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Spatially confined system interacting with Yukawa potential

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Hard wall confined fluid with Yukawa potential of interaction is considered. A solution of the inhomogeneous Ornstein-Zernike equation for the pair correlation function is obtained. The expression for the particle density profile is found by the method of functional differentiation of Helmholtz free energy with respect to the external field. The contribution to the behavior of particle density near the surface comes from the initial potential as well as from the collective screening interaction effects. It is shown that the contact value of the profile satisfies the condition of the contact theorem. Dependence of the adsorption coefficient on the particle density is calculated. It is also shown that in the case of repulsive Yukawa interaction the sign of the adsorption coefficient changes with the increase of the particle density.

Key words: *nonhomogeneous Ornstein-Zernike equation, hard wall, contact theorem, adsorption coefficient, Yukawa potential*

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1. Introduction

The study of systems with the long-range component of a Yukawa-like potential of interaction is of significant theoretical interest. Despite the simplicity of the actual potential, it allows one to describe structural and thermodynamic properties. In addition, there exist analytical solutions in the mean spherical approximation for a system of hard spheres with the Yukawa potential of interaction [1]. Recently, the density field theory was applied to the description of the fluid interacting with the Yukawa potential [2,3]. The Yukawa potential can be used in describing the systems of charged particles as well as neutral-particle systems. Sets of Yukawa potentials are used to approximate real interaction potentials in simple liquids [4], colloid fluids [5,6] and other systems [7].

Despite considerable progress in the study of spatially uniform systems of particles with the Yukawa potential, the research of non-uniform systems remains a relevant task. A lot more results have been obtained for spatially non-uniform systems of charged particles. Notably, expressions for the pair and singlet distribution functions for a system of point ions confined by a hard wall have been found [8–10]. The results of the pioneering work [11] have made it possible to obtain an analytical form of the contribution of short-range interactions to the structural properties of spatially confined systems. These and other works have significantly enhanced our understanding of surface effects in systems with electrostatic interaction.

When calculating structural properties of spatially non-uniform systems, it is important to verify that the results found satisfy certain exact relationships. Of special importance are exact relationships for the contact values of density profiles [12] and those of charge profiles [13], the so-called contact theorems. Specifically, in accordance with the contact theorem for the density profile, the contact value of particle density near a hard wall is determined by the pressure of a fluid without a wall. For a system of point ions it is shown that in the random phase approximation the expressions found for the density profile meet the requirements of the contact theorem [14].

Spatially non-uniform systems with the Yukawa potential have been studied primarily by computer simulations and numerical calculations of integral equations [15].

The present work focuses on the analytical research of thermodynamic and structural properties of a spatially non-uniform one-component system of particles with the Yukawa potential of interaction. We shall obtain expressions for the Helmholtz free energy, pair correlation function and density distribution for such a system. It will be shown that for the latter, the contact theorem is valid.

2. The model

We shall consider a two-phase system of particles within volume V, in which the phases are separated by the plain $z = 0$. The upper part of space ($z > 0$) is filled with the upper phase having the particle density ρ_+ , whereas the lower part of space ($z < 0$) is filled with the lower phase having the particle density ρ_- . The interaction potential between any two particles, the locations of which are given by radius vectors $\vec{R}_1$ and $\vec{R}_2$ in the Descartes coordinate system, is presented as the sum of short-range $u(R_{12})$ potential and long-range Yukawa potential

$$\Phi(R_{12}) = A\,\frac{\mathrm{e}^{-\alpha R_{12}}}{R_{12}}\,, \tag{1}$$

where A is the constant of interaction, R_{12} is the distance between two particles.

The potential energy of the system consists of the energy of inter-particle interaction and the energy of particles under an external field

$$U_{\mathrm{N}} = \sum_{j<i} u(R_{ij}) + \sum_{j<i} \Phi(R_{ij}) + \sum_{a,i}^{N} w_a(z_i)\,, \tag{2}$$

where $w_a(z_i)$ is the external field forming the phase interface, z_i is the distance between a wall and a particle. The index "a" indicates which phase a particle belongs to and takes the value "+" for the upper phase and "−" for the lower phase,

$$w_+(\vec{R}_i) = \begin{cases} 0, & z_i > 0\,, \\ \infty, & z_i < 0\,, \end{cases} \qquad w_-(\vec{R}_i) = \begin{cases} \infty, & z_i > 0\,, \\ 0, & z_i < 0\,. \end{cases} \tag{3}$$

From here on we shall consider only the long-range component of the potential energy similar to the way it had been done within the collective variables method when short-range interactions were taken into account using the method of functional differentiation [8]. Let us introduce the microscopic particle density

$$\hat{\rho}(\vec{R}) = \sum_{i=1}^{N} \delta(\vec{R} - \vec{R}_i). \tag{4}$$

In (1) let us do the Fourier transformation of the pair potential of interaction $\Phi(R_{ij})$

$$\tilde{\Phi}(k) = \int_V \Phi(R)\,\mathrm{e}^{\mathrm{i}\,\vec{k}\,\vec{R}}\,\mathrm{d}\vec{R} \tag{5}$$

and separate the self-energy part of the potential energy ($i = j$), then for the potential energy of the system we shall get the equality:

$$U_{\mathrm{N}}^{1} = \frac{1}{2}\frac{1}{V}\sum_{\vec{k}} \tilde{\Phi}(k)\hat{\rho}_{\vec{k}}\,\hat{\rho}_{-\vec{k}} - \frac{1}{2}\frac{N}{V}\sum_{\vec{k}} \tilde{\Phi}(k) + \sum_{a,\,i}^{N} w_a(z_i)\,, \tag{6}$$

where the index l indicates that the potential energy takes into account only the long-range components of inter-particle interaction, and

$$\hat{\rho}_{\vec{k}} = \sum_{a,i}^{N} \exp(\mathrm{i}\vec{k}\vec{R}_i) \tag{7}$$

is the Fourier transform of the microscopic particle density.

The Helmholtz free energy of the system can be determined from the relation

$$F_{\mathrm{N}}^{\mathrm{l}} = F_{\mathrm{N}}^{\mathrm{id}} + F_{\mathrm{N}}^{\mathrm{l,ex}} = F_{\mathrm{N}}^{\mathrm{id}} - T \ln Q_{\mathrm{N}}^{\mathrm{l}} , \tag{8}$$

where $F_{\mathrm{N}}^{\mathrm{id}}$ is the Helmholtz free energy of the system without particle interaction,

$$F_{\mathrm{N}}^{\mathrm{id}} = -T \sum_{a,i}^{N} N_a \left\{1 - \ln\left(\rho_a \Lambda^3\right)\right\} , \tag{9}$$

$Q_{\mathrm{N}}^{\mathrm{l}}$ is the configuration integral of a system of particles with the long-range interaction

$$Q_{\mathrm{N}}^{\mathrm{l}} = \frac{1}{V^N} \int\limits_V \prod_i^N \vec{R}_i \exp\left(-\frac{1}{T} U_{\mathrm{N}}^{\mathrm{l}}\right) , \tag{10}$$

and $F_{\mathrm{N}}^{\mathrm{l,ex}}$ is the contribution of long-range interactions to the Helmholtz free energy, T is the temperature measured in units of energy, N_+ and N_- are the numbers of particles in the upper and the lower half-space accordingly, and Λ is the thermal de Broglie wavelength.

