# Intermolecular forces and the structure of uniform and nonuniform fluids

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We discuss the ramifications of Widom's idea that attractive intermolecular forces essentially cancel in dense uniform liquids. This idea was used directly in the WCA theory of uniform liquids, where the structure of the liquid is approximated by that of a simpler reference fluid with purely repulsive intermolecular forces. To take account of the unbalanced attractive forces found in nonuniform fluids, Weeks, Selinger, and Broughton (WSB) developed a new method where the structure is related to that of a nonuniform reference fluid in an external field chosen to yield a self-consistent description of correlations induced by the repulsive forces and a mean field treatment of the attractive forces. Using simulations, we provide a quantitative test of the accuracy of both methods for the uniform fluid at different points in the phase diagram by relating correlation functions in the uniform fluid to those in a nonuniform fluid with a particle fixed at the origin. We find that at high densities the WSB approach can correct most of the small errors in the structure of the WCA reference fluid. At lower densities the WSB method provides a considerable improvement over the WCA theory. A simplified version of the WSB method is presented that is of comparable accuracy.

## I. INTRODUCTION

Ben Widom has made major contributions to the conceptual framework of almost every area of liquid state science. He is widely renowned both for the depths of his insights and for the clarity of his exposition. His ability to focus on the critical questions using the simplest possible physical models has shaped the research directions of the entire field. While Widom's work in the theory of interfaces and critical phenomena is perhaps better known, we focus here on the theory of *uniform* liquids *away* from the critical point, where his ideas have proven no less important. As an illustration of this fact, we examine herein the problem of determining the structural and thermodynamic properties of uniform liquids, based on a generalization of a physical picture presented by Widom in an exceptionally lucid article [1].

In the following, we first give in Sec. II a brief review of Widom's original picture and its quantitative implementation into the perturbation theory of dense uniform liquids [2] developed by Weeks, Chandler, and Andersen (WCA). Recently, Weeks, Selinger, and Broughton (WSB) developed an extension of these ideas to *nonuniform* liquids [3]. Initial applications to drying transitions near hard walls and to the liquid-vapor interface were quite encouraging, but further tests and simplifications of the basic method are needed. After describing the general WSB method and a simplified version in Sec. III, we apply both versions to a *uniform* fluid and compare the results to the usual WCA approach. This allows us to make a quantitative test of the new method and to clarify its relation to the original ideas of Widom and WCA. In Sec. IV we present the results of Molecular Dynamics simulations (MD) designed to test the various approaches. The results are given in Sec. V and we summarize in Sec. VI.

## II. REPULSIVE FORCE MODEL FOR UNIFORM FLUIDS

### A. Widom force cancellation argument

In the fundamental paper mentioned above [1], Widom first showed how attractive forces play the dominant role in determining the highly unusual density correlations found near the critical point. He then turned to a discussion of "ordinary" uniform liquids near the triple point. Highly nontrivial "excluded volume" correlations arise in the dense but disordered environment of such a liquid simply from the requirement that neighboring repulsive molecular cores cannot overlap. Widom argued that in typical configurations the vector sum of the longer ranged and relatively weak "attractive forces exerted on any molecule by its neighbors largely cancel, while the negative potentials largely add . . . . " Thus it is "fundamentally the molecular correlations that are due to the repulsive component of the intermolecular forces, and not those that are due to the attractive component, that determine the properties" of such a fluid. He idealized the repulsive interactions by hard spheres and the attractions by a constant uniform background potential, which exerts no force on the hard spheres immersed in it, and was able to provide an accurate parameter free prediction of several thermodynamic properties of a simple fluid such as Argon at the triple point.

Widom's idea that the attractive *forces* essentially cancel at high density is quite compelling. It allows us to understand why a mean field approach, where the effects of the attractive forces on the structure are ig-

nored completely, could be surprisingly accurate. This picture applies not only to an idealized model [4] with infinitely long ranged and weak interactions (where the attractions rigorously exert no force) but also to realistic models describing the finite ranged attractive interactions seen in simple liquids [1], where the force cancellation is mainly between oppositely situated neighbors of a given molecule. It is also easy to see why this picture would be less accurate at lower density, where the fluctuations in neighbor positions are more pronounced and the cancellation less complete.

### B. Repulsive force reference fluid

It was natural to embed these ideas for a uniform fluid in a more formal and quantitative approach. This was essentially the program followed by WCA [2]. Although the theory can be applied to any pair interaction, we will consider for concreteness in the following the Lennard-Jones (LJ) fluid. WCA first divided the LJ pair potential

$$w(r) = 4\epsilon\,[\,(\sigma/r)^{12} - (\sigma/r)^{6}\,] \qquad (1)$$

into repulsive and attractive components: $w(r) = u_0(r) + u_1(r)$, defining the *repulsive force reference potential* $u_0(r)$ uniquely by the requirement that it vanish for $r > r_0 \equiv 2^{1/6}\sigma$, where the LJ force is attractive, and that it reproduce exactly the full LJ repulsive force $-w'(r)$, for $r \leq r_0$. Thus $u_0(r) = w(r) + \epsilon$ for $r \leq r_0$, and is zero otherwise.

