Adsorption of Yukawa fluids on a hard wall

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INVITED ARTICLE

Adsorption of Yukawa fluids on a hard wall

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We construct a closure theory for the bridge functional based on the third-order Ornstein–Zernike (OZ3) equation. The new closure is tested on the adsorption of the hard-core Yukawa fluid on a planar hard wall and its results are compared with Monte Carlo computer simulation. We show that in the particularly challenging cases of depletive adsorption, the density profiles near the wall obtained from the OZ3 theory improve considerably over conventional liquid-state theories, such as the hypernetted-chain and the Percus–Yevick equations. Some technical details of the implementation of the procedure of re-normalisation of the non-uniform indirect correlation function are also provided.

Keywords: density functional theory; bridge function; Yukawa fluid; renormalisation; third-order Ornstein–Zernike equation

1. Introduction

We remark that when fluids adsorb on a solid surface, either of two situations may occur with regard to the singlet density function: (1) the contact value of the singlet density is higher than the bulk density. There is an abundance of molecules near the wall. We call this adhesion. (2) The contact density is lower than the bulk value; thus, there is a deficit of molecules at the wall. We call this depletion. We also do not rule out the third possibility of an even distribution. In statistical mechanics, the density profile near and not far from the wall is described by the singlet probability density \( \rho_w(z) \) (\( z \) being the distance normal to the wall). Far from the wall (\( z \to \infty \)), \( \rho_w(z) \) approaches the constant bulk density value \( \rho_0 \). Adhesion or depletion of molecules near the solid substrate is a general behaviour: present at either supercritical or subcritical states, with different substrate affinities, molecular species, and geometries of the inhomogeneities. Accumulation or detachment of molecules at the interface is the result of competition between the interfacial wall forces and the coherent fluid–fluid forces among the fluid molecules vis-à-vis the state conditions (phase diagrams, pressures, and temperatures, see the reviews [1,2]). It is the charge of the statistical mechanics discipline to delineate the interplay amongst these factors.

Compared to the weighted-function approaches [3] in the density functional theory (DFT) for inhomogeneous fluids, the conventional closure-based integral equations (based on an approximate bridge function or functional) have been less successful in dealing with the depletion adsorption. In a previous theoretical development [4] (hereafter referred to as Paper I), we have proposed a new formulation, the Ornstein–Zernike (OZ3) based closures for the bridge function (closures based on the OZ3 equations). An early test on the depletive adsorption of the Lennard-Jones fluid on a hard wall (HW) showed promise [4]. In this study, we shall further examine the adsorption of another simple fluid, exemplified by the hard-core attractive Yukawa potential (HCAY), on a simple HW. We shall pay special attention to cases of the depletive adsorption, precisely because these systems are more difficult to describe by the analytical theories. The traditional closures for uniform fluids, such as the Percus–Yevick (PY) and hypernetted-chain (HNC) equations, fall short to give quantitative answers for these non-uniform cases, as we shall see in detail in the next sections.

There have been a number of studies on the Yukawa fluid/hard wall (Yu/HW) systems [5–10]. While the approaches based on the fundamental measure theory (FMT [3]) have been quite accurate, attempts made employing the closure-based DFT have not yielded equally successful results for depletive absorptions. We shall test and ascertain the performance of the present OZ3-based bridge functions for the Yu/HW systems.

The theoretical basis has been laid out in Paper I [4]. Therefore, we shall be brief on the details of this approach. Section 2 gives an overview of the OZ3 equation. In Section 3, we outline the construction of the third-order term in the bridge functional expansion and the rationale
to generalise it to higher order terms. We apply the new bridge functional to the attractive Yukawa fluid adsorbed on an HW in Section 4. Five state conditions are examined. Most cases show the depletion type of adsorption. To determine the validity of the present approach, we also performed new Monte Carlo (MC) simulations for this non-uniform system in the constant number (N), volume (V), and temperature (T) ensemble (i.e. NVT). Some conclusions are drawn in Section 5.

