LETTER TO THE EDITOR

Critical behaviour of the restricted primitive model

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Abstract
We study a critical behaviour of systems dominated by Coulombic interaction.
For this purpose we use the method of collective variables with a reference
system. Starting from the Hamiltonian of the restricted primitive model (RPM),
the simplest model of ionic fluids, we obtain a functional of the grand partition
function given in terms of the two types of collective variable describing
fluctuations of the total number density and the charge density, respectively.
As the result of integration over the charge density variables, a microscopic
based effective Hamiltonian of the RPM in the vicinity of its gas–liquid critical
point is constructed. Coefficients of the effective Hamiltonian describing
the density fluctuations near the gas–liquid critical point are analysed. It is
shown that in spite of the long-range character of the Coulombic potential the
effective interactions appearing at this level of the description have a short-range
character. Consequently, the effective Hamiltonian obtained for the RPM in
the vicinity of the critical point is in the form of the Ginzburg–Landau–Wilson
Hamiltonian of an Ising-like model in a magnetic field. This confirms the fact
that the critical behaviour of the RPM near the gas–liquid critical point belongs
to the universal class of a 3D Ising model.

1. Introduction

Experimental investigations of the critical properties of electrolyte solutions displayed three
different types of behaviour: Ising-like and mean-field behaviour as well as a crossover
between the two [1–4]. In order to interpret the results, ionic systems were classified as either
solvophobic or Coulombic. In solvophobic systems, Coulombic forces are not supposed to
play a major role; the critical behaviour is that common for fluids and fluid mixtures, i.e.
Ising-like. By contrast, in Coulombic systems the phase separation is driven by electrostatic
interactions. In recent years the critical behaviour of the Coulombic systems has been a

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subject of active research. A theoretical model which demonstrates the phase separation driven exclusively by Coulombic forces is a restricted primitive model (RPM) [3, 4]. Early studies [5–7] established that the model has a gas–liquid (GL) phase transition. A reasonable theoretical description of the GL critical point in the RPM was accomplished at a mean-field (MF) level using integral equation methods [4, 8] and Debye–Hückel theory [9]. However, a systematic theoretical investigation of the criticality of the RPM requires a microscopic based effective Ginzburg–Landau–Wilson (GLW) Hamiltonian. Although some progress in this direction has been made [10–13] the GLW functional of the continuous RPM explicitly related to the microscopic characteristics has not been derived yet.

For the last decade, the GL critical point in the RPM has been much studied by computer simulation methods [14–26]. While the theory has not provided a clear picture of thermodynamic behaviour of the model in the critical region, very recent simulation studies have found strong evidence for an Ising universal class [25, 26].

In this letter we address an issue of criticality in the RPM using the functional representation of the grand partition function in terms of collective variables (CVs). Transformation from individual to collective coordinates (the Fourier transforms of the density fluctuations) is carried out via the corresponding Jacobian. Within the random phase approximation for the Jacobian one arrives at the Debye–Hückel approximation for the free energy [27]. The method of CVs was initially developed in the 1950s for the description of charged particle systems [28, 29]. The further development [30–33] of the method was related to the theory of phase transition.

According to the basic idea of universality [34], different systems which are described by similar effective GLW Hamiltonians (with the same symmetry) demonstrate the same critical behaviour. Thus, the knowledge of the effective Hamiltonian of the system is important in determining its critical behaviour. Our purpose here is to derive, from the first principles, the effective GLW Hamiltonian of the RPM in the vicinity of its GL critical point.

2. Functional representation of the grand partition function

The RPM consists of $N = N_+ + N_-$ hard spheres of diameter σ with N_+ carrying charges $+q$ and $N_-(=N_+)$ charges $-q$, in a medium of dielectric constant D. The interaction potential of the RPM is as follows:

$$U_{\gamma\delta}(r) = \begin{cases} \infty & \text{if } r < \sigma \\ \dfrac{q_\gamma q_\delta}{Dr} & \text{if } r \geqslant \sigma, \end{cases} \qquad q_i = \pm q. \tag{1}$$

