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Bridge Function and Cavity Correlation Function from Simulation: Implications on Closure Relations[1]

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In this paper we review recent molecular simulation results for the bridge function and cavity correlation function of the Lennard-Jones and soft-sphere fluids. We demonstrate that closures similar to the Percus Yevick (PY) closure are poor at short range and should only be valid for repulsive fluids. Finally, by comparing with our simulation results for the Lennard-Jones bridge function, we show how to rescale the Lennard-Jones bridge function so that it can be approximated with the bridge function for a repulsive fluid.

KEY WORDS: bridge function; cavity function; integral equation theory; thermodynamic properties.

1. INTRODUCTION

Integral equation theory is one of the most powerful methods in statistical mechanics for calculating fluid structure and thermodynamic properties. In many integral-equation-theory calculations, the Ornstein–Zernike equation is solved based on some closure relation. The Ornstein–Zernike equation for spherically symmetric molecules is given by [1, 2]

$$h(r_{12}) = c(r_{12}) + \rho \int h(r_{13})\, c(r_{23})\, d\mathbf{r}_3 \qquad (1)$$

where $c(r_{12})$ is the direct correlation function, $h(r_{12})$ is the total correlation function, ρ is the number density, and $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ is the distance between

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the centers of spherical molecules 1 and 2. A solution to Eq. (1) can be found given another equation relating the correlation functions; this is called a closure relation. In this sense, a closure relation is an approximation for a set of integrals known as the bridge function. The exact relationship between the bridge function and the other correlation functions is given by [2]

$$B(r_{12}) = c(r_{12}) + \ln[y(r_{12})] - h(r_{12}) \tag{2}$$

where $y(r_{12})$ is the cavity correlation function. The cavity correlation function is related to the total correlation function by

$$y(r_{12}) = g(r_{12}) \exp[\beta\phi(r_{12})] \tag{3}$$

where $g(r_{12}) = h(r_{12}) + 1$ is the pair correlation function, $\phi(r_{12})$ is the pair potential of interaction in the fluid, and $\beta = 1/k_B T$, where k_B is Boltzmann's constant and T is absolute temperature.

Many approximate closure relations have been proposed [2]. Two of the most commonly used integral equation theories are HNC theory [2] and Percus–Yevick (PY) theory [2, 3]. In HNC theory the bridge function is assumed to be zero for all r. PY theory assumes that $c(r_{12}) = f(r_{12})\, y(r_{12})$, where $f(r_{12}) = \exp[-\beta\phi(r_{12})] - 1$, which is equivalent to the assumption $B(r_{12}) = 1 - y(r_{12}) + \ln[y(r_{12})]$. Since the bridge function had not been accurately calculated for any fluid besides the hard-sphere fluid, these approximate closures have been tested by comparing with simulation results for the pair correlation functions and thermodynamic properties.

As an alternative to HNC or PY theory, Lado [4] proposed approximating the bridge function with the bridge function for a reference fluid at a suitably chosen temperature and density. The resulting theory is called reference hypernetted chain (RHNC) [4–6]. The thermodynamic properties and structure of a fluid can then be calculated given a suitable reference fluid and a prescription for determining the state point at which to calculate the reference-fluid bridge function. Until recently, the only fluid for which the bridge function had been accurately calculated was the hard-sphere fluid. In recent years, papers have focused on calculating the bridge function for the one-component plasma [7], hard spheres [8, 9], Lennard-Jones (LJ) spheres [10–13], the soft-sphere fluid [with pair potential given by $\phi(r) = 4\varepsilon(\sigma/r)^{12}$] [11], electrolytes [14], and liquid metals [15]. Two problems arise when trying to calculate the bridge function directly from molecular simulation: determining the cavity correlation function for the fluid at short range and obtaining an accurate direct correlation function. We have developed two techniques to determine the cavity correlation function at short range [10].

Our approach is to calculate the cavity correlation function and bridge function from molecular simulation as described in detail in a previous paper [10]. We have used both Henderson's equation [16] and a direct simulation method [10] to calculate the cavity correlation function. Henderson's equation provides accurate estimates of $y(r)$ for r near zero. The direct simulation method provides estimates for any range of r. We obtain the direct correlation function from the total correlation function through the Ornstein–Zernike equation, Eq. (1) [1, 2, 17], and use Eq. (2) to calculate the bridge function. The consistency of the direct correlation function is checked by means of the compressibility equation.

