Simple Integral Equation and Density Functional Study of a Hard Sphere Fluid in a Pore Formed by Two Hard Walls

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The structure of a hard sphere fluid in a pore formed by two parallel hard walls is studied as a function of the separation of the walls using the singlet theory of Henderson et al. and Lozada-Cassou with the Percus−Yevick (PY) and hypernetted chain (HNC) closures, which were studied previously, and a modified version of the Verlet (MV) closure. In addition, the density functional formalism of Tarazona et al. (TME) is employed. As noted earlier, the singlet theory yields poor results when the PY and HNC closures are used but yields quite good results when the MV closure is used. The TME approach also yields good results. The MV and singlet theory results are comparable in accuracy with those obtained from the second-order PY (PY2) theory but are much less demanding computationally.

Recently, we[1] studied a hard sphere fluid in a pore formed by two parallel hard walls, separated by a distance H using the singlet theory of Lozada-Cassou[2] with the Percus−Yevick (PY) and hypernetted chain (HNC) closures. This approach is a singlet level theory in the sense that the coordinates of only one hard sphere are considered; however, a total of three particles (one fluid particle and two giant, or surface, particles) are considered. The Lozada-Cassou theory is an extension of singlet theory of Henderson et al.[3] (HAB). It was found that the singlet theory gave poor results with these closures. This is not surprising since it is well-known that the HAB approach can be inaccurate when these closures are used. In contrast, good agreement with the simulations of Wertheim et al.[4] were obtained when a second-order Percus-Yevick (PY2) theory was used. The PY2 theory is a second-order theory in the sense that the coordinates of two hard spheres are considered. However, a total of four particles are considered. As a result, the calculations are difficult.

Some time ago, it was shown[5] that good results both for a hard sphere fluid and for a hard sphere fluid near a single wall, i.e., the HAB approach, were obtained with a modified Verlet[6] (MV) closure. This point has been made again in a recent paper.[7] Thus, one might hope that the MV closure might yield good results for a narrow pore. One aim of this work is to examine this hypothesis. In addition, we apply the density functional (DF) approach of Tarazona et al. (TME),[8,9] with the Carnahan−Starling free energy for hard spheres, to this system. This has been done previously; however, we include these results for comparison.

We consider a fluid of hard spheres of diameter d between two parallel hard walls, separated by the distance H. Thus, $H - d$ is the separation between the two planes of closest approach of the hard sphere fluid. The original version of the Ornstein−Zernike (OZ) equation, useful for bulk fluids, is well-known. HAB observed that the OZ formalism can be applied to inhomogeneous fluids. The HAB equation is

$$h(z_1) - c(z_1) = \rho\int_{-\infty}^{\infty} h(z_2)\, C(|z_1 - z_2|)\, \mathrm{d}z_2 \qquad (1)$$

where h and c are the total and direct correlation functions for the fluid−pore pair, ρ is the density of the bulk fluid,

$$C(s) = 2\pi\int_s^{\infty} t c_B(t)\, \mathrm{d}t \qquad (2)$$

and $c_B(t)$ is the direct correlation function of the bulk fluid, which is presumed to be known. Lozada-Cassou made the important observation that eq 1 can be applied to a pore as well as to a fluid near a single wall. The PY and HNC theories result from the combination of eq 1 and the PY closure,

$$\gamma(r) = y(r) - 1 \qquad (3)$$

or the HNC closure,

$$\gamma(r) = \ln y(r) \qquad (4)$$

In the above equations, $\gamma(r) = h(r) - c(r)$, and $y(r)$ is the cavity or background function. The function $C(s)$ *is* obtained using some approximation for the bulk fluid. We use the PY result because it is quite accurate and is analytic so that the integration in eq 2 can be performed analytically. Further details about the original OZ equation, closures, and the extensions discussed above can be found in a recent book on inhomogeneous fluids.[10]

The results of the singlet theory with the PY and HNC closures are displayed in Figures 1−3. The density profile is

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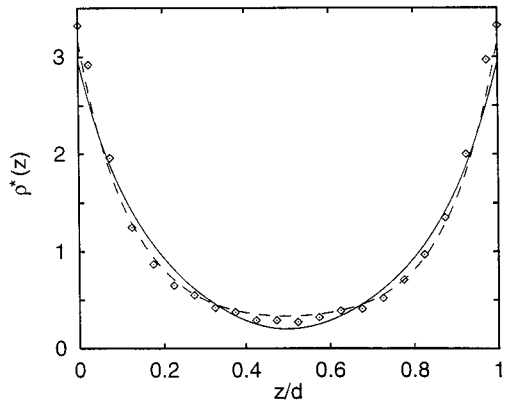

Figure 1. Density profile, $\rho^*(z) = \rho(z)d^3$, of a hard sphere fluid in a pore formed by two hard parallel walls whose separation is $H = 2d$. The fluid is in equilibrium with a bulk hard sphere fluid whose density is $\rho d^3 = 0.6$. The diamonds give the simulation results of Wertheim, and the solid and broken curves give the singlet MV and density functional results, respectively.

