Critical behaviour of ionic fluids

O.V. Patsahan
Institute for Condensed Matter Physics of the National Academy of Sciences of Ukraine,
1 Svientsitskii Str., 79011 Lviv, Ukraine
E-mail: oksana@icmp.lviv.ua
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Recently we proposed a microscopic approach to the description of the phase behaviour and critical phenomena in binary fluid mixtures. It was based on the method of collective variables (CV) with a reference system. The approach allowed us to obtain the functional of the Ginzburg-Landau-Wilson (GLW) Hamiltonian expressed in terms of the CV (fluctuating densities). The corresponding set of CV included the variable connected with the order parameter. In this paper we use this approach to the study of the critical behaviour of ionic fluids. For the restricted primitive model (RPM) we obtain the functional of the grand partition function in the phase space of the two fluctuating fields conjugate to the fluctuating densities. First we calculate the phase diagram of the RPM in the mean-field (MF) approximation and then we do this calculation taking into account the terms of the higher orders in the effective Hamiltonian. In the both cases the phase diagrams demonstrate the gas-liquid (GL) and charge ordering phase instabilities. In the latter case, the obtained value for the GL critical temperature is in good agreement with the MC simulation data whereas the critical density is underestimated. The explicit expression found for the grand thermodynamic potential in the vicinity of the GL critical point implies a classical critical behaviour of the RPM.

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I. INTRODUCTION

Nowdays the theory of phase transitions and critical phenomena is well developed in general. It enables one to predict both universal and non-universal properties for many model systems. However, a number of questions still remains open, among which the critical behaviour of ionic fluids is of great interest. Recent experiments have shown that both Ising-like and mean-field like criticality can be observed in such systems. For reviews of the experimental and theoretical situation see Refs. 1, 2, 3, 4, 5, 6. Numerous theoretical and computer simulation studies of the restricted primitive model (RPM), the simplest model for ionic systems, have not provided a clear picture of the thermodynamics in the critical region 7, 8, 9, 10, 11, 12, 13, 14, 15.

In this paper we address the issue of the critical behaviour of the RPM using the approach proposed in 16, 17 for the binary symmetrical mixture. The theory has its origin in the approach based on a functional representation of a partition function in the collective variables (CV) space 18, 19. Its particular feature is a choice of the phase space in which the system is considered. Among the independent variables of this space there could be the ones connected with the order parameters. This phase space is formed by a set of CV. Each of them is a mode of density fluctuations corresponding to the specificity of the model under consideration. This approach allows one to determine, on microscopic grounds, the explicit form of the effective GLW Hamiltonian and then to integrate the partition function in the neighborhood of the phase transition point taking into account the renormalization group symmetry. As a result, non-classical critical exponents and analytical expressions for thermodynamic functions are obtained 20, 21. More recently this theory was developed for a binary fluid mixture 14, 17, 22, 23, 24, 25.

The paper consists of two parts. In the first part we obtain the functional of the grand partition function (GPF) of the RPM given in the phase space of the two fluctuating fields: the fluctuating field $h_k=0$ conjugate to the fluctuating total number density $\rho_k=0$ and the fluctuating field $\gamma_k$ conjugate to the fluctuating charge density $c_k$. Restricting our consideration to the second powers of $\gamma_k$ (taking into account the higher powers of $h_k=0$) we derive the equation for the chemical potential. Based on the chemical potential obtained from the linearized equation (that corresponds to the mean-field (MF) approximation) we calculate the spinodal curve. Its run suggests that two types of phase instabilities can occur in the RPM. One part of the spinodal is the gas-liquid (GL) type while another one looks like a $\lambda$-line. We obtain the following values of the GL critical point: $T^*=0.084$ and $\eta^*=0.005$ which agree with the other MF theories 20. In order to study the nature of the criticality of the RPM as well as to get the best estimations for its GL critical point we go beyond the above mentioned approximation taking into account the terms of higher orders in the effective Hamiltonian. The second part of the paper is devoted to this end. First, we consider the Gaussian approximation of the functional of the GPF. It yields the equation for the boundary of stability with respect to the charge density fluctuations. Then, applying the procedure proposed in 16, 17 we obtain the expression for the grand thermodynamic potential in the vicinity of the GL critical point as a power series in the field $h_k=0$ (up to $h^4$) conjugate to the order parameter. The expression obtained has the form of the Landau free energy. We also
calculate the phase diagram demonstrating both GL and charge ordering phase instabilities. The data for the GL critical point are \( T_c^* = 0.0502 \) and \( \eta_c = 0.022 \).

II. FUNCTIONAL REPRESENTATION OF THE GPF OF THE RPM. AN EQUATION FOR THE CHEMICAL POTENTIAL; THE PHASE DIAGRAM IN THE MF APPROXIMATION

The RPM consists of \( N = N_+ + N_- \) hard spheres of diameter \( \sigma \) with \( N_+ \) carrying charges \( +q \) and \( N_- = N_+ \) charges \( -q \), in a medium of dielectric constant \( D \). The interaction potential of the RPM has the form

\[
U_{\gamma,\delta}(r) = \begin{cases} 
\infty & \text{if } r < \sigma \\
\frac{q_q k}{q_q} & \text{if } r \geq \sigma , \quad q_q = \pm q.
\end{cases}
\]

