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Weighted density functional theory of spherically inhomogeneous hard spheres

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The weighted density functional theory of hard sphere fluids proposed by Tarazona is applied to spherically inhomogeneous hard sphere fluids. The density profile of a hard sphere fluid around a hard sphere particle with structureless hard wall and varying radii is obtained. Our results are compared with previously obtained computer simulation with good agreement. We also calculate the density profile of a hard sphere fluid confined to spherical pores. We compare these results with those obtained by Calleja *et al.*, in which both theory and computer simulation are used. In this case the results are also in agreement.

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I. INTRODUCTION

The structural properties of an inhomogeneous fluid with a special geometrical symmetry, such as a fluid confined to a planar slit [1–3], a fluid bounded to a cylindrical channel [4–6] or spherical cavities [7,8], and a fluid around a large hard sphere [9], have been studied in the last two decades. Several theoretical methods have been applied for studying these kinds of system [10]. There are two main theoretical approaches for considering these types of problems: integral equations based on liquid theories and density functional theory [10–12]. A system of spherically inhomogeneous hard spheres has been studied theoretically and by using Monte Carlo simulation [13–15]. Attard [9] solved the inhomogeneous Ornstein-Zernike (OZ) equation and the Triezenberg-Zwanzwig expression for the density profile in the vicinity of an isolated hard sphere particle. For fluids in a spherically symmetric external field, he showed that the OZ convolution integral becomes a simple algebraic equation upon Legendre transformation [16]. Tang and Lu [13,14] expanded the radial distribution function of an arbitrary potential around the hard sphere and obtained a general solution of the OZ equation. The density profile of an inhomogeneous hard sphere fluid around a large colloidal hard sphere was calculated by Degreve and Henderson [15] using Monte Carlo simulation.

In the present article, we are interested in applying density functional theory to spherically inhomogeneous hard sphere fluids. This theory has been widely used in recent years to consider the structure of confined or homogeneous fluids [2,3,17]. Henderson and Sokolowski studied adsorption in spherical cavities using density functional theory [18]. Rickayzen and Augousti [1] introduced a modified hypernetted chain density functional containing a third order term in the density, chosen to ensure that the density functional gives the correct bulk pressure. This theory was then applied to study the density profile of hard spheres [1] and Lennard-Jones fluids [19,20] confined to a slit. Calleja *et al*. [11] obtained the density profile of hard sphere and Lennard Jones fluids confined to spherical pores, using both computer simulation and the density functional theory proposed by Rickayzen and Augousti. In the case of the hard sphere fluid, the results of the theory and simulation are in good agreement.

Tarazona and Evans [21] introduced a simple free energy functional, which includes both local thermodynamics and short range correlation, to find the density profile of a fluid near a hard wall. This functional is closely related to that studied by Nordholm *et al.* [22], where the theory is referred to as generalized van der Waals theory. Tarazona [23] developed a free energy density functional of the hard sphere fluid on a semiemprical basis following the preceding ideas [21]. In this formalism one tries to get a quantitatively good description of the hard sphere system in any likely situation, at the same time making it possible to use it for the description of the reference system in a perturbative analysis of any realistic model [24,25]. This functional theory, which is sometimes called the weighted density functional approximation (WDA), can be used to describe an inhomogeneous system of hard spheres. Even for uniform density distribution it gives the good description of the structure. It also gives a correct location of the solid-fluid phase transition, which implies a good description of the hard sphere crystal [23]. The theory has been applied to obtain the density profile and surface tension of hard sphere fluid in contact with a hard wall. The results are in good agreement with computer simulations, especially at high bulk density [23].

The purpose of the present work is to apply the WDA theory introduced by Tarazona to find the density profile of a hard sphere fluid around hard spheres with various radii and compare the results with previous computer simulations [15]. Furthermore, we study the structure of a hard sphere fluid confined to spherical pores and we compare our results with those obtained by Calleja *et al*. [11], where they used both theory and computer simulations.

