Adsorption of mixtures of the Yukawa-ions near a hard wall: A density functional study based on the third-order Ornstein-Zernike relation

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ABSTRACT

We examine the adsorption of the primitive-model “ionic” mixtures modeled in terms of the screened Debye potentials on a hard structureless wall. It is well-known that the screened Debye potentials are of the Yukawa form. They could approach the Coulomb potentials when the screen parameter $\lambda$ vanishes. Thus the study of the mixtures of repulsive and attractive Yukawa molecules can mimic the ionic fluid behavior at small $\lambda$. One of the advantages of using this Yukawa potential is that it avoids the long-range interactions and mitigates the complications inherent in the Coulomb potential.

We have previously developed a third-order Ornstein-Zernike relation (OZ3) and have adapted it to the adsorption of many types of fluids on hard walls. Specifically, a new generation of closures was developed for use in the Euler-Lagrange equations of the density functional theory (DFT) for determining the non-uniform densities of various fluid types such as the Lennard-Jones fluid, as well as the regular Yukawa fluids (with finite $\lambda$ values) on an inhomogeneous substrate. In this work, we examine the applicability of the OZ3-inspired bridge functions to the adsorption of the “small-$\lambda$” Yukawa fluids. The mixtures of these Yukawa fluids are, for simplicity, called the Yukawa ions, in contrast to the Coulomb ions. The results shall mimic the electrical double layers in electrochemistry.

The Euler-Lagrange equations for the binary mixtures are solved with new OZ3 closures. Two types of closures are investigated: one derived from the Jackson-Feenberg approximation, and the other derived from the linear cavity approximation. The results are compared with the Monte-Carlo results on primitive-model symmetric fluids. Satisfactory agreements are obtained. It is noted that the contact value theorems (i.e. the hard-wall sum rules) play an instrumental role in obtaining the accurate results.

1. Introduction

In the primitive model of electrolytes, the screened Debye potential (SDP) is well-known to be of the Yukawa form [1]. It will approach the Coulomb potential as the screen parameter, $\lambda$, tends to zero.

$$\beta u(r) = -\frac{1}{kT} \exp(-\lambda(r-\sigma))$$

where $u$ is the screened Debye potential, $\beta = 1/(kT)$, $k$ is Boltzmann constant, $T$ is the absolute temperature, $e$ is the energy parameter, $\sigma$ is the size parameter, and $\lambda$ is the screen parameter. $r$ is the intermolecular distance. When the sign is positive, we have repulsive interactions (cation-cation or anion-anion interactions); when the sign is negative, we have the attractive interaction (anion-cation interaction).

Lesser Blum was a major proponent and an originator of the premier rank in advancing the statistical mechanics of the Yukawa types of fluids. We propose here a study of the nonlinear mixtures of the Yukawa-charged molecules with attractive and repulsive interactions to mimic the electric double layers.

Our bulk fluid is composed of a binary mixture of two types of Yukawa particles: the Yukawa cations (subscript $p$) and the Yukawa anions (subscript $m$) (note that $p$ stands for plus or $+$, and $m$ for minus or $-$). The like-particles ($pp$ and $mm$) interact with the repulsive Yukawa potential and the unlike particles ($pm$) interact with the attractive Yukawa potential. These Yukawa potentials possess a hard core with diameters $\sigma_{pp}$, $\sigma_{mm}$, and $\sigma_{pm}$ respectively. Both symmetric mixtures (the 1–1 electrolytes) and asymmetrical mixtures (the 2–1 electrolytes) will be considered. Since the solvent molecules are “suppressed”, we are in the McMillan-Mayer picture; or we focus on the primitive models of electrolytes. A similar model has been considered by Rosenfeld [2].

In the uniform electrolyte theories, there is a long-standing corresponding-states hypothesis [3] that Coulomb systems are...
conformal to their corresponding Yukawa mixtures with regard to their excess thermodynamic properties, critical constants, and in the limit the structures. The rationale of the current proposal is to avoid the divergences in properties associated with the reciprocal-$r$ dependence in the Coulomb interaction. By choosing a finite $\lambda$, the exacerbating consequences of the long-ranged-ness of the Coulomb forces can be avoided. Thus the results of the SDP on a nonuniform wall can be considered as a surrogate to the full-ionic electric double layers.

There have been a number of recent studies on the adsorption of ions on charged and neutral surfaces [4]. Many of these were based on the fundamental-measure theory (FMT) derived from Rosenfeld’s formulation [5] of the weighting functions, originally designed for the structures of hard-sphere fluid on a hard wall. These have met with some degree of success. For charged hard ions (note that these are not simply neutral hard spheres), a perturbation theory [6] in FMT was formulated (based on a reference system of the hard-sphere/hard-wall system) in order to account for the additional effects of the Coulomb interactions. Here we propose an alternative approach. We shall construct a closure-based density functional theory (DFT), in which we develop a functional of the particle correlation (with subscript 0). Note that the kernel in (2.10) is the closure functional $\beta \mu_0$ (wall-particle) total correlation function.

\[ \frac{\delta \mu}{\delta \rho_w(r)} = 0 \quad \text{(at equilibrium)} \]  

(2.3)

From Eqs.(2.1) and (2.3), the Euler-Lagrange (EL) condition results

\[ - \frac{\delta \Psi}{\delta \rho_w(r)} = -\beta \mu_0(r) + \beta \mu_0 = C_0^{(1)}(r) - \ln \rho_w(r) \lambda^3 \]  

