Structure and thermodynamics of the dipolar hard sphere fluid from the reference-hypernetted chain equation with minimized free energy

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The reference-hypernetted chain equation, generalized to molecular fluids, is optimized by choosing the reference system so as to minimize the free energy. This procedure, which assures a significant improvement in the internal thermodynamic consistency of the theory, is here applied to a fluid of dipolar hard spheres, using both the complete dipolar potential and one with a reaction field (RF) truncation. We confirm that a recent reformulation of the relation between the dielectric constant $\varepsilon$ and the mean square dipole moment for the RF geometry indeed brings $\varepsilon$ for the truncated potential into reasonably good agreement with the infinite-range values, but that the important correlation functions nevertheless differ qualitatively in their long-range behavior. The method of solving the molecular integral equation, developed earlier, can be applied to other multipolar potentials, or alternatively, to molecules with distributed point charges.

I. INTRODUCTION

The reference-hypernetted chain (RHNC) integral equation,\(^1\) broadened in its scope by the Rosenfeld–Ashcroft\(^2\) insight of an adjustable reference tool, and optimized by requiring this adjustment to minimize the free energy,\(^3\) has proved to be a versatile and reliable tool in the study of simple fluids.\(^3,4\) The formal generalization of the same procedure to molecular fluids is straightforward;\(^5\) as yet, however, no actual calculation for anisotropic potentials has been carried out using this prescription. In this paper, we report the results of applying the optimized RHNC equation to a fluid of dipolar hard spheres.

To the usual difficulties of dealing with the additional degrees of freedom in molecular systems, particles with dipolar interactions add a special problem of their own, that of coping numerically with the comparatively long-ranged nature of this potential. This is particularly troublesome for numerical simulation studies, which most often adapt themselves to the finiteness of the simulated sample by truncation of the intermolecular potential and imposition of toroidal boundary conditions. Ironically, the macroscopic property of central interest for dipolar models, the dielectric constant $\varepsilon$, turns out to be very sensitive to such modifications, with the result that not only has there been some controversy over the correct way to compute $\varepsilon$ in finite geometries so as to simulate bulk values, but in practice the values of $\varepsilon$ that have been reported show discouraging scatter.\(^6\) More recently, rigorous expressions connecting $\varepsilon$ with the equilibrium dipole moment fluctuations in truncated geometries such as the reaction field method have been derived.\(^7,8\) Nevertheless, for the dipolar potential, computer simulation methods have so far played something less than their usual role as makers of touchstones.

Integral equations, on the other hand, can easily deal with such long-range functions as the dipolar potential; their shortcoming instead is that they are inherently approximate, often to an unknown extent until their results can be systematically contrasted with those of simulation studies. In the present context of complementary weaknesses, however, a reliable approximate integral equation can be a valuable aid to the simulation techniques themselves, in that it can provide an independent testbed for the study of the effects of the inevitable modifications of the model potential that the latter must accept. A small effort in this direction is included in this paper.

Recently, Fries and Patey\(^9\) have reported data obtained from the RHNC equation (without optimization) for three thermodynamic states of dipolar hard spheres. They find the results to be in much better agreement with simulation data than those of several earlier theories, especially for the dielectric constant. Here we repeat these calculations for comparison. We further obtain the solution of the optimized RHNC equation for a larger collection of thermodynamic states, using both the complete dipolar potential and the simulation version with reaction field (RF) truncation. In brief, we find that the (proposed) improvements from the optimization condition, here applied to a hard sphere reference system, mainly appear in the mechanical quantities of pressure and compressibility, with the dielectric constant being scarcely affected. Furthermore, we confirm that the recent RF formula for $\varepsilon ^{\dagger}$ brings its value into consonance with that of infinite samples (provided the cutoff distance is large enough), while the correlation functions using RF truncation nonetheless display anomalous long-range behavior.

For the sake of minimal completeness, Sec. II contains a
brief outline of the algorithm used to solve the optimized RHNC equation. (We note that essentially the identical procedure can be applied to other multipolar potentials, or alternatively, to molecules with distributed point charges, as well as to molecules with nonspherical cores.) The results of the calculation for dipolar hard spheres are given in Sec. III.

