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Free-energy density functional for hard spheres

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A free-energy density functional for a system of hard spheres is derived on a semiempirical basis. It is constructed to reproduce the thermodynamics and direct correlation function of a homogeneous fluid and then is tested in two highly inhomogeneous situations: the hard-wall—hard-sphere interface and the hard-sphere solid. The results are very good in both cases, showing that this density-functional model may be used with advantage in the study of the hard-sphere model by itself, or used as a reference system in a perturbative analysis.

I. INTRODUCTION

Wertheim's solution[1] for the correlation functions of hard spheres in the Percus-Yevick approximation was a milestone in the theory of liquids. The results for this system were used as the starting point to develop and test perturbation theories[2,3] and more sophisticated integral equations[4] for realistic models. At the present, one could say that there is a satisfactory understanding of most of the thermodynamics and structure of homogeneous simple liquids. Perturbation theories were also applied to inhomogeneous systems[5,6] but the knowledge of the structure and thermodynamics of inhomogeneous systems of hard spheres was much poorer, and the only feasible treatment for the hard-sphere reference system was the local-density approximation. This approach gives reasonable results for the surface tension and density profile of the free-liquid—vapor interface, but in a wall-fluid surface there is a strong short-ranged structure which is lost if the reference system in the perturbative analysis is treated with a local-density approximation. The most successful approach to this problem was the wall-particle integral equations,[7–9] which usually give good results for the structure of the fluid near the wall, although they failed in some specific situations[10] due to the inconsistency in the thermodynamics of this treatment.[11] For the same reason the integral equations also failed to reproduce the exact relation between the density of fluid at contact with a hard wall and the pressure in the bulk fluid.[8]

It is much easier to include the correct thermodynamics of homogeneous systems in density-functional theories, where the intrinsic free energy is considered as a functional $\mathscr{F}[\rho(\mathbf{r})]$ of the particle distribution $\rho(\mathbf{r})$. The problem now is to design a model for $\mathscr{F}[\rho(\mathbf{r})]$ which gives good account of the main characteristics of the real system. Nearly all the attempts to devise a free-energy functional start from the local-density approximation and add some nonlocal corrections.[12,13] These treatments give good results for weakly structured density distributions, $\rho(\mathbf{r})$, as is the case for the liquid-vapor interface or for a fluid in a weak external field, but they are not applicable to a strongly structured $\rho(\mathbf{r})$, because if a local-density term is present it would lead to unphysical estimations of $\mathscr{F}[\rho]$. A different approach was suggested by Nordholm and co-workers,[14] who used a nonlocal entropy for the inhomogeneous hard-sphere fluid, in terms of the excluded volume and described as a generalized van der Waals theory. A similar free-energy functional, although with a somehow different justification, was used to study the problem of complete wetting of a hard wall by a gas[15] and to describe the crystallization of a liquid,[16] problems in which the short-ranged repulsion plays a crucial role. The results obtained there were promising, giving the correct qualitative behavior and even a fairly good quantitative estimation with a very simple prescription for $\mathscr{F}[\rho]$.

In this paper a free-energy density functional for hard spheres is developed on a semiempirical basis, following the preceding ideas and trying to get a quantitatively good description of a hard-sphere system in any possible situation and, 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. The requirements imposed are, first of all, to recover the well-established results for the thermodynamics of the homogeneous fluid; second, to describe the structure and thermodynamics of highly inhomogeneous systems; and finally, to be a consistent density functional, so that any exact functional relation can be applied and the theory can be used both in a variational procedure or through the exact minimum principle for the equilibrium density, given by the Euler-Lagrange equation

$$\frac{\delta \mathscr{F}[\rho]}{\delta \rho(\mathbf{r})}+V_{\text{ext}}(\mathbf{r})=\mu\ , \tag{1.1}$$

where $V_{\text{ext}}(\mathbf{r})$ is the external potential and μ the chemical potential.

II. THE FREE-ENERGY FUNCTIONAL

The simplest free-energy functional one can develop is the local-density approximation

$$\mathscr{F}_{\text{LD}}[\rho]=\int dr\,\rho(\mathbf{r})\psi(\rho(\mathbf{r}))\ , \tag{2.1}$$

where $\psi(\rho)$ is the free energy per particle in a homogeneous system with density ρ. The idea behind (2.1) is quite simple: A particle at $\mathbf{r}$ is supposed to be affected by only the particles around it, in a range given by the interaction; if the range of the interparticle interaction is much smaller than the typical length for variations in $\rho(\mathbf{r})$, the system can be divided in small pieces of nearly constant density and each one of these pieces can be treated as part of a homogeneous system. The function $\psi(\rho)$ used in (2.1) is easily obtained from the equation of state.

Unfortunately, the assumption of smooth variations of $\rho(\mathbf{r})$ in the range of the interactions is only valid for fluids in very weak external fields, like gravity, and in the absence of first-order phase transitions. To approach more interesting interfacial problems, one has to improve the local-density approximation by adding some nonlocal corrections. In this way one gets the square-gradient approximation[12] and more refined treatments like the Ebner and Saam free-energy functional.[13] However, this route is restricted to not-too-strong inhomogeneities because, if $\rho(\mathbf{r})$ reaches very high peak values, the use of any local treatment involves the evaluation of $\psi(\rho)$ for a very large ρ and the behavior of a *homogeneous* system with such large density would be dramatically different from the real system and may even by impossible to achieve, as is the case for hard spheres with a homogeneous density larger than the close-packing limit.

