I. INTRODUCTION

Understanding the structure and phase behavior of colloidal dispersions is relevant to many traditional applications of colloids such as paints, inks and pharmaceutical dispersions as well as to recent interests in the fabrication of colloid-based nanostructured materials.\(^1\)–\(^3\) Current theories for that purpose are primarily based on an effective one-component model (OCM) where colloidal particles are represented by hard spheres with the interparticle potential taking into account the properties of all the remaining components in the dispersion, including the solvent, small ions, and probably polymers.\(^4\) OCM provides many valuable insights on the phase behavior of colloids, especially on the similarities between the colloidal phase diagrams and those corresponding to simple atomic systems.\(^5\)–\(^9\) However, application of OCM is often limited by an incomplete understanding of solvent-averaged colloidal forces.\(^10\),\(^11\) Besides, open questions remain on the pairwise additive assumption of the colloidal potentials.

Highly asymmetric binary hard-sphere mixtures, i.e., large hard spheres standing for colloidal particles and small spheres for solvent molecules (or polymers), provide the simplest model of colloidal dispersions beyond OCM.\(^12\) Despite its simplicity, a reliable statistical-thermodynamic model for highly asymmetric hard-sphere mixtures is yet to be established.\(^13\),\(^14\) The phase behavior of asymmetric binary hard-sphere mixtures has been hotly debated over the recent years and it remains unclear whether a fluid–fluid demixing exists at high overall densities.\(^15\)–\(^17\) Theoretical calculations are often inconclusive because the results are sensitive to the fine details of approximations. On the other hand, molecular simulations for the phase behavior of condensed highly asymmetric systems are notoriously difficult, not only because extremely large number of small particles are required to fill the space between the large particles, but also because updating the positions of large particles often causes ergodic problems.

The classical theories for the structures and thermodynamic properties of hard-sphere fluids were established in the 1960s and early 1970s, on the basis of two parallel but complementary approaches: the scaled-particle theory (SPT)\(^18\) and the integral equation theory.\(^19\) SPT was developed by interpolating classical and statistical considerations on the free energy for the creation of spherical cavities (scaled particles) in a hard-sphere fluid. Thermodynamic properties and the contact values of the pair distribution functions from SPT are in good agreement with simulation results. The integral equation theory, on the other hand, is primarily based on the Ornstein–Zernike equation coupled with the Percus–Yevick (PY) closure. Analytical solution to the PY equation was first developed by Thiele\(^20\) and independently by Wertheim for uniform hard spheres,\(^21\) and by Lebowitz and Rowlinson for hard-sphere mixtures.\(^19\) The pair distribution functions from the PY equation are in good agreement with simulation results (except near contact) but the thermodynamic properties derived from different routes do not always agree each other. It was recognized first by Carnahan and Starling\(^22\) and subsequently by Boublik,\(^23\) and by Mansoori, Carnahan, Starling, and Leland (BMCSL)\(^24\) that the thermodynamic properties from the PY equation could be significantly improved by an empirical combination of the results from the compressibility equation and from the virial equation. Improvements toward more accurate representations of the pair distribution functions of hard spheres were proposed semiempirically by Verlet and Weis for one-component fluids,\(^25\) and by Grundke and Henderson,\(^26\) Lee and Levesque,\(^27\) and Henderson and Blum\(^28\) for mixtures. Both the PY theory and SPT, as well as the subsequent modifications, predict no liquid–liquid phase separation in a binary mixture of hard spheres.

Different paths have been followed to obtain improved
expressions for the structure and thermodynamic properties of hard-sphere fluids. One approach is focused on the contact values of the radial distribution functions that, for a hard-sphere fluid, are directly related to the equation of state. Using the contact-value theorem and Monte Carlo simulation results, Henderson and co-workers proposed improved expressions for the contact values of the radial distribution functions of small–large spheres and of large–large spheres. A similar expression for the contact values of the small–large radial distribution functions was derived by Matyushov and Ladanyi on the basis of the exact geometrical relations from the scaled-particle theory. Barrio and Solana studied the thermodynamic consistency of various methods for the contact values of the radial distribution functions and proposed a semiempirical modification of the BMCSL equation of state. Regnaut et al. indicated that because the phase-equilibrium calculation requires accurate contact values as well as their derivatives with respect to the concentration, the contact-value approach yields inconclusive fluid–fluid phase transition in highly asymmetric hard-sphere mixtures. An alternative to the contact-value approach uses the exact expressions for the first five virial coefficients in the virial expansion. This approach indicates that hard-sphere demixing is possible in binary mixtures of any size asymmetry but the demixing transition is metastable with respect to the freezing transition where the large spheres form crystalline structures while the small spheres remain disordered.

