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Bridge functions near the liquid-vapor coexistence curve in binary Lennard-Jones mixtures

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We have carried out extensive *NPT* molecular-dynamics simulation studies of binary Lennard-Jones mixtures to calculate directly the bridge function at state points lying in a very narrow single fluid phase region between the vapor-liquid and solid-liquid coexistence lines [Lamm and Hall, Fluid Phase Equilib. **182**, 37 (2001); **194–197**, 197 (2002)]. By varying the density close to the liquid-vapor coexistence line, significant deviations are observed at intermediate distances between the simulated bridge function and two widely used approximate closures in the integral equation theory of liquids, viz. the hybrid mean spherical approximation and the Duh-Henderson closures. The overall qualitative agreement remains the same with small variation in temperature that brings the system closer to either the liquid-vapor or liquid-solid coexistence curve. We also report a comparison of the direct and indirect correlation functions obtained from our simulation studies as well as from the integral equation theory of liquids. Our results emphasize the need for developing new closures applicable to binary fluid mixtures over a wide range of thermodynamic parameters.

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I. INTRODUCTION

The binary Lennard-Jones (LJ) fluids have been widely investigated as model systems to study the structure and dynamics of multicomponent fluids [1–9]. The equilibrium structure of binary LJ fluids [10–12] as well as that of binary LJ solids [13,14] has been studied in detail. A variety of methods ranging from Gibbs ensemble Monte Carlo simulations [15] to integral equation theories of liquids [16,17] and density-functional theories [18] have been used to construct the phase diagram in binary LJ mixtures. This system has also been used to study interfacial phenomena such as wetting at the liquid-vapor interface [19,20] or surface tension at the interfaces between demixing liquids [21–23]. Molecular-dynamics simulation of the inherent structure of the binary LJ fluid in phase-separated binary LJ mixture [24] shows temporal evolution of microscopic domains during liquid-liquid phase separation. Recently, attempts have been made to rationalize the properties of such mixtures in bulk and in small clusters in terms of the underlying rugged energy landscape [25,26]. Importantly, much of our present understanding of relaxation dynamics in glass [27–29] and supercooled liquids [30–32] has been derived from studies on binary LJ mixtures.

In view of its wide range of applications, it often becomes necessary to have a detailed insight into the equilibrium structure (or equivalently, the equilibrium correlations) present in binary LJ fluids. These correlations may be obtained using molecular dynamics or Monte Carlo simulation studies [33,34]. On the other hand, extension of integral equation theories (IET) of liquids to binary mixtures is found to be computationally efficient, especially when investigating properties over a wide range of thermodynamic parameters [16,17]. The goal of the present paper is to investigate the static structure of binary Lennard-Jones mixture with variations in temperature T and pressure P using molecular-dynamics simulations. We shall focus here on the generation of key inputs to the IET of binary fluid mixtures.

Within the framework of IET, the total pair correlation between particles of type i and j separated by a distance r in a binary fluid mixture is given by the Ornstein-Zernike (OZ) equation [1]

$$h_{ij}(r) = c_{ij}(r) + \rho_0 \int d\mathbf{r}' c_{ij}(|\mathbf{r}-\mathbf{r}'|)h_{ij}(r'), \qquad (1)$$

where $c_{ij}(r)$ represents the distance-dependent direct correlation function between these particles. ρ_0 is the average number density of the fluid. $h_{ij}(r)$, on the other hand, is related to the interparticle pair potential $\phi_{ij}(r)$ by the following exact relation [1]:

$$h_{ij}(r) + 1 = \exp[-\beta\phi_{ij}(r) + \gamma_{ij}(r) + B_{ij}(r)], \qquad (2)$$

where $\gamma_{ij}(r)=h_{ij}(r)-c_{ij}(r)$ is known as the indirect correlation function between particles of type i and j. As usual, $\beta=(k_B T)^{-1}$ with k_B and T as the Boltzmann constant and absolute temperature, respectively. In Eq. (2), $B_{ij}(r)$ represents the bridge function that cannot be evaluated analytically. Therefore, semiempirical approximations for $B_{ij}(r)$ are introduced to close the numerical solution of Eqs. (1) and (2).

The accuracy of an approximate closure used is generally tested by comparing the correlation $h_{ij}(r)$ predicted by IET to that obtained from simulation [35,36]. However, a direct calculation of the bridge function and its dependence on the thermodynamic parameters are less frequently investigated [37,38]. In this paper, our aim is to extract $B_{ij}(r)$ directly from simulation and compare it to two of the most widely used closures for binary LJ mixtures. In particular, we shall discuss the variation of correlation between unlike species 1 and 2 in terms of $B_{12}(r)$ in a homogeneous liquid phase near the liquid-vapor coexistence curve.

