. Moreover, even for simple fluids in disordered confinements some questions have remained open [12]. At the same time, the phase behavior of systems comprised of charged particles confined in disordered matrices has received substantially less attention. This is mostly related to the fact that it is still a challenge to provide a good quantitative and, in some cases, a qualitative theoretical description of the phase behavior of ionic fluids even in the bulk. In particular, this concerns the effects of size and charge asymmetry of ions on the vapor-liquid phase diagram of ionic fluids with Coulomb-dominated interactions (see Ref. [13] and references cited therein). On the other hand, such fluids as ionic liquids are melted organic salts, which are usually characterized by a significant size asymmetry between cations and anions. Thus, in the present work we develop the method capable of describing the thermodynamics of model ionic liquids confined in disorder matrices in order to study the vapor-liquid transition in such systems.

The model most frequently used for ionic fluids is a two-component primitive model (PM) consisting of an electroneutral mixture of charged hard spheres (HSs) immersed in a structureless dielectric continuum. The simulation results for this model have shown that asymmetry in size and charge strongly affects the critical parameters, i.e., the suitably normalized critical temperature decreases with size and charge asymmetry while the critical density increases with charge asymmetry but decreases with size asymmetry [14–19].

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The original Debye-Hückel theory and the mean spherical approximation (MSA) are not capable of predicting the trends observed in simulations [20,21]. Moreover, both theories predict no dependence on charge asymmetry in the equisize case. Progress on a theoretical description of the effects of asymmetry on the vapor-liquid phase behavior has been made within the framework of the associative approach [22,23]. However, certain arbitrariness in determining the association constant is implied in these theories. On the other hand, the effect of asymmetry on the vapor-liquid phase diagram has been studied within the framework of the theory based on the method of collective variables (CVs) [24–28]. The theory allows one to take into account the effects of higher-order correlations between ions and, as a result, to obtain, on an analytical basis, the trends of the critical parameters with charge and size asymmetry that qualitatively agree with simulation findings.

It should be noted that the vapor-liquid phase behavior of a symmetric ionic model confined in uncharged pores of “simple geometry”, e.g., of a slit-like or cylindrical shape was studied numerically by using the density functional theory [8–10] and quite recently by the field-theoretical variational approach [11]. However, the case of size and charge asymmetry of ions was not considered in these studies. On the other hand, the behavior of ionic fluids in a disordered porous matrix is more complicated because one should take into account the effects of separate pores as well as the effects of correlations between the ions confined into different pores. Furthermore, a disordered porous matrix is characterized by specific features as porosity and pore surface area. Since the particles composing a matrix are of spherical shape, the mean pore surface curvature can play a role as well. To the best of our knowledge, no theoretical results have been obtained until recently for these rather complex systems.

Fluids confined in disordered porous materials can be treated as partly quenched systems in which some of the degrees of freedom are quenched while the others are annealed [29]. Partly quenched systems containing charges were mainly studied by using the replica Ornstein–Zernike (ROZ) theory (see review [30] and references cited therein). However, the phase behavior of such systems has not been considered within this approach. Moreover, unlike bulk fluids, no analytical result has been obtained from the ROZ theory even for a HS fluid confined in a HS matrix, being the model of particular importance for the development of perturbation theories. On the other hand, based on the scaled-particle theory (SPT) [31], a pure analytical approach has been recently proposed to describe the thermodynamics of the latter system [32–37]. An extension of the SPT developed for a HS fluid confined in a HS matrix, also referred to as the SPT2 approach [38], has already been successfully applied for the description of reference systems of different kinds of liquids including the systems with associative [36] and anisotropic interactions between particles [39]. More recently this approach has been generalized to the case of a multicomponent HS fluid confined in a multicomponent HS matrix [40].

In the previous paper [41], following the idea of Qin and Prausnitz [23] for the bulk PM, we developed a theoretical approach for the study of a vapor-liquid phase transition of a monovalent size-asymmetric PM confined in a disordered HS matrix. The approach combines a new extension of the SPT [40] and the associative MSA (AMSA) based on the simplified MSA [23]. While the SPT is used for the description of the HS subsystem presented as a two-component HS fluid confined in a HS matrix, the simplified MSA approximates the ionic subsystem by a symmetric ionic fluid with the effective ion diameter $\sigma_{+-} = (\sigma_+ + \sigma_-)/2$. However, the charge asymmetry cannot be taken into consideration within this approach.

In this paper, we continue our systematic studies of the vapor-liquid phase behavior of ionic systems confined in a disordered porous medium. Considering a two-component charge- and size-asymmetric ionic model confined in a disordered HS matrix, we exploit the idea of a partly quenched model and use the replica trick [42]. We extend the work [43] devoted to a symmetrical ionic model and develop a CV-based theory that allows one to simultaneously take into account charge and size asymmetry. Our approach enables us to formulate the perturbation theory using the SPT for a description of the thermodynamics of a reference system. In Ref. [40], different modifications derived from the basic SPT formulation are presented and their accuracy is evaluated against the simulation results. Here, we use the SPT2b approximation which provides more accurate results for excess chemical potentials.

First, we restrict our consideration to the Gaussian approximation and derive the grand potential of our partly quenched system. For a particular case where interactions between matrix particles and matrix and fluid particles can be neglected beyond the hard core, we derive an explicit expression for the relevant chemical potential conjugate to the order parameter in the approximation that takes into account the effects of correlations up to third order. To this end, we use the method proposed in Refs. [24,26] for the bulk PM. Based on this expression, we calculate the phase diagrams depending on the characteristics of an ionic fluid and a HS matrix. Here, we focus on the size-asymmetric case and consider, apart from an ion size asymmetry, different size ratios between the ion particles and the matrix obstacles. We analyze how variations in the size-asymmetry parameters and in the matrix porosity affect the vapor-liquid phase diagram of a confined ionic model.

The paper is arranged as follows: In Sec. II, we present a theoretical formalism. An explicit expression for the relevant chemical potential which takes into account the correlation effects beyond the Gaussian approximation is derived in this section. Section III is devoted to the reference system. In Sec. IV, the vapor-liquid phase diagrams of a size-asymmetric ionic fluid confined in HS matrices of different characteristics are presented and discussed in detail. We conclude in Sec. V.

II. MODEL AND THEORY

A. Model

We consider a two-component charge- and size-asymmetric ionic model confined in a disordered porous matrix formed by uncharged particles. The interaction potentials between the two matrix particles and between the ion (cation or anion) and the matrix particle include a short-range attraction or repulsion in addition to a hard-core repulsion. Furthermore, the ions themselves and the ions and the matrix particles differ in size. Therefore, the interactions in the matrix-ionic fluid system can be described by a set of pairwise interaction potentials: $u_{00}(x)$, $u_{++}(x)$, $u_{--}(x)$, $u_{+-}(x) = u_{-+}(x)$, $u_{0+}(x) = u_{+0}(x)$, $u_{0-}(x) = u_{-0}(x)$, where the subscript 0 refers to the matrix particles and the subscripts $+$, $-$ refer to the ions. We assume that the interaction potentials between different particles can be split into a reference part denoted by index "r" and a perturbation part denoted by index "p":

$$u_{ij}(x) = u_{ij}^{(r)}(x) + u_{ij}^{(p)}(x), \tag{1}$$

where $u_{ij}^{(r)}(x)$ is a potential of a short-range repulsion which, generally, describes the mutual impenetrability of the particles, while $u_{ij}^{(p)}(x)$ mainly describes the behavior at moderate and large distances. The system in which the particles interact via the potentials $u_{ij}^{(r)}(x)$ is regarded as the reference system, $u_{ij}^{(r)}(x)$ is specified in the form of the HS potential. We assume that the thermodynamic and structural properties of the reference system are known.

We follow the formalism originally proposed in Ref. [29] and consider our matrix-fluid system as a partly quenched model. This means that our system contains two subsystems: the first one, the matrix itself, is composed of particles quenched or frozen in place, while the second subsystem is an annealed (allowed to equilibrate) binary ionic fluid which is in equilibrium with the matrix. It is assumed that the matrix particles were quenched into an equilibrium configuration corresponding to the Gibbs distribution associated with a pairwise interaction potential. The ionic fluid is treated as a two-component charge- and size-asymmetric PM. In this case, statistical-mechanical averages used for calculations of thermodynamic properties become double ensemble averages: the first average is taken over all degrees of freedom of annealed particles keeping the quenched particles fixed, and the other average is performed over all realizations of a matrix. To treat the averages we use the replica method. It allows us to relate the matrix averaged quantities to the thermodynamic quantities of the corresponding fully equilibrated model, referred to as a replicated model. In our case, the replicated model consists of a matrix and of s identical copies or replicas of the two-component ionic model. Each pair of particles has the same pairwise interaction in this replicated system as in the partly quenched model except that a pair of particles from different replicas has no interaction. Thus, the interaction potentials between matrix particles, matrix and fluid particles and fluid and fluid particles can be presented as follows:

$$u_{00}(r_0 - r_0'), \quad u_{0A}^{\alpha}\left(r_0 - r_{\alpha}^{A}\right), \quad u_{AB}^{\alpha\beta}\left(r_{\alpha}^{A} - r_{\beta}^{B}\right)\delta_{\alpha\beta}, \tag{2}$$

where index "0" refers to matrix particles, Latin indices denote fluid (ion) species ($A,B = +,-$), and Greek indices denote replicas ($\alpha,\beta = 1,2,\ldots,s$). Furthermore, each interaction potential can be split into two terms in accordance with Eq. (1).