(2.4)

where we have supplied the definition [16] of the singlet direct correlation (DCF-1) $C_0^{(1)}(r)$, namely

\[ C_0^{(1)}(r) = \ln \rho_w(\lambda^3) + \beta \mu_0 = -\beta \mu_0 \]  

(2.5)

The symbol $\Lambda$ is de Broglie wavelength. In the limit that the external potential vanishes, $\rho_w(r) = 0$, $C_0^{(1)}(r)$ becomes the (negative) excess chemical potential $-\beta \mu_0^e$ of the uniform fluid:

\[ \lim_{w \to 0} C_w^{(1)}(r) = 0 \]  

(2.6)

Rearrangement of Eq. (2.5) gives

\[ \rho_w(\lambda^3) = \rho_0 \exp \left[ -\beta \mu_0(\lambda^3) + C_0^{(1)}(\lambda^3) - C_0^{(1)}(\lambda^3) \right] \]  

(2.7)

shown in terms of the bridge functional $B_w$, the Euler-Lagrange equation becomes

\[ \rho_0(\lambda^3) = \rho_0 \exp \left[ -\beta \mu_0(\lambda^3) + \gamma_w(\lambda^3) + B_w(\lambda^3) \right] \]  

(2.8)

where $B_w$ is the bridge functional in the presence of the external potential $w$. Comparing Eqs. (2.7) and (2.8) gives

\[ C_0^{(1)}(\lambda^3) - C_0^{(1)}(\lambda^3) = \gamma_w(\lambda^3) + B_w(\lambda^3) \]  

(2.9)

Note that the nonuniform indirect correlation function (icf) $\gamma_w(\lambda^3)$ is defined, by analogy with uniform fluids, as

\[ \gamma_w(\lambda^3) = \int d\lambda^3 \beta \mu_0(\lambda^3) \rho_w(\lambda^3) \]  

(2.10)

where the density derivative over the uniform value is given as $\delta \nu_w(\lambda^3) = \rho_0(\lambda^3) - \rho_0(\lambda^3) = \rho_0(\lambda^3)$. $h_w$ is the nonuniform (wall-particle) total correlation function. $\gamma_w(\lambda^3)$ as defined is a wall-particle correlation (with subscript $w$, and not a particle-particle correlation (not with subscript 0). Note that the kernel in (2.10) is the uniform fluid (particle-particle) pair direct correlation, $C_0^{(2)}$ (with subscript 0).

The IHFES can be separated into two parts, one part due to ideal gas contribution, $P^l$, and the other the excess, $P^e$

\[ \beta \Psi = \beta \Psi^l + \beta \Psi^e \]  

(2.11)

The ideal gas part is known as

\[ P^l = \int d\lambda^3 \rho_w(\lambda^3) \frac{\ln \rho_w(\lambda^3) \lambda^3 - 1}{\lambda^3} \]  

(2.12)

From the Euler-Lagrange equation Eq. (2.4) with incorporation of Eq. (2.12), one can show that the functional derivative of the excess IHFES is

\[ -\frac{\partial \Psi^e}{\partial \rho_w(r)} = C_0^{(1)}(r) \]  

(2.13)
Namely, the “primitive” of the singlet DCF is the (negative) excess IHFEF.

3. The third-order Ornstein-Zernike equations (OZ3)

We have shown earlier [7] the full derivation of the OZ3 equation in 2011. We shall give a brief summary here. As motivation we note that the second-order Ornstein-Zernike equation (the usual one used in the IETs) is equivalent to the contraction of the functional derivatives first proffered by Lebowitz and Percus [18]: i.e. the reciprocal relation between the fluctuation derivative $\delta \rho_w (1)/\delta \omega (2)$ and the susceptibility derivative $\delta \omega (2)/\delta \rho_w (1)$, where $\omega$ is the intrinsic chemical potential (ICP) defined by:

$$\omega (r!)=\beta \mu_0 - \beta w (r!)$$

Thereby

$$h_0^2 (\vec{r}, \vec{r}') - C_0^2 (\vec{r}, \vec{r}') = \int d\vec{r} \rho \frac{\partial h_0^2 (\vec{r}, \vec{r}')}{\partial \rho_w}$$

(3.2)

Noting

$$\frac{\delta \rho_w (1)}{\delta \omega (2)} = \delta_3 (1, 2) / \rho_w (1) + F^2 (1, 2)$$

(3.3a)

and

$$\frac{\delta \omega (1)}{\delta \rho_w (2)} = \delta_2 (1, 2) / \rho_w (1) - C^2 (1, 2)$$

(3.3b)

$\delta_3 (1, 2)$ is the 3-d Dirac delta function. The origination of OZ3 follows a similar pattern based on higher order functional derivatives, as an example one of them may be $\delta^2 \rho_w (1)/[\delta \omega (2) \delta \omega (3)]$. OZ3 has four alternative forms, because of the different choices of the differentiated