The first approximate closure being studied here is known as the hybrid mean spherical approximation (HMSA). This is based on a partitioning of the interaction potential, $\phi_{12}(r)$,

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between an unlike pair of particles into a soft core repulsive part, $\phi_R(r)$, and an attractive part, $\phi_A(r)$. $B_{12}(r)$ is then given by [35]

$$B_{12}(r) = \ln\left[1 + \frac{\exp\{f(r)[\gamma_{12}(r) - \beta\phi_A(r)]\} - 1}{f(r)}\right] - \gamma_{12}(r) + \phi_A(r) \tag{3}$$

with a Roger-Young "switching" function $f(r)=1-\exp(-\alpha r)$. The parameter α can be varied to impose thermodynamic consistency of the solution. We shall also consider the Duh-Henderson (DH) closure [36] that utilizes a semiphenomenological density dependence in the attractive part of the potential, $\phi_A(r)$ given by [39]

$$\phi_A(r) = -4\epsilon_{12}\left(\frac{\sigma_{12}}{r}\right)^6 \exp\left[-\frac{1}{\rho^*}\left(\frac{\sigma_{12}}{r}\right)^{6\rho^*}\right]. \tag{4}$$

Here, $\rho^*=\rho_0\sigma_{22}^3$ is the reduced density of the liquid scaled in terms of particle diameter σ_{22} of type 2. As explained below, σ_{12} and ϵ_{12} are the cross-species LJ parameters. It is also assumed that $B_{12}(r)\approx B_{12}(s)$, where $s_{12}(r)=\gamma_{12}(r)-\beta\phi_A(r)$ is the indirect correlation function renormalized in terms of $\phi_A(r)$. The resultant expression for the bridge function, free from any adjustable parameter, is given by

$$B_{12}(s) = \frac{-s_{12}^2}{2\left[1 + \left(\frac{5s_{12}+11}{7s_{12}+9}\right)s_{12}\right]}, \quad s_{12} \geqslant 0,$$

$$= -\frac{1}{2}s_{12}^2, \quad s_{12} < 0. \tag{5}$$

Applicability of both of these closures to calculate structure, thermodynamics, and phase equilibria in one- and multicomponent LJ fluids having moderate to high densities is well documented [16,36]. The assumption of a local dependence of B on γ plays a key role in the calculation of properties such as chemical potential [40] that is in turn used in predicting phase equilibria [16,17].

In order to evaluate the bridge function using computer simulation studies, the pair potential, $\phi_{ij}(r)$ $(i=1,2)$, in binary LJ mixture is generally modeled as

$$\phi_{ij}(r) = 4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r}\right)^{12} - \left(\frac{\sigma_{ij}}{r}\right)^6\right], \tag{6}$$

where ϵ_{ij} is the attractive well depth and σ_{ij} is the LJ diameter. The cross-species interaction parameters (ϵ_{12} and σ_{12}) may be determined, for example, by the Lorentz-Berthelot combination rules [41]

$$\sigma_{12} = \frac{1}{2}(\sigma_{11} + \sigma_{22}),$$

$$\epsilon_{12} = \delta_{12}\sqrt{\epsilon_{11}\epsilon_{22}}. \tag{7}$$

As is evident from the above equation, the binary interaction parameter δ_{12} reflects the deviation of unlike-pair interaction from the geometric mean of the like pair interactions. Recently, a detailed study was carried out on the complete phase diagram of binary LJ mixtures using Monte Carlo simulation and Gibbs-Duhem integration techniques [42] to understand the effect of δ_{12} on fluid phase behavior [42]. It was found that for $\delta_{12}=1.0$, $\epsilon_{11}/\epsilon_{22}=0.45$, and $\sigma_{11}/\sigma_{22}=0.85$, a completely miscible liquid phase exists in a narrow region between the solid-liquid and liquid-vapor coexistence curves. However, this phase disappears for $\delta_{12}=0.9$ where the above two coexistence regions interfere. In this paper, we shall focus on the applicability of HMSA and DH closures to binary LJ fluids in the narrow liquid phase at state points lying close to the liquid-vapor coexistence line.

It should be noted that both the closures mentioned above have originally been proposed to explain the properties of high-density, homogeneous single-component fluids [1] and extended later to describe correlations in homogeneous mixtures. However, in a binary mixture, an interchange of position of two particles, belonging to two different species, does not lead to an identical picture of phase space as it does if two identical particles are exchanged. Therefore, a careful analysis of the functional dependence of $B_{12}(r)$, e.g., on $\gamma_{12}(r)$, may be needed especially at regions close to phase coexistence. Recently, Fantoni and Pastore [43] have carried out an extensive Monte Carlo simulation study of the closure relations in hard-sphere fluid mixture where, depending on the system studied, the local dependence of the bridge function on γ is found to break down. Using a constant pressure integral equation theory to calculate phase diagrams [17], it has also been demonstrated that the accuracy of the predicted phase diagram in binary LJ fluids depends critically on the closure used.

With a view to estimating the accuracy of these approximate closures in the predictions of structural and thermodynamic properties, we have further carried out comparisons of our simulation results to approximate integral equation theories at the level of direct and indirect correlation functions, as well as the pair distribution function. Our results highlight the well-known accuracy of these closures in predicting the radial distribution function. The direct and indirect correlations are, however, not as accurately reproduced. As a consequence, it is found that quantities, such as chemical potentials, predicted using the indirect correlation functions derived from simulations as well as integral equation theories, exhibit significant deviations. These observations emphasize the need for developing new, improved closure relations for model systems. Our investigation is thus expected to be useful not only in assessing the applicability of these approximate closures over a wide range of thermodynamic parameters, but also in the context of calculation of fluid phase diagrams [17].

