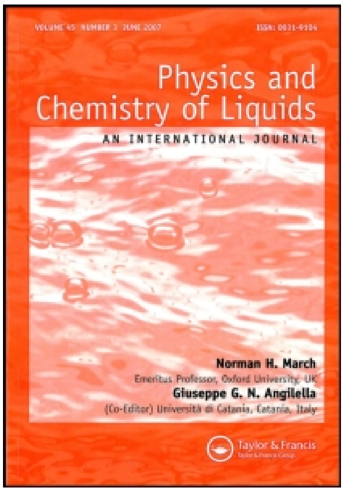

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THE BEHAVIOUR OF A FLUID MIXTURE IN CONTACT WITH A SURFACE

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The behaviour of a fluid mixture near a structureless hard wall is investigated. Following earlier work [D. Henderson, F.F. Abraham and J.A. Barker, Molec. Phys. **31**, 1291 (1976)] we consider the limiting case of a fluid mixture in which one of the species, representing the wall, is dilute and infinitely large. In this limit the Ornstein-Zernike equations yield the density distributions of each of the components with respect to the hard wall. The specific case of a mixture of hard spheres in contact with a hard wall is treated within the Percus-Yevick approximation and explicit results are obtained for a binary mixture. In addition to the density distributions simple expressions are obtained for the integrated densities. The density fluctuations in the fluid near the wall are small and short ranged for the hard sphere fluid. The effects of tails to the interatomic potentials outside the hard spheres can be incorporated approximately and could lead to much larger fluctuations in the densities.

Keywords: Hard spheres; Percus-Yevick method; binary mixture

1. INTRODUCTION

Some time ago Henderson, Abraham and Barker [1] [HAB] pointed out that a fluid in contact with a structureless surface can be regarded as a limiting case of a mixture (binary if the fluid is pure) in which one of the species is dilute and infinitely large. They developed the Ornstein-Zernike equations for the limiting case and went on to use the Percus-Yevick approximation for a mixture of hard spheres to obtain the density profile of a pure fluid in contact with a plane, hard wall. While there are alternative approaches for investigating the distribution of a fluid near a wall, such as density functional methods [2] or direct computer simulation using, for example, the Monte Carlo method [3], the approach of HAB is very simple and deserves more attention.

However, the behaviour of a fluid mixture in contact with a surface is also of interest because of the possibility of segregation taking place near the surface. The qualitative features of segregation of a binary alloy at a free surface have been studied by Bhatia and March [4] and at a container wall by Stott, Voice and Young [5], and density functional methods have been used to investigate adsorption and wetting transitions at the interface between a solid and a binary fluid mixture by Telo da Gama and Evans [6]. More recently Moradi and Rickayzen [2] have used density functional and Monte Carlo methods to study the structure of a hard sphere fluid mixture confined between a pair of hard walls forming a slit. The treatment of a fluid mixture near a structureless hard surface using the approach of HAB is already implicit in their original work, and in this paper we provide the details of the extension to a mixture and some general results which follow from the framework provided by HAB.

In the next section we reiterate the Ornstein-Zernike equations for a multicomponent fluid and follow the approach of HAB by letting the concentration of one component tend to zero and its size tend to infinity so that the surface of a molecule of this species plays the role of a plane wall. The density distributions of each of the other species with respect to the wall are given by the appropriate radial distribution functions. At this point a useful integrated measure of the degree of segregation due to the wall is obtained. In the next section results are obtained for the case of a mixture of hard spheres near a hard plane wall using the Percus-Yevick approximation, and numerical results for a binary mixture are presented. The paper closes with a discussion of the results and approximate extensions of the approach to more realistic fluid and fluid-wall interactions.

