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Gas–liquid critical point in ionic fluids

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Abstract

Based on the method of collective variables, we develop the statistical field theory for the study of a simple charge-asymmetric 1: z primitive model (SPM). It is shown that the well-known approximations for the free energy, in particular the DH limiting law (DHLL) and the optimized random phase approximation (ORPA), can be obtained within the framework of this theory. In order to study the gas–liquid critical point of the SPM we propose a method for the calculation of chemical potential conjugate to the total number density which allows us to take into account the higher-order fluctuation effects. As a result, the gas–liquid phase diagrams are calculated for $z = 2–4$. The results demonstrate a qualitative agreement with Monte Carlo (MC) simulation data: the critical temperature decreases when z increases and the critical density increases rapidly with z .

1. Introduction

Besides being of fundamental interest, ionic systems including electrolyte solutions, molten salts and ionic liquids deserve great attention from a practical point of view. For example, new ionic liquids with very low vapour pressure may find applications in an environmentally clean industry. Over the last ten years the phase and critical behaviour of ionic fluids has been a subject of intense research. For reviews of experimental and theoretical situation see [1–7] and the references cited therein. The basic properties of ionic systems can be described by the primitive model (PM) consisting of a mixture of m species of charged hard spheres. A two-component mixture of positive q_0 and negative $-zq_0$ charges having all the same diameter σ is a SPM. In the case $z = 1$ we have the well-known restricted primitive model (RPM). Early studies [8] established that the RPM has a gas–liquid (GL)-like critical point. A reasonable theoretical description of the GL critical point of the RPM was accomplished at a mean-field (MF) level using integral equation methods [4, 9] and Debye–Hückel (DH) theory [10]. Over the last decade numerous simulation studies have been devoted to the location of the GL

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phase transition of this model [11–19], and the most reliable current estimations turn out to be near $T_c^* = 0.049$, $\rho_c^* = 0.08$ when the temperature T^* and the density ρ^* are in standard dimensionless units. Due to controversial experimental findings, the critical behaviour of the RPM has also been under active debate [20–24] and strong evidence for an Ising universal class has been found by recent simulations [19–26] and theoretical [6, 27–29] studies.

In spite of significant progress in this field, ionic systems are far from being completely understood. The investigation of more complex models is very important in understanding the nature of critical and phase behaviour of real ionic fluids which demonstrate both the charge and size asymmetry as well as other complexities such as short-range attraction. The studies of the effects of charge-asymmetry on the phase diagram have been recently started using both computer simulations [18, 30, 31] and theoretical methods [32–35]. Monte Carlo (MC) simulations show that the SPM exhibits a GL-like phase transition, specifically $T_c^*(z)$ decreases with the increase of z while $\rho_c^*(z)$ rapidly increases. Unfortunately, the results obtained within the framework of both the original DH theory and the mean spherical approximation (MSA) are independent of z . The results for the z -dependence of the critical temperature, obtained within the framework of the field-theoretical analysis [32, 33], contradict the simulations displaying the increase of temperature with z . On the other hand, the recent results found based on the DH theory that have incorporated Bjerrum ion pairs and their solvation in the residual ionic fluid [34, 35] (theories DHBjCI and DHBjCIHC) demonstrate the decrease of T_c^* with charge asymmetry for $z = 1–3$ which agrees with MC data. This implies ‘... that recognizing ionic association is inescapable for a successful theory’ [35].

The motivation for this paper is the above-mentioned contradictory results for the z -dependence of the critical temperature. We study the GL phase diagrams of the charge asymmetric 1: z PM by means of the theory that exploits the method of collective variables (CVs) [36, 37] (see also [38, 39]). In particular, our aim is to answer the question: is the theory, which does not include the effects of association explicitly in the Hamiltonian, capable of correctly describing, at least on the qualitative level, the GL-like phase diagram of the SPM? To this end, we develop a theoretical approach which is based on the functional representation of configurational Boltzmann factor in terms of CVs. For a general case of a two-component model which includes both the short- and long-range interactions we derive an exact expression for the functional integral of the grand partition function (GPF). The CV action obtained depends upon the two sets of CVs: $\{\rho_{\mathbf{k}}\}$ (and conjugate $\{\omega_{\mathbf{k}}\}$) and $\{Q_{\mathbf{k}}\}$ (and conjugate $\{\gamma_{\mathbf{k}}\}$) describing the total number density and charge density fluctuations, respectively. We start with the saddle point (or MF) solutions $\bar{\rho}$ (and $\bar{\omega}$) and \bar{Q} (and $\bar{\gamma}$), and then we expand the CV action functionally around the MF solutions. As a result, we obtain an infinite expansion in terms of CVs $\delta\rho_{\mathbf{k}}$ and $\delta Q_{\mathbf{k}}$ (or $\delta\omega_{\mathbf{k}}$ and $\delta\gamma_{\mathbf{k}}$). For the SPM, based on the GPF in the Gaussian approximation, we propose a method for the calculation of the chemical potential conjugate to the total number density. The method allows us to take into account the higher-order fluctuation effects and consists in solving the equations for chemical potentials by means of successive approximations that correspond to the contributions of the higher-order correlations. Its initial idea to some extent resembles the idea sketched out by Hubbard in [40].

It should be noted that the CVs were first introduced in the 1950s [38, 39] and then on their basis the so-called CVs method was developed [36, 37]. Nearly at that time, other functional approaches based on the Stratonovich–Hubbard transformation [40, 41] were originated. As was shown recently [42], both groups of theories are in close relation.

The layout of the paper is as follows. In section 2, starting from the Hamiltonian of an asymmetric two-component model with long- and short-range interactions, we derive the exact functional representation of the GPF. We obtain an explicit expression for free energy of SPM in the random phase approximation (RPA) that leads to the well-known results, i.e. the

DH limiting law (DHLL) for the point charge particles and the free energy in the optimized random phase approximation (ORPA) (or MSA) for the SPM. In section 3 we study the GL critical point of the SPM, taking into account the correlation effects of higher order. The results obtained demonstrate qualitative agreement with the MC simulation data for both the critical temperature and the critical density. We conclude in section 4.

