Національна академія наук України

**ІНСТИТУТ
ФІЗИКИ
КОНДЕНСОВАНИХ
СИСТЕМ**

ICMP–13–03E

O.V.Patsahan

THE GINZBURG TEMPERATURE OF IONIC FLUIDS:
THE EFFECT OF COULOMB INTERACTIONS

Оксана Вадимівна Пацаган

Температура Гінзбурга для іонних плинів: вплив кулонівський взаємодій

ЛЬВІВ

Температура Гінзбурга для іонних плинів: вплив кулонівських взаємодій

О.В.Пацаган

Анотація. Використовуючи метод колективних змінних, досліджується вплив кулонівських взаємодій на температуру Гінзбурга для іонних систем. Для зарядово-асиметричної моделі з додатковими короткосяжними притягальними взаємодіями в околі критичної точки газ-рідина отримано ефективний гамільтоніан Ландау-Гінзбурга. Знайдено явні вирази для всіх коефіцієнтів гамільтоніану в однопетлевому наближенні. Отримане значення редукованої температури Гінзбурга t_G для обмеженої примітивної моделі (RPM) є приблизно в 20 разів менше, ніж для неіонної моделі. Для повної моделі, що включає як далекосяжні, так і короткосяжні взаємодії, t_G прямує до значення, знайденого для RPM, якщо сила кулонівських взаємодій стає достатньо великою.

The Ginzburg temperature of ionic fluids: the effect of Coulomb interactions

O.V.Patsahan

Abstract. Using the collective variables method we study the effect of Coulomb interactions on the Ginzburg temperature of ionic fluids. For the charge-asymmetric primitive model with additional short-range attractive interactions in the vicinity of the gas-liquid critical point, we derive the effective Landau-Ginzburg Hamiltonian. We obtain the explicit expressions for all the Hamiltonian coefficients within the framework of the one-loop approximation. We obtain the reduced Ginzburg temperature t_G for the restricted primitive model to be about 20 times smaller than for the nonionic model. For the full model including both the short-range attractive and long-range Coulomb interactions, we show that t_G approaches the value found for the pure Coulombic model when the strength of the Coulomb interactions becomes large enough.

1. Introduction

For the last two decades, much attention has been focused on the issue of critical and phase behaviour of fluids with Coulomb interactions. These studies were motivated by controversial experimental results that demonstrated the three types of the critical behaviour in ionic fluids: Ising-like critical behaviour, classical mean-field behaviour, and a crossover between these two regimes (see Refs [1–4]). In order to interpret the results, the ionic systems were classified as either solvophobic or Coulombic. The main attention has been paid to the criticality of Coulombic systems in which the phase separation is primarily driven by long-range electrostatic interactions.

It is now generally accepted that the critical behaviour of Coulombic systems belongs to the universality class of a three-dimensional Ising model. Earlier experiments that supported the expectation of mean-field critical behaviour could not be reproduced in later works (see Ref. [5,6] and references therein). Precise experiments indicate a crossover from Ising to mean-field behaviour characterized by an increase of the non-classical region with the polarity increase of the solvent [6,7].

Many theoretical and numerical works on Coulombic systems are based on a restricted primitive model (RPM), i.e., an equimolar mixture of equisized charged hard spheres immersed in a structureless dielectric continuum. It is established that the RPM undergoes a gas-liquid-like phase transition at low temperature and low density [8–11]. Reliable estimates of the location of the critical point have been obtained using simulations [12, 13]. Simulations also strongly support the Ising critical behaviour of the model [12–15].

The major part of theoretical studies of the criticality in the RPM is based on the mean-field theories and deals with calculations of the reduced Ginzburg temperature t_G [16, 17]. According to the Ginzburg criterion [18], the mean-field theory is valid only when $|t| \gg t_G$, where $t = (T - T_c)/T_c$ and T_c are the mean-field reduced temperature and the mean-field critical temperature, respectively. Generally, the previous estimates of the reduced Ginzburg temperature of the RPM suggest the non-classical region in the Coulombic systems to be of the same order, or even larger than in simple fluids [19–21]. Thus, excluding the possibility of mean-field behavior of the RPM, these results fail to explain the experimentally observed reduction of the crossover temperature in Coulombic systems. However, a very small value of t_G for the RPM (about 10^3 times smaller than for a simple fluid model) was found in Ref. [22]. It should be stressed that two conditions are to be taken into account to get a

reasonable result for the Ginzburg temperature. The fist condition consists in the choice of "a reference model" exhibiting typical Ising critical behaviour. The second one is the necessity to consider both the reference model and the model studied at the same level of approximation. In Refs. [19–21], the values of the Ginzburg temperature were calibrated by a typical model of simple fluids. However, they were mainly calculated at different, although often comparable, levels of approximation.

On the other hand, the criticality of Coulombic systems has been studied using the functional integration methods [23–27]. In particular, several attempts have been made in order to derive the effective Ginzburg-Landau-Wilson (GLW) Hamiltonian of the RPM [24, 25]. In Ref. [24], the effective Hamiltonian is obtained in terms of a scalar field conjugate to the charge density. However, a non-perturbative renormalization group analysis of such Hamiltonian does not allow one to make an unambiguous statement on the nature of the critical behaviour of the RPM. An attempt to derive the effective Hamiltonian of the RPM in terms of the number density field, strong fluctuating quantity in the vicinity of the gas-liquid critical point, was made using the collective variables (CVs) method in Ref. [25]. The analysis of the Hamiltonian coefficients shows that in spite of the long-range character of the Coulomb potential, the effective interactions are of a short-range character and describe attraction. The form of the Hamiltonian suggests the Ising-like criticality of the RPM. However, the numerical estimations of the relevant coefficients were not presented in this work. More recently, an effect of the long-range interactions on the Ginzburg temperature has been studied on the basis of the LGW Hamiltonian expressed in terms of the field conjugate to the order parameter [26]. The Hamiltonian coefficients are presented therein in the form of an expansion in powers of the ionicity measuring the strength of the Coulomb interaction, and the consideration is restricted to the second power. The results have shown that an increase in the Coulomb interactions leads to a decrease of the temperature region of the crossover regime which confirms the experimental observations [29]. A reduction of the reduced crossover temperature with an increase of the ionicity is also indicated in Ref. [27], though it is weak compared to the experimental data. The limiting system with the pure Coulomb interactions, which is the RPM, lies outside the range of validity of the perturbative treatments developed in Refs [26, 27].

Recently, non-classical critical exponents have been found for the RPM using the hierarchical reference theory [28]. However, an issue of the width of the critical region has not been addressed in this work.

Summarizing, we can state that the nature of the non-classical region in the Coulomb dominated systems remains of fundamental interest and presents a real challenge.

The purpose of the present paper is to derive a microscopic-based effective Hamiltonian of the ionic model supplemented by short-range attractive interactions and on its basis to consistently calculate the Ginzburg temperature for both the pure Coulombic model and the pure solvophobic model as well as for the model parameters ranging between the two limiting cases. To this end, we use the CVs-based theory developed for the description of phase transitions in ionic systems (see Refs. [30,31]). Following the ideas of Ref. [25], we integrate out the variables connected with the charge-density fluctuations and derive the effective Hamiltonian in terms of the variables describing the total number density fluctuations. In this paper, we find the explicit expressions for all the coefficients of the effective ϕ^4-model Hamiltonian at the same level of approximation, namely, in the one-loop approximation corresponding to a one sum over the wave vector. This enables us to get consistent estimates for the critical parameters as well as for the Hamiltonian coefficients for a whole range of the model parameters. The Ginzburg temperature for the pure Coulombic model obtained in this way appears to be about twenty times smaller than for a simple fluid. We also study the effect of the interplay of short-range and long-range interactions on the Ginzburg temperature.

The paper is arranged as follows. In Sec. II we give some brief background to the CVs-based theory for a charge-asymmetric primitive model with additional short-range attractive interactions included. Sec. III is devoted to the derivation of the effective Hamiltonian of the model in the vicinity of the gas-liquid critical point. In Sec. IV we calculate the Ginzburg temperature for the hard-sphere square-well model, the RPM as well as for the models including both short-range and long-range interactions. We conclude in Sec. V.

2. Background

We start with a classical two-component system consisting of 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:

$$U_{\alpha\beta}(r) = \phi_{\alpha\beta}^{HS}(r) + \phi_{\alpha\beta}^{C}(r) + \phi_{\alpha\beta}^{SR}(r), \qquad (2.1)$$

where $\phi_{\alpha\beta}^{HS}(r)$ is the interaction potential between the two additive hard spheres of diameters σ_α and σ_β. Here, $\phi_{\alpha\beta}^{C}(r)$ is the Coulomb potential: $\phi_{\alpha\beta}^{C}(r) = q_\alpha q_\beta \phi^C(r)$, where $\phi^C(r) = 1/(\epsilon r)$, ϵ is the dielectric

constant. The system consists of both positive and negative ions so that the electroneutrality condition is satisfied, i.e., $\sum_{\alpha=1}^{2} q_\alpha \rho_\alpha = 0$, where ρ_α is the number density of species α, $\rho_\alpha = N_\alpha/V$, V is the volume of the system. The ions of the species $\alpha = 1$ are characterized by their hard-sphere diameter σ_1 and by their electrostatic charge q_0 and those of species $\alpha = 2$ are characterized by diameter σ_2 and opposite charge $-zq_0$ (q_0 is an elementary charge and z is the parameter of charge asymmetry). Hereafter we consider the case $\sigma_1 = \sigma_2 = \sigma$. The potential $\phi_{\alpha\beta}^{SR}(r)$ describes the short-range attraction. We specify $\phi_{\alpha\beta}^{SR}(r)$ in the form of the square-well (SW) potential of the range λ and assume $\phi_{11}^{SR}(r) = \phi_{22}^{SR}(r) = \phi_{12}^{SR}(r) = \phi^{SR}(r)$. The system of hard spheres interacting through the SW potential with $\lambda = 1.5\sigma$ can serve as a reasonable model for simple fluids. Such a system undergoes a gas-liquid critical point which belongs to the universal class of a three-dimensional Ising model.