To describe Widom's "excluded volume" correlations quantitatively, they considered a uniform *repulsive force reference fluid* (indicated by the subscript 0) made up of particles interacting only through the pair potential $u_0(r)$ and under the *constraint* that it has the same (number) density $\rho$ [2] as the full LJ fluid. This requirement ensures that typical local environments in the two fluids are similar: both fluids then have identical repulsive cores at the same average separation determined by the fixed density. Fig. 1a and 1b give a pictorial representation of this idea. Both analytical and numerical calculations can be carried out more easily using the simpler reference fluid.

If Widom's picture were exact, and correlations were propagated only by repulsive forces, we would then expect that *all* correlation functions in the repulsive force fluid should equal those in the full LJ fluid. Thus, comparison of correlation functions in the two systems provides a direct test of these ideas. The most favorable case is the pair correlation function. WCA found that the full fluid's radial distribution function $g(r)$ (indicated by no subscript) is indeed very similar to the reference fluid's $g_0(r)$ at high density. The WCA perturbation theory of liquids uses this assumption in calculating the free energy, and this similarity is the fundamental reason for its accuracy at high density [2]. This provides a striking confirmation of the power and utility of Widom's original insight.

### C. Effects of attractive forces

However, as will be discussed in detail below, small differences can be seen in the correlation functions, even at the highest density. Moreover, at lower density, where the cancellation picture is clearly less applicable, the errors in the approximation $g_0(r) \approx g(r)$ become much more significant. As $\rho \to 0$, the approximation is not even qualitatively accurate. To improve on these results, we must take some account of the effects of *attractive forces* on the structure of the fluid, while still maintaining an accurate description of the important excluded volume correlations.

The standard approach to this problem uses integral equation methods [5]. The most accurate of these [6] are based on some type of perturbation treatment of the attractive forces, and have given quite satisfactory results for $g(r)$ except near the critical point where, as Widom points out, special techniques are needed. Thus, the practical task of determining $g(r)$ for a uniform simple fluid away from the critical point is essentially a solved problem. However, the physical basis for using a particular integral equation closure and the underlying reasons for their accuracy are not fully understood. Moreover, these methods have failed dramatically in other seemingly related applications, such as determining the structure of inhomogeneous fluids [7].

It was these latter difficulties that lead WSB to try to develop a more physically motivated theory of inhomogeneous and confined fluids, based on a generalization of the Widom and WCA ideas. As we will see below, the insights gained from that work will also allow us to gain a deeper understanding of the role of attractive forces on the structure of uniform fluids. We first review the WSB theory [3] for nonuniform fluids.

## III. THEORY OF NONUNIFORM FLUIDS

When considering the structure of a nonuniform fluid, at least two new complications arise. First, the full fluid with pair interactions $w(r)$ generally interacts also with an *external field* $\phi(\mathbf{r})$ describing, e.g., the effects of confining walls, etc. Perhaps conceptually more important is the fact that attractive forces must be treated more carefully, since their averaged effects clearly do not cancel by symmetry in a nonuniform fluid. This problem is more difficult precisely because we can no longer rely on Widom's cancellation argument to do most of the work for us! Thus, in general, *both* attractive and repulsive forces can have important effects on the structure of a nonuniform fluid.

### A. Nonuniform reference fluid

To deal with these issues, WSB introduced a *nonuniform* repulsive force reference fluid (denoted by the subscript R). In this model fluid, particles interact through the repulsive pair potential $u_0(r)$ and with a *self-consistently chosen effective field* $\phi_{\rm R}(\mathbf{r})$ which takes account of both the unbalanced attractive forces in the full fluid as well as the effects of the external field $\phi$. With this choice, the structure of the nonuniform reference fluid is again supposed to resemble that of the full fluid. Thus we still have the advantages of working with a simpler reference system with short-ranged purely repulsive intermolecular forces, but the proper choice of the external field $\phi_{\rm R}(\mathbf{r})$ can allow us to incorporate some of the important effects of the attractive forces on the fluid's structure.

To determine the effective field $\phi_{\rm R}(\mathbf{r})$, we follow WSB and take seriously Widom's insight that it is profitable to look at the balance of *forces* in liquids. The exact YBG hierarchy [5] permits a quantitative treatment [8] of this idea. In particular, consider both for the total system (shown here), and for the nonuniform reference system, the first equation of the YBG hierarchy. This can be written in the form

$$k_{\rm B}T\,\nabla_1 \ln \rho(\mathbf{r}_1;[\phi]) = -\nabla_1\phi(\mathbf{r}_1) - \int d\mathbf{r}_2 \rho(\mathbf{r}_2|\mathbf{r}_1;[\phi])\nabla_1 w(r_{12})\,. \quad (2)$$

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 density at $\mathbf{r}_2$ given that a particle is fixed at $\mathbf{r}_1$. The notation $[\phi]$ indicates that the correlation functions are functionals of the external field; for a given $\phi$ and $w$ *all* correlation functions are in principle determined. The right hand side gives the ensemble-averaged *mean force* acting on a particle fixed at $\mathbf{r}_1$; i.e., the vector sum of the direct force from the external field and the net force arising from the pair interactions with all the other particles. Note that this must be nonzero if there is a gradient at $\mathbf{r}_1$ in the singlet density $\rho(\mathbf{r}_1;[\phi])$.

