

Weighted-density-functional theory of nonuniform fluid mixtures: Application to the structure of binary hard-sphere mixtures near a hard wall

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A computationally practical density-functional theory of nonuniform fluid mixtures “designed primarily for the study of interfacial phenomena” is presented and applied to the structure of a binary hard-sphere mixture near a hard wall. The theory is based on a weighted-density approximation for the one-particle direct correlation functions of the nonuniform system, and requires as input only the one- and two-particle direct correlation functions of the corresponding uniform system. Numerical results for density and concentration profiles are presented and compared with available simulation data.

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I. INTRODUCTION

The physical properties of solid-fluid interfaces are of both fundamental theoretical interest and also of considerable practical importance in connection with phenomena such as adsorption, wetting, catalysis, and filtration. A characteristic feature of interfacial systems is the presence of a nonuniform (i.e., spatially varying) density profile in the vicinity of the interface. One reason for theoretical interest, then, is that such systems can serve as useful testing grounds for theories of nonuniform fluids.

The simplest imaginable model of a solid-fluid interface treats the solid as a smooth (i.e., structureless), hard (i.e., impenetrable) wall. Such a model is certainly a severe idealization of a real interface since it completely ignores any detailed microscopic interactions between solid and fluid. It does, however, capture one essential feature of the interface, namely the exclusion of the fluid from the region of space occupied by the solid. The role of exclusion in determining the density profile of the fluid may thus be studied in isolation from other contributing factors, such as, for instance, long-range fluid-solid interactions.

In recent years the wall-fluid model has been extensively studied by a variety of theoretical and computer-simulation techniques. On the theoretical side, the density-functional method has proven to be one of the more successful approaches. This method is actually a quite general approach to the equilibrium properties of nonuniform fluids, and has been widely applied to a variety of interfacial and bulk phenomena [1]. It usually proceeds by first approximating the thermodynamic potential of the nonuniform fluid, using known structural and thermodynamic information for the corresponding uniform fluid, and then minimizing the approximate thermodynamic potential with respect to the equilibrium density profile.

Numerous studies already have addressed problems involving simple one-component fluids near walls (see, for example, Refs. [2–9]). Relatively few studies, however,

have yet considered the more general case of fluid mixtures near walls. In comparison with one-component systems, mixtures naturally constitute a much richer class of systems because of the additional concentration variables. For the same reason, however, their quantitative study necessarily entails greater computational complexity. Recently Tan *et al.* [10] generalized one formulation of the density-functional method—one which is based on the smoothed density approximation of Tarazona [4]—from one-component systems to mixtures, and applied it to the structure of binary hard-sphere mixtures near a hard wall. Subsequently, Kierlik and Rosinberg proposed [8] a simplified version of the formulation of Rosenfeld [11] and applied it to the structure of the one-component hard-sphere fluid near a hard wall [8] and to adsorption at substrates of several simple binary mixtures [12]. The primary purpose of this paper is to present a corresponding generalization and application of a different formulation of the density-functional method—one which is based on a computationally simple version of the weighted-density approximation (WDA) of Curtin and Ashcroft [13].

The outline of the paper is as follows. In Sec. II we first describe our density-functional theory—based on a simple version of the WDA for the one-particle direct correlation function (DCF)—in the context of one-component fluids, and then propose its generalization to mixtures. In Sec. III we apply the theory to the special case of hard-sphere fluids near a smooth, hard wall, modeled as noted by a structureless, impenetrable, planar boundary, and then present results for density and concentration profiles. These results are compared with available simulation data, and some strengths and limitations of the theory are discussed. Finally, in Sec. IV we summarize and conclude.

II. THEORY

A. Density-functional theory of one-component fluids

Two central quantities in the density-functional method for nonuniform fluids [1,14] are the grand poten-

tial $\Omega[\rho]$, and the intrinsic Helmholtz free energy $F[\rho]$, both *unique* functionals of the spatially varying one-particle density $\rho(\mathbf{r})$, and related according to

$$\Omega[\rho] = F[\rho] + \int d\mathbf{r} \rho(\mathbf{r}) [u(\mathbf{r}) - \mu], \quad (1)$$

where $u(\mathbf{r})$ is an external potential and μ the chemical potential. The foundation of the method is a variational principle, according to which $\Omega[\rho]$ is minimized by the equilibrium density [14]. Thus, at *equilibrium*

$$\frac{\delta\Omega[\rho]}{\delta\rho(\mathbf{r})} = 0, \quad (2)$$

which implies [from Eq. (1)] the Euler-Lagrange relation

$$\frac{\delta F[\rho]}{\delta\rho(\mathbf{r})} = \mu - u(\mathbf{r}). \quad (3)$$