The rest of the paper is organized as follows. In Sec. II, we outline the method adopted to extract the bridge function from molecular-dynamics simulation of a binary LJ mixture whose phase diagram is completely known [42]. The results are presented and discussed in Sec. III, and Sec. IV summarizes the conclusions.

II. METHODOLOGY

We shall present here an overview of the method adopted to extract the bridge function from large-scale molecular-dynamics simulation of binary LJ fluids. Details of this method, applied to one-component LJ fluid, are available elsewhere [38].

In the first step, we calculate the unlike pair radial distribution function, $g_{12}(r)$, by an extensive sampling of equilibrated trajectories of molecular-dynamics simulation studies. We then Fourier transform $g_{12}(r)$ to obtain the structure factor, $S_{12}(k)$ [1,37,44]. The next step involves calculation of $\tilde{\gamma}_{12}(k)$, the indirect correlation function in the Fourier space, using the following expression:

$$\tilde{\gamma}_{12}(k) = \frac{[S_{12}(k) - 1]^2}{\rho_0 S_{12}(k)}. \tag{8}$$

Fourier inversion of $\tilde{\gamma}_{12}(k)$ yields $\gamma_{12}(r)$ that is finally used to calculate the bridge function as

$$B_{12}(r) = \ln g_{12}(r) + \beta\phi_{12}(r) - \gamma_{12}(r). \tag{9}$$

Note that $\gamma_{12}(r)$ is a smoothly decaying correlation function that goes to zero at large distances. The decay of $\phi_{12}(r)$ at large r may also be adjusted by shifting of the pair potential [33]. Therefore, for an accurate estimation of $B_{12}(r)$, one needs to employ a large enough simulation box whereby $g_{12}(r)$ effectively goes to its limiting value of unity well within the maximum distance probed. However, it is not possible to estimate $B_{12}(r)$ within the core region (that is, $r < \sigma_{12}$) using Eq. (9) as $g_{12}(r)$ is zero in this range. Alternatively, the bridge function may be evaluated from the cavity correlation function $y_{12}(r)$ as [1,16]

$$B_{12}(r) = \ln y_{12}(r) - \gamma_{12}(r). \tag{10}$$

We have estimated $y_{12}(r)$ using Henderson's equation [45], which is known to be accurate at small r [37,43]. In this method, for a binary mixture comprised of N_1 particles of type 1 and N_2 particles of type 2 present in a volume V, the unlike cavity function between particle 1 of type 1 and particle 1 of type 2 at a distance $r_{1_1 1_2}$ may be obtained from the following canonical average [43,45]:

$$y_{12}(r_{1_1 1_2}) = \frac{V z_1}{N_1} \langle \exp(-\beta\chi) \rangle_{N_1,N_2,V,T},$$

where

$$\chi = \sum_{i_2>1}^{N_2} \phi_{12}(r_{1_1 i_2}) + \sum_{i_1>1}^{N_1+1} \phi_{11}(r_{1_1 i_1}). \tag{11}$$

The summation χ and hence the average are evaluated by placing a hypothetical test particle (of type 1) at small distances over a grid near the particle 1 of type 1 and then near the particle 1 of type 2. In the above equation, $z_1 = \exp(\beta\mu_1)/\Lambda^3$ is the activity of specie 1 expressed in terms of its chemical potential μ_1 and thermal de Broglie wavelength, Λ. Thus the prefactor reduces to $Vz_1/N = \exp(\beta\mu_1^{\text{ex}})$ and is related to the excess chemical potential, μ_1^{ex}, of the specie 1. Note that the contribution of the prefactor to the average may be calculated from the limiting behavior of the cavity function [38,43]. Although computation of this probability is practically free in an *NVT* Monte Carlo simulation, it can also be evaluated without much computational cost from the equilibrium trajectories generated in MD simulation.

TABLE I. The three state points studied using *NPT* molecular-dynamics simulation characterized by reduced temperature, $T^* = k_B T/\epsilon_{22}$, reduced pressure, $P^* = P\sigma_{22}^3/\epsilon_{22}$, and molefraction x_2 of particles of type 2 having diameter σ_{22} and LJ-interaction parameter ϵ_{22}. For details, see text.

State	Pressure, P^*	Temperature, T^*	Molefraction, x_2
I	0.0366	1.21	0.55
II	0.0366	1.25	0.60
III	0.0366	1.29	0.65

The indirect correlation function thus extracted from the molecular-dynamics simulation studies has been further used to calculate the chemical potential of the two species present in the mixture. Here, we have adopted the well-known star function method [40] whereby the chemical potential is expressed as

$$\beta\mu_i^{\text{ex}} = \sum_{k=1}^{2} \rho_k \int d\vec{r} \Big[\gamma_{ik}(r) + B_{ik}(r) - h_{ik}(r) + \frac{1}{2} h_{ik}(r)\gamma_{ik}(r) + h_{ik}(r)B_{ik}(r) - S_{ik}(r) \Big]. \tag{12}$$

Under the assumption of a unique functionality $B = B(\gamma)$, the star function may be evaluated from the following expression:

$$S_{ik}(r) = \frac{h_{ik}(r)}{s_{ik}(r)} \int_0^{s_{ik}} d\gamma' B_{ik}(\gamma'). \tag{13}$$

The renormalized indirect correlation function, $s_{ik}(r)$ $(i,k = 1,2)$, may be obtained either from simulations or from the numerical solutions of OZ equation with a suitable closure.