2. Functional representation of the grand partition function of a two-component ionic model in the method of CVs

Let us consider a general case of a classical two-component system consisting of N particles among which there exist N_1 particles of species 1 and N_2 particles of species 2. The pair interaction potential is assumed to be of the following form:

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

where $\phi_{\alpha\beta}^{\text{HS}}(r)$ is the interaction potential between the two additive hard spheres of diameters $\sigma_{\alpha\alpha}$ and $\sigma_{\beta\beta}$. We call the two-component hard-sphere system a reference system (RS). The thermodynamic and structural properties of the RS are assumed to be known. $\phi_{\alpha\beta}^{\text{C}}(r)$ is the Coulomb potential: $\phi_{\alpha\beta}^{\text{C}}(r) = q_\alpha q_\beta \phi^{\text{C}}(r)$, where $\phi^{\text{C}}(r) = 1/(Dr)$, D is the dielectric constant; hereafter we put $D = 1$. The solution is made of both positive and negative ions so that the electroneutrality is satisfied, $\sum_{\alpha=1}^2 q_\alpha c_\alpha = 0$, and c_α is the concentration of the species α , $c_\alpha = N_\alpha/N$. The ions of the species $\alpha = 1$ are characterized by their hard-sphere diameter σ_{11} and their electrostatic charge $+q_0$ and those of species $\alpha = 2$, characterized by diameter σ_{22} , bear opposite charge $-zq_0$ (q_0 is elementary charge and z is the parameter of charge asymmetry). $\phi_{\alpha\beta}^{\text{SR}}(r)$ is the potential of the short-range interaction: $\phi_{\alpha\beta}^{\text{SR}}(r) = \phi_{\alpha\beta}^{\text{R}}(r) + \phi_{\alpha\beta}^{\text{A}}(r)$, where $\phi_{\alpha\beta}^{\text{R}}(r)$ is used to mimic the soft-core asymmetric repulsive interaction; $\phi_{\alpha\beta}^{\text{R}}(r)$ is assumed to have a Fourier transform; $\phi_{\alpha\beta}^{\text{A}}(r)$ describes a van der Waals-like attraction.

We consider the grand partition function (GPF) of the system, which can be written as follows:

$$\Xi[v_\alpha] = \sum_{N_1 \geq 0} \sum_{N_2 \geq 0} \prod_{\alpha=1,2} \frac{\exp(v_\alpha N_\alpha)}{N_\alpha!} \int (d\Gamma) \exp \left[-\frac{\beta}{2} \sum_{\alpha\beta} \sum_{i,j} U_{\alpha\beta}(r_{ij}) \right]. \quad (2)$$

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

Let us introduce operators $\hat{\rho}_{\mathbf{k}}$ and $\hat{Q}_{\mathbf{k}}$,

$$\hat{\rho}_{\mathbf{k}} = \sum_{\alpha} \hat{\rho}_{\mathbf{k},\alpha} \quad \hat{Q}_{\mathbf{k}} = \sum_{\alpha} q_{\alpha} \hat{\rho}_{\mathbf{k},\alpha},$$

which are combinations of the Fourier transforms of the microscopic number density of the species α : $\hat{\rho}_{\mathbf{k},\alpha} = \sum_i \exp(-i\mathbf{k}\mathbf{r}_i^\alpha)$. In this case a part of the Boltzmann factor in (2) which does not include the RS interaction can be presented as follows:

$$\begin{aligned} \exp \left[-\frac{\beta}{2} \sum_{\alpha\beta} \sum_{i,j} (U_{\alpha\beta}(r_{ij}) - \phi_{\alpha\beta}^{\text{HS}}(r_{ij})) \right] &= \exp \left[-\frac{1}{2} \sum_{\mathbf{k}} (\tilde{\Phi}_{NN} \hat{\rho}_{\mathbf{k}} \hat{\rho}_{-\mathbf{k}} \right. \\ &\quad \left. + \tilde{\Phi}_{QQ} \hat{Q}_{\mathbf{k}} \hat{Q}_{-\mathbf{k}} + 2\tilde{\Phi}_{NQ} \hat{\rho}_{\mathbf{k}} \hat{Q}_{-\mathbf{k}}) + \frac{1}{2} \sum_{\alpha} N_\alpha \sum_{\mathbf{k}} (\tilde{\Phi}_{\alpha\alpha}^{\text{SR}}(k) + q_\alpha^2 \tilde{\Phi}_{\alpha\alpha}^{\text{C}}(k)) \right], \quad (3) \end{aligned}$$

where

$$\begin{aligned}\tilde{\Phi}_{NN}(k) &= \frac{1}{(1+z)^2} \left[z^2 \tilde{\Phi}_{11}^{\text{SR}}(k) + 2z \tilde{\Phi}_{12}^{\text{SR}}(k) + \tilde{\Phi}_{22}^{\text{SR}}(k) \right] \\ \tilde{\Phi}_{QQ}(k) &= \frac{1}{(1+z)^2} \left[\tilde{\Phi}_{11}^{\text{SR}}(k) - 2\tilde{\Phi}_{12}^{\text{SR}}(k) + \tilde{\Phi}_{22}^{\text{SR}}(k) \right] + \tilde{\Phi}^{\text{C}}(k) \\ \tilde{\Phi}_{NQ}(k) &= \frac{1}{(1+z)^2} \left[z \tilde{\Phi}_{11}^{\text{SR}}(k) + (1-z) \tilde{\Phi}_{12}^{\text{SR}}(k) - \tilde{\Phi}_{22}^{\text{SR}}(k) \right]\end{aligned}\quad (4)$$

and we use the notations $\tilde{\Phi}_{\alpha\beta}^{X\cdots}(k) = \frac{\beta}{V} \tilde{\phi}_{\alpha\beta}^{X\cdots}(k)$ with $\tilde{\phi}_{\alpha\beta}^{X\cdots}(k)$ being a Fourier transform of the corresponding interaction potential.

In order to introduce the collective variables (CVs) we use the identity

$$\exp \left[-\frac{1}{2} \sum_{\mathbf{k}} \tilde{\Phi} \hat{\eta}_{\mathbf{k}} \hat{\eta}_{-\mathbf{k}} \right] = \int (d\eta) \delta_{\mathcal{F}}[\eta - \hat{\eta}] \exp \left[-\frac{1}{2} \sum_{\mathbf{k}} \tilde{\Phi} \eta_{\mathbf{k}} \eta_{-\mathbf{k}} \right], \quad (5)$$

where $\delta_{\mathcal{F}}[\eta - \hat{\eta}]$ denotes the functional delta function

$$\delta_{\mathcal{F}}[\eta - \hat{\eta}] \equiv \int (d\lambda) \exp \left[i \sum_{\mathbf{k}} \lambda_{\mathbf{k}} (\eta - \hat{\eta}_{\mathbf{k}}) \right],$$

$\eta_{\mathbf{k}} = \eta_{\mathbf{k}}^c - i\eta_{\mathbf{k}}^s$ ($\eta_{\mathbf{k}} = \rho_{\mathbf{k}}$, $Q_{\mathbf{k}}$) is the collective variable and

$$(d\eta) = d\eta_0 \prod_{\mathbf{k} \neq 0} d\eta_{\mathbf{k}}^c d\eta_{\mathbf{k}}^s, \quad (d\lambda) = d\lambda_0 \prod_{\mathbf{k} \neq 0} d\lambda_{\mathbf{k}}^c d\lambda_{\mathbf{k}}^s.$$

The indices c and s denote real and imaginary parts of $\eta_{\mathbf{k}}$ ($\lambda_{\mathbf{k}}$), respectively, and the product over \mathbf{k} is performed in the upper semi-space.