The goal of our work has been to provide accurate bridge functions from molecular simulation for a variety of model fluids over a range of conditions [10, 11]. The purpose is to provide accurate bridge function data to test approximate closure relations, to provide a bridge function correlation for a fluid other than the hard-sphere fluid (the soft-sphere fluid), and to study the effect of potential models on the bridge function and closure relations. Much of this has been accomplished [10, 11]. Although the bridge function is no longer thought to be universal, it might become useful to divide the bridge function into two parts: one due to short-range repulsion and the other due to long-range attraction as has been done for the Helmholtz free energy in perturbation theories for simple fluids [2, 14]. Our bridge function results will be essential to testing such a perturbation approach.

2. RESULTS AND DISCUSSION

It is well known that the configurational properties of the soft-sphere fluid scale with a single dimensionless parameter [2]

$$\Gamma = \frac{\rho\sigma^3}{(kT/\varepsilon)^{1/4}} \tag{4}$$

The correlation functions for the soft-sphere fluid also scale with Γ. These features make this an interesting fluid to study as a potential reference fluid for integral equation calculations. To facilitate this, we provided a correlation of the soft-sphere bridge function [11]. The bridge function oscillations grow in magnitude and shift to smaller distances with increasing Γ. We also note that the bridge function is always $\leqslant 0$ (nonpositive) for the soft-sphere fluid.

Based on our calculations of the soft-sphere bridge function and Lennard-Jones bridge function [10, 11], we have the opportunity to investigate various proposed closure relations. The PY closure can be written as

$$B^{\mathrm{PY}}(\tau) = -\tau + \ln(\tau + 1) \tag{5}$$

where $\tau(r) = h(r) - c(r)$. Other closures have been proposed in which the bridge function is written as a function of τ [14, 18 20]. Since the PY approximation has been found to be good for fluids with short-range interactions, some closures have attempted to match the PY bridge function at short range. As shown in the work by Duh and Haymet [14], it can be instructive to plot the bridge function versus τ. In Fig. 1, we have plotted $B(\tau)$ for the soft-sphere fluid at various state points. The functional form appears to be independent of state point. Also plotted in Fig. 1 is the PY approximation. The PY approximation is in poor agreement with the simulation results up to the first zero of the bridge function, but the PY approximation is in very good agreement with simulation results for all

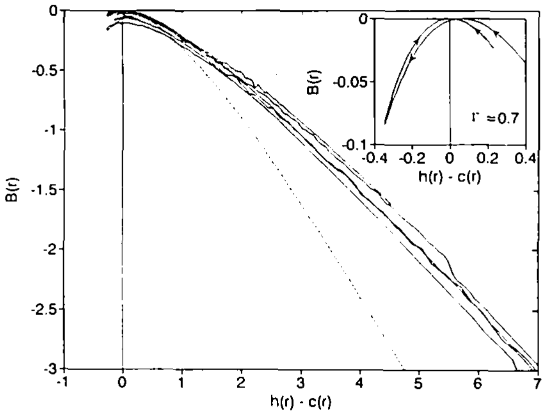

Fig. 1. The soft-sphere fluid bridge functions from simulation [11] (solid curves) at $\Gamma = 0.3$, 0.4, 0.5, 0.6, and 0.7 are shown to be primarily dependent on $h(r) - c(r)$. The Percus Yevick closure (dotted curve) is also shown, but it is in poor agreement with the soft-sphere-fluid simulation results for large $\tau = h(r) - c(r)$ (small separations). The inset shows the soft-sphere fluid bridge function from simulation at $\Gamma = 0.7$ to be a multivalued function of $h(r) - c(r)$ at small $h(r) - c(r)$. In terms of r, increasing from $r = 0$, the bridge function curve enters at the right, has a zero at $h(r) - c(r) \approx 0.063$, reaches a minimum, and finally oscillates along a single curve about $h(r) - c(r) = 0$ as the bridge function decays to zero.

oscillations beyond the first oscillation. We can fit the simulation bridge-function results with the function

$$B(\tau)=\begin{cases} A[-\tau+\ln(\tau+1)] & \text{for} \quad \tau\geqslant 0 \quad \text{up to the first zero of } B(\tau) \\ -\tau+\ln(\tau+1) & \text{otherwise} \end{cases} \tag{6}$$

where $A\approx 0.65$. The parameter A could be treated as an adjustable parameter to obtain thermodynamic consistency [2].