II. PROCEDURE

The numerical task at hand is to solve the Ornstein–Zernike (OZ) equation

\[ S(12) = \frac{\rho}{4\pi} \int dr_2 \omega_2 C(13) [S(32) + C(32)] , \]

(1)
coupled with the RHNC closure

\[ C(12) = \exp[-\beta\phi(12) + S(12) + B_0(12)] - 1 - S(12) \]

(2)
for the series function \( S(12) \) and the direct correlation function (DCF) \( C(12) \). The potential \( \phi(12) \) and the reference bridge function \( B_0(12) \) are assumed to be given. They are discussed below. With a solution in hand we may then construct the pair distribution function (PDF)

\[ g(12) = \exp[-\beta\phi(12) + S(12) + B_0(12)] , \]

(3)
and determine the thermodynamics of the molecular fluid at density \( \rho \) and temperature \( T = 1/k_B \beta \) through standard quadratures.

The pairs functions such as \( S(12) \) for linear molecules in these equations depend in general on the separation \( r_{12} \) between the molecular centers of mass and on the orientations \( \omega_1 = (\theta_1, \phi_1) \) and \( \omega_2 = (\theta_2, \phi_2) \) of the two molecular axes referred to some arbitrary coordinate frame,

\[ S(12) = S(r_{12}, \omega_1, \omega_2) . \]

(4)
The simplest such representation results from the choice of \( r_{12} \) as the z axis of the coordinate frame, for which now

\[ S(12) = S(r_{12}, \theta_1, \theta_2, \phi_{12}) \]

(5)
can be expanded in spherical harmonics as

\[ S(12) = 4\pi \sum_{l_1, i_{12}, m_{12}} S_{l_1 i_{12} m_{12}}(r_{12}) Y_{l_1 m_1}(\omega_1) Y_{l_2 m_2}(\omega_2) , \]

(6)
where \( m = -m \) and \( \phi_{12} = \phi_1 - \phi_2 \). The calculation is then to determine a finite but sufficient set of the axial \( S_{l_1 i_{12} m_{12}}(r) \) projections. Other orientation-dependent functions are handled similarly.

The solution of the nonlinear equations (1) and (2) is by iteration; the steps constituting one iteration are outlined below. For a more complete presentation of this procedure, as well as additional references, the interested reader is referred to Ref. 10.

(i) Compute the DCF coefficients

From the current set of \( S_{l_1 i_{12} m_{12}}(r) \) coefficients we construct the set

\[ C_{l_1 i_{12} m_{12}}(r) = g_{l_1 i_{12} m_{12}}(r) - \delta_{l_1 i_{12} m_{12} 000} - S_{l_1 i_{12} m_{12}}(r) , \]

(7)
using Eqs. (2) and (3), where

\[ g_{l_1 i_{12} m_{12}}(r) = \frac{1}{4\pi} \int d\omega_1 d\omega_2 g(12) Y_{l_1 m_1}(\omega_1) Y_{l_2 m_2}(\omega_2) \]

(8)
is evaluated with \( n \)-point Gaussian quadratures as

\[ g_{l_1 i_{12} m_{12}}(r) = \frac{1}{n} \sum_{k_1 k_2 \cdots j} w_k w_{k_2} \cdots (r r_{x_{k_2}, x_{k_2}, y_j}) \times P_{l_1 m_1}(x_{k_1}) P_{l_2 m_2}(x_{k_2}) (1 - 1)^m \]

(9)
Here \( x_{k_2} \) and \( y_j \) are the \( n \) zeros of the Legendre polynomial \( P_n(x) \) and Chebyshev polynomial \( T_n(y) \), respectively, the weights \( w_k \) are

\[ w_k = \left( \frac{1}{1 + x_k^2} \right) \left( \frac{1}{1 + x_k^2} \right) \]

(10)
and \( P_{l m}(x) \) is the associated Legendre function normalized to 2. The full angular dependence of \( g(12) \) is obtained through Eq. (3), with \( S(12) \) reconstructed from its coefficients using Eq. (6), which now reads

\[ S(r_{12}, \omega_1, \omega_2) = \sum_{l_1 i_{12} m_{12}} S_{l_1 i_{12} m_{12}}(r_{12}) P_{l_1 m_1}(x_{k_1}) P_{l_2 m_2}(x_{k_2}) (1 - 1)^m \]

(11)

In the present calculation, the dipolar potential is similarly represented while the reference bridge function \( B_0(12) \) has only a spherically symmetric term (see below). All \( r \)-dependent functions are evaluated at the points \( r_j = j \Delta r, j = 1, 2, ..., N_r, \Delta r \).

