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Solution of the Yukawa Closure of the Ornstein–Zernike Equation

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The solution of the Ornstein–Zernike equation with Yukawa closure $[c(r) = \sum_i K_i e^{-z_i(r-1)}/r$ for $r > 1]$ is generalized for an arbitrary number of Yukawas, using the Fourier transform technique introduced by Baxter. Full equivalence to the results of Waisman, Høye, and Stell is proved for the case of a single Yukawa. Finally, a convenient form of the Laplace transform of $\tilde{g}(s)$ is found, which can be easily inverted to give a stepwise, rapidly converging series for $g(r)$.

KEY WORDS: Mean spherical model; simple fluids; Ornstein–Zernike equation; Baxter method; generalized mean spherical model.

1. INTRODUCTION

While the theory of simple fluids with spherical potentials is rather well developed and little remains to be done as far as improving the agreement with known experiments (real life and computer), it is always interesting to be able to condense numerical results of long tables into simple analytical expressions that not only are simpler to handle, but also give physical insights that provide a basis for applications and extensions to more complicated systems.

A result of this nature is the solution of the mean spherical approximation[(1)] for a Yukawa tail recently obtained by Waisman,[(2)] which was later

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made into a rather exact theory for hard-sphere systems by Høye *et al.*,[3] the generalized mean spherical approximation. Further extensions and applications have also been published,[4–8] which show the potential of this approach; a review is given by Stell.[8]

The actual detailed solution[2] was done using the Laplace transform technique and was not published in full detail in the literature. What we propose to do is to apply a method of Baxter,[9] based on the Wiener–Hopf factorization of the Fourier transforms of the correlation function, to obtain a general solution of the Ornstein–Zernike (OZ) equation with a Yukawa closure.

More precisely, the OZ equation for a one-component fluid with spherically symmetric interaction is

$$h(r) = c(r) + \rho \int d\mathbf{r}' \, c(|\mathbf{r}'|)h(|\mathbf{r} - \mathbf{r}'|) \tag{1}$$

where $h(r) = g(r) - 1$ and $g(r)$ is the pair correlation function, while $c(r)$ ($r = |\mathbf{r}|$) is the direct correlation function. If the molecules have a hard, impenetrable core, then we know that

$$h(r) = -1 \qquad \text{for} \quad r < 1 \tag{2}$$

where we have taken the hard core diameter $\sigma = 1$. Now, to be able to solve (1), we need to know $c(r)$ for $r \geqslant 1$. We will call the particular assumption that $c(r)$ can be expressed by an arbitrary sum of Yukawas the "Yukawa closure." This means

$$c(r) = \sum_{i=1}^{n} K_i e^{-z_i(r-1)}/r \qquad \text{for} \quad r \geqslant 1 \tag{3}$$

Each term in (3) has the form of a Yukawa potential. When $n = 1, 2$, we recover the cases that were already solved[2,4–8] in the literature. However, in the case of one Yukawa, we will be able to show that the solution reduces to solving a quartic equation, which has an analytic, explicit solution.

The solution of the stated problem will consist in reducing the integral equation (1) with boundary conditions (2) and (3) to a set of $n + 2$ algebraic equations. By letting $n \to \infty$, we can express *any* reasonable $c(r)$ in the form of Eq. (3), but at the same time, the set of algebraic equations becomes just another integral equation, probably just as hard to deal with as (1).

The solution of (1) is done by utilizing Baxter's method[9] to obtain the closure (3). By his very elegant method Baxter solved in a rather simple way the Percus–Yevick equation for hard-sphere systems, in which the closure is simply $c(r) = 0$ ($r > 1$). While this gave a much simpler derivation of the Wertheim–Thiele[10] solution, its power became apparent by the generalization of Lebowitz's result[11] for hard-sphere mixtures.[12] Blum and Tibavisco[13] later showed that the Baxter method could be used to rederive the mean spherical approximation result for equal-size charged spheres of Waisman and Lebowitz[14] in a surprisingly simple manner. The key ingredient to this extension was to postulate a Yukawa closure of the form of Eq. (3), and take the limit $z_1 \to 0$ at the end of the calculation. This makes the Wiener–Hopf factorization possible, at the price of including poles in the previously entire Fourier transforms of $c(r)$. However, this approach proved quite powerful, since a number of interesting systems, such as mixtures of charged hard spheres and dipoles of equal[15],[4] and different[17] sizes, charged hard spheres of different charges and sizes,[18] and wall-charged hard spheres,[19] can be solved analytically.

