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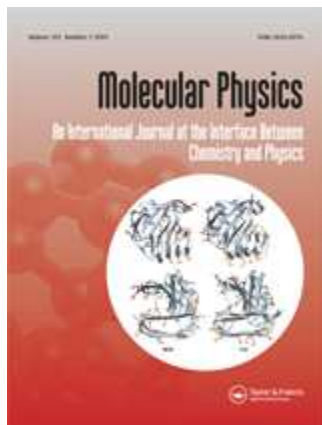
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RESEARCH ARTICLE

Yukawa fluid at a hard wall. Field theory description.

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We adopt a field-theoretical approach to study the structure and thermodynamics of a spatially confined fluid interacting with the Yukawa potential. We derive analytic expressions for the pressure, the Helmholtz free energy, the correlation function, the density profile, and the adsorption. Different simple analytic expressions of the density profile are compared with the numerical estimation of the mean field results. Beyond the mean field approximation, we show that fluctuations can contribute significantly to the properties of the system. Notably they lead to a desorption phenomenon regardless of the sign of the interaction. As a consequence, non monotonous density profile at the wall and adsorption curves as a function of the density are found for some systems. This behaviour rationalizes the ionic depletion phenomenon responsible for the anomalous behaviour of the electric capacitance as a function of temperature. Particular attention is given to the contact theorem condition.

Keywords: Inhomogeneous systems; Yukawa potential; Classical field theory; Contact theorem;

1. Introduction

Systems with a Yukawa-like potential of interaction are of considerable theoretical interest. The simplicity of the potential allows for a description of thermodynamics and structure of the Yukawa fluid. For hard spheres interacting with a Yukawa tail analytical solutions exist in the mean spherical approximation [1]. Any finite range interaction potential between point particles can be decomposed to a sum of Yukawa potentials with arbitrary accuracy. Such decompositions have been used for interaction potentials in simple liquids [2], colloid [3, 4] and other systems [5].

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1 The study on non-uniform systems of particles interacting with the Yukawa
2 potential remains well behind the research carried out on spatially uniform sys-
3 tems. One of the popular techniques of description of fluids near the surface is
4 the Henderson-Abraham-Barker approach [6]. In this approach the description of
5 a fluid near a surface reduces to that of a mixture of a fluid and of hard spheres
6 considered in the limit of infinite dilution and infinite hard sphere size. As a con-
7 sequence, the calculation of the fluid density profile reduces to the solution of the
8 Ornstein-Zernike integral equation for the fluid particle – wall distribution function
9 calculated from the known fluid particle distribution function in the bulk. Applica-
10 tion of this approach gave the possibility to evaluate the contribution of short-range
11 interactions to study the structural properties of spatially confined fluids. However
12 this approach in the simplest approximations like the mean spherical approxima-
13 tion does not take into account the contribution from the long range part of the
14 interactions. A better approach in this perspective is the use of inhomogeneous
15 integral equations which include in the convolution the density profile of fluid par-
16 ticles. For example, the application of a simple expression for the profile in the
17 form of step function provides the correct description of ionic fluids near a sur-
18 face. These results make use of the collective variables approach [7–9] to construct
19 cluster expansions for the pair and singlet distribution functions for a system of
20 point ions confined by a hard wall. In parallel, for the description of ionic systems
21 confined by wall, a density field theory has been developed [10–13] which also gave
22 the correct results for the description of the influence of ionic systems near a hard
23 wall.

24 These works, as well as computer simulations and numerical calculations of in-
25 tegral equations [14], have largely extended our understanding of surface effects
26 in systems confined by a hard wall and particularly in presence of electrostatic
27 interaction. The results for spatially non-uniform systems should satisfy certain
28 known exact relationships - sum rules. An important example is the so-called con-
29 tact theorem [15, 16]. It states for the neutral wall that the contact value of the
30 point particle density near a hard wall is determined by the pressure of the liquid
31 in the bulk volume. For a system of ions and charged wall there is an additional
32 contribution from the Maxwell pressure due to the force acting between charged
33 plates. The expressions found in the random phase approximation for the point
34 ion density profile, for instance, meet the requirements of the contact theorem [17].
35 They can be modified for non point ions by a simple change of the inverse Debye-
36 Hückel screening parameter κ to a new screening parameter Γ obtained in the
37 mean spherical description of homogeneous ionic systems [18]. Recently [19] the
38 collective variables technique was applied for the description of spatially confined
39 fluids with Yukawa potential of interaction. The principal difference between such
40 fluid with Yukawa interaction and an ionic fluid is connected with the electoneu-
41 trality condition for ionic systems which excludes some terms like Van der Waals
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1 contributions in the case of ions. Such contributions can play an important role in
2 the case of nonionic fluid. In [19], the contribution of such terms were taken into
3 account by construction in a simplified form.
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5 In this paper, we extend our previous work [20, 21] concerning the density field
6 theory description of a Yukawa fluid to the case of such a fluid near a hard wall.
7 The present work focuses on the analytical research of thermodynamic and struc-
8 tural properties of a spatially non-uniform one-component system of particles with
9 the Yukawa potential of interaction. We obtain expressions for the Helmholtz free
10 energy, pair correlation function and density distribution for such a system. It will
11 be shown that for the latter, the contact theorem is valid. The results obtained in
12 this paper, similar to [19], are presented for point particles with Yukawa interac-
13 tions. We hope in the future to modify them for non point particles with Yukawa
14 interactions using the mean spherical approximation result for homogeneous fluids
15 [1, 22] in a similar way as it was done for non point ionic systems [23].
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24 2. Model. Field theory formalism

25 We consider a fluid of particles interacting via a Yukawa potential given by
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$$27 \quad v(\mathbf{r}_{12}) = A \frac{e^{-\alpha r_{12}}}{r_{12}}. \quad (1)$$

28 We denote \mathbf{r}_{12} the vector between point 1 and point 2 and its length r_{12} . A is
29 the amplitude of the interaction, and α is the inverse range. We are interested in
30 the behaviour of such a fluid in the vicinity of a hard wall. For this purpose we
31 study this system in a finite slab of volume \mathcal{V} . The slab surface is \mathcal{S} parallel to
32 the wall and the slab width is L . One wall is situated at $z = 0$ and the other wall
33 is at $z = L$ where z is the coordinate perpendicular to the wall. Then we consider the
34 infinite width limit $L \rightarrow \infty$. In this limit, we do not make a distinction between
35 the average density in the system $\rho_t = N/V$ and the bulk density ρ_b that is far
36 from the interfaces, and use the latter when needed. For convenience, we use the
37 subscript b to denote the bulk value of the corresponding quantity.
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47 In a series of papers on ionic fluids [10–13, 24], we show that it is possible to
48 describe these systems using a field theoretical approach. The Hamiltonian of the
49 system is given by
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$$51 \quad \beta H[\rho] = \int \rho(\mathbf{r}_1) (\ln [\rho(\mathbf{r}_1)\Lambda^3] - 1) d\mathbf{r}_1 + \frac{\beta A}{2} \int \frac{e^{-\alpha r_{12}}}{r_{12}} \rho(\mathbf{r}_1)\rho(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \quad (2)$$

52 where $\rho(\mathbf{r})$ is the density and $\beta = 1/(k_B T)$ is the inverse temperature. We adopt
53 the canonical ensemble approach. We fix the number of particles. Thus we have
54 the condition: $\int \rho(\mathbf{r}) d\mathbf{r} = N$. To verify this condition in a formally unconstrained
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calculus we introduce the Lagrange multiplier λ such that

$$\left. \frac{\delta \beta H}{\delta \rho} \right|_{\rho_b} = \lambda. \quad (3)$$

It introduces the overall constraint on the number of particles. The partition function is

$$\Xi = \int \mathcal{D}\rho e^{-\beta H[\rho]} \quad (4)$$

where $\int \mathcal{D}\rho$ is the functional integral over all possible density distributions such that the total number of particles is N . The logarithm of the partition function gives the Helmholtz free energy

$$\beta F = -\ln \Xi. \quad (5)$$

For convenience we also introduce dimensionless quantities. We define the inverse length

$$B = \sqrt{4\pi\beta|A|\rho_b} \quad (6)$$

Note that the amplitude of potential can be positive or negative thus we take the absolute value of it. We will see further that for the negative attractive potentials there is a condition as shown in [19] to assure the stability of the system. From now on we introduce dimensionless lengths noted with a tilde $\tilde{\cdot}$ using B^{-1} as a unit of length. For instance a length \tilde{r} is defined $\tilde{r} = Br$. The inverse range of Yukawa potential in these units is $\tilde{\alpha} = \alpha/B$ and the dimensionless density $\tilde{\rho} = \rho/B^3$. For convenience it is also practical to introduce density normalised with respect to its bulk value $\hat{\rho} = \tilde{\rho}/\tilde{\rho}_b$. The length $1/B$ plays the role of the inverse Debye length, which in our previous papers has been used to define dimensionless quantities in the case of charged systems [10–13, 24]. This way we can use analogies between the present calculations for the Yukawa potential and the charged systems. This would not be possible if we adopted the alternative choice taken in [19] where the range of the potential $1/\alpha$ was used to define reduced quantities. This quantity is obviously diverging in the Coulomb systems because the interaction is long ranged ($\alpha \rightarrow 0$). In the formalism of statistical field theory we show [25, 26] that the entropic logarithmic term in the Hamiltonian does play an important role. The ionic density is selected as the field rather than a fictitious imaginary fluctuating potential [27–32]. In dimensionless quantities the Hamiltonian is

$$\beta H[\rho] = \int \tilde{\rho}(\tilde{\mathbf{r}}_1) \left(\ln \left[\tilde{\rho}(\tilde{\mathbf{r}}_1) \tilde{\Lambda}^3 \right] - 1 \right) d\tilde{\mathbf{r}}_1 + \frac{1}{8\pi\tilde{\rho}_b} \int \frac{e^{-\tilde{\alpha}\tilde{r}_{12}}}{\tilde{r}_{12}} \tilde{\rho}(\tilde{\mathbf{r}}_1) \tilde{\rho}(\tilde{\mathbf{r}}_2) d\tilde{\mathbf{r}}_1 d\tilde{\mathbf{r}}_2 \quad (7)$$