2. Theory of the third-order Ornstein–Zernike equation

For an $N$-body system under influence of an external one-body potential $u(1)$, the Hamiltonian $H_N$ is given by

$$H_N(p^N, r^N) \equiv \sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{i=1}^{N} \sum_{j<i}^{N} u(2)(r_{ij}) + \sum_{k=1}^{N} u(1)(r_k),$$

(2.1)

where $p^N$ is the $N$-vector of momenta, $r^N$ the $N$-vector of positions, $m$ = mass of molecules, $u(2)$ is the pair potentials among the fluid particles. $r_{ij}$ is the relative distance $|r_j - r_i|$, $r_k$ is the distance of the $k$th molecule. The commonly known second-order OZ equation

$$h_0^{(2)}(1, 2) - C_0^{(2)}(1, 2) \equiv \int d3C_0^{(2)}(1, 3)\rho_0 h_0^{(2)}(3, 2)$$

can be shown to result from the inverse relation of the fluctuation derivative and the compressibility derivative (as in the functional calculus of Lebowitz and Percus [11])

$$\int d3 \frac{\delta \rho_w(1)}{\delta W(3)} \frac{\delta W(3)}{\delta \rho_w(2)} = \delta_3(1, 2),$$

(2.2)

where $W$ is the intrinsic chemical potential defined by: $W(\vec{r}) \equiv \beta \mu_0 - \beta u^{(1)}(\vec{r})$. (Notation: arguments 1 $\equiv r_1$, and 2 $\equiv r_2$, etc.), and $\delta_3(1, 2)$ is the three-dimensional Dirac delta function. Note that $h$ is the total correlation, $C$ the direct correlation, $\beta \mu_0$ is the bulk chemical potential divided by $kT$ ($\mu_0/kT$): $k$ = Boltzmann constant and $T$ = absolute temperature. The functional derivatives are known explicitly from Lebowitz and Percus [11]

$$\frac{\delta \rho_w(1)}{\delta W(2)} = \delta_3(1, 2)\rho_w(1) + F^{(2)}(1, 2) \quad \text{and}$$

$$\frac{\delta W(1)}{\delta \rho_w(2)} = \frac{\delta_3(1, 2)}{\rho_w(1)} - C^{(2)}(1, 2),$$

(2.3)

where $F^{(2)}$ is the Ursell distribution function. Naturally, we can inquire about the relations among the higher functional derivatives. This has been done previously [12], and we shall cite only the results here. There are six equivalent forms of the third-order OZ relation. The one that we are interested in is the functional relation

$$\frac{\delta W(1)}{\delta \rho_w(2)} = \delta_3(1, 2)\rho_w(1) + F^{(2)}(1, 2) = -\int d4d5d6 \frac{\delta W(4)}{\delta \rho_w(3)} \frac{\delta W(6)}{\delta \rho_w(2)}$$

$$\times \frac{\delta W(1)}{\delta \rho_w(5)} \frac{\delta W(5)}{\delta \rho_w(4)} \cdot \frac{\delta W(4)}{\delta W(6)}. (2.4)$$

After some algebra, we obtain the OZ3 equation [11]

$$C_{123} = h_{123} - C_{12}C_{13} - C_{21}C_{23} - C_{31}C_{32}$$

$$- \rho^2 \int d4d5d6C_{14}C_{25}C_{36}h_{456}$$

$$+ \rho^2 \int d4d5d6C_{15}C_{26}h_{356} - \rho \int d5C_{15}h_{235}$$

$$+ \rho^2 \int d4d5d6C_{14}C_{26}h_{245} - \rho \int d6C_{26}h_{136} (OZ3)$$

$$+ \rho^2 \int d4d6C_{24}C_{36}h_{146} - \rho \int d4C_{34}h_{124}$$

$$+ 2\rho \int d4C_{14}C_{24}C_{34}. (2.5)$$

In (2.5), we dropped the superscripts and subscript ‘w’ to save space. Form (2.5) is exact. However, it is difficult to be implemented because of the higher order correlations contained therein. In Paper I [4], we simplified OZ3 by using a convolution approximation (CA) similar to that of Jackson and Feenberg [13] by setting $h^{(3)} \sim 0$. Thus

