

# On the Mean Field Treatment of Attractive Interactions in Nonuniform Simple Fluids<sup>†</sup>

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We study thermodynamic and structural properties of a Lennard-Jones liquid at a state very close to the triple point as the radius of a hard sphere solute is varied. Oscillatory profiles arise for small, molecular sized radii, whereas for large radii smooth interfaces with a “drying layer” of low vapor density near the solute are seen. We develop a quantitative theory for this process using a new mean field treatment where the effects of attractive interactions are described in terms of a self-consistently chosen effective single particle field. We modify the usual simple molecular field approximation for the effective field in a very natural way, so that exact results (consistent with a given accurate equation of state for the uniform fluid) arise in the “hydrostatic limit” of very slowly varying interfaces. Very good agreement with the results of computer simulations for a wide range of solute radii are found.

## 1. Introduction

In this paper, we are concerned with the interplay between oscillatory excluded volume correlations and the formation of smooth liquid–vapor interfaces in simple liquids. Broadly speaking, the former arise because the harshly repulsive molecular cores cannot overlap, whereas the latter are associated with the longer ranged and more slowly varying attractive intermolecular interactions. The theoretical challenge is to develop a general approach that can naturally explain the complete range of behavior. Early in his career, Bruce Berne and co-workers<sup>1</sup> examined some of these issues in a pioneering simulation study of the effects of confining a Lennard-Jones (LJ) liquid–vapor system in a slit with a varying width. This is a long-standing and very general problem, with work extending back to the time of van der Waals, and some interesting questions remain even now.

Here we consider a simpler geometry where the different correlations manifest themselves in a particularly clear way. We study the density response and associated thermodynamic properties of a LJ liquid at a state very close to the triple point as the radius of a hard sphere solute is varied. Let  $S$  denote the radius of the *solute cavity* within which the centers of fluid particles are excluded. As is shown in recent computer simulations by Huang and Chandler<sup>2</sup> (HC), for small molecular sized  $S$  of order unity (with the usual LJ parameter  $\sigma$  as the unit of length), the induced density profile is highly oscillatory and resembles the radial distribution function of the uniform LJ fluid, with a large density maximum near the solute. However, for much larger  $S$ , the solute approaches a hard wall and the density response is very different: a “drying layer” of low vapor density forms near the wall, and the transition to the bulk liquid density occurs through an essentially unperturbed and smooth vapor–

liquid interface. In general, as  $S$  increases from molecular size, the contact value of the density profile decreases and mixed states with increasingly damped oscillations are seen.

We will develop a quantitative description of this process, generalizing ideas based on mean field theory that we have developed in a series of recent papers.<sup>3–7</sup> Consider first the qualitative physics. As pointed out by Widom,<sup>8</sup> in most typical configurations in the uniform LJ fluid, the attractive intermolecular forces on a given particle tend to cancel in pairs between oppositely situated particles. This leaves only the excluded volume correlations induced by the harshly repulsive forces, which are well approximated by those in a uniform *hard sphere reference system*. This cancellation argument should also apply, though somewhat less accurately, to a small hard sphere solute of the same molecular size in the LJ fluid. The density response to such a fixed particle should thus closely resemble the oscillatory radial distribution in the associated hard sphere reference model, with a density *maximum* at contact.

However, because the hard core solute provides no balancing attractive forces, as its radius increases, LJ particles near the solute will increasingly experience a net “uncanceled” or “unbalanced” attractive force directed *away* from the solute arising from neighboring particles situated farther away.<sup>3,4</sup> This unbalanced attractive interaction induces a second more slowly varying “interfacial component” in the density response that competes with the oscillatory excluded volume correlations and tends to produce a *lower* density near the solute. The final density profile results from the interplay between these components and depends on how close the thermodynamic state of the initial uniform LJ fluid is to coexistence and on the magnitude of the unbalanced force, clearly related in this case to the size of the hard core solute.

The quantitative theory behind these ideas makes use of a fundamental approximation: the attractive interactions are described by a general *mean* or *molecular field* (MF) approach

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in which the locally averaged effects of the attractive intermolecular interactions are replaced by an effective single particle potential. Because the attractive interactions are relatively slowly varying, it seems plausible that such an averaged description could often provide a useful simplification. Thus, in the present case, the structure of the nonuniform LJ system is approximated by that of a (hard sphere) reference fluid in an appropriately chosen *effective reference field* (ERF) comprised of two parts: the bare external field from the hard core solute and a much more slowly varying part describing the unbalanced attractive interactions.

Of course, there are inherent errors in the theory arising from the use of an ERF to describe the effects of attractive interactions. In addition, other errors can arise from the numerical determination of the properties of the reference fluid in the presence of the ERF. However, we have previously introduced a new and generally very accurate way of calculating the structure and thermodynamics of the reference fluid in the presence of a *general* external field, based on a locally optimized application of linear response theory.<sup>6,7</sup> Thus, the latter source of error is very small (as will be verified later in this paper), and the quantitative validity of the theory for the LJ-hard core solute system depends mainly on the choice of the ERF.