3. Mean field approximation.

3.1. Mean field equations

To obtain the thermodynamic properties of the system we need to calculate the partition function. The lowest order approximation of the partition function eq. (4) is the saddle point approximation for the functional integral which is also a mean field approximation MFA from the physical point of view. In the canonical formalism, it corresponds to fixing the Lagrange parameter λ such that the following relation is true for the average bulk particle density:

$$\left. \frac{\delta \beta H}{\delta \rho} \right|_{\rho_b} = \lambda. \quad (8)$$

The MFA quantities will be indexed *MF*. In reduced units eq. (8) reads

$$\ln[\hat{\rho}(\tilde{\mathbf{r}}_1)] + \tilde{V}(\tilde{\mathbf{r}}_1) - \tilde{V}_b = 0 \quad (9)$$

where focusing on the inhomogeneous quantities we have subtracted the bulk value and introduced the MFA potential \tilde{V} defined as

$$\tilde{V}(\tilde{\mathbf{r}}_1) = \frac{\varepsilon}{4\pi} \int \hat{\rho}(\tilde{\mathbf{r}}_2) \frac{e^{-\tilde{\alpha}\tilde{r}_{12}}}{\tilde{r}_{12}} d\tilde{\mathbf{r}}_2 \quad (10)$$

where ε denotes the sign of the interaction (i.e. $\varepsilon = 1$ if $A > 0$ and $\varepsilon = -1$ otherwise). The bulk value of this quantity is

$$\tilde{V}_b = \frac{\varepsilon}{\tilde{\alpha}^2}. \quad (11)$$

Taking the gradient of eq. (9), we have

$$\frac{\tilde{\nabla} \hat{\rho}(\tilde{\mathbf{r}}_1)}{\hat{\rho}(\tilde{\mathbf{r}}_1)} - \tilde{\mathbf{E}}(\tilde{\mathbf{r}}_1) = 0, \quad (12)$$

where $\tilde{\nabla}$ is the gradient operator in terms of dimensionless distances and where we define an equivalent of the electric field by

$$\tilde{\mathbf{E}}(\tilde{\mathbf{r}}_1) \equiv -\tilde{\nabla} \tilde{V}(\tilde{\mathbf{r}}_1). \quad (13)$$

Owing to the properties of the Yukawa potential we have

$$(\tilde{\Delta} - \tilde{\alpha}^2) \tilde{V}(\tilde{\mathbf{r}}_1) = -\varepsilon \hat{\rho}(\tilde{\mathbf{r}}_1). \quad (14)$$

Using the translational invariance parallel to the wall, the functions depend only on \tilde{z}_1 and replacing eq. (14) in eq. (12) we finally obtain

$$\frac{d}{d\tilde{z}_1} \left[\hat{\rho}(\tilde{z}_1) - \varepsilon \frac{1}{2} \tilde{\mathbf{E}}^2(\tilde{z}_1) + \varepsilon \frac{\tilde{\alpha}^2}{2} \tilde{V}^2(\tilde{z}_1) \right] = 0. \quad (15)$$

To simplify results we give expressions of the inhomogeneous quantities with respect to the first wall situated at $\tilde{z} = 0$. We are not interested in the second wall at $\tilde{z} = \tilde{L}$ in the large \tilde{L} limit. However, when needed the dependence over the entire slab is detailed, for instance when applying the periodic boundary conditions we need to write the functions for the whole slab. Also we present final results in terms of both dimensionless and dimensioned quantities.

3.2. Pressure invariant of MFA equations

Eq. (15) tells us that the quantity in brackets is constant and therefore it can be evaluated for instance in the bulk as

$$1 + \varepsilon \frac{\tilde{\alpha}^2}{2} \tilde{V}_b^2 = 1 + \frac{\varepsilon}{2\tilde{\alpha}^2}, \quad (16)$$

where we use the fact that in the bulk $\hat{\rho}$ is 1 and $\tilde{\mathbf{E}}$ vanishes. This quantity is the pressure within MFA:

$$\beta P = \rho_b \left(1 + \frac{\varepsilon}{2\tilde{\alpha}^2} \right) = \rho_b \left(1 + \frac{2\pi\beta A \rho_b}{\alpha^2} \right). \quad (17)$$

This expression is the mean field approximation which corresponds to the Van der Waals contribution. Outside the system, where there are no particles, we have another invariant which is simply $(1/2)\tilde{\mathbf{E}}^2(\tilde{z}) - (\tilde{\alpha}^2/2)\tilde{V}^2(\tilde{z})$, its value far from the interface is zero and therefore also at the interface. From the continuity of the potential and of its derivative due to eq. (14), we have that this is also true just at the wall inside the system $\tilde{z} = 0_+$ thus

$$\hat{\rho}(0_+) - \frac{\varepsilon}{2} \left(\tilde{\mathbf{E}}^2(0_+) - \tilde{\alpha}^2 \tilde{V}^2(0_+) \right) = \hat{\rho}(0_+). \quad (18)$$

As this quantity is constant we obtain the so-called contact theorem

$$\frac{\beta P}{\rho_b} = \hat{\rho}(0_+). \quad (19)$$

We should like to emphasize two aspects. First, it is worth noting that in this approximation we obtain the contact theorem as a consequence of the existence of an invariant of the differential equations which corresponds to the pressure. The approximation in [19] also verifies the contact theorem, but it is somehow by construction. Indeed, the profile is written as the integral of the potential in the system. At the wall, we only have half the integral of the potential which corresponds immediately to the Van der Waals approximation. However, this approximation of the profile is as we shall see a rather crude approximation. The second aspect we note is that the validity of the contact theorem can by linearity be generalized to a sum of Yukawa type potentials and thus be applied to a variety of potentials which can be presented as a superposition of Yukawa potentials. Thus in the mean

field approximation systems of particles interacting with these potentials verify the contact theorem.

3.3. Density profiles

From equations (12) - (14), we obtain a set of differential equations

$$\frac{\partial \hat{\rho}(\tilde{z})}{\partial \tilde{z}} = \hat{\rho}(\tilde{z}) \tilde{E}(\tilde{z}) \quad (20)$$

$$\frac{\partial \tilde{V}(\tilde{z})}{\partial \tilde{z}} = -\tilde{E}(\tilde{z}) \quad (21)$$

$$\frac{\partial \tilde{E}(\tilde{z})}{\partial \tilde{z}} = \varepsilon \hat{\rho}(\tilde{z}) - \tilde{\alpha}^2 \tilde{V}(\tilde{z}). \quad (22)$$

These relations are first order differential equations which have been solved starting from the linear solution in the bulk, back integrating towards the wall [33–35]. The boundary condition is set from the fact that the final point is obtained when we have the contact theorem. To start the integration process we feed the solver starting far from the wall with the linear equations solution derived from

$$\frac{\partial \hat{\rho}(\tilde{z})}{\partial \tilde{z}} = \tilde{E}(\tilde{z}) \quad (23)$$

$$\frac{\partial \tilde{V}(\tilde{z})}{\partial \tilde{z}} = -\tilde{E}(\tilde{z}) \quad (24)$$

$$\frac{\partial \tilde{E}(\tilde{z})}{\partial \tilde{z}} = \varepsilon \hat{\rho}(\tilde{z}) - \tilde{\alpha}^2 \tilde{V}(\tilde{z}), \quad (25)$$

where we use $\hat{\rho}_b = 1$. Deriving the third equation and introducing the first one, we find

$$\tilde{E}''(\tilde{z}) = (\varepsilon + \tilde{\alpha}^2) \tilde{E}(\tilde{z}) \quad (26)$$

which can be solved with the boundary condition that \tilde{E} vanishes in the bulk. Setting the contact value of the density to be the pressure, we find that the solutions are

$$\begin{cases} \hat{\rho}(\tilde{z}) = 1 + \frac{\varepsilon}{2\tilde{\alpha}^2} e^{-\sqrt{\tilde{\alpha}^2 + \varepsilon} \tilde{z}} \\ \tilde{V}(\tilde{z}) = \tilde{V}_b - \frac{\tilde{\alpha}^2}{2\tilde{\alpha}^2} e^{-\sqrt{\tilde{\alpha}^2 + \varepsilon} \tilde{z}} \\ \tilde{E}(\tilde{z}) = -\varepsilon \frac{\sqrt{\tilde{\alpha}^2 + \varepsilon}}{2\tilde{\alpha}^2} e^{-\sqrt{\tilde{\alpha}^2 + \varepsilon} \tilde{z}} \end{cases} \quad (27)$$

We can verify that for the linear solution we have, as expected, the condition required by the contact theorem that $(1/2)\tilde{E}^2(0_+) - (\tilde{\alpha}^2/2)\tilde{V}^2(0_+) = 0$. As mentioned earlier, we only give the expressions related to the first wall at $\tilde{z} = 0$ similar expressions can be derived for $\tilde{z} = \tilde{L}$.