Improved radial distribution functions of hard spheres can be obtained by imposing the exact consistency conditions on the PY equation, as in the generalized mean spherical approximation (GMSA) theory first proposed by Blum and Hoye. In this approach, a Yukawa potential is empirically added to the direct correlation function beyond the collision diameter and the Yukawa parameters are determined from the consistency relations. GMSA corrects the key inconsistency problem of the PY equation but it is inconvenient for hard-sphere mixtures because it involves heavy algebra for solving the Yukawa parameters. Other closures, including those proposed by Martynov and Sarkisov, Rogers and Yong, and recently by Lee and Malijevsky, have also been applied to calculate the radial distribution functions of hard-sphere mixtures.

The correlation functions of a uniform fluid can also be obtained from a density-functional theory for the inhomogeneous distributions of molecules around a test particle fixed at the origin. The density distribution of a component \( i \) around a fixed particle of component \( j \), \( \rho_{i,j}(r) \), is directly related to the radial distribution function \( g_{ij}(r) \) by \( \rho_{i,j}(r) = \rho_{i,b} g_{ij}(r) \), where \( \rho_{i,b} \) is the density of component \( i \) in the bulk. Following the test-particle method, Patra and Ghosh applied the weighted density approximation of Denton and Ashcroft to calculate the radial distribution functions of hard-sphere fluids and ionic mixtures. They suggested that the test-particle method were not as accurate as the integral equation theory for representing the structural properties of uniform fluids. However, a different application by Rosenfeld indicated that the test-particle method is remarkably successful for uniform hard spheres. The mixed opinions on the test-particle method might be related to the application of different density functional theories.

In this work, we propose a variation of the fundamental-measure theory (FMT) by Rosenfeld to provide better descriptions of structural and thermodynamic properties of uniform as well as inhomogeneous hard-sphere fluids, including those of highly asymmetric hard-sphere mixtures. Probably, FMT represents the best density functional theory currently available for strongly inhomogeneous hard spheres. It has been successfully applied to describe the properties of hard spheres in the bulk and in slitlike pores, and has been extended to molecular fluids. In contrast to most alternative density functional approaches, FMT does not require the direct correlation function as an input, but rather reproduces the Percus–Yevick direct correlation function as an output in the limit of the homogeneous fluid. Because the weight functions are independent of density distributions, the weighted densities in FMT are more convenient to calculate than those in most nonlocal density-functional theories. Further, FMT is directly applicable to multicomponent systems using the same formulism for one-component fluids. There have been a few modified versions of FMT since it was proposed about 10 years ago. Most of previous modifications are focused on the limits of FMT for representing the properties of hard-sphere solids or hard spheres under strong confinement. While these modifications improve FMT for solid-related applications and for hard spheres in narrow pores, they give similar results for hard-sphere fluids and all overpredict the contact values of the density distributions. Our modification is intended to improve the accuracy of FMT for representing the structural and thermodynamic properties of hard-sphere fluids. A new excess free energy density is formulated based on the Boublik–Mansoori–Carnahan–Starling–Leland (BMCSL) equation of state instead of that from the scaled-particle theory or that from the PY theory. The new density functional theory gives improved contact densities for nonuniform hard-sphere fluids. The direct and pair distribution functions of bulk hard-sphere mixtures derived from the test-particle method are in excellent agreement with available simulation results.

The remainder of this paper is organized as follows: Sec. II briefly describes FMT and the rationale of our modification. In Sec. III, we apply the reformulated density functional theory to calculate the contact densities of inhomogeneous hard spheres, which provides a stringent comparison with the original FMT. Applications of the modified FMT for calculating the pair correlation functions of highly asymmetric hard sphere mixtures are discussed in Sec. IV. Finally, in Sec. V, we present the conclusions.

