Evaluation of the SSC/LHNC, SSCF and PY approximations for short ranged, anisotropic potentials

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Three approximations for the orientational correlation function of molecular fluids—the single super chain/linearized hypernetted chain (SSC/LHNC), single super chain $f$-expansion (SSCF) and Percus-Yevick (PY) approximation—are evaluated in the dense liquid state for a fluid interacting with short ranged anisotropic interactions. These interactions are prototypical of the forces that determine the non-spherical shape of symmetric linear molecules. We find that SSC/LHNC is very poor, failing to predict many of the structural features present in the Monte Carlo (MC) simulation results. The PY and SSCF approximations produce much better results; however, neither approximation is completely satisfactory.

1. INTRODUCTION

This paper is the first in a series of papers whose ultimate aim is the development of accurate integral equation approximations for molecular fluids. We have as our goal approximations that do justice both to the long ranged electrostatic and the short ranged anisotropic overlap forces that characterize molecular fluids. (For a review of molecular fluids, their interaction potentials and the approximate techniques available for calculating their structural and thermodynamic properties, see [1].)

In recent years, Wertheim [2] has developed an integral equation approximation for determining the structure and thermodynamics of polarizable fluids called the single super chain (SSC) approximation. For non-polarizable fluids,

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as pointed out by Smith and Henderson [3] and elaborated by Henderson and Gray [4], one realization of SSC, discussed in greater detail below, is equivalent to the linearized hypernetted chain (LHNC) approximation of Patey [5-7]. (Patey introduced LHNC for non-polarizable fluids interacting via potentials whose anisotropic parts consist only of electrostatic multipoles; for such fluids, and also for more general anisotropic perturbations, a simple derivation of SSC has been given by Henderson and Gray [4].)

We restrict our attention to non-polarizable fluids in the remainder of this paper. In discussing SSC, one begins by dividing the interaction potential $u(12)$ (where $i$ symbolizes both the position $r_i$ and the orientation $\omega_i$ of molecule $i$) into a reference part, $u_{\text{ref}}(12)$, and a perturbation, $u_{\text{pert}}(12)$, viz.

$$u(12) = u_{\text{ref}}(12) + u_{\text{pert}}(12).$$

(1.1)

At this point, the division of $u(12)$ into reference and perturbation parts is arbitrary. The key quantity of theoretical interest we wish to calculate is the molecular total correlation function $h(12)$ which is related to the pair correlation function $g(12)$ by

$$h(12) = g(12) - 1.$$  

(1.2)

The function $g(12)$ is proportional to the probability density of finding two distinct molecules in orientations and positions 1 and 2. Associated with $h(12)$ is the molecular direct correlation function $c(12)$ defined via the Ornstein-Zernike (OZ) equation, given by

$$h(12) = c(12) + \rho \int d3 c(13) h(32),$$

where $\rho$ is the number density of molecules. The notation $\int d3$ symbolizes $\int dr_2 d\omega_2/\Omega$, where $\Omega = \int d\omega_i = 4\pi$ for linear molecules and $8\pi^2$ for non-linear molecules. The general SSC closure is written in terms of $h(12)$ and $c(12)$ by decomposing these functions into two parts, viz.

$$h(12) = h_{\text{ref}}(12) + h_{\text{pert}}(12),$$

(1.4 a)

$$c(12) = c_{\text{ref}}(12) + c_{\text{pert}}(12).$$

(1.4 b)

The functions $h_{\text{ref}}(12)$ and $c_{\text{ref}}(12)$ are the total and direct correlation functions for a fluid interacting via the potential $u_{\text{ref}}(12)$ alone; $h_{\text{pert}}(12)$ and $c_{\text{pert}}(12)$ are then defined by (1.4). The SSC approximation for a fluid with interaction potential (1.1) is given by the exact OZ equation (1.3) supplemented with the approximate closure

$$c_{\text{pert}}(12) = -\beta g_{\text{ref}}(12) u_{\text{pert}}(12) + h_{\text{ref}}(12)[h_{\text{pert}}(12) - c_{\text{pert}}(12)],$$

(1.5)

where $\beta = (k_B T)^{-1}$ with $k_B$ Boltzmann's constant and $T$ the absolute temperature.

It should be emphasized at this point that the SSC approximation (1.5) is completely general: in particular, $u_{\text{ref}}(12)$ (and consequently $h_{\text{ref}}(12)$ and $c_{\text{ref}}(12)$) need not be spherically symmetric. For multipolar fluids interacting via a potential of the form

$$u(12) = u_0(r_{12}) + u_{\text{mult}}(12),$$

(1.6)

where $u_0(r_{12})$ is the unweighted angular average of $u(12)$,

$$u_0(r_{12}) = \langle u(12) \rangle_{u_{\text{ref}}},$$

(1.7)
and where $u_{\text{mult}}(12)$ consists only of electrostatic multipolar terms (dipole-dipole, dipole–quadrupole, etc.), then clearly one choice for $u_{\text{ref}}(12)$ and $u_{\text{pert}}(12)$ is the identification

$$u_{\text{ref}}(12) = u_0(r_{12}), \quad u_{\text{pert}}(12) = u_{\text{mult}}(12). \quad (1.8)$$

This choice of $u_{\text{ref}}(12)$ yields the LHNC approximation of Patey [5–7] and Henderson and Gray [4]. For multipolar fluids, one consequence of this choice is that

$$\langle h_{\text{pert}}(12) \rangle_{\omega_{120}} = 0, \quad \langle h(12) \rangle_{\omega_{120}} = h_{\text{ref}}(r_{12}). \quad (1.9)$$

This follows directly from the fact that multipolar potentials satisfy the strong angular condition

$$\langle u_{\text{mult}}(12) \rangle_{\omega_1} = \langle u_{\text{mult}}(12) \rangle_{\omega_2} = 0. \quad (1.10)$$

Hence an immediate test of the likely applicability of SSC to multipolar fluids with the identification (1.8) can be made by asking to what extent (1.9) is satisfied. For example, for dipolar hard spheres (where $u_{\text{ref}}(r_{12})$ is just the hard sphere potential) (1.9) is known to be quite accurate at high density; hence SSC/LHNC is not in any obvious error. In fact, as demonstrated by Patey [5–7] and by Henderson and Gray [4], SSC/LHNC is quite accurate for hard spheres or Lennard-Jones particles with low to moderate dipole and/or quadrupole moments. From the viewpoint of the various derivations [2, 4, 5], this success can be understood by noting that $u_{\text{pert}}(12)$ is long ranged and slowly varying compared to $u_{\text{ref}}(12)$; hence, the perturbative expansion implicit in these approaches is justified.

However, it is clearly of interest to be able to treat via an integral equation approximation not only the long ranged, slowly varying multipolar part of the pair potential, but also the anisotropic overlap which gives rise to the 'shape' of the molecule. This latter contribution to $u(12)$ is typically short ranged and rapidly varying. For the sake of discussion, we decompose $u(12)$ into constituent parts as follows [8]:

$$u(12) = u_0(r_{12}) + u_{\text{shape}}(12) + u_{\text{mult}}(12). \quad (1.11)$$

Here $u_0(r_{12})$ is defined in (1.7) and includes, for example, the spherically symmetric part of the overlap forces and contributions due to dispersion forces. Clearly, one method of implementing SSC for this potential is the identification

$$u_{\text{ref}}(12) = u_0(r_{12}) + u_{\text{shape}}(12), \quad u_{\text{pert}}(12) = u_{\text{mult}}(12). \quad (1.12)$$

However, this requires knowledge of $h_{\text{ref}}(12)$ and $c_{\text{ref}}(12)$ for the system with the non-spherical potential $u_{\text{ref}}(12)$, obtained either from computer simulation of the system or from an accurate theory such as an integral equation approximation or perturbation theory.

From the point of view of convenience in numerical computation, it would be particularly advantageous if the identification

$$u_{\text{ref}}(12) = u_0(r_{12}), \quad u_{\text{pert}}(12) = u_{\text{shape}}(12) + u_{\text{mult}}(12) \quad (1.13)$$
proved to be accurate. If this were the case, only properties of a spherically symmetric reference system would be required as input to the SSC formalism. The use of a spherically symmetric \( u_{ref}(12) \) is clearly in the spirit of LHNC; hence we refer to the identification (1.13) as SSC/LHNC.

One of the aims of this paper is to evaluate whether the identification (1.13) is at all tenable. To do this, we consider a prototypical model for \( u^{\text{shape}}(12) \) referred to as the ‘delta-model’ potential, and since our intention is to evaluate (1.13) mainly for \( u^{\text{shape}}(12) \) we consider a model for which \( u^{\text{mult}}(12) = 0 \). Specifically, the delta model (DM) potential is given by

\[
\begin{align*}
    u(12) &= u_0(r_{12}) + u^{\text{shape}}(12), \\
    u_0(r_{12}) &= 4\varepsilon \left[ \left( \frac{\sigma}{r_{12}} \right)^{12} - \left( \frac{\sigma}{r_{12}} \right)^{6} \right], \\
    u^{\text{shape}}(12) &= 4\varepsilon \delta \left( \frac{\sigma}{r_{12}} \right)^{12} (3 \cos^2 \theta_1 + 3 \cos^2 \theta_3 - 2), \\
    &= 4\varepsilon \delta \left( \frac{\sigma}{r_{12}} \right)^{12} 2[P_2(\cos \theta_1) + P_2(\cos \theta_3)],
\end{align*}
\]

where \( \sigma \) is the diameter and \( \varepsilon \) is the well depth of the isotropic Lennard-Jones (LJ) potential \( u_0(r_{12}) \), \( \theta_1 \) and \( \theta_3 \) are the polar angles made by the axes of symmetry of molecules 1 and 2 with the vector \( r_{12} \) joining the centres of the molecules, and \( P_2 \) is the Legendre polynomial of order 2. This model has a long history and is discussed in detail in Chapter 2 of [1]. The liquid state properties of this model have been investigated by Gray and Gubbins and coworkers [9]. For positive values of \( \delta \), (1.14c) is an approximation to the overlap potential for prolate (rod-shaped) molecules; negative \( \delta \) characterizes oblate (plate-shaped) molecules. We must have \(-\frac{1}{4} < \delta < \frac{1}{2}\) to ensure that at small separations the total potential is repulsive for all orientations. In this paper, we consider only \( \delta > 0 \).