Here, we also see that we have solutions only if $\tilde{\alpha}^2 + \varepsilon > 0$. This is always true for

repulsive potentials, whereas for attractive potentials we must have $\tilde{\alpha} > 1$. Using the reduced quantities used in [19], where the reduced density is $\rho^* = \rho/\alpha^3$ and the reduced temperature $T^* = k_B T/\alpha A$, we have

$$\tilde{\alpha} = \sqrt{\frac{T^*}{4\pi\rho^*}}. \quad (28)$$

We will now present a series of results for different values of ρ^* and T^* . For the sake of comparison we take the values used in [19]. They include both small and large values of $\tilde{\alpha}$. We compare the approximation in [19] and denote it by l_0 subscript

$$\hat{\rho}_{l_0}(\tilde{\alpha}\tilde{z}) = 1 + \frac{\varepsilon}{2\tilde{\alpha}^2} e^{-\tilde{\alpha}\tilde{z}}. \quad (29)$$

The linear mean field approximation eq. (27) denoted with subscript l_1

$$\hat{\rho}_{l_1}(\tilde{\alpha}\tilde{z}) = 1 + \frac{\varepsilon}{2\tilde{\alpha}^2} e^{-\sqrt{\tilde{\alpha}^2 + \varepsilon}\tilde{z}}. \quad (30)$$

And finally the MFA denoted $\hat{\rho}_{MFA}$ is computed numerically. Thus, the results for the approximation given in [19], the linearised equations (27) and the exact solution of the mean field equations (20)-(22) are shown in Figures 1-2. We note that for repulsive potential between particles ($T^* > 0$ or $\varepsilon > 0$) we obtain an effective attraction of the particles with the surface and vice versa for the attractive potential we have an effective repulsion with the surface. These trends are expected owing to the contact theorem. Also due to the fact that the solutions are monotonous, the adsorption coefficient is positive in the first case and negative in the second case. Analysing more in detail the results, for $\rho^* = 0.0005$ and $|T^*| = 0.1$, parameters taken from [19], we observe that there is no notable difference between the linearised profiles equations (29), (30) and the mean field equations (20)-(22). We choose not to show the corresponding profiles which are featureless. In this case, the parameter $\tilde{\alpha} = 3.99$ and we have that $\tilde{\alpha}^2 \gg 1$. This condition is the reason why all approximations predict similar profiles. On the contrary, for values of $\tilde{\alpha}$ of the order of 1, Figure 1, the linearised solution appears more accurate than the one given in [19]. In Figure 2, we present two other cases with $\tilde{\alpha}$ smaller or of the order of one. For repulsive potentials we have a small value of $\tilde{\alpha}$. The linear approximation and the approximation of ref. [19] are different from the mean field equations. In the other case when the potential is negative, the value of $\tilde{\alpha}$ close to one is bound by the condition $\tilde{\alpha} > 1$ and we have taken a value of the temperature so that $\tilde{\alpha}$ is close to its limiting value. Again the linear approximation and the approximation of ref. [19] are different from the mean field equations. However, in all cases, the linearised equations represent a simple and better approximation, although in the first case they over estimate the solution of MFA whereas they underestimate in the other. From eq. (28), we can note that the limit of large $\tilde{\alpha}$ corresponds to large

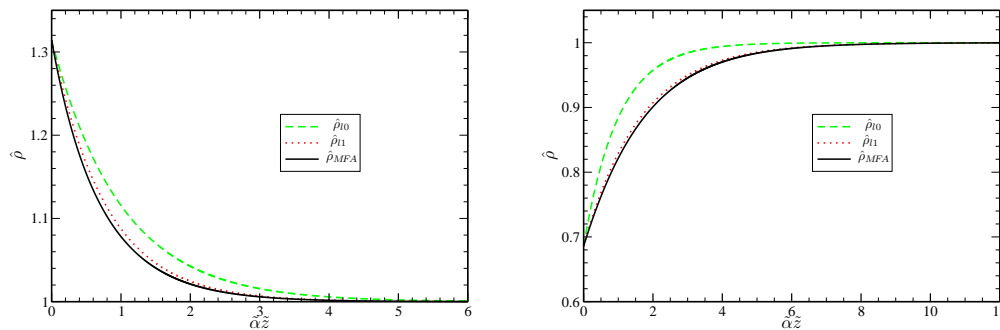


Figure 1. Mean field profiles in three different approximations for $\rho^* = 0.005$, $T^* = 0.1$ on the left and $T^* = -0.1$ on the right. The parameter $\tilde{\alpha} = 1.26$. In full line (black), we have the numerical solution of eq. (20)-(22), in dotted line (red), the linearised equations (27) and in dashed line (green), the approximation used in [19] eq. (29).

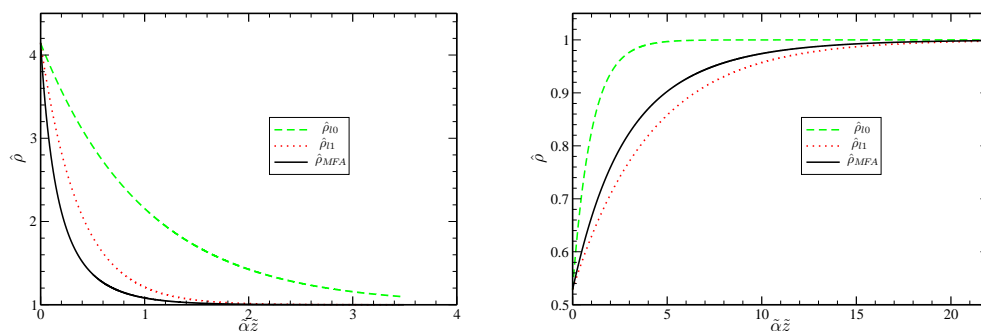


Figure 2. Identical quantities as shown in Figure 1 for $\rho^* = 0.005$, $T^* = 0.01$ on the left and $T^* = -1/15$ on the right with $\tilde{\alpha} = 0.399$ and $\tilde{\alpha} = 1.03$ respectively.

temperature or small density limits and in this regime all approximations are accurate. On the contrary, the linear approximation and the simple approximations of ref. [19] part from the mean field solution when the reduced temperature becomes small or the reduced density large. In these cases, it is worth solving the exact equations. As shown next in these domains the fluctuations also start becoming important.

4. Fluctuation and correlation effects on density profiles at the wall

In the previous Section, we have considered the mean field equations, where fluctuations are neglected. Here, we take them into account and therefore we have to expand the Hamiltonian.

4.1. Expansion of the Hamiltonian

Let us expand the Hamiltonian with respect to the bulk density of the system $\tilde{\rho}(\mathbf{r}) = \tilde{\rho}_b + d\tilde{\rho}(\mathbf{r})$. However, as the density fluctuates around the bulk density,

it is convenient to introduce the normalised density fluctuation $\delta\rho(\mathbf{r}) = d\tilde{\rho}(\mathbf{r})/\tilde{\rho}_b$. The expansion of the Hamiltonian is

$$\begin{aligned} \beta H[\rho] = & \beta H[\rho_b] + \int \delta\rho(\tilde{\mathbf{r}}_1) \left. \frac{\delta\beta H}{\delta(\delta\tilde{\rho}(\tilde{\mathbf{r}}_1))} \right|_{\rho_b} d\tilde{\mathbf{r}}_1 \\ & + \frac{1}{2} \int \delta\rho(\tilde{\mathbf{r}}_1)\delta\rho(\tilde{\mathbf{r}}_2) \left. \frac{\delta^2\beta H}{\delta(\delta\tilde{\rho}(\tilde{\mathbf{r}}_1))\delta(\delta\tilde{\rho}(\tilde{\mathbf{r}}_2))} \right|_{\rho_b} d\tilde{\mathbf{r}}_1 d\tilde{\mathbf{r}}_2 \\ & + \frac{1}{3!} \int \delta\rho(\tilde{\mathbf{r}}_1)\delta\rho(\tilde{\mathbf{r}}_2)\delta\rho(\tilde{\mathbf{r}}_3) \left. \frac{\delta^3\beta H}{\delta(\delta\tilde{\rho}(\tilde{\mathbf{r}}_1))\delta(\delta\tilde{\rho}(\tilde{\mathbf{r}}_2))\delta(\delta\tilde{\rho}(\tilde{\mathbf{r}}_3))} \right|_{\rho_b} d\tilde{\mathbf{r}}_1 d\tilde{\mathbf{r}}_2 d\tilde{\mathbf{r}}_3 + \dots \end{aligned} \quad (31)$$

In the canonical formalism fluctuations preserve the number of particles. Therefore $\int \delta\rho(\tilde{\mathbf{r}})d\tilde{\mathbf{r}} = 0$. The first term is simply the Hamiltonian functional from equation (2) for the bulk density in dimensionless units:

$$\beta H[\rho_b] = \tilde{V}\tilde{\rho}_b \left[\left(\ln[\tilde{\rho}_b\tilde{\Lambda}^3] - 1 \right) + \frac{\tilde{V}_b}{2} \right]. \quad (32)$$

The linear term is

$$\begin{aligned} \left. \frac{\delta\beta H}{\delta(\delta\rho(\mathbf{r}))} \right|_{\rho_b} &= \ln(\tilde{\rho}_b\tilde{\Lambda}^3) \int \delta\rho(\mathbf{r}_1)d\tilde{\mathbf{r}}_1 + \tilde{V}(z_1) - \tilde{V}_b \\ &= \frac{-e^{-\tilde{\alpha}z_1}}{2\tilde{\alpha}^2}, \end{aligned} \quad (33)$$

where we have used the fact that the integral of the density fluctuations vanishes in the canonical formalism and the mean potential eq. (10) in the vicinity of the wall is

$$\tilde{V}(\tilde{z}_1) = \frac{1}{2\tilde{\alpha}^2} (2 - e^{\tilde{\alpha}\tilde{z}_1}). \quad (34)$$