$$C^{(3)}(1, 2, 3) \equiv -C^{(2)}(1, 2)C^{(2)}(1, 3)$$

$$- C^{(2)}(2, 1)C^{(2)}(2, 3) - C^{(2)}(3, 2)C^{(2)}(3, 1)$$

$$+ 2\rho \int d4C^{(2)}(1, 4)C^{(2)}(2, 4)C^{(2)}(3, 4) \quad (CA - OZ3).$$

This appears to be a ‘drastic’ approximation for $h^{(3)}$. Other ‘milder’ and possibly better approximations for the triplet total correlation functions $h^{(3)}$ can also be made (see [14], referred to here as Paper II), and such will be investigated in the future.

3. Constructing the bridge function with aid of the OZ3 equation

Realising the ‘poor’ performance of the traditional PY and HNC closures, we intend to construct a more accurate closure. First, we should recognise that any DFT that contains or implies the Euler–Lagrange equation (EL) postulates a ‘bridge function’, either consciously or unconsciously, even though the particular approach was not based explicitly on ‘bridges’. The EL we are referring to is the equation [15–17]

$$\rho_w(\vec{r}) = \rho_0 \exp[-\beta u^{(1)}(\vec{r}) + C^{(1)}_w(\vec{r}) - C^{(1)}_0],$$

(3.1)

where $C^{(1)}_w(\vec{r})$ and $C^{(1)}_0$ are the singlet direct correlation functions, $s$-dfcs (subscript $w$ indicates the non-uniform
system, while 0 indicates the uniform system). The s-dcf is defined as the derivative of the excess free energy, $F^\text{ex}$, i.e.

$$- \frac{\delta \beta F^\text{ex}[\rho]}{\delta \rho_w(r)} \equiv c_w^{(1)}(r). \quad (3.2)$$

In our approach, the bridge function $B_w$ is defined in the following way

$$\rho_w(\vec{r}) \equiv \rho_0 \exp[-\beta w^{(1)}(\vec{r}) + \gamma_w(\vec{r}) + B_w(\vec{r})]. \quad (3.3)$$

Thus, we have the identity

$$c_w^{(1)}(\vec{r}) - c_0^{(1)}(\vec{r}) = \gamma_w(\vec{r}) + B_w(\vec{r}). \quad (3.4)$$

where the indirect correlation function $\gamma_w(\vec{r})$ (icf) is defined as the convolution integral

$$\gamma_w(\vec{r}) \equiv \int d\vec{r}^\prime c_0^{(2)}(\vec{r} - \vec{r}^\prime) \delta \rho_w(\vec{r}^\prime) \quad (3.5)$$

in analogy with the icf in uniform fluids, where $\delta \rho_w(\vec{r}) \equiv \rho_w(\vec{r}) - \rho_0 \equiv \rho_0 h_w(\vec{r})$, and $h_w(\vec{r})$ is the non-uniform total correlation function. Thus, if the DFT admits an EL equation (i.e. with an obvious expression for $c_w^{(1)}(\vec{r})$), then through Equation (3.4), we can extract the form of the bridge function for this DFT. This actually has been carried out by Rosenfeld and co-workers [18] in the FMT approach for hard spheres on an HW. A similar extraction can be made for a bridge function in the local molecular field approach of Rogers and Weeks [19] by applying Equation (3.4). Here it is opportune to remark on our usage of the terms (1) the bridge function (or bridge functional) and (2) the closure relation. (1) A bridge function $B_w$ is a well-defined quantity in statistical mechanics (either through the cluster integrals, or by eq. (3.4)). It ‘exists’, as remarked earlier, as a legitimate correlation function, just as the s-dcfs. (2) On the other hand, the closure relation is a theory, expressed as an equation that relates other correlation functions (such as the icf, $\gamma_w(\vec{r})$) to the bridge function $B_w(\vec{r})$. This equation $B_w = \Phi[\gamma_w]$ may or may not be exact. In fact, in almost all cases, it is an approximation. The symbol $\Phi$ can be a function relation, or can be a functional. The closure-based DFT is an attempt to construct an equation, $\Phi$, that hopefully will give a good representation of the bridge function in the particular application.

