On the mean field treatment of attractive interactions in nonuniform simple fluids

Kirill Katsov
Department of Physics, University of Washington
P.O. Box 351560, Seattle, WA 98195-1560

John D. Weeks
Institute for Physical Science and Technology, and
Department of Chemistry and Biochemistry
University of Maryland, College Park, MD 20742

Abstract

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 while 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 while 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 coworkers [1] 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 shown in recent computer simulations by Huang and Chandler [2] (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 [3, 4, 5, 6, 7]. Consider first the qualitative physics. As pointed out by Widom [8], 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 \textit{maximum} at contact.

However, since the hard core solute provides no balancing attractive forces, as its radius increases, LJ particles near the solute will increasingly experience a net “uncancelled” or “unbalanced” attractive force directed \textit{away} from the solute arising from neighboring particles situated farther away \cite{3, 4}. 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 \textit{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 \textit{mean} or \textit{molecular field} approach in which the locally averaged effects of the attractive intermolecular interactions are replaced by an effective single particle potential. Since 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 \textit{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 \textit{general} external field, based on a locally optimized application of linear response theory \cite{6, 7}. 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 [4, 5, 7] using the simplest possible mean or molecular field 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 molecular field 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 insures 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 [9] (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 like 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 so that all the harshly repulsive forces arise from $u_0$ and all the attractive forces from $u_1$.

The structure of the nonuniform LJ system is related to that of a simpler nonuniform reference fluid, with only repulsive intermolecular pair interactions $u_0(r)$ (equal to the LJ repulsions) and a chemical potential $\mu_0$ corresponding to the same bulk density $\rho$, but in a different renormalized or effective reference field $\phi_R(r)$. (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 as described in detail in earlier work. 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 $\phi_R(r)$? Since we want the reference fluid structure to approximate that of the full fluid to the extent possible, it seems reasonable to determine $\phi_R(r)$ formally by the requirement that it produces a local (singlet) density at every point $r$ in the reference fluid equal to that of the full nonuniform LJ fluid:

$$\rho_0(r; [\phi]) = \rho(r; [\phi]).$$

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 for the full and reference systems with $\phi_R$ chosen so that Eq. (1) is satisfied. The result appropriately focuses on forces and can be written exactly as

$$- \nabla_1 [\phi_R(r_1) - \phi(r_1)] = - \int dr_2 \rho_0(r_2|r_1; [\phi_R]) \nabla_1 u_1(r_{12})$$

$$- \int dr_2 \{\rho(r_2|r_1; [\phi]) - \rho_0(r_2|r_1; [\phi_R])\} \nabla_1 w(r_{12}).$$

Here $\rho_0(r_2|r_1; [\phi_R]) \equiv \rho_0^{(2)}(r_1, r_2; [\phi_R])$ is the conditional singlet density, i.e., the density at $r_2$ given that a particle is fixed at $r_1$.

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, Selinger and Broughton [3]. We focus here on the even simpler molecular field equation that arises from further approximating the conditional singlet density $\rho_0(r_2| r_1; [\phi_R])$ in the first term on the right side by the ordinary singlet density $\rho_0(r_2; [\phi_R])$. This approximation is much better than one might at first suppose, since the main difference in these two functions occurs when $r_2$ is close to $r_1$, but then for small $r_{12}$ 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 $\phi^{MF}_R$ vanishes far from the solute where the density equals $\rho^B$, we obtain the simple molecular field (MF) equation [4] for the ERF:

$$\phi^{MF}_R(r_1) - \phi(r_1) = \int d r_2 \rho_0(r_2; [\phi^{MF}_R]) u_1(r_{12}) + 2 \rho^B a,$$

where

$$a \equiv -\frac{1}{2} \int d r_2 u_1(r_{12})$$

(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, since the ERF $\phi^{MF}_R$ appears explicitly on the left side and implicitly on the right side through the dependence of the reference density $\rho_0(r_2; [\phi^{MF}_R])$ on $\phi^{MF}_R$. As mentioned above, we have developed new and generally very accurate ways of calculating $\rho_0(r; [\phi_R])$ for a given $\phi_R$. Since these methods have been described in some detail previously [6, 7], we will not review them here. Using these methods, it is straightforward to solve the molecular field equation (by iteration, for example) to determine the self-consistent $\phi^{MF}_R$ and the associated density $\rho_0(r; [\phi^{MF}_R])$, which from Eq. (1) approximates that of the original LJ-hard core solute system.
While the simple molecular field expression (3) often gives quite satisfactory results [4, 5, 7], 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 [14], 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 [15]. 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.

