Analytic solution of the RISM equation for
symmetric diatomics with Yukawa closure

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We present the site-site direct correlation function $c(r)$ for a fluid of hard diatomic symmetric molecules obtained from Monte Carlo simulation data via the RISM integral equation. This $c(r)$ ensures that the site-site correlation function given by the RISM equation is exact, and thus provides a basis for critically examining the usual closure for the RISM equation. As an example of an improved closure we present the analytic solution of the RISM integral equation with a Yukawa closure for $c(r)$.

1. INTRODUCTION

In a recent paper by Morriss et al. [1], the solution of the reference interaction site model (RISM) equation [2] was presented for symmetric diatomic molecules consisting of two fused hard spheres of diameter $\sigma$. The scalar RISM equation for this fluid is given by

$$[1 + \omega(k)]^{-1} - 2\rho^* \epsilon(k) [1 + \omega(k) + 2\rho^* h(k)] = 1,$$

(1.1)

where $\rho^*$ is the number density of molecules and $\omega(k)$ (the Fourier transform of the intramolecular correlation function) is given by

$$\omega(k) = \frac{\sin kl}{kl}. \tag{1.2}$$

Here $l$ is the distance between the centres of the two fused hard spheres; $\epsilon(k)$ and $h(k)$ are the Fourier transforms of the intramolecular site-site direct and total correlation functions respectively. The RISM theory consists of the RISM Ornstein–Zernike (OZ) equation (1.1), combined with the exact hard core condition

$$h(r) = -1 \quad r < \sigma \tag{1.3}$$

and the approximate closure

$$c(r) = 0 \quad r > \sigma. \tag{1.4}$$
The method of solution given by Morriss et al. [1, 6] involves a generalization of the Weiner–Hopf factorization technique developed by Baxter [3] for atomic fluids under the assumption of a finite ranged direct correlation function. The method of Morriss et al. [1] yields a formally exact solution for the RISM approximation involving an infinite sum of terms in the factored Baxter equations. In obtaining numerical solutions, Morriss and Smith [4] truncated this infinite series. This is to be contrasted with the numerical technique developed by Lowden and Chandler [5], which is based on a variational principle. This form of the variational principle, which simplifies considerably the numerical procedure required to solve the RISM OZ equation, is applicable only for the approximate closure (1.4). In general, close agreement was found between the results of Morriss and Smith [4] and those of Lowden and Chandler [5]. The agreement between the RISM results and Monte Carlo (MC) calculations [4, 7] for h(r) is known to be qualitatively good. Quantitatively, however, the agreement between RISM and MC results is significantly less good than that between the Percus–Yevick (PY) approximation for hard spheres and corresponding MC data. This inaccuracy of RISM can be thought of as an inaccuracy in the short range part of h(r).

Additional evidence for the inadequacy of the closure (1.4) is provided by the observation that the angular correlation parameter $G_a$ (defined in [8]) is precisely zero for any symmetric linear molecule in the RISM approximation (Chandler [9]; for a derivation of this result see Sullivan and Gray [10]). In deriving this result [10] it is clear that $G_a$ is zero not only for the usual closure (1.4) but in fact for any closure to the RISM OZ equation which ensures that

$$c_{\alpha\beta}(k) \sim c^{(0)} + c^{(2)} k^2 + c^{(4)} k^4 + \ldots, \quad k \rightarrow 0,$$

(1.5)

where $c_{\alpha\beta}(k)$ is the Fourier transform of the site–site direct correlation function between site $\alpha$ in one molecule and site $\beta$ in another. Hence, $G_a$ for a symmetric linear molecule can be made non-zero only by the addition to $c_{\alpha\beta}(r)$ of a part sufficiently long ranged to ensure that (1.5) is no longer satisfied. A related problem with the RISM theory arises in applications involving charged hard molecules where it has been shown that if $c_{\alpha\beta}(r)$ is assumed to have the asymptotic form of the Coulomb potential then the dielectric constant is simply the ideal gas result [10, 11]. This inaccuracy in RISM can be thus regarded as an error in the long range part of $h_{\alpha\beta}(r)$, the total correlation function in a general RISM problem between sites $\alpha$ and $\beta$.

