Use of the Ornstein-Zernike Percus-Yevick equation to extract interaction potentials from pair correlation functions

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(Received 22 March 2010; published 28 June 2010)

In this work, we test the ability of the Ornstein-Zernike equation in the Percus-Yevick approximation (OZPY) to generate interaction potentials from pair correlation functions (PCFs) of monatomic and diatomic Lennard-Jones fluids. The PCFs are generated by solving OZPY equation (monatomic fluid) and molecular-dynamics (MD) simulations (diatomic fluid). Since the interaction potentials are inputs in the OZPY method and the MD simulation, the extraction of the potential from the PCFs using OZPY is a test of self-consistency. This test is necessary if the procedure is to be used to generate coarse-grained (CG) potentials from PCFs. We find that the procedure is completely self-consistent for the monatomic fluid in the whole range of densities studied (reduced density up to 0.55, under reduced temperature of 2.0). In the diatomic case, we find that the procedure is generally self-consistent under both low and high densities, although there is a systematic deviation at high densities. The method is able to reproduce the two parameters (ε and σ) of the input Lennard-Jones potential model to within about 1%. This CG potential generating procedure can be straightforwardly extended to more complicated molecules.

DOI: 10.1103/PhysRevE.81.061204

PACS number(s): 61.20.Ja, 61.20.Gy, 05.10.—a

I. INTRODUCTION

In the development of coarse-grained (CG) potentials for polymers, one can perform the complete atomistic molecular-dynamics (MD) simulation (for which the interaction potentials are known) for a system of short chains and, based on the mapping of CG particles to the center of mass of polymer fragments, generate pair correlation functions (PCFs) for stretching, bending, torsion, and nonbonded interactions between CG particles. One then must extract the CG interaction potential for each mode from each PCF. For the stretching, bending, and torsion modes, there are straightforward approximations that relate the interaction potential directly to the PCF. For example, for the stretching mode, via the interaction energy between a particle of type α and a particle of type β, ϕαβγ as a function of the separation between particles, r, can (with proper validation) be related to the stretching pair correlation function gαβγ(r) via

\[
ϕ_{αβγ}(r) = -k_B T \ln \left[ g_{αβγ}(r) \right] + c_{αβγ},
\]

where \( k_B \) is the Boltzmann constant, \( T \) is the temperature, and \( c_{αβγ} \) is a constant. Similar expressions apply to the bending and torsion modes [1–3].

For the nonbonded interactions, this level of approximation is inadequate because the pairwise potential can give rise to large higher-order correlations. Thus, there is a need to develop a rigorous way to extract a CG nonbonded potential from the PCF.

There are two major methods currently used to extract the nonbonded CG potentials. First, the parameters of an analytical potential such as Lennard-Jones (L-J) are adjusted to closely reproduce the target PCF in the atomistic liquid or melt. Work of Harmandaris et al. [1,2,4] on coarse-grained modeling of polystyrene represents this approach in which target chain molecules are separated into fragments, so that the nonbonded interaction between different fragment types \{α, β, …\} is based on the fragment corresponding PCF, \( g_{αβγ} \). A problem with this method is that the difference of conformations and orientations between fragment molecules and target molecules may not be reflected correctly on the corresponding coarse-grained potentials [3,5]. For example, the conformations of phenol rings in liquid benzene and that in polystyrene (PS) melt where the rings are embedded into a long chain may be different. Consequently, these conformations would be misrepresented in the CG potential.

In the second method, a tabulated potential is numerically determined by iterative Boltzmann inversion [6]. The interaction potential is refined iteratively via

\[
ϕ_{αβγ}(r) = ϕ_{αβγ}(r) + k_B T \frac{g_{αβγ}(r)}{g_{αβγ}(r)},
\]

where \( g_{αβγ}(r, r') \) is the target PCF. The convergence of the procedure is guaranteed by the fact that there is a unique functional relationship between the PCF and the pairwise-additive potential. Potentials obtained from this procedure will closely reproduce the CG atomistic liquid PCFs. Using this method, Kamio et al. [7] performed CG end bridging Monte Carlo simulations of poly(ethylene terephthalate) melt and obtained CG melt density, characteristic ratio, and other conformational properties that agree with experiment. The challenging part of this method is obtaining PCFs from simulations in each iteration. As mentioned by Guenza [8], those simulations have to be performed on length scales and time scales large enough to ensure a reliable numerical predictions of the potential at the length scale characteristic of the

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coarse-graining procedure. This could strongly limit the computational gain of CG procedure. Thus, extraction of the nonbonded interaction potential for CG models remains an important problem.

