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Solution of the mean spherical approximation for the density profile of a hard-sphere fluid near a wall

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We investigate the density profile of a fluid of hard spheres in the vicinity of a (container) wall. Our analysis is based on the solution of an integral equation satisfied by this density profile in the Lebowitz–Percus mean spherical approximation or its generalization. The latter leads to a density profile in very good agreement with machine computations.

1. INTRODUCTION

Surface properties of various systems are currently a topic of considerable theoretical and practical interest. For fluids there are two common types of surfaces : those separating different phases of the system, such as the liquid and vapour below the critical temperature, and those adjacent to the walls of the container. While the first type of surfaces present even conceptually a difficult problem, the latter surface can, at least when the walls are suitably idealized, be readily treated by the standard methods of statistical mechanics [1]. Thus, at low bulk densities, it is possible to obtain virial expansions for the surface free energy and for the (non-uniform) density in the neighbourhood of the wall [2].

Virial expansions are however not suitable for liquid densities and it is therefore necessary to use some sort of approximation scheme even for the simplest of such surfaces. In the case of bulk fluid properties, much useful information has been gained from the use of integral equations. The availability of exact analytical solutions of the Percus–Yevick (PY) equation [3] and of the Lebowitz–Percus mean spherical approximation (MSA) equation [4] (and their generalizations) for various simple systems has been particularly useful. In this note we consider hard spheres near a flat structureless rigid wall and describe the solution of the MSA equation for the case where the wall–fluid direct correlation function (DCF) decays exponentially outside the wall. This is related to the work of Henderson [HAB] [5] and of Percus [6] who investigated the solution of the PY equation for such a system.

Recently, Blum and Stell [7] have solved the MSA equation using the HAB [5] form of the Ornstein–Zernike equation for a class of systems for which both the wall–fluid and fluid–fluid DCF's are non-zero outside their cores. For the wall–fluid system, their results are a generalization of those given here. However, the solution given here is valid for arbitrary, and not solely infinite, diameter of the solute molecule. The two solutions are in fact complementary.

2. FORMULATION OF THE PROBLEM

The basic idea of our approach is to treat a system in contact with a wall as a limit of a uniform mixture in which one of the components becomes infinitely dilute and then infinitely large. If we let ρ_i be the densities of the different components of the system, then the Ornstein–Zernike equation has the form

$$h_{ij}(r) = c_{ij}(r) + \sum_l \rho_l \int h_{il}(r')c_{lj}(|r'-r|)\,dr', \qquad (1)$$

where $h_{ij}(r) + 1 = h_{ji}(r) + 1 = g_{ij}(r)$ are the radial distribution functions (RDF's), i.e. $\rho_i g_{ij}(r)$ is the density of molecules of species i a distance r from the centre of a molecule of species j and $c_{ij}(r) = c_{ji}(r)$ are the DCF's. Equation (1) is, of course, just a definition of the $c_{ij}(r)$ and becomes useful only when supplemented by other equations for the $c_{ij}(r)$ (which may also involve the RDF's). It is, of course, these latter relations, which are of necessity approximate, that define the different theories.

Before going into these approximations we note that if we consider the simplest case of a binary mixture and let $\rho_2 \to 0$, then from (1)

$$h_{21} = c_{21} + \rho h_{21} * c_{11}, \qquad (2)$$

where the asterisk denotes a convolution, $\rho = \rho_1$ is the bulk fluid density, and $c_{11}(r)$ is the DCF in the uniform one-component fluid consisting entirely of molecules of species 1 with density ρ. We note again that (2) is still just an identity or definition of $c_{21}(r)$.

In order to relate (2) to the surface problem, we let $v_{12}(r) = v_{21}(r)$, the intermolecular potential between molecules of species 1 and 2 a distance r apart, have the form

$$v_{12}(r) = \begin{cases} \infty, & r < R_{12}, \\ w_{12}(x), & r = R_{12} + x > R_{12}. \end{cases} \qquad (3)$$

Letting $R_{12} \to \infty$ and setting $w(x)$ equal to the limit of $w_{12}(x)$ when $R_{12} \to \infty$, then $\rho g_{12}'(x) = \rho[h_{12}(x + R_{12}) + 1]$ will, in this limit, represent the density of molecules of species 1 a normal distance x from a rigid wall. Thus, we have a semi-finite one-component system in which the molecules (centres) are restricted to the region $x > 0$ and interact with the wall through a potential $w(x)$; x being the normal distance to the wall.