The plan of this article is as follows. In Sec. II we outline the weighted density functional theory of the hard sphere fluid introduced by Tarazona and we derive the Euler-Lagrange equation for an inhomogeneous hard sphere fluid. In Sec. III we discuss the weighted density functional theory of a spherically inhomogeneous hard sphere fluid and we calculate the density profile of the hard sphere fluid near hard spheres of varying radii. In Sec. IV the density profile of a hard sphere fluid confined to a spherical cavity is calculated. Finally, in Sec. V we describe and discuss the results.

II. WEIGHTED DENSITY FUNCTIONAL OF HARD SPHERES

Tarazona has introduced a free energy functional of smoothed density distribution $\overline{\rho}(\mathbf{r})$, which, at each point $\mathbf{r}$, is a nonlocal functional of $\rho(\mathbf{r})$. Any sharp change in the real density will be smeared down in $\overline{\rho(\mathbf{r})}$, which can be imagined as the mean density around a particle at point $\mathbf{r}$ and in a volume that can be related to the range of interaction. The Helmholtz free energy functional can be taken as

$$F[\rho]=F_{id}[\rho]+\int d\mathbf{r}\rho(\mathbf{r})\Delta\psi(\overline{\rho(\mathbf{r})}), \tag{1}$$

where $F_{id}[\rho]$ is the free energy functional of an ideal gas at temperature T and is exactly given by the local density approximation:

$$F_{id}[\rho(\mathbf{r})]=k_BT\int d\mathbf{r}\rho(\mathbf{r})\{\ln[\lambda^3\rho(\mathbf{r})]-1\}$$
$$=\int d\mathbf{r}\rho(\mathbf{r})\psi_{id}(\rho(\mathbf{r})). \tag{2}$$

Here $\lambda=h(2\pi m k_BT)^{-1/2}$ is the thermal de Broglie wavelength, k_B is the Boltzman constant, and $\Delta\psi(\rho)$ is the excess free energy per particle above the ideal gas,

$$\Delta\psi(\rho)\equiv\psi(\rho)-\psi_{id}(\rho), \tag{3}$$

where $\psi(\rho)$ and $\psi_{id}(\rho)$ are the free energy per particle of the liquid and ideal gas, respectively. In Eq. (1), we choose $\Delta\psi$ as a functional of $\overline{\rho(\mathbf{r})}$. To avoid purely local treatment of narrow peaks in $\rho(\mathbf{r})$ and to reach a really good description of direct correlation, we choose the function $\overline{\rho(\mathbf{r})}$ as

$$\overline{\rho(\mathbf{r})}=\int d\mathbf{r}'\rho(\mathbf{r}')w(|\mathbf{r}-\mathbf{r}'|,\overline{\rho(\mathbf{r})}). \tag{4}$$

This equation is an integral equation used to define $\overline{\rho(\mathbf{r})}$ in terms of $\rho(\mathbf{r})$. We assume that the analytic dependency of the function $w(r,\rho)$ on the density is given by

$$w(r,\rho)=w_0(r)+w_1(r)\rho+w_2(r)\rho^2+\cdots, \tag{5}$$

where the normalization condition of $w(r,\rho)$ at any density is

$$\int d\mathbf{r}w(r,\rho)=1, \tag{6}$$

which implies

$$\int d\mathbf{r}w_i(r,\rho)=\begin{cases}1 & \text{for} \quad i=0\\ 0 & \text{for} \quad i=1,2.\end{cases} \tag{7}$$

The weighting function $w_i(r)$ is obtained by requiring close agreement, over a range of densities, of the two-particle direct correlation function which is predicted by the Percus-Yevick approximation for the homogeneous hard-sphere fluid [23,24],

$$w_0(r)=\frac{3}{4\pi\sigma^3}\theta(\sigma-|\mathbf{r}|), \tag{8}$$

$$w_1(r)=\begin{cases}0.475-0.648(r/\sigma)+0.113(r/\sigma)^2, & r<\sigma\\ 0.288(\sigma/r)-0.924+0.764(r/\sigma)-0.187(r/\sigma)^2, & \sigma<r<2\sigma\\ 0, & r>2\sigma\end{cases} \tag{9}$$

