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Плин із подвійним потенціалом Юкави поблизу твердої поверхні: теоретико-польовий підхід

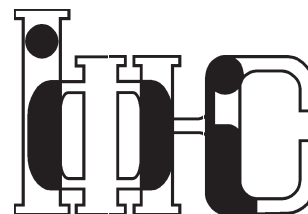
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ФІЗИКИ  
КОНДЕНСОВАНИХ  
СИСТЕМ

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FLUID INTERACTING WITH A TWO-YUKAWA POTENTIAL  
AT A HARD WALL: FIELD THEORY TREATMENT

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**Плин із подвійним потенціалом Юкави поблизу твердої поверхні: теоретико-польовий підхід**

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**Анотація.** В рамках теоретико-польового підходу досліджуються рівноважні властивості обмеженого твердою поверхнею плин з подвійним потенціалом Юкави. Отримано середньо-польові рівняння, внаслідок яких аналітичні вирази для профілю густини порівнюються з чисельно розрахованими значеннями. За межами наближення середнього поля виведено аналітичні вирази для вільної енергії та кореляційної функції. Знайдено вклад до профілю густини та коефіцієнту адсорбції від гаусівських флуктуацій. Як наслідок, для деяких систем спостерігаються коливальна поведінка профілю та немонотонна залежність коефіцієнта адсорбції від густини та температури. Аналітично показано, що середньо-польова та флуктуаційна частини профілю густини задовольняють умові контактної теореми.

**Fluid interacting with a two-Yukawa potential at a hard wall: field theory treatment**

I. Kravtsiv, M. Holovko, D. di Caprio, J. Stafiej

**Abstract.** In the framework of the field theory approach we study equilibrium properties of a two-Yukawa fluid confined by a hard wall. We derive mean field equations allowing for numerical evaluation of the density profile which is compared to different analytical estimations. Beyond the mean field approximation analytical expressions for the free energy and the correlation function are derived. Subsequently contributions to the density profile and the adsorption coefficient due to Gaussian fluctuations are found. As a result, an oscillating profile and a non-monotonic adsorption coefficient as a function of the density or the temperature are observed for some systems. Both the mean field and the fluctuation terms of the density profile are shown to satisfy the contact theorem.

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## 1. Introduction

Model systems with Yukawa-like potentials of interaction have been extensively used for the description of a large variety of liquids and soft matter materials. Any finite range interaction potential between point particles can be decomposed to a sum of Yukawa potentials with arbitrary accuracy. For instance, the Lennard-Jones potential used in the theory of simple fluids can be well approximated by the hard repulsion with two Yukawa tails [1, 2]. A hard core two-Yukawa model has been successfully used for the description of stability of charged colloidal dispersions [3] and the properties of solutions of globular charged proteins [4]. In this case the first Yukawa term describes the screened electrostatic interparticle repulsion and the second term approximates the Van der Waals interparticle attraction. Since the electrostatic intercolloidal repulsion is usually more long-ranged compared to the Van der Waals attraction, such a fluid demonstrates a very rich non-trivial phase behavior. Examples include various inhomogeneous structures such as spherical and cylindrical liquid-like clusters, single- and multi-liquid-like slabs, cylindrical and spherical bubbles [5, 6]. A hard core two-Yukawa model was also used to explain the formation of the extra low wave vector peak in the structure factor of cytochrome C protein solutions at moderate concentrations [7]. A hard core two-Yukawa model with the short-range strongly attractive interaction was used for the description of different clusterization phenomena in associated fluids [8]. Finally, a model with the isotropic Yukawa repulsion and the anisotropic Yukawa attraction has been used in the theory of nematogenic fluids [9, 10]. The simplicity of the Yukawa 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 [11, 12]. These analytical results were generalized for the description of hard sphere multi-Yukawa fluids [13, 14].

The study on inhomogeneous Yukawa fluids remains well behind the research carried out on homogeneous systems. One of the popular techniques of description of fluids near the surface is the Henderson-Abraham-Barker approach [15]. In this approach the description of a fluid near the surface reduces to that of a mixture of a fluid and of hard spheres considered in the limit of infinite dilution and infinite hard sphere size. In consequence, the calculation of the fluid density profile reduces to the solution of the Ornstein-Zernike integral equation for the fluid particle – wall distribution function calculated from the known fluid particle distribution function in the bulk. Application of this approach allowed

to evaluate the contribution of short-range interactions to the study of structural properties of spatially confined fluids. However, this approach in the simplest approximations like the mean spherical approximation does not take into account the contribution from the long range part of the interactions. A better approach in this perspective is the use of inhomogeneous integral equations which include in the convolution the density profile of fluid particles. For example, the application of a simple expression for the profile in the form of a step function provides the correct description of ionic fluids near the surface. These results make use of the collective variables approach [16,17] to construct cluster expansions for the pair and singlet distribution functions for a system of point ions confined by a hard wall. In parallel, for the description of ionic systems confined by a wall, the density field theory has been developed [18–21] which also gave the correct results for the description of ionic fluids near a hard wall.

The results for inhomogeneous fluids should satisfy certain known exact relationships - sum rules. An important example is the so-called contact theorem [22,23]. For a neutral fluid it states that the contact value of the point particle density near a hard wall is determined by the pressure of the liquid in the bulk volume. For a system of ions and charged wall there is an additional contribution from the Maxwell pressure due to the force acting between charged plates. The expressions found in the random phase approximation for the point ion density profile, for instance, meet the requirements of the contact theorem [24]. They can be modified for non-point ions by simply changing the inverse Debye-Hückel screening parameter  $\kappa$  to a new screening parameter  $\Gamma$  obtained in the mean spherical description of homogeneous ionic systems [25]. Recently the collective variables technique [26] was applied for the description of spatially confined fluids with the Yukawa potential of interaction. The principal difference between such a fluid with the Yukawa interaction and an ionic fluid is connected with the electroneutrality condition for ionic systems which excludes some terms like the Van der Waals contributions in the case of ions. Such contributions can play an important role in the case of a non-ionic fluid. In [26], the contribution of such terms was taken into account by construction in a simplified form. In [27] it was shown that the mean field treatment of a Yukawa fluid near the wall reduces to solving a non-linear differential equation for the density profile. Different simple analytical expressions for the density profile were obtained and compared with the numerical estimation of the mean field results. Beyond the mean field approximation it was shown that fluctuations can contribute significantly to the properties of a fluid. Notably they lead

to the desorption phenomenon regardless of the sign of interaction. The properties of hard sphere fluids with Yukawa interactions were also studied by computer simulations from numerical solutions of inhomogeneous integral equations [28] and also in the framework of the density functional theory and Grand Canonical Monte Carlo simulations [29,30]. In the latter paper the properties of an inhomogeneous hard core multi-Yukawa fluid were studied probably for the first time. Recently the structure and phase behavior of a fluid of the hard core model with a two-Yukawa tail potential in planar slit pores was studied [31].

In this paper we extend our previous work [27] concerning the field-theoretical description of a Yukawa fluid near a hard wall to the case of a fluid with two Yukawa potentials. We should mention that some preliminary results in this field were obtained by E. Soviak [32] in the framework of the collective variables approach [26]. Unfortunately he passed away before publication of his work [32].

We note that the results obtained in [27] for attractive potentials are not well defined for lower temperatures and higher densities. This problem is connected with the divergence of the bulk correlation function along the spinodal lines inside phase transitions of the mean field result. Such a divergence is the result of an incorrect treatment of short-range correlations in the bulk and can be removed by including repulsive interactions (see for example [33]). In this paper we generalize the model considered in [27] by adding a repulsive term to the potential of interaction and show that this step solves the problem of the correct description of the correlation function in the entire region of temperatures and densities.

The paper is organized as follows. The field theory formalism and the details of the model are presented in Section 2. The results of the mean field approximation are given in Section 3. The role of fluctuation and correlation effects on density profiles at the wall are presented and discussed in Section 4. Finally, in the last section we draw some conclusions.

## 2. The model and field theory formalism

We consider a neutral fluid of point particles in contact with a hard surface. The particles do not interact with the surface but interact with each other via a two-Yukawa potential

$$\nu(r_{12}) = \frac{A_1}{r_{12}} \exp(-\alpha_1 r_{12}) + \frac{A_2}{r_{12}} \exp(-\alpha_2 r_{12}), \quad (2.1)$$

where  $r_{12}$  denotes the distance between particles 1 and 2,  $A_1, A_2$  are the amplitudes of interaction and  $\alpha_1, \alpha_2$  are the inverse ranges. We associate the first term of the potential with the repulsion of particles (i.e.  $A_1 > 0$ ) and the second term with the attraction ( $A_2 < 0$ ).

In the formalism of statistical field theory the Hamiltonian  $H[\rho(\mathbf{r})]$  is a functional of field and consists of the ideal entropy and the interaction:

$$\begin{aligned} \beta H[\rho(\mathbf{r}_1)] &= \beta H^{entr}[\rho(\mathbf{r}_1)] + \beta H^{int}[\rho(\mathbf{r}_1)] = \\ & \int \rho(\mathbf{r}_1) (\ln [\rho(\mathbf{r}_1)\Lambda^3] - 1) d\mathbf{r}_1 + \\ & \frac{\beta}{2} \int \nu(r_{12}) \left[ \rho(\mathbf{r}_1)\rho(\mathbf{r}_2) - \rho(\mathbf{r}_1)\delta(\mathbf{r}_1 - \mathbf{r}_2) \right] d\mathbf{r}_1 d\mathbf{r}_2, \end{aligned} \quad (2.2)$$

where  $\beta = 1/kT$  is the inverse temperature,  $\rho(\mathbf{r})$  is the particle density, and  $\Lambda$  is the thermal de Broglie wavelength of the particles.

As in previous papers [18, 19, 27], we adopt the canonical ensemble approach. We fix the number of particles by the conditions  $\int \rho(\mathbf{r})d\mathbf{r} = N$  or  $\frac{1}{V} \int \rho(\mathbf{r})d\mathbf{r} = \rho_b$ , where  $V$  is the volume and  $\rho_b = N/V$  is the average value of the bulk density of the system. To verify this condition in a formally unconstrained calculus we introduce a Lagrange multiplier  $\lambda$  such that

$$\frac{\delta \beta H[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})} = \lambda. \quad (2.3)$$

The partition function  $Z_N[\rho(\mathbf{r})]$  can be expressed as

$$Z_N[\rho(\mathbf{r})] = \int D\rho(\mathbf{r}) \exp\{-\beta H[\rho(\mathbf{r})]\}, \quad (2.4)$$

where  $D\rho(\mathbf{r})$  denotes functional integration 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

$$\beta F = -\ln Z_N. \quad (2.5)$$

As we will see below, for further calculations it is convenient to introduce the following non-dimensional parameters: non-dimensional density  $\rho^* = \rho_b/\alpha_1^3$ , non-dimensional inverse temperature  $\beta^* = -\beta A_2\alpha_2 = 1/T^*$  and the ratios  $\omega = A_1/|A_2|$  and  $\tau = \alpha_1/\alpha_2$  similar to [27].

### 3. Mean field approximation

In order to obtain thermodynamic properties of the considered fluid we need to calculate the partition function. The lowest order approximation

for the partition function is the saddle point for the functional integral (2.4) which leads to the mean field approximation (MFA).

#### 3.1. Mean field equations

The condition for the mean field approximation is

$$\left. \frac{\delta \beta H}{\delta \rho} \right|_{\rho^{MFA}(\mathbf{r})} = \lambda. \quad (3.1)$$

In our case equation (3.1) reads

$$\ln \frac{\rho(\mathbf{r}_1)}{\rho_b} + V_1(\mathbf{r}_1) + V_2(\mathbf{r}_1) = \lambda, \quad (3.2)$$

where potentials  $V_i(\mathbf{r}_1)$  are defined as

$$V_i(\mathbf{r}_1) = \beta \int \rho(\mathbf{r}_2) \frac{A_i}{r_{12}} \exp(-\alpha_i r_{12}) d\mathbf{r}_2, \quad i = 1, 2. \quad (3.3)$$

We put

$$\lambda \equiv V_{1b} + V_{2b}, \quad (3.4)$$

where  $V_{ib}$  are the values of potentials  $V_i(\mathbf{r}_1)$  in the bulk:

$$V_{1b} = \frac{\varkappa_1^2}{\alpha_1^2}; \quad V_{2b} = \frac{\varkappa_2^2}{\alpha_2^2}, \quad (3.5)$$

and  $\varkappa_i^2 \equiv 4\pi\rho_b\beta A_i$ .