We start with the grand partition function for a two-component system ($\gamma, \delta = +, -$):

$$\Xi = \sum_{N_+ \geqslant 0} \sum_{N_- \geqslant 0} \prod_{\gamma=+,-} \frac{z_\gamma^{N_\gamma}}{N_\gamma!} \int (\mathrm{d}\Gamma) \exp\left[-\frac{\beta}{2} \sum_{\gamma\delta} \sum_{ij} U_{\gamma\delta}(r_{ij})\right],$$

where $(\mathrm{d}\Gamma) = \prod_\gamma \mathrm{d}\Gamma_{N_\gamma}$, $\mathrm{d}\Gamma_{N_\gamma} = \mathrm{d}\mathbf{r}_1^\gamma \mathrm{d}\mathbf{r}_2^\gamma \cdots \mathrm{d}\mathbf{r}_{N_\gamma}^\gamma$ ($\gamma = +, -$) is an element of the configurational space of the γth species; z_γ is the fugacity of the γth species: $z_\gamma = \exp(\beta\mu'_\gamma)$, $\mu'_\gamma = \mu_\gamma + \beta^{-1}\ln[(2\pi m_\gamma \beta^{-1})^{3/2}/h^3]$, μ_γ is the chemical potential of the γth species determined from the equation $\partial \ln \Xi/\partial\beta\mu_\gamma = \langle N_\gamma \rangle$. For the RPM we have $\mu_+ = \mu_-$.

Now we present the interaction potential $U_{\gamma\delta}(r)$ as a sum of two terms:

$$U_{\gamma\delta}(r) = \psi_{\gamma\delta}(r) + \Phi_{\gamma\delta}(r),$$

where $\psi_{\gamma\delta}(r)$ is a potential of a short-range repulsion and $\Phi_{\gamma\delta}(r)$ is a long-range attractive part of the potential. We split the potential $U_{\gamma\delta}(r)$ into short- and long-range parts using the

Weeks–Chandler–Andersen partition [35]:

$$\psi_{\gamma\delta}(r) = \begin{cases} \infty & \text{if } r \leqslant \sigma \\ 0 & \text{if } r > \sigma, \end{cases}$$

$$\Phi_{\gamma\delta}(r) = \begin{cases} \dfrac{q_\gamma q_\delta}{D\sigma} & \text{if } r \leqslant \sigma \\ \dfrac{q_\gamma q_\delta}{Dr} & \text{if } r > \sigma. \end{cases}$$

This simple form for $\Phi_{\gamma\delta}(r)$ inside the hard core changes the behaviour of the Fourier transform for large k from the usual Coulombic k^{-2} to k^{-3} decay. As has been shown [36], this choice of $\Phi_{\gamma\delta}(r)$ for $r < \sigma$ produces a rapid convergence of the series of the perturbation theory for the free energy. The Fourier transform of $\Phi_{\gamma\delta}(r) = \pm q^2/Dr = \pm\Phi_{\rm C}(r)$ has the form

$$\beta\rho\tilde{\Phi}_{\rm C}(x) = 24\beta^*\eta\frac{\sin x}{x^3}, \tag{2}$$

where $\beta^* = \beta q^2/D\sigma$, $\beta = 1/k_{\rm B}T$, $\eta = \pi\rho\sigma^3/6$ is the fraction density, and $x = k\sigma$.

Within the framework of the approach considered the interaction connected with a repulsion $\psi_{\gamma\delta}(r)$ is described in the space of the Cartesian coordinates of the particles. Here, the hard sphere system with the diameter σ is called a reference system (RS). The interaction connected with a long range potential $\Phi_{\gamma\delta}(r)$ is considered in the CV space. Transformation from the Cartesian coordinates to the CVs is performed by means of the transition Jacobian.

Using the method of CVs developed for a two-component continuous system [37, 38] we can rewrite the grand partition function of the RPM in the following way:

$$\Xi = \Xi_0 \int (\mathrm{d}\rho)(\mathrm{d}c) \exp\left(\beta\mu_1\rho_0 - \frac{\beta}{V}\sum_{\mathbf{k}}\tilde{\Phi}_{\rm C}(k)c_{\mathbf{k}}c_{-\mathbf{k}}\right)J(\rho, c). \tag{3}$$