In the inset to Fig. 1 we plot the soft-sphere bridge function for $\Gamma=0.7$ and we focus on the oscillations of the bridge function near $\tau=0$. In this case, we have replaced the simulation direct correlation function for $r>1.3\sigma$ with $-\beta\phi(r)$. As seen in Fig. 1, the soft-sphere bridge function is not a single-valued function of τ and the first zero of the function does not occur at $\tau=0$. Similar results are found for other values of Γ and prior to making the substitution of $-\beta\phi(r)$ for the direct correlation function; however, they are most easily seen for $\Gamma=0.7$. It is interesting to note that the PY bridge function provides an excellent fit to the soft-sphere bridge function after the first minimum. In the region where $c(r)$ can be approximated by $-\beta\phi(r)$, the bridge function can be written as

$$B(r)=-h(r)+\ln[h(r)+1] \tag{7}$$

Since the pair potential is small in this range, we have found that the function

$$B(\tau)=-\tau+1-\exp[-\beta\phi(r)]+\ln\{\tau+\exp[-\beta\phi(r)]\} \tag{8}$$

where $\phi(r)$ is the soft-sphere potential, provides an excellent correlation of the soft-sphere bridge function for all values of Γ if τ is not too large $(\tau<2)$.

The question arises, can the bridge function always be written as a function of τ? In Fig. 2 we plot bridge functions for the LJ fluid determined from simulation [10] for $\rho^*=0.8$ with $T^*=0.81$, 1.0, and 1.5 and $\rho^*=0.85$ with $T^*=0.72$. We observe that the LJ bridge function is not simply a function of τ; this may be due to the attractions between the LJ spheres. If the functional form is only universal for fluids without attractions, the PY approximation should be best for repulsive fluids; this is what has been observed [2]. If we can add information about the attractions between molecules into τ, it might be possible to develop a more universal closure.

For the Lennard-Jones fluid, we can separate the potential into reference (repulsive) and attractive parts as was done in the Weeks, Chandler, and Andersen (WCA) perturbation theory [21]. Separating the

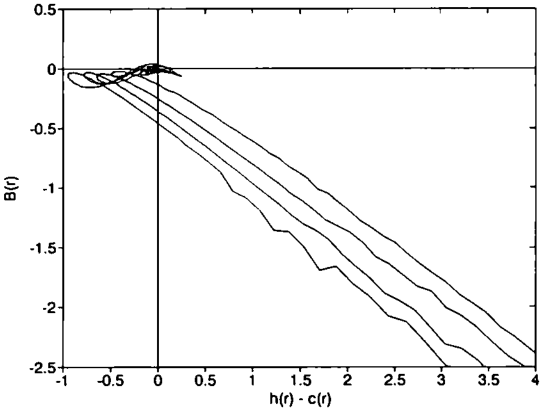

Fig. 2. The Lennard-Jones-fluid bridge functions from simulation [10] (curves) plotted versus $h(r)-c(r)$. The curves from left to right are for the conditions $\rho^* = \rho\sigma^3 = 0.85$ with $T^* = 0.72$, and $\rho^* = 0.8$ with $T^* = 0.81$, 1.0, and 1.5. No general correlation is apparent.