In § 2, we briefly outline the derivation of a new approximation for molecular fluids called the single super chain \( f \)-expansion (SSCF) approximation. It is an approximation which has greater promise for dealing accurately with the rapidly-varying anisotropic interactions that characterize \( u^{\text{shape}}(12) \) than the usual SSC. Both SSC and SSCF can be regarded as different linearizations of the hypernetted chain (HNC) approximation, an approximation which in the theory of simple fluids is known to be quite accurate for long ranged electrostatic interactions [10]. For short ranged, repulsive interactions, the Percus–Yevick (PY) approximation is generally regarded as more accurate than HNC [10]. Since \( u^{\text{shape}}(12) \) and \( u^{\text{mult}}(12) \) are the anisotropic generalizations of the short ranged repulsive and long ranged electrostatic interactions respectively found in simple fluids, it is natural to ask whether PY is superior to both SSC and SSCF in dealing with \( u^{\text{shape}}(12) \). Consequently, in § 4, we evaluate SSC/LHNC (SSC with the identification (1.13)), SSCF and PY for the DM fluid, having given details of their implementation in § 3. We conclude that SSC is very poor and that SSCF is reasonably good. The PY results are also quite good, and on balance we conclude that it is better than SSCF. In § 5, we summarize our findings and discuss future work.

Before continuing, however, it is worthwhile to consider the reasons for examining the fluid interacting via the DM potential (1.14), since clearly the
DM potential is a much simplified form of the shape interaction between linear symmetric molecules (in fact, for such molecules it represents the leading order terms in $u_{\text{shape}}(12)$). In general, one expects in principle to require an infinite number of spherical harmonics in $u_{\text{shape}}(12)$ (and in practice to require substantially more than those retained in (1.14)) to mimic faithfully the overlap interaction between two linear molecules. The same comment can be made in reference to the spherical harmonic expansion for the electrostatic interactions $u_{\text{mult}}(12)$ between the charge distributions in the two molecules, yet it is only in recent years that terms in $u_{\text{mult}}(12)$ beyond the leading one—the dipole–dipole term—have been considered. Our belief is that the use of a simplified shape model provides considerable insight into the adequacy of the approximations being evaluated; in particular, the linearity of the approximations such as SSC is made manifest when the potential contains only a small set of spherical harmonics. We return to this point in the discussion of our results in § 4.

2. THE SSCF APPROXIMATION

The derivation of the SSCF closure given here is based on a linearization of the HNC closure; alternative derivations along graph theoretical lines [10, 11] are given in Appendix A. Usually, $u_{\text{shape}}(12)$ is purely repulsive and large over a short range; consequently, $u_{\text{shape}}(12)$ can be comparable in magnitude to the repulsive part of $u_0(r_{12})$. For example, for $\delta = 0.25$ and $\theta_1 = \theta_2 = 0$, the DM potential at $r = 2^{1/6} \sigma$, the minimum of the LJ potential, has the value $+\varepsilon$, and so is of the same magnitude as $u_0(r_{12})$. Thus, it is difficult to regard $u_{\text{shape}}(12)$ as a small perturbation on $u_0(r_{12})$.

However, we can regard the Mayer $f$-function $f(12)$ for the DM potential to be a small perturbation on the Mayer $f$-function for a suitably defined reference system. We begin by writing (1.1) in terms of the Mayer $f$-functions as follows:

$$f(12) = \exp [-\beta u(12)] - 1 = f_{\text{ref}}(12) + [1 + f_{\text{ref}}(12)] f_{\text{pert}}(12).$$

In (2.1),

$$f_{\text{ref}}(12) = \exp [-\beta u_{\text{ref}}(12)] - 1, \quad f_{\text{pert}}(12) = \exp [-\beta u_{\text{pert}}(12)] - 1$$

are the (as yet arbitrary) reference and perturbation Mayer $f$-functions respectively. A specific choice for $f_{\text{ref}}(12)$ will be considered at the end of this section.

The HNC closure is given by

$$c(12) = -\beta u(12) + h(12) - \log [1 + h(12)],$$

$$= \log [1 + f(12)] + h(12) - \log [1 + h(12)].$$

We define $c_{\text{ref}}(12)$ and $h_{\text{ref}}(12)$, the parts of $c(12)$ and $h(12)$ induced by the perturbation $f_{\text{pert}}(12)$, by writing

$$c(12) = c_{\text{ref}}(12) + c_{\text{pert}}(12),$$

$$h(12) = h_{\text{ref}}(12) + h_{\text{pert}}(12),$$

where $h_{\text{ref}}(12)$ and $c_{\text{ref}}(12)$ are the total and direct correlation functions respectively for a fluid interacting via the potential $u_{\text{ref}}(12)$ defined in (2.2).
Substituting (2.1) and (2.5) into (2.4) we have

\[ c_{\text{ref}}(12) + c_{\text{pert}}(12) = \log \left[ \frac{1 + f_{\text{ref}}(12)}{1 + f_{\text{pert}}(12)} \right] \]

\[ + h_{\text{ref}}(12) + h_{\text{pert}}(12) \]

\[ - \log \left\{ \left[ 1 + h_{\text{ref}}(12) \right] \left[ 1 + h_{\text{pert}}(12) \right] \right\}, \tag{2.6} \]

where \( g_{\text{ref}}(12) = 1 + h_{\text{ref}}(12) \) is the reference system pair correlation function. The reference system quantities are assumed to be related by

\[ c_{\text{ref}}(12) = \log \left[ 1 + f_{\text{ref}}(12) \right] + h_{\text{ref}}(12) - \log \left[ 1 + h_{\text{ref}}(12) \right], \tag{2.7} \]

which would be the case if \( c_{\text{ref}}(12) \) and \( h_{\text{ref}}(12) \) were calculated using the HNC approximation. Using (2.7), (2.6) becomes

\[ c_{\text{pert}}(12) = \log \left[ 1 + f_{\text{pert}}(12) \right] + h_{\text{pert}}(12) - \log \left[ 1 + h_{\text{pert}}(12) \right]. \tag{2.8} \]

Expanding the logarithms to leading order, under the assumption that \( f_{\text{pert}}(12) \) and \( h_{\text{pert}}(12)/g_{\text{ref}}(12) \) are small, we obtain after rearrangement the SSCF closure:

\[ c_{\text{pert}}(12) = f_{\text{pert}}(12) g_{\text{ref}}(12) + h_{\text{pert}}(12) [ h_{\text{pert}}(12) - c_{\text{pert}}(12) ]. \tag{2.9} \]

Rather than calculate \( g_{\text{ref}}(12) \) via the HNC approximation, we assume that it is given exactly (via MC simulation, for example).

The relationship to the usual SSC closure (1.5) is clear: \( -\beta u_{\text{ref}}(12) \) in (1.5) is replaced by \( f_{\text{pert}}(12) \) in (2.9). For a given fluid interacting with potential \( u(12) \), one might choose a convenient \( u_{\text{ref}}(12) \) (for example, on the basis of access to readily available MC data or an approximate theory of demonstrated accuracy for the fluid interacting with potential \( u_{\text{ref}}(12) \)) and proceed to use either SSC (1.5) or SSCF (2.9). The choice of (1.5) or (2.9) would be governed by the relative sizes of \( u_{\text{pert}}(12)/u_{\text{ref}}(12) \) and \( f_{\text{pert}}(12)/f_{\text{ref}}(12) \), the smaller ratio (at least \textit{a priori}) indicating the favoured approximation. Note, however, that a given choice for \( u_{\text{ref}}(12) \) may lead to a very complicated \( f_{\text{ref}}(12) \) and vice versa.

In this paper, we choose \( f_{\text{ref}}(12) \) to be the spherically symmetric part of \( f(12) \); that is,

\[ f_{\text{ref}}(12) \equiv f_{s}(r_{12}) = \langle f(12) \rangle_{u_{s}(r_{12})}. \tag{2.10} \]

This is a numerically expedient choice of \( f_{\text{ref}}(12) \) in the same way that \( u_{0}(r_{12}) \) was a numerically expedient choice of \( u_{\text{ref}}(12) \) in the SSC theory. The Mayer \( f \)-function \( f_{s}(r_{12}) \) of (2.10) is related to a spherically symmetric potential \( u_{s}(r_{12}) \) given by

\[ u_{s}(r_{12}) = -k_{B} T \log \left[ 1 + f_{s}(r_{12}) \right] \tag{2.11} \]

which is equivalent to

\[ \exp \left[ -\beta u_{s}(r_{12}) \right] - 1 = f_{s}(r_{12}). \tag{2.12} \]

The potential \( u_{s}(r_{12}) \) is precisely the same potential that arises in the reference averaged Mayer \( f \)-function (RAM) perturbation theory for molecular fluids [12, 13]. For the DM potential, \( u_{s}(r) \) is shown in figure 1 for \( \delta = 0.1, 0.25 \) and 0.3 at \( T^{*} (=k_{B} T/\epsilon, \text{the reduced temperature}) \) of 0.719. It is clearly, in general, softer than the LJ potential, and is \( \delta \) and \( T^{*} \) dependent.
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\[ u_s(r)/\varepsilon \]

Figure 1. The LJ potential (---) and the potential \( u_s(r) \) [see (2.10) to (2.12) of the text] calculated at \( T^*=0.719 \) for \( \delta=0.1 \) (---), \( \delta=0.25 \) (\( \cdots \cdots \cdot \cdots \cdot \)) and \( \delta=0.3 \) (\( \cdots \cdots \cdots \cdots \cdots \)).

