

Using fundamental measure theory to treat the correlation function of the inhomogeneous hard-sphere fluid

Jeff B. Schulte, Patrick A. Kreitzberg, Chris V. Haglund, and David Roundy

Department of Physics, Oregon State University, Corvallis, Oregon 97331, USA

(Received 31 August 2012; published 28 December 2012)

We investigate the value of the correlation function of an inhomogeneous hard-sphere fluid at contact. This quantity plays a critical role in statistical associating fluid theory, which is the basis of a number of recently developed classical density functionals. We define two averaged values for the correlation function at contact and derive formulas for each of them from the White Bear version of the fundamental measure theory functional, using an assumption of thermodynamic consistency. We test these formulas, as well as two existing formulas, against Monte Carlo simulations and find excellent agreement between the Monte Carlo data and one of our averaged correlation functions.

DOI: [10.1103/PhysRevE.86.061201](https://doi.org/10.1103/PhysRevE.86.061201)

PACS number(s): 61.20.Ne, 61.20.Gy, 61.20.Ja

I. INTRODUCTION

There has been considerable recent interest in using statistical associating fluid theory (SAFT) to construct classical density functionals to describe associating fluids [1–10]. This approach has been successful in qualitatively describing the dependence of surface tension on temperature. A key input to these functionals is the correlation function evaluated at contact, which is identical to the contact value of the cavity correlation function for hard spheres, and is required for both the chain and association terms in the SAFT free energy. The chain term describes the chain formation energy in polymeric fluids, while the association term describes the effects of hydrogen bonding, both of which can be large. Yu and Wu introduced in 2002 a functional for the association term of the free energy, which included a functional for the contact value of the correlation function (described in Sec. III E) [8], which has subsequently been used in the development of other SAFT-based functionals [9,10]. Two functionals for the chain contribution have recently been introduced, one which uses the correlation function of Yu and Wu [10] and another which introduces a new approximation for the contact value of the correlation function [7].

Here we will briefly describe how the contact value of the correlation function has been used in two of these recent papers introducing SAFT-based classical density functionals. For simplicity, we will use our own notation to describe the work of these authors. In his paper presenting a density functional based on the PCP-SAFT equation of state [7], Gross introduces the chain free energy in SAFT as

$$\frac{A_{\text{chain}}}{kT} = -(m-1) \int n(\mathbf{r}) \{ \ln [n^A(\mathbf{r})g_\sigma^A(\mathbf{r})] - 1 \} d\mathbf{r}, \quad (1)$$

where $n^A(\mathbf{r})$ is a weighted density defined in Eq. (8) and $g_\sigma^A(\mathbf{r})$ is the local value of the correlation function at contact, which we define in Eq. (7). In Sec. III D, we describe Gross's approximation for this function. In a paper describing a classical density functional for inhomogeneous associating fluids [8], Yu and Wu define the association free energy as

$$\frac{A_{\text{assoc}}}{kT} = \sum_i \int \zeta(\mathbf{r}) n_0(\mathbf{r}) \left[\ln X_i(\mathbf{r}) - \frac{1}{2} X_i(\mathbf{r}) + \frac{1}{2} \right] d\mathbf{r} \quad (2)$$

$$X_i(\mathbf{r}) = \frac{1}{1 + \sum_j \frac{n_0(\mathbf{r})g_\sigma^S(\mathbf{r})}{\zeta(\mathbf{r})} X_j(\mathbf{r})\kappa_{ij}(e^{\beta\epsilon_{ij}} - 1)}, \quad (3)$$

where $X_i(\mathbf{r})$ is the fraction of interaction sites of type i at position \mathbf{r} that are unoccupied, $n_0(\mathbf{r})$ is a weighted density defined in Eq. (6), $\zeta(\mathbf{r})$ is a nonlocal measure of the density gradient defined in Eq. (32), and $g_\sigma^S(\mathbf{r})$ is a form of the correlation function at contact, which we define in Eq. (5). In Sec. III E, we present the approximation to $g_\sigma^S(\mathbf{r})$ introduced by Yu and Wu. Given these differing approaches, it seems valuable to examine this property of the hard-sphere fluid through direct simulation, in order to establish the advantages and disadvantages of each approach.

Although these recent works have introduced approximate functionals for the contact value of the correlation function for an inhomogeneous hard-sphere fluid [7,8], there has not been a study that specifically addresses this functional. In this paper, we introduce two definitions for the locally averaged correlation function of an inhomogeneous system. Given these definitions, we will present a thermodynamic derivation for each correlation function from the free energy functional. We will then discuss the correlation functions of Yu and Wu and of Gross and will end by comparing all four approximations with Monte Carlo simulations of the hard-sphere fluid at a variety of hard-wall surfaces.