2. THE ORNSTEIN-ZERNIKE EQUATIONS

Consider an m-component fluid mixture with total number density ρ and for which the number density of species i is $\rho_i = x_i\rho$. The Ornstein-

Zernike equations for this system are:

$$h_{ij}(r_{12}) = c_{ij}(r_{12}) + \rho \sum_{l=1}^{m} x_l \int h_{il}(r_{13}) c_{lj}(r_{32}) d\mathbf{r}_3 \tag{1}$$

where $h_{ij}(r_{1,2})$ and $c_{ij}(r_{12})$ are the total and direct correlation functions respectively for a molecule of species i at $\mathbf{r}_1$ and of j at $\mathbf{r}_2$. We assume that the intermolecular forces are central so that the correlation functions depend just on the distance between the molecules.

We now consider the dilute limit for the m'th component and let $x_m \to 0$ in which case the OZ equations become

$$h_{ij}(r_{12}) = c_{ij}(r_{12}) + \rho \sum_{l=1}^{m-1} x_l \int h_{il}(r_{13}) c_{lj}(r_{32}) d\mathbf{r}_3 \quad i,j \neq m \tag{2}$$

$$h_{im}(r_{12}) = c_{im}(r_{12}) + \rho \sum_{l=1}^{m-1} x_l \int h_{il}(r_{13}) c_{lm}(r_{32}) d\mathbf{r}_3 \quad i = m \tag{3}$$

The equations (2) are the OZ equations for an $m - 1$ component fluid mixture and we assume that the structure of this fluid is known, whereas (3) involves the density distribution of species i with respect to a member of the dilute species m through $h_{im}(r)$.

We assume that there is a well defined radius R_m associated with species m, and we shall be concerned with Eq.(3) in the limit of large R_m. For example, the m molecule could behave as a hard sphere of radius R_m along with weaker interactions with the other components. We now introduce $c'_{im}(z) = c_{im}(R_m + z)$ and $h'_{im}(z) = h_{im}(R_m + z)$, and perform the angular integrations in (3) to obtain in the limit $R_m \to \infty$

$$h'_{im}(z) = c'_{im}(z) + 2\pi\rho \sum_{l=1}^{m-1} x_l \int_0^{\infty} t h_{il}(t) dt \int_{z-t}^{z+t} s c'_{lm}(s) ds \tag{4}$$

The density distribution of species i measured from the hard surface of the dilute species m is given by

$$\rho_i(z) = \bar{\rho}_i [h'_{im}(z) + 1] \tag{5}$$

where $\bar{\rho}_i = \rho x_i$ is the average number density of species i; or alternatively we see that the fractional displaced density is

$$\frac{\delta\rho_i(z)}{\bar{\rho}_i} = h'_{im}(z) \tag{6}$$

Before proceeding beyond equation (4) to investigate the form of $\rho_i(z)$ for which we need a relationship between the total and direct correlation functions, we note that some progress can be made in relating integrated quantities to the properties of the homogeneous $m-1$ component fluid.

Returning to Eq.(3) and integrating over all space we obtain

$$\bar{h}_{im} = \bar{c}_{im} + \sum_{l=1}^{m-1} \bar{\rho}_l \bar{h}_{il} \bar{c}_{lm} \tag{7}$$

where

$$\bar{h}_{ij} = \int h_{ij}(r) d\mathbf{r} \tag{8}$$

and similarly for $\bar{c}_{ij}$. The $\bar{h}_{ij}$ can be written in terms of the $\mathbf{q}=0$ component of the partial structure factor $S_{ij}(\mathbf{q})$ using

$$S_{ij}(0) = \delta_{i,j} + \sqrt{\bar{\rho}_i \bar{\rho}_j}\,\bar{h}_{ij} \tag{9}$$

to give

$$\bar{h}_{im} = \sum_{l=1}^{m-1} \sqrt{\frac{\bar{\rho}_l}{\bar{\rho}_i}} S_{il}(0) \bar{c}_{l_m} \tag{10}$$