For the DM potential, we find that for \( T^*=0.719 \), \( f_{\text{pert}}(12)/f_s(r_{12}) \) is at most half the magnitude of \( u_{\text{pert}}(12)/u_s(r_{12}) \) for \( \delta \geq 0.1 \) (except, of course, in the vicinity of the zeros of \( f_s(r_{12}) \) and \( u_s(r_{12}) \)). Thus, on this basis alone, we expect that SSCF with identification (2.10) will be superior to SSC/LHNC ((1.5) with identification (1.13)).

3. IMPLEMENTATION OF THE SSC/LHNC, SSCF AND PY APPROXIMATIONS FOR THE DELTA MODEL FLUID

In Appendix B, we define the spherical harmonic coefficients \( A(l_1l_2; r) \) and \( A(l_1l_2m; r) \) in the laboratory frame (LF) and r-frame (RF) respectively for an arbitrary function \( A(12) \), and their k-space analogues. In terms of the k-frame (KF) harmonics (see (B 11)), the OZ equation has the particularly simple form [1, 4, 22].

\[ h(l_1l_2m; k) = c(l_1l_2m; k) + (-1)^m \frac{\rho}{4\pi} \sum_{l_3} h(l_1l_2m; k)c(l_2l_3m; k) \]  

(3.1)

where the summation is over the allowed values of \( l_3 \). We consider the SSC/LHNC, SSCF and PY approximations separately.

3.1. The SSC/LHNC approximation

We begin by considering the harmonics generated in the SSC/LHNC approximation for the DM fluid. The DM potential \( u(12) \) has the LF expansion

\[ u(12) = \sum_{l_1l_2} u(l_1l_2; r)\psi_{l_1l_2}(\omega_1\omega_2\omega) \]  

(3.2)
where \( \psi_{l_1 l_2}(\omega_1 \omega_2 \omega) \) is defined in Appendix B

\[
u(000 ; r) = (4\pi)^{3/2} u_{1,1}(r), \quad (3.3a)
\]

\[
u(l_1 l_2 ; r) = \frac{2}{(4\pi)^{3/2}} 4\pi \delta \left( \frac{\sigma}{r} \right)^{12} l_1 l_2 = 202,022, \quad (3.3b)
\]

\[= 0 \quad \text{otherwise.} \quad (3.3c)
\]

(The terms in (3.3b) can be easily derived by noting that (1.14d) is the RF form of \( u(12) \)—i.e., \( \theta_1 \) and \( \theta_2 \) are measured with respect to the RF axes—hence enabling the RF harmonics \( u(200 ; r) \) and \( u(020 ; r) \) to be identified. Equation (3.3b) follows from (B 6).)

Throughout this section, we find it useful to write \( h(12) \) and \( c(12) \) in the form

\[
h(12) = h_\theta(r_{12}) + h_a(12), \quad (3.4a)
\]

\[
c(12) = c_\theta(r_{12}) + c_a(12), \quad (3.4b)
\]

where \( h_\theta(r_{12}) \) and \( c_\theta(r_{12}) \) are the total and direct correlation functions associated with the spherically symmetric reference systems (with potential \( u_\theta(r_{12}) \) for SSC/LHNC, and with potential \( u_a(r_{12}) \) for SSCF). The functions \( h(12), c(12), h_a(12) \) and \( c_a(12) \) have LF expansions with LF harmonic coefficients \( h(l_1 l_2 ; r), c(l_1 l_2 ; r), h_a(l_1 l_2 ; r) \) and \( c_a(l_1 l_2 ; r) \) respectively. From (3.4), we can write down a relationship between these harmonics as follows:

\[
c(l_1 l_2 ; r) = (4\pi)^{3/2} c_\theta(r) + c_a(000 ; r) \quad l_1 l_2 = 000
\]

\[= c_a(l_1 l_2 ; r) \quad \text{otherwise,} \quad (3.5a)
\]

\[
h(l_1 l_2 ; r) = (4\pi)^{3/2} h_\theta(r) + h_a(000 ; r) \quad l_1 l_2 = 000
\]

\[= h_a(l_1 l_2 ; r) \quad \text{otherwise.} \quad (3.5b)
\]

We now consider the non-zero harmonics in SSC/LHNC. From the \( u(12) \) LF harmonics (3.3) and the SSC/LHNC closure (2.11), \( c(202 ; r) \) and \( c(022 ; r) \) are clearly non-zero. By considering the possible outcome of convolutions of LF 202 and 022 harmonics, one concludes that 000, 220, 222 and 224 harmonics will additionally be generated. The linearity of the SSC/LHNC closure ensures that no additional harmonics will be generated.

The harmonic coefficients \( A(l_1 l_2 ; r) \) satisfy the symmetry properties \( [1, 4] A(202 ; r) = A(022 ; r) \). Using this fact, we present in table 1 the relationship between the LF and RF expansions for a general function \( A(12) \), which may be either \( h_\theta(12) \) or \( c_\theta(12) \). Using these expansions, it is straightforward to verify that the KF harmonics of \( h(k \omega_1 \omega_2) \), the Fourier transform of \( h(r \omega_1 \omega_2) = h(12) \), are given by

\[
h(l_1 l_2 m ; k) = 4\pi h_\theta(k) + h_a(000 ; k) \quad l_1 l_2 m = 000
\]

\[= h_a(l_1 l_2 m ; k) \quad \text{otherwise,} \quad (3.6)
\]

where \( h_\theta(k) \) is the Fourier transform of \( h_\theta(r) \). There is an analogous result for \( c(l_1 l_2 m ; k) \). The functions \( h_\theta(k) \) and \( c_\theta(k) \) are related by

\[[1 + \rho h_\theta(k)][1 - \rho c_\theta(k)] = 1, \quad (3.7)
\]

which is the usual OZ equation for spherically symmetric total and direct correlation functions.
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Table 1. Conversion between the LF and RF harmonics of $A(r_{\omega_1\omega_2})$, obtained from (A 5) and (A 6) after evaluation of the relevant CG coefficients. Note that $m = -m$. A similar set of conversions between LF and KF harmonics of $A(k_{\omega_1\omega_2})$ is obtained simply by setting $r$ to $k$ in the above.

<table>
<thead>
<tr>
<th>LF</th>
<th>RF</th>
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<tbody>
<tr>
<td>$A(000; r)$</td>
<td>$2\pi^{1/2} A(000; r)$</td>
</tr>
<tr>
<td>$A(202; r)$</td>
<td>$2 \left( \frac{\pi}{5} \right)^{1/2} A(220; r)$</td>
</tr>
<tr>
<td>$A(220; r)$</td>
<td>$2 \left( \frac{\pi}{5} \right)^{1/2} A(220; r) - 4 \left( \frac{\pi}{5} \right)^{1/2} A(221; r) + 4 \left( \frac{\pi}{5} \right)^{1/2} A(222; r)$</td>
</tr>
<tr>
<td>$A(222; r)$</td>
<td>$-2 \left( \frac{2\pi}{35} \right)^{1/2} A(220; r) + 2 \left( \frac{2\pi}{35} \right)^{1/2} A(221; r) + 4 \left( \frac{2\pi}{35} \right)^{1/2} A(222; r)$</td>
</tr>
<tr>
<td>$A(224; r)$</td>
<td>$2 \left( \frac{2\pi}{35} \right)^{1/2} A(220; r) + 2 \left( \frac{2\pi}{35} \right)^{1/2} A(221; r) + 4 \left( \frac{2\pi}{35} \right)^{1/2} A(222; r)$</td>
</tr>
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</table>


We now derive the form of the OZ equation for the SSC/LHNC approximation. There are three values of $m$ to consider, $m = 0, 1$ and 2. After using (3.7) to simplify the $m = 0$ equations and to eliminate $c_\theta(k)$ in favour of $h_\theta(k)$, we find that the $m = 0$ equations are given by

$$
\begin{align*}
\frac{1}{2} \left( \frac{1}{\pi} \right)^{1/2} A(000; r) &= A(000; r) \\
\frac{1}{2} \left( \frac{5}{\pi} \right)^{1/2} A(202; r) &= A(200; r) \\
\frac{1}{2} \left( \frac{1}{70\pi} \right)^{1/2} A(220; r) + \frac{5}{14\pi} \left( \frac{1}{70\pi} \right)^{1/2} A(222; r) &= A(220; r) \\
\frac{1}{2} \left( \frac{1}{70\pi} \right)^{1/2} A(220; r) + \frac{5}{14\pi} \left( \frac{1}{70\pi} \right)^{1/2} A(222; r) &= A(221; r) \\
\frac{1}{2} \left( \frac{5}{70\pi} \right)^{1/2} A(220; r) + \frac{5}{14\pi} \left( \frac{1}{70\pi} \right)^{1/2} A(222; r) &= A(222; r)
\end{align*}
$$

(3.8)
where the two matrices $M_i$, $i = 1, 2$, are given by

$$M_1 = \begin{bmatrix}
1 - \frac{\rho}{4\pi} c_a(000 ; k) & -\frac{\rho}{4\pi} c_a(200 ; k) & 0 \\
\times [1 + \rho h_0(k)] & \times [1 + \rho h_0(k)] & 0 \\
-\frac{\rho}{4\pi} c_a(200 ; k) & 1 - \frac{\rho}{4\pi} c_a(220 ; k) & 0 \\
0 & -\frac{\rho}{4\pi} c_a(200 ; k) & 1 - \frac{\rho}{4\pi} c_a(220 ; k)
\end{bmatrix} \quad (3.9 \text{a})$$

$$M_2 = \begin{bmatrix}
1 - \frac{\rho}{4\pi} c_a(000 ; k) & -\frac{\rho}{4\pi} c_a(200 ; k) & 0 \\
\times [1 + \rho h_0(k)] & \times [1 + \rho h_0(k)] & 0 \\
0 & 1 - \frac{\rho}{4\pi} c_a(000 ; k) & -\frac{\rho}{4\pi} c_a(200 ; k) \\
0 & -\frac{\rho}{4\pi} c_a(200 ; k) & 1 - \frac{\rho}{4\pi} c_a(220 ; k)
\end{bmatrix} \quad (3.9 \text{b})$$