Taking into account (3)–(5), we can rewrite (2) as

$$\Xi[v_{\alpha}] = \int (d\rho) (dQ) (d\omega) (d\gamma) \exp(-\mathcal{H}[v_{\alpha}, \rho, Q, \omega, \gamma]), \quad (6)$$

where the CV action \mathcal{H} is as follows:

$$\begin{aligned}\mathcal{H}[v_{\alpha}, \rho, Q, \omega, \gamma] &= \frac{1}{2} \sum_{\mathbf{k}} [\tilde{\Phi}_{NN}(k) \rho_{\mathbf{k}} \rho_{-\mathbf{k}} + \tilde{\Phi}_{QQ}(k) Q_{\mathbf{k}} Q_{-\mathbf{k}} + 2\tilde{\Phi}_{NQ}(k) \\ &\quad \times \rho_{\mathbf{k}} Q_{-\mathbf{k}}] - i \sum_{\mathbf{k}} (\omega_{\mathbf{k}} \rho_{\mathbf{k}} + \gamma_{\mathbf{k}} Q_{\mathbf{k}}) - \ln \Xi_{\text{HS}}[\bar{v}_{\alpha}; -i\omega, -iq_{\alpha}\gamma].\end{aligned}\quad (7)$$

In (7) CVs $\rho_{\mathbf{k}}$ and $Q_{\mathbf{k}}$ describe fluctuations of the total number density and charge density, respectively. $\Xi_{\text{HS}}[\bar{v}_{\alpha}; -i\omega, -iq_{\alpha}\gamma]$ is the GPF of a two-component system of hard spheres with the renormalized chemical potential \bar{v}_{α} in the presence of the local field $\psi_{\alpha}(r_i)$,

$$\begin{aligned}\Xi_{\text{HS}}[\dots] &= \sum_{N_1 \geq 0} \sum_{N_2 \geq 0} \prod_{\alpha=1,2} \frac{\exp(\bar{v}_{\alpha} N_{\alpha})}{N_{\alpha}!} \int (d\Gamma) \exp \left[-\frac{\beta}{2} \sum_{\alpha\beta} \sum_{ij} \phi_{\alpha\beta}^{\text{HS}}(r_{ij}) \right. \\ &\quad \left. - \sum_{\alpha} \sum_i \psi_{\alpha}(r_i) \right],\end{aligned}\quad (8)$$

where

$$\bar{v}_{\alpha} = v_{\alpha} + \frac{1}{2} \sum_{\mathbf{k}} \tilde{\Phi}_{\alpha\alpha}^{\text{SR}}(k) + \frac{q_{\alpha}^2}{2} \sum_{\mathbf{k}} \tilde{\Phi}^{\text{C}}(k), \quad (9)$$

$$\psi_{\alpha}(r_i) = i\omega(r_i) + iq_{\alpha}\gamma(r_i). \quad (10)$$

Mean-field approximation. The MF approximation of functional (6) is defined by

$$\Xi_{\text{MF}}[v_{\alpha}] = \exp(-\mathcal{H}[v_{\alpha}, \bar{\rho}, \bar{Q}, \bar{\omega}, \bar{\gamma}]), \quad (11)$$

where $\bar{\rho}$, \bar{Q} , $\bar{\omega}$ and $\bar{\gamma}$ are the solutions of the saddle point equations:

$$\begin{aligned}\bar{\rho} &= \langle N[\bar{v}_\alpha; -i\bar{\omega}, -iq_\alpha\bar{\gamma}] \rangle_{\text{HS}}, & \bar{Q} &= 0, \\ \bar{\omega} &= -i\bar{\rho}\tilde{\phi}_{NN}(0), & \bar{\gamma} &= -i\bar{\rho}\tilde{\phi}_{NQ}(0).\end{aligned}\quad (12)$$

Substituting (12) in (11) we obtain

$$\Xi_{\text{MF}}[\nu_\alpha] = \exp\left[\frac{\beta}{2}\bar{\rho}^2\tilde{\phi}_{NN}(0)\right]\Xi_{\text{HS}}[\bar{v}_\alpha; -i\bar{\omega}, -iq_\alpha\bar{\gamma}].$$

The Legendre transform of $\ln \Xi_{\text{MF}}$ gives the free energy in the MF approximation,

$$\begin{aligned}\beta f_{\text{MF}} &= \frac{\beta\mathcal{F}_{\text{MF}}}{V} = \beta f_{\text{HS}}(\rho_\alpha) - \frac{\beta}{2V}\sum_\alpha\rho_\alpha\sum_{\mathbf{k}}\tilde{\phi}_{\alpha\alpha}^{\text{SR}}(k) \\ &\quad - \frac{\beta}{2V}\sum_\alpha q_\alpha^2\rho_\alpha\sum_{\mathbf{k}}\tilde{\phi}^C(k) + \frac{\beta}{2}\rho^2\tilde{\phi}_{NN}(0).\end{aligned}\quad (13)$$

It is worth noting that for $\phi_{\alpha\beta}^{\text{SR}}(r) = 0$ we arrive at the free energy of the SPM in a zero-loop approximation [43].

Beyond the MF approximation. First we present CVs $\rho_{\mathbf{k}}$ and $Q_{\mathbf{k}}$ ($\omega_{\mathbf{k}}$ and $\gamma_{\mathbf{k}}$) as

$$\begin{aligned}\rho_{\mathbf{k}} &= \bar{\rho}\delta_{\mathbf{k}} + \delta\rho_{\mathbf{k}}, & Q_{\mathbf{k}} &= \bar{Q}\delta_{\mathbf{k}} + \delta Q_{\mathbf{k}}, \\ \omega_{\mathbf{k}} &= \bar{\omega}\delta_{\mathbf{k}} + \delta\omega_{\mathbf{k}}, & \gamma_{\mathbf{k}} &= \bar{\gamma}\delta_{\mathbf{k}} + \delta\gamma_{\mathbf{k}},\end{aligned}$$

where the quantities with a bar are given by (12) and $\delta_{\mathbf{k}}$ is the Kronecker symbol.