In our earlier studies of nonuniform fluids in a variety of different geometries, we obtained very good qualitative and often even quantitative accuracy<sup>4,5,7</sup> using the simplest possible mean or MF description of the ERF, given in eq 3 below. However, in the present case, where an essentially unperturbed vapor–liquid interface with a very large change in density can form at large  $S$ , the usual MF theory will yield shifted (mean field) values for the coexisting vapor and liquid densities. The main problem with the theory is not so much its description of the local density gradients but its predictions for the thermodynamic properties of the coexisting *bulk* phases. In this paper, we introduce a simple modification of the mean field expression for the ERF that incorporates information from an accurate equation of state for the *uniform* fluid. The modified expression for the ERF ensures that *exact* thermodynamic results (consistent with the given uniform fluid equation of state) are found in the “hydrostatic limit” of a very slowly varying ERF, and it gives in particular accurate results for the coexisting vapor and liquid densities.

Using this modified expression for the ERF, we obtain excellent agreement with the simulations of HC for the density response to the hard sphere solute for all values of  $S$  tested. HC have already shown that good qualitative agreement can be obtained using a simplified version of the mean field theory introduced by Lum, Chandler, and Weeks<sup>9</sup> (LCW). The LCW theory does not require detailed information about the intermolecular potential (and, hence, can be applied to drying transitions in more complicated liquids such as water) but empirically fits a few key quantities using experimental data for properties of the liquid–vapor system. The present results suggest that the full theory can be used for quantitative calculations as well in simple liquids, requiring only the intermolecular potential and an accurate bulk equation of state along with known properties of the hard sphere reference system.

## 2. Simple Molecular Field Approximation for the ERF

Fluid particles interact with a known external field  $\phi(\mathbf{r})$  from the hard core solute. We consider a grand ensemble with fixed chemical potential  $\mu^B$ , which determines  $\rho^B$ , the uniform fluid density far from the solute where  $\phi(\mathbf{r}) = 0$ . The LJ pair potential  $w(r) \equiv u_0(r) + u_1(r)$  is separated into rapidly and slowly varying

parts associated with the intermolecular *forces*,<sup>10</sup> so that all of the harshly repulsive forces arise from  $u_0$  and all of the attractive forces from  $u_1$ .

The structure of the nonuniform LJ system is related to that of a simpler *nonuniform reference fluid*,<sup>3–5</sup> with only repulsive intermolecular pair interactions  $u_0(r)$  (equal to the LJ repulsions) and a chemical potential  $\mu_0^B$  corresponding to the same bulk density  $\rho^B$  but in a different renormalized or ERF  $\phi_R(\mathbf{r})$ . (In the numerical calculations that follow, the soft-sphere reference fluid is approximated by a hard sphere fluid of appropriately chosen diameter, with the finite softness of  $u_0$  taken into account by the usual “blip function” expansion,<sup>11,12</sup> as described in detail in earlier work.<sup>6,7</sup> The errors introduced by this treatment of the reference fluid are very small, and for most purposes, the reference system can be thought of simply as a hard sphere system.)

What is the best choice for  $\phi_R(\mathbf{r})$ ? Because we want the reference fluid structure to approximate that of the full fluid to the extent possible, it seems reasonable to determine  $\phi_R(\mathbf{r})$  formally by the requirement that it produces a *local* (singlet) density at every point  $\mathbf{r}$  in the reference fluid equal to that of the full nonuniform LJ fluid:<sup>13</sup>

$$\rho_0(\mathbf{r};[\phi_R]) = \rho(\mathbf{r};[\phi]) \quad (1)$$

In practice, we will make approximate choices for  $\phi_R$  motivated by mean field ideas. The subscript 0 in eq 1 denotes the reference fluid, and the notation  $[\phi_R]$  indicates that all distribution functions are functionals of the appropriate external field.

We can derive a formally exact equation for such a  $\phi_R$  by subtracting the first equations of the YBG hierarchy<sup>12</sup> for the full and reference systems with  $\phi_R$  chosen so that eq 1 is satisfied.<sup>3–5</sup> The result appropriately focuses on *forces*<sup>8,10</sup> and can be written exactly as

$$-\nabla_1[\phi_R(\mathbf{r}_1) - \phi(\mathbf{r}_1)] = -\int d\mathbf{r}_2 \rho_0(\mathbf{r}_2|\mathbf{r}_1;[\phi_R])\nabla_1 u_1(r_{12}) \\ - \int d\mathbf{r}_2 \{ \rho(\mathbf{r}_2|\mathbf{r}_1;[\phi]) - \\ \rho_0(\mathbf{r}_2|\mathbf{r}_1;[\phi_R]) \} \nabla_1 w(r_{12}) \quad (2)$$

Here  $\rho_0(\mathbf{r}_2|\mathbf{r}_1;[\phi_R]) \equiv \rho_0^{(2)}(\mathbf{r}_1, \mathbf{r}_2;[\phi_R])/\rho_0(\mathbf{r}_1;[\phi_R])$  is the *conditional* singlet density, i.e., the density at  $\mathbf{r}_2$  given that a particle is fixed at  $\mathbf{r}_1$ .

