Journal of Statistical Physics, Vol. 89, Nos. 1/2, 1997

Second-Order Percus–Yevick Theory for a Confined Hard-Sphere Fluid

Douglas Henderson,[1,2,4] Stefan Sokołowski,[3] and Darsh Wasan[2]

Received December 3, 1996; final February 11, 1997

A fluid of hard spheres confined between two hard walls and in equilibrium with a bulk hard-sphere fluid is studied using a second-order Percus–Yevick approximation. We refer to this approximation as second-order because the correlations that are calculated depend upon the position of two hard spheres in the confined fluid. However, because the correlation functions depend upon the positions of four particles (two hard spheres and two walls treated as giant hard spheres), this is the most demanding application of the second-order theory that has been attempted. When the two walls are far apart, this calculation reduces to our earlier second-order approximation calculations of the properties of hard spheres near a single hard wall. Our earlier calculations showed this approach to be accurate for the single-wall case. In this work we calculate the density profiles and the pressure of the hard-sphere fluid on the walls. We find, by comparison with grand canonical Monte Carlo results, that the second-order approximation is very accurate, even when the two walls have a small separation. We compare with a singlet approximation (in the sense that correlation functions that depend on the position of only one hard sphere are considered). The singlet approach is fairly satisfactory when the two walls are far apart but becomes unsatisfactory when the two walls have a small separation. We also examine a simple theory of the pressure of the confined hard spheres, based on the usual Percus–Yevick theory of hard-sphere mixtures. Given the simplicity of the latter approach the results of this simple (and explicit) theory are surprisingly good.

KEY WORDS: Confined fluid; pore; split pore; inhomogeneous fluid; integral equation; Percus–Yevick theory; hard-sphere fluid; colloid; interaction potential.

---

[1] Department of Chemistry and Biochemistry, Brigham Young University, Provo, Utah 84602.

[2] Department of Chemical Engineering, Illinois Institute of Technology, Chicago, Illinois 60616.

[3] Department for the Modelling of Physico-Chemical Properties, Faculty of Chemistry, MCS University, 20031 Lublin, Poland.

[4] To whom correspondence should be addressed at Department of Chemistry and Biochemistry, Brigham Young University, Provo, Utah 84602.

1. INTRODUCTION

It is a pleasure to participate in this volume celebrating Bernard Jancovici's birthday and career. We are interested in inhomogeneous fluids; Bernard's analytic solution for the profile and correlation functions of the two dimensional one component plasma is one of the few exact results that are available to guide our thinking. Bernard is also an amiable and gracious host.

The problem of the theory of a confined fluid is closely related to the problem of the theory of colloidal fluids. Colloidal fluids are of intrinsic scientific interest and are of great practical importance in the computer, chemical, food, petroleum, and environmental industries as well as in other industries.

The interaction between two colloidal particles (we assume them to be spherical for simplicity) in a fluid is usually described by the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory. In this theory, the potential interaction between the colloidal particles is sum of a long range repulsive electrostatic interaction and a short range attractive dispersion interaction. The electrostatic interaction is calculated by a simple Poisson–Boltzmann (PB) approximation that, in its linearized version, gives an exponential repulsion. Thus, the DLVO interaction is of the form

$$w(r) = -\frac{A}{r-2a} + B\exp[-\kappa(r-2a)], \tag{1}$$

where A and B are constants whose values are not of interest here. The first term comes from averaging the attractive dispersion energy, r^{-6}, over the volume of two large spheres of radii, a. The parameter, κ, is the usual Debye inverse screening length.

The experiments of Israelachvili and collaborators$^{(1)}$ have shown that the DLVO theory is reliable when the separation between the particles is large. However, as the separation becomes smaller, additional contributions to the interaction become apparent. Israelachvili has called these additional contributions the hydration force. In many cases, the hydration force consists of two terms. The first is an extra repulsion and the second is an oscillatory interaction. Henderson and Lozada-Cassou (HLC)$^{(2-3)}$ have argued that dielectric saturation in a polar solvent is responsible for the first term and that core effects are responsible for the second, oscillatory, term. In this paper, we study only the second oscillatory term. HLC have obtained an approximation to this term by using the hard sphere potential

$$u(r) = \begin{cases} \infty, & r < d \\ 0, & r > d \end{cases}, \tag{2}$$

where d is the diameter of the hard spheres, together with the results of Lebowitz$^{(4)}$ for the correlation functions of a hard-sphere mixture. One purpose of this note is to study the accuracy of the HLC result.