It is also known that the bridge functional admits an expansion in terms of the higher order (uniform) direct correlation functions [20]

$$B_w(1) \equiv \frac{1}{2!} \int d^2d^3c_0^{(3)}(1, 2, 3) \delta \rho_w(2) \delta \rho_w(3) + \frac{1}{3!} \int d^2d^3d^4c_0^{(4)}(1, 2, 3, 4) \delta \rho_w(2) \delta \rho_w(3) \delta \rho_w(4)$$

$$+ \frac{1}{4!} \int d^2d^3d^4d^5c_0^{(5)}(1, 2, 3, 4, 5) \delta \rho_w(2) \times \delta \rho_w(3) \delta \rho_w(4) \delta \rho_w(5) + \frac{1}{5!} + \ldots + \frac{1}{6!} + \ldots$$

$$= B_3 + B_4 + B_5 + B_6 + \ldots \quad \text{respectively,} \quad (3.6)$$

where $c_0^{(n)} (n = 3, 4, \ldots, n)$ are the uniform $n$th-order direct correlation functions. Since we have obtained an expression (2.6) for the third—order dcf, the $B_3$ term can be approximated (in the CA-OZ3 approximation) as

$$B_3(1) \equiv - \frac{\gamma_w(1)^2}{2} - \rho_0 \int d^2c_0^{(2)}(1, 2) \gamma_w(2) \delta \rho_w(2)$$

$$+ \rho_0 \int d^2c_0^{(2)}(1, 2) \gamma_w(2)^2. \quad (3.7)$$

This equation expresses $B_3$ both as a function and as a functional of the icf $\gamma_w$. We shall use this insight as the basis for constructing a full bridge functional. Upon considering (as in Paper I) that the higher order bridge terms $B_4, B_5, \text{etc.}$, assume similar forms as (3.7), we arrive at the following more complete expression

$$B_w(1) \equiv - \frac{\gamma_w(1)^2}{2} \left[ 1 - \phi + \frac{\phi}{1 + \alpha \gamma_w(1)} \right]$$

$$- \psi \rho_0 \left[ \int d^2c_0^{(2)}(1, 2) \gamma_w(2) \delta \rho_w(2) \right.$$

$$\left. - \int d^2c_0^{(2)}(1, 2) \gamma_w(2)^2 \right]. \quad (3.8)$$

where $\xi, \varphi, \alpha$, and $\psi$ are parameters to be determined from the state conditions. As explained earlier [4], the icf’s should be ‘renormalised’ to avoid multi-valued functions (or more precisely to convert a functional into a function), a new icf $\gamma_H$ is defined

$$\gamma_H(\vec{r}) \equiv \int d\vec{r} c_0^{(2)}(\vec{r} - \vec{r}^\prime) \delta \rho_w(\vec{r}^\prime), \quad (3.9)$$

where

$$c_0^{(2)}(r) = c_0^{(2)}(r), \quad \text{for } r \leq \sigma; \quad \text{and}$$

$$c_0^{(2)}(r) = 0, \quad \text{for } r > \sigma. \quad (3.10)$$

Therefore, the end product is the following renormalised closure for the bridge function

$$B_w(1) \equiv - \frac{\xi \gamma_H(1)^2}{2} \left[ 1 - \phi + \frac{\phi}{1 + \alpha \gamma_H(1)} \right]$$

$$- \psi \rho_0 \left[ \int d^2c_0^{(2)}(1, 2) \gamma_H(2) \delta \rho_w(2) \right.$$

$$\left. - \int d^2c_0^{(2)}(1, 2) \gamma_H(2)^2 \right]. \quad (3.11)$$
\[- \int d2C_H^{(2)}(1, 2)\gamma_w(2)^2 \]