To integrate this equation and obtain a simple expression for the effective field  $\phi_R$ , we make some physically motivated approximations. If we assume that eq 1 produces similar local environments for the (identical) repulsive cores in the two fluids, which then mainly determine density correlations through excluded volume effects, then when eq 1 is satisfied the conditional singlet densities in the two fluids should also be very similar. This suggests that the last term on the right side in eq 2 should be very small, at least at high densities where excluded volume correlations dominate. Moreover, the last term clearly vanishes at very low density where  $\phi_R = \phi$ .

If we ignore the last term entirely, we obtain an approximate equation for  $\nabla\phi_R$  suggested by Weeks et al.<sup>3</sup> We focus here on the even simpler *MF equation* that arises from further approximating the conditional singlet density  $\rho_0(\mathbf{r}_2|\mathbf{r}_1;[\phi_R])$  in the first term on the right side by the ordinary singlet density  $\rho_0(\mathbf{r}_2;[\phi_R])$ . This approximation is much better than one might at first suppose, because the main difference in these two functions occurs when  $\mathbf{r}_2$  is close to  $\mathbf{r}_1$  but then for small  $\mathbf{r}_{12}$  the multiplicative factor  $-\nabla_1 u_1(r_{12})$  (the *attractive* part of the LJ force) vanishes identically. The gradient  $\nabla_1$  can then be taken

outside the integral and the equation can be integrated. Choosing the constant of integration so that  $\phi_R^{\text{MF}}$  vanishes far from the solute where the density equals  $\rho^B$ , we obtain the simple MF equation<sup>4</sup> for the ERF:

$$\phi_R^{\text{MF}}(\mathbf{r}_1) - \phi(\mathbf{r}_1) = \int d\mathbf{r}_2 \rho_0(\mathbf{r}_2; [\phi_R^{\text{MF}}]) u_1(r_{12}) + 2\rho^B a \quad (3)$$

where

$$a \equiv -\frac{1}{2} \int d\mathbf{r}_2 u_1(r_{12}) \quad (4)$$

corresponds to the attractive interaction parameter  $a$  in the uniform fluid van der Waals equation, as discussed below.

A self-consistent solution of eq 3 must be found, because the ERF  $\phi_R^{\text{MF}}$  appears explicitly on the left side and implicitly on the right side through the dependence of the reference density  $\rho_0(r_2; [\phi_R^{\text{MF}}])$  on  $\phi_R^{\text{MF}}$ . As mentioned above, we have developed new and generally very accurate ways of calculating  $\rho_0(r; [\phi_R])$  for a given  $\phi_R$ . Because these methods have been described in some detail previously,<sup>6,7</sup> we will not review them here. Using these methods, it is straightforward to solve the MF equation (by iteration, for example) to determine the self-consistent  $\phi_R^{\text{MF}}$  and the associated density  $\rho_0(r; [\phi_R^{\text{MF}}])$ , which from eq 1 approximates that of the original LJ-hard core solute system.

Although the simple MF expression (3) often gives quite satisfactory results,<sup>4,5,7</sup> particularly for local density gradients, for quantitative accuracy in the present application, we require a better treatment of two phase coexistence. In the limit of a *uniform* system, eq 3 describes all effects of attractive interactions in terms of the *constant* parameter  $a$  as in the van der Waals equation. Indeed, the theory then reduces to the generalized van der Waals theory of Longuet-Higgins and Widom,<sup>14</sup> where one combines an accurate description of the uniform (hard sphere) reference system with the simple treatment of the attractive interactions in terms of the constant  $a$ . This very simple approximation captures much essential physics and gives a good qualitative description of the uniform fluid thermodynamic properties. To achieve quantitative agreement with bulk thermodynamic properties, one can replace the constant  $a$  by a *function*  $\alpha$  that depends (hopefully weakly, to the extent the van der Waals theory is reasonably accurate) on temperature and density.<sup>15</sup> We will adopt such a strategy here, modifying eq 3 so that it incorporates information from a given accurate bulk equation of state and gives exact results when  $\phi$  and  $\phi_R$  are very slowly varying.

Although the details differ, our method is similar in spirit to the procedure introduced in important work by van Swol and Henderson.<sup>16</sup> They modified the usual mean field description of attractive interactions in density functional theory<sup>17</sup> to ensure that accurate coexistence behavior is obtained in a density functional treatment of a square well fluid at a square well wall. The main idea behind both approaches is that, when repulsive forces are accurately described, relatively simple modifications of the van der Waals treatment of attractive forces can produce accurate thermodynamic and structural data in the limit of very slowly varying fields or in bulk phases. The modified theory combines the simplicity of mean field theory with an accurate description of two phase coexistence.