Another approach to the study of the interaction between two colloidal particles is through the use of simulations or of the theory of inhomogeneous fluids. Ideally, one would consider colloidal particles of large size and very small concentration in a fluid of small particles. This is not so easy. To perform computer simulations for a small concentration of large particles would require a very large system. A very large simulation cell is required to accomodate the large particles. In addition, because of the low concentration of the large particles, a large number of particles (and, hence, a large cell) would be required to have a sufficient number of large particles to yield good statistical averages.

In principle, the application of the theory of integral equations is not so formidable. One can obtain the form of the integral equations in the limit of very large colloidal, particles at small concentration and then solve this equations. Even though straightforward in principle, difficult numerical problems can be encountered. We are pursuing both simulations and integral equation theory for colloidal spheres and will report our results in due course.

A more straightforward approach is to consider a fluid adsorbed into a slit. The fluid in the slit is in thermodynamic equilibrium with the bulk fluid. This problem is related to the problem of the interaction between large colloidal spheres in small concentration by the Derjaguin approximations that relates the force, F, between two large colloidal particles, assumed to be spherical and of radius a, that are present in dilute concentration in a fluid of small particles to the interaction energy, $E(H)$, per unit area, A, between the walls of the slit.

$$\frac{F}{a} = \pi \frac{E(H)}{A} \tag{3}$$

The parameter, H is the separation of the two walls.

We consider the problem of a hard sphere fluid confined by two parallel hard walls in this publication. Thus the interaction between the fluid molecules is given by Eq. (2), and interaction of the hard spheres with the walls is given by

$$v(z) = \begin{cases} \infty, & z < d/2 \quad \text{or} \quad > H - d/2 \\ 0, & \text{otherwise} \end{cases} \tag{4}$$

In this coordinate system, $H < d$ corresponds to the situation where all the hard spheres have been "squeezed" from the pore. Not only is this problem of the confined fluid of interest because of its relation to colloids, it is an interesting problem in its own right. Wertheim *et al.*(6) have simulated this system. Evans and Marina Bettolo Marconi(7) have considered the thermodynamics of this system. Lozada-Cassou(8) and Zhou and Stell(9) have applied integral equations to this system. Very recently, Götzelmann and Dietrich (GD)(10) have studied this system by density functionals. When H is large, this system becomes the hard sphere fluid near a single wall studied by Henderson *et al.*,(11) Percus,(12) Sokolowski,(13) and Plischke and Henderson(14) by integral equations and by Snook and Henderson(15) and J. R. Henderson and van Swol(16) by simulations.

2. SIMPLE HLC THEORY

The simplest approach is to start with the well-known Ornstein–Zernike(OZ) relation

$$h_{ij}(r_{12}) = c_{ij}(r_{12}) + \sum_k \rho_k \int h_{ik}(r_{13})\, c_{jk}(r_{23})\, d\mathbf{r}_3, \tag{5}$$

where $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ is the scalar distance between two particles located at $\mathbf{r}_i$ and $\mathbf{r}_j$ and $\rho_k = N_k/V$ is the density of particles of species k, N_k, divided by the volume, V. The functions $h_{ij}(r) = g_{ij}(r) - 1$ and $c_{ij}(r)$ are the total and direct correlation functions, respectively, for a pair of particles of species i and j. The function $g_{ij}(r)$ is the radial distribution function, which is proportional to the probability of finding two particles of species i and j separated by a distance r. Equations (5) must be supplemented by a closure.

If the concentration of one species, say species C, is very small, then Eqs. (5) become

$$h(r_{12}) = c(r_{12}) + \rho \int d\mathbf{r}_3\, h(r_{13})\, c(r_{23}) \tag{6}$$

$$h_C(r_{12}) = c_C(r_{12}) + \rho \int d\mathbf{r}_3\, h_C(r_{13})\, c(r_{23}) \tag{7}$$

and

$$h_{CC}(r_{12}) = c_{CC}(r_{12}) + \rho \int d\mathbf{r}_3\, h_C(r_{13})\, c_C(r_{23}) \tag{8}$$

The subscript for the fluid (or solvent), which is present in high concentration, has been suppressed. The extension to the case where the solvent is a mixture is obvious.