We split the potential \( U_{\gamma,\delta}(r) \) into short- and long-range parts using the Weeks-Chandler-Andersen partition \[27\]. As a result, we have

\[
\psi_{\gamma,\delta}(r) = \begin{cases} 
\infty & \text{if } r \leq \sigma \\
0 & \text{if } r > \sigma .
\end{cases}
\]

\[
\Phi_{\gamma,\delta}(r) = \begin{cases} 
\frac{q_q k}{D_{\gamma,\delta}} & \text{if } r \leq \sigma \\
0 & \text{if } r > \sigma .
\end{cases}
\]

This simple form for \( \Phi_{\gamma,\delta}(r) \) inside the hard core changes the behaviour of the Fourier transform for large \( k \) from usual Colombic \( k^{-2} \) to \( k^{-3} \) decay. As was shown \[28\], this choice of \( \Phi_{\gamma,\delta}(r) \) for \( r < \sigma \) produces rapid convergence of the series of the perturbation theory for the free energy. The Fourier transform of \( \Phi_{\gamma,\delta}(r) = \hat{\Phi}_{\gamma,\delta}^{\gamma,\delta}(x) = \Phi_{\gamma,\delta}(r) \) has the form

\[
\beta \rho \hat{\Phi}_{\gamma,\delta}(x) = 24 \beta^* \eta \sin x
\]

where \( \beta^* = \frac{2 \beta}{2 \pi} \), \( \beta = \frac{1}{k_B T}, \) \( \eta = \frac{\pi \rho \sigma^3}{3} \) is fraction density, \( x = k x \).

We start with the GPF. We use the formulas obtained within the framework of the CV method for a binary continuous system (see \[RS\] in Appendix A). In the case of the RPM we have \( \hat{V}(k) \equiv 0, \hat{U}(k) \equiv 0, \hat{W}(k) = 2 \hat{\Phi}_{C}(k) \) and \( \mu_{1,+} = \mu_{1,-} \) (\( \mu_{1,i} \) is a part of the chemical potential of the 4th species, \( i = +, - \)). As a result, we can present the functional of the GPF of the RPM in the form (for details see Appendix A):

\[
\Xi = \Xi_0 \int (dp)(dc) \exp \left( \beta \mu_1 \rho_0 - \frac{\beta}{V} \sum_k \hat{\Phi}_{C}(k) c_k c_{-k} \right) J(p, c).
\]

(2)

Here \( \Xi_0 \) is the GPF of the RS. In the case of the RPM, the RS is a one-component hard-sphere system with the diameter \( \sigma \) (potential \( \psi_{\gamma,\delta}(r) = \psi(r) \)).

\( \rho_k \) and \( c_k \) are the CV connected with total density fluctuation modes and charge density fluctuation modes, respectively. \( \mu_1 \) \( (\mu_1 = (\mu_{1,+} + \mu_{1,-})/\sqrt{2}) \) is determined from the equation

\[
\frac{\partial \ln \Xi_1}{\partial \mu_1} = \frac{\langle N \rangle}{\sqrt{2}}.
\]

(3)

For the RPM \( J(p, c) \) has the same form as for the symmetrical binary fluid \[17\]:

\[
J(p, c) = \int (d\gamma)(d\omega) \exp \left\{ i \gamma \sum_k (\omega_k \rho_k + \gamma_k c_k) - i \frac{2 \pi}{\sqrt{2}} \sum_k \mathcal{M}_k^{(0)} \omega_k \delta_k \right. \\
+ \left. \frac{(-2 \pi)^2}{2!} \frac{1}{\sqrt{2}} \sum_k \mathcal{M}_k^{(0)} \omega_k \omega_{-k} + \mathcal{M}_k^{(2)} \gamma_{-k} \right\} \\
\times \sum_{k_1, k_2, k_3} \left( \mathcal{M}_k^{(0)} \omega_{k_1} \omega_{k_2} \omega_{k_3} + 3 \mathcal{M}_k^{(2)} \omega_{k_1} \gamma_{k_2} \gamma_{k_3} \delta_{k_1+k_2+k_3} + \frac{(-2 \pi)^4}{4!} \right)
\times \sum_{k_1, k_2, k_3} \mathcal{M}_k^{(0)} \omega_{k_1} \omega_{k_2} \omega_{k_3} \omega_{k_4} + 6 \mathcal{M}_k^{(2)} \omega_{k_1} \omega_{k_2} \gamma_{k_3} \gamma_{k_4} + \mathcal{M}_k^{(4)}
\]
functions \[ n \] Cumulants with \( S \) and condition (3) has the form:

\[
\times \omega_{k_1} \omega_{k_2} \omega_{k_3} \delta_{k_1 + \cdots + k_4} \times \left( \frac{-i2\pi}{5!} \frac{1}{\sqrt{2^5}} \sum_{k_1, \ldots, k_5} (\mathcal{M}^{(0)}_{k_1} \omega_{k_1} \omega_{k_2} \omega_{k_3} \omega_{k_4} \omega_{k_5} \omega_{k_6}) \right) + 150 \mathcal{M}^{(2)}_{n} \omega_{k_1} \omega_{k_2} \omega_{k_3} \omega_{k_4} \omega_{k_5} \omega_{k_6} + 150 \mathcal{M}^{(4)}_{n} \omega_{k_1} \omega_{k_3} \omega_{k_2} \omega_{k_4} \omega_{k_5} \omega_{k_6} \delta_{k_1 + \cdots + k_6} + \cdots ) .
\]

(4)

In (4) the cumulants \( \mathcal{M}^{(n)} \) with \( i_n = 0 \) are connected with the nth structure factors of the RS [23]:

\[
\mathcal{M}^{(0)}_{n} = (N) S_{\infty}.
\]