Now, any approximation scheme developed for mixtures with general densities ρ_i and potentials $v_{ij}(r)$ will automatically be applicable to the limiting case in which we are interested. Indeed, this is what was done by HAB [5] who considered the case of a mixture with diameters $R_{ij} = \frac{1}{2}(R_i + R_j)$. For this system $v_{ij}(r) = q_{ij}(r)$, where

$$q_{ij}(r) = \begin{cases} \infty, & r < R_{ij}, \\ 0, & r > R_{ij}. \end{cases} \qquad (4)$$

HAB used the PY approximation scheme for this mixture. This consists in setting $c_{ij}(r) = 0$ for $r > R_{ij}$ which when combined with the exact condition $h_{ij}(r) = 0$ for $r < R_{ij}$, permits an explicit solution [8] of (1). Letting $\rho_2 \to 0$ and $R_{12} \to \infty$ in that order (or requiring that $\rho_2 R_{12}{}^3 \to 0$ also) yields the PY approximation for a hard-sphere fluid in the neighbourhood of a rigid wall. This density, also obtained by Percus [6] in a different manner, is in remarkably good agreement with machine simulations [9] up to distances very close to the wall (see § 5).

When the intermolecular potential is of the form

$$v_{ij}(r) = q_{ij}(r) + w_{ij}(r), \tag{5}$$

where $q_{ij}(r)$ is given by (4) and w_{ij} is a soft potential, the MSA scheme consists in setting

$$c_{ij}(r) = -\beta w_{ij}(r), \quad r > R_{ij}, \tag{6}$$

where $\beta = 1/kT$ (T the temperature).

We shall now obtain the solution of (2) and (6), when

$$w_{11}(r) = 0, \quad r > R_1 \tag{7}$$

and

$$-\beta w_{12}(r) = B \exp(-zr)/r, \quad r > R_{12} \tag{8}$$

Taking the limit $R_2 \to \infty$ will yield the MSA result for the density of hard spheres in contact with a flat wall when the interaction between wall and hard sphere a normal distance x from the wall is $-\epsilon \exp(-zr)$, where $\beta\epsilon = \lim B \exp(-zR_{12}/R_{12})$ when $R_{12} \to \infty$. An alternative interpretation of our solution giving an improved (compared to PY) approximation for a system of hard spheres ($w_{12} = 0$) will be discussed in § 5.

3. Formal solution

Our task is to solve equation (2) with the conditions

$$h_{21}(r) = -1, \quad r < R_{12}, \tag{9}$$

$$c_{21}(r) = B \exp(-zr)/r, \quad r > R_{12}, \tag{10}$$

and c_{11} the PY DCF of a pure fluid of hard spheres of diameter R_1. For convenience, we set $R_1 = 1$ and $R_{12} = R$.

Define

$$h_{21}(r) = h_{21}{}^0(r) + \Delta h_{21}(r) \tag{11}$$

and

$$c_{21}(r) = c_{21}{}^0(r) + \Delta c_{21}(r), \tag{12}$$

where $h_{21}{}^0(r)$ and $c_{21}{}^0(r)$ are the known solutions [5, 8] to the problem when $B = 0$ (i.e. in the PY approximation). Setting

$$\Delta c_{21}(r) = \delta c_{21}(r) + B \exp(-zr)/r, \tag{13}$$

equation (2) becomes

$$\sigma_{21}(r) = b \exp(-zr) - \int_R^\infty \sigma_{21}(y) \, dy \int_{|r-y|<1}^1 \sigma(x) \, dx, \tag{14}$$

where

$$\sigma_{21}(r) = 12\eta r \begin{cases} -\delta c_{21}(r), & 2 < R, \\ \\ \Delta h_{21}(r), & r > R, \end{cases} \tag{15}$$

$$\sigma(r) = -12\eta r c_{11}(r), \tag{16}$$

and $b = 12\eta B$. We note that (14) is linear in $\sigma_{21}(r)$.

