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Density profiles of hard-sphere fluids restricted by hard and permeable walls

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Abstract. New hybrid weighted-density approximations (HWDA) based on both local and global average densities are proposed. In one of the approximations the weighting function is constructed to satisfy the same homogeneous properties as the local weighted-density approximation (LWDA) proposed by Tarazona; in the other, the weighting function is constructed to agree with that of Leidl and Wagner for the homogeneous fluid. Free energy functionals are derived from these proposed weighted-density approximations by using expansions in terms of the density. They are applied to predict the density profiles of hard-sphere fluids restricted by hard and permeable walls and in spherical cages. For the density profiles of fluids confined between hard flat walls, the results are in good agreement with the computer simulations and comparable with those of the free energy functional approximation of Tarazona even at the high density $\rho\sigma^3 = 0.9135$. For the density profiles of hard-sphere fluids restricted by permeable walls with a finite height and in spherical cages, the results are also in good agreement with the computer simulations. These results show that although the free energy functionals differ, the new approximations and LWDA produce equally accurate results for the inhomogeneous hard-sphere fluids investigated. The new approximations have the advantage of being simpler to apply.

1. Introduction

Over the past decade there has been considerable progress in the density-functional theory of inhomogeneous classical fluids. Many different types of density-functional approximation [1–8] have been proposed to describe the problems of inhomogeneous fluids of various sorts. These applications have been both qualitatively and, to varying degrees, quantitatively successful. Among these approximations, the weighted-density approximations developed can be generally categorized into three kinds of weighted density approximation: (i) weighted-density approximations based on a local averaged density called LWDA [2, 3, 5, 6] here, (ii) weighted-density approximations based on a globally averaged density (GWDA) [7], and (iii) hybrid weighted-density approximations (HWDA) based on both a locally weighted density and an additional globally averaged density [4].

It is generally known [1] that in actual applications of classical fluids the widely used weighted-density approximation (LWDA) was proposed by Tarazona yields very good results. It suffers, however, from two disadvantages: (a) in its pure form, it is not possible to derive an analytic weighting function which gives rise to a given direct correlation function, $c^{(2)}(r, \rho)$, such as the PY function, and (b) even when an analytic weighting function is used, the calculation of density profiles of the inhomogeneous fluid is computationally intensive.

To overcome the first disadvantage Tarazona and coworkers [6] expanded the weighted function in powers of the density and obtained an approximation to the direct correlation function which was good as long as the reduced density of the bulk fluid was less than about 0.9. The computer time is reduced by the HWDA but this approximation is less successful in the prediction of the density profiles.

The key to the success of Tarazona's approximation appears to lie in the choice of weighted function. We have therefore tried to find a good compromise between Tarazona's approximation and the other weighted-density approximations by seeking a new HWDA which uses Tarazona's weighting function but involves less computation. The consequences of this approximation for the density profile of an inhomogeneous fluid are compared with Tarazona's and with simulation results for the problems of hard-sphere (HS) fluid confined between hard walls and permeable walls. At the same time we have investigated a modification of the HWDA of Leidl and Wagner [4] and its consequences for the same problems.

In section 2, we consider the explicit forms of the density functionals and the weighting functions used in the various approximations. In section 3, we derive the density profiles of hard-sphere fluids confined between hard flat walls. We compare the results of the approximations to those of computer simulation. In section 4, we apply the approximations to calculate the density profiles of the hard-sphere fluids restricted by permeable walls of thickness of the order of a molecular diameter, in which the permeable walls are represented by the barriers with a finite height [9, 10]. We again compare our results with those of computer simulation. Section 5 contains a similar comparison for fluids confined to spherical cages. A brief discussion of the strengths and weaknesses of the various approximations is included in the conclusion.

2. The density functionals and weighted functions

In all the cases we consider, the free energy functional can be written as an ideal gas part plus an excess contribution $F[\rho]_{ex}$ originating from the particle interactions

$$F[\rho] = \beta^{-1} \int \mathrm{d}\boldsymbol{r}\, \rho(\boldsymbol{r})\{\ln[\rho(\boldsymbol{r})\Lambda^3] - 1\} + F[\rho]_{ex} \tag{1}$$

where β is the inverse temperature and Λ the de Broglie thermal wavelength. In the weighted-density approximations the excess contribution is assumed to be of the form

$$F[\rho]_{ex} = \int \mathrm{d}\boldsymbol{r}\, \rho(\boldsymbol{r}) f(\bar{\rho}(\boldsymbol{r})) \tag{2}$$

where $f(\rho)$ is the excess free energy per particle for the bulk fluid of density ρ and the weighted density $\bar{\rho}(\boldsymbol{r})$ is given by