Since our aim is to produce similar structures in the reference and full fluids, it is natural to choose $\phi_{\rm R}(\mathbf{r})$ so that the local (singlet) densities [7] at every point $\mathbf{r}$ in the two fluids are equal:

$$\rho_{\rm R}(\mathbf{r};[\phi_{\rm R}]) = \rho(\mathbf{r};[\phi]), \quad (3)$$

thus implying equality of the mean force at each $\mathbf{r}$ in the two fluids. It is known that such a field always exists in principle [9]; we derive below an approximate equation to determine its value explicitly.

To that end, let us examine physically the consequences of such a choice. As suggested by the arguments above for the uniform system, we assume that this condition produces similar local environments for the repulsive cores in the two fluids. Then if correlations are dominated by excluded volume effects, higher order correlation functions should again be very similar. In particular, we assume that if Eq. (3) is satisfied, then we also have

$$\rho_{\rm R}(\mathbf{r}_2|\mathbf{r}_1;[\phi_{\rm R}]) \approx \rho(\mathbf{r}_2|\mathbf{r}_1;[\phi])\,. \quad (4)$$

Eq. (4) is the basic structural hypothesis in the WSB method, and, as we will see, it represents the *only* approximation in the theory. This seems a natural extension of the WCA picture to a nonuniform system. Indeed, in a uniform system with $\phi = \phi_{\rm R} = 0$, we have the exact relation $\rho(\mathbf{r}_2|\mathbf{r}_1) = \rho g(r_{12})$, where $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$, and Eq. (4) reduces to the WCA approximation $g_0(r) \approx g(r)$. As is the case for uniform fluids, we expect Eq. (4) to be most accurate at high density.

### B. Inhomogeneous force equation

To get an explicit equation to determine $\phi_{\rm R}$, we use Eqs. (3) and (4) in (2), and subtract the exact YBG equation (2) for the nonuniform reference system. This yields the basic equation for $\phi_{\rm R}$ in the WSB method:

$$\nabla_1[\phi(\mathbf{r}_1) - \phi_{\rm R}(\mathbf{r}_1)] = -\int d\mathbf{r}_2\, \rho_{\rm R}(\mathbf{r}_2|\mathbf{r}_1;[\phi_{\rm R}])\nabla_1 u_1(r_{12})\,. \quad (5)$$

Some important benefits of the subtraction are that rapidly varying terms involving the repulsive pair interactions and the singlet density cancel by choice of $\phi_{\rm R}$, leaving an average only over the gradient of the slowly varying *attractive* potential $u_1(r_{12})$. The resulting self-consistent equation (5) has an obvious interpretation in terms of mean field ideas, which we will discuss in more detail later. However, it focuses directly on *forces*, and can appropriately be called the *inhomogeneous force* equation. In essence, Eq. (5) equates the net force generated by the external field and from attractive pair interactions to the inhomogeneous force $-\nabla\phi_{\rm R}$ in the reference system. In a uniform system with zero external field, this force cancels by symmetry and the theory reduces to the mean field picture of Widom [1] and WCA.

Perhaps the simplest way to solve (5) is by iteration. For fixed $u_0$ and *any* given "trial field" $\phi_t$, the associated correlation function $\rho_t(\mathbf{r}_2|\mathbf{r}_1;[\phi_t])$ is completely specified, and could in principle be calculated accurately. Eq. (5) then gives another non-trivial relation between $\phi_t$ and $\rho_t(\mathbf{r}_2|\mathbf{r}_1;[\phi_t])$ that can be iterated to self-consistency. The resulting self–consistent $\phi_{\rm R}$ yields a correlation function $\rho_{\rm R}(\mathbf{r}_2|\mathbf{r}_1;[\phi_{\rm R}])$ that reproduces the *same* $\phi_{\rm R}$ on the left hand side of (5). The self-consistent $\rho_{\rm R}(\mathbf{r};[\phi_{\rm R}])$ and $\rho_{\rm R}(\mathbf{r}_2|\mathbf{r}_1;[\phi_{\rm R}])$ offer approximations to the same functions in the full fluid.

Note that the approximation (4) is used only under the integral sign in Eq. (5). Any errors in (4) are important in

determining $\nabla\phi_{\rm R}(\mathbf{r}_1)$ from (5) only where the attractive forces are non-zero. Moreover, these vectorial quantities, weighted by the structure, are averaged over all space. Thus in many cases the main features of $\nabla\phi_{\rm R}(\mathbf{r}_1)$ are apparent from (5) using only crude approximations for $\rho_{\rm R}(\mathbf{r}_2|\mathbf{r}_1;[\phi_{\rm R}])$, and we expect the iteration process to converge rapidly.