II. CORRELATION FUNCTION WITH INHOMOGENEITY

We define our terms using the two-particle density $n^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$, which gives the probability per unit volume squared of finding one particle at position \mathbf{r}_1 and the other at position \mathbf{r}_2 . The pair correlation function is defined by

$$g(\mathbf{r}_1, \mathbf{r}_2) \equiv \frac{n^{(2)}(\mathbf{r}_1, \mathbf{r}_2)}{n(\mathbf{r}_1)n(\mathbf{r}_2)}. \quad (4)$$

In a homogeneous fluid, the pair correlation only depends on the distance $|\mathbf{r}_1 - \mathbf{r}_2|$ and can be expressed as a function of a single variable, and the contact value of the correlation function is its value when evaluated at a distance of the diameter σ . The pair correlation function of an *inhomogeneous* fluid is not as simple, but it is desirable for reasons of computational efficiency to construct classical density functionals using only

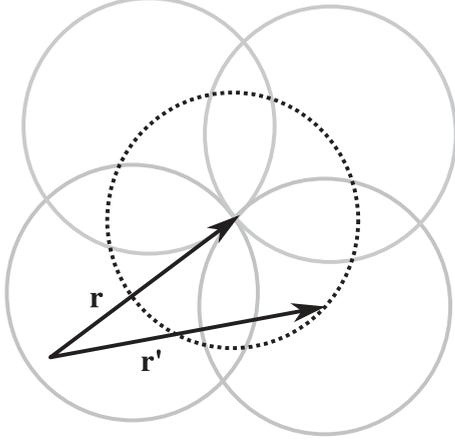


FIG. 1. Set of hard spheres that are included in $n_0(\mathbf{r})$, which consist of those which just touch the point \mathbf{r} .

one-center convolutions. Moreover, a local function is helpful when defining functionals based on perturbation theory, such as those in Eqs. (1)–(3). This leads us to seek a *local* value for g_σ that is dependent upon only one position variable \mathbf{r} . There are two reasonable options for defining such a local function: a symmetric formulation such as that used in Eqs. (2) and (3) (which we refer to as S) and an asymmetric formulation such as that used in Eq. (1) (which we refer to as A).

For the symmetric S case, the correlation function at contact is given by:

$$g_\sigma^S(\mathbf{r}) = \frac{1}{n_0(\mathbf{r})^2} \int n^{(2)}(\mathbf{r} - \mathbf{r}', \mathbf{r} + \mathbf{r}') \frac{\delta(\sigma/2 - |\mathbf{r}'|)}{\pi \sigma^2} d\mathbf{r}', \quad (5)$$

where σ is the hard sphere diameter and the density n_0 is one of the fundamental measures of fundamental measure theory (FMT). The functional $g_\sigma^S(\mathbf{r})$ is defined to treat the geometrically symmetric possibility of spheres touching at the position \mathbf{r} as illustrated in Fig. 1:

$$n_0(\mathbf{r}) = \int n(\mathbf{r}') \frac{\delta(\sigma/2 - |\mathbf{r} - \mathbf{r}'|)}{\pi \sigma^2} d\mathbf{r}'. \quad (6)$$

This functional $n_0(\mathbf{r})$ gives a density averaged over all spheres that touch at the position \mathbf{r} . Together, $n_0(\mathbf{r})$ and $g_\sigma^S(\mathbf{r})$ are used in the association free energy given in Eqs. (2) and (3).

In contrast, the asymmetrically averaged A correlation function is given by

$$g_\sigma^A(\mathbf{r}) = \frac{1}{n(\mathbf{r})n_A(\mathbf{r})} \int n^{(2)}(\mathbf{r}, \mathbf{r} + \mathbf{r}') \frac{\delta(\sigma - |\mathbf{r}'|)}{4\pi \sigma^2} d\mathbf{r}', \quad (7)$$

where the density $n_A(\mathbf{r})$ is analogous to $n_0(\mathbf{r})$, but measures the density of spheres that are touching a sphere that is located at point \mathbf{r} , as illustrated in Fig. 2.

$$n_A(\mathbf{r}) = \int n(\mathbf{r}') \frac{\delta(\sigma - |\mathbf{r} - \mathbf{r}'|)}{4\pi \sigma^2} d\mathbf{r}'. \quad (8)$$

Thus, g_σ^A corresponds to an average of the two-particle density over spheres touching a sphere that is located at the position \mathbf{r} . The functionals $n_A(\mathbf{r})$ and $g_\sigma^A(\mathbf{r})$ are used in the chain free energy given in Eq. (1).

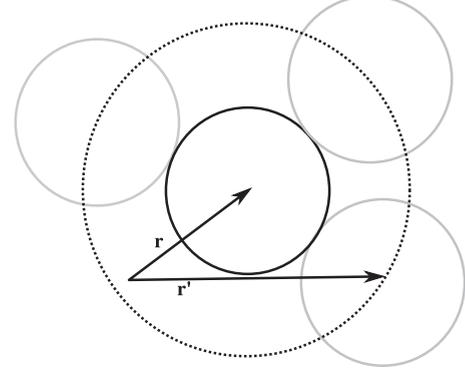


FIG. 2. Set of hard spheres that are included in $n_A(\mathbf{r})$, which consist of those that just touch a sphere centered at \mathbf{r} . The dashed line illustrates the surface over which contact is possible.

A. Fundamental measure theory

We use the White Bear version of the fundamental measure theory (FMT) functional [11], which describes the excess free energy of a hard-sphere fluid. The White Bear functional reduces to the Carnahan-Starling equation of state for homogeneous systems. It is written as an integral over all space of a local function of a set of “fundamental measures,” $n_\alpha(\mathbf{r})$, each of which is written as a one-center convolution of the density. The White Bear free energy is thus

$$A_{\text{HS}}[n] = k_B T \int [\Phi_1(\mathbf{r}) + \Phi_2(\mathbf{r}) + \Phi_3(\mathbf{r})] d\mathbf{r}, \quad (9)$$

with integrands

$$\Phi_1 = -n_0 \ln(1 - n_3) \quad (10)$$

$$\Phi_2 = \frac{n_1 n_2 - \mathbf{n}_{V1} \cdot \mathbf{n}_{V2}}{1 - n_3} \quad (11)$$