Using the CVs method, we can present the functional of the grand partition function of the above-described model in the form [30]:

$$\Xi[\nu_\alpha] = \int (\mathrm{d}\rho)(\mathrm{d}\omega) \exp\left(-\frac{\beta}{2V}\sum_{\mathbf{k}}[\widetilde{\phi}^{SR}(k)\rho_{\mathbf{k},N}\rho_{-\mathbf{k},N}\right.$$

$$+\widetilde{\phi}^C(k)\rho_{\mathbf{k},Q}\rho_{-\mathbf{k},Q}] + \mathrm{i}\sum_{\mathbf{k}}(\omega_{\mathbf{k},N}\rho_{\mathbf{k},N} + \omega_{\mathbf{k},Q}\rho_{\mathbf{k},Q})$$

$$\left.+\ln\Xi_{HS}[\bar{\nu}_N - \mathrm{i}\omega_N, \bar{\nu}_Q - \mathrm{i}q_\alpha\omega_Q]\right). \tag{2.2}$$

Here, the following notations are introduced. $\rho_{\mathbf{k},N}$ and $\rho_{\mathbf{k},Q}$ are the CVs which describe fluctuations of the total number density and the charge density, respectively:

$$\rho_{\mathbf{k},N} = \rho_{\mathbf{k},+} + \rho_{\mathbf{k},-}, \qquad \rho_{\mathbf{k},Q} = \rho_{\mathbf{k},+} - z\rho_{\mathbf{k},-},$$

CV $\rho_{\mathbf{k},\alpha} = \rho_{\mathbf{k},\alpha}^c - \mathrm{i}\rho_{\mathbf{k},\alpha}^s$ describes the value of the $\mathbf{k}$-th fluctuation mode of the number density of the αth species, the indices c and s denote real and imaginary parts of $\rho_{\mathbf{k},\alpha}$; CVs ω_N and ω_Q are conjugate to ρ_N and ρ_Q, respectively. $(\mathrm{d}\rho)$ and $(\mathrm{d}\omega)$ denote volume elements of the CV phase space

$$(\mathrm{d}\rho) = \prod_{A=N,Q} \mathrm{d}\rho_{0,A} \prod_{\mathbf{k}\neq 0}{}' \mathrm{d}\rho_{\mathbf{k},A}^c \mathrm{d}\rho_{\mathbf{k},A}^s,$$

$$(\mathrm{d}\omega) = \prod_{A=N,Q} \mathrm{d}\omega_{0,A} \prod_{\mathbf{k}\neq 0}{}' \mathrm{d}\omega_{\mathbf{k},A}^c \mathrm{d}\omega_{\mathbf{k},A}^s$$

and the product over $\mathbf{k}$ is performed in the upper semi-space ($\rho_{-\mathbf{k},A} = \rho_{\mathbf{k},A}^*$, $\omega_{-\mathbf{k},A} = \omega_{\mathbf{k},A}^*$). Coefficients $\widetilde{\phi}^{SR}(k)$ and $\widetilde{\phi}^C(k)$ are the Fourier

transforms of the corresponding interaction potentials. We use the Weeks-Chandler-Andersen (WCA) regularization scheme [32, 33] for the both potentials, $\phi^C(r)$ and $\phi^{SR}(r)$, inside the hard core.

$\Xi_{\mathrm{HS}}[\bar{\nu}_N - \mathrm{i}\omega_N, \bar{\nu}_Q - \mathrm{i}q_\alpha\omega_Q]$ is the grand canonical partition function of the hard-sphere system with the renormalized chemical potentials

$$\bar{\nu}_N = \frac{z\bar{\nu}_1 + \bar{\nu}_2}{1+z}, \qquad \bar{\nu}_Q = \frac{\bar{\nu}_1 - \bar{\nu}_2}{q_0(1+z)},$$

where $\bar{\nu}_\alpha$ is determined by

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

ν_α is the dimensionless chemical potential, $\nu_\alpha = \beta\mu_\alpha - 3\ln\Lambda_\alpha$ and μ_α is the chemical potential of the αth species; $\beta = 1/k_BT$ is the reciprocal temperature; $\Lambda_\alpha^{-1} = (2\pi m_\alpha\beta^{-1}/h^2)^{1/2}$ is the inverse de Broglie thermal wavelength. It is worth noting that $\phi_{\alpha\beta}^C(r=0)$ is a finite quantity due to the WCA regularization. We introduce

$$\mathrm{i}\omega_{\mathbf{k},N}^{'}\delta_{\mathbf{k}} = \mathrm{i}\omega_{\mathbf{k},N}\delta_{\mathbf{k}} - \Delta\nu_N, \tag{2.3}$$

where $\Delta\nu_N = \bar{\nu}_N - \nu_{N,\mathrm{HS}}$ with $\nu_{N,\mathrm{HS}}$ being the chemical potential of hard spheres.

In order to develop the perturbation theory, we present $\ln\Xi_{\mathrm{HS}}[\nu_{N,\mathrm{HS}} - \mathrm{i}\omega_N^{'}, \bar{\nu}_Q - \mathrm{i}q_\alpha\omega_Q]$ in the form of a cumulant expansion [31]

$$\ln\Xi_{\mathrm{HS}}[\ldots] = \sum_{n\geq 0}\frac{(-\mathrm{i})^n}{n!}\sum_{i_n\geq 0}\sum_{\mathbf{k}_1,\ldots,\mathbf{k}_n}\mathfrak{M}_n^{(i_n)}(k_1,\ldots,k_n)$$

$$\times\omega_{\mathbf{k}_1,Q}\ldots\omega_{\mathbf{k}_{i_n},Q}\omega_{\mathbf{k}_{i_n+1},N}\ldots\omega_{\mathbf{k}_n,N}\delta_{\mathbf{k}_1+\ldots+\mathbf{k}_n}, \tag{2.4}$$

where the prime on $\omega_{\mathbf{k},N}$ is omitted for the sake of simplicity. In Eq. (2.4), the nth cumulant $\mathfrak{M}_n^{(i_n)}(k_1,\ldots,k_n)$ is a linear combination of the partial cumulants $\mathfrak{M}_{\alpha_1\ldots\alpha_n}(k_1,\ldots,k_n)$, the superindex i_n indicates the number of variables $\omega_{\mathbf{k},Q}$ in the cumulant expansion. For details we refer the reader to Ref. [30]. The expressions for $\mathfrak{M}_1^{(i_n)}$ and $\mathfrak{M}_2^{(i_n)}$ are as follows:

$$\mathfrak{M}_1^{(0)} = \langle N\rangle_{\mathrm{HS}}, \qquad \mathfrak{M}_1^{(1)} = 0,$$

$$\mathfrak{M}_2^{(0)}(k) = \widetilde{G}_{2,\mathrm{HS}}(k), \qquad \mathfrak{M}_2^{(2)}(k) = q_0^2z\langle N\rangle_{\mathrm{HS}}\,\delta_{\mathbf{k}},$$

where $\langle N\rangle_{\mathrm{HS}}$ and $\widetilde{G}_{2,\mathrm{HS}}(k)$ are the average number of particles and the Fourier transform of the two-particle connected correlation function of

a one-component hard-sphere system. It is worth noting that $\mathfrak{M}_1^{(1)} \equiv 0$ due to the electroneutrality condition. The recurrence formulas for $\mathfrak{M}_n^{(i_n)}$ are derived in Ref. [30] (see Eqs. (46) in [30]).

Taking into account (2.3)-(2.4) and replacing $\rho_{\mathbf{k},N}$ by $\rho_{\mathbf{k},N} + \mathfrak{M}_1^{(0)}\delta_{\mathbf{k}}$ we can rewrite Eq. (2.2) as follows:

$$
\Xi[\nu_\alpha] = \Xi_{\mathrm{HS}}[\nu_{N,\mathrm{HS}}, \bar{\nu}_Q]\,\mathcal{C} \int (\mathrm{d}\rho)(\mathrm{d}\omega)\,\exp\left(\Delta\widetilde{\nu}_N \rho_{0,N} - \frac{\beta}{2V}\right.
$$

$$
\times \sum_{\mathbf{k}}[\widetilde{\phi}^{SR}(k)\rho_{\mathbf{k},N}\rho_{-\mathbf{k},N} + \widetilde{\phi}^C(k)\rho_{\mathbf{k},Q}\rho_{-\mathbf{k},Q}] + \mathrm{i}\sum_{\mathbf{k}}[\omega_{\mathbf{k},N}\rho_{\mathbf{k},N}
$$

$$
+\omega_{\mathbf{k},Q}\rho_{\mathbf{k},Q}] + \sum_{n\geq 2}\frac{(-\mathrm{i})^n}{n!}\sum_{i_n\geq 0}\sum_{\mathbf{k}_1,\ldots,\mathbf{k}_n}\mathfrak{M}_n^{(i_n)}(k_1,\ldots,k_n)
$$

$$
+\omega_{\mathbf{k}_1,Q}\ldots\omega_{\mathbf{k}_{i_n},Q}\,\omega_{\mathbf{k}_{i_{n+1}},N}\ldots\omega_{\mathbf{k}_n,N}\delta_{\mathbf{k}_1+\ldots+\mathbf{k}_n}\Big), \qquad (2.5)
$$

where

$$
\Delta\widetilde{\nu}_N = \Delta\nu_N - \beta\frac{\langle N\rangle_{\mathrm{HS}}}{V}\widetilde{\phi}^{SR}(0),
$$

$$
\mathcal{C} = \exp\left[\Delta\nu_N\langle N\rangle_{\mathrm{HS}} - \frac{\beta\langle N\rangle_{\mathrm{HS}}^2}{2V}\widetilde{\phi}^{SR}(0)\right],
$$

and $\ln\Xi_{\mathrm{HS}}[\nu_{N,\mathrm{HS}}, \bar{\nu}_Q] = \mathfrak{M}_0^{(0)}[\nu_{N,\mathrm{HS}}, \bar{\nu}_Q]$. It is worth noting that the Hamiltonian in Eq. (2.5) does not include direct pair interactions of number density fluctuations if $\widetilde{\phi}^{SR}(k) \equiv 0$.

