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Calculation of the density profile of a system of hard spheres near a hard wall using the Henderson–Plischke and related approximations§

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Abstract. The first Born–Green equation for an inhomogeneous fluid, which relates the density profile and an integral of the pair distribution of the fluid, is solved for the particular case of a system of hard spheres near a hard wall. The recent approximation of Henderson and Plischke, which is constructed from the Kirkwood superposition approximation and the Percus shielding approximation, is used for the pair distribution function. The results for the density profile are in reasonably good agreement with Monte Carlo simulations; they are very good near the wall but at larger distances are slightly worse than earlier analytic results obtained from the less sophisticated singlet theory which does not involve the inhomogeneous fluid pair correlation function.

Keywords. Density profile; Born–Green equation; Henderson–Plischke approximation; hard sphere/hard wall system.

1. Introduction

Some years ago, Henderson *et al* (1976) obtained the singlet Ornstein–Zernike equation for the density profile of an inhomogeneous fluid. The advantage and disadvantage of this approach is that only pair functions of the homogeneous (bulk) fluid and singlet density profiles of the inhomogeneous fluid appear and one is not faced with the need to approximate pair functions of the inhomogeneous fluid.

Henderson *et al* (1976) using the singlet Ornstein–Zernike equation and the Percus–Yevick approximation (Percus and Yevick 1958) obtained an analytic expression for the Laplace transform of the density profile. This transform was subsequently inverted analytically by Smith and Henderson (1978). Except in the immediate vicinity of the wall, this density profile is in good agreement with the computer simulations of Snook and Henderson (1978) and Henderson and van Swol (1984) of the hard sphere/hard wall system.

At contact with the hard wall, this singlet Percus–Yevick (hereinafter called PY1) density profile falls to satisfy the exact relation, obtained from force balance considerations,

$$n(0) = \beta p \ , \tag{1}$$

where $n(z)$ is the density and z is the perpendicular distance from the wall, $\beta = 1/kT$ (T is the temperature and k is the Boltzmann constant), and p is the pressure, but instead gives the incorrect result

§ Dedicated to Professor K S G Doss on his eightieth birthday.
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$$n(0) = \rho\left(\beta\frac{\partial p}{\partial \rho}\right)^{1/2}, \tag{2}$$

where $\rho = n(\infty)$ is the bulk density of the fluid. Waisman *et al* (1976) and Henderson and Plischke (1985) have proposed simple semiempirical corrections to the PY1 $n(z)$ for the hard sphere/hard wall system which satisfy (1) and are generally in good agreement with the simulation results at all z. The only remaining problem with these semiempirical $n(z)$ for the hard sphere/hard wall system is that the first minimum in $n(z)$, near $z = 0{\cdot}5d$, where d is the hard sphere diameter, is too deep. Generally this is a minor failing. However, at very high densities this minimum becomes negative, which is unphysical.

The singlet Ornstein–Zernike equation approach has been applied to electrochemical problems. Blum (1977) has used the mean spherical approximation to study the charged hard sphere/charged hard wall (double layer) system and Henderson *et al* (1979), Carnie *et al* (1981), Lozada-Cassou *et al* (1982), Lozada-Cassou and Henderson (1983), and Carnie (1985) have used the hypernetted chain approximation (hereinafter called HNC1) to study this system. The HNC1 results are generally quite good. However, instead of satisfying the exact contact condition,

$$n(0)kT = p + E^2/8\pi\varepsilon, \tag{3}$$

the HNC1 $n(z)$ satisfies

$$n(0)kT = \frac{1}{2}\rho kT\left(1+\beta\frac{\partial p}{\partial \rho}\right) + E^2/8\pi\varepsilon. \tag{4}$$

In many applications this error is not serious because the second term, $E^2/8\pi\varepsilon$, dominates. Also for electrolytes, if a continuum model of the solvent is used. the density of hard spheres is low and the difference between $\beta p/\rho$ and $\frac{1}{2}(1+\beta(\partial p/\partial\rho))$ is not too great. However, if discrete models of the solvent are used or if a high density system of charged hard sphere is used to describe a fused salt double layer, the error in the first term on the right hand side of (4) is much more serious.