It is standard to separate $F[\rho]$, according to

$$F[\rho] = F_{\text{id}}[\rho] + F_{\text{ex}}[\rho], \quad (4)$$

into an *ideal-gas* free energy $F_{\text{id}}[\rho]$, which is the free energy of the nonuniform system in the absence of internal interactions, and which is given by the exact relation

$$F_{\text{id}}[\rho] = k_B T \int d\mathbf{r} \rho(\mathbf{r}) \{ \ln[\rho(\mathbf{r})\lambda^3] - 1 \}, \quad (5)$$

where λ is the thermal de Broglie wavelength, and an *excess* free energy $F_{\text{ex}}[\rho]$, which originates in internal interactions and is in general unknown. The substitution of Eqs. (4) and (5) into Eq. (3) then leads to the following exact Euler-Lagrange relation for the equilibrium density:

$$\rho(\mathbf{r}) = z \exp \{ -\beta u(\mathbf{r}) + c^{(1)}(\mathbf{r}; [\rho]) \}, \quad (6)$$

where $z \equiv e^{\beta\mu}/\lambda^3$ (the fugacity), $\beta \equiv 1/k_B T$, and $c^{(1)}(\mathbf{r}; [\rho])$ denotes the one-particle direct correlation function [15]. The latter is a functional of the density, and the first of a hierarchy of DCF's defined by successive functional differentiation of $F_{\text{ex}}[\rho]$ according to

$$c^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_n; [\rho]) = -\beta \frac{\delta^n F_{\text{ex}}[\rho]}{\delta\rho(\mathbf{r}_1) \cdots \delta\rho(\mathbf{r}_n)}. \quad (7)$$

From Eq. (6) it is evident that $c^{(1)}(\mathbf{r}; [\rho])$ plays the role of an effective one-particle potential that acts self-consistently to determine $\rho(\mathbf{r})$.

The application of the density-functional method can now, in principle, proceed either by the minimization of $\Omega[\rho]$ with respect to $\rho(\mathbf{r})$ or alternatively by the search for a self-consistent solution of Eq. (6). In applications to interfacial properties of nonuniform fluids the latter approach is usually the more practical and is the approach followed in this paper. Equation (6) is a formally exact relation, which in principle may be solved for $\rho(\mathbf{r})$ if the functional $c^{(1)}$ is known. In practice, however, $c^{(1)}$ is generally unknown and so must be approximated. Here we adopt a simple version of the WDA of Curtin and Ashcroft [13], which we have previously proposed [16] and subsequently used [16,17] to study the structure of the uniform hard-sphere fluid. The approximation is expressed by the simple relation

$$c_{\text{WDA}}^{(1)}(\mathbf{r}; [\rho]) \equiv c_0^{(1)}(\bar{\rho}(\mathbf{r})), \quad (8)$$

which equates the one-particle DCF of a *nonuniform* fluid to its counterpart $c_0^{(1)}$ for the corresponding *uniform* fluid evaluated, however, at a *weighted* density $\bar{\rho}(\mathbf{r})$ defined according to

$$\bar{\rho}(\mathbf{r}) \equiv \int d\mathbf{r}' \rho(\mathbf{r}') w(|\mathbf{r} - \mathbf{r}'|; \bar{\rho}(\mathbf{r})), \quad (9)$$

that is, $\bar{\rho}(\mathbf{r})$ is a weighted average of the physical density $\rho(\mathbf{r})$ with respect to a weight function w . The basic physical assumption implicit in the approximation is that, at the level of $c^{(1)}$, the nonuniform fluid may be "mapped onto" an effective locally uniform fluid. The statement of the approximation is made complete by a specification of the weight function, a task to which we return below.

Several different but related formulations of the WDA have been proposed in recent years and applied to a variety of problems involving nonuniform fluids [2,4-13,16-19]. Generally the approximation is applied at the level of the excess Helmholtz free energy F_{ex} . A corresponding approximation for the one-particle DCF $c^{(1)}$ may then be obtained by functional differentiation according to Eq. (7). The resulting expression is normally difficult to evaluate in the numerical sense, however, and especially so in the case of fluid mixtures (for a generalization to mixtures of the WDA of Curtin and Ashcroft [13], see Ref. [19]). It is important to emphasize that the WDA for $c^{(1)}$ employed here [Eqs. (8) and (9)] is *not* derived from any corresponding higher-level approximation for F_{ex} , but is motivated primarily by a desire to facilitate computations (see Sec. III). In passing, we note that from our approximation for $c^{(1)}$ a corresponding approximation for F_{ex} can be obtained, in principle, by numerical functional integration. In practice, however, one of the earlier versions of the WDA explicitly formulated to approximate the excess free energy is actually better suited to this purpose.

