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1997 J. Phys.: Condens. Matter 9 2375

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Density functional theory for hard-sphere fluids: a generating function approach

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Received 28 November 1996

Abstract. A new density functional for the inhomogeneous hard-sphere fluid is proposed which expresses the free-energy density in terms of a set of derivatives, with respect to the particle radius, of a simple generating function. The three-dimensional version of the theory is used to calculate density profiles for hard spheres near walls and to investigate the bulk fluid $g(r)$, via the test particle procedure. While the performance of the theory is generally poorer than that of a related theory, the fundamental-measure approach of Rosenfeld, it is better than that of approaches based on a single, density-independent weight function. Unlike earlier approaches, the theory is remarkably successful at describing situations where the effective dimensionality \mathcal{D} is reduced below three. More specifically the three-dimensional functional yields rather accurate equations of state in the $\mathcal{D} = 1$ and $\mathcal{D} = 2$ limits and is exact for the $\mathcal{D} = 0$ limit (a cavity that cannot hold more than one particle). The strict one-dimensional version of the theory yields the exact free-energy functional for hard rods whilst the free-energy functional for $\mathcal{D} = 2$ is equivalent to that obtained from the fundamental-measure approach. The extension of the theory to hard-sphere mixtures is also described.

1. Introduction

The study of the equilibrium structure and thermodynamic properties of non-uniform fluids has become a field of growing interest and evolution. A spatially varying average one-particle density $\rho(r)$, characteristic of a non-uniform fluid, may appear in many situations. These can be associated with an external inhomogeneity such as occurs in adsorption and wetting at substrate–fluid interfaces or in confined fluids [1–3]. Another example is the interface between two coexisting bulk phases (liquid–vapour and liquid–liquid interface [4]). A bulk solid may also be regarded as a highly inhomogeneous (symmetry-broken) fluid (freezing) [5].

The reference model for classical fluids is the hard-sphere liquid in \mathcal{D} dimensions since it provides an excellent testing ground for any theory of the liquid state. This model is also of practical importance because it can be considered as a zeroth-order approximation in the statistical thermodynamics of an extensive variety of more realistic physical systems with *soft* repulsive cores and attractive interactions, both of which can often be handled perturbatively (e.g., Lennard-Jones fluids) or using more specific approximations (as in studies of molten salts or liquid metals).

The introduction of density functional theories (DFT) of non-uniform hard-sphere fluids is responsible for an appreciable part of the progress experienced in this field [1, 2, 4, 6–11]. The key aspect of a DFT is that the free energy of the fluid can be expressed

as a unique functional of the density $\rho(\mathbf{r})$. Once an explicit form for this functional is given, all of the thermodynamic quantities of interest can be easily obtained. Moreover, successive functional differentiation of the free-energy functional allows one to calculate the distribution functions which describe the microscopic structure of the fluid. One of the most important refinements in these theories has been the development of non-local free-energy density functionals for hard spheres [1, 2, 6–11], in which a coarse-grained or smoothed density is introduced in order to *smooth* the local density, which can exhibit very pronounced peaks in highly inhomogeneous situations such as adsorption of hard spheres at a wall. The resulting smoothed density can then be used in a local free-energy function.

Among the large variety of theories based on a coarse-grained density, perhaps the most successful one is the approximation derived by Rosenfeld [10, 12, 13], specifically designed for hard-sphere mixtures, and based on geometric considerations. In this theory one assumes that the excess free-energy density of the inhomogeneous fluid is a function of a set of six weighted densities: the system-averaged *fundamental geometric measures* of the particles [10, 12, 13], whose weights are functions characteristic of the geometry of the particles. This description is intimately related to the scaled-particle theory (SPT) [14, 15] for the homogeneous hard-sphere fluid, and thus one expects that in the uniform limit it should reproduce the SPT results; in fact, in that limit one recovers not only the SPT equation of state but also the Percus–Yevick (PY) (see, e.g., reference [16]) pair direct correlation function (DCF) $c^{(2)}(r)$ [10, 13]. (Note that for the uniform hard-sphere fluid in three dimensions, PY theory and SPT are equivalent theories.) This DFT has a number of advantages over other theories. First, by construction it is well suited for mixtures. Second, it gives excellent results for several different types of inhomogeneity. Third, it is easy to implement from a computational point of view. And fourth, it permits ready calculation of higher-order DCFs by functional differentiation of the excess free energy, and in particular, the triplet DCF of the uniform hard-sphere fluid is in good agreement with Monte Carlo simulations. Perhaps the most important drawback of this theory is its unsuitability for describing the freezing transition or the adsorption of liquids at strongly attractive walls, situations for which the oscillatory density profile becomes extremely peaked. The reason for its failure to describe the solid phase has been attributed to its failure to describe properly the zero-dimensional (0D) limit of a cavity that cannot hold more than one particle, and a modification has been proposed [17] which imposes the correct limiting behaviour and which does provide an accurate description of the hard-sphere freezing transition.

Based on the ideas of Rosenfeld, Kierlik and Rosinberg (KR) [11] introduced a seemingly different DFT in which they postulated a free-energy density in terms of a set of weighted densities. They assumed the functional form of the PY free-energy density (whereas in the Rosenfeld case this functional form is derived from the theory) and obtained the weight functions by fitting the uniform fluid pair DCF to the PY result. Although the two theories have different weight functions the equivalence between the Rosenfeld and the KR theories is now established [18].

In the present paper we propose a new DFT, which has its origins in the theories of Rosenfeld, and Kierlik and Rosinberg but which contains ingredients of SPT and free-volume theory. We present an approximation for the free energy of an inhomogeneous hard-sphere fluid in terms of derivatives with respect to the particle radius R of a function $G(\nu(\mathbf{r}, R))$ which depends on a single weighted density $\nu(\mathbf{r}, R)$ determined by a density-independent weight function. In one dimension, $\mathcal{D} = 1$, the theory, like that of Rosenfeld, yields the exact (Percus [19]) free-energy functional for hard rods while for $\mathcal{D} = 2$ it is equivalent to Rosenfeld's result for the $\mathcal{D} = 2$ hard-disk functional [10, 12, 13]. For $\mathcal{D} = 3$ the new functional, although not as accurate for density profiles and bulk correlations as the KR and

Rosenfeld functionals, performs better than earlier weighted-density approximations based on a single, density-independent weight function [2]. We show that when the approximate three-dimensional functional is applied in limiting cases of extreme inhomogeneity the free energy is given rather accurately for a wide range of packing fractions. In particular, our functional yields the exact 0D limit, results close to the exact free energy in the $\mathcal{D} = 1$ limit, and results comparable with those of Rosenfeld or KR in the $\mathcal{D} = 2$ limit. Thus, we argue that it should be well suited to tackling problems of extreme confinement, e.g. very narrow pores, small cavities or quasi-two-dimensional adsorbed layers where the effective dimensionality of the fluid is reduced below that of the bulk.

The paper is organized as follows. In section 2 we present the general structure of the theory. We start with a summary of the theories of Rosenfeld and KR. The present theory is then derived for the one-component three-dimensional hard-sphere fluid. Two different free-energy density functionals are obtained, one based on the PY theory and the other based on the Carnahan–Starling result for the free energy of the homogeneous hard-sphere fluid. In order to analyse the nature of this DFT, the pair DCF for the homogeneous fluid is derived and compared with the PY pair DCF. In section 3 several applications are considered and results are compared with those of Rosenfeld and KR. More explicitly, we address various cases of density profiles (adsorption) at walls, and we study the pair correlation function $g(r)$ of the homogeneous fluid obtained via the test particle method. Finally we obtain the zero-, one- and two-dimensional limits of the three-dimensional theory and compare the results for the free energy with other treatments. In section 4 the strict one- and two-dimensional versions of the theory are presented. We conclude with a brief summary of the results and their implications for DFT. In the appendix we extend the theory to mixtures of hard spheres.

2. Theory

Since this new DFT relies heavily on the Rosenfeld or KR theories, we begin with a brief account of these theories. More details can be found in the original papers [10, 11].

2.1. The theories of Rosenfeld and of Kierlik and Rosinberg

In both theories the excess contribution $\mathcal{F}_{ex}[\{\rho_i\}]$ to the free-energy functional of a mixture of hard spheres is postulated to be of the form

$$\beta\mathcal{F}_{ex}[\{\rho_i\}] = \beta\mathcal{F}[\{\rho_i\}] - \beta\mathcal{F}_{id}[\{\rho_i\}] = \int d\mathbf{r} \Phi[\{n_\alpha(\mathbf{r})\}] \quad (2.1)$$

where $\beta = 1/K_B T$, $\rho_i(\mathbf{r})$ is the density of component i , and

$$\beta\mathcal{F}_{id}[\{\rho_i\}] = \sum_i \int d\mathbf{r} \rho_i(\mathbf{r})(\log \Lambda_i^3 \rho_i(\mathbf{r}) - 1) \quad (2.2)$$

is the ideal-gas contribution with the Λ_i s being the thermal de Broglie wavelengths of component i . In equation (2.1), $\beta^{-1}\Phi$ is the excess free-energy density and it is expressed as a function of a set of weighted densities $n_\alpha(\mathbf{r})$ which are defined by

$$n_\alpha(\mathbf{r}) = \sum_i \int \rho_i(\mathbf{r}') \omega_i^{(\alpha)}(\mathbf{r} - \mathbf{r}') d\mathbf{r}'. \quad (2.3)$$

The main differences between the Rosenfeld and KR theories arise in the functional forms of Φ and the density-independent weight functions $\omega_i^{(\alpha)}(\mathbf{r})$.