The alternative we have followed before,[15,16] in the spirit of the generalized van der Waals theory of Nordholm and co-workers,[14] is to introduce the nonlocality of the free-energy functional through a smoothed (or coarse-grained) density distribution $\bar{\rho}(\mathbf{r})$, which is at each point a nonlocal functional of $\rho(\mathbf{r})$. Any narrow peak in the real density distribution $\rho(\mathbf{r})$ will be smeared down in $\bar{\rho}(\mathbf{r})$, which can be imagined as the mean density around a particle in $\mathbf{r}$ in a volume somehow related with the range of the interactions. The free-energy functional is taken as

$$\mathscr{F}[\rho]=\mathscr{F}_{\mathrm{id}}[\rho]+\int d\mathbf{r}\,\rho(\mathbf{r})\Delta\psi(\bar{\rho}(\mathbf{r}))\;, \tag{2.2}$$

where

$$\mathscr{F}_{\mathrm{id}}[\rho]\equiv kT\int d\mathbf{r}\,\rho(\mathbf{r})\psi_{\mathrm{id}}(\rho(\mathbf{r})) \tag{2.3}$$

is the free-energy functional for an ideal gas, which is exactly given by the local-density treatment, and the interactions are treated through the excess from ideal-gas free energy per particle,

$$\Delta\psi(\rho)\equiv\psi(\rho)-\psi_{\mathrm{id}}(\rho)\;, \tag{2.4}$$

taken locally in the smoothed $\bar{\rho}(\mathbf{r})$, so that the dangers of a purely local treatment of a narrow peak in $\rho(\mathbf{r})$ are avoided.

To complete the prescription for $\mathscr{F}[\rho]$ in (2.2), one requires a criterion for constructing $\bar{\rho}(\mathbf{r})$ from $\rho(\mathbf{r})$. In previous attempts[15,16] we used the formula

$$\bar{\rho}(\mathbf{r})=\int d\mathbf{r}'\rho(\mathbf{r}')w(|\mathbf{r}-\mathbf{r}'|)\;, \tag{2.5}$$

$w(r)$ being a normalized weight function, independent of the density, which was chosen to give a sensible response function of the system from a homogeneous density distribution. This is equivalent to saying that the direct correlation function, derived from (2.2) as

$$c(\mathbf{r},\mathbf{r}')=-\frac{1}{k_BT}\frac{\delta(\mathscr{F}[\rho]-\mathscr{F}_{\mathrm{id}}[\rho])}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')} \tag{2.6}$$

and evaluated for a homogeneous density $\rho(\mathbf{r})=\rho_0$, has to be in reasonable agreement with the established theories for the structure of bulk liquids.

In the case of hard spheres this reasoning leads to the simplest choice for $w(r)$ as a step function:

$$w(r)=\begin{cases}\dfrac{3}{4\pi}\sigma^{-3}, & r\le\sigma\\ 0, & r>\sigma\end{cases} \tag{2.7}$$

where σ is the hard-sphere diameter. This choice reproduces through (2.6) the discontinuity in $c(r)$ at $r=\sigma$, predicted by the Percus-Yevick approximation, but it overestimates the range of $c(r)$, especially at high density, by adding a negative tail for $\sigma<r<2\sigma$.

The use of the functional (2.2), with (2.5) and (2.7), for very inhomogeneous systems like the hard-wall—hard-sphere interface[15] and the hard-sphere solid[16] leads to qualitatively correct results, but the overestimation in the range of $w(r)$ produces too large a separation between layers of fluid close to the wall in the first case, and between the lattice positions in the second, giving a lower mean density for the fluid phase than that observed in computer simulations.[17]

If the prescription (2.7) for $w(r)$ is substituted by

$$w(r)=\begin{cases}\dfrac{3}{\pi}(r-\sigma)\sigma^{-4}, & r\le\sigma\\ 0, & r>\sigma\end{cases}$$

the range of $c(r)$ seems to be underestimated and the mean density of the hard-sphere solid at coexistence with the fluid is too large.

To reach a really good description of $c(r)$ we have to allow for a density-dependent weight function in (2.5). It would be easier to introduce the dependence on the smooth $\bar{\rho}(\mathbf{r})$, rather than in $\rho(\mathbf{r})$, so that we assume

$$\bar{\rho}(\mathbf{r})=\int d\mathbf{r}'\rho(\mathbf{r}')w(|\mathbf{r}-\mathbf{r}'|;\bar{\rho}(\mathbf{r}))\;, \tag{2.8}$$

which has to be considered as an integral equation used to define $\bar{\rho}(\mathbf{r})$ from $\rho(\mathbf{r})$.