As demonstrated in Ref. [17], in the context of the structure of uniform fluids, our approximation for $c^{(1)}$ may be interpreted as an approximate closure of the Ornstein-Zernike (OZ) equation. Similarly, in the present context, the approximation may be interpreted as an approximate closure of the wall-particle OZ equation. A distinction should be noted, however, between our approximation for $c^{(1)}$ and a previously proposed modified weighted-density approximation [18] for F_{ex} . Whereas the latter approximation has been shown by White and Evans [20] to correspond to the well-known hypernetted-chain (HNC) closure of the wall-particle OZ equation, our approximation for $c^{(1)}$ does not appear to correspond to any of the standard closures, but instead to a new closure [21].

We now return to the specification of the weight function. Normalization of w , according to

$$\int d\mathbf{r} w(r) = 1, \quad (10)$$

ensures that the approximation becomes exact in the uniform limit $[\rho(\mathbf{r}) \rightarrow \rho_0]$. The weight function is now *uniquely* specified by requiring that the first functional derivative of $c_{\text{WDA}}^{(1)}(\mathbf{r}; [\rho])$ with respect to the density yields, from Eq. (7), the exact two-particle DCF in the uniform limit, i.e.,

$$\lim_{\rho(\mathbf{r}) \rightarrow \rho_0} \left[\frac{\delta c_{\text{WDA}}^{(1)}(\mathbf{r}; [\rho])}{\delta \rho(\mathbf{r}')} \right] = c_0^{(2)}(|\mathbf{r} - \mathbf{r}'|; \rho_0). \quad (11)$$

Indeed, substitution of Eqs. (8) and (9) into Eq. (11) leads to the following analytic form for the weight function:

$$w(\mathbf{r}; \rho_0) = \frac{c_0^{(2)}(\mathbf{r}; \rho_0)}{\partial c_0^{(1)} / \partial \rho_0}. \quad (12)$$

Two important formal features of the approximation may now be noted. First, Eq. (11) ensures that a functional Taylor-series expansion of $c_{\text{WDA}}^{(1)}(\mathbf{r}; [\rho])$ about the uniform fluid is exact to first order and also includes a subset of certain exact terms to all higher orders, specifically those terms which may be derived from $c_0^{(2)}$ according to the hierarchy relation

$$\int d\mathbf{r}_3 \cdots \int d\mathbf{r}_n c_0^{(n)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_n; \rho_0) = \frac{\partial^{n-2}}{\partial \rho_0^{n-2}} c_0^{(2)}(|\mathbf{r}_1 - \mathbf{r}_2|; \rho_0). \quad (13)$$

In contrast, the HNC approximation, which is commonly used in integral equation theories of fluid structure [22], corresponds to a first-order *truncation* of the expansion [23]. Second, the self-consistent choice of the density argument of the weight function in Eq. (9) can be shown to ensure that Fourier transforms of $c_0^{(3)}$ and higher-order DCF's derived from $c_{\text{WDA}}^{(1)}(\mathbf{r}; [\rho])$ are smooth functions of their wave vector arguments [16].

Summarizing to this point, given as input the uniform-state functions $c_0^{(1)}$ and $c_0^{(2)}$, Eqs. (8)–(10) and (12) now constitute a closed, self-consistent set of equations for the density $\rho(\mathbf{r})$, which may be solved numerically by an iterative procedure (see Sec. III A). Next we turn to a generalization of the above theory to fluid mixtures.

B. Density-functional theory of fluid mixtures

The theory described above for one-component systems may be generalized to mixtures in a manner completely analogous to that proposed in Ref. [19] in a different context, namely a theory of freezing. In the simplest case of binary mixtures, the grand potential and the intrinsic Helmholtz free energy are unique functionals of the two spatially varying one-particle densities $\rho_1(\mathbf{r})$ and $\rho_2(\mathbf{r})$ of the two components, and related according to [cf. Eq. (1)]

$$\Omega[\rho_1, \rho_2] = F[\rho_1, \rho_2] + \sum_{i=1}^2 \int d\mathbf{r} \rho_i(\mathbf{r}) [u_i(\mathbf{r}) - \mu_i], \quad (14)$$

where the subscript i labels the component. The fundamental variational principle [Eq. (2)] can also be shown to apply to the density of each component, so that at equilibrium

$$\frac{\delta \Omega[\rho_1, \rho_2]}{\delta \rho_i(\mathbf{r})} = 0, \quad i = 1, 2. \quad (15)$$

The substitution of Eqs. (4), (14), and the generalization of Eq. (5) for the ideal-gas free energy, i.e.,

$$F_{\text{id}}[\rho_1, \rho_2] = k_B T \sum_{i=1}^2 \int d\mathbf{r} \rho_i(\mathbf{r}) \{ \ln[\rho_i(\mathbf{r}) \lambda_i^3] - 1 \}, \quad (16)$$

into Eqs. (15) then leads to a pair of coupled Euler-Lagrange relations [cf. Eq. (6)], namely,

$$\rho_i(\mathbf{r}) = z_i \exp\{ -\beta u_i(\mathbf{r}) + c_i^{(1)}(\mathbf{r}; [\rho_1, \rho_2]) \}, \quad i = 1, 2 \quad (17)$$

where $c_i^{(1)}(\mathbf{r}; [\rho_1, \rho_2])$ denotes the one-particle DCF of component i .