B. Collective-variables-based approach: Gaussian approximation

We consider a $(2s+1)$-component system with the interaction potentials given by Eq. (2) in the grand canonical ensemble. Then, using the method of CVs, we can present the equilibrium grand partition function of the system in the form of a functional integral (see Ref. [43] and the references therein):

$$\Xi^{\text{rep}}(s) = \Xi^{\text{mf}}\left[\tilde{\nu}_0, \tilde{\nu}_A^{\alpha}\right] \int (d\rho)(d\omega) \exp\left[-\frac{\beta}{2}\sum_{\mathbf{k}} \widehat{U}(k)\widehat{\rho}_{\mathbf{k}}\widehat{\rho}_{-\mathbf{k}} + i\sum_{\mathbf{k}} \widehat{\omega}_{\mathbf{k}}\widehat{\rho}_{\mathbf{k}} + \sum_{n\geqslant 2}\frac{(-i)^n}{n!}\sum_{\mathbf{k}_1,\ldots,\mathbf{k}_n} \widehat{\mathfrak{M}}_n \widehat{\omega}_{\mathbf{k}_1}\widehat{\omega}_{\mathbf{k}_2}\ldots\widehat{\omega}_{\mathbf{k}_n}\delta_{\mathbf{k}_1+\cdots+\mathbf{k}_n}\right]. \tag{3}$$

Here, the following notations are introduced: Ξ^{mf} is the mean-field (MF) part of the grand partition function which depends on the renormalized partial chemical potentials $\tilde{\nu}_0$ and $\tilde{\nu}_A^{\alpha}$ [see Eqs. (A1)–(A3) in Appendix A]; $\beta = 1/k_{\text{B}}T$ with k_{B} being the Boltzmann constant, T the absolute temperature; $(d\rho) = (d\rho_0)(d\rho_A^{\alpha})$ [$(d\omega) = (d\omega_0)(d\omega_A^{\alpha})$] denote volume elements of the phase space of CVs $\rho_{\mathbf{k},0}$ and $\rho_{\mathbf{k},A}^{\alpha}$ ($\omega_{\mathbf{k},0}$ and $\omega_{\mathbf{k},A}^{\alpha}$). CVs $\rho_{\mathbf{k},0}$ and $\rho_{\mathbf{k},A}^{\alpha}$ describe the fluctuation modes of the number density of the matrix and fluid species, respectively ($\omega_{\mathbf{k},0}$ and $\omega_{\mathbf{k},A}^{\alpha}$ are conjugate to $\rho_{\mathbf{k},0}$ and $\rho_{\mathbf{k},A}^{\alpha}$).

$\widehat{U}(k)$ denotes a symmetric $(2s+1)\times(2s+1)$ matrix of elements:

$$\begin{aligned}
u_{11} &= \widetilde{u}_{00}^{(p)}(k) = \widetilde{\varphi}_{00}(k),\\
u_{1i} &= u_{i1} = \widetilde{u}_{0+}^{\alpha(p)}(k) = \widetilde{\varphi}_{0+}(k), \quad i \in E,\\
u_{1i} &= u_{i1} = \widetilde{u}_{0-}^{\alpha(p)}(k) = \widetilde{\varphi}_{0-}(k), \quad i \in O,\\
u_{ii} &= \widetilde{u}_{++}^{\alpha\alpha(p)}(k) = \widetilde{\varphi}_{++}(k), \quad i \in E,\\
u_{ii} &= \widetilde{u}_{--}^{\alpha\alpha(p)}(k) = \widetilde{\varphi}_{--}(k), \quad i \in O,\\
u_{ij} &= u_{ji} = \widetilde{u}_{+-}^{\alpha\alpha(p)}(k) = \widetilde{\varphi}_{+-}(k), \quad i \in E, \quad j = i+1,\\
u_{ij} &= 0, \quad i \neq j, \quad j \neq i+1,
\end{aligned}$$

where the quantities with a "tilde" are the Fourier transforms of the corresponding interaction potentials and E (O) are even (odd) numbers. $\widehat{\rho}_{\mathbf{k}}$ indicates a column vector of elements $\rho_{\mathbf{k},0}$, $\rho_{\mathbf{k},+}^{1}$, …, $\rho_{\mathbf{k},+}^{s}$, $\rho_{\mathbf{k},-}^{1}$, …, $\rho_{\mathbf{k},-}^{s}$ and $\widehat{\omega}_{\mathbf{k}}$ is a row vector of elements $\omega_{\mathbf{k},0}$, $\omega_{\mathbf{k},+}^{1}$, …, $\omega_{\mathbf{k},+}^{s}$, $\omega_{\mathbf{k},-}^{1}$, …, $\omega_{\mathbf{k},-}^{s}$.

$\widehat{\mathfrak{M}}_n$ is a symmetric

$$\underbrace{(2s+1)\times(2s+1)\times\cdots\times(2s+1)}_{n}$$

matrix whose elements are cumulants: the nth cumulant coincides with the Fourier transform of the n-particle truncated correlation function [44] of the reference system. The elements of matrix $\widehat{\mathfrak{M}}_2$ read

$$\begin{aligned}
\mathfrak{M}_{11} &= \mathfrak{M}_{00}(k),\\
\mathfrak{M}_{1i} &= \mathfrak{M}_{i1} = \mathfrak{M}_{0+}(k), \quad i\in E, \quad \mathfrak{M}_{1i} = \mathfrak{M}_{i1} = \mathfrak{M}_{0-}(k), \quad i\in O,\\
\mathfrak{M}_{ii} &= \mathfrak{M}^{11}_{++}(k), \quad i\in E, \quad \mathfrak{M}_{ii} = \mathfrak{M}^{11}_{--}(k), \quad i\in O,\\
\mathfrak{M}_{ij} &= \mathfrak{M}_{ji} = \mathfrak{M}^{11}_{+-}(k), \quad i\in E, \quad j\in O, \quad j=i+1,\\
\mathfrak{M}_{ij} &= \mathfrak{M}_{ji} = \mathfrak{M}^{12}_{++}(k), \quad i,j\in E, \quad i\neq j,\\
\mathfrak{M}_{ij} &= \mathfrak{M}_{ji} = \mathfrak{M}^{12}_{--}(k), \quad i,j\in O, \quad i\neq j,\\
\mathfrak{M}_{ij} &= \mathfrak{M}_{ji} = \mathfrak{M}^{12}_{+-}(k), \quad i\in E, \quad j\in O, \quad j\neq i+1,
\end{aligned} \tag{4}$$

where

$$\begin{aligned}
&\mathfrak{M}_{00}(k) = \overline{\rho_0}\delta_{\mathbf{k}} + \overline{\rho_0}^2\tilde{h}^{(r)}_{00}(k), \quad \mathfrak{M}_{0A}(k) = \overline{\rho_0}\,\overline{\rho_A}\tilde{h}^{(r)}_{0A}(k),\\
&\mathfrak{M}^{\alpha\beta}_{AB}(k) = \overline{\rho^{\alpha}_A}\delta_{AB}\delta_{\alpha\beta}\delta_{\mathbf{k}} + \overline{\rho^{\alpha}_A}\,\overline{\rho^{\beta}_B}\tilde{h}^{\alpha\beta(r)}_{AB}(k),
\end{aligned} \tag{5}$$