Here Ξ_0 is the grand partition function of the RS. CVs $\rho_{\mathbf{k}}$ and $c_{\mathbf{k}}$ describe total density and charge density fluctuations, respectively: $\rho_{\mathbf{k}} = \rho_{\mathbf{k}}^{\rm c} - \mathrm{i}\rho_{\mathbf{k}}^{\rm s}$, $c_{\mathbf{k}} = c_{\mathbf{k}}^{\rm c} - \mathrm{i}c_{\mathbf{k}}^{\rm s}$; the indices c and s denote the real and imaginary parts of CVs $\rho_{\mathbf{k}}$ and $c_{\mathbf{k}}$. Each of $\rho_{\mathbf{k}}^{\rm c}$ $(c_{\mathbf{k}}^{\rm c})$ and $\rho_{\mathbf{k}}^{\rm s}$ $(c_{\mathbf{k}}^{\rm s})$ takes all the real values from $-\infty$ to $+\infty$, and $(\mathrm{d}\rho)$ and $(\mathrm{d}c)$ are volume elements of the CV phase space: $(\mathrm{d}\rho) = \mathrm{d}\rho_0\prod_{\mathbf{k}\neq 0}\mathrm{d}\rho_{\mathbf{k}}^{\rm c}\mathrm{d}\rho_{\mathbf{k}}^{\rm s}$, $(\mathrm{d}c) = \mathrm{d}c_0\prod_{\mathbf{k}\neq 0}\mathrm{d}c_{\mathbf{k}}^{\rm c}\mathrm{d}c_{\mathbf{k}}^{\rm s}$. The unknown parameter μ_1 $(\mu_1 = (\mu_{1,+} + \mu_{1,-})/\sqrt{2})$ is determined from the equation $\partial\ln\Xi_1/\partial\beta\mu_1 = \langle N\rangle/\sqrt{2}$.

For the RPM, the Jacobian of the transition to the CVs averaged over the RS, $J(\rho, c)$, is of the same form as that for the symmetrical binary fluid [38]:

$$J(\rho, c) = \int (\mathrm{d}\omega)\,(\mathrm{d}\gamma)\exp\left[\mathrm{i}2\pi\sum_{\mathbf{k}}(\omega_{\mathbf{k}}\rho_{\mathbf{k}} + \gamma_{\mathbf{k}}c_{\mathbf{k}}) + \sum_{n\geqslant 1}\sum_{i_n\geqslant 0}D_n^{(i_n)}(\omega, \gamma)\right], \tag{4}$$

$$D_n^{(i_n)}(\omega, \gamma) = \frac{(-\mathrm{i}2\pi)^n}{n!}\sum_{\mathbf{k}_1\cdots\mathbf{k}_n}\bar{\mathfrak{M}}_n^{(i_n)}(k_1, \cdots, k_n)\gamma_{\mathbf{k}_1}\cdots\gamma_{\mathbf{k}_{i_n}}\omega_{\mathbf{k}_{i_{n+1}}}\cdots\omega_{\mathbf{k}_n}\delta_{\mathbf{k}_1+\cdots+\mathbf{k}_n}, \tag{5}$$

where $\bar{\mathfrak{M}}_n^{(i_n)} = \mathfrak{M}_n^{(i_n)}/\sqrt{2}^n$ and the variable $\omega_{\mathbf{k}}$ $(\gamma_{\mathbf{k}})$ is conjugate to the CV $\rho_{\mathbf{k}}$ $(c_{\mathbf{k}})$. Index i_n $(i_n = 0, 2, 4, \ldots, 2n)$ is used to indicate the number of variables $\gamma_{\mathbf{k}}$ in the cumulant expansion (5). Cumulants $\mathfrak{M}_n^{(i_n)}$ are expressed as linear combinations of the partial cumulants $\mathfrak{M}_{\gamma_1\ldots\gamma_n}$ and are given for $\gamma_1, \ldots, \gamma_n = +, -$ and $n \leqslant 4$ in [33].