The gradient of (3.2) gives

$$\frac{\nabla \rho(\mathbf{r})}{\rho(\mathbf{r})} - \mathbf{E}_1(\mathbf{r}) - \mathbf{E}_2(\mathbf{r}) = 0, \quad (3.6)$$

where we define an equivalent of the electric field by

$$\mathbf{E}_1(\mathbf{r}_1) \equiv -\nabla V_1(\mathbf{r}_1); \quad \mathbf{E}_2(\mathbf{r}_1) \equiv -\nabla V_2(\mathbf{r}_1). \quad (3.7)$$

Due to the properties of Yukawa potential

$$(\Delta - \alpha_1^2) V_1(\mathbf{r}) = -4\pi\beta A_1 \rho(\mathbf{r}); \quad (3.8)$$

$$(\Delta - \alpha_2^2) V_2(\mathbf{r}) = -4\pi\beta A_2 \rho(\mathbf{r}). \quad (3.9)$$

Replacing (3.8) and (3.9) into (3.6) and using translational invariance parallel to the wall we obtain

$$\frac{d}{dz} \left[ \frac{\rho(z)}{\rho_b} + \frac{\alpha_1^2}{2\varkappa_1^2} [V_1(z)]^2 - \frac{1}{2\varkappa_1^2} E_1^2(z) + \frac{\alpha_2^2}{2\varkappa_2^2} [V_2(z)]^2 - \frac{1}{2\varkappa_2^2} E_2^2(z) \right] = 0. \quad (3.10)$$

### 3.2. Contact theorem

In the bulk  $\rho(z) \rightarrow \rho_b$ ,  $E_i(z) \rightarrow 0$ ,  $V_i(z) \rightarrow V_{ib}$ . From eq. (3.10) we see that the quantity in brackets is constant and therefore it can be evaluated for instance in the bulk as

$$1 + \frac{\varkappa_1^2}{2\alpha_1^2} + \frac{\varkappa_2^2}{2\alpha_2^2}. \quad (3.11)$$

This quantity is the reduced pressure  $\beta P/\rho_b$  within MFA:

$$\beta P = \rho_b \left( 1 + \frac{\varkappa_1^2}{2\alpha_1^2} + \frac{\varkappa_2^2}{2\alpha_2^2} \right). \quad (3.12)$$

Expression (3.12) 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  $\alpha_1^2 V_1^2(z)/2\varkappa_1^2 - E_1^2(z)/2\varkappa_1^2 + \alpha_2^2 V_2^2(z)/2\varkappa_2^2 - E_2^2(z)/2\varkappa_2^2$ , 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. (3.8) and (3.9), we have that this is also true at the wall just inside the system  $z = 0_+$  thus

$$\begin{aligned} \frac{\rho(0_+)}{\rho_b} + \frac{\alpha_1^2}{2\varkappa_1^2} [V_1(0_+)]^2 - \frac{1}{2\varkappa_1^2} E_1^2(0_+) + \frac{\alpha_2^2}{2\varkappa_2^2} [V_2(0_+)]^2 - \frac{1}{2\varkappa_2^2} E_2^2(0_+) \\ = \frac{\rho(0_+)}{\rho_b}. \end{aligned} \quad (3.13)$$

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

$$\beta P = \rho(0_+). \quad (3.14)$$

Thus, similar to the one-Yukawa case [27], in the MFA we obtain the contact theorem as the consequence of the existence of an invariant of the differential equations corresponding to the bulk pressure. The obtained result is in agreement with the note in [27] that in the MFA 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 that can be presented as a superposition of Yukawa potentials.

### 3.3. Density profiles

From (3.6)-(3.9) we obtain a set of five differential equations with five unknown functions  $\rho(z)$ ,  $E_1(z)$ ,  $E_2(z)$ ,  $V_1(z)$ ,  $V_2(z)$ :

$$\frac{\partial \rho(z)}{\partial z} = \rho(z) [E_1(z) + E_2(z)], \quad (3.15)$$

$$\frac{\partial V_1(z)}{\partial z} = -E_1(z), \quad (3.16)$$

$$\frac{\partial V_2(z)}{\partial z} = -E_2(z), \quad (3.17)$$

$$\frac{\partial E_1(z)}{\partial z} = -\alpha_1^2 V_1(z) + \frac{\varkappa_1^2}{\rho_b} \rho(z), \quad (3.18)$$

$$\frac{\partial E_2(z)}{\partial z} = -\alpha_2^2 V_2(z) + \frac{\varkappa_2^2}{\rho_b} \rho(z). \quad (3.19)$$

These relations are first-order differential equations that have been solved starting from the linear solution in the bulk, back integrating towards the wall [20,21,27]. The boundary condition is set from the fact that the final point is obtained when we have the contact theorem.

From (3.2) we have

$$\rho(z) = \rho_b \exp(-[V_1(z) - V_{1b}] - [V_2(z) - V_{2b}]). \quad (3.20)$$

If we approximate this as

$$\rho^L(z) = \rho_b (1 - [V_1(z) - V_{1b}] - [V_2(z) - V_{2b}]) \quad (3.21)$$

we obtain a linearized system

$$[\rho^L(z)]' = \rho_b [E_1(z) + E_2(z)], \quad (3.22)$$

$$V_1'(z) = -E_1(z), \quad (3.23)$$

$$V_2'(z) = -E_2(z), \quad (3.24)$$

$$E_1'(z) = -\alpha_1^2 V_1(z) + \frac{\varkappa_1^2}{\rho_b} \rho^L(z) \quad (3.25)$$

$$E_2'(z) = -\alpha_2^2 V_2(z) + \frac{\varkappa_2^2}{\rho_b} \rho^L(z), \quad (3.26)$$

where the prime denotes derivative by  $z$ .

The system (3.22)-(3.26) reduces to a system of two equations

$$\begin{aligned} E_1''(z) &= E_1(z) (\varkappa_1^2 + \alpha_1^2) + E_2(z) \varkappa_1^2 \\ E_2''(z) &= E_1(z) \varkappa_2^2 + E_2(z) (\alpha_2^2 + \varkappa_2^2) \end{aligned} \quad (3.27)$$

or in the matrix form

$$\mathbf{E}'' = \mathbf{A}\mathbf{E}, \quad (3.28)$$

where

$$\mathbf{E} = \begin{pmatrix} E_1(z) \\ E_2(z) \end{pmatrix}; \quad \mathbf{A} = \begin{pmatrix} (\varkappa_1^2 + \alpha_1^2) & \varkappa_1^2 \\ \varkappa_2^2 & (\alpha_2^2 + \varkappa_2^2) \end{pmatrix}. \quad (3.29)$$

Matrix  $\mathbf{A}$  can be presented in the form

$$\mathbf{A} = \mathbf{P}\mathbf{D}\mathbf{P}^{-1}, \quad (3.30)$$

where

$$\mathbf{D} = \begin{pmatrix} \lambda_2^2 & 0 \\ 0 & \lambda_1^2 \end{pmatrix} \quad (3.31)$$

is a diagonal matrix with eigenvalues

$$\lambda_1^2 = \frac{1}{2} \left( \varkappa_1^2 + \alpha_1^2 + \varkappa_2^2 + \alpha_2^2 + \sqrt{(\varkappa_1^2 + \alpha_1^2 - \varkappa_2^2 - \alpha_2^2)^2 + 4\varkappa_1^2\varkappa_2^2} \right) \quad (3.32)$$

$$\lambda_2^2 = \frac{1}{2} \left( \varkappa_1^2 + \alpha_1^2 + \varkappa_2^2 + \alpha_2^2 - \sqrt{(\varkappa_1^2 + \alpha_1^2 - \varkappa_2^2 - \alpha_2^2)^2 + 4\varkappa_1^2\varkappa_2^2} \right), \quad (3.33)$$

and matrix  $\mathbf{P}$  equals

$$\mathbf{P} = \begin{pmatrix} \frac{\lambda_2^2 - \varkappa_2^2 - \alpha_2^2}{\varkappa_2^2} & 1 \\ 1 & -\frac{(\lambda_2^2 - \varkappa_2^2 - \alpha_2^2)}{\varkappa_1^2} \end{pmatrix}. \quad (3.34)$$

The general solution for  $E_2(z)$  for instance is

$$E_2(z) = \tilde{B}_1 e^{-\lambda_1 z} + \tilde{B}_2 e^{-\lambda_2 z} + \tilde{B}_3 e^{\lambda_1 z} + \tilde{B}_4 e^{\lambda_2 z} = \tilde{B}_1 e^{-\lambda_1 z} + \tilde{B}_2 e^{-\lambda_2 z}, \quad (3.35)$$

where we used the fact that  $E(z)$  vanishes in the bulk. From (3.27)  $E_1(z)$  can be expressed in terms of  $E_2(z)$  as

$$E_1(z) = \frac{(\lambda_1^2 - \alpha_2^2 - \varkappa_2^2)}{\varkappa_2^2} \tilde{B}_1 e^{-\lambda_1 z} + \frac{(\lambda_2^2 - \alpha_2^2 - \varkappa_2^2)}{\varkappa_2^2} \tilde{B}_2 e^{-\lambda_2 z}. \quad (3.36)$$

Potentials  $V_i(z)$  then have the form

$$V_1(z) = V_{1b} + \frac{(\lambda_1^2 - \alpha_2^2 - \varkappa_2^2)}{\varkappa_2^2} B_1 e^{-\lambda_1 z} + \frac{(\lambda_2^2 - \alpha_2^2 - \varkappa_2^2)}{\varkappa_2^2} B_2 e^{-\lambda_2 z}, \quad (3.37)$$

$$V_2(z) = V_{2b} + B_1 e^{-\lambda_1 z} + B_2 e^{-\lambda_2 z}, \quad (3.38)$$

where  $B_1 \equiv \tilde{B}_1/\lambda_1$ ,  $B_2 \equiv \tilde{B}_2/\lambda_2$ . The constants  $B_1$  and  $B_2$  can be found from the boundary conditions given by the contact theorem (3.12) and equations (3.22),(3.23),(3.24):

$$V_{1b} - V_1(0) = \frac{\varkappa_1^2}{2\alpha_1^2}, \quad (3.39)$$

$$V_{2b} - V_2(0) = \frac{\varkappa_2^2}{2\alpha_2^2}, \quad (3.40)$$

resulting in

$$B_1 = \frac{\varkappa_2^2}{2(\lambda_1^2 - \lambda_2^2)} \left( -\frac{\varkappa_1^2}{\alpha_1^2} + \frac{\lambda_2^2 - \alpha_2^2 - \varkappa_2^2}{\alpha_2^2} \right) \quad (3.41)$$

$$B_2 = \frac{\varkappa_2^2}{2(\lambda_1^2 - \lambda_2^2)} \left( \frac{\varkappa_1^2}{\alpha_1^2} - \frac{\lambda_1^2 - \alpha_2^2 - \varkappa_2^2}{\alpha_2^2} \right).$$

Finally, for the linear approximation of the density profile we have

$$\begin{aligned} \frac{\rho^L(z)}{\rho_b} &= 1 - [V_1(z) - V_{1b}] - [V_2(z) - V_{2b}] \quad (3.42) \\ &= 1 - \frac{1}{2} \frac{(\lambda_1^2 - \alpha_2^2)}{(\lambda_1^2 - \lambda_2^2)} \left( -\frac{\varkappa_1^2}{\alpha_1^2} + \frac{\lambda_2^2 - \alpha_2^2 - \varkappa_2^2}{\alpha_2^2} \right) e^{-\lambda_1 z} \\ &\quad - \frac{1}{2} \frac{(\lambda_2^2 - \alpha_2^2)}{(\lambda_1^2 - \lambda_2^2)} \left( \frac{\varkappa_1^2}{\alpha_1^2} - \frac{\lambda_1^2 - \alpha_2^2 - \varkappa_2^2}{\alpha_2^2} \right) e^{-\lambda_2 z}. \end{aligned}$$

When  $\varkappa_1^2 = 0$  we have  $\lambda_1^2 = \alpha_1^2$  and  $\lambda_2^2 = \varkappa_2^2 + \alpha_2^2$ . Likewise, when  $\varkappa_2^2 = 0$  we have  $\lambda_1^2 = \varkappa_1^2 + \alpha_1^2$  and  $\lambda_2^2 = \alpha_2^2$ . In these cases we see that expression (3.42) reproduces the respective result obtained in [27] for a fluid interacting with a one-Yukawa potential.