The matrix $M_1$ is obtained by considering $l_1l_2m = 200$ in (3.1); the matrix $M_2$ is obtained by considering $l_1l_2m = 020$ in (3.1). These equations must be equivalent; however numerically we find it most useful to use (3.8) in the form

$$\begin{bmatrix}
h_a(000 ; k) \\
h_a(200 ; k) \\
h_a(220 ; k)
\end{bmatrix} = M^{-1} \begin{bmatrix}
c_a(000 ; k) \times [1 + \rho h_0(k)] \\
c_a(200 ; k) \times [1 + \rho h_0(k)] \\
c_a(220 ; k)
\end{bmatrix}, \quad (3.10)$$

where

$$M = \frac{1}{2}(M_1 + M_2). \quad (3.11)$$

The $m = 1, 2$ equations are given by

$$h_a(22m ; k) = \frac{c_a(22m ; k)}{1 - (-)^m \frac{\rho}{4\pi} c_a(22m ; k)}. \quad (3.12)$$

The SSC/LHNC closure, (2.11), implies the following conditions on the LF harmonics of $h(12)$ and $c(12)$:

$$c_a(202 ; r) = -\beta u_a(202 ; r) g_0(r) + h_0(r)[h_a(202 ; r) - c_a(202 ; r)], \quad (3.13 \text{a})$$

$$c_a(l_1l_2l ; r) = h_0(r)[c_a(l_1l_2l ; r) - c_a(l_1l_2l ; r)], \quad (3.13 \text{b})$$

The numerical scheme adopted is illustrated by the flowchart in figure 2. The functions $h_a(l_1l_2l ; r)$ and $c_a(l_1l_2l ; r)$ were evaluated for $0 \leq r/a \leq 10$ on a grid of points of width $\Delta r/a = 0.025$; thus, there were $N = 401$ values of $h_a(l_1l_2l ; r)$ and $c_a(l_1l_2l ; r)$ carried during the computation. The Hankel
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Figure 2. A flowchart illustrating the numerical scheme used for solving the SSC/LHNC approximation for the DM potential.

transforms \( h_a(l_1 l_2 ; k) \) and \( c_a(l_1 l_2 ; k) \) were calculated via the trapezoidal rule yielding \( N = 401 \) values on \( 0 \leq k \sigma \leq 40 \pi \) on a grid of width \( \Delta(k \sigma) = \pi/10 \). For a Fourier \((j_0)\) transform—as required by \( h_a(l_1 l_2 ; r) \) and \( c_a(l_1 l_2 ; r) \)—the use of the trapezoidal rule with this choice of \( k\)-space grid is equivalent to using the Lado method \[14\]. The Lado method ensures that inverse Fourier transformation of \( h(l_1 l_2 ; k) \), the transform of \( h(l_1 l_2 ; r) \) calculated numerically, gives back \( h(l_1 l_2 ; r) \) to within the accuracy of the computer (i.e. the accuracy dictated by the word length, evaluation of trigonometric functions and rounding error in floating point operations). By experimenting with a few sample functions, we
found that for \( j_2 \) and \( j_4 \)-transforms—required for \( h(l_1 l_2^2 ; r) \) and \( h(l_1 l_2^4 ; r) \)—the trapezoidal rule with Lado grid performed very well. That is, for a function \( p(r) \) we calculated numerically its \( j_2 \) and \( j_4 \)-transforms, \( p_2(k) \) and \( p_4(k) \) (see (B 9)), and then inverse transformed these latter functions numerically (see (B 10)) to form the functions \( p_2(r) \) and \( p_4(r) \). The difference between \( p_2(r) \), \( p_4(r) \) and \( p(r) \) was negligible, especially if \( p_2(r) \) and \( p_4(r) \) smoothly approached zero as \( r \to 0 \), a property that \( h(l_1 l_2^l ; r) \), \( l = 2, 4 \), satisfy [15]. The error criterion \( \gamma \) in figure 2 was usually of the order of 0.05 or less; with this criterion, \( |h(l_1 l_2^l ; r)| \leq 0.01 \) for \( r \) in the core region. As is often found with numerical solution of integral equations, mixing of the solutions (see figure 2) was required. The program was set up to automatically increase the mixing parameter \( \alpha \) if the error parameter ERR failed to decrease for three consecutive iterates. Significant mixing was required for the larger values of \( \delta (\delta = 0.25, 0.3) \).

The spherically symmetric reference system correlation function \( h_0(r) \) required for SSC/LHNC is the LJ total correlation function. The fitted formula of Goldman was used for this purpose [16]. The results are discussed in § 4.

### 3.2. The SSCF approximation

For the SSCF closure (2.10), we require the LF harmonics of \( f_0(12) \equiv f_{\text{pert}}(12) \), defined by (2.1). Even for the DM potential, there are an infinite number of such harmonics of the form \( f_0(l_1 l_2^l ; r) \) where \( l_1 \) and \( l_2 \) are both even by symmetry. In the work reported here, we have truncated the expansion of \( f_0(12) \) at \( l_2^1 = 2 \) and \( l_2 = 2 \). Thus, we have approximated \( f_0(12) \) by the function \( f_0^T(12) \) given by

\[
f_0^T(12) = f_0(202 ; r) \psi_{202} (\omega_1 \omega_2 \omega_0) + f_0(022 ; r) \psi_{022} (\omega_1 \omega_2 \omega_0) + f_0(222 ; r) \psi_{222} (\omega_1 \omega_2 \omega_0) + f_0(224 ; r) \psi_{224} (\omega_1 \omega_2 \omega_0),
\]

where the \( f_0(l_1 l_2^l ; r) \) are the LF harmonics of \( f_0(12) \). The approximation (3.14) can be evaluated by comparing \( f_0^T(12) \) and \( f_0(12) \) for various fixed orientations as a function of separation \( r \). We have performed such a comparison and find that \( f_0^T(12) \) is a very good approximation to \( f_0(12) \).

With the approximate \( f_0^T(12) \), the non-zero SSCF LF harmonics are exactly the same set as for SSC/LHNC. Thus the numerical scheme of figure 2 may be used for SSCF with an appropriate change in steps 0 and 6, the imposition of the closure condition. The SSCF closure (2.10) is given in terms of LF harmonics by

\[
c_a(000 ; r) = h_0(r)[h_a(000 ; r) - c_a(000 ; r)],
\]

\[
c_a(l_1 l_2^l ; r) = f_a(l_1 l_2^l ; r) g_0(r) + h_0(r)[h_a(l_1 l_2^l ; r) - c_a(l_1 l_2^l ; r)],
\]

\[
l_1 l_2^l = 202, 022, 220, 222, 224.
\]

The \( h_0(r) \) (and thus \( g_0(r) \)) required in (3.15) were calculated via MC simulation using the potential \( u_0(r) \) (see figure 1 and § 2). The results of this approximation are given in § 4.
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3.3. The PY approximation

The PY approximation can be written in various equivalent forms for fluids without hard cores [18]; the form that we favour here is

\[ c(12) = b(12)g(12), \] (3.16)

where

\[ b(12) = 1 - \exp[\beta u(12)]. \] (3.17)

As with \( f_\alpha(12) \) for the SSCF approximation, \( b(12) \) has an expansion in an infinite number of LF harmonics \( b(l_1l_2; r) \) with \( l_1 \) and \( l_2 \) even by symmetry. We must truncate this expansion and, as for SSCF, we do so at \( l_1 = 2 \) and \( l_2 = 2 \). That is, we use the approximation \( b^T(12) \) to \( b(12) \) given by

\[
\begin{align*}
b^T(12) &= b(000; r)\psi_{000}(\omega_1\omega_2\omega) + b(202; r)\psi_{202}(\omega_1\omega_2\omega) \\
&\quad + b(222; r)\psi_{222}(\omega_1\omega_2\omega) + b(224; r)\psi_{224}(\omega_1\omega_2\omega),
\end{align*}
\] (3.18)

where \( b(l_1l_2; r) \) are the LF harmonics of \( b(12) \). The approximation \( b^T(12) \) is as good an approximation to \( b(12) \) as \( f_\alpha(12) \) is to \( f_\alpha(12) \) as one might expect.

In solving the SSCF approximation, the set of harmonics in \( f_\alpha(12) \) was truncated; having truncated the \( f_\alpha(12) \) expansion, all the harmonics of \( h_\alpha(12) \) and \( c_\alpha(12) \) generated by the SSCF approximation were retained. In solving the PY approximation, the use of the assumption (3.18) is clearly analogous to using the truncated \( f_\alpha(12) \) expansion in SSCF. However, we make a further assumption which in general is not justified: we assume that the only non-zero harmonics of \( h_\alpha(12) \) and \( c_\alpha(12) \) are the set that appear in SSC/LHNC and the truncated SSCF approximations of §§ 3.1 and 3.2 above. That is, we assume that

\[ h(l_1l_2; r) = c(l_1l_2; r) = 0 \quad \text{for} \quad l_1l_2 \neq 000, 202, 220, 222, 224. \] (3.19)

This is clearly an extra approximation, due to (3.16). The assumption (3.19) is similar to that of Patey in going beyond LHNC to quadratic hypernetted chain (QHNC) [5-7]. A priori justification of (3.19) is difficult; in future work we intend to investigate systematically the effect of these truncations on the calculated LF harmonics.