### C. Results for fluids near walls

This was the case in the initial application [3] to fluids near repulsive walls studied by WSB, where a "drying region" of lower density near the wall can occur. To establish the accuracy of the basic equation (5) independent of any additional approximations made in determining $\rho_{\rm R}(\mathbf{r}_2|\mathbf{r}_1;[\phi_{\rm R}])$, they carried out MD simulations of the structure of the reference and the full LJ fluid next to a "hard" wall [modeled by the repulsive part of the LJ potential $u_0(z)$] for a few thermodynamic states of varying density along the critical isotherm. The effective wall potential $\phi_{\rm R}(z)$ in the reference fluid was computed self-consistently from (5) using *exact* (MD) values for $\rho_{\rm R}(\mathbf{r}_2|\mathbf{r}_1;[\phi_{\rm R}])$. Only two or three iterations were needed to achieve a self-consistent solution even starting from the "bare" $u_0(z)$. Approximate values of $\phi_{\rm R}(z)$ that were calculated by using much simpler estimates for the conditional density, including even a step function profile [10], were remarkably close to the fully self-consistent value.

Eq. (5) generates a *soft and smooth repulsive force* $-\nabla\phi_{\rm R}(z)$ 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 is the origin of the drying effect in this mean field approach. Sullivan and coworkers [7] have shown that standard integral equation methods cannot accurately describe these drying states. In contrast, the WSB 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 they found good qualitative agreement with simulations both for $\rho(z)$ and $\rho(\mathbf{r}_2|\mathbf{r}_1;[\phi_{\rm R}])$, and at high density nearly quantitative agreement.

In the WSB method, information about the structural effects of attractive intermolecular forces is encoded into an effective force field $-\nabla\phi_{\rm R}(\mathbf{r})$ that in many cases is easy to approximate and to understand physically. The WSB method logically separates the self–consistent calculation of the inhomogeneous force $-\nabla\phi_{\rm R}(\mathbf{r})$, which from (5) is often rather insensitive to errors in $\rho_{\rm R}(\mathbf{r}_2|\mathbf{r}_1;[\phi_{\rm R}])$, from the determination of the structure of the reference fluid itself in the presence of a given external field [11]. The latter becomes an appropriate focus for future research.

This indirect treatment of the effects of attractive intermolecular interactions through the use of an effective single particle potential is characteristic of a mean field approximation. Here we have incorporated mean field ideas into a formalism where *forces* appear naturally. This has allowed us to take the next step beyond Widom's profound insight that $\nabla\phi_{\rm R}(\mathbf{r})$ vanishes by symmetry for uniform systems with $\phi$=0 [1]. We can achieve the computational and conceptual simplifications of a model with purely repulsive intermolecular forces while still taking into account the averaged effects of the attractive forces in a physically sensible way.

## IV. UNIFORM FLUID REVISITED

### A. Wall particle picture

Using this perspective, we now return to the problem of determining the effects of attractive forces on the structure of *uniform* fluids. If we simply set the external field $\phi = 0$ in Eq. (5), then $\nabla\phi_{\rm R}(\mathbf{r})$ vanishes by symmetry, and we revert to the original Widom-WCA approach. However, we can obtain nontrivial results from Eq. (5) through the use of the exact relation [12] between pair correlations in a uniform fluid and the singlet distribution function in a nonuniform fluid in the external field $\phi_{\rm LJ}(r_1) \equiv w(r_{10})$ corresponding to a LJ-particle fixed at the origin $\mathbf{r}_0$:

$$\rho g(r_{10}) = \rho(\mathbf{r}_1|\mathbf{r}_0;[\phi=0]) \; = \rho(\mathbf{r}_1;[\phi_{\rm LJ}])\,. \qquad (6)$$

In the presence of this external field, the mean force at $\mathbf{r}_1$ no longer vanishes by symmetry in the full fluid and Eq. (5) will yield a nonzero $\phi_{\rm R}(r_1)$.

We can think of this field as arising from a special reference particle fixed at the origin which interacts with all the other particles through an effective pair potential $w_{\rm R}(r_{10}) \equiv \phi_{\rm R}(r_1)$; all other particles in the WSB reference system interact with each other through the repulsive pair potential $u_0(r_{ij})$. In the example studied by WSB of a fluid next to a wall, the wall interacted with the reference particles through an effective field $\phi_{\rm R}(z)$; in the present uniform fluid application, we can imagine the wall shrinking down to the special "wall particle" fixed at the origin.

It is convenient in what follows to define the analog of $u_1(r_{10})$ for the potential of the wall particle, $u_{1\rm R}(r_{10}) \equiv w_{\rm R}(r_{10}) - u_0(r_{10})$; note that $u_{1\rm R}$ in general may have both attractive and repulsive regions. The original WCA reference system corresponds to the particular choice of $w_{\rm R}(r_{10}) \equiv u_0(r_{10})$ or $u_{1\rm R}(r) = 0$ for the wall particle pair potential. The extra flexibility in the WSB method arising from the self-consistent choice of the potential $w_{\rm R}(r_{10})$ allows it to take account of some effects

of the attractive forces on the structure. See Fig. 1 for a pictorial representation of this idea.