Taking the Laplace transform of (14) gives

$$G_{21}(s) = \frac{s^2[b(s-z) - (s^2 - z^2)F_{21}(s)]}{(s^2 - z^2)[s^2 - sF^{\pm}(s)]}, \tag{17}$$

where

$$G_{21}(s) = \int_R^\infty \sigma_{21}(s) \exp(-sr) \, dr, \tag{18}$$

$$F_{21}(s) = \int_0^R \sigma_{21}(r) \exp(-sr) \, dr, \tag{19}$$

$$F^{\pm}(s) = F(s) - F(-s), \tag{20}$$

and

$$F(s) = \int_0^1 \sigma(r) \exp(-sr) \, dr. \tag{21}$$

We have solved (17) analytically, making use of the conditions that $F_{21}(s)$ is an entire function and $G_{21}(s)$ is analytic in the closed half plane Re $(s) \geqslant 0$. We do not give details of the procedure as it follows closely the techniques used in the solution of the PY equation for a pure-hard-sphere fluid [10] and for hard-sphere mixtures [8].

We find that

$$G_{21}(s) = 12\eta(1-\eta)^4 C \exp(-\lambda s) f(s, \eta)/(s+z), \tag{22}$$

where

$$C = B \exp(-\lambda z) f(z, \eta), \tag{23}$$

$$f(s, \eta) = \frac{s^3}{L(s) + S(s) \exp(s)}, \tag{24}$$

$$L(s) = 12\eta[1 + 2\eta + S(1 + \eta/2)], \tag{25}$$

and

$$S(s) = (1-\eta)^2 s^3 + 6\eta(1-\eta)s^2 + 18\eta^2 s - 12\eta(1+2\eta). \tag{26}$$

In addition,

$$\Delta c_{21}(r) = \begin{cases} 0, & r < \lambda, \\ \\ \dfrac{12\eta C}{r}\left[\dfrac{c_1 + zc_2}{z^2}\left(y + \dfrac{\exp(-zy) - 1}{z}\right) - \dfrac{c_1 y^2}{2z}\right], & \lambda < r < R, \\ \\ B \exp(-zr/r), & r > \lambda, \end{cases} \tag{27}$$

where $y = r - \lambda$, $c_1 = 1 + 2\eta$ and $c_2 = 1 + \eta/2$.

If use is made of the fact that

$$\Delta h_{21}(R^+) = \frac{B \exp(-zR)}{R} - \Delta c_{21}(R^-),\qquad(28)$$

we obtain for the contact value of the RDF

$$\Delta h_{21}(R^+) = C(1-\eta)^2/R.\qquad(29)$$

To complete the solution, we must obtain $\Delta h_{21}(r)$. If we return to (29) and expand in powers of $L(s)/S(s)$, we obtain

$$G_{21}(s) = 12\eta(1-\eta)^4 C \exp(-Rs)\frac{s^3}{(s+z)S(z)}$$

$$\times \sum_{n=0}^{\infty} (-1)^n \exp(-ns)\left[\frac{L(s)}{S(s)}\right]^n.\qquad(30)$$

Thus,

$$r\Delta h_{21}(r) = \sum_{n=1}^{\infty} \phi_n(r)u(r+1-R+n),\qquad(31)$$

where

$$u(x) = \begin{cases} 0, & x < 0, \\ 1, & x > 0. \end{cases}\qquad(32)$$

Hence, for $R < r < R+1$

$$r\Delta h_{21}(r) = \frac{1}{2\pi i} C(1-\eta)^4 \int_{\delta-i\infty}^{\delta+i\infty} \exp[s(r-R)]\frac{s^3 ds}{(s+z)S(s)}.\qquad(33)$$

Thus, using the residue theorem,

$$\Delta h_{21}(r) = \frac{C}{r}(1-\eta)^4\left\{ -\frac{z^3}{S(-z)} \exp[-z(r-R)]\right.$$

$$\left. + \sum_{i=1}^{\infty} \frac{s_i^3}{(s_i+z)S'(s_i)} \exp[s_i(r-R)]\right\}, \quad R < r < R+1,\qquad(34)$$

where the s_i are the roots of

$$S(s) = 0\qquad(35)$$

and $S'(s)$ is the derivative of $S(s)$. Simple expressions for the s_i have been obtained by Wertheim [11]. After a little manipulation, equation (29) can be obtained from (34).