2. METHOD OF SOLUTION

We take the Fourier transform (which is denoted by a tilde) of (1)

$$\tilde{h}(k) = \tilde{c}(k) + \rho\tilde{c}(k)\tilde{h}(k) \tag{4}$$

Equation (4) may be written as

$$1 - \rho\tilde{c}(k) = [1 + \rho\tilde{h}(k)]^{-1} = \tilde{Q}(k)\tilde{Q}(-k) \tag{5}$$

The (Wiener–Hopf) factorization with the function Q in (5) is the major step introduced by Baxter.[9] The $\tilde{Q}(k)$ may be written as

$$\tilde{Q}(k) = 1 - 2\pi\rho \int_0^R e^{ikr} Q(r)\, dr \tag{6}$$

Baxter then shows that $Q(r)$ has the following properties: The $Q(r)$ is a real function, and $Q(r) = 0$ for $r < 0$. Further, if $c(r) = 0$ for $r > R$, then $Q(r) = 0$ also for $r > R$. Thus the limits of integration in the one-dimensional Fourier transform given by (6) may be put equal to 0 and R, respectively. Finally, $Q(r)$ is a continuous function for $r > 0$. Accordingly,

$$Q(R) = 0 \tag{7}$$

By this introduction of $Q(r)$ the original integral equation can be transformed into[9]

$$rc(r) = -Q'(r) + 12\xi \int_0^R dt\, Q'(t)Q(t - r) \tag{8}$$

$$rh(r) = -Q'(r) + 12\xi \int_0^R dt\, (r - t)h(|r - t|)Q(t) \tag{9}$$

[4] Adelman and Deutch[16] solved the problem simultaneously, but using the Laplace transform technique. While the results seem to agree to lowest order in electrolyte concentration, it is still an open question to show that they are totally equivalent.

where $Q'(r)$ means the derivative of $Q(r)$ with respect to r, while $\xi = (\pi/6)\rho$. Equation (9) is a new integral equation, which, when solved, also gives $c(r)$ as given by (8). One advantage of (9) compared to (1) is that it is one dimensional instead of three dimensional. The second very great advantage of (9) is that here the special condition given by (2), namely that $h(r) = -1 =$ const for $r < 1$, can be utilized in a very profitable fashion, as we shall see. In this way one immediately gets the Percus–Yevick solution for hard spheres [$c(r) = 0$ for $r > 1$]. Then $R = 1$, and (9) needs to be considered only for $r < R = 1$, so $h(r)$ is involved only for $r < 1$. One then easily sees that [using (7)]

$$Q(r) = \tfrac{1}{2}ar^2 + br - (\tfrac{1}{2}a + b) \tag{10}$$

where a and b are found by insertion into (9), thus leading to the full solution of this problem.

However, in other problems, when $R > 1$, Eq. (9) again may look almost as difficult to solve as the original equation. Fortunately this is not as bad as it first appears, since we can profit somewhat from the knowledge of $c(r)$ for $r > 1$ as given by (3). The reason for this is that the form of $Q(r)$ for $r > 1$ is fully determined from (3).

Assume first that (3) holds for all r (>0). By Fourier transformations and by contour integration[13] (in both one and three dimensions), or most easily by use of (8), one then finds that $Q(r)$ must be of the form

$$Q(r) = \sum d_i e^{-z_i r} \qquad (r > 0) \tag{11}$$

Therefore

$$Q(r) = Q_0(r) + \sum d_i e^{-z_i r} \qquad (r > 0) \tag{12}$$

where

$$Q_0(r) = 0 \qquad \text{for} \quad r > 1 \tag{13}$$

and due to the condition of continuity

$$Q_0(1) = 0 \tag{14}$$

By study of Eq. (8) for $r > 1$ one finds that, with $Q(r)$ given by (12), the $c(r)$ will still be of the form given by (3), although the connection between the K_i and d_i will change. This connection is given by Eqs. (27) and (28). Accordingly, the $Q(r)$ that solves our problem can be written in the form given by (12), and then Eq. (9) with condition (2) again is very advantageous. One then sees that the $Q_0(r)$ will contain the terms given by (10) plus terms where the $e^{-z_i r}$ is involved. We find by use of (14)

$$Q_0(r) = \tfrac{1}{2}a(r^2 - 1) + b(r - 1) + \sum c_i(e^{-z_i r} - e^{-z_i}) \tag{15}$$

We now have to use Eq. (9) to determine the coefficients of (15). It is then convenient to introduce

$$g(r) = h(r) + 1 \qquad [\text{so } g(r) = 0 \quad \text{for} \quad r < 1] \tag{16}$$

Equation (9) then transforms into

$$rg(r) = r - Q'(r) - 12\xi \int_0^R (r - t)Q(t)\,dt + 12\xi \int_0^R (r - t)g(|r - t|)Q(t)\,dt \tag{17}$$

The limit of integration here means $R = 1$ for the part of $Q(r)$ that is $Q_0(r)$ and $R = \infty$ for the rest. The $Q(r)$ as given by (12) and (15) is then put into (17). For $r < 1$ one then finds

$$\begin{aligned} 0 = r - ar - b &+ \sum z_i(c_i + d_i)e^{-z_i r} - 12\xi r\Big[\tfrac{1}{3}a + \tfrac{1}{2}b \\ &- (\tfrac{1}{2}a + b + \sum c_i e^{-z_i}) + \sum c_i(1/z_i)(1 - e^{-z_i}) + \sum d_i(1/z_i)\Big] \\ &+ 12\xi\{\tfrac{1}{8}a + \tfrac{1}{3}b - \tfrac{1}{2}\Big(\tfrac{1}{2}a + b + \sum c_i e^{-z_i}\Big) + \sum c_i(1/z_i^2)[1 - (1 + z_i)e^{-z_i}] \\ &+ \sum d_i(1/z_i^2)\} - 12\xi \sum d_i e^{-z_i r}\hat{g}(z_i) \end{aligned} \tag{18}$$