Fig. 1. Comparison of the Boltzmann factors of the present Yukawa potentials (black lines) vs. the Boltzmann factors of the full Coulomb potential (the thick green lines). (a) for like-charge interactions, and (b) for the unlike-charge interaction.
We shall obtain the particular form of OZ3 to be used here. Upon replacing the functional derivatives by their equivalents in correlation functions, we shall obtain an "exact" third order Ornstein-Zernike equation (relating $h^{(3)}$ to $C^{(3)}$) [7]

$$C_{123} = h_{123} - C_{12}C_{13} - C_{21}C_{23} - C_{31}C_{32} - \rho^2 \int d\gamma C_{14}C_{25}C_{36} + \rho^2 \int d\gamma C_{15}C_{26} + \rho^2 \int d\gamma C_{16}C_{25} - \rho^2 \int d\gamma C_{14}C_{26} + 2\rho \int d\gamma C_{14}C_{24}C_{34} \tag{3.5}$$

(We have dropped the superscripts and subscript "w" to save space. We note that Eqs. (3.4) and (3.5) are equivalent forms of the OZ3: Eq. (3.4) is expressed in terms of the functional derivatives, and Eq. (3.5) will result after substituting the known expressions for the derivatives in Eq. (3.4). See ref. [7]. Just like the usual Ornstein-Zernike (OZ2) equation, that relates $C^{(2)}$ to $h^{(2)}$, Eq. (3.5) relates $C^{(3)}$ to $h^{(3)}$. Eq. (3.5) is formally exact. Note that $C^{(2)}$ and $h^{(3)}$ are numerically challenging, if not impossible, to evaluated from theories or from simulations at the present. Some efforts have been made to simulate $h^{(3)}$ for hard-sphere fluids. Approximate theoretical formulations for $C^{(3)}$ have also been attempted. Suitable approximations must be made to render Eq. (3.5) useful in calculations. This expression for the triplet direct correlation function $C^{(3)}$ will be used in constructing the new bridge function in this investigation.

4. Constructing the bridge function

We shall follow the following four steps in constructing a new type of closure for the bridge function: (1) functional expansion of the bridge function $B_n(r)$; (2) introducing the OZ3 relation (3.5) into the third order bridge term $B_3$; (3) making approximations to the resulting $B_3$ and (4) generalization to higher order bridge terms, $B_n (n > 3)$.

It is well-known that the bridge function $B_n(r)$ can be expanded as a Taylor series in terms of the singlet density as

$$B_n(r) = \frac{1}{2^n} \int d\gamma C_n^{(3)}(1, 2, 3) \int d\gamma C_n^{(3)}(1, 2, 3) \int d\gamma C_n^{(3)}(1, 2, 3) + \frac{1}{2^n} \int d\gamma C_n^{(4)}(1, 2, 3, 4) \int d\gamma C_n^{(4)}(1, 2, 3, 4) + \frac{1}{2^n} \int d\gamma C_n^{(5)}(1, 2, 3, 4, 5) \int d\gamma C_n^{(5)}(1, 2, 3, 4, 5) + \frac{1}{2^n} \int d\gamma C_n^{(6)}(1, 2, 3, 4, 5, 6) + \ldots \tag{4.1}$$

The first term on the RHS, i.e. the third-order bridge function $B_3$ contains the uniform triplet direct correlation $C_3^{(3)}$. If we substitute into $B_3$ the OZ3, Eq. (3.5), from the previous section for $C_3^{(3)}$, we shall obtain the (exact) third-order bridge terms:

$$2B_3^{(10)} = \rho^2 \int d\gamma C_{11}C_{22} + \rho^2 \int d\gamma C_{12}C_{31} + \rho^2 \int d\gamma C_{21}C_{13} - \rho^2 \int d\gamma C_{14}C_{25}C_{36} + \rho^2 \int d\gamma C_{15}C_{26} + \rho^2 \int d\gamma C_{16}C_{25} - \rho^2 \int d\gamma C_{14}C_{26} + 2\rho \int d\gamma C_{14}C_{24}C_{34} \tag{4.2}$$

Upon combining similar terms and simplifying the results, we obtain a short cluster representation of Eq. (4.2) (which remains exact) as

$$2B_3^{(10)} = -\gamma_4^{(10)} - 2 \gamma_9^{(9)} - 2 \gamma_6^{(6)} + 2 \gamma_4^{(4)}$$

$$\gamma_4^{(10)} = \frac{1}{2} \int d\gamma C_{11}C_{22} + \frac{1}{2} \int d\gamma C_{12}C_{31} + \frac{1}{2} \int d\gamma C_{21}C_{13} - \frac{1}{2} \int d\gamma C_{14}C_{25}C_{36} + \frac{1}{2} \int d\gamma C_{15}C_{26} + \frac{1}{2} \int d\gamma C_{16}C_{25} - \frac{1}{2} \int d\gamma C_{14}C_{26} + \gamma_4^{(4)}$$

$$\gamma_9^{(9)} = \frac{1}{2} \int d\gamma C_{11}C_{22} + \frac{1}{2} \int d\gamma C_{12}C_{31} + \frac{1}{2} \int d\gamma C_{21}C_{13} - \frac{1}{2} \int d\gamma C_{14}C_{25}C_{36} + \frac{1}{2} \int d\gamma C_{15}C_{26} + \frac{1}{2} \int d\gamma C_{16}C_{25} - \frac{1}{2} \int d\gamma C_{14}C_{26}$$