(the renormalised CA - OZ3 equation).

\[ u^{(2)}(r^*) = +\infty, \text{ for } r^* < 1, \]
\[ = -\epsilon \frac{e^{-\lambda(r^* - 1)}}{r^*}, \text{ for } r^* \geq 1, \]

where \(\epsilon\) and \(\sigma\) are the energy and size parameters of the potential, \(r^* = r/\sigma\). We study two cases of the range parameter \(\lambda\), namely at 1.8 and 3. The value \(\lambda = 3\), in combination with the chosen temperature and densities, gives us the depletive adsorption as observed in the MC calculations. The value \(\lambda = 1.8\) is for comparison with literature DFT data. The planar structureless HW is located at \(\sigma/2\):

4. Applications to the Yukawa fluid at a hard wall

The hard-core attractive Yukawa fluid has the pair potential

\[ u^{(2)}(r^*) = +\infty, \text{ for } r^* < 1, \]
\[ = -\epsilon \frac{e^{-\lambda(r^* - 1)}}{r^*}, \text{ for } r^* \geq 1, \]

\[ u^{(1)}(r) = +\infty, \text{ for } r < \sigma/2, \]
\[ = 0, \text{ for } r \geq \sigma. \]

We shall examine five state conditions: three cases at \(\lambda = 3\), reduced temperature \(T^* = 0.76\), and reduced densities \(\rho^* = 0.358, 0.473, \text{ and } 0.557\); and two cases at \(\lambda = 1.8\) and temperatures \(T^* = 1.25\) and 2.0 with density \(\rho^* = 0.7\). Most of these states have shown depletive behaviour at the HW. Thus, this poses a stringent test of the theory. The bridge function in Equation (3.11) is applied to all cases and the parameters \(\xi, \varphi, \alpha, \text{ and } \psi\) are allowed to vary until (1) they satisfy the hard-wall sum rule [21,22]; and (2) reproduce as closely as possible the MC singlet density profiles. In future work, we plan to determine their values self-consistently by using zero-separation theorems and thermodynamic consistency relationships. The hard-wall sum rule is

\[ \rho_w(\sigma = \sigma/2) = \frac{P_0}{kT}, \]

where \(P_0\) is the bulk fluid pressure, that can be obtained independently from MC data or from an accurate integral-equation theory for the homogeneous system. We list in Table 1 (1) the values of \(P_0\) obtained from integral-equation theory, (2) values of the contact density \(\rho_w(\sigma = \sigma/2)\) from the MC simulation; and (3) the contact density from the CA-OZ3 closure. The parameters used in the closure are given in Table 2.

In order to supply the homogeneous structural function \(C_0^{(2)}\) for the EL equation, we used three closure theories: the PY, the modified hypernetted-chain (MHNC), and the zero-separation closure (ZSEP) [23,24] closures via the homogeneous OZ equation:

\[ \gamma_0^{(2)}(r) \equiv \rho_0 \int dr' C_0^{(2)}(|\vec{r} - \vec{r}'|) h_0^{(2)}(r'). \]

Table 1. The bulk pressure, \(P_0/kT\) obtained from (1) an accurate integral equation for uniform fluids, i.e. MHNC, (2) the MC contact density \(\rho_w(\sigma = \sigma/2)\), and (3) \(\rho_w(\sigma = \sigma/2)\) obtained from solving the EL equation with the new bridge function CA-OZ3 (3.11).

<table>
<thead>
<tr>
<th>(T^*) = 0.76</th>
<th>(P_0/kT)</th>
<th>(\rho_w(\sigma = \sigma/2))</th>
<th>(\rho_w(\sigma = \sigma/2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\rho^* = 0.358)</td>
<td>0.13</td>
<td>0.13</td>
<td>0.14</td>
</tr>
<tr>
<td>(\rho^* = 0.473)</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
</tr>
<tr>
<td>(\rho^* = 0.557)</td>
<td>0.22</td>
<td>0.21</td>
<td>0.23</td>
</tr>
</tbody>
</table>

Table 2. Parameters used in the renormalised CA-OZ3 equation.