It is clear, then, from the above discussion, that there are errors in both the short range and long range parts of $h_{\alpha\beta}(r)$, and that these errors are attributable to the approximate closure (1.4). Thus it is of interest to evaluate critically the appropriateness of the closure (1.4) by examining exact site–site direct correlation functions which can be derived from MC values for $h_{\alpha\beta}(r)$. In § 2 we present exact site–site correlation functions for symmetric hard diatomics. Examination of these exact c(r)s then suggests functional forms for c(r) which may lead to an improvement over the usual closure (1.4). The simplest such improvement—i.e., the assumption of a Yukawa form for c(r), $r > \sigma$—is then examined in a detailed way in § 3, where the RISM OZ equation with this closure is solved exactly. The method used is a generalization of that used in [1]. In § 4 we discuss future applications of this analysis.
2. Estimates of the exact closure to the RISM OZ equation

Given the 'exact' site-site correlation function $h(r)$ from MC simulation, it is possible to determine the exact site-site direct correlation function $c_{E}(r)$, which when used in the RISM OZ equation (1.1) yields exact $h(r)$s. This is obtained by treating (1.1) as a definition of $c(r)$ [7]. Equation (1.1) may be rewritten as

$$\hat{c}(k) = \frac{\hat{h}(k)}{[1 + \hat{\omega}(k)][1 + \hat{\omega}(k) + 2\rho \hat{h}(k)]},$$

where $\hat{h}(k)$ and $\hat{\omega}(k)$ are given explicitly in terms of $h(r)$ and $c(r)$ as

$$\hat{h}(k) = \frac{4\pi}{k} \int_{0}^{\infty} dr \ r h(r) \sin kr,$$

and

$$\hat{\omega}(k) = \frac{4\pi}{k} \int_{0}^{\infty} dr \ c(r) \sin kr.$$

The MC simulation results give $g(r)$ on the range $0 < r < 3\sigma$, from which $\hat{h}(k)$ was calculated numerically on a grid of 3000 points using Lado’s method [12], noting that for $k = 0$,

$$\hat{h}(0) = 4\pi \int_{0}^{\infty} dr \ r^2 h(r).$$

Using (2.1), $\hat{c}(k)$ can be calculated on the same grid as $\hat{h}(k)$, and $c(r)$ obtained by Fourier inversion via

$$c(r) = \frac{1}{2\pi \sigma^2} \int_{0}^{\infty} dk \ k^2 \hat{c}(k) \frac{\sin kr}{kr}.$$

Figure 1. The exact site-site direct correlation function $c_{E}(r)$ obtained from the RISM OZ equation using the MC $g(r)$ for $l = \sigma/3$ and $\rho = 0.3, 0.45$ and 0.5.
The ‘exact’ site–site direct correlation function \( c_E(r) \) for the symmetric diatomic with \( l = \sigma/3 \) is shown in figure 1. A small value of \( l \) was chosen so that some measure of the long range structure \( (r \geq \sigma + 2l) \) could be obtained.

Several features of \( c_E(r) \) are noteworthy. The section of \( c_E(r) \) in the range \( \sigma < r < \sigma + l \) is negative. This is in direct contrast to the exact hard sphere \( c(r) \), which is positive outside, and in the vicinity of, the hard core. For hard spheres this has been interpreted as an effective ‘caging’ of the nearest neighbours [13]. In the RISM case, however, each sphere has another sphere protruding from its side which, on average, hinders the approach of nearest neighbours. This behaviour for \( c(r) \) was not observed by Streett and Tildesley [7], who found that, at the single symmetric diatomic result reported \( (\rho^*\sigma^3 = 0.53, l = 0.4\sigma) \), \( c(r) \) was positive for \( \sigma < r < \sigma + l \). Hence a method to check our calculated site–site direct correlation functions is desirable.

Rearranging (1.1) gives

\[
\rho_\infty \frac{1}{\gamma(k)} = (1 + \omega(k))^2 \gamma(k) + 2\rho(1 + \omega(k))\gamma(k)\rho_\infty(k).
\]

(2.6)

Performing the inverse transform, equation (2.6) can be written in the form

\[
h(r) = c(r) + \text{continuous functions of } r.
\]

(2.7)

Hence the discontinuity in \( h(r) \) (or equivalently \( g(r) = h(r) + 1 \), the site–site radial distribution function) at \( r = \sigma \) must equal the discontinuity in \( c(r) \) at \( r = \sigma \). We may in fact use this as a consistency requirement that the ‘exact’ \( c_E(r) \) must satisfy. Below we tabulate for comparison the discontinuities in \( g(r) \) and \( c_E(r) \).

