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Using mean field theory to determine the structure of uniform fluids

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The structure of a uniform simple liquid is related to that of a reference fluid with purely repulsive intermolecular forces in a self-consistently determined external reference field (ERF) ϕ_R . The ERF can be separated into a harshly repulsive part ϕ_{R0} generated by the repulsive core of a reference particle fixed at the origin and a more slowly varying part ϕ_{R1} arising from a mean field treatment of the attractive forces. We use a generalized linear response method to calculate the reference fluid structure, first determining the response to the smoother part ϕ_{R1} of the ERF alone, followed by the response to the harshly repulsive part. Both steps can be carried out very accurately, as confirmed by computer simulations, and good agreement with the structure of the full Lennard-Jones fluid is found. © 2001 American Institute of Physics. [DOI: 10.1063/1.1329881]

I. INTRODUCTION

In this paper we describe a new and physically motivated way to determine the structure of uniform fluids, based on a mean field treatment of the attractive intermolecular interactions. To apply this approximation to a general non-uniform system, attractive interactions are replaced by a spatially varying single particle “molecular field” potential, chosen to take account of variations in the average attractive energy density in different parts of the system.¹ Since the attractive interactions usually operate over an extended range, it seems plausible that an averaged description as given by mean field theory could often provide a useful simplification.

However, in real liquids, additional very important “excluded volume” correlations are generated by the short-ranged and harshly repulsive intermolecular forces;^{2,3} these cannot be accurately described using the same mean field averaging appropriate for the longer ranged attractive forces. Despite this additional complexity, the use of mean field theory allows us to consider an inherently simpler system: a *nonuniform reference fluid*. This consists of particles interacting only with repulsive intermolecular forces but in the presence of an *effective reference field* (ERF) chosen self-consistently to take account of the locally averaged effects of attractive interactions as well as any imposed external field.^{4–6} The uniform reference fluid is stable over the entire range of densities from vapor to liquid, and its structure in the presence of an appropriately chosen ERF approximates that of the original system.

In previous work^{4–6} we showed how these ideas can be used to give an accurate description of the structure of a nonuniform Lennard-Jones (LJ) fluid in a number of differ-

ent applications where the ERF is large and attractive forces strongly influence the structure, including the liquid-vapor interface and the structure of fluids near hard walls. In these cases conventional (singlet) integral equation methods have given poor results.⁷

In this paper we consider a different limit, that of the *uniform* LJ fluid. Here attractive forces produce relatively small structural changes at high density and integral equation methods have had their greatest successes. Indeed, in the simplest picture, the attractive forces on a given particle from oppositely situated neighbors essentially *cancel*⁸ in typical high density configurations, and the structure of the dense uniform LJ fluid is rather well approximated by that of a uniform reference fluid at the same density.³ The theoretical challenge is to improve on this rather accurate starting point at high density and to describe the larger structural changes attractive interactions induce at lower densities.

From this perspective the uniform LJ fluid provides an important and nontrivial test of our general approach. It is not clear that mean field averaging along with the approximate methods^{6,9} we use to calculate reference fluid structure will be accurate enough to determine the small but subtle changes induced by attractive interactions in the highly oscillatory structure of uniform fluids at high density or the more substantial changes seen at lower densities. Indeed, unlike the previous applications, it is difficult to guess even qualitative features of the ERF.

The plan of the paper is the following. In Sec. II we define the nonuniform reference fluid and the formal equation determining the ERF. In Sec. III we discuss the usual mean field approximation for the ERF and suggest a new generalized equation that incorporates exact results at low density.

In Sec. IV we first use computer simulations to carry out

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the determination of structure essentially exactly. This allows us to test the accuracy of the basic mean field description of the ERF without any further approximations. We generally find quite satisfactory results though small errors in the simplest mean field determination of the ERF can be seen at high density.

In Sec. V we introduce a new theory to calculate self-consistently both the ERF and the associated structure in the reference fluid, using a generalization of a physically motivated procedure first used to calculate the structure of a LJ fluid near a hard wall.⁶ The key idea is to divide the ERF into rapidly and slowly varying parts. We determine the response of the reference fluid density to each component of the ERF in successive steps, using appropriate methods in each step that can accurately describe the very different density responses, as discussed in Secs. VB and VC. In Sec. VI we discuss the results of the method and comparison to simulations. The theory generally gives quite satisfactory results. However, at the highest densities some small errors can be seen arising from the simple mean field treatment of attractive interactions. At lower densities, our simplest approximations give results comparable to the best integral equation methods.^{10,11} Final remarks are given in Sec. VII. Some technical details are presented in the Appendices.

II. NONUNIFORM REFERENCE FLUID

We first consider the case where fluid particles interact with a known external field $\phi(\mathbf{r})$ and through the LJ pair potential $w(r) \equiv u_0(r) + u_1(r)$, separated as usual³ into rapidly and slowly varying parts so that all the repulsive intermolecular forces arise from u_0 and all the attractive forces from u_1 .¹² We assume that the external field $\phi(\mathbf{r}) \equiv \phi_0(\mathbf{r}) + \phi_1(\mathbf{r})$ can be separated in a similar way, where the subscript 0 denotes a harshly repulsive interaction and the subscript 1 a much more slowly varying interaction usually associated with attractive forces. We consider a grand ensemble with fixed chemical potential μ^B , which determines ρ^B , the uniform fluid density when $\phi = 0$.

We relate the structure of the nonuniform LJ system to that of a simpler *nonuniform reference fluid*,⁴⁻⁶ with only repulsive intermolecular pair interactions $u_0(r_{ij})$ (equal to the LJ repulsions) in a different ERF $\phi_R(\mathbf{r})$. The replacement of attractive pair interactions by an approximate local “molecular field” is an essential step in mean field theory, but we can think of other more general prescriptions for $\phi_R(\mathbf{r})$. Here we determine $\phi_R(\mathbf{r})$ formally by the requirement that it has a functional form such that the *local* (singlet) density at every point $\mathbf{r}$ in the reference fluid equals that of the full LJ fluid:⁷

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

The subscript 0 in Eq. (1) reminds us that the reference system pair interactions arise only from u_0 and the notation $[\phi_R]$ indicates that all distribution functions are functionals of the appropriate external field. Since $\rho(\mathbf{r};[\phi])$ is a physically realizable distribution function, and the reference fluid is stable over a wide range of densities, it seems very plausible

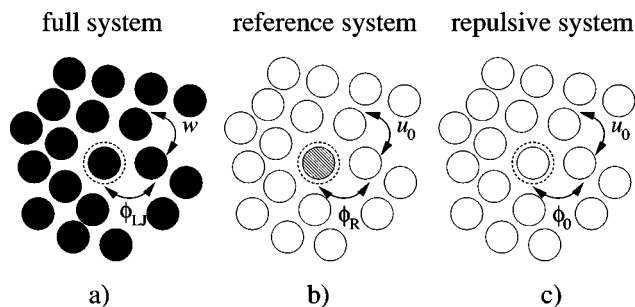


FIG. 1. Model systems considered. (a) is the full LJ system with a LJ particle fixed at the origin as indicated by the dashed circle. The interaction with the other particles can be described by an external field $\phi_{LJ}(r) = w(r)$. (b) is the nonuniform reference system with the special wall particle fixed at the origin with interaction $\phi_R(r)$. (c) is the original WCA repulsive force system with pair potential $u_0(r)$. Here the fixed particle interacts with the other particles through $\phi_0(r) = u_0(r)$.

sible that such a choice for the field ϕ_R can be made in principle.¹³ In practice we will make approximate choices motivated by mean field ideas.