<table>
<thead>
<tr>
<th>(\rho^*)</th>
<th>(\alpha)</th>
<th>(\varphi)</th>
<th>(\xi)</th>
<th>(\psi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(T^* = 0.76 (\lambda = 3.0))</td>
<td>(0.358)</td>
<td>0.01</td>
<td>-0.35</td>
<td>0.50</td>
</tr>
<tr>
<td></td>
<td>(0.473)</td>
<td>0.20</td>
<td>0.20</td>
<td>2.50</td>
</tr>
<tr>
<td></td>
<td>(0.557)</td>
<td>0.25</td>
<td>0.21</td>
<td>1.74</td>
</tr>
<tr>
<td>(T^* = 1.25 (\lambda = 1.8))</td>
<td>(0.70)</td>
<td>0.585</td>
<td>0.540</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>(T^* = 2.00 (\lambda = 1.8))</td>
<td>(0.70)</td>
<td>1.70</td>
<td>1.00</td>
</tr>
</tbody>
</table>
These closures provide additional relations linking the structural functions, whose general form is

\[ 1 + \kappa^{(2)}_0(r) = \exp\left[ -\beta u^{(2)}(r) + \gamma^{(2)}_0(r) + B_0(r) \right]. \] (4.5)

where \( B_0(r) \) is the homogeneous bridge function, whose specific formulation depends on the selected closure. For the MHNC closure, we input the bridge function of the hard spheres, and the hard-sphere diameter was used as a free parameter, as usual, to satisfy the thermodynamic consistency in the properties.

We start by considering the CA-OZ3-based closure at a moderate reduced density \( \rho^* = 0.358 \). Since we wanted to understand the effects of different inputs from
the homogeneous-fluid direct correlation function \( C_0^{(2)}(r) \) on the solution, we chose both the PY \( C_0^{(2)}(r) \) and MHNC \( C_0^{(2)}(r) \) as examples and gauged their influences on the eventual non-uniform density profiles \( y_w(z^*) \). In Figure 1, we compare these results for the inhomogeneous cavity function \( y_w(z^*) \) with MC computer simulation. We clearly see that the theoretical structural functions are quantitative for reduced distances \( z^* > 2 \), while they are slightly deviating from the MC data at lower \( z^* \)-distances where the cavity function develops a non-monotonic change in its slope. Overall, the two different homogeneous inputs (PY and MHNC [25]) provide a comparable performance, with the exception of
the MHNC one, that apparently develops a curious ‘hook’ at distances very close to the wall ($z^* \approx 0.5$). We will try to provide some insight into this feature later. Increasing the density to $\rho^* = 0.473$ does not seem to change the overall agreement significantly (Figure 2), with a peculiar behaviour observed at short distances similar to the case considered before (Figure 1).

Next, in Figure 3, we report the calculations at the density $\rho^* = 0.557$ with both PY and MHNC $C_0^{(2)}(r)$ as homogeneous inputs. For this case, we also report results from the so-called ZSEP closure [23,24] for $C_0^{(2)}(r)$. Overall, the calculations performed from $C_0^{(2)}(r)$ derived from the MHNC and ZSEP appear to be in better agreement with the MC data. Once again, at short distances, all theoretical inputs show deviations from MC, with a ‘hook’ particularly pronounced in the MHNC-derived $C_0^{(2)}(r)$.