Here $\hat{g}(z_i)$ is the Laplace transform,

$$\hat{g}(s) = \int_0^\infty rg(r)e^{-sr}\,dr \tag{19}$$

From (18) one immediately gets the following equations by equating terms with equal r dependence:

$$b = 12\xi\left\{-\frac{1}{8}a - \frac{1}{6}b + \sum c_i\left[\frac{1}{z_i^2} - \left(\frac{1 + z_i}{z_i^2} + \frac{1}{2}\right)e^{-z_i}\right] + \sum d_i \frac{1}{z_i^2}\right\} \tag{20a}$$

$$1 - a = 12\xi\left[-\frac{1}{3}a - \frac{1}{2}b + \sum c_i\left(\frac{1}{z_i} - \frac{1 + z_i}{z_i}e^{-z_i}\right) + \sum d_i \frac{1}{z_i}\right] \tag{20b}$$

$$z_i(c_i + d_i) = 12\xi d_i \hat{g}(z_i) \tag{20c}$$

The remaining obstacle to solving the integral equation as given by (1)–(3) is that we need some expression for $\hat{g}(z_i)$ [apart from the relation given by (20c)]. This we can obtain by taking the Laplace transform of (17). The Laplace transformation can be simplified by noting that since (18) holds for $r < 1$, it also holds for $r > 1$. Therefore we can subtract (18) from

(17) and then take the transform of the difference (which is different from zero for $r > 1$). One then notes that the latter integral of (17) will be the latter term of (18) for any r if the lower limit of integration, which is zero, is replaced by r. So for the difference we then find ($r > 1$)

$$rg(r) = ar + b - \sum z_i c_i e^{-z_i r} + 12\xi \int_0^r (r - t) g(|r - t|) Q(t)\, dt \tag{21}$$

The integral in (21) is just the convolution integral by Laplace transform, so from this we find

$$\hat{g}(s) = \left\{ \frac{1}{s^2} [a(s + 1) + bs] - \sum \frac{z_i c_i}{z_i + s} e^{-z_i} \right\} e^{-s} + 12\xi \hat{g}(s) q(s) \tag{22}$$

or

$$\hat{g}(s) = \frac{\{(1/s^2)[a(s + 1) + bs] - \sum [z_i c_i/(z_i + s)] e^{-z_i}\} e^{-s}}{1 - 12\xi q(s)} \tag{23}$$

where

$$q(s) = \int_0^R Q(t) e^{-st}\, dt = \sigma(s) - \tau(s) e^{-s}$$

$$\sigma(s) = a \frac{1}{s^3} + b \frac{1}{s^2} - \left(\frac{1}{2} a + b + \sum c_i e^{z_i} \right) \frac{1}{s} + \sum (c_i + d_i) \frac{1}{z_i + s} \tag{24}$$

$$\tau(s) = a \left(\frac{1}{s^3} + \frac{1}{s^2} \right) + b \frac{1}{s^2} - \frac{1}{s} \sum \frac{z_i}{z_i + s} c_i e^{-z_i}$$

From this one sees that $\hat{g}(s)$ also may be written as

$$\hat{g}(s) = s\tau(s) e^{-s}/[1 - 12\xi q(s)] \tag{25}$$

We observe, in passing, that (25) gives an explicit form of the binary correlation function $\hat{g}(s)$. A stripwise Laplace inversion can be easily achieved by expanding the e^{-s} term in $q(s)$.

By putting $s = z_i$, (25) gives the desired equations. Solution of Eqs. (20) and (25) then leads to the solution of the Ornstein–Zernike equation with the conditions (2) and (3). To complete the solution, we also need the connection between the parameters K_i in (3) and the a, b, c_i, and d_i. We will find it by investigating the direct correlation function $c(r)$.

3. THE DIRECT CORRELATION FUNCTION $c(r)$

We now will compute the form of $c(r)$ and establish the connection between parameters in $c(r)$ and $Q(r)$. It is then probably most simple to compute $c(r)$ by use of Eq. (8) with $Q(r)$ given by (12) and (15). For $r < 1$

the computation is somewhat tedious, as the integrand will consist of many terms that have to be integrated separately. Further, to bring $c(r)$ into the desired form, Eqs. (20) and (25) also have to be used. We will then find [Eq. (36)] that $c(r)$ has a form that generalizes the form found by Waisman when solving for one and two Yukawa terms. We find ($r < 1$)

$$-rc(r) = Q_0'(r) - \sum z_i d_i e^{-z_i r} - 12\xi \int_r^1 Q_0'(t)Q(t-r)\,dt + 12\xi \int_r^\infty \sum z_i d_i e^{-z_i t} Q(t-r)\,dt \quad (26)$$

