Self-Consistent Treatment of Repulsive and Attractive Forces in Nonuniform Liquids

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Structural and thermodynamic properties of a nonuniform liquid are related to those of a reference fluid with purely repulsive intermolecular forces in an external field. A new equation for that field derived from the Yvon-Born-Green hierarchy permits a self-consistent description of correlations induced by the exact repulsive forces and a mean field treatment of the attractive forces. Predictions of the theory for drying effects at repulsive walls and for the liquid-vapor interface are compared to molecular dynamics simulations.

The dominant source of correlations in a dense uniform nonassociated liquid arises from the short-ranged harshly repulsive intermolecular forces [1,2]. As argued by Widom [3], in the isotropic environment of a dense liquid the vector sum of the attractive forces on a given particle essentially *cancels* in most typical configurations. This suggests a mean field picture where this cancellation is exact and correlations are induced solely by the repulsive intermolecular forces [3,4]. Indeed, repulsive force models have provided an accurate description of a great many properties of both simple and complex fluids [5].

However, some qualitatively new ideas are needed to understand properties of nonuniform liquids. Attractive forces must be treated more carefully, since their averaged effects clearly do not cancel by symmetry. The most difficult cases arise when *both* attractive and repulsive forces have important effects on the structure of a nonuniform fluid and over comparable length scales of order the molecular size. Examples discussed below include partial wetting and drying effects at walls, and the interface between a dense liquid and its vapor [6]. The basic problem is to take account of the new and substantial effects of attractive forces while still maintaining an accurate description of repulsive force correlations.

We introduce here a new theory of nonuniform fluids based on an analysis of the balance of forces [7] as expressed by the first equation of the exact Yvon-Born-Green (YBG) hierarchy [1]. To motivate the theory, first consider a dense uniform liquid. Highly nontrivial correlations on the molecular length scale arise in the dense but disordered environment of a liquid simply from the requirement that neighboring repulsive molecular cores cannot overlap. To describe these "excluded volume" correlations quantitatively it is useful to consider a *reference fluid* made up of particles with purely repulsive intermolecular forces identical to the repulsive forces in the real fluid of interest and *constrained to have the same (number) density ρ* [4]. This constraint ensures that typical local environments in the two fluids are similar: both fluids then have identical re-

pulsive cores at the same average separation determined by the fixed density. Excluded volume correlations in the reference fluid manifest themselves in the oscillatory behavior of the *conditional singlet density* $\rho_0(\mathbf{r}_2|\mathbf{r}_1)$—the density at $\mathbf{r}_2$ given that there is a particle fixed at $\mathbf{r}_1$. If correlations in the full fluid are dominated by excluded volume effects as well, we then expect $\rho(\mathbf{r}_2|\mathbf{r}_1) \equiv \rho\, g(r_{12}) \approx \rho_0(\mathbf{r}_2|\mathbf{r}_1)$. The full fluid's radial distribution function $g(r)$ is indeed very similar to the reference system's $g_0(r)$; this is the fundamental reason for the accuracy of modern perturbation theories of liquids [1,4].

We now extend these ideas about excluded volume correlations to dense nonuniform liquids. We discuss here the simple case of pairwise additive intermolecular forces. Particles in the total system of interest interact with a known external field $\phi(\mathbf{r})$, incorporating confining walls, etc., if present, and through a pair potential $w(r_{ij}) \equiv u_0(r_{ij}) + u(r_{ij})$, divided as usual so that all the repulsive intermolecular forces arise from u_0 [4]. The reference system has only the repulsive pair interaction $u_0(r_{ij})$ and a *different* external field $\phi_0(\mathbf{r})$, to be determined later. Consider now both for the total system (shown here), and for the reference system, the first equation of the exact YBG hierarchy [1]. This can be written in the form

$$k_B T \nabla_1 \ln\rho(\mathbf{r}_1; [\phi]) = -\nabla_1 \phi(\mathbf{r}_1)$$
$$ -\int d\mathbf{r}_2\, \rho(\mathbf{r}_2|\mathbf{r}_1; [\phi]) \nabla_1 w(r_{12}). \quad (1)$$

Here $\rho(\mathbf{r}_2|\mathbf{r}_1; [\phi]) \equiv \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2; [\phi])/\rho(\mathbf{r}_1; [\phi])$ is the conditional singlet density. The notation $[\phi]$ indicates that the correlation functions are functionals of the external field; for a given ϕ *all* correlation functions are in principle determined. The right-hand side (r.h.s.) gives the ensemble-averaged *mean force* on a particle fixed at $\mathbf{r}_1$; this must be nonzero for a gradient in the density $\rho(\mathbf{r}_1; [\phi])$ to exist. Suppose we now choose $\phi_0(\mathbf{r})$ so that the *local* (singlet) densities [8] at every point $\mathbf{r}$ in the two fluids are equal: $\rho_0(\mathbf{r}; [\phi_0]) = \rho(\mathbf{r}; [\phi])$, thus implying

equality of the mean force at each $\mathbf{r}$. It is known that such a field always exists [9]. Assuming again that this condition produces similar local environments for the repulsive cores in the two fluids, and that correlations are dominated by excluded volume effects, we then expect the conditional densities to be very similar:

$$\rho(\mathbf{r}_2|\mathbf{r}_1;[\phi]) \approx \rho_0(\mathbf{r}_2|\mathbf{r}_1;[\phi_0]). \tag{2}$$