Since we are interested in the gas-liquid critical point, the small-$\mathbf{k}$ expansion of the cumulants can be considered. Hereafter we will put

$$
\mathfrak{M}_2^{(0)}(k) \simeq \mathfrak{M}_2^{(0)}(0) + \frac{k^2}{2}\mathfrak{M}_{2,2}^{(0)} \qquad (2.6)
$$

and approximate cumulants for $n \geq 3$ by their values in the long-wavelength limit

$$
\mathfrak{M}_n^{(i_n)}(k_1,\ldots,k_n) \simeq \mathfrak{M}_n^{(i_n)}(0,\ldots). \qquad (2.7)
$$

3. Effective Hamiltonian in the vicinity of the gas-liquid critical point

In this section, based on Eqs. (2.5)-(2.7), we derive the effective Hamiltonian of the model (2.1) in the vicinity of the gas-liquid critical point.

We obtain consistently all the coefficients, including the square-gradient term, within the framework of the same approximation.

First, we integrate over CVs $\omega_{\mathbf{k},N}$ and $\omega_{\mathbf{k},Q}$ in Eq. (2.5) using the Gaussian density measure as the basic one [25]. As a result, we get

$$
\Xi[\nu_\alpha] = \Xi_{\mathrm{HS}}\,\mathcal{C}\prod_{\mathbf{k}}\frac{1}{\pi\mathfrak{M}_2^{(0)}}\prod_{\mathbf{k}}\frac{1}{\pi\mathfrak{M}_2^{(2)}}\int(\mathrm{d}\rho)\,\exp\left(-\mathcal{H}[\nu_\alpha,\rho_N,\rho_Q]\right), \quad (3.1)
$$

where

$$
-\mathcal{H}[\nu_\alpha,\rho_N,\rho_Q] = -a_1^{(0)}\rho_{0,N} - \frac{1}{2!}\sum_{\mathbf{k}}\left(a_2^{(0)}\rho_{\mathbf{k},N}\rho_{-\mathbf{k},N}\cdot + a_2^{(2)}\rho_{\mathbf{k},Q}\right.
$$

$$
\times\rho_{-\mathbf{k},Q}\Big) - \frac{1}{3!}\sum_{\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3}\left(a_3^{(0)}\rho_{\mathbf{k}_1,N}\rho_{\mathbf{k}_2,N}\rho_{\mathbf{k}_3,N} + 3a_3^{(2)}\rho_{\mathbf{k}_1,N}\rho_{\mathbf{k}_2,Q}\rho_{\mathbf{k}_3,Q}\right.
$$

$$
+a_3^{(3)}\rho_{\mathbf{k}_1,Q}\rho_{\mathbf{k}_2,Q}\rho_{\mathbf{k}_3,Q}\Big)\delta_{\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3} - \frac{1}{4!}\sum_{\mathbf{k}_1,\ldots,\mathbf{k}_4}\left(a_4^{(0)}\rho_{\mathbf{k}_1,N}\ldots\rho_{\mathbf{k}_4,N}\right.
$$

$$
+6a_4^{(2)}\rho_{\mathbf{k}_1,N}\rho_{\mathbf{k}_2,N}\rho_{\mathbf{k}_3,Q}\rho_{\mathbf{k}_4,Q} + 4a_4^{(3)}\rho_{\mathbf{k}_1,N}\rho_{\mathbf{k}_2,Q}\rho_{\mathbf{k}_3,Q}\rho_{\mathbf{k}_4,Q}
$$

$$
+a_4^{(4)}\rho_{\mathbf{k}_1,Q}\rho_{\mathbf{k}_2,Q}\rho_{\mathbf{k}_3,Q}\rho_{\mathbf{k}_4,Q}\Big)\delta_{\mathbf{k}_1+\ldots+\mathbf{k}_4} + \ldots \qquad (3.2)
$$

and the coefficients $a_n^{(i_n)}$ ($n \leq 4$) are given by

$$
a_1^{(0)} = -\Delta\widetilde{\nu}_N, \qquad a_1^{(1)} = 0, \qquad (3.3)
$$

$$
a_2^{(0)} = \frac{\beta}{V}\widetilde{\phi}^{SR}(k) + \frac{1}{\mathfrak{M}_2^{(0)}(k)}, \qquad a_2^{(2)} = \frac{\beta}{V}\widetilde{\phi}^C(k) + \frac{1}{\mathfrak{M}_2^{(2)}}, \qquad (3.4)
$$

$$
a_3^{(0)} = -\frac{\mathfrak{M}_3^{(0)}}{(\mathfrak{M}_2^{(0)})^3}, \qquad a_3^{(2)} = -\frac{\mathfrak{M}_3^{(2)}}{\mathfrak{M}_2^{(0)}(\mathfrak{M}_2^{(2)})^2}, \qquad a_3^{(3)} = -\frac{\mathfrak{M}_3^{(3)}}{(\mathfrak{M}_2^{(2)})^3}, \qquad (3.5)
$$

$$
a_4^{(0)} = -\frac{1}{(\mathfrak{M}_2^{(0)})^4}\left(\mathfrak{M}_4^{(0)} - 3\frac{(\mathfrak{M}_3^{(0)})^2}{\mathfrak{M}_2^{(0)}}\right),
$$

$$
a_4^{(2)} = -\frac{1}{(\mathfrak{M}_2^{(0)})^2(\mathfrak{M}_2^{(2)})^2}\left(\mathfrak{M}_4^{(2)} - \frac{\mathfrak{M}_3^{(0)}\mathfrak{M}_3^{(2)}}{\mathfrak{M}_2^{(0)}} - 2\frac{(\mathfrak{M}_3^{(2)})^2}{\mathfrak{M}_2^{(2)}}\right),
$$

$$
a_4^{(3)} = -\frac{1}{\mathfrak{M}_2^{(0)}(\mathfrak{M}_2^{(2)})^3}\left(\mathfrak{M}_4^{(3)} - 3\frac{\mathfrak{M}_3^{(2)}\mathfrak{M}_3^{(3)}}{\mathfrak{M}_2^{(2)}}\right),
$$

$$
a_4^{(4)} = -\frac{1}{(\mathfrak{M}_2^{(2)})^4}\left(\mathfrak{M}_4^{(4)} - 3\frac{(\mathfrak{M}_3^{(2)})^2}{\mathfrak{M}_2^{(0)}} - 3\frac{(\mathfrak{M}_3^{(3)})^2}{\mathfrak{M}_2^{(2)}}\right). \qquad (3.6)
$$

A distinguishing feature of the Hamiltonian(3.2)-(3.6), unlike that for the RPM [25], is the presence of the coefficients $a_n^{(3)}$ due to the charge-asymmetry of the model. Using the recurrence formulae from Ref. [30], Eqs. (3.3)-(3.6) can be reduced to the form given in Appendix A.

3.1. Gaussian approximation

Let us consider the Gaussian approximation, which corresponds to Eq. (3.2) where only the terms with $n \leq 2$ are taken into account. In this case, the integration over CVs $\rho_{\mathbf{k},N}$ and $\rho_{\mathbf{k},Q}$ in Eq. (3.1) leads to the following expression for the logarithm of the grand partition function

$$\ln \Xi_{\mathrm{G}} = \ln \Xi_{\mathrm{HS}} + \frac{\beta \langle N \rangle_{\mathrm{HS}}^2}{2V} \widetilde{\phi}^{\mathrm{SR}}(0) - \frac{1}{2} \sum_{\mathbf{k}} \ln \left[1 + \frac{\beta}{V} \widetilde{\phi}^{\mathrm{SR}}(k) \mathfrak{M}_2^{(0)}(k) \right]$$
$$- \frac{1}{2} \sum_{\mathbf{k}} \ln \left[1 + \frac{\beta}{V} \widetilde{\phi}^{C}(k) \mathfrak{M}_2^{(2)} \right].$$

The Legendre transform of $\ln \Xi_G$ yields the Helmholtz free energy in the one-loop approximation. The result is

$$\beta f_{\mathrm{RPA}} = \frac{\beta F_{\mathrm{RPA}}}{V} = \beta f_{\mathrm{HS}} - \frac{\beta \rho}{2V} \sum_{\mathbf{k}} \widetilde{\phi}^{\mathrm{SR}}(k) - \frac{\beta q_0^2 z \rho}{2V} \sum_{\mathbf{k}} \widetilde{\phi}^{\mathrm{C}}(k)$$
$$+ \frac{1}{2} \beta \rho^2 \widetilde{\phi}^{\mathrm{SR}}(0) + \frac{1}{2V} \sum_{\mathbf{k}} \ln \left[1 + \beta \rho \widetilde{\phi}^{\mathrm{SR}} S_{2,\mathrm{HS}}(k) \right]$$
$$+ \frac{1}{2V} \sum_{\mathbf{k}} \ln \left[1 + \beta q_0^2 z \rho \widetilde{\phi}^{C}(k) \right], \qquad (3.7)$$

where $f_{...}$ denotes the Helmholtz free energy density. Again, the subscript HS refers to the hard-sphere system, $S_{2,\mathrm{HS}}(k)$ is the pair structure factor of a one-component hard-sphere system [34]. The one-loop free energy (3.7) coincides with the free energy in the random phase approximation (RPA) of the theory of liquids [34].

