

Structure of Nonuniform Hard Sphere Fluids from Shifted Linear Truncations of Functional Expansions[†]

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Percus showed that approximate theories for the structure of nonuniform hard sphere fluids can be generated by linear truncations of functional expansions of the nonuniform density $\rho(\mathbf{r})$ about that of an appropriately chosen uniform system. We consider the most general such truncation, which we refer to as the shifted linear response (SLR) equation, where the density response $\rho(\mathbf{r})$ to an external field $\phi(\mathbf{r})$ is expanded to linear order at each \mathbf{r} about a different uniform system with a locally shifted chemical potential. Special cases include the Percus–Yevick (PY) approximation for nonuniform fluids, with no shift of the chemical potential, and the hydrostatic linear response (HLR) equation, where the chemical potential is shifted by the local value of $\phi(\mathbf{r})$. The HLR equation gives exact results for very slowly varying $\phi(\mathbf{r})$ and reduces to the PY approximation for hard core $\phi(\mathbf{r})$, where generally accurate results are found. We show that a truncated expansion about the bulk density (the PY approximation) also gives exact results for localized fields that are nonzero only in a “tiny” region whose volume V^ϕ can accommodate at most one particle. The SLR equation can also exactly describe a limit where the fluid is confined by hard walls to a very narrow slit. This limit can be related to the localized field limit by a simple shift of the chemical potential, leading to an expansion about the ideal gas. We then try to develop a systematic way of choosing an optimal local shift in the SLR equation for general $\phi(\mathbf{r})$ by requiring that the predicted $\rho(\mathbf{r})$ is insensitive to small variations about the appropriate local shift, a property that the exact expansion to all orders would obey. The resulting insensitivity criterion (IC) gives a theory that reduces to the HLR equation for slowly varying $\phi(\mathbf{r})$ and is much more accurate than HLR both for very narrow slits, where the IC agrees with exact results, and for fields confined to “tiny” regions, where the IC gives very accurate (but not exact) results. However, the IC is significantly less accurate than the PY and HLR equations for single hard core fields. Only a small change in the predicted reference density is needed to correct this remaining limit.

I. Introduction

In this paper, we discuss approximate methods for determining the structure and thermodynamics of nonuniform hard sphere fluids in a general external field $\phi(\mathbf{r})$. The field can directly describe the effects of fixed solute particles, confining walls, and other sources of nonuniformity on the hard sphere fluid,^{1–3} and the model serves as a reference system through which properties of nonuniform simple liquids can be determined by density functional theory⁴ or molecular field theory.⁵

We start from a general theoretical perspective first described in a classic article by Percus⁶ and reviewed below in section 2. Percus suggested that approximate theories for the density response to $\phi(\mathbf{r})$ could be generated by truncations of formally exact functional Taylor series expansions of the nonuniform density $\rho(\mathbf{r})$ about that of an appropriately chosen uniform system. In particular, he argued that the density response to a hard core $\phi(\mathbf{r})$ could be accurately described by a simple linear truncation of an expansion about the bulk density. This yields

the Percus–Yevick (PY) approximation for nonuniform fluids,⁷ discussed in section 3, and indeed, this gives rather accurate results for hard core solutes of varying diameters.^{8–11} The linear truncation is the key to developing a practically useful theory, since higher order terms in the expansions are very complicated. Unfortunately, the results of the PY approximation deteriorate very quickly for more extended fields, especially ones with attractive regions, where the linear extrapolation from the bulk becomes very inaccurate.

In sections 4 and 5, we exploit an exact property of the grand canonical ensemble, where both the chemical potential μ^B and external field $\phi(\mathbf{r})$ can be shifted by a constant without changing any properties.⁴ This allows us to consider a more flexible expansion where the density response $\rho(\mathbf{r})$ at each \mathbf{r} is expanded to linear order about a different uniform system with a locally shifted chemical potential.^{5,10,11} We can use the additional freedom permitted by this local shift to minimize errors arising from the linear truncation of the expansion. Indeed, we show below that there are several different limits where exact results can be obtained from a linearly truncated expansion by using an appropriate shift.

When the field $\phi(\mathbf{r})$ is very slowly varying, it is natural to expand about a uniform system where the chemical potential is

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shifted by the local value of the field. This leads to the hydrostatic linear response (HLR) equation, which we derived earlier using physically motivated arguments.^{5,10,11} The HLR equation gives exact results for very slowly varying $\phi(\mathbf{r})$ and turns out also to give the same predictions as the PY approximation for hard core $\phi(\mathbf{r})$. Thus, it can be successfully used for a much wider class of fields (both repulsive and attractive). However, the specific choice for the shift made in the HLR equation is based on the local value of the field, and this can give poor results in certain special cases, particularly when there are rapid variations in $\phi(\mathbf{r})$ in a confined region of space much smaller than the correlation length of the bulk fluid.

However, we show in section 5 that in two such cases a linearly truncated expansion can again give exact results with different choices of the locally shifted system. In particular, we show that exact results can be found by expanding about the bulk density (i.e., the PY approximation) for external fields $\phi(\mathbf{r})$ that are nonzero only in a tiny region of space whose volume V^ϕ is so small that the center of at most one hard sphere can be accommodated within it. The fact that the PY approximation can give exact results for such confined or “tiny fields” does not seem to be known in the literature. This limit is of more than academic interest since some recent advances in density functional theory have resulted from requiring that it be satisfied.¹² Moreover, we show how expansions used in the tiny field theory can be easily modified to exactly describe a seemingly very different problem, a narrow slit, where the potential is infinite except in a narrow rectangular slit of width L_s . In the limit as $L_s \rightarrow 0$, we show that a truncated expansion about the ideal gas can give exact results,¹³ whereas the PY (and HLR) equation gives very poor results in this limit.⁹

The fact that different shifted linear truncations can exactly satisfy all of these distinct limits suggests that a generally useful theory might arise from finding a local shift that in some sense minimizes the errors arising from the linear truncation. In section 6, we present our first attempt along these lines, where the local shift is chosen self-consistently so that the predicted density response $\rho(\mathbf{r})$ is insensitive to small variations about the proper local choice, a property that an exact expansion to all orders would satisfy. This “insensitivity criterion” (IC) effectively generates an expansion about a local uniform system whose density can be interpreted as a smoothed weighted average of the full density $\rho(\mathbf{r})$, reminiscent of results in certain versions of weighted density functional theory.^{4,14}

Results of the various theories for the density response to several different fields are presented in section 7. In general the IC performs very well: it reduces to the exact HLR equation for slowly varying fields, gives exact results in the narrow slit limit, and gives generally accurate (though not exact) results for tiny fields. However, the IC approach is significantly less accurate than the PY or HLR equations for a single hard core field, where it substantially overestimates the contact density at high density. Since this is one limit where the PY and HLR equations do give satisfactory results, this may not be of much practical importance. However, it would be better to have a general approach that remains accurate for these cases as well. Suggestions for further work along these lines and final remarks are given in section 8.

II. Exact Expansions for the Density Response to an External Field

The potential distribution theorem of Widom¹⁵ relates the density $\rho(\mathbf{r})$ of a single component hard sphere fluid in an

external field $\phi(\mathbf{r})$ to the probability $P(\mathbf{r}; [\rho])$ of inserting a hard sphere test particle at the position \mathbf{r}

$$\rho(\mathbf{r}) = \Lambda^{-3} e^{\beta[\mu^B - \phi(\mathbf{r})]} P(\mathbf{r}; [\rho]) \quad (1)$$