$$\Phi_3 = (n_2^3 - 3n_2 \mathbf{n}_{V2} \cdot \mathbf{n}_{V2}) \frac{n_3 + (1 - n_3)^2 \ln(1 - n_3)}{36\pi n_3^2 (1 - n_3)^2}, \quad (12)$$

using the fundamental measures

$$n_3(\mathbf{r}) = \int n(\mathbf{r}') \Theta(\sigma/2 - |\mathbf{r} - \mathbf{r}'|) d\mathbf{r}' \quad (13)$$

$$n_2(\mathbf{r}) = \int n(\mathbf{r}') \delta(\sigma/2 - |\mathbf{r} - \mathbf{r}'|) d\mathbf{r}' \quad (14)$$

$$\mathbf{n}_{V2}(\mathbf{r}) = \int n(\mathbf{r}') \delta(\sigma/2 - |\mathbf{r} - \mathbf{r}'|) \frac{\mathbf{r} - \mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \quad (15)$$

$$\mathbf{n}_{V1} = \frac{\mathbf{n}_{V2}}{2\pi\sigma}, \quad n_1 = \frac{n_2}{2\pi\sigma}, \quad n_0 = \frac{n_2}{\pi\sigma^2}. \quad (16)$$

III. THEORETICAL APPROACHES

A. Homogeneous limit

In order to motivate our derivation of the correlation function at contact for the *inhomogeneous* hard-sphere fluid, we begin by deriving the well-known formula for g_σ for the *homogeneous* fluid that comes from the Carnahan-Starling free energy. The contact value of the correlation function density can be found by using the contact-value theorem, which states that the pressure on any hard surface is determined by the

density at contact:

$$p_{\text{SAS}}(\mathbf{r}_c) = k_B T n(\mathbf{r}_c), \quad (17)$$

where \mathbf{r}_c is a position of a sphere that would be in contact with the hard surface, $n(\mathbf{r}_c)$ is the density at this point \mathbf{r}_c , and $p_{\text{SAS}}(\mathbf{r}_c)$ is the pressure that the spheres exert on the surface at the same point. This pressure is understood as the ratio of force to an infinitesimal element of *solvent accessible surface* (SAS) area. In the homogeneous fluid, the contact-value theorem implies that

$$p_{\text{SAS}} = k_B T n g_\sigma, \quad (18)$$

where p_{SAS} is the pressure on a hard sphere's solvent accessible surface. This pressure can be readily computed from the dependence of the Carnahan-Starling free energy on hard sphere radius,

$$A_{\text{HS}} = N k_B T \frac{4\eta - 3\eta^2}{(1 - \eta)^2}, \quad (19)$$

where $\eta \equiv \frac{\pi}{6} \sigma^3 n$ is the filling fraction. We compute the pressure using the total force with respect to a changing radius of all the spheres. To find the pressure, we divide this force by $4\pi\sigma^2$, which is the SAS area of a single hard sphere, illustrated in Fig. 2. Finally, we divide by N to account for the total area of all the spheres in the fluid:

$$p_{\text{SAS}} = \frac{1}{N 4\pi\sigma^2} \frac{dA_{\text{HS}}}{dR}, \quad (20)$$

$$= \frac{1}{N 4\pi\sigma^2} \frac{1}{2} \frac{dA_{\text{HS}}}{d\sigma}, \quad (21)$$

$$= k_B T n \frac{1 - \frac{\eta}{2}}{(1 - \eta)^3}. \quad (22)$$

Using the contact-value theorem, we thus find the well-known correlation function evaluated at contact:

$$g_\sigma = \frac{1 - \frac{\eta}{2}}{(1 - \eta)^3}. \quad (23)$$

Extending this derivation to the inhomogeneous fluid requires that we find the pressure felt by the surface of particular spheres.

B. Asymmetrically averaged correlation function

We will begin our derivation of the locally averaged correlation function with the asymmetric definition of $g_\sigma^A(\mathbf{r})$ given in Eq. (7), which is averaged over contacts in which one of the two spheres is located at position \mathbf{r} . This correlation function is related to the contact density averaged over the solvent accessible surface of a sphere located at \mathbf{r} and can thus be determined by finding the pressure on that surface. We find this pressure from the change in free energy resulting from an infinitesimal expansion of spheres located at position \mathbf{r} . From this pressure, we derive a formula for the correlation function $g_\sigma^A(\mathbf{r})$ as was done in the previous section:

$$p_{\text{SAS}}(\mathbf{r}) = \frac{1}{n(\mathbf{r}) 4\pi\sigma^2} \frac{1}{2} \frac{\delta A_{\text{HS}}}{\delta\sigma(\mathbf{r})} \quad (24)$$

$$g_\sigma^A(\mathbf{r}) = \frac{1}{n(\mathbf{r}) n_A(\mathbf{r})} \frac{1}{k_B T 4\pi\sigma^2} \frac{1}{2} \frac{\delta A_{\text{HS}}}{\delta\sigma(\mathbf{r})}, \quad (25)$$

where $\sigma(\mathbf{r})$ is the diameter of spheres located at position \mathbf{r} . Details regarding the evaluation of the functional derivative $\frac{\delta A_{\text{HS}}}{\delta\sigma(\mathbf{r})}$ are discussed in the Appendix. Equation (25) is an exact expression for $g_\sigma^A(\mathbf{r})$ as defined in Eq. (7). However, since we do not know the exact hard-sphere free energy, we approximate A_{HS} using FMT. The equation for g_σ^A found using FMT requires finding convolutions of local derivatives of the free energy, making this formulation computationally somewhat more expensive than the free energy itself.