2.1.1. *The Rosenfeld theory.* In the work of Rosenfeld [10] the six weight functions are characteristic functions for the geometry of a three-dimensional sphere of radius R_i . They are both scalar and vector quantities and are defined as

$$\omega_i^{(3)}(\mathbf{r}) = \theta(R_i - r) \quad (2.4)$$

$$\omega_i^{(2)}(\mathbf{r}) = \delta(R_i - r) \quad \boldsymbol{\omega}_i^{(2)}(\mathbf{r}) = \frac{\mathbf{r}}{r} \delta(R_i - r) \quad (2.5)$$

$$\omega_i^{(1)}(\mathbf{r}) = \frac{\omega_i^{(2)}(\mathbf{r})}{4\pi R_i} \quad \boldsymbol{\omega}_i^{(1)}(\mathbf{r}) = \frac{\boldsymbol{\omega}_i^{(2)}(\mathbf{r})}{4\pi R_i} \quad (2.6)$$

$$\omega_i^{(0)}(\mathbf{r}) = \frac{\omega_i^{(2)}(\mathbf{r})}{4\pi R_i^2} \quad (2.7)$$

where θ and δ are, respectively, the Heaviside step and the Dirac delta function. The excess free-energy density $\beta^{-1}\Phi$ is derived [10] as a sum of vector and scalar contributions:

$$\Phi = \Phi_S + \Phi_V \quad (2.8)$$

$$\Phi_S = -n_0 \log(1 - n_3) + \frac{n_1 n_2}{1 - n_3} + \frac{n_2^3}{24\pi(1 - n_3)^2} \quad (2.9)$$

$$\Phi_V = -\frac{\mathbf{n}_1 \cdot \mathbf{n}_2}{1 - n_3} - \frac{n_2(\mathbf{n}_2 \cdot \mathbf{n}_2)}{8\pi(1 - n_3)^2} \quad (2.10)$$

where the dot denotes the scalar product. For a uniform hard-sphere mixture one has $\rho_i(\mathbf{r}) = \rho_i$, the integrals over the two vector weight functions vanish so $\mathbf{n}_1 = \mathbf{n}_2 = 0$, and the remaining four scalar functions yield the weighted densities

$$n_\alpha = \sum_i \rho_i R_i^{(\alpha)} \quad (2.11)$$

where

$$R_i^{(0)} = 1 \quad R_i^{(1)} = R_i \quad R_i^{(2)} = 4\pi R_i^2 \quad R_i^{(3)} = \frac{4}{3}\pi R_i^3. \quad (2.12)$$

The resulting $\Phi = \Phi_S$ is the scaled-particle theory or Percus–Yevick excess free-energy density of the uniform hard-sphere mixture [10]. Note that n_3 is simply the packing fraction.

The direct correlation function is given by the second functional derivative of the excess free-energy functional:

$$-c^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \beta \frac{\delta^2 \mathcal{F}_{ex}}{\delta \rho(\mathbf{r}_1) \delta \rho(\mathbf{r}_2)}. \quad (2.13)$$

In the uniform limit one has

$$-c_{ij}^{(2)}(r) = \chi^{(3)} \Delta V_{ij}(r) + \chi^{(2)} \Delta S_{ij}(r) + \chi^{(1)} \Delta R_{ij}(r) + \chi^{(0)} \theta((R_i + R_j) - r) \quad (2.14)$$

where $\chi^{(\alpha)} = \partial^2 \Phi_S / \partial n_3 \partial n_\alpha$ and $\Delta V_{ij}(r)$, $\Delta S_{ij}(r)$, and $\Delta R_{ij}(r)$ are functions of the distance r between two spheres of radius R_i and R_j . These quantities are given by geometrical measures [10]. Expression (2.14) coincides with the PY direct correlation function for a three-dimensional hard-sphere mixture [10].

2.1.2. *The Kierlik–Rosinberg theory.* In the work of Kierlik and Rosinberg [11] the PY form is postulated for the excess free-energy density:

$$\Phi = \Phi_{PY} = -n_0 \log(1 - n_3) + \frac{n_1 n_2}{1 - n_3} + \frac{n_2^3}{24\pi(1 - n_3)^2} \quad (2.15)$$

where again the n_α s are averaged densities (2.3) but now with different weight functions obtained by requiring that in the uniform limit the above functional gives rise to the PY direct correlation function (2.14). Then KR obtained four scalar weight functions [11]:

$$\omega_i^{(3)}(r) = \theta(R_i - r) \tag{2.16}$$

$$\omega_i^{(2)}(r) = \delta(R_i - r) \tag{2.17}$$

$$\omega_i^{(1)}(r) = \frac{1}{8\pi} \delta'(R_i - r) \tag{2.18}$$

$$\omega_i^{(0)}(r) = -\frac{1}{8\pi} \delta''(R_i - r) + \frac{1}{2\pi r} \delta'(R_i - r) \tag{2.19}$$

where the prime denotes differentiation w.r.t. r . Notice that in the uniform limit the n_α s arising from this theory are identical to those of the Rosenfeld theory.

2.2. Present theory

For the sake of clarity we present the theory for the case of a hard-sphere fluid with only one component; the extension to mixtures is straightforward and is reported in the appendix.

2.2.1. The functional of the one-component fluid. In accordance with Rosenfeld and KR we assume the following expression for the excess part of the free energy $\mathcal{F}_{ex}[\rho]$:

$$\beta\mathcal{F}[\rho] - \beta\mathcal{F}_{id}[\rho] = \beta\mathcal{F}_{ex}[\rho] = \int \Phi(\mathbf{r}; \rho) \, d\mathbf{r} \tag{2.20}$$

where

$$\mathcal{F}_{id}[\rho] = \beta^{-1} \int d\mathbf{r} \, \rho(\mathbf{r})(\log \Lambda^3 \rho(\mathbf{r}) - 1) \tag{2.21}$$

is again the free energy of the ideal gas. In the spirit of scaled-particle theory the excess free-energy density $\beta^{-1}\Phi$ is assumed to be of the form

$$\Phi(\mathbf{r}; \rho) = D_R G(R; \mathbf{r}; \rho) \tag{2.22}$$

where G is a dimensionless generating function which depends on the radius R of the particles and whose explicit functional form will be proposed later. D_R is a differential operator of order \mathcal{D} , where \mathcal{D} is the dimension of the system ($\mathcal{D} = 1, 2, \text{ or } 3$):

$$D_R = \sum_{i=1}^{\mathcal{D}} q_i(R) \frac{\partial^i}{\partial R^i} \tag{2.23}$$

and the $q_i(R)$ are undetermined functions of the radius R , with dimension $R^{i-\mathcal{D}}$. The simplest choice for these functions is $q_i(R) = a_i R^{i-\mathcal{D}}$, the a_i s being dimensionless constants. With this choice, we have

$$D_R = \sum_{i=1}^{\mathcal{D}} \frac{a_i}{R^{\mathcal{D}-i}} \frac{\partial^i}{\partial R^i}. \tag{2.24}$$

Our proposal for the generating function is

$$G = (1 - \nu(\mathbf{r}, R))(\log(1 - \nu(\mathbf{r}, R)) - 1) \tag{2.25}$$

where ν is a weighted density:

$$\nu(\mathbf{r}, R) = \int d\mathbf{r}' \, \rho(\mathbf{r} - \mathbf{r}') \omega(\mathbf{r}', R) \tag{2.26}$$

and $\omega(\mathbf{r}', R)$ is a density-independent weight function which determines the dependence on R . Following the Rosenfeld and KR theories and earlier approaches [2] we take the simplest weight function:

$$\omega(\mathbf{r}', R) = \theta(R - r') \quad (2.27)$$

so that for $\mathcal{D} = 3$, $\nu(\mathbf{r}, R)$ coincides with the average density $n_3(\mathbf{r}, R)$ which appears in the Rosenfeld and KR theories.

The proposed form of G is motivated by making comparison with the ideal-gas free-energy density

$$f_{id}(\rho(\mathbf{r})) = \beta^{-1} \rho(\mathbf{r})(\log(\Lambda^3 \rho(\mathbf{r})) - 1). \quad (2.28)$$

Since in the uniform limit ν reduces to the packing fraction $\eta = (4/3)\pi R^3 \rho$, which represents the fraction of volume occupied by the molecules, for the inhomogeneous fluid $1 - \nu$ can be taken as the fraction of free volume. One then assumes that G as a function of $1 - \nu$ is just the free-energy density of the ideal gas. Going further with the analogy, one could then consider the excess free-energy density $\beta^{-1} D_R G$ as being the geometrical contributions to the free-energy density of an *ideal 'interstitial' fluid* with the packing fraction given by $1 - \nu$. Other choices of G are possible but we first explore the consequences of this simple prescription.

The next step is to determine appropriate values for the coefficients a_i . To this end we follow the usual procedure of *imposing* the known homogeneous limit, i.e., we choose the a_i s in such a way that for $\rho(\mathbf{r}) = \rho = \text{constant}$, $\beta^{-1} \Phi$ in (2.22) coincides with a known excess free-energy density. For $\mathcal{D} = 3$ this can be carried out for the Percus–Yevick excess free-energy density (the natural choice because of its equivalence to SPT) but also for the more accurate Carnahan–Starling result [16].

From (2.22)–(2.25) we obtain

$$\begin{aligned} \Phi = D_R G = & - \left(\frac{a_1}{R^2} v' + \frac{a_2}{R} v'' + a_3 v''' \right) \log(1 - \nu) \\ & + \left(\frac{a_2}{R} (v')^2 + 3a_3 v' v'' \right) \frac{1}{1 - \nu} + a_3 (v')^3 \frac{1}{(1 - \nu)^2} \end{aligned} \quad (2.29)$$

where the prime denotes differentiation w.r.t. R . Equating term by term in (2.29) and in the Percus–Yevick result (2.15) and taking into account that $\nu = n_3$, we obtain the following set of equations:

$$\begin{aligned} n_0 &= \frac{a_1}{R^2} v' + \frac{a_2}{R} v'' + a_3 v''' \\ n_1 n_2 &= \frac{a_2}{R} (v')^2 + 3a_3 v' v'' \\ \frac{n_2^3}{24\pi} &= a_3 (v')^3. \end{aligned} \quad (2.30)$$

Given that in the homogeneous limit we have

$$n_3 = \frac{4}{3} \pi R^3 \rho \quad n_2 = 4\pi R^2 \rho \quad n_1 = R\rho \quad n_0 = \rho \quad (2.31)$$

and

$$\nu = \frac{4}{3} \pi R^3 \rho \quad \nu' = 4\pi R^2 \rho \quad \nu'' = 8\pi R \rho \quad \nu''' = 8\pi \rho \quad (2.32)$$

it follows that in that limit (2.30) has the unique solution

$$a_1 = \frac{1}{6\pi} \quad a_2 = 0 \quad a_3 = \frac{1}{24\pi}. \quad (2.33)$$

Substitution of (2.33) into (2.29) allows us to write

$$\Phi = -\left(\frac{1}{6\pi R^2}v' + \frac{1}{24\pi}v'''\right)\log(1-v) + \frac{v'v''}{8\pi(1-v)} + \frac{(v')^3}{24\pi(1-v)^2}. \quad (2.34)$$