$$\bar{\rho}(\boldsymbol{r}) = \int \mathrm{d}\boldsymbol{s}\, \rho(\boldsymbol{s})\omega(\boldsymbol{r}-\boldsymbol{s}, \hat{\rho}(\boldsymbol{r})); \tag{3}$$

the weighting function $\omega(\boldsymbol{r}-\boldsymbol{s}, \rho)$ is related to the direct correlation function of the fluid through the second derivative of the excess free energy with respect to the density:

$$c^{(2)}(\boldsymbol{r}, \boldsymbol{s}; [\rho]) = -\frac{\beta\delta^2 F[\rho]_{ex}}{\delta\rho(\boldsymbol{r})\delta\rho(\boldsymbol{s})}. \tag{4}$$

Equation (4) is used only after the density has been made uniform.

In the homogeneous state where no averaging is necessary one requires, for (2) to be correct, that

$$\bar{\rho} = \hat{\rho} = \rho. \tag{5}$$

Hence

$$\int \mathrm{d}\boldsymbol{r}\,\omega(r,\rho) = 1. \tag{6}$$

The differences between the functionals arise from the different definitions of the density $\hat{\rho}(\boldsymbol{r})$ on which the weighting function depends. We consider these in turn.

2.1. The LWDA of Tarazona

For this approximation

$$\hat{\rho}(\boldsymbol{r}) = \bar{\rho}(\boldsymbol{r}). \tag{7}$$

Then equation (4) becomes explicitly

$$c^{(2)}(\boldsymbol{r}-\boldsymbol{s},\rho) = -2\beta f'(\rho)\omega(\boldsymbol{r}-\boldsymbol{s},\rho) - \rho\beta f''(\rho)\int \mathrm{d}\boldsymbol{t}\,\omega(\boldsymbol{r}-\boldsymbol{t},\rho)\omega(\boldsymbol{t}-\boldsymbol{s},\rho)$$
$$-\rho\beta f'(\rho)\int \mathrm{d}\boldsymbol{t}\,[\omega'(\boldsymbol{r}-\boldsymbol{t},\rho)\omega(\boldsymbol{t}-\boldsymbol{s},\rho) + \omega(\boldsymbol{r}-\boldsymbol{t},\rho)\omega'(\boldsymbol{t}-\boldsymbol{s},\rho)] \tag{8}$$

where ω' and f' indicates differentiation with respect to the bulk density and $\rho = \rho_b$. (1)–(8) constitute the LWDA proposed by Tarazona and extended by Curtin and Ashcroft. In practice, even if $c^{(2)}(\boldsymbol{r},\rho)$ can be given explicitly as a function of r and ρ, the weighting function, which satisfies (6) and (8), cannot. This increases enormously the complexity of calculations which use this approximation. In order to avoid this Tarazona and coworkers [6] have proposed an expansion for $\omega(r,\rho)$ of the form

$$\omega(r,\rho) = \omega_0(r) + \omega_1(r)\rho + \omega_2(r)\rho^2 \tag{9}$$

where

$$\omega_0(r) = \frac{3}{4\pi\sigma^3}\theta(\sigma - r) \tag{10}$$

$$\begin{aligned}\omega_1(r) &= 0.475 - 0.648\left[\frac{r}{\sigma}\right] + 0.113\left[\frac{r}{\sigma}\right]^2 \qquad r < \sigma\\ &= 0.288\left[\frac{\sigma}{r}\right] - 0.924 + 0.764\left[\frac{r}{\sigma}\right] - 0.187\left[\frac{r}{\sigma}\right]^2 \qquad \sigma < r < 2\sigma\\ &= 0 \qquad r > 2\sigma\end{aligned} \tag{11}$$

and

$$\omega_2(r) = \frac{5\pi\sigma^3}{144}\left(6 - 12\left[\frac{r}{\sigma}\right] + 5\left[\frac{r}{\sigma}\right]^2\right)\theta(\sigma - r) \tag{12}$$

where $\theta(x)$ is the Heaviside step function and σ the hard-sphere diameter. Substituted into equation (8), one obtains an approximation for $c^{(2)}(\boldsymbol{r},\rho)$ which is good up to a reduced density of ~ 0.9.

2.2. A new HWDA

The object of this approximation is to use a simpler approximation for $\hat{\rho}(\boldsymbol{r})$ than equation (7), but to simplify in such a way that the weighting function still satisfies (8). This can be achieved by taking it to be the global average defined by

$$\hat{\rho}(\boldsymbol{r}) = \int \mathrm{d}\boldsymbol{s}\,\rho(\boldsymbol{s})\omega(\boldsymbol{r}-\boldsymbol{s},\rho_b) \tag{13}$$

where ρ_b is the bulk density. This is simpler to use than equation (7) because it provides an explicit definition for $\hat{\rho}(\boldsymbol{r})$. (7) provides a circular definition because $\hat{\rho}(\boldsymbol{r})$ depends on $\bar{\rho}(\boldsymbol{r})$ which itself depends on $\hat{\rho}(\boldsymbol{r})$. Thus $\bar{\rho}(\boldsymbol{r})$ has to be found self-consistently. Because the weighted function still satisfies equation (8), one can use Tarazona's solution as given by equations (9)–(12).