The direct influence of the external field on the test particle is excluded in determining $P(\mathbf{r}; [\rho])$, which depends only on the intermolecular interaction energy between the test particle and the hard sphere fluid. Equivalently, $P(\mathbf{r}; [\rho])$ is the probability that a cavity whose radius is equal to or greater than the diameter d of the hard sphere particles exists at the particular point \mathbf{r} , since only then can the test particle be inserted. Here μ^B is the chemical potential, Λ is the thermal de Broglie wavelength, and $[\rho]$ specifies the functional dependence on the density profile. $P(\mathbf{r}; [\rho])$ can be formally reexpressed^{2,3} in terms of the one-body direct correlation function $c^{(1)}(\mathbf{r}; [\rho])$ as

$$P(\mathbf{r}; [\rho]) = e^{c^{(1)}(\mathbf{r}; [\rho])} \quad (2)$$

By expanding $P(\mathbf{r}_1; [\rho])$ at a given \mathbf{r}_1 in a functional Taylor series about a uniform fluid at some density $\bar{\rho}$, we arrive at a formal expansion for the nonuniform density directly related to an expansion suggested by Percus:^{6,16}

$$\rho(\mathbf{r}_1) = \Lambda^{-3} e^{\beta[\mu^B - \phi(\mathbf{r}_1)] + c^{(1)}(\mathbf{r}_1; \bar{\rho})} \left\{ 1 + \int d\mathbf{r}_2 c^{(2)}(r_{12}; \bar{\rho})(\rho(\mathbf{r}_2) - \bar{\rho}) + Q(\mathbf{r}_1) + \dots \right\} \quad (3)$$

where the quadratic term in the expansion is

$$Q(\mathbf{r}_1) \equiv \int d\mathbf{r}_2 \int d\mathbf{r}_3 \{ c^{(2)}(r_{12}; \bar{\rho}) c^{(2)}(r_{13}; \bar{\rho}) + c^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3; \bar{\rho}) \} (\rho(\mathbf{r}_2) - \bar{\rho})(\rho(\mathbf{r}_3) - \bar{\rho}) \quad (4)$$

The $c^{(n)}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n; [\rho])$ are defined by successive functional derivatives of $c^{(1)}(\mathbf{r}; [\rho])$ with respect to the singlet density, i.e.

$$c^{(n)}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n; [\rho]) \equiv \frac{\delta c^{(n-1)}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_{n-1}; [\rho])}{\delta \rho(\mathbf{r}_n)} \quad (5)$$

Since we expand about a uniform fluid state, $c^{(2)}(\mathbf{r}_1, \mathbf{r}_2; [\rho]) = c^{(2)}(r_{12}; \bar{\rho})$, where $r_{12} = |\mathbf{r}_2 - \mathbf{r}_1|$, due to translational invariance. Although the density $\rho(\mathbf{r})$ can have discontinuities caused by the discontinuities in the external field $\phi(\mathbf{r})$, representing, e.g., a hard wall or a spherical cavity, $P(\mathbf{r}; [\rho])$ is always continuous and smooth.³ The expansion in eq 3 is designed to take advantage of the smoothness of $P(\mathbf{r}; [\rho])$. The hope is that with proper choice of $\bar{\rho}$ the expansion can be truncated at some low order and a relatively simple theory for $\rho(\mathbf{r})$ will result.

Percus considered many other expansions as well, some of which might seem even more promising.⁶ For example, by directly expanding $c^{(1)}(\mathbf{r}_1; [\rho])$ in eq 2 in a Taylor series, we are guaranteed that the resulting approximation for the density after a truncation is always nonnegative, an exact and desirable property not always produced by truncations of eq 3. However, as discussed in sections 3 and 5, there is a well-defined limit where the expansion in eq 3 truncates exactly, in contrast to the corresponding expansion for $c^{(1)}$. Moreover, we will show that both the HLR and the PY equations can be derived from eq 3. This suggests that it offers a versatile starting point for further research.

III. Confined Fields and the PY Approximation

One limit where the expansion in eq 3 is particularly useful is when the external field ϕ is nonzero only a region much

smaller than the correlation length of the fluid. The analyticity of $P(\mathbf{r}; [\rho])$ then ensures that its values in the tiny region where ϕ is nonzero can be accurately determined by making use of a low order extrapolation of its values outside, i.e., where ϕ vanishes. For such locally confined fields, it seems clear that the expansion in eq 3 should be about $\tilde{\rho} = \rho^B \equiv \rho(\mu^B)$, where $\rho(\mu)$ gives the density of the uniform system with $\phi = 0$ as a function of the chemical potential μ . In terms of the quantities appearing in eqs 1 and 2, this can also be written as

$$\rho^B = \Lambda^{-3} e^{\beta\mu^B + c^{(1)}(\rho^B)} \quad (6)$$

It seems plausible that expansion only to linear order in eq 3 could then give an accurate description of the fluid's density response to a very confined field

$$\rho(\mathbf{r}_1) = \Lambda^{-3} e^{\beta[\mu^B - \phi(\mathbf{r}_1)] + c^{(1)}(\rho^B)} [1 + \int d\mathbf{r}_2 c^{(2)}(r_{12}; \rho^B)(\rho(\mathbf{r}_2) - \rho^B)] \quad (7)$$

This qualitative argument will be made more precise in section 5. Using eq 6, this equation can be rewritten as

$$\rho(\mathbf{r}_1) = \rho^B e^{-\beta\phi(\mathbf{r}_1)} [1 + \int d\mathbf{r}_2 c^{(2)}(r_{12}; \rho^B)(\rho(\mathbf{r}_2) - \rho^B)] \quad (8)$$

If the direct correlation function $c^{(2)}(r_{12}; \rho^B)$ of the uniform bulk fluid is known, eq 8 can be solved for the density $\rho(\mathbf{r})$ induced by the external field $\phi(\mathbf{r})$.

Equation 8 is the PY approximation for nonuniform fluids.⁶ We argue below that it gives exact results for any sufficiently localized $\phi(\mathbf{r})$, as suggested by the extrapolation argument. Moreover, the PY approximation is known to give reasonably accurate results for the density response to larger spherical cavities (including the hard wall limit), where $\phi(\mathbf{r})$ is infinitely repulsive inside a spherical region of radius R , but zero elsewhere. For such potentials, the exact result $\rho(\mathbf{r}) = 0$ is trivially obtained from eq 8 in regions where $\phi(\mathbf{r})$ is infinite because of the Boltzmann factor $e^{-\beta\phi(\mathbf{r})}$.

Despite this success, the linear extrapolation using the bulk fluid in eq 8 would be expected to give poor results for external fields that remain finite and vary over extended regions, especially in negative regions of the field where errors in the truncated series can be greatly magnified by the Boltzmann factor $e^{-\beta\phi(\mathbf{r})}$. These are limits where the PY approximation is known to be very inaccurate.⁹

IV. Exact Shifting Property of the Grand Ensemble

When the linear truncation is inaccurate, it may seem difficult to make further progress, since the higher order terms in eq 3 are too complicated to use in practical calculations. However, as noted by Percus,⁶ one does not have to expand eq 3 about the bulk density defined by eq 6, nor does one have to expand about the same bulk state for each \mathbf{r} value of $\rho(\mathbf{r})$. We can use this additional flexibility to greatly extend the accuracy of different linear truncations of eq 3.

As is well-known, it is the combination $\mu^B - \phi(\mathbf{r})$ that determines the density profile in the grand canonical ensemble, and not μ^B and $\phi(\mathbf{r})$ separately.⁴ When both the chemical potential and the external field are shifted by the same constant, the system's properties should thus remain unchanged. This exact shifting property¹⁰ of the grand ensemble will play a key role in what follows.

Using this shifting property in eq 3, we consider a general shifted chemical potential

$$\tilde{\mu}^{\mathbf{r}_1} = \mu^B - a^{\mathbf{r}_1} \quad (9)$$

and a shifted external field

$$\tilde{\phi}^{\mathbf{r}_1}(\mathbf{r}) = \phi(\mathbf{r}) - a^{\mathbf{r}_1} \quad (10)$$

both of which are shifted from the original μ^B and $\phi(\mathbf{r})$ by a constant $a^{\mathbf{r}_1}$ that in principle can depend parametrically on the point \mathbf{r}_1 about which the expansion is carried out, as indicated by the superscript \mathbf{r}_1 . The shifted chemical potential $\tilde{\mu}^{\mathbf{r}_1}$ defines at each \mathbf{r}_1 an associated bulk system with a uniform density

$$\tilde{\rho}^{\mathbf{r}_1} \equiv \rho(\tilde{\mu}^{\mathbf{r}_1}) \quad (11)$$

whose correlation functions are used in the expansion. Equation 3 thus becomes

$$\rho(\mathbf{r}_1) = \Lambda^{-3} e^{\beta[\tilde{\mu}^{\mathbf{r}_1} - \tilde{\phi}^{\mathbf{r}_1}(\mathbf{r}_1)] + c^{(1)}(\tilde{\rho}^{\mathbf{r}_1})} \{1 + \int d\mathbf{r}_2 c^{(2)}(r_{12}; \tilde{\rho}^{\mathbf{r}_1})(\rho(\mathbf{r}_2) - \tilde{\rho}^{\mathbf{r}_1}) + Q(\mathbf{r}_1) + \dots\} \quad (12)$$

In principle (assuming convergence of the infinite series), if we could accurately evaluate all terms in the Taylor series, the same exact result for $\rho(\mathbf{r}_1)$ would be found for any choice of $a^{\mathbf{r}_1}$ due to the shifting property. However, this is hopelessly complicated in general and approximate values for $\rho(\mathbf{r}_1)$ from truncations of the series do depend on the choice of the $a^{\mathbf{r}_1}$.