Then we write $\ln \Xi_{\text{HS}}[\bar{v}_\alpha; -i\bar{\omega}, -iq_\alpha\bar{\gamma}]$ (see (8)–(10)) in the form of the cumulant expansion

$$\begin{aligned}\ln \Xi_{\text{HS}}[\dots] &= \sum_{n\geq 0}\frac{(-i)^n}{n!}\sum_{i_n\geq 0}\sum_{\mathbf{k}_1, \dots, \mathbf{k}_n}\mathfrak{M}_n^{(i_n)}(k_1, \dots, k_n)\delta\gamma_{\mathbf{k}_1}\dots\delta\gamma_{\mathbf{k}_{i_n}} \\ &\quad \times \delta\omega_{\mathbf{k}_{i_n+1}}\dots\delta\omega_{\mathbf{k}_n}\delta_{\mathbf{k}_1+\dots+\mathbf{k}_n},\end{aligned}\quad (14)$$

where $\mathfrak{M}_n^{(i_n)}(k_1, \dots, k_n)$ is the n th cumulant defined by

$$\mathfrak{M}_n^{(i_n)}(k_1, \dots, k_n) = \frac{\partial^n \ln \Xi_{\text{HS}}[\dots]}{\partial\delta\gamma_{\mathbf{k}_1}\dots\partial\delta\gamma_{\mathbf{k}_{i_n}}\partial\delta\omega_{\mathbf{k}_{i_n+1}}\dots\partial\delta\omega_{\mathbf{k}_n}}|_{\delta\gamma_{\mathbf{k}}=0, \delta\omega_{\mathbf{k}}=0}.\quad (15)$$

The expressions for the cumulants (for $i_n \leq 3$) are given in appendix A.

We can integrate (6) over $\delta\omega_{\mathbf{k}}$ and $\delta\gamma_{\mathbf{k}}$ and obtain for $\Xi[\nu_\alpha]$ (see [29])

$$\begin{aligned}\Xi[\nu_\alpha] &= \Xi_{\text{MF}}[\bar{v}_\alpha]\Xi'\int(d\delta\rho)(d\delta Q)\exp\left\{-\frac{1}{2!}\sum_{\mathbf{k}}\left[L_{NN}(\bar{v}_\alpha; k)\delta\rho_{\mathbf{k}}\delta\rho_{-\mathbf{k}}\right.\right. \\ &\quad \left.\left.+ 2L_{NQ}(\bar{v}_\alpha; k)\delta\rho_{\mathbf{k}}\delta Q_{-\mathbf{k}} + L_{QQ}(\bar{v}_\alpha; k)\delta Q_{\mathbf{k}}\delta Q_{-\mathbf{k}}\right]\right. \\ &\quad \left.+\sum_{n\geq 3}\sum_{i_n\geq 0}\mathcal{H}_n^{(i_n)}(\bar{v}_\alpha; \delta\rho, \delta Q)\right\}.\end{aligned}\quad (16)$$

It is worth noting that the above expression is of the same form as that obtained within the framework of the mesoscopic field theory [6, 27]. The main difference is that $\Xi[\nu_\alpha]$ in (16) is a function of full chemical potentials, rather than just a function of their mean field parts.

2.1. Gaussian approximation. A two-component primitive model (PM)

In the Gaussian approximation, which corresponds to taking into account in (16) only terms with $n \leq 2$ ($\mathcal{H}_n^{(i_n)} \equiv 0$), we have $L_{AB}(\bar{v}_\alpha; k) = C_{AB}(\bar{v}_\alpha; k)$ ($A, B = N, Q$), where

$$\begin{aligned}C_{NN} &= \tilde{\Phi}_{NN}(k) + 1/\mathfrak{M}_2^{(0)}(\bar{v}_\alpha; k), & C_{QQ} &= \tilde{\Phi}_{QQ}(k) + 1/\mathfrak{M}_2^{(2)}(\bar{v}_\alpha), \\ C_{NQ} &= \tilde{\Phi}_{NQ}(k).\end{aligned}\quad (17)$$

$C_{NN}(k)$, $C_{QQ}(k)$ and $C_{NQ}(k)$ are the Fourier transforms of the density–density, charge–charge and charge–density direct correlation functions, respectively. It is worth noting that $\mathfrak{M}_2^{(2)}(\bar{v}_\alpha)$ does not depend on \mathbf{k} (see appendix A). After integrating in (16) over $\delta\rho_{\mathbf{k}}$ and $\delta Q_{\mathbf{k}}$ taking into account (17) we arrive at the GPF in the Gaussian approximation.

Let us consider a two-component simple primitive model (SPM) [43] consisting of charged hard spheres of the same diameter ($\sigma_{11} = \sigma_{22} = \sigma$) with $\tilde{\Phi}_{\alpha\beta}^{\text{SR}}(k) = 0$ which differ by their respective charges ($z \neq 1$). We have for the SPM (see (4))

$$\tilde{\Phi}_{NN}(k) = 0, \quad \tilde{\Phi}_{NQ}(k) = 0, \quad \tilde{\Phi}_{QQ}(k) = \tilde{\Phi}^C(k). \quad (18)$$

It should be noted here that the Hamiltonian of the SPM, as for the RPM [29], does not include a direct pair interaction of number density fluctuations. Integration over $\delta\rho_{\mathbf{k}}$ and $\delta\omega_{\mathbf{k}}$ in (6) is trivial in this case and leads to the KSSHE action obtained in [43] by performing the Hubbard–Stratonovich transformation. Starting from this expression the free energy of the SPM in a two-loop order approximation was derived by Caillol [43]. As was shown [33], the z -dependence of the critical temperature calculated within the framework of this approximation disagrees with the results obtained by MC simulations. Below we propose an alternate way of taking into account the fluctuation effects near the GL critical point.

Expressions (17), under conditions (18), are reduced to

$$C_{NN} = 1/\mathfrak{M}_2^{(0)}(\bar{v}_\alpha; k), \quad C_{QQ} = \tilde{\Phi}^C(k) + 1/\mathfrak{M}_2^{(2)}(\bar{v}_\alpha), \quad C_{NQ} \equiv 0 \quad (19)$$

and the logarithm of the GPF in the Gaussian approximation is as follows:

$$\ln \Xi_G(\bar{v}_\alpha) = \ln \Xi_{\text{HS}}(\bar{v}_\alpha) - \frac{1}{2} \sum_{\mathbf{k}} \ln \left[1 + \tilde{\Phi}^C(k) \mathfrak{M}_2^{(2)}(\bar{v}_\alpha) \right]. \quad (20)$$

After the Legendre transform of $\ln \Xi_G(\bar{v}_\alpha)$ we obtain the well-known expression (see e.g. [43]) for the free energy in the RPA,

$$\beta f_{\text{RPA}} = \beta f_{\text{MF}} + \frac{1}{2V} \sum_{\mathbf{k}} \ln(1 + \kappa_D^2 \phi^C(k)), \quad (21)$$

where βf_{MF} has the form (13) under conditions (18), and $\kappa_D^2 = 4\pi\rho\beta q_0^2 z$ is the squared Debye number. It is worth noting that the use of a momentum cutoff $|\mathbf{k}_\Lambda| = 2\pi/a$ in (21) leads to the same expression for the βf_{DH} as in [32]. For point charge particles, (21) yields the free energy in the DHLL approximation $\beta f_{\text{DHLL}} = \beta f_{\text{id}} - \frac{\kappa_D^3}{12\pi}$. Using the optimized regularization of the Coulomb potential inside the hard core [47], we arrive at the free energy in the ORPA (or MSA).