This application of the inhomogeneous force equation to a uniform fluid provides a stringent test of its accuracy. Unlike the previous examples studied by WSB where the qualitative form of $\phi_{\rm R}(z)$ was easy to guess, it was not obvious (to us at least) what the proper form of $w_{\rm R}(r_{10})$ should be, at least at high density where the differences in $g(r)$ and $g_0(r)$ are rather small and subtle. Nevertheless, given its sound physical foundations, we would expect Eq. (5) to give improved results over a wide range of density.

Indeed, while the direct structural approximation in Eq. (4) should be most accurate at high density, its use in Eq. (5) can yield accurate predictions for $\phi_{\rm R}$ even at much lower densities. It is clear that in the extreme low density limit $\rho \to 0$, the r.h.s. of Eq. (5) vanishes. Thus in this limit it predicts $w_{\rm R}(r_{10}) = w(r_{10})$ or $u_{1{\rm R}}(r_{10}) = u_1(r_{10})$, which gives the *exact* low density limit for the correlation function $g_{\rm R}(r) = \exp(-w(r)/k_{\rm B}T) = g(r)$. This stands in marked contrast to the poor results of the WCA approximation $g_0(r) \approx g(r)$ in this limit. (However, as we will see below, the next order correction in the density from Eq. (5) is incorrect, and overall the theory is better at higher density.)

We emphasize that we are not proposing to apply Eq. (5) to uniform fluids in order to arrive at a simpler or computationally more efficient method than the successful integral equation approaches. Rather we view the uniform fluid as an important testing ground for the physical ideas that lead to Eq. (5); this equation has proved accurate in other applications where the integral equations have failed.

We can also use the uniform fluid to test various simplifications of the basic equation (5). It is quite difficult to accurately determine the full conditional singlet density $\rho_{\rm R}(\mathbf{r}_2|\mathbf{r}_1;[\phi_{\rm R}])$ appearing in Eq. (5), but in the applications studied by WSB, many basic features of the effective field $\phi_{\rm R}(\mathbf{r})$ could be found using relatively crude approximations to this function. If this remains true in the more subtle application to the uniform fluid, this suggests we may be able to simplify the theory with little loss of accuracy. Moreover, this approach could lead to a better physical understanding of the existing integral equation closures and could suggest new ones.

### B. Simplified mean field equation

To that end, we also examine for the uniform fluid case the much simpler equation that results when the conditional density $\rho_{\rm R}(\mathbf{r}_2|\mathbf{r}_1;[w_{\rm R}])$ is replaced by the ordinary singlet density $\rho_{\rm R}(\mathbf{r}_2;[w_{\rm R}])$ on the r.h.s. of Eq. (5). This approximation is much less drastic than one might at first suppose, since the main differences in the two functions occur when $\mathbf{r}_2$ is close to $\mathbf{r}_1$, but then for small $r_{12} < r_0 = 2^{1/6}\sigma$, the multiplicative factor $\nabla_1 u_1(r_{12})$ vanishes identically. If this approximation is made, then the gradient $\nabla_1$ can be taken outside the integral in Eq. (5) and the equation can be integrated. If we choose the constant of integration so that $w_{\rm R}(r_{10})$ vanishes far from the origin, then the simplified equation can be written in the following suggestive mean field [13] form:

$$u_{1{\rm R}}(r_{10}) = u_1(r_{10}) + \rho \int d\mathbf{r}_2 \, [g_{\rm R}(r_{20}) - 1] \, u_1(r_{12}) \,, \quad (7)$$

where

$$g_{\rm R}(r_{20}) = \rho(\mathbf{r}_2;[w_{\rm R}])/\rho \quad (8)$$

is the radial distribution function in the nonuniform reference fluid with respect to the wall particle fixed at the origin. Note that Eq. (7), like Eq. (5), yields *exact* results for $u_{1{\rm R}}$ as $\rho \to 0$. Although we will not pursue this further herein, Eq. (7) can be solved by standard integral equation methods and can be used to derive new closures [14]. In any case, it is clear that Eq. (7) is significantly easier to deal with than Eq. (5) and we expect it to play an important role in future developments of the theory.

### C. Method of solution

In order to test the accuracy of the basic equations (5) and (7) without any further approximations, we carried out MD simulations for the three model systems shown in Fig.1: the full LJ system, the original WCA repulsive force system, and the inhomogeneous reference system. To determine the effective potential in the latter case, we solved Eqs. (5) and (7) by iteration using the MD results. In the following all results will be given in reduced LJ-units, i.e., the unit of energy is $\epsilon$, the unit of length is $\sigma$ and the unit of time is $(m\sigma^2/\epsilon)^{1/2}$. In order to cover a broad range of the phase diagram, several states along the critical isotherm with $T$=1.35 and $\rho$=0.78 / 0.54 / 0.45 / 0.1 as well as a state near the triple point with $T$=0.88 and $\rho$=0.85 were investigated.