From (3.7) one can find the chemical potential ν_N in the RPA

$$\nu_N^{\mathrm{RPA}} = \nu_{N,\mathrm{HS}} - \frac{\beta}{2V} \sum_{\mathbf{k}} \widetilde{\phi}^{\mathrm{SR}}(k) - \frac{\beta q_0^2 z}{2V} \sum_{\mathbf{k}} \widetilde{\phi}^{\mathrm{C}}(k) + \beta \rho \widetilde{\phi}^{\mathrm{SR}}(0)$$
$$+ \frac{1}{2V} \sum_{\mathbf{k}} \frac{\beta q_0^2 z \widetilde{\phi}^{C}(k)}{1 + \beta q_0^2 z \rho \widetilde{\phi}^{C}(k)}. \qquad (3.8)$$

and obtain on its basis the mean-field gas-liquid phase diagram. The gas-liquid critical parameters of the charge-asymmetric PM ($\phi^{\mathrm{SR}}(r) =$

0) were calculated in Ref. [10] using the above equations and different regularization schemes for the Coulomb potential inside the hard core.

3.2. Coefficients of the Landau-Ginzburg-Wilson Hamiltonian

Our aim is to derive the effective Hamiltonian in terms of CVs $\rho_{\mathbf{k},N}$ related to the order parameter associated with the gas-liquid critical point. To this end, we integrate out CVs $\rho_{\mathbf{k},Q}$ in Eq. (3.2) following the programme outlined for the RPM [25]. As a result, we arrive at the effective LGW Hamiltonian of the following form:

$$-\mathcal{H}^{eff}[\rho_N] = -\sum_{n \geq 1} \frac{1}{n! \langle N \rangle^{n-1}} \sum_{\mathbf{k_1}, \ldots, \mathbf{k_n}} a_n \, \rho_{\mathbf{k_1},N} \, \rho_{\mathbf{k_2},N} \cdots \rho_{\mathbf{k_n},N}$$
$$\times \delta_{\mathbf{k_1}+\ldots+\mathbf{k}_n}. \qquad (3.9)$$

Coefficient a_n can be presented as

$$a_n = a_n^{(0)} + \Delta a_n, \qquad (3.10)$$

where the second addend is the correction obtained after integration over CVs $\rho_{\mathbf{k},Q}$. Each correction Δa_n has the form of infinite series. In particular, after some algebra we find the following expressions for Δa_n in the approximation corresponding to a one sum over the wave vector $\mathbf{q}$

$$\Delta a_1 = -\frac{1}{2 < N >} \sum_{\mathbf{q}} \widetilde{G}_{QQ}(q) + \ldots, \qquad (3.11)$$

$$\Delta a_2(k) = \frac{1}{< N >} \sum_{\mathbf{q}} \widetilde{G}_{QQ}(q) - \frac{1}{2 < N >} \sum_{\mathbf{q}} \widetilde{G}_{QQ}(q)$$
$$\times \widetilde{G}_{QQ}(|\mathbf{q} + \mathbf{k}|) + \ldots, \qquad (3.12)$$

$$\Delta a_3(k_1, k_2) = -\frac{3}{< N >} \sum_{\mathbf{q}} \widetilde{G}_{QQ}(q) + \frac{3}{< N >} \sum_{\mathbf{q}} \widetilde{G}_{QQ}(q)$$
$$\times \widetilde{G}_{QQ}(|\mathbf{q} + \mathbf{k_1}|) - \frac{1}{< N >} \sum_{\mathbf{q}} \widetilde{G}_{QQ}(q)$$
$$\times \widetilde{G}_{QQ}(|\mathbf{q} + \mathbf{k_1}|) \widetilde{G}_{QQ}(|\mathbf{q} - \mathbf{k_2}|) + \ldots, \qquad (3.13)$$

$$\Delta a_4(k_1, k_2, k_3) = \frac{12}{<N>} \sum_{\mathbf{q}} \widetilde{G}_{QQ}(q) - \frac{6}{<N>} \sum_{\mathbf{q}} \widetilde{G}_{QQ}(q)$$

$$\times \widetilde{G}_{QQ}(|\mathbf{q} + \mathbf{k_1} + \mathbf{k_2}|) - \frac{12}{<N>} \sum_{\mathbf{q}} \widetilde{G}_{QQ}(q)\widetilde{G}_{QQ}(|\mathbf{q} + \mathbf{k_1}|)$$

$$+\frac{12}{<N>} \sum_{\mathbf{q}} \widetilde{G}_{QQ}(q)\widetilde{G}_{QQ}(|\mathbf{q} + \mathbf{k_1}|)\widetilde{G}_{QQ}(|\mathbf{q} - \mathbf{k_2} - \mathbf{k_3}|)$$

$$-\frac{3}{<N>} \sum_{\mathbf{q}} \widetilde{G}_{QQ}(q)\widetilde{G}_{QQ}(|\mathbf{q} + \mathbf{k_1}|)\widetilde{G}_{QQ}(|\mathbf{q} - \mathbf{k_2}|)$$

$$\times \widetilde{G}_{QQ}(|\mathbf{q} - \mathbf{k_2} - \mathbf{k_3}|) + \dots, \tag{3.14}$$

where we have made use of the formulas from Appendix A. Hereafter, for notation simplicity, the subscript HS is omitted.

$\widetilde{G}_{QQ}(q)$ is the Fourier transform of a charge-charge connected correlation function of the charge-asymmetric PM determined in the Gaussian approximation

$$\widetilde{G}_{QQ}(q) = \frac{1}{1 + \beta\rho q_0^2 z \widetilde{\phi}^C(q)}.$$

For the WCA regularization [33],

$$\widetilde{\phi}^C(q) = 4\pi \frac{\sin q\sigma}{\epsilon q^3}. \tag{3.15}$$

Now, we are in a position to study Eqs. (3.11)-(3.14) in detail. As is seen from Eqs (3.11)-(3.14), corrections Δa_n for $n \geq 2$ depend on the wave vectors. Expanding the second term of Δa_2 at small k one can readily see that the linear term vanishes. As a result, Δa_2 can be presented as follows:

$$\Delta a_2 = \Delta a_{2,0} + k^2 \Delta a_{2,2} + \mathcal{O}(k^4), \tag{3.16}$$

where

$$\Delta a_{2,0} = \frac{1}{\langle N \rangle} \sum_{\mathbf{q}} \widetilde{G}_{QQ}(q) - \frac{1}{2\langle N \rangle} \sum_{\mathbf{q}} [\widetilde{G}_{QQ}(q)]^2,$$

$$\Delta a_{2,2} = -\frac{1}{4\langle N \rangle} \sum_{\mathbf{q}} \widetilde{G}_{QQ}(q)\widetilde{G}_{QQ}^{(2)}(q) \tag{3.17}$$

and the superscript (2) refers to the second-order derivative with respect to the wave vector k: $\widetilde{G}_{QQ}^{(2)}(q) = \partial^2 \widetilde{G}_{QQ}(|\mathbf{q} + \mathbf{k}|)/\partial k^2|_{k=0}$. The appearance of the factor k^2 in Eq. (3.16) is caused by the charge-charge

correlations being taken into account. It should be noted that the expression for $\Delta a_{2,2}$ has the same form as that obtained for the RPM in Ref. [25]. However, the numerical estimates of the effective Hamiltonian coefficients were not made in that work. It will be done below.

The integrals $\int_0^\infty \left[\widetilde{G}_{QQ}(q)\right]^n d\mathbf{q}$ entering Eqs. (3.11)-(3.14) are divergent at $q \to \infty$. This divergence can be avoided by introducing the cutoff wave-vector which, however, leads to the cutoff-dependent results. Another way is to rearrange the terms in Eqs. (3.11)-(3.14) expressed by infinite series. Here, we will follow the second way.