<table>
<thead>
<tr>
<th>( \rho^*\sigma^3 )</th>
<th>( g(\sigma^+) )</th>
<th>( c_E(\sigma^+) - c_E(\sigma^-) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td>0.688</td>
<td>0.680</td>
</tr>
<tr>
<td>0.4</td>
<td>0.885</td>
<td>0.884</td>
</tr>
<tr>
<td>0.45</td>
<td>1.053</td>
<td>1.063</td>
</tr>
<tr>
<td>0.5</td>
<td>1.252</td>
<td>1.320</td>
</tr>
</tbody>
</table>

Another test of the quality of the computed \( c_E(r) \) comes from the work of Ladanyi and Chandler [14] who showed that \( c(r) \) rigorously has a cusp at \( \sigma - l \) and could be expected to have another cusp at \( \sigma + l \). The cusp at \( \sigma - l \) is clearly seen in figure 1, and there is strong evidence in figure 2 of a cusp at \( \sigma + l \). This, combined with the agreement between the discontinuities in \( g(r) \) and \( c(r) \) at \( r = \sigma \), gives us reason to be confident in our computed \( c_E(r) \), at least on the range \( 0 < r < 2\sigma \).

These computed \( c_E(r) \)s are suggestive of ways in which the closure (1.4) can be improved. From the discussion in § 1, there are clearly two regions over which \( h(r) \) needs to be improved—namely, the short range part and the long range part—and as pointed out there, the latter can only be improved by the addition of a long ranged correction to \( c(r) \). It therefore seems likely, that the short range deficiencies of \( h(r) \) can be corrected by the addition of a short range part to \( c(r) \). The form of this short range correction should be suggested by the form of \( c_E(r) \) on the range \( \sigma < r < \sigma + l \). Høye and Stell [15] have suggested that a suitable short range correction to \( c(r) \) can be obtained by assuming \( c(r) \) has a Yukawa form outside the hard core, i.e.

\[
c(r) = \frac{A^* \exp \left[ -z^*(r-\sigma) \right]}{r} \quad r > \sigma.
\]

(2.8)
One or both of the parameters $A^*$ and $z^*$ can be determined from such constraints as thermodynamic consistency with a good, semiempirical equation of state (such as that derived by Tildesley and Streett [16]) and/or MC values of $g(\sigma^+)$. This suggestion is based on the successful approach in simple fluids known as the generalized mean spherical approximation (GMSA) [17], which consists of adding one or more Yukawa terms to the form of $c(r)$ expected on the basis of the Mean Spherical Approximation (MSA) and determining the Yukawa parameters through thermodynamic consistency criteria. Of particular interest to the hard diatomic problem being considered here, is the success of the GMSA for hard spheres [18].

It can be seen from figures 1 and 2 that a Yukawa term such as that in (2.8) could be used as an ansatz for $c(r)$ on the range $\sigma < r < \sigma + l$ when $A^*$ is negative (in contrast to the GMSA for hard spheres [18]). The adequacy of this short range correction to $c(r)$ is difficult to assess a priori, and from figures 1 and 2 will depend on how large a contribution the positive part of $c(r)$ (on the range $\sigma + l \leq r \leq 2.5\sigma$) makes to the short range behaviour of $h(r)$. Clearly if this contribution is significant then a more appropriate form of $c(r)$—such as an oscillatory form—may be required.

In the following section we present the formally exact solution of the RISM OZ equation with closures (1.3) and (2.8). We emphasize that, in the absence
of a variational principle for this closure (2.8) of the type derived by Chandler and Andersen [2], the analysis presented in the following section represents the only feasible method for solution applicable to the GMSA problem.

3. METHOD OF SOLUTION

Before proceeding to the solution of the RISM OZ equation with Yukawa closure, it is convenient to rewrite the defining equations for the problem in terms of dimensionless quantities. The distances are scaled with respect to the hard core diameter \( \sigma \) — i.e., \( r = \alpha x \) where \( x \) is now dimensionless. It is easily seen that if \( f(r) \) is any function of \( r \) then its Fourier transform satisfies

\[
f(k') = \sigma^3 f(k),
\]

where \( k = k' \sigma \). Thus the RISM OZ equation can be written as

\[
[(1 + \omega(k))^{-1} - 2\rho c(k)] [1 + \omega(k) + 2\rho \bar{h}(k)] = 1,
\]

where \( \rho = \rho^* \sigma^3 \) is the dimensionless density and \( k \) is now dimensionless. In terms of dimensionless quantities, the closure relations to the RISM OZ equation are given by

\[
h(x) = \begin{cases} 
1 & x < 1, \\
-1 & x > 1,
\end{cases}
\]

\[
e(x) = \frac{A \exp \left[ -z(x-1) \right]}{x}, \quad x > 1,
\]

where \( A = A^*/\sigma \) and \( z = z^*/\sigma \). Equation (3.1) may be written as

\[
\tilde{A}(k) [1 + \omega(k) + 2\rho \bar{h}(k)] = 1,
\]

where \( \tilde{A}(k) \) is given by

\[
\tilde{A}(k) = (1 + \omega(k))^{-1} - 2\rho \tilde{c}_0(k) - \frac{8\pi \rho A e^z}{k^2 + z^2}.
\]