$$\gamma_6^{(6)} = \frac{1}{2} \int d\gamma C_{11}C_{22} + \frac{1}{2} \int d\gamma C_{12}C_{31} + \frac{1}{2} \int d\gamma C_{21}C_{13} - \frac{1}{2} \int d\gamma C_{14}C_{25}C_{36} + \frac{1}{2} \int d\gamma C_{15}C_{26} + \frac{1}{2} \int d\gamma C_{16}C_{25} - \frac{1}{2} \int d\gamma C_{14}C_{26} + \gamma_4^{(4)}$$

$$\gamma_4^{(4)} = \frac{1}{2} \int d\gamma C_{11}C_{22} + \frac{1}{2} \int d\gamma C_{12}C_{31} + \frac{1}{2} \int d\gamma C_{21}C_{13} - \frac{1}{2} \int d\gamma C_{14}C_{25}C_{36} + \frac{1}{2} \int d\gamma C_{15}C_{26} + \frac{1}{2} \int d\gamma C_{16}C_{25} - \frac{1}{2} \int d\gamma C_{14}C_{26}$$

Fig. 2. Case (i) Symmetric ions: comparison of the cation cavity functions, $y_p(z)$, calculated by Version 1 (CA-OZ3) theory (dotted line) and from the MC data (orange diamonds) of Gillespie et al. [13] for the cation adsorption at the hard neutral wall.

Fig. 3. Case (i) Symmetric ions: comparison of the anion cavity functions, $y_m(z)$, calculated by Version 1 (CA-OZ3) theory (dotted line) and from the MC data (orange diamonds) of Gillespie et al. [13] for the anion adsorption at the hard neutral wall.
where the filled black circles are the (integrated) field points and the orange circles are the open root points (not integrated). The bonds represent the following correlation functions.

\[
\begin{align*}
\mathbf{h} & \quad \mathbf{C} \\
\hbar(3) & \quad \gamma
\end{align*}
\]

(4.4)

This exact expression contains the triplet correlation function \( h^{(3)} \) and is thus impractical for numerical calculations. It seems that so far we have traded one triplet \( C^{(3)} \) for another triplet \( h^{(3)} \). However, we are in fact more than ready to make approximations to the triplet total correlation \( h^{(3)} \). The first idea that comes to mind \([12]\) is the Kirkwood superposition approximation for \( h^{(3)} \). Before considering the Kirkwood route, which shall engender more intractable diagrams, we try two alternatives: (i) the Jackson-Feenberg convolution approximation \([11]\) and (ii) the linear approximation \([12]\). We designate the Jackson-Feenberg approximation as Version 1 (V1) and the linear approximation as Version 2 (V2).

4.1. Convolution approximation to \( h^{(3)} \)-Version 1

Setting

\[
\hbar^{(3)}(1,2,3) \approx 0
\]

(4.5)

results in

\[
\begin{align*}
\hbar^{(3)}(1,2,3) & = -C^{(2)}(1,2)C^{(2)}(1,3) - C^{(2)}(2,1)C^{(2)}(2,3) - C^{(2)}(3,2)C^{(2)}(3,1) \\
& \quad + 2\rho \int d4 \, C^{(2)}(1,4)C^{(2)}(2,4)C^{(2)}(3,4)
\end{align*}
\]

(4.6)

When incorporated into the bridge-expansion, the \( B_{h} \) term now assumes the form.

\[
B_{h}(1,0) \equiv -\frac{\gamma^{2}(1,0)}{2} \quad \text{(V1)}
\]

(4.7)

which is precisely

\[
B_{h}(1,0) = -\frac{\gamma^{2}(1,0)}{2} - \rho \int d3 \, C^{(2)}(1,3)C^{(2)}(3,0) \gamma(3,0) \quad \text{(V1)}
\]

(4.8)

Version 1 has been developed previously and tried out for a couple of adsorptive systems. This V1 will also be employed in this work, for example, for the symmetric primitive electrolytes adsorbed at a hard wall.

4.2. Linear approximation to \( h^{(3)} \)-Version 2

The linear approximation (LA) for the triplet correlation is expressed in terms of the cavity function \( y^{(3)} \) as \([12]\)

\[
\ln y^{(3)}(1,2,3) \approx \ln y^{(2)}(1,2) + \ln y^{(2)}(2,3)
\]

(4.9)

This approximation to \( y^{(3)} \) is often used in one-dimensional adsorptive systems. We remark that this form lacks the symmetry in the three arguments \((1,2,3)\). (We shall call this the symmetry-breaking property). Generally speaking, the linear approximation is used when the length connecting 1 and 3, \( r_{13} \), is greater than either \( r_{12} \) or \( r_{13} \), being the longest bond. We have previously assessed performance of LIN in some detail for hard-sphere triplets (see 2013 \([12]\)). Substituting the LIN for \( h^{(3)} \) \((1,2,3)\) in Eq. (4.9), we obtain

\[
h^{(3)}_{\text{LIN}} = f_{13} - h_{13} + f_{13}h_{12} + h_{12}h_{23} + f_{13}h_{12}h_{23} \quad \text{(LIN)}
\]

(4.10)

In order for Eq. (4.10) to be applicable in the homogeneous fluids it must maintain the inequalities, i.e. \( r_{13} \) be greater than either \( r_{12} \) or \( r_{13} \). This inequality is difficult to keep in practice for arbitrary configurations of three molecules 1, 2, and 3. We make a further approximation (valid at low densities) that \( f_{13} \approx h_{13} \). Then Eq. (4.10) will become fully symmetrical in positions \( r_{1}, r_{2}, \) and \( r_{3} \). We shall call the resulting approximation “LIN/Symm”.

