Roles of Repulsive and Attractive Forces in Determining the Structure of Nonuniform Liquids: Generalized Mean Field Theory

John D. Weeks,[1,2] Kirill Katsov,[1] and Katharina Vollmayr[1]
[1]*Institute for Physical Science and Technology, University of Maryland, College Park, Maryland 20742*
[2]*Department of Chemistry, University of Maryland, College Park, Maryland 20742*
(Received 9 June 1998)

The structure of a nonuniform Lennard-Jones (LJ) liquid near a hard wall is approximated by that of a reference fluid with repulsive intermolecular forces in a self-consistently determined external mean field incorporating the effects of attractive forces. We calculate the reference fluid structure by first determining the response to the slowly varying part of the field alone, followed by the response to the harshly repulsive part. Both steps can be carried out very accurately, as confirmed by Monte Carlo simulations, and good agreement with the structure of the full LJ fluid is found. [S0031-9007(98)07606-6]

PACS numbers: 61.20.Gy, 68.10.Cr, 68.45.Gd

Dense liquids have highly nontrivial density correlations arising because the harshly repulsive molecular cores cannot overlap [1–3]. Because of the constantly changing molecular arrangements, such correlations play a much more fundamental role in liquids than they do in other condensed phases such as glasses and solids, which sample only a few basic configurations. Indeed, a model with only repulsive intermolecular forces [2] can give a surprisingly accurate description of the full density correlations seen in a uniform dense simple liquid like Ar because the vector sum of the longer ranged attractive forces on a given particle essentially *cancels* [1] in most typical configurations.

Nonuniform liquids present a greater and qualitatively different challenge, since even the averaged effects of attractive forces clearly do not cancel [4]. We discuss here an example where *both* attractive and repulsive forces can greatly influence the liquid's structure: a Lennard-Jones (LJ) fluid next to a hard wall. We obtain accurate numerical results using a physically suggestive generalized mean field description of the attractive forces [5]. We consider first the effects of these slowly varying forces on the liquid's structure before taking account of the response to the rapidly varying (hard-core-like) part of the external field. This treatment of attractive interactions is quite different from that used in conventional integral equation and density functional methods [6], and we believe it offers important conceptual and computational advantages.

Fluid particles interact with a known external (wall) field $\phi(\mathbf{r})$ and through the LJ pair potential $w(r_{ij}) \equiv u_0(r_{ij}) + u_1(r_{ij})$, divided as usual [2] so that all the repulsive intermolecular forces arise from u_0 and all the attractive forces from u_1. 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 in all that follows a harshly repulsive interaction and the subscript 1 a much more slowly varying interaction usually associated with attractive forces. Here we take $\phi(\mathbf{r})$ to be a hard wall potential, setting $\phi_1(\mathbf{r}) = 0$ and $\phi_0(\mathbf{r}) = \phi_{\mathrm{HW}}(z)$, where $\phi_{\mathrm{HW}} = \infty$ for $z \le 1$ (in reduced units) and 0 otherwise, and we let ρ_B be the bulk density far from the wall.

We relate the structure of the nonuniform LJ system to that of a simpler *nonuniform reference fluid* [4,7], with only repulsive intermolecular pair interactions $u_0(r_{ij})$ (equal to the LJ repulsions) in a different *effective reference field* (ERF) $\phi_R(\mathbf{r})$. While the replacement of attractive pair interactions by an approximate "molecular field" is an essential step in mean field theory, we can think of other more general choices. 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 [8]:

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

The subscript 0 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.

To find ϕ_R explicitly, we subtract the first equations of the YBG hierarchy [3] for the full and reference systems with ϕ_R chosen so that Eq. (1) is satisfied [4,7]. The result can be written exactly as

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

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

If we assume that Eq. (1) produces similar local environments for the (identical) repulsive cores in the two fluids, which mainly determine density correlations through excluded volume effects, then the conditional singlet densities in the two fluids should also be very similar. This key structural assumption introduces a generalized mean