V. Shifted Linear Truncations

Our strategy is to try to choose the $a^{\mathbf{r}_1}$ or the $\tilde{\rho}^{\mathbf{r}_1}$ at each \mathbf{r}_1 in such a way that a self-consistent solution for $\rho(\mathbf{r}_1)$ based on a simple low order truncation of the series in eq 3 can give accurate results. In particular, we suppose that the $a^{\mathbf{r}_1}$ can be chosen by some argument to be specified later so that the expansion can be truncated at linear order to a good approximation. We thus arrive at a very general starting point, which we refer to as the shifted linear response (SLR) equation

$$\begin{aligned} \rho(\mathbf{r}_1) &= \Lambda^{-3} e^{\beta[\tilde{\mu}^{\mathbf{r}_1} - \tilde{\phi}^{\mathbf{r}_1}(\mathbf{r}_1)] + c^{(1)}(\tilde{\rho}^{\mathbf{r}_1})} \\ &\quad [1 + \int d\mathbf{r}_2 c^{(2)}(r_{12}; \tilde{\rho}^{\mathbf{r}_1})(\rho(\mathbf{r}_2) - \tilde{\rho}^{\mathbf{r}_1})] \\ &= \tilde{\rho}^{\mathbf{r}_1} e^{-\beta\tilde{\phi}^{\mathbf{r}_1}(\mathbf{r}_1)} [1 + \int d\mathbf{r}_2 c^{(2)}(r_{12}; \tilde{\rho}^{\mathbf{r}_1})(\rho(\mathbf{r}_2) - \tilde{\rho}^{\mathbf{r}_1})] \end{aligned} \quad (13)$$

Specific choices of the $a^{\mathbf{r}_1}$ or $\tilde{\rho}^{\mathbf{r}_1}$ will lead to different approximations for $\rho(\mathbf{r}_1)$. The PY approximation arises from the choice $a^{\mathbf{r}_1} = 0$ or $\tilde{\rho}^{\mathbf{r}_1} = \rho^B$. As we argued above, this choice should give very accurate results for sufficiently localized fields, and it is known to give a good description of the response to hard core solutes.

However, when the external field is extended but slowly varying, a different choice of $a^{\mathbf{r}_1}$ is clearly more appropriate. As discussed in detail in refs 5, 10, and 11, the HLR equation is very accurate in such cases. This uses the hydrostatic shift, where the external field is locally shifted at each \mathbf{r}_1 to be zero. This corresponds to the choice

$$a^{\mathbf{r}_1} = \phi(\mathbf{r}_1) \quad (14)$$

in eq 13 so that $\tilde{\phi}^{r_1}(\mathbf{r}_1) = 0$. The associated uniform density given by the shifted chemical potential for this particular choice of a^{r_1} is denoted ρ^{r_1} and it satisfies

$$\rho^{r_1} = \rho(\mu^B - \phi(\mathbf{r}_1)) \quad (15)$$

Unlike the PY approximation, the HLR equation builds in the invariance of the grand canonical ensemble when both the chemical potential and the external field are shifted by a constant. It is an excellent approximation when the external field is slowly varying, and the expansion in eq 12 about the hydrostatic density eq 15 converges rapidly.¹⁷ Moreover, the HLR equation gives the same results as the PY equation for hard core fields. In general, the HLR approximation is much more accurate than the PY approximation for a wide range of external fields.^{10,11}

The SLR eq 13 with the particular choice $a^{r_1} = \phi(\mathbf{r}_1)$ thus provides an alternative derivation of the HLR equation, in addition to the previous physical arguments based on optimizing linear response by use of the hydrostatic shift.^{5,10,11} However, as discussed below, there are some limits where the HLR choice for a^{r_1} gives poor results. The SLR equation permits other choices for a^{r_1} and thus provides additional flexibility that can lead to improvements of the HLR equation. With proper choice of a^r , eq 13 can be used to describe and bridge several limits that both the PY and the HLR equations fail to capture. These limiting cases will be addressed in the following.

A. Tiny Fields. Consider first a very localized field $\phi(\mathbf{r})$ that is nonvanishing only within a spherical volume V^ϕ of radius $d/2$, with d the hard sphere diameter

$$\begin{aligned} \phi(\mathbf{r}) &\neq 0, \quad |\mathbf{r}| < \frac{d}{2} \\ &= 0, \quad \text{otherwise} \end{aligned} \quad (16)$$

This volume is so small that it can simultaneously accommodate the centers of at most one hard sphere particle. We call localized fields that are nonzero only in such a tiny region tiny fields. A special case is a tiny cavity, where ϕ is infinite in V^ϕ . The density response of a hard sphere fluid to any tiny field can be determined exactly, as we now show.

We start with the grand partition function $\Xi[\phi]$ when a general external field ϕ is present in the fluid

$$\begin{aligned} \Xi[\phi] &= \sum_{N=0}^{\infty} \frac{z^N}{N!} Z_N[\phi] \\ &= \sum_{N=0}^{\infty} \frac{z^N}{N!} \int d\mathbf{r}_1 \dots d\mathbf{r}_N e^{-\beta \sum_{n=1}^N \phi(\mathbf{r}_n) - \beta V_N\{\mathbf{r}\}} \end{aligned} \quad (17)$$

Here $Z_N[\phi]$ is the canonical partition in the presence of the field, $Z_N[0]$ refers to that of the uniform fluid when the external field is zero, $z \equiv \exp(\beta\mu^B)/\Lambda^3$, and $V_N\{\mathbf{r}\}$ is the intermolecular interaction potential between the N fluid particles. Introducing the Mayer f -function for the external field

$$f^\phi(\mathbf{r}) \equiv e^{-\beta\phi(\mathbf{r})} - 1 \quad (18)$$

eq 17 can be rewritten in terms of an expansion about the uniform fluid with $\phi = 0$

$$\begin{aligned} \Xi[\phi] &= \sum_{N=0}^{\infty} \frac{z^N}{N!} \sum_{n=0}^N \int d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_n \frac{N!}{(N-n)!n!} \\ &\quad f^\phi(\mathbf{r}_1) f^\phi(\mathbf{r}_2) \dots f^\phi(\mathbf{r}_n) \int d\mathbf{r}_{n+1} \dots d\mathbf{r}_N e^{-\beta V_N\{\mathbf{r}\}} \\ &= \sum_{n=0}^{\infty} \frac{1}{n!} \int d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_n f^\phi(\mathbf{r}_1) f^\phi(\mathbf{r}_2) \dots f^\phi(\mathbf{r}_n) \\ &\quad \sum_{N \geq n} \frac{z^N}{(N-n)!} \int d\mathbf{r}_{n+1} \dots d\mathbf{r}_N e^{-\beta V_N\{\mathbf{r}\}} \\ &= \Xi[0] \sum_{n=0}^{\infty} \frac{1}{n!} \int d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_n f^\phi(\mathbf{r}_1) f^\phi(\mathbf{r}_2) \dots f^\phi(\mathbf{r}_n) \\ &\quad \rho^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_n; [0]) \end{aligned} \quad (19)$$

Here $\rho^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_n; [0])$ is the n -particle distribution function in the uniform grand canonical ensemble with chemical potential μ^B .