\[
h^{(3)}_{\text{LIN/Symm}} = h_{13}h_{12} + h_{13}h_{23} + h_{12}h_{23} + h_{13}h_{12}h_{23} \quad \text{(LIN/Symm)}
\]

(4.11)

After incorporating this \( h^{(3)} \) (Eq. (4.11)) into \( B_{h} \), we obtain the clusters
very lengthy and involve even higher-order correlation functions: $h(4)$, in the bridge expansion. First of all, these higher order terms are associated with the hard wall. There are two possibilities for further developments: (i) we can stop at $B_3$, and ignore the higher order terms (setting $B_n = 0$, $n > 3$), or (ii) we can assume that the higher order terms (such as $B_4, B_5, a_n$ and $B_6$ etc.) have similar functionality as $B_3$ (as far as the particle functional) but with different numerical values, in such a way that they are anion). All Yukawa ions contain a hard-sphere core.

In contrast to the $V_1$, Eq. (4.8), the difference lies in the integrand (replacing the $C(2)$ with the $\gamma$ term). This formula will be used in the study of the asymmetric primitive mixtures adsorbed on the hard wall.

The final Version 2 formula is

$$B_3(1,0) = -\psi \int d3 \ C(2)(1,3) \gamma^2(3,0) \quad (V2) \quad (4.14)$$

4.3. The new closure theories

We have developed two versions for the third-order bridge term $B_3$. To proceed, we need also the higher order terms: $B_4, B_5, B_6$, etc., in the bridge expansion. First of all, these higher order terms are very lengthy and involve even higher-order correlation functions: $h(4)$, $h(5)$, ... and $C(4), C(5)$, etc. At present there are no ready and easy ways to evaluate these terms. To obviate these obstacles, we explore at least two possibilities for further developments: (i) we can stop at $B_3$, and ignore the higher order terms (setting $B_n = 0$, $n > 3$), or (ii) we can assume that the higher order terms (such as $B_4, B_5, B_6$ etc.) have similar functionality as $B_3$ (as far as the functional part is concerned) but with different numerical values, in such a way that they are multiples of $B_3$.

We use the coefficient $\psi$ as this multiplier

$$B_w(1,0) \propto \text{function}(\gamma) - \psi \cdot \rho \int d3 \ C(2)(1,3) \gamma^2(3,0) \quad (V2) \quad (4.15)$$

Note that $\alpha, \psi$, and $\zeta$ are parameters to be determined by some appropriate sum rules. We remark that the direct correlation $C_w(3)$ for the nonuniform (wall-particle) correlation is defined as the difference: $C_w(3) = [h_w(3) - \gamma_w(3)]$. The details of the derivation are given in Appendix A.

5. The adsorption of “primitive-model” Yukawa-ions on a hard wall: the potentials

We shall examine two cases of adsorption of primitive model ions on a structureless hard wall. The first case (i) is the adsorption of symmetric 1–1 electrolytes ($\sigma_{mp} = \sigma_{mm} = \sigma_{pp}$, $p = \text{cation}$, $m = \text{anion}$) on the hard wall, and the second case (ii) is adsorption of asymmetric 2–1 electrolytes ($\sigma_{mm} = 2.12 \, \sigma_{pp}$). For the symmetric case, we shall apply Version 1 (Eq. (4.18)) of the closure; for the asymmetric case, we shall use the new closure Versions 2 (Eq. (4.19)). The reasons are that for the symmetric electrolytes, Version 1 was found to be adequate. However, for the asymmetric case, Version 1 was found to be insufficient and we need to use the newly improved closure Version 2.

The screened Debye potentials for the bulk Yukawa-type ions are of two types: (1) the repulsive Yukawa potential (simulating like-ion interactions) and (2) the attractive Yukawa potential (simulating unlike-ion interactions) (where $p$ (plus) = cation and $m$ (minus) = anion). All Yukawa ions contain a hard-sphere core.
5.1. Repulsive “Cation-Cation” Yukawa Potential in the Bulk

\[ \beta \mu_{pp}(r) = -\frac{e}{kT} \exp\left[ -\lambda \left( \frac{r}{\sigma_{pp}} - 1 \right) \right] \quad \text{for} \quad r > r' = r/\sigma_{pp} \] (5.1)

5.2. Repulsive “Anion-Anion” Yukawa Potential in the Bulk

\[ \beta \mu_{mm}(r) = -\frac{e}{kT} \exp\left[ -\lambda \left( \frac{r}{\sigma_{mm}^*} - 1 \right) \right] \quad \text{for} \quad r > \sigma_{mm}^*, r' = r/\sigma_{pp} \] (5.2)

5.3. Attractive “Cation-Anion” Yukawa Potential in the Bulk

\[ \beta \mu_{pm}(r) = -\frac{e}{kT} \exp\left[ -\lambda \left( \frac{r}{\sigma_{pm}^*} - 1 \right) \right] \quad \text{for} \quad r > \sigma_{pm}^*, r' = r/\sigma_{pp} \] (5.3)

For all pairs: \( ij = pp, mm, pm, \beta \mu_{ij} = +\infty, \) for \( r^* < a_0^* \) (i.e. hard core ions).