The density dependence of the weight function introduces some new terms in the direct correlation function obtained from $\mathscr{F}[\rho]$ through (2.6). Beside those obtained with the simpler prescription of density-independent $w(r)$,[15] now we have from (2.2), evaluated for a homogeneous system with density ρ_0,

$$\begin{aligned}c(|\mathbf{r}-\mathbf{r}'|)=&-\frac{2\Delta\psi'(\rho_0)}{k_BT}\frac{\delta\bar{\rho}(\mathbf{r})}{\delta\rho(\mathbf{r}')}\bigg|_{\rho_0}\\&-\frac{\Delta\psi''(\rho_0)\rho_0}{k_BT}\int d\mathbf{r}''\frac{\delta\bar{\rho}(\mathbf{r}'')}{\delta\rho(\mathbf{r})}\bigg|_{\rho_0}\frac{\delta\bar{\rho}(\mathbf{r}'')}{\delta\rho(\mathbf{r}')}\bigg|_{\rho_0}\\&-\frac{\Delta\psi'(\rho_0)}{k_BT}\rho_0\int d\mathbf{r}''\frac{\delta^2\bar{\rho}(\mathbf{r}'')}{\delta\rho(\mathbf{r}')\delta\rho(\mathbf{r}'')}\;,\end{aligned} \tag{2.9}$$

$\Delta\psi'(\rho_0)$ and $\Delta\psi''(\rho_0)$ being the first and second derivatives of $\Delta\psi(\rho_0)$. The functional derivatives of $\bar{\rho}(\mathbf{r})$ with respect to $\rho(\mathbf{r}')$ are easily obtained from (2.8) as

$$\left.\frac{\delta\bar{\rho}(\mathbf{r})}{\delta\rho(\mathbf{r}')}\right|_{\rho_0}=w(\,|\,\mathbf{r}-\mathbf{r}'\,|\,,\rho_0) \tag{2.10}$$

and

$$\left.\frac{\delta^2\bar{\rho}(\mathbf{r}'')}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')}\right|_{\rho_0}=w'(\,|\,\mathbf{r}''-\mathbf{r}\,|\,,\rho_0)w(\,|\,\mathbf{r}''-\mathbf{r}'\,|\,,\rho_0)+w'(\,|\,\mathbf{r}''-\mathbf{r}'\,|\,,\rho_0)w(\,|\,\mathbf{r}''-\mathbf{r}\,|\,,\rho_0)\;, \tag{2.11}$$

where $w'(r,\rho)$ is the derivative of $w(r,\rho)$ with respect to ρ. In the earlier theory,[15] with a weight function independent of ρ, the last term in (2.9) vanishes and $c(r)$ is given in terms of $w(r)$ and its self-convolution. Now, a new term appears with the convolution of $w(r,\rho)$ with its derivative with respect to ρ.

The first step to determine the function $w(r,\rho)$ is to assume that it has an analytic dependence on the density and to expand it in a power series

$$w(r,\rho)=w_0(r)+w_1(r)\rho+w_2(r)\rho^2+\cdots\;, \tag{2.12}$$

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

$$\int w(r,\rho)d\mathbf{r}=1\;, \tag{2.13}$$

implies that $w_0(r)$ is normalized and all the higher-order terms have zero integral

$$\int w_i(r)dr=\begin{cases}1, & i=0\\ 0, & i=1,2,\ldots\,.\end{cases} \tag{2.14}$$

By introducing (2.12) in (2.9) together with the virial expansion of $\Delta\psi(\rho)$ one gets the powers of density series for $c(r)$ in this theory, which can be compared with the results obtained in the cluster expansion.[4] Term by term, equalities will provide information on the coefficients in (2.12). Thus, from the zero-order term we get

$$w_0(r)=\frac{3}{4\pi\sigma^3}\Theta(\sigma-r)\;, \tag{2.15}$$

$\Theta(x)$ being the Heaviside step function. This exact expression for $w_0(r)$ is the simple step weight (2.7) used in Ref. 15, so that our earlier theory corresponds to the zero-order term in the density expansion of $w(r,\rho)$.

The equivalence between the first-order terms in (2.9) and in the virial expansion of $c(r)$ for hard spheres gives the following equation:

$$20w_0(r)+8w_1(r)+10\int d\mathbf{r}'w_0(r)w_0(r+r')+8\int d\mathbf{r}'w_0(r')w_1(r+r')=\frac{6}{\pi}\left[8-6\frac{r}{\sigma}+\tfrac{1}{2}\left[\frac{r}{\sigma}\right]^3\right]\Theta(\sigma-r)\;, \tag{2.16}$$

$w_0(r)$ being known from the zero-order term, (2.15). This is an integral equation for $w_1(r)$ which can be easily solved numerically by Fourier transforms, to factorize the convolution between $w_0(r)$ and $w_1(r)$. The result for this exact first-order term in (2.12) is shown in Fig. 1; it is nearly linear for $r<\sigma$ and has an oscillating tail for $r>\sigma$ which decays exponentially. A polynomial approximation is given in the Appendix.

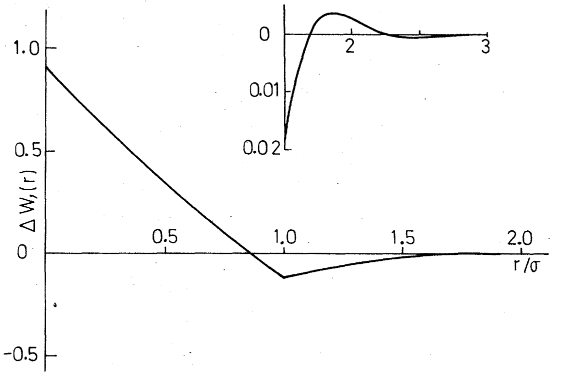

FIG. 1. The first-order weight function as described in Eq. (2.16). The inset shows the oscillating structure of the tail.