The function \( \tilde{c}_0(k) \) is the Fourier transform of the finite ranged function

\[
\tilde{c}_0(x) = e(x) - \frac{A \exp \left[ -z(x-1) \right]}{x}.
\]

Using the Weiner–Hopf method (see [1] for details) (3.5) may be factorized to give

\[
\tilde{A}(k) = \tilde{Q}(k) \tilde{Q}(-k),
\]

where \( \tilde{Q}(k) \) is the Fourier transform of a real function \( Q(r) \) defined by

\[
2\pi \rho Q(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dk \exp (-ikx) [1 - \tilde{Q}(k)].
\]

For \( x < 0 \), (3.8) can be closed in the upper half plane, and for \( x > 1 \), closed in the lower half plane to give

\[
2\pi \rho Q(x) = \begin{cases} 
0 & x < 0, \\
\sum_{n=-\infty}^{\infty} \zeta_n \exp (-i\lambda_n x) & x > 1,
\end{cases}
\]

\[

\]
where

\[ \zeta_n = i[\dot{\omega}(\lambda_n)\dot{Q}(\lambda_n)] \quad n \neq 0, \]  
\[ \zeta_0 = -6\eta\mu_0 = \frac{12\eta A\epsilon}{z\dot{Q}(iz)}, \]
\[ \lambda_0 = -iz, \]
\[ \eta = \frac{\pi}{3} \rho. \]

As in [1], for \( n \neq 0 \), the parameters \( \lambda_n \) are complex roots of the equation

\[ 1 + \frac{\sin \lambda_n l}{\lambda_n l} = 0. \]  

Defining

\[ \zeta_n^0 = \zeta_n - 6\eta\mu_n \]  
and

\[ 2\pi\rho \dot{Q}_0(x) = 2\pi\rho \dot{Q}(x) - \sum_{n=-\infty}^{\infty} \zeta_n \exp(-i\lambda_n x) \]

equation (3.8) can be inverse transformed to give

\[ \dot{Q}(k) = 1 + \sum_{n=-\infty}^{\infty} \frac{\zeta_n}{i(k-\lambda_n)} - 6\eta \int_0^1 dx \dot{Q}_0(x) \exp(ikx). \]

Combining (3.4), (3.7) and (3.17) gives

\[ \dot{Q}(k)[1 + \dot{\omega}(k) + 2\rho\dot{h}(k)] = [\dot{Q}(-k)]^{-1}, \]

which on Fourier inversion yields (see [1] for details)

\[ Q_0(x) + \frac{1}{2l} \int_0^l dt \dot{Q}_0(x-t) \]
\[ = 2J(x) - 12\eta \int_0^1 dt \dot{Q}_0(t)J(|x-t|) - 2 \sum_{n=-\infty}^{\infty} \zeta_n \int_0^x dt \exp(-i\lambda_n t) \]
\[ \times J(|x-t|) - \mu_0 \exp(-i\lambda_0 x) \left( 1 + \frac{\sin \lambda_0 l}{\lambda_0 l} - \frac{\theta(l-x)}{2l} \right) \]
\[ \times \sum_{n=-\infty}^{\infty} \frac{\mu_n}{i\lambda_n} \left( 1 - \exp[i\lambda_n(l-x)] \right), \]

where

\[ J(x) = \int_x^\infty dt \theta(t) = \int_x^\infty dt (g(t) - 1) \]

and \( \theta(x) \) is the Heaviside step function—i.e.