II. EXCESS HELMHOLTZ ENERGY DENSITY OF INHOMOGENEOUS HARD SPHERES

In FMT, Rosenfeld postulates that the excess Helmholtz energy functional of an inhomogeneous hard-sphere mixture, \( F_{ex} \), can be expressed in the form of a weighted density approximation: 
\[ F_{cv} / k_B T = \int \Phi(\mathbf{r}) d\mathbf{r}, \]  
where \( k_B \) is the Boltzmann constant and \( T \) is absolute temperature. The reduced excess Helmholtz energy density \( \Phi \) is a function of only the weighted averages of the density distribution functions \( \rho_i(\mathbf{r}) \), 
\[ n_a(\mathbf{r}) = \sum_i n_{a,i}(\mathbf{r}) = \sum_i \int \rho_i(\mathbf{r'}) \omega_i^{(a)}(\mathbf{r'} - \mathbf{r}) d\mathbf{r'} . \]  
The weight functions \( \omega_i^{(a)}(\mathbf{r}) \) in Eq. (2) characterize the geometry of a hard sphere: two scalar functions are related to, respectively, the volume and the surface area 
\[ \omega_i^{(3)}(\mathbf{r}) = \delta(\sigma_i / 2 - \mathbf{r}), \]  
and a surface vector function characterizes the variance across the particle surface 
\[ \omega_i^{(2)}(\mathbf{r}) = \delta(\sigma_i / 2 - \mathbf{r}). \]  
Three additional weight functions are given by 
\[ \omega_i^{(1)}(\mathbf{r}) = \omega_i^{(2)}(\mathbf{r}) / (2 \pi \sigma_i), \]  
\[ \omega_i^{(0)}(\mathbf{r}) = \omega_i^{(2)}(\mathbf{r}) / (\pi \sigma_i^2), \]  
\[ \omega_i^{(1)}(\mathbf{r}) = \omega_i^{(2)}(\mathbf{r}) / (2 \pi \sigma_i). \]  
In Eqs. (3)–(6), \( \sigma_i \) is the hard-sphere diameter, \( \delta(\mathbf{r}) \) is the Dirac delta function, and \( \theta(\mathbf{r}) \) is the Heaviside step function. The vector weighted densities, \( \mathbf{n}_{v1} \) and \( \mathbf{n}_{v2} \), vanish in the limit of a bulk fluid.

An analysis of the function space and the dimensionality of the weighted densities leads to the expression for the Helmholtz energy density, \( \Phi \), as 
\[ \Phi = f_0 n_0 + f_1 n_1 + n_2^3 + f_{22}^V n_{v1} \cdot \mathbf{n}_{v2} + f_{222}^V n_{v2} \cdot \mathbf{n}_{v2}, \]  
where the \( n_3 \)-dependent coefficients \( f_0, f_{12}, f_{222}, f_2^V, \) and \( f_{222}^V \) are determined from the properties of the corresponding low-density uniform fluid and from the scaled-particle differential equation for hard spheres. An important feature of Eq. (7) is that the free energy density depends on the scalar- as well as the vector-weighted densities. The final expression for the excess Helmholtz energy density is given by \( \Phi \) as 
\[ \Phi = -n_0 \ln(1 - n_3) + \frac{n_1 n_2}{1 - n_3} + \frac{n_2^3}{8 \pi (1 - n_3)^2}. \]  
In the limit of homogeneous hard spheres, Eq. (8) reduces to that from the corresponding scaled-particle theory or that from the PY theory via the compressibility approach. Different from most other density functional theories, the excess Helmholtz energy density in the FMT includes scalar and the vector contributions.

FMT and subsequent modifications) persistently overpredicts contact densities in comparison with Monte Carlo simulations. Because the contact densities of a hard-sphere fluid links directly to the thermodynamic properties, we assume that the FMT can be systematically improved by replacing the scalar part of the excess Helmholtz energy density in Eq. (8) with the more accurate expression from the BMCSL equation of state. It is worth mentioning that similar ideas had been attempted without success a few years ago by Kierlik and Rosinberg.\(^6\) The reason is that when the scalar part of the excess Helmholtz energy density is reformulated, a corresponding change must be applied to the vector part.