We approximate Δa_2 by Eqs. (3.16)-(3.17) and replace $\Delta a_3(k_1, \dots)$ and $\Delta a_4(k_1, \dots)$ by their values in the long-wavelength limit putting $\Delta a_3(k_1, \dots) \simeq \Delta a_{3,0}$ and $\Delta a_4(k_1, \dots) \simeq \Delta a_{4,0}$. It is convenient to calculate Δa_n using Feynman diagram presentation. Limiting the series in Eqs. (3.11)-(3.14) to the order of one sum over $\mathbf{q}$ one can present the part of the effective Hamiltonian (3.9) in the following diagrammatic form

$$\Delta a_1 \rho_{0,N} = -\frac{1}{2} \,\text{---}\bullet\!\bigcirc, \tag{3.18}$$

$$\frac{1}{2!\langle N \rangle} \sum_{\mathbf{k}} \Delta a_{2,0} \rho_{\mathbf{k},N} \rho_{-\mathbf{k},N} = \bigcirc - \frac{1}{2} \,\text{---}\bullet\!\bigcirc\!\bullet\text{---}, \tag{3.19}$$

$$\frac{1}{3!\langle N \rangle^2} \sum_{\mathbf{k_1},\mathbf{k_2}} \Delta a_{3,0} \rho_{\mathbf{k_1},N} \rho_{\mathbf{k_2},N} \rho_{-\mathbf{k_1}-\mathbf{k_2},N} = -3 \,\text{-}\!\bigcirc$$

$$+3 \,\text{--}\!\bigcirc\!\!\!\times - \triangle , \tag{3.20}$$

$$\frac{1}{4!\langle N \rangle^3} \sum_{\mathbf{k_1},\mathbf{k_2},\mathbf{k_3}} \Delta a_{4,0} \rho_{\mathbf{k_1},N} \rho_{\mathbf{k_2},N} \rho_{\mathbf{k_3},N} \rho_{-\mathbf{k_1}-\mathbf{k_2}-\mathbf{k_3},N}$$

$$= 12 \,\bigcirc - 6 \,\bigcirc\!\!\!\times - 12 \,\text{--}\!\bigcirc\!\!\!\times + 12 \,\triangle$$

$$-3 \,\square . \tag{3.21}$$

In Eqs. (3.18)-(3.21), each external leg represents CV $\rho_{\mathbf{k},N}$, the vertex represents the factor $\frac{a_n^{(i_n)}}{n!}\delta_{\mathbf{k_1}+\dots+\mathbf{k_n}}$ and each internal line corresponds

to the propagator $\widetilde{G}_{QQ}(q)$. Integrals over wave vectors are implied here. As is seen, the restriction to a one sum over $\mathbf{q}$ in the expressions for Δa_n leads to the one-loop diagrams having the same number of vertices and bonds.

Now, introducing

$$\widetilde{g}(q) = -\frac{\beta\rho q_0^2 z\widetilde{\phi}^C(q)}{1 + \beta\rho q_0^2 z\widetilde{\phi}^C(q)},$$

we substitute

$$\widetilde{G}_{QQ}(q) = 1 + \widetilde{g}(q) \tag{3.22}$$

into Eqs. (3.11)-(3.14). Then, adding all the terms corresponding to the one-loop diagrams in Eqs (3.18)-(3.21) we present Δa_n in the form:

$$\Delta a_1 = -\frac{1}{2 <N>} \sum_{\mathbf{q}} \widetilde{g}(q), \tag{3.23}$$

$$\Delta a_2(k) = -\frac{1}{2 <N>} \sum_{\mathbf{q}} [\widetilde{g}(q)]^2 - \frac{k^2}{4\langle N\rangle} \sum_{\mathbf{q}} \widetilde{g}^{(2)}(q) [1 + \widetilde{g}(q)], \tag{3.24}$$

$$\Delta a_3 = -\frac{1}{<N>} \sum_{\mathbf{q}} [\widetilde{g}(q)]^3, \tag{3.25}$$

$$\Delta a_4 = -\frac{3}{<N>} \sum_{\mathbf{q}} [\widetilde{g}(q)]^4. \tag{3.26}$$

The integrals entering Eqs. (3.23)-(3.26) are convergent in the lower and upper limits. Again, the superscript (2) denotes the second-order derivative with respect to k. Comparing Eqs. (3.24) and (3.17) it is easy to check that substitution (3.22) does not change the coefficient $\Delta a_{2,2}$. Finally, inserting Eqs. (3.23)-(3.26) in (3.10) we arrive at explicit expressions for the coefficients a_n in the one-loop approximation:

$$a_{1,0} = -\Delta\widetilde{\nu}_N - \widetilde{\mathcal{C}}_{1,\text{C}}, \tag{3.27}$$

$$a_{2,0} = -\rho\widetilde{\mathcal{C}}_{2,\text{HS}} + \beta\rho\widetilde{\phi}^{SR}(0) - \rho\widetilde{\mathcal{C}}_{2,\text{C}}, \tag{3.28}$$

$$a_{2,2} = -\frac{1}{2}\rho\widetilde{\mathcal{C}}_{2,\text{HS}}^{(2)} + \frac{1}{2}\beta\rho\widetilde{\phi}^{SR,(2)}$$

$$-\frac{1}{4\langle N\rangle} \sum_{\mathbf{q}} \widetilde{g}^{(2)}(q) [1 + \widetilde{g}(q)], \tag{3.29}$$

$$a_{3,0} = -\rho^2\widetilde{\mathcal{C}}_{3,\text{HS}} - \rho^2\widetilde{\mathcal{C}}_{3,\text{C}}, \tag{3.30}$$

$$a_{4,0} = -\rho^3\widetilde{\mathcal{C}}_{4,\text{HS}} - \rho^3\widetilde{\mathcal{C}}_{4,\text{C}}, \tag{3.31}$$

where $a_{n,0} = a_n|_{k_i=0}$, $a_{2,0}$ and $a_{2,2}$ are the coefficients of the expansion $a_2 = a_{2,0} + k^2 a_{2,2}$, and $\widetilde{\mathcal{C}}_{2,\text{HS}}(k) = \widetilde{\mathcal{C}}_{2,\text{HS}} + \frac{1}{2}k^2\widetilde{\mathcal{C}}_{2,\text{HS}}^{(2)}$. $\widetilde{\mathcal{C}}_{n,\text{HS}}$ is the Fourier transform of the n-particle direct correlation function of a one-component hard-sphere system in the long-wavelength limit

$$-\rho\widetilde{\mathcal{C}}_{2,\text{HS}} = \frac{1}{S_{2,\text{HS}}(0)}, \quad \rho^{n-1}\widetilde{\mathcal{C}}_{n,\text{HS}} = \rho^{n-1}\widetilde{\mathcal{C}}_{n,\text{HS}}(0,\ldots) = a_n^{(0)}, \quad n \geq 3$$

and $\widetilde{\mathcal{C}}_{2,\text{HS}}^{(2)} = \partial^2\widetilde{\mathcal{C}}_{2,\text{HS}}(k)/\partial k^2|_{k=0}$. Using the formulas from Appendix A, one can establish a link between the direct correlation functions $\widetilde{\mathcal{C}}_{n,\text{HS}}$ and the connected correlation functions $\widetilde{G}_{n,\text{HS}}$ for $n \leq 4$.

$\widetilde{\mathcal{C}}_{n,\text{C}}$ denotes the contribution to the n-particle direct correlation function from the charge subsystem

$$\rho^{n-1}\widetilde{\mathcal{C}}_{n,\text{C}} = \rho^{n-1}\widetilde{\mathcal{C}}_{n,\text{C}}(k = 0) = \frac{(n-1)!}{2}\frac{1}{\langle N\rangle} \sum_{\mathbf{q}} [\widetilde{g}(q)]^n. \tag{3.32}$$

It is easy to check that the coefficients $a_{n,0}$ for $n \geq 2$ can be obtained from the one-loop free energy (see Eq. (3.7))

$$a_{n,0} = \rho^{n-1}\frac{\partial^n(-\beta f_{\text{RPA}})}{\partial\rho^n} = \rho^{n-1}\widetilde{\mathcal{C}}_n(0,\ldots),$$

where $\widetilde{\mathcal{C}}_n(0,\ldots)$ denotes the Fourier transform of the n-particle direct correlation function of the full system in the long-wavelength limit. It is worth noting that the functions $\widetilde{\mathcal{C}}_n$ differ from the ordinary direct correlation functions $\widetilde{c}_n$ by an ideal term [34, 35].

Coefficient $a_{1,0}$ is the excess part of the chemical potential ν_N connected with the short-range attractive and long-range Coulomb interactions. Equation $a_{1,0} = 0$ leads to the expression for ν_N in the RPA (see Eq. (3.8)). Coefficient $a_{2,2}$ describes the square-gradient term. We emphasize that all the coefficients given by Eqs (3.27)-(3.31) are found in the one-loop approximation corresponding to a one sum over the wave vector. The charge asymmetry does not manifest itself in the above equations and, therefore, there is no difference between the RPM and the charge-asymmetric PM at this level of approximation. The resulting effective Hamiltonian reads as

$$\mathcal{H}^{eff} = a_{1,0}\rho_{0,N} + \frac{1}{2!\langle N\rangle} \sum_{\mathbf{k}} \left(a_{2,0} + k^2 a_{2,2}\right) \rho_{\mathbf{k},N}\rho_{-\mathbf{k},N}$$

$$+\frac{1}{3!\langle N\rangle^2} \sum_{\mathbf{k_1},\mathbf{k_2}} a_{3,0}\rho_{\mathbf{k_1},N}\rho_{\mathbf{k_2},N}\rho_{-\mathbf{k_1}-\mathbf{k_2},N} + \frac{1}{4!\langle N\rangle^3}$$

$$\times \sum_{\mathbf{k_1},\mathbf{k_2},\mathbf{k_3}} a_{4,0}\rho_{\mathbf{k_1},N}\rho_{\mathbf{k_2},N}\rho_{\mathbf{k_3},N}\rho_{-\mathbf{k_1}-\mathbf{k_2}-\mathbf{k_3},N}.$$

Therefore, within the framework of the same approximation, we have derived the microscopic-based expressions for the coefficients of the effective Hamiltonian. Taking into account the charge-charge correlations through integration over the charge subsystem (the CVs $\rho_{\mathbf{k},Q}$) we get a contribution to the coefficients at the second order which describes the effective attraction of short-range character. The resulting Hamiltonian has the structure of the LGW Hamiltonian of an Ising model in an external magnetic field. Eqs. (3.27)-(3.32) will be used below for the calculation of the Ginzburg temperature.