LJ potential at the minimum, the WCA attractive part of the potential is given by

$$\phi_a(r) = \begin{cases} -\varepsilon, & 0 \leqslant r \leqslant r_{\min} \\ 4\varepsilon\left[\left(\dfrac{\sigma}{r}\right)^{12} - \left(\dfrac{\sigma}{r}\right)^{6}\right], & r \geqslant r_{\min} \end{cases} \tag{9}$$

If we assume that the functional form of $B(\tau)$ is universal for fluids without attractions, the bridge function for the WCA reference fluid is only dependent on τ_{WCA}. The WCA perturbation theory is successful for dense fluids in part because the pair correlation function for the WCA reference fluid is approximately the same as the pair correlation function for the LJ fluid [2]. If we write $g_{\mathrm{LJ}}(r) \approx g_{\mathrm{WCA}}(r)$ for a dense fluid, then the cavity correlation function for the LJ fluid is approximately

$$\ln[y_{\mathrm{LJ}}(r)] \approx \ln[y_{\mathrm{WCA}}(r)] + \beta\phi_a(r) \tag{10}$$

If we use the random-phase approximation [2, 22, 23]

$$c_{\mathrm{LJ}}(r) + \beta\phi_a(r) \approx c_{\mathrm{WCA}}(r) \tag{11}$$

then from Eqs. (2), (10), and (11) we have

$$B_{\mathrm{LJ}}(\tau_{\mathrm{LJ}}) = \ln[y_{\mathrm{WCA}}(r)] + \beta\phi_a(r) - [h_{\mathrm{LJ}}(r) - c_{\mathrm{LJ}}(r)] \approx B_{\mathrm{WCA}}(\tau_{\mathrm{LJ}} - \beta\phi_a(r)) \tag{12}$$

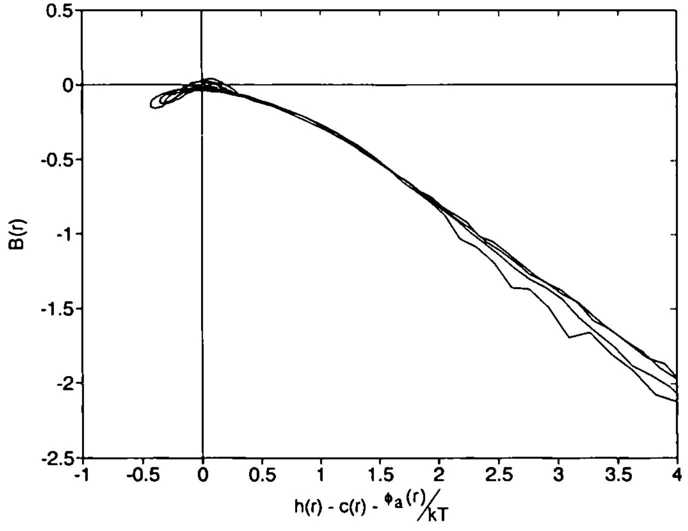

Fig. 3. The Lennard-Jones-fluid bridge functions from simulation [10] (solid curves) at $\rho^* = \rho\sigma^3 = 0.8$ with $T^* = 0.81$, 1.0, and 1.5, and at $\rho^* = 0.85$ with $T^* = 0.72$, plotted versus $h_{\mathrm{LJ}}(r) - c_{\mathrm{LJ}}(r) - \phi_{\mathrm{a}}(r)/kT$.

The LJ bridge function at τ_{LJ}, $B(\tau_{\mathrm{LJ}})$, is approximately equal to the WCA bridge function evaluated at $\tau' = \tau_{\mathrm{LJ}} - \beta\phi_{\mathrm{a}}(r)$. As shown in Fig. 3, by plotting the LJ bridge function versus τ', we find that $B_{\mathrm{LJ}}(\tau')$ appears to be nearly the same function as plotted in Fig. 1. Equation (6) provides a good correlation of the LJ bridge function results [10] when τ is replaced by τ' and A is set equal to ρ^*. Because the approximations developed above for the LJ fluid are based in part on WCA theory, this closure should be valid at intermediate densities. It is not our intent to develop rigorous new closures, but to point out interesting features of our calculated bridge functions.

3. CONCLUSIONS

The simulation distribution functions were used to examine the validity of closures based on $\tau = h(r) - c(r)$. Neither the soft-sphere bridge function nor the Lennard-Jones fluid bridge function are single-valued in τ. The results imply that the bridge function for fluids with weak, short-ranged attractions is primarily determined by the short-ranged repulsive part of the potential. We conclude that the PY closure is best for nonattracting fluids; however, a semiempirical closure based on simulation should provide the best agreement for a variety of fluids. These simulation results should provide a strong test for proposed bridge function approximations.

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