The quadratic term is

$$\frac{\tilde{\rho}}{2} \int \delta\rho(\tilde{\mathbf{r}}_1)\delta\rho(\tilde{\mathbf{r}}_2) \left[\tilde{\delta}(\tilde{\mathbf{r}}_1 - \tilde{\mathbf{r}}_2) + \frac{e^{-\tilde{\alpha}\tilde{r}_{12}}}{4\pi\tilde{r}_{12}} \right] d\tilde{\mathbf{r}}_1 d\tilde{\mathbf{r}}_2. \quad (35)$$

The first term comes from the expansion of the logarithmic term in the Hamiltonian. More generally, we have shown in [26] that these terms coming from the logarithm can be written for $n \geq 2$

$$(-1)^n \frac{(n-2)!}{n!} \int \delta\rho^n(\tilde{\mathbf{r}}_1)d\tilde{\mathbf{r}}_1. \quad (36)$$

Finally, we summarize the first terms in the expansion of the Hamiltonian

$$\begin{aligned} \beta H[\rho] = \tilde{\rho} \left[\tilde{V} \left(\ln(\tilde{\rho}\tilde{\Lambda}^3) - 1 + \frac{\tilde{V}_b}{2} \right) + \frac{1}{2} \int \delta\rho^2(\tilde{\mathbf{r}}_1) d\tilde{\mathbf{r}}_1 \right. \\ \left. + \frac{1}{2} \int \delta\rho(\tilde{\mathbf{r}}_1) \frac{e^{-\tilde{\alpha}\tilde{r}_{12}}}{\tilde{r}_{12}} \delta\rho(\tilde{\mathbf{r}}_2) d\tilde{\mathbf{r}}_1 d\tilde{\mathbf{r}}_2 \right. \\ \left. + \int \delta\rho(\tilde{\mathbf{r}}_1) (\tilde{V}(\tilde{z}_1) - \tilde{V}_b) - \frac{1}{3!} \int \delta\rho^3(\tilde{\mathbf{r}}_1) d\tilde{\mathbf{r}}_1 + \dots \right]. \end{aligned} \quad (37)$$

Note that we perform the expansion around a constant density $\tilde{\rho}_b$ and not the mean field profile which is inhomogeneous and known numerically only. In the Hamiltonian, the quadratic term is used to calculate the gaussian integrals and the linear and higher than quadratic terms are treated as coupling terms which are calculated perturbatively expanding the exponential. It is the linear term, in the expansion of the exponential treated as a perturbation, which allows to include the interaction with the wall in a non trivial way with terms of higher levels than a linear approximation.

4.2. The diagonal basis for the quadratic Hamiltonian operator

To calculate the functional integral using the gaussian integrals, it is necessary to have the quadratic term in a diagonal form. In the slab we expand the functions in the bases of eigenfunctions of the Yukawa potential operator, see [10] and appendix A

$$\delta\rho(\tilde{\mathbf{r}}_1) = \sum_{\tilde{\mathbf{K}}, \tilde{\mu} > 0} e^{i\tilde{\mathbf{K}}\tilde{\mathbf{R}}_1} \phi_{\tilde{K}, \tilde{\mu}}(\tilde{z}_1) \rho_{\tilde{\mathbf{K}}, \tilde{\mu}} \quad (38)$$

where $\tilde{\mathbf{R}}_1$ is vector component of $\tilde{\mathbf{r}}_1$ parallel to the wall, $\tilde{\mathbf{K}}$ and $\tilde{\mu}$ are the wave vectors in the directions parallel and orthogonal to the wall and the functions ϕ given in appendix A are

$$\phi_{\tilde{K}, \tilde{\mu}}(\tilde{z}) = \frac{1}{\sqrt{\tilde{L}(\tilde{\alpha}^2 + \tilde{K}^2 + \tilde{\mu}^2)}} \left((\sqrt{\tilde{\alpha}^2 + \tilde{K}^2} + i\tilde{\mu}) e^{i\tilde{\mu}\tilde{z}} - (\sqrt{\tilde{\alpha}^2 + \tilde{K}^2} - i\tilde{\mu}) e^{-i\tilde{\mu}\tilde{z}} \right) \quad (39)$$

As shown in appendix B, the Hamiltonian in this basis is

$$\begin{aligned} \beta H = \tilde{\rho}_b \left[\tilde{V} \left(\ln(\tilde{\rho}\tilde{\Lambda}^3) - 1 + \frac{\tilde{v}_0}{2} \right) + \frac{\tilde{S}}{2} \sum_{\tilde{\mathbf{K}}, \tilde{\mu} > 0} \left(1 + \frac{1}{\tilde{\alpha}^2 + \tilde{K}^2 + \tilde{\mu}^2} \right) \rho_{\tilde{\mathbf{K}}, \tilde{\mu}} \rho_{\tilde{\mathbf{K}}', \tilde{\mu}'} \right. \\ \left. + \int \delta\rho(\tilde{\mathbf{r}}_1) (\tilde{v}(z_1) - \tilde{v}_0) d\tilde{\mathbf{r}}_1 - \frac{1}{3!} \int \delta\rho^3(\tilde{\mathbf{r}}_1) d\tilde{\mathbf{r}}_1 + \dots \right] \end{aligned} \quad (40)$$

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where $\delta\rho(\tilde{\mathbf{r}}_1)$ is given by eq. (38).

5. Helmholtz free energy.

The free energy can be computed calculating

$$\frac{\beta F}{\mathcal{V}} = -\ln \left[\int \mathcal{D}\rho e^{-\beta H[\rho]} \right]. \quad (41)$$

The free energy is

$$\begin{aligned} \frac{\beta F}{\mathcal{V}} &= \rho_b (\ln(\rho_b \Lambda^3) - 1) + \frac{\rho_b \tilde{V}_b}{2} + \frac{B^3}{(2\pi)^2} \int_0^\infty \tilde{k}^2 d\tilde{k} \left[\ln \left(1 + \frac{1}{\tilde{k}^2 + \tilde{\alpha}^2} \right) - \frac{1}{\tilde{k}^2 + \tilde{\alpha}^2} \right] \\ &= \rho_b (\ln(\rho_b \Lambda^3) - 1) + \frac{\rho_b \tilde{V}_b}{2} + \frac{1}{8\pi} \left[\varepsilon \tilde{\alpha} - \frac{2}{3} \left[(\varepsilon + \tilde{\alpha}^2)^{3/2} - \tilde{\alpha}^3 \right] \right] B^3. \end{aligned} \quad (42)$$

We calculate the pressure using

$$-\beta P \mathcal{V} = \beta F - \beta \hat{\mu} N \quad (43)$$

where $\hat{\mu}$ here is the chemical potential, its value is given by

$$\beta \hat{\mu} = \left. \frac{\partial \beta F / \mathcal{V}}{\partial \rho} \right|_{T, \mathcal{V}} \quad (44)$$

$$= \ln(\rho_b \Lambda^3) + \tilde{V}_b + \frac{1}{8\pi \rho_b} \left[\varepsilon \tilde{\alpha} - \varepsilon \sqrt{\varepsilon + \tilde{\alpha}^2} \right] \quad (45)$$

so that we obtain for the pressure

$$\beta P = \rho_b + \rho_b \frac{B^2}{2\tilde{\alpha}^2} + \frac{B^3}{12\pi} \left[\tilde{\alpha}^2 \sqrt{\varepsilon + \tilde{\alpha}^2} - \frac{\varepsilon}{2} \sqrt{\tilde{\alpha}^2 + \varepsilon} - \tilde{\alpha}^3 \right]. \quad (46)$$

This expression is identical to that derived in [19]. As noted there, the second term $\rho_b B^2 / (2\tilde{\alpha}^2)$ is absent for ionic systems due to electroneutrality and in the infinite range limit $\alpha \rightarrow 0$ the pressure is the Debye limiting law

$$\beta P = \rho_b - \frac{B^3}{24\pi}, \quad (47)$$

where B plays the role of K_D the inverse Debye length used for ionic systems.

6. Correlation functions and density profile

6.1. Correlation functions

The expression of the correlation function is

$$\langle \delta\rho(\tilde{\mathbf{r}}_1)\delta\rho(\tilde{\mathbf{r}}_2) \rangle = \sum_{\tilde{\mathbf{K}},\tilde{\mu}>0} e^{i\tilde{\mathbf{K}}\tilde{\mathbf{R}}_1} \phi_{\tilde{\mathbf{K}},\tilde{\mu}}(\tilde{z}_1) \sum_{\tilde{\mathbf{K}}',\tilde{\mu}'>0} e^{i\tilde{\mathbf{K}}'\tilde{\mathbf{R}}_2} \phi_{\tilde{\mathbf{K}}',\tilde{\mu}'}^\dagger(\tilde{z}_2) \langle \rho_{\tilde{\mathbf{K}},\tilde{\mu}} \rho_{\tilde{\mathbf{K}}',\tilde{\mu}'} \rangle \quad (48)$$

where \dagger stands for the complex conjugate quantity. The gaussian averages are simple to calculate as in the diagonal basis they are

$$\langle \rho_{\tilde{\mathbf{K}},\tilde{\mu}} \rho_{\tilde{\mathbf{K}}',\tilde{\mu}'} \rangle = \frac{1}{\tilde{\rho}\tilde{\mathcal{S}}} \delta_{\tilde{\mathbf{K}},\tilde{\mathbf{K}}'} \delta_{\tilde{\mu},\tilde{\mu}'} \left(\frac{\tilde{\alpha}^2 + \tilde{K}^2 + \tilde{\mu}^2}{1 + \tilde{\alpha}^2 + \tilde{K}^2 + \tilde{\mu}^2} \right) \quad (49)$$

where the $\delta_{*,*}$ are Kronecker symbols. The correlation function is then

$$\langle \delta\rho(\mathbf{r}_1)\delta\rho(\mathbf{r}_2) \rangle = \frac{1}{(2\pi)^2 \tilde{\rho}_b} \int d\tilde{\mathbf{K}} \sum_{\tilde{\mu}>0} \phi_{\tilde{\mathbf{K}},\tilde{\mu}}(\tilde{z}_1) \phi_{\tilde{\mathbf{K}},\tilde{\mu}}^\dagger(\tilde{z}_2) e^{i\tilde{\mathbf{K}}(\tilde{\mathbf{R}}_1 - \tilde{\mathbf{R}}_2)} \left(\frac{\tilde{\alpha}^2 + \tilde{K}^2 + \tilde{\mu}^2}{1 + \tilde{\alpha}^2 + \tilde{K}^2 + \tilde{\mu}^2} \right) \quad (50)$$