Equation (6) is the usual OZ relation for the pure solvent. The inhomogeneous density in the vicinity of a particle of species C can be obtained from the solution of Eq. (7)

$$\rho(r) = \rho g_C(r), \tag{9}$$

where $\rho = \rho(\infty)$ is the density of the bulk fluid. Equation (7) is the basis of the singlet approach of Henderson *et al.*(11) and Percus.(12) The approach is called a singlet approach because the correlation functions depend only on the position of a single solvent particle. The other particle, of species C, is regarded as the source of an inhomogeneity. The energy of interaction between two particles of species C, in the presence of the solvent molecules, is obtained from the results of Eq. (8)

$$w(r) = -kT \ln g_{CC}(r), \tag{10}$$

where k is Boltzmann's constant and T is the temperature. The force F in Eq. (3) is the derivative of $w(r)$ with respect to r.

Following Henderson *et al.*(11) and Percus,(12) Eqs. (7) and (8) can be written the form appropriate for the case of colloid particles, where the particles of species C are very large.

Using the results of Lebowitz,(4) HLC have obtained analytic formulae for the solutions of Eqs. (6–8) for large and small hard spheres. They used the Percus–Yevick (PY) closure,

$$h(r) - c(r) = y(r) - 1, \tag{11}$$

or, equivalently,

$$c(r) = f(r)\, y(r) \tag{12}$$

where

$$f(r) = \exp[-\beta u(r)] \tag{13}$$

is the Mayer function,

$$y(r) = \exp[\beta u(r)]\, g(r) \tag{14}$$

and $\beta = 1/kT$, for Eqs. (6–7) and the hypernetted chain (HNC) closure,

$$h(r) - c(r) = \ln y(r), \tag{15}$$

for Eq. (8). The PY closure is used because, generally speaking, it is a good approximation for hard spheres. However, the use of the PY closure in Eq. (8) would result in an interaction energy, $w(r)$, between large colloidal particles that is proportional to the logarithm of the size of the colloidal particles, a result in contradiction both with experiment and the Derjaguin approximation. The HNC closure gives the correct linear dependence of $w(r)$ on the size of the colloidal particles. We refer to this mixture of PY and HNC closures as the HNC/PY/PY approximation.

The HLC procedure, involving a mixture of closures, is rather ad hoc and has not been tested directly. The comparison with experiment is pleasing but there is some question about the applicablity of the hard sphere potential to the real fluids, especially water. A direct test of the HLC approach is needed. The most direct test would be a comparison of the HLC procedure with simulation results or highly accurate integral equations for a mixture of dilute large hard spheres in a solvent of small hard spheres. Such studies are in progress and will be reported in due course. In this note, we use the HLC results for $w(r)$, together with the Derjaguin approximation, to obtain the pressure, the derivative of $E(H)$, with respect to H, for a hard sphere fluid confined between two hard walls and in equilibrium with a hard sphere fluid and compare with the results of more sophisticated integral equations and simulations.(6)

3. SINGLET AND PAIR THEORIES

One such sophisticated integral equation is the singlet theory of Lozada-Cassou(8) who used Eq. (7) but took the fluid of species C to be a pair of large particles. These could be two large spheres but this geometry is rather complex; generally two flat walls are used. This is a singlet theory because the coordinates of only one hard sphere appear. However, the coordinates of three particles, one hard sphere and two walls, are involved. Lozada-Cassou refers to this approach as the three point extension (TPE). For confined hard spheres, Eq. (6) is solved with the PY closure and Eq. (7) is solved with either the PY or the HNC approximation. The resulting scheme can be referred to as the PY/PY or the HNC/PY approximation, respectively. At large separation of the two walls, this theory reduces to that of Henderson *et al.*(11). They have observed that for a fluid near a hard wall, the singlet approach gives a contact density that is equal to the geometric or arithmetic mean, respectively, of unity and the inverse of the compressibility of the fluid for the PY/PY and HNC/PY approximations rather the correct result of the pressure. This means that at large separation, Lozada-Cassou's theory will have some error for the profiles at contact. However, one might hope that the situation will be no worse at small separation. The excess pressure required to squeeze the confined fluid is

$$p = kT[\rho_c(h) - \rho_c(\infty)], \tag{16}$$

where $\rho_c(H)$ is the contact density of the profile for wall separated by the distance H. One might hope that a cancellation of errors might result in good values of the pressure.