In principle this process could be carried on for higher-order terms, getting each time an integral equation for $w_i(r)$ involving the preceding functions $w_j(r)$, for $j<i$, and the i-order term in the virial expansion for the exact direct correlation function. The process would also require the exact virial expansion of $\Delta\psi(\rho)$, which can be easily obtained from the well-known series for the pressure of the hard-sphere fluid,

$$\left.\frac{\Delta\psi(\rho)}{k_BT}\right|_{\text{exact}}=4\eta+5\eta^2+\frac{3673}{600}n^3+\frac{353}{50}\eta^4+\cdots=4\eta+5\eta^2+6.121\,666\eta^3+7.06\eta^4+\cdots\;, \tag{2.17}$$

where $\eta=\pi\sigma^3\rho/6$ is the volume fraction. However, if we want to use in (2.2) the free energy per particle derived from the quasiexact Carnaham-Starling (CS) equation of state,

$$\left.\frac{\Delta\psi(\rho)}{k_BT}\right|_{\text{CS}}=\frac{2}{(1-\eta)}+\frac{1}{(1-\eta)^2}-3\;, \tag{2.18}$$

we find that its series expansion,

$$\left.\frac{\Delta\psi(\rho)}{k_BT}\right|_{\text{CS}}=4\eta+5\eta^2+6\eta^3+7\eta^4+\cdots\;, \tag{2.19}$$

agrees with the exact (2.17) only for the first two terms, being the next integer approximation for the others. We should note here that the volume integral of $c(\mathbf{r})$ in this theory is completely determined by the function $\Delta\psi(\rho)$, through the compressibility rule

$$\int c(\mathbf{r})d\mathbf{r}=-\frac{1}{k_BT}\,|\,2\Delta\psi'(\rho_0)+\Delta\psi''(\rho)\rho\,|=-\frac{1}{\rho k_BT}\frac{d(p-p_{\text{id}})}{d\rho}\;, \tag{2.20}$$

as is easily obtained from (2.9)—(2.11) by using the normalization of $w(r,\rho)$, (2.13). That means that the use of the Carnaham-Starling equation of state to fix $\Delta\psi(\rho)$ as in (2.18) will be inconsistent with the exact virial expansion for $c(r)$ for order higher than 1 and that invalidates the term-by-term identification used to get $w_i(r)$, for $i \geq 2$. On the other hand, we know that the difference between (2.18) and (2.17) is small for all the known terms in (2.17) and, in fact, for high values of the density the compact formula (2.18) is much better than any truncated series expansion with the exact coefficients, as implied by the adjective "quasiexact" usually applied to Carnaham-Starling equations of state. We thus advice keeping $\Delta\psi(\rho)$ as given in (2.18), even if that means that we cannot get the exact $w_i(r)$ for $i \geq 2$. In fact, the weight function $w(r,\rho)$ has only to establish the "shape" of the function $c(r)$, because the overall scale, which contains the most important part of the dependence on the density, is determined by $\Delta\psi(\rho)$, through (2.20). Then we can expect that using a good description of $\Delta\psi(\rho)$, the expansion of $w(r,\rho)$ in powers of ρ, (2.12) may be truncated with only a few terms.

In the earlier theory[15] the series (2.12) was effectively truncated at the zero-order term. The results for $c(r)$ in a homogeneous system were in reasonable agreement with Percus-Yevick theory for $\rho \lesssim 0.2\sigma^{-3}$ but became much worse for larger density. If the exact first-order term is included, the results improve, but there are still serious discrepancies at $\rho \gtrsim 0.6$ (see Fig. 2). The higher-order terms cannot be exactly evaluated as explained above, and the alternative used here is to truncate the expansion (2.12) at the second-order term and find an empirical form for $w_2(r)$ to get a good description of $c(r)$ in all the range of fluid density.

The best result was obtained with

$$w_2(r) = \frac{5}{4\pi}\left[6 - 12\frac{r}{\sigma} + 5\left[\frac{r}{\sigma}\right]^2\right]\Theta(\sigma - r)\ , \qquad (2.21)$$

and the results for the direct correlation function can be seen in Fig. 2. They compare very well with the Percus-Yevick approximation up to $\rho = 0.8\sigma^{-3}$ and present slight differences at higher densities, where the Percus-Yevick result also starts deviating from the exact values.

To summarize this section, we have constructed a free-energy functional for hard spheres, which gives the correct thermodynamics of a homogeneous system, by using the functional form (2.2) and the quasiexact $\Delta\psi(\rho)$, (2.18). It also gives the nearly correct response function of the homogeneous phase to an external field, as implied by having a good direct correlation function and hence a good structure factor.

This is obtained by using a "smoothed" profile, $\bar{\rho}(\mathbf{r})$, defined through (2.8) with the weight function

$$w(r,\rho) = w_0(r) + w_1(r)\rho + w_2(r)\rho^2\ , \qquad (2.22)$$

where $w_0(r)$ is given in (2.15), $w_1(r)$ is exactly defined through (2.16) and can be taken as (A3) and (A4), and $\rho_2(r)$ is empirically taken as (2.21).