In density-functional theory, the equilibrium particle density distribution is, in general, found by minimizing the grand potential functional $\Omega[\rho]$ with respect to variations in $\rho(\boldsymbol{r})$

$$\beta\mu - \beta u^{ext}(\boldsymbol{r}) = \frac{\beta\delta F[\rho]}{\delta\rho(\boldsymbol{r})} \tag{14}$$

where μ is the chemical potential of the system and $u^{ext}(\boldsymbol{r})$ the external potential. From (1) and (14), one obtains

$$\beta\mu - \beta u^{ext}(\boldsymbol{r}) = \ln\rho(\boldsymbol{r}) - c^{(1)}(\boldsymbol{r};[\rho]) \tag{15}$$

where $c^{(1)}(\boldsymbol{r};[\rho])$ is the one-particle direct correlation function

$$c^{(1)}(\boldsymbol{r};[\rho]) = -\beta f(\bar{\rho}(\boldsymbol{r})) - \beta\int \mathrm{d}\boldsymbol{s}\,\rho(\boldsymbol{s})f'(\bar{\rho}(\boldsymbol{s}))\frac{\delta\bar{\rho}(\boldsymbol{s})}{\delta\rho(\boldsymbol{r})} \tag{16}$$

and

$$\frac{\delta\bar{\rho}(\boldsymbol{s})}{\delta\rho(\boldsymbol{r})} = \omega(\boldsymbol{r}-\boldsymbol{s},\hat{\rho}(\boldsymbol{s})) + \omega(\boldsymbol{r}-\boldsymbol{s},\rho_b)\int \mathrm{d}\boldsymbol{t}\,\rho(\boldsymbol{t})\omega'(\boldsymbol{s}-\boldsymbol{t},\hat{\rho}(\boldsymbol{s})). \tag{17}$$

Here, the locally weighted density $\bar{\rho}(\boldsymbol{r})$ is simply given as

$$\bar{\rho}(\boldsymbol{r}) = \rho_0(\boldsymbol{r}) + \rho_1(\boldsymbol{r})\hat{\rho}(\boldsymbol{r}) + \rho_2(\boldsymbol{r})\hat{\rho}(\boldsymbol{r})^2 \tag{18}$$

where

$$\hat{\rho}(\boldsymbol{r}) = \rho_0(\boldsymbol{r}) + \rho_1(\boldsymbol{r})\rho_b + \rho_2(\boldsymbol{r})\rho_b^2 \tag{19}$$

with coefficients

$$\rho_i(\boldsymbol{r}) = \int \mathrm{d}\boldsymbol{s}\,\rho(\boldsymbol{s})\omega_i(\boldsymbol{r}-\boldsymbol{s}) \qquad i = 0, 1, 2. \tag{20}$$

In a homogeneous state $\bar{\rho}(\boldsymbol{r}) = \hat{\rho}(\boldsymbol{r}) = \rho_b$, equation (16) yields for the chemical potential

$$\beta\mu = \ln\rho_b - c^{(1)}(\rho_b) \tag{21}$$

where

$$c^{(1)}(\rho_b) = -\beta f(\rho_b) - \beta\rho_b f'(\rho_b). \tag{22}$$

Combining (15) and (21) and eliminating the chemical potential μ, we have the density profile equation

$$\rho(\boldsymbol{r}) = \rho_b \exp[-\beta u^{ext}(\boldsymbol{r}) + c^{(1)}(\boldsymbol{r};[\rho]) - c^{(1)}(\rho_b)]. \tag{23}$$

The density profiles were obtained by numerical iteration between the old density profiles on the right-hand side and the new one on the left-hand side of equation (23).