For $r > 1$ it is easy to find $c(r)$. In that case (26) reduces to [since $Q_0(r) = 0$ for $r > 1$]

$$rc(r) = \sum z_i d_i [1 - 12\xi q(z_i)] e^{-z_i r} \quad (27)$$

where $q(s)$ is given by (24). This establishes the relation to the coefficients of Eq. (3),

$$K_i e^{z_i} = z_i d_i [1 - 12\xi q(z_i)] \quad (28)$$

For $r < 1$ we find by a more tedious computation

$$\begin{aligned} -rc(r) &+ K_i e^{z_i} e^{-z_i r} \\ &= b - 12\xi \Big\{ -\tfrac{1}{2}\Big[\tfrac{1}{2}a + b + \sum c_i e^{-z_i} - \sum (c_i + d_i)\Big]^2 \\ &\quad + \sum z_i (c_i + d_i)\sigma(z_i) + \sum z_i c_i e^{-z_i}\tau(z_i)\Big\} \\ &\quad + \Big\{ a - 12\xi a \Big[-\tfrac{1}{3}a - \tfrac{1}{2}b - \sum [(1 + z_i)/z_i] c_i e^{-z_i} \\ &\quad + \sum (1/z_i)(c_i + d_i)\Big]\Big\} r \\ &\quad - 12\xi\Big[\tfrac{1}{2}(a+b)^2 + a\sum c_i e^{-z_i}\Big] r^2 + \tfrac{1}{2}\xi a^2 r^4 \\ &\quad + 12\xi\Big[\sum z_i (c_i + d_i)\tau(z_i) e^{-z_i} e^{z_i r}\Big] - \sum z_i c_i [1 - 12\xi\sigma(z_i)] e^{-z_i r} \end{aligned} \quad (29)$$

The $\sigma(z_i)$ and $\tau(z_i)$ are given by Eq. (24). To go further with expression (29), we have to utilize Eqs. (20) and (25). Consider first Eq. (8) for $r = 0$. In this case the computations are very simple, resulting

$$\begin{aligned} -rc(r)|_{r=0} &= Q'(0) + 6\xi[Q(0)]^2 \\ &= b - \sum z_i (c_i + d_i) + 6\xi\Big[\tfrac{1}{2}a + b + \sum c_i e^{-z_i} - \sum (c_i + d_i)\Big]^2 \end{aligned} \quad (30)$$

One sees that result (29) from the more tedious computation agrees with this when Eq. (28) is used for $K_i e^{z_i}$ and Eq. (24) for $q(z_i)$. Now $rc(r)$ should be zero for $r = 0$, as one expects $c(0)$ to be finite. From Eq. (30) this is not automatically fulfilled. As this does not hold for general a, b, c_i, and d_i, one instead will expect it to hold when these coefficients are found from Eqs. (20) and (25). Therefore, we will try to find a combination of these that results in expression (30). By use of (25), Eq. (20c) may be transformed into

$$c_i + d_i = 12\xi[\sigma(z_i)(c_i + d_i) - \tau(z_i)c_i e^{-z_i}] \tag{31}$$

To find the proper combination, we now have to do the following: Multiply Eq. (20a) with a, multiply Eq. (20b) with b, and multiply Eq. (31) with $-z_i$. Then add these equations together. The result is

$$b - \sum z_i(c_i + d_i) = -6\xi\left[\tfrac{1}{2}a + b + \sum c_i e^{-z_i} - \sum (c_i + d_i)\right]^2 \tag{32}$$

From this one sees that $-rc(r) = 0$ for $r = 0$, as it should.

By use of Eq. (20b) one sees that the coefficient of the r term of (29) is the same as a^2. To investigate the $e^{z_i r}$ and $e^{-z_i r}$ terms, let us introduce

$$v_i = 24\xi K_i e^{z_i} \int rg(r)e^{-z_i r}\, dr = 24\xi K_i e^{z_i}\hat{g}(z_i) \tag{33}$$

One then finds by use of (20c), (25), and (28)

$$\begin{aligned}
\tfrac{1}{4}v_i^2/K_i e^{z_i} z_i^2 &= (1/4z_i^2)K_i e^{z_i}[24\xi\hat{g}(z_i)]^2 \\
&= 12\xi\tau(z_i)e^{-z_i}[12\xi\hat{g}(z_i)/z_i]d_i \\
&= 12\xi(c_i + d_i)\tau(z_i)e^{-z_i}
\end{aligned} \tag{34}$$

$$\begin{aligned}
K_i e^{z_i}[1 - (v_i/2K_i e^{z_i} z_i)]^2 &= K_i e^{z_i}\{1 - [12\xi\hat{g}(z_i)/z_i]\}^2 \\
&= z_i d_i[1 - 12\xi\sigma(z_i)]\{1 - [12\xi\hat{g}(z_i)/z_i]\} \\
&= -z_i c_i[1 - 12\xi\sigma(z_i)]
\end{aligned} \tag{35}$$

One sees that (34) and (35) are the coefficients of the $e^{z_i r}$ and $e^{-z_i r}$ terms of (29). Accordingly, $c(r)$ may be written for $r < 1$ as

$$\begin{aligned}
-rc(r) &= a_0 r + b_0 r^2 + \tfrac{1}{2}\xi a_0 r^4 \sum (v_i^2/4K_i e^{z_i} z_i^2)(e^{z_i r} - 1) \\
&\quad + \sum K_i e^{z_i}\{[1 - (v_i/2K_i e^{z_i} z_i)]^2 - 1\}(e^{-z_i r} - 1) \\
&= a_0 r + b_0 r^2 + \tfrac{1}{2}\xi a_0 r^4 + \sum (v_i/z_i)(1 - e^{-z_i r}) \\
&\quad + \sum \{v_i^2[\cosh(z_i r) - 1]/2K_i e^{z_i} z_i^2\}
\end{aligned} \tag{36}$$