 0031-9007/98/81(20)/4400(4)$15.00

field theory in which the reference fluid still has nontrivial pair and higher order correlations induced by the repulsive forces. This suggests that the last term on the right-hand side of Eq. (2) is often very small. If we ignore it completely [9] we obtain the approximate equation for the field ϕ_R suggested by Weeks, Selinger, and Broughton [4]:

$$\nabla_1[\phi_R(\mathbf{r}_1) - \phi(\mathbf{r}_1)] = \int d\mathbf{r}_2\, \rho_0(\mathbf{r}_2 \mid \mathbf{r}_1; [\phi_R]) \times \nabla_1 u_1(r_{12}). \quad (3)$$

Equation (3) incorporates mean field ideas, but it appropriately focuses on *forces* [1,2]. The relation to ordinary mean field theory becomes clearer [7] if we replace $\rho_0(\mathbf{r}_2 \mid \mathbf{r}_1; [\phi_R])$ by $\rho_0(\mathbf{r}_2; [\phi_R])$ in Eq. (3). This approximation is much better than one might at first suppose, since the main difference in these two functions occurs when $\mathbf{r}_2$ is close to $\mathbf{r}_1$, but then for small r_{12} the multiplicative factor $-\nabla_1 u_1(r_{12})$ (the *attractive* part of the LJ force) vanishes identically. The gradient ∇_1 can then be taken outside the integral and Eq. (3) can be integrated. Choosing the constant of integration so that the density far from the wall equals ρ_B, we obtain the simplified mean field equation [7]:

$$\phi_R(\mathbf{r}_1) - \phi(\mathbf{r}_1) \equiv \phi_s(\mathbf{r}_1) = \int d\mathbf{r}_2\, [\rho_0(\mathbf{r}_2; [\phi_R]) - \rho_B] u_1(r_{12}). \quad (4)$$

Because of the integration over the slowly varying attractive potential "weighting function" $u_1(r_{12})$, $\phi_s(\mathbf{r})$ in Eq. (4) extends smoothly into the repulsive core region where $\rho_0(\mathbf{r}; [\phi_R])$ vanishes. Outside the wall it is smooth and relatively slowly varying even when $\rho_0(\mathbf{r}; [\phi_R])$ itself has pronounced oscillations. Physically $\phi_s(\mathbf{r})$ mimics the effects of the unbalanced attractive forces in the LJ system, giving a soft *repulsive* interaction [4] that tends to push the reference particles away from the wall.

In order to solve equations like (3) or (4) to obtain the self-consistent ERF $\phi_R(\mathbf{r})$, we must determine the required reference fluid distribution functions arising from a given external field. In previous work [4,7], computer simulations were used for this purpose. We now introduce a simple and accurate numerical method for calculating these distribution functions and illustrate it here by solving (4) for the case of the LJ fluid near the hard wall.

We note that the ERF $\phi_R(\mathbf{r}) \equiv \phi_{R0}(\mathbf{r}) + \phi_{R1}(\mathbf{r})$ in Eq. (4) (and other related equations) can be naturally separated into the sum of a harshly repulsive part, $\phi_{R0}(\mathbf{r})$, and a much more slowly varying "smooth" part $\phi_{R1}(\mathbf{r})$, arising physically mainly from the attractive interactions in the original system. Equation (4) suggests the identification $\phi_{R0}(\mathbf{r}) = \phi_0(\mathbf{r})$ and $\phi_{R1}(\mathbf{r}) = \phi_s(\mathbf{r}) + \phi_1(\mathbf{r})$. More generally, we can define $\phi_{R0}(\mathbf{r}) = \phi_0(\mathbf{r}) - \phi_{0s}(\mathbf{r})$ and $\phi_{R1}(\mathbf{r}) = \phi_s(\mathbf{r}) + \phi_{0s}(\mathbf{r}) + \phi_1(\mathbf{r})$, where $\phi_{0s}(\mathbf{r})$ is an essentially arbitrary smooth function that is nonzero only in the repulsive core region but with $\phi_{0s}(\mathbf{r}) \ll \phi_0(\mathbf{r})$, so that ϕ_{R0} remains a harshly repulsive interaction. In the present case it is sufficient to take the separation suggested by Eq. (4), with $\phi_{R0} = \phi_{\mathrm{HW}}$ and $\phi_{R1} = \phi_s$.