III. RESULTS AND DISCUSSION

We have performed an extensive *NPT* molecular-dynamics simulation study of the equilibrium correlations present in a completely miscible liquid phase lying in the narrow intervening region between the liquid-vapor and solid-liquid coexistence lines as observed in the simulated phase diagram of a binary LJ mixture [42]. For this purpose, we have used the following parameters to model the binary interaction potential: diameter ratio $\sigma_{11}/\sigma_{22} = 0.85$, well depth ratio $\epsilon_{11}/\epsilon_{22} = 0.45$, and binary interaction parameter $\delta_{12} = 1.0$. The simulations were carried out with a total of 5000 particles at three typical state points lying near the liquid-vapor coexistence curve to obtain the bridge function for this liquid phase. The details of the state points studied are summarized in Table I. In all the cases studied here, length is scaled by σ_{22}, and the diameter of particles of type 2 and energy by the LJ energy parameter ϵ_{22}. The thermodynamic state of the system is characterized accordingly by the reduced density, $\rho^* = \rho_0\sigma_{22}^3$, and the reduced temperature, $T^* = k_B T/\epsilon_{22}$, along with the variation in molefraction x_2.

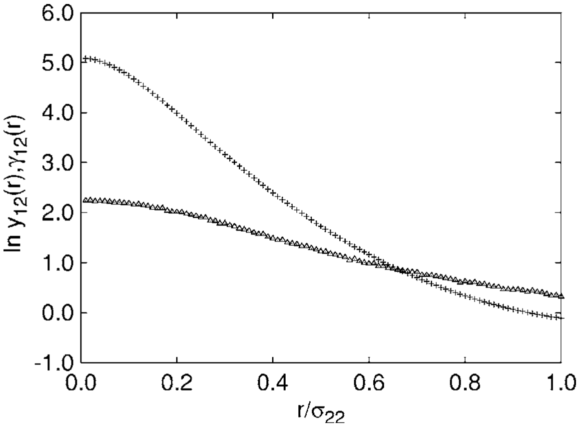

FIG. 1. The indirect correlation function, $\gamma_{12}(r)$, and log of the cavity correlation function, $\ln y_{12}(r)$, in binary LJ fluid obtained from *NPT* molecular-dynamics studies at $T^*=1.21$, $P^*=0.0366$, and $x_2=0.55$ (state I of Table I). $\ln y_{12}(r)$ calculated using Henderson's method [45] is shown using triangles, and $\gamma_{12}(r)$ obtained from Fourier inversion of structure factor is represented +.

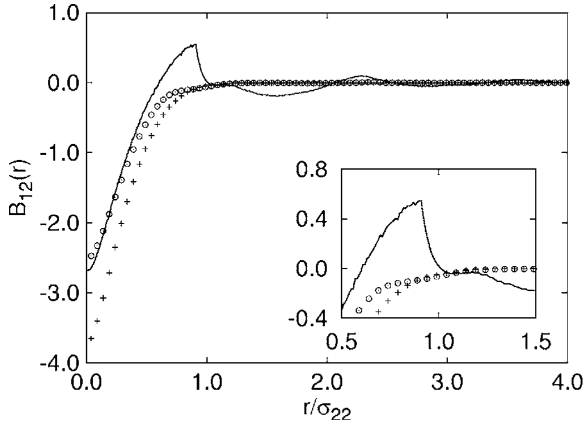

FIG. 2. Comparison of simulated bridge function (*NPT*, solid line) of binary LJ fluid in state I with the approximate IET closures, DH (open circle), and HMSA (+). The inset highlights stronger correlation predicted by *NPT* MD in comparison to the closures at intermediate distances near the core.

Choosing the mass m, diameter σ_{22}, and energy parameter ϵ_{22} to be equal to those characteristic of Ar, time t is found to be scaled by $\tau=\sqrt{m\sigma_{22}^2/\epsilon_{22}}\sim 2$ ps.

It is important to note that the cavity correlation function $y_{12}(r)$ can be obtained exactly from *NVT* MD simulations by using Eq. (11). The approximate cavity correlations derived from our *NPT* simulation studies have been checked for accuracy against the corresponding exact *NVT* results and we get identical estimates of $y_{12}(r)$ from both simulations. The simulation package DL_POLY [46] has been used to generate the trajectories in the *NPT* ensemble using a Nosé-Hoover thermostat [47]. Efficient fast Fourier transform routines have been used to calculate $S_{12}(k)$ directly from $g_{12}(r)$. $\gamma_{12}(r)$ is subsequently calculated by Fourier inversion of $S_{12}(k)$. It is well known that estimates of $y_{12}(r)$ become statistically unreliable at distances $r\sim\sigma_{12}$, and hence $B_{12}(r)$ obtained directly from MD is used to represent $B_{12}(r)$ at larger distances. $B_{12}(r)$ within the core derived from Henderson's method is found to extend smoothly and continuously to $B_{12}(r)$ outside the core calculated from the MD simulation. To facilitate a direct comparison to the simulated bridge function, the approximate functional forms of $B_{12}(r)$ as in HMSA or DH have been evaluated using the simulated $\gamma_{12}(r)$ as input.