Structure factors \( S_{\infty}(0) \) with \( n > 2 \) can be obtained from \( S_{\infty}(0) \) by means of a chain of equations for correlation functions [29]. Cumulants with \( i_n \neq 0 \) can be expressed in terms of \( \mathcal{M}^{(0)}_{n} \) (see also formulae (4.8) in [23]):

\[
\mathcal{M}^{(2)}_{n} = \mathcal{M}^{(0)}_{n - 1}, \quad \mathcal{M}^{(4)}_{n} = 3 \mathcal{M}^{(0)}_{n - 2} - 2 \mathcal{M}^{(0)}_{n - 3}, \quad \mathcal{M}^{(6)}_{n} = 15 \mathcal{M}^{(0)}_{n - 3} - 30 \mathcal{M}^{(0)}_{n - 4} + 16 \mathcal{M}^{(0)}_{n - 5}.
\]

(5)

First we integrate in (2) over the variables \( \rho_k \) and \( \omega_k \). As a result, we have

\[
\Xi = \Xi_0 \exp \left( \sum_{n \geq 1} \frac{\mathcal{M}^{(n)}_{n}}{n!} h_0^n \right) \int (dc) \exp \left( \frac{\beta}{V} \sum_k \Phi_C(k) c_k e^{-k} \right) J(c, h_0),
\]

where

\[
J(c, h_0) = \int (d\gamma) \exp \left( i2\pi \sum_k \gamma_k c_k + \frac{-i2\pi}{2!} \sum_{k_1, \ldots, k_4} \gamma_{k_1} \gamma_{k_2} \gamma_{k_3} \gamma_{k_4} \delta_{k_1 + \cdots + k_4} \sum_{n \geq 0} \frac{\mathcal{M}^{(2)}_{n+2} h_0^n}{n!} \right)
\]

(7)

and condition (9) has the form:

\[
\frac{\partial \ln \Xi_1}{\partial h_0} = (N).
\]

(9)

Expressions (6) - (7) do not include the "field" variable \( h_k \) with \( k \neq 0 \). As one can see below, this fact will give rise to the Landau type free energy of the RPM in the vicinity of the GL critical point.

Performing in (6) - (7) integration over \( c_k \) we obtain (up to \( \gamma^4 \))

\[
\Xi_1 = \prod_k \sqrt{\frac{\pi V}{\beta \Phi_C(k)}} \int (d\gamma) \exp \left\{ \mathcal{F}(h_0) + \frac{-i2\pi}{2!} \sum_k \gamma_{k} \gamma_{-k} \frac{1}{2 \beta V \Phi_C(k)} \right\} \times \left( 1 + \frac{\beta}{V \Phi_C(k)} \frac{\partial \mathcal{F}(h_0)}{\partial h_0} \right) + \frac{-i2\pi}{4!} \frac{1}{\sqrt{2}} \sum_{k_1, \ldots, k_4} \gamma_{k_1} \gamma_{k_2} \gamma_{k_3} \gamma_{k_4} \delta_{k_1 + \cdots + k_4} \sum_{n \geq 0} \frac{\mathcal{M}^{(4)}_{n+4} h_0^n}{n!} \right) ,
\]

(10)

where

\[
\mathcal{F}(h_0) = \sum_{n \geq 1} \frac{\mathcal{M}^{(n)}_{n}}{n!} h_0^n, \quad \frac{\partial \mathcal{F}(h_0)}{\partial h_0} = \sum_{n \geq 1} \frac{\mathcal{M}^{(n)}_{n}}{(n-1)!} h_0^{n-1},
\]

(11)
\[ \frac{\partial^2 F(h_0)}{\partial h_0^2} = \sum_{n \geq 2} \frac{\mathcal{M}_n^{(n)}}{(n - 2)!} h_0^{n-2} \] \hspace{1cm} (12)

and formulas (5) are used for \( \mathcal{M}_n^{(n)} \).

It should be point out that this integration makes sense for a positive function \( \Phi_C(k) \). In our study \( \Phi_C(k) \) (see (11)) can change the sign and the transition from (5) to (11) has to be regarded as an algebraic formal way of deriving the expansion in terms of \( h_0 \) and \( \gamma_k \) solely. As a result, in (10) in the exponent we have the expression in terms of the two fluctuating fields, namely, the fluctuating field \( h_{k=0} \) conjugate to the fluctuating total density \( \rho_{k=0} \) and the fluctuating field \( \gamma_k \) (for all of \( k \)) conjugate to the fluctuating charge density \( \sigma_k \).

a. Equation for the chemical potential. Restricting our consideration in (7) to the second power of \( \rho \) and formulas (5) are used for \( \gamma_k \). As a result, we obtain for \( \Xi_1 \)

\[ \Xi_1 = \prod_k \left[ 1 + \beta \frac{\Phi_C(k)}{V} \frac{\partial F(h_0)}{\partial h_0} \right]^{-1/2} \exp(F(h_0)). \] \hspace{1cm} (13)

Using (11) and (13) we can write the following equation for the chemical potential

\[ \frac{\partial F(h_0)}{\partial h_0} = \mathcal{M}_1^{(0)} \] \hspace{1cm} (14)

where \( h_0, F(h_0), \frac{\partial F(h_0)}{\partial h_0} \) and \( \frac{\partial^2 F(h_0)}{\partial h_0^2} \) are given by (8) and (11)-(12), respectively.