Now we expect that this functional can be successfully used to determine the structure and thermodynamics of very inhomogeneous systems. At least it has not the strong disadvantages of any purely local-density treatment to evaluate the free energy of a narrow and high peak in $\rho(\mathbf{r})$. In Secs. III and IV this free-energy functional is used to describe two of the most important inhomogeneous systems with hard spheres: the interface with a hard wall and the hard-sphere solid.

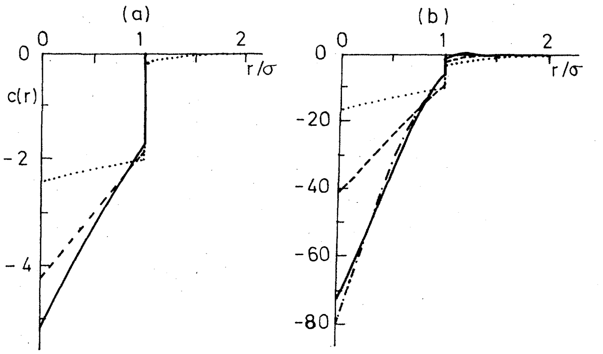

FIG. 2. The direct correlation function for two values of the density: (a) $\rho = 0.4\sigma^{-3}$ and (b) $\rho = 0.8\sigma^{-3}$. The solid line is the present theory to second-order expansion of $w(r,\rho)$ with respect to ρ. The dotted and dashed lines are the zero- and first-order expansions, respectively. The dot-dashed line is the Percus-Yevick approximation, which for the lower density is indistinguishable from the present theory.

III. THE HARD-WALL–HARD-SPHERE INTERFACE

This is one of the most interesting problems concerning inhomogeneous distributions of hard spheres. Quite different approaches have been used[7–9] and all of them give good results for low bulk density. However, as the density increases, the layering structure of the fluid near the wall becomes stronger and the discrepancies between the theory and the computer simulations grow fast. The wall-particle Percus-Yevick and hypernetted-chain approximations[8,9] do not satisfy the well-known exact rule relating the fluid density at contact, $\rho(0)$, with the bulk pressure, P_0, as

$$\rho(0) = \frac{P_0}{k_B T}\ . \qquad (3.1)$$

This failure of the integral equations is due to their lack of thermodynamical consistency.

The use of the Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY) hierarchy with a superposition approximation closure[18] gives exact results for the density at contact but overestimates the propagation of the layering structure into the bulk fluid. The scaled particle theory can be used to evaluate the surface tension of the hard-wall—hard-sphere interface[19] and the result has a good agreement with recent computer simulations.[20] However, this approach cannot be used to calculate the structure of the fluid near the wall.

To study this problem with the free-energy functional described above, we use the minimization principle, through the Euler-Lagrange equation (1.1), with the external field

$$V_{\text{ext}}(z) = \begin{cases} \infty, & z < 0 \\ 0, & z > 0 \end{cases} \qquad (3.2)$$

which imposes $\rho(z)=0$ for $z<0$.

The first functional derivative of $\mathscr{F}[\rho]$ in (2.2) is

$$\frac{\delta\mathscr{F}}{\delta\rho(\mathbf{r})}=\mu_{\text{id}}(\rho(\mathbf{r}))+\Delta\psi(\bar{\rho}(\mathbf{r}))+\int d\mathbf{r}'\rho(\mathbf{r}')\Delta\psi'(\bar{\rho}(\mathbf{r}'))\frac{\delta\bar{\rho}(\mathbf{r}')}{\delta\rho(\mathbf{r})}\ , \tag{3.3}$$

where $\mu_{\text{id}}(\rho)$ is the ideal-gas chemical potential. The coarse-grained density profile $\bar{\rho}(\mathbf{r})$ has to be evaluated from $\rho(\mathbf{r})$ through the integral equation (2.8), but the choice made for the weight function (2.22) simplifies that, allowing us to rewrite (2.8) as

$$\bar{\rho}(\mathbf{r})=\bar{\rho}_0(\mathbf{r})+\bar{\rho}_1(\mathbf{r})\bar{\rho}(\mathbf{r})+\bar{\rho}_2(\mathbf{r})(\bar{\rho}(\mathbf{r}))^2\ , \tag{3.4}$$

where

$$\bar{\rho}_i(\mathbf{r})=\int d\mathbf{r}'\rho(\mathbf{r}')w_i(\,|\mathbf{r}-\mathbf{r}'\,|\,) \tag{3.5}$$

for $i=0,1,2$, which are the smoothed profiles evaluated with the density-independent weights $w_i(r)$. In this way Eq. (2.8) reduces to a second-degree algebraic equation for $\bar{\rho}(\mathbf{r})$, with the dependence on $\rho(\mathbf{r})$ through the coefficients (3.5).