The pair theory results from the second order OZ relation

$$h(\mathbf{r}_1, \mathbf{r}_2) = c(\mathbf{r}_1, \mathbf{r}_2) + \int d\mathbf{r}_3\, \rho(\mathbf{r}_3)\, c(\mathbf{r}_1, \mathbf{r}_3)\, h(\mathbf{r}_2, \mathbf{r}_3), \tag{17}$$

where $h(\mathbf{r}_1, \mathbf{r}_2) = g(\mathbf{r}_1, \mathbf{r}_2) - 1$ is the pair level total correlation function, $c(\mathbf{r}_1, \mathbf{r}_2)$ is the pair level direct correlation function, and $\rho(\mathbf{r}_1)$ is the local density. The exact relation between the local density and the pair correlation function is

$$\nabla_1 \ln \rho(\mathbf{r}_1) = \int d\mathbf{r}_2\, \rho(\mathbf{r}_2)\, c(\mathbf{r}_1, \mathbf{r}_2) = -\int d\mathbf{r}\, \nabla_2 v(\mathbf{r}_2)\, h(\mathbf{r}_1, \mathbf{r}_2), \tag{18}$$

where $v(\mathbf{r})$ is the external potential field. The PY closure supplements Eqs. (17) and (18) with the approximate relations

$$c(\mathbf{r}_1, \mathbf{r}_2) = y(\mathbf{r}_1, \mathbf{r}_2)\, f(\mathbf{r}_1, \mathbf{r}_2) \tag{19}$$

or, equivalently,

$$h(\mathbf{r}_1, \mathbf{r}_2) = y(\mathbf{r}_1, \mathbf{r}_2)[f(\mathbf{r}_1, \mathbf{r}_2) + 1] - 1, \tag{20}$$

where $y(\mathbf{r}_1, \mathbf{r}_2)$ is the pair level cavity function and $f(\mathbf{r}_1, \mathbf{r}_2)$ is the Mayer function. We refer to this combination of the second order OZ equation and the PY closure as the PY2 theory. We regard this as a pair theory because the coordinates of two hard spheres appear. However, the coordinates of four particles, two hard spheres and two walls, are involved. As a result, this is a demanding calculation.

Substituting Eq. (19) or (20) into Eq. (17) we obtain

$$Y(\mathbf{r}_1, \mathbf{r}_2) = \int d\mathbf{r}_3\, \rho(\mathbf{r}_3)\, Y_f(\mathbf{r}_1, \mathbf{r}_3)[Y(\mathbf{r}_2, \mathbf{r}_3) + Y_f(\mathbf{r}_2, \mathbf{r}_3)], \tag{21}$$

where $Y(\mathbf{r}_1, \mathbf{r}_2) = y(\mathbf{r}_1, \mathbf{r}_2) - 1$ and $Y_f(\mathbf{r}_1, \mathbf{r}_2) = y(\mathbf{r}_1, \mathbf{r}_2)\, f(\mathbf{r}_1, \mathbf{r}_2)$.

Assuming that the external potential has the form we model adsorption of a fluid inside the slit like pore of the width H. Equation (18) takes the form

$$d \ln \rho(z_1)/dz_1 = \int d\mathbf{r}_2\, \rho(z_2)\, c(\mathbf{r}_1, \mathbf{r}_2)$$

$$= -\int dx_2\, dy[h(z_1=0, z_2, r_{12}) + h(z_1=H, z_2, r_{12})] \qquad (22)$$

The quantities Y, Y_f, g and c are now the functions of the variables z_1, z_2 and the planar distance between the points r_1 and r_2, $R_{12}^2 = r_{12}^2 - (z_1 - z_2)^2$. Defining the Fourier–Bessel transform with respect to horizontal coordinates as

$$\tilde{F}(z_1, z_2, k) = \int dR_{12}\, F(z_1, z_2, R_{12}) \exp(i\mathbf{k}\mathbf{R}_{12})$$

$$= 2\pi \int_0^\infty F(z_1, z_2, R_{12})\, J_o(kR_{12})\, R_{12}\, dR_{12}, \qquad (23)$$

where J_o is a Bessel function of the first kind of the zero-th order and F stands for Y and for Y_f, Eq. (21) can be rewritten

$$\tilde{Y}(z_1, z_2, k) = \int dz_3\, \tilde{Y}_f(z_1, z_3, k)[\tilde{Y}(z_2, z_3, k) + Y_f(z_2, z_3, k)]\, \rho(z_3), \qquad (24)$$

whereas Eq. (22) becomes

$$d \ln \rho(z_1)/dz_1 = -[Y(z_1=0, z_2, k=0) + Y_f(z_1=0, z_2, k=0)$$

$$+ Y(z_1=H, z_2, k=0) + Y_f(z_1=H, z_2, k=0)] \quad (25)$$

Let λ_i be the set of the positive roots of $J_o(x) = 0$. From the theory of Bessel functions we know that the system of the functions $J_o(\lambda_n x/l)$, $n = 1, 2, \ldots$ is orthogonal set in the Hilbert space $L_{2,x}(0, l)$. These functions also constitute a complete system in this space. Thus, the function $F(z_1, z_2, R_{12})$ can be expanded into a Fourier–Bessel series