4. Ginzburg temperature

We present $a_{2,0}$ in the form:

$$a_{2,0} = \bar{a}_{2,0} + a_{2,t}\, t, \qquad t = \frac{T - T_c}{T_c},$$

where $a_{2,0} = \bar{a}_{2,0}(t = 0)$ and $a_{2,t} = \left. \dfrac{\partial a_{2,0}}{\partial t} \right|_{t=0}$. Hereafter, the subscript c refers to the critical value.

At the critical point, the system of equations

$$\bar{a}_{2,0} = 0, \qquad a_{3,0} = 0 \qquad (4.1)$$

holds yielding the critical temperature and the critical density. After the substitution of T_c and ρ_c in the equation $a_{1,0} = 0$ one gets the critical value of the chemical potential ν_N.

Following [18,19], the reduced Ginzburg temperature can be written as follows:

$$t_G = \frac{1}{32\pi^2} \frac{a_{4,0}^2}{a_{2,\tau} a_{2,2}^3}, \qquad (4.2)$$

where all the coefficients should be calculated at the critical temperature and the critical density determined from Eqs. (4.1).

4.1. Hard-core square-well model

First, we consider a one-component system of hard spheres interacting through the SW potential of depth ε and range $\lambda = 1.5\sigma$. This system

exhibits a typical Ising critical behaviour. For the WCA regularization, the Fourier transform of the SW potential has the form [32]

$$\widetilde{\phi}^{SR}(k) = \widetilde{\phi}^{SR}(0)\frac{3}{(\lambda x)^3}[-\lambda x\,\cos(\lambda x) + \sin(\lambda x)], \qquad (4.3)$$

where $x = k\sigma$ and $\widetilde{\phi}^{SR}(0) = -\varepsilon\sigma^3\frac{4\pi}{3}\lambda^3$.

For this model $\Delta a_n \equiv 0$, and we get from Eqs. (3.27)-(3.31) and Eq. (4.3) simple expressions for the coefficients of the LGW Hamiltonian

$$a_{1,0} = -\Delta\nu_N + \frac{1}{2T^{\mathrm{SR}}} - \frac{8\eta\lambda^3}{T^{\mathrm{SR}}}, \qquad (4.4)$$

$$\bar{a}_{2,0} = -\rho\widetilde{\mathcal{C}}_{2,\mathrm{HS}} - \frac{8\eta\lambda^3}{T_c^{\mathrm{SR}}}, \qquad a_{2,t} = \frac{8\eta\lambda^3}{T_c^{\mathrm{SR}}},$$

$$a_{2,2} = -\frac{1}{2}\rho\widetilde{\mathcal{C}}_{2,\mathrm{HS}}^{(2)} + \frac{4}{5}\frac{\eta\lambda^5}{T^{\mathrm{SR}}}, \qquad (4.5)$$

$$a_{3,0} = -\rho^2\widetilde{\mathcal{C}}_{3,\mathrm{HS}}, \qquad a_{4,0} = -\rho^3\widetilde{\mathcal{C}}_{4,\mathrm{HS}}, \qquad (4.6)$$

where $\Delta\nu_N = \nu_N - \nu_{N,\mathrm{HS}}$. The reduced temperature in the hard-core square-well (HCSW) model, T^{SR}, is defined as the ratio between the thermal energy and the interaction strength of the two hard spheres at contact $T^{\mathrm{SR}} = k_{\mathrm{B}}T/\varepsilon$, and $\eta = \pi\rho\sigma^3/6$ is the packing fraction. We use the Percus-Yevick (PY) approximation for the n-particle direct correlation functions of the hard-sphere system [34,36]. As a result, we have

$$-\rho\widetilde{\mathcal{C}}_{2,\mathrm{HS}} = \frac{(1 + 2\eta)^2}{(1-\eta)^4}, \qquad -\rho\widetilde{\mathcal{C}}_{2,\mathrm{HS}}^{(2)} = \frac{\eta(16 - 11\eta + 4\eta^2)}{10(1-\eta)^4},$$

$$-\rho^2\widetilde{\mathcal{C}}_{3,\mathrm{HS}} = \frac{(1 - 7\eta - 6\eta^2)(1 + 2\eta)}{(1-\eta)^5},$$

Table 1. The reduced gas-liquid critical parameters, the coefficients of the effective Hamiltonian and the reduced Ginzburg temperature t_G for the hard-core square-well model (HCSW model) and for the restricted primitive model (RPM) in the one-loop approximation. The superscripts SR and C refer to the HCSW model and RPM, respectively.

Model	$T_c^{\mathrm{SR/C}}$	ρ_c^*	$a_{2,t}$	$a_{2,2}$	$a_{4,0}$	t_G
HCSW	1.2667	0.2457	2.7426	0.4536	2.7421	0.0937
RPM	0.08446	0.0088	1.0758	0.2570	0.1752	0.0053

$$-\rho^3 \widetilde{\mathcal{C}}_{4,\mathrm{HS}} = \frac{2(1 - 6\eta + 15\eta^2 + 56\eta^3 + 24\eta^4)}{(1 - \eta)^6}$$

Using Eqs. (4.1), (4.2) and (4.4)-(4.6) one can easily calculate the reduced Ginzburg temperature. The corresponding results are presented in Table 1 (the first row). It should be noted that we get $t_G = 1.55$ if we pass to the expression for the the reduced Ginzburg temperature used in Ref. [20] which differs from Eq. (4.2) by the factor $(\rho_c^*)^{-2}$. This agrees with the result $t_G = 1.57$ obtained in [20] for the same system in the RPA.

4.2. Restricted primitive model

Now, we consider the RPM setting $\phi^{\mathrm{SR}} \equiv 0$ in Eqs. (3.27)-(3.31). Using Eq. (3.15), we get the following explicit expressions for the coefficients of the effective Hamiltonian

$$a_{1,0} = -\Delta\nu_N - \frac{1}{2T^C} + i_1, \tag{4.7}$$

$$\bar{a}_{2,0} = \frac{(1 + 2\eta)^2}{(1 - \eta)^4} + i_2, \qquad a_{2,t} = \frac{2\kappa_c^2}{\pi T_c^C} i_{2,t}, \tag{4.8}$$

$$a_{2,2} = \frac{\eta(16 - 11\eta + 4\eta^2)}{20(1 - \eta)^4} - \frac{1}{6\pi T^C} i_{12}, \tag{4.9}$$

$$a_{3,0} = \frac{(1 - 7\eta - 6\eta^2)(1 + 2\eta)}{(1 - \eta)^5} + i_3, \tag{4.10}$$

$$a_{4,0} = \frac{2(1 - 6\eta + 15\eta^2 + 56\eta^3 + 24\eta^4)}{(1 - \eta)^6} + i_4. \tag{4.11}$$

In Eqs. (4.7)-(4.11) the following notation are introduced:

$$i_n = \frac{(n-1)!(-\kappa^2)^{n-1}}{\pi T^C} \int_0^\infty x^2 \left[\frac{\sin(x)}{x^3 + \kappa^2 \sin(x)}\right]^n \mathrm{d}x,$$

$$i_{2,t} = \int_0^\infty \frac{x^5 \sin^2(x)}{(x^3 + \kappa_c^2 \sin(x))^3} \mathrm{d}x,$$

$$i_{12} = \int_0^\infty x^6 \left[\kappa^2 x^2 (1 + \cos^2(x)) + 2(x^3 - 2\kappa^2 \sin(x))(2x\cos(x)\right.$$
$$\left. -3\sin(x)) + x^5 \sin(x)\right] / (x^3 + \kappa^2 \sin(x))^4 \mathrm{d}x,$$

where $\kappa = \kappa_D \sigma$ with $\kappa_D^2 = 4\pi\rho\beta q^2 z$ being the Debye number.

The reduced temperature T^C is defined in the standard way as the ratio between the thermal energy and the interaction strength of the

opposite charged hard spheres at contact

$$T^C = \frac{k_{\mathrm{B}} T \epsilon \sigma}{z q_0^2}. \tag{4.12}$$

The loci of equations $\bar{a}_{2,0} = 0$ and $a_{3,0} = 0$ are shown in Fig. 1. The two lines intersect at a maximum of the gas-liquid spinodal yielding the coordinates of the critical point in the one-loop approximation (see Table 1).