2.3. A new global hybrid weighted-density approximation (GHWDA)

This density functional is based upon that due to Leidl and Wagner [4]. A simplified version based upon an expansion of the weighting function in powers of density akin to Tarazona's expansion has already been proposed and explored by Lee *et al* [11]. In this paper, we propose a further simplification, similar to that in subsection 2.2, which leads to an explicit formula for the average density which exploits the weighting function of Lee *et al.*

For the new functional, we take $\hat{\rho}(\boldsymbol{r})$ to be the globally averaged function

$$\hat{\rho}(\rho) = \frac{1}{N}\int \mathrm{d}\boldsymbol{r}\,\rho(\boldsymbol{r})\int \mathrm{d}\boldsymbol{s}\,\rho(\boldsymbol{s})\omega(\boldsymbol{r}-\boldsymbol{s};\rho_b) \tag{24}$$

where N is the number of particles. Then, from the definition of $c^{(2)}(\boldsymbol{r}-\boldsymbol{s},\rho)$ we simply obtain the same relationship with the weighted function as given by Leidl and Wagner [4], namely

$$c^{(2)}(\boldsymbol{r}-\boldsymbol{s},\rho) = -2\beta f'(\rho)\omega(\boldsymbol{r}-\boldsymbol{s},\rho) - \rho\beta f''(\rho)\int \mathrm{d}\boldsymbol{t}\,\omega(\boldsymbol{r}-\boldsymbol{t},\rho)\omega(\boldsymbol{t}-\boldsymbol{s},\rho). \tag{25}$$

In the homogeneous fluid, the average densities will equal the bulk density and the weighted function will again be normalized by equation (6). One can easily check that the proposed weighted-density approximation exactly generates the same higher-order direct correlation functions $c^{(n)}(\boldsymbol{r},\ldots,\boldsymbol{t},\rho)$ [4, 12, 13] as those of the HWDA of Leidl and Wagner because in the thermodynamic limit

$$\lim_{\rho(\boldsymbol{r})\to\rho_b}\frac{\delta^{(n)}\hat{\rho}[\rho]}{\delta\rho(\boldsymbol{s})\cdots\delta\rho(\boldsymbol{t})} \to 0 \qquad \text{for} \qquad n \geqslant 1. \tag{26}$$

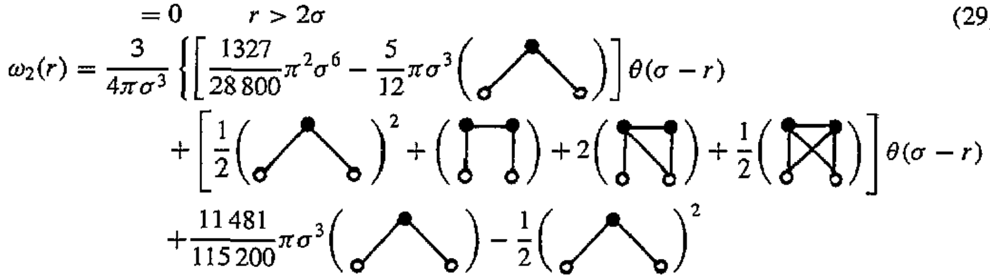
On the other hand, it is expected that in applications such as to the properties of inhomogeneous classical fluids the proposed weighted-density approximation will give different results from the HWDA of Leidl and Wagner because of the different average density. To reduce the computational problem in actual applications, we use the weighted function derived from the density expansion method by Lee *et al* [11]. In this case, the weighting function is given by

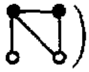
$$\omega(r,\rho) = \omega_0(r) + \omega_1(r)\rho + \omega_2(r)\rho^2 + \omega_3(r)\rho^3 \tag{27}$$

with the coefficients

$$\omega_0(r) = \frac{3}{4\pi\sigma^3}\theta(\sigma - r) \tag{28}$$

$$\begin{aligned}\omega_1(r) &= \frac{81}{128\sigma^3}\left(\frac{4}{3} - \left[\frac{r}{\sigma}\right] + \frac{1}{12}\left[\frac{r}{\sigma}\right]^3\right) - \frac{5}{16} \qquad r < \sigma \\ &= -\frac{15}{128\sigma^3}\left(\frac{4}{3} - \left[\frac{r}{\sigma}\right] + \frac{1}{12}\left[\frac{r}{\sigma}\right]^3\right) \qquad \sigma < r < 2\sigma \\ &= 0 \qquad r > 2\sigma\end{aligned} \tag{29}$$



$$-\frac{25}{512}\Big($$  $$\Big)-\frac{5}{16}\Big($$  $$\Big)-\frac{1}{2}\Big($$  $$\Big)\Big\} \tag{30}$$

$$\omega_3(r)=\frac{55\sigma^6}{1000}\left(6-12\left[\frac{r}{\sigma}\right]+5\left[\frac{r}{\sigma}\right]^2\right)\theta(\sigma-r) \tag{31}$$

where we have used the graphical representations of the Mayer–Montroll formalism [14]; $\theta(x)$ is the Heaviside step function and σ is the hard-sphere diameter. Taken together, equations (24)–(31) constitute the GHWDA derived from the proposed weighted-density approximation. In this approximation, the density profiles are again obtained as solutions to equation (23) with the one-particle direct correlation function defined by (16), but equations (17)–(19) are replaced by