### 3. Constant Fields and Chemical Potential Changes

Consider first the important special case where the external field  $\phi$  is a *constant* everywhere. Because in the grand ensemble one encounters only the difference between the chemical

potential and the external field, the effect of such a field just amounts to a change in the chemical potential of the uniform LJ fluid from  $\mu^B$  to  $\mu^B - \phi$ , which then changes the bulk density.<sup>12,6</sup> Equation 3 then reduces to the simple MF *approximation* for the analogous field  $\phi_R$  (or the reference chemical potential change) that from eq 1 is supposed to produce the same density change in the uniform reference fluid. In general, there will be errors arising from the MF approximation even in this simple limit. However, if an accurate equation of state for the uniform fluid is known, we can calculate these density changes exactly, and this will suggest how to modify eq 3 so that it gives exact results for very slowly varying fields.

To that end, let  $\mu(\rho)$  denote the chemical potential as a function of density  $\rho$  for the uniform LJ fluid. (This also depends on the temperature, but we are interested in density variations along particular isotherms, so we will not indicate the temperature dependence explicitly.) We determine  $\mu(\rho)$  from the accurate 33-parameter equation of state given by Johnson et al.<sup>18</sup> This provides a very good global description of the stable liquid and vapor phases in the (cutoff and shifted) LJ fluid used in the simulations of HC and provides a smooth interpolation between by using analytic fitting functions. Thus, it naturally produces a modified “van der Waals loop” in the two phase region and seems quite appropriate for our use here in improving the simplest mean field or van der Waals description of the uniform fluid. One could alternately use the method of van Swol and Henderson<sup>16</sup> and achieve essentially identical results. If  $\phi(\rho)$  denotes the magnitude of the uniform external field that yields a particular density  $\rho$  when applied to the LJ system with chemical potential  $\mu^B$ , then its value is exactly given by

$$\phi(\rho) = \mu^B - \mu(\rho) \quad (5)$$

Using known properties of the hard sphere fluid, we also have essentially exact expressions for  $\mu_0(\rho)$ , the chemical potential as a function of density in the uniform reference fluid, and for the inverse function  $\rho_0(\mu)$ , giving the uniform reference density as a function of chemical potential. The analogous uniform reference field yielding the same density  $\rho$  as in eq 5 is then exactly given by

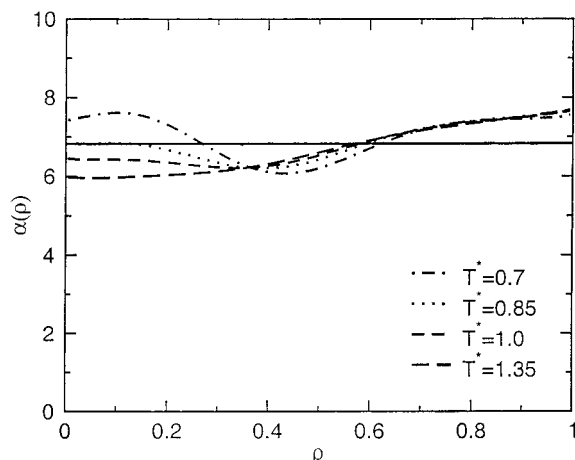
$$\phi_R(\rho) = \mu_0^B - \mu_0(\rho) \quad (6)$$

Finally, the exact  $\mu(\rho)$  and  $\mu_0(\rho)$  can be related through a function  $\alpha(\rho)$  defined so that

$$\mu(\rho) = \mu_0(\rho) - 2\rho\alpha(\rho) \quad (7)$$

Thus, the exact chemical potentials in the uniform LJ and reference systems are related in the same way as predicted by the simple mean field approximation of eq 3 except that the constant  $a$  in eq 4 is replaced by a (temperature and density dependent) function  $\alpha(\rho)$  chosen so that eq 7 holds. Because even the simplest mean field theory is qualitatively accurate, we expect that the ratio  $\alpha(\rho)/a$  will be of order unity and rather weakly dependent on density and temperature.

In Figure 1, we give the calculated effective  $\alpha(\rho)$  from the equation of state of Johnson et al.,<sup>18</sup> together with the value  $a$  of the van der Waals constant in eq 4 for a number of different isotherms. The value of the constant  $a = -2\pi \int_0^\infty dr r^2 u_1(r)$  seems to be a good overall compromise and may suffice for many qualitative purposes. Our derivation resulting from approximately integrating the force balance in eq 2 indicates why this expression with  $u_1$  giving all the attractive *forces* and integrated from 0 to infinity is appropriate. This gives much



**Figure 1.** Density and temperature dependence of the effective van der Waals parameter  $\alpha(\rho)$  of the truncated and shifted LJ fluid obtained from the accurate equation of state.<sup>18</sup> Also shown with a solid line is the prediction of the simple van der Waals mean field theory from eq 4.

better results than the earlier intuitive suggestion  $a' = -2\pi \int_{\sigma}^{\infty} dr r^2 w(r)$  which integrates only the *negative part* of the LJ potential from the point  $\sigma$  where the potential changes sign.<sup>19</sup> However, the true  $\alpha(\rho)$  exhibits some noticeable variations in density and temperature, illustrating the need for an accurate equation of state for quantitative accuracy. We note that some of the thermodynamic states plotted in Figure 1 are in the two phase region of the bulk LJ fluid and, thus, are not thermodynamically or sometimes even mechanically stable. The analytic equation of state provides a smooth interpolation through these states and produces behavior analogous to the van der Waals loop in the simplest mean field description. By introducing a function  $\alpha(\rho)$  that reduces to the *constant*  $a$  in the van der Waals theory, we hopefully have removed much of the (temperature and) density dependence otherwise arising from the loops, leaving the relatively smooth  $\alpha(\rho)$  suitable for interpolation.<sup>20</sup>