As is seen, βf_{RPA} does not explicitly depend on the charge asymmetry factor z . The same is true for the MSA and the DH theories. The detailed analysis of the GL phase equilibrium using (21) and different regularizations of the Coulomb potential inside the hard core was fulfilled in [33]. As was shown [32, 43], the z -dependent free energy can be found only in the higher-order approximations.

Below we study the GL phase diagram of SPMs when fluctuation effects of order higher than the two are taken into account.

3. Gas–liquid critical point of the primitive models (PMs) of ionic fluids

Let us consider equation (20). Introducing \bar{v}_N and \bar{v}_Q

$$\bar{v}_N = \frac{z}{1+z} \bar{v}_1 + \frac{1}{1+z} \bar{v}_2, \quad \bar{v}_Q = \frac{1}{q_0(1+z)} (\bar{v}_1 - \bar{v}_2) \quad (22)$$

we can present (20) as follows:

$$\ln \Xi_G(\nu_\alpha) = \ln \Xi_{\text{HS}}(\bar{\nu}_N, \bar{\nu}_Q) - \frac{1}{2} \sum_{\mathbf{k}} \ln \left[1 + \tilde{\Phi}^C(k) \mathfrak{M}_2^{(2)}(\bar{\nu}_N, \bar{\nu}_Q) \right], \quad (23)$$

where the new chemical potentials $\bar{\nu}_N$ and $\bar{\nu}_Q$ (see (22)) are conjugate to the total number density and charge density, respectively. Since near the GL critical point the fluctuations of the number density play a crucial role, $\bar{\nu}_N$ is of special interest in this study.

We present $\bar{\nu}_N$ and $\bar{\nu}_Q$ as

$$\bar{\nu}_N = \nu_N^0 + \lambda \Delta \nu_N, \quad \bar{\nu}_Q = \nu_Q^0 + \lambda \Delta \nu_Q,$$

with ν_N^0 and ν_Q^0 being the MF values of $\bar{\nu}_N$ and $\bar{\nu}_Q$, respectively and $\Delta \nu_N$ and $\Delta \nu_Q$ being the solutions of the equations

$$\frac{\partial \ln \Xi_G(\nu_N, \nu_Q)}{\partial \Delta \nu_N} = \lambda \langle N \rangle_{\text{HS}}, \quad (24)$$

$$\frac{\partial \ln \Xi_G(\nu_N, \nu_Q)}{\partial \Delta \nu_Q} = 0. \quad (25)$$

Expanding (23) in powers of $\Delta \nu_N$ and $\Delta \nu_Q$, we obtain

$$\ln \Xi_G(\nu_N, \nu_Q) = \sum_{n \geq 0} \sum_{i_n \geq 0} C_n^{i_n} \frac{\mathcal{M}_n^{(i_n)}(\nu_N^0, \nu_Q^0)}{n!} \Delta \nu_Q^{i_n} \Delta \nu_N^{n-i_n}, \quad (26)$$

where

$$\mathcal{M}_n^{(i_n)}(\nu_N^0, \nu_Q^0) = \frac{\partial^n \ln \Xi_G(\nu_N, \nu_Q)}{\partial \Delta \nu_Q^{i_n} \partial \Delta \nu_N^{n-i_n}} \Big|_{\Delta \nu_N=0, \Delta \nu_Q=0}.$$

The expressions for the coefficients $\mathcal{M}_n^{(i_n)}$ are given in appendix B.

We solve equations (24) and (25) approximately, taking into account (26) and keeping terms of a certain order in parameter λ . The procedure is as follows. First, we calculate $\Delta \nu_Q$ from (25) in the approximation which corresponds to a certain order of λ e.g., order s . Then, we substitute this $\Delta \nu_Q$ into equation (24) in order to find $\Delta \nu_N$ in the approximation corresponding to λ^{s+1} . In (24) we take into account only the linear terms with respect to $\Delta \nu_N$, keeping terms with *all powers of* $\Delta \nu_Q$ within a given approximation in terms of λ .

As is readily seen, the first nontrivial solution for $\Delta \nu_N$ is obtained in the approximation of the first order of λ . It is the result of substitution in (24) of the solution $\Delta \nu_Q = 0$. As a result, we have

$$\Delta \nu_N = -\frac{\mathfrak{M}_3^{(2)}}{2\mathfrak{M}_2^{(0)}} \sum_{\mathbf{k}} \tilde{g}(k), \quad (27)$$

where

$$\tilde{g}(k) = -\frac{\tilde{\Phi}^C(k)}{1 + \tilde{\Phi}^C(k) \mathfrak{M}_2^{(2)}} = -\frac{1}{V} \frac{\beta \tilde{\phi}^C(k)}{1 + \kappa_D^2 \tilde{\phi}^C(k)}. \quad (28)$$

Equations (27) and (28) can be rewritten as (see appendix C)

$$\Delta \nu_N = \frac{1}{2N} \sum_{\mathbf{k}} \frac{\kappa_D^2 \tilde{\phi}^C(k)}{1 + \kappa_D^2 \tilde{\phi}^C(k)} \quad (29)$$

which corresponds to the RPA. As was mentioned above, $\Delta \nu_N$ given by (29) does not depend on the charge asymmetry factor z . In order to obtain the z -dependent expression for the chemical potential related to the number density fluctuations we should consider the next approximation in λ for $\Delta \nu_N$.

In order to obtain $\Delta\nu_N$ in the approximation corresponding to λ^2 , we substitute in (24) the solution $\Delta\nu_Q$ as follows (see appendix C):

$$\Delta\nu_Q = -\frac{\mathfrak{M}_3^{(3)}}{2\mathfrak{M}_2^{(2)}} \sum_{\mathbf{k}} \tilde{g}(k) = -\frac{(1-z)}{2} \sum_{\mathbf{k}} q_0 \tilde{g}(k), \quad (30)$$

which is found from (25) in the first approximation of λ . Taking into account only a linear term with respect to $\Delta\nu_N$, we get

$$\Delta\nu_N = -\frac{1}{\mathfrak{M}_2^{(0)}} \left[\frac{1}{2} \sum_{\mathbf{k}} \tilde{g}(k) \mathfrak{M}_3^{(2)} + \frac{1}{2} \sum_{\mathbf{k}} \tilde{g}(k) \mathfrak{M}_4^{(3)} \Delta\nu_Q + \frac{1}{2} \mathfrak{M}_3^{(2)} \Delta\nu_Q^2 + \frac{1}{3!} \mathfrak{M}_4^{(3)} \Delta\nu_Q^3 \right]. \quad (31)$$

Let us consider (31) in detail. The correlation effects of order higher than two enter the equation through the cumulants $\mathfrak{M}_n^{(i_n)}$ for $n \geq 3$ and $i_n \neq 0$. The appearance of these cumulants reflects the fact that the terms proportional to $\omega\gamma^2$, γ^3 and $\omega\gamma^3$ are taking into account in the cumulant expansion (14) ($n \leq 4$). Recall that $\omega_{\mathbf{k}}$ and $\gamma_{\mathbf{k}}$ are conjugate to the CVs $\rho_{\mathbf{k}}$ and $Q_{\mathbf{k}}$ describing the total number density and charge density fluctuations, respectively. This means that in order to determine $\Delta\nu_N$ we take into account in (14), besides the terms of the second order, the contribution corresponding to the pure charge density fluctuations for $n = 3$ ($\mathfrak{M}_3^{(3)}$) and the contributions corresponding to the correlations between the charge density and the total number density fluctuations for $n \leq 4$ ($\mathfrak{M}_3^{(2)}$ and $\mathfrak{M}_4^{(3)}$) which are linear in $\omega_{\mathbf{k}}$. Therefore, the analysis of (31) establishes a link between the approximations considered above (in terms of λ) and the approximations formulated in terms of CVs.