In terms of the variables used in Eq. (7), the excess free energy density according to the BMCSL equation is given by 
\[ \Phi^{(CS)} = -n_0 \ln(1 - n_3) + \frac{n_1 n_2}{1 - n_3} \]  
\[ + \left[ \frac{1}{36 \pi n_3^3} \ln(1 - n_3) + \frac{1}{36 \pi n_3 (1 - n_3)^2} \right] n_2^3. \]  
To derive the contribution to the excess Helmholtz energy density from the vector weighted densities, a comparison of Eqs. (7) and (8) suggests that \( f_2^V = f_{12} \) and \( f_{222}^V = -3 f_{222}^V \). With the assumption that these two equations hold after the scalar Helmholtz energy density in Eq. (8) is replaced with Eq. (9), we obtained a new expression for the excess Helmholtz energy density from the vector-weighted densities 
\[ \Phi^{(CS)} = -n_0 \ln(1 - n_3) - \frac{n_1 n_2}{1 - n_3} \]  
\[ + \left[ \frac{1}{12 \pi n_3} \ln(1 - n_3) \right] + \frac{1}{12 \pi n_3 (1 - n_3)^2} n_2^2 \mathbf{n}_{v2} \cdot \mathbf{n}_{v2}. \]  
The reformulated overall excess free energy density includes both the scalar and vector contributions 
\[ \Phi = \Phi^{(CS)} + \Phi^{(CS)}. \]  
As in the original FMT, the vector-related Helmholtz energy density disappears in the limit of a homogeneous fluid. Because the BMCSL equation is more accurate than the PY theory, the improvement of the reformulated density functional theory over the original FMT is guaranteed for representing thermodynamic properties of bulk hard-sphere fluids.

III. INHOMOGENEOUS HARD SPHERES

A. Hard-spheres in slit pores

We first apply the modified FMT to a one-component hard-sphere fluids confined in slit hard pores. The external potential due to the slit walls is given by 
\[ \Psi(z) = \begin{cases} 
0, & 0 < z < H, \\
\infty, & \text{otherwise},
\end{cases} \]  
where \( H \) stands for the pore width, and \( z \) is the distance from one of the slit walls. In this case, the weighted densities from Eq. (2) are 
\[ n_0(z) = \frac{2 n_1(z)}{1 - \frac{z}{z'}} / \pi \sigma^2, \]  
\[ n_2(z) = \frac{\pi \sigma^2}{-\sigma^2} \int_{-\sigma^2}^{\sigma^2} \rho(z + z') dz'. \]
FIG. 1. The wall pressure ($P_w$) as a function of the pore width ($H$) for hard spheres confined in slit pores at the reduced bulk density $\rho_0\sigma^3 = 0.7$. The points are from Monte Carlo simulation (Ref. 61), the solid line is from this work, and the dashed line is from the original FMT.

\[ n_s(z) = \pi \int_{-\sigma/2}^{\sigma/2} \rho(\sigma + z') [\sigma^2/4 - (z')^2], \]  
\[ n_{V1}(z) = n_{V2}(z)/2\pi \sigma, \]  
\[ n_{V2}(z) = 2 \pi e_z \int_{-\sigma/2}^{\sigma/2} \rho(\sigma + z') dz', \]

where $e_z$ is the unit vector at the $z$ direction.

The equilibrium distribution of hard spheres $\rho(z)$ is obtained by minimization of the grand potential:

\[ \Omega = k_B T \int d\mathbf{r} \rho(\mathbf{r}) [\ln \rho(\mathbf{r}) - 1] \]
\[ + \int d\mathbf{r} \rho(\mathbf{r}) [\Psi(\mathbf{r}) - \mu] + F_{ex}, \]

which yields

\[ \rho(z) = \exp \left\{ - \int d\mathbf{r} \sum_a \frac{\partial \Phi}{\partial n_a}(\mathbf{r} - \mathbf{r}') \right\} \]
\[ + [\mu - \Psi(z)]/(k_B T). \]

The chemical potential in Eq. (15) can be related to the density of a uniform hard-sphere fluid via the Carnahan–Starling equation of state\(^{22}\)

\[ \frac{\mu}{k_B T} = \ln(\rho_0) + \frac{8 - 9 \eta + 3 \eta^2}{(1 - \eta)^2}, \]

where $\rho_0$ is the number density of the uniform fluid, and $\eta = \pi \rho_0 \sigma^3/6$ is the corresponding packing fraction.