Analyzing expressions (3.32) and (3.33) we note that coefficients  $\lambda_1^2$  and  $\lambda_2^2$  are real-valued if the expression under the square root is positive, i.e.

$$(\varkappa_1^2 - |\varkappa_2^2| + \alpha_1^2 - \alpha_2^2)^2 \geq -4|\varkappa_2^2|(\alpha_1^2 - \alpha_2^2). \quad (3.43)$$



For the case when the repulsive part of the interaction potential has a shorter range than the attractive part, i.e.  $\alpha_1 > \alpha_2$ , condition (3.43) is always true and coefficients  $\lambda_1^2$ ,  $\lambda_2^2$  cannot be complex.

For the density profile to have physical sense, we should also have the coefficient  $\lambda_2^2$  positive. This fact leads to two conditions

$$\frac{\varkappa_1^2}{\alpha_1^2} \geq \frac{\alpha_2^2}{\alpha_1^2} \left( \frac{|\varkappa_2^2|}{\alpha_2^2} - 1 \right) - 1, \quad (3.44)$$

$$\frac{\varkappa_1^2}{\alpha_1^2} \geq \frac{|\varkappa_2^2|}{\alpha_2^2} - 1, \quad (3.45)$$

where relation (3.44) comes from the fact that in (3.32) the expression in front of the square root should be positive.

For the case when  $\alpha_1 > \alpha_2$  and  $A_1 > |A_2|$ , one can see that inequality (3.45) contains inequality (3.44) and therefore condition (3.45) is sufficient. Furthermore, when  $|\varkappa_2^2| \leq \alpha_2^2$  the right-hand side of (3.45) is negative and parameters  $\varkappa_1^2$  and  $\alpha_1^2$  can take on any positive values. In [27] it was shown that for a one-Yukawa fluid the decay of the linearized profile in the MFA has the form  $(\varkappa_i^2 + \alpha_i^2)^{-1/2}$  ( $i = 1$  or  $2$ ). Consequently, a fluid interacting with an attractive Yukawa potential can be stable only if the condition  $|\varkappa_2^2| \leq \alpha_2^2$  applies, i.e. the interaction potential cannot be too attractive. This problem is related to the divergence of the correlation function in the bulk which is caused by the incorrect treatment of short-range correlations [33]. Since in the present model we are not bound by this restriction, we see that generalization of the interaction potential to the sum of a repulsive and an attractive parts removes limitations on the values of the attractive interaction.

In Figure 1 we show three different estimations of the mean field density profile using the parameter  $r_d = 1/|\varkappa_2^2|^{1/2}$  as a unit of length. We give the exact numerical solution of the system (3.15)-(3.19), the analytical solution (3.42) of the linearized system of equations, and the simplified linearized solution  $\rho^{sl}(z)$  as was done in [26, 32]:

$$\frac{\rho^{sl}(z)}{\rho_b} = 1 + \frac{\varkappa_1^2}{2\alpha_1^2} \exp(-\alpha_1 z) + \frac{\varkappa_2^2}{2\alpha_2^2} \exp(-\alpha_2 z). \quad (3.46)$$

In this last approximation the profile is written as the integral of the potential of interparticle interaction  $\nu(r_{12})$

$$\frac{\rho^{sl}(z_1)}{\rho_b} = 1 - \beta \rho_b \int_{z_2 \geq 0} d\mathbf{r}_{12} \nu(r_{12}) + \beta \rho_b \int d\mathbf{r}_{12} \nu(r_{12}), \quad (3.47)$$

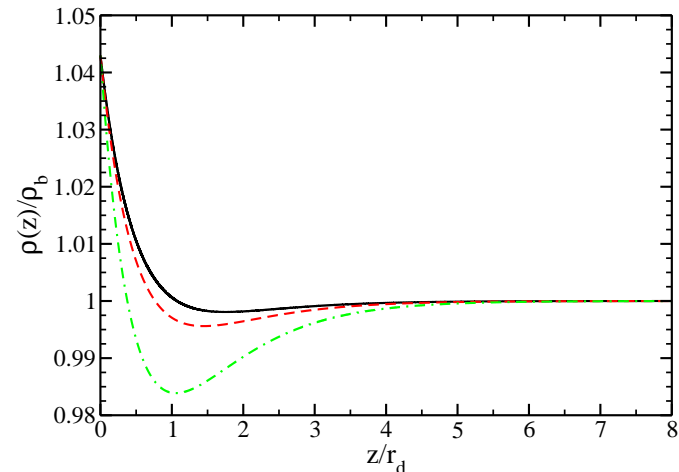


Figure 1. Mean field density profiles in three different approximations for  $\rho^* = 0.005$ ,  $T^* = 0.2$ ,  $\omega = 2$ , and  $\tau = 1.25$ . For the solid black line we have the exact numerical solution of equations (3.15)-(3.19), for the dashed red line the analytical solution (3.42) of the linearized system of equations, and for the dash dotted green line the simplified linearized solution (3.46).

where the last term subtracts the bulk value of the integral corresponding to the Van der Waals contribution to the free energy.

At the wall we have only one half of the integral of the potential which corresponds to the Van der Waals approximation. As a result, this approximation satisfies the contact theorem. However, as we see from Figure 1 this approximation is rather crude, whereas the linearized equations represent a better approximation.

Comparing Figure 1 to the results of [27], we see that generalization of the one-Yukawa potential to the sum of a repulsive and an attractive Yukawa potentials leads to non-monotonic behavior of the density profile even in the simplest mean field approximation. Due to the contact theorem we also have that the contact value of the density is larger than the bulk value if  $\omega > \tau^2$  whereas for a one-Yukawa fluid it was larger for all repulsive interactions and smaller for all attractive interactions.

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

In the previous section we have considered mean field equations, where the fluctuations are neglected. Here we take them into account and therefore we have to expand the Hamiltonian with respect to the mean field density  $\rho^{MFA}(\mathbf{r})$ . For this aim we put  $\rho(\mathbf{r}) = \rho^{MFA}(\mathbf{r}) + \delta\rho(\mathbf{r})$ .

##### 4.1. Expansion of the Hamiltonian

Expansion of the Hamiltonian around the mean field density  $\rho^{MFA}(\mathbf{r})$  gives

$$\begin{aligned} \beta H[\rho] &= \beta H[\rho^{MFA}] + \int \delta\rho(\mathbf{r}_1) \frac{\delta\beta H}{\delta(\delta\rho(\mathbf{r}_1))} \Big|_{\rho^{MFA}} d\mathbf{r}_1 + \\ &\frac{1}{2} \int \delta\rho(\mathbf{r}_1) \delta\rho(\mathbf{r}_2) \frac{\delta^2\beta H}{\delta(\delta\rho(\mathbf{r}_1))\delta(\delta\rho(\mathbf{r}_2))} \Big|_{\rho^{MFA}} d\mathbf{r}_1 d\mathbf{r}_2 + \\ &\sum_{n \geq 3} (-1)^n \frac{(n-1)!}{n!} \int \delta\rho(\mathbf{r}_1) \dots \delta\rho(\mathbf{r}_n) \frac{\delta^n \beta H}{\delta(\delta\rho(\mathbf{r}_1)) \dots \delta(\delta\rho(\mathbf{r}_n))} \Big|_{\rho^{MFA}} d\mathbf{r}_1 \dots d\mathbf{r}_n. \end{aligned} \quad (4.1)$$

The first term is the Hamiltonian functional (2.2) for the mean field density

$$\begin{aligned} \beta H[\rho^{MFA}] &= \int \rho^{MFA}(\mathbf{r}_1) (\ln[\rho^{MFA}(\mathbf{r}_1)\Lambda^3] - 1) d\mathbf{r}_1 \\ &+ \frac{\beta}{2} \int \nu(r_{12}) \left[ \rho^{MFA}(\mathbf{r}_1) \rho^{MFA}(\mathbf{r}_2) - \rho^{MFA}(\mathbf{r}_1) \delta(\mathbf{r}_1 - \mathbf{r}_2) \right] d\mathbf{r}_1 d\mathbf{r}_2. \end{aligned} \quad (4.2)$$

The linear term disappears as in the canonical formalism fluctuations preserve the number of particles and  $\int \delta\rho(\mathbf{r}) d\mathbf{r} = 0$ .

The quadratic term is

$$\beta H_2[\rho] = \frac{1}{2} \int \delta\rho(\mathbf{r}_1) \delta\rho(\mathbf{r}_2) \left[ \frac{\delta(\mathbf{r}_1 - \mathbf{r}_2)}{\rho^{MFA}(\mathbf{r}_1)} + \beta\nu(r_{12}) \right] d\mathbf{r}_1 d\mathbf{r}_2, \quad (4.3)$$

where the first term comes from the expansion of the logarithmic term in the Hamiltonian.

Due to translational invariance parallel to the wall, we expand the fluctuations of the density as

$$\delta\rho(\mathbf{r}) = \sum_{\mathbf{K}} \delta\rho_{\mathbf{K}}(z) e^{i\mathbf{K}\mathbf{R}}, \quad (4.4)$$

where  $\mathbf{R}$  is the vector component of  $\mathbf{r}$  parallel to the wall,  $\mathbf{K}$  is the wave vector in the direction parallel to the wall.

The entropic term equals

$$\begin{aligned} \beta H_2^{entr}[\rho_{\mathbf{K}}(z)] &= \frac{1}{2} \int \frac{\delta\rho^2(\mathbf{r})}{\rho^{MFA}(z)} d\mathbf{r} \\ &= \frac{1}{2} \sum_{\mathbf{K}, \mathbf{K}'} \int \frac{\delta\rho_{\mathbf{K}}(z) \delta\rho_{\mathbf{K}'}(z)}{\rho^{MFA}(z)} e^{i\mathbf{R}(\mathbf{K} + \mathbf{K}')} d\mathbf{R} dz \\ &= \frac{S}{2} \sum_{\mathbf{K}} \int dz_1 dz_2 \delta\rho_{\mathbf{K}}(z_1) \delta\rho_{-\mathbf{K}}(z_2) \frac{\delta(z_1 - z_2)}{\rho^{MFA}(z)}, \end{aligned} \quad (4.5)$$

where  $S$  is the surface area.

The interaction term gives

$$\beta H_2^{int}[\rho_{\mathbf{K}}(z)] = \frac{S\beta}{2} \sum_{\mathbf{K}} \int dz_1 \int dz_2 \delta\rho_{\mathbf{K}}(z_1) \delta\rho_{-\mathbf{K}}(z_2) \nu(\mathbf{K}, |z_1 - z_2|), \quad (4.6)$$

where  $\nu(\mathbf{K}, |z_1 - z_2|) = \int d\mathbf{R}_{12} \nu(r_{12}) \exp(-i\mathbf{K}\mathbf{R}_{12})$ .

Finally, for the quadratic term of the Hamiltonian we obtain

$$\begin{aligned} \beta H_2[\rho] &= \\ &\frac{S}{2} \sum_{\mathbf{K}} \int dz_1 \int dz_2 \delta\rho_{\mathbf{K}}(z_1) \delta\rho_{-\mathbf{K}}(z_2) \left[ \frac{\delta(z_1 - z_2)}{\rho^{MFA}(z_1)} + \beta\nu(\mathbf{K}, |z_1 - z_2|) \right]. \end{aligned} \quad (4.7)$$

##### 4.2. Thermodynamic properties: free energy, pressure, and chemical potential

We start our calculations from consideration of thermodynamic properties of the fluid in the bulk.