On the other hand, from equations (2.26) and (2.27), and the definitions (2.3) for the averaged densities n_α , and (2.16)–(2.19) for the corresponding weight functions $\omega^{(\alpha)}$ in the Kierlik–Rosinberg theory, it is easy to establish the following relations:

$$\begin{aligned} n_3 &= v \\ n_2 &= v' \\ n_1 &= \frac{1}{8\pi}v'' \\ n_0 &= -\frac{1}{8\pi}v''' + \frac{1}{2\pi}\left(\frac{v'}{R}\right)' \end{aligned} \quad (2.35)$$

that allow us to rewrite (2.34) as

$$\Phi = \left(\frac{1}{3}n_0 - \frac{4}{3R}n_1\right)\log(1-n_3) + \frac{n_1n_2}{1-n_3} + \frac{n_2^3}{24\pi(1-n_3)^2}. \quad (2.36)$$

In this functional the only difference from Φ^{PY} in (2.15) appears in the first term, this difference vanishing in the homogeneous limit. The functional Φ in equation (2.36) is our proposal for the excess free-energy density for $\mathcal{D} = 3$, and unless otherwise stated, it will be the functional used in the calculations that we present later.

Proceeding in an analogous way we can obtain a functional that yields the Carnahan–Starling free energy in the homogeneous limit. The starting point is the extension to mixtures [20] of the C–S expression, written in terms of scaled-particle variables [11]:

$$\Phi^{CS} = \left(\frac{n_2^3}{36\pi n_3^2} - n_0\right)\log(1-n_3) + \left(n_1n_2 + \frac{n_2^3}{36\pi n_3}\right)\frac{1}{1-n_3} + \frac{n_2^3}{36\pi(1-n_3)^2}. \quad (2.37)$$

Note that the coefficient of the first log term vanishes for the uniform fluid. Now, equating term by term in (2.29) and (2.37), the constants a_i take the following values:

$$a_1 = -\frac{7}{18\pi} \quad a_2 = \frac{1}{6\pi} \quad a_3 = \frac{1}{36\pi} \quad (2.38)$$

giving the new functional

$$\begin{aligned} \Phi = & -\left(\frac{-7}{18\pi R^2}v' + \frac{1}{6\pi R}v'' + \frac{1}{36\pi}v'''\right)\log(1-v) \\ & + \left(\frac{1}{6\pi R}(v')^2 + \frac{1}{12\pi}v'v''\right)\frac{1}{1-v} + \frac{1}{36\pi}\frac{(v')^3}{(1-v)^2} \end{aligned} \quad (2.39)$$

or, in terms of the n_α s given by (2.35)

$$\begin{aligned} \Phi = & -\left(-\frac{1}{2\pi R^2}n_2 + \frac{20}{9R}n_1 - \frac{2}{9}n_0\right)\log(1-n_3) \\ & + \left(\frac{1}{6\pi R}n_2^2 + \frac{2}{3}n_1n_2\right)\frac{1}{1-n_3} + \frac{n_2^3}{36\pi(1-n_3)^2} \end{aligned} \quad (2.40)$$

which, as in the previous case, differs from Φ^{CS} in (2.37) but agrees with it in the homogeneous limit.

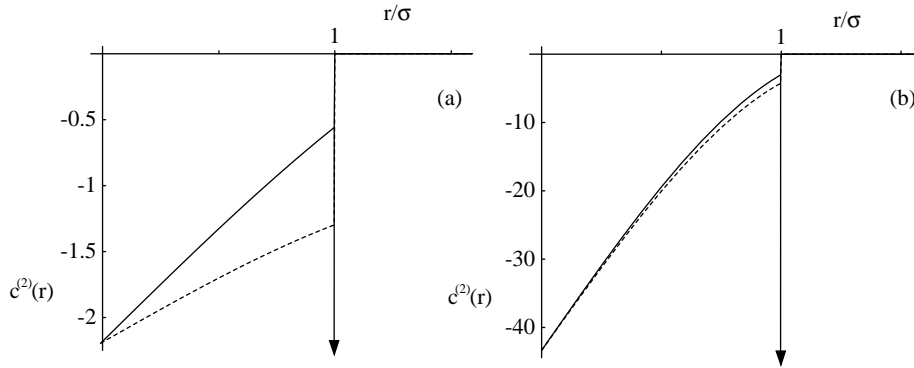


Figure 1. The two-body direct correlation function $c^{(2)}(r)$ of the homogeneous hard-sphere fluid; (a) packing fraction $\eta = 0.1$ and (b) $\eta = 0.46$. The solid lines are the results of our theory (2.45) and the dashed lines show the PY DCF (2.14).

2.2.2. The direct correlation function. In this section we study the structure of the uniform fluid as obtained from the above theory, i.e., we shall compare the pair DCF $c^{(2)}(r)$ with the PY pair DCF. From definition (2.13) and (2.20)–(2.25) we obtain

$$-c^{(2)}(r_1, r_2) = D_R \int \frac{1}{1 - v(r, R)} \omega(r - r_1, R) \omega(r - r_2, R) dr. \quad (2.41)$$

For a homogeneous fluid both $c^{(2)}$ and ω depend only on $r_{ij} = |r_i - r_j|$, so the Fourier transform of (2.41) reads

$$-c^{(2)}(k) = D_R \left(\frac{(\omega(k, R))^2}{1 - v} \right). \quad (2.42)$$

A simple calculation using the a_i s in (2.33) allows us to write

$$-c^{(2)}(k) = \chi^{(3)} \Delta V(k) + \chi^{(2)} \Delta S(k) + \chi^{(1)} \Delta R(k) + \chi^{(0)} \bar{\theta}(k) \quad (2.43)$$

with

$$\bar{\theta}(k) = \theta(k, 2R) + \theta(k, R) \frac{4}{3} \left(\frac{\sin(kR)}{kR} - \cos(kR) - kR \sin(kR) \right) \quad (2.44)$$

and where the $\chi^{(\alpha)}$ s have the same meaning as in equation (2.14). $\Delta V(k)$, $\Delta S(k)$, and $\Delta R(k)$ are the Fourier transforms of the functions appearing in (2.14), and $\theta(k, R)$ is the Fourier transform of $\theta(R - r)$. Explicit expressions for these functions have been given elsewhere [11]. Back in real space, from (2.43) and (2.44) we find

$$c^{(2)}(r) = c_{PY}^{(2)}(r) + \frac{2}{3} \frac{1}{1 - \eta} \frac{r}{\sigma} \theta \left(1 - \frac{r}{\sigma} \right) - \frac{1}{6} \frac{1}{1 - \eta} \delta \left(1 - \frac{r}{\sigma} \right) \quad (2.45)$$

where $c_{PY}^{(2)}(r)$ is the PY pair DCF (2.14) for a one-component homogeneous fluid and $\sigma = 2R$ is the hard-sphere diameter. The most remarkable (and unphysical) feature of $c^{(2)}(r)$ in (2.45) is the presence of a Dirac δ -function at $r = \sigma$. Figure 1 shows a comparison between the PY pair DCF and the result (2.45) for two different densities. The agreement between the results of the two theories is fairly good, especially at high densities. Notice that $c^{(2)}(r)$ in (2.45) coincides with $c_{PY}^{(2)}(r)$ for $r = 0$. This is related to the fact that the two theories give rise to the same equation of state in the homogeneous limit—see (3.18) and the discussion that follows.

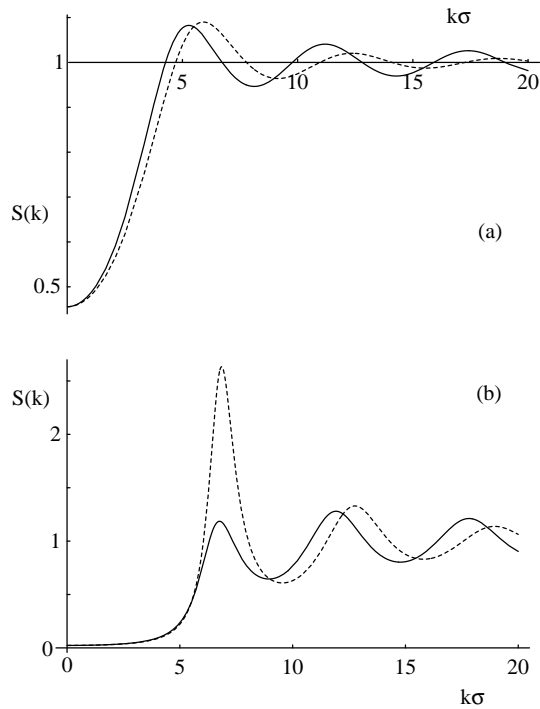


Figure 2. The structure factor $S(k)$ of a homogeneous hard-sphere fluid; (a) packing fraction $\eta = 0.1$ and (b) $\eta = 0.46$. The solid lines are the results of our theory and the dashed lines show the PY structure factor.

Figure 2 exhibits the structure factor $S(k) = 1/(1 - \rho c^{(2)}(k))$ for both theories and the same two densities. As can be observed, a dephasing occurs, and the first peak is not adequately described for the higher density in the present theory. This failing is due to the large contribution from the second term in (2.44), reflecting the unphysical delta function. Note that $c^{(2)}(k = 0)$ and $S(k = 0)$ coincide for the two theories, since they have the same compressibility equation of state.