(ii) Convert to space-fixed frame

The OZ equation is deconvoluted using Fourier transformation. To compute the Fourier transform of \( C(12) \) we must represent it in some coordinate frame other than the axial one. This amounts to generating a new set of space-fixed coefficients from the axial ones by a Clebsch–Gordon (CG) transformation,

\[ C(r_{12} l_{12} l_0) = \left( \frac{4\pi}{2l + 1} \right)^{1/2} \sum_{l m} \langle l m l_0 | l_{12} l_0 \rangle C_{l_1 i_{12} m_{12}}(r) , \]

(12)
where the angular brackets are Clebsch–Gordon coefficients.

(iii) "Lower" the \( l > 0 \) members

The Fourier transform of \( C(r_{12} l_0 l_{12}) \) involves a spherical Bessel function kernel \( j_{l_0}(kr) \). To avoid the complexity of several different transform algorithms, those coefficients with \( l > 0 \) are first "lowered" to new functions \( C^{(0)}(r_{12} l_{12}) \), which can be transformed with a \( j_{l_0}(kr) \) kernel, by repeated application of

\[ C^{(k-2)}(r_{12} l_{12}) = C^{(k)}(r_{12} l_{12}) - (2k - 1) r^{k-2} \]

\[ \times \int R \frac{C^{(k)}(r_{12} l_{12})}{x^{k-1}} , \]

(13)
starting from \( C^{(0)}(r_{12} l_{12}) \). In the present calculation, the coefficients of \( C(12) \) have a finite discontinuity at the core diameter which must be taken into account in evaluating Eq. (13). The trapezoidal rule is used to evaluate the integral.
(iv) Compute Fourier transforms

The transforms
\[ \tilde{C}(k; l_1 l_2) = 4\pi \int_0^\infty dr \ r^2 C^{(0)}(r; l_1 l_2) j_0(kr) \tag{14} \]
are computed using the fast Fourier transform (FFT). At the core discontinuity, \( C^{(0)}(r; l_1 l_2) \) is assigned its mean value. Fourier transforms are determined at the points \( k_j = j\pi/N, \Delta r, j = 1, 2, ..., N_r - 1.\)

(v) Convert to axial frame

Having obtained the transform of \( C(12) \), we must now solve the OZ equation for the transform of \( S(12) \). This turns out to be simpler if done in terms of an axial set of coefficients, with \( k \) as the \( z \) axis. Thus, we perform another Clebsch–Gordon transformation (the inverse of Eq. (12)) to generate the set
\[ \tilde{C}_{l_1 l_2 m}(k) = \sum_l \langle l m l \bar{m} | l_1 m l_2 \rangle \left( \frac{2l + 1}{4\pi} \right)^{1/2} \tilde{C}(k; l_1 l_2) \]. \tag{15} \]

(vi) Solve the OZ equation for \( \tilde{S}(12) \)

The solution of the OZ equation is now effected as a set of matrix equations,
\[ \tilde{S}_m(k) = (-1)^m [I - (-1)^m \rho \tilde{C}_m(k)]^{-1} [\tilde{C}_m(k)]^2, \tag{16} \]
where the matrices \( \tilde{S}_m(k), \tilde{C}_m(k) \) have elements \( \tilde{S}_{l_1 l_2 m}(k), \tilde{C}_{l_1 l_2 m}(k) \), respectively, with \( l_1, l_2, m \geq m \).

(vii) Convert to space-fixed frame

We now seek to Fourier invert \( \tilde{S}(12) \) to get \( S(12) \). Again, this requires a nonaxial frame of reference, so the axial coefficients \( \tilde{S}_{l_1 l_2 m}(k) \) are converted to a space-fixed set through another CG transformation,
\[ \tilde{S}(k; l_1 l_2) = \left( \frac{4\pi}{2l + 1} \right)^{1/2} \sum_m \langle l_1 m \bar{m} | l_2 \rangle S_{l_1 l_2 m}(k) \]. \tag{17} \]

(viii) Compute inverse Fourier transforms

We can now perform the Fourier inversion to get
\[ S^{(0)}(r; l_1 l_2) = \frac{1}{2\pi^2} \int_0^\infty dr \ r^2 \tilde{S}(k; l_1 l_2) j_{0}(kr) \tag{18} \]
using again the FFT algorithm.