Although $\Delta h_{21}(r)$ cannot be written in a closed form which is valid for all r, the moments of $\Delta h_{21}(r)$ can be obtained from (22) by expanding in power of s and equating coefficients of like powers of s. Thus,

$$\int_R^{\infty} r\Delta h_{21}(r)\, dr = \frac{C(1-\eta)^4}{z(1+2\eta)}\qquad(36)$$

and

$$\int_R^{\infty} r^2\Delta h_{21}(r)\, dr = \frac{C(1-\eta)^4}{z(1+2\eta)}\left[\lambda + \frac{1}{z} + \frac{1+\eta/2}{1+2\eta}\right].\qquad(37)$$

Finally, by setting $s = z$ in (22) and using (23), we obtain

$$-\beta \int_R^\infty r^2 \Delta h_{21}(r) w_{21}(r)\, dr = C^2(1-\eta)^4/2z, \tag{38}$$

where

$$-\beta w_{21}(r) = B \exp(-zr/r).$$

4. Solution in the limit of infinite R

The solution in the limit $R \to \infty$ can be obtained easily. However, because of the importance of this limit, we give an explicit summary.

For infinite R, (10) becomes

$$-\beta w_{12}'(x) = B' \exp(-zx), \tag{39}$$

where $w_{12}'(x) = w_{12}(R + x)$, $B' = B \exp(-zR)/R$ is finite, and $x = r - R$ is the normal distance from the wall. Thus, (23) is replaced by

$$C' = C/R = B' \exp(z) f(z, \eta) \tag{40}$$

The DCF is given by

$$\Delta c_{12}'(x) = \begin{cases} 0, & x < -1, \\ 12\eta C'[-c_1 y^2/2z \\ \quad + (c_1 + z c_2)\{y + (\exp(-zy) - 1)/z\}/z^2], & 1 < x < 0, \\ B' \exp(-zx), & x > 0, \end{cases} \tag{41}$$

where $y = x - 1$ and $\Delta c_{12}'(x)$ is defined similarly to $w_{12}'(x)$.

In this limit,

$$\Delta h_{21}'(0) = C'(1-\eta)^2, \tag{42}$$

where $\Delta h_{21}'(x)$ is defined similarly to $w_{12}'(x)$. Also

$$\Delta h_{21}'(x) = C'(1-\eta)^4 \left[-\frac{z^3}{S(-z)} \exp(-zx) \right.$$
$$\left. + \sum_{i=1}^3 \frac{s_i^3}{(s_i + z) S'(s_i)} \exp(s_i x) \right] \quad 0 < x < 1. \tag{43}$$

Finally, (36) and (37) become

$$\int_0^\infty \Delta h_{21}'(x)\, dx = \frac{C'(1-\eta)^4}{z(1+2\eta)} \tag{44}$$

and (38) becomes

$$-\beta \int_0^\infty \Delta h_{21}'(x) w_{21}'(x)\, dx = (C')^2(1-\eta)^4/2z. \tag{45}$$

5. Generalized MSA for hard-sphere fluid near a wall

The preceding results can be used to describe, in the MSA, a fluid of hard spheres with a soft exponential interaction with the wall. Alternatively, and

this is what we shall do now, we can use these results to give a generalized mean spherical approximation (GMSA) for a fluid of hard spheres (with no soft interactions) near a wall.

The essence of GMSA approximation is to solve the Ornstein–Zernike relation, equation (1), for a fluid (mixture or single component), with interaction potential (5), under the assumption that $g_{ij}(r) = 0$ for $r < R_{ij}$ and $c_{ij}(r)$ has a prescribed form containing unspecified parameters for $r < R_{ij}$. The form is chosen to make the problem soluble and the unspecified parameters are then adjusted for 'best' results [12]. In our problem we assume (10) to be the functional form of the wall–fluid DCF outside the wall and then adjust the parameters B and z occurring in $c_{12}(r)$ according to the procedure outlined below (for the case when R is infinite). This leads to better agreement with the results of machine computations [9] than those obtained from the solution of the PY equation for this system [5, 6].