The free energy is

$$\beta F = -\ln \left[ \int \mathcal{D}\rho e^{-\beta H[\rho]} \right]. \quad (4.8)$$

In order to calculate the functional integral using the Gaussian integrals with such a Hamiltonian, it is necessary to have the quadratic term in a diagonal form. For bulk properties such as the Helmholtz free energy we can expand density on the Fourier components

$$\delta\rho(\mathbf{r}) = \sum_{\mathbf{k}} \delta\rho_{\mathbf{k}} e^{i\mathbf{k}\mathbf{r}}. \quad (4.9)$$



In this basis the quadratic Hamiltonian is

$$\beta H_2[\rho] = \frac{V}{2\rho_b} \sum_{\mathbf{k}>0} \delta\rho_{\mathbf{k}} \delta\rho_{-\mathbf{k}} \left[ 1 + \frac{\varkappa_1^2}{\mathbf{k}^2 + \alpha_1^2} + \frac{\varkappa_2^2}{\mathbf{k}^2 + \alpha_2^2} \right] \quad (4.10)$$

and after integration the excess free energy equals

$$\begin{aligned} \beta F^{ex} &= \beta(F - F^{id}) = \\ &\rho_b V \frac{\varkappa_1^2}{2\alpha_1^2} + \rho_b V \frac{\varkappa_2^2}{2\alpha_2^2} + \frac{1}{2} \sum_{\mathbf{k}} \ln[1 + \rho_b \nu(k)] - \frac{1}{2} \rho_b \sum_{\mathbf{k}} \nu(k), \end{aligned} \quad (4.11)$$

where

$$\nu(k) = \frac{4\pi\beta A_1}{k^2 + \alpha_1^2} + \frac{4\pi\beta A_2}{k^2 + \alpha_2^2} \quad (4.12)$$

is the Fourier transform of the interaction potential (2.1) multiplied by  $\beta$ .

The first and the second terms on the right-hand side of (4.11) are mean field contributions with the other two terms coming from Gaussian fluctuations. In order to calculate the third and the fourth terms we switch from summation to integration and then integrate by parts

$$\begin{aligned} \beta F^{fluct} &= \frac{1}{2} \sum_{\mathbf{k}} \ln[1 + \rho_b \nu(k)] - \frac{1}{2} \rho_b \sum_{\mathbf{k}} \nu(k) \\ &= \frac{V}{4\pi^2} \int_0^\infty k^2 dk \left[ \ln[1 + \rho_b \nu(k)] - \rho_b \nu(k) \right] \\ &= \frac{\rho_b^2 V}{12\pi^2} \int_0^\infty k^3 dk \frac{\nu(k)}{1 + \rho_b \nu(k)} \frac{d\nu(k)}{dk}. \end{aligned} \quad (4.13)$$

For further calculations it is helpful to express parameters  $\varkappa_1^2$  and  $\varkappa_2^2$  in terms of  $\lambda_1$  and  $\lambda_2$ . From (3.32) and (3.33) we have

$$\varkappa_1^2 = \frac{(\alpha_2^2 - \lambda_1^2)(\alpha_1^2 - \lambda_2^2)}{\alpha_2^2 - \alpha_1^2}, \quad \varkappa_2^2 = \frac{(\alpha_2^2 - \lambda_1^2)(\alpha_2^2 - \lambda_2^2)}{\alpha_1^2 - \alpha_2^2}. \quad (4.14)$$

Using identities (4.14), after integration we obtain

$$\begin{aligned} \frac{\beta F^{ex}}{V} &= \frac{\rho_b}{2} \left( \frac{\varkappa_1^2}{\alpha_1^2} + \frac{\varkappa_2^2}{\alpha_2^2} \right) - \frac{1}{12\pi} (\lambda_1^3 + \lambda_2^3) - \frac{1}{24\pi} (\alpha_1^3 + \alpha_2^3) \\ &+ \frac{1}{8\pi} (\lambda_1^2 + \lambda_2^2) (\alpha_1 + \alpha_2) - \frac{1}{8\pi} \frac{(\lambda_1^2 + \alpha_1 \alpha_2)(\lambda_2^2 + \alpha_1 \alpha_2)}{\alpha_1 + \alpha_2}. \end{aligned} \quad (4.15)$$

The pressure can be found from the free energy as

$$\beta P = -\beta \frac{\partial F}{\partial V} \Big|_{T,N}. \quad (4.16)$$

Differentiation of (4.15) with respect to volume gives the fluctuation part of the bulk pressure as

$$\begin{aligned} \beta P^{fluct} &= -\frac{d}{dV} \left[ \frac{\rho_b^2 V}{12\pi^2} \int_0^\infty k^3 dk \frac{\nu(k)}{1 + \rho_b \nu(k)} \frac{d\nu(k)}{dk} \right] \\ &= \frac{\rho_b^2}{12\pi^2} \int_0^\infty k^3 dk \frac{\nu(k)}{[1 + \rho_b \nu(k)]^2} \frac{d\nu(k)}{dk}. \end{aligned} \quad (4.17)$$

After integration and due to identities (4.14) the excess pressure equals

$$\begin{aligned} \beta P^{ex} &= \frac{\rho_b}{2} \left( \frac{\varkappa_1^2}{\alpha_1^2} + \frac{\varkappa_2^2}{\alpha_2^2} \right) - \frac{1}{24\pi} (\lambda_1^3 + \lambda_2^3) - \frac{1}{12\pi} (\alpha_1^3 + \alpha_2^3) \\ &+ \frac{1}{8\pi} (\alpha_1^2 + \alpha_2^2) (\lambda_1 + \lambda_2) - \frac{1}{8\pi} \frac{1}{\lambda_1 + \lambda_2} (\alpha_1^2 + \lambda_1 \lambda_2) (\alpha_2^2 + \lambda_1 \lambda_2). \end{aligned} \quad (4.18)$$

Finally, the excess chemical potential can be derived directly from (4.15) and (4.18) as  $\mu^{ex} = (F^{ex} + P^{ex}V)/N$  giving

$$\begin{aligned} \beta \mu^{ex} &= \frac{\varkappa_1^2}{\alpha_1^2} + \frac{\varkappa_2^2}{\alpha_2^2} - \frac{1}{8\pi\rho_b} (\lambda_1^3 + \lambda_2^3) - \frac{1}{8\pi\rho_b} (\alpha_1^3 + \alpha_2^3) \\ &+ \frac{1}{8\pi\rho_b} (\lambda_1^2 + \lambda_2^2) (\alpha_1 + \alpha_2) + \frac{1}{8\pi\rho_b} (\alpha_1^2 + \alpha_2^2) (\lambda_1 + \lambda_2) \\ &- \frac{1}{8\pi\rho_b} \frac{(\lambda_1^2 + \alpha_1 \alpha_2)(\lambda_2^2 + \alpha_1 \alpha_2)}{\alpha_1 + \alpha_2} - \frac{1}{8\pi\rho_b} \frac{(\alpha_1^2 + \lambda_1 \lambda_2)(\alpha_2^2 + \lambda_1 \lambda_2)}{\lambda_1 + \lambda_2}. \end{aligned} \quad (4.19)$$

For  $A_1 = 0$  or  $A_2 = 0$  expressions (4.15) for the free energy, (4.18) for the pressure, and (4.19) for the chemical potential reduce to the respective expressions obtained in [26, 27] for a one-Yukawa fluid.

### 4.3. Correlation function

The expression for the pair correlation function  $h(\mathbf{r}_1, \mathbf{r}_2)$  is [34]

$$h(\mathbf{r}_1, \mathbf{r}_2) \langle \rho(\mathbf{r}_1) \rangle \langle \rho(\mathbf{r}_2) \rangle = \langle \delta\rho(\mathbf{r}_1) \delta\rho(\mathbf{r}_2) \rangle - \delta(\mathbf{r}_1 - \mathbf{r}_2) \langle \rho(\mathbf{r}_1) \rangle. \quad (4.20)$$

In  $\mathbf{K}$ -space this expression reads

$$\begin{aligned} \frac{1}{S} \left[ \rho^{MFA}(z_1) \rho^{MFA}(z_2) h(K, z_1 z_2) + \rho^{MFA}(z_1) \delta(z_1 - z_2) \right] \\ = \langle \delta \rho_{\mathbf{K}}(z_1) \delta \rho_{-\mathbf{K}}(z_2) \rangle, \end{aligned} \quad (4.21)$$

where

$$h(K, z_1 z_2) = \int d\mathbf{R}_{12} h(R_{12}, z_1, z_2) \exp(i\mathbf{K}\mathbf{R}_{12}). \quad (4.22)$$

The right-hand side of equation (4.21) can be calculated from expression (4.7) and gives the inverse Hamiltonian matrix  $\beta H_2^{-1} [\rho_{\mathbf{K}}(z)] / 2$

$$\begin{aligned} \langle \delta \rho_{\mathbf{K}}(z_1) \delta \rho_{-\mathbf{K}}(z_2) \rangle &= \frac{\int D(\delta \rho_{\mathbf{K}}(z)) \delta \rho_{\mathbf{K}}(z_1) \delta \rho_{-\mathbf{K}}(z_2) \exp(-\beta H_2[\rho_{\mathbf{K}}(z)])}{\int D(\delta \rho_{\mathbf{K}}(z)) \exp(-\beta H_2[\rho_{\mathbf{K}}(z)])} \\ &= \frac{1}{2} \beta H_2^{-1} [\rho_{\mathbf{K}}(z)]. \end{aligned} \quad (4.23)$$

Hence the product of the Hamiltonian matrix and the matrix on the left-hand side of (4.21) yields unity, so we have

$$\begin{aligned} \int dz_3 \left( \left[ \rho^{MFA}(z_1) \rho^{MFA}(z_3) h(K, z_1 z_3) + \rho^{MFA}(z_1) \delta(z_1 - z_3) \right] \right. \\ \left. \left[ \frac{\delta(z_3 - z_2)}{\rho^{MFA}(z_3)} + \beta \nu(\mathbf{K}, |z_3 - z_2|) \right] \right) = \delta(z_1 - z_2), \end{aligned} \quad (4.24)$$

or

$$\begin{aligned} h(K, z_1, z_2) + \int dz_3 \rho^{MFA}(z_3) h(K, z_1, z_3) \beta \nu(\mathbf{K}, |z_3 - z_2|) \\ = -\beta \nu(\mathbf{K}, |z_1 - z_2|). \end{aligned} \quad (4.25)$$

Relation (4.25) is a convolution-type equation. It can be reduced to the so-called Riemann problem [35] if we assume the density profile to be a step-function. In this approximation  $\rho^{MFA}(z) = 0$  for  $z < 0$  and  $\rho^{MFA}(z) = \rho_b$  for  $z > 0$ .