$\overline{\rho_0} = \langle N_0\rangle_r/V$, $\overline{\rho^{\alpha}_A} = \langle N^{\alpha}_A\rangle_r/V$, $\langle\cdots\rangle_r$ indicates the average taken over the reference system and we put $\overline{\rho^1_A} = \overline{\rho^2_A} = \cdots = \overline{\rho^s_A} = \overline{\rho_A}$. $\tilde{h}^{\cdots(r)}_{\cdots}(k)$ is the Fourier transform of the corresponding pair correlation function of a $(2s+1)$-component reference system, $h^{11(r)}_{AB}(r)$ describes the correlations between particles within the same replica, whereas $h^{12(r)}_{AB}(r)$ describes correlations between the particles from different replicas. The determinant of the matrix $\widehat{\mathfrak{M}}_2$ is of the form

$$\begin{aligned}
\det[\widehat{\mathfrak{M}}_2(s)] = {} & [(\mathfrak{M}^{11}_{++} - \mathfrak{M}^{12}_{++})(\mathfrak{M}^{11}_{--} - \mathfrak{M}^{12}_{--}) - (\mathfrak{M}^{11}_{+-} - \mathfrak{M}^{12}_{+-})^2]^{s-1}(\mathfrak{M}_{00}\{[\mathfrak{M}^{11}_{++} + (s-1)\mathfrak{M}^{12}_{++}][\mathfrak{M}^{11}_{--} + (s-1)\mathfrak{M}^{12}_{--}]\\
& - [\mathfrak{M}^{11}_{+-} + (s-1)\mathfrak{M}^{12}_{+-}]^2\} - s\mathfrak{M}^2_{0+}[\mathfrak{M}^{11}_{--} + (s-1)\mathfrak{M}^{12}_{--}] - s\mathfrak{M}^2_{0-}[\mathfrak{M}^{11}_{++} + (s-1)\mathfrak{M}^{12}_{++}]\\
& + 2s\mathfrak{M}_{0+}\mathfrak{M}_{0-}[\mathfrak{M}^{11}_{+-} + (s-1)\mathfrak{M}^{12}_{+-}]).
\end{aligned}$$

We restrict our consideration to the second-order cumulants in Eq. (3). In this case, after integration we obtain the grand partition function of the replicated system in the Gaussian approximation

$$\frac{1}{V}\ln\Xi^{\mathrm{rep}}_{\mathrm{G}}(s) = \frac{1}{V}\ln\Xi^r + \frac{\beta}{2}(\overline{\rho_0})^2\widetilde{\varphi}_{00}(0) + s\beta\bar{\rho}_0\sum_A\overline{\rho_A}\widetilde{\varphi}_{0A}(0) - \frac{1}{2V}\sum_{\mathbf{k}}\ln[\det(\widehat{U}\widehat{\mathfrak{M}}_2 + \underline{1})], \tag{6}$$

where Ξ^r is the grand partition function of a $(2s+1)$-component reference system.

Using the Legendre transform, from Eq. (6) one can derive the Helmholtz free energy in the random-phase approximation (RPA):

$$\begin{aligned}
\beta f_{\mathrm{RPA}}(s) = \frac{\beta F^{\mathrm{rep}}_{\mathrm{RPA}}(s)}{V} = {} & \beta f^r - \frac{\rho^{\mathrm{rep}}_0}{2V}\sum_{\mathbf{k}}\beta\widetilde{\varphi}_{00}(k) + \frac{\left(\rho^{\mathrm{rep}}_0\right)^2}{2}\beta\widetilde{\varphi}_{00}(0) - \frac{s}{2V}\sum_{A=+,-}\sum_{\mathbf{k}}\rho^{\mathrm{rep}}_A\beta\widetilde{\varphi}_{AA}(k) + s\rho_0\sum_{A=+,-}\rho^{\mathrm{rep}}_A\beta\widetilde{\varphi}_{0A}(0)\\
& + \frac{1}{2V}\sum_{\mathbf{k}}\ln[\det(\widehat{U}\widehat{\mathfrak{M}}_2 + \underline{1})],
\end{aligned}$$

where f^r is the free energy of the reference system, ρ^{rep}_0 and ρ^{rep}_A denote the number densities of the matrix and fluid particles (cations and anions), respectively.

Here, we consider a particular case where interactions between the matrix particles can be neglected beyond the hard core. Taking a replica limit of Eq. (6) $-\beta\overline{\Omega}^G = \ln\overline{\Xi}^G = \lim_{s\to 0}\frac{d}{ds}\ln\Xi^{\mathrm{rep}}_G(s)$ we derive, after some algebra, an expression for the grand potential of a partly quenched system in the Gaussian approximation:

$$\begin{aligned}
-\beta\overline{\Omega}^G = {} & -\beta\overline{\Omega}^r + \rho_0\sum_A\rho_A\beta\widetilde{\varphi}_{0A}(0) - \frac{1}{2}\sum_{\mathbf{k}}\ln\left[\det\left(\widehat{\Phi}_2\widehat{\mathfrak{M}}^c_2 + \underline{1}\right)\right] - \frac{1}{2}\sum_{\mathbf{k}}\frac{1}{\det\left(\widehat{\Phi}_2\widehat{\mathfrak{M}}^c_2 + \underline{1}\right)}\Bigg\{\det(\widehat{\Phi}_2)(\mathfrak{M}^c_{++}\mathfrak{M}^b_{--}\\
& + \mathfrak{M}^c_{--}\mathfrak{M}^b_{++} - 2\mathfrak{M}^c_{+-}\mathfrak{M}^b_{+-}) + 2\beta^2[\widetilde{\varphi}_{0+}(k)\widetilde{\varphi}_{+-}(k) - \widetilde{\varphi}_{0-}(k)\widetilde{\varphi}_{++}(k)][\overline{\mathfrak{M}}_{0+}\mathfrak{M}^c_{+-} - \overline{\mathfrak{M}}_{0-}\mathfrak{M}^c_{++}]\\
& + 2\beta^2[\widetilde{\varphi}_{0+}(k)\widetilde{\varphi}_{--}(k) - \widetilde{\varphi}_{0-}(k)\widetilde{\varphi}_{+-}(k)][\overline{\mathfrak{M}}_{0+}\mathfrak{M}^c_{--} - \overline{\mathfrak{M}}_{0-}\mathfrak{M}^c_{+-}] + \det(\widehat{\Phi}_3)\overline{\mathfrak{M}}_{00}\det\left(\widehat{\mathfrak{M}}^c_2\right)\\
& - \overline{\mathfrak{M}}_{00}\sum_{A,B=+,-}\beta\widetilde{\varphi}_{0A}(k)\mathfrak{M}^c_{AB}\beta\widetilde{\varphi}_{0B}(k) + 2\sum_{A=+.-}\beta\widetilde{\varphi}_{0A}(k)\overline{\mathfrak{M}}_{0A} + \sum_{A,B=+.-}\beta\widetilde{\varphi}_{AB}(k)\mathfrak{M}^b_{AB}\Bigg\}.
\end{aligned} \tag{7}$$

Here, the following notations are introduced: $\overline{\Omega}^r$ is the grand potential of the reference system consisting of a two-component HS fluid confined in a HS matrix, $\rho_0 = \overline{\rho_0}|_{s=0}$, and $\rho_A = \overline{\rho_A}|_{s=0}$. Matrices $\widehat{\Phi}_2$ and $\widehat{\Phi}_3$ are of the form

$$\widehat{\Phi}_2 = \begin{pmatrix} \beta\widetilde{\varphi}_{++}(k) & \beta\widetilde{\varphi}_{+-}(k) \\ \beta\widetilde{\varphi}_{+-}(k) & \beta\widetilde{\varphi}_{--}(k) \end{pmatrix},$$

$$\widehat{\Phi}_3 = \begin{pmatrix} 0 & \beta\widetilde{\varphi}_{0+}(k) & \beta\widetilde{\varphi}_{0-}(k) \\ \beta\widetilde{\varphi}_{0+}(k) & \beta\widetilde{\varphi}_{++}(k) & \beta\widetilde{\varphi}_{+-}(k) \\ \beta\widetilde{\varphi}_{0-}(k) & \beta\widetilde{\varphi}_{+-}(k) & \beta\widetilde{\varphi}_{--}(k) \end{pmatrix}.$$

$\mathfrak{M}^c_{AB}$ and $\mathfrak{M}^b_{AB}$ are elements of the matrices

$$\widehat{\mathfrak{M}}^c_2 = \begin{pmatrix} \mathfrak{M}^c_{++}(k) & \mathfrak{M}^c_{+-}(k) \\ \mathfrak{M}^c_{+-}(k) & \mathfrak{M}^c_{--}(k) \end{pmatrix},$$

$$\widehat{\mathfrak{M}}^b_2 = \begin{pmatrix} \mathfrak{M}^b_{++}(k) & \mathfrak{M}^b_{+-}(k) \\ \mathfrak{M}^b_{+-}(k) & \mathfrak{M}^b_{--}(k) \end{pmatrix}. \tag{8}$$