We first note that the density of a fluid in contact with a flat hard wall is, when multiplied by kT, just the momentum transfer to the wall and hence equal to the pressure p of the fluid [1, 2]. Hence, when $w_{12} = 0$, the pressure of the bulk hard sphere fluid is given by

$$p/kT = \lim_{\substack{\rho_2 \to 0 \\ R \to \infty}} \rho g_{12}(R) = \rho g'_{12}(0). \tag{46}$$

It is therefore natural to adjust the parameters B and z in such a way that (46) is satisfied. Thus making the GMSA $g_{12}'(x)$ exact at $x = 0$. While we do not know the hard-sphere fluid pressure exactly, an accurate approximation to it is given by

$$P/\rho kT = \frac{1 + \eta + \eta^2 - \eta^3}{(1-\eta)^3}. \tag{47}$$

On the other hand, the PY expression for $g_{12}'(0)$ is

$$[g_{12}'(0)]_{\mathrm{PY}} = \frac{1 + 2\eta}{(1-\eta)^2}. \tag{48}$$

Thus, if in (42) we set

$$C' = \eta^2 \frac{3 - \eta}{(1-\eta)^5}, \tag{49}$$

then the GMSA $g_{12}(r)$ will satisfy (47).

We note in passing that besides the familiar thermodynamic inconsistency between the pressure and compressibility equations of state, the PY theory of hard-sphere mixtures has the additional inconsistency that the PY $g_{12}(R)$ does not satisfy (46) in the sense that (48) does not equal either PY equation of state of bulk hard spheres [8]. On the other hand, the scaled-particle theory (SPT) expression [14, 1] for $g_{12}(R)$ in the limit $R \to \infty$,

$$[g_{12}'(0)]_{\mathrm{SPT}} = \frac{1 + \eta + \eta^2}{(1-\eta)^3}, \tag{50}$$

does satisfy (46) because it is equal to the SPT equation of state for bulk hard spheres. This means that the procedure of Grundke and Henderson [15], of writing in analogy to Carnahan and Starling,

$$g_{ij}(R_{ij}) = \tfrac{1}{3}[g_{ij}(R_{ij})]_{\mathrm{PY}} + \tfrac{2}{3}[g_{ij}(R_{ij})]_{\mathrm{SPT}}, \tag{51}$$

although reliable for the region of interest to them ($R \sim 1$), must fail for R large because of the failure of the PY $g_{12}(r)$ to satisfy (46).

In order to 'adjust' our second parameter, z, we need an additional reliable relation involving $h_{12}(r)$, e.g. its integral. Using some general relations [8] for the integrals of $c_{ij}(r)$ it is easy to show that in the limit $\rho_2 \to 0$

$$\int h_{12}\, d\mathbf{r} = \rho^{-1}\{[1 - \beta\, \partial p/\partial\rho_2]/[\beta\, \partial p/\partial\rho_1]\}_{\rho_2 = 0} \tag{52}$$

where $p(\rho_1, \rho_2)$ is the pressure of a mixture of hard spheres. The difficulty now arises of finding an expressin for $p(\rho_1, \rho_2)$ which would be reliable to use in (52) when $R_2 \to \infty$. Using the PY compressibility (or, equivalently, the SPT) equation of state yields

$$\int_0^\infty h_{12}'(x)\, dx = 3\eta/2(1 + 2\eta) \tag{53}$$

a relation already satisfied by $[h_{12}'(x)]_{\mathrm{PY}}$. To obtain an improvement we should therefore use an equation of state based on an ansatz like (51) which is the mixture analogue of (47). Unfortunately however the PY virial pressure does not (as already mentioned) have the right asymptotic form as $R_2 \to \infty$. What we have therefore done is to assume that the deviation of the right side of (52) from its SPT value is of the form $\alpha R_2^2 + \gamma R_2^3$ but to determine α and γ, not from the PY pressure isotherm (which suggested this form), but by requiring that the result be finite in the limit $R \to \infty$ and be equal to the Carnahan and Starling expression for the integral of $h(r)$ when $R = 1$. In this manner we obtain (in the limit $R \to \infty$)

$$\int_0^\infty h_{12}'(x)\, dx = \frac{9\eta(1 + 2\eta) + \eta^2(4 - \eta)(1 - 4\eta)}{6[(1 + 2\eta)^2 - \eta^3(4 - \eta)]}. \tag{54}$$