Due to the spatial non-homogeneousness of the system we introduce one-sided pair correlation functions  $h_{\pm}(R_{12}, z_1, z_2)$  such that

$$\begin{aligned} h(R_{12}, z_1, z_2) &= h_+(R_{12}, z_1, z_2) - h_-(R_{12}, z_1, z_2), \\ h_+(R_{12}, z_1, z_2) &= \begin{cases} h(R_{12}, z_1, z_2), & z_1 > 0, \\ 0, & z_1 < 0, \end{cases} \\ h_-(R_{12}, z_1, z_2) &= \begin{cases} 0, & z_1 > 0, \\ -h(R_{12}, z_1, z_2), & z_1 < 0. \end{cases} \end{aligned} \quad (4.26)$$

The function  $h(K, z_1, z_2)$  can then be presented as the difference of one-sided functions  $h_{\pm}(K, z_1, z_2)$  such that

$$\begin{aligned} h(K, z_1, z_2) &= h_+(K, z_1, z_2) - h_-(K, z_1, z_2), \\ h_+(K, z_1, z_2) &= \begin{cases} h(K, z_1, z_2), & z_1 > 0, \\ 0, & z_1 < 0, \end{cases} \\ h_-(K, z_1, z_2) &= \begin{cases} 0, & z_1 > 0, \\ -h(K, z_1, z_2), & z_1 < 0. \end{cases} \end{aligned} \quad (4.27)$$

Equation (4.25) now reads

$$\begin{aligned} h_+(K, z_1, z_2) - h_-(K, z_1, z_2) + \rho_b \int_0^{\infty} dz_3 h_+(K, z_1, z_3) \beta \nu(\mathbf{K}, |z_3 - z_2|) \\ = -\beta \nu(\mathbf{K}, |z_1 - z_2|). \end{aligned} \quad (4.28)$$

Expanding the functions  $h_{\pm}(K, z_1, z_2)$  and  $\nu(\mathbf{K}, |z_1 - z_2|)$  on Fourier harmonics with respect to the wave vector  $\mu$  in the direction perpendicular to the wall and switching from summation to integration we obtain

$$\begin{aligned} \left[ 1 + \frac{\chi_1^2}{K^2 + \mu_1^2 + \alpha_1^2} + \frac{\chi_2^2}{K^2 + \mu_1^2 + \alpha_2^2} \right] h_+(K, \mu_1 \mu_2) - h_-(K, \mu_1 \mu_2) \\ = - \left( \frac{4\pi\beta A_1}{K^2 + \mu_2^2 + \alpha_1^2} + \frac{4\pi\beta A_2}{K^2 + \mu_2^2 + \alpha_2^2} \right) \delta(\mu_1 + \mu_2), \end{aligned} \quad (4.29)$$

where

$$h_{\pm}(K, \mu_1, \mu_2) = \int_S d\mathbf{R}_{12} e^{i\mathbf{K}\mathbf{R}_{12}} \int_{-\infty}^{\infty} dz_1 e^{i\mu_1 z_1} \int_{-\infty}^{\infty} dz_2 e^{i\mu_2 z_2} h_{\pm}(R_{12}, z_1 z_2) \quad (4.30)$$

and we have used the relation

$$\begin{aligned} \int_{-\infty}^{\infty} dz_1 e^{i\mu_1 z_1} \int_{-\infty}^{\infty} dz_2 e^{i\mu_2 z_2} \beta \nu(\mathbf{K}, |z_1 - z_2|) = \\ = - \left( \frac{4\pi\beta A_1}{K^2 + \mu_2^2 + \alpha_1^2} + \frac{4\pi\beta A_2}{K^2 + \mu_2^2 + \alpha_2^2} \right) \delta(\mu_1 + \mu_2). \end{aligned} \quad (4.31)$$

Equation (4.29) is known as the Riemann problem [35]. Using the technique proposed in [26, 32] we solve this problem for  $h_+(K, \mu_1, \mu_2)$  (refer to Appendix A for the details of calculation) and obtain

$$h_+(K, \mu_1, \mu_2) = \frac{1}{\rho_b} \frac{\varkappa_1^2(\mu_2^2 + \alpha_2^2(K)) + \varkappa_2^2(\mu_1^2 + \alpha_1^2(K))}{(\mu_2 - i\alpha_1(K))(\mu_2 - i\alpha_2(K))(\mu_2 + i\lambda_1(K))(\mu_2 + i\lambda_2(K))} \frac{(\mu_1 + i\alpha_1(K))(\mu_1 + i\alpha_2(K))}{(\mu_1 + i\lambda_1(K))(\mu_1 + i\lambda_2(K))} \delta_+(\mu_1 + \mu_2), \quad (4.32)$$

where  $\delta_+(\mu_1 + \mu_2)$  is a one-sided delta-function. The expression for the correlation function in  $\mathbf{r}$ -space is

$$\begin{aligned} h_+(R_{12}, z_1, z_2) = & \beta \frac{A_1(\lambda_2^2 - \alpha_2^2) + A_2(\lambda_2^2 - \alpha_1^2)}{(\lambda_1^2 - \lambda_2^2)} \frac{e^{-\lambda_2 r_{12}}}{r_{12}} \\ & - \beta \frac{A_1(\lambda_1^2 - \alpha_2^2) + A_2(\lambda_1^2 - \alpha_1^2)}{(\lambda_1^2 - \lambda_2^2)} \frac{e^{-\lambda_1 r_{12}}}{r_{12}} \\ & - \beta \int_0^\infty 2K J_0(KR_{12}) dK \left\{ \frac{A_1(\lambda_2^2 - \alpha_2^2) + A_2(\lambda_2^2 - \alpha_1^2)}{2\lambda_2(K)(\lambda_1(K) - \lambda_2(K))^2} \right. \\ & \quad \frac{(\lambda_2(K) - \alpha_1(K))(\lambda_2(K) - \alpha_2(K))}{(\lambda_2(K) + \alpha_1(K))(\lambda_2(K) + \alpha_2(K))} e^{-\lambda_2(K)(z_1+z_2)} \\ & \quad - \frac{A_1(\lambda_1^2 - \alpha_2^2) + A_2(\lambda_1^2 - \alpha_1^2)}{(\lambda_1(K) + \lambda_2(K))(\lambda_1(K) - \lambda_2(K))^2} \\ & \quad \frac{(\lambda_2(K) - \alpha_1(K))(\lambda_2(K) - \alpha_2(K))}{(\lambda_1(K) + \alpha_1(K))(\lambda_1(K) + \alpha_2(K))} e^{-\lambda_2(K)z_1 - \lambda_1(K)z_2} \\ & \quad - \frac{A_1(\lambda_2^2 - \alpha_2^2) + A_2(\lambda_2^2 - \alpha_1^2)}{(\lambda_1(K) + \lambda_2(K))(\lambda_1(K) - \lambda_2(K))^2} \\ & \quad \frac{(\lambda_1(K) - \alpha_1(K))(\lambda_1(K) - \alpha_2(K))}{(\lambda_2(K) + \alpha_1(K))(\lambda_2(K) + \alpha_2(K))} e^{-\lambda_1(K)z_1 - \lambda_2(K)z_2} \\ & \quad \left. + \frac{A_1(\lambda_1^2 - \alpha_2^2) + A_2(\lambda_1^2 - \alpha_1^2)}{2\lambda_1(K)(\lambda_1(K) - \lambda_2(K))^2} \right. \\ & \quad \left. \frac{(\lambda_1(K) - \alpha_1(K))(\lambda_1(K) - \alpha_2(K))}{(\lambda_1(K) + \alpha_1(K))(\lambda_1(K) + \alpha_2(K))} e^{-\lambda_1(K)(z_1+z_2)} \right\}, \end{aligned} \quad (4.33)$$

where

$$\alpha_i(K) = \sqrt{\alpha_i^2 + K^2}; \quad \lambda_i(K) = \sqrt{\lambda_i^2 + K^2} \quad (4.34)$$

and

$$J_0(KR_{12}) = \frac{1}{\pi} \int_0^\pi d\varphi e^{iKR_{12} \cos \varphi} \quad (4.35)$$

is a Bessel function of the first kind.

The first two terms of expression (4.33) correspond to the homogeneous part  $h_+^b(R, z_1, z_2)$  of the correlation function. The rest of the terms are the non-homogeneous part. Setting  $A_1 = 0$  or  $A_2 = 0$ , this expression reduces to that obtained in [26, 27] for a fluid interacting with a one-Yukawa potential.

From expression (4.33) we see that  $\lambda_1$  and  $\lambda_2$  play the role of parameters characterizing the screening of the repulsive and the attractive interactions respectively. In contrast, for one-Yukawa fluids [27] these parameters have a simple form  $\varkappa_i^2 + \alpha_i^2$  ( $i = 1, 2$ ). This means that for an attractive one-Yukawa case the pair correlation function is not defined for low temperatures, high densities, or strongly attractive potentials due to condition  $\varkappa_2^2 + \alpha_2^2 < 0$ . Note that the quantities  $\lambda_1$  and  $\lambda_2$  appear in the bulk part of the pair correlation function as well as in the inhomogeneous contribution to the MFA density profile (3.42). Consequently, if condition (3.45) is satisfied the pair correlation function of a two-Yukawa fluid becomes well-defined for all temperatures and densities as well as for strongly attractive interactions between the particles.

#### 4.4. Density profile

In the Gaussian approximation the inhomogeneous density profile can be written as the sum of the mean field profile  $\rho^{MFA}(z)$  and the quadratic fluctuation term  $\rho^{fluct}(z)$

$$\rho(z) = \rho^{MFA}(z) + \rho^{fluct}(z). \quad (4.36)$$

The contribution of quadratic fluctuations to the profile corresponds to the one-particle irreducible diagram in the field theory [36, 37] and can be found as:

$$\frac{\rho^{fluct}(z_1)}{\rho_b} = \frac{1}{2} [h_+(R, z_1, z_2) - h_+^b(R, z_1, z_2)] \Big|_{\substack{z_2 \rightarrow z_1 \\ R \rightarrow 0}}, \quad (4.37)$$

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

As a result

$$\begin{aligned}
\frac{\rho^{fluct}(z_1)}{\rho_b} = & -\frac{1}{8\pi\rho_b} \int_0^\infty K dK \left\{ \frac{\varkappa_1^2(\lambda_1^2 - \alpha_2^2) + \varkappa_2^2(\lambda_1^2 - \alpha_1^2)}{\lambda_1(K)(\lambda_2(K) - \lambda_1(K))^2} \times \right. \\
& \frac{(\lambda_1(K) - \alpha_1(K))(\lambda_1(K) - \alpha_2(K))}{(\lambda_1(K) + \alpha_1(K))(\lambda_1(K) + \alpha_2(K))} e^{-2\lambda_1(K)z_1} \\
& - 2 \left[ \frac{\varkappa_1^2(\lambda_2^2 - \alpha_2^2) + \varkappa_2^2(\lambda_2^2 - \alpha_1^2)}{(\lambda_2(K) + \lambda_1(K))(\lambda_2(K) - \lambda_1(K))^2} \times \right. \\
& \frac{(\lambda_1(K) - \alpha_1(K))(\lambda_1(K) - \alpha_2(K))}{(\lambda_2(K) + \alpha_1(K))(\lambda_2(K) + \alpha_2(K))} \\
& + \left. \frac{\varkappa_1^2(\lambda_1^2 - \alpha_2^2) + \varkappa_2^2(\lambda_1^2 - \alpha_1^2)}{(\lambda_2(K) + \lambda_1(K))(\lambda_2(K) - \lambda_1(K))^2} \times \right. \\
& \left. \frac{(\lambda_2(K) - \alpha_1(K))(\lambda_2(K) - \alpha_2(K))}{(\lambda_1(K) + \alpha_1(K))(\lambda_1(K) + \alpha_2(K))} \right] e^{-[\lambda_1(K) + \lambda_2(K)]z_1} \\
& + \left. \frac{\varkappa_1^2(\lambda_2^2 - \alpha_2^2) + \varkappa_2^2(\lambda_2^2 - \alpha_1^2)}{\lambda_2(K)(\lambda_2(K) - \lambda_1(K))^2} \times \right. \\
& \left. \frac{(\lambda_2(K) - \alpha_1(K))(\lambda_2(K) - \alpha_2(K))}{(\lambda_2(K) + \alpha_1(K))(\lambda_2(K) + \alpha_2(K))} e^{-2\lambda_2(K)z_1} \right\}.
\end{aligned} \quad (4.38)$$

Note that the constant  $1/(8\pi\rho_b)$  in front of the fluctuation term (4.38) can be rewritten in the form  $\eta \equiv 1/(8\pi\rho_b r_d^3)$ . In terms of reduced parameters  $\eta = \beta^* \tau (\pi \rho^* \beta^* \tau)^{1/2}$  and similar to the one-Yukawa fluid [27] the corrections due to fluctuations become more significant with increasing bulk density  $\rho^*$  and/or decreasing temperature  $T^* = 1/\beta^*$ .