Another important issue to be discussed is the limiting case $z = 1$ that corresponds to the RPM. For $z = 1$ only the first term survives in (31). Furthermore, in this case the conditions $\mathfrak{M}_n^{(3)} \equiv 0$ and $\Delta\nu_Q = 0$ hold simultaneously (they are equivalent for the RPM) due to the model symmetry (see formulae in appendixes A and C). As a result, we arrive at the expression for the chemical potential of the RPM in the RPA [33, 48]. On the other hand, when we set solely $\Delta\nu_Q = 0$ in (31) we obtain (27) which also corresponds to the RPA and is valid for $z \neq 1$. The latter reflects the fact that the correlations between fluctuations of the charge density and the total number density are not taken into account at the RPA level. Therefore, for $\Delta\nu_Q = 0$ all the terms, except the first one, in (31) become equal to zero and we get the expressions for the chemical potential conjugate to the total number density in the same approximation for the both models. The equation (31) is obtained in the approximation when only the linear terms with respect to ω in the cumulant expansion (14) are taken into account. However, for $z = 1$ these contributions are equal to zero. This means that the approximation considered in this paper for the SPM does not have an analogy for the RPM. In order to include the fluctuations in the simplest model (RPM) the higher-order terms should be taken into account. This issue was considered in [48] where a good agreement for the critical temperature was obtained.

Based on (31) the coexistence curves for the SPM for different values of z can be calculated. 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 [6, 33]. Within the framework of the Gaussian approximation of the GPF the best estimation for the critical temperature is achieved for the optimized regularization [47] that leads to the ORPA (MSA). However, this approximation does not work properly in the higher orders of the perturbation theory [33]. In this study we use the Weeks–Chandler–Andersen (WCA) regularization [45]. As was shown [46], this choice of $\phi^C(r)$ for $r < \sigma$ produces rapid convergence of the series of the perturbation theory for the free energy. For the WCA, the Fourier transform of $\phi^C(r)$ is of the form $\phi^C(x) = \sin(x)/x^3$ with $x = k\sigma$. As a result, (31)

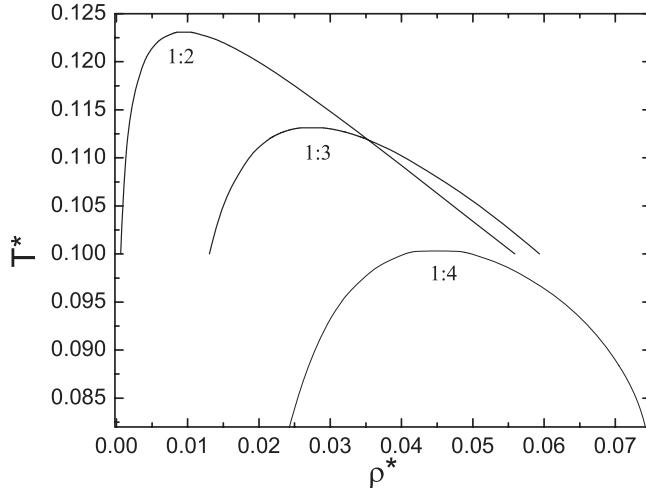


Figure 1. Coexistence curves of the (1:z) charge-asymmetric ionic model.

can be written as (see appendix C)

$$\Delta\nu_N = \frac{i_1}{\pi} \left[1 + \frac{i_1(1-z)^2}{2z\pi} \left(1 - \frac{i_1(1-z)^2}{3z\pi} \right) \right]. \quad (32)$$

In (32)

$$i_1 = \frac{1}{T^*} \int_0^\infty \frac{x^2 \sin x dx}{x^3 + \kappa^{*2} \sin x} \quad (33)$$

with $\kappa^* = \kappa_D \sigma$ being the reduced Debye number. Hereafter the standard notations are introduced for the temperature and the density: $T^* = \frac{k_B T \sigma}{z q_0^2}$, $\rho^* = \rho \sigma^3$.

Finally, we get the expression for the full chemical potential ν_N conjugate to the total number density,

$$\nu_N - 3 \ln \Lambda / \sigma = \ln \rho^* + \frac{\eta(8 - 9\eta + 3\eta^3)}{(1 - \eta)^3} + \frac{z}{1 + z} \ln z - \ln(1 + z) - \frac{1}{2T^*} + \Delta\nu_N, \quad (34)$$

where $\Delta\nu_N$ is given in (32) and (33) and $\eta = \pi \rho^* / 6$. In (34) the Carnahan–Starling approximation for the hard-sphere system is used.

Figure 1 shows the coexistence curves for $z = 2\text{--}4$ calculated based on the isotherms of chemical potential (34) supplemented with the Maxwell construction. The estimations for the critical point are as follows:

$$\begin{aligned} z = 2: \quad T_c^* &= 0.123\,10, & \rho_c^* &= 0.009\,46 \\ z = 3: \quad T_c^* &= 0.113\,13, & \rho_c^* &= 0.027\,40 \\ z = 4: \quad T_c^* &= 0.100\,30, & \rho_c^* &= 0.045\,01. \end{aligned}$$

These results demonstrate the qualitative agreement with the MC data: the critical temperature decreases when z increases and the critical density increases rapidly with z . Moreover, a comparison of the coexistence curve forms for $z = 2$ and $z = 3$ (results for the coexistence curve for $z = 4$ are not available by now) with the DHBjCIHC theory indicates their similarity. It is also worth noting that the above data for the critical temperature lie about in the same region as those obtained in [33] within the framework of the two-loop expansion.

4. Conclusions

In this paper we have studied the GL phase behaviour of a charge-asymmetric primitive ionic model. For this purpose we have derived the exact expression for the functional of the GPF of a two-component asymmetric ionic model which includes both the short- and long-range interactions among charged hard spheres. We have shown that the well-known approximations for the free energy, in particular DHLL and ORPA, can be reproduced within the framework of this approach. On the other hand, the GPF functional can be reduced to the form found in the KSSHE theory [43]. This means that the field-theoretical analysis of the expression for the GPF given by (6) and (7) has to lead in the two-loop approximation to the same z -dependence for the critical temperatures as in [33], which does not agree with the MC simulations. Here, we have proposed an alternative method for the study of the GL phase equilibria in the SPM. It consists in the calculation of the chemical potential ν_N conjugate to the total number density by means of successive approximations.