b. Phase diagram of the RPM in the MF approximation. We solve equation (14) in the simplest approximation. Neglecting terms \( h_0^2, h_0^3 \) and etc. in the right hand side of (14) and setting

\[ \frac{\partial F(h_0)}{\partial h_0} = \mathcal{M}_1^{(0)} \] \hspace{1cm} (15)

in the left hand side of (14) we obtain for \( \mu_{1,+} (= \mu_{1,-}) \)

\[ \mu_{1,+} = -\frac{1}{2\beta} \hat{\alpha}(\beta), \] \hspace{1cm} (16)

where

\[ \hat{\alpha}(\beta) = -\sum_k \frac{\Phi_C(k)}{1 + \frac{\beta \Phi_C(k)}{V} \mathcal{M}_1^{(0)}}. \] \hspace{1cm} (17)

On the other hand, we can get the same result for \( \mu_{1,+} \) taking into account the terms proportional to \( \gamma^2 \) and \( \gamma^2 h_0 \) in the exponent of (7) and setting \( \mathcal{M}_3^{(2)} = 0 \) in the final result (\( \mathcal{M}_3^{(2)} \) is the coefficient of \( \gamma^2 h_0 \)). Therefore, we may say that \( \mu_{1,+} \) given by (13)-(17) is obtained in the MF approximation.

The full chemical potential \( \mu_+ \) is equal to \( \mu_{0,+} + \mu_{1,+} \),

where \( \mu_{0,+} (= \mu_{0,-}) \) is the chemical potential of a one-component hard sphere system.

The equation \( \beta \rho \frac{\partial \mu_+}{\partial \rho} = 0 \), where \( \rho \) is the total number density, gives the spinodal of the RPM in the approximation considered. Using (11) for \( \Phi_C(k) \) and the Perkus-Yevick approximation for the RS, the equation for the spinodal curve can be written as

\[ \int_0^\infty \frac{x^2 \sin x^2 \sin x}{(x^8 T^* + 24 \eta \sin x^2) \sin x} dx = \frac{\pi}{24 \eta (1 - \eta)^4} \] \hspace{1cm} (18)

The phase diagram calculated from (18) is shown in Fig. 1. The obtained data for the GL critical point are \( T_c^* \approx 0.084 \) (\( T_c^* = 1/\beta_c^* \)) and \( \eta_c \approx 0.005 \).

It is evident that in the considered approximation (corresponding to the MF theory) we get the overestimated value for the GL critical temperature and the underestimated value for the critical density. But, in contrast to the previous results, the spinodal curve changes its run (at \( \eta \approx 0.047 \)) and then it directs to the higher temperature. The second positive slop of the spinodal indicates another type of the phase instability appearing in the RPM (similarly to the \( \lambda \)-line in a symmetrical binary fluid). Below, we shall calculate the phase diagram of the RPM taking into account in (7) the terms of the higher orders.
Now let us rewrite (6)-(7) as

\[
\Xi_1 = \exp\left(\mathcal{F}(h_0)\right) \int (dc) \exp\left(-\frac{\beta}{V} \sum_k \Phi_C(k)c_k c_{-k}\right)
\]

\[
\times \int (d\gamma) \exp\left\{i2\pi \sum_k \gamma_k c_k + \frac{(-i2\pi)^2}{2!} \sum_k \gamma_k \gamma_{-k} \Psi^{(0)}_1 + \frac{(-i2\pi)^4}{4!} \frac{1}{\sqrt{2}} \right. \\
\times \left. \sum_{k_1, \ldots, k_4} \gamma_{k_1} \gamma_{k_2} \gamma_{k_3} \gamma_{k_4} \left(3 \frac{\partial^2 \mathcal{F}(h_0)}{\partial h_0^2} - 2 \frac{\partial \mathcal{F}(h_0)}{\partial h_0} \right) \delta_{k_1 + \ldots + k_4}\right\}
\]

and the notations in (19) are the same as those in the previous section.

a. Gaussian approximation. First, we restrict our attention to the second powers of variables \(h_0\) and \(\gamma_k\) which corresponds to neglecting the terms proportional to \(h_0^3, \gamma_k \gamma_{-k} h_0, \gamma_k \gamma_{-k} h_0^2, h_0^4\), etc. After integration in (19) over \(\gamma_k\) we obtain

\[
\Xi_1 = \exp\left(\mathcal{F}(h_0)\right) \prod_k \left(\pi \Psi^{(0)}_1\right)^{-1/2} \int (dc) \exp\left\{-\sum_k \frac{c_k c_k}{\Psi^{(0)}_1} \right. \\
\times \left. \left(1 + \frac{\beta}{V} \Phi_C(k) \Psi^{(0)}_1\right)\right\}
\]

As is seen from (20), the equality

\[
1 + \frac{\beta}{V} \Phi_C(k) \Psi^{(0)}_1 = 0
\]

holds at some values of the wave-vector \(k\), temperature and density. Equation (21) determines the boundary of stability connected with the charge fluctuations (the field variable \(\gamma_k\) is conjugate to the CV \(c_k\)):

\[
T^* = -24\eta \frac{\sin x^*}{x^*}, \quad T^* = \frac{1}{\beta^*},
\]

or

\[
T_c^*(x^*, \eta) = -8\eta \frac{\cos x^*}{x^* + 2},
\]

where \(x^*\) is determined from the condition

\[
\tan x^* = \frac{x^*}{3},
\]

which yields \(x^* \approx 4.0783\). Substituting \(x^*\) in (20) we obtain the boundary of stability with respect to fluctuations of the local charge density

\[
T_{c}^*(x = x^*) \approx 0.285\eta.
\]

A similar result (for another choice of interaction inside the hard core) was obtained in [9, 10] within the framework of the field-theoretical approach. The possibility of the charge-ordering transition in the continuous-space RPM model was discussed therein.