3. Random phase approximation for the Helmholtz free energy of the system

Let us evaluate the configuration integral $Q_{\mathrm{N}}^{\mathrm{l}}$, which has the following form in terms of the collective variables method:

$$\begin{aligned} Q_{\mathrm{N}}^{\mathrm{l}} = {} & \frac{1}{V^N} \int \prod_i \mathrm{d}\vec{R}_i \int \prod_{\vec{k}} \mathrm{d}\rho_{\vec{k}} \int \prod_{\vec{k}} \mathrm{d}\omega_{\vec{k}} \exp\left\{ -\frac{1}{2} \sum_{\vec{k}} \tilde{\nu}(k) \rho_{\vec{k}}\, \rho_{-\vec{k}} \right. \\ & \left. + \frac{1}{2} N \sum_{\vec{k}} \tilde{\nu}(k) - \frac{1}{T} \sum_{a,\, i}^{N} w_a(z_i) + 2\mathrm{i}\pi \sum_{\vec{k}} \omega_{-\vec{k}} \left(\rho_{-\vec{k}} - \hat{\rho}_{-\vec{k}}\right) \right\} , \end{aligned} \tag{11}$$

where for convenience we have introduced

$$\tilde{\nu}(k) = \frac{1}{T\,V} \tilde{\Phi}(k) = \frac{A}{T\,V} \frac{4\pi}{k^2 + \alpha^2} . \tag{12}$$

Integration of Gaussian form with respect to collective variables and making use of the cumulative development technique [8] for the repulsive interaction makes it possible to do the integration in the space of individual variable particles. Then, by taking into account only the zero, the first, and the second cumulants, for the configuration integral in the random phase approximation we shall get

$$\begin{aligned} Q_{\mathrm{N}}^{\mathrm{l,RPA}} = {} & \exp\left\{ \mathfrak{M}_0 + \frac{1}{2} N \sum_{\vec{k}} \tilde{\nu}(k) + \frac{1}{2} \sum_{\vec{k}} \ln \frac{2\pi}{\tilde{\nu}(k)} \right\} \int \prod_{\vec{k}} \mathrm{d}\omega_{\vec{k}} \\ & \times \exp\left\{ 2\pi^2 \sum_{\vec{k}_1,\, \vec{k}_2} \tilde{g}^{-1}(\vec{k}_1, \vec{k}_2) \omega_{\vec{k}_1} \omega_{\vec{k}_2} - 2\pi\mathrm{i} \sum_{\vec{k}} \mathfrak{M}_1(\vec{k}) \omega_{\vec{k}} \right\} , \end{aligned} \tag{13}$$

where $\mathfrak{M}_0(\vec{k})$, $\mathfrak{M}_1(\vec{k})$, $\mathfrak{M}_2(\vec{k}_1,\vec{k}_2)$ denote the zero, the first, and the second cumulants, respectively

$$\mathfrak{M}_0 = N_+ \ln\left\{\frac{1}{V}\int\limits_V \mathrm{d}\vec{R}\,\mathrm{e}^{-\frac{1}{T}w_+(z)}\right\} + N_- \ln\left\{\frac{1}{V}\int\limits_V \mathrm{d}\vec{R}\,\mathrm{e}^{-\frac{1}{T}w_+(z)}\right\}, \tag{14}$$

$$\mathfrak{M}_1(\vec{k}) = \delta_{\vec{p},0}\left\{\rho_+\int\limits_V \mathrm{d}\vec{R}\,\mathrm{e}^{-\frac{1}{T}w_+(z)}\mathrm{e}^{\mathrm{i}qz} + \rho_-\int\limits_V \mathrm{d}\vec{R}\,\mathrm{e}^{-\frac{1}{T}w_-(z)}\mathrm{e}^{\mathrm{i}qz}\right\}, \tag{15}$$

$$\begin{aligned}\mathfrak{M}_2(\vec{k}_1,\vec{k}_2) = {} & \delta_{\vec{p}_1+\vec{p}_2,0}\rho_+\int\limits_V \mathrm{d}\vec{R}\,\mathrm{e}^{-\frac{1}{T}w_+(z)}\,\mathrm{e}^{\mathrm{i}(q_1+q_2)z} + \delta_{\vec{p}_1+\vec{p}_2,0}\rho_-\int\limits_V \mathrm{d}\vec{R}\,\mathrm{e}^{-\frac{1}{T}w_-(z)}\,\mathrm{e}^{\mathrm{i}(q_1+q_2)z}\\ & - \delta_{\vec{p}_1,0}\delta_{\vec{p}_2,0}\rho_+\frac{1}{\mathcal{V}_+}\int\limits_V \mathrm{d}\vec{R}\,\mathrm{e}^{-\frac{1}{T}w_+(z)}\,\mathrm{e}^{\mathrm{i}q_1z}\int\limits_V \mathrm{d}\vec{R}\,\mathrm{e}^{-\frac{1}{T}w_+(z)}\mathrm{e}^{\mathrm{i}q_2z}\\ & - \delta_{\vec{p}_1,0}\delta_{\vec{p}_2,0}\rho_-\frac{1}{\mathcal{V}_-}\int\limits_V \mathrm{d}\vec{R}\,\mathrm{e}^{-\frac{1}{T}w_-(z)}\,\mathrm{e}^{\mathrm{i}q_1z}\int\limits_V \mathrm{d}\vec{R}\,\mathrm{e}^{-\frac{1}{T}w_-(z)}\,\mathrm{e}^{\mathrm{i}q_2z}.\end{aligned} \tag{16}$$

$$\mathcal{V}_+ = \int\limits_V \mathrm{d}\vec{R}\,\mathrm{e}^{-\frac{1}{T}w_+(z)}, \qquad \mathcal{V}_- = \int\limits_V \mathrm{d}\vec{R}\,\mathrm{e}^{-\frac{1}{T}w_-(z)}, \tag{17}$$

and $\vec{k} = \vec{p} + \vec{i}_z q$ ($\vec{i}_z$ is a unit basis vector perpendicular to the surface and $\vec{p}$ is a vector parallel to the surface), $\delta_{\vec{p},0}, \delta_{\vec{p}_1+\vec{p}_2,0}$ is the Kroneker delta.