We have obtained the expression for the chemical potential ν_N in which the effects of indirect correlations between the number density fluctuations are taken into consideration via a charge subsystem. This fact is reflected in expression (31) which includes the higher-order cumulants (cumulants $\mathfrak{M}_3^{(2)}$, $\mathfrak{M}_3^{(3)}$ and $\mathfrak{M}_4^{(3)}$). The cumulants in turn are related to the higher-order truncated correlation functions of a hard-sphere system (see appendix A). In particular, this is the main distinctive feature of the method proposed in comparison with the field-theoretical analysis of Netz and Orland [32]. In [32], the system of charged point particles is considered and hard-core effects are taken into account only by an effective high-momentum cutoff. In addition, the perturbative consideration used in [32] is solely based on the charge density fluctuations. Within the framework of the approach proposed both the charge density and number density fluctuations are taken into consideration simultaneously and the equations for the relevant chemical potentials are solved self-consistently.

In conclusion, based on the expression for ν_N supplemented with the Maxwell construction the coexistence curves for $z = 2-4$ have been calculated. The z -dependences obtained for both the critical temperature and the critical density qualitatively agree with MC simulations. The results demonstrate that the terms responsible for the charged clustering need not be included in the Hamiltonian explicitly in order to describe, at least qualitatively, the GL phase diagram of the SPM. Instead, the interaction between charge and density fluctuations should be properly taken into account. To achieve a quantitative agreement, the higher-order terms should be taken into consideration in the CV action. This task will be considered elsewhere.

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Appendix A. Recurrence formulae for the cumulants in the Fourier space representation

$$\mathfrak{M}_n^{(0)}(k_1, k_2, \dots, k_n) = \tilde{G}_n(k_1, k_2, \dots, k_n) \quad (A.1)$$

$$\mathfrak{M}_n^{(1)}(k_1, k_2, \dots, k_n) = 0 \quad (A.2)$$

$$\mathfrak{M}_n^{(2)}(k_1, k_2, \dots, k_n) = \sum_{\alpha} q_{\alpha}^2 c_{\alpha} \tilde{G}_{n-1}(k_1, k_2, \dots, |\mathbf{k}_{n-1} + \mathbf{k}_n|) \quad (A.3)$$

$$\mathfrak{M}_n^{(3)}(k_1, k_2, \dots, k_n) = \sum_{\alpha} q_{\alpha}^3 c_{\alpha} \tilde{G}_{n-2}(k_1, k_2, \dots, |\mathbf{k}_{n-2} + \mathbf{k}_{n-1} + \mathbf{k}_n|) \quad (A.4)$$

where $\tilde{G}_n(k_1, k_2, \dots, k_n)$ is the Fourier transform of the n -particle truncated correlation function [44] of a one-component hard-sphere system.

Appendix B. Explicit expressions for $\mathcal{M}_n^{(i_n)}$

$$\begin{aligned}
\mathcal{M}_1^{(0)} &= \lambda \mathfrak{M}_1^{(0)} + \frac{\lambda^3}{2} \mathfrak{M}_3^{(2)} \sum_{\mathbf{k}} \tilde{g}(k), \\
\mathcal{M}_1^{(1)} &= \frac{\lambda^3}{2} \mathfrak{M}_3^{(3)} \sum_{\mathbf{k}} \tilde{g}(k), \\
\mathcal{M}_2^{(0)} &= \lambda^2 \mathfrak{M}_2^{(0)} + \frac{\lambda^4}{2} \mathfrak{M}_4^{(2)} \sum_{\mathbf{k}} \tilde{g}(k) + \frac{\lambda^6}{2} \left[\mathfrak{M}_3^{(2)} \right]^2 \sum_{\mathbf{k}} \tilde{g}^2(k), \\
\mathcal{M}_2^{(1)} &= \frac{\lambda^4}{2} \mathfrak{M}_4^{(3)} \sum_{\mathbf{k}} \tilde{g}(k) + \frac{\lambda^6}{2} \mathfrak{M}_3^{(2)} \mathfrak{M}_3^{(3)} \sum_{\mathbf{k}} \tilde{g}^2(k), \\
\mathcal{M}_2^{(2)} &= \lambda^2 \mathfrak{M}_2^{(2)} + \frac{\lambda^4}{2} \mathfrak{M}_4^{(4)} \sum_{\mathbf{k}} \tilde{g}(k) + \frac{\lambda^6}{2} \left[\mathfrak{M}_3^{(3)} \right]^2 \sum_{\mathbf{k}} \tilde{g}^2(k), \\
\mathcal{M}_3^{(0)} &= \lambda^3 \mathfrak{M}_3^{(0)} + \frac{\lambda^5}{2} \mathfrak{M}_5^{(2)} \sum_{\mathbf{k}} \tilde{g}(k) + \frac{3\lambda^7}{2} \mathfrak{M}_3^{(2)} \mathfrak{M}_4^{(2)} \sum_{\mathbf{k}} \tilde{g}^2(k) + \lambda^9 \left[\mathfrak{M}_3^{(2)} \right]^3 \sum_{\mathbf{k}} \tilde{g}^3(k), \\
\mathcal{M}_3^{(1)} &= \frac{\lambda^5}{2} \mathfrak{M}_5^{(2)} \sum_{\mathbf{k}} \tilde{g}(k) + \frac{\lambda^7}{2} \left[\mathfrak{M}_3^{(3)} \mathfrak{M}_4^{(2)} + \mathfrak{M}_3^{(2)} \mathfrak{M}_4^{(3)} \right] \sum_{\mathbf{k}} \tilde{g}^2(k) \\
&\quad + \lambda^9 \left[\mathfrak{M}_3^{(2)} \right]^2 \mathfrak{M}_3^{(3)} \sum_{\mathbf{k}} \tilde{g}^3(k), \\
\mathcal{M}_3^{(2)} &= \lambda^3 \mathfrak{M}_3^{(2)} + \frac{\lambda^5}{2} \mathfrak{M}_5^{(4)} \sum_{\mathbf{k}} \tilde{g}(k) + \frac{\lambda^7}{2} \left[\mathfrak{M}_3^{(2)} \mathfrak{M}_4^{(4)} + 2\mathfrak{M}_3^{(3)} \mathfrak{M}_4^{(3)} \right] \\
&\quad \times \sum_{\mathbf{k}} \tilde{g}^2(k) + \lambda^9 \left[\mathfrak{M}_3^{(3)} \right]^2 \mathfrak{M}_3^{(2)} \sum_{\mathbf{k}} \tilde{g}^3(k), \\
\mathcal{M}_3^{(3)} &= \lambda^3 \mathfrak{M}_3^{(3)} + \frac{\lambda^5}{2} \mathfrak{M}_5^{(5)} \sum_{\mathbf{k}} \tilde{g}(k) + \frac{3\lambda^7}{2} \mathfrak{M}_3^{(3)} \mathfrak{M}_4^{(4)} \sum_{\mathbf{k}} \tilde{g}^2(k) + \lambda^9 \left[\mathfrak{M}_3^{(3)} \right]^3 \sum_{\mathbf{k}} \tilde{g}^3(k), \\
\mathcal{M}_4^{(0)} &= \lambda^4 \mathfrak{M}_4^{(0)} + \frac{\lambda^6}{2} \mathfrak{M}_6^{(2)} \sum_{\mathbf{k}} \tilde{g}(k) + \frac{\lambda^8}{2} \left(3 \left[\mathfrak{M}_4^{(2)} \right]^2 + 4 \mathfrak{M}_3^{(2)} \mathfrak{M}_5^{(2)} \right) \\
&\quad \times \sum_{\mathbf{k}} \tilde{g}^2(k) + 6\lambda^{10} \left[\mathfrak{M}_3^{(2)} \right]^2 \mathfrak{M}_4^{(2)} \sum_{\mathbf{k}} \tilde{g}^3(k) + 3\lambda^{12} \left[\mathfrak{M}_3^{(2)} \right]^4 \sum_{\mathbf{k}} \tilde{g}^4(k), \\
\mathcal{M}_4^{(1)} &= \frac{\lambda^6}{2} \mathfrak{M}_6^{(3)} \sum_{\mathbf{k}} \tilde{g}(k) + \frac{\lambda^8}{2} \left(3 \mathfrak{M}_4^{(2)} \mathfrak{M}_4^{(4)} + \mathfrak{M}_3^{(2)} \mathfrak{M}_5^{(3)} + \mathfrak{M}_3^{(3)} \mathfrak{M}_5^{(2)} \right) \\
&\quad \times \sum_{\mathbf{k}} \tilde{g}^2(k) + 3\lambda^{10} \left(\mathfrak{M}_3^{(2)} \mathfrak{M}_3^{(3)} \mathfrak{M}_4^{(4)} + \left[\mathfrak{M}_3^{(2)} \right]^2 \mathfrak{M}_4^{(3)} \right) \sum_{\mathbf{k}} \tilde{g}^3(k) \\
&\quad + 3\lambda^{12} \left[\mathfrak{M}_3^{(2)} \right]^3 \mathfrak{M}_3^{(3)} \sum_{\mathbf{k}} \tilde{g}^4(k), \\
\mathcal{M}_4^{(2)} &= \lambda^4 \mathfrak{M}_4^{(2)} + \frac{\lambda^6}{2} \mathfrak{M}_6^{(4)} \sum_{\mathbf{k}} \tilde{g}(k) + \frac{\lambda^8}{2} \left(2 \mathfrak{M}_3^{(3)} \mathfrak{M}_5^{(3)} + 2 \mathfrak{M}_3^{(2)} \mathfrak{M}_5^{(3)} \right)
\end{aligned}$$