The PY closure has been investigated in the present notation by Gray and Gubbins in Appendix A of [1]. The closure is most succinctly expressed in RF harmonics [17] and is given by

\[
\begin{align*}
\sum_{l',l''} \frac{1}{4\pi} \left[ \frac{2l'+1)(2l''+1)(2l'''+1)(2l'''+1)}{(2l_1+1)(2l_2+1)} \right]^{1/2} \\
\times C(l',l'',l_1; 000)C(l''l''',l_2; 000) \\
\times \sum_{m',m''} C(l',l'',l_1; m'm'') \\
\times C(l''l'''l_2; m'm''m) b(l'_1l''_2m'; r)g(l''_1l'''_2m''; r),
\end{align*}
\] (3.20)

where \( C(l_1l_2; m_1m_2m) \) is a Clebsch–Gordan coefficient, and the summation is over allowed values of \( l'_1, l''_1, l''_2, m', m'' \). In solving the PY, we have not corrected the approximation to build in the exact \( \delta = 0 \) limit; thus the full \( c, h \) and \( b \) occur in (3.19) and (3.20) (and not \( c_\alpha, h_\alpha \) and \( b_\alpha \)). For the restricted
harmonic subspace (3.19), (3.20) yields the following closures in terms of RF harmonics:

\[ c(000; r) = \frac{1}{4\pi} [b(000; r)g(000; r) + 2b(200; r)g(200; r) + b(220; r)g(220; r)], \quad (3.21 \text{ a}) \]

\[ c(200; r) = \frac{1}{4\pi} [b(200; r)[g(000; r) + g(220; r)] + g(200; r)[b(000; r) + b(220; r)]] + \frac{1}{14\pi} 5^{1/2} [b(200; r)g(200; r) + b(220; r)g(220; r)], \quad (3.21 \text{ b}) \]

\[ c(220; r) = \frac{1}{4\pi} [b(220; r)g(000; r) + 2b(200; r)g(200; r) + b(000; r)g(220; r)] + \frac{5}{49\pi} b(220; r)g(220; r), \quad (3.21 \text{ c}) \]

\[ c(221; r) = \frac{1}{4\pi} b(000; r)g(221; r) + \frac{5^{1/2}}{14\pi} b(200; r)g(221; r) + \frac{5}{196\pi} b(220; r)g(221; r), \quad (3.21 \text{ d}) \]

\[ c(222; r) = \frac{1}{4\pi} b(000; r)g(222; r) - \frac{5^{1/2}}{7\pi} b(200; r)g(222; r) + \frac{5}{49\pi} b(220; r)g(222; r). \quad (3.21 \text{ e}) \]

The numerical scheme adopted in solving the PY approximation is the same as that given in figure 2 with two changes: the insertion of a step between steps 5 and 6 to obtain the RF harmonics of \( h(12) \), \( h(l_d m; r) \); and step 6 now becomes the imposition of the PY closure, (3.21). (Note that, for the PY approximation, the full \( h(12) \) and \( c(12) \), rather than \( h_\alpha(12) \) and \( c_\alpha(12) \), are computed numerically.) The results of the PY approximation are given in the following section.

4. Results for the Delta-Model Fluid

The state condition at which we report results is at \( \rho^* = \rho_0^* = 0.8 \) and \( T^* = 0.719 \), a typical high density liquid state of the LJ fluid. MC simulations of the DM fluid were performed at \( \delta = 0.1, 0.25 \) and \( 0.3 \); details of the simulations are given in Appendix C. In figure 3 we exhibit \( g(r) \), the angle average of \( g(12) \),

\[ g(r) = \langle g(12) \rangle_{\omega_1 \omega_2} \quad (4.1) \]
as calculated in the simulations, and compare it with \( g_{\text{LJ}}(r) \) at the same \( \rho^* \) and \( T^* \). Clearly, the short ranged anisotropic part of the DM potential significantly alters the spatial distribution of the molecules from its \( \delta = 0 \) (LJ) form: this is in contrast to the multipolar fluids discussed in § 1. One obvious test of the three approximations—SSC/LHNC, SSCF and PY—is the extent to which they reproduce this spatial structure. Note that in figure 3 we have also included the pair correlation function for the LJ fluid calculated in the PY approximation. The PY result is quite accurate, except that it exaggerates the first peak and is a little out of phase. It should be kept in mind that the PY approximation, as solved in § 3.3, yields the PY approximation for the LJ \( g(r) \) in the limit \( \delta = 0 \). The SSC/LHNC and SSCF approximations, on the other hand, yield the exact \( g_{\text{LJ}}(r) \) in the limit \( \delta = 0 \).

We present complete results at \( \delta = 0.25 \)—i.e. the full set of calculated harmonics—and \( g(r) \), \( h(202; r) \) and \( h(220; r) \) at \( \delta = 0.1 \) and 0.3. In figures 4 through 8, the functions \( g(r) \), \( h(202; r) \), \( h(220; r) \), \( h(222; r) \) and \( h(224; r) \) calculated via the SSC/LHNC, SSCF and PY approximations are compared with the MC results for \( \delta = 0.25 \). From figure 4, it is clear that the SSC/LHNC approximation is worst at reproducing the spatial distribution of molecule centres. In fact, on the scale of these figures, the SSC/LHNC \( g(r) \) is indistinguishable from \( g_{\text{LJ}}(r) \) for each of the values of \( \delta \), which from figure 3 is a considerable error. The SSCF approximation is best at predicting \( g(r) \), yielding results that lie along the MC simulation values except at the first peak which is overestimated by about 10 per cent and slightly displaced towards small
Figure 4. The angle averaged pair correlation function $g(r)$ for the DM potential calculated at $\rho^*=0.8$, $T^*=0.719$ and $\delta=0.25$ using the SSC/LHNC (---), SSCF (----) and PY (-----) approximations. The circles are MC results.

Figure 5. The spherical harmonic coefficient $h(202; r)$ for the DM potential for the same state conditions and using the same legend as figure 4.
Figure 6. The spherical harmonic coefficient $h(220; r)$ for the DM potential for the same state conditions and using the same legend as figure 4.

Figure 7. The spherical harmonic coefficient $h(222; r)$ for the DM potential for the same state conditions and using the same legend as figure 4.
The spherical harmonic coefficient $h(224 ; r)$ for the DM potential for the same state conditions and using the same legend as figure 4.

The PY result is reasonably good; it has a significantly diminished peak height from its $\delta = 0$ value. The relationship between the PY and MC results at $\delta = 0.25$ for $g(r)$ is very similar to that between the corresponding results at $\delta = 0$ (the LJ fluid, figure 3).

The LF harmonic $h(202 ; r)$ is shown in figure 5 for $\delta = 0.25$. Here there is no clear cut best approximation. The SSC/LHNC has the best magnitudes for the first trough and second peak; however, because of the poor spatial distribution, $h(202 ; r)$ is badly out of phase for $r < \sigma$. The SSCF result is in phase, but is consistently low in magnitude; the PY approximation is also in phase, but in contrast to SSCF it has exaggerated magnitudes.

The $h(220 ; r)$, $h(222 ; r)$ and $h(224 ; r)$ harmonics (figures 6 to 8) show that SSC/LHNC is badly in error, with these harmonics being effectively zero. The SSCF approximation is much better than SSC/LHNC, qualitatively predicting the first peak (or trough) for each harmonic. However, SSCF consistently misses completely the second trough (or peak) in each harmonic, although the second trough in $h(224 ; r)$ is barely resolved in the MC results. The best approximation for these harmonics is clearly PY, which qualitatively predicts each of the predominant structures in the MC results, albeit with exaggerated magnitudes as before.

The results at $\delta = 0.1$ present a similar trend as those at $\delta = 0.25$, as figures 9 to 11 reveal, with some slight differences. Firstly, for $g(r)$, figure 9, SSC/LHNC must be regarded as superior to PY. This is an artifact of $\delta = 0.1$ being close enough to $\delta = 0$ that $g(r)$ is close to its $\delta = 0$ (i.e., LJ) form. Since SSC/LHNC has this limit built in exactly and PY has not, the results for $g(r)$ favour SSC/LHNC somewhat fortuitously at this value of $\delta$. The SSCF result at $\delta = 0.1$ is
within the MC error. The result for \( h(202; r) \) at \( \delta = 0.1 \), figure 10, is also clouded by the proximity of the \( \delta = 0.1 \) spatial structure being very close to that of \( \delta = 0 \). SSC/LHNC and SSCF are both very good, with SSC/LHNC having a small edge. The PY result, as at \( \delta = 0.25 \), is qualitatively correct with peaks in the correct position but of exaggerated magnitude.

Figure 9. As for figure 4 except that \( \delta = 0.1 \).

Figure 10. As for figure 5 except that \( \delta = 0.1 \).
Most of the results for $h(220; r)$ are expected from the $\delta = 0.25$ analysis given above: the SSC/LHNC result is effectively zero, the SSCF result is qualitative for the first peak and misses the second trough completely and the PY result is qualitatively correct with peaks in the correct position but of exaggerated magnitude. There is one significant difference, however, and that is the relative size of the SSCF compared to the PY and MC results. Here, SSCF is larger in magnitude than either of the latter two quantities, whereas at $\delta = 0.25$ the opposite is true. This is also true of the other harmonics, $h(222; r)$ and $h(224; r)$. We have been unable to find a satisfactory explanation for this reversal, although it is certain that its origin must lie in the fact that as $\delta$ changes, $f_0(r)$, $g_0(r)$ and $f_{\alpha}(12)$ are all changing as well. This fact renders SSCF less predictable in its behaviour as a function of $\delta$.

The SSC/LHNC results for the DM potential at $\delta = 0.1$ and $0.25$ have a number of noteworthy features. The first is: comparison of the results at $\delta_1 = 0.1$ and $\delta_2 = 0.25$ indicates that the coefficients $h_0(202; r)$ satisfy the scaling relation

$$h_0(202; r)\big|_{\delta = \delta_2} \approx \frac{\delta_2}{\delta_1} h_0(202; r)\big|_{\delta = \delta_1}. \tag{4.2}$$

An analogous result holds for $c_0(202; r)$. This scaling relation is consistent with the SSC/LHNC closure but, in view of the non-linearity of the OZ equation, it is not necessarily implied by this closure. The extent to which (4.2) is satisfied is such that the left and right hand sides of (4.2) are indistinguishable on the scale of figure 5. We find that for the DM potential, (4.2) is satisfied quite generally ($0.1 \leq \delta_1$, $\delta_2 \leq 0.35$) by SSC/LHNC. In addition, as noted above,

$$h_0(l_1l_2l; r) \approx 0, \quad l_1l_2l \neq 202, 220. \tag{4.3}$$

Figure 11. As for figure 6 except that $\delta = 0.1$. 
We find results (4.2) and (4.3) fascinating for the following reason: the application of first order Gray-Gubbins (GG) perturbation theory [24] to the DM potential yields spherical harmonic coefficients $h_a(l/2l_{1/2}; r)$ which satisfy (4.2) and (4.3) exactly (rather than approximately, as in SSC/LHNC). Although not shown in figures 5 and 10, the first-order GG perturbation theory results for $h(202; r)$ are similar but a little inferior to the SSC/LHNC.