and

$$w_2(r)=\frac{5\pi\sigma^3}{144}[6-12(r/\sigma)+5(r/\sigma)^2]\theta(\sigma-r), \tag{10}$$

where σ is the diameter of the hard sphere and $\theta(r)$ is the Heaviside step function. By using Eqs. (4) and (5), we can derive the relation

$$\overline{\rho(\mathbf{r})}=\overline{\rho_0}(\mathbf{r})+\overline{\rho_1}(\mathbf{r})\overline{\rho(\mathbf{r})}+\overline{\rho_2}(\mathbf{r})[\overline{\rho(\mathbf{r})}]^2, \tag{11}$$

where

$$\overline{\rho_i}(\mathbf{r})=\int d\mathbf{r}'\rho(\mathbf{r}')w_i(|\mathbf{r}-\mathbf{r}'|). \tag{12}$$

The function $\overline{\rho(\mathbf{r})}$ can be obtained from Eq. (11),

$$\overline{\rho(\mathbf{r})}=\frac{2\overline{\rho_0}(\mathbf{r})}{[1-\overline{\rho_1}(\mathbf{r})]+[|1-\overline{\rho_1}(\mathbf{r})|^2-4\overline{\rho_0}(\mathbf{r})\overline{\rho_2}(\mathbf{r})]^{1/2}}. \tag{13}$$

The functional derivative of $\overline{\rho(\mathbf{r})}$ with respect to $\rho(\mathbf{r})$ can be expressed as

$$\frac{\delta\overline{\rho(\mathbf{r})}}{\delta\rho(\mathbf{r}')}=\frac{w(|\mathbf{r}-\mathbf{r}'|,\overline{\rho(\mathbf{r})})}{1-\overline{\rho_1}(\mathbf{r})-2\overline{\rho_2}(\mathbf{r})\overline{\rho(\mathbf{r})}}. \tag{14}$$

In density functional theory, the grand canonical potential $\Omega[\rho]$ and intrinsic (Helmholtz) free energy functional $F[\rho]$, both unique functionals of the one-particle density $\rho(\mathbf{r})$, are related by

$$\Omega[\rho]=F[\rho]+\int d\mathbf{r}\rho(\mathbf{r})[u_{ext}(\mathbf{r})-\mu], \tag{15}$$

where μ is the chemical potential of the system and $u_{ext}(\mathbf{r})$ is an external potential. The equilibrium density distribution of the inhomogeneous fluid corresponds to the minimum of the grand potential satisfying

$$\frac{\delta\Omega[\rho]}{\delta\rho(\mathbf{r})}=0, \tag{16}$$

which leads to the Euler-Lagrange equation

$$\mu-u_{ext}(\mathbf{r})=\frac{\delta F[\rho]}{\delta\rho(\mathbf{r})}. \tag{17}$$

According to Eq. (1), the functional derivative of $F[\rho]$ with respect to the density is

$$\frac{\delta F[\rho]}{\delta\rho(\mathbf{r})}=\mu_{id}(\rho(\mathbf{r}))+\Delta\psi(\overline{\rho}(\mathbf{r}))+\int d\mathbf{r}'\rho(\mathbf{r}')\Delta\psi'(\overline{\rho}(\mathbf{r}'))\frac{\delta\overline{\rho}(\mathbf{r}')}{\delta\rho(\mathbf{r})}, \tag{18}$$

where $\mu_{id}(\rho(\mathbf{r}))$ is the ideal-gas chemical potential and $\Delta\psi'(\overline{\rho}(\mathbf{r}'))$ is the first derivative of $\Delta\psi(\overline{\rho}(\mathbf{r}'))$ with respect to $\overline{\rho}(\mathbf{r}')$.

