Reference-hypernetted chain equation with anisotropic bridge function for fluids of diatomic molecules

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Modeling the bridge function in the reference-hypernetted chain equation with that of a hard-sphere fluid has proven to be highly successful for simple liquids, particularly when the reference-hard-sphere diameter is treated as an adjustable parameter. In this paper, we examine the generalization of this technique to liquids of diatomic molecules, with the reference bridge function taken from that of the corresponding hard-diatomic-molecule fluid. Specifically, the diatomic molecules of the system of interest interact through an atom–atom Lennard-Jones potential while the hard-diatomic-reference model is solved in Percus–Yevick approximation. We find that variation of the sphere diameter of the hard-diatomic molecule makes possible excellent agreement with simulation results for the two-center Lennard-Jones fluid, just as it does for simple fluids.

I. INTRODUCTION

Ideally, techniques and equations developed for the study of simple liquids should be transferable to the more complex molecular liquids[1] without additional approximations, even if not without additional effort. Thus, e.g., the Ornstein–Zernike (OZ) equation with arbitrary closure can be solved for arbitrary molecular potentials in a straightforward manner.[2] This solution algorithm has been used in earlier work to solve the reference-hypernetted chain[3] (RHNC) equation fluids of hard-diatomic molecules[4] and dipolar hard spheres.[5] In both these cases, the reference system for the bridge function was a fluid of hard spheres. While this choice seems reasonable for the dipolar hard spheres case, it is less plausible for hard-diatomic molecules, since the dominant repulsive potential is there itself anisotropic. These intuitive expectations are borne out by the quality of the results obtained.[4,5] In this brief note, we examine the effect of generalizing the reference system bridge function so as to reflect the short-range anisotropy of the system of interest.

This system is here a fluid of diatomic molecules interacting through an atom–atom Lennard-Jones potential, for which Monte Carlo (MC) data are available.[6] The logical reference model for such a system is a fluid of hard-diatomic molecules. Adopting Rosenfeld and Ashcroft's[7] insight on reference system properties, both the interatomic separation $l_{\rm HD}$ and hard-sphere diameter $\sigma_{\rm HD}$ of the hard-diatomic molecule may be treated as variable parameters, to be chosen by some prescription. For computational simplicity, however, only the sphere diameter $\sigma_{\rm HD}$ is varied in the present work, which is intended as illustrative, rather than exhaustive. Even so, we find that excellent agreement with simulation results can be obtained in this way.

II. CALCULATION

The RHNC approximation is defined by the closure

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

coupled with the OZ equation for linear molecules[1]:

$$S(12) = \frac{\rho}{4\pi}\int d\mathbf{r}_3\, d\omega_3 [S(13) + C(13)]C(32), \qquad (2)$$

which are to be solved for the series function $S(12) = g(12) - 1 - C(12)$. In these equations, $g(12)$ is the usual pair distribution function of the molecular fluid[1] at density ρ and temperature $T = (k_B\beta)^{-1}$, $C(12)$ the corresponding direct correlation function, $\phi(12)$ the intermolecular potential energy, and $B_0(12)$ the molecular bridge function obtained from a reference system with potential $\phi_0(12)$.

As noted, we are interested in the model of diatomic molecules defined by atom–atom Lennard-Jones interactions, which have been extensively studied with numerical simulation techniques by Streett and Tildesley.[6] The question addressed here is whether the successful modeling of the reference bridge function $B_0(12)$ that has been developed for simple fluids[7–9] can be generalized to such diatomic molecular fluids. It seems clear that to do so the reference potential should reflect the same steric repulsion as the potential of interest. Thus, just as the hard-sphere fluid is the primitive model for all simple liquids, we may take the hard-diatomic fluid as the elementary model for all diatomic liquids.

The hard-diatomic fluid, with distance parameters $l_{\rm HD}$ and $\sigma_{\rm HD}$ for the interatomic separation and sphere diameter, respectively, is treated in Percus–Yevick[1] (PY) approximation, which yields the bridge function in the form

$$B_0(12) = \ln[1 + S_0(12)] - S_0(12). \qquad (3)$$

Here the reference series function $S_0(12)$ is reconstructed from the computed axial coefficients $S^{(0)}_{l_1 l_2 m}(r)$ through the standard expansion

$$S_0(12) = 4\pi \sum_{l_1 l_2 m} S^{(0)}_{l_1 l_2 m}(r_{12}) Y_{l_1 m}(\omega_1) Y_{l_2 \underline{m}}(\omega_2), \qquad (4)$$

where $\underline{m} = -m$, while the needed axial harmonic coefficients of $B_0(12)$ are in turn obtained by the numerical evaluation[2] of

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TABLE I. Computed pressure and internal energy of fluid of Lennard-Jones diatomic molecules as a function of the reference system sphere diameter σ_{HD} for the state $\rho d^3 = 0.869$, $k_B T/\epsilon = 2.36$, and $l/\sigma = 0.5741$.