### D. Simulation Details

We performed molecular dynamics (MD) simulations in the (NVT)-ensemble using the velocity form of the Verlet algorithm with a time step of $\Delta t$=0.001. Constant temperature was maintained by choosing new velocities for all particles every 150 MD-steps with the probability of the corresponding Boltzmann distribution. The LJ potential was cut off at $r$=2.5$\sigma$ and shifted in the usual manner. We used $N$=3000 for the high density states with $T$=1.35, $\rho$=0.78 and $T$=0.88, $\rho$=0.85 and $N$=450 for all other simulations. The absence of finite size effects was verified. To measure $\rho(\mathbf{r}_2;[w_{\rm R}])$ we first equilibrated

for at least $5 \cdot 10^5$ MD-steps and calculates $\rho(\mathbf{r}_2;[w_{\rm R}])$ in the following $3 \cdot 10^6$ and in the longest runs $5.5 \cdot 10^7$ MD-steps. In the cases of the inhomogeneous reference system we iterate until we see a convergence in $\rho(\mathbf{r}_2;[w_{\rm R}])$.

## V. RESULTS

The figures 2-4 show the simulation results for the radial distribution function $g_{\rm R}(r_{20})$ at the temperature $T$=1.35 and the densities $\rho$=0.78 , $\rho$=0.45 and $\rho$=0.1 respectively. For each density we compare the $g(r_{20})$ of the full LJ system (solid line, filled circles), the homogeneous WCA repulsive system (dotted line, filled squares) and the inhomogeneous reference system (WSB approximation) as determined using both Eq. (5) (dashed line, open circles) and Eq. (7) (long dashed line, open diamonds).

At the highest density ($\rho$=0.78) all curves are very similar (Fig.2a) and even the enlargement of the first peak (Fig.2b) shows only small differences. We also find that there is very little difference in the results from the full and the simplified WSB equations. Similar results were found near the triple point ($T$=0.88 , $\rho$=0.85). For these high density states, the original WCA approximation, i.e., the homogeneous repulsive system, is a rather good approximation to the full LJ system, as suggested by Widom's cancellation argument.

However, as Figs.2b) shows, even these small differences between the full and the repulsive force system can be improved by using the WSB approximations. The first term of Eq. (5) corrects the force of the wall particle on its first and second neighbors. Instead of using $\nabla w_{\rm R}(r_1) = \nabla \phi_{\rm R}(r_1) = \nabla u_0(r_1)$ as in the homogeneous repulsive system, the WSB approximations self-consistently take account of attractive forces. Thus they use to lowest order in $\rho$, $\nabla w_{\rm R}(r_1) \approx \nabla w(r_1)$. As a consequence, particles with separations $r_1 > r_0$ are pulled into the first neighbor peak of the wall particle at $r_0$. Therefore the first minimum of the WSB approximations is lower than the first minimum of the repulsive system, and the right wing of the first peak is shifted to the right, in agreement with the full LJ system (Fig.2b). Thus, while small differences remain, the use of the inhomogeneous reference system corrects the main qualitative defects in the WCA approximation. This is strong evidence that the underlying physical picture is valid.

Even though the WCA approximation described in Sec. II B gives a fairly good description at high densities, it breaks down noticeably at $T$=1.35 and $\rho$=0.54 and $\rho$=0.45 (Fig.3). Both peak positions and peak heights are clearly different for the full and the repulsive force system. On the other hand, both WSB approximations describe the full LJ system very well. As before, at $\rho = 0.45$ both the right wing of the first peak and even the peak height are corrected by choosing $\nabla w_{\rm R}$ instead of $\nabla u_0$. Again we find that the simplified Eq. (7) gives as good results as the full Eq. (5). Thus these equations are capable of describing the much more significant effects of attractive forces on the structure seen at moderate densities. Moreover, as pointed out earlier, both equations are *exact* in the extreme low density limit as $\rho \to 0$.

However, at slightly higher, but still very low densities, noticeable errors in the WSB approximations can be seen. Thus for $\rho$=0.1 (Fig.4), the first peak height is overestimated and the right wing shifted too far to the right. (Of course the results are still much better than the WCA approximation.) The small second peak in the LJ $g(r_{20})$ is completely missing. It is still the case that Eq. (7) gives essentially the same results as the full Eq. (5). The reason for this is again the strong influence of the force of the wall particle on the particles of the first and second neighbor shell. It is clear that if we require a general theory that is accurate in this low density regime, we must reexamine the use of the basic approximation (4) in Eq. (2). Work along these lines will be reported elsewhere [14].

## VI. SUMMARY

In this paper we have examined theories building on Widom's key idea of the cancellation of attractive forces in dense liquids. This idea was embedded in the WCA theory of uniform liquids. A more general treatment of the roles of attractive and repulsive forces in nonuniform liquids led WSB to the basic inhomogeneous force equation (5). After reviewing these ideas, we tested their accuracy on the uniform fluid by relating its correlation function to that of a nonuniform fluid with a particle fixed at the origin. Via simulations we have tested quantitatively at different points of the phase diagram the WCA and the WSB approaches, using both Eq. (5) and a simplified version, Eq. (7).

The WCA approximation $g_0(r) \approx g(r)$ is reasonably accurate only for very dense liquids; the WSB method considerably improves these high density results. Moreover, it remains accurate for such moderate density states as $\rho$=0.45, $T$=1.35, and is exact in the low density limit $\rho \to 0$. However, noticeable errors are seen at slightly higher density states such as $\rho$=0.1, $T$=1.35. A potentially very useful finding is that the much simpler effective field equation (7) gave nearly as accurate results as did the use of (5). Since this was also the case in the examples studied by WSB of a fluid near a hard wall and for the liquid-vapor interface [3], we believe it may prove useful in a variety of other applications.