While the details differ, our method is similar in spirit to the procedure introduced in important work by van Swol and Henderson [17]. They modified the usual mean field description of attractive interactions in density functional theory 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. Since 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 [12, 6]. Equation (3) then reduces to the simple molecular field approximation for
the analogous field $\phi_R$ (or the reference chemical potential change) that from
Eq. (4) is supposed to produce the same density change in the uniform reference fluid. In general there will be errors arising from the molecular field 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 \cite{18} given by Johnson, et al. 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 in 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 \cite{17} 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. (6) holds. Since 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 Fig. 1 we give the calculated effective $\alpha(\rho)$ from the equation of state of Johnson et al. [18], 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 $a = -2\pi \int_0^\infty r^2 u_1(r) \, dr$ 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 better results than the earlier intuitive suggestion $a' = -2\pi \int_\sigma^\infty r^2 w(r) \, dr$, which integrates only the negative part of the LJ potential from the point $\sigma$ where the potential changes sign [19]. 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 Fig. 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 [20].

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 by [21, 6] by the local hydrostatic density $\rho^{\star 1} \equiv \rho_0(\mu_0^{\star 1})$, the density of the uniform reference fluid at the shifted
chemical potential \( \mu_{\text{r}}(r_1) \equiv \mu_0^B - \phi_R(r_1) \). Since in the hydrostatic approximation the density at any given point responds only to the local value of the field, all 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. (3) 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:

\[
\phi_R(r_1) = \phi(r_1) - 2\rho^r_1 \alpha(\rho^r_1) + 2\rho^B \alpha(\rho^B).
\] (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:

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

Thus the molecular field integral in Eq. (3) is multiplied by a factor \( \alpha(\rho^r_1)/a \) of order unity that depends on \( r_1 \) through the dependence of the hydrostatic density \( \rho^r_1 \) on the local value of the field \( \phi_R(r_1) \), 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 \( \phi_R(r_1) \) 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 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 (6, 7) 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. (4). By construction from Eq. (4), 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. (4) by iteration. In Fig. 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 [2] of the same LJ system by HC. There is very good agreement between theory and simulation.

Figure 3 shows the corresponding ERF’s 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 iterations 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 $\phi_R(r; S)$. 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 Fig. 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 order-
ing (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 Fig. 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 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 Fig. 2 is not the result of some fortuitous cancellation of errors associated with our treatment of the reference fluid, we have carried out computer simulations of the reference fluid structure in the presence of the self-consistently determined ERF’s. This directly tests our theory for reference system correlations in the presence of a given external field. Results of these calculations are shown in Fig. 5 and demonstrate a very good agreement between our theory for the reference fluid structure 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, 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. 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. 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, since 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:

$$\Omega = -k_B T \ln \Xi.$$  \hfill (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

$$\rho(r; \mu_B, [\phi]) = k_B T \delta \ln \Xi(\mu_B, [\phi]) \delta[\mu - \phi(r)].$$  \hfill (12)

We now specialize to the hard core solute $\phi(r; S)$ and introduce a coupling-parameter dependent external field $\phi_\lambda(r) \equiv \phi(r/\lambda)$ with corresponding density $\rho_\lambda(r) \equiv \rho(r; \mu_B, [\phi_\lambda])$. 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 [22]. As is well-known, the free energy change for the hard core field then takes the particularly simple form:

$$\beta \Delta \Omega_S = 4\pi S^d \int_0^1 d\lambda \lambda^2 \rho_\lambda(\lambda S^+),$$  \hfill (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 $\mu_B$. 

13
In Fig. 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 [23] 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 Fig. 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 practically constant plateau in agreement with the simulation results. The small slope of the curves in Fig. 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 [2] as discussed by HC:

$$\Delta \Omega_S \approx V_S p^B + A_S \gamma_S.$$  \hspace{1cm} (14)

The first term in this expression corresponds to the work required to remove liquid particles from the volume occupied 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 how relatively simple modification of the simple molecular field 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. 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.