III. DENSITY PROFILE OF A HARD SPHERE FLUID AROUND A HARD SPHERE PARTICLE

We use Eq. (18) to find the density profile of a hard sphere fluid around a hard sphere particle. In this case the external potential has spherical symmetry,

$$u_{ext}(\mathbf{r})=\begin{cases}\infty, & |\mathbf{r}|\leqslant R\\ 0, & |\mathbf{r}|>R,\end{cases} \tag{19}$$

where R is the radius of the hard sphere particle. The number density $\rho(r)$ is a function of r only and

$$\rho(\mathbf{r})=0,\quad |\mathbf{r}|<R. \tag{20}$$

Combining Eqs. (17) and (18) and using the external potential given by Eq. (19), we have

$$\mu=\mu_{id}(\mathbf{r})+\Delta\psi(\overline{\rho}(\mathbf{r}))+\int d\mathbf{r}'\rho(\mathbf{r}')\Delta\psi'(\overline{\rho}(\mathbf{r}'))\frac{\delta\overline{\rho}(\mathbf{r}')}{\delta\rho(\mathbf{r})}. \tag{21}$$

For an inhomogeneous fluid in contact with a homogeneous bulk fluid, the chemical potential μ is equal to that of the homogeneous bulk fluid, and hence using Eq. (21) we have

$$\mu_{id}(\rho(\mathbf{r}))+\Delta\psi(\overline{\rho}(\mathbf{r}))+\int d\mathbf{r}'\rho(\mathbf{r}')\Delta\psi'(\overline{\rho}(\mathbf{r}'))\frac{\delta\overline{\rho}(\mathbf{r}')}{\delta\rho(\mathbf{r})}=\mu_{id}(\rho_0)+\Delta\psi(\rho_0)+\rho_0\Delta\psi'(\rho_0), \tag{22}$$

where $\Delta\psi'(\rho_0)$ is the derivative of $\Delta\psi(\rho_0)$ with respect to ρ_0. If we use the definition of $\mu(\rho_0)$ and $\mu_{id}(\rho_0)$,

$$\mu_{id}(\rho_0)=k_BT\ln\lambda^3\rho_0, \tag{23a}$$

$$\mu_{id}(\rho(\mathbf{r}))=k_BT\ln\lambda^3\rho(\mathbf{r}), \tag{23b}$$

we obtain the density of the hard sphere fluid,

$$\rho(\mathbf{r})=\rho_0\exp\left\{-\beta\left[\Delta\psi(\overline{\rho}(\mathbf{r}))+\int d\mathbf{r}'\rho(\mathbf{r}')\Delta\psi'(\overline{\rho}(\mathbf{r}'))\frac{\delta\overline{\rho}(\mathbf{r}')}{\delta\rho(\mathbf{r})}-\Delta\psi(\rho_0)-\rho_0\Delta\psi'(\rho_0)\right]\right\}. \tag{24}$$

We insert $\delta\overline{\rho}(\mathbf{r}')/\delta\rho(\mathbf{r})$ from Eq. (14) in Eq. (24) and obtain

$$\rho(\mathbf{r})=\rho_0\exp\left\{-\beta\left[\Delta\psi(\overline{\rho}(\mathbf{r}))+\int d\mathbf{r}'\rho(\mathbf{r}')\Delta\psi'(\overline{\rho}(\mathbf{r}'))\times\frac{w(|\mathbf{r}-\mathbf{r}'|,\overline{\rho}(\mathbf{r}'))}{1-\overline{\rho_1}(\mathbf{r}')-2\overline{\rho_2}(\mathbf{r}')\overline{\rho}(\mathbf{r}')}-\Delta\psi(\rho_0)-\rho_0\Delta\psi'(\rho_0)\right]\right\}. \tag{25}$$

If we want to find the density profile around the hard sphere particle, it is required to calculate the integral in Eq. (25) numerically. We insert the function $w(|\mathbf{r}-\mathbf{r}'|,\overline{\rho}(\mathbf{r}'))$ from Eq. (5) in the integral given in Eq. (25) and write

$$I(R,r)=\int_{R+\sigma/2}^{\infty}\frac{d\mathbf{r}'\rho(\mathbf{r}')\Delta\psi'(\overline{\rho}(\mathbf{r}'))}{1-\overline{\rho_1}(\mathbf{r}')-2\overline{\rho_2}(\mathbf{r}')\overline{\rho}(\mathbf{r}')}[w_0(|\mathbf{r}-\mathbf{r}'|)+w_1(|\mathbf{r}-\mathbf{r}'|)\overline{\rho}(\mathbf{r}')+w_2(|\mathbf{r}-\mathbf{r}'|)\overline{\rho}^2(\mathbf{r}')]. \tag{26}$$