σ_{HD}/σ	$p\sigma^3/\epsilon$	$U/N\epsilon$
1.00	0.13	−12.48
0.96	1.79	−12.11
0.94	2.41	−11.97
0.93	2.68	−11.91
0.92	2.97	−11.84

$$B^{(0)}_{l_1 l_2 m}(r_{12}) = \frac{1}{4\pi}\int d\omega_1\, d\omega_2 \times B_0(12)\, Y^*_{l_1 m}(\omega_1)\, Y^*_{l_2 m}(\omega_2). \quad (5)$$

These coefficients are then used in the solution of the RHNC equation for the two-center Lennard-Jones fluid. The algorithm for these calculations is described in Refs. 2 and 4.

To illustrate the effect of these $B_0(12)$ coefficients, we have solved the RHNC equation for the Lennard-Jones diatomic molecule fluid at the relatively high density

$$\rho d^3 = \rho\sigma^3\left[1 + \frac{3}{2}\frac{l}{\sigma} - \frac{1}{2}\left(\frac{l}{\sigma}\right)^3\right] = 0.869, \quad (6)$$

with $k_B T/\epsilon = 2.36$ and $l/\sigma = 0.5471$. Here l, σ, and ϵ are, respectively, the interatomic separation and usual Lennard-Jones distance and energy scales of the diatomic molecule. The resulting pressure p and internal energy U are shown in Table I for various values of σ_{HD}. (The length l_{HD} was set equal to l in all cases.) As with simple fluids, it is clear that the pressure is particularly sensitive to changes in the reference model. These results were obtained using five spherical harmonic coefficients in the expansions which are evaluated at 256 points with a grid interval $\Delta r/\sigma = 0.04$.

Comparing the computed results in Table I with the Monte Carlo[6] values cited in Table II, we see that the best agreement occurs for σ_{HD}/σ around 0.93. Refining the calculation by going to 14 coefficients evaluated at 512 points with $\Delta r/\sigma = 0.02$, we arrive finally at the values given in Table II for $\sigma_{HD}/\sigma = 0.931$. We include in this table the corresponding values obtained from a separate solution of the PY equation for the same Lennard-Jones molecular model. Clearly, it is possible to duplicate for molecular liquids the successful use of a variable reference system developed earlier for simple liquids.

The improvement extends to the pair correlation function as well. We show in Fig. 1 the first few axial coefficients of $g(12)$ for the same three cases of Table II. We note that a

TABLE II. Pressure and internal energy of a fluid of Lennard-Jones diatomic molecules for the state of Table I. The RHNC results were obtained with $\sigma_{HD}/\sigma = 0.931$.

	$p\sigma^3/\epsilon$	$U/N\epsilon$
MC	2.65	−11.89
RHNC	2.655	−11.91
PY	3.958	−11.73