In (13) we have introduced an infinite matrix $\mathbb{G}^{-1}$ whose elements are

$$\tilde{g}^{-1}(\vec{k}_1,\vec{k}_2) = -\frac{1}{\tilde{\nu}(k)_1}\delta_{\vec{k}_1+\vec{k}_2,0} - \mathfrak{M}_2(\vec{k}_1,\vec{k}_2) \tag{18}$$

and the elements of the inverse matrix $\mathbb{G}$ are the Fourier transforms of the so-called screened potentials and can be determined from the equation

$$\tilde{g}(\vec{k}_1,\vec{k}_2) = -\tilde{\nu}(k_1) - \tilde{\nu}(k_1)\sum_{\vec{k}} M_2(-\vec{k}_1,\vec{k}_2)\tilde{g}(\vec{k}_1,\vec{k}_2). \tag{19}$$

In (13) we shall convert the square matrix form with respect to variables $\omega_{\vec{k}}$ into the diagonal form similar to the way it was done in work [10]. Then, as a result of integration in the random phase approximation, the configuration integral of a two-phase spatially non-uniform system of point particles with the Yukawa interaction can be written in the form

$$Q_{\mathrm{N}}^{\mathrm{l,RPA}} = \exp\left\{\mathfrak{M}_0 + \frac{1}{2}N\sum_{\vec{k}}\tilde{\nu}(k) - \frac{1}{2}\ln\det\{\mathbf{1}+\tilde{\nu}\mathbf{M_2}\} + \frac{1}{2}\sum_{\vec{k}_1,\vec{k}_2}\tilde{g}(\vec{k}_1,\vec{k}_2)\mathfrak{M}_1(\vec{k}_1)\mathfrak{M}_1(\vec{k}_2)\right\}. \tag{20}$$

Let us examine the last term in the equality (20) taking (19) into account. We have

$$\begin{aligned}\sum_{\vec{k}_1,\vec{k}_2}\tilde{g}(\vec{k}_1,\vec{k}_2)\mathfrak{M}_1(\vec{k}_1)\,\mathfrak{M}_1(\vec{k}_2) &= -\sum_{\vec{k}_1}\tilde{\nu}(k_1)\mathfrak{M}_1(\vec{k}_1)\,\mathfrak{M}_1(-\vec{k}_1)\\ &\quad - \sum_{\vec{k}_1,\vec{k}_2,\vec{k}}\tilde{\nu}(k_1)\mathfrak{M}_2(-\vec{k}_1,\vec{k})\tilde{g}(\vec{k},\vec{k}_2)\mathfrak{M}_1(\vec{k}_1)\,\mathfrak{M}_1(\vec{k}_2)\\ &= -\sum_{\vec{k}_1}\tilde{\nu}(k_1)\mathfrak{M}_1(\vec{k}_1)\,\mathfrak{M}_1(-\vec{k}_1),\end{aligned} \tag{21}$$

at the thermodynamic limit ($N \to \infty$, $V \to \infty$, $\rho = \mathrm{const}$)

$$\sum_{\vec{k}_1,\,\vec{k}_2,\,\vec{k}} \tilde{\nu}(k_1)\mathfrak{M}_2(-\vec{k}_1,\vec{k})\tilde{g}(\vec{k},\vec{k}_2)\mathfrak{M}_1(\vec{k}_1)\,\mathfrak{M}_1(\vec{k}_2) \;=\; 0. \tag{22}$$

Then, taking into account only the long-range inter-particle interactions, for the Helmholtz free energy of the system in the random phase approximation we shall have

$$\frac{1}{T}\,F_{\mathrm{N}}^{\mathrm{l,RPA}} = \frac{1}{T}\,F_{\mathrm{N}}^{\mathrm{l,id}} - \mathfrak{M}_0 - \frac{1}{2}\,N\sum_{\vec{\mathrm{k}}}\tilde{\nu}(k) + \frac{1}{2}\ln\det\left\{\mathbf{1} + \tilde{\nu}\mathbf{M_2}\right\} + \frac{1}{2}\sum_{\vec{k}}\tilde{\nu}(k)\mathfrak{M}_1(\vec{k})\,\mathfrak{M}_1(-\vec{k})\,, \tag{23}$$

where $\mathbf{1} + \tilde{\nu}\mathbf{M_2}$ is a matrix whose elements can be determined from the following expression

$$\delta_{\vec{k}_1+\vec{k}_2,\,0} \;+\; \tilde{\nu}(k_1)\,\mathfrak{M}_2(-\vec{k}_1,\vec{k}_2). \tag{24}$$

4. Particle density profile

We shall be looking for the density of the system using the method of functional differentiation of Helmholtz free energy $F_{\mathrm{N}}^{\mathrm{l}}$ (23) of the system with respect to the external field

$$\rho(z_1) \;=\; \frac{1}{T}\,\frac{\delta}{\delta w_a(z_1)}\,F_{\mathrm{N}}^{\mathrm{l}}\,. \tag{25}$$

The functional derivative applies only to the terms that contain cumulants. Then, in the random phase approximation

$$\frac{1}{T}\,\frac{\delta F_{\mathrm{N}}^{\mathrm{l,RPA}}}{\delta w_a(\vec{R}_1)} = -\,\frac{\delta\mathfrak{M}_0}{\delta w_a(\vec{R}_1)} + \frac{1}{2}\,\frac{\delta}{\delta w(\vec{R}_1)}\ln\det\{\mathbf{1} + \tilde{\nu}\mathbf{M_2}\} + \frac{1}{2}\,\frac{\delta}{\delta w(\vec{R}_1)}\sum_{\vec{k}}\tilde{\nu}(k)\mathfrak{M}_1(\vec{k})\,\mathfrak{M}_1(-\vec{k})\,. \tag{26}$$

The first term in (26) is equal to

$$-\,\frac{\delta\mathfrak{M}_0}{\delta w_a(\vec{R}_1)} \;=\; \rho_a\,\mathrm{e}^{-\frac{1}{T}w_a(\vec{R}_1)}\,. \tag{27}$$

In the second term, it should be taken into account that the derivative of $\mathfrak{M}_2(\vec{k}_1,-\vec{k}_1)$ in the thermodynamic limit is equal to zero. Then,

$$\frac{\delta}{\delta w_a(\vec{R}_1)}\ln\det\{\mathbf{1} + \tilde{\nu}\mathbf{M_2}\} = \sum_{\vec{k}_1,\,\vec{k}_2}\frac{\delta\mathfrak{M}_2(\vec{k}_1,\vec{k}_2)}{\delta w_a(\vec{R}_1)}\,\frac{\delta\ln\det\{\mathbf{1} + \tilde{\nu}\mathbf{M_2}\}}{\delta\mathfrak{M}_2(\vec{k}_1,\vec{k}_2)} = \rho_a\,\mathrm{e}^{-\frac{1}{T}w_a(\vec{R}_1)}\,g_a(\vec{R}_1), \tag{28}$$

where $g_a(\vec{R}_1)$ is the regular part of the screened potential

$$g_a(\vec{R}_1) \;=\; \sum_{\vec{k}_1,\,\vec{k}_2}\Big[1 \;-\; \delta_{\vec{k}_1\,+\,\vec{k}_2,\,0}\Big]\;\tilde{g}(\vec{k}_1,\vec{k}_2)\,\mathrm{e}^{-\mathrm{i}\vec{k}_1\vec{R}_1-\mathrm{i}\vec{k}_2\vec{R}_1}\,. \tag{29}$$