We present an alternative procedure based on the Ornstein-Zernike equation with the Percus-Yevick approximation (OZPY) to extract the CG nonbonded potential from the PCFs. This method is approximate only because of the approximate nature of the Percus-Yevick (PY) assumption for the direct correlation function. On the other hand, it is simple and fast compared to methods of comparable accuracy. It is a step forward from Eq. (1) in theoretical rigor; it acknowledges the influence of interactions with surrounding particles that should be present in the determination of pairwise potentials from the PCF.

The OZPY equation is typically used to generate PCFs given the interaction potential. We refer to this as the OZPY procedure. The use of the OZPY equation to extract the interaction potential from the PCFs will be called inverse OZPY or OZPY$^{-1}$. Before the OZPY$^{-1}$ procedure can be applied to the development of CG potentials, it must first demonstrate the capability to reproduce known results. To this end, we apply it to two fluids: a monatomic Lennard-Jones fluid and a flexible diatomic Lennard-Jones fluid. We point out that while the OZPY is nonlinear in the PCF, it is linear in the exponential of the interaction potential, making the inverse OZPY equation relatively straightforward to solve.

The OZPY theory is well established for simple fluids, both pure and in mixtures. The challenging part of OZPY$^{-1}$ is formulating the OZPY theory to account for the presence of a stretching potential between some of the atoms. The Ornstein-Zernike (OZ) integral has been under study for several decades in the fields of monatomic, diatomic, and polyatomic fluids theories. Most of the research focuses on the calculation of structural properties of the fluids. A literature survey shows that OZPY gives results that match well the PCFs from molecular simulation of low-density monatomic fluids but deviate at high density [9]. For this reason, Verlet and Weis [10] proposed several empirical corrections. Tang and Lu [11] and Bravo Yuste et al. [12] developed improved expressions that can reproduce the simulation data. These expressions are somewhat more cumbersome than the PY approximation. In the diatomic case, a numerical procedure [13] and sophisticated models [14,15] have been developed to solve the OZ equation to exactly reproduce the structural properties of diatomic Lennard-Jones [13,15] and hard dumbbell fluids [14].

The application of integral equation theories to polymers has a long history [16,17] and continues to be used in the development of modern multiscale models of polymers [18,19]. The polymer reference interaction site model (PRISM) [20,21] has become the most fully developed and widely used integral equation approach [22], with areas of application that include polymer solutions [23], colloid-polymer suspensions [24], and CG procedures [8,21,22,25]. Most of these applications are related to the calculation of structural properties such as PCFs [21,22] or other correlation functions [8,25].

In the application to CG potentials, Zhao et al. [22] adopted an approach similar to iterative Boltzmann inversion method to obtain the two optimized parameters of a CG Lennard-Jones potential model of atactic PS melt, using PRISM to calculate intermolecular PCFs with intramolecular PCFs with atomistic MD simulation as input. Since it is still a numerical procedure, it suffers the same disadvantage as the iterative Boltzmann inversion method.

The OZPY equation [26,27] used here is relatively simple and can be easily inverted. The use of OZPY$^{-1}$ method [28] to obtain the interaction potential is currently limited to monatomic systems [29–32]. In this paper, we demonstrate that this method can also be applied to the diatomic Lennard-Jones fluid.

To this end, using known atomistic interaction potentials, we generated PCFs for two systems, a monatomic Lennard-Jones fluid and a flexible diatomic Lennard-Jones fluid, in which each atom interacts with other nonbonded atoms via the Lennard-Jones interaction potential. For each system we use the OZPY$^{-1}$ procedure to regenerate the nonbonded interaction potential. Given that the nonbonded interaction potential is known a self-consistency test is provided, establishing the reliability of the procedure for generating CG potentials. Note that we are not generating a CG potential in this work; rather we are reproducing atomistic potentials via the same OZPY$^{-1}$ procedure that could be used to generate a CG potential. The procedure is illustrated in Fig. 1.

