Density fluctuations and the structure of a nonuniform hard sphere fluid

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We derive an exact equation for density changes induced by a general external field that corrects the hydrostatic approximation where the local value of the field is adsorbed into a modified chemical potential. Using linear response theory to relate density changes self-consistently in different regions of space, we arrive at an integral equation for a hard sphere fluid that is exact in the limit of a slowly varying field or at low density and reduces to the accurate Percus-Yevick equation for a hard core field. This and related equations give accurate results for a wide variety of fields.

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Determining the structure and thermodynamics of a hard sphere fluid in a general external field is a basic problem in the theory of nonuniform fluids [1]. When the field represents walls, slits, or pores, this is the simplest model system describing the interplay between excluded volume correlations in the bulk fluid and the effects of confining geometries. Other choices for the field can represent fixed fluid particles and thus give information about multiparticle correlation functions [2,3]. Moreover, within mean field theory, a hard sphere fluid in the presence of an appropriately chosen “molecular field” potential can also describe a liquid-vapor interface and wetting and drying phenomena near walls or other solutes for simple liquids [4–6].

There are two limits where accurate solutions to this problem are already known. The simplest limit occurs when the external field \( \phi \) varies so slowly that it is essentially constant over the range of a correlation length in the bulk hard sphere fluid [6]. The partition function and the density \( \rho(\mathbf{r}; [\phi], \mu^B) \) in the grand ensemble are functionals of the external field \( \phi \) and functions of the chemical potential \( \mu^B \), and depend only on the difference between these quantities [3]. Thus we can subtract any constant from both \( \mu^B \) and \( \phi \) with no effect on the exact structural or thermodynamic properties of the fluid. In particular, for any fixed position \( \mathbf{r}_1 \) we can define a shifted field

\[
\phi^{r_1}(\mathbf{r}) \equiv \phi(\mathbf{r}) - \phi(\mathbf{r}_1),
\]

and shifted chemical potential

\[
\mu^{r_1} \equiv \mu^B - \phi(\mathbf{r}_1)
\]

whose parametric dependence on \( \mathbf{r}_1 \) is denoted by a superscript, and we have for all \( \mathbf{r} \) the exact relation \( \rho(\mathbf{r}; [\phi], \mu^B) = \rho(\mathbf{r}; [\phi^{r_1}], \mu^{r_1}) \). However, by construction the shifted field \( \phi^{r_1}(\mathbf{r}) \) vanishes at \( \mathbf{r} = \mathbf{r}_1 \) and it remains very small for \( \mathbf{r} \) near \( \mathbf{r}_1 \) when \( \phi \) is very slowly varying. In such a case we have

\[
\rho(\mathbf{r}_1; [\phi], \mu^B) \approx \rho(\mathbf{r}_1; [0], \mu^{r_1}) \equiv \rho(\mu^{r_1}).
\]

From Eq. (2) this depends only on the local value of the field \( \phi \) at \( \mathbf{r}_1 \). Equation (3) is exact in the limit of a very slowly varying \( \phi \), even when its magnitude is very large [7]. However Eq. (3) must fail if \( \phi \) has significant gradients over the range of a correlation length in the bulk fluid.

Accurate results can also be found in the limit of a hard core field, where \( \phi \) varies as rapidly as possible. Then the Percus-Yevick (PY) equation is often very accurate, particularly at low to moderate densities [3]. Simple corrections to the PY approximation for hard core fields such as the generalized mean spherical approximation (GMSA) are available [8] and give even more accurate results.

Recent work [8] has provided a new interpretation of the PY approximation for hard sphere fluids that is physically suggestive and suitable for generalization. Computer simulations have shown that even large spontaneous density fluctuations in a uniform hard sphere fluid can be accurately described using the same Gaussian probability distribution that controls small fluctuations [10]. Small density changes induced by small changes in the field \( \phi \) for a general system with chemical potential \( \mu^B \), temperature \( k_B T \equiv \beta^{-1} \), and density \( \rho(\mathbf{r}; [\phi], \mu^B) \equiv \rho(\mathbf{r}) \) are linearly related:

\[
-\beta \delta \phi(\mathbf{r}_1) = \int d\mathbf{r}_2 \chi^{-1}(\mathbf{r}_1, \mathbf{r}_2; [\rho]) \delta \rho(\mathbf{r}_2)
\]

through the linear response function [11]

\[
\chi^{-1}(\mathbf{r}_1, \mathbf{r}_2; [\rho]) \equiv \delta(\mathbf{r}_1 - \mathbf{r}_2)/\rho(\mathbf{r}_1) - c(\mathbf{r}_1, \mathbf{r}_2; [\rho]).
\]