The third term in (26), considering the expression for the first cumulant (15), can be written in the form

$$\begin{aligned}\frac{\delta}{\delta w_a(\vec{R}_1)}\sum_{\vec{k}}\tilde{\nu}(k)\mathfrak{M}_1(\vec{k})\,\mathfrak{M}_1(-\vec{k}) &= -\rho_a\,\mathrm{e}^{-\frac{1}{T}w_a(\vec{R}_1)}\sum_{\vec{k}}\tilde{\nu}(k)\,[1 \;-\; \delta_{\vec{k},\,0}]\,\mathrm{e}^{-\mathrm{i}\vec{k}\vec{R}_1}\,\mathfrak{M}_1(-\vec{k})\\ &= \;-\,\rho_a\,\frac{1}{T}\,\mathrm{e}^{-\frac{1}{T}w_a(\vec{R}_1)}\sum_{b}\rho_b\int\limits_V \mathrm{d}\vec{R}_2\,\Phi_{ab}(|\vec{R}_1 - \vec{R}_2|)\left[\mathrm{e}^{-\frac{1}{T}\,w_b(\vec{R}_2)} \;-\; 1\right].\end{aligned} \tag{30}$$

Thus, considering (25–30) the density profile of a spatially non-uniform system of point particles with the Yukawa interaction in the random phase approximation is:

$$\rho_a(\vec{R}_1) = \rho_a\, \mathrm{e}^{-\frac{1}{T} w_b(\vec{R}_1)} \left\{ 1 + \frac{1}{2}\, g_a(\vec{R}_1) - \frac{1}{T} \sum_b \rho_b \int_V \mathrm{d}\vec{R}_2 \Phi_{ab}\left(|\vec{R}_1 - \vec{R}_2|\right) \left[\mathrm{e}^{-\frac{1}{T} w_b(\vec{R}_2)} - 1\right] \right\}. \quad (31)$$

The last term in (30) represents the potential of interaction between the surface and the particles. In a similar way one can get the surface "3–9" potential from the spatially uniform Lennard-Jones "6–12" potential. It should be noted that in ionic systems the last term, which comes from the contribution of the initial potential to the density profile, is absent due to the condition of general electroneutrality of the system.

5. The pair correlation function of the system

Equation (19) for Fourier-transforms of screened potentials in the coordinate space has the form

$$g_{ab}(\vec{R}_1, \vec{R}_2) \,=\, -\frac{1}{T}\, \Phi_{ab}(R_{12}) \,-\, \frac{1}{T} \sum_c \rho_c \int_V d\vec{R}_3\, \mathrm{e}^{-\frac{1}{T} w_c(\vec{R}_3)}\, \Phi_{ac}(|\vec{R}_1 \,-\, \vec{R}_3|)\, g_{cb}(\vec{R}_3,\, \vec{R}_2)\,. \quad (32)$$

This equation coincides with the spatially non-uniform Ornstein-Zernike equation

$$h_{ab}(\vec{R}_1, \vec{R}_2) \,=\, c_{ab}(\vec{R}_1,\, \vec{R}_2) + \sum_c \int_V \mathrm{d}\vec{R}_3\, \rho_c(\vec{R}_3)\, c_{ac}(\vec{R}_1,\, \vec{R}_3)\, h_{cb}(\vec{R}_3,\, \vec{R}_2)\,, \quad (33)$$

if, like it is done in the mean spherical approximation for a system of point particles, we set the direct correlation function equal to the potential of particle interaction and if for a zero approximation we use the density of free particles under an external field $w(\vec{R})$.

$$\rho_a(\vec{R}_1) \,=\, \rho_a \mathrm{e}^{-\frac{1}{T} w_a(\vec{R}_1)}\,, \qquad c_{ab}(\vec{R}_1,\, \vec{R}_2) \,=\, -\frac{1}{T}\, \Phi_{ab}(R_{12}). \quad (34)$$

In this case the screened potential and the pair correlation function coincide $h_{ab}(\vec{R}_1, \vec{R}_2) = h^{\mathrm{l}}_{ab}(\vec{R}_1, \vec{R}_2) = g_{ab}(\vec{R}_1, \vec{R}_2)$.

Let us solve the spatially non-uniform Ornstein-Zernike equation for a system of point particles in the approximation (35). Considering the symmetry of the potential energy, we shall express the pair correlation function and the Yukawa potential as follows

$$h^{\mathrm{l}}_{ab}(\vec{R}_1, \vec{R}_2) \,=\, h^{\mathrm{l}}(s_{12}, z_1, z_2)\,, \qquad \Phi_{ab}(R_{12}) \,=\, A\frac{\exp\left(-\alpha\sqrt{s_{12}^2 + (z_1 - z_2)^2}\right)}{\sqrt{s_{12}^2 + (z_1 - z_2)^2}}\,. \quad (35)$$

where $\vec{s}_1$, $\vec{s}_2$ are the projections of radius vectors $\vec{R}_1$ and $\vec{R}_2$ onto the plane $z = 0$, $s_{12} = |\vec{s}_1 - \vec{s}_2|$ is the distance between projections and z_1, z_2 are particle coordinates in the direction perpendicular to the surface.

Then, considering the step-like approximation for the particle density of the system, the OZ equation will look as follows

$$\begin{aligned} h^{\mathrm{l}}(s_{12}, z_1, z_2) \quad &= \quad -\frac{A}{T}\frac{\exp\left(-\alpha\sqrt{s_{12}^2 + (z_1 - z_2)^2}\right)}{\sqrt{s_{12}^2 + (z_1 - z_2)^2}} \\ &\quad - \frac{A\rho_+}{T} \int_{\mathcal{S}} \mathrm{d}\vec{s}_3 \int_0^{\infty} \mathrm{d}z_3 \frac{\exp\left(-\alpha\sqrt{s_{13}^2 + (z_1 - z_3)^2}\right)}{\sqrt{s_{13}^2 + (z_1 - z_3)^2}} h^{\mathrm{l}}(s_{32}, z_3, z_2) \\ &\quad - \frac{A\rho_-}{T} \int_{\mathcal{S}} \mathrm{d}\vec{s}_3 \int_{-\infty}^{0} \mathrm{d}z_3 \frac{\exp\left(-\alpha\sqrt{s_{13}^2 + (z_1 - z_3)^2}\right)}{\sqrt{s_{13}^2 + (z_1 - z_3)^2}} h^{\mathrm{l}}(s_{32}, z_3, z_2), \end{aligned} \quad (36)$$

where integration with respect to $\vec{s}_3$ is given in an infinite plane $\mathcal{S}$.