For general extended fields, this formal expansion does not converge rapidly. However, it can be very useful when the field is confined to a small localized region of space since $f^\phi(\mathbf{r})$ is nonzero only where ϕ is nonzero. In particular for tiny fields, the expansion eq 19 must truncate *exactly* due to the vanishing of the $\rho^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_n; [0])$ when more than one hard particle is simultaneously within the volume V^ϕ . By functional differentiation of eq 19 we can also find an expansion for $\rho(\mathbf{r}; [\phi])$ that similarly truncates. Thus we have exactly for tiny fields

$$\Xi[\phi] = \Xi[0] [1 + \int d\mathbf{r}_1 \rho^B f^\phi(\mathbf{r}_1)] \quad (20)$$

and

$$\begin{aligned} \rho(\mathbf{r}_1; [\phi]) &= \\ &= \frac{\rho^B e^{-\beta\phi(\mathbf{r}_1)}}{1 + \int d\mathbf{r}_2 \rho^B f^\phi(\mathbf{r}_2)} [1 + \int d\mathbf{r}_2 \rho^B g^{(2)}(r_{12}; \rho^B) f^\phi(\mathbf{r}_2)] \end{aligned} \quad (21)$$

The exact result for the density response to a tiny cavity was originally derived in a different way by Reiss and Casberg.¹⁸ Here $g^{(2)}(r_{12}; \rho^B)$ is the exact radial distribution for the uniform hard sphere fluid. This same formula clearly holds for a more general model with longer ranged pair interactions outside the hard core if the appropriate $g^{(2)}$ is used.

As would be expected by the appearance of ρ^B in this equation, one can show that the PY approximation eq 8 is consistent with this exact result for *any* tiny field. See ref 19 for a straightforward but tedious derivation. In accord with the qualitative argument above, the linear extrapolation from the bulk into the tiny region is exact in this case. This corresponds in the SLR equation to the choice $a^r = 0$, i.e., $\tilde{\rho}^r = \rho^B$ and shows that the series indeed truncates exactly in this special case.

However, a closely related limit highlights a general problem with the PY approximation. Consider a field $\phi^c(\mathbf{r})$ that is a nonzero constant c outside a tiny region V^ϕ and any value $\phi(\mathbf{r})$ inside. This can immediately be shifted to be the type for which eqs 20 and 21 hold by making the choice $a^r = c$. For such a field ϕ^c , we then have

$$\begin{aligned} \rho(\mathbf{r}_1; [\phi]) &= \\ &= \frac{\tilde{\rho}^c e^{-\beta\phi^c(\mathbf{r}_1)}}{1 + \int d\mathbf{r}_2 \tilde{\rho}^c \tilde{f}^c(\mathbf{r}_2)} [1 + \int d\mathbf{r}_2 \tilde{\rho}^c g^{(2)}(r_{12}; \tilde{\rho}^c) \tilde{f}^c(\mathbf{r}_2)] \end{aligned} \quad (22)$$

Here $\tilde{\rho}^c = \rho(\mu^B - c)$ and \tilde{f}^c is defined as in eq 18 with the shifted tiny field $\tilde{\phi}^c(\mathbf{r}) = \phi^c(\mathbf{r}) - c$.

For a perturbation that varies significantly only in a very local region (compared with the correlation length of the particles), a particle situated in the perturbed region, though directly affected by the field, should screen the perturbation from the rest of the fluid. The fluid's response thus essentially remains that of the uniform fluid outside the local region. The shifted field represents such a localized perturbation. Thus, choosing the density $\tilde{\rho}^c$ to be that of the bulk environment, i.e., $\rho(\mu^B - c)$, will truncate eq 19 at low order, leading to eq 22. And again, the choice $a^r = c$ in the SLR eq 13 gives this exact result.

In this essentially equivalent case however, the PY approximation, which always uses the unshifted ρ^B , will give an incorrect result, even though it can exactly describe the tiny field limit when $c = 0$. Unlike the SLR equation, the PY approximation does not build in the exact shifting feature of the grand canonical ensemble. This can cause significant errors for extended slowly varying fields.

However, the HLR approximation uses the hydrostatic shift eq 14 and thus will correctly describe the shifted bulk density $\tilde{\rho}^c$ in this case. Moreover it is exact for tiny cavities (tiny fields that are infinitely repulsive inside V^0) since any finite value for a^r inside the cavity will still give the correct zero density. However, the HLR equation is not exact for more general finite tiny fields. The HLR reference density ρ^r would follow the variations in ϕ inside the tiny region, contrary to the exact result with a constant $\tilde{\rho}^c$ everywhere. Rapidly varying tiny fields can thus generate noticeable errors in the HLR approximation, as will be shown in a later section where computational results are reported.

B. Narrow Slits. Another application that may at first seem to be very different from the tiny field case is when an extended external field confines the fluid to a region of reduced dimensions. For example, consider a hard sphere fluid confined between two planar hard walls forming a narrow slit. We can get exact results for this case from eq 19 by exploiting the shifting property of the grand ensemble. The confining field can be taken to be the limit of piecewise constant potentials defined so that

$$\begin{aligned} \phi^c(z) &= 0, \quad 0 < z < L_s \\ &= c, \quad \text{otherwise} \end{aligned} \quad (23)$$

in the limit where $c \rightarrow \infty$. In this limit, the fluid's density will be zero except in the narrow region between the walls. Here, L_s is the effective width of the slit as seen by the centers of the fluid particles.

If we formally introduce the uniform shift $a^z = c$, we have

$$\begin{aligned} \tilde{\phi}^c(z) &= -c, \quad 0 < z < L_s \\ &= 0, \quad \text{otherwise} \end{aligned} \quad (24)$$

and the shifted external field $\tilde{\phi}^c(z)$ is nonzero only in the narrow slit region, similar to a tiny field. However, the shifted slit field is not strictly a tiny field as defined in the previous section where the expansion exactly truncates, because even when $L_s \rightarrow 0$, many particles in principle can still be found in the slit, aligned in a two-dimensional layer along the walls of the slit. However, once this shift has been made, the expansion in eqs 19 and 22 converges rapidly for small L_s since the contributions from the integration over the \tilde{f}^c tend to zero. The shifted chemical potential $\tilde{\mu}^c = \mu^B - c$ tends to $-\infty$, corresponding to an

expansion about the ideal gas limit where the shifted bulk density $\tilde{\rho}^c$ tends to zero and $c^{(1)}(\tilde{\rho}^c) = 0$.

Inside the slit where $\tilde{\mu}^c - \tilde{\phi}^c(\mathbf{r}_1) = \mu^B - \phi^c(\mathbf{r}_1) = \mu^B$, we have a finite limiting density as $L_s \rightarrow 0$ given by

$$\tilde{\rho}^c e^{-\beta \tilde{\phi}^c(\mathbf{r}_1)} = \Lambda^{-3} e^{\beta[\tilde{\mu}^c - \tilde{\phi}^c(\mathbf{r}_1)] + c^{(1)}(\tilde{\rho}^c)} = \Lambda^{-3} e^{\beta \mu^B} \quad (25)$$

Equation 22 then gives the first two terms in an exact (but nontruncating) virial-like expansion valid for narrow slits. Higher order terms can be determined straightforwardly from eq 19. In agreement with previous work,¹³ there is a constant limiting lowest order density profile in the narrow slit given by

$$\begin{aligned} \rho(z) &= \Lambda^{-3} e^{\beta \mu^B}, \quad 0 < z < L_s \\ &= 0, \quad \text{otherwise} \end{aligned} \quad (26)$$

For a value of μ^B corresponding to a dense uniform hard sphere fluid, this yields a very large limiting value for the reduced density in the slit $\rho^{3D} d^3 \equiv \Lambda^{-3} e^{\beta \mu^B} d^3 \gg 1$. However, the density of fluid particles per unit area of the wall $\rho^{2D} d^2 \equiv \Lambda^{-3} e^{\beta \mu^B} d^2 L_s$ tends to zero as $L_s \rightarrow 0$. Thus, particles in the narrow slit are very far apart laterally, and an expansion about the ideal gas limit is physically appropriate.