Our task is now to determine the local density $\rho_0(\mathbf{r}; [\phi_R]) \equiv \rho_{0,R}(\mathbf{r})$ produced by a given ERF ϕ_R. We provide a new way to solve this basic problem, quite independent of its origins in the mean field equation (4). Initially we treat the LJ repulsive potential u_0 as a hard core interaction but then use standard methods [3] to correct for its finite softness in our final numerical results. We expect that there will be very different responses of the reference fluid density to the rapidly and slowly varying parts of the ERF $\phi_R \equiv \phi_{R0} + \phi_{R1}$ and anticipate that any large oscillations arise mainly from the harshly repulsive part ϕ_{R0}. These oscillations cause problems in density functional methods, which use a variety of somewhat arbitrary weighting functions to arrive at some underlying "smooth density" for use in a free energy functional [6].

Instead, we first determine the response to the *slowly varying part of the ERF alone*, followed by the response to the harshly repulsive part, using different methods in each step appropriate for the different density responses. In the first step, we determine the associated "smooth interface" $\rho_0(\mathbf{r}; [\phi_{R1}]) \equiv \rho_{0,R1}(\mathbf{r})$ that arises naturally from the slowly varying part $\phi_{R1} = \phi_s$ of the ERF *alone*. Physically, this takes account of the effects of the attractive interactions modeled by ϕ_{R1}. We start from the basic equation relating small changes in the potential and density [3]:

$$-\beta\, \delta\phi_{R1}(\mathbf{r}_1) = \int d\mathbf{r}_2\, \chi_0^{-1}(\mathbf{r}_1, \mathbf{r}_2; [\rho_{0,R1}]) \delta\rho_{0,R1}(\mathbf{r}_2), \quad (5)$$

through the generalized linear response function $\chi_0^{-1}(\mathbf{r}_1, \mathbf{r}_2; [\rho_{0,R1}]) \equiv \delta(\mathbf{r}_1 - \mathbf{r}_2)/\rho_{0,R1}(\mathbf{r}_1) - c_0(\mathbf{r}_1, \mathbf{r}_2; [\rho_{0,R1}])$. Here $c_0(\mathbf{r}_1, \mathbf{r}_2; [\rho_{0,R1}])$ is the direct correlation function of the reference fluid with density $\rho_{0,R1}$ and $\beta = 1/k_B T$. Specializing to the case when the change is a small displacement of the field, we find the exact equation [10]:

$$\nabla_1 \rho_{0,R1}(\mathbf{r}_1)/\rho_{0,R1}(\mathbf{r}_1) = -\beta \nabla_1 \phi_{R1}(\mathbf{r}_1) + \int d\mathbf{r}_2\, c_0(\mathbf{r}_1, \mathbf{r}_2; [\rho_{0,R1}]) \times \nabla_2 \rho_{0,R1}(\mathbf{r}_2). \quad (6)$$

If $\rho_{0,R1}$ is relatively slowly varying, we can accurately approximate $c_0(\mathbf{r}_1, \mathbf{r}_2; [\rho_{0,R1}])$ under the integral in Eq. (6) by the *uniform fluid* function $c_0(r_{12}; \bar{\rho}_{12})$, where $\bar{\rho}_{12}$ is some intermediate density associated with the two points [11]. A natural choice that gives very good results when $\rho_{0,R1}$ is reasonably smooth is $\bar{\rho}_{12} = [\rho_{0,R1}(\mathbf{r}_1) + \rho_{0,R1}(\mathbf{r}_2)]/2$. Starting with a given ϕ_{R1}, we can then solve Eq. (6) for the associated $\rho_{0,R1}$ by iteration, making use of the analytic and accurate Percus-Yevick (PY) expressions for the direct correlation function of the uniform hard sphere fluid [3,11]. If necessary, we can choose ϕ_{R1} inside the repulsive core region to help ensure that $\rho_{0,R1}$ is

smooth enough for the expansion method to be accurate; this procedure is important in some other applications [5].

A special case where this step can be carried out analytically arises when $\rho_{0,R1}$ varies so slowly that it is accurate to keep only the first term in the expansion of $\nabla_2 \rho_{0,R1}(\mathbf{r}_2)$ in Eq. (6) about $\mathbf{r}_1$. After integrating, we arrive at the simple *local hydrostatic relation* [11] between $\rho_{0,R1}$ and ϕ_{R1}:

$$\mu_0(\rho_{0,R1}(\mathbf{r})) + \phi_{R1}(\mathbf{r}) = \mu_{0B}\,, \tag{7}$$

where $\mu_0(\rho)$ is the chemical potential of the uniform (hard sphere) reference fluid at density ρ and $\mu_{0B} = \mu_0(\rho_B)$.