$$\frac{\delta\bar{\rho}(s)}{\delta\rho(\boldsymbol{r})}=\omega(\boldsymbol{r}-\boldsymbol{s};\hat{\rho})+\int \mathrm{d}\boldsymbol{t}\,\rho(\boldsymbol{t})\omega'(\boldsymbol{t}-\boldsymbol{s};\hat{\rho})\frac{\delta\hat{\rho}}{\delta\rho(\boldsymbol{r})} \tag{32}$$

where the locally weighted density $\bar{\rho}(\boldsymbol{r})$ is simply given by

$$\bar{\rho}(\boldsymbol{r})=\rho_0(\boldsymbol{r})+\rho_1(\boldsymbol{r})\hat{\rho}+\rho_2(\boldsymbol{r})\hat{\rho}^2+\rho_3(\boldsymbol{r})\hat{\rho}^3 \tag{33}$$

and

$$\hat{\rho}=\frac{1}{N}\int \mathrm{d}\boldsymbol{s}\,\rho(\boldsymbol{s})[\rho_0(\boldsymbol{s})+\rho_1(\boldsymbol{s})\rho_b+\rho_2(\boldsymbol{s})\rho_b^2+\rho_3(\boldsymbol{s})\rho_b^3]. \tag{34}$$

3. Density profiles of hard-sphere fluids confined between hard flat walls

As a simple application of the new functionals, we apply them to derive the density profiles of a hard-sphere fluid confined between two hard, parallel and structureless walls. Because of the symmetry of the problem, all quantities depend upon only one coordinate, say z, and not on x, y, where the z = constant planes lie parallel to the walls. Hence, $\rho=\rho(z)$, $\bar{\rho}=\bar{\rho}(z)$, etc. Then, the weighting function $\omega(z)$ is given by

$$\omega(z)=\int \mathrm{d}x\,\mathrm{d}y\,\omega([x^2+y^2+z^2]^{1/2}). \tag{35}$$

The density profile equation with a hard wall situated at the origin is given by

$$\begin{aligned}\rho(z)&=\rho_b\exp[c^{(1)}(z;[\rho])-c^{(1)}(\rho_b)] \qquad z>\sigma/2\\ &=0 \qquad z<\sigma/2.\end{aligned} \tag{36}$$

Three sets of densities, $\rho\sigma^3=0.715$, 0.183 and 0.9135 are investigated in this work for the density profiles of the hard-sphere fluid. In applying (36) together with equations (16) and (22), the excess free energy per particle of the hard-sphere fluid, $f(\rho)$, is taken according to the quasi-exact Carnahan–Starling equation of state [15]

$$\beta f(\rho)=\frac{\eta(4-3\eta)}{(1-\eta)^2} \tag{37}$$

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

The resulting density profiles are displayed in figures 1–3, and compared with the results of the LWDA of Tarazona and computer simulation [16]. Because of the symmetries of the density profiles, we show the density profiles only to one side of the wall. The origin for the coordinate z is at the closest distance of approach of a molecule to the wall. In fact, the results from the two new weighting approximations are so close to each other that they cannot be distinguished in the figures and only those due to the HWDA (case B) are displayed. As can be seen from figure 1, at $\rho\sigma^3=0.715$ the hard-sphere oscillatory

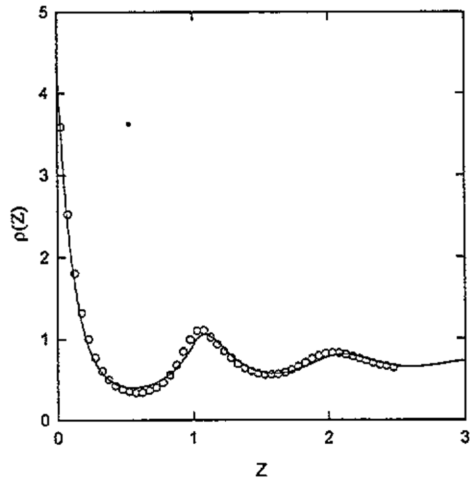


Figure 1. Density profile of a hard-sphere fluid confined in hard flat walls ($\rho\sigma^3 = 0.715$). The open circles are from the computer simulations [10]. The solid and dotted lines correspond to the LWDA of Tarazona and our approximation, respectively. Notice here that our approximation is indistinguishable from the LWDA of Tarazona.