Using this perspective, let us consider the problem of determining the effects of attractive forces on the structure of *uniform* fluids. The simplest approximation by Weeks, Chandler and Anderson (WCA) assumes complete cancellation of attractive forces and approximates the radial distribution function $g(r)$ of the uniform LJ fluid by the $g_0(r)$ of the uniform repulsive force fluid at the same density. To improve on this, we make use of the exact relation¹⁴ between $\rho^B g(r)$ in the uniform LJ fluid and the singlet density in a nonuniform fluid with a particle fixed at $\mathbf{r}_0$, which we take to be the origin of our coordinate system:

$$\rho^B g(r_1) = \rho(\mathbf{r}_1|\mathbf{r}_0;[\phi=0]) = \rho(r_1;[\phi_{LJ}]). \quad (2)$$

Here $\rho(\mathbf{r}_1|\mathbf{r}_0;[\phi=0])$ is the *conditional* singlet density — the density in zero external field at $\mathbf{r}_1$ given that a particle is fixed at $\mathbf{r}_0$. By symmetry this depends only on the radial distance $r_1 \equiv |\mathbf{r}_1|$ from the fixed “wall particle” at $\mathbf{r}_0 = 0$. This in turn must equal the nonuniform singlet density induced by the external field $\phi_{LJ}(r_1) \equiv w(r_1)$.

By choosing $\phi_R(r_1)$ in Eq. (1) to fit the nonuniform LJ density $\rho(r_1;[\phi_{LJ}])$, we obtain a *nonuniform reference system* in which the density $\rho_0(r_1;[\phi_R])$ is modified by the effects of attractive forces. In particular this can be used in Eq. (2) to calculate the radial distribution function $g(r_1)$ of the uniform LJ system. The original WCA approximation³ arises from the particular choice $\phi_R = u_0$. See Fig. 1.

III. MEAN FIELD APPROXIMATION FOR THE ERF

In previous work⁴⁻⁶ we started from the balance of forces as described by the exact Yvon–Born–Green hierarchy² and arrived at a generalized mean field equation for the ERF by a series of physically motivated approximations. We will not repeat these arguments here and instead focus on the simplest final approximation, the *molecular field equation* for the ERF, which proved surprisingly accurate in a number of different applications. This is just a transcription of the usual molecular field equation for the Ising model¹ to a continuum fluid with attractive interactions $u_1(r)$ and can be immediately written down:

$$\phi_R^{\text{MF}}(r_1) = \phi_{\text{LJ}}(r_1) + \int d\mathbf{r}_2 [\rho_0(r_2; [\phi_R^{\text{MF}}]) - \rho^B] u_1(r_{12}). \quad (3)$$

The effective field ϕ_R^{MF} at a particular distance r_1 from the fixed wall particle is comprised of the bare field $\phi_{\text{LJ}}(r_1)$ from the fixed particle plus the integral over all positions $\mathbf{r}_2$ of the attractive interactions $u_1(r_{12})$ from other particles weighted by the deviation of the nonuniform reference density $\rho_0(r_2; [\phi_R^{\text{MF}}])$ from its limiting value ρ^B . Use of the density deviation ensures that ϕ_R^{MF} vanishes at large r_1 .

Let ϕ_s denote the second term on the right in Eq. (3):

$$\phi_s(r_1) \equiv \int d\mathbf{r}_2 [\rho_0(r_2; [\phi_R^{\text{MF}}]) - \rho^B] u_1(r_{12}). \quad (4)$$

It provides an estimate of the averaged effects of attractive pair interactions arising from the other (mobile) particles in the full LJ fluid at a distance $\mathbf{r}_1$ from a particle fixed at the origin. Because of the convolution with the slowly varying attractive potential “weighting function” $u_1(r_{12})$ in Eq. (4), $\phi_s(r_1)$ extends smoothly into the repulsive core region of the wall particle where $\rho_0(r_1; [\phi_R^{\text{MF}}])$ vanishes. Outside the core it is a smooth, basically repulsive and relatively slowly varying interaction even when $\rho_0(r_1; [\phi_R^{\text{MF}}])$ itself has pronounced oscillations.

More complicated, but sometimes more accurate, equations for the ERF are available,⁵ but in practice the simple mean field approximation (3) often gives quite satisfactory results. In Appendix A we discuss a simple modification of Eq. (4) that gives somewhat more accurate results at low density. In the following we will use Eq. (3) to determine the ERF unless otherwise indicated.

IV. RESULTS FROM MD SIMULATIONS

We now must solve Eq. (3) to determine the ERF ϕ_R^{MF} and associated density $\rho_0(r; [\phi_R^{\text{MF}}])$. As is typical in mean field theory, a self-consistent solution must be found, since the ERF ϕ_R appears explicitly on the left side and implicitly on the right side through the dependence of the density $\rho_0(r_2; [\phi_R])$ on ϕ_R . If we can find the reference structure $\rho_0(r; [\phi_R])$ produced by a given ERF ϕ_R accurately, then it is straightforward to solve the mean field equation (by iteration, for example) to determine the self-consistent ϕ_R^{MF} and the associated density $\rho_0(r; [\phi_R^{\text{MF}}])$. In Sec. V we will discuss new theoretical methods to calculate $\rho_0(r; [\phi_R])$ for a given ϕ_R . However, since these could introduce additional errors, it is useful first to assess the accuracy of the basic mean field equation (3) without any further approximations.

We carried out MD simulations in the canonical ensemble using the three model systems shown in Fig. 1: the full LJ system, the WCA repulsive force system, and the inhomogeneous reference system with the special wall particle fixed at the origin.¹⁵ To determine the effective potential in the latter case, we solved Eq. (3) by iteration,¹⁶ using (essentially exact) MD results for $\rho_0(r; [\phi_R])$. The errors in $\rho_0(r; [\phi_R^{\text{MF}}])$ when compared to $\rho(r; [\phi_{\text{LJ}}])$ then arise solely from the mean field approximation for the ERF ϕ_R^{MF} .

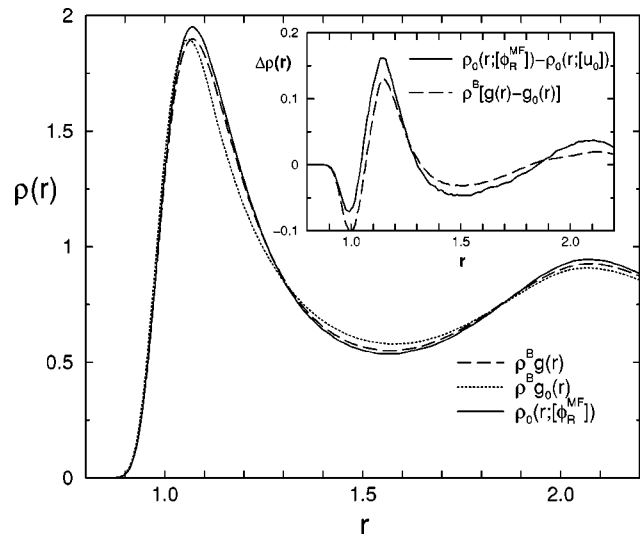


FIG. 2. Densities with a particle fixed at the origin as determined by MD simulations for the three systems in Fig. 1 at $T=1.35$ and $\rho^B=0.78$. The inset gives the difference in density between the LJ fluid and the WCA repulsive force fluid as determined by simulations and by self-consistent solution of the mean field equation (3), again using simulation data.