Here \( c \) is the direct correlation function of the system; it is a functional of the density \( \rho(\mathbf{r}) \). Note that the external potential appears explicitly only on the left side of Eq. (4). In most standard applications, one considers perturbations about \( \phi = 0 \), so \( \rho(\mathbf{r}) = \rho^B \) and \( \chi^{-1} \) reduces to the uniform fluid function \( \chi^{-1}(\mathbf{r}_2; \rho^B) \). By the fluctuation-dissipation theorem, this same function controls the small Gaussian density fluctuations in the uniform fluid [11].

Can Eq. (1) also be used to calculate the response to a large (hard core) field? Certainly this linear relation between a finite external field perturbation and the induced
density must fail for values of \( r_1 \) where the field is very large. Conversely, Eq. (4) should be most accurate for those values of \( r_1 \) where the field is small — in particular where the field vanishes, and the simulations suggest that even large fluctuations in the absence of a field are well described by a linear fluctuation theory.

If we use Eq. (4) only for those values of \( r_1 \) where the field perturbation vanishes, then the integration over all \( r_2 \) relates density changes in the region where the field vanishes to the density change in the region where the field is nonzero \( \left[ 3 \right] \). For a hard core perturbation the density in the latter (hard core) region must vanish exactly and we can use Eq. (4) to determine the induced density changes in the region of zero field outside the core if the \( \chi^{-1}(r_{12}; \rho^B) \) for the uniform fluid is known.

For a general hard core solute (e.g., a hard wall), this is equivalent to the PY approximation for the solute-particle direct correlation function \( \left[ 3 \right] \). An equation equivalent to the PY equation for hard spheres results from a self-consistent application of this procedure for a potential representing a hard sphere fixed at the origin. By making use of the exact relation between the density induced by such a fixed particle and the pair correlation function of the uniform hard sphere fluid \( \left[ 3 \right] \), one obtains the PY approximations for both the induced density and \( \chi^{-1}(r_{12}; \rho^B) \).

Progress was possible in this special case because we could impose the exact “core condition” \( \left[ 3 \right] \) that the density vanishes in the hard core region. But what can be done for a general finite external field where the associated density response is not known in advance?

We note that there is a common feature of both limits discussed above. *Simple and accurate approximations are available wherever the local value of the field vanishes.* Thus depending on the value of the external field we can apply the exact hydrostatic shift in Eqs. (1) and (2) at each point of space to ensure that this optimal condition holds true. The hydrostatic limit for a slowly varying field is automatically satisfied. At the same time we can use accurate methods based on linear response theory that relate only densities in different parts of space to take into account nonlocal effects of the external field. In contrast, standard methods generally use only the response function of the bulk fluid and try to prescribe nonlinear closures that directly relate the field and the density \( \left[ 4 \right] \).

To develop a quantitative theory we first note that if \( \phi \) depends on a parameter \( \lambda \) (denoted by \( \phi_\lambda \); the associated density is \( \rho_\lambda \)) then Eq. (4) can be rewritten exactly by setting \( d\phi(r_1) = [d\phi_\lambda(r_1)]/d\lambda d\lambda \) and \( d\rho(r_2) = [d\rho_\lambda(r_2)]/d\lambda d\lambda \). In view of the discussion above we want to remove the explicit appearance of the field on the left side of Eq. (4). To that end we rewrite Eq. (4) using the shifted field and chemical potential of Eqs. (1) and (2). Then we introduce a modified potential \( \phi_\lambda^r(r) \) depending on a coupling parameter \( \lambda \) with \( 0 \leq \lambda \leq 1 \) such that \( d\phi_\lambda^r(r)/d\lambda \) vanishes everywhere and the associated density \( \rho_\lambda^r(r) = \rho^r \), the uniform hydrostatic density at \( r_1 \), while for \( \lambda = 1 \), \( \phi_\lambda^r = \phi^r \) and the associated density is \( \rho(r; [\phi^r], \mu^r) = \rho(r) \), the desired density of the fluid in the general external field \( \phi \). One possible choice is \( \phi_\lambda^r(r) \equiv \lambda \phi^r(r) \), but the linear dependence on \( \lambda \) is not essential in the following.