Note that \( r^* \) is the reduced distance in units of cation diameter \( \sigma_{pp} \) while \( a_0^* \) are the diameter ratios: \( \sigma_{mm}^* = \sigma_{mm}/\sigma_{pp}, \sigma_{pp}^* = \sigma_{pp}/\sigma_{pp}, = 1, \) and \( \sigma_{pm}^* = \theta (\sigma_{pp} + \sigma_{mm})/\sigma_{pp}. \) We adjusted \( \theta \) to be: \( \theta = 0.499, \) a bit smaller than 0.500. When \( \theta = 0.500 \) we would have the arithmetic mean, i.e., additive diameter. Our combining rule is smaller than the arithmetic mean. This was done to facilitate numerical solution. The screened parameter is set to \( \lambda = 0.01. \) This small value enables the approach to the behavior of the Coulomb potential. The reduced temperature \( T^* \) is defined as \( kT/\epsilon. \) The reduced (bulk-phase) ion densities are \( \rho_{pp}^* = \rho_{pp}/\rho_{pp}, \) (cation number density), and \( \rho_{mm}^* = \rho_{mm}/\rho_{pp}, \) (anion number density). We shall study two cases of ion adsorption on a hard wall.

Case (1) Symmetric 1:1-type ions at a hard wall

Cations and anions are of different sizes: \( \sigma_{pp} = 2 \sigma_0 = 4.25 \AA, = \sigma_{mm} = 4.05 \AA, \) thus \( \sigma_{mm}^* = \sigma_{mm}/\sigma_{pp} = 2.125, \sigma_{pp}^* = 1, \) and \( \sigma_{pm}^* = 0.970. \) The number densities are \( \rho_{pp}^* = \rho_{pp}/\rho_{pp}, = 0.004818, \) and \( \rho_{mm}^* = \rho_{mm}/\rho_{pp}, = 0.004818. \) These values correspond to 1 M of the salt solution. Given the temperature at 298.15 K, and the relative dielectric constant \( D = 78.5, \) the \( T^* \) is 0.08 and the Bjerrum length is calculated to be \( \beta = e^2/(\epsilon D_0 m kT), = 3.575. \) This case is studied in this work using the Closure Version V1.

Case (2) Asymmetric 2:1-type ions at a hard wall

Cations and anions are of different sizes: \( \sigma_{pp} = 2 \sigma_0 = 4.25 \AA, = \sigma_{mm} = 4.05 \AA, \) thus \( \sigma_{mm}^* = \sigma_{mm}/\sigma_{pp} = 2.125, \sigma_{pp}^* = 1, \) and \( \sigma_{pm}^* = 0.970. \) The number densities are \( \rho_{pp}^* = \rho_{pp}/\rho_{pp}, = 0.004818, \) and \( \rho_{mm}^* = \rho_{mm}/\rho_{pp}, = 0.009636. \) The valences are \( z = 2, \) and \( z = 1. \) Given the temperature at 298.15 K, and the relative dielectric constant \( D = 78.5, \) the \( T^* \) is 0.28 and the Bjerrum length is calculated to be \( \beta = e^2/(\epsilon D_0 m kT), = 3.575. \) This case is studied here using the Closure Version V2.

5.4. The hard wall-ion interactions

The wall is a hard structureless wall occupying the half-space \( z < 0. \) The wall potentials, \( w(z), z \) being the vertical distance from the wall, distinguish between the cations and anions by their sizes

\[ \beta w_p(z) = +\infty, \quad \forall z < \frac{1}{2}\sigma_{pp} \] (for cations) (5.4)

\[ \beta w_m(z) = +\infty, \quad \forall z < \frac{1}{2}\sigma_{mm} \] (for anions) (5.5)

6. The Euler-Lagrange equations for the wall-particle system and the numerical solution

The Euler-Lagrange equations for the adsorption of the Yukawa ions at the hard wall are given below:

The Euler-Lagrange equation for cationic adsorption

\[ \rho_p(z) = \rho_{pp} \exp \left[ -\beta w_p(z) + \gamma_p(z) + B_p(z) \right] \] (6.1)

The Euler-Lagrange equation for anionic adsorption

\[ \rho_m(z) = \rho_{mm} \exp \left[ -\beta w_m(z) + \gamma_m(z) + B_m(z) \right] \] (6.2)

where \( \rho_p(z) \) is the nonuniform cation singlet-density at the hard wall; and \( \rho_m(z) \) the nonuniform anion singlet-density at the hard wall. On the other hand, \( \rho_{pp} \) is the uniform (bulk) cation density; and \( \rho_{mm} \) the uniform (bulk) anion density. \( B_p \) and \( B_m \) are the respective nonuniform \( \langle wall-particle\rangle \) bridge functions. \( \gamma_p \) and \( \gamma_m \) are the nonuniform indirect correlations defined as

\[ \gamma_i (\vec{r}) \equiv \sum_j \int d\vec{r}' \ C_p^{ij} \left( \vec{r} - \vec{r}' \right) \hat{\rho}_p (\vec{r}') \] (6.3)

where \( \hat{\rho}_p (\vec{r}') \equiv \rho_p^{(1)} (\vec{r}') - \rho_{pp} h_p (\vec{r}') \), and \( h_p (\vec{r}') \) is the nonuniform total correlation function \( \langle ij \rangle \) (wall-particle) bridge functions. The bridge functions in Eqs. (6.1) and (6.2) are now functionals of \( \gamma_i (\vec{r}). \)