Superscripts "c" and "b" in Eq. (8) denote the connected and blocking parts of the cumulants $\mathfrak{M}_{AB}$ (or structure factors of the reference system):

$$\mathfrak{M}_{AB}(k) = \mathfrak{M}^c_{AB}(k) + \mathfrak{M}^b_{AB}(k) = \rho_A\delta_{AB} + \rho_A\rho_B\widetilde{h}^r_{AB}(k),$$
$$A,B = +,-\,, \tag{9}$$

where

$$\begin{aligned} \mathfrak{M}^c_{AB}(k) &= \lim_{s\to 0}\left[\mathfrak{M}^{11}_{AB}(k) - \mathfrak{M}^{12}_{AB}(k)\right] \\ &= \rho_A\delta_{AB} + \rho_A\rho_B\widetilde{h}^{r,c}_{AB}(k), \\ \widetilde{h}^{r,c}_{AB}(k) &= \lim_{s\to 0}\left[\widetilde{h}^{11(r)}_{AB}(k) - \widetilde{h}^{12(r)}_{AB}(k)\right], \end{aligned} \tag{10}$$

and

$$\begin{aligned} \mathfrak{M}^b_{AB}(k) &= \lim_{s\to 0}\mathfrak{M}^{12}_{AB} = \rho_A\rho_B\widetilde{h}^{r,b}_{AB}(k), \\ \widetilde{h}^{r,b}_{AB}(k) &= \lim_{s\to 0}\widetilde{h}^{12(r)}_{AB}(k). \end{aligned} \tag{11}$$

In Eq. (9), $\widetilde{h}^r_{AB}(k) = \widetilde{h}^{r,c}_{AB} + \widetilde{h}^{r,b}_{AB}$ is the Fourier transform of the partial pair correlation function with $\widetilde{h}^{r,c}_{AB}$ ($\widetilde{h}^{r,b}_{AB}$) being its connected (blocking) part. The connected correlation function accounts for correlations between a pair of the fluid particles transmitted through successive layers of fluid particles while the blocking correlation function accounts for correlations between two fluid particles separated from each other by matrix particles [42,45].

For $\overline{\mathfrak{M}}_{00}$ and $\overline{\mathfrak{M}}_{0A}$, we have

$$\begin{aligned} \overline{\mathfrak{M}}_{00}(k) &= \lim_{s\to 0}\mathfrak{M}_{00} = \rho_0 + \rho_0^2\widetilde{h}^r_{00}(k), \quad \widetilde{h}^r_{00}(k) = \lim_{s\to 0}\widetilde{h}^{(r)}_{00}(k), \\ \overline{\mathfrak{M}}_{0A}(k) &= \lim_{s\to 0}\mathfrak{M}_{0A} = \rho_0\rho_A\widetilde{h}^r_{0A}(k), \quad \widetilde{h}^r_{0A}(k) = \lim_{s\to 0}\widetilde{h}^{(r)}_{0A}(k), \end{aligned} \tag{12}$$

where $\widetilde{h}^r_{00}(k)$ and $\widetilde{h}^r_{0A}(k)$ are Fourier transforms of the matrix-matrix and matrix-fluid correlation functions in a partly quenched reference system. In Eqs. (10)–(12), $\mathfrak{M}^{\alpha\beta}_{AB}$, $\mathfrak{M}_{00}$, and $\mathfrak{M}_{0A}$ are the elements of the matrix $\widehat{\mathfrak{M}}_2$ [see Eqs. (4) and (5)].

Similarly, one can find the RPA free energy of a two-component ionic system confined in a disordered porous matrix. It should be noted that the expression for free energy of a binary model liquid in a disordered porous matrix in the RPA was derived in Ref. [46] in terms of direct correlation functions.

C. Charge- and size-asymmetric primitive model confined in a disordered hard-sphere matrix: Beyond the Gaussian approximation

We are interested in the vapor-liquid phase diagram of an asymmetric PM confined in a disordered HS matrix. We assume that interactions between matrix particles and matrix and fluid particles can be neglected beyond the hard core. In this case we have

$$\varphi_{00}(r) = 0, \quad \varphi_{0+}(r) = 0, \quad \varphi_{0-}(r) = 0. \tag{13}$$

The system is electrically neutral: $\sum_{A=+,-} q_A\rho_A = 0$ where q_A is a charge of the ion of the Ath species, $q_+ = +zq$, $q_- = -q$, ρ_A is the number density of the Ath species.

The model is characterized by the parameters

$$\lambda = \frac{\sigma_+}{\sigma_-}, \quad z = q_+/|q_-| \tag{14}$$

describing charge and size asymmetry of ions (σ_A is the diameter of the Ath species). In addition, we introduce the parameter λ_0 which describes the size asymmetry between ions and matrix particles defined as a size ratio of matrix and negatively charged ions:

$$\lambda_0 = \sigma_0/\sigma_-. \tag{15}$$

We use the Weeks–Chandler–Andersen regularization scheme for the Coulomb potentials $\varphi_{AB}(r)$ inside the hard core [47]. Then, we have for $\beta\widetilde{\varphi}_{AB}(k)$:

$$\begin{aligned} \beta\widetilde{\varphi}_{++}(k) &= \frac{4\pi z\sigma^3_{+-}}{T^*}\frac{(1+\lambda)}{2\lambda}\frac{\sin[2x\lambda/(1+\lambda)]}{x^3}, \\ \beta\widetilde{\varphi}_{--}(k) &= \frac{4\pi\sigma^3_{+-}}{T^*z}\frac{(1+\lambda)}{2}\frac{\sin[2x/(1+\lambda)]}{x^3}, \\ \beta\widetilde{\varphi}_{+-}(k) &= -\frac{4\pi\sigma^3_{+-}}{T^*}\frac{\sin(x)}{x^3}, \end{aligned}$$

where $T^* = \frac{k_BT\sigma_{+-}}{q^2z}$ is the dimensionless temperature, $x = k\sigma_{+-}$, and $\sigma_{+-} = (\sigma_+ + \sigma_-)/2$.

Our aim here is to derive an analytical expression for the chemical potential conjugate to the order parameter which takes into account the correlation effects of the order higher than the second one. To this end, we follow a theoretical scheme proposed in Ref. [24] for the bulk PM. We start with the grand potential of a partly quenched model in the Gaussian approximation (7) under condition (13) and we pass from the initial chemical potentials ν_+ and ν_- to their linear combinations

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

As was shown in Ref. [26], ν_1 is conjugate to the order parameter of the vapor-liquid critical point

$$\xi_0 = \frac{1}{\sqrt{1+z^2}}\left(\frac{1+z^2}{1+z}\rho_N + \frac{1-z}{1+z}\rho_Q\right), \tag{16}$$

where $\rho_N = \rho_+ + \rho_-$ and $\rho_Q = z\rho_+ - \rho_-$ describe long-wavelength fluctuations of the total number density and charge density, respectively. ν_2 is conjugate to ρ_Q. It follows from Eq. (16) that $\xi_0 \sim \rho_N$ for $z = 1$.

Then, we present ν_1 and ν_2 as

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

where ν_1^0 and ν_2^0 are the MF parts of ν_1 and ν_2, respectively, and $\Delta\nu_1$ and $\Delta\nu_2$ are solutions of the equations for chemical potentials. We self-consistently solve the equations for the relevant chemical potential $\Delta\nu_1$ by means of successive approximations. The procedure of searching for a solution is described in Refs. [13,24,26].

The expression for the relevant chemical potential ν_1 found in the first nontrivial approximation corresponding to $\nu_2 = \nu_2^0$ is of the form

$$\begin{aligned}\nu_1 = \nu_1^0 &+ \frac{\sqrt{1+z^2}}{2[\mathfrak{M}^c_{++} + 2z\mathfrak{M}^c_{+-} + z^2\mathfrak{M}^c_{--}]}\\ &\times \sum_{\mathbf{k}} \frac{1}{\det\left[\widehat{\Phi}_2\widehat{\mathfrak{M}}^c_2 + \underline{1}\right]}\\ &\times [\beta\tilde{\varphi}_{++}(k)\mathcal{F}_1 + \beta\tilde{\varphi}_{--}(k)\mathcal{F}_2 + 2\beta\tilde{\varphi}_{+-}(k)\mathcal{F}_3], \qquad (17)\end{aligned}$$

where $\nu_1^0 = \nu_1^r + \nu_1^{se}$ with ν_1^r being the combination of the HS chemical potentials

$$\nu_1^r = \frac{\nu_+^r + z\nu_-^r}{\sqrt{1+z^2}}$$

and ν_1^{se} being the combination of self-energy parts of chemical potentials ν_+ and ν_-,

$$\nu_1^{se} = -\frac{1}{2V\sqrt{1+z^2}}\sum_{\mathbf{k}}[\beta\tilde{\phi}_{++}(k) + z\beta\tilde{\phi}_{--}(k)].$$

In addition to the second-order cumulants $\mathfrak{M}^c_{AB}$, Eq. (17) includes the connected parts of the third-order cumulants $\mathfrak{M}^c_{ABC}$:

$$\begin{aligned}&\mathcal{F}_1 = \mathfrak{M}^c_{+++} + z\mathfrak{M}^c_{++-}, \quad \mathcal{F}_2 = \mathfrak{M}^c_{+--} + z\mathfrak{M}^c_{---},\\ &\mathcal{F}_3 = \mathfrak{M}^c_{++-} + z\mathfrak{M}^c_{+--}. \qquad (18)\end{aligned}$$

In Eq. (17), $\mathfrak{M}^c_{AB}$ and $\mathfrak{M}^c_{ABC}$ are approximated by their values in the long-wavelength limit. A general form of Eq. (17) is similar to that for the bulk case obtained in Ref. [26]. However, the main difference concerns the reference system. Below, we consider the reference system in more detail.