A. Simulation details

In the following we use reduced Lennard-Jones units where the unit of length is σ , the unit of energy is ϵ and the unit of time is $\sqrt{m\sigma^2/\epsilon}$. We carried out MD simulations in the canonical ensemble using the velocity Verlet algorithm with a time step of $\Delta t=0.001$. To maintain constant temperature, every 150 MD steps we chose new velocities for all particles from the corresponding Boltzmann distribution.

We simulated states along the near critical isotherm at $T=1.35$ for densities $\rho^B=0.78, 0.54, 0.45$ and 0.1 , and a state near the triple point with $T=0.88$ and $\rho^B=0.85$. We used $N=3000$ particles for $T=1.35, \rho^B=0.78$ and for $T=0.88, \rho^B=0.85$, and $N=450$ for all other states. To eliminate the possibility of finite size effects we made test runs for $T=1.35$ and $\rho^B=0.54, 0.45$ and 0.1 with $N=3000$ particles, which led to the same density distributions as for $N=450$. Each state was first equilibrated for 5×10^5 MD steps. Subsequently we calculated $g(r)$ for the uniform systems and $\rho_0(r; [\phi_R^{\text{MF}}])$ for the nonuniform reference system for at least 3.5×10^6 and up to 7.5×10^7 MD steps.

B. Simulation results for the ERF

We first concentrate on the high density state $\rho^B=0.78$ and $T=1.35$, which will illustrate many basic features of the mean field approach. Figure 2 gives simulation results for the full LJ density $\rho^B g(r)$, the WCA reference density $\rho^B g_0(r)$, and the inhomogeneous reference density $\rho_0(r; [\phi_R^{\text{MF}}])$ for this state. We see that the mean field prediction $\rho_0(r; [\phi_R^{\text{MF}}]) \approx \rho^B g(r)$ is able to correct the main quantitative errors in the already rather accurate WCA approximation $g_0(r) \approx g(r)$, describing in particular the slight shift outward of the first peak. However, some small errors remain, due solely to the mean field approximation for the ERF from Eq. (3). These are focused on in the inset to Fig. 2, which compares the density change $\rho_0(r; [\phi_R^{\text{MF}}]) - \rho^B g_0(r)$ due to at-

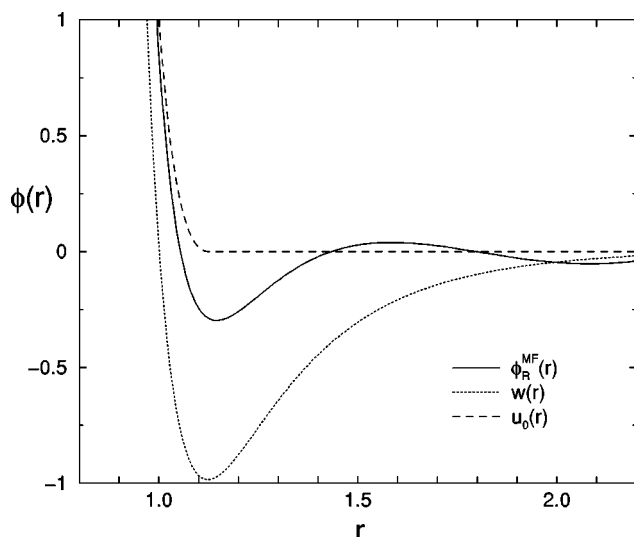


FIG. 3. The self-consistent ERF $\phi_R^{MF}(r)$ determined from the mean field equation (3) for $T=1.35$ and $\rho^B=0.78$ compared to the full LJ potential $w(r)$ and the repulsive force reference potential $u_0(r)$.

tractive forces as predicted by Eq. (3) to the actual change $\rho^B[g(r)-g_0(r)]$ given by the simulations. Any further improvements in these results will require a better approximation for the ERF.

Figure 3 shows the corresponding self-consistent ERF $\phi_R^{MF}(r)$ from Eq. (3), compared to the bare LJ potential $w(r)$ and the repulsive reference potential $u_0(r)$. At low density ϕ_R^{MF} reduces exactly to w , and if the force cancellation argument were exact, then at high density ϕ_R^{MF} would equal u_0 as assumed in the WCA approximation. However, there is a weak negative region in $\phi_R^{MF}(r)$ for r between about 1.1 and 1.4. This results from the nonuniform attractive energy density experienced by a particle in this region in the LJ system, which is slightly lower than average because of the fixed particle and its neighbors even at this high density. This produces the slight shift in the first peak noted above.

Figure 4 shows the ERF for a series of states along the

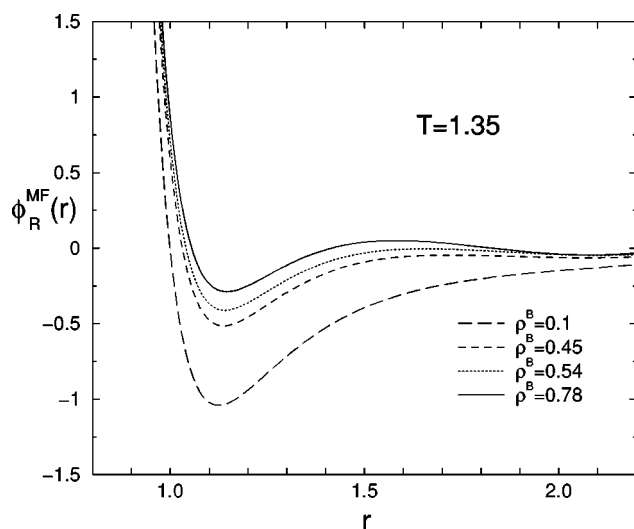


FIG. 4. The self-consistent ERF from Eq. (3) for the indicated densities along the $T=1.35$ isotherm.

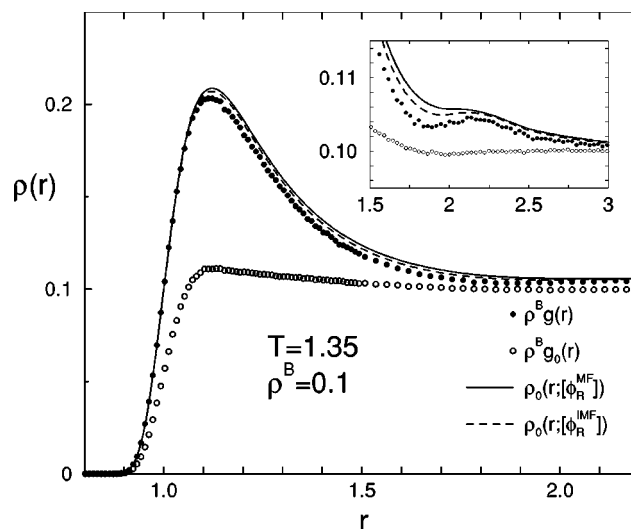


FIG. 5. Densities for $\rho^B=0.10$ and $T=1.35$ for the LJ system, the WCA reference system and the nonuniform reference system with the ERF determined from Eq. (3) and from Eq. (A1). The inset focuses in the region around the second peak.

$T=1.35$ isotherm. The attractive force cancellation from further neighbors becomes increasingly less effective at lower densities, and attractive interactions produce much larger structural changes, as will be shown later.