The weighted-density approximation described above for the one-component $c^{(1)}$ now may be generalized to $c_i^{(1)}$ in the same manner as a similar generalization proposed in Ref. [19]. The generalized approximation is expressed by

$$c_{i\text{WDA}}^{(1)}(\mathbf{r}; [\rho]) \equiv c_{i0}^{(1)}(\bar{\rho}^{(i)}(\mathbf{r}), \mathbf{x}), \quad i = 1, 2 \quad (18)$$

where $c_{i0}^{(1)}$ is the uniform-fluid counterpart of $c_i^{(1)}$, \mathbf{x} is the average concentration of the mixture, and $\bar{\rho}^{(i)}(\mathbf{r})$ is the weighted density associated with component i , defined in terms of weight functions w_{ij} ($i, j = 1, 2$; $w_{12} = w_{21}$) according to

$$\bar{\rho}^{(i)}(\mathbf{r}) \equiv \sum_{j=1}^2 \int d\mathbf{r}' \rho_j(\mathbf{r}') w_{ij}(|\mathbf{r} - \mathbf{r}'|; \bar{\rho}^{(i)}(\mathbf{r})), \quad i = 1, 2. \quad (19)$$

Physically, $\bar{\rho}^{(i)}(\mathbf{r})$ may be interpreted as the *total* density of an effective locally uniform mixture, associated with component i at position \mathbf{r} , onto which the nonuniform fluid is mapped. For simplicity, the concentration of the effective mixture is taken to be the same for each component.

The weight functions are specified first by normalization conditions [cf. Eq. (10)]

$$\int d\mathbf{r} w_{ij}(\mathbf{r}) = 1, \quad i, j = 1, 2 \quad (20)$$

thus ensuring again that the approximation is exact in the limit of a uniform mixture $[\rho(\mathbf{r}) \rightarrow \rho_0]$, and second by requiring that the first functional derivatives of $c_i^{(1)}$ with respect to the densities yield the exact two-particle DCF's in the uniform limit, i.e. [cf. Eq. (11)],

$$\lim_{\rho(\mathbf{r}) \rightarrow \rho_0} \left[\frac{\delta c_{i\text{WDA}}^{(1)}(\mathbf{r}; [\rho_1, \rho_2])}{\delta \rho_j(\mathbf{r}')} \right] = c_{ij}^{(2)}(|\mathbf{r} - \mathbf{r}'|; \rho_0, \mathbf{x}), \quad i, j = 1, 2. \quad (21)$$

The substitution of Eqs. (18) and (19) into Eq. (21) leads to the following analytic forms for the weight functions [24] [cf. Eq. (12)]:

$$w_{ij}(\mathbf{r}; \rho_0, \mathbf{x}) = \frac{c_{ij}^{(2)}(\mathbf{r}; \rho_0, \mathbf{x})}{\partial c_{i0}^{(1)} / \partial \rho_0}. \quad (22)$$

Summarizing again, given as input the uniform-state functions $c_0^{(1)}$ and $c_{ij}^{(2)}$, Eq. (18), together with Eqs. (19), (20), and (22), may be solved for the densities $\rho_1(\mathbf{r})$ and $\rho_2(\mathbf{r})$ by a numerical iterative procedure (see Sec. III B). In the following section we proceed to an application of the theory described above to the specific case of hard-sphere fluids.

III. APPLICATION TO HARD-SPHERE FLUIDS NEAR HARD WALLS

In this section we study the density profiles of both one- and two-component hard-sphere fluids in the presence of a wall which is both smooth and hard in the sense described earlier. We locate the wall at $z=0$ and describe the corresponding external potential by

$$\begin{aligned} u(z) &= \infty, & z < \sigma/2 \\ u(z) &= 0, & z > \sigma/2 \end{aligned} \quad (23)$$

where σ is the hard-sphere diameter. For simplicity, we assume planar symmetry and concern ourselves here with spatial density variations only in the direction perpendicular to the wall. In making this assumption, we implicitly ignore the possibility of fluid structure in directions parallel to the wall.