3. Applications

3.1. Adsorption at a wall

This is a prototypical problem for examining the performance of any theory of inhomogeneous fluids. We investigate first the structure (density profile) of a one-component hard-sphere fluid in contact with a hard wall. In this case the external potential is given by

$$V_{ext}(\mathbf{r}) = V_{ext}(z) = \begin{cases} \infty & z < 0 \\ 0 & z > 0. \end{cases} \quad (3.1)$$

The minimization of the grand potential

$$\Omega[\rho] = \mathcal{F}[\rho] + \int dz \rho(z)[V_{ext}(z) - \mu]$$

gives rise to the following expression for the density profile:

$$\rho(z) = \begin{cases} \rho_B \exp[c^{(1)}(z) - c_0^{(1)}(\rho_B)] & z > 0 \\ 0 & z < 0 \end{cases} \quad (3.2)$$

where ρ_B is the bulk density (the density of the fluid far away from the wall), $c^{(1)}(z)$ is the first functional derivative of the excess free energy, and $c_0^{(1)}$ is its homogeneous limit ($\rho(z) \rightarrow \rho_B$). For our particular functional

$$c^{(1)}(\mathbf{r}) = -\beta \frac{\delta \mathcal{F}_{ex}}{\delta \rho(\mathbf{r})} = - \int \sum_{\alpha} \frac{\partial \Phi}{\partial n_{\alpha}} \omega^{(\alpha)}(\mathbf{r}' - \mathbf{r}) d\mathbf{r}' \quad (3.3)$$

where Φ is given by (2.36) and the weights $\omega^{(\alpha)}$ come from the KR theory (2.16)–(2.19) restricted to a one-component fluid. By defining $S_{\alpha}(z) \equiv \int \Phi_{\alpha} \omega^{(\alpha)}(\mathbf{r}' - \mathbf{r}) d\mathbf{r}'$, with $\Phi_{\alpha} = \partial \Phi / \partial n_{\alpha}$, we have

$$c^{(1)}(z) = - \sum_{\alpha} S_{\alpha}(z) \quad (3.4)$$

where the S_{α} s can be rewritten in the following simplified form:

$$\begin{aligned} S_3(z) &= \pi \int_{-R}^R \Phi_3(z+z') [R^2 - z'^2] dz' \\ S_2(z) &= 2\pi R \int_{-R}^R \Phi_2(z+z') dz' \\ S_1(z) &= \frac{R}{4} (\Phi_1(z+R) + \Phi_1(z-R)) + \frac{1}{4} \int_{-R}^R \Phi_1(z+z') dz' \\ S_0(z) &= \frac{1}{2} (\Phi_0(z+R) + \Phi_0(z-R)) - \frac{R}{4} (\Phi_0'(z+R) - \Phi_0'(z-R)) \end{aligned} \quad (3.5)$$

and the weighted densities can be written as in KR theory [11]. The term $c_0^{(1)}(\rho_B)$ is easily expressed as

$$c_0^{(1)}(\rho_B) = - \sum_{\alpha} \Phi_{\alpha}(\{n_{\beta} = \rho_B R^{(\beta)}\}) R^{(\alpha)} \quad (3.6)$$

where $R^{(0)} = 1$, $R^{(1)} = R$, $R^{(2)} = 4\pi R^2$, and $R^{(3)} = (4/3)\pi R^3$.

Equation (3.2) for the profile $\rho(z)$ is readily solved by iteration. Figure 3 shows a comparison between the solution of equation (3.2) and the result of the KR theory (equivalent to that of Rosenfeld) which is known to give very accurate results for the present problem [11, 2]. The solutions are plotted for different bulk densities, and are in better agreement as the density decreases. The most striking feature of the solutions obtained from the new theory is the appearance of a *kink* at $z = \sigma$ (and discontinuities in higher derivatives at $z = 2\sigma, 3\sigma, \dots$) which can be traced back to the delta function term in the DCF (2.45). The delta function contribution *propagates* the discontinuity in the profile at $z = 0$ to $z = \sigma$ in the form of a discontinuity in the first derivative of $\rho(z)$ (the kink). Although this unphysical kink is the main difference between the theories, there is also some dephasing of the maxima.

It should be mentioned that the present theory obeys the contact sum rule for a fluid near a hard wall:

$$\beta P = \rho(\text{contact}). \quad (3.7)$$

This sum rule is satisfied by any (non-local) DFT. In this case (as in the Rosenfeld or KR theories) the bulk pressure P is that given from the compressibility PY equation of state.

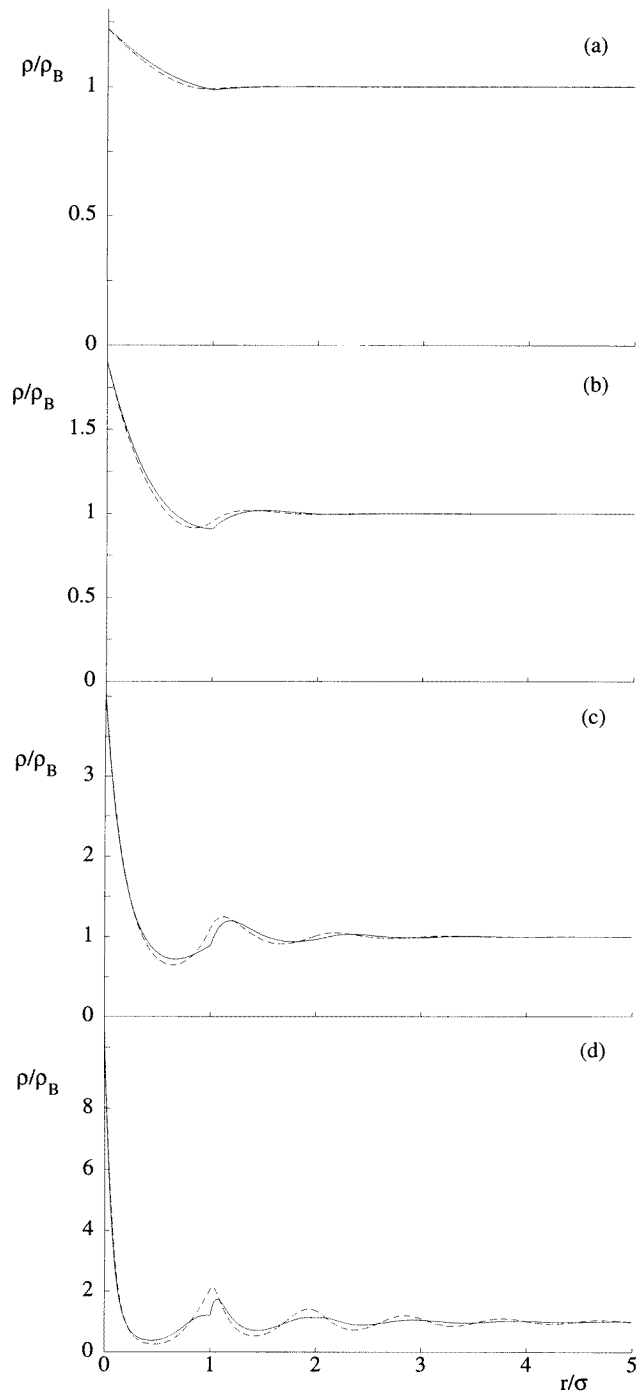


Figure 3. Density profiles for a hard-sphere fluid near a planar hard wall; (a) bulk packing fraction $\eta_B = 0.05$, (b) $\eta_B = 0.15$, (c) $\eta_B = 0.30$, and (d) $\eta_B = 0.46$. The solid lines are the results of our theory and the dashed lines are those of the KR theory.

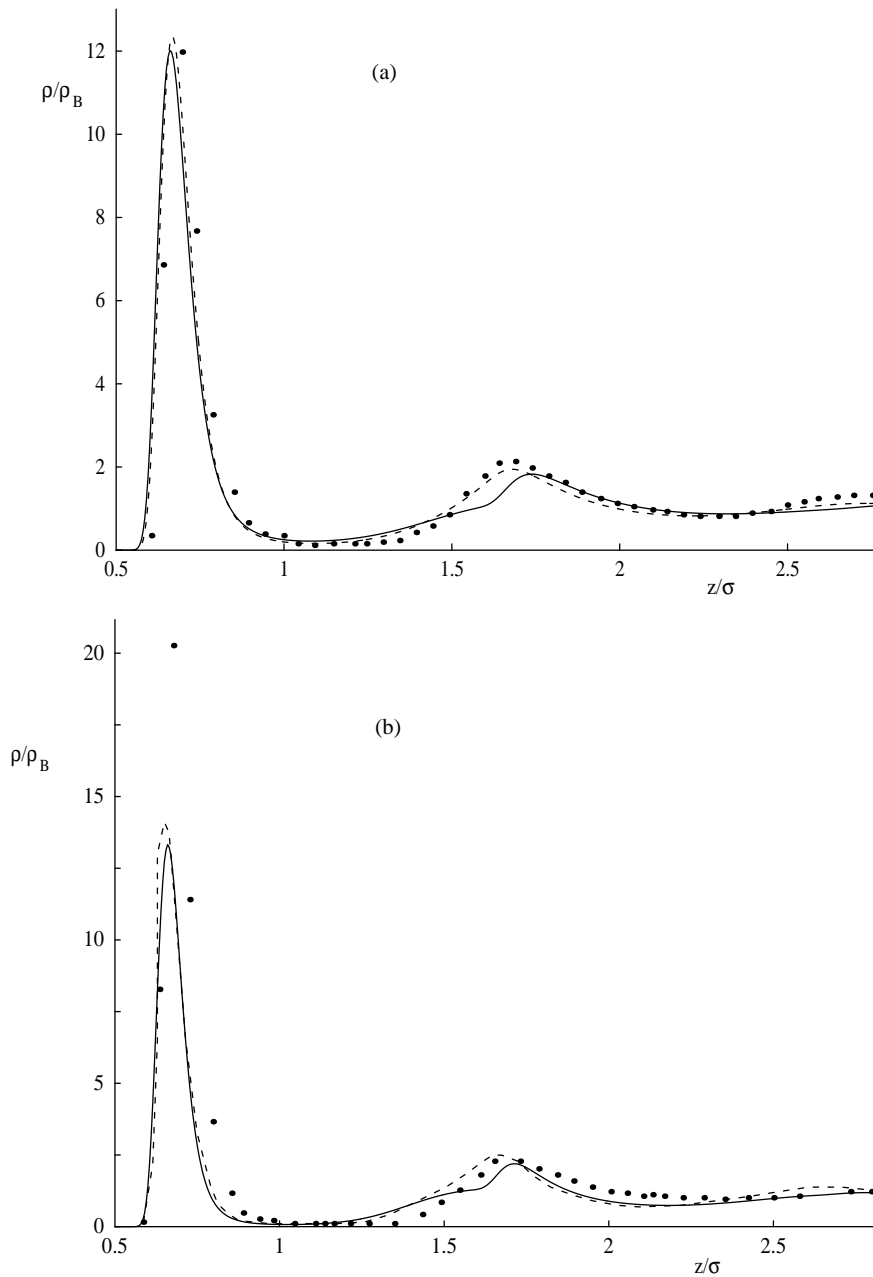


Figure 4. Density profiles of hard spheres near a Lennard–Jones 9–3 wall; (a) $\eta_B = 0.244$, $\epsilon/k_B = 2876$ K, $z_0 = 0.562\sigma$, $T = 150$ K, and (b) $\eta_B = 0.32$, $\epsilon/k_B = 2876$ K, $z_0 = 0.562\sigma$, $T = 100$ K. The points are the Monte Carlo results of reference [21], the solid lines are the results of the present theory, and the dashed lines are those of the KR theory [11].