Finally we obtain

$$\langle \delta\rho(\tilde{\mathbf{r}}_1)\delta\rho(\tilde{\mathbf{r}}_2) \rangle = \frac{1}{\tilde{\rho}_b} \left(\tilde{\delta}(\tilde{\mathbf{r}}_{12}) - \frac{1}{4\pi} \frac{e^{-\sqrt{1+\tilde{\alpha}^2}\tilde{r}_{12}}}{\tilde{r}_{12}} \right) \quad (51)$$

$$- \frac{1}{\tilde{\rho}_b} \int \tilde{K} d\tilde{K} J_0(\tilde{K}\tilde{R}_{12}) \frac{\tilde{\alpha}_+(\tilde{K}) - \tilde{\alpha}_-(\tilde{K})}{\tilde{\alpha}_+(\tilde{K})(\tilde{\alpha}_+(\tilde{K}) + \tilde{\alpha}_-(\tilde{K}))} e^{-\tilde{\alpha}_+(\tilde{K})(\tilde{z}_1 + \tilde{z}_2)} \quad (52)$$

where J_0 is a Bessel function of the first kind [36], $\tilde{\alpha}_+(\tilde{K}) = \sqrt{\varepsilon + \tilde{\alpha}^2 + \tilde{K}^2}$ and $\tilde{\alpha}_-(\tilde{K}) = \sqrt{\tilde{\alpha}^2 + \tilde{K}^2}$, the details of the calculation are given in Appendix C. The first term is the contribution from the bulk correlation function whereas the second term is purely inhomogeneous. With dimensions we have

$$\begin{aligned} \langle \rho(\mathbf{r}_1)\rho(\mathbf{r}_2) \rangle &= \rho_b^2 \langle \delta\rho(\tilde{\mathbf{r}}_1)\delta\rho(\tilde{\mathbf{r}}_2) \rangle \quad (53) \\ &= \rho_b \left(\delta(\mathbf{r}_{12}) - \beta A \rho \frac{e^{-\sqrt{1+\alpha^2}r_{12}}}{r_{12}} \right) \\ &\quad - \beta A \rho \int K dK J_0(KR_{12}) \frac{\alpha_+(K) - \alpha_-(K)}{\alpha_+(K)(\alpha_+(K) + \alpha_-(K))} e^{-\alpha_+(K)(z_1 + z_2)}. \end{aligned}$$

The expression is identical to that of ref. [19] where in this work the correlation function was calculated from the inhomogeneous integral equation theory in which direct correlation function is equal to $-\beta v(\mathbf{r})$ and the profile is considered as a step

function. This integral equation is equivalent to the differential equation considered in this paper and this is why results in both cases are the same.

6.2. Density profile

The inhomogeneous profile in the canonical framework is given by two contributions which correspond to one particle irreducible diagrams in field theory [37–39]. Thus the profile is

$$\begin{aligned} \langle \delta\rho(\tilde{\mathbf{r}}_1) \rangle = & \frac{\tilde{\rho}_b}{2\tilde{\alpha}^2} \int \langle \delta\rho(\tilde{\mathbf{r}}_1)\delta\rho(\tilde{\mathbf{r}}_2) \rangle e^{-\tilde{\alpha}\tilde{z}_2} d\tilde{\mathbf{r}}_2 \\ & + \frac{1}{2} \langle \delta\rho(\tilde{\mathbf{r}}_1)\delta\rho(\tilde{\mathbf{r}}_1) \rangle - \frac{1}{2} \langle \delta\rho(\tilde{\mathbf{r}}_1)\delta\rho(\tilde{\mathbf{r}}_1) \rangle \Big|_b \end{aligned} \quad (54)$$

where calculating the inhomogeneous profile we have subtracted the homogeneous bulk part.

The first contribution is related to the linear term in eq. (33), that is the interaction with the wall which is seen here as an external potential acting on the density via the correlation function. Its expression is

$$\frac{\tilde{\rho}_b}{2\tilde{\alpha}^2} \int \langle \delta\rho(\tilde{\mathbf{r}}_1)\delta\rho(\tilde{\mathbf{r}}_2) \rangle e^{-\tilde{\alpha}\tilde{z}_2} d\tilde{\mathbf{r}}_2 = \frac{1}{\tilde{\alpha}^2} \frac{e^{-\sqrt{\varepsilon+\tilde{\alpha}^2}z_1}}{1 + \sqrt{1 + \varepsilon/\tilde{\alpha}^2}} \quad (55)$$

$$= \frac{4\pi\beta A\rho}{\alpha^2} \frac{e^{-\sqrt{\varepsilon B^2 + \alpha^2}z_1}}{1 + \sqrt{1 + \varepsilon B^2/\alpha^2}}. \quad (56)$$

Refer to appendix C.1 for the details of calculation. In field theory, this term is a zero loop level contribution and is therefore comparable with a mean field term contribution. Thus, we note that it is similar to the expression in [19] in the limit $\tilde{\alpha} \gg 1$ in this case

$$\frac{\tilde{\rho}_b}{2\tilde{\alpha}^2} \int \langle \delta\rho(\tilde{\mathbf{r}}_1)\delta\rho(\tilde{\mathbf{r}}_2) \rangle e^{-\tilde{\alpha}\tilde{z}_2} d\tilde{\mathbf{r}}_2 \approx \frac{1}{2\tilde{\alpha}^2} e^{-\tilde{\alpha}\tilde{z}_1} = \frac{2\pi\beta A\rho}{\alpha^2} e^{-\alpha z_1} \quad (57)$$

Unfortunately the approximation does not satisfy the contact theorem as its value at the wall is $1/(\tilde{\alpha}^2(1 + \sqrt{1 + \varepsilon\tilde{\alpha}^2}))$ instead of $1/(2\tilde{\alpha}^2)$. The contact theorem is reached only asymptotically when $\tilde{\alpha} \gg 1$. For this reason, in the following, we will replace this approximate mean field like approximation with the exact mean field result derived in Section 3.3.

The second contribution to the profile is the one loop irreducible diagram written

as

$$\begin{aligned} \frac{1}{2} \langle \delta\rho(\mathbf{r}_1)\delta\rho(\mathbf{r}_1) \rangle - \frac{1}{2} \langle \delta\rho(\mathbf{r}_1)\delta\rho(\mathbf{r}_1) \rangle \Big|_b &= -\eta \int \tilde{K} d\tilde{K} \frac{(\tilde{\alpha}_+(\tilde{K}) - \tilde{\alpha}_-(\tilde{K}))e^{-2\tilde{\alpha}_+(\tilde{K})\tilde{z}_1}}{\tilde{\alpha}_+(\tilde{K})(\tilde{\alpha}_+(\tilde{K}) + \tilde{\alpha}_-(\tilde{K}))} \\ &= -\frac{\beta A}{2} \int K dK \frac{(\alpha_+(K) - \alpha_-(K))e^{-2\alpha_+(K)z_1}}{\alpha_+(K)(\alpha_+(K) + \alpha_-(K))}. \end{aligned} \tag{58}$$

Note that the constant in front of the first form of the expression is $\eta \equiv 1/(8\pi\tilde{\rho}_b) = B^3/(8\pi\rho)$ which similar to what is obtained in the case of the Coulomb for the first loop density profile correction. In terms of the reduced parameters we have $\eta = \sqrt{\pi\rho^*}/(T^*)^{3/2}$, we thus see that the corrections due to fluctuations become significant when ρ^* increases or T^* is small. These are also the limits where $\tilde{\alpha}$ is not much greater than 1 and the approximation in [19] and the linear approximation are no longer accurate. We therefore present results for the profiles where we substitute the linear type approximation of the mean field eq. (55) with the more accurate solution of the mean field equations presented in Section 3.3.

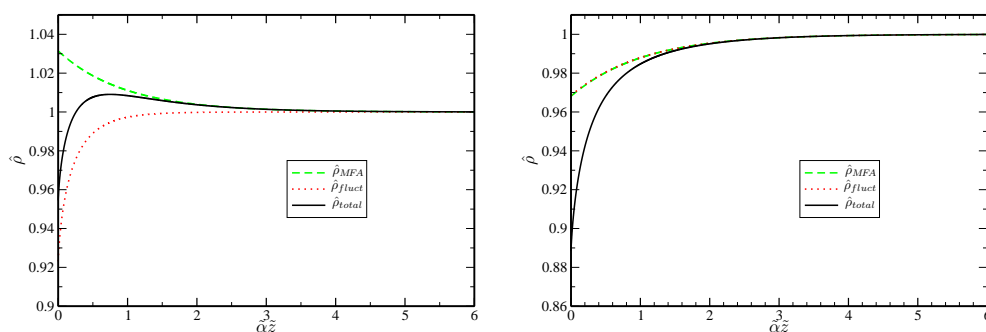


Figure 3. Density profiles for $\rho^* = 0.0005$, $T^* = 0.1$ on the left and $T^* = -0.1$ on the right with $\tilde{\alpha} = 3.99$. The curve in dashed line (green) is the mean field solution $\tilde{\rho}_{MFA}$, in dotted line (red) we have the contribution from the fluctuations $\tilde{\rho}_{fluct}$ and in full line (black) the combination of the two $\tilde{\rho}_{total}$.