Again mean field theory can yield accurate results. This is illustrated in Fig. 5 for the low density state $\rho^B=0.1$, and $T=1.35$. This figure shows simulation results for the full LJ density $\rho^B g(r)$, the WCA repulsive fluid density $\rho^B g_0(r)$, and the inhomogeneous reference density $\rho_0(r;[\phi_R^{MF}])$. Also shown is $\rho_0(r;[\phi_R^{IMF}])$, with the ERF calculated from Eq. (A1) in Appendix A [using $I_2(\rho)$ as the interpolation function], which does a slightly better job at reproducing the second peak than does Eq. (3). Theoretical values for correlation functions for all the states in Fig. 4 and comparison to results for the full LJ fluid will be discussed in Sec. VI.

As the density tends to zero, the ERF reduces to the bare potential $w(r)$ as correctly predicted by Eq. (3). The increased “screening” of attractive forces as the density is increased was first demonstrated using diagrammatic resummation techniques in the derivation of the optimized random phase (ORPA) and exponential (EXP) integral equations.¹⁷ Mean field theory provides a very simple and physically suggestive way of understanding these results.

V. TWO STEP METHOD

We now discuss theoretical methods^{6,9} for determining the density $\rho_0(\mathbf{r};[\phi_R]) \equiv \rho_R(\mathbf{r})$ produced by a given ERF ϕ_R . We use a generalization of the two step method first introduced in Ref. 6. Initially we treat the LJ repulsive potential u_0 as a hard core interaction with diameter d , but then use the standard “blip function” expansion² to correct for its finite softness in our final numerical results. Let us concentrate on the mean field equation (3) for the ERF. Recall that $\phi_{LJ}(r) \equiv w(r) = u_0(r) + u_1(r)$.

A. Separation of ERF

The two step method introduces a similar division of the full ERF,

$$\phi_R(r) \equiv \phi_{R0}(r) + \phi_{R1}(r), \quad (5)$$

and determines the density response to each part of the ERF in separate steps. As this notation suggests, ϕ_{R0} is supposed to take account of the harshly repulsive part of the ERF associated mainly with the repulsive core of the fixed wall particle at the origin. The other component ϕ_{R1} is much more slowly varying and physically incorporates the averaged effects of attractive interactions.

The mean field equation (3) naturally separates into two such parts by setting

$$\phi_{R0}(r) \equiv u_0(r) \quad (6)$$

and

$$\phi_{R1}(r) \equiv u_1(r) + \phi_s(r), \quad (7)$$

with ϕ_s given by Eq. (4). We call this the *basic* separation and will use it in most of what follows.

However, other choices can be made. As discussed in Appendix B, there exists considerable freedom to vary $\phi_{R1}(r)$ inside the harshly repulsive core region where $u_0(r)$ is very large, without affecting the final result when both parts of the ERF are taken into account. This flexibility can be used to increase the accuracy of approximations introduced there that require a slowly varying density response.

B. First step

The key idea in the two step method is to compute in an initial step the density response to the *slowly varying part* $\phi_{R1}(r)$ of the ERF *alone*. Physically, this takes account of the averaged effects of the attractive interactions modeled by ϕ_{R1} and we can exploit the fact that the density response can be expected to be reasonably slowly varying. The response to the remaining harshly repulsive interaction ϕ_{R0} is then determined in a second step.

1. Hydrostatic approximation

Let us first consider the special case where ϕ_{R1} varies so slowly that it is essentially constant over the range of a correlation length in the bulk fluid. The associated density $\rho_0(r; [\phi_{R1}], \mu_0^B)$ is a functional of the external field ϕ_{R1} and a function of the chemical potential μ_0^B and depends only on the difference between these quantities. Thus for any fixed position r_1 we can define a shifted chemical potential

$$\mu_0^{r_1} \equiv \mu_0^B - \phi_{R1}(r_1) \quad (8)$$

and shifted field

$$\phi_{R1}^{r_1}(r) \equiv \phi_{R1}(r) - \phi_{R1}(r_1), \quad (9)$$

whose parametric dependence on r_1 is denoted by a superscript, and we have for all r the exact relation

$$\rho_0(r; [\phi_{R1}], \mu_0^B) = \rho_0(r; [\phi_{R1}^{r_1}], \mu_0^{r_1}). \quad (10)$$

By construction the shifted field $\phi_{R1}^{r_1}(r)$ vanishes at $r = r_1$ and it remains very small for r near r_1 when ϕ_{R1} is very

slowly varying. Thus to determine the density at r_1 we can approximate the rhs of Eq. (10) by $\rho_0(r_1; [0], \mu_0^{r_1}) \equiv \rho_0(\mu_0^{r_1})$, the density of the *uniform* fluid (in zero field) at the shifted chemical potential $\mu_0^{r_1}$. We arrive at the *hydrostatic approximation*^{18,19} for the density arising from a very slowly varying field ϕ_{R1} :

$$\rho_0(r_1; [\phi_{R1}], \mu_0^B) \approx \rho_0(\mu_0^{r_1}). \quad (11)$$

We refer to $\rho_0(\mu_0^{r_1}) \equiv \rho_0^{r_1}$ as the *hydrostatic density* at r_1 ; from Eqs. (8) and (11) it depends only on the *local* value of the field ϕ_{R1} at r_1 . The hydrostatic approximation is exact for sufficiently slowly varying ϕ_{R1} and has been used in more approximate applications of these ideas to hydrophobic interactions in water.²⁰ However, in the present application ϕ_{R1} varies rapidly enough that for quantitative accuracy we must use more accurate methods to determine the full non-local response.

We now show that the generalized linear response method introduced in Ref. 9 provides a simple and accurate way to determine both the density ρ_{R1} induced in the first step as well as the response to ϕ_{R0} taken into account in the second step. In Appendix B we discuss an alternate but somewhat more complicated approach suggested in Ref. 6, which requires that ρ_{R1} is sufficiently slowly varying that gradient-type expansions give accurate results.

We start from the exact linear response equation that relates *small* changes in the potential and density for a system with external potential ϕ , chemical potential μ , and associated density $\rho_0(r; [\phi], \mu) \equiv \rho_\phi(r)$:^{2,6}

$$-\beta \delta \phi(\mathbf{r}_1) = \int d\mathbf{r}_2 \chi_0^{-1}(\mathbf{r}_1, \mathbf{r}_2; [\rho_\phi]) \delta \rho_\phi(\mathbf{r}_2) \quad (12)$$

through the linear response function $\chi_0^{-1}(\mathbf{r}_1, \mathbf{r}_2; [\rho_\phi]) \equiv \delta(\mathbf{r}_1 - \mathbf{r}_2) / \rho_\phi(\mathbf{r}_1) - c_0(\mathbf{r}_1, \mathbf{r}_2; [\rho_\phi])$. Here c_0 is the direct correlation function of the system with density $\rho_\phi(r)$.

2. Linear response of hydrostatic fluid

The simple hydrostatic method discussed earlier approximates $\rho_{R1}(r_1)$ at each r_1 by the density $\rho_0^{r_1}$ of the uniform hydrostatic fluid with chemical potential $\mu_0^{r_1}$, and thus ignores the *nonlocal* effects of the shifted field $\phi_{R1}^{r_1}$ on the density at r_1 . To get a more accurate approximation, we can use Eq. (12) to take into account the *linear response* of the density of the uniform hydrostatic fluid to the shifted field $\phi_{R1}^{r_1}$. Thus we set $\rho_\phi = \rho_0^{r_1}$ and take $\delta \phi = \phi_{R1}^{r_1}$ in Eq. (12). This idea was first suggested in Ref. 9 and was shown to give accurate results in a number of different applications. While a more formal derivation can be given,⁹ here we focus on physical considerations.