Here

$$a_0 = a^2; \qquad b_0 = -12\xi\left[\tfrac{1}{2}(a+b)^2 + a\sum c_i e^{-z_i}\right] \tag{37}$$

The a^2 can be given a direct physical interpretation. From Eqs. (6), (20b), and (24) [Eq. (20b) is the same as the coefficient of the r term of (17)]

$$\tilde{Q}(0) = 1 - 12\xi q(0) = a \tag{38}$$

So from Eq. (5)

$$1 - \rho\tilde{c}(0) = \tilde{Q}(0)\tilde{Q}(0) = a^2 = a_0 \tag{39}$$

From (39) one sees that $a_0 = a^2$ is the same as the inverse compressibility if the equation of state is computed via the fluctuation theorem. Now one sees that the $c(r)$ as given by (36) is exactly the same as found by Waisman by his method to solve the Ornstein–Zernike equation for one and two Yukawas, where v_i and a are defined by (33) and (39). Equation (36) generalizes the form of $c(r)$ for one and two Yukawas to an arbitrary number of Yukawa terms.

4. COMPARISON WITH EARLIER SOLUTION

The cases with one and two Yukawas have been solved by Waisman[2,4] by a quite different method, leading to solutions with $c(r)$ as given by (36), but with completely different algebraic equations. These solutions were simplified by Høye *et al.*[5–7] as part of a general investigation of the OZ equation. We would like to show the equivalence between these earlier solutions and the solutions found here. In a preceding section we have already shown that the form of the $c(r)$ agrees in full, but we have not shown that the determination of its coefficients gives the same result.

Here we will not try to do this explicitly for the two-Yukawa case, since, as far as we can see, this will be a rather tedious computation. However, we will indicate that it should be possible to perform such a comparison explicitly in the two-Yukawa case, too. This is based upon the observation that Eqs. (20) and (25) form a set of linear equations if the a, b, c_i, and d_i are all considered as unknown while the $\hat{g}(z_i)$ (besides z_i and ξ) are considered as the known quantities. This means that the equations can be solved explicitly with respect to a, b, c_i, and d_i in terms of $\hat{g}(z_i)$, giving a unique solution. (However, when other quantities, e.g., K_i, are considered known, then the resulting equations are no longer linear, and multiple solutions will occur, of which only one is acceptable.) Despite its complexity, the earlier solution also turns out to form a set of linear equations for a certain combination of variables.[5] The resulting equations, Eqs. (30)–(32) of Ref. 5, are linear in A, U_0, and W_0 and are thus solvable with respect to these variables when $S_1 = U_1/U_0$ and

$S_2 = W_1/W_0$ (besides z_i and ξ) are considered known. The resulting solutions can be compared since A, U_0, and W_0 can be expressed explicitly in terms of a, b, c_i, d_i, and $\hat{g}(z_i)$ (via K_i) and S_1 and S_2 can be expressed explicitly in terms of $\hat{g}(z_i)$ alone.[5]

Now we turn to the one-Yukawa case, for which we will perform the comparison in a way different from the one outlined above. For given K_1, z_1, and ξ we need three independent equations to determine a_0, b_0, and v_1. One of those is Eq. (39). Accordingly, we have to show the equivalence of two additional equations. This may be performed in the following way $(z_i, c_i, d_i \to z, c, d)$: One equation in the earlier solution to compare with is Eq. (2.30) of Ref. 6:

$$(U_0 + A - p)(U_0 + A) - \tfrac{1}{4}z^2(p - A) + zA^{1/2}(U_0 + A - p) = 0 \quad (40)$$

where from Eqs. (2.9) and (2.22) of Ref. 6 ($U_0 = u_0 + u$)

$$p = [(1 - 2\xi)/(1 - \xi)]^2, \qquad A = (1 - \xi)^2 a^2, \qquad 6\xi y_0 = U_0 + A - 1 \quad (41)$$

The y_0 is the contact value $y_0 = g(1+)$. (Note that a^2 is the same as the a of Ref. 6.) In terms of a and y_0, Eq. (40) reads

$$36\xi^2 y_0^2 + 6\xi \frac{1 - 8\xi - 2\xi^2}{(1 - \xi)^2} y_0 - 6\xi \frac{1 + \frac{1}{2}\xi}{(1 - \xi)^2} - \frac{1}{4} z^2 \frac{(1 + 2\xi)^2}{(1 - \xi)^2}$$
$$+ \frac{1}{4} z^2 (1 - \xi)^2 a^2 + 6\xi z(1 - \xi) a y_0 - 6\xi z a \frac{1 + \frac{1}{2}\xi}{1 - \xi} = 0 \quad (42)$$