In (4) and (5), the cumulants $\mathfrak{M}_n^{(i_n)}$ with $i_n = 0$ are connected with the nth structure factors of the RS. For $i_n \neq 0$, $\mathfrak{M}_n^{(i_n)}$ can be expressed in terms of $\mathfrak{M}_n^{(0)}$ (see formulae (4.8) in [33]):

$$\begin{aligned} \mathfrak{M}_n^{(0)} = \langle N\rangle S_n, \qquad \mathfrak{M}_n^{(2)} = \mathfrak{M}_{n-1}^{(0)}, \qquad \mathfrak{M}_n^{(4)} = 3\mathfrak{M}_{n-2}^{(0)} - 2\mathfrak{M}_{n-3}^{(0)}, \\ \mathfrak{M}_n^{(6)} = 15\mathfrak{M}_{n-3}^{(0)} - 30\mathfrak{M}_{n-4}^{(0)} + 16\mathfrak{M}_{n-5}^{(0)}. \end{aligned} \tag{6}$$

In general, the dependence of $\mathfrak{M}_n^{(i_n)}(\mathbf{k}_1, \ldots, \mathbf{k}_n)$ on wavevectors $\mathbf{k}_1, \ldots, \mathbf{k}_n$ is too complicated. Since we are interested in the critical behaviour, the small-$\mathbf{k}$ expansion of the cumulant can be considered. Hereafter we shall replace $\bar{\mathfrak{M}}_n^{(i_n)}(\mathbf{k}_1, \ldots, \mathbf{k}_n)$ by their values in the long-wavelength limit $\bar{\mathfrak{M}}_n^{(i_n)}(0, \ldots, 0)$. Structure factors $S_n(0, \ldots, 0)$ with $n > 2$ can be obtained from $S_2(0)$ by means of a chain of equations for correlation functions [39].

Let us present $J(\rho, c)$ as

$$
J(\rho, c) = \int (\mathrm{d}\omega)\,(\mathrm{d}\gamma) \exp\bigg[\mathrm{i}2\pi \sum_{\mathbf{k}} (\omega_{\mathbf{k}}\rho_{\mathbf{k}} + \gamma_{\mathbf{k}} c_{\mathbf{k}})
$$
$$
+ \frac{(-\mathrm{i}2\pi)^2}{2!} \sum_{\mathbf{k}} (\bar{\mathfrak{M}}_2^{(0)} \omega_{\mathbf{k}}\omega_{-\mathbf{k}} + \bar{\mathfrak{M}}_2^{(2)} \gamma_{\mathbf{k}}\gamma_{-\mathbf{k}}) + \sum_{n \geqslant 3} \sum_{i_n \geqslant 0} D_n^{(i_n)}(\omega, \gamma) \bigg], \tag{7}
$$

where $D_n^{(i_n)}(\omega, \gamma)$ has the following form (up to $n = 4$):

$$
D_n^{(i_n)}(\omega, \gamma) = \frac{(-\mathrm{i}2\pi)^3}{3!} \sum_{\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3} (\bar{\mathfrak{M}}_3^{(0)} \omega_{\mathbf{k}_1}\omega_{\mathbf{k}_2}\omega_{\mathbf{k}_3} + 3\bar{\mathfrak{M}}_3^{(2)} \omega_{\mathbf{k}_1}\gamma_{\mathbf{k}_2}\gamma_{\mathbf{k}_3})
$$
$$
\times \delta_{\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3} + \frac{(-\mathrm{i}2\pi)^4}{4!} \sum_{\mathbf{k}_1, \ldots, \mathbf{k}_4} (\bar{\mathfrak{M}}_4^{(0)} \omega_{\mathbf{k}_1}\omega_{\mathbf{k}_2}\omega_{\mathbf{k}_3}\omega_{\mathbf{k}_4}
$$
$$
+ 6\bar{\mathfrak{M}}_4^{(2)} \omega_{\mathbf{k}_1}\omega_{\mathbf{k}_2}\gamma_{\mathbf{k}_3}\gamma_{\mathbf{k}_4} + \bar{\mathfrak{M}}_4^{(4)} \gamma_{\mathbf{k}_1}\gamma_{\mathbf{k}_2}\gamma_{\mathbf{k}_3}\gamma_{\mathbf{k}_4}) \delta_{\mathbf{k}_1 + \cdots + \mathbf{k}_4}.
$$

In (7) the linear term is eliminated by the shift $\rho_{\mathbf{k}} = \rho_{\mathbf{k}}' + \bar{\mathfrak{M}}_1^{(0)} \delta_{\mathbf{k}}$ (the prime on $\rho_{\mathbf{k}}$ is omitted for clarity). According to (6), $\bar{\mathfrak{M}}_2^{(0)}(k) = \langle N \rangle S_2(k)/2$ and $\bar{\mathfrak{M}}_2^{(2)} = \langle N \rangle/2$, where $S_2(k)$ is a two-particle structure factor of a one-component hard-sphere system.