C. Symmetrically averaged correlation function

We now address the symmetrically averaged correlation function, which is defined in Eq. (5). This corresponds to the correlation function averaged for spheres *touching at a given point*. In this case, we conceptually would like to evaluate the pressure felt by the surface of spheres where that surface is located at point \mathbf{r} . We can approximate this value by assuming that this pressure will be simply related to the free energy density at point \mathbf{r} . Through a process similar to the previous derivations, this leads to the expression

$$g_\sigma^S(\mathbf{r}) = \frac{1}{n_0(\mathbf{r})^2} \frac{1}{4\pi\sigma^2} \frac{1}{2} \frac{\partial\Phi(\mathbf{r})}{\partial\sigma}, \quad (26)$$

where $\Phi(\mathbf{r}) = \Phi_1(\mathbf{r}) + \Phi_2(\mathbf{r}) + \Phi_3(\mathbf{r})$ is the dimensionless free energy density. This expression is an approximation—unlike the analogous Eq. (25)—because it assumes that we have available a local functional $\Phi(\mathbf{r})$ whose derivative provides the pressure needed to compute $g_\sigma(\mathbf{r})$. Equation (26) requires that we evaluate the derivatives of the fundamental measures $n_\alpha(\mathbf{r})$ with respect to diameter, which leads us to derivatives of the δ function, which we can simplify and approximate using an assumption of a reasonably smooth density:

$$\frac{\partial n_2(\mathbf{r})}{\partial\sigma} = \frac{1}{2} \int \delta' \left(\frac{\sigma}{2} - |\mathbf{r} - \mathbf{r}'| \right) n(\mathbf{r}') d\mathbf{r}' \quad (27)$$

$$= \frac{2}{\sigma} n_2(\mathbf{r}) - \frac{1}{2} \int \delta \left(\frac{\sigma}{2} - |\mathbf{r} - \mathbf{r}'| \right) \times \frac{\mathbf{r} - \mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} \cdot \nabla n(\mathbf{r}') d\mathbf{r}' \quad (28)$$

$$\approx \frac{2}{\sigma} n_2(\mathbf{r}). \quad (29)$$

In the systems that we study, the density is *not* reasonably smooth, but we can state empirically making this approximation nevertheless improves the predictions of our functional g_σ^S , while at the same time reducing its computational cost by avoiding the need to calculate any additional weighted densities or convolutions.

D. Gross's asymmetrically averaged correlation functional

One approximation for the correlation function is that of Gross [7], which is of the asymmetrically averaged variety (g_σ^A):

$$g_\sigma^{\text{Gross,A}}(\mathbf{r}) = \frac{1 - \frac{\pi}{12} \sigma^3 n_A(\mathbf{r})}{\left[1 - \frac{\pi}{6} \sigma^3 n_A(\mathbf{r}) \right]^3}, \quad (30)$$

where n_A is the averaged density defined in Eq. (8). This formula is arrived at by using the density averaged over all spheres that could be touching a sphere at point \mathbf{r} in the Carnahan-Starling equation for the correlation function at contact, given in Eq. (23).

E. Yu and Wu's symmetrically averaged functional

Yu and Wu developed a functional for the correlation function evaluated at contact, which is symmetrically averaged [8]. However, instead of using n_0 as the corresponding density, they use a density given by

$$n_{\text{Yu}}(\mathbf{r}) = n_0(\mathbf{r})\zeta(\mathbf{r}) \quad (31)$$

$$\zeta = 1 - \frac{\mathbf{n}_{V2} \cdot \mathbf{n}_{V2}}{n_2^2}, \quad (32)$$

where the function ζ is a measure of local inhomogeneity at the point of contact and has the effect of reducing this density at interfaces. Because of this difference, the correlation function of Yu and Wu cannot be directly compared with g_σ^S as defined in Eq. (5). Therefore, in order to make a comparison, we move the factors of ζ in Eq. (31) from the density into the correlation function itself,

$$g_\sigma^{\text{Yu},S} = \zeta^2 g_\sigma^{\text{Yu}} \quad (33)$$

$$= \zeta^2 \left[\frac{1}{1-n_3} + \frac{1}{4} \frac{\sigma n_2 \zeta}{(1-n_3)^2} + \frac{1}{72} \frac{\sigma^2 n_2^2 \zeta}{(1-n_3)^3} \right], \quad (34)$$

where g_σ^{Yu} is the correlation function as defined in Ref. [8], and $g_\sigma^{\text{Yu},S}$ is the function we will examine in this paper.

IV. COMPARISON WITH SIMULATION

We performed a Monte Carlo simulation of the hard sphere fluid to measure the contact value of the correlation function for several simple inhomogeneous configurations. For each configuration, we compute the mean density, and the contact values of the correlation function, averaged as defined in Eqs. (7) and (5). We compare these with the functionals presented in Secs. III B–III E. We constructed our functionals using both the original White Bear functional [11] as well as the mark II version of the White Bear functional [12], but the results were essentially indistinguishable on our plots, so we exclusively show the results due to the original White Bear functional.