Similar to [16], let us introduce one-sided pair correlation functions $h^1_{+(-)}(s_{12}, z_1, z_2)$.

$$\begin{aligned} h^1(s_{12}, z_1, z_2) &= h^1_+(s_{12}, z_1, z_2) - h^1_-(s_{12}, z_1, z_2), \\ h^1_+(s_{12}, z_1, z_2) &= \begin{cases} h^1(s_{12}, z_1, z_2), & z_1 > 0, \\ 0, & z_1 < 0, \end{cases} \\ h^1_-(s_{12}, z_1, z_2) &= \begin{cases} 0, & z_1 > 0, \\ -h^1(s_{12}, z_1, z_2), & z_1 < 0. \end{cases} \end{aligned} \tag{37}$$

After the Fourier transformation of (36) and a few additional simple transformations we shall obtain the equation for the Fourier transforms of one-sided pair correlation functions

$$P_+(p, q_1)\,\tilde{h}^1_+(p, q_1, q_2) - P_-(p, q_1)\,\tilde{h}^1_-(p, q_1, q_2) = -4\pi\frac{A}{T}\,\delta(q_1 + q_2), \tag{38}$$

where

$$\tilde{h}^1_{+(-)}(p, q_1, q_2) = \int\limits_{\mathcal{S}} \mathrm{d}\vec{s}_{12}\mathrm{e}^{\mathrm{i}\vec{p}\vec{s}_{12}} \int\limits_{-\infty}^{\infty} \mathrm{d}z_1 \mathrm{e}^{\mathrm{i}q_1 z_1} \int\limits_{-\infty}^{\infty} \mathrm{d}z_2 \mathrm{e}^{\mathrm{i}q_2 z_2} h^1_{+(-)}(s_{12}, z_1, z_2) \tag{39}$$

and the coefficients $P_+(p, q_1)$ and $P_-(p, q_1)$ are quadratic polynomials of variable q_1

$$\begin{aligned} P_+(p, q_1) &= p^2 + q_1^2 + \gamma_+^2, \qquad P_-(p, q_1) = p^2 + q_1^2 + \gamma_-^2, \\ \gamma_+^2 &= \alpha^2 + \varkappa_+^2, \qquad \gamma_-^2 = \alpha^2 + \varkappa_-^2, \qquad \varkappa_+^2 = 4\pi A\frac{\rho_+}{T}, \qquad \varkappa_-^2 = 4\pi A\frac{\rho_-}{T}. \end{aligned} \tag{40}$$

The indexes "+" and "−" in these coefficients do not correspond to the regions of their analyticity but indicate where they belong to in the equality (38).

Equation (38) is known as the Riemann problem [18]. We shall use the technique proposed in [16,17], to factorize the equation. From here on we shall restrict the problem to the case of $A > -\alpha T/(4\pi\rho)$, since a strongly attractive Yukawa potential $A < -\alpha T/(4\pi\rho)$ requires a separate study. We shall present the fraction $P_-(p, q_1)/P_+(p, q_1)$ in the form

$$\frac{P_-(p, q_1)}{P_+(p, q_1)} = \frac{Q_+(p, q_1)}{Q_-(p, q_1)}, \tag{41}$$

where the functions $Q_+(p, q_1)$, $Q_-(p, q_1)$, being the functions of the variable q_1, are analytical and have no zeros in the upper + or the lower − semi-planes of the complex plane. They are easy to find since the coefficients of equation (38) are second degree polynomials of a variable q_1

$$Q_+(p, q_1) = \frac{q_1 + \mathrm{i}\alpha_-(p)}{q_1 + \mathrm{i}\alpha_+(p)}, \qquad Q_-(p, q_1) = \frac{q_1 - \mathrm{i}\alpha_+(p)}{q_1 - \mathrm{i}\alpha_-(p)}, \qquad \alpha_{+(-)}(p) = \sqrt{(p^2 + \gamma^2_{+(-)})}. \tag{42}$$

Equation (38) can be rewritten as follows

$$\frac{\tilde{h}^1_+(p, q_1, q_2)}{Q_+(p, q_1)} - \frac{\tilde{h}^1_-(p, q_1, q_2)}{Q_-(p, q_1)} = -4\pi\frac{A}{T}\frac{1}{Q_+(p, -q_2)\,P_+(p, -q_2)}\,\delta(q_1 + q_2). \tag{43}$$

In equality (38) let us present the Dirac δ-function as the difference of one-sided functions $\delta(q_1 + q_2) = \delta_+(q_1 + q_2) - \delta_-(q_1 + q_2)$, which are analytical in the upper and the lower semi-planes of the complex plane, respectively. Since the index of problem (43) is equal to zero [18] for the Fourier-transforms of one-sided pair correlation functions we obtain

$$\begin{aligned} \tilde{h}^1_+(p, q_1, q_2) &= -4\pi\frac{A}{T}\,Q_+(p, q_1)\,\frac{\delta_+(q_1 + q_2)}{Q_+(p, -q_2)\,P_+(p, -q_2)}, \\ \tilde{h}^1_-(p, q_1, q_2) &= -4\pi\frac{A}{T}\,Q_-(p, q_1)\,\frac{\delta_-(q_1 + q_2)}{Q_+(p, -q_2)\,P_+(p, -q_2)}. \end{aligned} \tag{44}$$

Substituting (40) and (42) into (44), then for $\tilde{h}^1_{+(-)}(p, q_1, q_2)$ we get

$$\begin{aligned}\tilde{h}^1_+(p, q_1, q_2) &= -4\pi \frac{A}{T} \frac{q_1 + i\alpha_-(p)}{q_1 + i\alpha_+(p)} \frac{\delta_+(q_1+q_2)}{(q_2 - i\alpha_-(p))(q_2 + i\alpha_+(p))}\,,\\ \tilde{h}^1_-(p, q_1, q_2) &= -4\pi \frac{A}{T} \frac{q_1 - i\alpha_+(p)}{q_1 - i\alpha_-(p)} \frac{\delta_-(q_1+q_2)}{(q_2 - i\alpha_-(p))(q_2 + i\alpha_+(p))}\,. \end{aligned} \tag{45}$$

Let us now find the originals of the one-sided pair correlation functions. To this end we shall do the inverse Fourier transformation

$$h^1(s_{12}, z_1, z_2) = \int \frac{\mathrm{d}\vec{p}}{(2\pi)^2} \mathrm{e}^{-\mathrm{i}\vec{p}\vec{s}_{12}} \int\limits_{-\infty}^{\infty} \frac{\mathrm{d}q_1}{2\pi} \mathrm{e}^{-\mathrm{i}q_1 z_1} \int\limits_{-\infty}^{\infty} \frac{\mathrm{d}q_1}{2\pi} \mathrm{e}^{-\mathrm{i}q_2 z_2} \left\{ \tilde{h}^1_+(p, q_1, q_2) - \tilde{h}^1_-(p, q_1, q_2) \right\}. \tag{46}$$

Let us calculate the integral with respect to the variable q_2. One-sided δ-functions can be presented as follows

$$\delta_+(\zeta) = \lim_{\varepsilon\to+0} \frac{\mathrm{i}}{\zeta + \mathrm{i}\varepsilon}\,, \qquad \delta_-(\zeta) = \lim_{\varepsilon\to+0} \frac{\mathrm{i}}{\zeta - \mathrm{i}\varepsilon}\,. \tag{47}$$