Since $\phi_{R1}^{r_1}(r)$ is zero at r_1 , the left side of Eq. (12) vanishes by construction. We would expect the linear response relation between an external field and induced density to be most accurate where the field is small — in particular where the field vanishes — and at each r_1 we will use the appropriate shifted (hydrostatic) chemical potential and shifted field so that this optimal condition continues to hold locally. This shift is crucial for the accuracy of this method

and is its main new feature over previous approaches. Moreover, it has been shown that even large density fluctuations in a (field free) hard sphere fluid can be accurately described using the *same* Gaussian probability distribution that controls small fluctuations²¹ and that yields the basic linear response relation (12) for a uniform system.

This suggests that we can accurately determine the desired $\rho_{R1}(r_1)$ by using the linear response function $\chi_0^{-1}(\mathbf{r}_{12}; \rho_0^{r_1})$ of the uniform hydrostatic fluid in Eq. (12) even when the field $\phi_{R1}^{r_1}$ produces significant density changes. Assuming a linear density response, we replace $\delta\rho_\phi(r)$ in (12) by the full density change $\rho_{R1}(r) - \rho_0^{r_1}$, thus yielding our final result:

$$[\rho_{R1}(r_1) - \rho_0^{r_1}] / \rho_0^{r_1} = \int d\mathbf{r}_2 c_0(r_{12}; \rho_0^{r_1}) [\rho_{R1}(r_2) - \rho_0^{r_1}]. \quad (13)$$

Here $c_0(r_{12}; \rho_0^{r_1})$ is the direct correlation of the uniform reference fluid at the hydrostatic density $\rho_0^{r_1}$. Note that the external field appears only implicitly in Eq. (13) through its local effect on the hydrostatic density $\rho_0^{r_1}$.

Equation (13) is a *linear* integral equation relating the density $\rho_{R1}(r_1)$ at a given r_1 on the left side to an integral involving the density $\rho_{R1}(r_2)$ at all other points and a *uniform fluid* kernel $c_0(r_{12}; \rho_0^{r_1})$ that depends implicitly on r_1 through $\rho_0^{r_1}$. This new feature presents no technical difficulties in determining a numerical solution and Eq. (13) can be solved by any number of standard methods. We found that Picard iteration works very well. See Appendix C for details.

C. Second step

We now determine in a second step the response $\Delta\rho_R(r) \equiv \rho_0(r; [\phi_R]) - \rho_0(r; [\phi_{R1}])$ of the relatively slowly varying density field $\rho_0(r; [\phi_{R1}]) \equiv \rho_{R1}(r)$ to the remaining harshly repulsive component ϕ_{R0} of the ERF, which we approximate initially as a hard core of range d . We take $\rho_\phi = \rho_{R1}$ in Eq. (12) and again assume a linear density response in the “out” region $r_1 > d$ where the perturbing potential $\phi_{R0}(r_1)$ vanishes. This is consistent with the simulation results²¹ showing that the Gaussian probability distribution gave a good description even of the formation of voids in uniform fluids.

This linear response assumption gives the approximate equation, valid for $r_1 > d$:

$$0 = \int d\mathbf{r}_2 \chi_0^{-1}(\mathbf{r}_1, \mathbf{r}_2; [\rho_{R1}]) \Delta\rho_R(r_2), \quad (14)$$

where we impose the exact condition $\rho_0(r_2; [\phi_R]) = 0$ from the hard core interaction for $r_2 < d$ in the integration over r_2 . Again we approximate $\chi_0^{-1}(\mathbf{r}_1, \mathbf{r}_2; [\rho_{R1}])$ by the response function of an appropriately chosen uniform system. As in Sec. V B 2 and as shown in Ref. 9, we find that the use of the hydrostatic fluid with density $\rho_0^{r_1}$ gives accurate results even when ρ_{R1} varies rather rapidly. Some alternate but less generally useful choices are discussed in Appendix B. Thus we arrive at the basic equation for the second step of our theory, valid for $r_1 > d$:

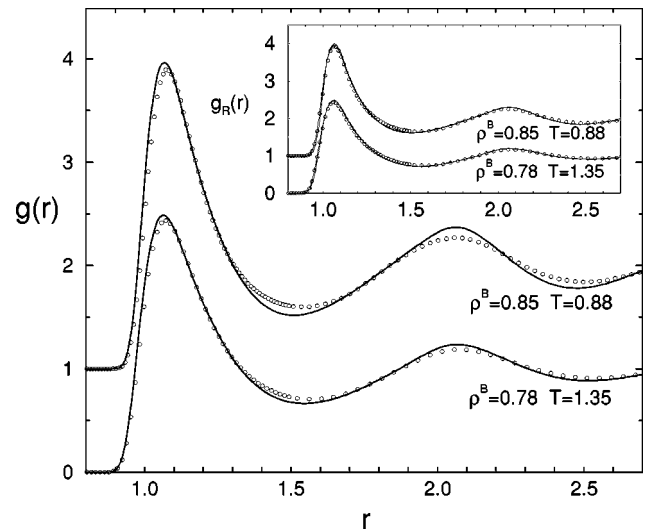


FIG. 6. Radial distribution functions $g_0(r_2; [\phi_R^{\text{MF}}]) = \rho_0(r_2; [\phi_R^{\text{MF}}]) / \rho^B$ for two high density states (solid lines with the origin shifted for clarity) as given by the two step method using Eq. (3) for the ERF along with Eqs. (13) and (15) compared to the results of MD simulations (open circles) of the LJ fluid. In the inset the two step results are compared directly to simulations of the *reference fluid* in the self-consistent potential ϕ_R^{MF} . The latter tests the accuracy of the two-step method for reference fluid correlations induced by the given ϕ_R^{MF} , while the former tests the accuracy of the mean field equation for determining ϕ_R^{MF} .

$$\Delta\rho_R(r_1) / \rho_0^{r_1} = \int d\mathbf{r}_2 c_0(r_{12}; \rho_0^{r_1}) \Delta\rho_R(r_2). \quad (15)$$

Equation (15) is a *linear* equation for $\Delta\rho_R(r_1)$, which we can directly solve by iteration or other means. When $\rho_{R1}(r) = \rho^B$, and c_0 is assumed to vanish for $r > d$, Eq. (15) reduces to the standard PY equation²² for the uniform hard sphere fluid. This has an analytic solution^{18,2} and is known to give very good results overall, with small errors in the height of the first peak at very high densities. If still more accuracy is required, we can use modified generalized mean spherical approximation (GMSA)-type equations²³ related to the Percus–Yevick (PY) equation to describe c_0 , as discussed in Appendix D. Again we can solve Eq. (15) by iteration.

This constitutes the second step of our method. The net result of this two step process is the desired $\rho_0(r; [\phi_R])$ arising from a given ϕ_R . This can be substituted into Eq. (3), which can then be iterated to determine the final self-consistent ϕ_R^{MF} and $\rho_0(r; [\phi_R^{\text{MF}}])$. See Appendix C for further details of the calculations.