3. The effective Hamiltonian of the RPM in the vicinity of the GL critical point

Because $\bar{\mathfrak{M}}_2^{(0)}(0)$ is a positive and smooth function in the region under consideration and $\bar{\mathfrak{M}}_2^{(2)}$ is equal to a constant, we can integrate in (7) over $\omega_{\mathbf{k}}$ and $\gamma_{\mathbf{k}}$ using the Gaussian density measures as basic ones. Using the Euler equations we can determine $\omega_{\mathbf{k}}^*$ (and $\gamma_{\mathbf{k}}^*$) which provide a maximum for the functional in the exponent of (7):

$$
\omega_{\mathbf{k}}^* = \frac{\rho_{-\mathbf{k}}}{-\mathrm{i}2\pi \bar{\mathfrak{M}}_2^{(0)}} + \cdots, \qquad \gamma_{\mathbf{k}}^* = \frac{c_{-\mathbf{k}}}{-\mathrm{i}2\pi \bar{\mathfrak{M}}_2^{(2)}} + \cdots. \tag{8}
$$

This leads to the expression

$$
\Xi = \Xi_0 \mathcal{C} \int (\mathrm{d}\rho)(\mathrm{d}c) \exp\bigg[a_1^{(0)}\rho_0 - \frac{1}{2!} \sum_{\mathbf{k}} \Big(a_2^{(0)} \rho_{\mathbf{k}}\rho_{-\mathbf{k}} + a_2^{(2)} c_{\mathbf{k}}c_{-\mathbf{k}} \Big)
$$
$$
+ \frac{1}{3!} \sum_{\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3} \Big(a_3^{(0)} \rho_{-\mathbf{k}_1}\rho_{-\mathbf{k}_2}\rho_{-\mathbf{k}_3} + a_3^{(2)} \rho_{-\mathbf{k}_1} c_{-\mathbf{k}_2} c_{-\mathbf{k}_3} \Big) \delta_{\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3}
$$
$$
+ \frac{1}{4!} \sum_{\mathbf{k}_1, \ldots, \mathbf{k}_4} \Big(a_4^{(0)} \rho_{-\mathbf{k}_1}\rho_{-\mathbf{k}_2}\rho_{-\mathbf{k}_3}\rho_{-\mathbf{k}_4} + a_4^{(2)} \rho_{-\mathbf{k}_1}\rho_{-\mathbf{k}_2} c_{-\mathbf{k}_3} c_{-\mathbf{k}_4}
$$
$$
+ a_4^{(4)} c_{-\mathbf{k}_1} c_{-\mathbf{k}_2} c_{-\mathbf{k}_3} c_{-\mathbf{k}_4} \Big) \delta_{\mathbf{k}_1 + \cdots + \mathbf{k}_4} \bigg], \tag{9}
$$

where superscript i_n indicates the number of variables $c_{\mathbf{k}}$ at $a_n^{(i_n)}$. Here

$$
\mathcal{C} = \prod_{\mathbf{k}} \frac{1}{\pi \bar{\mathfrak{M}}_2^{(0)}} \prod_{\mathbf{k}} \frac{1}{\pi \bar{\mathfrak{M}}_2^{(2)}} \exp(\beta \mu_1 \bar{\mathfrak{M}}_1^{(0)}), \tag{10}
$$

and the coefficients $a_n^{(i_n)}$, taking into account the first terms in (8), can be written as

$$a_1^{(0)} = \beta\mu_1, \qquad a_2^{(0)} = \frac{1}{\bar{\mathfrak{M}}_2^{(0)}}, \qquad a_2^{(2)} = \frac{1 + 2\frac{\beta}{V}\tilde{\Phi}_C(k)\bar{\mathfrak{M}}_2^{(2)}}{\bar{\mathfrak{M}}_2^{(2)}}, \qquad (11)$$