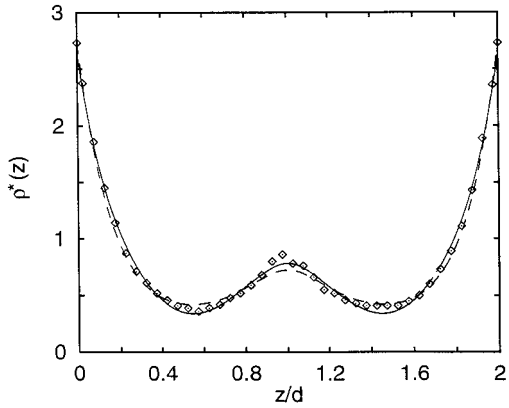

Figure 2. Density profile, $\rho^*(z) = \rho(z)d^3$, of a hard sphere fluid in pore formed by two hard parallel walls whose separation is $H = 3d$. The fluid is in equilibrium with a bulk hard sphere fluid whose density is $\rho d^3 = 0.6$. The diamonds and curves have the same meaning as in Figure 1.

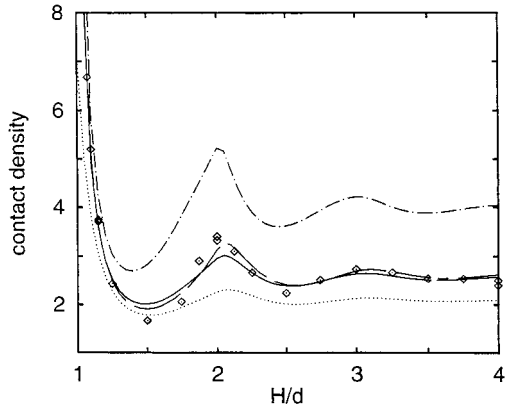

Figure 3. Contact density of a hard sphere fluid in a pore formed by two hard parallel walls as a function of the separation. The fluid is in equilibrium with a bulk hard sphere fluid whose density is $\rho d^3 = 0.6$. The diamonds and solid and broken curves have the same meaning as in Figure 1. The dot-dashed and dotted curves give the singlet HNC and PY results, respectively.

given by $\rho(z) = \rho[h(z) + 1]$. The contact values of $\rho(z)$, shown in Figure 3, are directly related to the salvation force between the walls. The pressure acting on the walls is equal to kT times the difference between the contact value at H and at $H = \infty$. The quantity k is the Boltzmann constant, and T is the temperature. The HNC and PY density profiles are too large and too small, respectively. This point has already been made[1] and is consistent with the general tendencies of these closures for hard spheres.

The Verlet closure is

$$\gamma(r) = \ln y(r) + \frac{\gamma^2(r)}{2[1 + \alpha\gamma(r)]} \tag{5}$$

where α is a parameter. Verlet[6] assigned a value to α that, presumably, he determined by trial and error. More recently, it has been suggested by Henderson et al.[5] that α should be state dependent. For hard spheres, they use

$$\alpha = \frac{17}{120\eta} + 0.5150 - 0.2210\eta \tag{6}$$

where

$$\eta = \pi\rho d^3/6 \tag{7}$$

The first term in eq 6 reproduces, to order ρ^2, the easily calculated value of $y(r)$ at zero separation of a pair of hard spheres. This modified Verlet closure works well for a fluid of hard spheres and for a hard sphere fluid at a single hard wall. It is hoped that it will also be satisfactory for a hard sphere fluid in a pore, i.e., for small values of H.

Some results of the singlet theory with the MV closure are given in Figures 1−3. The results are very pleasing, even at small values of H. It is to be noticed in Figure 2 that the simulations results are slightly asymmetric about the midpoint of the pore. Taking this asymmetry as a measure of the statistical error in the simulations, we conclude that the MV closure results agree with the simulation results, within their statistical error.

For comparison, we display results, obtained from the TME density functional theory in Figures 1−3; we used the algorithm of Tarazona and the Evans−Tarazona weight function. As well as comparing contact values in Figure 3, we can compare the numerical values of the contact value at $H = d$, when all the hard spheres have been "squeezed out" of the pore. The PY, HNC, MV, and TME values are 7.19, 35 344, 135.9, and 124.9, respectively. The MV and TME values compare well with the exact result, 123.3, obtained from the chemical potential of a hard sphere fluid. The density functional theory is constrained to give the exact result, within the accuracy of the Carnahan−Starling expression, when $H = d$. The TME and MV results are both very good, the TME results being somewhat better. The MV and TME results are of about the same accuracy as the PY2 results that we have obtained recently.[1] The PY2 theory is more sophisticated than any of the theories discussed here and has the advantage of not being too sensitive to the closure that is employed but is much more demanding computationally. We hope to define satisfactory bridge functions for other systems and use the singlet theory and density functional theory to study solvation forces for more realistic fluids and pores.

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