#### 4. Slowly Varying Fields and the Hydrostatic Density

These results for a strictly constant field can be used to determine simple and accurate approximations for very slowly varying fields. In particular, when the field  $\phi_R(\mathbf{r})$  varies so slowly that it is essentially *constant* over the range of a correlation length in the reference fluid, then the density  $\rho_0(\mathbf{r}_1; [\phi_R])$  at a given point  $\mathbf{r}_1$  is very accurately approximated<sup>21,6</sup> by the *local hydrostatic density*  $\rho^{r_1} \equiv \rho_0(\mu^{r_1})$ , the density of the *uniform* reference fluid at the shifted chemical potential  $\mu^{r_1} \equiv \mu_0^B - \phi_R(\mathbf{r}_1)$ . Because in the hydrostatic approximation the density at any given point responds only to the *local* value of the field, all of the equations defined above for constant fields and uniform densities also hold for very slowly varying fields and the corresponding hydrostatic densities.

By subtracting eq 5 from eq 6 and using eq 7, we then arrive at an equation analogous to the simple mean field equation (3) that gives essentially exact results in the hydrostatic limit of very slowly varying fields:

$$\phi_R(\mathbf{r}_1) = \phi(\mathbf{r}_1) - 2\rho^{r_1}\alpha(\rho^{r_1}) + 2\rho^B\alpha(\rho^B) \quad (8)$$

#### 5. Modified Molecular Field Equation

We now compare this exact result to the hydrostatic limit of the simple mean field equation (3). It is easy to see that this takes the same form as eq 8 except that the function  $\alpha(\rho)$  is

replaced by the constant  $a$ . Our goal is to modify eq 3 so that in the hydrostatic limit it reduces exactly to eq 8, while still giving reasonable results for more rapidly varying fields.

There is no unique way to do this, but the following simple prescription seems most natural and gives our final result, which we will call the *modified molecular field* (MMF) approximation for the ERF:

$$\phi_R(\mathbf{r}_1) - \phi(\mathbf{r}_1) = \frac{\alpha(\rho^{r_1})}{a} \int d\mathbf{r}_2 \rho_0(\mathbf{r}_2; [\phi_R]) u_1(r_{12}) + 2\rho^B\alpha(\rho^B) \quad (9)$$

Thus, the MF integral in eq 3 is multiplied by a factor  $\alpha(\rho^{r_1})/a$  of order unity that depends on  $\mathbf{r}_1$  through the dependence of the hydrostatic density  $\rho^{r_1}$  on the local value of the field  $\phi_R(\mathbf{r}_1)$ , and the constant of integration  $2\rho^B a$  is replaced by the appropriate limiting value of the modified integral. Note that the hydrostatic density  $\rho^{r_1}$  remains smooth and relatively slowly varying even when  $\phi_R(\mathbf{r}_1)$  contains a hard core. The nonlocal oscillatory excluded volume correlations that can exist in the full density  $\rho_0(\mathbf{r}_1; [\phi_R])$  do not appear in  $\rho^{r_1}$  because of the strictly local response to  $\phi_R$ .

The next sections report results for the structure and thermodynamics of the LJ-hard core solute system studied by HC with the ERF determined from eq 9. We use methods based on generalized linear response theory<sup>6,7</sup> to determine the structure of the nonuniform reference fluid.

## 6. Results

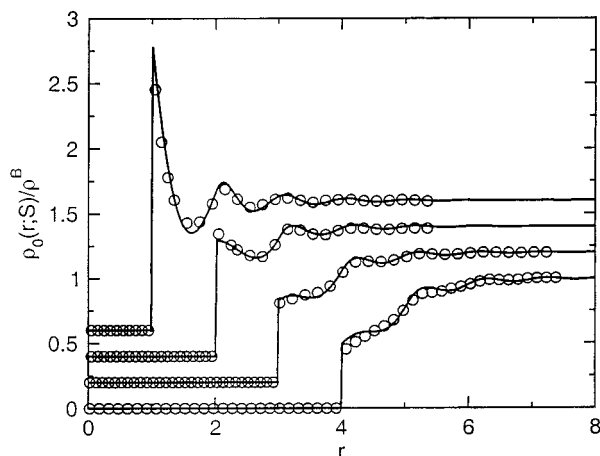
**6.1. Structure.** To make contact with the work of HC, we study the LJ liquid at a state near the triple point with  $\rho^B = 0.70$  and  $T = 0.85$  in the presence of a hard sphere solute. (We use the standard LJ reduced units.) By definition the solute centered at the origin interacts with the LJ particles through the hard core potential:

$$\phi(r; S) = \begin{cases} \infty, & r \leq S \\ 0, & r > S \end{cases} \quad (10)$$