Whereas the $\bar{h}_{im}$ and $\bar{c}_{im}$ in (10) involve correlations with the dilute species the structure factors $S_{ij}(0)$, in the limit of $x_m \to 0$, are for the homogeneous $m-1$ component fluid. Recalling that a molecule of species m is a hard sphere with large radius R_m we may write

$$\bar{h}_{im} = 4\pi \int_0^{R_m} r^2 h_{im}(r) dr + 4\pi \int_{R_m}^{\infty} r^2 h'_{im}(r) dr \tag{11}$$

but $h_{im}(r) = -1$ for $r < R_m$, and $h_{im}(R_m + z) = h'_{im}(z)$, and so

$$\bar{h}_{im} = -\frac{4\pi}{3}R_m^3 + 4\pi R_m^2 \int_0^\infty h'_{im}(z)dz + O(R_m) \tag{12}$$

The integral of the direct correlation functions involved in (9) can be written in a similar form to (11):

$$\bar{c}_{im} = 4\pi R_m^3 c_i^{(3)} + 4\pi R_m^2 c_i^{(2)} + O(R_m) \tag{13}$$

where the coefficients $c_i^{(n)}$ in the expansion depend on the details of the direct correlations with the dilute species. Substituting (12) and (13) in (10) and using (6) we have

$$\frac{\overline{\delta\rho_i}}{\bar{\rho}_i} = \sum_{l=1}^{m-1} \sqrt{\frac{\bar{\rho}_l}{\bar{\rho}_i}}\, c_l^{(2)} S_{il}(0) \tag{14}$$

where

$$\overline{\delta\rho_i} = \int_0^\infty \delta\rho_i(z)dz \tag{15}$$

The result (14) for the total displaced density is reminiscent of the expression for the linear response of an $m-1$ component fluid to external perturbations; the S_{ij} are the density response functions of the fluid and the perturbing effect of the wall are contained in the coefficients $c_l^{(2)}$, but the result goes beyond linear response.

As a specific example for which detailed results can be obtained we consider a two component hard sphere fluid in contact with a hard, plane wall and use the Percus-Yevick approximation to link the direct and total correlation functions.

3. HARD SPHERE FLUID

Simple analytic forms have been obtained for the direct correlation functions for a multicomponent fluid of additive hard spheres within the Percus-Yevick approximation. Results for the binary hard sphere case were first obained by Lebowitz [7] and for the multicomponent case by Hiroike [8] whose results we adopt.

For a system of hard spheres with m components and the labelling such that hard sphere diameters, σ_i, are ordered with $\sigma_j > \sigma_i$ for $j > i$. Hiroike [8] obtained for the direct correlation functions within the Percus-Yevick approximation

$$-c_{ii}(r) = \left.\begin{array}{ll} a_i + b_i r + dr^3 & r < \sigma_i \\ 0 & r > \sigma_i \end{array}\right\} \tag{16}$$

and for $j > i$

$$-c_{ij}(r) = \left.\begin{array}{ll} a_i & r < \frac{\sigma_j - \sigma_i}{2} \\ a_{ij} + b_{ij} r + dr^3 + f_{ij}/r & \frac{\sigma_j - \sigma_i}{2} < r < \frac{\sigma_j + \sigma_i}{2} \\ 0 & r > \frac{\sigma_j + \sigma_i}{2} \end{array}\right\} \tag{17}$$

where $a_{ij} = (a_i + a_j)/2$ and $b_{ij} = (b_i + b_j)/2$,

$$\begin{aligned} a_i &= 1/(1-\eta) + a\sigma_i + b\sigma_i^2 + \frac{c}{3}\sigma_i^3 \\ b_i &= -\frac{a}{2} - b\sigma_i - \frac{c}{2}\sigma_i^2 \\ a &= 3\xi_2/(1-\eta)^2 \\ b &= 3(\xi_1/(1-\eta)^2 + 3\xi_2^2/(1-\eta)^3) \\ c &= 3(\xi_0/(1-\eta)^2 + 6\xi_1\xi_2/(1-\eta)^3 + 9\xi_2^3/(1-\eta)^4) \\ d &= c/6 \\ \xi_l &= \sum_{i=1}^{m} \frac{1}{6}\pi\bar{\rho}_i\sigma_i^l \end{aligned}$$