Then we turn to the equations found here. First we eliminate b by introducing y_0. Due to the continuity of $h(r) - c(r)$ at $r = 1$ [which is obvious from (1)] the y_0 is also the same as the discontinuity of $c(r)$ at $r = 1$, which from (8) again must be equal to the discontinuity of $Q'(r)$ or $Q_0'(r)$ at $r = 1$. So

$$y_0 = Q'(1-) - Q'(1+) = a + b - zce^{-z} \quad (43)$$

By this elimination of b, Eqs. (20a) and (20b) read

$$12\xi(1/z^2)[c + d - (1 + z + \tfrac{1}{2}z^2)ce^{-z}] - (1 + 2\xi)zce^{-z}$$
$$= (1 - 2\xi)y_0 - (1 + \tfrac{1}{2}\xi)a - 12\xi(1/z)[c + d - (1 + z + \tfrac{1}{2}z^2)ce^{-z}]$$
$$= -6\xi y_0 + (1 - 2\xi)a - 1 \quad (44)$$

By solution of these equations with respect to c and d one finds

$$\tfrac{1}{2}a + b + ce^{-z} - (c + d)$$
$$= -\tfrac{1}{2}a + y_0 + [c(1 + z)e^{-z} - (c + d)]$$
$$= [1/12\xi(1 + 2\xi)][12\xi(1 - \xi)y_0 + (1 - \xi)^2 za - (1 + 2\xi)z - 6\xi] \quad (45)$$

and

$$b - z(c + d) = y_0 - a + z[(1 + z)ce^{-z} - (c + d)] - z^2ce^{-z}$$

$$= \frac{1 - 4\xi}{1 + 2\xi} y_0 - \frac{1 - \xi}{2(1 + 2\xi)} za - \frac{1}{1 + 2\xi} + \frac{1 - \xi}{(1 + 2\xi)} zy_0$$

$$+ \frac{(1 - \xi)^2}{12\xi(1 + 2\xi)} z^2a - \frac{z^2}{12\xi} - \frac{z}{2(1 + 2\xi)} \tag{46}$$

When Eqs. (45) and (46) are used in Eq. (32) one obtains Eq. (42), as we wanted to show.

To show full equivalence, we need another equation, too, as argued above. This can be obtained as follows: We need the derivative to contact $y_1 = (d/dr)[rg(r)]|_{r=1+}$. From (1) one can conclude that $h'(r) - c'(r)$ as well as $h(r) - c(r)$ is continuous at $r = 1$. Therefore

$$y_1 = \frac{d}{dr}[rc(r)]\bigg|_{r=1+} - \frac{d}{dr}[rc(r)]\bigg|_{r=1-} \tag{47}$$

The y_1 can then be obtained by differentiation of Eq. (8):

$$y_1 = Q''(1-) - Q''(1+) + 12\xi Q(0)[Q'(1-) - Q'(1+)]$$

$$= a + z^2ce^{-z} + 12\xi y_0[c + d - (\tfrac{1}{2}a + b + ce^{-z})] \tag{48}$$

We obtain the desired equation from Ref. 6 by using its Eqs. (2.24) and (2.26) together with Eqs. (2.9) and (2.30) to eliminate $U_1 = u_1 + u$ and $\frac{1}{4}z^2(p - A)$. This gives with use of Eq. (41)

$$3\xi y_1 = (2 - \sqrt{p})(A + U_0) - 1 - \frac{1}{\sqrt{p}}[(U_0 + A - p)(U_0 + A + \tfrac{1}{2}z\sqrt{A})]$$

$$= -\frac{1 - \xi}{1 + 2\xi}(6\xi y_0)^2 + \frac{6\xi}{1 + 2\xi}6\xi y_0 + \frac{3\xi}{1 + 2\xi}$$

$$- \left[\frac{(1 - \xi)^2}{2(1 + 2\xi)}6\xi y_0 - \frac{1 + \frac{1}{2}\xi}{1 + 2\xi}3\xi\right]za \tag{49}$$

One finds that Eq. (48) is identical to this when b, c, and d are eliminated by use of (45) and (46). Thus we can conclude that the solution of the OZ equation is the same for one Yukawa whether it is solved by Waisman's method or via the extension of Baxter's method used here.

5. A SPECIAL SOLUTION IN THE ONE-YUKAWA CASE

Let us finally consider a special explicit solution in the case of one Yukawa; e.g., when the solution of the Ornstein–Zernike equation is used in the mean spherical approximation one will consider ξ, z, and K as known quantities and solve for the others. In this case the term $(z = z_1)$

$$\gamma = 12\xi\hat{g}(z)/z \tag{50}$$

will be proportional to, and thus correspond to, the internal energy. We will here find a quartic equation for γ. This quartic equation does have an explicit solution for $\hat{g}(z)$ or γ, which can be obtained by reducing it first to a cubic equation and then solving a set of two quadratic equations,[20] or else solving numerically on a digital computer. Among the four solutions one has to choose the physically acceptable one.