VI. RESULTS

We now give a detailed comparison of the radial distribution functions $g_0(r_2; [\phi_R^{\text{MF}}]) = \rho_0(r_2; [\phi_R^{\text{MF}}]) / \rho^B$ given by the two step method to the results of MD simulations of the full LJ fluid. In Fig. 6 we consider two high density states with $\rho^B = 0.78$ and $T = 1.35$ and $\rho^B = 0.85$ and $T = 0.88$. At these high densities small errors can be seen in the linear response treatment (equivalent to the hard core PY equation) of even the uniform hard sphere reference fluid. For greater accuracy therefore we used an improved GMSA description as briefly described in Appendix D. We find by direct comparison with simulations of the reference fluid in the pres-

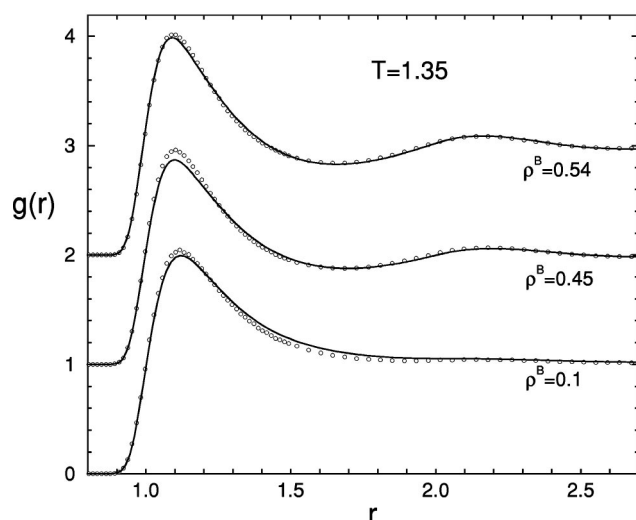


FIG. 7. Radial distribution functions for the lower density states indicated compared to the results of MD simulations (open circles) of the LJ fluid. The symbols have the same meaning as in Fig. 6.

ence of the self-consistent ERF that the two step method indeed gives a very accurate description of the nonuniform reference fluid density, as illustrated in the inset to Fig. 6.

The main remaining errors in describing the full LJ fluid are thus associated with the mean field approximation for the ERF. As already indicated in Fig. 2, this properly describes the basic shift in the first peak when compared to the WCA uniform reference fluid, but it also produces slight overshoots in the peaks and minima for these high density states, as can be seen in Fig. 6.

Figure 7 gives results for states at $T=1.35$ and a series of lower densities: $\rho^B=0.54$, $\rho^B=0.45$, and $\rho^B=0.10$. Here the linear response treatment of the reference system is sufficiently accurate and the attractive interactions produce large changes in the correlation functions. The results seem quite satisfactory, and are comparable to those given by the best standard integral equation methods.^{10,11} Results from the alternate methods discussed in Appendix B are equally good and essentially indistinguishable on the scale of the graph.

VII. FINAL REMARKS

These results thus give us additional confidence in the utility of our general approach. While we certainly do not advocate replacing standard and successful integral equation methods for the specific problem of the structure of uniform simple fluids, these ideas do suggest new ways of thinking about some basic issues. We can view the simple mean field approximation for the attractive interactions along with the generalized linear response treatment of correlations in the reference fluid as providing reasonably accurate and computationally practical first approximations for correlations induced by attractive and repulsive interactions. For qualitative and often quantitative work they have proved useful in a variety of different applications, including cases such as drying near walls⁶ where attractive forces induce large structural changes and standard integral equation methods fail.

For quantitative accuracy, improvements in both approximations may be called for in some cases. Incorporation of GMSA-type corrections²³ for reference fluid correlations is straightforward, as discussed in Appendix D, and alternate and probably more accurate treatments of the effects of soft cores can be used if needed.²⁴ Some corrections to the simplest mean field equation for the ERF, as discussed in Appendix A or in Ref. 5, can also be introduced. However, there are some fundamental errors arising from the use of any mean field approximation for the attractive interactions that cannot be easily avoided. The inherent limitations of mean field theory in treating long wavelength correlations such as those seen at the critical point or arising from capillary waves at the liquid-vapor interface are well known. Fortunately in many applications of interest such correlations do not play an important role, or their effects can be taken into account separately. In such cases the ideas discussed here provide a unified and physically suggestive perspective capable of giving a good qualitative and often a quantitative description of the structure of both uniform and nonuniform fluids.

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APPENDIX A: INTERPOLATED MEAN FIELD EQUATION

Equation (3) is *exact* as the density ρ tends to zero, where ϕ_R^{MF} reduces to the bare field ϕ_{LJ} . However, the next order term [of $O(\rho)$] in a density expansion is incorrect. This can most easily be seen by comparing the known density expansions² for the LJ system's $\rho(r_1; [\phi_{\text{LJ}}])$ with a LJ particle fixed at the origin, and the reference system's $\rho_0(r_1; [\phi_R])$ with the special wall particle with pair interaction $w_R(r_{01}) = \phi_R(r_1)$ fixed at the origin.

We examined an empirical modification of Eq. (3) that at low density gives the next term of $O(\rho)$ exactly but then quickly goes over to Eq. (3) at higher density:

$$\beta\phi_R^{\text{IMF}}(r_1) = \beta\phi_{\text{LJ}}(r_1) - \int d\mathbf{r}_2 \{ [\rho_0(r_2; [\phi_R^{\text{IMF}}]) - \rho^B] \times [1 + I(\rho)f_0(r_{12})]F_1(r_{12}; \rho^B) \}. \quad (\text{A1})$$

Here $I(\rho)$ is an *interpolation function* that tends to unity at low density and to zero at high density, $f_0(r) \equiv \exp[-\beta u_0(r)] - 1$, and

$$F_1(r; \rho) \equiv [\exp\{-\beta u_1(r)I(\rho)\} - 1]/I(\rho). \quad (\text{A2})$$

Possible choices for $I(\rho)$ include $I_1(\rho) = (\partial\rho/\partial\beta p)_0 \equiv S_{0,\rho}$,²⁵ proportional to the reference fluid isothermal compressibility, and $I_2(\rho) = S_{0,\rho}^2$, as suggested by a crude argument²⁶ based on perturbing the hard sphere Ornstein-Zernike equation by a very weak and slowly varying potential. At the lowest density studied, $\rho=0.1$, Eq. (A1) with

$I_2(\rho)$ gave a slightly better description of the weak second peak than does the simple mean field equation (3). See Fig. 5.

APPENDIX B: ALTERNATE EQUATIONS FOR SLOWLY VARYING ρ_{R1}

In Sec. V we exploited the Gaussian nature of fluctuations in the uniform reference system in carrying out both steps of the two step method. While this is a good approximation for LJ reference system, it may not always hold true. In our initial work in Ref. 6 we proposed a different and very general way of carrying out the first step, which, however, requires that ρ_{R1} varies sufficiently slowly that gradient type expansions give good results.

We started from an exact equation²⁷ first derived by Lovett, Mou and Buff (LMB):²⁸

$$\begin{aligned} \nabla_1 \rho_{R1}(r_1) / \rho_{R1}(r_1) = & -\beta \nabla_1 \phi_{R1}(r_1) \\ & + \int d\mathbf{r}_2 c_0(\mathbf{r}_1, \mathbf{r}_2; [\rho_{R1}]) \nabla_2 \rho_{R1}(r_2). \end{aligned} \quad (\text{B1})$$

The $c_0(\mathbf{r}_1, \mathbf{r}_2; [\rho_{R1}])$ for a general nonuniform ρ_{R1} is difficult to determine, so Eq. (B1) is generally not very useful for practical calculations. However, if ρ_{R1} is relatively slowly varying, then we can accurately approximate $c_0(\mathbf{r}_1, \mathbf{r}_2; [\rho_{R1}])$ under the integral in Eq. (B1) by the uniform fluid function $c_0(r_{12}; \bar{\rho}_{12})$,²⁹ where $\bar{\rho}_{12}$ is some average density associated with the two points. Then Eq. (B1) can be solved to determine ρ_{R1} .