and $\eta = \xi_3$ is the overall packing fraction. The key results we need in order to apply Eqs. (4) and (14) and obtain $\rho_i(z)$ and $\overline{\delta\rho_i}$ are $c'_{im}(z) \overset{R_m \to \infty}{=} c_{im}(R_m + z)$ and the coefficient $c_i^{(2)}$ in the expansion of $\bar{c}_{im}$ both for $x_m \to \infty$. Some tedious algebra yields

$$-c'_{im} = \left.\begin{array}{ll} a_i & z < -\frac{\sigma_i}{2} \\ a_i - (b + c\sigma_i)(z + \frac{\sigma_i}{2})^2 & -\frac{\sigma_i}{2} < z < \frac{\sigma_i}{2} \\ 0 & \frac{\sigma_i}{2} < z \end{array}\right\} \tag{18}$$

and

$$-\frac{1}{4\pi}\bar{c}_{im}=\frac{1}{3}R_m^3a_i+\frac{1}{2}R_m^2(1/(1-\eta)+a\sigma_i+b\sigma_i^2/3)+O(R_m) \quad (19)$$

so that the coefficients incorporating the effects of the wall in the density response (14) are

$$c_i^{(2)}=-\frac{1}{2}\sigma_i(1/(1-\eta)+a\sigma_i+b\sigma_i^2/3) \quad (20)$$

If we specialize to the case of $m=3$ and consider a binary mixture in contact with a hard wall then in addition to $c'_{im}(z)$ and $c_i^{(2)}$ we also require the $h_{ij}(r)$ and $S_{ij}\,(\boldsymbol{q}=0)$ for the homogeneous two component fluid for use in Eqs. (4) and (14) respectively, and these are readily obtained from (16) and (17) using the Ornstein-Zernike equations for the binary hard sphere mixture.

4. RESULTS AND DISCUSSION

We have performed calculations for a two component system of hard spheres in contact with a hard wall within the Percus-Yevick approximation as described above. A packing fraction $\eta=0.4$ was chosen, and the units of length were such that the diameter of the smaller hard sphere $\sigma_1=1$. Results for $\rho_i(z)/\bar{\rho}_i, i=1,2$ for a range of mixture concentrations, x_1, and with the ratio of hard sphere diameters σ_2/σ_1 equal to 1, 1.4 and 1.8 are shown in Figures 1, 2 and 3 respectively.

The results illustrated in Figure 1 with $\sigma_1/\sigma_2=1$ are the same as for a pure hard sphere fluid in contact with a hard wall and only differ from the results illustrated in HAB because of the slightly larger packing fraction of $\eta=0.42$ which those authors used. The main features of the results for the mixtures, illustrated in Figures 2 and 3, are similar to those reported for the pure fluid by HAB. The values of $\rho_i/\bar{\rho}_i$ at nearest approach to the wall are almost twice the values of g_{ii} at closest approach for the two component fluid. The subsequent oscillations in $\rho_i/\bar{\rho}_i$ also have larger amplitude than those in g_{ii}, so much so that for $\sigma_2/\sigma_1=1.8$ the first minimum in $\rho_2/\bar{\rho}_2$ is deep enough to drive the density slightly negative. This unphysical feature we take to be a consequence of the Percus-Yevick approximation, and

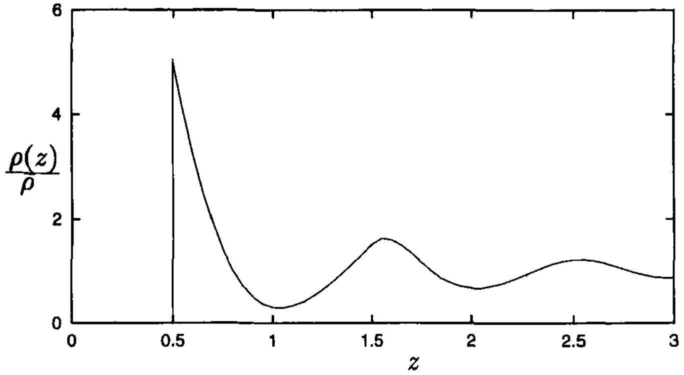

FIGURE 1 Density, $\rho(z)/\bar{\rho}$, as a function of distance z from the hard wall in units where $\sigma_1 = 1$, for the case $\sigma_2/\sigma_1 = 1$.