Thus we find \( 0 = \int dr_2 \chi^{-1}(r_1, r_2; [\rho_\lambda^r]) d\rho_\lambda^r(r_2)/d\lambda \) from Eq. (4) and we can integrate with respect to \( \lambda \) to obtain the formally exact result:

\[
0 = \int dr_2 \int_0^1 d\lambda \chi^{-1}(r_1, r_2; [\rho_\lambda^r]) d\rho_\lambda^r(r_2)/d\lambda .
\]

(6)

This equation has the desired features that the external field does not appear explicitly and the induced density changes in different parts of space are related to one another through a linear response function.

For practical calculations we must approximately carry out the \( \lambda \) integration. The simplest treatment approximates \( \chi^{-1}(r_1, r_2; [\rho_\lambda^r]) \) for all \( \lambda \) by \( \chi^{-1}(r_{12}; \rho^F) \), its value at \( \lambda = 0 \), consistent with the idea that even large changes in the density are controlled by the same response function as in the case of small changes. The \( \lambda \) integration involving the density can then be carried out exactly, and using Eq. (6) we obtain our final result, the *hydrostatic linear response (HLR) equation*:

\[
\rho(r_1) = \rho^F + \rho^r \int dr_2 c(r_{12}; \rho^r) [\rho(r_2) - \rho^F].
\]

(7)

Equation (6) is a linear integral equation relating the density \( \rho(r_1) \) at a given \( r_1 \) to an integral involving the density \( \rho(r_2) \) at all other points and a uniform fluid kernel \( c(r_{12}; \rho^F) \) that depends implicitly on \( r_1 \) through \( \rho^F \). This new feature presents no technical difficulties in determining a self-consistent numerical solution. We found that Picard iteration works very well. See Refs. \( \left[ 1 \right] \) and \( \left[ 2 \right] \) for details about the numerical solution.

Equation (6) has the following remarkable properties. i) It is exact when \( \phi(r) \) is very slowly varying. ii) It is exact for any \( \phi(r) \) at low enough density, where there is a local relation between the potential and induced density. iii) For a field \( \phi(r) \) from a general hard core solute, Eq. (6) reduces to the PY approximation, as discussed above. Any desired representation of the uniform fluid \( c \) can be used.

Other equations can be derived by making different approximations while carrying out the \( \lambda \) integration in Eq. (4). We note from Eq. (6) that the local (\( \delta \)-function) part of \( \chi^{-1} \) becomes relatively more important as the density \( \rho(r_1) \) tends to zero either because of a harshly repulsive \( \phi(r_1) \) or because \( \rho^B \) is small. A somewhat inconsistent approximation that does however exactly describe the local part of \( \chi^{-1} \) sets \( \chi^{-1}(r_1, r_2; [\rho_\lambda^0]) \approx \delta(r_1-r_2)/\rho_\lambda^0(r_1) - c(r_{12}; \rho^F) \), thus keeping the exact \( \lambda \)-dependence in the local part of \( \chi^{-1} \) but setting \( \lambda = 0 \) in the nonlocal part. The \( \lambda \) integration can then be carried out exactly and we arrive at an alternative *hydrostatic mixed (HM) equation*:
The hydrostatic density \( \rho \) of spherical parabolic potentials shown in the inset (solid lines) as given by theory and simulation. The upper curve corresponds to the smaller potential and has been displaced upward by one unit. Also shown in the inset (crosses) are the potentials predicted by Eq. (8) given the simulation data.

\[
\rho(r_1) = \rho^f \exp\{\int dr_2 c(r_{12}; \rho^f) [\rho(r_2) - \rho^f]\}. \tag{8}
\]

In regions where the external field \( \phi(r_1) \) is infinite both the hydrostatic density \( \rho^f \) and the exact density \( \rho(r_1) \) must vanish; the solutions to both Eqs. (7) and (8) clearly satisfy this condition. Moreover, the \( \rho(r_1) \) solving Eq. (8) is always nonnegative, which is not the case for Eq. (7), and properties i) and ii) above still hold true. As we will see, Eq. (8) also gives very good results for a wide variety of potentials. However, for a hard sphere potential Eq. (8) reduces to the hypernetted chain (HNC) equation [3] for hard spheres, which is known to be much less accurate than the PY equation at high density [2].