We calculate each integral in Eq. (26) as

$$\int d\mathbf{r}'g(\mathbf{r}')w_i(|\mathbf{r}-\mathbf{r}'|)=2\pi\int dr'r'^2\int_{-1}^{1}d\xi g(\mathbf{r}')w_i(|\mathbf{r}-\mathbf{r}'|)=2\pi\int dr'r'^2g(r')W_i(r,r'), \tag{27}$$

where

$$|\mathbf{r}-\mathbf{r}'|^2=r^2+r'^2-2\xi rr', \tag{28}$$

$$W_i(r,r')=\int_{-1}^{1}d\xi w_i(|\mathbf{r}-\mathbf{r}'|)=\frac{1}{rr'}\int_{|\mathbf{r}-\mathbf{r}'|}^{|\mathbf{r}+\mathbf{r}'|}dr''r''w_i(r''), \tag{29}$$

and $g(\mathbf{r}')$ is an arbitrary function of $\mathbf{r}'$. Equation (26) can be written as

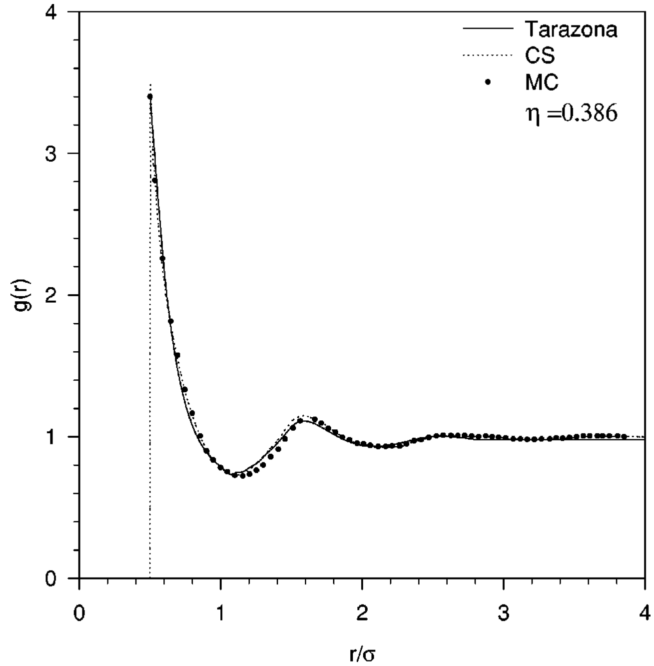

FIG. 1. Radial distribution function of the hard sphere fluid at $\eta=0.386$. The solid line corresponds to the Tarazona theory (present work), the solid circles are taken from the Monte Carlo (MC) simulation of Degreve and Henderson, and the dashed line corresponds to the Carnahan-Starling (CS) calculation.