We simulate the inhomogeneous hard sphere fluid at four hard-wall interfaces. The first and simplest is a flat hard wall. We then study two convex hard surfaces. One is an excluded sphere with diameter 2σ , which corresponds to a “test particle” simulation with one of a hard sphere at the origin with diameter σ . The second is an excluded sphere with diameter 6σ , which demonstrates behavior typical of mildly convex hard surfaces. Finally, we study a concave surface given by a hard cavity in which our fluid is free to move up to a diameter of 16σ , which demonstrates behavior typical of mildly concave surfaces. In each case, we performed a low-density (filling fraction 0.1) and high-density (filling fraction 0.4) simulation. We performed additional computations over a wider range of curvatures and densities but chose these as typical examples.

A. Low density

We begin by presenting our low-density results, corresponding to a filling fraction of 0.1, which are shown in Fig. 3. At this low density, the contact value of the correlation function in the bulk is only 1.3, indicating that correlations are indeed small and that the fluid should be relatively easy to model. Indeed, the contact density at the hard surface is only around 50% higher than the bulk, and the FMT predicted density is close to indistinguishable from the true density for each of the four configurations, as seen in the bottom subpanel of each subfigure within Fig. 3.

The g_σ^A correlation function in each configuration (plotted in the top panel of each subfigure within Fig. 3) is very flat, with only small, smooth changes as the surface is approached. Our functional g_σ^A very closely matches the Monte Carlo predictions in each case, while that of Gross consistently underestimates the correlation at the interface by a significant margin. We note that the theoretical curves extend into the region from which the fluid is excluded. This value corresponds to the correlation function that would be observed in the vanishingly unlikely scenario in which there was a sphere present at that location. Naturally, we are unable to observe this quantity in our Monte Carlo simulations.

The g_σ^S correlation function (plotted in the middle panels of Fig. 3) shows considerably more structure, as well as additional variation due to the curvature of the hard surface. The symmetric correlation function is nonzero at locations where spheres may touch, which for a convex hard surface means that g_σ^S may be nonzero in the volume in which hard spheres are excluded. In every configuration studied, the agreement between the theoretical predictions and the Monte Carlo simulation in each case is very poor in the region where there should be no contacts at all. Because n_0 is comparable to its bulk value in this region, this means that these functionals predict a significant number of contacts in the region where there should be none. The correlation function of Yu and Wu [8] and ours, described in Sec. III C, give similar results, with slightly larger errors in our prediction.

B. High density

At a higher density corresponding to a filling fraction of 0.4, correlations are much stronger, with the bulk contact value of the correlation function of 3.7, as seen in Fig. 4. This results in larger oscillations in the density at the hard surfaces and correspondingly more interesting behavior in the correlation function near the interface, as shown in the bottom panels of the plots in Fig. 4. The density predicted by the White Bear functional agrees reasonably well with the simulation results, although not so well as it did at lower density. The discrepancies are largest in the case of the spherical cavity [Fig. 4(d)], in which the DFT considerably underestimates the range of the density oscillations.

The asymmetric version of the correlation function (plotted in the top panels of Fig. 4) once again displays relatively smooth behavior with a few small oscillations near the interface and a somewhat elevated value within a diameter of the hard surface, with the magnitude of this elevation somewhat different in each configuration. As was the case