The smooth profile $\rho_{0,R1}$ is analogous to one that could be calculated using a single occupancy lattice gas (Ising) model, where correlations arise *only* from attractive interactions [1]. A realistic fluid has additional short wavelength correlations due to the repulsive intermolecular forces. These show up primarily in the second step of our method, where we take account of the response to ϕ_{R0}, the remaining harshly repulsive part of the ERF.

Consider first a *small* perturbing potential $\delta\phi_{R0}$ that is nonzero only inside the wall region with $z < 1$. Evaluating Eq. (5) for $z_1 > 1$ gives an exact relation between the small induced density changes inside and outside the wall region. However, it has been shown that even large density fluctuations in a hard sphere fluid are accurately described by Gaussian fluctuation theory [12]. This suggests that if we could somehow *impose* the proper values on the wall density field for $z < 1$ arising from the *full* ϕ_{R0}, we could then still use the linear response relation to determine the large density change $\Delta\rho_{0,R}(\mathbf{r}) \equiv \rho_{0,R}(\mathbf{r}) - \rho_{0,R1}(\mathbf{r})$ induced for $z > 1$. Imposing accurate density values in general is very difficult [13], but for the hard wall potential $\phi_{R0} = \phi_{\mathrm{HW}}$ we have the exact result $\rho_{0,R}(\mathbf{r}) = 0$ for all $z \le 1$. Thus replacing $\delta\rho_{0,R1}$ by $\Delta\rho_{0,R}$ in (5) and setting $\rho_{0,R} = 0$ for all $z \le 1$, we find for $z_1 > 1$:

$$\Delta\rho_{0,R}(\mathbf{r}_1)/\rho_{0,R1}(\mathbf{r}_1) = \int d\mathbf{r}_2\, c_0(\mathbf{r}_1, \mathbf{r}_2; [\rho_{0,R1}]) \times \Delta\rho_{0,R}(\mathbf{r}_2)\,. \tag{8}$$

Equation (8) is a linear equation for $\Delta\rho_{0,R}(\mathbf{r}_1)$, which we can directly solve by iteration or other means, approximating $c_0(\mathbf{r}_1, \mathbf{r}_2; [\rho_{0,R1}])$ by that of an appropriate uniform system, just as we did before. When $\rho_{0,R1}(\mathbf{r}) = \rho_B$, Eq. (8) is equivalent to the usual hard-wall, hard-particle PY equation, which has an analytic solution [14]. Equation (8) is quite adequate for our purposes here, though small errors can be seen at the highest densities. If still more accuracy is required, we could use modified generalized mean-spherical approximation-type equations related to the PY equation [14]. It may also be possible to use new and very accurate density functional methods for hard core fluids in this step of our method [15].

The net result of this two step process is the desired $\rho_{0,R}$ arising from a given ϕ_R. This can be substituted into Eq. (4), which can then be iterated to determine the final self-consistent ϕ_R. In Fig. 1 we give the self-consistent

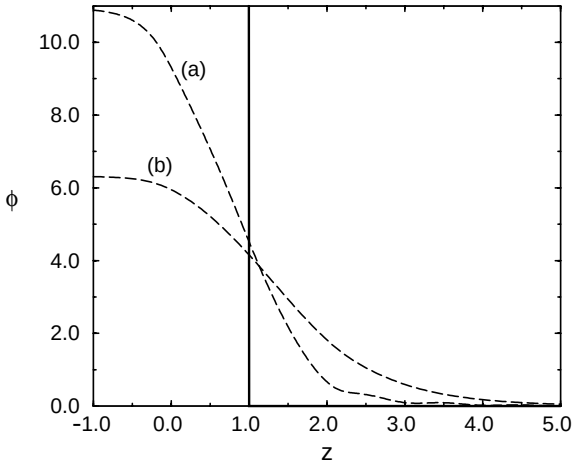

FIG. 1. Self-consistent potential $\phi_{R1} = \phi_s$ (dashed line) for $\rho_B = 0.785$ (a) and $\rho_B = 0.45$ (b), $T = 1.35$, and bare wall potential $\phi_{R0} = \phi_{\mathrm{HW}}$ (solid line). The ERF $\phi_R = \phi_{R0} + \phi_{R1}$.