In order to gain some insight into this discrepancy vis-à-vis the MC data, we further compared the inhomogeneous bridge functions from CA-OZ3 and from inversion of the MC data, by using the defining equation: $B_w(z) = \ln y_w(z) - \gamma_w(z)$, in such manner that the cavity function $y_w(z)$ was obtained directly from the MC computer simulations, and the indirect correlation function $\gamma_w(z)$ was calculated from Equation (3.5) by using the inputs $\rho_w(z)$ from MC and $C_0^{(2)}(r)$ from one of the selected uniform closures. Results are reported in Figure 4. If we examine the behaviour of the theoretical bridge functions $B_w(z)$ (CA-OZ3), they drop to zero slopes when approaching the wall (at $z^* = 0.5$), i.e., at the contact distance. On the other hand, the MC bridge function $B_w(z)$ (MC) reported in Figure 4 does not show such ‘flattening’ near $z^* = 0.5$. $B_w(z)$ (MC) terminates at $z^* = 0.5$, as MC simulation should, not to ‘pen-
Inhomogeneous indirect correlation and bridge functions as a function of the distance from the wall for $\rho^* = 0.557$.

Theoretical $B_w(z)$ (CA-OZ3) can, of course, enter the wall due to the removal of wall potential in the cavity function $y_w(z)$, just as in the uniform case.

Thus, the inversion trend in the cavity function $y_w(\vec{r})$ (the hooking behaviour) is a reflection of the $B_w(z)$ (CA-OZ3) behaviour. Even though this appears to be a theoretical problem, it is worth comparing what would happen when the PY and HNC theories were applied here as the non-uniform closures. In Figure 5, we show the calculation [25] done at $\rho^* = 0.557$ by using the non-uniform PY and HNC theories.
HNC bridge functions (obviously, $B_w(\vec{r}) = 0$ in the HNC case). It is evident that these theories fail to reproduce even qualitatively the MC profile (the MC data are reported as triangles in Figure 5). Both PY and HNC show oscillatory behaviour as a function of the distance and clearly over-estimate MC data. In fact, PY and HNC predict adhesive adsorption when approaching the wall, a wrong behaviour. These observations are contrary to the depletive adsorption as shown by the MC data. The MC $y_w(z_0) \sim 0.37$ at the wall of $z = z_0$, or $\rho_w(z_0)$ (MC) = 0.21, which is less than the bulk density $\rho^*_0 = 0.557$. Clearly, the adsorption is depletive.

Whilst, the contact values of the cavity functions $y_w(z_0)$ of the naive PY and HNC theories are at much higher values: being 1.6 and 1.8, respectively, as compared to 0.37 from MC. The (wall-particle) bridge function $B_w$ (dotted line) from PY is shown in Figure 5, and is much subdued, being smaller (in magnitude) than the MC-inverted bridge function $B_w$ (MC) (circles). This is symptomatic of the behaviour of many approximate closure equations derived from the uniform fluids. They are not applicable to the non-uniform case. The presence of the solid substrate exacerbates the inadequacies in the original PY and HNC equations. The new CA-OZ3-based closure is capable of curing this defect. We are able to show depletion effects and attain remarkable agreement with the MC data.

Additional details about the benefit of the renormalisation procedure described in the previous section (Equations (3.9) and (3.10)) can be observed if we compare the $y_w(\vec{r})$ and $\gamma_H(\vec{r})$ as a function of the distance outside the wall, as shown for at $\rho^* = 0.557$ in Figure 6 (representative of all of the densities considered). We notice that the renormalised $\gamma_H(\vec{r})$ are higher than the original $y_w(\vec{r})$, owing to the core values $C^{(2)}_H(\vec{r})$ that enhance the function’s values. $\gamma_H(\vec{r})$ is for most part positive and non-oscillatory. The importance of this treatment is easily revealed if we construct a so-called Duh–Haymet (DH) plot [26] for $B_w$ vs. $\gamma_H$, as we compare it to the pair, $B_w$ vs. $y_w$ (see Figure 7). While $B_w - \gamma_H$ is a well-behaved function, the un-renormalised $B_w - y_w$ develops some kinks with multiple function values. These features come to show that $B_w$ is a functional of $y_w$ and cannot be a simple function of $\gamma_w$. The relation is clearly not single-valued.

From our perspective, these considerations highlight the importance of extracting out the extra-functional contributions in constructing the closure theory by implementing the re-normalisation of $y_w$, as is done here. The use of the base function $\gamma_H$ is essential.