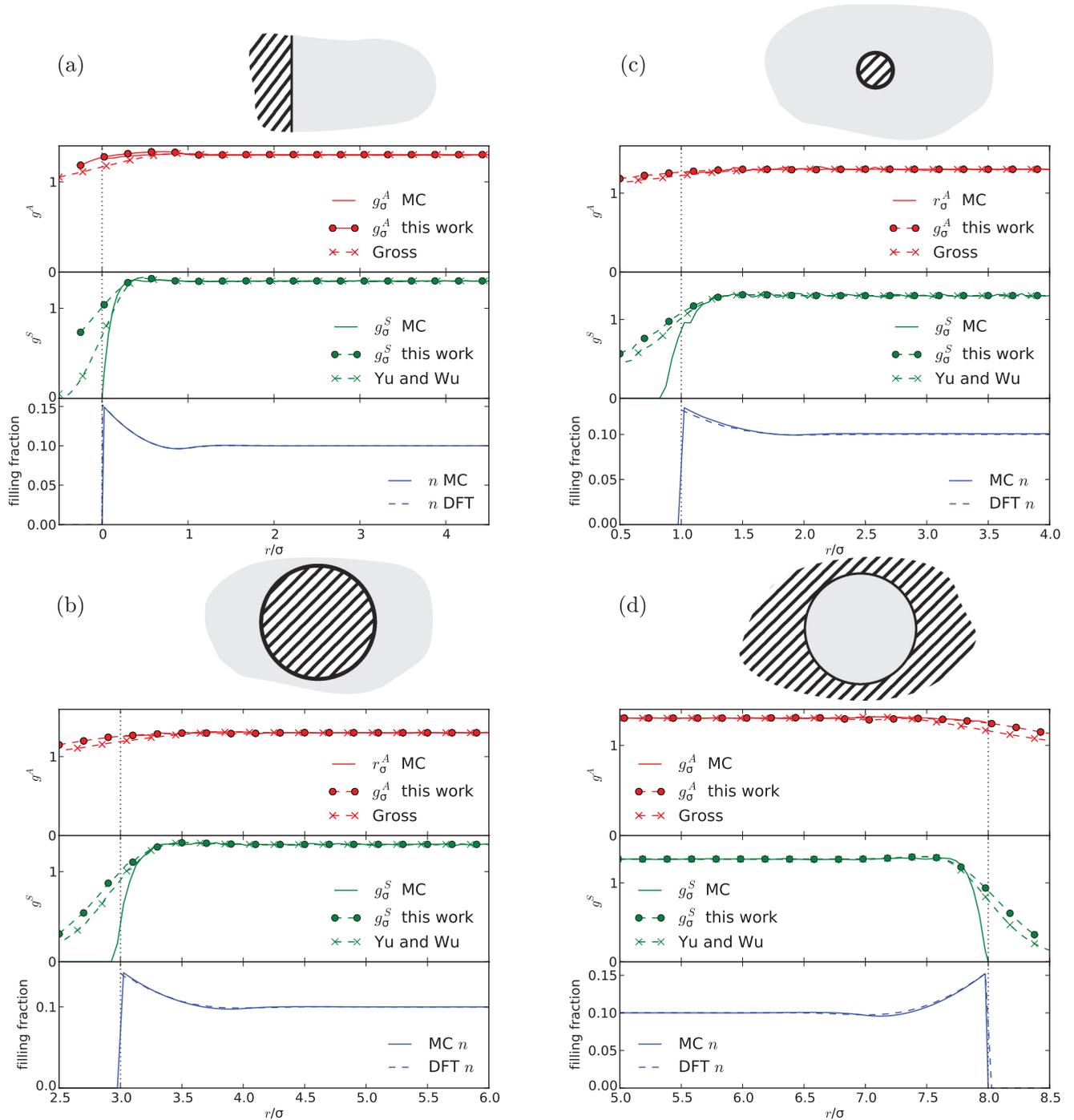


FIG. 3. (Color online) Density and correlation function in systems with a “low-density” bulk filling fraction of 0.1. The subplots each show a different system: (a) next to a flat hard wall, (b) around a hard sphere with an excluded diameter of 6σ , (c) around a hard sphere with an excluded diameter of 2σ , and (d) within a spherical cavity with an included diameter of 16σ . In the top and middle panels of each subfigure, respectively, are the asymmetrically averaged correlation function g_{σ}^A [defined in Eq. (7)] and the symmetrically averaged correlation function g_{σ}^S [defined in Eq. (5)]. The results of Monte Carlo, our functional, and one previously published functional [7,8] are compared in each case. The bottom panels show the density computed with Monte Carlo and with DFT.

at low density, our correlation function g_{σ}^A matches very closely the Monte Carlo data, reproducing quite well the structure near the interface in each configuration, although in the spherical cavity there is a small but significant discrepancy, comparable to the discrepancy found in the density itself. In each case, the correlation of Gross dramatically

underestimates the correlation at the interface, at one extreme by 40% in the case of the spherical cavity [Fig. 4(d)] and at the other extreme by 15% in the test-particle scenario [Fig. 4(c)].

The symmetrically averaged correlation function (plotted in the middle panels of Fig. 4) shows considerably more