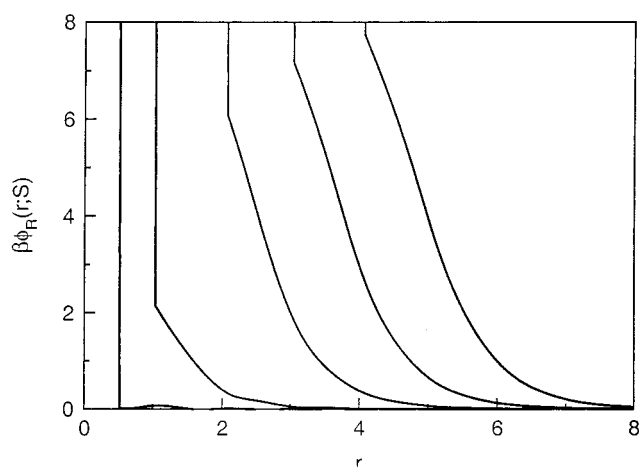
The MMF theory discussed above allows us to reduce this problem to that of the *reference* fluid in the presence of the effective field  $\phi_R(r; S)$  satisfying eq 9. By construction from eq 1, the density profile of the full LJ fluid subjected to the “bare” external field  $\phi(r; S)$  and the profile of the reference LJ fluid in the presence of the external field  $\phi_R(r; S)$  “dressed” by the attractive interactions are supposed to be identical to each other.

We have calculated *self-consistently* the ERF  $\phi_R(r; S)$  and the associated density response  $\rho_0(r; S)$  of the reference fluid, solving eq 9 by iteration. In Figure 2, we compare these results for the density profiles in the presence of the hard sphere solutes with  $S$  equal to 1.0, 2.0, 3.0, and 4.0 in reduced units with the simulation results<sup>2</sup> of the same LJ system by HC. There is very good agreement between theory and simulation.

Figure 3 shows the corresponding ERFs obtained in these calculations. For small solutes with  $S$  less than about 0.7, attractive interactions do not give rise to any substantial modification of the bare external field, as can be seen from the plot of  $\phi_R(r; S)$  for  $S = 0.5$ . (Clearly, for  $S = 0$ , there are no solute induced interactions of any kind and the profile reduces to the constant  $\rho^B$ ). However, the effects due to unbalanced attractions begin to become important even for  $S = 1.0$ , which is about the same size as the LJ core, and all larger sizes give rise to a very strong and relatively soft repulsion in  $\phi_R(r; S)$ .



**Figure 2.** Density profiles of the LJ fluid ( $T = 0.85$  and  $\rho^B = 0.70$ ) in the presence of the hard sphere solute with  $S = 1.0, 2.0, 3.0,$  and  $4.0$ . Circles denote simulation results.<sup>2</sup> Lines are results of the self-consistent approach based on the modified mean field determined from eq 9. For ease of viewing, the density profiles for  $S = 1.0, 2.0,$  and  $3.0$  have been shifted vertically by  $0.6, 0.4,$  and  $0.2$  units, respectively.

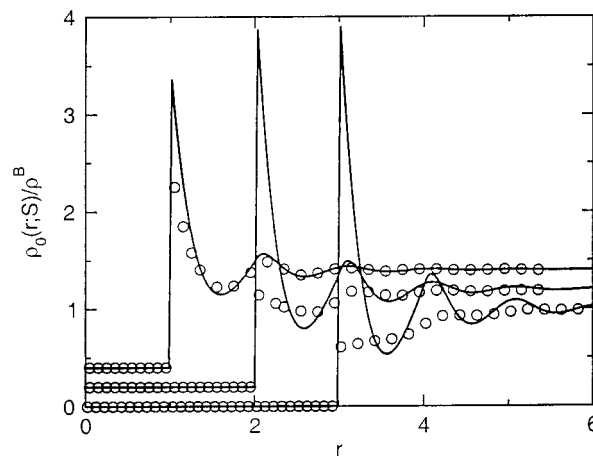


**Figure 3.** Self-consistent mean MF of the LJ fluid for the solute with  $S = 0.5, 1.0, 2.0, 3.0,$  and  $4.0$ , obtained from eq 9.

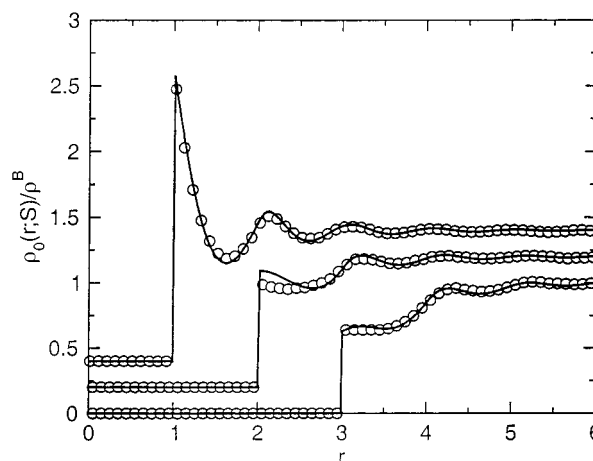
The corresponding density profiles show pronounced depletion near the surface of the solute, characteristic of surface induced drying.