(ix) "Raise" the \( l > 0 \) members

As the inverse of Eq. (14), Eq. (18) generates the lowered version of the \( S(12) \) coefficients. These must next be raised by the inverse of the operation in Eq. (13). This is
\[ S^{(k)}(r; l_1 l_2) = S^{(k-2)}(r; l_1 l_2) \]
\[ -\frac{2k - 1}{r^{k+1}} \int_0^\infty dx \ x^k S^{(k-2)}(x; l_1 l_2) \], \tag{19} \]
applied recursively until reaching \( k = l \). To avoid magnifying quadrature errors at small \( r \) upon dividing by \( r^{k+1} \), the integral in Eq. (19) is evaluated using a modified trapezoidal rule, whereby only \( S(x) \) is fitted by linear interpolation.

(x) Convert to axial frame

The final step completing one iteration is to generate the new axial projections of \( S(12) \) by a CG transformation like that of Eq. (15),
\[ S_{l_1 l_2 m}(r) = \sum_m \langle l_1 m l \bar{m} | l_2 \rangle \frac{2l + 1}{4\pi} \tilde{S}(r; l_1 l_2) \]. \tag{20} \]
Here a test is made of the differences between the new and old axial coefficients of \( S(12) \); if they are not small enough, we return to step (1). To speed the convergence, we have adopted Gillan's\(^13\) method of performing Newton–Raphson iterations, but for simplicity only for the dominant radial term \( S_{00}(r) \). Broyles'\(^4\) method of mixing iterations is also helpful in coaxing convergence in the more stubborn cases.

The dipolar hard sphere potential is
\[ \phi(12) = \phi_{HS}(r) + \phi_{DD}(12), \tag{21} \]
where
\[ \phi_{HS}(r) = \infty, \quad r < \sigma \]
\[ = 0, \quad r > \sigma \tag{22} \]
for hard spheres of diameter \( \sigma \), and where the dipole–dipole part \( \phi_{DD}(12) \) has axial coefficients
\[ \phi_{n0}(r) = -\frac{2}{3} \frac{\mu^2}{r}, \tag{23} \]
\[ \phi_{11}(r) = \frac{2}{3} \frac{\mu^2}{r}, \]
with \( \mu \) the dipole moment. The leading nonvanishing axial coefficients of, say, \( S(12) \) are then (arranged in \( S_m \) matrix format):
\[
\begin{array}{ccc}
S_{00} & \cdots & S_{30} \\
S_{10} & \cdots & S_{31} \\
S_{20} & \cdots & S_{32} \\
S_{30} & \cdots & S_{40} \\
S_{11} & \cdots & S_{31} \\
S_{21} & \cdots & S_{32} \\
S_{31} & \cdots & S_{41} \\
S_{22} & \cdots & S_{42} \\
S_{32} & \cdots & S_{43} \\
S_{42} & \cdots & S_{44} \\
S_{33} & \cdots & S_{44} \\
\end{array}
\]
By symmetry, \( S_{l_1 l_2 m}(r) = S_{l_2 l_1 m}(r) = S_{l_1 l_2 m}(r) \) for the nonvanishing coefficients, so the displayed elements are the only independent ones through index 4. The number of coefficients employed in the calculation is determined by the choice of the largest value of \( m \) to be used; for \( m = 0, 1, 2, 3, 4,... \) we need, respectively, \( 1, 3, 7, 13, 22,... \).
coefficients (the cumulative sum in the successive columns above). Our calculation can use all the displayed coefficients; in practice, we find the set of 13 for max \( m = 3 \) to be entirely adequate, as did Fries and Patey\(^9\) for their similar calculation.

The reference system from which \( B_m(r) \) is obtained for use in Eq. (3) is here the hard sphere fluid, as modeled by Verlet–Weis\(^{12}\) and Henderson–Grundke,\(^16\) for spheres of diameter \( \sigma_0 \). The choice \( \sigma_0 = \sigma \) constitutes the usual RHNC approximation.\(^1\) The reference system can be optimized, however, by treating \( \sigma_0 \) as a variable parameter\(^2\) and requiring that its choice satisfy the constraint\(^3\)

\[
\rho \int dr [g_{00}(r) - g_0(r)] \sigma_0 \frac{\partial B_m(r)}{\partial \sigma_0} = 0, \tag{24}
\]

where \( g_{00}(r) \) is the radial part of the dipolar hard spheres PDF and \( g_0(r) \) the reference PDF. This condition for \( \sigma_0 \) has two effects. First, it minimizes the free energy functional associated with the RHNC equation and, second, it removes the inconsistency, otherwise present in the RHNC approximation, between the pressure obtained by differentiation of the free energy and that obtained from the virial theorem.