Version I (CA-OZ3)

\[ B_p (1) = -\frac{c}{2} \frac{\zeta}{2} \gamma_i^{(1)} \left[ 1 - \psi_i - \frac{q_i}{1 + \psi_i / \gamma_i^{(1)}} \right] \sum_{j:p,m} \rho_j \int d\vec{r} \ C_p^{ij} (1, 3) \hat{h}_j (3) - \gamma_j (3) \gamma_3 (3) \] (6.4)
Note that in the bridge functions (6.4) and (6.5) the uniform fluid second-order direct correlation functions (dcfs) $C_{ij}^{(2)}$ are involved in the integrands. We must know the bulk mixture properties beforehand in order to solve the Euler-Lagrange equations. They are three types of the uniform dcfs, $C_{i}^{(2)}$ and $C_{ij}^{(2)}$ since $C_{i}^{(2)} = C_{ij}^{(2)}$. These homogeneous dcfs for the Yukawa fluid mixtures were supplied by solving the uniform case OZ2 equations using the HNC closures.

Numerical solution

The Euler-Lagrange Eqs. (6.1) and (6.2) were discretized in the $z$-coordinate. Since the attenuated Yukawa potentials ($\lambda = 0.01$) are long-ranged, we used 8192 grids of size $\Delta z = 0.005s_{0}$ in the $z$-direction (which is perpendicular to the hard wall). Thus the $z$-coordinate spanned up to 40.96. At times, we increased the maximum $z$-ranges up to 81.92 and 163.84 to ascertain convergence. Trapezoidal rule was used for integration to minimize numerical mismatch at convolution integral boundaries (that might have happened in Simpson’s rules if not carefully done). Numerical relaxation with a mixing parameter “relax” = 0.999 or higher was carried out by Picard’s iterative procedure. (Note relax was chosen to favor old solutions). A numerical solution was considered achieved in the Cauchy convergence sequence with the convergence criterion $\epsilon < 0.00011$ (or $< 0.00021$).

7. Results and discussions

As discussed above, we investigate two adsorptive systems: (i) Symmetrical Yukawa-ions and (ii) Asymmetrical Yukawa-ions.

Case (i): Symmetrical Yukawa-ions

We recapitulate the conditions of Case i: Cations and anions are of different sizes: $s_{0p} = 2A$, $s_{0m} = 4.25A$, thus $s_{0p} / s_{0m} = 2.125$, $a_{i}^{pp} = 1$, and $a_{i}^{pm} = 1.06$. The number densities are $\rho_{p} = \rho_{0} / s_{0pp} = 0.004818$, and $\rho_{m} = \rho_{0} s_{0pm} = 0.004818$. These values correspond to 1 Molar of the salt solution. Given the temperature at 298.15 K, the number of parameters is still larger than the contact conditions. We have extra degrees of freedom. We have “frozen” four parameters ($a_{i}^{pp}$ and $a_{i}^{pm}$) and adjusted the other four parameters ($s_{0p}$ and $s_{0m}$). We treat out cases as a first-time feasibility study, to determine if the OZ3-based closures can at least mimic the adsorption of ionic species. Additional conditions [23] will be formulated in future studies.

Fig. 2 shows the $y_{i}(z)$, the singlet cavity function, for the adsorption of cations at the hard wall. The wall-particle singlet cavity function $y(z)$ is defined in terms of the singlet density $\rho_{i}(z)$ as

$$y(z) = \rho_{i}(z) \exp[+-\beta W_{i}(z)] / \rho_{0i}, \quad i = p, m$$

Thus by matching the cavity functions, we can tell how well the singlet densities of adsorption will also match. Fig. 2 shows that there is quite close match between the present theory (using V1 closure) and the MC results.

Fig. 3 shows the $y_{i}(z)$, the singlet cavity function, for the adsorption of anions at the hard wall. Again we see the close reproduction of the MC data by the present theory of V1.

Case (2): Asymmetrical Yukawa-ions

To recapitulate: in Case ii, cations and anions are of different sizes: $s_{0p} = 2A$, $s_{0m} = 4.25A$, thus $a_{i}^{pm} = s_{0m} / 0pp = 2.125$, $a_{i}^{pp} = 1$, and $a_{i}^{pm} = 1.06$. The number densities are $\rho_{p} = \rho_{0} s_{0pp} = 0.004818$, and $\rho_{m} = \rho_{0} s_{0pm} = 0.004818$. These values correspond to 1 Molar for cations and 2 Molar for anions. The charge valences are $Z_{p} = 2$,
and $Z_m = 1$. The temperature $T^*$ is 0.28. This case is modeled with the closure Version V2.

Fig. 4 shows the singlet cavity function of cations, $y_p(z)$, at the hard wall. The orange colored diamonds are from the MC of Gillespie [13]. The dash-dot line is from the present theory (Version 2). The hard wall is located at $z^* = 0.5$ (or 1 Å). The theoretical prediction shows some oscillatory behavior and the V1 contact value at the wall is too high (compared with the MC value). Thus there are discrepancies due to inaccuracies in the theory.

Fig. 5 shows the $y_{yi}(z)$, the singlet cavity function, for the adsorption of anions at the hard wall. Here we have satisfactory agreement between the theory (V2) and MC.