It is of interest to compare the present OZ3-based theory with conventional DFTs based on the weighted-functions such as the FMT [3], and the non-uniform integral equation theory (e.g. the Lovett-Mou-Buff-Wertheim equation – LMBW-1) [5]. Olivares-Rivas et al. [5] have reported the LMBW results, and Kim et al. [9] reported the FMT calculations for this Yukawa fluid at an HW. The $\lambda$ range parameter they used was $\lambda = 1.8$. We examine two cases at temperatures $T^* = 1.25$ and 2.0. Both are at $\rho^* = 0.70$. In Figure 8, we report the comparison for $\rho^* = 0.7$ and $T^* = 2$. The MC data are available from Ref. [5]. The predictions

![Figure 8](https://example.com/image8.png)

Figure 8. Inhomogeneous cavity functions as a function of the distance from the wall for $\lambda = 1.8$, $T^* = 2.0$, and $\rho^* = 0.7$. 

of the CA-OZ3 theory with MHNC-\(C_0^{(2)}\) input and FMT show comparable agreement with the MC profile of \(y_w(z^*)\). The FMT is slightly superior in capturing the depth of the first minimum of \(y_w(z^*)\).

A slightly worse agreement is given by the CA-OZ3-based on the PY-\(C_0^{(2)}\) input (solid line, Figure 8) in reproducing the second peak, although the first minimum is well predicted. The LMBW-1 theory shows the worst agreement with the MC data, as it misses location and magnitude of the first valley.

In Figure 9, we present the comparison for a more challenging thermodynamic state for the theoretical approaches, namely, the temperature is reduced to \(T^* = 1.25\) (close to the critical temperature of the homogeneous hard-core attractive Yukawa fluid at \(\lambda = 1.8\)). At this temperature, the LMBW-1 theory (dotted line) is very poor, unable to capture the correct phase of the oscillations of the cavity function as the distance from the wall is increased. However, both versions (PY and MHNC \(C_0^{(2)}\)) of the CA-OZ3 theory reproduce the MC data quite accurately (see the full line and short dots, Figure 9), and are shown to be even superior to the FMT approach, which overestimates the MC profile at reduced distance \(r^* < 2\).

5. Conclusions
We have shown that the bridge function constructed based on the OZ3 theory can improve over traditional closures, such as the PY or the HNC equations. The CA-OZ3 formulation can reproduce the depletion behaviour in the Yukawa fluids near an HW. Comparisons are made with other density functional theories in existence: the FMT and the inhomogeneous integral equation of Lovett-Mou-Buff-Wertheim for the same non-uniform system. The CA-OZ3 compares favourably to these alternatives when checked with MC data. We achieve quantitative agreement, in general, for wall distances \(z^* > 2\). For \(z^* < 2\), there are some discrepancies in the curvatures. The source lies in the short-separation values of the bridge functions used. Clearly, improvement is needed. From the study of the triplet correlation functions in Paper II [14], we can develop a better approximation to the \(h^{(3)}\) function than the simple CA of Jackson and Feenberg. This will be investigated in the future.

To solve the EL equation, an input function, the uniform-fluid pair direct correlation function \(C_0^{(2)}\) is needed. Its accuracy critically affects the adsorption profile \(y_w(z^*)\). This fact has been known, but has not been well documented. In most studies, some mention was made of the construction of \(C_0^{(2)}\) but no details were given. No rigorous testing was reported. In this work, for the uniform Yukawa fluid, we studied three uniform closures, MHNC, PY, and ZSEP. Their effects on the density profile \(y_w(z^*)\) are clearly shown and results ranked.

We examined the functional dependence of the bridge function \(B_w\) on the indirect correlation function \(\gamma_w\). The DH plot is constructed. Clearly, the renormalised \(\gamma_H\) gives a better, smoother fit for the \(B_w\) as a function (see Figure 7); this being done without any reference to the form of the closure function. It demonstrates the necessity of renormalisation.
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