we expect that a better approximation would flatten off the minima in $\rho_i/\bar{\rho}_i$, reduce the amplitude of the oscillations, or otherwise yield a non-negative density. A new feature appearing in the density is the irregularity near the second maximum for the cases with intermediate concentration. This is not present in the case of the pure fluid and is more pronounced for the larger σ_2/σ_1 ratio. This is a real effect due to the registration of the first fluid layers which is provided by the wall. For a mixture of different sized spheres the centres of the two sorts can be as close as $\sigma_1/2$ and $\sigma_2/2$ to the wall and the spheres in contact with the wall form a mixed first layer. If now we consider the density distribution of a particular species, say 1, the spheres in the second layer of type 1 forming the second peak in $\rho_1(z)$ will be affected by the registered first layer for z roughly in the range $3\sigma_1/2$ to $(\sigma_1 + \sigma_2)/2$, which is the range where we see the irregularities in Figures 2 and 3. The effect becomes washed out the further we move from the wall. Similar registration effects in the radial distribution functions for the homogeneous fluid mixture are smaller near the second peak and are washed out more rapidly because the volume available increases as z^2.

Direct integration of the calculated density distributions or application of Eq. (14) gives $\overline{\delta\rho_i}$ and results for this quantity as a function of concentration are presented in Figure 4. The results for both species are smooth functions of concentration, are negative for the chosen parameters, and are small in magnitude, with a significant contribution coming from the excluded region against the wall of

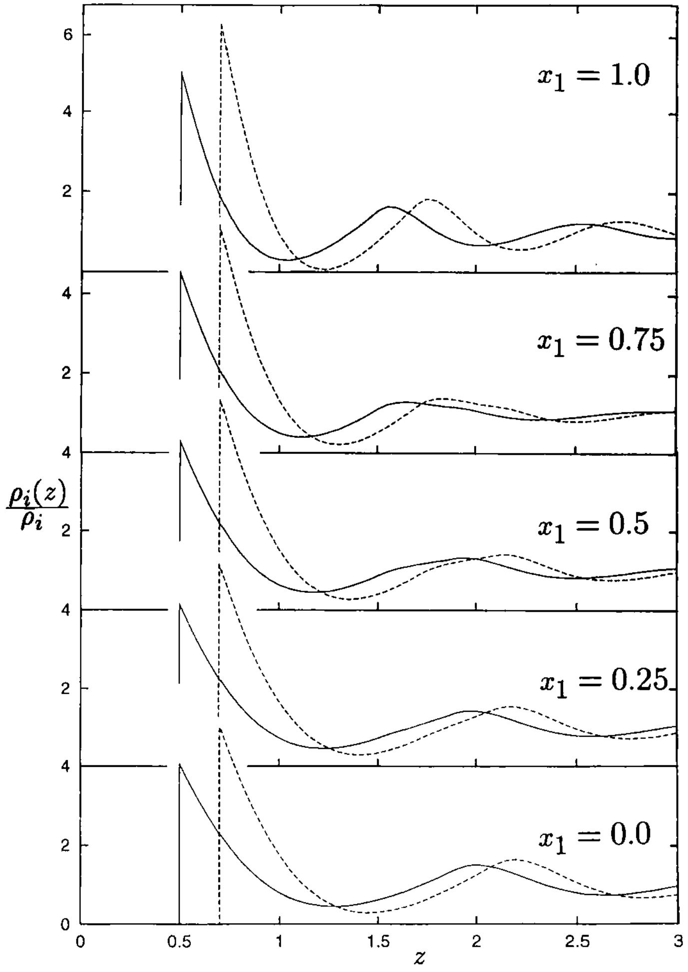

FIGURE 2 Density, $\rho_i(z)/\bar{\rho}_i$, as a function of distance z from the hard wall in units where $\sigma_1 = 1$, for the case $\sigma_2/\sigma_1 = 1.4$. The concentrations of the mixtures, x_1, are as given on the figures, and results are shown for species 1,____ ; and species 2_ _ _ _.