Kierlik and Rosinberg [11] applied their approach to the very inhomogeneous case of a hard-sphere fluid near a Lennard-Jones wall with the potential given by

$$V_{ext}(z) = \epsilon \left(\left(\frac{z_0}{z} \right)^9 - \left(\frac{z_0}{z} \right)^3 \right). \quad (3.8)$$

Figure 4 shows a comparison between Monte Carlo and KR results, and the results of the present theory for two different bulk states. In general the KR theory is accurate except in case (b), a high-density, low-temperature state where it cannot reproduce adequately the extremely high first peak of the profile. The new theory gives results similar to those of KR but with poorer agreement with simulations which again can be related to the delta function term in the DCF (2.45). In this case the wall potential is soft, there is no discontinuity at contact, and the kink is smoothed. Notice that the kink appears at a distance of approximately σ from the main peak. Once again there seems to be significant dephasing of the maxima.

3.2. The radial distribution function $g(r)$ of a homogeneous hard-sphere fluid from the test particle method

The test particle method is based on an idea of Percus [22] which allows one to study the structure of the homogeneous fluid using theories for inhomogeneous liquids. The idea is to consider one of the particles as fixed at the origin, thereby creating an inhomogeneity in the one-body density profile. The resulting density profile $\rho(r)$ is then related to the radial distribution function $g(r)$ of the homogeneous fluid by the following relation:

$$\rho(r) = \rho_B g(r). \quad (3.9)$$

From this viewpoint we consider a fluid in an external potential equal to the intermolecular potential (created by the particle at the origin). For hard spheres this potential is given by

$$V_{ext}(\mathbf{r}) = V_{ext}(r) = \begin{cases} \infty & r < 2R \\ 0 & r > 2R. \end{cases} \quad (3.10)$$

Since this potential has spherical symmetry, the resulting density profile will also have spherical symmetry. In this case, the convolutions defining the weighted densities (and those convolutions appearing in $c^{(1)}(\mathbf{r})$) can be easily handled by Fourier transform methods by noticing that all of the Fourier transforms (FT) involved can be reduced to one-dimensional FTs on the radial coordinate r . The calculations can then be done using a fast-Fourier-transform (FFT) procedure. This method can also be implemented in the previous case of adsorption at a wall.

Figure 5 shows a comparison between the results obtained from KR theory (or equivalently, from the Rosenfeld theory) and from the present theory for several bulk densities. In general, the behaviour is similar to that found in the case of adsorption at a wall. $g(r)$ is characterized by the appearance of a kink for $r = 2\sigma$ (and discontinuities in higher derivatives for $r = 3\sigma, 4\sigma, \dots$), i.e., at a distance σ from the contact. This kink is enhanced as the density is increased and can be traced back to the delta function term in the DCF.

The reason for comparing with the KR theory is that we know that this provides accurate results for the radial distribution function. This can be ascertained in figure 6 where we plot our results for $g(r)$ for $\eta = 0.46$ from KR theory using the test particle method and the PY result obtained as usual from the PY pair DCF through the Ornstein–Zernike equation. Since the PY pair DCF is also the KR DCF, figure 6 illustrates the great degree of consistency of the KR theory. The main differences between the results from the test particle method and the inversion of the Ornstein–Zernike equation appear at or close to the contact, where the test particle result is closer to the simulation result.

As in the wall–particle problem, in the test particle case there is an exact sum rule linking the contact value of the profile $g(\sigma)$ with the equation of state of the hard-sphere

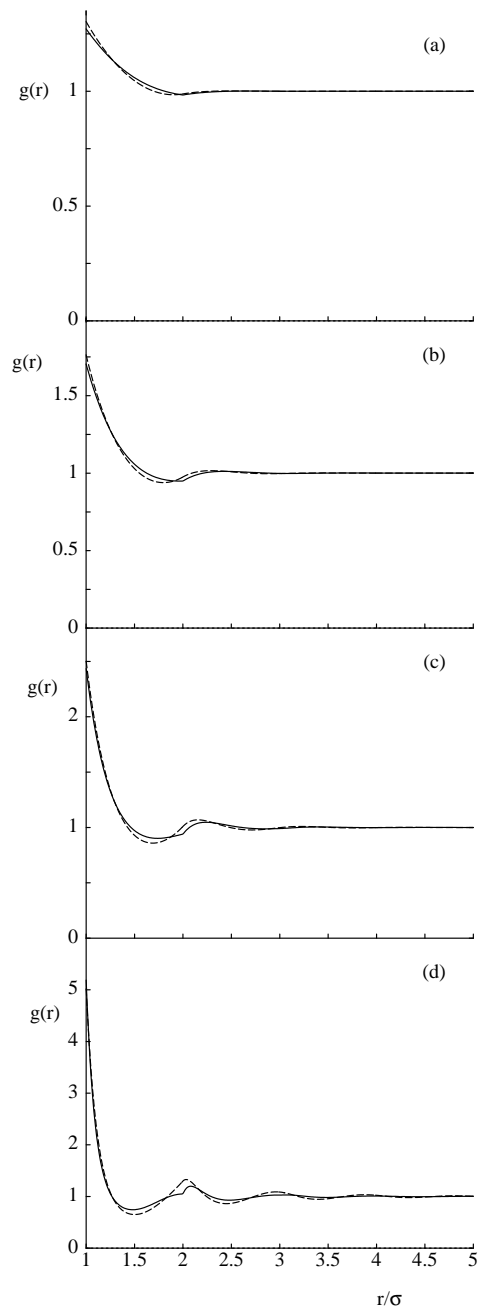


Figure 5. Pair correlation functions $g(r)$ of the homogeneous hard-sphere fluid obtained from the test particle method; (a) bulk packing fraction $\eta_B = 0.1$, (b) $\eta_B = 0.2$, (c) $\eta_B = 0.3$, and (d) $\eta_B = 0.46$. The solid lines are the predictions of the present theory and the dashed lines are those of the KR theory.

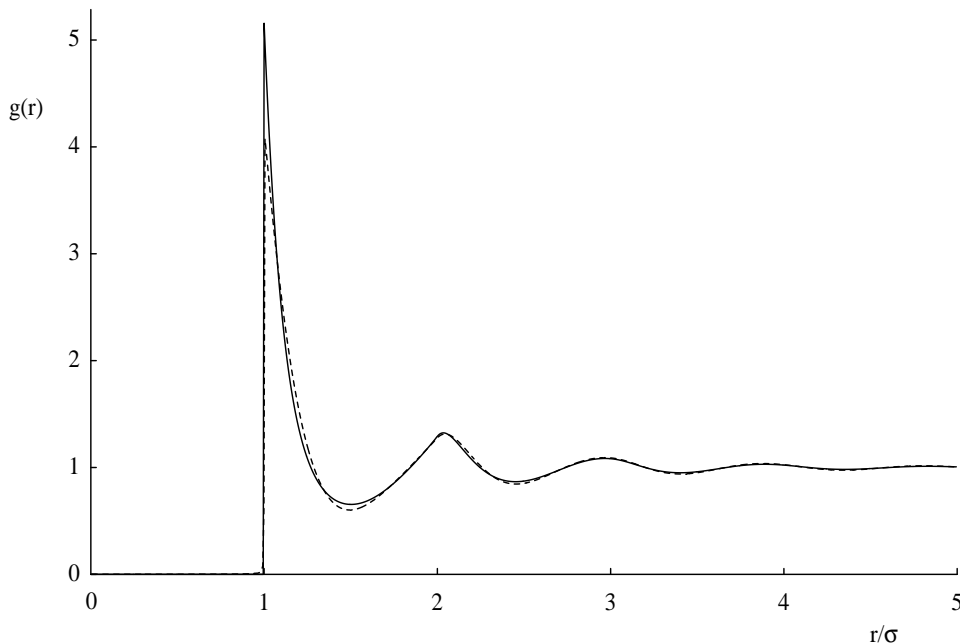


Figure 6. The pair correlation function $g(r)$ for the homogeneous hard-sphere fluid at a packing fraction $\eta_B = 0.46$. The solid line is the result of the KR theory obtained using the test particle method. The dashed line is the PY $g(r)$.

fluid. This is the virial equation of state [16]:

$$\frac{\beta P}{\rho} = 1 + \frac{2}{3}\pi\rho\sigma^3 g(\sigma). \quad (3.11)$$

However, for this problem our theory yields contact values different from the KR theory (see figure 5). This observation is related to the fact that the DCFs of the two theories are different. Nevertheless, as can be seen in figure 7, the contact values obtained in our theory, when used in equation (3.11), give rise to pressures P (equations of state) in remarkable agreement with the corresponding homogeneous fluid equations of state. More precisely, in figure 7 we compare the test particle results from our theory using Φ from equation (2.36) (\diamond) with the PY compressibility equation of state (solid line) and find that these are very close. We also compare the test particle results from our theory with Φ derived from the Carnahan–Starling free energy (2.40) (+) with the accurate Carnahan–Starling equation of state (dashed line). Again these are very close. In this context we mention that replacement of Φ from equation (2.36) (coming from PY theory) by Φ from equation (2.40) (coming from Carnahan–Starling theory) gives rise to density profiles $\rho(z)$ or $g(r)$ that are almost identical except for the values near the contact which are much more accurate in the Carnahan–Starling case.