A. One-component hard-sphere fluid

We first test the theory of Sec. II on the relatively simple (but well-studied) one-component hard-sphere fluid. Under the assumption of planar symmetry, the one-particle density is a function of z only and, from Eqs. (6) and (23), it may be expressed in the form

$$\rho(z) = \rho_0 \exp\{c^{(1)}(z; [\rho]) - c_0^{(1)}(\rho_0)\}, \quad (24)$$

where ρ_0 is the bulk fluid density far from the wall. Applying the weighted-density approximation described in Sec. II A to the functional $c^{(1)}$ in Eq. (24), $\rho(z)$ may be approximated by the relation

$$\rho(z) = \rho_0 \exp[c_0^{(1)}(\bar{\rho}(z)) - c_0^{(1)}(\rho_0)], \quad (25)$$

where the weighted density $\bar{\rho}(z)$ is defined by

$$\bar{\rho}(z) \equiv \int dz' \rho(z') \bar{w}(|z-z'|; \bar{\rho}(z)), \quad (26)$$

and where $\bar{w}(z)$ is a planar average of the weight function $w(r)$, i.e.,

$$\bar{w}(z) \equiv \int dx \int dy w(r). \quad (27)$$

For the required uniform-state functions $c_0^{(1)}$ and $c_0^{(2)}$, we adopt the expressions which conveniently follow from the analytic solution of the Percus-Yevick (PY) integral equation for hard spheres [25], explicitly,

$$c_0^{(1)} = -\frac{7\eta - 13\eta^2/2 + 5\eta^3/2}{(1-\eta)^3} + \ln(1-\eta), \quad (28)$$

$$c_0^{(2)}(x) = a + bx + cx^3, \quad x < 1 \quad (29)$$

$$c_0^{(2)}(x) = 0, \quad x > 1$$

where $\eta = (\pi/6)\rho_0\sigma^3$, $x = r/\sigma$, $a = -(1+2\eta)^2/(1-\eta)^4$, $b = 6\eta(1+\frac{1}{2}\eta)^2/(1-\eta)^4$, and $c = \frac{1}{2}\eta a$.

The integrals in Eq. (27) may be evaluated analytically, and they yield the result

$$\begin{aligned} \bar{w}(z) &= \frac{\pi}{\partial c_0^{(1)}/\partial \rho_0} [a(\sigma^2 - z^2) + \frac{2}{3}b(\sigma^3 - z^3) \\ &\quad + \frac{2}{5}d(\sigma^5 - z^5)], \quad z < \sigma \end{aligned} \quad (30)$$

where $a = -(1+2\eta)^2/(1-\eta)^4$, $b = 6\eta(1+\frac{1}{2}\eta)^2/(1-\eta)^4$, and $d = \frac{1}{2}\eta a$. Figure 1 shows an illustrative plot of $\bar{w}(z)$ vs z . Notice in particular that $\bar{w}(z)$ has a range σ equal to the range of the PY direct correlation function. This ensures that the range of nonlocality of the approximate $c^{(1)}$, that is, the range over which $c_{\text{WDA}}^{(1)}$ depends on $\rho(z)$, is accurately represented by the WDA.

Using this $\bar{w}(z)$, we next compute profiles of the density $\rho(z)$ and the weighted-density $\bar{\rho}(z)$ by the following iterative procedure. Beginning with initial estimates of $\rho(z)$ and $\bar{\rho}(z)$, a new estimate of $\bar{\rho}(z)$ is computed from Eqs. (26) and (30). We find it sufficient to begin with flat profiles, discretized with a step size of 0.02σ . The substitution of the new $\bar{\rho}(z)$ into Eq. (25) then immediately yields a new estimate of $\rho(z)$. Using the new $\rho(z)$ and $\bar{\rho}(z)$, the procedure is then iterated until it converges [i.e., until $\rho(z)$ and $\bar{\rho}(z)$ change insignificantly from one iteration to the next]. To obtain convergence, we find it essential to use the standard technique of mixing the old solution with the new, according to [26]

$$\rho_{\text{in}}^{n+1}(z) = \alpha \rho_{\text{out}}^n(z) + (1-\alpha) \rho_{\text{in}}^n(z). \quad (31)$$

Figure 2 shows a sample of the resulting density and weighted density profiles at bulk density $\rho_0\sigma^3 = 0.81$, together with the corresponding simulation data of Snook and Henderson [27]. Several features of the profiles may be noted. First, the density profile $\rho(z)$ vanishes as expected in the region $z < \sigma/2$ because of exclusion of the fluid by the wall (at $z=0$); moving away from the wall it oscillates with a period equal to the hard-sphere diameter σ . Second, the oscillations in the weighted density profile $\bar{\rho}(z)$ are much weaker than, and out of phase with, those of $\rho(z)$, a consequence of the exponential relation between $\rho(z)$ and $c_0^{(1)}(\bar{\rho}(z))$ [see Eq. (25)] and also the fact that $c_0^{(1)}$ is always negative. Finally, both $\rho(z)$ and $\bar{\rho}(z)$ asymptotically approach ρ_0 far from the wall; this trend serves as a numerical check on the computations.