III. REFERENCE SYSTEM: THERMODYNAMIC PROPERTIES FROM SCALED PARTICLE THEORY

We start with general relationships valid for a multicomponent system; in particular, a recurrent formula allowing us to derive the third-order cumulants in the long-wavelength limit [48]:

$$\mathfrak{M}_{\alpha_1\alpha_2\ldots\alpha_n} = \mathfrak{M}_{\alpha_1\alpha_2\ldots\alpha_n}(0,\ldots) = \frac{\partial\mathfrak{M}_{\alpha_1\alpha_2\ldots\alpha_{n-1}}(0,\ldots)}{\partial\nu_{\alpha_n}}, \qquad (19)$$

and the equation given by Kirkwood and Buff which relates the thermodynamic properties with the partial structure factors at $k = 0$ [49],

$$S_{\alpha_1\alpha_2}(0) = \frac{1}{\sqrt{\rho_{\alpha_1}\rho_{\alpha_2}}}\mathfrak{M}_{\alpha_1\alpha_2}(0) = \frac{1}{\sqrt{\rho_{\alpha_1}\rho_{\alpha_2}}}\frac{|A|_{\alpha_1\alpha_2}}{\det(A)}. \qquad (20)$$

In Eq. (20), A is a matrix with elements given by $A_{\alpha_1\alpha_2} = (\partial\nu_{\alpha_1}/\partial\rho_{\alpha_2})_{T,\rho_{\alpha_3}}$, $|A|_{\alpha_1\alpha_2}$ indicates the cofactor of the elements $A_{\alpha_1\alpha_2}$. Using the Ornstein–Zernike equation we obtain from Eq. (20)

$$\left(\frac{\partial\nu_{\alpha_1}}{\partial\rho_{\alpha_2}}\right)_{T,\rho_{\alpha_3}} = \frac{\delta_{\alpha_1\alpha_2}}{\rho_{\alpha_1}} - \tilde{c}_{\alpha_1\alpha_2}(0), \qquad (21)$$

where $\tilde{c}_{\alpha_1\alpha_2}(0)$ is the Fourier transform of the partial direct correlation functions [50] at $k = 0$. In Ref. [46], general expressions were presented for thermodynamic quantities and relations for a two-component system confined in a disordered matrix. In particular, it was shown that, in this case, Eq. (21) are satisfied for the connected parts of $\tilde{c}_{\alpha_1\alpha_2}(0)$ [see Eqs. (47)–(49) in Ref. [46]]. Using Eq. (19), $\mathfrak{M}_{\alpha_1\alpha_2\alpha_3}(0,0)$ can be expressed in terms of the partial structures factors $S_{\alpha_1\alpha_2}(0)$ and their derivatives. The corresponding formulas for a two-component system are given in Appendix B. The same formulas hold for the connected parts of the quantities entering Eqs. (B1) and (B2).

Now we turn back to our reference system which consists of a two-component HS fluid confined in a one-component HS matrix. The matrix is characterized by HS obstacles of diameter σ_0 and different types of porosity; namely, geometrical porosity ϕ_0 and two probe-particle porosities ϕ_+ and ϕ_- for the two-fluid species. The probe-particle porosity ϕ_+ (ϕ_-) is defined by the excess value of the chemical potential of a fluid particle with diameter σ_+ (σ_-) in the limit of infinite dilution and, hence, takes into account the size of adsorbate species [40]. The geometrical porosity ϕ_0 is independent of adsorbate. It defines a "bare" pore volume of the matrix and can be considered as a more general characteristic. For the HS matrix $\phi_0 = 1 - \eta_0$, where $\eta_0 = \pi\rho_0\sigma_0^3/6$, $\rho_0 = N_0/V$ is the number density of matrix particles.

Using the results obtained for an n-component HS fluid in an m-component HS matrix [40] we find analytical expressions for the chemical potentials ν_+^r and ν_-^r. The expression for ν_+^r in the SPT2b approximation providing the best accuracy reads

$$\begin{aligned}\nu_+^r = \nu_+^{SPT2b} &= \ln(\Lambda_+^3\eta_+) - \ln(\phi_+) + k_+^1\frac{\eta_i/\phi_0}{1-\eta_i/\phi_0} + k_+^2\left(\frac{\eta_i/\phi_0}{1-\eta_i/\phi_0}\right)^2 + k_+^3\left(\frac{\eta_i/\phi_0}{1-\eta_i/\phi_0}\right)^3 - \ln\left(1-\frac{\eta_i}{\phi}\right)\\ &\times\left\{1-\frac{\phi}{\eta_i}\left[1-\frac{\phi}{\phi_+}\frac{(\eta_+ + \lambda^3\eta_-)}{\eta_i}\right]\right\} - \frac{\phi_0}{\eta_i}\ln\left(1-\frac{\eta_i}{\phi_0}\right)\left(1-\frac{\eta_+ + \lambda^3\eta_-}{\eta_i}\right) + \frac{(\eta_+ + \lambda^3\eta_-)}{\eta_i}\left(1-\frac{\phi}{\phi_+}\right), \qquad (22)\end{aligned}$$

where $\eta_i = \eta_+ + \eta_-$, $\eta_A = \frac{\pi}{6}\rho_A\sigma_A^3$ $(A = +,-)$, and

$$\phi^{-1} = \frac{1}{\eta_i}\left(\frac{\eta_+}{\phi_+} + \frac{\eta_-}{\phi_-}\right). \tag{23}$$

For ϕ_+, we have

$$\phi_+ = (1-\eta_0)\exp\left(-\frac{6\tau\lambda}{(1+\lambda)}\frac{\eta_0}{(1-\eta_0)}\left\{1 + \frac{\tau\lambda}{1+\lambda}\left(2 + \frac{3\eta_0}{1-\eta_0}\right) + \frac{4}{3}\left(\frac{\tau\lambda}{1+\lambda}\right)^2\left[1 + \frac{3\eta_0}{1-\eta_0} + 3\left(\frac{\eta_0}{1-\eta_0}\right)^2\right]\right\}\right), \tag{24}$$

where the parameter

$$\tau = \frac{\sigma_{+-}}{\sigma_0} = \frac{1+\lambda}{2\lambda_0} \tag{25}$$

is introduced. ϕ_- is obtained from Eq. (24) by replacing λ with $1/\lambda$.

The expressions for coefficients k_+^i are as follows:

$$k_+^1 = \frac{\eta_-\lambda(\lambda^2 + 3\lambda + 3) + 7\eta_+}{\eta_i} + \frac{3\tau\lambda\eta_0[\eta_-(\lambda^2 + 6\lambda + 1) + 8\eta_+]}{\eta_i(1+\lambda)(1-\eta_0)} + \frac{6\tau^2\lambda^2\eta_0(1 + 2\eta_0)[\eta_-(1+\lambda) + 2\eta_+]}{\eta_i(1+\lambda)^2(1-\eta_0)^2}, \tag{26}$$

$$\begin{aligned} k_+^2 = {} & \frac{3}{2}\frac{[\eta_-^2\lambda^2(2\lambda + 3) + 2\eta_+\eta_-\lambda(\lambda + 4) + 5\eta_+^2]}{\eta_i^2} + \frac{3\tau\lambda\eta_0[2\eta_-^2\lambda(2 + 3\lambda) + \eta_+\eta_-(\lambda^2 + 14\lambda + 5) + 10\eta_+^2]}{\eta_i^2(1+\lambda)(1-\eta_0)} \\ & + \frac{6\tau^2\lambda^2\eta_0[\eta_-(4\eta_0\lambda + \eta_0 + \lambda) + \eta_+(5\eta_0 + 1)]}{(1+\lambda)^2(1-\eta_0)^2\eta_i}, \end{aligned} \tag{27}$$

$$k_+^3 = 3\left[\frac{2\tau\lambda\eta_0}{(1+\lambda)(1-\eta_0)} + \frac{\eta_+ + \lambda\eta_-}{\eta_i}\right]^2\frac{\eta_+ + \lambda\eta_-}{\eta_i}. \tag{28}$$

The expression for ν_-^r can be obtained from Eqs. (22)–(28) by replacing η_+ with η_- and vice versa as well as by replacing λ with $1/\lambda$, ϕ_+ with ϕ_-, and k_+^i with k_-^i $(i = 1,2,3)$.