Recently, Croxton and McQuarrie (1979, 1981), Henderson *et al* (1981), Lozada (1981), Blum *et al* (1983) and Caccamo *et al* (1986) have used the first Born–Green (BG) equation (Born and Green 1946) to study double layer problems. They obtain results which are as reliable as those of the HNC1 approach. In contrast to the HNC1 approach, the BG theory requires that the pair correlation function be approximated. However, because the BG equation is obtained from force balance considerations, the density profile obtained from the BG equation automatically gives the correct value for the density profile at contact, no matter what approximation is used for the pair correlation function, provided, of course, that this approximate pair correlation function is correct in the bulk.

The modified Poisson–Boltzmann (MPB) approximation (Outhwaite 1978, 1983; Levine and Outhwaite 1978; Outhwaite *et al* 1979, 1980, 1981; Bhuiyan *et al* 1979, 1981; Levine *et al* 1981; Outhwaite and Bhuiyan 1982, 1983) is also accurate for electrolytes and is similar in spirit to the BG approximation in as much as an approximation for the pair correlation function must be introduced before $n(z)$ can be calculated.

In the above applications of the BG and MPB theories, the pair correlation

function was approximated in a relatively simple manner. Plischke and Henderson (1986) have used a more systematic approach. They solve the pair Ornstein–Zernike equation for the inhomogeneous fluid self consistently with the first BG equation, or an equivalent relation between pair and single functions, to obtain the pair correlation function and the density profile. Depending upon whether the Percus–Yevick or hypernetted chain approximations are used in the inhomogeneous Ornstein–Zernike equation, we refer hereinafter to these systems of equations as the PY2 of HNC2 equations.

To date PY2 and HNC2 results have been obtained only for the hard sphere/hard wall system and the Lennard–Jones fluid/hard wall system. However, in principle at least, the method can be applied to electrochemical problems. The Plischke–Henderson procedure is very promising but computationally very difficult. As a result, simple approximations for the pair correlation functions are still of great interest.

Because of the relative complexity of the charged hard sphere/charged hard wall system, the approximations used for the pair correlation function in the Croxton–McQuarrie and Caccamo *et al* BG calculations and in the MPB calculations cannot be tested directly (at present, at least). Instead the approximations are tested by examination of the resulting density profile.

Values for the pair correlation function of an inhomogeneous fluid, obtained by computer simulation, exist only for the hard sphere/hard wall system (Snook and Henderson 1978; Henderson and van Swol 1984). As a result it seems worthwhile to consider this system and examine available approximations for the pair correlation function both by direct comparison with the simulation results and by study of the density profiles obtained by a self consistent solution of the BG equation.

2. Theory

The first Born–Green (BG) equation is obtained by formally differentiating the density profile $n(z)$ with respect to z,

$$-kT\frac{\partial \ln n(z)}{\partial z} = \frac{\partial V(z)}{\partial z} + 2\pi\int_{-\infty}^{\infty}(z-z')n(z')\mathrm{d}z' \times \int_0^{\infty} g(r', z, z')\frac{\partial u(R')}{\partial R'} r'\mathrm{d}r' , \tag{5}$$

where cylindrical coordinates, r' and z', have been used. In (5) $V(z)$ is the external potential due to the wall and $u(R)$ is the pair potential between fluid particles separated by a distance R, $g(r', z, z')$ is the pair correlation for 2 particles at z and z' separated by a distance, R' which is related to r' and z' by

$$R'^2 = r'^2 + (z-z')^2. \tag{6}$$

For the specific case of the hard sphere/hard wall system, (5) becomes

$$\frac{\partial \ln n(z)}{\partial z} = 2\pi \int_{[0,\, z-d]}^{z+d} (z-z')n(z')G(z,z')\mathrm{d}z', \tag{7}$$

where $[0, z-d]$ indicates that the maximum of 0 and $z-d$ is to be used, d is the hard sphere diameter, and $G(z, z')$ is the value of $g(r', z, z')$ when the two spheres at z and z' are in contact.