Equation (2) is our basic structural hypothesis and represents the only approximation in the theory. As is the case for uniform fluids, it should be most accurate at high density.

To get an explicit equation to determine ϕ_0, we use Eq. (2) in (1), and subtract the exact YBG equation (1) for the reference system. This yields our basic result,

$$\nabla_1[\phi(\mathbf{r}_1) - \phi_0(\mathbf{r}_1)] = -\int d\mathbf{r}_2 \, \rho_0(\mathbf{r}_2|\mathbf{r}_1;[\phi_0])\nabla_1 u(r_{12}). \tag{3}$$

Some important benefits of the subtraction are that rapidly varying terms involving the repulsive pair interactions and the singlet density cancel by choice of ϕ_0, leaving an average only over the gradient of the slowly varying *attractive* potential $u(r_{12})$. The resulting Eq. (3) has an obvious interpretation in terms of mean field ideas, but directly involves *forces*; it can appropriately be called the *inhomogeneous force* equation. In essence, Eq. (3) equates the net force generated by the external field and from attractive pair interactions to the inhomogeneous force $-\nabla\phi_0$ in the reference system. This force cancels by symmetry in a uniform system, and the theory reduces to the mean field picture of Widom [3].

Perhaps the simplest way to solve (3) is by iteration. For *any* given "trial field" ϕ_t, the associated correlation function $\rho_t(\mathbf{r}_2|\mathbf{r}_1;[\phi_t])$ is completely specified and can in principle be calculated accurately. Equation (3) then gives another nontrivial relation between ϕ_t and $\rho_t(\mathbf{r}_2|\mathbf{r}_1;[\phi_t])$ that can be iterated to self-consistency. The resulting self-consistent ϕ_0 yields a correlation function $\rho_0(\mathbf{r}_2|\mathbf{r}_1;[\phi_0])$ that reproduces the *same* ϕ_0 on the left-hand side (l.h.s.) of (3). The self-consistent $\rho_0(\mathbf{r})$ and $\rho_0(\mathbf{r}_2|\mathbf{r}_1)$ offer approximations to the same functions in the full fluid; their accuracy can be checked against computer simulation data. Note that any errors in (2) are important in determining $\nabla\phi_0(\mathbf{r})$ from (3) only where the attractive forces are nonzero. Moreover, these vectorial quantities, weighted by the structure, are averaged over all space. Thus the main features of $\nabla\phi_0(\mathbf{r})$ are apparent from (3) using only crude approximations for $\rho_0(\mathbf{r}_2|\mathbf{r}_1)$, and we expect the iteration process to converge rapidly. This also suggests that simplified treatments of the correlation function $\rho_0(\mathbf{r}_2|\mathbf{r}_1)$ in (3) may still yield rather accurate approximations to $\nabla\phi_0(\mathbf{r})$. This will be examined in future work.

The above described the lowest order structural implications of the theory. We can also derive the asso-

ciated mean field expression for the *free energy*, using a coupling parameter method. Consider a partially coupled system with pair potential $w_\lambda(r) \equiv u_0(r) + \lambda u(r)$, $0 \le \lambda \le 1$, and single particle potential $\phi_\lambda(r)$ chosen so that $\rho_\lambda(\mathbf{r};[\phi_\lambda]) = \rho(\mathbf{r};[\phi])$ for all λ, where $\phi = \phi_{\lambda=1}$. Differentiating and then integrating the canonical partition function with respect to λ gives an exact expression for the Helmholtz free energy A. Assuming as in (2) that with this choice of ϕ_λ the pair correlation function is essentially independent of λ then gives the final result,

$$A = A_0 + \int d\mathbf{r}[\phi(\mathbf{r}) - \phi_0(\mathbf{r})]\rho_0(\mathbf{r})$$
$$+ \frac{1}{2} \int d\mathbf{r}_1 \, d\mathbf{r}_2 \, u(r_{12})\rho_0^{(2)}(\mathbf{r}_1, \mathbf{r}_2). \tag{4}$$

If properties of the inhomogeneous reference system can be accurately determined, this relation could lead to more accurate estimates for thermodynamic properties than would be found using (2) directly in the standard correlation function expressions. This approach also allows direct contact with other free energy based methods including, in particular, density functional theory.