II. SIMULATION

For the monatomic fluid, PCFs can be generated either from MD simulation or from solution of the OZPY equation. Using the PCFs from OZPY can provide a cleaner test of the OZPY$^{-1}$ procedure than using them from simulation. Therefore, PCFs used here for monatomic fluid were generated by solving the OZPY integral equation, using an established method and code developed by Lee [27]. Different state points were investigated for the monatomic fluid; the corresponding states vary from low-density gas to high-density liquid. The dimensionless temperature of the simulation was $T^*=2.00$ and the dimensionless densities were $\rho^*=0.005$, 0.15, 0.25, 0.35, 0.45, and 0.55. Classical MD simulations were also run at some of these state points in order to compare the PCFs from simulation and integral equation theory. As a point of reference, the critical point for the Lennard-Jones fluid lies at a reduced temperature of 1.293 and reduced density of 0.313 [33].
For the diatomic fluid, PCFs were generated from classical MD simulations rather than from the OZPY integral equation because of the additional complexity introduced by the internal structure of the molecule. For both the monatomic and diatomic fluids, the MD simulations were performed on an in-house code, using a two-time step reversible RESPA algorithm \cite{34}. The diatomic molecules are fully flexible. The stretching potential is a Hookian equation in its present form implicitly allows for a different potential, when the same particle can interact via different potentials (e.g., stretching or nonbonded). We shall address this shortly.

For the diatomic fluid, we need to modify the OZ equation, so that it can account for some particles interacting via a stretching potential and some particles interacting via a nonbonded potential. In the case of the single-component diatomic fluid investigated here, the summation over \( \gamma \) becomes explicitly a summation over interaction potentials. In order to emphasize this, we rewrite the OZ equation, replacing the \( \alpha \beta \) subscripts with \( \psi \) subscripts,

\[
g_{\psi_1}(r, r') - 1 = c_{\psi_1}(r, r') + \sum_{\gamma} \sum_{\phi_2} \int c_{\phi_2}(r, r'') n_\gamma(r'') \times [g_{\psi_3}(r'', r') - 1] d^3 r''.
\]

There are some ambiguities associated with the PCF of a given potential, when the same particle can interact via different potentials (e.g., stretching or nonbonded). We shall address this shortly.

For the purposes of our work here, we will use this equation to solve for the nonbonded potential, assuming the stretching potential is obtained from Eq. (1). As such \( \psi_1 \) is always the nonbonded potential, while the summations of \( \psi_2 \) and \( \psi_3 \) include both nonbonded and stretching potentials. Some combinations of \( \psi_2 \) and \( \psi_3 \) are not permitted. For the case of a homonuclear diatomic fluid, the three possible combinations are illustrated in Fig. 2 (see also Table I). The

![FIG. 2. (Color online) Schematic of allowed interaction combinations of diatomic case. The three choices for particle 3 are shown for a diatomic molecule. The red springs represent an interaction via stretching. The black lines represent an interaction via the nonbonded potential. Additional atoms are shown for completeness, although they do not appear in the OZPY equation.](image)

### III. Theory

The Ornstein-Zernike integral equation for a mixture of simple fluids is \cite{26}

\[
g_{\alpha\beta}(r, r') = 1 + c_{\alpha\beta}(r, r') + \sum_{\gamma} \int c_{\alpha\gamma}(r, r'') n_\gamma(r'') \times [g_{\psi_2}(r'', r') - 1] d^3 r''.
\]

where the pair correlation function between particles of types \( \alpha \) and \( \beta \) located, respectively, at \( r \) and \( r' \), \( g_{\alpha\beta}(r, r') \), is related to the direct correlation \( c_{\alpha\beta}(r, r') \) and an integral including the interactions of the \( \alpha \) and \( \beta \) particles with a third particle, \( \gamma \), located at \( r'' \) with a singlet density \( n_\gamma(r'') \). There is a summation over \( \gamma \) spanning all types of particles. This equation in its present form implicitly allows for a different interaction potential between each pair of types of particles. In essence, the summation over \( \gamma \) is a summation over interaction potentials.