Based on the equations for ν_+^r and ν_-^r obtained above one can derive analytic expressions for $\mathfrak{M}_{AB}^c(0)$ and $\mathfrak{M}_{ABC}^c(0,0)$ which enter the equation (17) for the relevant chemical potential. In particular, for $S_{AB}^c = \mathfrak{M}_{AB}^c(0)/\sqrt{\rho_A\rho_B}$ we have

$$S_{++}^c = \left(\frac{\partial\nu_-^r}{\partial\eta_-}\right)_{\eta_+}\frac{\eta_-}{\det\left(A_2^r\right)}, \quad S_{--}^c = \left(\frac{\partial\nu_+^r}{\partial\eta_+}\right)_{\eta_-}\frac{\eta_+}{\det\left(A_2^r\right)}, \quad S_{+-}^c = -\left(\frac{\partial\nu_-^r}{\partial\eta_+}\right)_{\eta_-}\frac{\sqrt{\lambda^3\eta_+\eta_-}}{\det\left(A_2^r\right)}, \tag{29}$$

where

$$\det\left(A_2^r\right) = \eta_+\eta_-\left[\left(\frac{\partial\nu_+^r}{\partial\eta_+}\right)_{\eta_-}\left(\frac{\partial\nu_-^r}{\partial\eta_-}\right)_{\eta_+} - \left(\frac{\partial\nu_+^r}{\partial\eta_-}\right)_{\eta_+}\left(\frac{\partial\nu_-^r}{\partial\eta_+}\right)_{\eta_-}\right]. \tag{30}$$

Taking into account Eq. (18) and formulas (B1) and (B2) from Appendix B, the coefficients $\mathcal{F}_1$, $\mathcal{F}_2$, and $\mathcal{F}_3$ can be written in the form

$$\begin{aligned} \frac{\mathcal{F}_1}{\rho_+} &= \left(S_{++}^c + \eta_+\frac{\partial S_{++}^c}{\partial\eta_+}\right)\left(S_{++}^c + z\sqrt{z}S_{+-}^c\right) + \frac{\eta_-}{\sqrt{z}}\frac{\partial S_{++}^c}{\partial\eta_-}\left(S_{+-}^c + z\sqrt{z}S_{--}^c\right), \\ \frac{\mathcal{F}_2}{\rho_-} &= \frac{1}{\sqrt{z}}\left(S_{--}^c + \eta_-\frac{\partial S_{--}^c}{\partial\eta_-}\right)\left(S_{+-}^c + z\sqrt{z}S_{--}^c\right) + \eta_+\frac{\partial S_{--}^c}{\partial\eta_+}\left(S_{++}^c + z\sqrt{z}S_{+-}^c\right), \\ \frac{\mathcal{F}_3}{\sqrt{\rho_+\rho_-}} &= S_{+-}^c\left(S_{++}^c + \eta_+\frac{\partial S_{++}^c}{\partial\eta_+}\right) + zS_{+-}^c\left(S_{--}^c + \eta_-\frac{\partial S_{--}^c}{\partial\eta_-}\right) + \frac{1}{\sqrt{z}}S_{--}^c\eta_-\frac{\partial S_{++}^c}{\partial\eta_-} + z\sqrt{z}S_{++}^c\eta_+\frac{\partial S_{--}^c}{\partial\eta_+}. \end{aligned} \tag{31}$$

Explicit expressions for Eqs. (29)–(31) are too long to be presented here.

IV. RESULTS AND DISCUSSION

Using the equations (17) and (18) (as well as the expressions from Sec. III), we study the vapor-liquid phase diagrams of the PM confined in a HS matrix. Here, we focus on a monovalent size-asymmetric PM. Because of symmetry with respect to the exchange of "+" and "−" ions, only $\lambda > 1$ or $\lambda < 1$ need be considered in this case. Supplementing the above-mentioned equations by the Maxwell construction, we calculate the coexistence curves and the corresponding critical parameters for different values of size ratios λ and λ_0 [see Eqs. (14) and (15)] and for different matrix porosities ϕ_0. Estimates of the critical temperature and the critical density are given by their values for which the maxima and minima of the van der Waals loops coalesce. The reduced temperature and the reduced density are chosen in the conventional form, which is common to the works dealing with the phase behavior of an

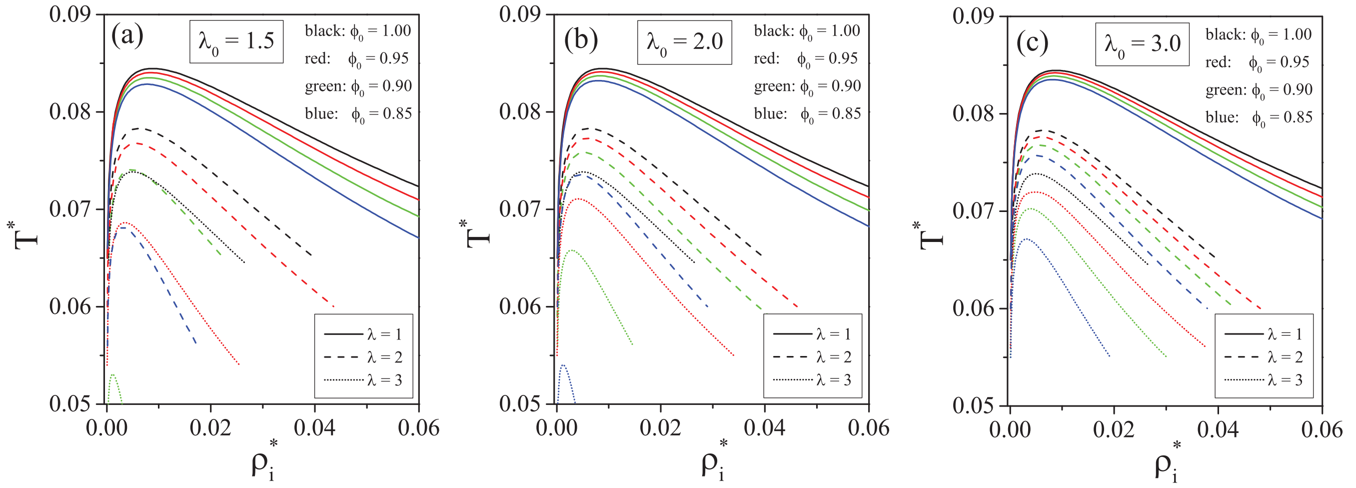

FIG. 1. Vapor-liquid phase diagrams at the fixed size ratios (a) $\lambda_0 = 1.5$, (b) $\lambda_0 = 2.0$, and (c) $\lambda_0 = 3.0$ [see Eq. (15)]. In each case, data are shown for different ratios of ion size asymmetry λ as indicated in the legends and for different matrix porosities ϕ_0. At the fixed λ, $\phi_0 = 1$, 0.95, 0.9, and 0.85 (from top to bottom). The bulk case ($\phi_0 = 1$) is presented for comparison. Temperature T^* and the ion density ρ_i^* are in dimensional reduced units defined in Eqs. (32).

asymmetric PM in the bulk state (see, for example, Ref. [14]):

$$T^* = \frac{k_B T \sigma_{+-}}{q^2 z}, \quad \rho_i^* = \rho_i \sigma_{+-}^3, \tag{32}$$

where $\rho_i = \rho_+ + \rho_-$ is the total ionic number density. It should be noted that, for the bulk PM, our theory predicts a reduction of the coexistence regions as well as a decrease of the critical parameters T_c^* and $\rho_{i,c}^*$ with an increase of size asymmetry [26,27]. This behavior qualitatively agrees with simulation results [14–19].

The calculated phase diagrams in the (T^*-ρ_i^*) plane for $\lambda_0 = 1.5$, 2, and 3 are shown in Figs. 1(a)–1(c). In each figure, for the given λ_0, we show the coexistence curves for $\lambda = 1$, 2, and 3 and for the three values of matrix porosity $\phi_0 = 0.85$, 0.9, and 0.95. The bulk case, $\phi_0 = 1.0$, is shown for comparison. For the fixed λ_0 and λ, the phase diagrams demonstrate the usual behavior of confined fluids, i.e., both the critical temperature and the critical density decrease when the porosity decreases and simultaneously the coexistence region becomes narrower. An increase of size asymmetry of the ions which corresponds to an increase of the parameter λ essentially strengthens the tendency of T_c^* and $\rho_{i,c}^*$ towards lower values. By contrast, an increase of the size of matrix particles, i.e., an increase of the parameter λ_0, leads to the opposite effect. Hence, in Figs. 1(a)–1(c) one can observe a competition between different effects controlled by the parameters ϕ_0, λ, and λ_0. Since the matrix is totally defined by its porosity and by the size of matrix particles σ_0, the parameters ϕ_0 and $\lambda_0 = \sigma_0/\sigma_-$ are responsible for the confinement effects. It is seen from Fig. 1 that the strongest confinement effect is obtained for the lowest porosity and for the smallest size of matrix particles, i.e., for $\phi_0 = 0.85$ and $\lambda_0 = 1.5$ [see Fig. 1(a)]. In this case, the critical parameters T_c^* and $\rho_{i,c}^*$ dramatically decrease with an increase of the ion size asymmetry λ. Moreover, for $\lambda = 3$, the critical temperature T_c^* is so low that the vapor-liquid phase transition gets beyond the temperature range considered in our