For simple fluids, Eq. (24) is further found in practice to improve the computed results.\(^3,4\)

General expressions\(^12\) for the internal energy \( U \) and the pressure \( p \) become, for dipolar hard spheres,

\[
\beta U / N = 2\pi \rho \int_0^\infty dr r^2 [g_{110}(r)\beta \phi_{110}(r) + 2g_{111}(r)\beta \phi_{111}(r)] \tag{25}
\]

and

\[
\beta p / \rho = 1 + \frac{3}{2} \pi \rho \sigma^3 g_{000}(\sigma) + \beta U / N, \tag{26}
\]

while the isothermal compressibility \( \chi \) is given by the usual expression

\[
\rho k_B T \chi = \left[ 1 - 4\pi \rho \int_0^\infty dr r^2 C_{000}(r) \right]^{-1}. \tag{27}
\]

The RHNC equation provides the free energy \( A \) in the form\(^11\)

\[
\beta A / N = \beta A_0 / N + (\beta \Delta A / N - \beta \Delta A_0 / N), \tag{28}
\]

where \( A_0 \) is the reference system free energy and

\[
\beta \Delta A / N = \frac{1}{2} \int \frac{d \mathbf{k}}{(2\pi)^3} \left\{ \ln \det(I + \rho \mathbf{h}(k)) - \rho \text{Tr} \mathbf{h}(k) \right\}.
\]

\[
\beta \Delta A_0 / N = \frac{1}{2} \int \frac{d \mathbf{k}}{(2\pi)^3} \left\{ \ln(1 + \rho \mathbf{h}_0(k)) - \rho \mathbf{h}_0(k) + \rho^2 \mathbf{h}_0(k) [\frac{1}{2} \mathbf{h}_0(k) - \mathbf{S}_0(k)] \right\}.
\]

\[
(\epsilon - 1)(2\epsilon + 1) = yg, \tag{31}
\]

with

\[
y = 4\pi \rho \beta \mu y^2 / 9 \]

\[
g = 1 + \frac{1}{2} \rho \mathbf{h}^{110}(0), \tag{32}
\]

and from the asymptotic form\(^18,19\)

\[
h^{112}(r) \sim \frac{(\epsilon - 1)^2}{4\pi \rho \epsilon v^3}. \tag{33}
\]

In these expressions, we have introduced variants of the space-fixed coefficients defined by the CG transformation, Eq. (12) to conform with common usage. Specifically, we have

\[
h^{110}(r) = -3^{1/2}(r10) = h_{110}(r) - 2h_{111}(r), \tag{34}
\]

\[
h^{112}(r) = (\eta)^{1/2}(r12) = h_{110}(r) + h_{111}(r), \tag{35}
\]

and similarly for the transforms. [These functions have also been called \( h_{11}(r) \) and \( h_{12}(r) \), respectively, in many works.] As noted, Eqs. (31) and (33) should produce the same value for the dielectric constant, which provides a useful internal check on the calculation. [For large values of \( \mu \), however, Eq. (31) is the more reliable numerically.] It should be remarked that the transform at \( k = 0 \) in Eq. (32) must be calculated from those of the corresponding \( C^{110}(0) \) and \( \tilde{S}^{110}(0) \) obtained by step (vi) of the procedure outlined above; the direct evaluation of \( \tilde{h}^{110}(0) \) by integrating over \( h^{110}(r) \) is numerically unreliable. This is especially true for the truncated potential discussed next.

Simulation methods using toroidal boundary conditions\(^4\) must, as noted earlier, use potentials of finite range, enforced by truncation if necessary. The reaction field method of Barker and Watts\(^20\) is an attempt to heal the effects of this cutoff of the dipolar potential that is equivalent\(^21\) to an effective dipole–dipole interaction with axial coefficients

\[
\phi_{110}^{\text{ef}}(r) = \phi_{110}(r) - \frac{\mu^2}{3R_c^3}, \tag{36}
\]

\[
\phi_{111}^{\text{ef}}(r) = \phi_{111}(r) + \frac{\mu^2}{3R_c^3}, \quad r < R_c
\]

and

\[
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\]