The GG perturbation theory calculates the properties of a fluid interacting with potential (1.1) by using a spherically symmetric reference system (a fluid interacting with potential $u_0(r_{12})$ defined by (1.7)) and expanding about this reference system in powers of $u_{vert}(12)$. As evidenced by (1.13), SSC/LHNC has much of the same conceptual basis, so it is very interesting that two theories, which are quite disparate in their derivation and implementation, yield such similar results.

In the introduction, we alluded to the usefulness of the DM potential in probing the linearity of the SSC/LHNC closure. The results in figures 4–11 demonstrate this quite forcefully: despite the fact that within SSC/LHNC the harmonic coefficients $h_a(000; r)$, $h_a(220; r)$, $h_a(222; r)$ and $h_a(224; r)$ are in principle non-zero, in practice they are effectively zero. The only significantly non-zero harmonic coefficient is $h_a(202; r)$, corresponding to the only non-zero potential harmonic. We conclude that the coupling between harmonic coefficients in SSC/LHNC is sufficiently weak that in-effect in the resulting structure we see only a linear response to the perturbing potential. Such an observation would have been obscured had a more realistic model for $u^{shape}(12)$ been employed.

Figure 12. The angle averaged pair correlation function $g(r)$ for the DM potential calculated at $\rho^* = 0.8$, $T^* = 0.719$ and $\delta = 0.3$ using the SSCF (----) and PY (-----) approximations. The circles are the MC results. The RAM result for $g(r)$ is indistinguishable from the SSCF result on the scale of this graph.
Figure 13. The spherical harmonic coefficient $h(202; r)$ for the DM potential for the same state conditions and using the same legend as figure 12, compared to the results from the low-order RAM perturbation theory given by (4.4) (---).

Figure 14. The spherical harmonic coefficient $h(220; r)$ for the DM potential at the same state conditions and using the same legend as figure 13.
For SSCF, if there is to be any link with perturbation theory one expects that link to be with RAM perturbation theory [12, 13] rather than GG perturbation theory. Consequently, for the $\delta = 0.3$ results shown in figures 12 to 14, we do not show SSC/LHNC results and instead exhibit the result of a leading-order RAM perturbation theory [26]. In the notation of this paper, the latter theory predicts

$$g(r) = g_0(r),$$

$$h_a(l_1l_2l; r) = f_{\text{pert}}(l_1l_2l; r)g_0(r).$$ \hspace{1cm} (4.4)

We find that for $g(r)$ at $\delta = 0.3$, shown in figure 12, SSCF and RAM are indistinguishable. The PY results are quite good for the first peak in $g(r)$ but are out of phase at larger values of $r$.

For $h(202 ; r)$, shown in figure 13, SSCF is quite good, although the depth of the first trough and the height of the first peak are a little exaggerated. The RAM result substantially disagrees with SSCF and is quite bad, especially since the first peak is completely absent. The PY result has the correct troughs and peaks but with magnitudes approximately a factor of two bigger than the MC results.

Figure 14 shows $h(220 ; r)$ at $\delta = 0.3$. Interestingly, the SSCF and RAM results are very similar, both missing the trough just beyond $r = 1$ shown by the MC and PY results. The PY results have the correct troughs and peaks but again with spuriously high magnitudes. The agreement shown here between the SSCF and RAM results is found to hold for the other non-potential harmonics. In fact, we find in general that

$$h_a(l_1l_2l; r)_{\text{SSCF}} \approx h_a(l_1l_2l; r)_{\text{RAM}}, \quad l_1l_2l \neq 202, 022. \hspace{1cm} (4.5)$$

Thus, SSCF produces results that, except for the harmonic in the potential, are similar to RAM results. This indicates that the SSCF closure is linear in the harmonics of $f_{\text{pert}}(12)$ except for the harmonic contained in the potential.

We should note that SSCF represents a considerable improvement over RAM in that $h_a(202 ; r)$ is predicted much more accurately by SSCF. In contrast, SSC/LHNC represents only a small improvement over GG perturbation theory.

5. CONCLUSION

Our results indicate the SSC/LHNC is not a good approximation for the short ranged anisotropic interactions that characterize overlap (shape) forces. The new approximation introduced here, SSCF, is clearly superior to SSC/LHNC but is nevertheless unable to predict certain features that PY correctly exhibits. The PY approximation must, on balance, be regarded as the best of the three approximations, although there is clearly room for improvement.

The relationships between SSC/LHNC and SSCF and the corresponding perturbation theories (GG and RAM) point to the linearity of these approximations in $u_{\text{pert}}(12)$ and $f_{\text{pert}}(12)$ respectively. This accounts for the behaviour of these approximations for the harmonics not contained in $u(12)$, as discussed in the previous section. The PY approximation is sensitive to the finer features of these very harmonics apparently because the closure strongly mixes the coefficients of $g(12)$ and $h(12)$. 
In future work, we intend to explore a corrected PY approximation in the belief that such an approximation may still have the qualitatively correct features of the uncorrected PY approximation combined with quantitatively more correct magnitudes. In addition, we are applying SSCF to multipolar fluids (dipolar hard spheres, the Stockmayer fluid, etc.) with high dipole moments, since for such fluids the spatial structure can differ appreciably from that of the reference system (that is, (1.9) is not well satisfied by these systems).

APPENDIX A

Alternative derivations of SSCF and SSC

From an analysis of their respective cluster expansions, we derive two approximate relations between \( g(12) \) and \( c(12) \) that are motivated by the PY and HNC approximations. These closures, suggested and derived by one of us (MSW), are called the Percus–Yevick excess (PYX) and hypernetted chain excess (HNCX) approximations respectively, since the classes of diagrams neglected in each case have topological properties similar to those neglected in the usual PY and HNC approximations. Although these closures are of interest in their own right, our purpose in introducing them here is to demonstrate how linearizations of these approximations immediately yield the SSCF and SSC closures, hence showing that these closures are not uniquely related to the HNC approximation.

For convenience, we follow the notation and definitions of Hansen and McDonald [10], to which the reader is referred for detailed descriptions of the cluster expansions referred to below. From (5.53) of [10], we have

\[
g(12) = e(12)\gamma(12), \tag{A 1}
\]

where \( e(12) = f(12) + 1 \) and \( \gamma(12) \) has an expansion in terms of diagrams, each of which may or may not contain a nodal circle. We rewrite (A 1) as

\[
g(12) = e(12)[1 + m(12) + z(12)], \tag{A 2}
\]

where

\[
m(12) = \text{sum of diagrams in } \gamma(12) \text{ containing nodal circles} \tag{A 3}
\]

and

\[
z(12) = \text{sum of diagrams in } \gamma(12) \text{ with no nodal circles} \tag{A 4}
\]

(Note that the function denoted \( m(12) \) here is called \( b(12) \) in [10].) Now, \( c(12) \) is defined so that it contains only those diagrams of \( g(12) \) without nodal circles (see equations (5.40) and (5.63) of [10]) so that

\[
c(12) = g(12) - 1 - m(12) \tag{A 5 a}
\]

or equivalently

\[
c(12) = f(12)[1 + m(12)] + e(12)z(12). \tag{A 5 b}
\]

The PY approximation consists of setting \( z(12) = 0 \) [11]; elimination of \( m(12) \) between (A 2) and (A 5 b) yields

\[
e(12)c(12) = g(12)f(12), \tag{A 6}
\]

which can be written in the form (3.16).
To derive PYX, we rewrite (A 2) in the following (exact) form:

\[ g(12) = g_{\text{ref}}(12) + e_{\text{ref}}(12)[1 + M(12) + Z(12)]. \]  

(A 7)

In (1.7), \( e_{\text{ref}}(12) = \exp [-\beta u_{\text{ref}}(12)] \) and \( g_{\text{ref}}(12) \) is as defined in (1.2) and (1.4). The diagrams in \( M(12) \) and \( Z(12) \) are no longer simple graphs, since circles in these diagrams can be connected either by an \( f_{\text{ref}} \) or by an \( f_{\text{pert}} \)-bond or by both. The diagrams in \( Z(12) \) are free of nodal circles, whilst the diagrams in \( M(12) \) contain at least one nodal circle. The actual diagrams in \( M(12) \) and \( Z(12) \) can be found by comparing each side of (A 7) term-by-term in density and using the fact that

\[ f(12) = f_{\text{ref}}(12) + f_{\text{pert}}(12) + f_{\text{ref}}(12)f_{\text{pert}}(12) \]  

(A 8)

to expand out the diagrams in \( g(12) \). It is relatively straightforward to establish that

\[ M(12) = m(12) - m_{\text{ref}}(12) \]  

(A 9)

where \( m_{\text{ref}}(12) \) is the same set of diagrams as \( m(12) \) but with each \( f \)-bond replaced by an \( f_{\text{ref}}(12) \)-bond (i.e., it is \( m(12) \) for the reference system); note that the analogous expression for \( Z(12) \) does not hold. One consequence of this fact is that linearization of the PYX closure (discussed below) in either \( f_{\text{pert}}(12) \) or \( u_{\text{pert}}(12) \) yields closures that are different to those obtained by direct linearization of the PY closure itself.