Let us consider a case when the first particle is in the upper phase $z_1 > 0$. Since the function $\tilde{h}^1_-(p, q_1, q_2)$ is an analytical function of the variable q_1 in the lower half of the complex plane, integration of this function with respect to q_1 yields zero. Subsequently for $z_2 > 0$, closing the contour of integration with respect to q_2 in the lower half of the complex plane, we find

$$\begin{aligned}&\lim_{\varepsilon\to+0} \int\limits_{-\infty}^{\infty} \frac{\mathrm{d}q_2}{2\pi} \frac{\mathrm{i}\,\mathrm{e}^{-\mathrm{i}q_2 z_2}}{(q_2 - \mathrm{i}\alpha_-(p))(q_2 + \mathrm{i}\alpha_+(p))(q_1 + q_2 + \mathrm{i}\varepsilon)}\\ &\qquad = \frac{\mathrm{i}\mathrm{e}^{-\alpha_+(p) z_2}}{(\alpha_+(p) + \alpha_-(p))(q_1 - \mathrm{i}\alpha_+(p))} + \frac{\mathrm{e}^{\mathrm{i}q_1 z_2}}{(q_1 + \mathrm{i}\alpha_-(p))(q_1 - \mathrm{i}\alpha_+(p))}\,. \end{aligned} \tag{48}$$

Now, let us integrate with respect to q_1. Since $z_1 > 0$, we have

$$\begin{aligned}&\int\limits_{-\infty}^{\infty} \frac{\mathrm{d}q_1}{2\pi} \left\{ \frac{\mathrm{i}\mathrm{e}^{-\alpha_+(p) z_2 - \mathrm{i}q_1 z_1}}{(\alpha_+(p) + \alpha_-(p))(q_1 - \mathrm{i}\alpha_+(p))} + \frac{\mathrm{e}^{\mathrm{i}q_1(z_2 - z_1)}}{(q_1 + \mathrm{i}\alpha_-(p))(q_1 - \mathrm{i}\alpha_+(p))} \right\} \frac{q_1 + \mathrm{i}\alpha_-(p))}{q_1 + \mathrm{i}\alpha_+(p))}\\ &\qquad = \frac{1}{2} \left\{ \frac{1}{\alpha_+(p))} \mathrm{e}^{-\alpha_+(p))|z_1 - z_2|} + \frac{1}{\alpha_+(p))} \frac{\alpha_+(p)) - \alpha_-(p))}{\alpha_+(p)) + \alpha_-(p))} \mathrm{e}^{-\alpha_+(p))(z_1 + z_2)} \right\}. \end{aligned} \tag{49}$$

By the inverse Fourier transformation with respect to the surface vector $\vec{p}$, we can obtain an expression for the pair correlation function for the case when both particles are in the upper half of space $z_1 > 0$, $z_2 > 0$.

$$h^1_{++}(s_{12}, z_1, z_2) = -\frac{A}{T} \frac{\mathrm{e}^{-\gamma_+ R_{12}}}{R_{12}} - \frac{A}{T} \int\limits_0^{\infty} J_0(p s_{12}) \frac{p\mathrm{d}p}{\alpha_+(p))} \frac{\alpha_+(p)) - \alpha_-(p))}{\alpha_+(p)) + \alpha_-(p))} \mathrm{e}^{-\alpha_+(p))(z_1 + z_2)}\,, \tag{50}$$

where the first term in (50) represents the spatially uniform part of the pair correlation function and the second term – the regular part of the pair correlation function contributed by spatial non-uniformity. $J_0(x)$ is the first order Bessel function

$$J_0(p s_{12}) = \frac{1}{\pi} \int\limits_0^{\pi} \mathrm{d}\varphi\, \mathrm{e}^{\mathrm{i}\, p s_{12}\, \cos\varphi}\,. \tag{51}$$

In a similar way, we can calculate the pair correlation function for other regions of space. Finally, for the pair correlation function of a two-phase system of point particles with the Yukawa potential of inter-particle interaction we obtain the expressions:

$$h^{\mathrm{l}}_{++}(s_{12},z_1,z_2) = -\frac{A}{T}\frac{\mathrm{e}^{-\gamma_+ R_{12}}}{R_{12}} - \frac{A}{T}\int\limits_0^\infty J_0(ps_{12})\,\frac{p\,dp}{\alpha_+(p))}\,\frac{\alpha_+(p)) - \alpha_-(p))}{\alpha_+(p)) + \alpha_-(p))}\,\mathrm{e}^{-\alpha_+(p))(z_1+z_2)}, \qquad \text{for} \quad z_1\,,z_2\,>\,0\,, \tag{52}$$

$$h^{\mathrm{l}}_{+-}(s_{12},z_1,z_2) = -\frac{A}{T}\int\limits_0^\infty J_0(ps_{12})p\mathrm{d}p\frac{\mathrm{e}^{-\alpha_+(p)z_1+\alpha_-(p)z_2}}{\alpha_+(p)) + \alpha_-(p))} \qquad \text{for} \quad z_1\,>\,0\,,z_2\,<\,0\,, \tag{53}$$

$$h^{\mathrm{l}}_{-+}(s_{12},z_1,z_2) = -\frac{A}{T}\int\limits_0^\infty J_0(ps_{12})p\mathrm{d}p\frac{\mathrm{e}^{\alpha_-(p)z_1-\alpha_+(p)z_2}}{\alpha_+(p)) + \alpha_-(p))} \qquad \text{for} \quad z_1\,<\,0\,,z_2\,>\,0\,, \tag{54}$$

$$h^{\mathrm{l}}_{--}(s_{12},z_1,z_2) = -\frac{A}{T}\frac{\mathrm{e}^{-\gamma_- R_{12}}}{R_{12}} + \frac{A}{T}\int\limits_0^\infty J_0(ps_{12})\,\frac{p\mathrm{d}p}{\alpha_-(p))}\,\frac{\alpha_+(p)) - \alpha_-(p))}{\alpha_+(p)) + \alpha_-(p))}\,\mathrm{e}^{\alpha_-(p))(z_1+z_2)}\,, \qquad \text{for} \quad z_1\,<\,0\,,z_2\,>\,0\,. \tag{55}$$

From (52–55) it is easy to derive the pair correlation functions for Coulomb systems of point particles [16,17]. This this end one should set $\alpha = 0$ and $A = Q_1Q_2$, where Q_1, Q_2 are the electric charges of particles 1 and 2.

6. Equation of state for a spatially uniform system with a Yukawa-like potential of interaction

If there are no external fields forming the interface, the equality (23) turns into the expression for the Helmholtz free energy of a spatially uniform system. At the same time, the part of the Helmholtz free energy responsible for the inter-particle interaction in the random phase approximation can be found by integrating with respect to the coupling parameter ξ [8]

$$F_{\mathrm{N}}^{\mathrm{l,RPA,ex}} = \frac{1}{2}\,\rho\,N\int\limits_V \mathrm{d}\vec{R}_{12}\,\Phi(R_{12})\int\limits_0^1 \mathrm{d}\xi\,\left[1\,+\,h(\xi,R_{12})\right]. \tag{56}$$

The spatially uniform part of the pair correlation function can be found from the respective spatially non-uniform expression by setting $\rho_+ = \rho_- = \rho$. Inclusion of the interaction parameter means that the constant of interaction A gets substituted for $\xi\,A$. Then, integrating with respect to $\vec{R}_{12}$, we have

$$A\int_0^\infty \mathrm{e}^{-\alpha\,R_{12}}\left(R_{12}\,-\,\xi\,\frac{A}{T}\,\mathrm{e}^{-R_{12}\sqrt{\alpha^2+\xi\,\varkappa^2}}\right) \,=\, \frac{A}{\alpha^2}\,+\,\frac{A}{4\pi\rho}\left(\sqrt{\alpha^2+\xi\,\varkappa^2}\,-\,\alpha\right)\,. \tag{57}$$