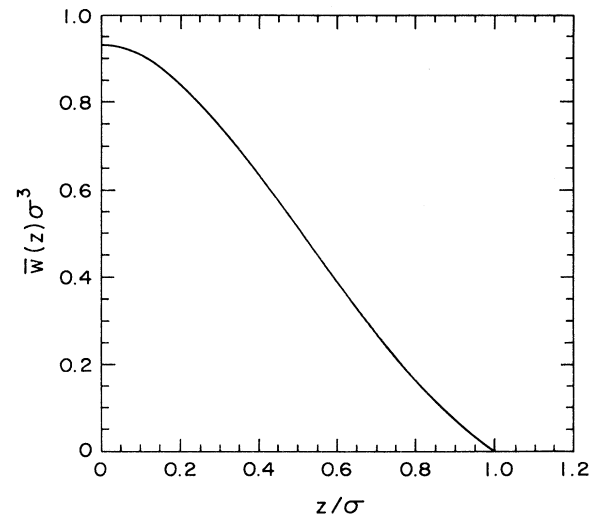


FIG. 1. Planar-averaged weight function for one-component hard-sphere fluid at bulk density $\rho_0\sigma^3 = 0.8$.

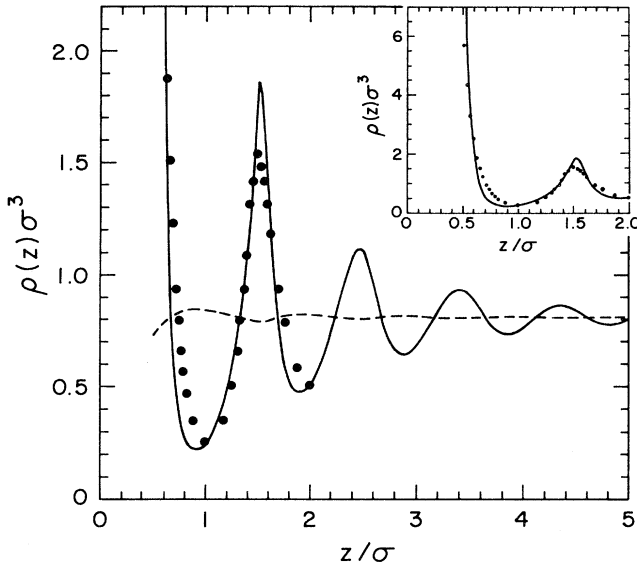


FIG. 2. Density profile of one-component hard-sphere fluid, of bulk density $\rho_0\sigma^3=0.81$, near a hard wall (at $z=0$). The solid and dashed curves are the theoretical results for the density and weighted-density profiles, respectively, and the symbols are the simulation data of Snook and Henderson [27].

In comparison with the simulation data, the theory accurately predicts the position of the first peak of the profile but it somewhat overpredicts the corresponding amplitude. The theory also overpredicts somewhat the peak in the density at contact [28], which reveals a notable limitation of the theory, namely its failure to satisfy the exact relation between the bulk pressure P of a fluid and the density at contact with a hard wall, i.e.,

$$\beta P = \rho(\sigma/2). \quad (32)$$

At present, we know of no explicit formula for the contact density predicted by our theory. It is important to note that some earlier density-functional theories [4–7,9,13] based on weighted-density approximations for F_{ex} , rather than for $c^{(1)}$, do indeed satisfy Eq. (32), albeit at the expense of greater computational complexity. On the other hand, some other theories, such as integral equation theories based on PY or HNC approximations [22], also fail to satisfy Eq.(32). A major feature of the present theory is that it appears to accurately capture at least the qualitative trends of the density profile, while demanding minimum computational effort. This takes on added importance when the theory is applied to the intrinsically more complex fluid mixtures, as we next proceed to demonstrate.