To demonstrate the importance of the renormalization of the effective field, we show in Figure 4 the density profiles of the reference fluid in the presence of the *bare* external field  $\phi(r;S)$ , thus, neglecting all effects due to the attractions. These density profiles reflect the characteristic packing effects associated with excluded volume correlations, which result in a local ordering (or layering) of fluid particles next to the solute. We would also expect such behavior from the LJ system at very high temperatures, but for the state near the triple point considered here, the strong ordering is absent even though the density is high. The unbalanced attractive interactions generate an additional strong repulsive component in the ERF as shown in Figure 3. This is capable of destroying the ordering and effectively places a layer of the metastable low-density vapor next to the solute's surface for states near coexistence.

In the self-consistent theory discussed above, we make approximations both in determining the ERF and in calculating the structure of the reference fluid in the presence of a given ERF. To make sure that in the present case the agreement with the simulation results for the LJ fluid given in Figure 2 is not the result of some fortuitous cancellation of errors associated



**Figure 4.** Predicted density profiles of the *reference* LJ fluid in the presence of the *bare* external field  $\phi(r;S)$  for the solute with  $S = 1.0, 2.0,$  and  $3.0$  (lines). For ease of viewing, the density profiles for  $S = 1.0$  and  $2.0$  have been shifted vertically by  $0.4$  and  $0.2$  units, respectively. Circles denote simulation results of the *full* LJ fluid.<sup>2</sup>



**Figure 5.** Density profiles of the *reference* LJ fluid in the presence of the self-consistently determined mean MF given by eq 9 for the solute with  $S = 1.0, 2.0,$  and  $3.0$ . For ease of viewing, the density profiles for  $S = 1.0$  and  $2.0$  have been shifted vertically by  $0.4$  and  $0.2$  units, respectively.

with our treatment of the reference fluid, we have carried out computer simulations<sup>6</sup> of the *reference* fluid structure in the presence of the self-consistently determined ERFs. This directly tests our theory<sup>6,7</sup> for reference system correlations in the presence of a given external field. Results of these calculations are shown in Figure 5 and demonstrate a very good agreement between our theory for the reference fluid structure<sup>6,7</sup> and the simulations.

**6.2. Solvation Free Energy.** Another quantity of great interest is the free energy of the nonuniform system. This is the main focus of attention in density functional theory,<sup>17</sup> where one tries to approximate the “intrinsic” free energy as a functional of the nonuniform singlet density. The equilibrium density and value of the free energy for a given external field and set of intermolecular interaction potentials is determined by minimizing an appropriate free energy functional of the density and those potentials.<sup>12</sup> By starting from the free energy, certain exact *sum rules* relating integrals of those correlation functions to the thermodynamic properties are automatically and consistently satisfied.<sup>17</sup> Of course consistency does not necessarily imply correctness—a poor functional will give consistently poor values for the thermodynamic properties—and the physical implications

of particular approximations made in DFT can sometimes be hard to understand.

In contrast, our approach focuses first on the liquid *structure*, as do most integral equation methods. We believe this permits physical insight to play a more direct role. However, because we can determine the density response to an arbitrary external field, the free energy can be easily calculated from a coupling parameter type integration that connects some initial state (e.g., the bulk fluid) whose free energy is known to the final state as the field is varied. Of course, our structural predictions, though generally accurate, are not exact, and different routes to the same thermodynamic property can give different answers. Fortunately, in the present case, there is a very simple route to the free energy of the nonuniform LJ system that uses structural features that we know from simulations are accurately determined.

**6.3. Virial Route.** The basis for our calculation lies in the definition of the grand canonical free energy (thermodynamic potential) in the LJ fluid, which is related to the partition function  $\Xi$  through the following equation:

$$\Omega = -k_B T \ln \Xi \quad (11)$$

We also use the property that the partition function is the generating function for the density correlation functions; in particular, the density profile in the presence of a general field  $\phi$  is given by

$$\rho(\mathbf{r}; \mu^B, [\phi]) = k_B T \frac{\delta \ln \Xi(\mu^B, [\phi])}{\delta [\mu^B - \phi(\mathbf{r})]} \quad (12)$$

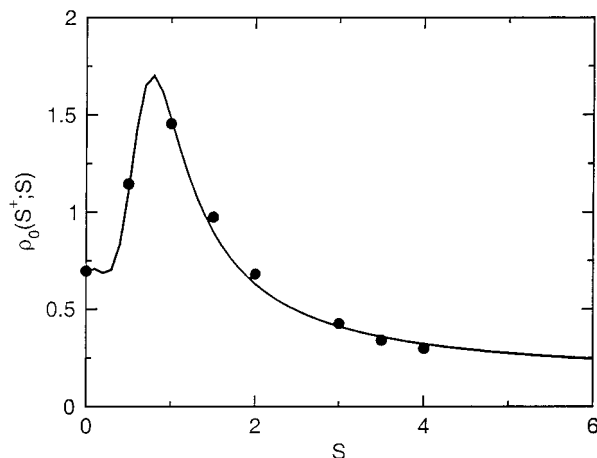
We now specialize to the hard core solute  $\phi(r; S)$  and introduce a coupling-parameter dependent external field  $\phi_\lambda(\mathbf{r}) \equiv \phi(\mathbf{r}/\lambda)$  with corresponding density  $\rho_\lambda(\mathbf{r}) \equiv \rho(\mathbf{r}; \mu^B, [\phi_\lambda])$ . This  $\lambda$  dependence corresponds to growing the range of the external field from zero at  $\lambda = 0$  to the full external field at  $\lambda = 1$ . This construction is the basis of scaled particle theory.<sup>22</sup> As is well-known, the free energy change for the hard core field then takes the particularly simple form