Clearly the SLR equation can reproduce these exact limiting results if the proper choice $a^z = c$ (where $c \rightarrow \infty$) for all z is made. However, the PY approximation uses $a^z = 0$ everywhere in the SLR equation, whereas the HLR equation assumes $a^z = c$ outside the slit but $a^z = 0$ inside, and hence, they both give incorrect results in the limit $L_s \rightarrow 0$. Both theories correctly predict zero density outside the slit, since for any choice of a^z , the factor $\tilde{\rho}^c e^{-\beta \tilde{\phi}^c(z_1)}$ in eq 13 immediately makes $\rho(z_1)$ zero outside the slit. However, inside the slit, both the PY and the HLR equations take $\tilde{\rho}^c = \rho^B$ and thus expand about the uniform bulk reference state, which gives a very poor description of the dilute 2D gas in the slit. As $L_s \rightarrow 0$ they predict a much lower limiting density²⁰ than given by eq 26. These problems arise only at small separations of the order or smaller than that of the hard sphere diameter d . At larger separations and in the one wall limit both theories give much more satisfactory results.

VI. New Criterion for Choosing the Reference Density in the SLR Equation

The above discussion has shown the versatility of the SLR equation and its ability to give exact limiting results in several specific cases with proper choice of the $\tilde{\rho}^r$. It has also shown that inaccuracies arise in some cases from the prescribed local choices made by the PY and HLR equations. Thus, we need a more general and systematic way to choose $\tilde{\rho}^r$ in the SLR equation. To that end, we first look more closely at the reasons why HLR fails in some cases.

A. Limitations of the HLR Prescription. The HLR equation expands about the hydrostatic density $\rho^r = \rho(\mu^B - \phi(\mathbf{r}))$. This depends on the external field too locally in cases where the external fields varies significantly in local regions much smaller than the correlation length of the fluid. In such cases, the proper density $\tilde{\rho}^r$ to expand about is often not the hydrostatic density, but a nonlocal extrapolation using the density of the surroundings, as illustrated by the tiny field and narrow slit examples discussed above. To use the SLR eq 13 to improve on the HLR approximation, we need a new way to choose $\tilde{\rho}^r$ that can account for this extrapolation of the local uniform system in such cases, while not spoiling the good results of the HLR equation in most other limits. We describe below our first attempt to develop such a computationally useful criterion.

B. Insensitivity Criterion. If all terms are exactly retained in eq 12, it should be invariant with respect to a simultaneous shift of the chemical potential μ^B and the external field ϕ . Thus, eq 12 should hold for all choices of $\tilde{\rho}^r$. However, only certain choices of $\tilde{\rho}^r$ can efficiently truncate the series at low orders. One possible criterion for a truncation is to choose $\tilde{\rho}^r$ that minimize the contribution from the quadratic term $Q(\mathbf{r}_1)$ in eq 12. However, unlike $c^{(2)}(r_{12}; \rho)$, $c^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3; \rho)$ is often not available analytically (and accurately) and the 6-dimensional integral of $Q(\mathbf{r}_1)$ in eq 4 is very computational demanding.

To circumvent the difficulty of dealing with $Q(\mathbf{r})$ directly, a reasonable alternative is to consider how the predictions of the SLR equation change as $\tilde{\rho}^r$ is varied. Since the SLR equation is a truncation of the exact series in eq 12, it is certainly not invariant with respect to variation of any $\tilde{\rho}^r$. However, if the truncation is accurate for some particular choice of $\tilde{\rho}^r$, then in effect the higher order terms in the series have been taken into account. Thus, the SLR equation should be relatively insensitive to small variations about the particular $\tilde{\rho}^r$ that make the higher order corrections to the SLR equation small. This condition need not be exact, even in the case of a tiny field where the series truncates exactly, but it seems likely that it could produce reasonable choices for $\tilde{\rho}^r$ in many cases.

This leads to the following self-consistent condition for the density given by the SLR eq 13

$$\delta\rho(\mathbf{r}_1)/\delta\tilde{\rho}^{r_2} = 0, \quad \forall \mathbf{r}_1, \mathbf{r}_2 \quad (27)$$

expressing the insensitivity of the density with respect to variations in $\tilde{\rho}^r$. Differentiating both sides of the SLR eq 13 and collecting the terms arising from $\delta\rho(\mathbf{r}_1)/\delta\tilde{\rho}^{r_2}$ (for details of the derivation, see the appendix), the insensitivity criterion (IC) arising from eq 27 can be written as

$$\tilde{\rho}^{r_1} = \frac{\int d\mathbf{r}_2 W(|\mathbf{r}_1 - \mathbf{r}_2|; \tilde{\rho}^{r_1}) \rho(\mathbf{r}_2)}{\int d\mathbf{r}_2 W(|\mathbf{r}_1 - \mathbf{r}_2|; \tilde{\rho}^{r_1})} \quad (28)$$

where

$$W(r_{12}; \rho) \equiv \dot{c}^{(1)}(\rho) c^{(2)}(r_{12}; \rho) + \dot{c}^{(2)}(r_{12}; \rho) \quad (29)$$

and

$$\dot{c}^{(1)}(\rho) \equiv dc^{(1)}(\rho)/d\rho; \quad \dot{c}^{(2)}(r_{12}; \rho) \equiv dc^{(2)}(r_{12}; \rho)/d\rho \quad (30)$$

Because the function $W(|\mathbf{r}_1 - \mathbf{r}_2|; \rho)$ in eq 29 has range of $c^{(2)}(|\mathbf{r}_1 - \mathbf{r}_2|; \rho)$, eq 28 shows that $\tilde{\rho}^{r_1}$ can be interpreted as the full density $\rho(\mathbf{r})$ averaged over the range of the fluid's correlation length around the point \mathbf{r}_1 , using a self-consistent weighting function W that itself depends on $\tilde{\rho}^{r_1}$. We will refer to the resulting $\tilde{\rho}^r$ as the smoothed reference density in what follows. Some versions of weighted density functional theory have used similar weighted densities, though the detailed implementation and justification are rather different.^{4,14}

Equation 28 derived from the IC can then be solved along with the SLR equation to determine both the full density $\rho(\mathbf{r})$ and the smoothed density $\tilde{\rho}^r$. We refer to these coupled equations as the IC equations. The IC equations can be solved numerically by iteration with the same methods used to solve the PY or HLR equations.

C. Behavior of IC Equations in Limiting Cases. We first verify that the IC equations can give accurate results in limiting cases where the proper choice of $\tilde{\rho}^r$ is known. In the hydrostatic limit where the external field is very slowly varying, $\rho(\mathbf{r})$ will

reduce to the hydrostatic density $\rho^r = \rho(\mu^B - \phi(\mathbf{r}))$, as given by the HLR equation. In this same limit, $\rho(\mathbf{r}_2)$ in the IC eq 28 can be approximated by $\rho(\mathbf{r}_1)$ and taken outside the integral. This gives $\tilde{\rho}^r = \rho(\mathbf{r})$ and hence $\tilde{\rho}^r = \rho^r$. The IC equations thus reduce to the HLR equation for slowly varying fields and recover the hydrostatic limit correctly. However, because of the averaging in eq 28, in other limits the IC choice of $\tilde{\rho}^r$ is less local than the HLR choice ρ^r and tends to smear out the nonuniformity caused by external perturbations in small regions.

For the narrow slit limit discussed above, the $\tilde{\rho}^r$ given by eq 28 correctly approaches zero as $L_s \rightarrow 0$, since the Boltzmann factor $e^{-\beta\phi(\mathbf{r})}$ ensures that $\rho(\mathbf{r})$ is zero inside the walls. Thus the IC equations are *exact* in the narrow slit limit as $L_s \rightarrow 0$ and correct the poor predictions of both the HLR and PY equations.

For tiny fields, the IC choice in eq 28 strictly reproduces the exact bulk density choice $\tilde{\rho}^r = \rho(\mu^B - \phi(\infty))$ only in the limit where $V^\phi \rightarrow 0$, and is not exact for general tiny fields. However $\tilde{\rho}^r$ is generally very close to that of the bulk density because the tiny field volume V^ϕ has little weight in the averaging. Thus the IC equations can be expected to agree reasonably well with exact results for general tiny fields, as will be shown in the next section.

VII. Numerical Results

We first consider the density response of a hard sphere fluid at a moderate packing fraction $\eta = 0.3$ to a series of spherical model potentials of varying ranges and different signs. In particular we studied repulsive (attractive) step functions of height $3k_B T$ ($-3k_B T$) and different ranges and "triangular" fields that start with the same height at the origin and vary linearly in r to the cutoff. Hard sphere cavities with the same cutoffs were also studied. Numerical solutions of the IC, HLR, and PY equations are presented, together with results of Monte Carlo simulations for the fluid's density response. The PY bulk direct correlation function $c^{(2)}(r_{12}; \rho)$, which is very accurate at these densities, was used in the theoretical calculations.² The Carnahan–Starling²¹ equation of state was used for computing the density $\tilde{\rho}^r = \rho(\mu^B - a^r)$ of the locally shifted uniform system.