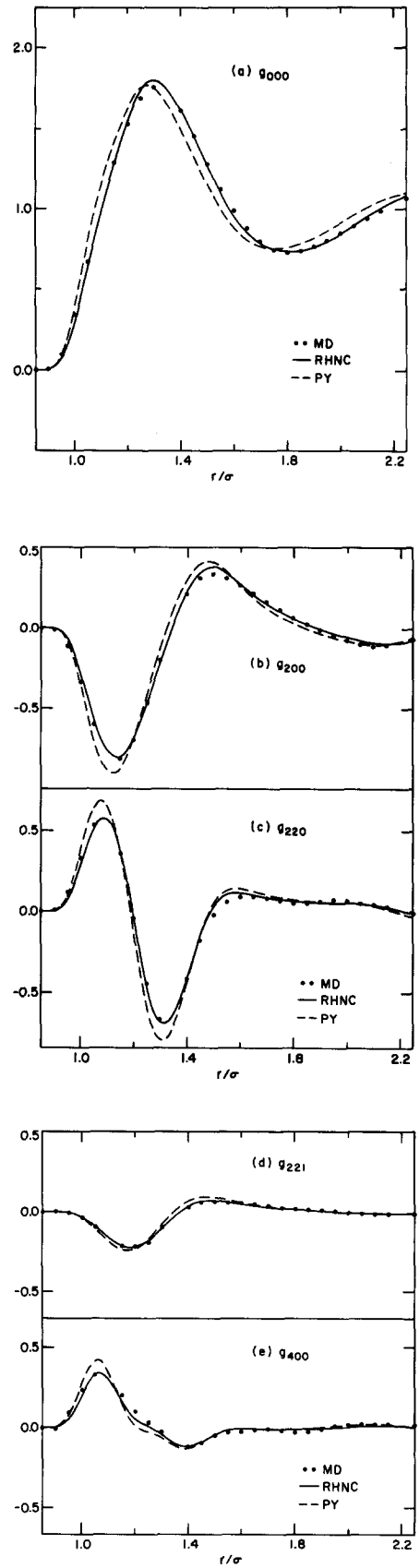

FIG. 1. (a) Radial part of the pair distribution function $g(12)$ for a fluid of Lennard-Jones diatomic molecules for the state $\rho d^3 = 0.869$, $k_B T/\epsilon = 2.36$, and $l/\sigma = 0.5741$. (b), (c) Higher coefficients of the pair distribution function $g(12)$ for a fluid of Lennard-Jones diatomic molecules for the state of Fig. 1(a). (d), (e) Higher coefficients of the pair distribution function $g(12)$ for a fluid of Lennard-Jones diatomic molecules for the state of Fig. 1(a).

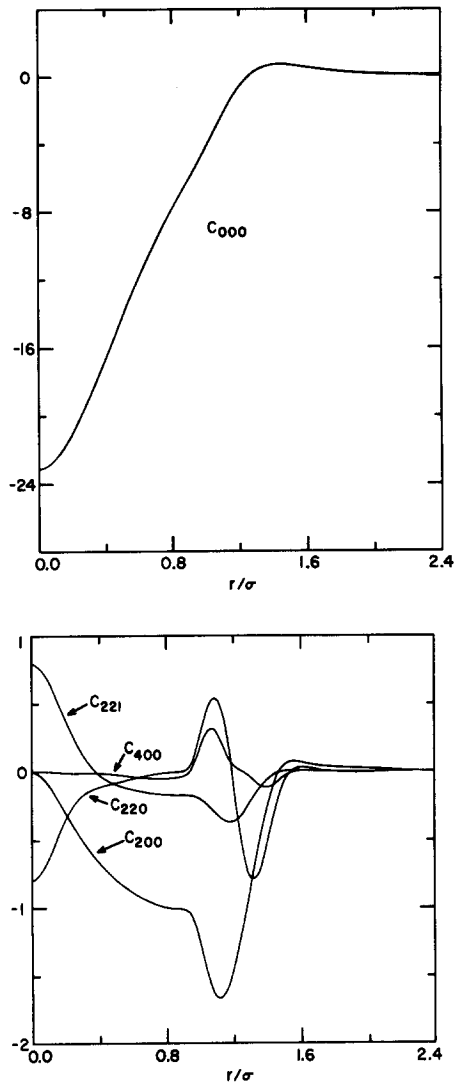

FIG. 2. (a) Radial part of the direct correlation function $C(12)$ for a fluid of Lennard-Jones diatomic molecules from the RHNC equation for the state of Fig. 1(a). (b) Higher coefficients of the direct correlation function $C(12)$ for a fluid of Lennard-Jones diatomic molecules from the RHNC equation for the state of Fig. 1(a).

subsidiary benefit of an accurate RHNC calculation is that it also provides an accurate set of coefficients of the direct correlation function $C(12)$, which are needed in modern density functional theories of phase transitions[10] and are not available from simulation. Figure 2 displays the same subset of these coefficients of $C(12)$.

The calculation as described above is relatively tedious, in that a separate integral equation must be solved for the reference system. An alternative procedure would be to use instead a modeled solution of the PY equation for hard diatomics. While such an analytic solution is not yet available, an empirical fit to $C_0(12)$ proposed by Pynn[11] has proven highly successful[12] and can be used for this purpose.

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