3.3. Very inhomogeneous situations

In this subsection we consider the zero-, one-, and two-dimensional limits of the three-dimensional theory. If a theory based on a full three-dimensional functional can provide an accurate account of results for lower dimensions, it should, in principle, be able to deal

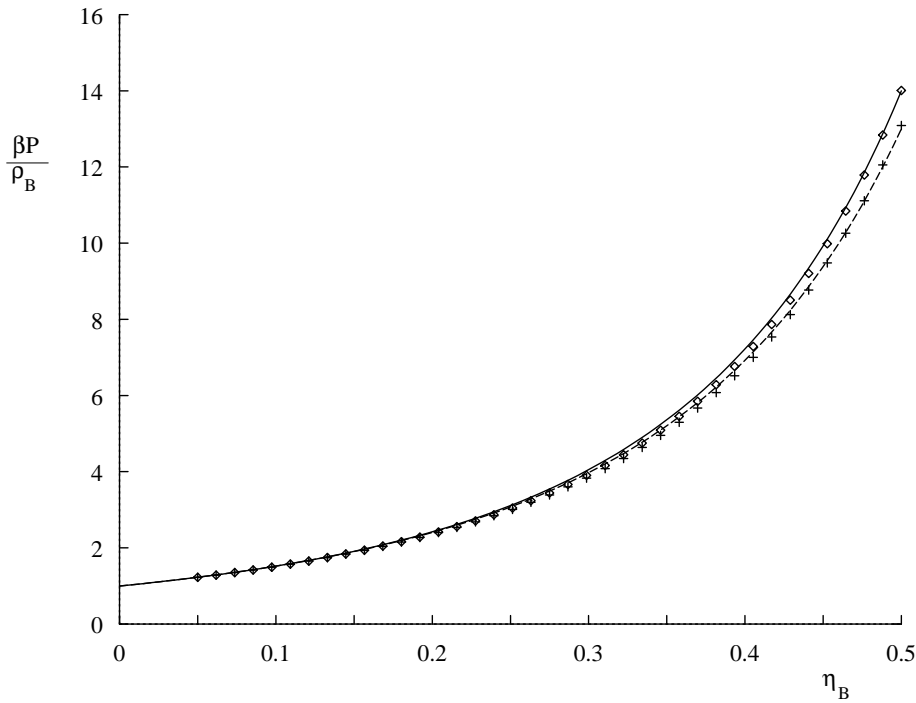


Figure 7. The equation of state for a hard-sphere fluid plotted as a function of packing fraction η_B . The solid line is the PY compressibility equation of state, the dashed line is the Carnahan–Starling equation of state; \diamond : the results of this theory (using the test particle method and the virial equation (3.11)) in the PY version, and $+$: this theory in the Carnahan–Starling version.

with highly inhomogeneous situations in which the effective dimension of the problem is reduced. For example, if we consider adsorption at very attractive walls, the first layer of molecules behaves as a near-two-dimensional fluid.

3.3.1. The zero-dimensional limit. In a recent paper [17] Rosenfeld *et al* have proposed a modified geometrically based free-energy functional for hard spheres. In that work the authors analyse a situation of extreme confinement in which one considers cavities that cannot hold more than one particle. This is the 0D limit. The modified free-energy functional is constructed in such a way that it recovers the exact excess free energy for this situation. This is given by [17]

$$\beta\mathcal{F}_{ex}(\eta) = \eta + (1 - \eta) \log(1 - \eta) \quad (3.12)$$

where the 0D packing fraction η represents the average occupation of the cavity ($0 \leq \eta \leq 1$). We note that the exact 0D excess free energy (3.12) is essentially our generating function G (see (2.25)) expressed in terms of the average occupation η . More specifically, $\beta\mathcal{F}_{ex}(\eta) = G(\eta) + 1$. Thus, one might argue that our present theory is constructed so that the exact 0D limit is achieved. This was not how we came to our approximation, however; rather it was motivated by the simple free-volume ideas described earlier. As such, our approach is in a somewhat different spirit from the very recent work of Tarazona and Rosenfeld [23], which presents an elegant derivation of fundamental-measure-theory functionals based on the exact 0D free energy. Note that the original Rosenfeld theory does

not recover the correct 0D limit; rather it leads to a divergence. As we shall see below, a remarkable property of our theory is that it yields the above exact 0D excess free energy when we consider the (PY-fitted) functional (2.29) with coefficients (2.33).

The density in the 0D limit is $\rho(\mathbf{r}) = \eta\delta(\mathbf{r})$, and therefore

$$v(\mathbf{r}) = \eta \int \delta(\mathbf{r}')\theta(R - |\mathbf{r} - \mathbf{r}'|) d\mathbf{r}' = \eta\theta(R - |\mathbf{r}|). \quad (3.13)$$

From (2.20) and (2.22) one has

$$\beta\mathcal{F}_{ex} = D_R \int G(v) d\mathbf{r} \quad (3.14)$$

and then, using (3.13), one can divide $\int G(v) d\mathbf{r}$ into two parts, one inside the sphere $r = R$ for which $G(v) = G(\eta) = \text{constant}$ and the other outside this sphere for which $G(v) = G(0) = -1$. Since η (the average occupation) is independent of R in 0D we find

$$\beta\mathcal{F}_{ex}(\eta) = D_R((-1)(V - V_3(R)) + G(\eta)V_3(R)) = (1 + G(\eta))D_R(V_3(R)) \quad (3.15)$$

where V is the volume of the system ($V = \int d\mathbf{r}$) and $V_3(R) = (4/3)\pi R^3$ is the volume of a sphere of radius R . From (2.25), equation (3.15) is the exact result (3.12) provided that

$$D_R(V_3(R)) = 1. \quad (3.16)$$

Considering the general expression for D_R (2.24), condition (3.16) requires that

$$4\pi(a_1 + 2a_2 + 2a_3) = 1 \quad (3.17)$$

and this is fulfilled by the set (2.33), i.e. the set which in the homogeneous limit recovers the PY free energy from our functional. Surprisingly, using the set (2.38) that gives the Carnahan–Starling version of our theory we obtain $D_R(V_3(R)) = 0$, i.e. we do not recover the correct 0D limit. This indicates that our theory is intimately linked to the PY (or SPT) structure. This feature is also present if one considers the following relation:

$$-c^{(2)}(r=0) + \rho c^{(2)}(k=0) = D_R(V_3(R)) \quad (3.18)$$

which is valid for the homogeneous fluid DCF in the framework of our theory. It can be derived by recognizing that equation (2.42) yields $-\rho^2 c^{(2)}(k=0) = D_R(\eta^2/(1-\eta))$ (note that $\eta/\rho = (4/3)\pi R^3$) and equation (2.41) implies $-\rho c^{(2)}(r=0) = D_R(\eta/(1-\eta))$. Expression (3.18) reduces to $-c^{(2)}(r=0) + \rho c^{(2)}(k=0) = 1$ for the PY version of our theory. This last result is a well-known requirement on the PY pair DCF; it is easily obtained from the Ornstein–Zernike relation, noting that $c^{(2)}(r) = 0$ for $r > \sigma$ and $g(r) = 0$ for $r < \sigma$.

It is important to note that (3.18) generalizes to other dimensions \mathcal{D} . The derivation sketched above yields, for all \mathcal{D} ,

$$-c^{(2)}(r=0) + \rho c^{(2)}(k=0) = D_R\left(\frac{\eta}{\rho}\right) \quad (3.19)$$

where η is the appropriate packing fraction and D_R is the operator appropriate to the particular dimension \mathcal{D} . In section 4 we show that the r.h.s. of (3.19) reduces to unity for $\mathcal{D} = 1$ and $\mathcal{D} = 2$ as well as for $\mathcal{D} = 3$.

3.3.2. *The one-dimensional limit.* In this case the particles are restricted to the line ($x = y = 0$) and the density profile can be written as

$$\rho(\mathbf{r}) = \rho_z(z)\delta(x)\delta(y) \quad (3.20)$$

and thus

$$\nu(\mathbf{r}) = \int \rho_z(z')\delta(x')\delta(y')\theta(R - |\mathbf{r} - \mathbf{r}'|) d\mathbf{r}' = \theta(R - \varrho) \int_{z-l}^{z+l} \rho_z(z') dz' \quad (3.21)$$

where $\varrho^2 = x^2 + y^2$ and $l^2 = R^2 - \varrho^2$. In order to derive the corresponding excess free energy we use again equation (3.14). The integral in (3.14) can be evaluated taking into account the cylindrical symmetry of $\nu(\mathbf{r})$ and the fact that for $\varrho > R$, $\nu = 0$ and $G(\nu = 0) = -1$. We find

$$\int G(\nu) d\mathbf{r} = 2\pi \int dz \int_0^R G(\nu)\varrho d\varrho + \pi LR^2 - V \quad (3.22)$$

where again V is the volume of the system and L is its length ($L = \int dz$).

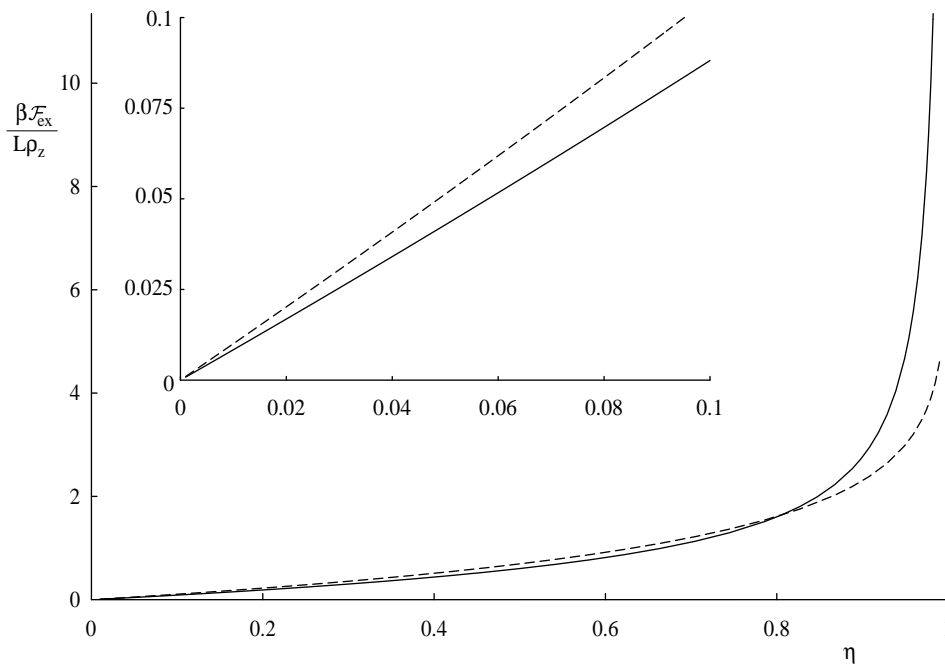


Figure 8. The excess free energy of a uniform one-dimensional hard-rod fluid. The solid line is obtained from the one-dimensional limit of the present three-dimensional functional. The dashed line corresponds to the exact solution. In the inset we show the results for low densities. η is the 1D packing fraction.