In the bulk fluid, $\rho(\mathbf{r})$ goes to a constant value, $\rho(\mathbf{r})=\rho_0$, and because of the normalization conditions (2.14), we have

$$\begin{aligned}&\bar{\rho}_0=\rho_0\ ,\\&\bar{\rho}_1=\bar{\rho}_2=0\ ,\end{aligned} \tag{3.6}$$

and this limit allows us to identify the root of (3.4) with physical sense, as

$$\bar{\rho}(\mathbf{r})=\frac{[1-\bar{\rho}_1(\mathbf{r})]-[\,|1-\bar{\rho}_1(\mathbf{r})|^2-4\bar{\rho}_0(\mathbf{r})\bar{\rho}_2(\mathbf{r})]^{1/2}}{2\bar{\rho}_2(\mathbf{r})}=\frac{2\bar{\rho}_0(\mathbf{r})}{[1-\bar{\rho}_1(\mathbf{r})]+[\,|1-\bar{\rho}_1(\mathbf{r})|^2-4\bar{\rho}_0(\mathbf{r})\bar{\rho}_2(\mathbf{r})]^{1/2})} \tag{3.7}$$

where the last form is more convenient for numerical calculations when $\bar{\rho}_1(\mathbf{r})$ and $\bar{\rho}_2(\mathbf{r})$ approach zero.

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

$$\frac{\delta\bar{\rho}(\mathbf{r})}{\delta\rho(\mathbf{r}')}=\frac{w(\,|\mathbf{r}-\mathbf{r}'\,|,\bar{\rho}(\mathbf{r}))}{1-\bar{\rho}_1(r)-2\bar{\rho}_2(\mathbf{r})\bar{\rho}(\mathbf{r})}\ , \tag{3.8}$$

which in the bulk fluid reduces to (2.10).

With (3.3), (3.7), and (3.8), the Euler-Lagrange equation for the equilibrium profile is

$$\mu_{\text{id}}[\rho(z)]+\Delta\psi(\bar{\rho}(z))+\int_0^\infty dz'\rho(z')\Delta\psi'(\bar{\rho}(z'))\times\frac{W(\,|z-z'\,|,\bar{\rho}(z'))}{1-\bar{\rho}_1(z')-2\bar{\rho}_2(z')\bar{\rho}(z')}=\mu\ , \tag{3.9}$$

where we have made explicit that $\rho(\mathbf{r})$ does only depend on the coordinate z, normal to the wall, fixed at $z=0$, and

$$W(z,\rho_0)\equiv\int d\mathbf{R}\,w((R^2+z^2)^{1/2},\rho_0) \tag{3.10}$$

is the weight function integrated over the transverse coordinates. Equation (3.9) can be rearranged for numerical solution as

$$\rho(z)=\rho_0\exp\left[-\frac{1}{k_BT}\left[\Delta\psi(\bar{\rho}(z))+\int_0^\infty dz'\rho(z')\Delta\psi'(\bar{\rho}(z'))\frac{W(\,|z-z'\,|,\bar{\rho}(z'))}{1-\bar{\rho}_1(z')-2\bar{\rho}_2(z')\bar{\rho}(z')}-\Delta\psi(\rho_0)-\rho_0\Delta\psi'(\rho_0)\right]\right]\ , \tag{3.11}$$

ρ_0 being the bulk density. This equation can be solved by iterations, by putting in the right-hand side of the old profile and getting the new one in the left-hand side.

The iteration process is not very efficient, especially at high bulk density, and if the full new profile obtained from (3.11) is used in the next iteration the process usually diverges in a few steps. To avoid that, I used a mixing scheme between the results of an iteration, $\rho_{\text{out}}^{(i)}(z)$, and its initial guess, $\rho_{\text{in}}^{(i)}(z)$, to get the next-step initial guess as

$$\rho_{\text{in}}^{(i+1)}(z)=\rho_{\text{out}}^{(i)}(z)f(z)+\rho_{\text{in}}^{(i)}(z)[1-f(z)]\ , \tag{3.12}$$

with a careful choice of the mixing function $f(z)$ to avoid the divergence. The function $f(z)$ was fixed by trial and error, and sometimes it has to be as small as 0.01; in this case the process requires several hundred iterations before reaching convergence.

At the same time the iterations of (3.11) were performed, I evaluated the surface tension of each configuration as the excess of grand potential energy over the bulk fluid extended to the wall,

$$\gamma=\int_0^\infty dz\{\rho(z)[\psi_{\text{id}}(\rho(z))+\Delta\psi(\bar{\rho}(z))-\mu]+p\}\ , \tag{3.13}$$

which has to be minimum for the equilibrium profile so that its evaluation at each step provides a different way to check the convergence of the process; successive iterations have to give decreasing values for γ, and only when it stabilizes has the equilibrium value been reached.