Combining this with (44) and (52) gives

$$z^{-1} = \frac{(1 + 2\eta)(1 - \eta)}{\eta^2(3 - \eta)}\left[\frac{9\eta(1 + 2\eta) + \eta^2(4 - \eta)(1 - 4\eta)}{6[(1 + 2\eta)^2 - \eta^3(4 - \eta)]} - \frac{3\eta}{2(1 + 2\eta)}\right]. \tag{55}$$
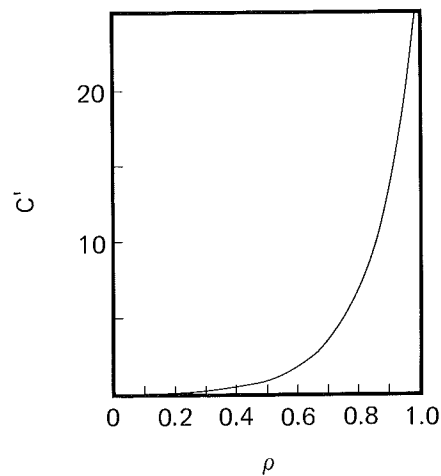

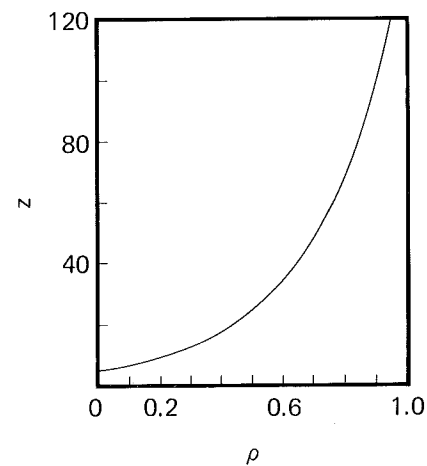Figure 1. C' for GMSA for hard spheres of diameter $\sigma_{11} = 1$ near a wall.

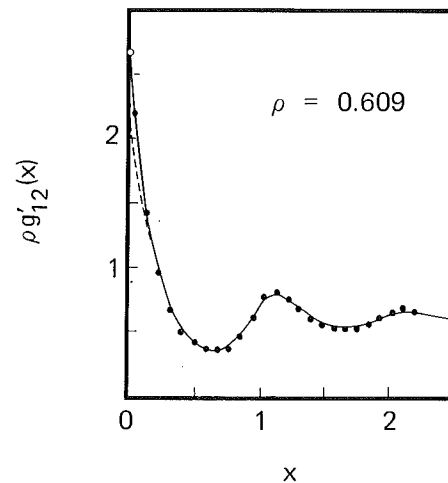Figure 2. z for GMSA for hard spheres of diameter $\sigma_{11} = 1$ near a wall.

Figure 3. Density profile for hard spheres of diameter $\sigma_{11}=1$ near a wall. The points give the MC results of Liu *et al.* [9] and solid and broken curves give the GMSA and PY results, respectively. The asymptotic bulk density $\rho = 0.609$ corresponds to the average density $\rho_{av} = 0.7$ of the Monte Carlo calculations.

The values of C' and z, obtained from (49) and (55), are plotted in figures 1 and 2. In figure 3 we compare the resulting GMSA g_{12} with the PY [5] and Monte Carlo [9] values. The PY g_{12} shows appreciable error for $x \sim 0$ but is otherwise in excellent agreement with the Monte Carlo values. The GMSA g_{12} is in excellent agreement with the Monte Carlo values for all x.

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