Using the PY coefficients (2.33) it follows that

$$D_R = \frac{1}{6\pi R^2} \frac{\partial}{\partial R} + \frac{1}{24\pi} \frac{\partial^3}{\partial R^3} \quad (3.23)$$

and from (3.14) and (3.22) we obtain

$$\begin{aligned} \beta \mathcal{F}_{ex} = & \frac{L}{3R} + \frac{1}{3R} \int G(\bar{v}) \, dz - \frac{1}{6} \int (\rho_z(z+R) + \rho_z(z-R)) \log(1 - \bar{v}) \, dz \\ & - \frac{R}{12} \int (\rho'_z(z+R) - \rho'_z(z-R)) \log(1 - \bar{v}) \, dz \\ & + \frac{R}{12} \int \frac{(\rho_z(z+R) + \rho_z(z-R))^2}{1 - \bar{v}} \, dz \end{aligned} \quad (3.24)$$

where

$$\bar{v}(z) = v(x=0, y=0, z) = \int_{z-R}^{z+R} \rho_z(z') \, dz'. \quad (3.25)$$

For a uniform fluid the density is constant: $\rho_z(z) = \rho_z = N/L$ and $\bar{v}(z) = 2R\rho_z$, giving

$$\frac{\beta \mathcal{F}_{ex}(\rho_z)}{L\rho_z} = -\log(1 - 2R\rho_z) + \frac{1}{3R\rho_z} \log(1 - 2R\rho_z) + \frac{2}{3} + \frac{R\rho_z}{3(1 - 2R\rho_z)}. \quad (3.26)$$

The first term in the above equation is the exact free energy for the homogeneous hard-rod fluid [19]. The remaining terms constitute, therefore, deviations of the present approximation from the exact result. In general, up to a packing fraction of $\eta \equiv 2R\rho_z \approx 0.8$, the deviations are small (see figure 8). The theory does not predict the correct second virial coefficient as can be deduced from (3.26) (or see the inset in figure 8). Moreover the free energy diverges faster at $\eta = 1$ than the exact result. We stress, however, that we are dealing with a highly inhomogeneous problem for which very versatile theories such as the weighted-density approximation of Tarazona [8] and of Rosenfeld [13] fail. For example, in the original Rosenfeld theory there are non-integrable singularities in the calculation of the 1D free energy [13, 24]. The modified version of Rosenfeld *et al* [17] removes the singularities and yields free energies which are of a similar accuracy to those obtained from our present theory.

3.3.3. The two-dimensional limit. Now the particles are restricted to the plane $z = 0$ and the density is given by

$$\rho(\mathbf{r}) = \rho_2(x, y)\delta(z). \quad (3.27)$$

Proceeding in the same manner as in the previous case we obtain in the uniform limit ($\rho_2(x, y) = \rho_2 = N/A$) the following expression for the free energy:

$$\frac{\beta \mathcal{F}_{ex}}{A\rho_2} = -\frac{2}{3} \log \eta - \frac{1}{3} \int_{-1}^1 \log(a^2 + \zeta^2) \, d\zeta + \frac{\eta}{3} + \frac{1}{2} \int_{-1}^1 \frac{d\zeta}{a^2 + \zeta^2} + \frac{1}{3} \int_{-1}^1 \frac{d\zeta}{(a^2 + \zeta^2)^2} \quad (3.28)$$

where $A = \int dx \, dy$, the two-dimensional packing fraction is $\eta = \rho_2\pi R^2$, $\zeta = z/R$, and $a = ((1 - \eta)/\eta)^{1/2}$. This result should be compared with the two-dimensional limit of the KR or Rosenfeld theory [24, 13]:

$$\frac{\beta \mathcal{F}_{ex}^{KR}}{A\rho_2} = \eta + \frac{1}{2} \int_{-1}^1 \frac{d\zeta}{a^2 + \zeta^2} + \frac{1}{3} \int_{-1}^1 \frac{d\zeta}{(a^2 + \zeta^2)^2} \quad (3.29)$$

and with the accurate result of the scaled-particle theory (SPT) for $\mathcal{D} = 2$ [15]:

$$\frac{\beta \mathcal{F}_{ex}^{SPT}}{A\rho_2} = \frac{\eta}{1 - \eta} - \log(1 - \eta). \quad (3.30)$$

Figure 9 shows the three cases. Our result is very close to that of KR except for at low densities (see the inset) where KR theory is in better agreement with SPT.

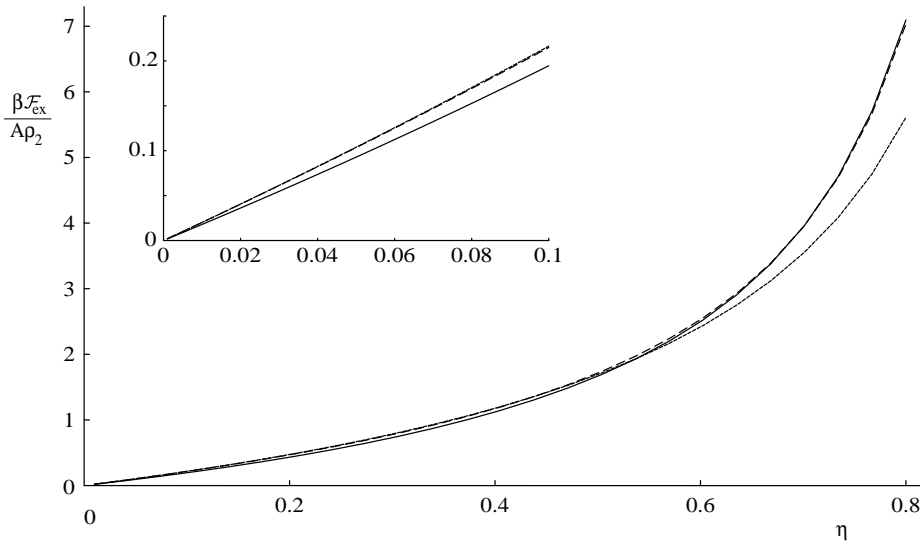


Figure 9. The excess free energy of a uniform two-dimensional hard-disk fluid. The solid line is obtained from the two-dimensional limit of the present three-dimensional functional. The dashed line corresponds to the same limit of the Rosenfeld (or KR) theory. The dotted line represents the *near exact* SPT result [15]. In the inset we show the results for low densities. η is the 2D packing fraction.

4. Theory in dimensions one and two

In this section we derive the one- and two-dimensional versions of the present theory, following the procedure employed for the three-dimensional case.

4.1. Dimension one

For $\mathcal{D} = 1$ the weighting function is $\omega(r) = \theta(R - |r|)$ where $|r|$ is the absolute value of the one-dimensional variable r and $D_R = a_1 \partial/\partial R$. Then

$$\Phi = -a_1 v' \log(1 - v) \quad (4.1)$$

which in the uniform limit takes the value

$$\Phi = -2a_1 \rho \log(1 - \eta) \quad (4.2)$$

where now $\eta = 2R\rho$ is the one-dimensional packing fraction. Equating with the exact result $\Phi^{\text{exact}} = -\rho \log(1 - \eta)$ we obtain $a_1 = 1/2$, which inserted in (4.1) gives rise to

$$\beta \mathcal{F}_{ex} = -\frac{1}{2} \int (\rho(r+R) + \rho(r-R)) \log \left(1 - \int_{r-R}^{r+R} \rho(r') dr' \right) dr \quad (4.3)$$

and this is the exact free-energy functional for the one-dimensional inhomogeneous hard-rod fluid [2, 19]. Note that for $\mathcal{D} = 1$, $D_R(\eta/\rho) = 2a_1 = 1$, so (3.19) reduces to $-c^{(2)}(r=0) + \rho c^{(2)}(k=0) = 1$. This relation is exact for $\mathcal{D} = 1$.

4.2. Dimension two

Applying the two-dimensional version of D_R :

$$D_R = \frac{a_1}{R} \frac{\partial}{\partial R} + a_2 \frac{\partial^2}{\partial R^2} \tag{4.4}$$

to $G = (1 - \nu)(\log(1 - \nu) - 1)$ we obtain

$$\Phi = -\left(\frac{a_1 \nu'}{R} + a_2 \nu''\right) \log(1 - \nu) + a_2 \frac{(\nu')^2}{1 - \nu}. \tag{4.5}$$

In the uniform limit (4.5) reads

$$\Phi = -2\pi\rho(a_1 + a_2) \log(1 - \eta) + a_2 \frac{(2\pi R\rho)^2}{1 - \eta} \tag{4.6}$$

where $\eta = \pi R^2 \rho$ is the two-dimensional packing fraction. Equating (4.6) with the SPT free-energy density for two dimensions (3.30), re-expressed as

$$\Phi^{SPT} = \rho^2 \frac{\pi R^2}{1 - \eta} - \rho \log(1 - \eta) \tag{4.7}$$

we obtain $a_1 = a_2 = 1/4\pi$. The functional (4.5) can then be expressed in the form

$$\Phi = -n_0 \log(1 - n_2) + \frac{1}{4\pi} \frac{(n_1)^2}{1 - n_2} \tag{4.8}$$

where $n_i(\mathbf{r}) = \int d\mathbf{r}' \omega^{(i)}(|\mathbf{r} - \mathbf{r}'|)\rho(\mathbf{r}')$ and we have defined the weights $\omega^{(i)}$ as

$$\begin{aligned} \omega^{(2)}(r) &= \Theta(R - r) \\ \omega^{(1)}(r) &= \delta(R - r) \\ \omega^{(0)}(r) &= \frac{1}{4\pi} \left(\frac{1}{R} \delta(R - r) + \delta'(R - r) \right). \end{aligned} \tag{4.9}$$

The two-dimensional functional (4.8) with the scalar weight functions (4.9) can be viewed as the two-dimensional version of the KR theory. Note however that there is only one weight function (2.27)—the structure of this $\mathcal{D} = 2$ theory is the same as for $\mathcal{D} = 3$ —and the $\omega^{(i)}$ (4.9) are simply derivatives of this one. This is somewhat different from the genesis of the weight functions in Rosenfeld’s theory.