A. Tiny Fields. For tiny fields, all results should be compared to the PY approximation, which is exact for such fields (subject only to the very small errors in the PY bulk direct correlation function). As can be seen in Figures 1 and 2, the HLR equation is exact only for tiny cavities. For finite tiny fields, its major errors occur in the tiny region where the field is nonvanishing and rapidly varying. The density response predicted by the HLR equation often exhibits a negative region where the external field varies most rapidly. The IC approximation, on the other hand, in general agrees with the PY approximation much better in the tiny field region and in particular eliminates the negative densities given by HLR. However the IC equations are not exact for tiny fields, and tend to overestimate the contact densities.

B. Extended Fields. For more extended fields, none of the approximations are exact, so Monte Carlo simulations were carried out to test the various theories. As shown in Figures 3 and 4, as the range of the step and the triangle potentials becomes wider, the HLR approximation becomes more accurate. However, it can still exhibit negative densities in its solution for both repulsive and attractive step potentials, especially for the narrower steps. For the same width of the potentials, the HLR equation does better in predicting the response to the triangle potentials than to the step potentials. This agrees with the expectation that the HLR equation should be more accurate when the external field is more slowly varying.

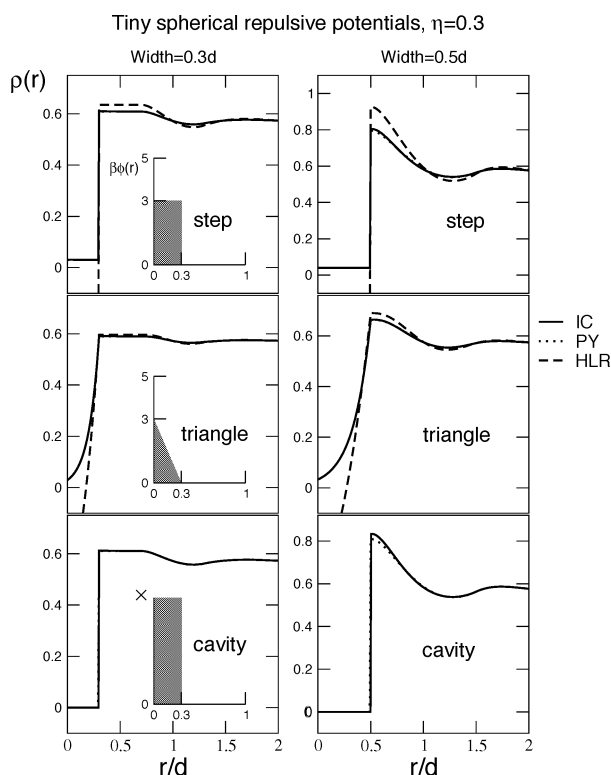


Figure 1. Plot of the density response to tiny repulsive external fields of different widths W . The curves are the predictions by the IC, PY, and HLR approximations. The PY approximation is exact for the density values inside the nonzero field region. All the external fields are spherical. “Step” denotes a spherical step function where $\beta\phi(r) = 3$, $\forall r < W$ and $\beta\phi(r) = 0$, otherwise. “Triangle” refers to the potential $\beta\phi(r) = 3 - 3r/W$ that has the same height as the step potentials but decays linearly to zero at $r = W$ with $\beta\phi(r) = 0$, otherwise. “Cavity” refers to the hard core potential $\beta\phi(r) = \infty$, $\forall r < W$ and $\beta\phi(r) = 0$, otherwise. The form of the potentials $\beta\phi(r)$ are illustrated in the insets. For the cavity potentials, the PY and HLR approximations give identical density solutions. The bulk fluid’s packing fraction $\eta \equiv \pi\rho^b d^3/6$ is $\eta = 0.3$.

The PY approximation, on the contrary, becomes less accurate when the field’s width increases, as is seen in Figure 3. This is because the PY expansion about the bulk density and extrapolation into the region where the external field is nonvanishing becomes less and less justified when the range of the potential increases. This problem with the PY approximation becomes much more acute for attractive potentials, where its errors are magnified by the large Boltzmann factor in eq 8, and the results are so poor that we do not show them in Figure 4. Indeed, the PY approximation for nonuniform fluid is hardly ever applied in practice except for strongly repulsive potentials, where the value of $\bar{\rho}^r$ in the repulsive region is essentially irrelevant.

The IC approximation is able again to correct the negative densities given by HLR and, most notably, to capture the highly nontrivial density profile inside both positive and negative step potentials due to the packing of the hard spheres. However, for spherical cavities, although it is known that the PY (and HLR) approximation consistently predicts a contact density lower than the exact value,^{2,11} the IC noticeably over-corrects the contact densities. This has a deleterious effect on the rest of the profile, especially near the cavity region.

In Figures 5 and 6, we consider the density response of a hard sphere fluid with bulk packing fraction $\eta = 0.25656$ to two deep attractive parabolic bowl potentials. Figure 5 shows the bowl potentials on the left and the reference densities ρ^r and $\bar{\rho}^r$ for the HLR and IC equations on the right. Results for

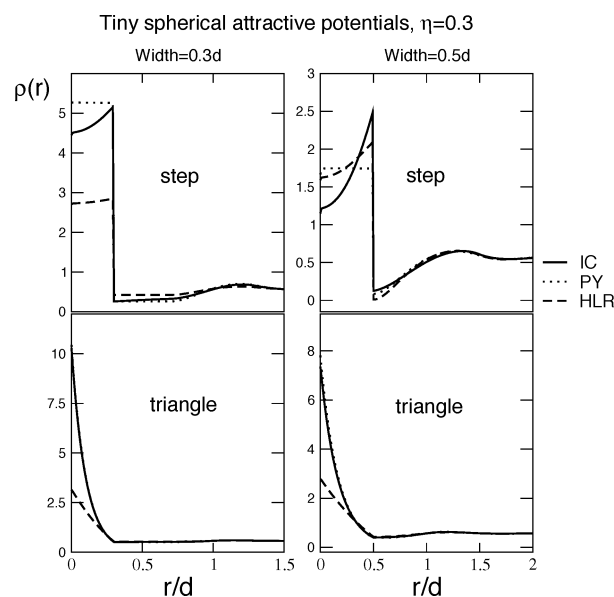


Figure 2. Curves following the same legend conventions used in Figure 1 and that are computed at the same bulk packing fraction $\eta = 0.3$. The external fields calculated here are all tiny spherical attractive potentials. Step and triangle potentials are defined as in Figure 1, except that the sign of the potential is negative.

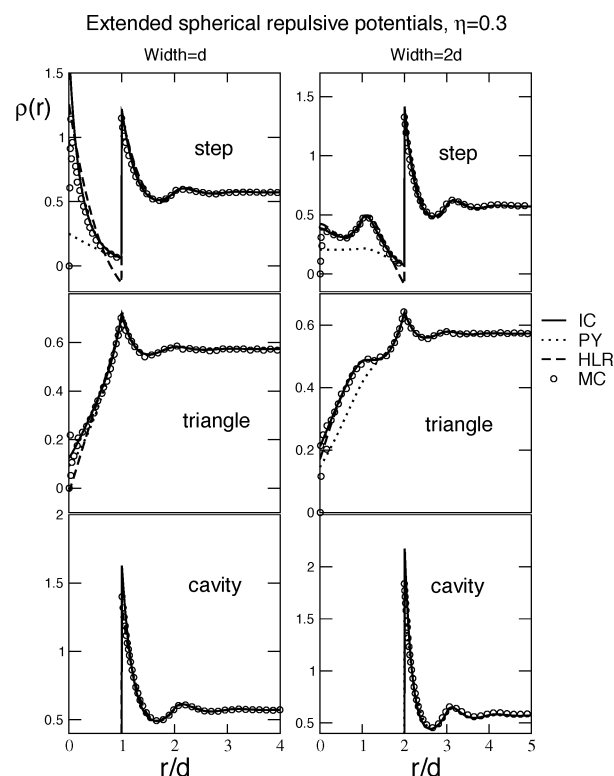


Figure 3. Density response to extended spherical repulsive potentials of varying widths. Conventions and bulk packing fraction are those of Figures 1 and 2.

the HLR and IC approximations are compared to MC simulations¹⁰ in Figure 6. For the shallower bowl potential, both the IC and HLR approximations agree well with the Monte Carlo simulations. The reference density $\bar{\rho}^r$ of the IC approximation is very close to that of the hydrostatic density ρ^r , as can be seen in the right graph of Figure 5, except that $\bar{\rho}^r$ varies smoothly near the edge of the bowl, whereas the hydrostatic density has a discontinuous derivative.