\[ \theta(x) = \begin{cases} 0 & x < 1 \\ 1 & x > 1 \end{cases} \]
Differentiating equation (3.14) with respect to \( x \) we obtain

\[
Q'(x) + \frac{1}{2l} \{Q_0(x + l) - Q_0(x - l)\} = 2x(1 - g(x)) - 12\eta \int_0^\infty \frac{dt}{t} Q_0(t)(x-t)(1-g(|x-t|))
\]

\[
-2 \sum_{n=\infty}^{\infty} \zeta_n \int_0^\infty dt \exp (-i\lambda_n t)(x-t)(1-g(|x-t|))
\]

\[
+i\lambda_0 \mu_0 \exp (-i\lambda_0 x) \times \left( 1 + \frac{\sin \lambda_0 l}{\lambda_0 l} \right)
\]

\[-\frac{\theta(l-x)}{2l} \sum_{n=\infty}^{\infty} \mu_n \exp [-i\lambda_n (x-1)]. \quad (3.20)
\]

This equation is central to the solution as, using the hard core condition \( g(x) = 0 \) for \( x < 1 \) gives

\[
Q'(x) + \frac{1}{2l} \{Q_0(x + l) - Q_0(x - l)\} = ax + b + \sum_{n=\infty}^{\infty} i\lambda_n (e_n \zeta_n + d_n \mu_n) \exp (-i\lambda_n x)
\]

\[-\theta(l-x) \sum_{n=\infty}^{\infty} i\lambda_n f_n \mu_n \exp (-i\lambda_n x), \quad (3.21)
\]

where

\[
a = 2 - 12\eta \int_0^\infty \frac{dt}{t} Q_0(t) - 2 \sum_{n=\infty}^{\infty} \frac{\zeta_n}{i\lambda_n}, \quad (3.22)
\]

\[
b = 12\eta \int_0^\infty \frac{dt}{t} tQ_0(t) - 2 \sum_{n=\infty}^{\infty} \frac{\zeta_n}{\lambda_n^2}, \quad (3.23)
\]

\[
e_n = \frac{-2\tilde{G}(i\lambda_n)}{i\lambda_n} (1 - \delta_{n0}), \quad (3.24)
\]

\[
d_n = -12\eta \frac{\tilde{G}(i\lambda_n)}{i\lambda_n} n \neq 0, \quad (3.25)
\]

\[
d_0 = 1 + \frac{\sin \lambda_0 l}{\lambda_0 l} - 12\eta \frac{\tilde{G}(i\lambda_0)}{i\lambda_0}, \quad (3.26)
\]

\[
f_n = \frac{\exp (i\lambda_n l)}{2i\lambda_n l}, \quad (3.27)
\]

and \( \tilde{G}(s) \) denotes the Laplace transform of \( xg(x) \)

\[
\tilde{G}(s) = \int_0^\infty dx \exp (-sx)xg(x). \quad (3.28)
\]

Two independent sets of parameters—the \( \tilde{G}(i\lambda_n) \) and \( \zeta_n \)—have so far been generated by the solution. One set of equations relating these parameters is given by equations (3.10) and (3.11). A second independent relation between
RISM equation for diatomics

\[ \mathcal{G}(i\lambda_n) \] and \( \zeta_n \) can be obtained by considering equation (3.20) for \( x > 1 \). That is,

\[
2xg(x) - 12\eta \int_0^1 dt \mathcal{Q}_0(t)(x-t)g(x-t) - 2 \sum_{n=0}^{\infty} \zeta_n \int_0^x dt \exp(-i\lambda_n t) \times (x-t)g(x-t) = \frac{1}{2t} \mathcal{Q}_0(x-l) + ax + b
\]

\[ + \sum_{n= - \infty}^{\infty} i\lambda_n (e_n \xi_n^0 + d_n \mu_n) \exp(-i\lambda_n x). \quad (3.29) \]

Multiplying both sides by \( \exp(-sx) \) and integrating from 1 to \( \infty \) gives

\[
2\mathcal{G}(s)\mathcal{Q}(is) = \frac{1}{2l} \int_1^{1+l} dx \exp(-sx)\mathcal{Q}_0(x-l) + \int_1^\infty dx \exp(-sx)
\times \left\{ ax + b + \sum_{n= - \infty}^{\infty} i\lambda_n (e_n \xi_n^0 + d_n \mu_n) \exp(-i\lambda_n x) \right\}. \quad (3.30) \]

Using (3.7) this becomes

\[
\mathcal{G}(i\lambda_m) = \frac{\xi_m \mathcal{Q}'(\lambda_m)}{2i} \left[ \frac{1}{2l} \int_1^{1+l} dx \exp(-sx)\mathcal{Q}_0(x-l) + \int_1^\infty dx \exp(-sx)
\times \left\{ ax + b + \sum_{n= - \infty}^{\infty} i\lambda_n (e_n \xi_n^0 + d_n \mu_n) \exp(-i\lambda_n x) \right\} \right. \quad (3.31) \]