## VII. ACKNOWLEDGMENTS

It is our pleasure to dedicate this paper to Ben Widom on the happy occasion of his 70th birthday. We are grate-

ful to Hans Andersen and David Chandler for many helpful remarks. This work was supported in part by the NSF Grant No. CHE9528915. KV greatfully acknowledges support from the Deutsche Forschungsgemeinschaft.

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## Figure Captions

**Fig.1** This figure summarizes the three models used. a) corresponds to the full system with interactions of Eq. (1), b) corresponds to the homogeneous repulsive WCA system and c) corresponds to the inhomogeneous reference system. In the original Widom-WCA interpretation the circled particle represents a typical particle in the uniform fluid; the force cancellation in a) is mainly between oppositely situated neighbors. In the WSB interpretation the circled particles in a), b) and c) represent special particles fixed at the origin. The pair potential of the fixed particle in c) is $w_{\rm R}$.

**Fig.2** $g(r_{20})$ at $T$=1.35 and $\rho$=0.78. Shown are the simulation results of the homogeneous full LJ system (solid line in a), filled circles in b)), of the homogeneous repulsive system (dotted line in a), filled squares in b)) and of the inhomogeneous reference system with $\nabla w_{\rm R}$ determined iteratively via simulations with Eq. (5) (dashed line in a), open circles in b)) and with Eq. (7) (long-dashed line in a), open diamonds in b)). Fig. b) is an enlargement of the first peak.

**Fig.3** $g(r_{20})$ at $T$=1.35 and $\rho$=0.45. Symbols are as in Fig. 1. Fig. b) is an enlargement of the first peak.

**Fig.4** $g(r_{20})$ at $T$=1.35 and $\rho$=0.1. Symbols are as in Fig. 1. Fig. b) and c) are enlargements of the first and second peaks respectively.

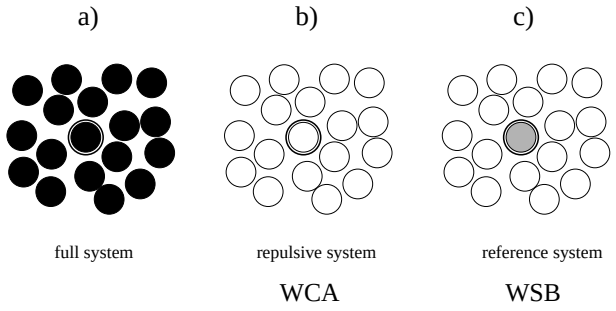
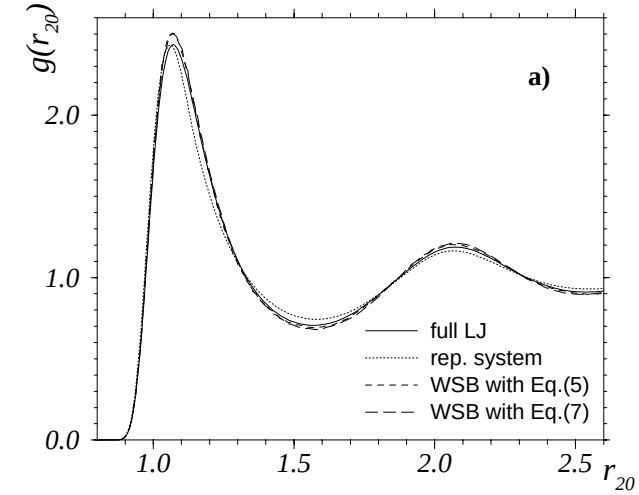



FIG. 1.



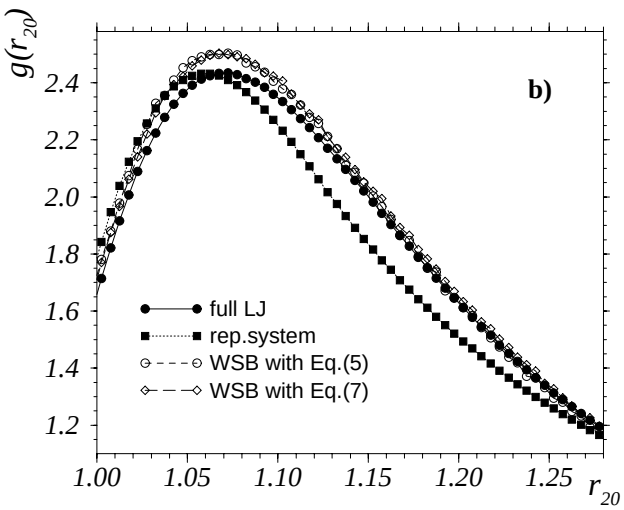
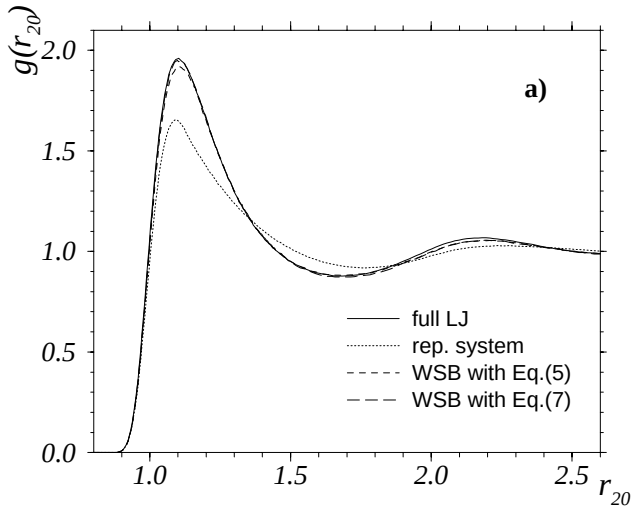