$$F(z_1, z_2, R_{12}) = \sum_{n \geqslant 1} \phi_n(z_1, z_2)\, J_o(\lambda_n R_{12}/l) \qquad (26)$$

where

$$\phi_n(z_1, z_2) = \int_0^l F(z_1, z_2, R_{12})\, J_o(\lambda_n R_{12}/l)\, R_{12}\, dR_{12} \Big/ \int_0^l R_{12} J_o^2(\lambda_n R_{12}/l)\, dR_{12}. \tag{27}$$

In the above we have assumed that $F(z_1, z_2, R_{12})$ effectively vanishes for $R_{12} > l$; this implies that the Fourier–Bessel transform need not be calculated for values of k more closely spaced than some finite minimum, about π/l.

In our numerical procedure we calculate F and $\tilde{F}$ at the selected points $z_1 = i\delta$ and $z_2 = j\delta$, $i, j = 1, 2, \ldots, N$. With the aid of the equations given above, the matrices $[\tilde{F}_{ijk}] = [\tilde{F}(z_i, z_j, k_s)]$ and $[F_{ijm}] = [\tilde{F}(z_i, z_j, R_m)]$ are given by

$$F_{ijm} = (1/\pi l^2) \sum_{s=1}^{M-1} \tilde{F}_{ijs} J_o(\lambda_s \lambda_m / \lambda_M)\, J_1^2(\lambda_s) \tag{28}$$

and

$$\tilde{F}_{ijs} = (4\pi/K^2) \sum_{m=1}^{M-1} F_{ijm} J_o(\lambda_s \lambda_m / \lambda_M) / J_1^2(\lambda_m) \tag{29}$$

where $k_s = \lambda_s/l$, $R_m = \lambda_m l/\lambda_M$, $K = k_M$ and the summation is terminated at $n = M$. The last two relations allow efficiency in the transform calculations. We stress that the matrices $[F_{ijk}]$ and $[\tilde{F}_{ijm}]$ are symmetric with respect to the indices i and j.

The integration of the inhomogeneous or nonuniform pair level Percus–Yevick equation requires the specification of the constant of the integration of Eq. (25). In the case of a fluid in contact with a single wall, the density profile is constant and equal to the bulk fluid density, ρ, if the distance from the surface is sufficiently large. Obviously, in the case of slit-like pores there exists no "bulk" part of the system within the slit. Consequently, ρ cannot be taken as the integration constant.

However, the confined fluid is in equilibrium with the bulk system and the equilibrium condition requires a constant chemical potential value for both the confined and bulk fluids. It is well known, that the one-particle cavity or background correlation function, $y(z)$, defined by $\rho(z) = \exp[-\beta v(z)]\, y(z)$, must satisfy, independently of H, the following sum rule

$$\begin{gathered} \lim_{z \to -\infty} y(z) = \exp(\beta\mu), \\ \lim_{z \to \infty} y(z + H) = \exp(\beta\mu), \end{gathered} \tag{30}$$

where μ is the chemical potential. Thus, in the case of the system that we are considering, the value of the background correlation function "inside the wall" should be taken as the integration constant. In order to remove possible sources of error, our strategy for the calculations is the following. First, we consider a wide pore, $H = 10d$. Within the range of the densities that we studied, the most inner part of the pore could be treated as a "bulk fluid." Consequently, for such a wide pore, we can take the value of $\rho(z) = \rho_b$ as the integration constant of Eq. (9). Continuing the integration of this equation for $z < d/2$ (or for $z > H - d/2$), we evaluate the limiting value of the background function $y(z = -\infty)$. This value is used as the integration constant for narrow pores.

In most of our calculations, we used 75 terms in the Fourier–Bessel series (28) and (29); the grid size along the z-axis was $\delta = 0.02d$. However, for very narrow pores we reduced the grid size to $\delta = 0.002d$. The solutions of the equations were obtained using at iterational procedure. The iterations were continued until the maximum difference between two subsequent iterations was lower than 10^{-4}.