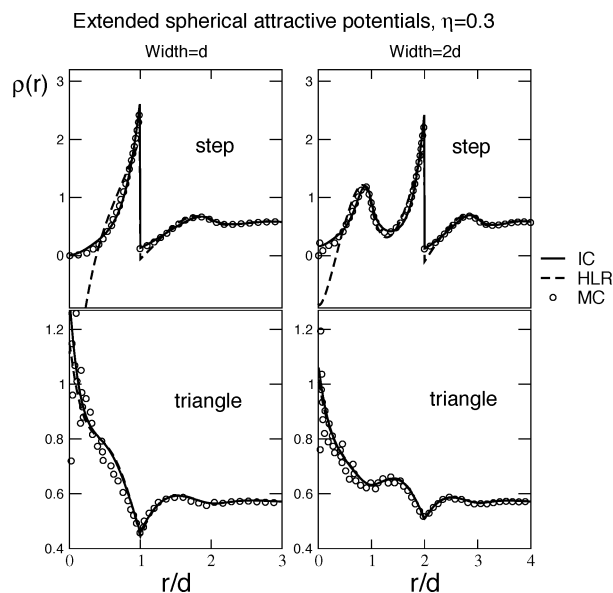


Figure 4. Density response to extended spherical attractive potentials of varying widths. Conventions and bulk packing fraction are those of Figures 1 and 2.

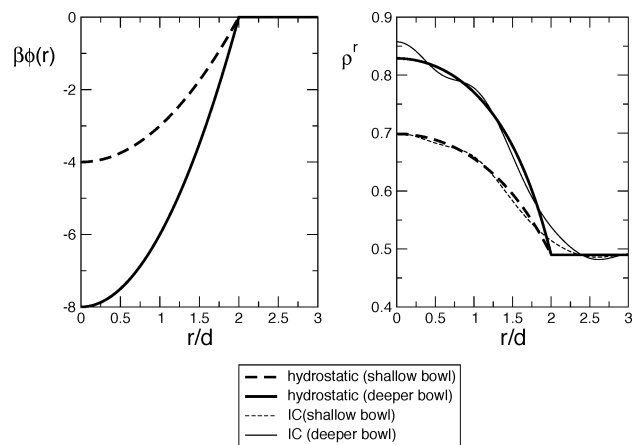


Figure 5. (Left) bowl potentials $\beta\phi(r) = A(r^2 - 4)$, with $A = 1$ for the shallow bowl and $A = 2$ for the deeper bowl. (Right) comparison of the hydrostatic densities ρ^r of the external fields to the ρ^r given by the IC equations.

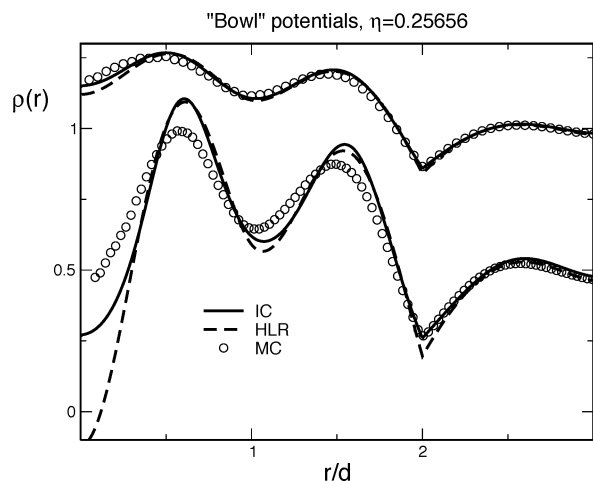


Figure 6. Density responses to attractive parabolic bowl potentials. Here $\eta = 0.25656$.

For the deeper bowl potential, both approximations deviate noticeably from the simulation data, but nonetheless capture the nontrivial oscillatory density profile inside the bowl. In

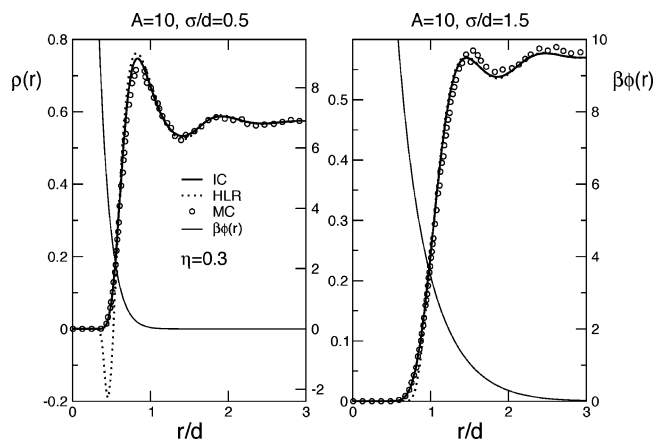


Figure 7. Density response to two external fields of the form $A \text{erfc}(r/\sigma)/r$. Note that the left vertical axis refers to the density curves while the right vertical axis labels $\beta\phi(r)$. Here $\eta = 0.3$.

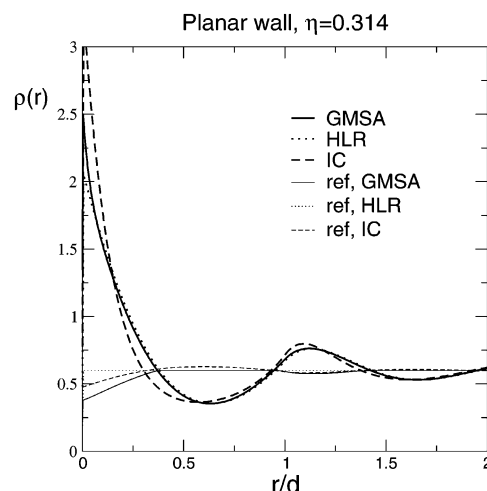


Figure 8. Density response to one planar hard wall positioned at $z = 0$. The bulk packing fraction is $\eta = 0.314$. The “ref” curves give the $\tilde{\rho}^r$ used with the different approximations. The $\tilde{\rho}^r$ for the GMSA approximation is obtained by using the GMSA $\rho(z)$ in the IC equation and solving inversely for the corresponding $\tilde{\rho}^r$.

particular, both reproduce the density minimum at the center of the bowl, where the external field is actually most attractive, due to nonlocal effects from packing of the hard spheres. However, the HLR density becomes negative at the bottom of the bowl, whereas the IC density remains positive, though somewhat lower than the MC result. The reference density $\tilde{\rho}^r$ for the IC method for the deeper bowl potential has more oscillations than that of the shallow bowl potential, and exhibits a maximum at the center, which is the key for keeping its predicted full density positive. Once outside the bowl, all approximations agree well with the MC result.

Figure 7 plots the density response to a soft continuous repulsive potential of the form $\beta\phi(r) = A \text{erfc}(r/\sigma)/r$. This potential is important in our theory of ionic fluids²² but, for our purposes here, just serves as an example of a soft repulsive potential. Here all the approximate results agree quite well with the simulations, except that the HLR equation again shows a narrow negative density region for the more rapidly varying potential (left graph of Figure 7).

Finally, in Figure 8, the density response to a planar hard wall determined using the IC and HLR approximations is compared to the results of the generalized mean spherical approximation (GMSA).²³ The GMSA fits the contact density at the wall to the bulk equation of state using an exact sum

rule, and is known to be very accurate for such systems. Thus it can be used as a benchmark for the other approximations. As is well-known, the HLR approximation (equivalent in this case to the PY approximation) agrees well with the GMSA except for its consistent underestimate of the contact density.