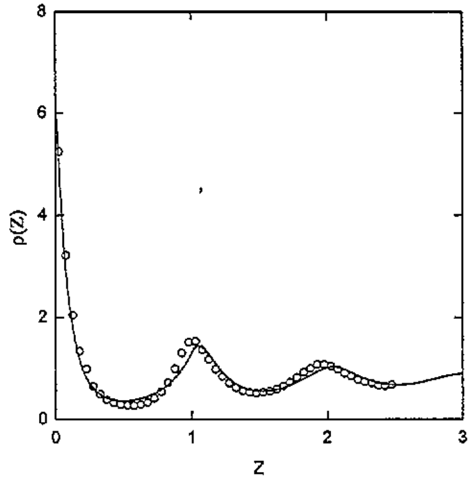


Figure 2. Same as figure 1 except that $\rho\sigma^3 = 0.813$.

structures are well reproduced when compared with simulation results. Notice here that the HWDA is indistinguishable from Tarazona's approximation. At $\rho\sigma^3 = 0.9135$ the deviation from the simulation results becomes, as expected, more marked; the position of the first peak is slightly shifted and the first oscillation is slightly underestimated. In this case too, the HWDA is almost indistinguishable from the approximation of Tarazona, with the differences being small. The surprising feature of these results is how close the results of the HWDA are to those calculated via Tarazona's functional. The overall picture shows that the HWDA describes the inhomogeneous properties of the hard-sphere fluids well.

4. Density profiles of hard-sphere fluids restricted by permeable walls

As a second application of the HWDA, we consider density profiles of hard-sphere fluids restricted by permeable walls. For the wall–fluid potential, we have used the same potential as Powles and Pagoda [9, 10]. In this case, there is an infinite array of semipermeable walls uniform and stretching to infinity in the x and y direction with a separation h between the central planes of neighbouring walls. Then,

$$u^{ext}(z) = H \sum_{n=-\infty}^{\infty} \left[1 + \left(\frac{|z - h/2 + nh|}{\omega/2} \right)^9 \right]^{-1} \tag{38}$$

where H is the height of the barrier and ω the width of the barrier. In practice, it is only necessary to determine the density profiles of hard-sphere fluids in the range $0 < z < h/2$. The required values outside this range are then given by the symmetry of the problem. Because the wall has a finite height, H, there is a finite probability of finding a molecule within the wall and this depends on the temperature $k_B T$. Thus, although the fluid comprises

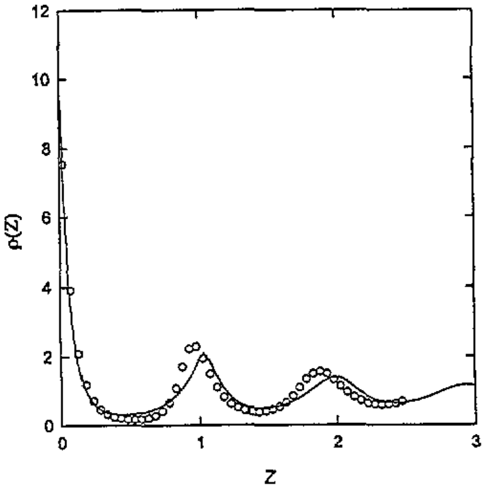


Figure 3. Same as figure 1 except that $\rho\sigma^3 = 0.9135$.

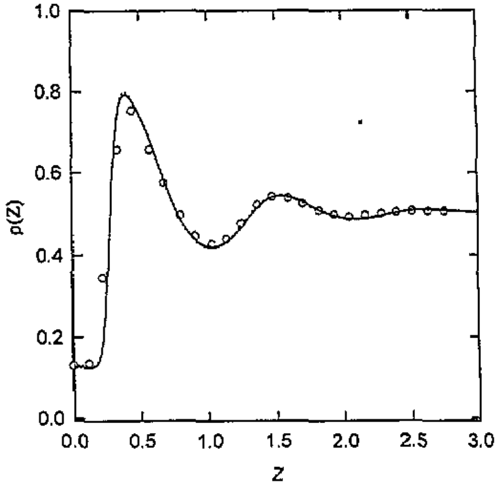


Figure 4. Density profile of a hard-sphere fluid restricted by permeable walls. $\rho\sigma^3 = 0.50364$, $H = 2.0$ and $\omega = 0.5$. The open circles are from computer *simulation [16]. The solid and dotted lines correspond* to the LWDA of Tarazona and our approximation, respectively. Notice that our approximation is almost indistinguishable from the LWDA of Tarazona.

hard spheres, the density profile will depend on the temperature. Then, the density profile equation is

$$\rho(z) = \rho_b \exp[-\beta u^{ext}(z) + c^{(1)}(z; [\rho]) - c^{(1)}(\rho_b)] \qquad 0 < z < h. \tag{39}$$

Since the lengths in the problem can be measured in terms of a molecular diameter σ, and energies can be measured in terms of $k_B T$, the problem is characterized by the three reduced parameters

$$H^* = \beta H \qquad \omega^* = \frac{w}{\sigma} \qquad h^* = \frac{h}{\sigma}. \tag{40}$$

As these are the only parameters used in the remainder of this paper we drop the asterisks. To obtain results to compare with those in [10] h is chosen as $h = 16$. With this value for h, the hard-sphere fluid is essentially homogeneous midway between two permeable walls and the shape of the density profile is unaffected by the exact value h.