### Table I. Necessary combinations for single component diatomic case.

<table>
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<th>( \alpha )</th>
<th>( \beta )</th>
<th>( \gamma )</th>
<th>( \alpha\beta )</th>
<th>( \alpha\gamma )</th>
<th>( \gamma\beta )</th>
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<td>N</td>
<td>S</td>
<td>S</td>
<td>SS</td>
<td>No, not in a diatomic system</td>
</tr>
</tbody>
</table>

* Symbol for atom.
* Nonbonded interaction.
* Stretching interaction.
* Nonbonded + nonbonded interaction.
* Stretching + nonbonded interaction.
* Nonbonded + stretching interaction.
third particle can interact with the first via a nonbonded interaction and the second via a nonbonded interaction, (2) with the first via a stretching interaction and the second via a nonbonded interaction, and (3) with the first via a nonbonded interaction and the second via a stretching interaction. The fourth combination, that of the third particle interacting with both the first and second particles via a stretching interaction, does not exist in a diatomic fluid, where each particle has a stretching interaction with one and only one other particle.

The Percus-Yevick approximation expresses the direct correlation function as

$$c_{\phi}(r,r') = g_{\phi}(r,r') \left[ 1 - \exp \left( \frac{\Phi(r,r')}{k_BT} \right) \right]. \quad (5)$$

We follow the convention in defining the cavity function [36] and total correlation function,

$$y_{\phi}(r,r') = g_{\phi}(r,r') \exp \left( \frac{\Phi(r,r')}{k_BT} \right), \quad (6)$$

$$h_{\phi}(r,r') = g_{\phi}(r,r') - 1. \quad (7)$$

Substitution of Eqs. (5)–(7) into Eq. (4) yields the Ornstein-Zernike equation with the Percus-Yevick approximation or the OZPY equation,

$$y_{\phi}(r,r') = 1 + \sum_{\varphi_2} \sum_{\varphi_3} \int c_{\phi_2}(r,r)m(r')h_{\phi_3}(r',r')d^3r'. \quad (8)$$

If the fluid is homogeneous in space, the positions can be replaced with displacements,

$$r = |r - r'|, \quad s = |r' - r''|, \quad t = |r'' - r|, \quad (9)$$

and Eq. (8) can be rewritten as

$$y_{\phi}(r) = 1 + \sum_{\varphi_2} \sum_{\varphi_3} \int c_{\phi_2}(s)n_{\phi_3}(t)dV, \quad (10)$$

where the integral is over all volume. Following Lee [27], it is convenient to convert the volume integral to bipolar coordinates, which yields

$$y_{\phi}(r) = 1 + \sum_{\varphi_2} \sum_{\varphi_3} \frac{2\pi n}{r} \int_0^\infty ds \int_0^{\pi} \int_{\rho}^{\infty} dt \phi_3(t). \quad (11)$$

Substitution of the PY approximation into the integrand yields

$$y_{\phi}(r) = 1 + \sum_{\varphi_2} \sum_{\varphi_3} \frac{2\pi n}{r} \int_0^\infty ds \int_0^{\pi} \int_{\rho}^{\infty} dt \phi_3(t) \times [h_{\phi_2}(s) - y_{\phi_2}(s) + 1] dt \phi_3(t). \quad (12)$$

Conceptually, then we measure all $h_{\phi}(t)$ in the simulation and we solve Eq. (12) for $y_{\phi}(r)$ from which the potential can be directly extracted.

We now resolve the ambiguity of the PCF for a given potential, which was introduced above. The PCF for an arbitrary interaction potential is equal to the number of pairs of particles of types $\alpha$ and $\beta$ interacting via that potential at a distance $r$, averaged over all $\alpha$ particles and normalized by the average density of the $\beta$ particles,

$$g_{\alpha\beta,\phi}(r) = \frac{N_{\phi,\text{pairs}}(r)}{N_\alpha N_\beta} \frac{V(r)}{V} = \frac{N_{\phi,\text{pairs}}(r)}{N_\alpha V(r)} n_{\beta,\phi}, \quad (13)$$