4. RESULTS

We report results for the case where the bulk density is $\rho d^3 = 0.6$ since simulation (grand canonical Monte Carlo) results$^{(6)}$ are available for this density. Density profiles, calculated from the PY2 theory for 5 values of H, are shown in Figs. 1–5. The results for the largest value of H, $H = 10d$, are virtually identical to what what be obtained for a hard sphere fluid at a single wall and are the same as those obtained from the methods of Sokołowski$^{(13)}$ and Plischke and Henderson.$^{(14)}$ The agreement of the PY2 results with the simulation results, also shown in Figs. 1–5, is very pleasing, even for small H. The density functional results (calculated for a different density), reported by GD,$^{(10)}$ seem promising but the reported results are for fairly large values of H. The accuracy of their approach for small H is unknown. Lozada-Cassou$^{(8)}$ and Alejandre *et al.*$^{(17)}$ have reported density profiles from the singlet theory. Except at contact, they obtain good results. However, they consider fairly large slits. As is seen in Fig. 1, the density profile is almost flat when H is small. Since the singlet theory is poor for the contact value (see Fig. 6), the singlet theory will not be satisfactory for small slits.

Contact values are shown it Fig. 6. The PY2 results are in quite good agreement with the simulation results. On the other hand, the singlet HNC/PY results are too small whereas the HNC/PY results are too large. At small H, the HNC/PY results seem not too bad. However, this is deceptive.

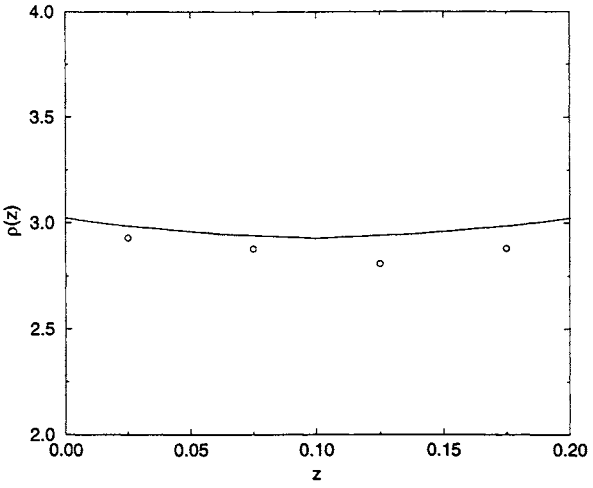

Fig. 1. Density profile of a hard sphere fluid confined by a slit formed by two parallel hard walls whose separation is $H = 1.2d$ and which is in equilibrium with a bulk hard sphere fluid whose density is $\rho d^3 = 0.6$. The density and distance are in units of d^3 and d, respectively. The circles give the simulation results[6] and curve gives the PY2 results.

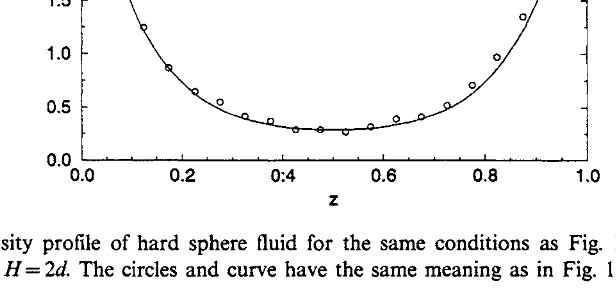

Fig. 2. Density profile of hard sphere fluid for the same conditions as Fig. 1, except that $H = 2d$. The circles and curve have the same meaning as in Fig. 1.

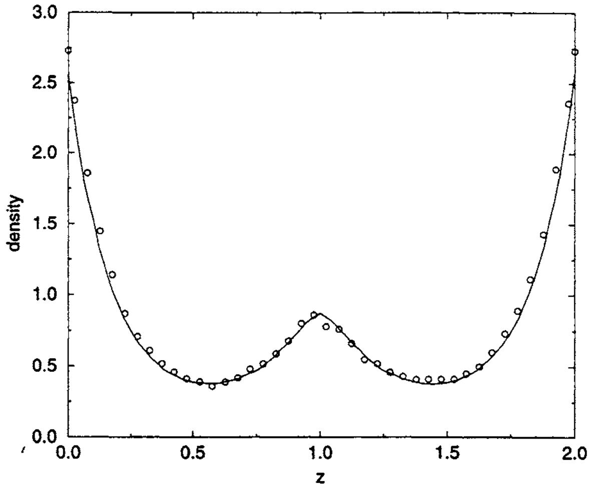

Fig. 3. Density profile. The conditions and the meaning of the circles and curve are the same as Fig. 1, except that $H = 3d$.