It is worth noting that the RPM does not demonstrate the GL phase transition in the Gaussian approximation. In order to obtain the GL spinodal curve we should take into consideration the terms of the order higher than the second one (\(\gamma^2 h, \gamma^2 h^2\), etc.).
b. Beyond the Gaussian approximation (model $\varphi^4$). We restrict our consideration in (19) to the terms of the fourth order. In this case $\Xi$ has the form:

$$
\Xi = \Xi_0 \exp (\mathcal{F}(h_0)) \int (dc) \exp \left( -\beta \sum_k \tilde{\Phi}_C(k)c_k c_{-k} \right) \int (d\gamma) \exp \{ i2\pi \sum_k \gamma_k c_k + \frac{(-2\pi)^2}{2!} \sum_k \gamma_k \gamma_{-k} \left( \mathcal{M}_1^{(0)} + h_0 \mathcal{M}_2^{(0)} + h_0^2 \mathcal{M}_3^{(0)} \right) \} + \frac{(-2\pi)^4}{4!} \sum_{k_1, \ldots, k_4} \gamma_{k_1} \gamma_{k_2} \gamma_{k_3} \gamma_{k_4} \left( 3 \mathcal{M}_2^{(0)} - 2 \mathcal{M}_1^{(0)} \right) \delta_{k_1 + \ldots + k_4} \right),
$$

where the summation in (11) over $n$ is restricted to 4.

Now we follow the programme proposed in [16, 23] for a two-component fluid system. First, we separate the two types of variables: the essential variables (which include the variable connected with the order parameter) and the 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 variable $h_0$ (conjugate to the CV $\rho_0$) turns out to be the essential variable [17]. Thus, we can present (26) as

$$
\Xi_1 = \prod_k \left( \pi \mathcal{M}_1^{(0)} \right)^{-1/2} \exp (\mathcal{F}(h_0)) \int (dc) \exp \left( -\beta \sum_k \tilde{\Phi}_C(k)c_k c_{-k} \right) \times \left( 1 + \hat{A} + \frac{1}{2!} \hat{A}^2 + \ldots \right) \exp \left( -\sum_k c_k c_{-k} / \mathcal{M}_1^{(0)} \right),
$$

where

$$
\hat{A} = \left( h_0 \mathcal{M}_2^{(0)} + h_0^2 \mathcal{M}_3^{(0)} \right) \frac{\partial^2}{\partial c_k c_{-k}}.
$$

After integration in (27) we get

$$
\Xi_1 = \prod_k \frac{1}{\sqrt{1 + \beta \mathcal{M}_n^{(0)}}} \exp \left( \sum_{n \geq 1} \mathcal{M}_n \frac{h_0^n}{n!} \right),
$$

where

$$
\mathcal{M}_n = \mathcal{M}_n^{(0)} + \Delta \mathcal{M}_n,
$$

$\Delta \mathcal{M}_n$ are the corrections obtained as the result of integration over variables $c_k$:

$$
\Delta \mathcal{M}_1 = \frac{1}{2} \mathcal{M}_2^{(0)} \hat{a}(\beta), \quad \Delta \mathcal{M}_2 = \frac{1}{2} \mathcal{M}_3^{(0)} \hat{a}(\beta), \quad \Delta \mathcal{M}_3 \equiv 0, \quad \Delta \mathcal{M}_4 \equiv 0.
$$

and $\hat{a}(\beta)$ is given by (17).

It is worth noting that the non-zero corrections $\Delta \mathcal{M}_n$ (see (29)) are those which include only one sum over $k$. Next, the shift is carried out in order to eliminate the cubic term in (28)

$$
h_0 = \tilde{h}_0 + \Delta,
$$

where $\Delta = - \frac{\Delta \mathcal{M}_4}{\Delta \mathcal{M}_4}$. Then (28) has the form

$$
\Xi_1 = C \exp \left( \sum_{n \geq 1} \hat{\mathcal{M}}_n \frac{\tilde{h}_0^n}{n!} \right),
$$

(30)
where

\[ C = \prod_k \frac{1}{\sqrt{1 + \beta \frac{\hat{\omega}}{\hat{\omega}^*} \tilde{\Phi}_C(k)}} \exp \left( \frac{m_1^{(0)}}{2} + \frac{1}{2} \left( \frac{m_3^{(0)}}{m_4^{(0)}} \right)^2 \left( \frac{m_2^{(0)} - (m_3^{(0)})^2}{4m_4^{(0)}} \right) \right) \]

\[ + \frac{1}{2} \tilde{a}(\beta) \left( \frac{m_2^{(0)}}{m_4^{(0)}} + \frac{(m_3^{(0)})^3}{2(m_4^{(0)})^2} \right) \],

\[ \hat{M}_1 = m_1^{(0)} - \frac{m_3^{(0)}}{m_4^{(0)}} \left( \frac{m_2^{(0)} - (m_3^{(0)})^2}{3m_4^{(0)}} \right) + \frac{1}{2} \tilde{a}(\beta) \left( \frac{m_2^{(0)} - (m_3^{(0)})^2}{m_4^{(0)}} \right) \],

\[ \hat{M}_2 = m_2^{(0)} - \frac{(m_3^{(0)})^2}{2m_4^{(0)}} + \frac{1}{2} \tilde{a}(\beta)m_3^{(0)}, \quad \hat{M}_4 = m_4^{(0)} \].