potentials $\phi_{R1} = \phi_s$ that satisfy Eqs. (4), (6), and (8) for two different states along the near critical isotherm $T = 1.35$. We see that ϕ_{R1} is indeed a slowly varying repulsive interaction in both cases. In Fig. 2 we give the associated smooth density profiles $\rho_{0,R1}$ from (6) for each state, as well as the full profiles $\rho_{0,R}$ determined from Eq. (8). These are compared to Monte Carlo (MC) simulations we carried out [5] of the reference system in the ERFs of Fig. 1. This directly tests the accuracy of our two step procedure for calculating the effects of ϕ_R on the reference system. The agreement is excellent.

In Fig. 3 we test the simplified mean field treatment of the attractive interactions in Eq. (4) by comparing the reference profiles $\rho_{0,R}$ to those of the full LJ fluid in the presence of the hard wall, as determined by MC calculations. There is good agreement, though small quantitative differences can be seen. Thus even the simplest mean field treatment of attractive interactions is capable of capturing the major changes in the density profile as the

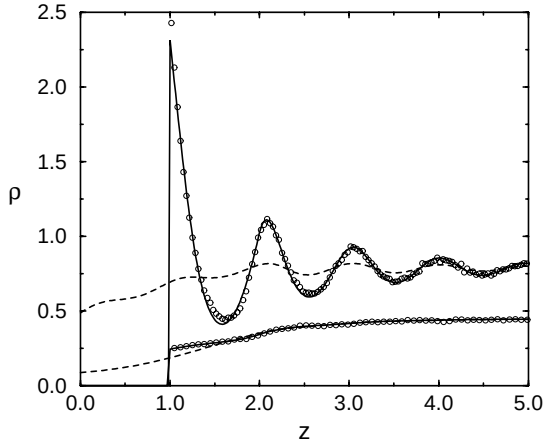

FIG. 2. Density profiles $\rho_{0,R1}$ (dashed line) and $\rho_{0,R}$ (solid line) compared to MC simulations of the reference fluid in potential ϕ_R (circles) for the same states as in Fig. 1.

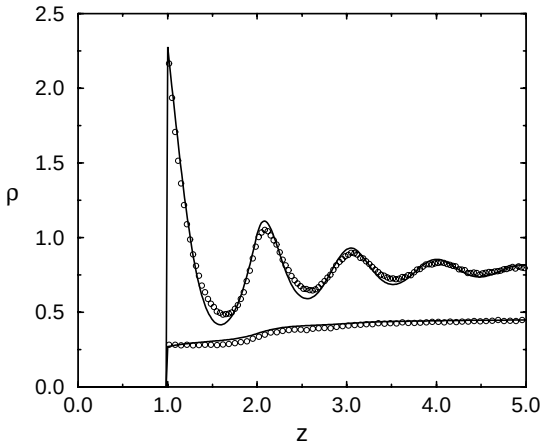

FIG. 3. Density profiles $\rho_{0,R}$ compared to MC simulation of the full LJ fluid (circles) for the same states as in Fig. 1.

density is decreased, and at lower temperature at coexistence we find complete drying states where a stable vapor-liquid interface can exist arbitrarily far from the wall [5].

Our emphasis thus far has been on quantitative numerical calculations. However, the qualitative features of our method are equally important. A long-standing problem of liquid state theory, well illustrated by the nonuniform fluid example studied here, is how to treat consistently the oscillating molecular scale "excluded volume" correlations arising from repulsive intermolecular forces and the more slowly varying and longer ranged correlations arising from attractive forces and often associated with the formation of interfaces. In principle these issues are addressed by modern density functional and integral equation methods, but in practice a number of uncontrolled and often mathematically motivated approximations are made. It is often difficult to assess their physical implications and to determine where the major sources of error lie. Here, we have divided this problem into several distinct parts, whose accuracy can be examined separately, and where the physical content and limitations of the methods used are clearer. We used here the simplest mean field equation to determine the ERF ϕ_R but more accurate (though more complicated) equations derived from (2) are available [5].