The resulting density profiles for the hard-sphere fluid are displayed in figures 4–8, and compared with the results of the LWDA of Tarazona and computer simulation [10]. Again, the results of the two new approximations are so close to each other that only those from the HWDA are displayed. As can be discerned from figures 4–8, over most of the range of the parameters, the HWDA reproduces the density profiles of hard-sphere fluids very well when compared with the computer simulations. Also over most of the range of the parameters the HWDA is indistinguishable from the LWDA of Tarazona although we can see slight differences between two approximations in figures 4 and 5. Even though we do not show the density profiles for other density-functional approximations for clarity, the comparisons show that the HWDA gives better results than the other density-functional approximations which were tested by Marsh *et al* [10]. Once again, the overall picture shows that over most

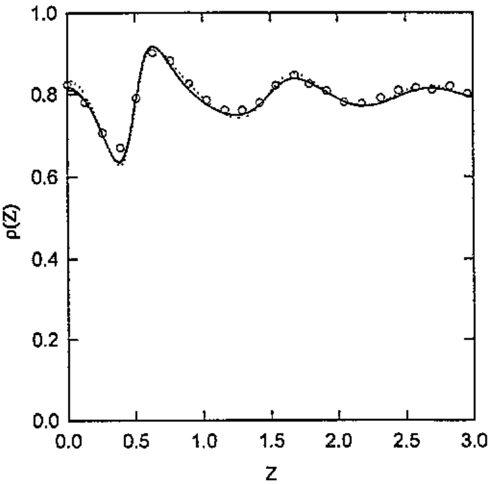


Figure 5. Same as figure 4 but with the parameters $\rho\sigma^3 = 0.8022$, $H = 1$ and $\omega = 1$. In this case, some difference between the LWDA of Tarazona and our approximation can be seen, but it is very small.

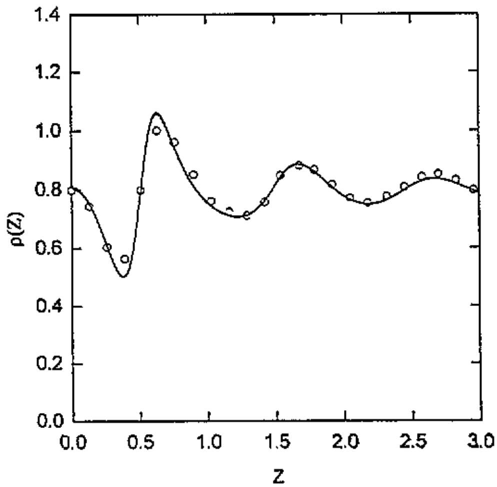


Figure 6. Same as figure 4 but with the parameters $\rho\sigma^3 = 0.8046$, $H = 2$ and $\omega = 1$.

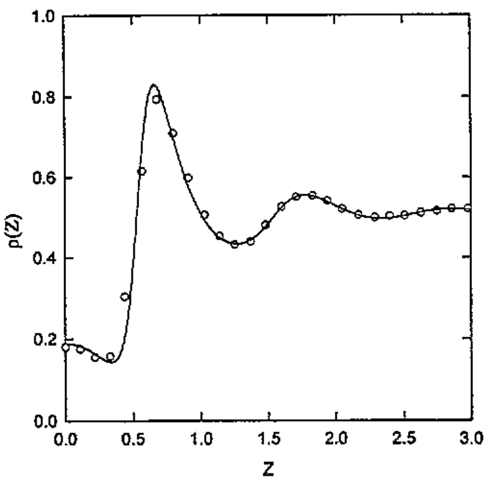


Figure 7. Same as figure 4 but with the parameters $\rho\sigma^3 = 0.5142$, $H = 3$ and $\omega = 1$.

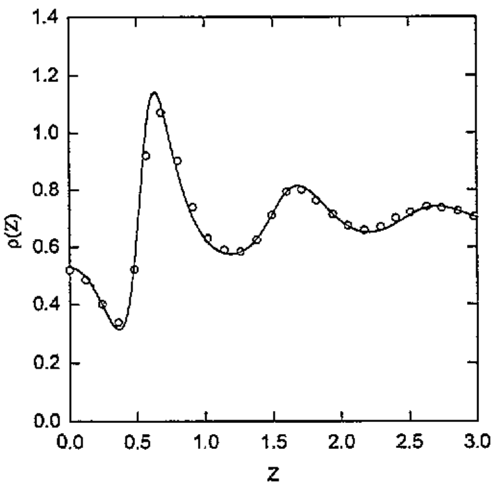


Figure 8. Same as figure 4 but with the parameters $\rho\sigma^3 = 0.7099$, $H = 3$ and $\omega = 1$.

of the range of the parameters the HWDA describes the structural properties of hard-sphere fluids restricted by permeable walls very well.