After integrating with respect to the parameter of interaction inclusion, for $F_{\mathrm{N}}^{\mathrm{l,RPA,ex}}$ we get the following expression

$$F_{\mathrm{N}}^{\mathrm{l,RPA,ex}} = VT\left(\frac{\alpha^3}{12\pi} - \frac{\left(\alpha^2+\varkappa^2\right)^{3/2}}{12\pi} + \frac{\alpha\,\varkappa^2}{8\pi} + \frac{\rho\,\varkappa^2}{2\alpha^2}\right). \tag{58}$$

Equation of state for a spatially uniform system can be found by differentiating the Helmholtz free energy with respect to the system's volume at a constant temperature and a constant number of particles.

$$P = -\left[\frac{\partial}{\partial V}F_{\mathrm{N}}\right]_{T,N} = -\left[\frac{\partial}{\partial V}\left(F_{\mathrm{N}}^{\mathrm{id}} + F_{\mathrm{N}}^{ex}\right)\right]_{T,N}. \tag{59}$$

This differentiation applies only to density ρ and the parameter $\varkappa$. Consequently, in the random phase approximation for the contribution of long-range inter-particle interaction to the pressure we have

$$\frac{1}{T}P^{\mathrm{l,RPA,ex}} = \frac{\rho\,\varkappa^2}{2\alpha^2} + \frac{\alpha^2\sqrt{\alpha^2+\varkappa^2}}{12\pi} - \frac{\sqrt{\alpha^2+\varkappa^2}\varkappa^2}{24\pi} - \frac{\alpha^3}{12\pi}. \tag{60}$$

Finally, since $\frac{1}{T}P^{\mathrm{id}} = \rho$, the pressure in the system equals

$$\frac{1}{T}P^{\mathrm{l,RPA}} = \rho + \rho\frac{\varkappa^2}{2\alpha^2} + \frac{\alpha^2\sqrt{\alpha^2+\varkappa^2}}{12\pi} - \frac{\varkappa^2\sqrt{\alpha^2+\varkappa^2}}{24\pi} - \frac{\alpha^3}{12\pi}. \tag{61}$$

It should be noted that in the case of ionic systems, the term $\rho\frac{\varkappa^2}{2\alpha^2}$ is absent due to the condition of electric neutrality of the system. Then, setting $\alpha = 0$, we get the equation of state for an ionic system

$$\frac{1}{T}P^{\mathrm{l,RPA}} = \rho - \rho\frac{\varkappa^3}{24\pi}, \tag{62}$$

which coincides with the results of the Debye-Huckel theory.

7. The contact theorem

For systems of particles that are spatially confined by a hard wall, certain exact relationships hold true. These relationships establish the connection between structural properties of the system near the surface and its thermodynamic properties. Notably, the contact theorem connects the value of the particle density with the pressure

$$\rho_a(z_1 = 0) = \frac{1}{T}P. \tag{63}$$

In [14], in the random phase approximation, the validity of this relation was shown for a spatially confined system of charged point particles. Let us now show that the particle density profile found satisfies the condition of the contact theorem.

In the case of a system confined by a hard wall we shall set the particle density in the lower phase equal to zero and for density profile in the upper phase $z > 0$ of the system with (31), setting $\rho_+ = \rho,\;\; \rho_- = 0$, we get

$$\frac{\rho(z_1)}{\rho} = 1 - \rho\frac{1}{T}\int\limits_{-\infty}^{0}\mathrm{d}z_2\int\limits_{S}\mathrm{d}\vec{s}_{12}\Phi\left(\sqrt{s_{12}^2+(z_1-z_2)^2}\right) + \frac{1}{2}g_+(z_1). \tag{64}$$

Taking into account the form of the Yukawa potential (1) and that of the regular part of the pair correlation function (29),

$$g_+(z_1) = -\frac{A}{T}\int\limits_0^\infty\frac{p\,\mathrm{d}p}{\alpha_+(p))}\frac{\alpha_+(p))-\alpha_-(p))}{\alpha_+(p))+\alpha_-(p))}\,\mathrm{e}^{-2\alpha_+(p)z_1}. \tag{65}$$

For $\rho(z_1)$ we get the following expression

$$\rho(z_1) = \rho\left\{1 + \frac{2\pi A\rho}{\alpha^2 T}\mathrm{e}^{-\alpha z_1} - \frac{A}{2T}\int\limits_0^\infty\frac{p\,\mathrm{d}p}{\alpha_+(p))}\frac{\alpha_+(p))-\alpha_-(p))}{\alpha_+(p))+\alpha_-(p))}\mathrm{e}^{-2\,\alpha_+(p)\,z_1}\right\}, \tag{66}$$

where

$$\alpha_+(p)) \;=\; \sqrt{p^2 \,+\, \alpha^2 + \varkappa^2}, \qquad \alpha_-(p)) \;=\; \sqrt{p^2 \,+\, \alpha^2}\,, \qquad \varkappa^2 \;=\; \frac{4\pi A\rho}{T}\,. \tag{67}$$

From equality (66), setting $z_1 = 0$, we obtain the value of particle density at the surface

$$\rho(0) \;=\; \rho + \rho\,\frac{\varkappa^2}{2\alpha^2} \;+\; \frac{\alpha^2\sqrt{\alpha^2+\varkappa^2}}{12\pi} \;-\; \frac{\varkappa^2\sqrt{\alpha^2+\varkappa^2}}{24\pi} \;-\; \frac{\alpha^3}{12\pi}\,, \tag{68}$$

which is identical to the expression (61) for the pressure of a spatially uniform system with the Yukawa potential of interaction. Therefore, we have proven the validity of the contact theorem for a system with the Yukawa-like inter-particle interaction in the random phase approximation.

8. Adsorption

Expression (66) established for the density profile can be written in the form

$$\frac{\rho(z_1)}{\rho} \;=\; 1 + \frac{\varkappa^2}{2\alpha^2\,T}\,\mathrm{e}^{-\alpha\,z_1} \;-\; \varkappa^2\frac{A}{2T}\int\limits_0^\infty \frac{p\,\mathrm{d}p}{\alpha_+(p)}\,\frac{1}{(\alpha_+(p)+\alpha_-(p))^2}\mathrm{e}^{-2\,\alpha_+(p)\,z_1}\,. \tag{69}$$

Contribution of the Yukawa potential to the particle distribution function increases with the increase of the system's density. It should be noted that the change of the sign of interaction does not reverse the sign of the term responsible for collective effects while the contribution of the initial potential reverses that sign. This property causes significant distinctions between surface properties of Coulomb systems and those of neutral particle systems.

Before moving on to computational calculations, we would like to point out that a system with the Yukawa potential of inter-particle interaction is characterized by two unitless parameters: the unitless inverse temperature $\alpha A/T = 1/T^*$, which characterizes the intensity of interaction, and the unitless density of the system $\rho^* = \rho/\alpha^3$.