The density profile was evaluated for three different bulk densities, $\rho_0\sigma^3=0.57$, 0.755, and 0.81, for which computer-simulation results exist[21] and have been used before checking other theories.[14,15] The results are shown in Fig. 3, compared with the simulation and with the BBGKY results. The present theory gives a fair agreement with the simulations and the values for the density at the wall satisfy the relation (3.1), as a signature of being a consistent functional theory with the correct thermodynamics; the agreement in the position and value of the next minimum and maximum are in much better agreement with the earlier theory[16] with the density-independent weight function. The only systematic difference which can be appreciated is the position of the peak in $\rho(z)$ around $z=\sigma$, which in the simulation is closer to the wall than in the present calculation. That suggests the presence of a transverse ordering which couples successive

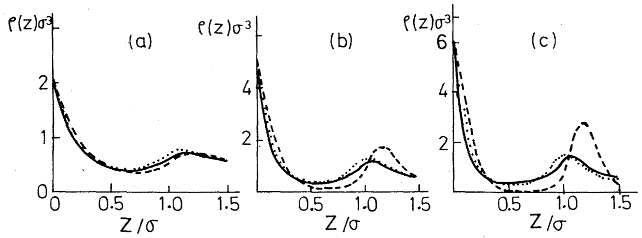

FIG. 3. Density profiles for the hard-sphere fluid against a hard wall. The bulk density is (a) $0.57\sigma^{-3}$, (b) $0.755\sigma^{-3}$, and (c) $0.81\sigma^{-3}$. The dots are the simulation results (Ref. 17). The solid line is the present theory and the dashed line is the result in BBGKY, as in Ref. 18 recalculated for these bulk densities.

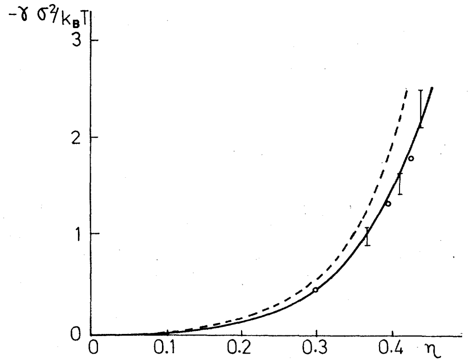

FIG. 4. Surface tension of the hard-wall—hard-sphere interface. The circles are the results of the present theory corresponding to the density profiles in Fig. 3. The solid line is the scaled particle result (Ref. 19), the dashed line is the Kirkwood-Buff formula with the BBGKY density profiles (Ref. 18), and the bars are the estimations from the computer simulation (Ref. 20).

layers allowing them to get closer. This effect is not considered in this calculation because in (3.9) and (3.11) I have imposed the complete homogeneity in the (x,y) plane. Nevertheless, that effect can be considered in this functional theory by exploring density distributions with transverse order.

Despite this problem, the present results still can be favorably compared with other theories, especially at high bulk density. The generalized mean spherical approximation (GMSA) result reported by Waisman *et al.*[22] for $\rho_B=0.609$ is in even better agreement with computer simulations, but I am not aware of any calculation for higher ρ_B. A further advantage of the present theory is that it gives in a perfectly consistent way the surface tension of the interface. The results for γ corresponding to the three systems are shown in Fig. 4, compared with a recent computer simulation,[20] with the Kirkwood-Buff formula applied to the superposition approximation profile[18] and with the scaled particle theory.[19] The agreement of the present results with the latter and with the simulation is quite good, indicating that the free-energy functional described in this paper gives not only the right position for the minimum of the grand potential energy in the density-functional space, but also gives the correct value for the free energy at the minimum.

IV. THE HARD-SPHERE SOLID

In an earlier paper[16] the simpler functional model, with the density-independent weight function, was used to describe the solid of hard spheres and to find the density of the solid and fluid coexisting phases. The same is done here with the more refined theory to check how it behaves when used to describe such an extremely inhomogeneous density distribution.

The process followed here is completely equivalent to the one followed before.[16] The density distribution is parametrized in terms of normalized Gaussian peaks at each lattice site

$$\rho(\mathbf{r})=\left[\frac{\alpha}{\pi}\right]^{3/2}\sum_{\substack{\mathbf{R}\\ \text{fcc lattice}}} e^{-\alpha(\mathbf{r}-\mathbf{R})^2}\,, \tag{4.1}$$

where the lattice constant is fixed by the mean density in the crystal and the only free parameter is the decay constant α, which gives the fluid phase in the limit $\alpha\to 0$. If the free energy, for fixed mean density, has a minimum at $\alpha\neq 0$ it will represent a stable or metastable solid structure. In fact, if one observes these structures for any mean density larger than some value around $0.9\sigma^{-3}$, it becomes the stable structure at high mean density, with preference to the disordered fluid. The values for the solid and fluid densities which can coexist is given by the usual double tangent construction.

The results are presented in Table I and compared with the earlier theory,[16] with computer simulations,[17] and with Haymet's results[23] in a refined version of Ramakrishnan-Yussouff theory,[24] based on an expansion of $\mathscr{F}[\rho]$ around the homogeneous density of the fluid at coexistence with the solid (see *Note added in proof.*) It can be observed that the present functional model gives an important improvement with respect to the earlier results and puts the theory in fairly good agreement with the

TABLE I. Coexisting fluid and solid densities for hard spheres.