The IC result is now significantly worse than it was in the other cases. The main problem arises from a severe overestimate of the contact density, which goes on to spoil the rest of the density profile. The state shown is at a moderate packing fraction $\eta = 0.314$, and the errors get even larger at higher densities. This problem is similar to that seen for the cavity potentials presented before.

The IC method can also be used in an inverse way to determine what $\tilde{\rho}^r$ is needed to obtain a given density $\rho(\mathbf{r})$ as a solution. We determined the $\tilde{\rho}^r$ associated with the accurate GMSA $\rho(\mathbf{r})$ in this way, and it can be seen in Figure 8 that this GMSA $\tilde{\rho}^r$ deviates from the bulk density (used in the HLR equation) only very near the wall. The IC $\tilde{\rho}^r$ shows a similar deviation, but has more oscillations away from the wall and dips less low near the wall.

This example shows that relatively small changes in $\tilde{\rho}^r$ near the wall can have large effects on the predicted density profile near the wall in the SLR equation. The fact that the HLR choice, clearly appropriate for slowly varying fields, continues to give reasonably good results for single hard walls and hard cavities seems somewhat fortuitous, as illustrated by the errors HLR produces for rapidly varying but finite repulsive potentials. See, for example, the left graph in Figure 7. The IC method, which gives very good results in most other limits, correctly predicts a positive correction to the HLR/PY contact density but overestimates its magnitude. Only a small change in $\tilde{\rho}^r$ would be needed to produce very good results, but the IC prescription is not able to determine this in advance.

VIII. Final Remarks

The SLR equation provides a versatile framework for computing the density response of hard sphere fluids to general external fields. Since it satisfies the exact shifting property of the grand ensemble, it can accurately describe two important limits: slowly varying external fields (hydrostatic limit) and the opposite limit where field can be very rapidly varying but only perturbs the fluid in tiny or narrow regions. Errors in specific predictions arising from the linear truncation in the SLR equation in other cases can be minimized by expanding about a different uniform system at every point in space.

In practice there could be different prescriptions for how these local uniform systems could best be chosen in particular applications and for specific properties. In many cases the simple local HLR choice is quite sufficient. However this has problems for rapidly varying but finite fields and the SLR equation allows other choices. A general idea often used in other expansions in liquid state theory is to choose a reference density $\tilde{\rho}^r$ that at least minimizes the quadratic correction to the SLR equation in eq 4. However, this is very complicated, and there will still be unknown contributions from the higher order terms.

Here, as a first attempt, we have devised a computationally efficient insensitivity criterion (IC), based on the idea that the SLR equation should be insensitive to small variations of $\tilde{\rho}^r$. This property would be exactly satisfied if all terms in the expansion were taken into account, and by imposing it self-consistently on the SLR equation we hope to generate a truncation where the contributions from higher order terms are indeed small. The resulting IC method is extremely successful in correcting the negative density regions that the HLR often

exhibits for rapidly varying finite fields, and although not exact, the IC method also shows considerable improvement over HLR for the tiny field cases. Moreover, the IC method is exact for narrow slits as the slit width $L_s \rightarrow 0$, whereas the HLR and PY approximations have very significant errors in this limit.

However, the IC method tends to overestimate the contact value of the density response to single hard core cavities of all sizes, and this damages the accuracy of the rest of the density profile. In practice this need not be a significant limitation, since these cases are reasonably well treated by the HLR and PY approximations. Other specific conditions for hard core potentials, such as the sum rule used in the GMSA approximation, could be taken into account to improve the IC method in this limit.

However, it seems conceptually worthwhile to try to choose $\tilde{\rho}^r$ more generally within the SLR framework so that accurate results naturally arise in this limit as well. To that end, we believe it would be profitable to further study the tiny field limit, where similar problems are encountered, to gain additional insights into the optimal choice of the reference density for the SLR equation. We also need more information about the analytic nature and uniqueness of solutions the IC or similar criteria can provide. We have solved the resulting nonlinear equations numerically by iteration and have found a stable self-consistent solution. But there could be other solutions, or other branches that only a small change in the IC could favor. We have preliminary evidence that in the hard wall limit an alternative branch may exist for high density states that could give much better results, and plan further research along these lines.

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Appendix: Insensitivity Condition for the SLR Equation

After carrying out the functional derivative $\delta\rho(\mathbf{r}_1)/\delta\tilde{\rho}^r$ in eq 27 on the $\rho(\mathbf{r}_1)$ given by the SLR eq 13, one can rewrite the resulting expression as

$$\begin{aligned} \int d\mathbf{r}_3 [\delta(\mathbf{r}_1 - \mathbf{r}_3) - \tilde{\rho}^r e^{-\beta\tilde{\phi}^r(\mathbf{r}_1)} c^{(2)}(r_{13}; \tilde{\rho}^r)] \frac{\delta\rho(\mathbf{r}_3)}{\delta\tilde{\rho}^r} = \\ \tilde{\rho}^r e^{-\beta\tilde{\phi}^r(\mathbf{r}_1)} \delta(\mathbf{r}_1 - \mathbf{r}_2) \{ \dot{c}^{(1)}(\tilde{\rho}^r) - \int d\mathbf{r}_3 c^{(2)}(r_{13}; \tilde{\rho}^r) + \\ \int d\mathbf{r}_3 [\dot{c}^{(1)}(\tilde{\rho}^r) c^{(2)}(r_{13}; \tilde{\rho}^r) + \dot{c}^{(2)}(r_{13}; \tilde{\rho}^r)] (\rho(\mathbf{r}_3) - \tilde{\rho}^r) \} \end{aligned} \quad (\text{A.1})$$

A special case of eq 5 relating the $n-1$ and n th order direct correlation functions can be written as⁶

$$\dot{c}^{(n-1)}(\mathbf{r}_1, \dots, \mathbf{r}_{n-1}; \rho) = \int d\mathbf{r}_n c^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_{n-1}, \mathbf{r}_n; \rho) \quad (\text{A.2})$$

Using this on the right-hand side of eq A.1, the first two terms in the curly brackets cancel. Thus, the requirement that $\delta\rho(\mathbf{r}_3)/\delta\tilde{\rho}^r$ in eq A.1 vanish for all \mathbf{r}_2 and \mathbf{r}_3 as in eq 27 then implies that

$$\int d\mathbf{r}_3 [\dot{c}^{(1)}(\tilde{\rho}^r) c^{(2)}(r_{13}; \tilde{\rho}^r) + \dot{c}^{(2)}(r_{13}; \tilde{\rho}^r)] (\rho(\mathbf{r}_3) - \tilde{\rho}^r) = 0 \quad (\text{A.3})$$

for all \mathbf{r}_1 , from which eq 28 follows. Note that by using eq A.2, the equation above can be written as

$$\int d\mathbf{r}_2 \int d\mathbf{r}_3 [c^{(2)}(r_{12}; \tilde{\rho}^{\mathbf{r}_1}) c^{(2)}(r_{13}; \tilde{\rho}^{\mathbf{r}_1}) + c^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3; \tilde{\rho}^{\mathbf{r}_1})] (\rho(\mathbf{r}_3) - \tilde{\rho}^{\mathbf{r}_1}) = 0 \quad (\text{A.4})$$

This could also be derived by making the following approximation for $Q(\mathbf{r})$ in eq 4

$$Q(\mathbf{r}_1) \approx (\rho(\mathbf{r}_1) - \tilde{\rho}^{\mathbf{r}_1}) \int d\mathbf{r}_2 \int d\mathbf{r}_3 [c^{(2)}(r_{12}; \tilde{\rho}^{\mathbf{r}_1}) c^{(2)}(r_{13}; \tilde{\rho}^{\mathbf{r}_1}) + c^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3; \tilde{\rho}^{\mathbf{r}_1})] (\rho(\mathbf{r}_3) - \tilde{\rho}^{\mathbf{r}_1}) \quad (\text{A.5})$$

i.e., by assuming that $\rho(\mathbf{r}_2)$ differs little from $\rho(\mathbf{r}_1)$ in the region of integration near \mathbf{r}_1 in the definition for Q . Requiring that this approximation for the quadratic term vanish then gives eq A.4.

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