In \( \tilde{\eta}_0 \) is the field conjugate to the order parameter for the GL critical point (see (1.8)-(1.10) in \[21\] and (15)-(20) in \[17\]).

Now we can obtain the grand thermodynamic potential of the RPM in the vicinity of the GL critical point

\[ \Omega - \Omega_0 + k_B T \ln C = -k_B T \left( \sum_{n \geq 1} \hat{M}_n \frac{\tilde{\eta}_0^n}{n!} \right). \] (31)

The right hand side in (31) has the form of the Landau free energy expressed in terms of the field \( \tilde{\eta}_0 \) conjugate to the order parameter. From the equation \( \hat{M}_2 = 0 \) we obtain the equation for the GL spinodal curve

\[ \tilde{a}(\beta) = -2 \frac{m_1^{(0)}}{m_3^{(0)}} + \frac{m_2^{(0)}}{m_4^{(0)}}, \]

or

\[ \frac{2}{\pi} \int_0^\infty \frac{x^2 \sin x dx}{x^3 T + 24 \eta \sin x} = 2 \frac{S_2(0)}{S_3(0)} - \frac{S_3(0)}{S_4(0)}. \] (32)

where \( S_n(0) \) is the \( n \)th structure factor of the one-component hard-sphere system at \( k = 0 \).

The phase diagram of the RPM is shown in Fig. 2. The curve with the maximum is the GL spinodal calculated using \[52\]. The Percus-Yevick approximation is used for \( S_2(0) \) (the expressions for \( S_2(0) \), \( S_3(0) \) and \( S_4(0) \) are given in Appendix B). The straight line calculated by \[40\] (the Gaussian approximation) corresponds to the charge ordering phase transition. The GL critical point is located at \( T_c^* = 0.0502 \) and \( \eta_c = 0.022 \). While the value for \( T_c^* \) is in good agreement with the recent data of computer simulations \[12\] \[13\] \( T_c^* \simeq 0.05 \), the critical density is underestimated \( (\eta_c \simeq 0.04) \).

We can also obtain from \[51\] (using \[31\]) the expression for \( \mu_{+,1} \)

\[ \mu_{+,1} = - \frac{1}{2} \frac{m_2^{(0)}}{m_4^{(0)}} \tilde{a}(\beta) \left( \frac{m_2^{(0)} - (m_3^{(0)})^2}{m_4^{(0)}} \right) \] (33)

If we set \( m_3^{(0)} = 0 \) the expression \[33\] reduces to \[16\].

It should be pointed out that the above described scheme of integration in the vicinity of the GL critical point cannot be used in the region close to the line defined by \[40\] (dotted line in Fig. 2): the variables \( \gamma_k \) appear to be the essential variables in this region.

IV. CONCLUSIONS

We use the recently developed approach in the study of the critical behaviour of ionic fluids. For the RPM we obtain the functional of the GPF in terms of the two fluctuating fields, namely, the field \( h_0 \) conjugate to the total density fluctuations and the field \( \gamma_k \) conjugate to the charge density fluctuations. The phase diagram of the system
is calculated in the MF approximation (that corresponds to setting \( \mu_n^{(i_n)} = 0 \) for \( n \geq 3 \) in the expression for the chemical potential) as well as taking into account the higher powers of the field \( h_0 \). In the both cases the phase diagram demonstrates the GL and charge ordering phase instabilities. In the latter case the obtained value for the GL critical temperature correlates well with the MC simulation data.

Following the scenario proposed in \[16, 17\] for a binary fluid we integrate over \( \gamma_k \) (non-essential variables) with the Gaussian density measure. As a result, we obtain an explicit expression for the grand thermodynamic potential of the RPM in the vicinity of the GL critical point as an expansion in terms of the field conjugate to the order parameter. The expression implies the classical critical behaviour of the RPM.

**Appendix A**

Let us consider a classical two-component system of interacting particles consisting of \( N_a \) particles of species \( a \) and \( N_b \) particles of species \( b \). The system is in volume \( V \) at temperature \( T \).

Let us assume that an interaction in the system has a pairwise additive character. The interaction potential between a \( \gamma \) particle at \( r'_{ij} \) and a \( \delta \) particle at \( r'_{ij} \) may be expressed as a sum of two terms:

\[
U_{\gamma\delta}(r_{ij}) = \psi_{\gamma\delta}(r_{ij}) + \phi_{\gamma\delta}(r_{ij}),
\]

where \( \psi_{\gamma\delta}(r) \) is a potential of a short-range repulsion that can be chosen as an interaction between two hard spheres \( \sigma_{\gamma\delta} \) and \( \phi_{\gamma\delta}(r) \) is an attractive part of the potential which dominates at large distances.

Let us start with a grand partition function of a two-component continuous system

\[
\Xi = \sum_{N_a=0}^{\infty} \sum_{N_b=0}^{\infty} \prod_{\gamma=1}^{N_a} z_{a}^{N_{\gamma}} \prod_{\delta=1}^{N_b} z_{b}^{N_{\delta}} \int (d\Gamma) \exp \left[ -\frac{\beta}{2} \sum_{\gamma\delta} \sum_{ij} U_{\gamma\delta}(r_{ij}) \right],
\]

(34)

where \( (d\Gamma) = \prod_{\gamma} d\Gamma_{N_{\gamma}}, d\Gamma_{N_{\gamma}} = d\vec{r}_{1\gamma}^a d\vec{r}_{2\gamma}^a \cdots d\vec{r}_{N_{\gamma}}^a \) is an element of the configurational space of the \( \gamma \)th species; \( z_{a} \) is the fugacity of the \( \gamma \)th species: \( z_{\gamma} = \exp(\beta \mu_{\gamma}') \), \( \mu_{\gamma} = \mu_{\gamma}' + \beta^{-1} \ln([2\pi m_{\gamma} \beta^{-1}]^{3/2}/2) \); \( \beta = \frac{1}{k_B T} \) is the Boltzmann constant, \( T \) is temperature; \( m_{\gamma} \) is mass of the \( \gamma \)th species, \( h \) is the Planck constant. \( \mu_{\gamma}' \) is determined from

\[
\frac{\partial \ln \Xi}{\partial \beta \mu_{\gamma}} = \langle N_{\gamma} \rangle,
\]

where \( \langle N_{\gamma} \rangle \) is the average number of the \( \gamma \)th species.