	ρ_F	ρ_S	ρ_S-ρ_F
Present theory	0.9433	1.0609	0.1176
Zero-order theory, Ref. 16	0.8917	0.9662	0.0745
Haymet's theory, Ref. 23	0.976	1.035	0.059
Computer simulation, Ref. 27	0.939—0.948	1.036—1.045	0.106—0.088

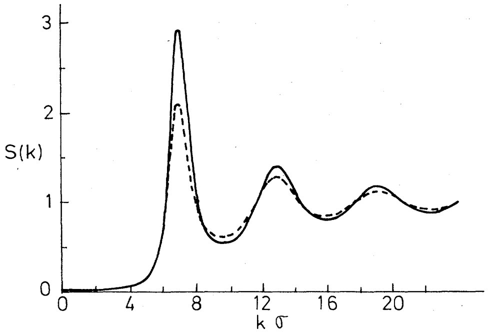

FIG. 5. Structure factor for the hard-sphere fluid at the crystallizing density, $\rho_b = 0.943\,28\sigma^{-3}$, in the present theory (solid line) compared with the Percus-Yevick result for the same density. The first peak in $S(k)$ is about 3, in good agreement with the Hansen-Verlet rule.

computer simulations. Probably the agreement would be even better if a more sophisticated description of the solid structure were used, instead of the single parameter formula (4.1). That indicates that the free-energy functional described here is quite appropriate to describe a very inhomogeneous situation, with peak values of $\rho(\mathbf{r})$ one hundred times larger than the complete packing mean density.

As a final test, I have calculated the structure factor of the fluid at the coexisting density, $\rho_F = 0.943\,28\sigma^{-3}$, and it is shown in Fig. 5, in comparison with Percus-Yevick theory for the same density. At lower density the agreement between the two theories would be much better, as a direct consequence of the good agreement presented between the respective $c(r)$, as shown in Fig. 2, but at higher density the structure in $S(k)$ becomes much stronger in the present theory than in the Percus-Yevick approximation; and at the crystallization density the first peak in $S(k)$ reaches a value just below 3, in perfect agreement with the empirical rule established by Hansen and Verlet,[25] while the Percus-Yevick approximation gives a much lower value. This is proof of the consistency of this functional model, which recovers any relationship between different magnitudes which may be proven on general grounds, as is the case with the Hansen-Verlet rule (see Baus[26]).

V. DISCUSSION

The free-energy functional model presented here can be used with advantage over any existing theory to describe an inhomogeneous system of hard spheres. First of all, for uniform density distributions it gives, by construction, the correct thermodynamics and a very good description of the structure. It also gives a very good location of the solid-fluid phase transition, which implies a good description of the hard-sphere crystal. The results for the hard-wall—hard-sphere interface are, especially at high bulk density, the best—to my knowledge—both for the density profile $\rho(z)$ and the surface tension.

All these results, referred to very different physical situations, are obtained with the same, relatively simple formula for $\mathcal{F}[\rho]$, which is perfectly consistent as a free-energy functional, and as such reproduces all the exact relations, such as Eq. (3.1), which can be derived in a general density-functional formalism.

This free-energy functional can also be used to describe the reference system in a perturbative analysis, as was shown with the earlier version,[16] and it provides in that case the first theory able to describe the full solid-liquid-vapor phase diagram.

The functional model can be used in a variational procedure, by minimizing the grand potential energy with respect to a set of parameters used to describe the density distribution or by solving the integral equation for $\rho(\mathbf{r})$ given by the Euler-Lagrange minimum principle (1.1). Both of these routes can be used for the pure hard-sphere fluid or together with any perturbative contribution from the attractive interactions, in more realistic models.

Note added in proof. A recent work by G. L. Jones and U. Mohanty (unpublished) gives an important improvement from Ref. 23 by allowing a density of vacancies in the solid and using it as a variational parameter.

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APPENDIX

The integral equation (2.16) for the first-order weight function is easily solved by Fourier transforms:

$$w_1(q) = \frac{f(q) + 20w_0(q) + 10[w_0(q)]^2}{8[1 + w_0(q)]}, \tag{A1}$$

where $w_0(q)$ is the Fourier transform of the zero-order weight (2.15) and

$$f(q) = \frac{24}{q}\left[\left[\frac{2}{q^2} + \frac{12}{q^4}\right]\sin q + \left[\frac{5}{2q} + \frac{6}{q^3} + \frac{12}{q^5}\right]\cos q - 12\left[\frac{1}{q^3} + \frac{1}{q^5}\right]\right]. \tag{A2}$$

The numerical inverse Fourier transform of $w_1(q)$ gives the function $w_1(r)$, shown in Fig. 1. For $r < \sigma$ the result is very well fitted by the second-degree polynomial

$$w_1(x) = a_0 + a_1 x + a_2 x^2, \quad x = r/\sigma \le 1 \tag{A3}$$

with

$$a_0 = 0.907\,24, \quad a_1 = -1.237\,17, \quad a_2 = 0.216\,16 .$$

The oscillating tail for larger r requires a more complex fitting:

$$w_1(x) = c e^{-\beta_1(x-1)} \sin[\alpha(x-1)] + e^{-\beta_2(x-1)}(b_0 + b_1 x + b_2 x^2 + b_3 x^3), \quad x = r/\sigma > 1 \tag{A4}$$

with

$$c=-0.10244,\quad b_0=35.134\ ,$$
$$\alpha=4.934,\quad b_1=-98.684\ ,$$
$$\beta_1=3.5621,\quad b_2=92.693\ ,$$
$$\beta_2=12,\quad b_3=-29.257\ .$$

For most numerical applications of this formalism the oscillating tail for $r>2\sigma$ has very little effect, so that $w(r)$ may be truncated at $r=2\sigma$ with a slight correction to ensure the normalization requirements (2.14).

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