B. Binary hard-sphere mixtures

We now apply the theory to the more interesting and complex case of binary hard-sphere mixtures. The system may be completely characterized by the hard-sphere diameter ratio $\alpha \equiv \sigma_1/\sigma_2$, the concentration x , and the

bulk packing fraction η , related to the bulk density ρ_0 according to

$$\eta = \frac{\pi}{6} [x + (1-x)\alpha^3] \rho_0 \sigma_2^3. \quad (33)$$

Here we follow the conventions $\sigma_1 < \sigma_2$ ($\alpha < 1$) and $x = \rho_{02}/\rho_0$ (concentration of larger spheres). Equations (25)–(27) for the one-component fluid generalize quite naturally to

$$\rho_i(z) = \rho_{i0} \exp [c_{i0}^{(1)}(\bar{\rho}^{(i)}(z), x) - c_{i0}^{(1)}(\rho_{i0}, x)], \quad i=1,2 \quad (34)$$

$$\bar{\rho}^{(i)}(z) = \sum_{j=1}^2 \int dz' \rho_j(z') \bar{w}_{ij}(|z-z'|; \bar{\rho}^{(i)}(z), x), \quad i=1,2 \quad (35)$$

and

$$\bar{w}_{ij}(z) \equiv \int dx \int dy w_{ij}(r), \quad (36)$$

where ρ_{i0} is the density of component i in the bulk. For the required uniform-state functions $c_0^{(1)}$ and $c_{ij}^{(2)}$, we adopt the expressions which follow from Lebowitz's analytic solution [29] of the PY integral equation for hard-sphere mixtures. Evaluating the integrals in Eq. (36), we obtain

$$\bar{w}_{11}(z) = \frac{\pi}{\partial c_{10}^{(1)}/\partial \rho_0} [a_1(\sigma_1^2 - z^2) + \frac{2}{3}b_1(\sigma_1^3 - z^3) + \frac{2}{3}d(\sigma_1^5 - z^5)], \quad z < \sigma_1 \quad (37)$$

$$\bar{w}_{12}(z) = \frac{\pi}{\partial c_{10}^{(1)}/\partial \rho_0} [a_1(\sigma_{12}^2 - z^2) + \frac{2}{3}b\sigma_1^3 + 2d\lambda\sigma_1^4 + \frac{2}{3}d\sigma_1^5], \quad z < \sigma_{12} \quad (38)$$

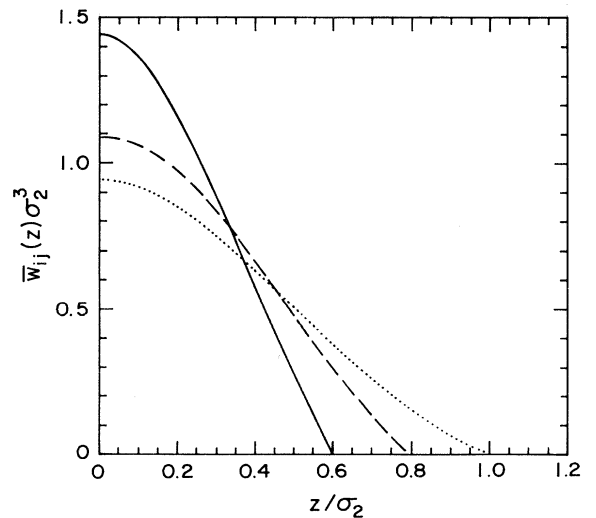


FIG. 3. Planar-averaged weight functions for binary hard-sphere mixture at diameter ratio $\alpha=0.6$, concentration $x=0.5$, and bulk packing fraction $\eta=0.4$. The solid, dashed, and dotted curves correspond, respectively to \bar{w}_{11} , \bar{w}_{12} , and \bar{w}_{22} .

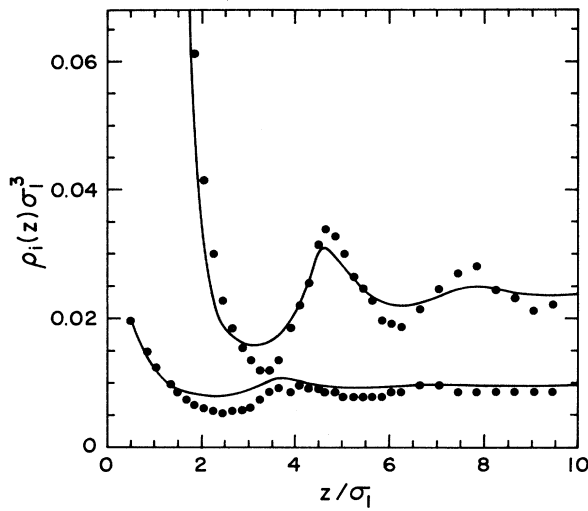


FIG. 4. Density profiles of a binary hard-sphere mixture near a hard wall at diameter ratio $\alpha = \frac{1}{3}$, concentration $x = 0.2856$, and bulk packing fraction $\eta \equiv \pi[x + (1-x)\alpha^3]\rho_0\sigma_2^3/6 = 0.3435$. The curves are the theoretical results—the bottom curve $\rho_1(z)$, the density of *smaller* spheres, and the top curve $\rho_2(z)$ —and the symbols are the simulation data given in Fig. 8 of Tan *et al.* [10].