where $V$ is the system volume and $N_\alpha$ and $N_\beta$ are the numbers of particles involved in interaction $\phi$ in the system and we define a component density as $n_{\beta,\phi} = N_\beta/V$, which itself now is tied to a given potential. In a mixture of simple fluids all of the quantities in Eq. (13) are completely unambiguous; the number of particles of types $\alpha$ and $\beta$ are independent of the potential. However, when one looks even at a single-component homonuclear diatomic fluid, the number of $\alpha$ particles is well defined, but the density of $\beta$ particles interacting only with a single given potential is unclear since all $\beta$ particles interact with both stretching and nonbonded potentials. We define an unambiguous pair correlation function, with the local density of particles interacting via interaction potential $\phi$: $g'_{\alpha\beta,\phi}(r)$, which is directly calculated in an MD simulation,

$$g'_{\alpha\beta,\phi}(r) = n_{\beta,\phi} n_{\alpha,\phi}(r) = \frac{N_{\phi,\text{pairs}}(r)}{N_\alpha V(r)}, \quad (14)$$

where $V(r)$ is the volume of the spherical shell. Now the PCF has units of density and there is no ambiguity in the meaning or evaluation of this quantity because $n_{\beta,\phi}$ has been eliminated. This is the local density of particles of type $\beta$ around particles of type $\alpha$ interacting via $\phi$. We define analogous variables for the cavity, total, and direct correlation functions,

$$y'_{\alpha\beta,\phi}(r) = n_{\beta,\phi} y_{\alpha\beta,\phi}(r) = g'_{\alpha\beta,\phi}(r) \exp \left( \frac{\Phi(r)}{k_BT} \right), \quad (15)$$

$$h'_{\alpha\beta,\phi}(r) = n_{\beta,\phi} h_{\alpha\beta,\phi}(r) = g'_{\alpha\beta,\phi}(r) - n_{\beta,\phi}, \quad (16)$$

$$c'_{\alpha\beta,\phi}(r) = n_{\beta,\phi} c_{\alpha\beta,\phi}(r) = g'_{\alpha\beta,\phi}(r) \left[ 1 - \exp \left( \frac{\Phi(r)}{k_BT} \right) \right]. \quad (17)$$

We then recast the OZPY equation in terms of these new variables, where we drop the extraneous $\alpha\beta$ subscripts used in the derivation since in this work we only have one type of particle,

$$y'_{\phi}(r) = n_{\beta,\phi} + \sum_{\varphi_2} \sum_{\varphi_3} \frac{2\pi n}{r} \int_0^\infty ds \int_0^{\pi} \int_{\rho}^{\infty} dt \phi_3(t) \times [h_{\phi_2}(s) - y_{\phi_2}(s) + 1] \int_{\rho}^{\infty} dt \phi_3(t). \quad (18)$$

In this rearrangement, we have introduced $n_{\beta,\phi}$ into Eqs. (16) and (18). For the monatomic case where only nonbonded interactions are present, this density is the density of atoms in the system. For the stretching potential, we used the following function:
For the monatomic case, we solved the OZPY equation, which is linear in \( y'_{g}(r) \). We discretize the radial dimension in increments of 0.05 \( \AA \) and use the trapezoidal rule to evaluate the integrals. We then solve the system of linear algebraic equations for \( y'_{g}(r) \) from which the nonbonded potential is easily obtained from Eq. (15).

**IV. RESULTS**

**A. Simple fluid monatomic molecule**

For the monatomic case, we can obtain the PCF either from MD simulation or from solution of the OZPY equation directly. In Fig. 3, we compare the PCFs from these two methods at reduced densities of 0.55 and 0.9. At the higher density, there is a visible discrepancy between the two methods, attributed to the Percus-Yevick approximation. Up to a density of 0.55 the agreement between simulation and integral equation theory is very good. Similar simulation results are available in Ref. [15]. For the monatomic case, we choose to use the PCF from the OZPY equation as the input into the potential generating procedure. This is the preferred approach because it avoids errors due to disagreements between PY theory and simulation and provides a test of self-consistency for the procedure.

For the monatomic case, we solved the OZPY equation directly to obtain the PCF for reduced densities from 0.005 to 0.55 and a reduced temperature of 2.0. The PCFs are shown in Fig. 4. They are shifted by increments of 0.25 on the \( y \) axis for visual clarity. We see that the low-density PCF reflects a single peak feature that is typical for a low-density monatomic gas. The high-density PCF has two peaks with a more pronounced first peak.