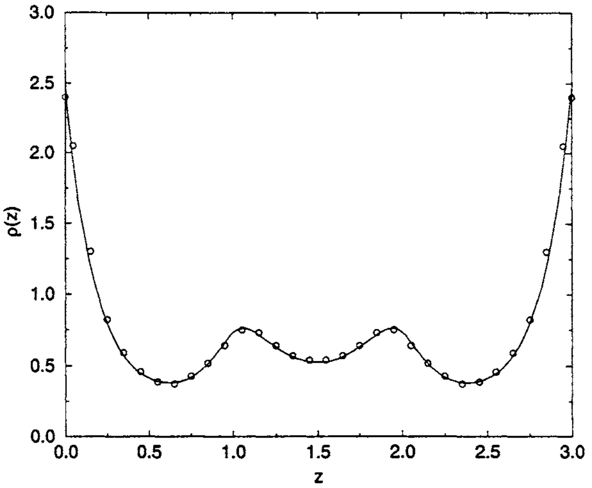

Fig. 4. Density profile. The conditions and the meaning of the circles and curve are the same as in Fig. 1, except that $H = 4d$.

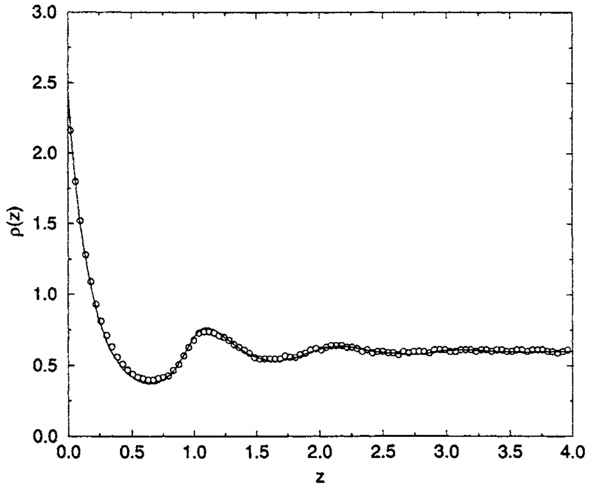

Fig. 5. Density profile. The conditions and the meaning of the circles and curve are the same as in Fig. 1, except that $H = 9d$, which is large enough that the two walls do not interact.

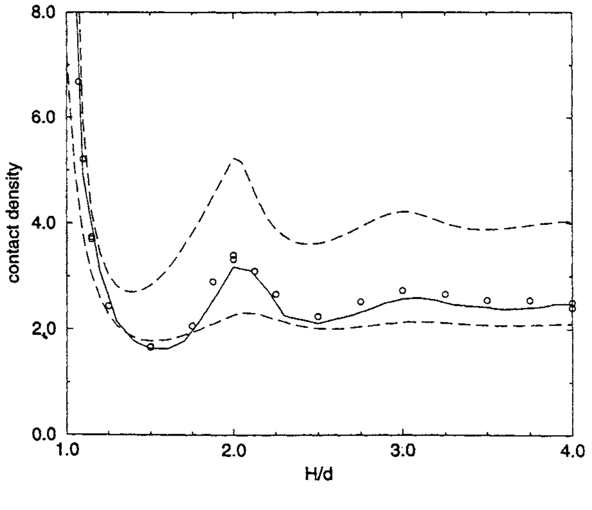

Fig. 6. Contact density of a hard sphere fluid confined by two parallel hard walls as a function of the separation of the walls. The conditions are the same as in Fig. 1. The circles give simulation results.[(6)] The solid and dashed curves give the PY2 and singlet theory[(8)] results, respectively. The upper dashed,curve gives the HNC/PY results and the lower dashed curve gives the PY/PY results.

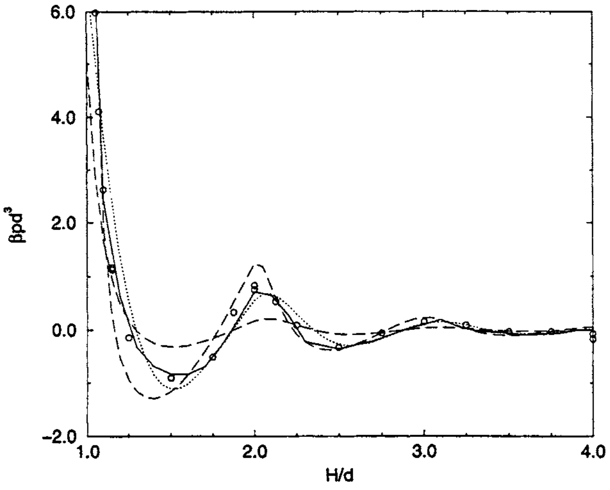

Fig. 7. Excess pressure of a hard sphere fluid confined by two parallel hard walls as a function of the separation of the walls. The conditions are the same as Fig. 1. The meaning of the solid and dashed curves is as in Fig. 6. The short dashed curve gives the HNC/PY/PY of HLC.(11)

At $H = 1$, when all the hard spheres have been squeezed out, the HNC/PY result is orders of magnitude too large.