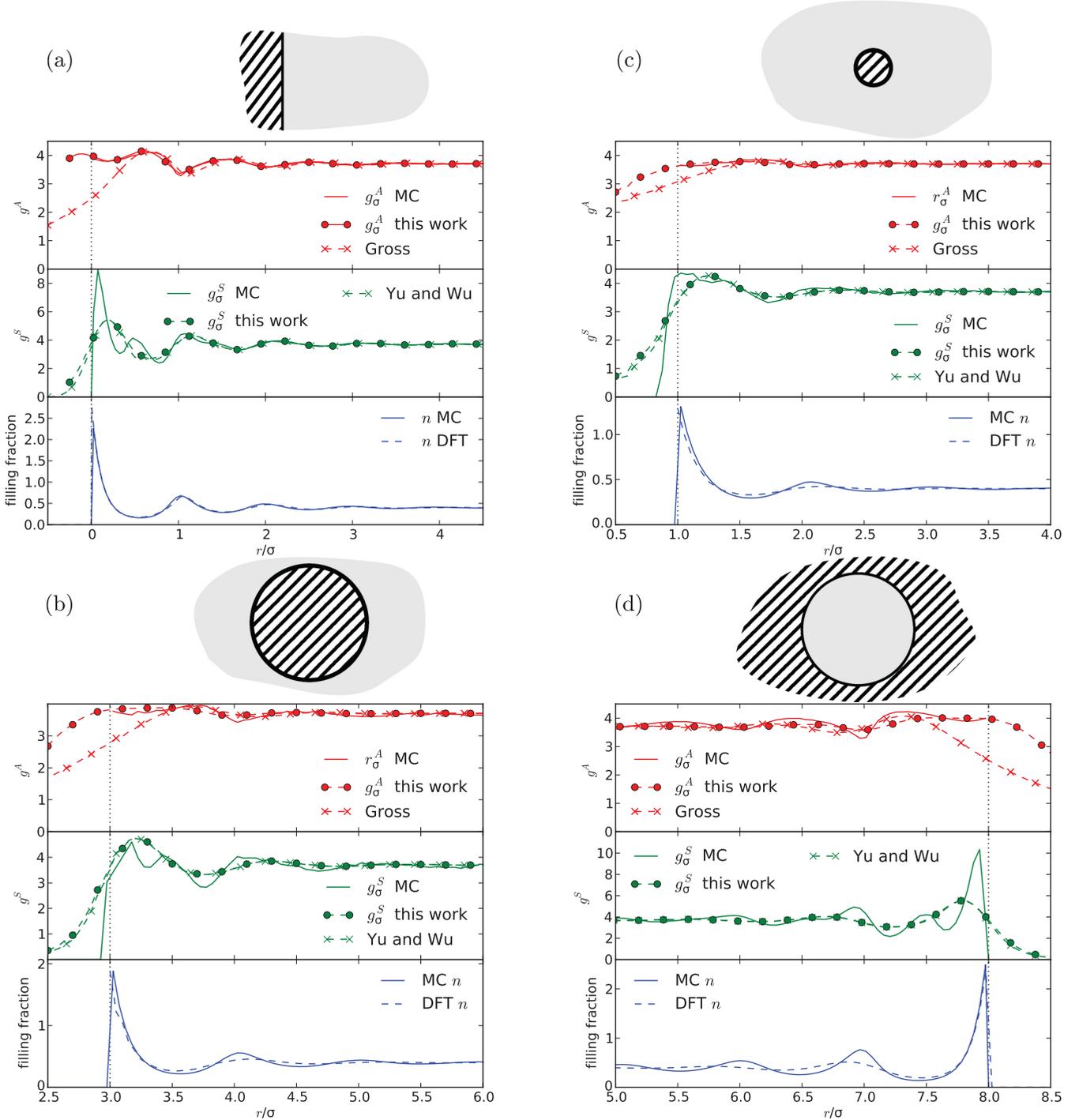


FIG. 4. (Color online) Density and correlation function in systems with a “high-density” bulk filling fraction of 0.4. The subplots each show a different system: (a) next to a flat hard wall, (b) around a hard sphere with an excluded diameter of 6σ , (c) around a hard sphere with an excluded diameter of 2σ , and (d) within a spherical cavity with an included diameter of 16σ . In the top and middle panels of each subfigure, respectively, are the asymmetrically averaged correlation function g_σ^A [defined in Eq. (7)] and the symmetrically averaged correlation function g_σ^S [defined in Eq. (5)]. The results of Monte Carlo, our functional, and one previously published functional [7,8] are compared in each case. The bottom panels show the density computed with Monte Carlo and with DFT.

structure near the interface at high density, and this structure varies considerably depending on the curvature of the hard surface. In each case, this structure is not reflected in the theoretical predictions, neither that of this paper, nor that of Yu and Wu [8]. As was the case at low density, both functionals

give significant and finite values in the region in which there are no contacts, but at high density they also miss the large oscillations that are present near the flat wall and the concave surface [Figs. 4(a) and 4(d)]. As was the case at low density, the functional of Yu and Wu [8] gives slightly better agreement

with the simulation results than that which we derive in Sec. III C.

V. CONCLUSION

We investigated several approximations to the contact value of the correlation function for inhomogeneous fluid distributions corresponding to flat, concave, and convex walls. We defined and simulated two averages of the correlation function, an asymmetric A average centered at the location of one of the two spheres that is in contact and a symmetric S average centered at the point of contact of touching spheres. For each average, we derived a functional form from FMT and also found an approximation that has been used in the literature. When compared with essentially exact Monte Carlo simulations, the A correlation function derived from fundamental measure theory in Sec. III B gives excellent results for each surface, at both high and low density. The other three approximations that we studied all showed significant and systematic deviations under some circumstances. Thus, we recommend that creators of SAFT-based classical density functionals consider using the g_σ^A functional defined in Sec. III B.

APPENDIX

The expression for the asymmetric correlation function $g_\sigma^A(\mathbf{r})$ [Eq. (25)] involves the functional derivative $\frac{\delta A_{\text{HS}}}{\delta \sigma(\mathbf{r})}$. In this appendix we will explain how this derivative is evaluated. We begin by applying the chain rule in the following way:

$$\frac{\delta A_{\text{HS}}}{\delta \sigma(\mathbf{r})} = \int \left[\sum_{\alpha} \frac{\delta A_{\text{HS}}}{\delta n_{\alpha}(\mathbf{r}')} \frac{\delta n_{\alpha}(\mathbf{r}')}{\delta \sigma(\mathbf{r})} \right] d\mathbf{r}'. \quad (\text{A1})$$

This expression requires us to evaluate $\frac{\delta A_{\text{HS}}}{\delta n_{\alpha}(\mathbf{r}'')}$ and $\frac{\delta n_{\alpha}(\mathbf{r}')}{\delta \sigma(\mathbf{r})}$. The former is straightforward, given Eqs. (10)–(12), and we will write no more about it. The functional derivatives of the fundamental measures, however, require a bit more subtlety, and we will address them here.

We begin with the derivative of n_3 , the filling fraction, which we will discuss in somewhat more detail than the remainder, which are similar in nature. Because the diameter $\sigma(\mathbf{r})$ is the diameter of a sphere at position \mathbf{r} , we write the fundamental measure $n_3(\mathbf{r}')$ as

$$n_3(\mathbf{r}') = \int n(\mathbf{r}'') \Theta \left(\frac{\sigma(\mathbf{r}'')}{2} - |\mathbf{r}' - \mathbf{r}''| \right) d\mathbf{r}'', \quad (\text{A2})$$

where we note that $\sigma(\mathbf{r}'')$ and $n(\mathbf{r}'')$ are the diameter and density, respectively, of spheres centered at position \mathbf{r}'' . Thus,

the derivative with respect to the diameter of spheres at position \mathbf{r} is

$$\frac{\delta n_3(\mathbf{r}')}{\delta \sigma(\mathbf{r})} = \frac{1}{2} \int n(\mathbf{r}'') \delta \left[\frac{\sigma(\mathbf{r}'')}{2} - |\mathbf{r}' - \mathbf{r}''| \right] \delta(\mathbf{r} - \mathbf{r}'') d\mathbf{r}'' \quad (\text{A3})$$

$$= n(\mathbf{r}) \delta[\sigma(\mathbf{r})/2 - |\mathbf{r}' - \mathbf{r}|]. \quad (\text{A4})$$