$$\bar{w}_{22}(z) = \frac{\pi}{\partial c_{20}^{(1)}/\partial \rho_0} [a_2(\sigma_2^2 - z^2) + \frac{2}{3}b_2(\sigma_2^3 - z^3) + \frac{2}{3}d(\sigma_2^5 - z^5)], \quad z < \sigma_2 \quad (39)$$

where $\lambda = \frac{1}{2}(\sigma_2 - \sigma_1)$, $\sigma_{12} = \frac{1}{2}(\sigma_1 + \sigma_2)$, and the coefficients a_i , b_i , b , and d are functions of η , α , and x , given explicitly in Ref. [29]. Figure 3 shows illustrative plots of the planar-averaged weight functions. Again it is important to notice that each weight function has a range

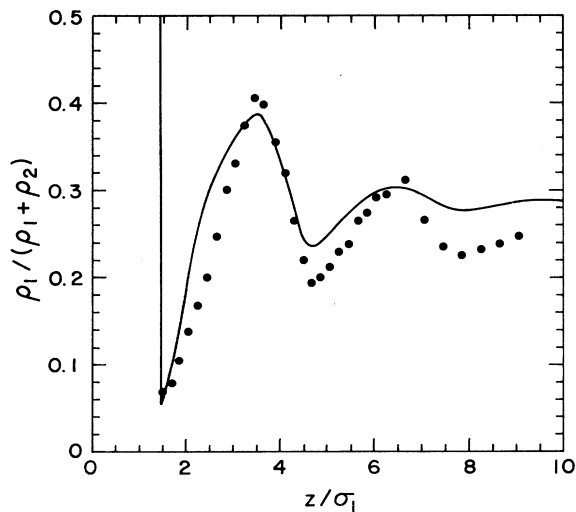


FIG. 5. Concentration profile (of *smaller* spheres) corresponding to Fig. 4.

equal to that of its corresponding DCF. Using these $\bar{w}_{ij}(z)$, we compute profiles of the densities $\rho_i(z)$ and weighted-densities $\bar{\rho}_i(z)$ by the same type of iterative procedure as described above for the one-component case.

Figure 4 shows a sample of the resulting density profiles together with the corresponding simulation data of Tan *et al.* [10]. As in the one-component case (Fig. 2), the theory again accurately predicts the periodicity of the oscillations in the density profiles, but is less accurate in predicting the amplitudes and contact values. Figure 5 shows the corresponding concentration profile; it clearly exhibits the phenomenon of surface segregation, with the density of the larger spheres exceeding that of the smaller spheres near the wall. The origin of this phenomenon in our theory may be traced to the differing ranges of the weight functions associated with each of the two components and the different magnitudes of the functions $c_{10}^{(1)}$ and $c_{20}^{(1)}$.

IV. SUMMARY AND CONCLUSIONS

In summary, we have presented a density-functional theory of nonuniform fluid mixtures, designed primarily for the study of interfacial phenomena. The theory is parameter free and is based on a weighted-density approximation for the one-particle direct correlation functions, which enter in the Euler-Lagrange relations for the one-particle density profiles of the fluid. It requires as input only the one- and two-particle direct correlation functions of the corresponding uniform system. A significant strength of the theory compared with earlier related density-functional theories is its relative computational simplicity.

We have tested this approach by applying it to both a one-component hard-sphere fluid and a binary hard-sphere mixture near a hard wall, modeled as a structureless, impenetrable boundary. Comparison of numerical results for the density and concentration profiles with available simulation data indicates that the main qualitative features of the profiles are predicted satisfactorily, although some quantitative discrepancies exist. Notably, the theory fails to satisfy the exact relation between the bulk pressure and the density at contact. We note, however, that satisfaction of this important relation might be ensured by introducing free parameters into the theory, an option we mention for future consideration.

Beyond the relatively idealized case of hard-sphere fluids near a hard wall, the theory may also be straightforwardly applied to study the structure of other simple fluids (e.g., Lennard-Jones or soft-sphere fluids and mixtures) near walls or in confined geometries [30] (e.g., slits, cylindrical or spherical pores, etc.) with various wall-fluid potentials. Finally, an important issue is whether the theory can accurately describe wetting behavior [31]. Although we do not address this issue here, we note, on the basis of the higher-order terms included by the WDA in the Taylor-series expansion of $c^{(1)}$ (see Sec. II A), that any predictions of the theory are expected to differ at least from those of standard integral equation theories (e.g., theories based on HNC or PY approximations).

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