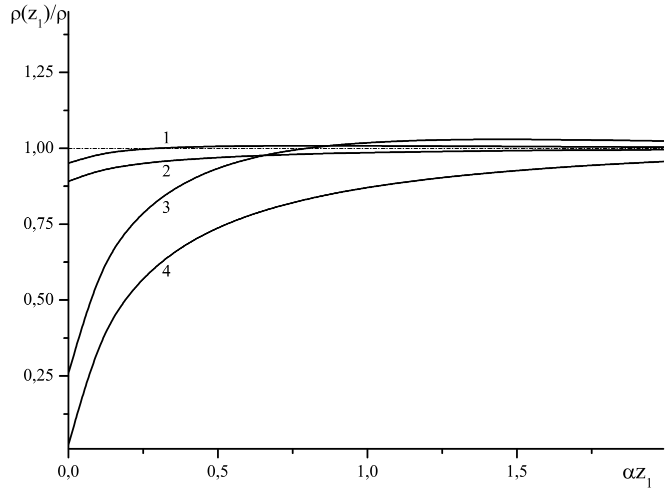

Figure 1. The profile of particle density. Curves are labeled by: (1) for $\frac{1}{T^*} = 10.0$ and $\rho^* = 0.0005$, (2) for $\frac{1}{T^*} = -10.0$ and $\rho^* = 0.0005$, (3) for $\frac{1}{T^*} = 10.0$ and $\rho^* = 0.005$, (4) for $\frac{1}{T^*} = -10.0$ and $\rho^* = 0.005$.

In figure 1 the unitless profile of particle density $\rho(\alpha z_1)/\rho$ versus the unitless distance to the hard wall $z = \alpha z_1$. is shown. At small values of the unitless interaction coefficient $\alpha\,A/T < 1$ the term associated with the Yukawa potential plays the major role in the behaviour of the density profile. With the rise of the coefficient, the contribution of collective effects increases. At the same time, it remains negative regardless of the nature of interaction. For this reason, at small distances to the surface, where collective interactions are more important than the initial Yukawa potential, the value of the singlet function is less than the one for both the attractive and the repulsive interactions.

As the distance to the hard wall increases, the contribution of collective interactions decreases at a rate faster than $\frac{\varkappa^2}{2\alpha^2}\,\mathrm{e}^{-\alpha z_1}$. Consequently, with increasing distance of a particle from the surface, the density of the system becomes higher than the bulk value for repulsive interaction and remains lower than the bulk value for attractive interaction.

Another important characteristic of the surface properties of a system is the adsorption coefficient

$$\Gamma = \int_0^\infty \mathrm{d}z\,[\,\rho(z) - \rho\,]\,. \tag{70}$$

Substitution of the expression (66) into the equality for the adsorption coefficient (70) yields

$$\Gamma = \frac{\rho\,\varkappa^2}{2\alpha^3} - \frac{\varkappa^2}{32\pi}\,(\,2\ln 2 - 1\,) + \frac{\varkappa^2}{16\pi}\,\ln\left(1 + \frac{\alpha}{\sqrt{\alpha^2+\varkappa^2}}\right) - \frac{\alpha\,\left(\sqrt{\alpha^2+\varkappa^2} - \alpha\right)}{16\pi}\,. \tag{71}$$

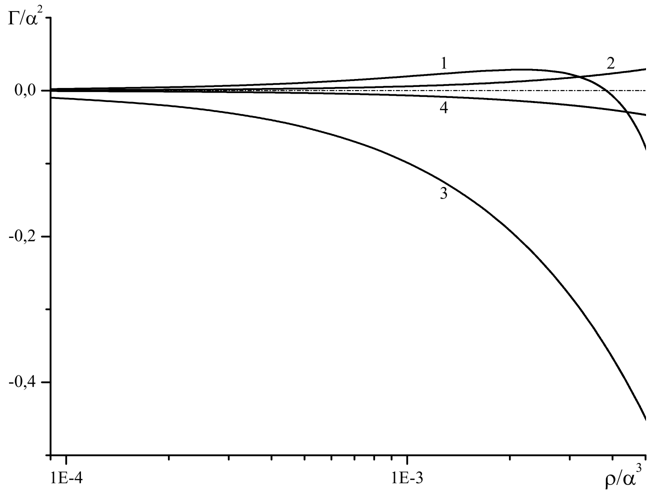

Figure 2. Density dependence of adsorption. Curves are labeled by: (1) for $\frac{1}{T^*}\alpha = 10$, (2) for $\frac{1}{T^*} = 1$, (3) for $\frac{1}{T^*} = -10$, (4) for $\frac{1}{T^*} = -1$.

In figure 2, the dependences of adsorption on the particle density ρ/α^3 are presented. The adsorption in the system considerably depends on the sign of interaction as well as on the range of the Yukawa potential. For systems with an repulsive interaction it is distinctive that the sign of adsorption reverses with transition to higher densities. As the interaction parameter $1/T^*$ increases, the point of sign reversal for the adsorption coefficient moves to the region of the higher densities.

9. Summary

In this work we have studied a spatially non-uniform system of point particles with the Yukawa potential of interaction. Such a system allows one to reveal distinctions between structural and thermodynamic properties of charged-particle systems and those of neutral-particle systems. These distinctions are also present in spatially uniform systems, in particular due to the inter-particle interaction contributing to the expression for the Helmholtz free energy. In systems of charged particles such a term is absent due to the condition of general electric neutrality [8]. For spatially non-uniform systems, this term leads to the appearance in density profiles of a coordinate dependence related to the effective interaction; in addition, density profiles acquire a dependence caused by the finiteness of the range of the initial potential. In the pair correlation function of neutral particles, no additional functional coordinate dependences appear compared to spatially non-uniform systems of charged particles. The expression for the density profile of a system obtained via functional differentiation of Helmholtz free energy with respect to the external field contains terms from the initial potential and the pair correlation function. At the same time, the profile of the particle density satisfies the condition of the contact theorem. Analysis of the expression found for the adsorption coefficient shows that in the case of an repulsive interaction, the sign of adsorption reverses with the increase in density. For sufficiently dense systems, adsorption remains negative regardless of the nature of interaction.

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Просторово обмежений плин із потенціалом взаємодії Юкави

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Розглянуто обмежений твердою стінкою плин з потенціалом взаємодії Юкави. Отримано розв'язок просторово неоднорідного рівняння Орнштейна-Церніке для парної кореляційної функції. Методом функціонального диференціювання вільної енергії за зовнішнім полем знайдено вираз для профілю густини частинок. Показано, що вклад у поведінку густини частинок поблизу поверхні вносить як вихідний потенціал, так і колективні ефекти екранування взаємодії. Розраховано залежність коефіцієнта адсорбції від густини числа частинок. Показано, що у випадку притягувальної взаємодії із збільшенням густини числа частинок системи змінюється знак коефіцієнта адсорбції.

Ключові слова: *просторово неоднорідне рівняння Орнштейна-Церніке, тверда стінка, контактна теорема, коефіцієнт адсорбції, потенціал Юкави*

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