From (A 5 a), considered for the reference system only,

\[ m_{\text{ref}}(12) = c_{\text{ref}}(12) - g_{\text{ref}}(12) + 1. \]  

(A 10)

Combining (A 9) with (A 5 a) yields

\[ e(12) = g(12) - [g_{\text{ref}}(12) - c_{\text{ref}}(12)] - M(12) \]  

(A 11 a)

or, equivalently,

\[ c_{\text{pert}}(12) = h_{\text{pert}}(12) - M(12). \]  

(A 11 b)

The PYX approximation is defined by analogy with PY; that is, it corresponds to setting \( Z(12) = 0 \). In this case, (A 7) and (A 11 b), upon elimination of \( M(12) \), yield the closure

\[ g_{\text{ref}}(12)[c_{\text{pert}}(12)c_{\text{pert}}(12) - f_{\text{pert}}(12)] = h_{\text{pert}}(12)[g_{\text{ref}}(12)e_{\text{pert}}(12) - 1]. \]  

(A 12)

For \( f_{\text{pert}}(12) \) small, we retain the lowest order terms throughout, yielding

\[ g_{\text{ref}}(12)[c_{\text{pert}}(12) - f_{\text{pert}}(12)] = h_{\text{pert}}(12)h_{\text{ref}}(12). \]  

(A 13)

This is the SSCF closure introduced in § 2 on the basis of linearizing the HNC closure in both \( f_{\text{pert}}(12) \) and \( h_{\text{pert}}(12) \). If (A 12) is linearized in \( u_{\text{pert}}(12) \), the SSC closure (1.5) results.

The HNCX approximation is derived along principles similar to those used above for PYX. We begin with the exact equation

\[ g(12) = \epsilon(12) \exp [m(12) + d(12)] \]  

(A 14)

where \( d(12) \) is a set of diagrams free of nodal circles generally known as the bridge diagrams (see equations (5.61) to (5.65) of [10]). The usual HNC approximation (2.3)–(2.4) results from setting \( d(12) = 0 \).
As for PYX, (A 14) may be replaced by another exact equation

\[ g(12) = g_{\text{ref}}(12) e_{\text{pert}}(12) \exp [M(12) + D(12)] \]  

(A 15)

where again \( M(12) \) and \( D(12) \) respectively contain some or no nodal circles, and furthermore term-by-term comparison establishes (A 9). The HNCX approximation corresponds to setting \( D(12) = 0 \), yielding (after eliminating \( M(12) \) and taking logarithms)

\[ \log \left[ \frac{g(12)}{g_{\text{ref}}(12)} \right] = \log \left[ 1 + f_{\text{pert}}(12) \right] + h_{\text{pert}}(12) - c_{\text{pert}}(12) \]  

(A 16)

which is (2.8). Linearization in \( f_{\text{pert}}(12) \) yields SSCF; linearization in \( u_{\text{pert}}(12) \) yields SSC.

A simplified graphical derivation of SSCF can be obtained by replacing \( - \beta u_\alpha \) by \( f_{\text{pert}}(12) \) in the derivation of SSC given by Henderson and Gray \([4]\).

It is interesting to compare the PYX and HNCX approximations with the Corrected Percus–Yevick (CPY) and Corrected Hypernetted Chain (CHNC) approximations of Lado \([27]\) and Smith and Henderson \([3]\). Smith and Henderson \([3]\) have derived both CPY and CHNC approximations in the context of cluster expansions. Consequently, it is perhaps not unexpected to find that the HNCX and CHNC approximations are identical.

Surprisingly, however, the CPY and PYX approximations are not equivalent. The CPY approximation ((22) of \([3]\)) can be written in the form

\[ c_{\text{pert}}(12) = f_{\text{pert}}(12) \left[ g_{\text{ref}}(12) + \left[ 1 + f_{\text{ref}}(12) \right] \times [h_{\text{pert}}(12) - c_{\text{pert}}(12)] \right] \]

+ \( f_{\text{ref}}(12) [h_{\text{pert}}(12) - c_{\text{pert}}(12)] \) \hspace{1cm} (A 17)

In order to emphasize the difference between it and CPY, the PYX approximation can be written as

\[ c_{\text{pert}}(12) = f_{\text{pert}}(12) \left[ g_{\text{ref}}(12) + g_{\text{ref}}(12) \times [h_{\text{pert}}(12) - c_{\text{pert}}(12)] \right] \]

+ \( h_{\text{ref}}(12) [h_{\text{pert}}(12) - c_{\text{pert}}(12)] \) \hspace{1cm} (A 18)

Thus, CPY corresponds to PYX when certain occurrences of \( h_{\text{ref}}(12) \) are replaced by that function’s zero density form \( f_{\text{ref}}(12) \). In view of its somewhat richer structure, we are currently investigating the accuracy of PYX for molecular fluids.

**APPENDIX B**

*Definitions of spherical harmonic expansions*

In this Appendix, we follow the definitions used by Gray and Gubbins and coworkers over the last decade. The most complete summary of this formalism is given in Chapters 3 and 5 and Appendices A and 3B of \([1]\). Here we quote the required results.

Consider a function \( A(12) = A(r_{\omega_1 \omega_2}) \) which depends on \( r \), the vector joining the centre of two linear molecules 1 and 2, and the molecules’ orientations \( \omega_1 \) and \( \omega_2 \). If \( A(r_{\omega_1 \omega_2}) \) is invariant under rotation of the two molecule system \( A(r_{\omega_1 \omega_2}) \) can be written in the following form

\[ A(r_{\omega_1 \omega_2}) = \sum_{l,d} A(l, \ell, d; r) \psi_{l,\ell, d}(\omega_1 \omega_2). \]  

(B 1)
Here, $\omega$ and $r$ are the orientation and magnitude respectively of $\mathbf{r}$ and $\psi_{l_1l_2}(\omega_1\omega_2\omega)$ is a rotational invariant given by
\[
\psi_{l_1l_2}(\omega_1\omega_2\omega) = \sum_{m_1m_2m} C(l_1l_2l; m_1m_2m) Y_{l_1m_1}(\omega_1) Y_{l_2m_2}(\omega_2) Y_{lm}(\omega). \tag{B 2}
\]
In (B 2), $C(l_1l_2l; m_1m_2m)$ is a Clebsch–Gordan (CG) coefficient and $Y_{lm}(\omega)$ is a spherical harmonic in the convention of Rose [19]. The summations in (B 1) and (B 2) are restricted by symmetry considerations and the values over which the CG coefficients are non-zero (in (B 3), for example, $m = m_1 + m_2$ is one restriction). The reader is referred to [1] for details. The coefficients $A(l_1l_2l; r)$ are projections of $A(\omega_1\omega_2\omega)$ and are given by
\[
A(l_1l_2l; r) = \frac{(4\pi)^{3/2} [(2l_1 + 1)(2l_2 + 1)(2l + 1)]^{1/2}}{C(l_1l_2l; 000)} \times \int \frac{d\omega_1}{4\pi} \int \frac{d\omega_2}{4\pi} \int \frac{d\omega}{4\pi} P_{l_1}(\cos \theta_1) P_{l_2}(\cos \theta_2) P_l(\cos \theta) A(\omega_1\omega_2\omega), \tag{B 3}
\]
where $P_l$ is the Legendre polynomial of order $l$ and $\theta_1$, $\theta_2$ and $\theta$ are the polar angles from the orientations $\omega_1$, $\omega_2$ and $\omega$, respectively. The orientations are measured with respect to an arbitrary set of axes fixed in space, called the laboratory frame (LF); the $A(l_1l_2l; r)$ are called the LF harmonic coefficients.

The function $A(\omega_1\omega_2)$ can be expanded in another set of basis functions, which corresponds to choosing a particular LF for which the $z$-axis coincides with $\mathbf{r}$. This yields the $\mathbf{r}$-frame (RF) expansion given by
\[
A(\omega_1\omega_2) = \sum_{l_1l_2m} A(l_1l_2m; r) Y_{l_1m}(\omega_1) Y_{l_2m}(\omega_2), \tag{B 4}
\]
where $m = -m$ and $\omega_1$, $\omega_2$ are now the orientations referred to the RF axes. The $A(l_1l_2m; r)$ are called the RF harmonics and are related to the LF harmonics by
\[
A(l_1l_2m; r) = \sum_{l} \left( \frac{2l+1}{4\pi} \right)^{1/2} C(l_1l_2l; m_1m_2m) A(l_1l_2l; r), \tag{B 5}
\]
\[
A(l_1l_2l; r) = \sum_{m} \left( \frac{4\pi}{2l+1} \right)^{1/2} C(l_1l_2l; m_1m_2m) A(l_1l_2m; r). \tag{B 6}
\]
The relation (B 5) follows trivially from (B 1)–(B 4) by noting that the RF is an LF with $\omega \equiv 0\hat{\mathbf{r}}$; (B 6) follows from (B 5) and the unitarity properties of the CG coefficients.

The usefulness of the expansion (B 1) becomes apparent under Fourier transformation. Let $A(\omega_1\omega_2)$ be the three-dimensional Fourier transform of $A(\omega_1\omega_2)$—i.e.
\[
A(k\omega_1\omega_2) = \int d\mathbf{r} \exp(ik \cdot \mathbf{r}) A(\omega_1\omega_2). \tag{B 7}
\]
Then, clearly $A(k\omega_1\omega_2)$ can be written in the LF expansion
\[
A(k\omega_1\omega_2) = \sum_{l_1l_2} A(l_1l_2l; k) \psi_{l_1l_2}(\omega_1\omega_2\omega), \tag{B 8}
\]
where $\omega$ and $k$ are the orientation and magnitude of the vector $k$; $A(l_1l_2l; k)$ are the LF harmonics of $A(k\omega_1\omega_2)$. The remarkable aspect of the expansions
(B 1) and (B 8) is that \( A(l_1 l_2^l ; r) \) and \( A(l_1 l_2^l ; k) \) are related in the following way:

\[
A(l_1 l_2^l ; k) = 4\pi (i)^l \int_0^\infty j_l(kr)A(l_1 l_2^l ; r)r^2 dr, \tag{B 9}
\]

\[
A(l_1 l_2^l ; r) = \frac{1}{2\pi^2} (-i)^l \int_0^\infty j_l(kr)A(l_1 l_2^l ; k)k^2 dk. \tag{B 10}
\]

Here, \( j_l \) is the spherical Bessel function of order \( l \); (B 9) indicates that \( A(l_1 l_2^l ; k) \) is the Hankel transform of \( A(l_1 l_2^l ; r) \), (B 10) being the inverse transform relation.