Further consideration of the problem is done in the extended phase space: in the phase space of the Cartesian coordinates of the particles and in the CV phase space. An interaction connected with the repulsion (potential \( \psi_{\gamma\delta}(r) \)) is considered in the space of the Cartesian coordinates of the particles. We call this two-component hard-spheres system a reference system (RS). The thermodynamic and structural properties of the RS are assumed to be known. The interaction connected with an attraction (potential \( \phi_{\gamma\delta}(r) \)) is considered in the CV space. The phase space overflow is cancelled by introduction of a Jacobian of the transition to CV. The contribution of the short-range forces to the long-range interaction screening is ensured by averaging this Jacobian over the RS.

Let us introduce the grand partition function of the RS

\[
\Xi_0 = \sum_{N_a=0}^{\infty} \sum_{N_b=0}^{\infty} \prod_{\gamma=1}^{N_a} \prod_{\delta=1}^{N_b} \exp \left( \beta \mu_0^\gamma N_{\gamma} \right) \int (d\Gamma) \exp \left[ -\frac{\beta}{2} \sum_{\gamma\delta} \sum_{ij} \psi_{\gamma\delta}(r_{ij}) \right],
\]

(35)

where \( \mu_0^\gamma \) is the chemical potential of the \( \gamma \)th species in the RS.

Then the grand partition function \( \Xi \) can be written as \( \Xi = \Xi_0 \Xi_1 \) :

\[
\Xi = \Xi_0 \Xi_1,
\]

where \( \Xi_0 \) is given in \( \Xi_0 \). The part of the grand partition function which is defined in the CV phase space has the form of the functional integral:

\[
\Xi_1 = \int (dp) \exp \left[ \beta \sum_{\gamma} \mu_0^\gamma \rho_{a,\gamma} - \frac{\beta}{2V} \sum_{\gamma\delta} \sum_{k} \phi_{\gamma\delta}(k) \rho_{k,\gamma} \rho_{-k,\delta} \right] J(\rho_a, \rho_b).
\]

(36)
Here,

1) \( \mu_1^r \) is a part of the chemical potential of the \( \gamma \)-th species

\[
\mu_1^r = \mu_1 - \mu_1^0 + \frac{\beta}{2V} \sum_k \tilde{\phi}_{\gamma\gamma}(k)
\]

and is determined from the equation

\[
\frac{\partial \ln \Xi_1}{\partial \beta \mu_1^r} = \langle N_\gamma \rangle,
\]

\( \mu_\gamma \) is the full chemical potential of the \( \gamma \)-th species;

2) \( \rho_{k,\gamma} = \rho_{k,\gamma}^r - i \rho_{k,\gamma}^s \) is the collective variable of the \( \gamma \)-th species, the indices \( c \) and \( s \) denote the real part and the coefficient at the imaginary part of \( \rho_{k,\gamma} \); \( \rho_{k,\gamma}^r \) and \( \rho_{k,\gamma}^s \) describe the value of \( k \)-th fluctuation mode of the number of \( \gamma \)-th species particles. Each of \( \rho_{k,\gamma}^r \) and \( \rho_{k,\gamma}^s \) takes all the real values from \(-\infty\) to \(+\infty\). \( (dp) \) is a volume element of the CV phase space:

\[
(dp) = \prod_\gamma dp_{0,\gamma} \prod_{k \neq 0} dp_{k,\gamma} dp_{k,\gamma}^s.
\]

The prime means that the product over \( k \) is performed in the upper semispace;

3) \( J(\rho_a, \rho_b) \) is the transition Jacobian to the CV averaged on the RS [22, 23]:

\[
J(\rho_a, \rho_b) = \int (dv) \prod_\gamma \exp \left[ i 2 \pi \sum_k \nu_{k,\gamma} \rho_{k,\gamma} \right] \exp \left[ \sum_{n \geq 1} \frac{(-i\pi)^n}{n!} \sum_{\gamma_1=\gamma_2} M_{\gamma_1...\gamma_n}(k_1, \ldots, k_n) \nu_{k_1,\gamma_1} \cdots \nu_{k_n,\gamma_n} \right],
\]

where variable \( \nu_{k,\gamma} \) is conjugated to CV \( \rho_{k,\gamma} \). \( M_{\gamma_1...\gamma_n}(k_1, \ldots, k_n) \) is the \( n \)-th cumulant connected with \( S_{\gamma_1...\gamma_n}(k_1, \ldots, k_n) \), the \( n \)-particle partial structure factor of the RS, by means of the relation

\[
M_{\gamma_1...\gamma_n}(k_1, \ldots, k_n) = \sqrt{N_{\gamma_1} \cdots N_{\gamma_n}} S_{\gamma_1...\gamma_n}(k_1, \ldots, k_n) \delta_{k_1+\cdots+k_n},
\]

where \( \delta_{k_1+\cdots+k_n} \) is the Kronecker symbol.