A natural choice for $\bar{\rho}_{12}$ suggested by a gradient expansion¹⁸ is $\bar{\rho}_{12} = [\rho_{R1}(r_1) + \rho_{R1}(r_2)]/2$. This gives very good results when ρ_{R1} is reasonably smooth. This is the only approximation we make and we can check its accuracy by seeing if similar results arise from other approximations such as $\bar{\rho}_{12} = \rho_{R1}(r_1)$ or $\bar{\rho}_{12} = \rho_{R1}(r_2)$. Starting with a given ϕ_{R1} , we can then solve Eq. (B1) for the associated ρ_{R1} by iteration, making use of the analytic and accurate Percus–Yevick (PY) expressions for the direct correlation function of the uniform hard sphere fluid.^{18,22} If more accuracy is required we can use GMSA-type equations related to the PY equation²³ to describe c_0 . See Appendix D.

In our previous study of the LJ fluid near a hard wall,⁶ we used the basic separation of ϕ_R in Eqs. (6) and (7), and found that it indeed produced a slowly varying density response. As expected Eq. (B1) then gave very accurate results. However, in the present application, the size of the excluded volume region of the fixed particle (of order σ of the LJ potential) is also the same order as the range of the attractive interactions as well as the average spacing between particles at high density. If the basic separation is used, this “resonance” produces a ϕ_{R1}^B at very high density with small but noticeable oscillations of period $2\pi/\sigma$ outside the core and a pronounced minimum inside the core at $r_1=0$. The associated density response $\rho_0(r_1; [\phi_{R1}^B])$ will have a pronounced maximum at $r_1=0$ and oscillations outside the core, which will cause errors in the local expansion method used in Eq. (B1) and in Eq. (B4) to follow.

Fortunately, we can use the flexibility in the choice of the field $\phi_{R1}(r)$ in the core region to produce a much smoother density response. More precisely, we can define an extended separation of $\phi_R(r)$ in Eq. (5) by

$$\phi_{R0}^E(r) \equiv u_0(r) - \phi_0^E(r) \quad (\text{B2})$$

and

$$\phi_{R1}^E(r) \equiv u_1(r) + \phi_s(r) + \phi_0^E(r), \quad (\text{B3})$$

where $\phi_0^E(r)$ is an essentially arbitrary smooth function that is nonzero only in the repulsive core region but with $\phi_0^E(r) \ll u_0(r)$, so that ϕ_{R0}^E remains a harshly repulsive (essentially hard core) interaction. This separation still divides the ERF $\phi_R(r)$ into two parts with the physical meaning discussed in Sec. V, but provides some additional flexibility in the choice of $\phi_{R1}(r)$ in the core region that can be used to produce a smoother density response in the first step. An exact treatment of the response to both components of $\phi_R(r)$ would of course be independent of how the potential was separated.

We found best results by requiring that density response to ϕ_{R1}^E inside the (hard) core region be constant and continuous across the core. In a sense this is the smoothest possible choice, at least in the vicinity of the core region. This choice can easily be implemented numerically during the iterative solution of Eq. (B1) by simply setting $\nabla_1 \rho_{R1}(r_1)$ to be zero for all r_1 inside the core on each iteration and solving for the associated $\nabla_1 \phi_{R1}^E(r_1)$. At convergence, the self-consistent $\rho_{R1}^E(r)$ is constant inside the core and smoother outside the core than that produced by the basic separation.

Using the same extended separation, we have verified by comparison with the hydrostatic linear response method and with direct simulations that Eq. (B1) now gives accurate results for all the states tested here. Thus it offers an alternative (though numerically slightly more complicated) way of carrying out the first step.

In Ref. 6 we also carried out the second step in a slightly different way, effectively combining a local expansion of ρ_{R1} with a linear response treatment of the density induced by ϕ_{R0} . In particular, in Eq. (14) we treated the δ -function part of $\chi_0^{-1}(\mathbf{r}_1, \mathbf{r}_2; [\rho_{R1}])$ exactly and approximated the c_0 part by the uniform fluid function at the intermediate density $\bar{\rho}_{12} = [\rho_{R1}(r_1) + \rho_{R1}(r_2)]/2$. The accuracy of this approximation can again be checked by comparing with other choices such as $\bar{\rho}_{12} = \rho_{R1}(r_1)$. This yields the alternate equation for the second step:

$$\Delta \rho_R(r_1) / \rho_{R1}(r_1) = \int d\mathbf{r}_2 c_0(r_{12}; \bar{\rho}_{12}) \Delta \rho_R(r_2). \quad (\text{B4})$$

When $\rho_{R1}(r_1)$ is slowly varying, as was the case in all the examples studied in the previous work, Eq. (B4) gives accurate results, essentially identical to those of Eq. (15). This is also true for most of the states studied in the present application, provided that the appropriate extended separation is used. In such cases Eqs. (B1) and (B4) can be used as alternate ways of implementing the two step method, and for the states shown in Fig. 7 they give results on the scale of the graph essentially identical to those shown. However, for the high density states $\rho^B=0.78$ and $T=1.35$ and $\rho^B=0.85$ and $T=0.88$ in Fig. 6 the results using Eq. (B4) vary significantly

when different choices for $\bar{\rho}_{12}$ are made. This indicates that for these states ρ_{R1}^E is too rapidly varying for Eq. (B4) to be trusted. Since Eq. (15) gives accurate results even for these high density states, and makes fewer assumptions about the smooth behavior of ρ_{R1} , it is the preferred way to carry out the second step.³⁰

APPENDIX C: DETAILS OF THE NUMERICAL CALCULATIONS

We give here some details of the numerical solution of the basic equations (3), (13), and (15). Equations (B1) and (B4) could be used as alternates in the first and second step respectively except at the highest densities. We exploit the spherical symmetry of the density and the ERF about the center of the fixed wall particle, which we take as the origin of a spherical coordinate system. Since all these equations are used iteratively, we need an efficient and accurate method to calculate three dimensional integrals over $\mathbf{r}_2$ of the general form

$$I(r_1) = \int d\mathbf{r}_2 k(r_2) K(r_{12}; \bar{\rho}), \quad (\text{C1})$$

where due to the spherical symmetry $k(r_2)$ depends only on $r_2 = |\mathbf{r}_2|$, and $K(r_{12}; \bar{\rho})$ is a function only of $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ and r_1 and r_2 through our choice of the effective density $\bar{\rho}$ which equals either the hydrostatic density $\bar{\rho} = \rho_0^{r_1}$ or the average density $\bar{\rho} = \bar{\rho}_{12} = [\rho_{R1}(r_1) + \rho_{R1}(r_2)]/2$.

These properties make it advantageous for us to use *bipolar coordinates*³¹ with the substitution $y^2 = r_{12}^2 = r_1^2 + r_2^2 - 2r_1r_2\cos\theta$ and reduce the three dimensional integration to two:

$$I(r_1) = \frac{2\pi}{r_1} \int_0^\infty dr_2 r_2 k(r_2) \int_{|r_1-r_2|}^{r_1+r_2} dy y K(y; \bar{\rho}). \quad (\text{C2})$$

This transformation is particularly useful if the dependence of $K(y; \bar{\rho})$ on y is known analytically, since then we can explicitly carry out the y integration, and Eq. (C2) further reduces to a one dimensional integral. All relevant equations have K 's that satisfy this condition, thus permitting very efficient numerical computations.