This pattern will hold for each fundamental measure: because we are seeking the change in free energy when spheres at point \mathbf{r} are expanded, the integral over density is eliminated. To compute the correlation function g_σ^A , we convolve this delta function with the product of the density and a local derivative of $\Phi(\mathbf{r})$:

$$\frac{\delta A_{\text{HS}}}{\delta \sigma(\mathbf{r})} = \int \frac{\partial \Phi(\mathbf{r}')}{\partial n_3(\mathbf{r}')} n(\mathbf{r}') \delta[\sigma(\mathbf{r})/2 - |\mathbf{r}' - \mathbf{r}|] d\mathbf{r}' + \dots \quad (\text{A5})$$

As we shall see, there are only four convolution kernels, leading to four additional convolutions beyond those required for FMT.

The functional derivative of n_2 introduces our second convolution kernel, which is a derivative of the delta function:

$$\frac{\delta n_2(\mathbf{r}')}{\delta \sigma(\mathbf{r})} = \frac{1}{2} n(\mathbf{r}) \delta'[\sigma(\mathbf{r})/2 - |\mathbf{r}' - \mathbf{r}|]. \quad (\text{A6})$$

The derivatives of the remaining scalar densities n_1 and n_0 reduce to sums of the terms above:

$$\begin{aligned} \frac{\delta n_1(\mathbf{r}')}{\delta \sigma(\mathbf{r})} &= \frac{n(\mathbf{r})}{4\pi\sigma(\mathbf{r})} \delta'[\sigma(\mathbf{r})/2 - |\mathbf{r}' - \mathbf{r}|] \\ &\quad - \frac{n(\mathbf{r})}{2\pi\sigma(\mathbf{r})^2} \delta[\sigma(\mathbf{r})/2 - |\mathbf{r}' - \mathbf{r}|] \end{aligned} \quad (\text{A7})$$

and

$$\begin{aligned} \frac{\delta n_0(\mathbf{r}')}{\delta \sigma(\mathbf{r})} &= \frac{n(\mathbf{r})}{2\pi\sigma(\mathbf{r})^2} \delta'[\sigma(\mathbf{r})/2 - |\mathbf{r}' - \mathbf{r}|] \\ &\quad - 2 \frac{n(\mathbf{r})}{\pi\sigma(\mathbf{r})^3} \delta[\sigma(\mathbf{r})/2 - |\mathbf{r}' - \mathbf{r}|]. \end{aligned} \quad (\text{A8})$$

The vector-weighted densities \mathbf{n}_{V1} and \mathbf{n}_{V2} give terms analogous to those of n_1 and n_2 :

$$\frac{\delta \mathbf{n}_{V2}(\mathbf{r}')}{\delta \sigma(\mathbf{r})} = -\frac{1}{2} n(\mathbf{r}) \delta'(\sigma(\mathbf{r})/2 - |\mathbf{r}' - \mathbf{r}|) \frac{\mathbf{r} - \mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|}, \quad (\text{A9})$$

$$\begin{aligned} \frac{\delta \mathbf{n}_{V1}(\mathbf{r}')}{\delta \sigma(\mathbf{r})} &= -\frac{n(\mathbf{r})}{4\pi\sigma(\mathbf{r})} \delta'(\sigma(\mathbf{r})/2 - |\mathbf{r}' - \mathbf{r}|) \frac{\mathbf{r} - \mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} \\ &\quad + \frac{n(\mathbf{r})}{2\pi\sigma(\mathbf{r})^2} \delta(\sigma(\mathbf{r})/2 - |\mathbf{r}' - \mathbf{r}|) \frac{\mathbf{r} - \mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|}. \end{aligned} \quad (\text{A10})$$

Thus, there are four convolution kernels used in computing g_σ^A : one scalar and one vector delta function, and one scalar and one vector derivative of the delta function.

[1] J. Felipe, E. del Río, E. De Miguel, and G. Jackson, *Mol. Phys.* **99**, 1851 (2001).

[2] G. Gloor, F. Blas, E. del Rio, E. de Miguel, and G. Jackson, *Fluid Phase Equilib.* **194**, 521 (2002).

[3] G. Gloor, G. Jackson, F. Blas, E. del Río, and E. de Miguel, *J. Chem. Phys.* **121**, 12740 (2004).

[4] G. Clark, A. Haslam, A. Galindo, and G. Jackson, *Mol. Phys.* **104**, 3561 (2006).

- [5] G. Gloor, G. Jackson, F. Blas, E. del Río, and E. de Miguel, *J. Phys. Chem. C* **111**, 15513 (2007).
- [6] H. Kahl and J. Winkelmann, *Fluid Phase Equilib.* **270**, 50 (2008).
- [7] J. Gross, *J. Chem. Phys.* **131**, 204705 (2009).
- [8] Y. X. Yu and J. Wu, *J. Chem. Phys.* **116**, 7094 (2002).
- [9] D. Fu and J. Wu, *Ind. Eng. Chem. Res.* **44**, 1120 (2005).
- [10] P. Bryk, S. Sokółowski, and O. Pizio, *J. Chem. Phys.* **125**, 024909 (2006).
- [11] R. Roth, R. Evans, A. Lang, and G. Kahl, *J. Phys.: Condens. Matter* **14**, 12063 (2002).
- [12] H. Hansen-Goos and R. Roth, *J. Phys.: Condens. Matter* **18**, 8413 (2006).