It is necessary to specify $G(z, z')$. The best known approximation for $g(r, z, z')$ is the superposition approximation (Kirkwood 1935),

$$g(r, z, z') = g(r), \tag{8}$$

where $g(r)$ is the radial distribution function of the bulk fluid. Recently, Percus (1980) has proposed the approximation

$$g(r, z, z') = [\rho/n(z_{\max})]g(r), \tag{9}$$

where $\rho = n(\infty)$ and $z_{\max}$ is the height of the sphere which is furthest from the wall. Physically, (9) implies that the inner sphere shields the outer sphere from the wall and for this reason Percus called (9) the shielding approximation.

Comparison with computer simulations shows that (8) is best (at high densities, at least) for $z_1 = z_2$ while (9) is best for $r = 0$ or $R = |z-z'|$. This suggests that a hybrid approximation incorporating the best features of the superposition and shielding approximations would be useful. Henderson and Plischke (Plischke and Henderson 1984; Henderson and Plischke 1985) have constructed such an approximation. They write

$$\begin{aligned} G(z_1, z_2) = {} & |z_1 - z_2|\,[\rho d^{-1}/n(z_{\max})]g(d) \\ & + (1 - |z_1 - z_2|/d)\,[1 + c(z_1, z_2)h(d)], \end{aligned} \tag{10}$$

where $n(z_{\max}) = n(0{\cdot}75d)$ for $z_{\max} < 0{\cdot}75d$, $h(d) = g(d) - 1$, $g(d)$ is the radial distribution function at contact for the bulk fluid, and

$$c(z_1, z_2) = \begin{cases} c - \dfrac{1-c}{2}\,[3(z_1+z_2) - (z_1+z_2)^3], & z_1 + z_2 < d \\ 1, & z_1 + z_2 > d. \end{cases} \tag{11}$$

The function $A\ (z_1, z_2)$ of Caccamo *et al* (1986) seems to play the same role as $c(z_1, z_2)$. The parameter c has been determined from theoretical considerations by Henderson and Plischke (1985). For simplicity, the fit

$$c = 0{\cdot}5 + 1{\cdot}03\rho d^3 - 0{\cdot}5\rho^2 d^6, \tag{12}$$

can be used. To complete (10) we must specify $g(d)$. We use the essentially exact Carnahan and Starling (1969) result,

$$g(d) = (1 - \eta/2)/(1-\eta)^3, \tag{13}$$

where $\eta = \pi\rho d^3/6$.

When $|z_1 - z_2| = d$

$$G(z_1, z_2) = [\rho/n(z_{\max})]\, g(d), \tag{14}$$

which is the shielding approximation. When $z_1 = z_2$

$$G(z_1, z_2) = 1 + c(z_1, z_2)h(d). \tag{15}$$

At high densities $c(z_1, z_2) \simeq 1$ and (14) becomes the superposition approximation. At low densities

$$G(0,0) = 1 + \frac{1}{2} h(d), \tag{16}$$

which is exact, the factor of $\frac{1}{2}$ accounting for the exclusion of the hard spheres from half of the space.

Thus, (10) yields the correct limits. Direct comparison with computer simulations shows it to be a reliable approximation.

3. Results

We have calculated $n(z)$ by numerical integration, with 1001 Trapezoid rule integration points, of either

$$n(z) = \rho - 2\pi \int_z^\infty n(z')\mathrm{d}z' \int_{[0, z'-d]}^{z'+d} (z'-z'')n(z'')G(z', z'')\mathrm{d}z'' \tag{17}$$

or

$$\ln n(z) = \ln \rho - 2\pi \int_z^\infty n(z')\,\mathrm{d}z'$$

$$\times \int_{[0, z'-d]}^{z'+d'} (z'-z'')n(z'')G(z', z'')\mathrm{d}z'' \tag{18}$$

It is worth noting that for the shielding and superposition approximations, one integral in (17) or (18) can be obtained analytically by reversing the order of integration (Henderson *et al* 1981; Wertheim 1986). Wertheim (1986) further gives analytic results for $n(z)$ for the shielding approximation for the hard sphere/hard wall system but gives no numerical results for this system. Since our main interest is the Henderson-Plischke approximation, we do not make use of any of these simplifications since they do not apply to this approximation.