As mentioned previously, our Eqs. (20) and (25) are linear and are thus explicitly solvable in analytic form when a, b, c_i, and d_i are considered as unknown. So our method of solution will be to solve Eqs. (20) and (25) for a, b, c, and d $(c = c_1, d = d_1)$. This solution is then used to eliminate these quantities in Eq. (28), which then gives the sought quartic equation for γ. From (28) it is obvious that solution of the quartic equation may be avoided if the γ can be considered as known and K $(=K_1)$ as unknown (i.e., in cases where K does not have to be fixed to a specific value) since (28) must give K explicitly in terms of γ. We do the solution as follows: The c is eliminated by means of Eqs. (20c) and (50),

$$c = (\gamma - 1)d \tag{51}$$

Next we eliminate a and b by solution of Eqs. (20a) and (20b) using (51). We find

$$a + b = a_0 + b_0 - d(\gamma B_1 + C_1 e^{-z}), \qquad a = a_0 - d(\gamma B_2 + C_2 e^{-z}) \tag{52}$$

where a_0 and b_0 are the coefficients in Eq. (10) for the Percus–Yevick hard-core case (i.e., $d = 0$),

$$a_0 = (1 + 2\xi)/(1 - \xi)^2; \qquad a_0 + b_0 = (1 + \tfrac{1}{2}\xi)/(1 - \xi)^2 \tag{53}$$

and the B_i and C_i $(i = 1, 2)$ are coefficients related to them by the equations

$$\begin{aligned} B_1 &= (12\xi/z)(-z^2 e^{-z})[\varphi_1(-z)(a_0 + b_0) + \varphi_2(-z)a_0] \\ C_1 e^{-z} &= -B_1 + (12\xi/z)[a_0 + b_0 - (1/z)a_0] \\ B_2 &= (12\xi/z)(-z^2 e^{-z})[\varphi_1(-z)a_0 - 4\varphi_2(-z)b_0] \\ C_2 e^{-z} &= -B_2 + (12\xi/z)[a_0 + (4/z)b_0] \end{aligned} \tag{54}$$

where we have used the incomplete gamma functions

$$\varphi_1(z) = (1/z^2)(1 - z - e^{-z}), \qquad \varphi_2(z) = (1/z^3)(1 - z + \tfrac{1}{2}z^2 - e^{-z}) \tag{55}$$

Finally, the d is found by solution of Eq. (25) (with $s = z$), where a, b, c, and γ are replaced by expressions (50)–(52). The result, after some computation, is

$$d = -(\gamma X_1 + X_0)/[\gamma^2 D_2 + \gamma(D_1' + D_1'') + D_0] \tag{56}$$

where

$$\begin{aligned} D_2 &= 12\xi[\varphi_2(z)B_2 + \varphi_1(z)B_1 - (1/2z)(1 - e^{-z})^2] \\ D_1' &= 12\xi e^{-z}[\varphi_2(z)C_2 + \varphi_1(z)C_1 - (1/2z)(2 - e^{-z})] \\ D_1'' &= 12\xi e^{-z}[(1/z^3)(B_2 + zB_1) + (1/2z)e^{-z}] \\ D_0 &= 12\xi e^{-2z}[(1/z^3)(C_2 + zC_1) - (1/2z)] \\ X_1 &= 1 - 12\xi[\varphi_2(z)a_0 + \varphi_1(z)(a_0 + b_0)] \\ X_0 &= -12\xi(e^{-z}/z^3)[a_0 + z(a_0 + b_0)] \end{aligned} \tag{57}$$

By some computation it can be shown that $D_1'' = D_1' + (12\xi/z)e^{-z}$. When this is put into Eq. (28), we get the sought quartic equation for γ,

$$Ke^z = zd[X_1 + (\gamma D_2 + D_1')d] \tag{58}$$

or by use of (56)

$$\begin{aligned} &K(e^z/z)[\gamma^2 D_2 + \gamma(D_1' + D_1'') + D_0]^2 \\ &\qquad = (\gamma X_1 + X_0)[X_0(\gamma D_2 + D_1') - X_1(\gamma D_1'' + D_0)] \end{aligned} \tag{59}$$

Besides being a quartic equation in γ, Eq. (58) may also be considered as an explicit expression for K in terms of γ, as concluded before. It is of interest to note that Eq. (25) yields an explicit, rapidly converging, and easy to handle zone-by-zone expression for the binary correlation function $g(r)$. This expression is in a way the extension of the explicit solution for the equations for $g(r)$ proposed by Perram.[21] From (24) and (25) we can write

$$\frac{1}{s}\hat{g}(s) = \frac{1}{12\xi}\frac{V(s)e^{-s}}{1 + V(s)e^{-s}} \tag{60}$$

$$V(s) = \frac{N(s)}{P(s)} \tag{61}$$

where $N(s) = \tau(s)s^3 \prod_i (s + z_i)$ and $P(s) = [1 - 12\xi\sigma(s)]s^3 \prod_i (s + z_i)$ are $(n + 1)$th- and $(n + 3)$th-order polynomials, respectively, where n is the number of Yukawas. From the form of $\sigma(s)$ [Eqs. (24)] we know that

$$P(s) = \prod_{i=1}^{n+3} (s - \mu_i) \tag{62}$$

where μ_i are the roots of $P(s)$; in general, some of the roots are real while others may form complex conjugate pairs for small enough ρ and sufficiently large s, $e^{-s}V(s) < 1$; the following expansion of (60) converges

$$\frac{1}{s}\hat{g}(s) = \sum_{l=1}^{\infty} \frac{1}{12\xi} (-1)^{l-1} [V(s)]^l e^{-sl} \tag{63}$$