Nevertheless we now show that Φ given by (4.8) is completely equivalent to the Rosenfeld functional in two dimensions [12, 13]:

$$\hat{\Phi} = -\hat{n}_0 \log(1 - \hat{n}_2) + \frac{1}{4\pi} \frac{\hat{n}_1^2}{1 - \hat{n}_2} - \frac{1}{4\pi} \frac{\hat{n}_1 \cdot \hat{n}_1}{1 - \hat{n}_2} \tag{4.10}$$

where the \hat{n}_i s are again given by $\hat{n}_i(\mathbf{r}) = \int d\mathbf{r}' \hat{\omega}^{(i)}(r - r')\rho(\mathbf{r}')$ with the $\mathcal{D} = 2$ set of weights

$$\begin{aligned} \hat{\omega}^{(2)}(\mathbf{r}) &= \Theta(R - r) \\ \hat{\omega}^{(1)}(\mathbf{r}) &= |\nabla\Theta(R - r)| = \delta(R - r) \\ \hat{\omega}^{(1)}(\mathbf{r}) &= -\nabla\Theta(R - r) = \frac{\mathbf{r}}{r} \delta(R - r) \\ \hat{\omega}^{(0)}(\mathbf{r}) &= \frac{1}{2\pi R} \hat{\omega}^{(1)}(\mathbf{r}) = \frac{1}{2\pi R} \delta(R - r). \end{aligned} \tag{4.11}$$

The demonstration of the equivalence of the two theories is very similar to the one used by Phan *et al* [18] to establish the equivalence of the KR and Rosenfeld theories in three dimensions. Let us consider the difference

$$\int d\mathbf{r} (\hat{\Phi} - \Phi) = \int d\mathbf{r} \left(-(\hat{n}_0 - n_0) \log(1 - n_2) - \frac{1}{4\pi} \frac{\hat{\mathbf{n}}_1 \cdot \hat{\mathbf{n}}_1}{1 - n_2} \right) \quad (4.12)$$

in which the identities $\hat{n}_1 = n_1$ and $\hat{n}_2 = n_2$ have been applied. Also, since $\hat{\mathbf{n}}_1 = -\nabla n_2$ one has

$$\int d\mathbf{r} \frac{\hat{\mathbf{n}}_1 \cdot \hat{\mathbf{n}}_1}{1 - n_2} = \int d\mathbf{r} \hat{\mathbf{n}}_1 \cdot \nabla \log(1 - n_2) = - \int d\mathbf{r} \nabla \cdot \hat{\mathbf{n}}_1 \log(1 - n_2) \quad (4.13)$$

where we have performed an integration by parts, neglecting the surface terms. We get therefore

$$\int d\mathbf{r} (\hat{\Phi} - \Phi) = \int d\mathbf{r} \left(-(\hat{n}_0 - n_0) + \frac{1}{4\pi} \nabla \cdot \hat{\mathbf{n}}_1 \right) \log(1 - n_2). \quad (4.14)$$

This expression vanishes provided that $-(\hat{n}_0 - n_0) + (1/4\pi) \nabla \cdot \hat{\mathbf{n}}_1 = 0$, and this can be verified by noticing that

$$\begin{aligned} -(\hat{\omega}^{(0)} - \omega^{(0)}) + \frac{1}{4\pi} \nabla \cdot \hat{\omega}^{(1)} &= \frac{1}{4\pi} \left(-\frac{\omega^{(1)}}{R} + \omega^{(1)'} + \nabla \cdot \hat{\omega}^{(1)} \right) \\ &= \frac{1}{4\pi} \left(-\frac{\delta(R-r)}{R} + \delta'(R-r) + \nabla \cdot \hat{\mathbf{r}} \delta(R-r) + \hat{\mathbf{r}} \cdot \nabla \delta(R-r) \right) \end{aligned} \quad (4.15)$$

where $\hat{\mathbf{r}} = \mathbf{r}/r$ and equations (4.9) and (4.11) have been used. Recalling that $\nabla \cdot \hat{\mathbf{r}} = 1/r$ for $\mathcal{D} = 2$, it is straightforward to see that this expression vanishes on integration. Finally we note that for $\mathcal{D} = 2$, $D_R(\eta/\rho) = 2\pi(a_1 + a_2) = 1$ and, once more, equation (3.19) reduces to $-c^{(2)}(r=0) + \rho c^{(2)}(k=0) = 1$.

5. Conclusions

We have proposed a new density functional for the inhomogeneous hard-sphere fluid which is close in spirit to the theories of Rosenfeld [10] and of Kierlik and Rosinberg [11] but which employs a simple *ansatz* (2.22) for the excess free-energy density. The assumption is that the latter can be written as a set of derivatives of a generating function G w.r.t. the particle radius R . Our choice of G was motivated by simple free-volume considerations and involves a single weighted density $\nu(\mathbf{r}, R)$. In contrast to the Rosenfeld and KR theories whose structure is, in some sense, predetermined by that of PY theory or SPT for the hard-sphere system, our approach builds in some flexibility. It is designed so that the coefficients of the differential operator can be fitted to different uniform fluid free-energy densities. The results presented here are obtained by fitting to the PY free energy, in order to effect a fair comparison with the Rosenfeld and KR theories. The application of our theory with coefficients determined by the Carnahan–Starling free energy (see (2.40) and above) gives rise to almost identical results for density profiles and for $g(r)$ but with significant improvement near the contact.

In applications to three-dimensional problems (density profiles at walls or the calculation of $g(r)$ from the test particle procedure) our new functional is generally less accurate than the Rosenfeld or KR functionals. However, it does fare somewhat better than other functionals based on a single density-independent weight function, which suggests that the generating procedure does contain some of the essential physics. We have traced the failings of our theory to the fact that it does not generate an adequate pair DCF for the uniform fluid.

There is an unphysical delta function term at $r = \sigma$ which is responsible for the appearance of a kink at $z = \sigma$ in the density profile at a hard wall and a similar kink in $g(r)$ at $r = 2\sigma$. These kinks are not present in the results of more sophisticated approximations or in simulations. Such observations reinforce the conjecture [2] that for a DFT to give an accurate description of the density profile of the inhomogeneous fluid it should generate an accurate pair DCF in the uniform case.

The main strength of our present theory lies in its ability to describe successfully limiting cases of extreme inhomogeneity. The three-dimensional functional yields equations of state for one- and two-dimensional systems that are comparable in accuracy to those from the latest modification [17] of Rosenfeld's fundamental-measure theory. Given that it also yields the exact OD limit (a demanding test [17]) this suggests that the present functional could find useful applications in problems of extreme confinement. These are currently under investigation.

At the risk of losing the overall simplicity of the theory, modifications could be made by introducing other generating functions, i.e. modifying the ideal-gas form in (2.25). It remains to be seen what the consequences of such modifications will be and whether these will lead to improved pair DCFs and density profiles for $\mathcal{D} = 3$.

Acknowledgments

JAW wishes to acknowledge financial support by the Dirección General de Investigación Científica y Técnica (DGICYT) of Spain under Grant No PB 95-0934 and by the Junta de Castilla y León (Spain) under Grant No SA78/96. RE is grateful to Y Rosenfeld for supplying preprints of his work and many stimulating discussions. We are also grateful to P Tarazona for sending a preprint [23] and helpful correspondence.

Appendix

In this appendix we extend the theory formulated in section 2 for a one-component fluid to the general case of fluid mixtures. We assume an excess free-energy density $\beta^{-1}\Phi$ of the form

$$\Phi(\mathbf{r}; \{\rho_i\}) = D_R G(\mathbf{r}; \{\rho_i, R_i\}) \quad (\text{A.1})$$

where ρ_i and R_i are, respectively, the density and the radius of component i of the mixture. Also, for dimension $\mathcal{D} = 3$, we define

$$D_R = k_1 \sum_i \frac{1}{R_i^2} \frac{\partial}{\partial R_i} + k_2 \sum_i \frac{1}{R_i} \frac{\partial}{\partial R_i} \left(\sum_j \frac{\partial}{\partial R_j} \right) + k_3 \sum_i \frac{\partial}{\partial R_i} \left(\sum_j \frac{\partial}{\partial R_j} \left(\sum_k \frac{\partial}{\partial R_k} \right) \right) \quad (\text{A.2})$$

and

$$G = (1 - v(\mathbf{r}; \{\rho_i, R_i\})) (\log(1 - v(\mathbf{r}; \{\rho_i, R_i\})) - 1) \quad (\text{A.3})$$

where v is a weighted density

$$v(\mathbf{r}; \{\rho_i, R_i\}) = \sum_i \int \rho(\mathbf{r} - \mathbf{r}') \omega(\mathbf{r}', R_i) d\mathbf{r}' \quad (\text{A.4})$$

and

$$\omega(\mathbf{r}', R_i) = \theta(R_i - r'). \quad (\text{A.5})$$

Performing the differentiation indicated in the above equations and comparing term by term with the PY functional in the homogeneous fluid limit, we find

$$k_1 = \frac{1}{6\pi} \quad k_2 = 0 \quad k_3 = \frac{1}{24\pi} \quad (\text{A.6})$$

which coincides with the result for the one-component fluid.

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