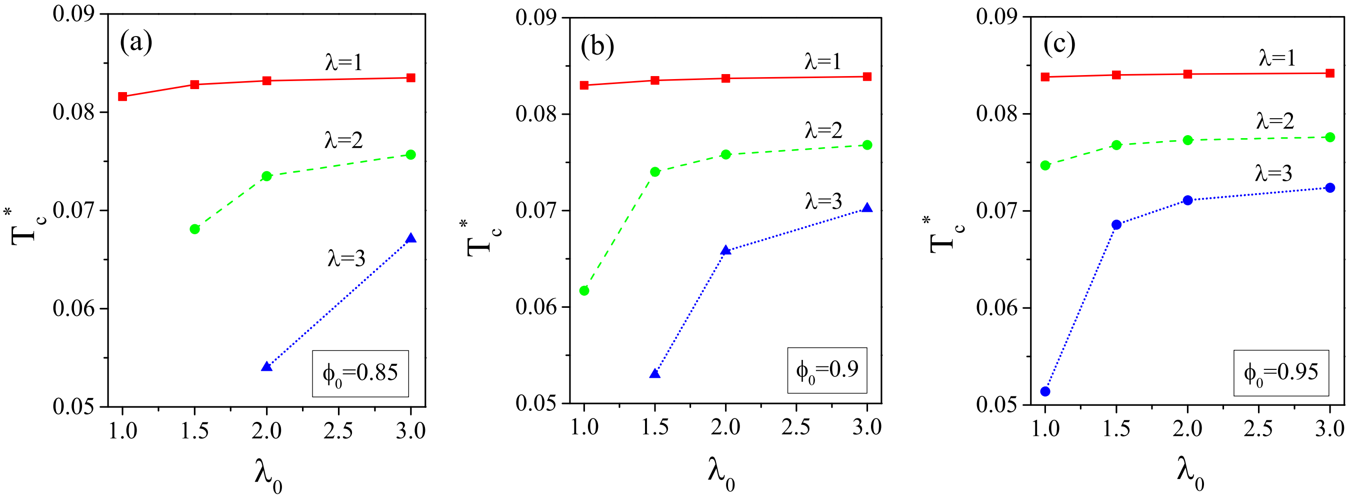

FIG. 2. Dependence of the critical temperature T_c^* on the size of matrix particles λ_0 [see Eq. (15)] for different matrix porosities: (a) $\phi_0 = 0.85$, (b) $\phi_0 = 0.9$, and (c) $\phi_0 = 0.95$. In each case, data are shown for different values of the ion size ratio λ.

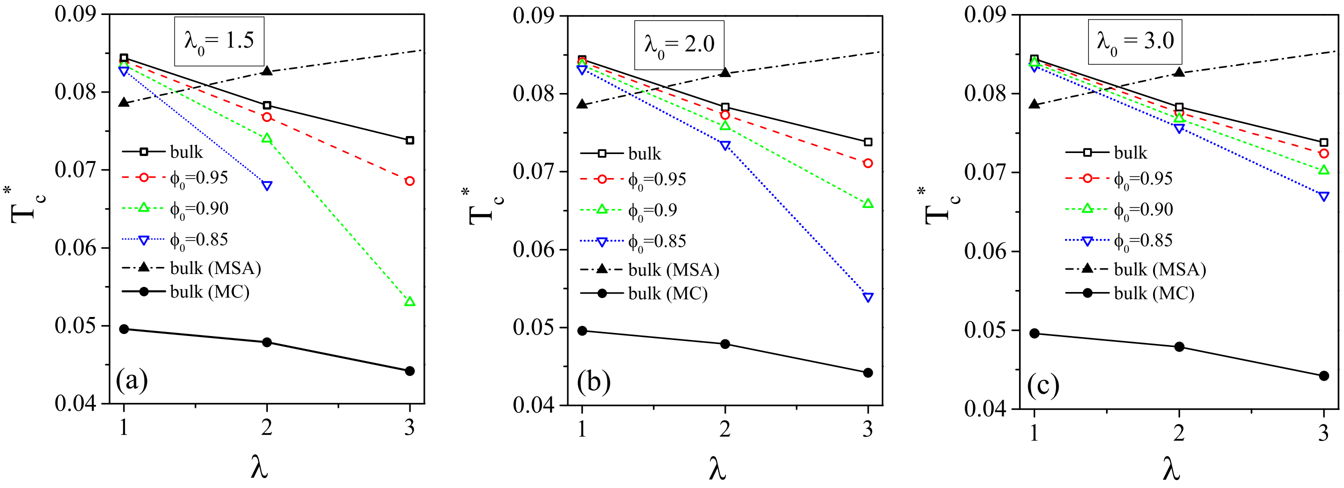

FIG. 3. Dependence of the critical temperature T_c^* on the ion size ratio λ at the fixed size ratios (a) $\lambda_0 = 1.5$, (b) $\lambda_0 = 2.0$, and (c) $\lambda_0 = 3.0$ [see Eq. (15)]. In each case, data are for different values of the matrix porosity as indicated in the legends. Open symbols denote the results obtained in this study using the CV approach, filled triangles are MSA results [20], and filled circles denote simulation results [14].

study. On the other hand, the phase transition has been obtained for larger matrix particles [see Figs. 1(b) and 1(c)], although for $\lambda_0 = 2$, the coexistence region is rather small.

In Figs. 2(a)–2(c), we present the dependence of the critical temperature T_c^* on λ_0 in more detail. It is seen that, for a symmetric ionic fluid ($\lambda = 1$), the dependence of T_c^* on λ_0 is weak, especially for large porosity ($\phi_0 = 0.95$). For an asymmetric ionic fluid ($\lambda = 2$ and 3), this dependence drastically changes, i.e., T_c^* starts to sharply decrease at small values of λ_0. This trend is more prominent when the porosity ϕ_0 is lower.

Similar to the bulk case, the critical temperature T_c^* of a confined ionic fluid decreases with an increase of size asymmetry of ions λ. The corresponding results are shown in Figs. 3(a)–3(c) for the matrix porosities $\phi_0 = 0.85$, 0.9, and 0.95 and for different sizes of the matrix particles $\lambda_0 = 1.5$, 2.0, and 3.0. By comparison, in these figures we show the critical temperatures of a bulk PM fluid obtained from the grand canonical Monte Carlo simulations [14] and from the calculations performed in the MSA [20]. It is seen that the dependence of the critical temperature of a PM fluid on the ion size asymmetry provided within our theoretical approach is in a qualitative agreement with the simulation studies, while the MSA leads to the results with the opposite trend which is considered to be wrong. For a confined PM fluid, the slopes of the dependence of T_c^* on λ indicate that at lower matrix porosities, the critical temperature decreases faster with λ. The same effect is noticed when the size of matrix particles is smaller.

The critical density $\rho_{i,c}^*$ of the confined PM fluid depending on λ is shown in Figs. 4(a)–4(c) for the same matrix porosities and sizes of matrix particles as in the previous figures. As one can see, general conclusions on the behavior of the critical density $\rho_{i,c}^*$ qualitatively repeat the conclusions on the behavior of the critical temperature T_c^*. It should be noted that our theoretical predictions of the trend of $\rho_{i,c}^*$ with λ is in qualitative

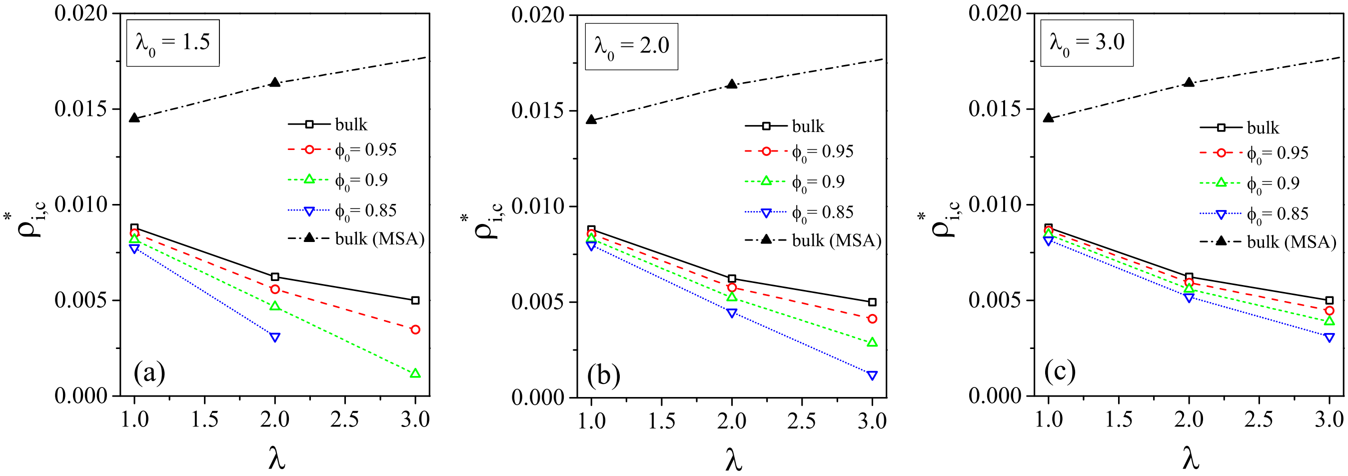

FIG. 4. Dependence of the critical density $\rho_{i,c}^*$ on the ion size ratio λ at the fixed size ratios (a) $\lambda_0 = 1.5$, (b) $\lambda_0 = 2.0$, and (c) $\lambda_0 = 3.0$ [see Eq. (15)]. In each case, data are for different values of the matrix porosity as indicated in the legends. Open symbols denote the results obtained in this study using the CV approach and filled triangles are MSA results [20].

agreement with the simulation findings for the bulk PM [14]. On the other hand, the MSA approach again provides a wrong trend.