In Figures 2-3 we present the density profiles for different values of parameter  $\eta$  which correspond to different values of reduced bulk density and temperature. We give the mean field profile  $\rho^{MFA}(z)/\rho_b$ , the contribution from fluctuations  $\rho^{fluct}(z)/\rho_b$ , and the sum of the two  $\rho(z)/\rho_b$ . The contribution from fluctuations has a negative sign which is expected since in [27] it was shown that for a one-Yukawa fluid the fluctuation part of the density profile is negative for both attractive and repulsive interactions. Due to the fact that in the present model the mean field contribution is non-monotonic, we see that for some parameters the full profile has a minimum and a maximum between the contact value and the bulk value. This means that the fluid can have a layered-type structure, which was not observed in the one-Yukawa case. As parameter  $\eta$

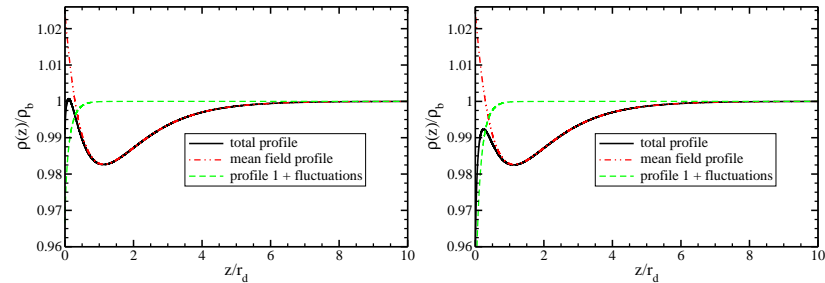


Figure 2. Density profile in the Gaussian approximation for  $\omega = 2$ ,  $\tau = 1.35$  and different values of parameter  $\eta$ . On the left  $\eta = 0.5$  ( $T^* = 1$ ,  $\rho^* = 0.0325$ ). On the right  $\eta = 1.0$  ( $T^* = 0.5$ ,  $\rho^* = 0.0163$ ). The curve denoted by the dash-dotted red line is the mean field solution of equations (3.15)–(3.19), for the dashed green line we have the contribution from the fluctuations, and the solid black line is the sum of the two.

is increased, the profile exhibits smaller oscillations and monotonically decreases at the approach of the surface. We also observe that with increasing  $\eta$  the density depletion effect becomes more pronounced. At low values of  $\eta$  fluid particles accumulate near the wall while for higher values of  $\eta$  they are held back from the wall. These results are in qualitative agreement with [30], where a hard core two-Yukawa fluid was studied by means of Monte-Carlo simulations and the density functional theory.

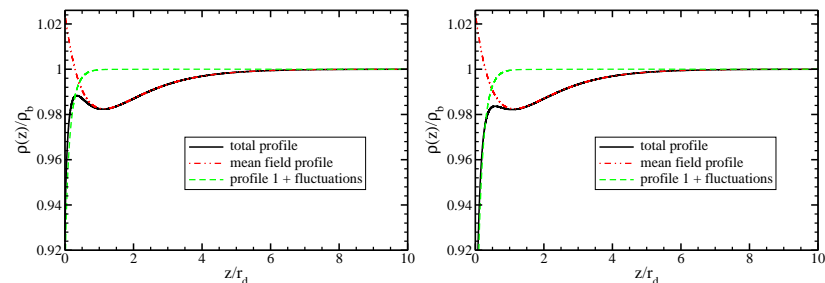


Figure 3. Identical quantities as shown in Figure 2 for  $\eta = 1.5$  ( $T^* = 0.335$ ,  $\rho^* = 0.011$ ) on the left and  $\eta = 2.0$  ( $T^* = 0.167$ ,  $\rho^* = 0.0055$ ) on the right.

#### 4.5. Contact theorem

In Section 3.2 we have shown the validity of the contact theorem in the mean field approximation. Here we will show that for the considered model the contact theorem is also satisfied when the fluctuations are taken into account.

Setting  $z_1 = 0$  in expression (4.38) and using identities (4.14), we obtain the contact value of density

$$\rho^{fluct}(0_+) = \frac{1}{4\pi} \int_0^\infty K dK \left[ \alpha_1(K) + \alpha_2(K) - \frac{1}{2} [\lambda_1(K) + \lambda_2(K)] \right. \\ \left. - \frac{1}{2} \frac{[\alpha_1^2(K) + \lambda_1(K)\lambda_2(K)] [\alpha_2^2(K) + \lambda_1(K)\lambda_2(K)]}{\lambda_1(K)\lambda_2(K) [\lambda_1(K) + \lambda_2(K)]} \right]. \quad (4.39)$$

Going back to expression (4.17) for the pressure we can calculate the fluctuation part of the pressure using the cylindrical coordinate system instead of the spherical one. Then we have

$$\beta P^{fluct} = \frac{\rho_b^2}{12\pi^2} \int_0^\infty k^3 dk \frac{\nu(k)}{[1 + \rho\nu(k)]^2} \frac{d\nu(k)}{dk} \quad (4.40) \\ = \frac{\rho_b^2}{4\pi^2} \int_0^\infty K dK \int_{-\infty}^\infty \mu d\mu \frac{\nu(K, \mu)}{[1 + \rho_b \nu(K, \mu)]^2} \frac{d\nu(K, \mu)}{d\mu} \\ = -\frac{1}{2\pi^2} \int_0^\infty K dK \int_{-\infty}^\infty \mu^2 d\mu \frac{[\varkappa_1^2 (\mu^2 + \alpha_2^2(K)) + \varkappa_2^2 (\mu^2 + \alpha_1^2(K))]}{[\mu^2 + \lambda_1^2(K)]^2 [\mu^2 + \lambda_2^2(K)]^2} \\ \frac{[\varkappa_1^2 (\mu^2 + \alpha_2^2(K))^2 + \varkappa_2^2 (\mu^2 + \alpha_1^2(K))^2]}{[\mu^2 + \alpha_1^2(K)] [\mu^2 + \alpha_2^2(K)]}.$$

After integration with respect to  $\mu$  and taking into account relations (4.14) we obtain

$$\beta P^{fluct} = \frac{1}{4\pi} \int_0^\infty K dK \left[ \alpha_1(K) + \alpha_2(K) - \frac{1}{2} [\lambda_1(K) + \lambda_2(K)] \right. \\ \left. - \frac{1}{2} \frac{[\alpha_1^2(K) + \lambda_1(K)\lambda_2(K)] [\alpha_2^2(K) + \lambda_1(K)\lambda_2(K)]}{\lambda_1(K)\lambda_2(K) [\lambda_1(K) + \lambda_2(K)]} \right], \quad (4.41)$$

which is exactly the expression (4.39).

We have therefore proved the validity of the contact theorem for the fluctuation term of the density profile.

#### 4.6. Adsorption

We can calculate the adsorption coefficient defined as

$$\Gamma = \int_0^\infty dz [\rho(z) - \rho_b] = \Gamma_{MFA} + \Gamma_{fluct} \quad (4.42)$$

according to different approximations of the mean field density profile presented in Section 3.3.

Hence the exact mean field contribution can be determined only numerically.

The linearized equation (3.42) gives

$$\Gamma_{MFA}^L = -\frac{\rho_b}{2\lambda_1} \frac{(\lambda_1^2 - \alpha_2^2)}{(\lambda_1^2 - \lambda_2^2)} \left( -\frac{\varkappa_1^2}{\alpha_1^2} + \frac{\lambda_2^2 - \alpha_2^2 - \varkappa_2^2}{\alpha_2^2} \right) \\ - \frac{\rho_b}{2\lambda_2} \frac{(\lambda_2^2 - \alpha_2^2)}{(\lambda_1^2 - \lambda_2^2)} \left( \frac{\varkappa_1^2}{\alpha_1^2} - \frac{\lambda_1^2 - \alpha_2^2 - \varkappa_2^2}{\alpha_2^2} \right), \quad (4.43)$$

and the simplified linear approximation (3.46) gives

$$\Gamma_{MFA}^{sl} = \frac{\rho_b \varkappa_1^2}{2\alpha_1^3} + \frac{\rho_b \varkappa_2^2}{2\alpha_2^3}. \quad (4.44)$$

As we can see from Figure 1 the linear approximation (3.42) interpolates the mean field result for the density profile quite well. Due to this we can consider the linear approximation (4.43) for the adsorption coefficient as a correct enough result in the framework of the MFA. At the same time we can see from Figure 1 that the simplified linear approximation (3.46) is rather crude. However, expression (4.44) gives a simple estimate of the sign of the adsorption coefficient. This expression tells us that  $\Gamma_{MFA}^{sl}$  is positive if  $\omega > \tau^3$  and negative if  $\omega < \tau^3$ .

In order to determine the sign of  $\Gamma_{MFA}^L$  we use identities (4.14) to rewrite expression (4.43) as

$$\Gamma_{MFA}^L = \frac{\rho_b |\varkappa_2^2|}{2(\lambda_1 + \lambda_2)\lambda_1\lambda_2\tau^2} \left[ \omega - \tau^4 + (\omega - \tau^2) \sqrt{4\pi\rho_b^*\beta^*\tau^3(\omega - \tau^2) + \tau^2} \right]. \quad (4.45)$$

The function outside of the square brackets is positive, therefore the sign of  $\Gamma_{MFA}^L$  is determined by the sign of the function inside the square

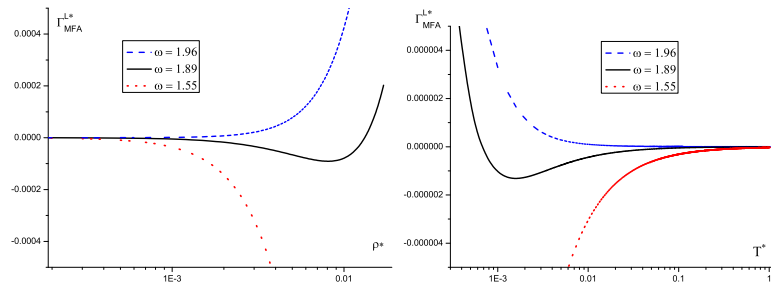


Figure 4. Reduced adsorption coefficient  $\Gamma_{MFA}^{L*}$  as a function of the reduced density at  $T^* = 0.083$  on the left and as a function of the reduced temperature at  $\rho^* = 0.0001$  on the right. The lines correspond to different values of parameter  $\omega$  at a fixed  $\tau = 1.25$  ( $\tau^2 = 1.56$ ,  $\tau^3 = 1.95$ ). The dashed blue lines correspond to  $\omega = 1.96$ , the solid black lines to  $\omega = 1.89$ , and the dotted red lines to  $\omega = 1.55$ .

brackets. The expression under the square root is also positive if we choose the parameters to satisfy the condition (3.45). Then we see that the expression inside the square brackets is a monotonic function of  $\beta^* \rho_b^*$  at a fixed  $\omega$  and  $\tau$ . Furthermore, this expression increases if  $\omega > \tau^2$  and decreases if  $\omega < \tau^2$ . At  $\beta^* \rho_b^* = 0$  the expression inside the square brackets equals  $(\tau + 1)(\omega - \tau^3)$ . This means that for the case of  $\omega < \tau^2$   $\Gamma_{MFA}^L$  is negative for all values of  $\beta^* \rho_b^*$ . At  $\omega > \tau^3$  we have that  $\Gamma_{MFA}^L$  is positive for all values of  $\beta^* \rho_b^*$ . For the case when  $\tau^2 < \omega < \tau^3$  we have that  $\Gamma_{MFA}^L$  is negative at low values of  $\beta^* \rho_b^*$  and positive at higher values of  $\beta^* \rho_b^*$ . These relationships are illustrated in Figure 4 where we present the reduced adsorption coefficient  $\Gamma_{MFA}^{L*} = \Gamma_{MFA}^L / \alpha_1^2$  as a function of the reduced density and the reduced temperature for different values of  $\omega$  at a given value of  $\tau$ . One can see at  $\tau^2 < \omega < \tau^3$  the adsorption coefficient displays non-monotonic behavior with the density at a fixed temperature as well as with the temperature at a fixed density.  $\Gamma_{MFA}^{L*}$  is negative for lower values of the density and becomes positive for higher values of the density. Likewise, at a fixed density it is positive for lower temperatures and negative for higher temperatures. This effect was not observed in one-Yukawa systems [27] where the mean field contribution to the adsorption coefficient was strictly monotonic.