In particular, Eq. (3) becomes

$$\begin{aligned} \phi_R^{\text{MF}}(r_1) - \phi_{\text{LJ}}(r_1) &= \frac{2\pi}{r_1} \int_0^\infty dr_2 r_2 [\rho_0(r_2; [\phi_R^{\text{MF}}]) - \rho^B] \\ &\quad \times \int_{|r_1-r_2|}^{r_1+r_2} dy y u_1(y), \end{aligned} \quad (\text{C3})$$

while Eq. (15) is transformed to

$$\begin{aligned} \Delta\rho_R(r_1)/\rho_0^{r_1} &= \frac{2\pi}{r_1} \int dr_2 r_2 \Delta\rho_R(r_2) \\ &\quad \times \int_{|r_1-r_2|}^{r_1+r_2} dy y c_0(y; \rho_0^{r_1}). \end{aligned} \quad (\text{C4})$$

Equations (13) and (B4) can be similarly rewritten.

The vector equation (B1) can be transformed into scalar form by taking the scalar product with the unit vector $\mathbf{r}_1/r_1$ and using the identity $2\mathbf{r}_1 \cdot \mathbf{r}_2 = r_1^2 + r_2^2 - r_{12}^2$. Thus we find

$$\begin{aligned} \frac{d\ln\rho_{R1}(r_1)}{dr_1} &= -\frac{\beta d\phi_{R1}(r_1)}{dr_1} + \frac{\pi}{r_1^2} \int dr_2 \frac{d\rho_{R1}(r_2)}{dr_2} \\ &\quad \times \int_{|r_1-r_2|}^{r_1+r_2} dy y (r_1^2 + r_2^2 - y^2) c_0(y; \bar{\rho}_{12}). \end{aligned} \quad (\text{C5})$$

In all these equations the integration over the variable y can be performed analytically, since we use the PY hard sphere direct correlation function $c_0(y)$, which is a polynomial in y ,² and the $u_1(y)$ of the Lennard-Jones potential, which is a sum of y^{-6} and y^{-12} terms.¹² Integrals involving an improved GMSA approximation for c_0 can also be carried out analytically. The resulting one dimensional integral equations can be solved by Picard iteration, where to enforce convergence we use the usual mixing technique.

In solving these equations the reference potential u_0 is initially taken to be a hard core potential with diameter d given by the accurate Verlet-Weiss expressions.³² As in the blip function method,² the result for $\rho_0(r; [\phi_R])$ with u_0 approximated by a hard core is linearly extrapolated into the core region and multiplied by the Boltzmann factor of the true soft core potential u_0 to give the final results for ρ_0 shown in Figs. 6 and 7. The errors introduced by this simplified treatment of soft cores are much smaller than those arising from our use of the mean field approximation for the ERF ϕ_R .

APPENDIX D: GENERALIZED MEAN SPHERICAL TREATMENT OF REFERENCE SYSTEM

The description of the reference system presented here relies on accuracy of the uniform hard sphere fluid direct correlation function $c_0(r)$. The generalized linear response treatment of Eq. (15) with $\rho_0^{r_1} = \rho^B$ and c_0 vanishing outside the core is equivalent to the PY approximation, and is surprisingly accurate at intermediate and low densities. However, at high density it has noticeable errors, especially in the region of the first peak near contact, and for quantitative results should be corrected.

Since the uniform fluid direct correlation function is just an input in our approach we can use other, more accurate approximations (even results of molecular simulations, if such are available). We have found that use of the generalized mean spherical approximation (GMSA) of Waisman,²³ as implemented by Hoyer and Stell,³³ gives considerable improvement over the original PY approximation. Moreover, it still preserves the analytic simplicity of the resulting $c_0(r)$ so that the methods of Appendix C can be used.

The GMSA approximates $c_0(r)$ outside the hard core (we set $d=1$ here), where PY assumes c_0 vanishes, by a Yukawa function:

$$c_0(r>1) = K \frac{e^{-z(r-1)}}{r}. \quad (\text{D1})$$

The exact core condition $g(r < 1) = 0$ then allows one to obtain $c_0(r)$ inside the core and satisfy the Ornstein–Zernike equation:

$$c_0(r < 1) = -a - br - \frac{\eta a}{2} r^3 - v \frac{1 - e^{-zr}}{zr} + v^2 \frac{\cosh zr - 1}{2Kz^2 e^z}. \quad (\text{D2})$$

Requiring consistency between compressibility and virial routes for the pressure and agreement with simulations gives explicit analytic expressions for a , b , v , K and z as functions of the packing fraction $\eta \equiv \pi \rho / 6$, as discussed in Ref. 33. We can use this improved expression for $c_0(r_{12}; \rho_0^{r_1})$ in Eq. (15) to describe the hard sphere reference fluid.

We can also amend our description of the wall particle in a similar way by adding the tail correction Eq. (D1) as given by the GMSA on the right side of Eq. (15). In the absence of attractive forces this equation then reduces exactly to a GMSA description of the response of a hard sphere fluid to a hard sphere fixed at the origin, and we neglect any changes in this correction when attractions are taken into account through $\phi_{R1}(r)$. These GMSA corrections to the usual linear response treatment are numerically significant only for the high density states studied in Fig. 6.

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¹² To compare with simulations, we actually used the standard cutoff and shifted LJ potential with cutoff radius at $r = 2.5\sigma$.

¹³ For a general review, see R. Evans, in *Fundamentals of Inhomogeneous Fluids*, edited by D. Henderson (Dekker, New York, 1992).

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¹⁵ A preliminary account of this part of our work was published in Ref. 5.

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¹⁷ H. C. Andersen and D. Chandler, *J. Chem. Phys.* **57**, 1918 (1972).

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²⁶ J. D. Weeks (unpublished).

²⁷ This follows immediately from Eq. (12) by considering the density response to a small shift in the external potential. See Ref. 28.

²⁸ R. A. Lovett, C. Y. Mou, and F. P. Buff, *J. Chem. Phys.* **65**, 570 (1976). See also M. Wertheim, *ibid.* **65**, 2377 (1976).

²⁹ Because of its simple structure and short range for the repulsive force reference system, interpolation of c_0 using this version of the LMB equation is more accurate than the use of the alternate Wertheim equation, which involves h_0 . See S. Iatsevitch and F. Forstmann, *J. Chem. Phys.* **107**, 6925 (1997) for further discussion of this point.

³⁰ Note that Eq. (15) requires only information about the hydrostatic density $\rho_0^{r_1}$ for $r_1 > d$, which in turn depends only on the local value of $\phi_s(r_1)$ outside the core. $\rho_0^{r_1}$ is more slowly varying than $\rho_{R1}(r_1)$ and from Eq. (4) depends only on the final density $\rho_0(r; [\phi_R^{MF}])$, which by assumption is not affected by any of the core changes made in $\phi_{R1}^E(r)$. Thus, assuming the linear response treatment is accurate, any separation, including in particular the basic separation, will give the same final result when the two step method is implemented using Eq. (13) and (15). This invariance, which also would hold for an exact two step treatment of the response to ϕ_R^{MF} , gives another reason for preferring the use of these equations.

³¹ See, e.g., M. S. Wertheim, *J. Math. Phys.* **5**, 643 (1964).

³² L. Verlet and J.-J. Weis, *Phys. Rev. A* **5**, 939 (1972).

³³ J. S. Hoye and G. Stell, *Mol. Phys.* **32**, 195 (1976).