Substituting the critical temperature and the critical density into Eqs (4.8)-(4.11) we calculate the coefficients of the effective Hamiltonian. Then, we get from Eq. (4.2) the reduced Ginzburg temperature of the RPM. The results are presented in Table 1 (the second row). As is seen, the reduced Ginzburg temperature found for the RPM is about twenty times smaller than that obtained for the HCSW model. Therefore, contrary to the previous findings [19–21], our results suggest that the critical region for the RPM is much narrower than the critical region for a non-ionic model.
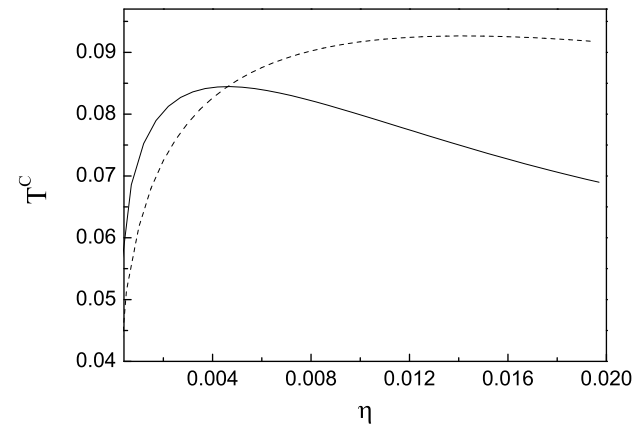

Figure 1. Restricted primitive model: the loci of equations $\bar{a}_{2,0} = 0$ (solid line) and $a_{3,0} = 0$ (dashed line). Temperature T^C is given by Eq. (4.12) and $\eta = \pi\rho\sigma^3/6$ is the packing fraction.

4.3. Coulomb interactions versus short-range attractive interactions

Here, we consider the full system given by Eq. (2.1) and study the effect of the interplay of short- and long-range interactions on the Ginzburg temperature. We briefly call the model as a RPM-SW model. For the RPM-SW model, we get explicit expressions for the coefficients of the effective Hamiltonian combining Eqs. (4.4)-(4.6) and Eqs. (4.7)-(4.11). We also introduce the parameter

$$\alpha = \frac{T^{SR}}{T^C} = \frac{q_0^2 z}{\epsilon \sigma \varepsilon},$$

measuring the strength of the Coulomb interaction with respect to the short-range attractive interaction.

As before, we first solve the equations for the critical parameters. The loci of these equations are shown in Fig. 2 for $\alpha = 25, 50, 100$ and ∞ (RPM) and in Fig. 3 for $\alpha = 0.5, 1, 2, 5$ and 10. As for the RPM, the curve $a_{3,0} = 0$ intersects the gas-liquid spinodals at a maximum. The results for the critical parameters, the Hamiltonian coefficients and the reduced Ginzburg temperature are presented in Table 2. As is seen, the reduced Ginzburg temperature first decreases with an increase of α and then begins to increase slowly approaching the RPM value for $\alpha \gtrsim 100$.
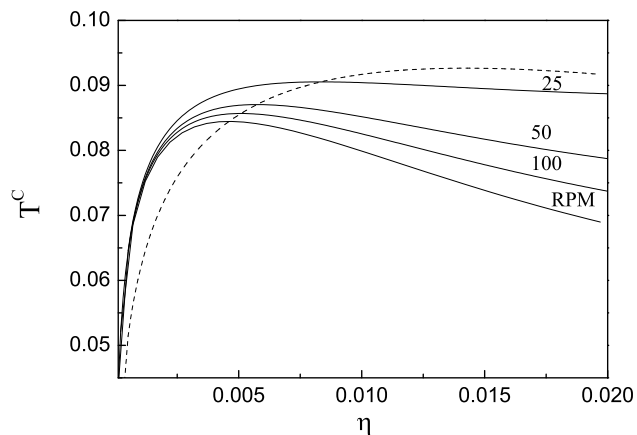

Figure 2. RPM-SW model: the loci of equations $\bar{a}_2 = 0, 0$ (solid lines) and $a_{3,0} = 0$ (dashed line) for $\alpha = 25, 50, 100$ and ∞ (RPM). T^C is given by Eq. (4.12), $\eta = \pi \rho \sigma^3/6$ is the packing fraction and $\alpha = q_0^2 z/(\epsilon \sigma \varepsilon)$.
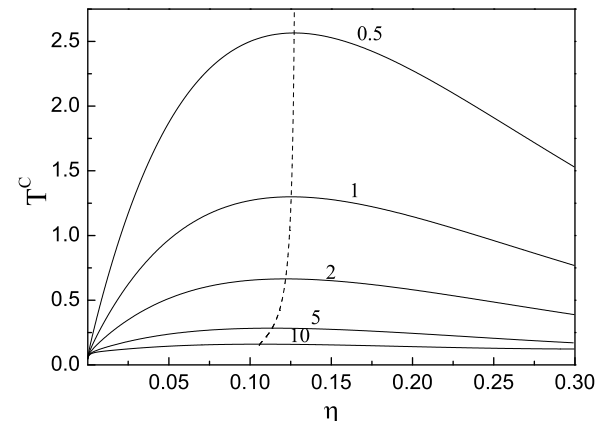

Figure 3. RPM-SW model: the loci of equations $\bar{a}_{2,0} = 0$ (solid lines) and $a_{3,0} = 0$ (dashed line) for $\alpha = 0.5, 1, 2, 5$ and 10. The meaning of the symbols is the same as in Fig. 2.

Quite probably, the RPM-SW model with a certain value of α lying between 10 and 25 undergoes a tricritical point (see, e.g., Ref. [37,38]). This issue deserves a separate study. All the coefficients have the same trend with an increase of α from 0 to ∞, and their trend coincides with the trend of t_G. Both T_c^C and ρ_c^* (or η_c) decrease when α increases and reach the critical values of the RPM. The trend of T_c^{SR} is opposite to the trend of T_c^C.

Table 2. The reduced gas-liquid critical parameters, the coefficients of the effective Hamiltonian and the reduced Ginzburg temperature t_G for the RPM-SW model (see the text) in the one-loop approximation.

| α	T_c^C	T_c^{SR}	ρ_c^*	$a_{2,t}$	$a_{2,2}$	$a_{4,0}$	t_G
0.5	2.56537	1.28269	0.2429	2.7132	0.4506	2.6606	0.0903
1	1.29904	1.29904	0.2393	2.6694	0.4427	2.5441	0.0885
2	0.66471	1.32943	0.2328	2.5908	0.4288	2.3275	0.0840
5	0.28387	1.41935	0.2170	2.4320	0.3986	1.8133	0.0676
10	0.16012	1.6012	0.2026	2.4104	0.3740	1.2586	0.0398
25	0.09054	2.2636	0.0159	1.0406	0.2175	0.0906	0.0024
50	0.08705	4.3524	0.0109	1.0597	0.2396	0.1472	0.0047
100	0.08568	8.568	0.0097	1.0676	0.2481	0.1602	0.0050
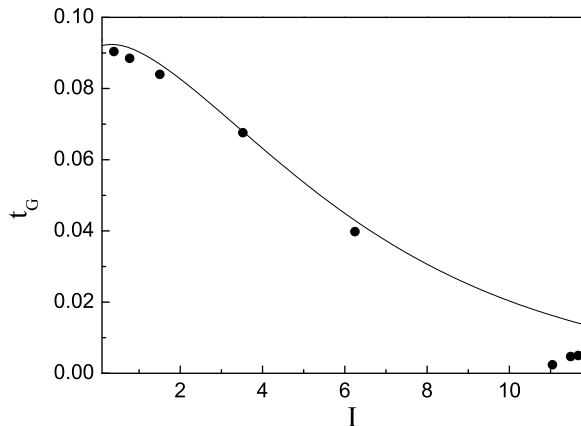
Figure 4. The reduced Ginzburg temperature as a function of the ionicity (see the text). The symbols indicate the results of the present work and the line represents the results from Ref. [26]. $\mathcal{I}$ is given by Eq. (4.13).

In order to establish a link to our previous results (see Ref. [26]) we pass from α to the ionicity $\mathcal{I}$ by means of the relation

$$\alpha = T^{SR}\mathcal{I}, \qquad \text{where} \qquad \mathcal{I} = \frac{1}{T^C}. \qquad (4.13)$$

Fig. 4 presents the dependence of the reduced Ginzburg temperature on the ionicity. The results of the present work are shown by solid circles while the line represents the results from Ref. [26]. As is seen, the both groups of results agree well for $\mathcal{I} \leq 6.25$ corresponding to $\alpha \leq 10$. The deviations between the results that appear for large values of $\mathcal{I}$ are due to the different approximations used in calculating the Hamiltonian coefficients in the present and previous works. Therefore, the results of this paper generally agree with the previous results obtained within the framework of a different perturbative treatment and, in turn, confirm a key role of the Coulomb interactions in the reduction of the crossover region in ionic systems when compared to the nonionic systems.

5. Conclusions

In this paper, we have revisited the issue of the criticality of the Coulomb dominated systems. The model considered, besides Coulomb interactions, includes short-range attractive interactions. Using the CVs-based theory we have derived the ϕ^4-model LGW Hamiltonian in terms of the CVs describing the fluctuation modes of the total number density. The resulting form of the effective Hamiltonian confirms the fact that the criticality of the Coulombic models belongs to the universal class of a three dimensional Ising model. The important feature of the developed approach is that it enables us to obtain all the coefficients, including the square-gradient term, within the framework of the same approximation.

The LGW Hamiltonian obtained has been used for the calculation of the gas-liquid critical parameters and the Ginzburg temperature for a number of models, in particular, the pure solvophobic model, the pure Coulombic model as well as for the models including both the Coulomb interactions and the short-range attractive interactions. In the present paper, all quantities, the critical parameters, the relevant coefficients of the effective Hamiltonian, and, accordingly, the Ginzburg temperature, for all the models considered have been calculated in the one-loop approximation. This approximation leads to the mean-field values for the reduced critical parameters. It is worth noting that the charge-asymmetry does not manifest itself at this level of approximation.