We next examine the level of agreement of the contact values. Table 1 shows the comparison of the contact values for Case (1)—symmetric ions, and Table 2 for the contact values of Case (2)—asymmetric ions. Note that we have three sources of the contact values: (i) derived from the contact value theorems Eqs.(7.3a) & (7.3b) that are based on the bulk pressure; (ii) obtained from the Monte Carlo simulation [13]; and (iii) calculated from the present theories (CA-OZ3 and LIN/Symm).

We note that for the entries (i), (ii) and (iv), the three values from different sources are quite close, meaning satisfactory agreement with the contact value theorem. Due to this close match, an overall agreement (from $z = contact$ to $z = \infty$ at large distances) between our theory and Monte Carlo data is achieved. For Entry (iii), in the asymmetrical mixture, the cation contact value ($=0.5$) obtained from the LIN/Symm theory is off by 12% from MC value ($=0.446$); and 25% off from the contact theorem value ($=0.4$), despite efforts at enforcing the contact-value consistency. Thus Entry (iii) shows the highest deviation from the MC data. We note that the requirement of contact value consistency is essential in the present approach for obtaining accurate correlation functions. This fact has been previously observed and was used to good effect by di Caprio et al. [24], Kravtsiv et al. [25], and Jiang et al. [26].

8. Conclusions

In this study we have incorporated the third-order Ornstein-Zernike relation (OZ3) in the derivation of the third-order term $B_3$ of the bridge function. To make it work for a new bridge function theory, we make further approximations by introducing the inverse Jackson-Feenberg ansatz (Version 1) or the so-called linear approximation—LIN (Version 2) for the triplet correlations. From this $B_3$, we construct the complete bridge functional $B_m$ by adding the ZSEP function and the newly minted $\psi$-functional. The resulting bridge correlation is a “functional” that depends on all values of the $\gamma_i$ function.

The conventional closure-based density functional theories usually failed for the so-called depletive type of adsorptions (the contact density is lower than the bulk density. See e.g. Ref. [7]). Here we have shown, even for the Yukawa ions, the new theories (Version 1 and Version 2) are able to achieve reasonable agreement when compared with Monte Carlo simulated data (See Figs. 2 and 4, both are depletive adsorption). In summary, the new versions perform remarkably well for symmetric ions (cations and anions adsorptions—see Figs. 2 and 3), and also quite well for asymmetric ions with regard to the anionic adsorption (see Fig. 5). The exception is the asymmetric cationic adsorption (Fig. 4). There the contact value obtained from theory does not match the contact value from MC [13]. However, for larger $z$ values, the theory recovers and gives reasonably accurate values for the cations. Our theory captures the main trends of the Monte-Carlo data, although there are differences in the detailed curvatures. We remark that, strictly speaking, our Yukawa ions are not Coulomb ions. According to Holovko et al. [27,28], the contact value is dependent on the pair correlation function $g_{ij}(r)$ at long distances, $r \rightarrow \infty$. Calculating the Coulomb contact values with the Yukawa contact values is be bound to have discrepancies (due to lack of long-range contributions).

There are several areas that need improvements: (1) we have excessively more numbers of parameters than available consistency conditions to assure “unique” solution. In the future, other known adsorptive theorems will be incorporated. For example the Gibbs adsorption theorem [23] will be satisfied. (2) The Yukawa potentials are not the Coulomb potentials. For “real” ions, one needs to use the full Coulomb potential in the calculation. We shall develop new numerical procedures to treat complications arising from the long-range nature of the Coulomb potential. (3) The OZ3 approach promises to give insights into the closure behavior. New closure relations will be developed for the more recalcitrant cases.

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Appendix A

In this Appendix, we show the detailed derivations in order to incorporate the LIN approximation into the $B_3$ expression. The LIN approximation is given by the simple formula

$$\ln y^{(3)}(1, 2, 3) \approx \ln y^{(2)}(1, 2) + \ln y^{(2)}(2, 3)$$

(4.9)

It is predicated on that the bond $r_{13}$ is the longest of the three bonds. The triplet cavity function $y^{(3)}(1,2,3)$ is related to the triplet total correlation $h^{(3)}(1,2,3)$ via

$$h^{(3)}_{123} = y^{(3)}_{123} e^{g_{122}e_{31} - g_{12} - g_{23} - g_{31} + 2}$$

(A.1)

where $e_i$ are the Boltzmann factors and $g_i$ the pair correlations. Thus from Eq. (4.9), we have

$$h^{(3)}_{123} = f_{13} - h_{13} + f_{13}h_{12} + f_{13}h_{23} + h_{12}h_{23} + f_{13}h_{12}h_{23}$$

(4.10)

Substituting Eq. (4.10) into the exact $B_3$ expression Eq. (4.3), we obtain the approximate cluster diagrams (approximate because it has incorporated the LIN approximation):

$$2B_3(10) \leq \rho \int dA dS \langle f_{i_4} - h_{i_4} \rangle C_{10}C_{10} - \gamma_{10}^2$$

(A.2)
where the bonds are the correlation functions

\[ h \quad C \quad h^{(3)} \quad \gamma \quad f \]

Eq. (A.2) is not “symmetrical” in its arguments because the uneven distribution of the Mayer bonds, \( f_{ij} \). To make it symmetrical, we equate the bonds \( f_{ij} = h_{ij} \). Thus we have

\[ 2B_1 \equiv \quad \text{(LIN/Symm)} \quad (4.12) \]

This is the final LIN/Symm approximation.

References