The calculation proceeded by using the Henderson *et al* (1976) PY1 $n(z)$ as an initial guess and then iterating, using as subsequent iterates

$$n_{\mathrm{in}}^k(z) = \alpha n_{\mathrm{out}}^k(z) + (1-\alpha)\, n_{\mathrm{in}}^{k-1}(z), \tag{19}$$

with $\alpha = 0{\cdot}05$, until self consistency was achieved. The solution was deemed self consistent if

$$\sum_{i=1}^{1001} \{n_{\mathrm{out}}^k(z_i) - n_{\mathrm{out}}^{k-1}(z_i)\}^2 < 10^{-5}. \tag{20}$$

At low densities the iteration was very fast. Even at high densities only slightly more than 100 iterations were needed, requiring no more than a few minutes of CPU time on an IBM 3081 computer.

The results obtained from (17) or (18) were virtually identical. Generally, (18)

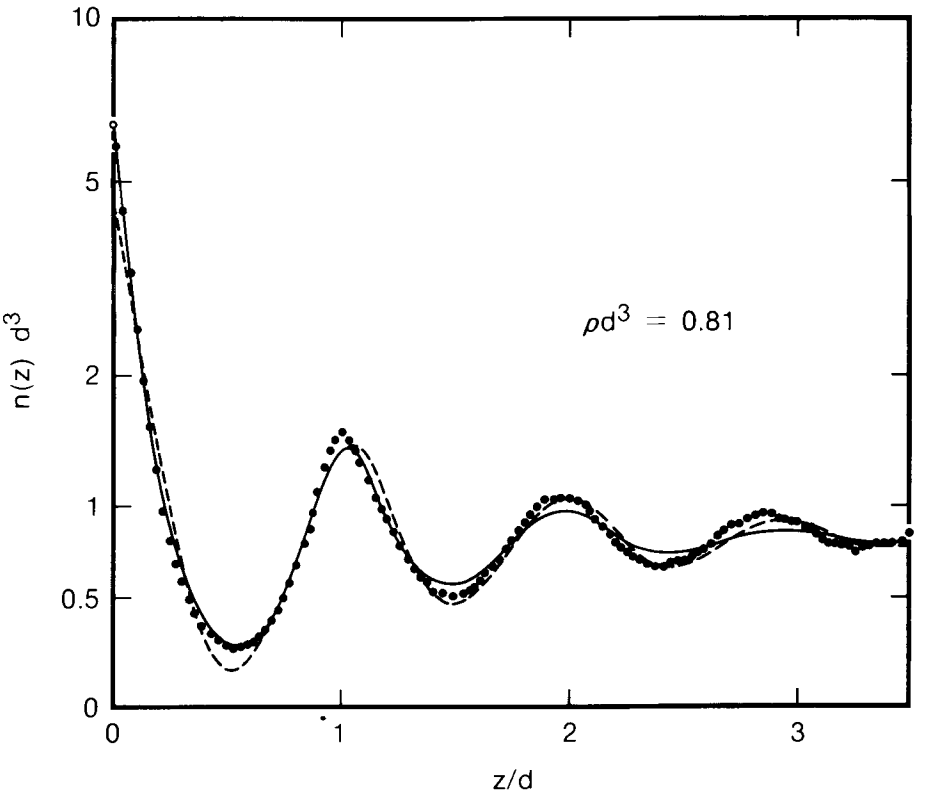

Figure 1. Density profile for hard spheres of diameter d near a hard wall for $\rho d^3 = 0{\cdot}81$. The points given over the computer simulation values of Snook and Henderson (1978) and the solid and broken curves gives the values obtained from (7) and (10), the Henderson–Plischke approximation, and from the PY1 theory (Henderson *et al* 1976), respectively.

required slightly fewer iterations and gave slightly more accurate results, judged from the values of $n(0)$.

In figure 1 we give the resulting values of $n(z)$ at $\rho d^3 = 0{\cdot}81$, calculated using the Henderson–Plischke approximation. The agreement with computer simulation results (Snook and Henderson 1978) is good. It is better than the PY1 result at small z but is somewhat inferior at larger z.