In general, the dependence of \( M_{\gamma_1...\gamma_n}(k_1, \ldots, k_n) \) on wave vectors \( k_1, \ldots, k_n \) is complicated. Hereafter we shall replace \( M_{\gamma_1...\gamma_n}(k_1, \ldots, k_n) \) by their values in long-wave length limit \( M_{\gamma_1...\gamma_n}(0, \ldots, 0) \).

4) \( \tilde{\phi}_{\gamma\delta}(k) \) is the Fourier transform of attractive potential \( \phi_{\gamma\delta}(r) \). The behaviour of \( \phi_{\gamma\delta}(r) \) in the region of the core \( r < \sigma_{\gamma\delta} \) must be determined from the conditions of optimal separation of the interaction.

We pass in [36] to CV \( \rho_k \) and \( c_k \) (according to \( \omega_k \) and \( \gamma_k \)) by means of the orthogonal linear transformation:

\[
\rho_k = \frac{\sqrt{2}}{2} (\rho_{k,a} + \rho_{k,b}), \quad c_k = \frac{\sqrt{2}}{2} (\rho_{k,a} - \rho_{k,b}),
\]

\[
\omega_k = \frac{\sqrt{2}}{2} (\nu_{k,a} + \nu_{k,b}), \quad \gamma_k = \frac{\sqrt{2}}{2} (\nu_{k,a} - \nu_{k,b}).
\]

As a result, we obtain for \( \Xi \) [14, 17]

\[
\Xi = \Xi_0 \int (dp) (dc) \exp \left[ \beta \mu_1^+ \rho_0 + \beta \mu_1^- c_0 - \frac{\beta}{2V} \sum_k \tilde{V}(k) \rho_k \rho_{k,-k} + \tilde{W}(k) c_k c_{-k} + \tilde{U}(k) \rho_k c_{-k} \right] J(\rho, c).
\]

Here the following notations are introduced:

\[
\Xi = \Xi_0 \int (dp) (dc) \exp \left[ \beta \mu_1^+ \rho_0 + \beta \mu_1^- c_0 - \frac{\beta}{2V} \sum_k \tilde{V}(k) \rho_k \rho_{k,-k} + \tilde{W}(k) c_k c_{-k} + \tilde{U}(k) \rho_k c_{-k} \right] J(\rho, c).
\]
\( \rho_k \) and \( \phi_k \) are the CV connected with total density fluctuation modes and relative density (or concentration) fluctuation modes in the binary system. \((d\rho)\) and \((dc)\) are volume elements of the CV phase space:

\[
(d\rho) = d\rho_0 \prod_{k \neq 0} d\rho_k^c d\rho_k^a, \quad (dc) = dc_0 \prod_{k \neq 0} dc_k^c dc_k^a.
\]

Functions \( \mu_1^+ \) and \( \mu_1^- \) have the form:

\[
\mu_1^+ = \frac{\sqrt{2}}{2} (\mu_{1,a} + \mu_{1,b}), \quad \mu_1^- = \frac{\sqrt{2}}{2} (\mu_{1,a} - \mu_{1,b})
\]

\[
\begin{align*}
\tilde{V}(k) &= (\tilde{\phi}_{aa}(k) + \tilde{\phi}_{ab}(k) + 2\tilde{\phi}_{ab}(k))/2 \\
\tilde{W}(k) &= (\tilde{\phi}_{aa}(k) + \tilde{\phi}_{bb}(k) - 2\tilde{\phi}_{ab}(k))/2 \\
\tilde{U}(k) &= (\tilde{\phi}_{aa}(k) - \tilde{\phi}_{bb}(k))/2
\end{align*}
\]

\[
J(\rho,c) = \int (d\omega) (d\gamma) \exp \left[ \frac{i2\pi}{2} \sum_k (\omega_k \rho_k + \gamma_k c_k) \right] J(\omega,\gamma),
\]

\[
J(\omega,\gamma) = \exp \left[ \sum_n \sum_{i_n \geq 0} \frac{(-i2\pi)^n}{n!} \sum_{k_1...k_n} M_{i_n}^{(n)}(0,...,0) \times \gamma_{k_1} \cdots \gamma_{k_n} \omega_{k_{n+1}} \cdots \omega_{k_n} \right].
\]

Index \( i_n \) is used to indicate the number of variables \( \gamma_k \) in the cumulant expansion (42). Cumulants \( M_{i_n}^{(n)} \) are expressed as linear combinations of the partial cumulants \( M_{\gamma_1,...,\gamma_n} \) (see (37)) and are presented for \( \gamma_1,...,\gamma_n = a,b \) and \( n \leq 4 \) in [23] (see Appendix B in [23]).

\section*{Appendix B}

\[
S_2(0) = \frac{(1 - \eta)^4}{(1 + 2\eta)^2},
\]

\[
S_3(0) = \frac{(1 - \eta)^7(1 - 7\eta - 6\eta^2)}{(1 + 2\eta)^3},
\]

\[
S_4(0) = \frac{(1 - \eta)^{10}(1 - 30\eta + 81\eta^2 + 140\eta^3 + 60\eta^4)}{(1 + 2\eta)^8}
\]

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FIGURE CAPTIONS

FIG. 1. The phase diagram of the RPM calculated from (18) (see the text for explanation).

FIG. 2. The phase diagram of the RPM calculated from (30) (see the text for explanation).
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FIG. 2: The phase diagram of the RPM calculated from (30) (see the text for explanation).