4. Discussion

Algebraically, the simplest case to consider is when \( l = 1 \). (For other values of \( l \), see [1].) This corresponds to a dumb-bell consisting of two hard spheres which just touch one another. For this case equation (3.20) becomes

\[
\mathcal{Q}_0(x) = ax + b + \sum_{n= - \infty}^{\infty} (e_n \xi_n^0 + (d_n - f_n) \mu_n) \exp(-i\lambda_n x) \quad (4.1) \]

so that \( \mathcal{Q}_0(x) \) is given by

\[
\mathcal{Q}_0(x) = \frac{1}{2}(a(x^2 - 1) + b(x - 1)) = \left( e_n \xi_n^0 + (d_n - f_n) \mu_n \right) \exp(-i\lambda_n) - \exp(-i\lambda_n x). \quad (4.2) \]

Substituting this equation into (3.31) yields

\[
\mathcal{G}(i\lambda_m) = \frac{\xi_m \mathcal{Q}'(\lambda_m)}{2i} \left\{ aE_m + bF_m + \sum_{n= - \infty}^{\infty} (e_n \xi_n^0 + d_n \mu_n) I_{m,n}
+ \sum_{n= - \infty}^{\infty} (e_n \xi_n^0 + (d_n - f_n) \mu_n) J_{m,n} \right\}, \quad (4.3) \]

where

\[
E_m = \left[ \frac{3}{4} \cdot \frac{1}{i\lambda_m} + \frac{1}{\lambda_m^2} - \frac{1}{2i\lambda_m^3} \right] + \frac{\exp(-i\lambda_m)}{2\lambda_m^2} \left( 1 + \frac{1}{i\lambda_m} \right) \exp(-i\lambda_m), \quad (4.4) \]

\[
F_m = \left[ \frac{1}{2i\lambda_m} - \frac{1}{2\lambda_m^2} \right] \exp(-i\lambda_m), \quad (4.5) \]

\[
I_{m,n} = \frac{\lambda_n \exp[-i(\lambda_n + \lambda_m)]}{\lambda_n + \lambda_m}, \quad (4.6) \]
The parameters $\tilde{G}(i\lambda_n)$ are linearly related to the parameters $e_n$ and $d_n$ via (3.20) and (3.21). Therefore, (4.3) can be used to eliminate these parameters.

The solution obtained thus far is a function of the parameters $z$, $A$, $\zeta_n$ and $\mu_n$. As our intention is to improve the consistency of the RISM theory developed previously [1], it seems appropriate to use the parameters $\zeta_n$ and $\mu_n$ from the solution of the RISM OZ equation with closure (1.4), although this is only one of a number of ways that the analysis of $\rho_z$ can be implemented. In particular, at high density, the results of Morriss and Smith [4] show that the theory is relatively insensitive to the parameters $\zeta_n$ and $\mu_n$ and that these terms can be dropped without any significant loss of accuracy in $h(r)$. Thus in this regime, at least, the analysis in § 3 can be simplified dramatically by setting $\zeta_n = \mu_n = 0$ for all $n$ except $n = 0$, which corresponds to the retention of the Yukawa term in $c(r)$. In this case we expect the analysis to yield a fully analytic theory of similar structure to that developed by Cummings and Smith [19, 20] for the case of hard spheres with Yukawa closure.

In the GMSA for hard spheres two conditions are needed to set the two parameters $z$ and $A$. These are chosen to ensure that the virial and compressibility pressures are internally consistent and also agree with the Carnahan–Starling equation of state (see Henderson and Blum [18]). It is not possible to follow a completely analogous procedure in the RISM case, as there is no route to the virial pressure from the site-site correlation functions only [21]. There does exist a semiempirical equation of state for hard symmetric diatomics [16] so that at least by requiring that the compressibility be consistent with this, one of the Yukawa parameters could be assigned in the spirit of the GMSA.

Tildesley [22] has suggested that the two parameters be chosen to ensure that the value of $g(x)$ at contact and cusp equal their respective MC values. Consistency could then be assessed by comparing $g(x)$ over the rest of the range and also by comparing the compressibility with the MC result.

We are presently investigating a variety of assignment schemes for the parameters $z$ and $A$. It is hoped that by a judicious choice of what should and should not be retained of the $A = 0$ (RISM) factorization, a semianalytic theory which retains much of the simplifying features which follow from the application of Baxter’s factorization to the simple fluid case [19, 20], can be obtained.

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