extent $\sigma_i/2$ as we have chosen to integrate out from the wall itself rather than from the distance of closest approach. Changing the fluid parameters within reasonable limits does not change the results much, for example, a larger σ_2/σ_1 ratio of 2.2 increases slightly the spread between the results for the different species, and a larger packing fraction of $\eta = 0.45$ reduces the magnitude of both.

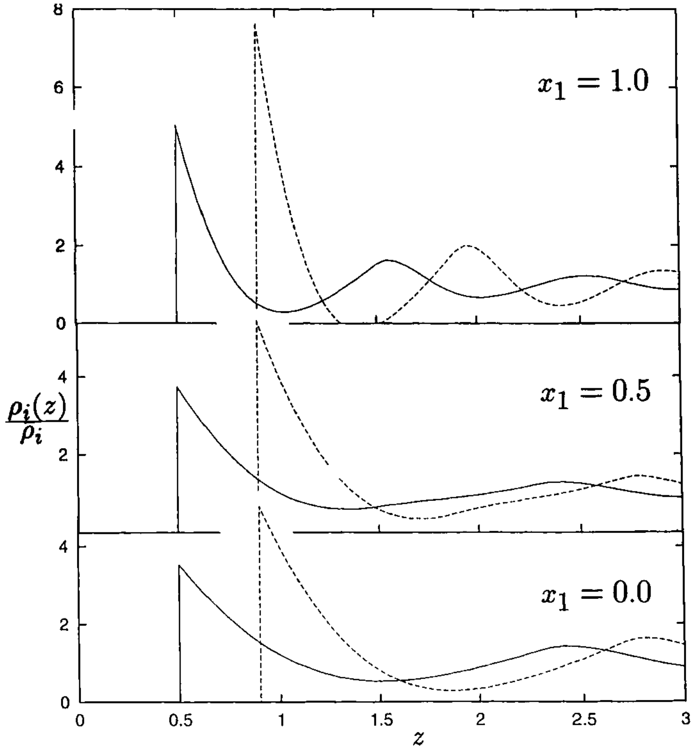

FIGURE 3 Density, $\rho_i(z)/\bar{\rho}_i$, as a function of distance z from the hard wall in units where $\sigma_1 = 1$, for the case $\sigma_2/\sigma_1 = 1.8$. The concentrations of the mixtures, x_1, are as given on the figures, and results are shown for species 1,____; and species 2_ _ _ _.

The results for $\delta\bar{\rho}_i/\bar{\rho}_i$ give no indication that segregation or other large effects might take place near the hard wall for a mixture of hard spheres, at least within the limitations of the Percus-Yevick approximation, and this is not unexpected. However, Eq. (14) is not restricted to a hard sphere fluid. We may consider a more general system by using in Eq. (14) the long wavelength limit of the partial structure factors, $S_{ij}(\mathrm{q} = 0)$, for the mixture obtained from calculations employing realistic interactions, or from scattering experiments, or using thermodynamic relations. These quantities given the susceptibility of the homogeneous fluid mixture to the presence of the wall. The interactions between the fluid molecules and the wall affect the density distributions near the wall through the direct correlation functions $c_{im}(r)$. The effect of the addition of tails to the