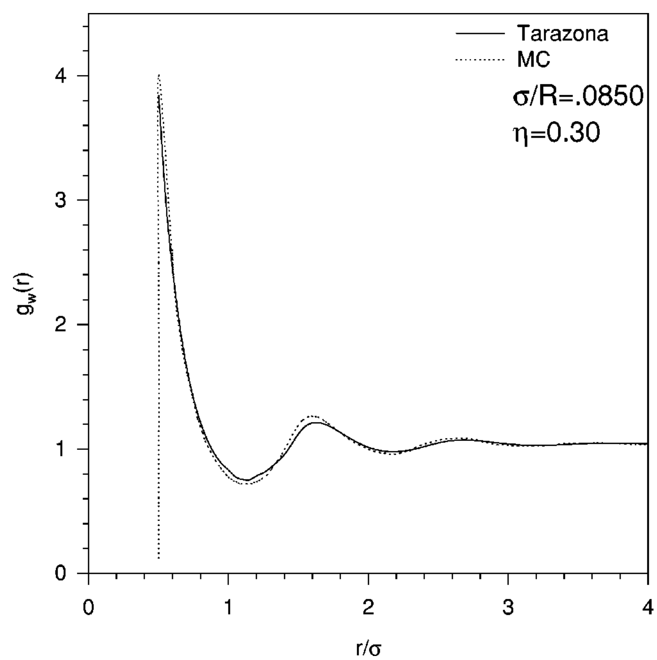

FIG. 2. The normalized density profile about the hard sphere particle, where the inverse diameter of the particle is $\sigma/R=0.0850$ and $\eta=0.30$. The solid line corresponds to present work and the dotted line is taken from the Monte Carlo (MC) simulation of Degreve and Henderson.

$$I(R,r)=2\pi\int_{R+\sigma/2}^{\infty}\frac{dr'r'^2\,\rho(r')\Delta\psi'(\overline{\rho}(r'))}{1-\overline{\rho_1}(r')-2\overline{\rho_2}(r)\overline{\rho}(r)}[W_0(r,r')+W_1(r,r')\overline{\rho}(r')+W_2(r,r')\overline{\rho}^2(r')], \tag{30}$$

and the density profile is given by

$$\rho(r)=\rho_0\exp\{-\beta[\Delta\psi(\overline{\rho}(r))+I(R,r)-\Delta\psi(\rho_0)-\rho_0\Delta\psi'(\rho_0)]\}. \tag{31}$$

We calculate the density profile $\rho(r)$ for the case $R=\sigma/2$ and $\eta=\pi\rho_0\sigma^3/6=0.386$; then we obtain the radial distribution function $g(r)=\rho(r)/\rho_0$ for a hard sphere fluid. In Fig. 1, the function $g(r)$ is displayed and compared with the Monte Carlo simulation results of Degreve and Henderson [15] and those obtained by Carnahan and Starling [26]. The reduced density profile $g_w(r)=\rho(r)/\rho_0$ for a hard sphere fluid near a large hard sphere particle is calculated for $\sigma/R=0.0850$ and $\eta=0.30$. In Fig. 2, we compare the result with those obtained by computer simulation [15]. The origin in Fig. 1 and 2 is taken at the wall of the particle.

IV. HARD SPHERE FLUID CONFINED TO SPHERICAL PORES

We assume the hard sphere fluid is confined to a spherical cavity with a hard structureless wall; thus

$$u_{ext}(\mathbf{r})=\begin{cases}\infty, & |\mathbf{r}|\geqslant R\\ 0, & |\mathbf{r}|<R,\end{cases}$$

where R is the radius of the cavity, the number density is a function of r only, and

$$\rho(r)=0,\quad |\mathbf{r}|>R.$$

Again, we can use Eq. (31) to find the density profile, but Eq. (30) is changed to the expression:

$$I(R,r)=2\pi\int_{0}^{R-\sigma/2}\frac{dr'r'^2\,\rho(r')\Delta\psi'(\overline{\rho}(r'))}{1-\overline{\rho_1}(r')-2\overline{\rho_2}(r)\overline{\rho}(r)}[W_0(r,r')+W_1(r,r')\overline{\rho}(r')+W_2(r,r')\overline{\rho}^2(r')]. \tag{32}$$

For the reduced density $\rho_0^*=\sigma^3\rho_0=0.62$ and $R=5\sigma$, we calculate the density profile inside the cavity and we compare our results with those obtained by Calleja *et al.* [11], who applied both density functional theory and computer simulation. The result are displayed and compared in Fig. 3. The same calculation is done for $\rho_0^*=\sigma^3\rho_0=0.75$ and the results are compared in Fig. 4. As is seen in both cases, the results obtained by Tarazona theory are in agreement with those obtained by other methods.