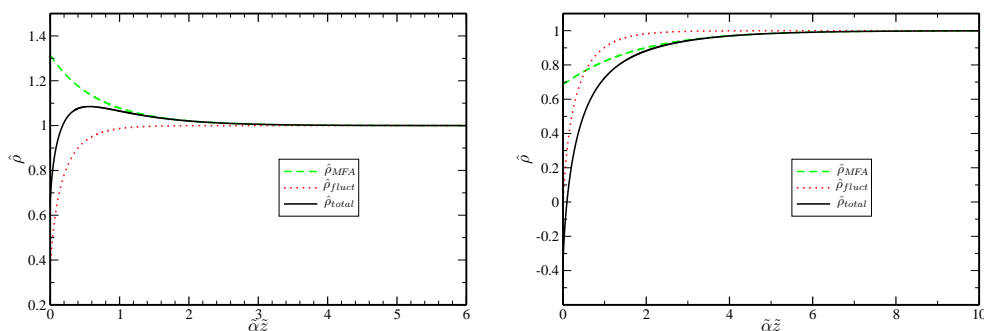


Figure 4. Identical quantities as shown in Figure 1 for $\rho^* = 0.005$, $T^* = 0.1$ on the left and $T^* = -0.1$ on the right with $\tilde{\alpha} = 1.26$.

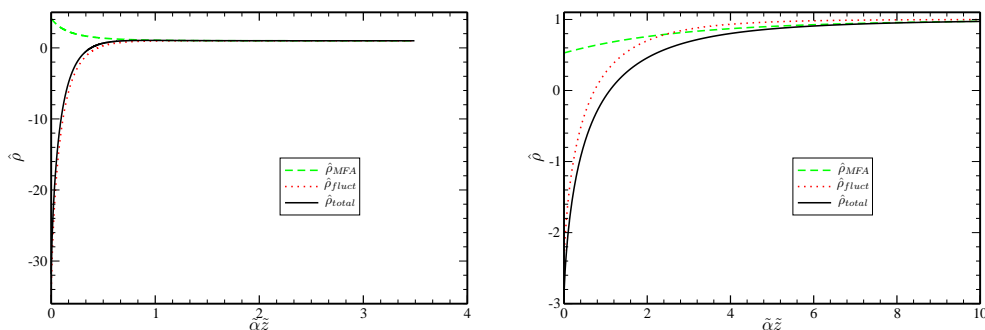


Figure 5. Identical quantities as shown in Figure 1 for $\rho^* = 0.005$, $T^* = 0.01$ on the left and $T^* = -1/15$ on the right with $\tilde{\alpha} = 0.399$ and $\tilde{\alpha} = 1.03$.

In Figures 3-5, we present the density profiles for different values of reduced parameters of density and temperature as used in [19]. We give the mean field density profile $\tilde{\rho}_{MFA}$, the contribution from fluctuations $\tilde{\rho}_{fluct}$ and the combination of the two $\tilde{\rho}_{total}$. In the figures, we observe that the mean field profile departs from one with a sign which depends on the sign of the interaction. Whereas the density profile associated to the fluctuations is always smaller than the bulk value. As a result for repulsive potentials we can have a non monotonous profile. In this event we can foresee that the sign of the adsorption it is not easy to assume the sign of the adsorption. The contribution from the fluctuations is proportional to η and becomes important when the reduced density is large and the reduced temperature small. This is the case for the values of the parameters ρ^* and T^* presented. It is interesting to note that the term from the fluctuations can dominate even for relatively small densities as long as the reduced temperature is small. In real units, this corresponds to rather low temperature or rather high the amplitude of the interaction. This effect amounts to a depletion of the density profile from the wall. It has already been pointed out for ionic systems and shown to be the origin of the anomalous behaviour of the electric capacitance with the temperature. In this context, numerical simulations and the field theoretical approach [40, 41] have shown that the anomalous capacitance behaviour can be seen for low value of the reduced density.

6.3. Adsorption

We can also calculate the reduced adsorption defined

$$\Gamma^* \equiv \frac{\Gamma}{\alpha^2} = \frac{1}{\alpha^2} \int dz (\rho(z) - \rho_b) \quad (59)$$

$$= \rho^* \tilde{\alpha} \int d\tilde{z} (\tilde{\rho}(z) - 1). \quad (60)$$

according to the different approximations of the density profile. We first start with the mean field like contributions presented in Section 3.3. The approximation from reference [19] gives

$$\frac{\Gamma_{l0}}{\alpha^2} = \varepsilon \frac{\rho^*}{2\tilde{\alpha}^2}. \quad (61)$$

The linearised equations give

$$\frac{\Gamma_{l1}}{\alpha^2} = \varepsilon \frac{\rho^*}{\tilde{\alpha}^2} \left(\frac{1}{\sqrt{1 + \varepsilon/\tilde{\alpha}^2}} \right) \left(\frac{1}{1 + \sqrt{1 + \varepsilon/\tilde{\alpha}^2}} \right). \quad (62)$$

The mean field contribution can only be determined numerically.

From the contribution to the density profile from the fluctuations eq. (58), we calculate the corresponding adsorption contribution

$$\frac{\Gamma_{fluct}}{\alpha^2} = \frac{-1}{32\pi\tilde{\alpha}^2} \left[\varepsilon(2 \ln 2 - 1) - 2\varepsilon \ln \left(1 + \frac{\tilde{\alpha}}{\sqrt{\tilde{\alpha}^2 + \varepsilon}} \right) + 2\tilde{\alpha}(\sqrt{\tilde{\alpha}^2 + \varepsilon} - \tilde{\alpha}) \right] \quad (63)$$

The expression is identical to that given in ref. [19]. Note that this contribution is always negative, irrespective of the sign of the interaction.

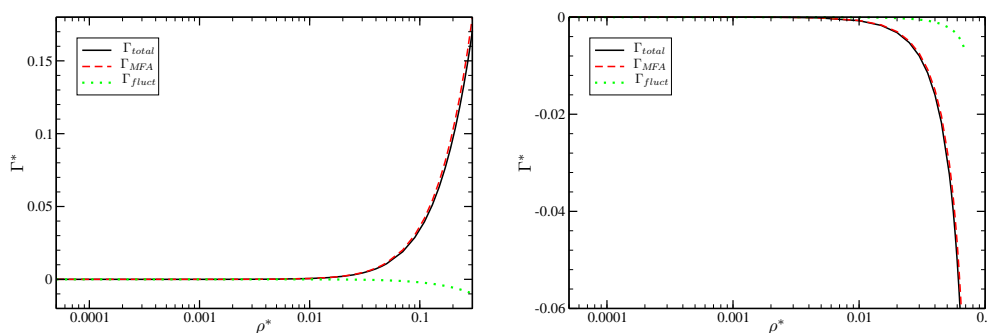


Figure 6. Adsorption as a function of reduced density ρ^* for different values of $T^* = +1$ on the left and $T^* = -1$ on the right.

In Figures 6-8, we present the adsorption as the sum of the mean field contribution and of the contribution from fluctuations as a function of ρ^* for different values of T^* . In Figure 6, we can observe that for not too small values of T^* of the order of one or even larger, the mean field solution dominates. However, the contribution from fluctuations becomes increasingly important when T^* becomes small. Clearly both contributions from the mean field and the fluctuations have the same sign and add to each other when the potential is attractive. But the case when the potential is repulsive is of interest because we have competition between the two contributions. This is seen in Figure 7 and 8 for $T^* = 0.1$ and $T^* = 1/20$. In the first example, we have a monotonous behaviour of the adsorption with the density,

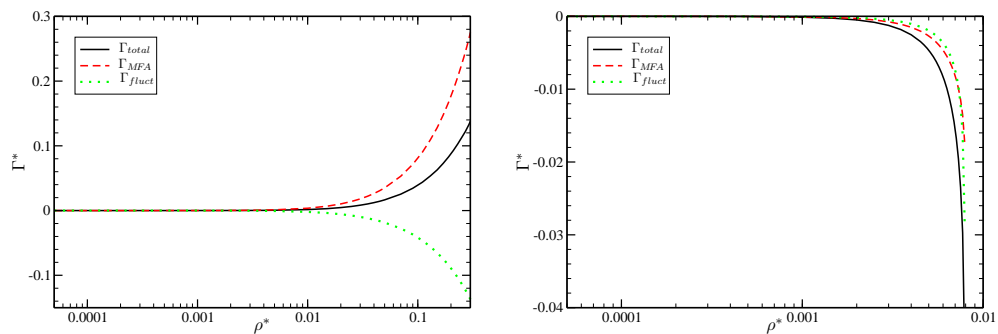


Figure 7. Adsorption as a function of reduced density ρ^* for different values of $T^* = 0.1$ on the left and $T^* = -0.1$ on the right.

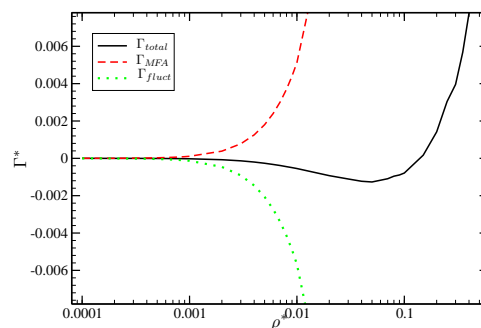


Figure 8. Adsorption as a function of reduced density ρ^* for $T^* = 1/20$.

in the second case we can see that the adsorption changes sign. The two contributions mostly compensate each other, however for the $T^* = 1/20$, the remaining part can have positive or negative sign.