It is a pleasure to dedicate this paper to Bruce Berne on the happy oc-
casion of his 60th birthday. This work was supported in part by NSF Grant
No. CHE9528915.

References

[1] Rao, M.; Berne, B. J.; Percus, J. K.; Kalos, M. H. J. Chem. Phys. 1979, 71, 3802.
[2] Huang, D. M.; Chandler, D. Phys. Rev. E 2000, 61, 1501.
[3] Weeks, J. D.; Selinger, R. L. B.; Broughton, J. Q. Phys. Rev. Lett. 1995, 75, 2694.
[4] Weeks, J. D.; Vollmayr, K.; Katsov, K. Physica A 1997, 244, 461.
[5] Weeks, J. D.; Katsov, K.; Vollmayr, K. Phys. Rev. Lett. 1998, 81, 4400.
[6] Katsov, K.; Weeks, J. D. Phys. Rev. Lett. 2001, 86, 440.
[7] Vollmayr-Lee, K.; Katsov, K.; Weeks, J. D. J. Chem. Phys. 2001, 114, 416.
[8] Widom, B. Science 1967, 157, 375.
[9] Lum, K.; Chandler, D.; Weeks, J. D. J. Phys. Chem. B 1999, 103, 4570.
[10] Weeks, J. D.; Chandler, D.; Andersen, H. C. J. Chem. Phys. 1971, 54, 5237.
[11] Andersen, H. C.; Weeks, J. D.; Chandler, D. Phys. Rev. A 1971, 4, 1597.
[12] Hansen, J. P.; McDonald, I. R. *Theory of Simple Liquids*; Academic Press: London, 1986.

[13] Sullivan, D.; Stell, G. *J. Chem. Phys*. **1978**, *69*, 5450.

[14] Longuet-Higgins, H. C.; Widom, B. *Mol. Phys.* **1964**, *8*, 549.

[15] Weeks, J. D.; Broughton, J. Q. *J. Chem. Phys.* **1983**, *78*, 4197.

[16] For a general review see Evans, R. In *Fundamentals of Inhomogeneous Fluids*; Henderson, D., Ed.; Dekker: New York, 1992.

[17] van Swol, F.; Henderson, J. R. *Phys. Rev. A* **1991**, *43*, 2932.

[18] Johnson, J. K.; Zollweg, J. A.; Gubbins, K. E. *Mol. Phys.* **1993**, *78*, 591.

[19] For the cutoff and shifted LJ potential, $a = 6.83$ and $a' = 4.55$.

[20] Near the critical point much more sophisticated interpolation schemes are required. See, e.g., Fisher, M. E.; Shun-Yong, Z.; Upton, P. J. *Phys. Rev. B* **1999**, *59*, 14533.

[21] Percus, J. K. In *The Equilibrium Theory of Classical Fluids*; Frisch, H. L.; Lebowitz, J. L., Eds.; W.A. Benjamin: New York, 1964; p. II.33.

[22] Reiss, H.; Frisch, H. L.; Lebowitz, J. L. *J. Chem. Phys.* **1959**, *31*, 369.

[23] Stillinger, F. H. *J. Soln. Chem.* **1973**, *2*, 141.
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 \[18\]. Also shown with a solid line is the prediction of the simple van der Waals mean field theory from Eq. (4).
Figure 2: Density profiles of the LJ fluid ($T = 0.85$, $\rho^B = 0.70$) in the presence of the hard sphere solute with $S = 1.0$, 2.0, 3.0 and 4.0. Circles denote simulation results [2]. 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 molecular field of the LJ fluid for the solute with $S = 0.5, 1.0, 2.0, 3.0$ and $4.0$, obtained from Eq. (9).
Figure 4: 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 [2].
Figure 5: Density profiles of the reference LJ fluid in the presence of the self-consistently determined mean molecular field 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.
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 [2]. 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 [2]. Lines are obtained from Eq. (13) by using the results of the mean field Eqs. (11) (solid), and by neglecting the mean field (dotted).