It is important to establish the accuracy of the basic inhomogeneous force equation (3) independent of any additional approximations made in determining $\rho_0(\mathbf{r}_2|\mathbf{r}_1)$. To that end, we carried out molecular dynamics (MD) simulations [10] of the structure of the reference and the full Lennard-Jones (LJ) fluids next to a "hard" planar wall [modeled by the repulsive part of the LJ potential $u_0(z)$] for thermodynamic states of varying bulk density along the $T = 1.35$ isotherm. This is a typical example where a careful treatment of the effects of both attractive and repulsive forces is required. Indeed, the attractive interparticle interactions combined with the repulsive wall-particle interactions can stabilize a lower density *drying region* near the wall even under conditions where heterophase fluctuations in the bulk liquid are relatively small [6]. Sullivan and co-workers [8] have shown that standard integral equation methods cannot accurately describe these drying states. Density functional methods have had more success, but a self-consistent treatment based on (3) has never been carried out [11].

The effective wall potential $\phi_0(z)$ in the reference fluid was computed self-consistently from (3) using *exact* (MD) values for $\rho_0(\mathbf{r}_2|\mathbf{r}_1)$. Only two or three iterations were needed to achieve a self-consistent solution even starting from the "bare" $u_0(z)$. As shown in Fig. 1, Eq. (3) generates a *soft and smooth repulsive force* $-\nabla\phi_0(z)$ that tends to push particles away from the hard wall, opposing the natural tendency of repulsive particles to produce partially ordered layers with a density maximum near the wall. This produces the drying effect in our reference system model. As Eq. (3) makes clear, the physical origin of this effective repulsive force arises from the unbalanced attractive pair forces in the full nonuniform liquid near the
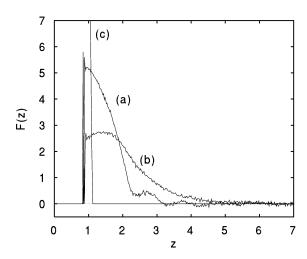
FIG. 1. The (dimensionless) self-consistent force $F(z)$ given by the r.h.s. of Eq. (3) near a repulsive planar wall with bare potential $u_0(z)$ is shown for two states along the $T = 1.35$ isotherm: (a) bulk density 0.78, (b) bulk density 0.54. Also shown in (c) is the force $F_{\text{bare}}(z) = -\nabla u_0(z)$ from the bare wall. The *total* force $-\nabla\phi_0(z)$ is given by $F(z) + F_{\text{bare}}(z)$. The units of length and energy are the usual σ and ε of the LJ potential.

wall. Figure 2 shows that the method correctly reproduced the pronounced change in behavior in $\rho(z)$ from significant layering remaining near the wall at high bulk density to the formation of a relatively structureless profile with a density maximum well away from the wall at lower bulk density. In general, there is good qualitative agreement with simulations both for $\rho(z)$ and $\rho(\mathbf{r}_2|\mathbf{r}_1)$, and at high density nearly quantitative agreement.

One of the most theoretically interesting applications of these ideas is to the *free* liquid-vapor interface with $\phi = 0$. In this case the approximation (2) is fundamentally in

error for an infinite system. Because of long wavelength capillary wave fluctuations [12,13], there exist long-ranged correlations along the interface in $\rho(\mathbf{r}_2|\mathbf{r}_1)$ that are impossible to reproduce in any repulsive fluid's $\rho_0(\mathbf{r}_2|\mathbf{r}_1)$. In an infinite system these fluctuations also lead to a washing out of the true density profile $\rho(z)$. This basic distinction between free interfaces and interfaces near rigid walls cannot be captured in mean field theory, which attempts to describe both situations in terms of some effective field $\phi_0(z)$.

Nevertheless, self-consistent liquid-vapor solutions of Eq. (3) exist, yielding a well-defined profile $\rho_0(z)$ of finite width. This can legitimately be called an *intrinsic interface profile*: a profile unbroadened by capillary wave fluctuations [14]. We had argued earlier [13] that interfaces in *finite* systems, where significant capillary wave fluctuations cannot occur, should be well described by such a mean field $\rho_0(z)$. Figures 3 and 4 report the results of MD simulations [15] for free interfaces in the full and reference LJ systems that suggest this is indeed the case. For states away from the critical region, there is good qualitative agreement between the full (finite system) $\rho(z)$ produced by computer simulations and the self-consistent $\rho_0(z)$. Both simulations and theory produce smooth profiles with no indication of oscillatory behavior even at the lowest (triple point) temperature. However, the self-consistent solution to (3) yields values for the coexisting bulk vapor and liquid densities as well as the shape of the profile between them, and differences can be seen in the predicted bulk densities. The main errors in these mean field predictions arise from the inaccuracy of (2) in describing the relatively simple correlations seen
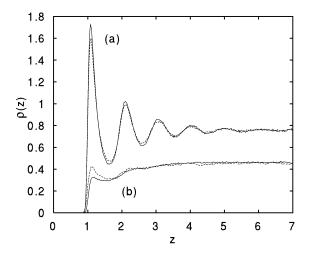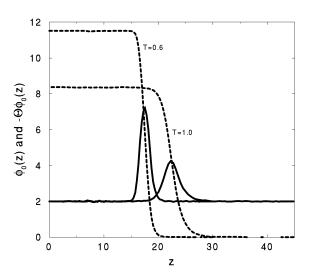