$$\begin{aligned}
& + \mathfrak{M}_4^{(2)} \mathfrak{M}_4^{(4)} + 2 \left[\mathfrak{M}_4^{(3)} \right]^2 + 2 \mathfrak{M}_4^{(2)} \left[\mathfrak{M}_3^{(3)} \right]^2 \right) \sum_{\mathbf{k}} \tilde{g}^2(k) + 2\lambda^{10} \\
& \times \left(2 \mathfrak{M}_3^{(2)} \mathfrak{M}_3^{(3)} \mathfrak{M}_4^{(3)} + \left[\mathfrak{M}_3^{(2)} \right]^2 \mathfrak{M}_4^{(4)} \right) \sum_{\mathbf{k}} \tilde{g}^3(k) + 3\lambda^{12} \left[\mathfrak{M}_3^{(2)} \right]^2 \\
& \times \left[\mathfrak{M}_3^{(3)} \right]^2 \sum_{\mathbf{k}} \tilde{g}^4(k), \\
\mathcal{M}_4^{(3)} = & \lambda^4 \mathfrak{M}_4^{(2)} + \frac{\lambda^6}{2} \mathfrak{M}_6^{(5)} \sum_{\mathbf{k}} \tilde{g}(k) + \frac{\lambda^8}{2} \left(3 \mathfrak{M}_3^{(3)} \mathfrak{M}_5^{(4)} + \mathfrak{M}_3^{(2)} \mathfrak{M}_5^{(5)} \right. \\
& \left. + 3 \mathfrak{M}_4^{(3)} \mathfrak{M}_4^{(4)} \right) \sum_{\mathbf{k}} \tilde{g}^2(k) + 3\lambda^{10} \left(\mathfrak{M}_3^{(2)} \mathfrak{M}_3^{(3)} \mathfrak{M}_4^{(4)} + \left[\mathfrak{M}_3^{(3)} \right]^2 \mathfrak{M}_4^{(3)} \right) \\
& \times \sum_{\mathbf{k}} \tilde{g}^3(k) + 3\lambda^{12} \mathfrak{M}_3^{(2)} \left[\mathfrak{M}_3^{(3)} \right]^3 \sum_{\mathbf{k}} \tilde{g}^4(k).
\end{aligned}$$

In the above formulae $\mathfrak{M}_n^{(i_n)} = \mathfrak{M}_n^{(i_n)}(\nu_N^0, \nu_Q^0)$.

Appendix C. Some explicit relations obtained for a 1: z asymmetric PM

Let us consider the expressions (A.1)–(A.4). For a 1: z asymmetric PM we have

$$\sum_{\alpha} q_{\alpha}^2 c_{\alpha} = q_0^2 z, \quad \sum_{\alpha} q_{\alpha}^3 c_{\alpha} = q_0^3 z(1-z).$$

Using the above relations and (A.1)–(A.4) we can obtain the following explicit relations for the SPM:

$$\begin{aligned}
\frac{\mathfrak{M}_3^{(2)}}{\mathfrak{M}_2^{(0)}} &= q_0^2 z, \quad \left(\frac{\mathfrak{M}_3^{(3)}}{\mathfrak{M}_2^{(2)}} \right)^2 = q_0^2 z \frac{(1-z)^2}{z}, \quad \frac{\mathfrak{M}_4^{(3)} \mathfrak{M}_3^{(3)}}{\mathfrak{M}_2^{(2)} \mathfrak{M}_3^{(2)}} = q_0^2 z \frac{(1-z)^2}{z}, \\
\left(\frac{\mathfrak{M}_3^{(3)}}{\mathfrak{M}_2^{(2)}} \right)^3 \frac{\mathfrak{M}_4^{(3)}}{\mathfrak{M}_3^{(2)}} &= \left(q_0^2 z \frac{(1-z)^2}{z} \right)^2.
\end{aligned}$$

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