These PCFs were input into the OZPY\(^{-1}\) procedure to obtain the interaction potentials. The interaction potentials are compared with the original Lennard-Jones 12-6 potential in Fig. 5. The potentials are shifted by increments of 0.25 on the \( y \) axis for clarity. As expected, excellent agreement is shown in Fig. 5 for low-density cases. As the density increases there is a small but growing discrepancy between the original potential and the potential from the OZPY\(^{-1}\) procedure, which we attribute to numerical approximations in the evaluation of the integrals. This source of error was confirmed by increasing the size of the discretization and observing that the noise in the data also increased. Generally, we see that the OZPY\(^{-1}\) procedure is able to satisfactorily reproduce the interaction potential.

It is of interest to see where a simple approximation of the nonbonded potential, such as that given in Eq. (1), is valid. In Fig. 6, we compared the potential obtained from Eq. (1), using the PCF from the OZPY method, with the input Lennard-Jones potential. As expected, the two potentials match very well at low densities but deviate at high densities. A simple expression like Eq. (1) fails dramatically at high loading because it introduces one or more longer-ranged repulsive components to the potential that are not part of the

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**FIG. 3.** Comparison of pair correlation functions (PCFs) obtained by solving OZPY equation directly and MD simulation of a Lennard-Jones fluid at \( T' = 2.0, \rho' = 0.55 \) and 0.90; here, \( T' = T/e, \rho' = \rho r^2 \). The data have been shifted in the vertical direction for clarity.

**FIG. 4.** PCFs obtained by solving OZPY equation directly, under \( T' = 2.0, \rho' \) from 0.005 to 0.55. The data have been shifted in the vertical direction for clarity.
repulsive core. If one assumes that there are no three-body interactions in the system, then these repulsive regions in the potential are required to generate the observed structure in the PCF.

Figure 7 shows the cavity function $y_N(r)$ obtained from the OZPY$^{-1}$ procedure. $y_N(r)$ is an important property in the OZPY$^{-1}$ algorithm since it is directly related to the interaction potential. The OZPY$^{-1}$ is very sensitive to this function. A small error in $y_N(r)$ may cause a significant deviation in the potential. Notice that when $g_N(r)$ goes to zero, the definition of $y_N(r)$ becomes ambiguous since the corresponding potential goes to infinity. Approximations from both simulation and theory have been applied to get $y_N(r)$ at short range. Our results for the short-range $y_N(r)$ are similar to those of Law and Buzza [28], who used a two-dimensional predictor-corrector method to obtain the interaction potential of a colloidal monolayer, in which $y_N(r)$ for small $r$ was approximated by hard-sphere fluid theory. The similarity indicates that the short-range $y_N(r)$ is fairly insensitive to the interaction potential, as noted elsewhere [37]. The results for $y_N(r)$ here were calculated directly by the OZPY$^{-1}$, in which $y_N(r)$ is the unknown variable. This reduces the extra computational work on the approximation of $y_N(r)$ in short range.

**B. Diatomic fluid at low density**

In the diatomic case, the stretching and nonbonded radial density functions (RDFs), $g_S'(r)$ and $g_N'(r)$, were generated via MD simulation (of $N_2$). At low density ($T^*=8.3333$ and $\rho^*=0.07341$), the nonbonded RDF has a single peak (Fig. 8). Note that the plateau for the nonbonded RDF is twice the reduced density since we are examining a diatomic molecule. The stretching RDF shows a sharp peak around its equilibrium bond distance ($r_{eq}$). We note that there are relatively few nonzero points in the stretching RDF due to the fact that it is resolved on the same discretization as the nonbonded RDF. The smooth curve is a Gaussian, which is the theor-
FIG. 9. Comparison of nonbonded potentials for the diatomic fluid at $T^*=5.5556$ and $\rho^*=0.5057$. We show the input Lennard-Jones potential, the data from the OZPY$^{-1}$ procedure, and a L-J fit to the data.

FIG. 10. Bonded and nonbonded RDFs obtained from MD simulation of the diatomic fluid at $T^*=5.5556$ and $\rho^*=0.5057$. That Eq. (1) is true for the stretching potential. Equation (1) implies the stretching distribution is independent of the nonbonded distribution. This error can be determined to be small in this case since the stretching potential extracted from Eq. (1) matches the stretching potential used in the MD simulation.