In Fig. 1, we present the indirect correlation function $\gamma_{12}(r)$ and the unlike cavity correlation function $y_{12}(r)$ obtained from simulation of the binary LJ fluid at the state point I. The resultant variation of $B_{12}(r)$ is shown in Fig. 2, where $B_{12}(r)$ obtained from *NPT* simulation has been compared to HMSA and DH closures. It is found that while the DH closure reproduces the bridge function quantitatively inside the core, both the closures significantly underestimate $B_{12}(r)$ at the distances $r_{12}\sim\sigma_{22}$. The overall quality of agreement remains the same as we go from state I to state II (shown in Figs. 3 and 4) and state III (Figs. 5 and 6). It should also be noted that both the closures predict a singular lack of structure in $B_{12}(r)$ at distances $r\gtrsim\sigma_{22}$ while the simulation results indicate a slower decay with small oscillations. Therefore, any attempt toward the improvement of these closure relations would warrant a better modeling at intermediate distances. The Duh-Henderson closure appears to provide a marginally better estimate of $B_{12}(r)$ in comparison to HMSA, especially within the core.

We have also investigated the presence of anisotropy, if any, in the liquid phase being studied here. For this purpose, we have calculated the radial distribution function, $g_{12}(r,\theta,\phi)$, by sampling the unlike pair of particles at different pair separations $\vec{r}$ with varying orientations (θ,ϕ) of $\vec{r}$. In Fig. 7, we show the typical behavior of $g(r,\theta,\phi)$ as a function of (r,θ) for $\phi=0$ in a one-component LJ fluid in a high-density, homogeneous state. Similar to its one-component analogue, the binary LJ fluid in the narrow region under investigation also shows a completely isotropic distribution of the neighboring particles both in first- and second-neighbor shells. This has been highlighted in Fig. 8.

We next present the "Duh-Henderson" plot [36,38,43] and the results are shown in Fig. 9 to understand the dependence

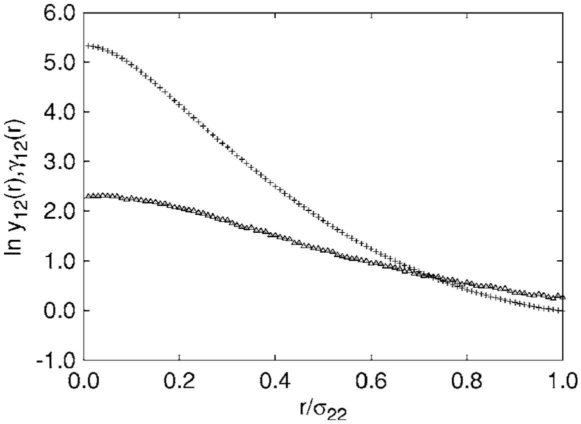

FIG. 3. The indirect correlation function, $\gamma_{12}(r)$ (+), and log of the cavity correlation function, $\ln y_{12}(r)$ (triangle), in binary LJ fluid at $T^*=1.25$, $P^*=0.0366$, and $x_2=0.6$ (state II of Table I).

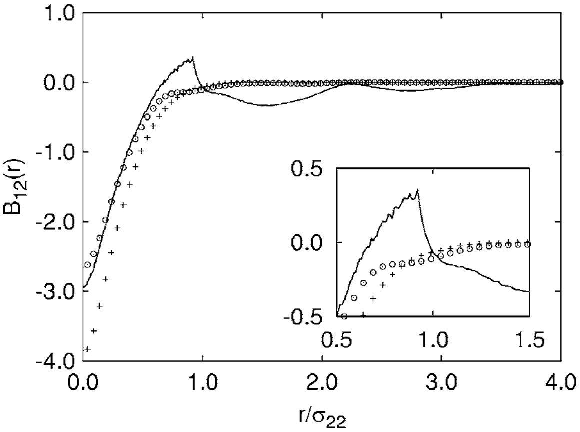

FIG. 4. Comparison of simulated bridge function (from *NPT* MD, solid line) in binary LJ fluid at state II with IET closures HMSA (+) and DH (open circle). The inset as before highlights stronger correlation predicted by *NPT* MD at distances $r \sim \sigma_{22}$.

of the bridge function $B_{12}(r)$ on the indirect correlation function, $\gamma_{12}(r)$. It is found that similar to the predictions of both HMSA and DH closures, the bridge function shows a unique local dependence on $\gamma_{12}(r)$ for higher values of the indirect correlation function. However, a significant deviation is observed for small values of $\gamma_{12}(r)$ at all the three state points.

In order to compare the effect of variation of temperature on $B_{12}(r)$, we show in Fig. 10 the bridge functions extracted from molecular-dynamics simulation of a binary LJ mixture at temperatures $T^*=1.24$, 1.21, and 1.17, respectively, with all other parameters remaining the same as those of state I (see Table I). It should be noted that while the state with $T^*=1.24$ lies in close proximity to the liquid-vapor coexistence curve, that with $T^*=1.17$ is close to the liquid-solid coexistence line. It is found that as expected, lowering of temperature increases the correlation at the intermediate distances followed by small but slow oscillations setting in at larger distances. There is no other significant change.