V. CONCLUSIONS

We have studied the vapor-liquid phase equilibrium of an asymmetric binary ionic model confined in a disordered porous medium formed by a HS matrix. To this end, considering the whole system as a partly quenched model, we have developed a theoretical approach that enables us to formulate a perturbation theory. The approach is based on the CV method with a reference system. For an asymmetric PM in the bulk state, it allowed us to obtain the correct trends of both the critical temperature and the critical density with size and charge asymmetry. Following the ideas earlier proposed for the bulk PM, we have derived an explicit expression for the relevant chemical potential conjugate to the order parameter which includes the effects of correlations up to third order. It should be emphasized that the expression takes into account both charge and size asymmetry at the same level of approximation.

In this paper, the reference system is considered to be a two-component HS fluid confined in a disordered HS matrix. The HS fluid is characterized by the parameter of size asymmetry $\lambda = \sigma_+/\sigma_-$ while the matrix is characterized by the diameter of obstacles σ_0 and different types of matrix porosity, geometrical porosity ϕ_0, and two probe-particle porosities ϕ_+ and ϕ_-. The description of the reference system has been carried out by using the recent generalization of the SPT theory for a multicomponent fluid in a multicomponent matrix. Here, we have presented explicit expressions for the partial chemical potentials in the approximation that provides the best accuracy against the simulation results. Based on these expressions, we have found analytical formulas for the two- and three-body correlation functions of the reference system in the long-wavelength limit.

Using an expression for the relevant chemical potential, we have calculated the vapor-liquid phase diagrams of a monovalent PM with $\lambda = 1$, 2, and 3 confined in the HS matrix of different porosities $\phi_0 = 0.85$, 0.90, and 0.95 and with different size ratios between the matrix obstacles and the negatively charged ions, $\lambda_0 = \sigma_0/\sigma_- = 1$, 1.5, 2, and 3. Based on the phase diagrams, the critical parameters T_c^* and $\rho_{i,c}^*$ of a confined PM fluid have been obtained. It has been shown that both the critical temperature and the critical density lower when the matrix porosity decreases. On the other hand, at a fixed porosity, the critical parameters T_c^* and $\rho_{i,c}^*$ are higher in a matrix of large particles than in a matrix of small particles. An increase in the ratio of ion size asymmetry λ leads to the lowering of T_c^* and $\rho_{i,c}^*$, and this trend is essentially strengthened by the confinement effect at lower porosities, especially when a matrix is composed of the particles of small sizes. It should be noted that variations in the critical parameters T_c^* and $\rho_{i,c}^*$ with λ and ϕ_0 confirm our previous results obtained within the framework of the AMSA where, however, only the case of fixed $\lambda_0 = 2$ is considered. A distinguishing feature of the present approach is the possibility to derive, without additional assumptions such as the presence of ion pairs, an analytical expression for the chemical potential conjugate to the order parameter which provides a qualitatively correct phase behavior of a rather complex system.

Finally, for the asymmetric PM confined in a disordered porous matrix, we have proposed an analytical approach which allows one to make qualitative predictions of the vapor-liquid phase behavior depending on size and charge asymmetry of ions and on matrix characteristics such as a geometrical porosity and a diameter of solid obstacles. We expect that taking into account of higher-order correlations will lead to quantitative, but not qualitative, changes to our results. It should be noted that the present approach can be extended for more complex models, e.g., for the models which include attractive or repulsive ion-matrix interactions in addition to a hard-core repulsion.

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APPENDIX A: GRAND PARTITION FUNCTION OF A (2s + 1)-COMPONENT REPLICATED MODEL IN THE MEAN-FIELD APPROXIMATION

The MF part of the grand partition function is of the form

$$\begin{aligned}\Xi^{\mathrm{mf}} &= \Xi^{r}\left[\tilde{\nu}_0, \tilde{\nu}_A^{\alpha}\right]\\ &\quad \times \exp\left\{\langle N_0\rangle_r\left[\frac{\beta}{2}\overline{\rho_0}\tilde{u}_{00}^{(p)}(0) + \sum_{\alpha}\sum_{A}\beta\overline{\rho_A^{\alpha}}\tilde{u}_{0A}^{\alpha(p)}(0)\right]\right\},\end{aligned} \tag{A1}$$

where Ξ^r is the grand partition function of a $(2s+1)$-component reference system with the renormalized partial chemical potentials

$$\begin{aligned}\tilde{\nu}_0 &= \nu_0 + \frac{\beta}{2V}\sum_{\mathbf{k}}\tilde{u}_{00}^{(p)}(k) - \overline{\rho_0}\beta\tilde{u}_{00}^{(p)}(0)\\ &\quad - \sum_{\alpha}\sum_{A}\overline{\rho_A^{\alpha}}\beta\tilde{u}_{0A}^{\alpha(p)}(0),\end{aligned} \tag{A2}$$

$$\begin{aligned}\tilde{\nu}_A^{\alpha} &= \nu_A^{\alpha} + \frac{\beta}{2V}\sum_{\mathbf{k}}\tilde{u}_{AA}^{\alpha\alpha(p)}(k) - \overline{\rho_0}\beta\tilde{u}_{0A}^{\alpha(p)}(0)\\ &\quad - \sum_{B}\overline{\rho_B^{\alpha}}\beta\tilde{u}_{AB}^{\alpha\alpha(p)}(0),\end{aligned} \tag{A3}$$

where $\nu_0 = \beta\mu_0 - \ln\Lambda_0^3$ and $\nu_A^{\alpha} = \beta\mu_A^{\alpha} - \ln\Lambda_A^3$ are the dimensionless chemical potentials of the corresponding species (Λ_0 and Λ_A are the de Broglie thermal wavelengths), $\overline{\rho_0} = \langle N_0\rangle_r/V$, $\overline{\rho_A^{\alpha}} = \langle N_A^{\alpha}\rangle_r/V$, $\langle\ldots\rangle_r$ indicates the average taken over the reference system, $\tilde{u}_{00}^{(p)}(k)$, $\tilde{u}_{0A}^{\alpha(p)}(k)$, and $\tilde{u}_{AB}^{\alpha\alpha(p)}(k)$ are the Fourier transforms of the perturbative parts of the corresponding interaction potentials.

APPENDIX B: EXPRESSIONS FOR $\mathfrak{M}_{\alpha_1\alpha_2\alpha_3}(0,0)$

For a two-component system, the expressions for the third-order cumulants in the long-wavelength limit are as follows:

$$\mathfrak{M}_{+++}(0,0) = \rho_+\left\{S_{++}(0)\left[S_{++}(0)+\eta_+\left(\frac{\partial S_{++}(0)}{\partial\eta_+}\right)_{\eta_-}\right]+\sqrt{\frac{\rho_+}{\rho_-}}S_{+-}(0)\,\eta_-\left(\frac{\partial S_{++}(0)}{\partial\eta_-}\right)_{\eta_+}\right\}, \tag{B1}$$

$$\mathfrak{M}_{++-}(0,0) = \sqrt{\rho_+\rho_-}\left\{S_{+-}(0)\left[S_{++}(0)+\eta_+\left(\frac{\partial S_{++}(0)}{\partial\eta_+}\right)_{\eta_-}\right]+\sqrt{\frac{\rho_+}{\rho_-}}S_{--}(0)\,\eta_-\left(\frac{\partial S_{++}(0)}{\partial\eta_-}\right)_{\eta_+}\right\}. \tag{B2}$$

The expressions for $\mathfrak{M}_{---}(0,0)$ and $\mathfrak{M}_{+--}(0,0)$ can be obtained replacing indices "+" by indices "−" and vice versa. The same formulas are valid for the connected parts of the corresponding quantities.

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