In this work, Eq. (15) is solved using the Picard iterative method and the weighted densities and the integral are evaluated using a trapezoidal rule with a mesh width equal to 0.01 \(\sigma\) for a satisfactory numerical accuracy. To test the performance of the modified FMT, we calculated the wall pressure for hard spheres confined in slitlike pores. According to the contact-value theorem, the contact density $\rho(0)$ in a slit pore is directly proportional to the wall pressure $P_w$.

\[ P_w = \rho(0) k_B T. \]

Figure 1 shows the wall pressure as a function of the slit-pore width for the chemical potential specified by a reduced bulk density $\rho_0\sigma^3 = 0.7$. The improvement of the reformulated FMT over the original one is apparent. The original FMT overpredicts the wall pressure systematically in comparison with the results from Monte Carlo simulation.\(^6^1\)

For hard spheres in contact with a single wall, the wall pressure is identical to the bulk pressure. In this case, the wall pressure from the original FMT is that corresponding to the PY compressibility equation, while in the reformulated FMT, the wall pressure is that from the more accurate Carnahan–Starling equation of state.

B. Distribution of hard spheres around a spherical particle

A spherical hard particle of diameter $D$ dissolved in fluid hard spheres of diameter $\sigma$ introduces an external potential given by

\[ \Psi(r) = \begin{cases} 0, & r \geq (D + \sigma)/2, \\ \infty, & r < (D + \sigma)/2. \end{cases} \]

where $r$ is the center-to-center distance from the fixed particle. In this case, the density profile of free hard spheres has a spherical symmetry and the weighted densities are given by\(^{50}\)

\[ n_0(r) = 2n_1(r)/\sigma = n_2(r)/\pi \sigma^2, \]
\[ n_2(r) = \frac{\pi \sigma}{r} \int_{r - \sigma/2}^{r + \sigma/2} dr' r' \rho(r'), \]
\[ n_3(r) = \frac{\pi}{r} \int_{r - \sigma/2}^{r + \sigma/2} dr' r' [\sigma^2/4 - (r - r')^2] \rho(r'), \]
\[ n_{V1}(r) = n_{V2}(r)/2\pi \sigma, \]
\[ n_{V2}(r) = \frac{\pi}{r} \int_{r - \sigma/2}^{r + \sigma/2} dr' r' [r^2 - r'^2 + \sigma^2/4] \rho(r'). \]

The equation for calculating the density profiles in this case is the same as Eq. (15) except that the coordinate $z$ is now replaced by the radial distance $r$. In solving the density
profiles, we use a step length $\Delta r=0.01\sigma$. The maximum value of $r$ is chosen sufficiently large such that the density distribution $\rho(r)$ decays to the asymptotic value $\rho_b$.

Figure 2 presents the reduced contact densities of hard spheres distributed around a fixed sphere of diameter $\sigma$. The contact density increases when the diameter of the fixed sphere or the bulk density rises. For $D/\sigma=1$ the fixed hard sphere has the same diameter of small spheres and for $D/\sigma=\infty$ the fixed sphere corresponds to a hard wall. The agreement between the modified FMT and simulations\textsuperscript{62,63} is reasonably satisfactory for all the three situations considered here. The discrepancy at high density for $D/\sigma=0.4252$ is related to the well-known deficiency of the BMCSL equation of state for large impurities of low concentration. This discrepancy also appears in Fig. 3, which shows the density distribution of a hard-sphere fluid at the bulk packing fraction $\eta=0.324$ around a large hard-sphere particle of diameter $D/\sigma=11.8$. While the density profile is accurate at large separations, the density functional theory underpredicts the contact value. Figures 2 and 3 indicate that, in general, the reformulated FMT provides satisfactory density profiles and contact densities for hard spheres near a spherical particle of arbitrary size.

IV. DIRECT AND PAIR CORRELATION FUNCTIONS OF UNIFORM HARD-SPHERE FLUIDS

Many years ago, Percus indicated that the pair correlation functions of a uniform fluid could be calculated from the density profiles around a fixed molecule.\textsuperscript{64} The pair correlation function, i.e., the radial distribution function $g_{i,j}(r)$ for a pair of species $i$ and $j$, specifies the reduced density of particle $i$, $\rho_{i,j}(r)/\rho_{i,b}$, at a position $r$ from a particle $j$ fixed at the origin. The density profile $\rho_{i,j}(r)$ is equivalent to the inhomogeneous distribution of particle $i$ in an external field of the fixed particle $j$, which is the same as the two-body interaction potential in the bulk fluid. Following this connection between the density distribution of the inhomogeneous fluid and the structure of the corresponding uniform fluid, we now apply the reformulated FMT to calculate the direct and pair distribution functions of uniform hard-sphere fluids that are self-consistent with the BMCSL equation of state.