$$\beta \Delta \Omega_s = 4\pi S^3 \int_0^1 d\lambda \lambda^2 \rho_\lambda(\lambda S^+) \quad (13)$$

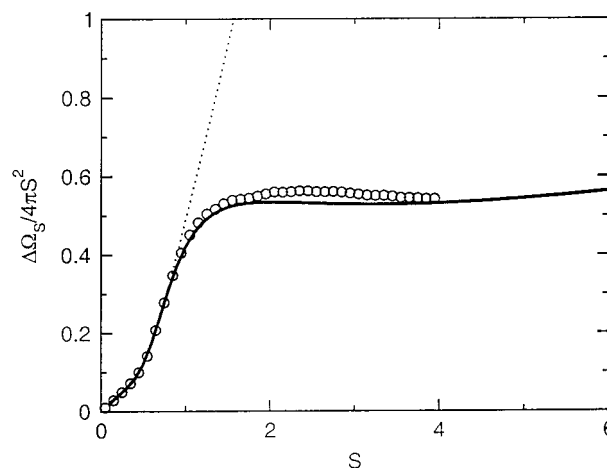
which requires only the *contact value*  $\rho_\lambda(\lambda S^+)$  of the density profile. This is very accurately given by the theory described above. To use this “virial route”, we can discretize the  $\lambda$  integration and calculate the density profile for several values of  $\lambda$  at the fixed bulk chemical potential  $\mu^B$ .

In Figure 6, we plot the contact values as a function of the size  $S$ . For solvent fluids with purely repulsive interactions, such as the hard sphere fluid, the contact value monotonically increases because the fluid particles increasingly tend to order next to the surface of the solute and the density profile always has a sharp peak at contact. A nonmonotonic dependence of the contact values is a very characteristic feature of surface induced drying and has been predicted for the case of water in contact with hydrophobic objects by Stillinger<sup>23</sup> and in the present case by the LCW theory.

Using eq 13, we obtain the dependence of solvation free energy on the size of the hard sphere solute. The free energy per unit surface area of the solute  $\Delta \Omega_s / 4\pi S^2$  we obtain is shown in Figure 7. For small solutes, attractive interactions do not play an important role and the solvation free energy agrees well with a pure hard sphere model, which completely neglects attractions by using the bare solute potential, as shown by the dotted line. At the solute size of about 0.7, the behavior changes drastically and the reduced free energy rapidly crosses over to the



**Figure 6.** Dependence of the contact value of the density profiles of the LJ fluid on the cavity size  $S$ . Circles denote results of simulations.<sup>2</sup> The line is the result of the present theory.



**Figure 7.** Dependence of the solvation free energy on the cavity size  $S$ . Circles denote results of simulations.<sup>2</sup> Lines are obtained from eq 13 by using the results of the mean field eq 9 (solid) and by neglecting the mean field (dotted).

practically constant plateau in agreement with the simulation results. The small slope of the curves in Figure 7 for large  $S$  can be understood by separating the free energy into volume ( $V_s = 4\pi S^3/3$ ) and surface ( $A_s = 4\pi S^2$ ) contributions<sup>2</sup> as discussed by HC:

$$\Delta \Omega_s \approx V_s p^B + A_s \gamma_s \quad (14)$$

The first term in this expression corresponds to the work required to remove liquid particles from the volume occupied by the solute, where  $p^B$  is the bulk liquid pressure, and is very small for the values of  $S$  considered here. The second term determines the cost of forming the liquid-solute interface and is proportional to the interface tension  $\gamma_s$ , which is essentially independent of the solute size for large solutes.

## 7. Conclusions

The theory described here combines an accurate treatment of correlations induced in the nonuniform hard sphere reference system by a general external field with a mean field description of the effects of attractive interactions in terms of an appropriately chosen ERF. We have shown here how a relatively simple modification of the simple MF expression for the ERF can ensure that accurate results are found in the hydrostatic limit

of very slowly varying fields and for properties of coexisting bulk phases. Of course there are important limitations inherent in any mean field treatment of long wavelength fluctuations, such as those seen near the critical point or the capillary wave fluctuations of the liquid–vapor interface.<sup>12</sup> However, in many other applications where such fluctuations do not play an important role, mean field theory provides a simple and often very accurate starting point. In future work, we will discuss properties of the liquid–vapor interface and of fluids confined in slits and cylinders from this perspective.

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