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\[ \phi_{110}^{\text{eff}}(r) = 0, \]
\[ \phi_{111}^{\text{eff}}(r) = 0, \quad r > R_c, \]
where
\[ f = \frac{2(\varepsilon_{\text{RF}} - 1)}{2\varepsilon_{\text{RF}} + 1}, \]
and \( R_c \) is the cutoff separation, while \( \varepsilon_{\text{RF}} \) is the dielectric constant of the infinite continuum surrounding the truncation sphere. For this interaction, Eq. (33) is no longer valid and Eq. (31) must be replaced with \(^{14}\)
\[ \frac{(e - 1)(2e_{\text{RF}} + 1)}{3(e + 2e_{\text{RF}})} = yg, \]
with \( g \) still determined by Eq. (32). The other thermodynamic formulas are not affected by this change, with the exception of the pressure, which picks up an additional contribution from the new delta function in \( \phi'(12) \) at \( r = R_c \).

This is a small effect which has been included in the data reported below. The new discontinuities in \( C(12) \) and \( g(12) \) at \( r = R_c \) also call for special treatment in integrals such as those of steps (iii) and (iv).

**III. RESULTS**

The iterative solutions were typically started from the converged solution of a neighboring thermodynamic state and continued until the largest difference between successive iterates of \( sS_{110}(r) \) was less than \( 10^{-5} \) for all 13 coefficients used. With Gillan's method\(^{19}\) accelerating the convergence of \( sS_{100}(r) \), the last coefficient to converge was generally \( sS_{110}(r) \). To ensure a sufficient range, we used \( N_r = 1024 \) points with an interval \( \Delta r = 0.02\sigma \) in the solutions with the complete dipolar potential. With the truncated potential, an adequate range is more of a problem and the number of points was doubled to 2048 with the same grid size. The Gaussian quadratures of step (i) were done with \( n = 10 \).

The computed thermodynamic properties of the dipolar hard sphere fluid at density \( \rho \sigma^3 = 0.8 \) are shown in Table I for seven values of the reduced dipole moment. Results from both the usual RHNC equation (\( \sigma_0 = \sigma \)) and the optimized RHNC equation (\( \sigma_0 < \sigma \)) are given, with the value of \( \sigma_0 \) needed to satisfy Eq. (24) also tabulated. The greatest effect of the optimization is on the radial functions, which is reflected here in the larger changes it produces in the computed pressure and compressibility. The dielectric constant, on the other hand, is scarcely affected. The first few axial projections of \( g(12) \) and \( h(12) \) are shown, respectively, in Fig. 1 and as the solid curves in Fig. 2 for the (optimized) case at \( \rho \sigma^3 = 0.8 \) and \( \beta \mu^2 / \sigma^3 = 2.0 \).

Computed properties for the truncated potential, Eq. (35), with \( R_c = 4.5\sigma \) and \( \varepsilon_{\text{RF}} = 50 \), obtained from the optimized RHNC equation are listed in Table II. There is generally excellent agreement with the corresponding data in Table I, including quite good correspondence of the dielectric constant computed using Eq. (37) with the infinite sample value from Eq. (31) for the first two states of Table II. For the last state with the largest dipole moment there is significant difference in \( \varepsilon \). To check if this is due to the cutoff

![FIG. 1. Axial coefficients of g(12) for the dipolar hard sphere fluid at \( \rho \sigma^3 = 0.8 \) and \( \beta \mu^2 / \sigma^3 = 2.0 \), obtained from the optimized RHNC equation. Results for the complete and truncated potentials are identical on this scale.](http://jcp.aip.org/jcp/copyright.jsp)
separation of $4.5\sigma$ becoming more inadequate as $\mu$ increases, as seemed likely, we have recomputed this state using $R_c = 6.0\sigma$ with other parameters unchanged. The effect of this on $\epsilon$ is indeed large and is seen to move the finite sample value much closer to the bulk value. Such an increase in $R_c$ would require roughly a doubling of the sample size (number of molecules) in a computer simulation.

While the reaction field correction does produce a dielectric constant in consonance with that of an infinite sample, the long-range behavior of the correlation functions for the truncated potential is nevertheless anomalous. This would not at all be evident on the scale of Fig. 1, which indeed could as well be that of the truncated potential data. It shows up strikingly, however, in the short-range behavior of some Fourier transforms, as seen in Fig. 2, where the dashed curves are for the RF potential. For very small $k$, the axial coefficients most significant for the dipole potential,