It is of interest to examine the BG results using the superposition approximation and the shielding approximation. We were unable to obtain a solution at $\rho d^3 = 0{\cdot}81$ using the superposition approximation. For this reason we examine the results of these approximations at lower density, $\rho d^3 = 0{\cdot}7028$, in figure 2. Comparison with the simulation results (Henderson and van Swol 1984) shows that the superposition approximation results in an overestimation of the oscillations in $n(z)$ whereas the shielding approximation underestimates these oscillations. Both approximations result in $n(z)$ which are out of phase with the computer simulation results. On the whole the shielding approximation yields better results.

Finally, it is interesting to examine the superposition, shielding, and Henderson–Plischke approximations for $G(z_1, z_2)$. We do this at $\rho d^3 = 0{\cdot}81$ because we do not have simulation values for $G(z_1, z_2)$ at $\rho d^3 = 0{\cdot}7028$ and because self consistent

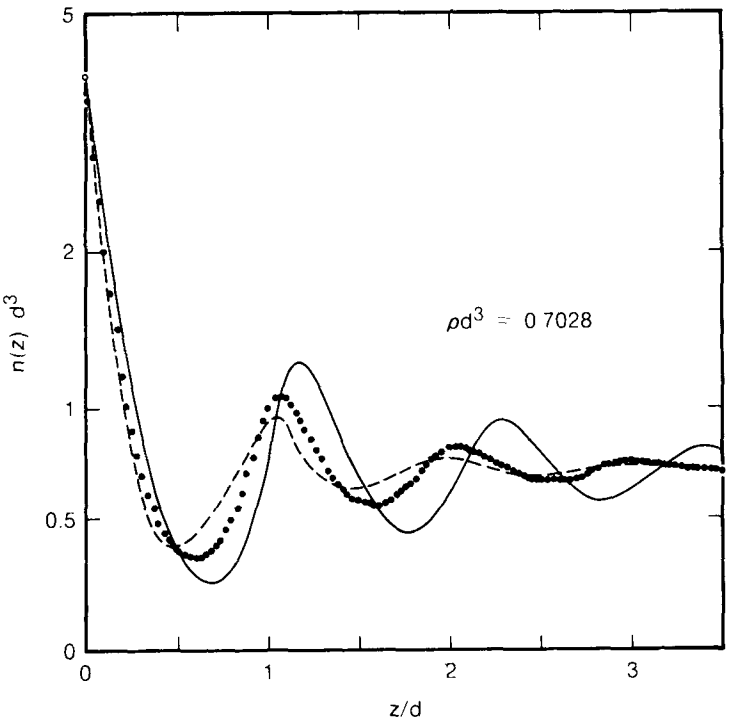

Figure 2. Density profile for hard spheres of diameter d near a hard wall for $\rho d^3 = 0{\cdot}7028$. The points give the computer simulation values of Henderson and van Swol (1984) and the solid and broken curves give the values obtained from (7) with the superposition and shielding approximations, respectively.

values of $n(z)$ are not needed to produce $G(z_1, z_2)$ from the superposition approximation.

As pointed out by J R Henderson and van Swol, the Snook and D Henderson simulation values for $g(r_{12}, z_1, z_2)$ are somewhat in error near the wall. It would be preferable to use their values. However, the only available values, at least to us, from their simulation are for $z_1 = z_2 = 0$. Thus, we have no alternative but to use the Snook and D Henderson results for $G(z_1, z_2)$. They are plotted for $z_1 = 0$, $0 < z_2 < d$ in figure 3. We corrected the Snook and D Henderson simulation results in an *ad hoc* but reasonable manner. The results of J R Henderson and van Swol indicate that near $\rho d^3 \sim 0{\cdot}81$, $G(0, 0) \sim g(d)$. Therefore, we have subtracted from the Snook and D Henderson results an amount sufficient to make $G(0, 0) = g(d)$ and have subtracted a linearly decreasing correction such that the Snook and D Henderson results are uncorrected when $z_2 = d$. Although *ad hoc*, this procedure seems reasonable and probably preferable to using the uncorrected results. The correction is not large and does not affect our conclusions.