Having excluded the Coulomb interaction, we first calculate the reduced Ginzburg temperature for a simple fluid model, the one-component system of hard spheres interacting via the square-well potential of the range $\lambda = 1.5$. This well-known model is used to calibrate the Ginzburg temperature for the models having Coulomb interactions. Then, neglecting the short-range attraction we study the criticality in the RPM. Our calculations have shown that the reduced Ginzburg temperature of the Coulombic systems is much smaller (although it is not extremely small) than for simple fluids. We have obtained the fluctuation dominated region for the RPM to be much narrower (reduced by a factor of ~ 20) than for the HCSW fluid.

We have also studied the Ginzburg temperature depending on the interplay between the Coulombic and short-range attractive interactions. Having introduced the ratio α that determines the strength of the Coulomb interaction with respect to the short-range interactions (SW potential), we calculate both the reduced critical temperature and critical density, the Hamiltonian coefficients and the reduced Ginzburg temperature for a set of the α values ranging from 0.5 to 100. For the model under consideration, the Ginzburg temperature shows a non-monotonous behaviour with the variation of α. In particular, t_G first decreases approaching its minimum in the region $10 < \alpha < 25$ and then starts to increase approaching the RPM value for $\alpha > 100$. The present results generally agree with our previous results obtained within the framework

of the different perturbative treatment. Moreover, they are in good quantitative agreement for $\alpha \leq 10$.

In conclusion, within the framework of the unified approach we have derived the Ising-like effective Hamiltonian which enables us to make reliable estimates of the reduced Ginzburg temperature for the RPM as well as for the model with the competing short-range and Coulomb interactions. For the model including both the short-range attractive interactions and the long-range Coulomb interactions, we have shown that the reduced Ginzburg temperature approaches the value obtained for the RPM when the strength of the Coulomb interactions becomes large enough. This suggests the key role of the Coulomb interactions in the crossover behaviour observed experimentally in ionic fluids. We believe that our results provide new insights into the nature of the non-classical region in the Coulomb-dominated systems.

6. Appendix

6.1. Expressions for coefficients $a_n^{(i_n)}$

Taking into account the recurrence formulae for $\mathfrak{M}_n^{(i_n)}$ (see (46) in Ref. [30]) we get the following expressions for coefficients $a_n^{(i_n)}$ for $n \leq 4$

$$a_2^{(0)} = \beta\rho\widetilde{\phi}^{SR}(k) + \frac{1}{S_{2,\mathrm{HS}}(k)}, \qquad a_2^{(2)} = \beta\rho\widetilde{\phi}^{C}(k) + \frac{1}{q_0^2 z},$$

$$a_3^{(0)} = -\frac{S_{3,\mathrm{HS}}}{S_{2,\mathrm{HS}}^3}, \qquad a_3^{(2)} = -\frac{1}{q_0^2 z}, \qquad a_3^{(3)} = -\frac{(1-z)}{q_0^3 z^2},$$

$$a_4^{(0)} = -\frac{1}{S_{2,\mathrm{HS}}^4}\left(S_{4,\mathrm{HS}} - \frac{3S_{3,\mathrm{HS}}^2}{S_{2,\mathrm{HS}}}\right), \qquad a_4^{(2)} = \frac{2}{q_0^2 z},$$

$$a_4^{(3)} = \frac{2(1-z)}{q_0^3 z^2}, \qquad a_4^{(4)} = -\frac{2(1-z+z^2)}{q_0^4 z^3},$$

where $S_{n,\mathrm{HS}} = \widetilde{G}_{n,\mathrm{HS}}/\langle N\rangle_{\mathrm{HS}}$, $\widetilde{G}_{n,\mathrm{HS}}$ is the Fourier transform of the n-particle connected correlation function of a one-component hard-sphere system.

In order to get the corrections Δa_3 and Δa_4 (Eqs. (3.13)-(3.14)) we also need coefficients $a_5^{(2)}$ and $a_6^{(2)}$ presented by

$$a_5^{(2)} = -\frac{3!}{q_0^2 z}, \qquad a_6^{(2)} = \frac{4!}{q_0^2 z}.$$

References

1. M. Buback and E.U. Franck, Ber. Bunsenges. Phys. Chem. **76**, 350 (1972).
2. P. Chieux and M.J. Sienko, J.Chem.Phys. **53**, 566 (1970).
3. R.R. Singh and K.S. Pitzer, J. Chem. Phys. **92**, 6775 (1990).
4. J.M.H. Levelt Sengers and J.A. Given, Mol. Phys. **80**, 899 (1993).
5. W. Schröer, in *Ionic Soft Matter: Modern Trends and Applications*, edited by D. Henderson, M.Holovko, and A. Trokhymchuk (Dordrecht: NATO ASI Series II, Springer, 2004) P. 143.
6. W. Schröer, Contrib. Plasma Phys. **52**, 78 (2012).
7. J.V. Sengers and J.G. Shanks, J. Stat. Phys. **137**, 857 (2009).
8. G. Stell, J. Stat. Phys. **78**, 197 (1995).
9. Y. Levin and M.E. Fisher, Physica A **225**, 164 (1996).
10. J.-M. Caillol, Mol. Phys. **103**, 1271 (2005).
11. O.V. Patsahan, Condens. Matter Phys. **7**, 35 (2004).
12. A.-P. Hynninen and A.Z. Panagiotopoulos, Mol. Phys. **106**, 2039 (2008).
13. J.-M. Caillol, D. Levesque, and J.-J. Weis, J. Chem. Phys. **116**, 10794 (2002).
14. E. Luijten, M.E. Fisher, and A.Z. Panagiotopoulos, Phys. Rev. Lett. **88**, 185701 (2002).
15. Y.C. Kim, M.E. Fisher, and A.Z. Panagiotopoulos, Phys. Rev. Lett. **95**, 195703 (2005).
16. A. P. Levanyuk, Sov. Phys. JETP **36**, 571 (1959) [Zh. Eksp. Teor. Fiz. **36**, 810 (1959)].
17. V.L. Ginzburg, Sov. Phys. Solid State **2**, 1824 (1960) [Fiz. Tverd. Tela **2**, 2031-2043 (1960)].
18. N. Goldenfeld, *Lectures on phase transitions and the renormalization group* (Addison-Wesley, New-York, 1992).
19. M.E. Fisher and B.P. Lee, Phys. Rev. Lett. **77**, 3561 (1996).
20. J.F. Leote de Carvalho and R. Evans, J. Phys.: Condens. Matter **7**, L57 (1995).
21. W. Schröer and V.C. Weiss, J. Chem. Phys. **109**, 8504 (1998).
22. V.C. Weiss and W. Schröer, J. Chem. Phys. **106**, 1930 (1997).
23. A. Ciach, Phys. Rev.E **73**, 066110 (2006).
24. N.V. Brilliantov, C. Bagnuls, and C. Bervillier, Phys. Lett. A **245**, 274 (1998).
25. O.V. Patsahan and I.M. Mryglod, J. Phys.: Condens. Matter **16**, L235 (2004).
26. O.V. Patsahan, J.-M. Caillol, and I.M. Mryglod, Europ. Phys. Jour-

nal B **58**, 449 (2007).

27. A.G. Moreira, M.M. Telo de Gama, and M.E. Fisher, J. Chem. Phys. **110**, 10058 (1999).
28. A. Parola and D. Pini, Mol. Phys. **109**, 2989 (2011).
29. M.Kleemeier, S. Wiegand, W. Schröer, and H. Weingärtner, J. Chem. Phys. **110**, 3085 (1999).
30. O. Patsahan, and I. Mryglod, Condens. Matter Phys. **9**, 659 (2006).
31. O.V. Patsahan, I.M. Mryglod, and T.M. Patsahan, J.Phys.: Condens. Matter **18**, 10223 (2006).
32. J. D. Weeks, D. Chandler, and H.C. Andersen, J. Chem. Phys. **54**, 5237 (1971).
33. D. Chandler and H.C. Andersen, J. Chem. Phys. **54**, 26 (1971).
34. J.P. Hansen and I.R. McDonald *Theory of simple liquids* (Academic Press, 1986).
35. G. Stell, in *Phase transitions and critical phenomena*, edited by C. Domb and M.S. Green (Academic Press, London, 1975) vol. 5B, p. 205.
36. N.W. Ashcroft and J. Lekner, Phys. Rev. B **145**, 83 (1966).
37. A. Ciach and G. Stell, Physica A, **306**, 220 (2002).
38. A. Ciach and G. Stell, J. Chem Phys. **114**, 3617 (2001).

CONDENSED MATTER PHYSICS

The journal **Condensed Matter Physics** is founded in 1993 and published by Institute for Condensed Matter Physics of the National Academy of Sciences of Ukraine.

AIMS AND SCOPE: The journal **Condensed Matter Physics** contains research and review articles in the field of statistical mechanics and condensed matter theory. The main attention is paid to physics of solid, liquid and amorphous systems, phase equilibria and phase transitions, thermal, structural, electric, magnetic and optical properties of condensed matter. Condensed Matter Physics is published quarterly.

ABSTRACTED/INDEXED IN: Chemical Abstract Service, Current Contents/Physical, Chemical&Earth Sciences; ISI Science Citation Index-Expanded, ISI Alerting Services; INSPEC; "Referatyvnyj Zhurnal"; "Dzherelo".

EDITOR IN CHIEF: Ihor Yukhnovskii.