Now, calling $W_l(r)$ the inverse Laplace transform of $[V(s)]^l$, we get, with $\theta_l(x) = 0$ for $x \leqslant 0$ and $\theta_l(x) = 1$ for $x > 0$,

$$rg(r) = \frac{1}{12\xi} \sum_{l=1}^{\infty} (-1)^{l-1} \frac{\partial}{\partial r} [W_l(r-l)\theta(r-l)] \tag{64}$$

The explicit form of $W_l(r)$ can be obtained from standard analysis (Bromwhich–Laplace inversion formula)

$$\begin{aligned} W(r) &= \sum_{i=1}^{n+3} \text{Residue}\{[V(s)]^l e^{sr}\} \\ &= \sum_{i=1}^{n+3} \lim_{s\to\mu_i} \frac{1}{(l-1)!} \left(\frac{d}{ds}\right)^{l-1} \frac{(s-\mu_i)^l}{P(s)^l} e^{sr} [N(s)]^l (12\xi)^l \end{aligned} \tag{65}$$

where

$$N(s) = \tau(s) s^3 \prod_{l=1}^{n} (s + z_l) \tag{66}$$

Expanding the polynomial $P(s)$ around its solutions, we easily get

$$W_l(r) = \sum_{i=1}^{n+3} \frac{1}{(l-1)!} \left(\frac{d}{d\mu_i}\right)^{l-1} e^{\mu_i r} \left[\frac{N(\mu_i)}{P'(\mu_i)}\right]^l \tag{67}$$

from which

$$rg(r) = \sum_{l=1}^{\infty} \frac{1}{12\xi} \frac{(-1)^{l-1}}{(l-1)!} \sum_{i=1}^{n+3} \left(\frac{d}{d\mu_i}\right)^{l-1} \mu_i e^{\mu_i (r-l)} \left[\frac{N(\mu_i)}{P'(\mu_i)}\right]^l \theta(r-l) \tag{68}$$

where we have used the standard formula of calculus for residues of l-order poles, which implies that we are restricted to the situation in which $\mu_i \neq \mu_j$ $(i \neq j)$. The expansion formula (68) is rather rapidly convergent. Therefore, instead of giving the explicit general derivation of (65), let us just quote the first terms:

$$W_1(r) = 12\xi \sum_{i=1}^{n+3} [N(\mu_i) e^{\mu_i r} / P'(\mu_i)] \mu_i \tag{69}$$

$$W_2(r) = (12\xi)^2 \sum_{i=1}^{n+3} \mu_i e^{\mu_i r} \left[\frac{N(\mu_i)}{P'(\mu_i)}\right]^2 \left[r + 2\frac{N'(\mu_i)}{N(\mu_i)} - 2\frac{P''(\mu_i)}{P'(\mu_i)}\right] \tag{70}$$

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REFERENCES

1. J. L. Lebowitz and J. K. Percus, *Phys. Rev.* **144**:251 (1966).
2. E. Waisman, *Mol. Phys.* **25**:45 (1973).
3. J. S. Høye, J. L. Lebowitz, and G. Stell, *J. Chem. Phys.* **61**:3253 (1974).
4. E. Waisman, J. S. Høye, and G. Stell, *Chem. Phys. Lett.* **40**:514 (1976).
5. J. S. Høye, G. Stell, and E. Waisman, *Mol. Phys.* **32**:209 (1976).
6. J. S. Høye and G. Stell, *Mol. Phys.* **32**:195 (1976).
7. J. S. Høye and G. Stell, SUSB Report #271, to be published.
8. G. Stell, Fluids with long range forces: toward a simple analytic theory, in *Modern Theoretical Chemistry*, Vol. IV, *Statistical Mechanics*, B. J. Berne, ed., Plenum Press, New York (1976).
9. R. J. Baxter, *Austral. J. Phys.* **21**:563 (1968).
10. M. Wertheim, *Phys. Rev. Lett.* **10**:321 (1963); E. Thiele, *J. Chem. Phys.* **38**:1959 (1963).
11. J. L. Lebowitz, *Phys. Rev.* **133**:A895 (1964).
12. R. S. Baxter, *J. Chem. Phys.* **52**:4559 (1970).
13. L. Blum and H. Tibavisco, unpublished; H. Tibavisco, Thesis, University of Puerto Rico, Rio Piedras, Puerto Rico (1974).
14. E. Waisman and J. L. Lebowitz, *J. Chem. Phys.* **56**:3086, 3093 (1972).
15. L. Blum, *Chem. Phys. Lett.* **26**:200 (1974); *J. Chem. Phys.* **61**:2129 (1974).
16. S. A. Adelman and J. M. Deutch, *J. Chem. Phys.* **60**:3935 (1974).
17. L. Blum, Solution of a model of arbitrary size solvent-electrolyte interaction (unpublished).
18. L. Blum, *Mol. Phys.* **30**:1529 (1975).
19. L. Blum and G. Stell, *J. Stat. Phys.* **15**:439 (1976).
20. M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions*, Dover, New York (1965), p. 13.
21. J. Perram, Hard Sphere Correlation Functions, preprint (1975).