FIG. 2.



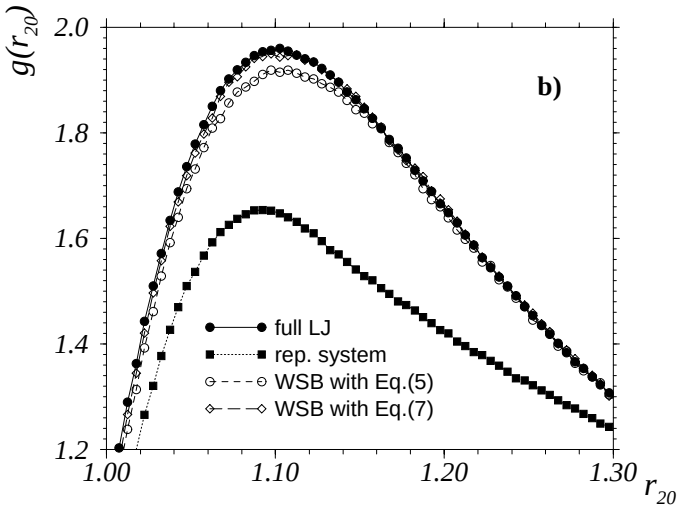




FIG. 3.

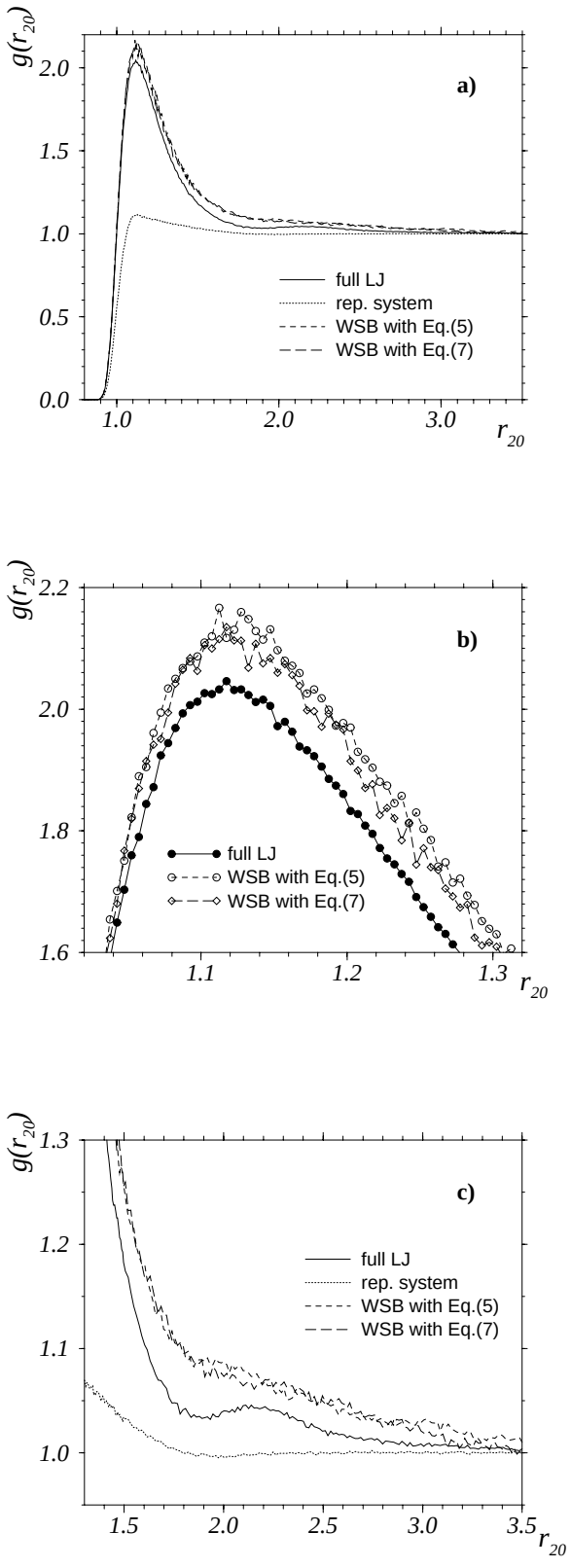



FIG. 4.