For the fluctuation part of the adsorption coefficient due to identities

(4.14) we obtain an analytical result

$$\begin{aligned} \Gamma_{fluct} = & \frac{1}{32\pi} (\lambda_1 + \lambda_2)^2 + \frac{1}{32\pi} (\alpha_1^2 + \alpha_2^2) - \frac{1}{16\pi} (\lambda_1 + \lambda_2) (\alpha_1 + \alpha_2) \\ & - \frac{1}{16\pi} \frac{(\lambda_2 \lambda_1 + \alpha_2^2)(\lambda_2 \lambda_1 + \alpha_1^2)}{(\lambda_1 + \lambda_2)^2} + \frac{1}{16\pi} \frac{(\alpha_1 + \alpha_2)(\lambda_2 \lambda_1 + \alpha_2 \alpha_1)}{\lambda_1 + \lambda_2} \\ & + \frac{1}{16\pi} (\lambda_1^2 + \lambda_2^2 - \alpha_1^2 - \alpha_2^2) \ln \left[ \frac{(\lambda_2 + \alpha_1)(\lambda_2 + \alpha_2)}{2\lambda_2(\lambda_1 + \lambda_2)} \right] \\ & + \frac{1}{16\pi} \frac{(\lambda_1^2 - \alpha_1^2)(\lambda_1^2 - \alpha_2^2)}{\lambda_2^2 - \lambda_1^2} \ln \left[ \frac{\lambda_1 (\lambda_2 + \alpha_1)(\lambda_2 + \alpha_2)}{\lambda_2 (\lambda_1 + \alpha_1)(\lambda_1 + \alpha_2)} \right]. \end{aligned} \quad (4.46)$$

Unlike the mean field contribution, the contribution from fluctuations  $\Gamma_{fluct}$  is always negative. This result is expected as in [27] it was shown that for a one-Yukawa fluid at a wall the fluctuation effects lead to density depletion for both repulsive and attractive interactions. In the region where  $\Gamma_{MFA}$  is negative the value of the total adsorption coefficient  $\Gamma$  will be negative. It is therefore more interesting to consider the region in which  $\Gamma_{MFA}$  is positive. In this case we will have the competition between the MFA contribution and the contribution from fluctuations. Such a situation is illustrated in Figures 5 and 6, where we present the reduced adsorption coefficient  $\Gamma^* = \Gamma / \alpha_1^2$  as a function of the reduced temperature  $T^*$  and of the reduced bulk density  $\rho_b^*$  respectively. The mean field contributions are calculated in the framework of the linearized approximation (4.43). In Figure 5 we observe compensation from

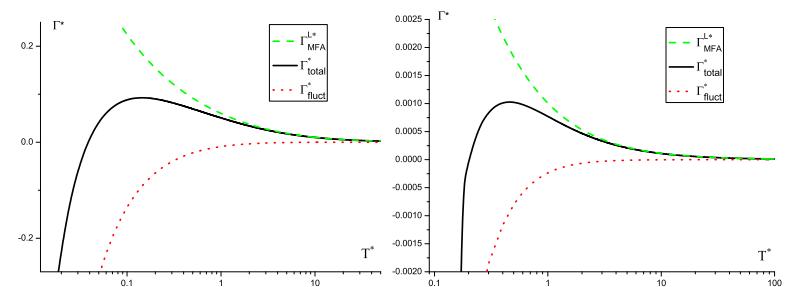


Figure 5. Adsorption isochore as a function of the reduced temperature at  $\omega = 3.4$ ,  $\tau = 1.25$  for  $\rho_b^* = 0.1$  on the left and  $\rho_b^* = 0.01$  on the right. The curve in dashed line (green) is the linearized mean field solution  $\Gamma_{MFA}^{L*}$ , in dotted line (red) we have the contribution from the fluctuations  $\Gamma_{fluct}^*$  and in full line (black) the sum of the two  $\Gamma_{total}^*$ .



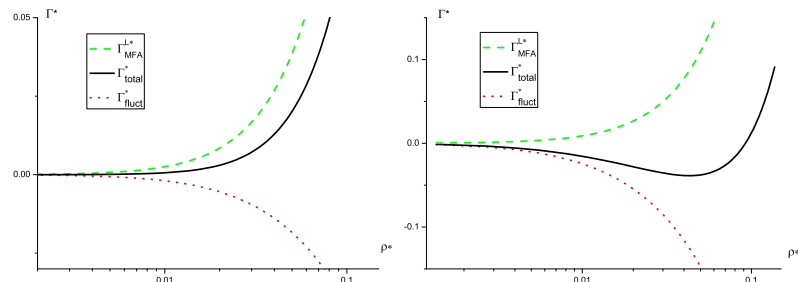


Figure 6. Adsorption isotherm as a function of the reduced density at  $\omega = 3.4$ ,  $\tau = 1.25$  for  $T^* = 0.3$  on the left and  $T^* = 0.05$  on the right. The curve in dashed line (green) is the linearized mean field solution  $\Gamma_{MFA}^{L*}$ , in dotted line (red) we have the contribution from the fluctuations  $\Gamma_{fluct}^*$  and in full line (black) the sum of the two  $\Gamma_{total}^*$ .

the two contributions resulting in non-monotonic dependence of  $\Gamma^*$  on the temperature for both higher and lower values of the bulk density. In Figure 6 we show dependence of  $\Gamma^*$  on  $\rho_b^*$  for two different values of  $T^*$ ,  $T^* = 0.3$  and  $T^* = 0.05$ . One can see that for  $T^* = 0.3$  the mean field term dominates. The fluctuation part becomes increasingly more important with decreasing temperature. In consequence, at certain values of the temperature the adsorption isotherm displays non-monotonic behavior with the bulk density. In [30] a similar result was obtained for a hard core two-Yukawa fluid in the framework of the density functional theory and Monte Carlo simulations.

## 5. Conclusions

In this work the field theoretical approach is applied to the description of a fluid interacting with a repulsive and an attractive Yukawa potentials in the vicinity of a hard wall. The results obtained are compared to a more simple one-Yukawa model considered in our previous work [27]. We derive mean field equations that allow for a numerical evaluation of the density profile. Subsequently the contact theorem is validated employing a scheme that can by linearity be generalized to a multi-Yukawa fluid. The numerical result of the density profile is then compared to different analytical estimations. We find that unlike a one-Yukawa fluid, a two-Yukawa fluid can have a non-monotonic profile even in the mean field approximation. The linearized version of the profile contains two

generalized decays  $\lambda_1$  and  $\lambda_2$  which have a more complicated form than in the one-Yukawa case. For the case of  $\alpha_1 > \alpha_2$  we determine that these decays cannot be complex and establish a simple condition on the free parameters of the fluid for them to be real-valued. In contrast, the results obtained in [27] for an attractive one-Yukawa case are not defined when  $\alpha_2^2 + \alpha_2^2 < 0$ , that is for low temperatures, high densities, or strongly attractive potentials. This peculiarity is related to general problems in the description of phase transitions in the framework of the Gaussian fluctuations theory in the bulk. More specifically, it is the so-called RPA-catastrophe which is caused by the incorrect treatment of short-range correlations and can be removed by including the repulsive interactions [33]. Compared to an attractive one-Yukawa case we thus show that generalization of the interaction potential to the sum of a repulsive and an attractive parts makes the profile decays well defined for all temperatures and densities.

Beyond the mean field approximation we study an impact of Gaussian fluctuations on thermodynamical and structural properties of the fluid. Analytical expressions for the free energy, the pressure, the chemical potential, and the correlation function are derived. Subsequently we find a correction to the density profile due to fluctuations and show that fluctuations always lead to depletion. This effect can cause an oscillatory behavior of the density profile which was not observed in the one-Yukawa case [27]. With a decreasing temperature the oscillations become smaller and the profile becomes more monotonic. We show analytically that the fluctuation terms of the pressure and of the density contact value satisfy the contact theorem. Next we study the adsorption coefficient and its dependence on the bulk density and the temperature. A simple condition on the parameters of the pair potential is established to determine the sign and the monotonicity of the linearized mean field contribution. An analytical expression for the fluctuation part of the adsorption coefficient is then presented. Unlike the mean field part, the contribution from fluctuations is always negative. We consider the case when there is a competition between the two contributions. It is found that at higher temperatures the mean field term dominates, but as the temperature decreases the fluctuation effects become increasingly more important. As a result, non-monotonic adsorption curves are found for some systems. The behaviors of the density profile and of the adsorption isotherm described in this paper are in qualitative agreement with the results of [30], where a hard core two-Yukawa fluid was studied by means of Monte-Carlo simulations and the density functional theory.

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## A. The Riemann problem

Equation (4.29) can be represented in the form

$$P_+(K, \mu_1) h_+(K, \mu_1, \mu_2) - P_-(K, \mu_1) h_-(K, \mu_1, \mu_2) = -L(\mu_2) \delta(\mu_1 + \mu_2) \quad (1.1)$$

where

$$L(\mu_2) = 4\pi\beta \{A_1(\mu_2^2 + p^2 + \alpha_2^2) + A_2(\mu_2^2 + p^2 + \alpha_1^2)\}, \quad (1.2)$$

$$P_+(K, \mu_1) = (K^2 + \mu_1^2 + \alpha_1^2)(K^2 + \mu_1^2 + \alpha_2^2) + \varkappa_1^2(K^2 + \mu_1^2 + \alpha_2^2) + \varkappa_2^2(K^2 + \mu_1^2 + \alpha_1^2), \quad (1.3)$$

$$P_-(K, \mu_1) = (K^2 + \mu_1^2 + \alpha_1^2)(K^2 + \mu_1^2 + \alpha_2^2),$$

Equation (1.1) is known as the Riemann problem [35]. It can be solved by factorization, for which purpose we write the fraction  $P_-(K, \mu_1)/P_+(K, \mu_1)$  as

$$\frac{P_-(K, \mu_1)}{P_+(K, \mu_1)} = \frac{Q_+(K, \mu_1)}{Q_-(K, \mu_1)}, \quad (1.4)$$

where  $Q_+(K, \mu_1)$ ,  $Q_-(K, \mu_1)$  are analytical functions of  $\mu_1$  and cannot be zero in the upper + or lower - halves of the complex plane. The latter are easy to find:

$$\begin{aligned} Q_+(K, \mu_1) &= \frac{(\mu_1 + i\alpha_1(K))(\mu_1 + i\alpha_2(K))}{(\mu_1 + i\lambda_2(K))(\mu_1 + i\lambda_1(K))}, \\ Q_-(K, \mu_1) &= \frac{(\mu_1 - i\lambda_2(K))(\mu_1 - i\lambda_1(K))}{(\mu_1 - i\alpha_1(K))(\mu_1 - i\alpha_2(K))}, \end{aligned} \quad (1.5)$$

where

$$\begin{aligned} \alpha_1(K) &= \sqrt{K^2 + \alpha_1^2}, & \alpha_2(K) &= \sqrt{K^2 + \alpha_2^2}, \\ \lambda_2(K) &= \sqrt{K^2 + \lambda_2^2}, & \lambda_1(K) &= \sqrt{K^2 + \lambda_1^2}. \end{aligned} \quad (1.6)$$

Coefficients  $\lambda_1$ ,  $\lambda_2$  are found from equation

$$\lambda^4 - (\alpha_1^2 + \alpha_2^2 + \varkappa_1^2 + \varkappa_2^2)\lambda^2 + (\alpha_1^2 + \varkappa_1^2)(\alpha_2^2 + \varkappa_2^2) - \varkappa_1^2 \varkappa_2^2 = 0 \quad (1.7)$$

giving

$$\lambda_{1,2}^2 = \frac{1}{2} \left( \varkappa_1^2 + \alpha_1^2 + \varkappa_2^2 + \alpha_2^2 \pm \sqrt{(\varkappa_1^2 + \alpha_1^2 - \varkappa_2^2 - \alpha_2^2)^2 + 4\varkappa_1^2 \varkappa_2^2} \right) \quad (1.8)$$

and coinciding with expressions (3.32) obtained in the framework of the mean field approximation.

We choose  $i\lambda_2(K)$ ,  $i\lambda_1(K)$  to be in the upper and  $-i\lambda_2(K)$ ,  $-i\lambda_1(K)$  in the lower halves of the analytical plane.