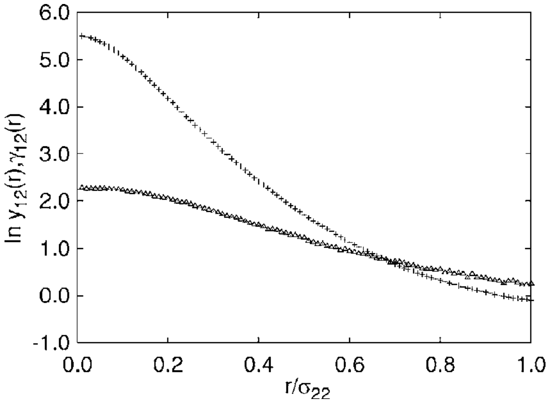

FIG. 5. The indirect correlation function, $\gamma_{12}(r)$ (+), and log of the cavity correlation function, $\ln y_{12}(r)$ (triangle), in binary LJ fluid at $T^*=1.29$, $P^*=0.0366$, and $x_2=0.65$ (state III of Table I).

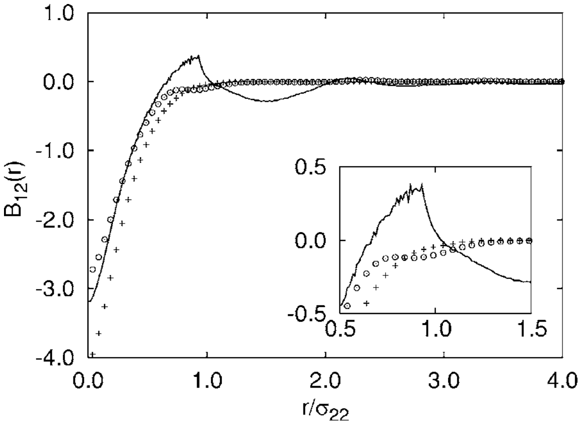

FIG. 6. Comparison of simulated bridge function (*NPT*, solid line) of binary LJ fluid in state III with the approximate IET closures, DH (open circle), and HMSA (+). As in Figs. 2 and 4 the inset highlights stronger correlation predicted by *NPT* MD at distances close to $r \sim \sigma_{22}$.

As expected, at the level of radial distribution function $g(r)$, both of the closures being discussed here produce a quantitative agreement with the simulated $g(r)$ that has not been shown here. However, our ultimate goal is to predict properties such as the chemical potential. Therefore, it may be more useful to know the accuracy of these closure relations in providing the direct or indirect correlation functions. For this purpose, we have obtained these correlation functions by solving Eq. (1) in conjunction with HMSA as the approximate closure employing Gillan's algorithm [48]. In Fig. 11, we present a comparison of the indirect correlation function, $\gamma_{12}(r)$, for binary LJ fluid thus obtained with that calculated from our MD simulation studies. It is clearly seen that both simulation and HMSA predict a qualitatively similar, smooth decay of $\gamma_{12}(r)$ with HMS markedly underestimating $\gamma_{12}(r)$ at small distances. In Fig. 12, we present a comparison of the direct correlation function, $c_{12}(r)$, for binary LJ fluid obtained by MD simulation and by solving the IET for HMSA. Interestingly, it is found that the use of an approximate closure leads to an overestimation of the direct correlation function in the core region. At the intermediate distances, as expected from our studies on the bridge func-

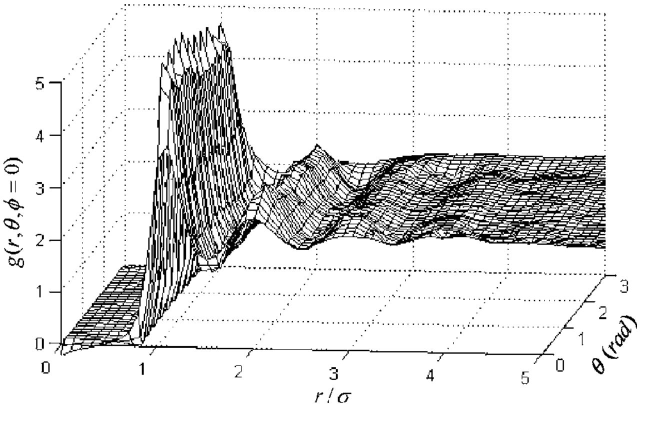

FIG. 7. Isotropic distribution of the pair correlation function, $g(r,\theta,\phi)$, in one-component LJ fluid in a high-density homogeneous fluid phase with $T^*=1.04$, $\rho^*=\rho_0\sigma^3=0.8442$ having 5000 particles. For the sake of simplicity, we show the variation of g as a function of r and θ keeping $\phi=0$.