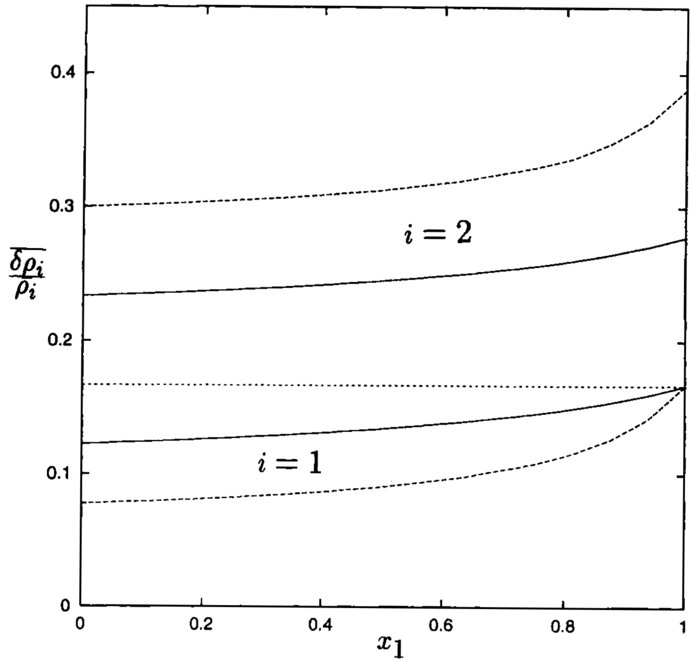

FIGURE 4 Total displaced density, $\overline{\delta\rho_i}/\bar{\rho}_i$ as a function of mixture concentration, x_1, for $\sigma_2/\sigma_1 = 1$.........; $\sigma_2/\sigma_1 = 1.4$_ _ _ _; and $\sigma_2/\sigma_1 = 1.8$_____.

hard wall-fluid interaction can be treated within perturbation theory. At the level of the random phase approximation (RPA) we would have

$$c_{im}(r) = c_{im}^{hs}(r) - v_{im}^{tail}(r)/k_BT \tag{21}$$

where c_{im}^{hs} is the direct correlation function for hard spheres given by (17) and v_{im}^{tail} is the interaction potential extending beyond the hard sphere. It straightforward to find the corresponding tail corrections to the coefficients, $c_i^{(2)}$, in the expansion given by equation (13) which enter the result, (14), for the total displaced density. We have

$$c_i^{(2)} = -\frac{1}{2}\sigma_i(1/(1-\eta) + a\sigma_i + b\sigma_i^2/3) - \bar{v}_i/k_BT \tag{22}$$

where

$$\bar{v}_i = \int_0^\infty v'_{im}(z)dz \tag{23}$$

and in the notation used earlier $v_{im}(R_m + z) = v'_{im}(z)$, so that the intergral in (23) is taken out from the hard wall. However, we note that the small values for $\delta\bar{\rho}_i/\bar{\rho}_i$ for the binary hard sphere mixture against a hard wall which are shown in Figure 2 result after cancellation between the two terms (for the binary mixture) in Eq. (14). This is particularly marked for the smaller species where the individual terms in (14) are at least a factor of 10 larger in magnitude than the results. This cancellation present for hard spheres could be upset if the interactions with the surface differ from hard wall by the addition of a tail outside the wall, and larger total displaced densities could results. In these cases the net effect of the hard wall terms in Eq. (16) should be negligible because of the cancellation, and a good approximation should be

$$\frac{\overline{\delta\rho_i}}{\bar{\rho}_i} \simeq -\frac{1}{k_B T}\sum_{l=1}^{m-1}\sqrt{\frac{\bar{\rho}_l}{\bar{\rho}_i}}\,\bar{v}_i\; S_{il}(0) \tag{24}$$

This is, of course, the result linear response would give, but it would seem to be a reasonable approximation in circumstances where linear response theory would not normally work because of the strong interactions with the hard wall.

Finally, we point out that it is straightforward in the case of a binary mixture near a wall to use as variables the total number density and the concentration (N and C) rather than the densities of the species. This change would lead to the expression of the total displaced quantities, (16), in terms of the structure factors: $S_{NN}(0), S_{CC}(0)$, and $S_{NC}(0)$, introduced by Bhatia and Thornton [9], which may be more useful in some circumstances.

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