The error could be due to the fact that the MD simulation and the OZPY description of the diatomic fluid are not the same. In other words, the error is a manifestation of the approximation in the integral equation theory. Such errors have been noted before. For example, using the hypernetted chain (HNC) closure, Bresme et al. [13] proved that the bond length and stretching interaction potential could affect the comparison of structural properties of diatomic Lennard-Jones fluids calculated by OZ integral theory with simulation data. This is because solving the OZ integral with HNC closure using a central force model cannot satisfy the condition that the number of bonds per atom is unity, compared with the real diatomic Lennard-Jones fluid. In our inverse proce-

FIG. 11. Comparison of nonbonded potentials for the diatomic fluid under $T^*=5.5556$ and $\rho^*=0.5057$. We show the input Lennard-Jones potential, the data from the OZPY$^{-1}$ procedure, and a L-J fit to the data.

The PCs generated from MD simulations at high density for $(T^*=5.5556$ and $\rho^*=0.5057$) are shown in Fig. 10. The nonbonded RDF shows four peaks within a distance of $5\sigma$. Similar structural features under both low and high densities can be found in the work of Lue and Blankschein [38] in Monte Carlo simulation of a flexible diatomic Lennard-Jones fluid, indicating that our MD simulation correctly captured the structure of the fluid. The peak of $g_{\text{S}}(r)$ is much higher than at low density. We compare the potential from the OZPY$^{-1}$ procedure with the input potential in Fig. 11. The potentials agree well at distances below 1.2 and above 1.7. From 1.2 to 1.3, the extracted potential is slightly low, and from 1.4 to 1.7 it is significantly high. Again, for the stretching interaction, the smooth curve is a Gaussian, which is expected if the stretching mode is independent of the nonbonded interaction.

We now discuss the possible sources of error and their impact. A potential source of error is that we have assumed that Eq. (1) is true for the stretching potential. Equation (1) implies the stretching distribution is independent of the nonbonded distribution. This error can be determined to be small in this case since the stretching potential extracted from Eq. (1) matches the stretching potential used in the MD simulation.

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C. Diatomic fluid at high density

The PCs generated from MD simulations at high density for $(T^*=5.5556$ and $\rho^*=0.5057$) are shown in Fig. 10. The nonbonded RDF shows four peaks within a distance of $5\sigma$. Similar structural features under both low and high densities can be found in the work of Lue and Blankschein [38] in Monte Carlo simulation of a flexible diatomic Lennard-Jones fluid, indicating that our MD simulation correctly captured the structure of the fluid. The peak of $g_{\text{S}}(r)$ is much higher than at low density. We compare the potential from the OZPY$^{-1}$ procedure with the input potential in Fig. 11. The potentials agree well at distances below 1.2 and above 1.7. From 1.2 to 1.3, the extracted potential is slightly low, and from 1.4 to 1.7 it is significantly high. Again, for the stretching interaction, the smooth curve is a Gaussian, which is expected if the stretching mode is independent of the nonbonded interaction.

We now discuss the possible sources of error and their impact. A potential source of error is that we have assumed
In this work, we have demonstrated that the OZPY equation can be used to extract interaction potentials given distribution functions for monatomic and diatomic fluids. In the monatomic fluid case, the procedure is able to reliably reproduce the original Lennard-Jones 12-6 potential up to moderate densities. In the diatomic case, we first obtained the density distributions for stretching and nonbonded interaction sites from classical equilibrium MD simulation of nitrogen under low- and high-density cases. By incorporating the stretching potential into the OZPY equation, we extracted a nonbonded interaction potential which matched the original Lennard-Jones 12-6 potential at low densities. At higher densities, there was a systematic difference between the original potential and that extracted from the OZPY procedure, which we attribute to the PY approximation. However, the short-range portion of the potential is reproduced sufficiently well that the $\varepsilon$ and $\sigma$ parameters can be reproduced to within 1.1% and 1.0%, respectively. This level of accuracy would represent an improvement in the development of coarse-grained potentials. Application to polymeric systems is underway.

ACKNOWLEDGMENTS

This research was supported by the Eastman Chemical Co. and by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering. This research project used resources of the National Institute for Computational Sciences (NICS) supported by NSF under Agreement No. OCI 07-11134-5.

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