To determine the structure of the reference fluid in the presence of a given ERF, we first calculated the response to ϕ_{R1}, the slowly varying part of the ERF, by expanding about a uniform system. Next we used a Gaussian field model [12] (equivalent to a modified wall-particle PY equation) to calculate the response to the remaining harshly repulsive part ϕ_{R0} of the ERF. More accurate methods could be used in both steps if necessary, and for qualitative purposes both steps can be simplified considerably. For example, Lum, Chandler, and Weeks [16] have developed very simple approximations for use with continuum Landau-Ginsburgh-type equations that give good qualitative results in a number of different cases, including hydrophobic interactions in water. Application of these ideas to a variety of different problems is underway [5,16].

This work was supported by NSF Grant No. CHE9528915. K. V. acknowledges support from the Deutsche Forshungsgemeinschaft. We thank D. Chandler, K. Lum, and J. Broughton for helpful discussions.

[1] B. Widom, Science **157**, 375 (1967).
[2] J. D. Weeks, D. Chandler, and H. C. Andersen, J. Chem. Phys. **54**, 5237 (1971); D. Chandler, J. D. Weeks, and H. C. Andersen, Science **220**, 787 (1983).
[3] See, e.g., J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic, London, 1986).
[4] J. D. Weeks, R. L. B. Selinger, and J. Q. Broughton, Phys. Rev. Lett. **75**, 2694 (1995).
[5] A more complete discussion of this problem and of other applications involving wetting at walls and the liquid-vapor interface is given by K. Katsov, K. Vollmayr, J. D. Weeks, and J. Broughton (to be published). Studies of the uniform fluid, and confined fluids in slits and cylinders are also being carried out [K. Vollmayr, K. Katsov, and J. D. Weeks (to be published)].
[6] For a general review, see R. Evans, in *Fundamentals of Inhomogeneous Fluids*, edited by D. Henderson (Dekker, New York, 1992).
[7] J. D. Weeks, K. Vollmayr, and K. Katsov, Physica (Amsterdam) **244A**, 461 (1997).
[8] D. E. Sullivan and G. Stell, J. Chem. Phys. **69**, 5450 (1978); D. E. Sullivan, D. Levesque, and J. J. Weis, *ibid.* **72**, 1170 (1980).
[9] We expect that this approximation will be most accurate at high density, as is the case for the uniform fluid. However, it also gives *exact* results as the density tends to zero, since then the last term vanishes. But the next order term in a density expansion can be evaluated exactly and does not vanish. As discussed in [5], we can use this result in Eq. (2) to derive modified equations that improve on the predictions of Eqs. (3) and (4) at very low but nonzero densities, and in some cases such as the liquid-vapor interface, these corrections can be quantitatively important.
[10] R. A. Lovett, C. Y. Mou, and F. P. Buff, J. Chem. Phys. **65**, 570 (1976); M. Wertheim, *ibid.* **65**, 2377 (1976).
[11] J. K. Percus, in *The Equilibrium Theory of Classical Fluids*, edited by H. L. Frisch and J. L. Lebowitz (W. A. Benjamin, Inc., New York, 1964), p. II-33.
[12] D. Chandler, Phys Rev. E **48**, 2989 (1993); G. E. Crooks and D. Chandler, Phys. Rev. E **56**, 4217 (1997); see also G. Hummer *et al.*, Proc. Natl. Acad. Sci. **93**, 8951 (1996).
[13] By definition [11], the *exact* density change $\Delta\rho_{0,R}(\mathbf{r}) \equiv \rho_{0,R}(\mathbf{r}) - \rho_{0,R1}(\mathbf{r})$ that arises when ϕ_{R0} is taken into account satisfies Eq. (5) when the factor $-\beta\delta\phi_{R1}(\mathbf{r})$ is replaced by the (wall-particle) *direct correlation function* $C_{R0}(\mathbf{r};[\rho_{0,R1}])$. Accurately determining this for a general potential is very difficult. However, for the *hard wall*, if we make the PY assumption that C_{R0} has the same range as ϕ_{R0} and hence vanishes for $z > 1$, we again arrive at Eq. (8) for $z > 1$.
[14] J. L. Lebowitz, Phys. Rev. **133**, A895 (1964); E. Waisman, Mol. Phys. **25**, 45 (1973).
[15] Y. Rosenfeld *et al.*, Phys. Rev. E **55**, 4245 (1997).
[16] K. Lum, D. Chandler, and J. D. Weeks (to be published).