Equation (1.1) now reads

$$\frac{h_+(K, \mu_1, \mu_2)}{Q_+(K, \mu_1)} - \frac{h_-(K, \mu_1, \mu_2)}{Q_-(K, \mu_1)} = -\frac{L(\mu_2) \delta(\mu_1 + \mu_2)}{Q_+(K, -\mu_2) P_+(K, -\mu_2)}. \quad (1.9)$$

In (1.1) we present the Dirac function as the difference of one-sided Dirac functions

$$\delta(\mu_1 + \mu_2) = \delta_+(\mu_1 + \mu_2) - \delta_-(\mu_1 + \mu_2), \quad (1.10)$$

which are analytical in the upper and lower halves of the complex plane respectively. Since the index of the problem (1.1) is zero [35], we obtain

$$\begin{aligned} h_+(K, \mu_1, \mu_2) &= -\frac{L(\mu_2) Q_+(K, \mu_1)}{Q_+(K, -\mu_2) P_+(K, -\mu_2)} \delta_+(\mu_1 + \mu_2) \\ h_-(K, \mu_1, \mu_2) &= -\frac{L(\mu_2) Q_-(K, \mu_1)}{Q_+(K, -\mu_2) P_+(K, -\mu_2)} \delta_-(\mu_1 + \mu_2). \end{aligned} \quad (1.11)$$

Replacing (1.2), (1.4) and (1.5) into (1.11), we have

$$\begin{aligned} h_+(K, \mu_1, \mu_2) &= \\ &= -4\pi\beta \frac{A_1(\mu_2^2 + \alpha_2^2)(K) + A_2(\mu_2^2 + \alpha_1^2)(K)}{(\mu_2 - i\alpha_1(K))(\mu_2 - i\alpha_2(K))(\mu_2 + i\lambda_2(K))(\mu_2 + i\lambda_1(K))} \\ &\quad \frac{(\mu_1 + i\alpha_1(K))(\mu_1 + i\alpha_2(K))}{(\mu_1 + i\lambda_2(K))(\mu_1 + i\lambda_1(K))} \delta_+(\mu_1 + \mu_2), \end{aligned} \quad (1.12)$$

$$\begin{aligned} h_-(K, \mu_1, \mu_2) &= \\ &= -4\pi\beta \frac{A_1(\mu_2^2 + \alpha_2^2) + A_2(\mu_2^2 + \alpha_1^2)}{(\mu_2 - i\alpha_1(K))(\mu_2 - i\alpha_2(K))(\mu_2 + i\lambda_2(K))(\mu_2 + i\lambda_1(K))} \\ &\quad \frac{(\mu_1 - i\lambda_2(K))(\mu_1 - i\lambda_1(K))}{(\mu_1 - i\alpha_1(K))(\mu_1 - i\alpha_2(K))} \delta_-(\mu_1 + \mu_2). \end{aligned} \quad (1.13)$$

Performing the inverse Fourier transformation

$$h(R_{12}, z_1, z_2) = \int \frac{d\mathbf{K}}{(2\pi)^2} e^{-i\mathbf{K}R_{12}} \int_{-\infty}^{\infty} \frac{d\mu_1}{2\pi} e^{-i\mu_1 z_1} \int_{-\infty}^{\infty} \frac{d\mu_2}{2\pi} e^{-i\mu_2 z_2} \{h_+(K, \mu_1, \mu_2) - h_-(K, \mu_1, \mu_2)\}, \quad (1.14)$$

we can find the originals of one-sided pair correlation functions. Due to the considered model we are interested in the case when both particles are in the upper half-space  $z_1 > 0$ ,  $z_2 > 0$ . We present one-sided  $\delta$ -functions as

$$\begin{aligned} \delta_+(\mu_1 + \mu_2) &= \lim_{\varepsilon \rightarrow 0} \frac{i}{\mu_1 + \mu_2 + i\varepsilon}, \\ \delta_-(\mu_1 + \mu_2) &= \lim_{\varepsilon \rightarrow 0} \frac{i}{\mu_1 + \mu_2 - i\varepsilon} \end{aligned} \quad (1.15)$$

and integrate by  $\mu_1$ . Then for  $z_1 > 0$ , closing the integration contour in the lower half of the complex plane, we have

$$\begin{aligned} \lim_{\varepsilon \rightarrow 0} \int_{-\infty}^{\infty} \frac{d\mu_1}{2\pi} \frac{(\mu_1 + i\alpha_1(K))(\mu_1 + i\alpha_2(K))}{(\mu_1 + i\lambda_2(K))(\mu_1 + i\lambda_1(K))} \frac{i}{\mu_1 + \mu_2 + i\varepsilon} e^{-i\mu_1 z_1} = \\ \frac{(\mu_2 - i\alpha_1(K))(\mu_2 - i\alpha_2(K))}{(\mu_2 - i\lambda_2(K))(\mu_2 - i\lambda_1(K))} e^{i\mu_2 z_1} - \\ i \frac{(\lambda_2(K) - \alpha_1(K))(\lambda_2(K) - \alpha_2(K))}{((\lambda_2(K) - \lambda_1(K))(\mu_2 - i\lambda_2(K)))} e^{-\lambda_2(K)z_1} + \\ i \frac{(\lambda_1(K) - \alpha_1(K))(\lambda_1(K) - \alpha_2(K))}{(\lambda_2(K) - \lambda_1(K))(\mu_2 - i\lambda_1(K))} e^{-\lambda_1(K)z_1}. \end{aligned} \quad (1.16)$$

Now we integrate by  $\mu_2$ . We consider the case  $z_2 > 0$ .

$$\begin{aligned} \int_{-\infty}^{\infty} \frac{d\mu_2}{2\pi} \frac{[A_1(\mu_2^2 + \alpha_2^2(K)) + A_2(\mu_2^2 + \alpha_1^2(K))] e^{-i\mu_2 z_2}}{(\mu_2 - i\alpha_1(K))(\mu_2 - i\alpha_2(K))(\mu_2 + i\lambda_2(K))(\mu_2 + i\lambda_1(K))} \\ \left\{ \frac{(\mu_2 - i\alpha_1(K))(\mu_2 - i\alpha_2(K))}{(\mu_2 - i\lambda_2(K))(\mu_2 - i\lambda_1(K))} e^{i\mu_2 z_1} - \right. \\ \left. i \frac{(\lambda_2(K) - \alpha_1(K))(\lambda_2(K) - \alpha_2(K))}{(\lambda_2(K) - \lambda_1(K))(\mu_2 - i\lambda_2(K))} e^{-\lambda_2(K)z_1} + \right. \\ \left. i \frac{(\lambda_1(K) - \alpha_1(K))(\lambda_1(K) - \alpha_2(K))}{(\lambda_2(K) - \lambda_1(K))(\mu_2 - i\lambda_1(K))} e^{-\lambda_1(K)z_1} \right\} = \\ - \frac{A_1(\lambda_2^2 - \alpha_2^2) + A_2(\lambda_2^2 - \alpha_1^2)}{2\lambda_2(K)(\lambda_1^2 - \lambda_2^2)} e^{-\lambda_2(K)|z_1 - z_2|} + \\ \frac{A_1(\lambda_1^2 - \alpha_2^2) + A_2(\lambda_1^2 - \alpha_1^2)}{2\lambda_1(K)(\lambda_1^2 - \lambda_2^2)} e^{-\lambda_1(K)|z_1 - z_2|} + \quad (1.17) \\ \frac{A_1(\lambda_2^2 - \alpha_2^2) + A_2(\lambda_2^2 - \alpha_1^2)}{2\lambda_2(K)(\lambda_1(K) - \lambda_2(K))^2} \\ \frac{(\lambda_2(K) - \alpha_1(K))(\lambda_2(K) - \alpha_2(K))}{(\lambda_2(K) + \alpha_1(K))(\lambda_2(K) + \alpha_2(K))} e^{-\lambda_2(K)(z_1 + z_2)} - \\ \frac{A_1(\lambda_1^2 - \alpha_2^2) + A_2(\lambda_1^2 - \alpha_1^2)}{(\lambda_1(K) + \lambda_2(K))(\lambda_1(K) - \lambda_2(K))^2} \\ \frac{(\lambda_2(K) - \alpha_1(K))(\lambda_2(K) - \alpha_2(K))}{(\lambda_1(K) + \alpha_1(K))(\lambda_1(K) + \alpha_2(K))} e^{-\lambda_2(K)z_1 - \lambda_1(K)z_2} - \\ \frac{A_1(\lambda_2^2 - \alpha_2^2) + A_2(\lambda_2^2 - \alpha_1^2)}{(\lambda_1(K) + \lambda_2(K))(\lambda_1(K) - \lambda_2(K))^2} \\ \frac{(\lambda_1(K) - \alpha_1(K))(\lambda_1(K) - \alpha_2(K))}{(\lambda_2(K) + \alpha_1(K))(\lambda_2(K) + \alpha_2(K))} e^{-\lambda_1(K)z_1 - \lambda_2(K)z_2} + \\ \frac{A_1(\lambda_1^2 - \alpha_2^2) + A_2(\lambda_1^2 - \alpha_1^2)}{2\lambda_1(K)(\lambda_1(K) - \lambda_2(K))^2} \\ \frac{(\lambda_1(K) - \alpha_1(K))(\lambda_1(K) - \alpha_2(K))}{(\lambda_1(K) + \alpha_1(K))(\lambda_1(K) + \alpha_2(K))} e^{-\lambda_1(K)(z_1 + z_2)} \end{aligned}$$

Taking the inverse Fourier transform with respect to vector  $K$ , we obtain the following expression for the case when particles 1 and 2 are in the

upper half-space, i.e.  $z_1 > 0$ ,  $z_2 > 0$

$$\begin{aligned}
 h_+(R_{12}, z_1, z_2) = & \beta \frac{A_1(\lambda_2^2 - \alpha_2^2) + A_2(\lambda_2^2 - \alpha_1^2)}{(\lambda_1^2 - \lambda_2^2)} \frac{e^{-\lambda_2 R_{12}}}{R_{12}} - \\
 & \beta \frac{A_1(\lambda_1^2 - \alpha_2^2) + A_2(\lambda_1^2 - \alpha_1^2)}{(\lambda_1^2 - \lambda_2^2)} \frac{e^{-\lambda_1 R_{12}}}{R_{12}} - \\
 & 2\beta \int_0^\infty p J_0(K R_{12}) dp \left\{ \frac{A_1(\lambda_2^2 - \alpha_2^2) + A_2(\lambda_2^2 - \alpha_1^2)}{2\lambda_2(K)(\lambda_1(K) - \lambda_2(K))^2} \right. \\
 & \frac{(\lambda_2(K) - \alpha_1(K))(\lambda_2(K) - \alpha_2(K))}{(\lambda_2(K) + \alpha_1(K))(\lambda_2(K) + \alpha_2(K))} e^{-\lambda_2(K)(z_1+z_2)} - \\
 & \frac{A_1(\lambda_1^2 - \alpha_2^2) + A_2(\lambda_1^2 - \alpha_1^2)}{(\lambda_1(K) + \lambda_2(K))(\lambda_1(K) - \lambda_2(K))^2} \\
 & \frac{(\lambda_2(K) - \alpha_1(K))(\lambda_2(K) - \alpha_2(K))}{(\lambda_1(K) + \alpha_1(K))(\lambda_1(K) + \alpha_2(K))} e^{-\lambda_2(K)z_1 - \lambda_1(K)z_2} - \\
 & \frac{A_1(\lambda_2^2 - \alpha_2^2) + A_2(\lambda_2^2 - \alpha_1^2)}{(\lambda_1(K) + \lambda_2(K))(\lambda_1(K) - \lambda_2(K))^2} \\
 & \frac{(\lambda_1(K) - \alpha_1(K))(\lambda_1(K) - \alpha_2(K))}{(\lambda_2(K) + \alpha_1(K))(\lambda_2(K) + \alpha_2(K))} e^{-\lambda_1(K)z_1 - \lambda_2(K)z_2} \\
 & \left. + \frac{A_1(\lambda_1^2 - \alpha_2^2) + A_2(\lambda_1^2 - \alpha_1^2)}{2\lambda_1(K)(\lambda_1(K) - \lambda_2(K))^2} \right. \\
 & \left. \frac{(\lambda_1(K) - \alpha_1(K))(\lambda_1(K) - \alpha_2(K))}{(\lambda_1(K) + \alpha_1(K))(\lambda_1(K) + \alpha_2(K))} e^{-\lambda_1(K)(z_1+z_2)} \right\},
 \end{aligned} \tag{1.18}$$

where  $J_0(K R_{12})$  is a Bessel function of the first kind given by expression (4.35).

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