7. Conclusion

In this paper, we study the behaviour of a fluid with Yukawa interactions in the vicinity of a wall. We calculate the pressure and Helmholtz free energy and present expressions for the correlation function, the density profile and for the adsorption. We compare different simple analytical expressions with the numerical estimation of the MFA equations. For the MFA equations we find an invariant corresponding to the pressure. We can demonstrate the validity of the contact theorem for this approximation. One interesting aspect is that the mean field solution and the contact theorem proof presented can be generalized to potentials which can be expanded as sums of Yukawa potentials. We also present results beyond the mean field approximation studying the effects of the fluctuations. The results beyond the MFA show that the fluctuations decrease the density profile whatever the character of the interaction - repulsive or attractive. This effect for the ionic density profiles

1 is just the depletion from a neutral wall responsible for the anomalous capacity
2 behaviour as a function of the temperature [40, 41]. Here we have the opportunity
3 to show that it exists for both attractive and repulsive interactions. We are able to
4 study systems with a competition between the intuitive mean field effects and the
5 correction due to fluctuations. As a consequence certain systems can have negative
6 or positive adsorption depending on the value of the density for a given value of
7 the potential.
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13
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Appendix A. Density distribution in the eigen functions of the Yukawa potential

In a similar way to what has been presented in [42] for the Coulomb potential, due to the translational invariance parallel to the wall, we expand the fluctuations of the density as follows

$$\delta\rho(\tilde{\mathbf{r}}_1) = \sum_{\tilde{\mathbf{K}}, \tilde{\mu}} \rho_{\tilde{\mathbf{K}}, \tilde{\mu}} e^{i\tilde{\mathbf{K}}\tilde{\mathbf{R}}_1} \phi_{\tilde{\mathbf{K}}, \tilde{\mu}}(\tilde{z}_1), \quad (\text{A1})$$

where the $\rho_{\tilde{\mathbf{K}}, \tilde{\mu}}$ are the amplitudes and the functions ϕ are eigenfunctions of the Yukawa potential such that

$$\int \frac{e^{-\alpha\tilde{r}}}{\tilde{r}} \delta\rho(\tilde{\mathbf{r}}) d\tilde{\mathbf{r}} = \lambda_{\tilde{\mathbf{K}}, \tilde{\mu}} \delta\rho(\tilde{\mathbf{r}}). \quad (\text{A2})$$

Owing to the properties of the Yukawa potential, we have $\lambda_{\tilde{\mathbf{K}}, \tilde{\mu}} = 1/(\tilde{\alpha}^2 + \tilde{K}^2 + \tilde{\mu}^2)$ and eigenvalues which verify

$$\tan\left(\frac{\tilde{\mu}\tilde{L}}{2}\right) = -\frac{\tilde{\mu}}{\sqrt{\tilde{\alpha}^2 + \tilde{K}^2}} \quad \text{and} \quad \tan\left(\frac{\tilde{\mu}\tilde{L}}{2}\right) = \frac{\sqrt{\tilde{\alpha}^2 + \tilde{K}^2}}{\tilde{\mu}}, \quad (\text{A3})$$

with $\tilde{\mu} > 0$. Using the fact that outside the slab we must have decaying functions, the function should be written

$$\phi_{\tilde{\mathbf{K}}, \tilde{\mu}}(\tilde{z}) = \begin{cases} A_1 e^{\sqrt{\tilde{\alpha}^2 + \tilde{K}^2}\tilde{z}} & \text{if } \tilde{z} < 0, \\ A_2 e^{i\tilde{\mu}\tilde{z}} + A_3 e^{-i\tilde{\mu}\tilde{z}} & \text{if } 0 < \tilde{z} < \tilde{L}, \\ A_4 e^{-\sqrt{\tilde{\alpha}^2 + \tilde{K}^2}\tilde{z}} & \text{if } \tilde{z} > \tilde{L}. \end{cases} \quad (\text{A4})$$

From the continuity of the functions at the walls and using periodic boundary conditions, we finally obtain inside the slab

$$\phi_{\tilde{\mathbf{K}}, \tilde{\mu}}(\tilde{z}) = \frac{1}{\sqrt{\tilde{L}(\tilde{\alpha}^2 + \tilde{K}^2 + \tilde{\mu}^2)}} \left((\sqrt{\tilde{\alpha}^2 + \tilde{K}^2} + i\tilde{\mu}) e^{i\tilde{\mu}\tilde{z}} - (\sqrt{\tilde{\alpha}^2 + \tilde{K}^2} - i\tilde{\mu}) e^{-i\tilde{\mu}\tilde{z}} \right), \quad (\text{A5})$$

where we have used periodic boundary conditions and normalised the function in the slab according to

$$\int_0^{\tilde{L}} \phi_{\tilde{\mathbf{K}}, \tilde{\mu}}(\tilde{z}) \phi_{\tilde{\mathbf{K}}, \tilde{\mu}}^\dagger(\tilde{z}) d\tilde{z} = 1. \quad (\text{A6})$$

These functions represent a complete set of orthonormal functions.

Appendix B. Diagonal terms

The quadratic terms can be written

$$\begin{aligned} \frac{1}{2} \int \delta\rho^2(\tilde{\mathbf{r}}_1) d\tilde{\mathbf{r}}_1 &= \int d\tilde{\mathbf{r}}_1 \sum_{\tilde{\mathbf{K}}, \tilde{\mu} > 0} e^{i\tilde{\mathbf{K}}\tilde{\mathbf{R}}_1} \phi_{\tilde{K}, \tilde{\mu}}(\tilde{z}_1) \rho_{\tilde{\mathbf{K}}, \tilde{\mu}} \sum_{\tilde{\mathbf{K}}', \tilde{\mu}' > 0} e^{-i\tilde{\mathbf{K}}'\tilde{\mathbf{R}}_1} \phi_{\tilde{K}', \tilde{\mu}'}^\dagger(\tilde{z}_1) \rho_{\tilde{\mathbf{K}}', \tilde{\mu}'}^\dagger \\ &= \tilde{S} \sum_{\tilde{\mathbf{K}}, \tilde{\mu} > 0} \rho_{\tilde{\mathbf{K}}, \tilde{\mu}} \rho_{\tilde{\mathbf{K}}, \tilde{\mu}}^\dagger, \end{aligned} \quad (\text{B1})$$

where \tilde{S} is the dimensionless surface parallel to the walls and we have used the normalisation condition eq. (A6).

The interaction quadratic term

$$\begin{aligned} \frac{1}{4\pi} \int \delta\rho(\tilde{\mathbf{r}}_1) \frac{e^{-\tilde{\alpha}\tilde{r}_{12}}}{\tilde{r}_{12}} \delta\rho(\tilde{\mathbf{r}}_2) d\tilde{\mathbf{r}}_1 d\tilde{\mathbf{r}}_2 &= \int d\tilde{\mathbf{r}}_1 d\tilde{\mathbf{r}}_2 \sum_{\tilde{\mathbf{K}}, \tilde{\mu} > 0, \tilde{\mathbf{K}}', \tilde{\mu}' > 0} e^{i\tilde{\mathbf{K}}\tilde{\mathbf{R}}_1 - i\tilde{\mathbf{K}}'\tilde{\mathbf{R}}_2} \frac{e^{-\tilde{\alpha}\tilde{r}_{12}}}{\tilde{r}_{12}} \\ &\quad \phi_{\tilde{K}, \tilde{\mu}}(\tilde{z}_1) \phi_{\tilde{K}', \tilde{\mu}'}^\dagger(\tilde{z}_2) \rho_{\tilde{\mathbf{K}}, \tilde{\mu}} \rho_{\tilde{\mathbf{K}}', \tilde{\mu}'}^\dagger. \end{aligned} \quad (\text{B2})$$

We can change variables using $d\tilde{\mathbf{R}}_1 d\tilde{\mathbf{R}}_{12}$ and integrating over $\tilde{\mathbf{R}}_1$ we obtain due to the orthogonality of $e^{i\tilde{\mathbf{K}}\tilde{\mathbf{R}}}$: the Kronecker symbol $\delta_{\tilde{\mathbf{K}}, \tilde{\mathbf{K}}'}$. Which can then be summed over $\tilde{\mathbf{K}}'$. We can integrate over $\tilde{\mathbf{R}}_{12}$ and we obtain an integral of the form

$$\int_0^{\tilde{L}} \frac{e^{-\sqrt{\tilde{K}^2 + \tilde{\alpha}^2}|\tilde{z}_1 - \tilde{z}_2|}}{2\sqrt{\tilde{K}^2 + \tilde{\alpha}^2}} \phi_{\tilde{K}, \tilde{\mu}}(\tilde{z}_2) d\tilde{z}_2 = \frac{1}{\tilde{\alpha}^2 + \tilde{K}^2 + \tilde{\mu}^2} \phi_{\tilde{K}, \tilde{\mu}}(\tilde{z}_1), \quad (\text{B3})$$

where we have used the properties of the $\phi_{\tilde{K}, \tilde{\mu}}$ functions which are eigenfunctions of the Yukawa potential. Finally we have

$$\frac{1}{4\pi} \int \delta\rho(\tilde{\mathbf{r}}_1) \frac{e^{-\tilde{\alpha}\tilde{r}_{12}}}{\tilde{r}_{12}} \delta\rho(\tilde{\mathbf{r}}_2) d\tilde{\mathbf{r}}_1 d\tilde{\mathbf{r}}_2 = \sum_{\tilde{\mathbf{K}}, \tilde{\mu} > 0} \frac{1}{\tilde{\alpha}^2 + \tilde{K}^2 + \tilde{\mu}^2} \rho_{\tilde{\mathbf{K}}, \tilde{\mu}} \rho_{\tilde{\mathbf{K}}, \tilde{\mu}}^\dagger. \quad (\text{B4})$$