To give some indications of the accuracy of Eqs. (7) and (8) we report solutions for a number of different external fields and compare with the results of computer simulations [4]. We first consider two model potentials designed to show both the strengths and the weaknesses of the present methods. Then we consider more realistic potentials arising from a mean field treatment of wetting and drying phenomena in the Lennard Jones (LJ) fluid.

Fig. 1 shows the correlation function \( g(r) \equiv \rho(r)/\rho^B \) for a hard sphere system at a moderately high bulk density \( \rho^B = 0.49 \) in the presence of two deep attractive spherical parabolic model potentials shown in the inset. (Reduced units, with distances measured in units of the hard sphere diameter are used.) Both equations reproduce the increased density inside the well, and the nonlocal oscillatory excluded volume correlations, which show a local density minimum at the center of the well due to packing effects.

Since the external field enters Eqs. (7) and (8) only locally through its effect on \( \rho^f \), it is also easy to use these equations for the inverse problem of determining the field associated with a given density profile. As an example, the crosses in the inset gives the potentials predicted by Eq. (8) given the simulation data for \( g(r) \).

One would expect methods based on expanding about the uniform hydrostatic fluid to be least accurate for potentials with very steep gradients, exemplified by the repulsive planar triangular barrier potential shown in the inset to Fig. 2. Even here reasonably good results are found from Eqs. (7) and (8) at the moderately high density of \( \rho^B = 0.55 \) (with excellent results at lower densities). However, at \( \rho^B = 0.75 \) very noticeable errors are seen in the shape and height of the first peak and the amplitude and phase of subsequent peaks in both approximations.

Results actually improve as the barrier height increases and the potential approaches a hard wall potential: the theory does better for hard cores because there is no region of space where there is a large gradient in the external field while at the same time the local density is nonzero. Equation (7) then reduces to the accurate hard core PY wall-particle equation, and Eq. (8) describes subsequent peaks better, though the characteristic HNC overshoot of the height of the first peak for hard core systems becomes very evident as the slope increases. Large repulsive potentials with very steep gradients are better treated by “blip function” methods [2] or other expansions about a hard core system.

In most realistic applications we can envision, the external potential can be divided into a harshly repulsive, essentially hard core, region well treated by the present methods (with “blip function” corrections for finite core softness), and an extended interaction region where the potential varies slowly enough that the theory again gives good results. This is the basis of the two step method used to solve the mean field equations for the LJ fluid in Refs.
In Fig. 3 we show the reference system $g(r)$ as predicted by the HLR equation induced by the repulsive external fields shown in the inset. These fields arise from a generalized mean field treatment \([12]\) describing the density distribution in a LJ fluid. The upper curve shows a molecularly sized solute, which induces density oscillations like those seen in the radial distribution function. For larger excluded volume regions, the unbalanced attractive forces \([4]\) in the LJ fluid contribute a stronger and longer ranged repulsive component to the effective potential in the associated hard sphere system as seen in the inset and partial drying occurs. This manifests itself in the middle and lower curves by smoother profiles, with a density minimum near the solute. Other limits of this problem, such as hard spheres near a hard wall or the mean field approximation to the smooth vapor-liquid interface of a LJ fluid, are well described using the same HLR equation in the presence of the appropriate effective mean field.

While we have concentrated on the structure \([16]\) of hard sphere systems here, even large density fluctuations in more complicated liquids like water are also well described by a Gaussian model \([17, 18]\) in the presence of an effective field \([19]\) describing the unbalanced attractive forces arising when interfaces form. By taking this field into account, Lum, Chandler and Weeks \([19]\) were able to extend the (field free) Gaussian theory of hydrophobicity of Pratt and Chandler \([17, 18]\) for small hydrophobic solutes to large hydrophobic solutes, where drying inter-

 faces, very similar to those seen in Fig. 3, are predicted to occur. More generally, we believe that extensions of linear response methods or Gaussian fluctuation theory \([20]\) to include the effects of appropriately chosen external fields, with optimal treatment of the field by equations similar to the HLR equation \([7]\), will prove useful in a variety of different problems. This work was supported by the National Science Foundation, Grant No. CHE9528915.

FIG. 3. Correlation functions (vertically displaced by 0.1 unit) induced by the potentials shown in the insets. These potentials arise from a generalized mean field treatment of the response of a LJ fluid to a hard sphere solute with varying size. Circles indicate simulation data and the solid line give the predictions of Eq. \([8]\).

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