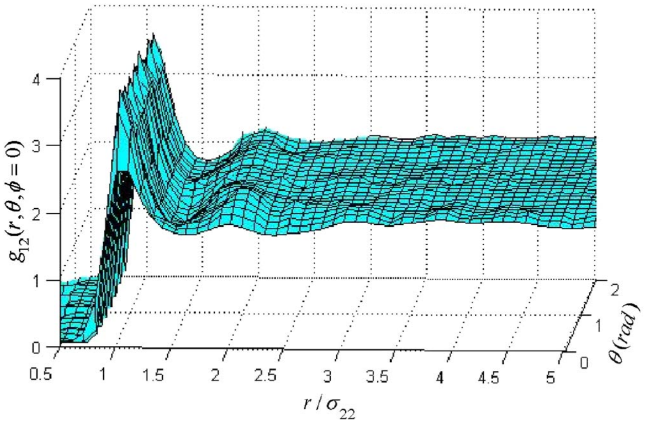

FIG. 8. (Color online) Isotropic distribution of the unlike pair correlation function, $g_{12}(r,\theta,\phi)$, in a completely miscible liquid phase of a binary LJ mixture at the state III of Table I. As in Fig. 7, we show the variation of g as a function of r and θ keeping $\phi=0$.

tion, the extent of correlation predicted by the IET is less than that obtained from the simulation.

An immediate consequence of these observed deviations on the calculated thermodynamic properties has been presented in Table II. Here, we have calculated the nonideal contribution to the chemical potential of both species 1 and 2 using Lee's star function method [40]. The evaluations are carried out starting with $\gamma_{ij}(r)$ derived from both MD simulations at the three state points mentioned above and also from the solution of the OZ equation in conjunction with the HMSA closure. It is found that the estimate of $\beta\mu_i^{\mathrm{ex}}$ obtained from HMSA is higher than that observed in our simulation studies.

IV. CONCLUSION

In this paper, we have presented a molecular-dynamics study of the bridge function in a completely miscible liquid phase near the liquid-vapor coexistence curve in binary LJ fluid mixtures. The results have been compared to two of the most widely used approximate closures of the integral equation theories of liquids. It is found that both HMSA and DH closures provide a qualitatively accurate description of the bridge function especially within the core. However, correlations at contact distances are substantially underestimated. Both of the closures predict practically structureless variation of the bridge function outside the core. The overall accuracy of the closures may be primarily attributed to the homogeneous and isotropic distribution of the fluid particles. It may be recalled that in liquids at supercritical states near the criti-

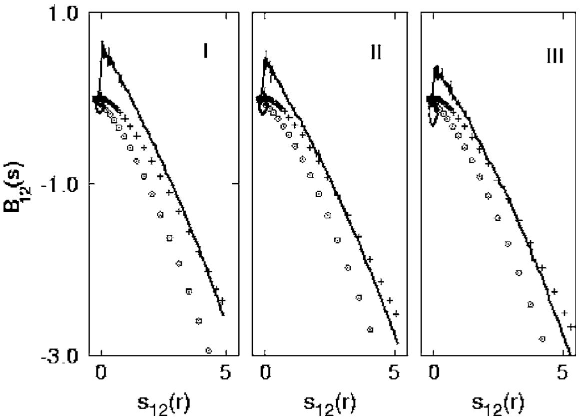

FIG. 9. The Duh-Henderson plot of the bridge function, $B_{12}(s)$, where it is plotted as a function of the renormalized indirect correlation function, $s_{12}(r)$, of binary Lennard-Jones fluid at the three state points I, II, and III (see Table I). The solid line represents the results of *NPT* MD simulation. The circles and + correspond to the prediction of DH and HMSA closures, respectively. In the case of HMSA, the bridge function has been plotted as a function of $\gamma_{12}(r)$ instead of $s_{12}(r)$.

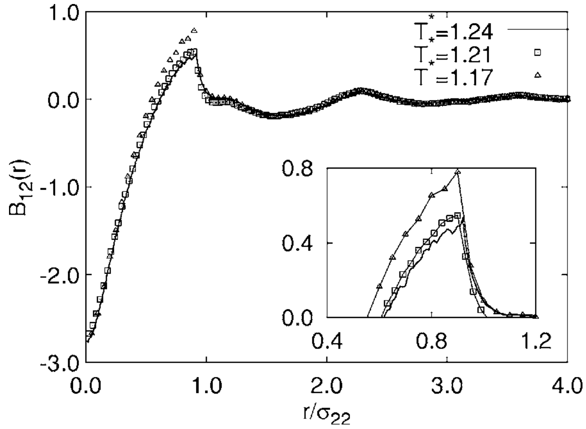

FIG. 10. Comparison of simulated bridge function $B_{12}(r)$ (*NPT* MD) of binary LJ fluid at three different temperature for $x_2=0.55$ and $P^*=0.0366$. As the temperature changes from $T^*=1.24$ (solid line) to $T^*=1.21$ (open squares) and finally to $T^*=1.17$ (triangles), the correlations at intermediate distances progressively increase. The inset highlights this increment with a decrease in temperature that takes the system along a constant pressure-constant composition line from near the liquid-vapor coexistence line ($T^*=1.24$) close to the liquid-solid coexistence line ($T^*=1.17$).