Appendix C. Correlation function

From eq. (50), we introduce the following notations $\tilde{\alpha}_+(\tilde{K}) = \sqrt{\varepsilon + \tilde{\alpha}^2 + \tilde{K}^2}$ and $\tilde{\alpha}_-(\tilde{K}) = \sqrt{\tilde{\alpha}^2 + \tilde{K}^2}$ so that

$$\langle \delta\rho(\tilde{\mathbf{r}}_1) \delta\rho(\tilde{\mathbf{r}}_2) \rangle = \frac{1}{(2\pi)^2 \tilde{\rho}_b} \int d\tilde{\mathbf{K}} \sum_{\tilde{\mu} > 0} \phi_{\tilde{K}, \tilde{\mu}}(\tilde{z}_1) \phi_{\tilde{K}, \tilde{\mu}}^\dagger(\tilde{z}_2) e^{i\tilde{\mathbf{K}}(\tilde{\mathbf{R}}_1 - \tilde{\mathbf{R}}_2)} \left(\frac{\tilde{\alpha}_-^2(\tilde{K}) + \tilde{\mu}^2}{\tilde{\alpha}_+^2(\tilde{K}) + \tilde{\mu}^2} \right). \quad (\text{C1})$$

We need to compute

$$\sum_{\tilde{\mu}>0} \phi_{\tilde{K},\tilde{\mu}}(\tilde{z}_1) \phi_{\tilde{K}',\tilde{\mu}'}^\dagger(\tilde{z}_2) \left(\frac{\tilde{\alpha}_-^2(\tilde{K}) + \tilde{\mu}^2}{\tilde{\alpha}_+^2(\tilde{K}) + \tilde{\mu}^2} \right) = \sum_{\tilde{\mu}>0} \frac{1}{\tilde{L}} \left(\frac{\tilde{\alpha}_-^2(\tilde{K}) + \tilde{\mu}^2}{\tilde{\alpha}_+^2(\tilde{K}) + \tilde{\mu}^2} \right) \quad (C2)$$

$$\left[\begin{aligned} & (e^{i\tilde{\mu}(\tilde{z}_1-\tilde{z}_2)} + e^{-i\tilde{\mu}(\tilde{z}_1-\tilde{z}_2)}) \\ & - \frac{(\tilde{\alpha}_-(\tilde{K}) + i\tilde{\mu})^2}{\tilde{\alpha}_+^2(\tilde{K})} e^{i\tilde{\mu}(\tilde{z}_1+\tilde{z}_2)} \\ & - \frac{(\tilde{\alpha}_-(\tilde{K}) - i\tilde{\mu})^2}{\tilde{\alpha}_+^2(\tilde{K})} e^{-i\tilde{\mu}(\tilde{z}_1+\tilde{z}_2)} \end{aligned} \right]. \quad (C3)$$

We introduce the continuous integral in the $\tilde{L} \rightarrow \infty$ limit where $\sum_{\tilde{\mu}>0} \rightarrow L/(4\pi) \int_{-\infty}^{\infty} d\tilde{\mu}$ where we have extended the integral over all reals, the contribution from $\tilde{\mu} = 0$ vanishes as it is of zero measure and non singular for $\tilde{z}_1 \neq \tilde{z}_2$. The first two terms in the brackets depend on $\tilde{z}_1 - \tilde{z}_2$ and give the known homogeneous contribution

$$\frac{1}{\tilde{\rho}_b} \left(\tilde{\delta}(\tilde{\mathbf{r}}_{12}) - \frac{\varepsilon}{4\pi} \frac{e^{-\sqrt{\varepsilon+\tilde{\alpha}^2}\tilde{r}_{12}}}{\tilde{r}_{12}} \right), \quad (C4)$$

where we have separated $(\tilde{\alpha}_-^2(\tilde{K}) + \tilde{\mu}^2)/(\tilde{\alpha}_+^2(\tilde{K}) + \tilde{\mu}^2) = 1 - \varepsilon/(\tilde{\alpha}_+^2(\tilde{K}) + \tilde{\mu}^2)$, the term related to 1 giving the Dirac distribution. The inhomogeneous contribution is

$$\langle \delta\rho(\tilde{\mathbf{r}}_1) \delta\rho(\tilde{\mathbf{r}}_2) \rangle = \frac{1}{(2\pi)^2 \tilde{\rho}} \int d\tilde{\mathbf{K}} \frac{-1}{4\pi} \int_{-\infty}^{\infty} d\tilde{\mu} \frac{\left[(\tilde{\alpha}_-(\tilde{K}) + i\tilde{\mu})^2 e^{i\tilde{\mu}(\tilde{z}_1-\tilde{z}_2)} + (\tilde{\alpha}_-(\tilde{K}) - i\tilde{\mu})^2 e^{-i\tilde{\mu}(\tilde{z}_1-\tilde{z}_2)} \right]}{\tilde{\mu}^2 + \tilde{\alpha}_+^2(\tilde{K})}. \quad (C5)$$

For the integration over $\tilde{\mu}$, we have two poles at $\pm i\tilde{\alpha}_+(\tilde{K})$, we can perform contour integrations with the semi-circles in the upper plane and the lower plane and we obtain

$$\langle \delta\rho(\tilde{\mathbf{r}}_1) \delta\rho(\tilde{\mathbf{r}}_2) \rangle = -\frac{1}{\tilde{\rho}_b} \int \tilde{K} d\tilde{K} J_0(\tilde{K} \tilde{R}_{12}) \frac{(\tilde{\alpha}_+(\tilde{K}) - \tilde{\alpha}_-(\tilde{K})) e^{-\tilde{\alpha}_+(\tilde{K})(\tilde{z}_1+\tilde{z}_2)}}{\tilde{\alpha}_+(\tilde{K})(\tilde{\alpha}_+(\tilde{K}) + \tilde{\alpha}_-(\tilde{K}))} \quad (C6)$$

where J_0 is a Bessel function of the first kind [36], the result is identical to the one obtained in [19].

C.1. Density profile

To calculate the first term in the density profile, it is convenient to expand all terms in the $e^{i\mathbf{K}\tilde{\mathbf{R}}}$, $\phi_{\tilde{\mu}}(\tilde{z})$ basis. We first decompose $e^{-\tilde{\alpha}\tilde{z}}$ on this basis

$$e^{-\tilde{\alpha}\tilde{z}} = \sum_{\tilde{\mathbf{K}}, \tilde{\mu} > 0} \delta_{\tilde{\mathbf{K}}, 0} \frac{4i\tilde{\mu}\tilde{\alpha}}{(\tilde{\alpha}^2 + \tilde{\mu}^2)^{3/2}} e^{-i\tilde{\mathbf{K}}\tilde{\mathbf{R}}} \phi_{\tilde{\mathbf{K}}, \tilde{\mu}}^{\dagger}(\tilde{z}). \quad (\text{C7})$$

Introducing this expression, we have

$$\begin{aligned} \frac{\tilde{\rho}_b}{2\tilde{\alpha}^2} \int \langle \delta\rho(\tilde{\mathbf{r}}_1)\delta\rho(\tilde{\mathbf{r}}_2) \rangle e^{-\tilde{\alpha}\tilde{z}_2} d\tilde{\mathbf{r}}_2 &= \frac{\tilde{\rho}_b}{2\tilde{\alpha}^2} \frac{1}{\tilde{\rho}_b\tilde{S}} \int d\tilde{\mathbf{R}}_2 d\tilde{z}_2 \sum_{\tilde{\mathbf{K}}, \tilde{\mu} > 0} \sum_{\tilde{\mathbf{K}'}, \tilde{\mu}' > 0} \phi_{\tilde{\mathbf{K}}, \tilde{\mu}}(\tilde{z}_1) \phi_{\tilde{\mathbf{K}'}, \tilde{\mu}'}^{\dagger}(\tilde{z}_2) e^{-i\tilde{\mathbf{K}}(\tilde{\mathbf{R}}_1 - \tilde{\mathbf{R}}_2)} \delta_{\tilde{\mathbf{K}'}, 0} \frac{4i\tilde{\mu}'\tilde{\alpha}}{(\tilde{\alpha}^2 + \tilde{\mu}'^2)^{3/2}} e^{-i\tilde{\mathbf{K}'}\tilde{\mathbf{R}}_2} \\ &= -\frac{1}{2\tilde{\alpha}^2} \sum_{\tilde{\mu} > 0} \frac{4i\tilde{\mu}\tilde{\alpha}}{(\tilde{\alpha}^2 + \tilde{\mu}^2)^{3/2}} \frac{\tilde{\alpha}^2 + \tilde{\mu}^2}{\varepsilon + \tilde{\alpha}^2 + \tilde{\mu}^2}. \end{aligned} \quad (\text{C9})$$

Taking the limit $\tilde{L} \rightarrow \infty$, we can go from discrete summation to continuous integral $\sum_{\tilde{\mu} > 0} \rightarrow L/(4\pi) \int_{-\infty}^{\infty} d\tilde{\mu}$. Performing contour integration in the upper and lower complex plane according to the poles, we obtain

$$\frac{\tilde{\rho}_b}{2\tilde{\alpha}^2} \int \langle \delta\rho(\tilde{\mathbf{r}}_1)\delta\rho(\tilde{\mathbf{r}}_2) \rangle e^{-\tilde{\alpha}\tilde{z}_2} d\tilde{z}_2 = \frac{1}{\tilde{\alpha}^2} \frac{e^{-\sqrt{\varepsilon + \tilde{\alpha}^2}\tilde{z}_1}}{1 + \sqrt{1 + \varepsilon/\tilde{\alpha}^2}} \quad (\text{C10})$$

$$= \frac{4\pi\beta A\rho}{\alpha^2} \frac{e^{-\sqrt{\varepsilon B^2 + \alpha^2}z_1}}{1 + \sqrt{1 + \varepsilon B^2/\alpha^2}}. \quad (\text{C11})$$

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