FIG. 2. Density profiles $\rho(z)$ for the full LJ fluid (solid line) and the self-consistent reference fluid (dashed line) for the same two states along the $T = 1.35$ isotherm as in Fig. 1: (a) bulk density 0.78, (b) bulk density 0.54. The LJ fluid experiences the bare external force $-\nabla u_0(z)$, while the reference fluid experiences the external force $-\nabla\phi_0(z)$ shown in Fig. 1.

FIG. 3. Self-consistent force $-\nabla\phi_0(z)$ (solid line) and potential $\phi_0(z)$ (dashed line) for the liquid-vapor interface at $T = 0.6$ and $T = 1.0$. Different simulation cell sizes in the z direction of 60σ at $T = 0.6$ and 90σ at $T = 1.0$ were used, so the curves at different temperatures are naturally displaced along the z axis. For ease in viewing, the force has also been displaced vertically by two units.
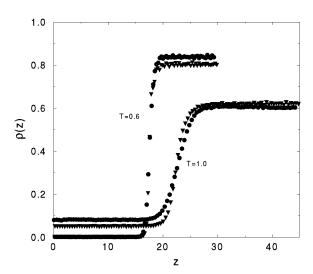
FIG. 4. Density profiles $\rho(z)$ for the liquid-vapor interface for the same two states as in Fig. 3. Circles denote the LJ fluid and triangles the reference fluid. The two profiles are shown with the same location for the Gibbs dividing surface.

in the *vapor* phase [16]. In future work we plan to incorporate simple virial-like corrections to the theory at low density that should improve these results.

The method introduced here logically separates the self-consistent calculation of the inhomogeneous force $\nabla\phi_0(\mathbf{r})$, which from (3) is rather insensitive to errors in $\rho_0(\mathbf{r}_2|\mathbf{r}_1)$, from the determination of the structure of the reference fluid itself in the presence of a given external field [17]. The latter becomes an appropriate focus for future research. This indirect treatment of the effects of attractive forces allows us to focus on a simpler model with purely repulsive intermolecular forces. Theoretical methods such as integral equation and density functional theories have proved most accurate in such applications. This approach ensures that the physically sensible results of mean field theory are reproduced while still allowing for an accurate representation of the important excluded volume correlations. We believe it will often prove more successful than a direct attack using standard integral equation closures or density functional methods that explicitly incorporate the attractive interactions.

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[10] MD simulations were carried out under fixed N, V, T (number of particles, volume, temperature) conditions with periodic boundary conditions in the x, y directions and bounded by walls in the z direction. The box size was 22.5σ on a side. The LJ potential was truncated at 2.5σ. For the densities under consideration N fell in the range $\approx 5000-10\,000$. Simulations were carried out for both the Lennard-Jones and repulsive reference potentials at $T = 1.35$ for a range of densities.

[11] In the usual density functional approach, attractive interactions are analyzed using a crude approximation where the inhomogeneous pair correlation function is replaced by a product of singlet functions [9]. Such inconsistent approximations used for the attractive interactions "contaminate" the description of the repulsive forces and reduce the accuracy of the overall theory.

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[14] For an excellent discussion, see B. Widom, in *Phase Transitions and Critical Phemomena,* edited by C. Domb and M. S. Green (Academic, New York, 1972), Vol. 2, p. 79.

[15] Simulations for $N = 3000$ particles at $T = 0.60$ and $T = 1.0$ were carried out. The former is very slightly below the triple point ($T = 0.61$) for the truncated LJ potential. A box size up to $10 \times 10 \times 90\sigma$, the largest dimension being normal to the interface, was used. A small field was applied to the LJ system to stop any slight center of gravity drift.

[16] The mean field theory consistently underestimates the vapor density. This can be understood from the underestimation of correlations implied by the use of Eq. (2) at low density. This in turn affects the mean field prediction for the coexisting bulk liquid density.

[17] This is the same procedure used in uniform fluids. In that case the calculation of the inhomogeneous force field is trivial. Then the structure of the reference fluid in the presence of that (vanishing) force field is calculated using as accurate a theory as possible.