$$a_3^{(0)} = \frac{\bar{\mathfrak{M}}_3^{(0)}}{(\bar{\mathfrak{M}}_2^{(0)})^3}, \qquad a_3^{(2)} = \frac{3\bar{\mathfrak{M}}_3^{(2)}}{\bar{\mathfrak{M}}_2^{(0)}(\bar{\mathfrak{M}}_2^{(2)})^2}, \qquad (12)$$

$$a_4^{(0)} = \frac{\bar{\mathfrak{M}}_4^{(0)}}{(\bar{\mathfrak{M}}_2^{(0)})^4}, \qquad a_4^{(2)} = \frac{6\bar{\mathfrak{M}}_4^{(2)}}{(\bar{\mathfrak{M}}_2^{(0)})^2(\bar{\mathfrak{M}}_2^{(2)})^2}, \qquad a_4^{(4)} = \frac{\bar{\mathfrak{M}}_4^{(4)}}{(\bar{\mathfrak{M}}_2^{(2)})^4}. \qquad (13)$$

Let us analyse expression (9). Restricting our consideration to the Gaussian approximation (neglecting the terms proportional to ρ^3, ρc^2, etc in the exponent of (9)) we obtain the boundary of stability with respect to fluctuations of the charge density [40]. The fact that the RPM does not demonstrate the GL phase instability in this approximation is attributed to the absence of direct pair interactions of density fluctuations in the model as well as to the neglect of the effects of non-direct correlations via a charge subsystem at this level. In order to obtain the GL spinodal curve we should take into consideration the terms of the higher order [13, 40].

Now we follow the programme proposed in [33, 37] for a two-component fluid system. First, we distinguish the two types of variable: essential variables connected with the order parameter and non-essential variables. Then, integrating over the non-essential variables with the Gaussian density measure, we construct the basic density measure (the GLW Hamiltonian) with respect to the essential variables. For the RPM in the vicinity of the GL critical point the density variables $\rho_{\mathbf{k}}$ (describing fluctuations of the total number density) turn out to be essential variables [38]. Thus, we can rewrite (9) (under the condition $a_2^{(2)} > 0$) as follows:

$$\Xi = \Xi_0 \mathcal{C} \int (\mathrm{d}\rho) \exp\left[\bar{a}_1\rho_0 - \frac{1}{2!\langle N\rangle}\sum_{\mathbf{k}}\bar{a}_2\rho_{\mathbf{k}}\rho_{-\mathbf{k}} + \frac{1}{3!\langle N\rangle^2}\right.$$

$$\times \sum_{\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3}\bar{a}_3\rho_{-\mathbf{k}_1}\rho_{-\mathbf{k}_2}\rho_{-\mathbf{k}_3}\delta_{\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3} + \frac{1}{4!\langle N\rangle^3}\sum_{\mathbf{k}_1,\ldots,\mathbf{k}_4}\bar{a}_4$$

$$\left.\times \rho_{-\mathbf{k}_1}\rho_{-\mathbf{k}_2}\rho_{-\mathbf{k}_3}\rho_{-\mathbf{k}_4}\delta_{\mathbf{k}_1+\cdots+\mathbf{k}_4}\right], \qquad (14)$$

where

$$\bar{a}_n = \bar{a}_n^{(0)} + \Delta a_n, \qquad \bar{a}_n^{(0)} = a_n^{(0)}\langle N\rangle^{n-1} \qquad (15)$$

and Δa_n are correction terms obtained as the result of integration over CVs $c_{\mathbf{k}}$:

$$\Delta a_1 = \frac{1}{\sqrt{2}\langle N\rangle}\sum_{\mathbf{q}}\tilde{G}(q),$$

$$\Delta a_2 = \frac{S_3}{S_2^2}\frac{1}{\langle N\rangle}\sum_{\mathbf{q}}\tilde{G}(q) + \frac{1}{2\langle N\rangle}\sum_{\mathbf{q}}\tilde{G}(q)\tilde{G}(|\mathbf{q}-\mathbf{k}|) + \cdots,$$

$$\Delta a_3 = \frac{6S_3}{\sqrt{2}S_2^2}\frac{1}{\langle N\rangle}\sum_{\mathbf{q}}\tilde{G}(q)\tilde{G}(|\mathbf{q}+\mathbf{k}_1|) + \cdots, \qquad (16)$$