5. Hard-sphere fluids in a spherical cage

The GHWDA becomes identical to an approximation already discussed by Lee *et al* [11] for systems with a planar geometry. However, this is no longer the case in a spherical geometry. To test whether the two produce similar results in such a geometry, we have studied the profile of a hard-sphere fluid confined to a spherical cage with a hard wall and radius $R + \sigma/2$. In this case, the resulting density profile satisfies the equation

$$\begin{aligned} \rho(r) &= \rho_b \exp[c^{(1)}(r;[\rho]) - c^{(1)}(\rho_b)] \qquad r < R \\ &= 0 \qquad r > R. \end{aligned} \tag{41}$$

Two bulk densities ($\rho\sigma^3 = 0.62$ with $N = 277$ and $\rho\sigma^3 = 0.75$ with $N = 342$) have been investigated. In figure 9 we compare the result of the GHWDA with computer simulation at the higher density; it can be seen that the agreement is very good, comparable with that provided by the earlier and more complex theory [11]. Comparable agreement is found at the lower density.

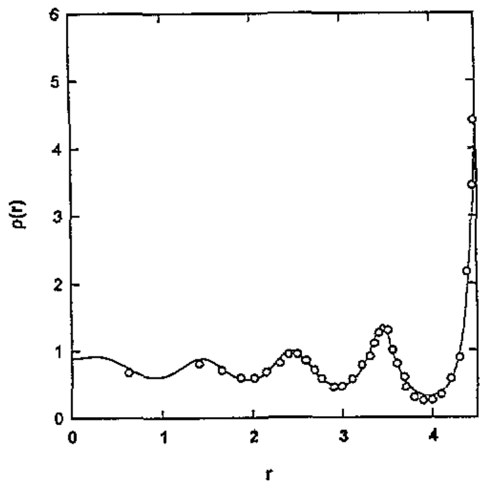


Figure 9. Density profile of a hard-sphere fluid confined within a spherical cage with a hard structureless wall ($\rho\sigma^3 = 0.75$). The open circles are from computer simulation [21].

6. Results and discussion

We have proposed two new weighted-density approximations based on local and global average densities and have implemented than using density expansions for the weighting function. The main advantage of the new approximations is that they are computationally much simpler to use than the LWDA because of the analytic form of the weight function. We have applied the approximation to calculate the density profiles of hard-sphere fluids confined in certain types of pore and have compared our results both with those of other model approximations and with computer simulations. For the particular problems studied the two approximations give almost identical results.

For the hard-sphere fluid confined between planar hard walls, the results are almost indistinguishable from those of the LWDA of Tarazona, although at the highest density investigated the new approximation is in closer agreement with simulation.

When the walls are permeable, the new approximations produce profiles again almost indistinguishable from that due to Tarazona's theory except near the centre of a permeable wall. In this region, Tarazona's theory agrees better with simulation.

The GHWDA approximation has been applied to a hard-sphere fluid confined to a spherical cage and again the profile agrees very well with the simulated one. From the various applications we conclude that the new approximations provide nearly as reliable density profiles as Tarazona's LWDA. They have the advantage of being less intense computationally.

One can calculate the higher-order direct correlation functions, $c^{(n)}(r, s, \ldots, t, \rho)$, from the HWDA by taking the functional derivative of the free energy functional with respect to the density [12, 13, 17, 18]. It is expected that in the homogeneous state the higher-order direct correlation functions derived from the HWDA will be different from those of the LWDA since

$$\lim_{\rho(r)\to\rho_b} \frac{\delta^{(n)}\hat{\rho}(r)}{\delta\rho(s)\cdots\delta\rho(t)} = 0 \qquad \text{for} \qquad n \geqslant 2. \tag{42}$$

On the other hand, the free energy functional approximation presented here can generally be used as a reference system for a perturbative analysis of bulk hard-sphere systems and can be applied to the liquid–solid freezing transition of other systems such as Lennard-Jones fluids; such systems with soft repulsions are notoriously difficult to study *vis-à-vis* freezing transitions and constitute a stern test for any theory [19, 20]. Therefore, we intend to use the proposed HWDA to study the homogeneous and inhomogeneous properties of liquids as well as the freezing problem of classical fluids. We hope to investigate these problems in the near future.

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