V. CONCLUSIONS

The weighted density functional theory for a hard sphere fluid near a hard wall [23], proposed by Tarazona, has been extended to a spherically inhomogeneous hard sphere fluid. The theory appears to be fairly accurate for describing the structure of this kind of inhomogeneous hard sphere fluid. According to the results obtained in this and other articles such as [23,27], one can claim that the density functional

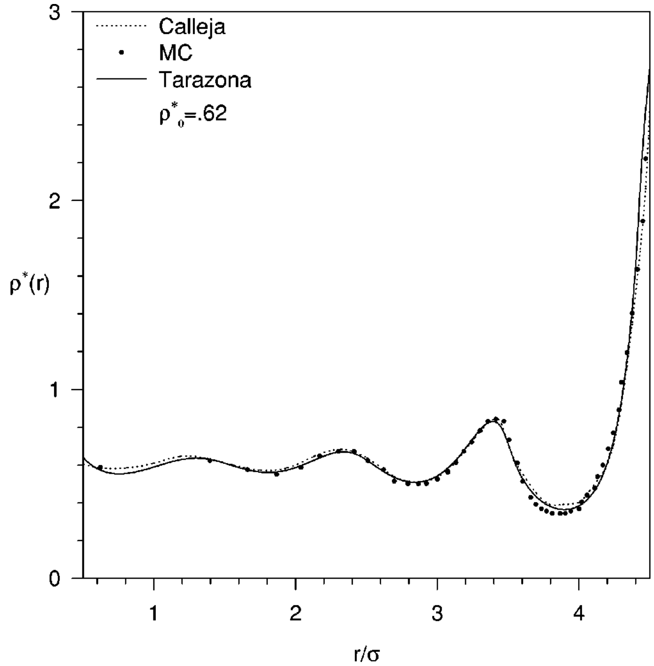

FIG. 3. The reduced density profile $\rho^*(\mathbf{r})=\rho(\mathbf{r})\sigma^3$ inside the cavity where the radius of the cavity is $R=5\sigma$ and $\rho_0^*=0.62$. The solid line corresponds to the Tarazona theory, the solid circles are taken from the Monte Carlo (MC) simulation, and the dashed line is taken from theory, both from Calleja *et al* [11].

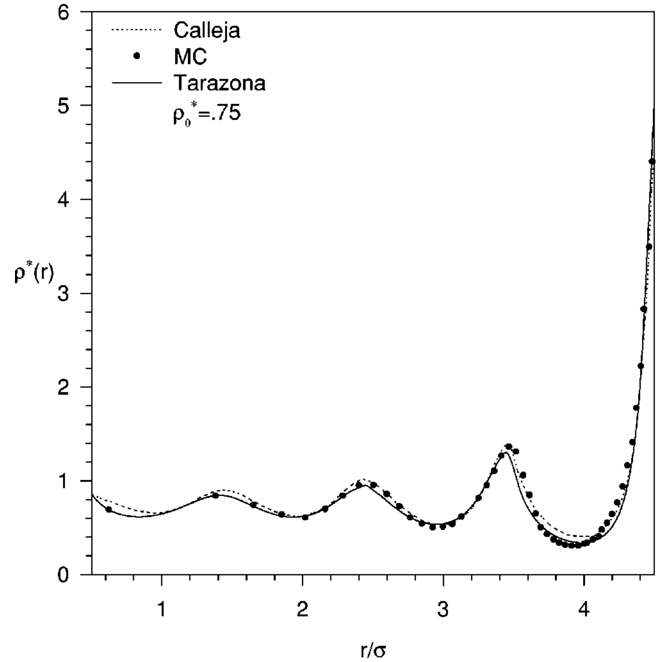

FIG. 4. Same as Fig. 3 except for $\rho_0^*=0.75$.

theory introduced by Tarazona works quite well for a variety of inhomogeneous hard sphere fluids. Of course, these calculations may be used for the hard sphere part of a fluid with interaction such as a charged hard sphere, a dipolar hard sphere, a hard sphere with Yukawa tail, a sticky hard sphere fluid, and others. Kim and Suh [24] have considered such fluids confined to a planar slit. They introduced a density functional perturbative approximation that is based on both the weighted density approximation for the hard sphere contribution and the density functional of Rickayzen and Augousti [1]. We plan to apply these calculations to inhomogeneous fluids with special spherical symmetries.

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