$$\Delta a_4 = \frac{6S_3^2}{S_2^4}\frac{1}{\langle N\rangle}\sum_{\mathbf{q}}\tilde{G}(q)\tilde{G}(|\mathbf{k}_3+\mathbf{k}_4-\mathbf{q}|) + \cdots,$$

where

$$\tilde{G}(q) = \frac{1}{1 + \beta\frac{\langle N\rangle}{V}\tilde{\Phi}_C(q)} \qquad (17)$$

is a charge–charge structure factor of the RPM determined in the Gaussian approximation. It is worth noting that $\tilde{G}(q)$ is of the same form as the function $\tilde{G}^0_{\phi\phi}(k)$ introduced in [13]. In the next part we restrict our attention to the GL critical point where $\tilde{G}(q)$ remains a smooth function.

Now let us consider the coefficient $\bar{a}_2$ in more detail. Expanding this coefficient at small k one can readily see that the linear term vanishes. Thus, we obtain

$$\bar{a}_2 = \bar{a}_{2,0} + \tfrac{1}{2}k^2 \bar{a}_{2,2} + \cdots, \tag{18}$$

where

$$\bar{a}_{2,0} = a_2^{(0)} + \frac{S_3}{S_2^2} \frac{1}{\langle N \rangle} \sum_{\mathbf{q}} \tilde{G}(q) + \frac{1}{2\langle N \rangle} \sum_{\mathbf{q}} \tilde{G}(q)^2,$$
$$\bar{a}_{2,2} = \frac{1}{2\langle N \rangle} \sum_{\mathbf{q}} \tilde{G}(q) \frac{\partial^2 \tilde{G}(q)}{\partial q^2}. \tag{19}$$

It is worth noting that the dependence on $\mathbf{k}$ results from the second order of the perturbation theory in $\tilde{G}(q)$. Inserting expansion (18) into (14) one arrives at the effective Hamiltonian of the RPM in the neighbourhood of the GL critical point. The coefficients of the Hamiltonian are explicitly given in (11)–(13) and (15)–(19). As is seen, the effective interaction that has appeared in (14) is of a short-range character, and the effective Hamiltonian has a structure quite similar to the effective Hamiltonian of an Ising model in an external magnetic field.

4. Conclusions

In this letter we have studied the critical behaviour of the RPM in the vicinity of the GL critical point. For this purpose the method of CVs with a reference system was used. First we obtain the functional of the grand partition function given in terms of the two CVs $\rho_{\mathbf{k}}$ and $c_{\mathbf{k}}$ describing fluctuations of the total number density and the charge density, respectively. As is known, the Gaussian approximation of the functional of the grand partition function of simple fluids and their mixtures produces a qualitative picture of their phase behaviour. In contrast, the full phase diagram of the RPM cannot be obtained within the framework of this approximation. In order to describe the GL phase transition, terms of higher order should be taken into account in the effective Hamiltonian [13, 40]. Actually, the non-direct correlations which are formed through the mediation of the charge subsystem cause an effective attraction between the ions which, in turn, leads to the GL phase transition in the RPM.

After the integration over CV $c_{\mathbf{k}}$ with the Gaussian basic density measure we construct an effective Hamiltonian in terms of $\rho_{\mathbf{k}}$ connected with the order parameter. All the coefficients of the effective Hamiltonian consist of two parts: the part depending solely on the characteristics of the RS (through the n-particle structure factors of the RS in the long-wavelength limit) and the part of mixed type. The latter is in the form of an expansion in terms of the charge–charge structure factors. Allowance for the charge–charge correlations (through the integration over CVs $c_{\mathbf{k}}$) leads to the contribution Δa_2 to the coefficient a_2 (at the second power of CVs $\rho_{\mathbf{k}}$) which describes the effective attraction of short-range character.

Finally, the original Hamiltonian is mapped onto the GLW Hamiltonian of an Ising-like model in a magnetic field. We conclude that the form of the effective Hamiltonian of the RPM confirms the fact that the critical behaviour of the RPM near the GL critical point belongs to the universal class of a 3D Ising model. A more comprehensive analysis of the coefficients $\bar{a}_n$ will be done elsewhere.

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