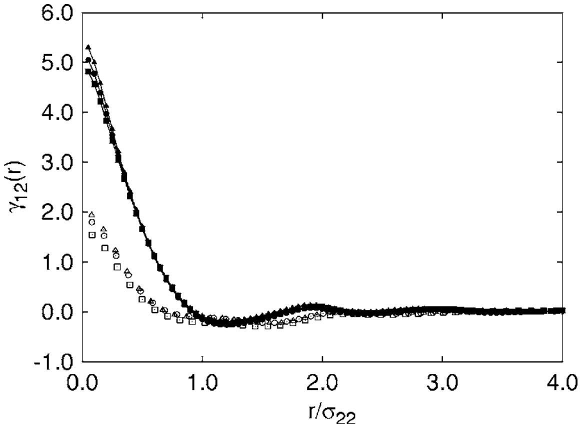

FIG. 11. Comparison of simulated indirect correlation function $\gamma_{12}(r)$ (*NPT* MD) of binary LJ fluid with the results obtained by solving the OZ equation with HMSA closure at states I, II, and III of Table I. The simulated values are shown using lines connecting solid squares (state I), solid circles (state II), and solid triangles (state III). The variation of $\gamma_{12}(r)$ predicted by HMSA is represented using open squares, circles, and triangles at states I, II, and III, respectively.

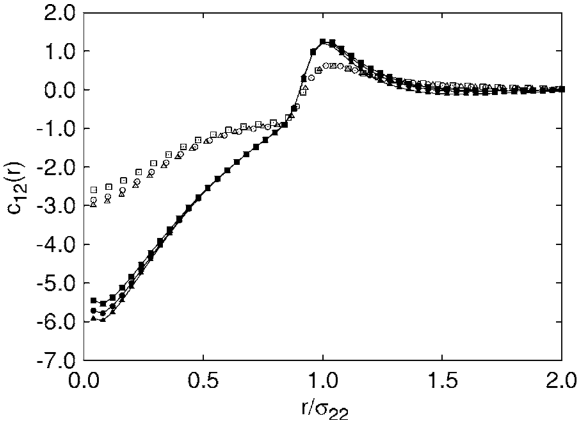

FIG. 12. Comparison of simulated direct correlation function $c_{12}(r)$ (*NPT* MD) of binary LJ fluid with the results obtained by solving the OZ equation with HMSA closure at the three state points I, II, and III (see Table I). The representation remains the same as in Fig. 11.

TABLE II. Values of the excess chemical potentials obtained using Lee's star function method [40] at the state points I, II, and III of Table I. μ_{ii} represents the chemical potential of the ith specie in the binary mixture at a reduced density ρ^* and temperature T^*. The requisite input of the indirect correlation function, $\gamma_{ij}(r)$, has been calculated both from our *NPT*–molecular-dynamics (MD) simulations and from a solution of OZ equation with HMSA closure. For further details, see text.

State	$\beta\mu_1^{\mathrm{ex}}$ (MD)	$\beta\mu_1^{\mathrm{ex}}$ (HMSA)	$\beta\mu_2^{\mathrm{ex}}$ (MD)	$\beta\mu_2^{\mathrm{ex}}$ (HMSA)
I	4.7307	4.7449	0.2265	0.1602
II	3.2439	3.2692	0.2202	0.2146
III	2.7585	2.8602	0.2162	0.1738

cal point [38], an anomalous positive segment is observed for the bridge function in the core possibly as a result of local-density augmentation. No such deviation is observed here. The Duh-Henderson plots presented here seem to indicate a nontrivial dependence of the bridge function on the indirect correlation function beyond the widely used local approximation. We have also investigated the effect of temperature variation for a fixed composition that brings the state point closer to the neighboring coexistence lines. It would have been interesting to see if the onset of a phase transition gets reflected in the structure of the bridge function as a result of changes in the binary interaction parameter δ_{12}. Variation of δ_{12} from 1.0 to 0.9 leads to a coalescence of the liquid-vapor and liquid-solid coexistence regions [42]. Our preliminary investigations at δ_{12}=0.95 (keeping all other parameters the same) do not seem to reveal any marked change in the overall behavior of $B_{12}(r)$.

In view of the results presented here, it should be realized that the deviations observed may not induce any significant difference between the simulated radial distribution function and that predicted by using these closures in IET. However, it is the direct correlation function or the structure factor, rather than the radial distribution function, that governs the effect of equilibrium correlations, for example, on system dynamics [1]. We have reported in this study how the use of an approximate closure like HMSA leads to an underestimation of $\gamma(r)$ and an overestimation of $c(r)$ at small distances. It is also shown how these can be correlated to the observation of marginally larger values of chemical potential. Therefore, one must employ the utmost caution in choosing an approximate closure especially if the application needs either the direct or the indirect correlation function as an input. It has already been shown [17] that use of thermodynamically consistent and state-sensitive closures may induce significant improvements in estimating chemical potentials. Any such improvement may help in providing quantitative descriptions of phenomena determined by chemical potential such as phase equilibria and chemical reaction equilibrium. The use of a density-dependent attractive part of the potential seems to hold a key to the wide applicability of the Duh-Henderson closure. For accurate prediction of phase transitions and critical behavior of simple fluids and their mixtures, one may also use, for instance, the self-consistent Ornstein-Zernike approximation (SCOZA) [49] that provides an accurate estimate of the equilibrium correlations near the liquid-vapor coexistence curve. It will further be of wide interest to investigate how such different approaches may be extended to treat inhomogeneous fluids [50] in reference to interfacial phenomena such as surface wetting.

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