The pressure, calculated from Eq. (16), is plotted in Fig. 7. One might have hoped that the errors in the singlet theory contact values might have subtracted out. However this is not the case. The PY2 results are very good. This is not surprising since the PY2 contact values are very good. What is perhaps surprising, and certainly pleasing, is that the simple HNC/PY/PY results are fairly accurate. These are obtained from the formulae of Henderson and Lozada-Cassou(2) and the Derjaguin approximation, Eq. (3), which relates the interaction between two flat walls to that of two large spheres.

5. CONCLUSIONS

The simple HNC/PY/PY approximation of HLC, based on the usual OZ relation and the Derjaguin approximation, is fairly accurate. The results given here are the first unambiguous test of this approach. It certainly seems worthy of use in other applications The density functional approach of GD has merit but results for small H are needed before more can be said.

The singlet approach is not satisfactory at small H. The statements of Lozada-Cassou and Alejandre *et al.*, based on comparisons with simulation results for large H, seem too optimistic. The problem with the singlet approach is due the failure of this theory (with simple closures) to give good contact values for the density profile. For the hard sphere fluid, the pressure and compressibility are at least somewhat similar. This places a limit on the error in the singlet theory contact values. For other systems, such as a liquid in coexistence with its vapor, the pressure and compressibility can be very different. As a result, the singlet theory would be rather worse for such a system in a slit than for the confined hard sphere system examined here. We hasten to add that the singlet theory does deal with electrostatic forces correctly, at least at contact. As a result, the singlet approach should be quite useful for systems in which electrostatics dominates, for example, the primitive model electrolyte. Fortunately, this is Lozada-Cassou's main interest.

The PY2 approach gives very good results but with a penalty of numerical complexity. An advantage of both the PY2 and the density functional approach is that both yield pair inhomogeneous functions. However, we do not report pair functions here and defer this issue to a later publication.

ACKNOWLEDGMENTS

The financial support of the National Science Foundation, Grants CTS94-023584 and CHE96-01971 is gratefully acknowledged.

REFERENCES

1. J. N. Israelachvili, *Intermolecular and Surfaces Forces*, Academic Press, London (1992).
2. D. Henderson and M. Lozada-Cassou, *J. Colloid Interface Sci.* **114**:180 (1986).
3. D. Henderson, *J. Colloid Interface Sci.* **121**:486 (1988).
4. J. Lebowitz, *Phys. Rev.* **133**:A895 (1964).
5. B. V. Derjaguin, *Kolloid Z.* **69**:155 (1934).
6. M. Wertheim, L. Blum, and D. Bratko, in *Micellar Solutions and Microemulsions* (S.-H. Chen and R. Rajagopalan, Eds.), Springer-Verlag, New York, NY (1990) Chapt. 6.
7. R. Evans and U. Marini Bettolo Marconi, *J. Chem. Phys.* **86**:7138 (1987).
8. M. Lozada-Cassou, in *Fundamentals of Inhomogeneous Fluids* (D. Henderson, Ed.), Dekker, New York, NY (1992) Chapt. 8.
9. Y. Zhou, and G. Stell, *Mol. Phys.* **66**:767 (1989).
10. B. Götzelmann and S. Dietrich, Report WUB96-35, Fachbereich Physik, Bergische Universität Gesamthochschule Wuppertal (1996).
11. D. Henderson, F. F. Abraham, and J. A. Barker, *Mol. Phys.* **31**:1291 (1976).
12. J. K. Percus, *J. Stat. Phys.* **15**:505 (1976).
13. S. Sokołowski, *J. Chem. Phys.* **73**:3507 (1980).
14. M. Plischke and D. Henderson, *Proc. Roy. Soc.* (*London*) **A404**:323 (1986).
15. I. K. Snook and D. Henderson, *J. Chem. Phys.* **68**:2134 (1978).
16. J. R. Henderson and F. van Swol, *Mol. Phys.* **51**:991 (1984).
17. J. Alejandre, M. Lozada-Cassou, and. L. Degreve, *Mol. Phys.* **88**:1317 (1996).