One choice of the LF for \( A(k_1 \omega_1 \omega_2) \) is the k-frame (KF) which yields the KF harmonics:

\[
A(k_1 \omega_1 \omega_2) = \sum_{l_1, l_2, m} A(l_1 l_2^m ; k) Y_{l_1m}(\omega_1) Y_{l_2m}(\omega_2). \tag{B 11}
\]

Here \( \omega_1 \) and \( \omega_2 \) are now the orientations of molecules 1 and 2 referred to the KF axes, which of course will in general be different from the RF axes. The LF and KF coefficients of \( A(k_1 \omega_1 \omega_2) \), \( A(l_1 l_2^l ; k) \) and \( A(l_1 l_2^m ; k) \), are related in the same way as the LF and RF coefficients of \( A(r_1 \omega_1 \omega_2) \), viz.

\[
A(l_1 l_2^m ; k) = \sum_T \left( \frac{2l+1}{4\pi} \right)^{1/2} C(l_1 l_2^m ; m_1 m_2 m)A(l_1 l_2^l ; k), \tag{B 12}
\]

\[
A(l_1 l_2^l ; k) = \sum_m \left( \frac{4\pi}{2l+1} \right)^{1/2} C(l_1 l_2^l ; m_1 m_2 m)A(l_1 l_2^m ; k). \tag{B 13}
\]

While there is a direct relation between \( A(l_1 l_2^l ; r) \) and \( A(l_1 l_2^l ; k) \) (B 9), (B 10)), the relation between \( A(l_1 l_2^m ; r) \) and \( A(l_1 l_2^m ; k) \) is an indirect one via (B 12), (B 13), (B 9), (B 10), (B 5) and (B 6).

We require each of the expansions introduced above for the following reasons: the closure relations (SSC, SSCF and PY) are most readily expressed in terms of the LF harmonics of \( h(r_1 \omega_1 \omega_2) \) and \( c(r_1 \omega_1 \omega_2) \); the OZ equation, on the other hand, is most succinctly expressed in terms of the KF harmonics of \( h(k_1 \omega_1 \omega_2) \) and \( c(k_1 \omega_1 \omega_2) \) (see (3.1)). We can summarize the relations among these various expansions schematically as follows:

\[
\begin{align*}
A(l_1 l_2^l ; r) &\leftrightarrow A(l_1 l_2^l ; k) \quad \text{(B 9)} \\
A(l_1 l_2^m ; r) &\leftrightarrow A(l_1 l_2^m ; k) \quad \text{(B 5)} \\
A(l_1 l_2^l ; r) &\leftrightarrow A(l_1 l_2^l ; k) \quad \text{(B 10)} \\
A(l_1 l_2^m ; r) &\leftrightarrow A(l_1 l_2^m ; k) \quad \text{(B 6)} \\
&\quad \text{(B 12)} \quad \text{(B 13)}
\end{align*}
\]

There are further relations—in particular, an alternative relation between \( A(l_1 l_2^l ; r) \) and \( A(l_1 l_2^l ; k) \), see chapter 5 of [1]. However, the scheme (B 14) is sufficient for our present requirements.

In conclusion, we note that expansion in rotational invariants has its origin in the work of Gray [20] and Wertheim [21]; see also Blum [22]. Wertheim introduced a cartesian form of rotational invariants—the functions \( \Delta(\omega_1 \omega_2) \) and \( D(\omega_1 \omega_2) \)—which are related to the present \( \psi_{110}(\omega_1 \omega_2) \) and \( \psi_{112}(\omega_1 \omega_2) \) by trivial multiplicative constants. The rotational invariants \( \phi_{1112}(\omega_1 \omega_2) \) of Blum are also related to the \( \psi_{1111}(\omega_1 \omega_2) \) by trivial multiplicative factors.
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APPENDIX C

Summary of MC simulations

The MC calculations were performed for the DM potential \( u(12) \) given by (1.14) in an NVT ensemble simulation at \( p^* = 0.8 \) and \( T^* = 0.719 \). The system consisted of 128 molecules within a duodecahedronal simulation cell subject to the usual periodic boundary conditions. Each of the simulations began with the particles placed randomly without overlap inside the simulation cell, and the first 25,000 configurations were used to equilibrate the system. Table 2 gives the number of configurations making up each run and the average internal configurational energy obtained from block averages of 1280 configurations.

Table 2. Summary of MC runs.

<table>
<thead>
<tr>
<th>( \delta )</th>
<th>Number of configurations</th>
<th>Average internal energy ((U/N_e))(\dagger)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>1,408,000</td>
<td>(-5.877 \pm 0.091)</td>
</tr>
<tr>
<td>0.25</td>
<td>1,996,800</td>
<td>(-6.270 \pm 0.093)</td>
</tr>
<tr>
<td>0.3</td>
<td>2,662,400</td>
<td>(-6.607 \pm 0.102)</td>
</tr>
<tr>
<td>0.35</td>
<td>1,250,000</td>
<td>(-7.310 \pm 0.132)</td>
</tr>
</tbody>
</table>

\(\dagger\) A LJ tail correction of \(-0.237 \pm 0.05\) has been added to the raw average internal energy obtained directly from the MC simulation.

To monitor each run for bottlenecks and an insufficient number of equilibrating configurations, the internal configurational energy averaged over the last 1280 configurations, the mean squared displacement, and an orientational correlation coefficient were outputted every 1280 configurations. Periodically, the radial distribution function, four LF harmonics and four RF harmonics were calculated and examined for the degree of scatter. At this point, when the harmonics were sufficiently smooth, the calculation was terminated.

Several years ago, Wang et al. [23] calculated the internal configurational energy for several potentials including the DM potential (1.14) to test the

Table 3. Comparison of MC and perturbation theory.

<table>
<thead>
<tr>
<th>( \delta )</th>
<th>((U/N_e)_{\text{total}})</th>
<th>((U/N_e)_{\text{orientational}})</th>
<th>Perturbation theory(\dagger)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>(-6.270 \pm 0.093)</td>
<td>(-0.394 \pm 0.169)</td>
<td>(-0.873)</td>
</tr>
<tr>
<td></td>
<td>((-6.250 \pm 0.169))(\dagger)</td>
<td>((-0.425 \pm 0.182))</td>
<td></td>
</tr>
<tr>
<td>0.35</td>
<td>(-7.310 \pm 0.132)</td>
<td>(-1.434 \pm 0.182)</td>
<td>(-1.710)</td>
</tr>
<tr>
<td></td>
<td>((-7.204 \pm 0.831))(\dagger)</td>
<td>((-1.379 \pm 0.844))</td>
<td></td>
</tr>
</tbody>
</table>

\(\dagger\) The MC results in parentheses and the perturbation theory results are taken from [23]. For the definition of \((U/N_e)_{\text{orientational}}\), see [23].

\(\dagger\) These results differ from those quoted in [23] due to the addition of a LJ tail correction of \(-0.459 \pm 0.05\). This correction, which is appropriate for the system size used in [23], was not included in the earlier study.
accuracy of Gray–Gubbins perturbation theory [24] in determining the internal configurational energy. In those calculations, the length of each simulation run (80,000 configurations) was quite short. Our results for δ = 0.25 and 0.35 are given in Table 3, and compared with the previous simulation results and those of the perturbation theory reported in [23]. Our present results are consistent with the earlier study and alter none of its conclusions; however, due to the much greater length of the simulation runs, the statistical errors have been greatly reduced.

The LF harmonics can be calculated by two methods. The most straightforward method conceptually is by the direct route—that is, calculating $h(l_{pq}; r)$ as ensemble averages inferred from (B.3). The other indirect route is to calculate the RF harmonics as the relevant ensemble averages, and calculate the LF harmonics via (B.6). Recently, Haile and Gray [25] have shown that for two potential models, the indirect route leads to less scatter in the LF harmonics. For all the runs reported here, both the direct and indirect routes were used to calculate $h(220; r)$, $h(222; r)$ and $h(224; r)$. We find, in agreement with Haile and Gray, that the indirect route yields smoother space fixed harmonics.

Note that simulations were performed at δ = 0.35, but there is no discussion of this value of δ in §4. This is because the PY approximation failed to converge adequately at this value of δ.

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REFERENCES


[8] Strictly speaking, there are further contributions to u(12)—in particular, anisotropic dispersion interactions. However, the principles we wish to discuss are illustrated sufficiently well by consideration of the model potential (1.11).
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[15] Thus our numerical method contrasts with Patey’s [5–7] in its treatment of \( j \)-transforms, \( l > 0 \). Patey transforms the \( h(l_1 l_2 l; r) \) and \( c(l_1 l_2 l; r) \) harmonics to related functions introduced by Wertheim [21] defined in such a way that the Fourier transform of these latter functions is equal to the relevant \( j \)-transform of \( h(l_1 l_2 l; r) \) and \( c(l_1 l_2 l; r) \).

[16] Goldman, S., 1979, J. phys. Chem., 83, 3033. The Goldman formula is a ‘best’ statistical fit of available MD data to an analytic functional form. For the state condition reported in this paper, some smoothing of the Goldman \( g_b(r) \) was necessary at \( r \approx \sigma \) and \( r \approx 1.8 \sigma \). The resulting \( g_b(r) \) is within the uncertainty of the MD results.

[17] For low density site-site model fluids, Y. D. Chen and W. A. Steele (1969, J. chem. Phys., 50, 1428) solved the PY approximation using RF harmonics in both the OZ and the closure relations.

[18] For fluids with hard cores, these forms are not equivalent. For a detailed discussion, see Stell, [11 (b)].


[26] Equation (4.4) corresponds to retaining those terms linear in \( f_{pert}(12) \) which do not depend on the reference fluid triplet correlation functions. Equation (4.4) is sometimes referred to in the literature as zeroth order RAM perturbation theory (e.g., Nezbeda, I. and Smith, W. R., 1981, J. chem. Phys., 75, 4060).