As is seen in figure 3, the Henderson–Plischke approximation for $G(z_1, z_2)$ is very good whereas neither the superposition approximation nor the shielding approximation are satisfactory, except near $z_2 = 0$ and $z_2 = d$, respectively. Although the Henderson–Plischke and shielding approximations become identical in form at $z_2 = d$ the two approximations give different $G(z_1, z_2)$ at $z_1 = 0$ and $z_2 = 0$ because they yield different self consistent $n(z)$.

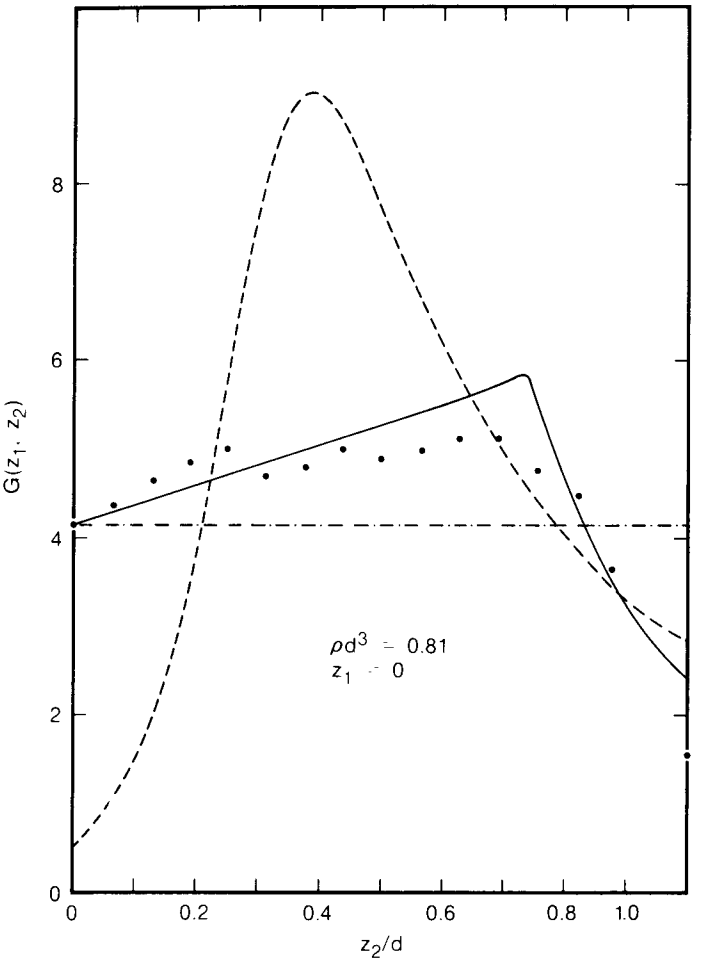

Figure 3. $G(z_1, z_2)$ for hard spheres of diameter d near a hard wall for $z_1 = 0$ and $\rho d^3 = 0{\cdot}81$. The points give the computer simulation values of Snook and Henderson (1978), corrected as described in the text, and the solid, broken and dot dash curves give the Henderson–Plischke, shielding and superposition approximations, respectively.

4. Conclusions

Despite the fact that the Henderson–Plischke approximation is quite good, the resulting self consistent $n(z)$ is a little disappointing at larger z. The oscillations at larger z are damped compared to the simulation results. Evidently there is still a little too much of the screening approximation in the Henderson–Plischke approximation.

The results are a little disappointing for the hard sphere/hard wall system because a simple, analytic, reasonably reliable result (PY1) is available. However, in a larger sense the present results are not so disappointing, since for most systems, although the PY1 and HNC1 theories still will be simple, they will not be analytic and may not even be reliable, whereas the BG theory will always be satisfactory, at least

near the wall, provided that an approximation for the pair correlation function is used which is reasonable in the bulk.

However, the present results seem to indicate that for overall good results, a very accurate approximation for $g(r_{12}, z_1, z_2)$ is required. This seems not to have been the case in the BG and MPB double layer calculations. Perhaps the low densities used in these calculations or the overwhelming influence of the electric field makes a difference. Possibly the hard sphere/hard wall system is particularly sensitive to the approximation used for $G(r_{12}, z_1, z_2)$. In any case the method is worth pursuing.

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