Consider first a uniform hard-sphere mixture with a test particle $j$ fixed at the origin. The grand potential (of all the remaining hard spheres) is given by

$$\Omega=k_B T \sum_i \int dr \rho_i(r) [\ln \rho_i(r) - 1] + \sum_i \int dr \rho_i(r) [\Psi_i(r) - \mu_i] + F_{ex},$$

where the external potential $\Psi_i(r) = \phi_{ij}(r)$ is the pair potential between particle $i$ and the fixed test particle $j$. In Eq. (20), the chemical potential $\mu_i$ is calculated from the BMCSL equation of state, and the excess Helmholtz energy is given by Eq. (1) and Eqs. (9)–(11). The density distribution functions of the remaining particles around the test particle satisfy $\delta \Omega/\delta \rho_i(r) = 0$, and from which we obtain an expression for the radial distribution functions.

![Graph of direct correlation functions for uniform hard-sphere fluids at reduced densities (from top to bottom) $\rho\sigma^3=0.7$, 0.8, and 0.9. The solid lines are from this work, the dashed lines are from the PY theory and the symbols are from simulation (Ref. 65).](image)

![Graph of radial distribution functions of uniform hard-sphere fluids at reduced densities $\rho\sigma^3=0.9$, 0.8, and 0.7. The points are from MC simulation (Ref. 68), the solid lines are calculated in this work and the dashed lines are from the PY theory. For clarity, curves for $\rho\sigma^3=0.8$ and 0.9 are shifted upward by 0.5 and 1, respectively.](image)
of the excess free-energy functional with respect to the density distributions

$$-c_{ij}^{(2)}(r_1, r_2) = \frac{\delta^2 F_{ex}/(k_BT)}{\delta \rho_i(r_1) \delta \rho_j(r_2)}.$$  \hspace{1cm} (22)

For a uniform fluid, the derivatives of the excess Helmholtz energy density $\Phi$ with respect to weighted densities are independent of $r$. Introducing Fourier transforms with respect to $r$, we obtain from Eq. (1), (9)–(11), and (22) the direct correlation function

$$-c_{ij}^{(2)}(k) = \sum_{\alpha, \gamma} \frac{\delta^2 \Phi}{\delta \rho_\alpha \delta \rho_\gamma} \omega_i^{(\alpha)}(k) \omega_j^{(\gamma)}(k),$$  \hspace{1cm} (23)

where in Fourier space the weight functions are given by

$$\omega_i^{(\alpha)}(k) = 2 \sin(k \sigma_i / 2) / k \sigma_i,$$  \hspace{1cm} (24)
Equation (23) can be calculated following a straightforward algebra. Alternatively, the direct correlation functions can be obtained from the Ornstein–Zernike equation using the radial distribution functions obtained from Eq. (21). Because the excess Helmholtz energy functional is not exact, the pair and direct correlation functions calculated from these two approaches do not necessarily agree with each other.

Figure 4 shows the direct correlation functions calculated from Eq. (23) for a uniform one-component hard-sphere fluid at the reduced densities $\rho \sigma^3 = 0.7, 0.8$, and 0.9. Also shown in this figure are the results from the PY theory (which is identical to that from the original FMT) and from MC simulation. While the modified FMT is more accurate than the PY theory for all densities, the deviation from Monte Carlo results increases slightly at high densities, probably due to the inherited limits of the FMT for representing the properties of strongly confined hard spheres. Interestingly, a recent generating function approach based also on the BMCSL equation of state gives accurate direct correlation functions of hard spheres only at high densities but not at low densities.
Figure 5 compares the radial distribution functions calculated from Eq. (21) with those from Monte Carlo simulation for a uniform hard-sphere fluid at three reduced densities \(\rho r^2 = 0.7, 0.8,\) and 0.9. Here the numerical integrals are evaluated by a trapezoidal rule with a mesh width equal to 0.01\(\sigma\). The modified FMT predicts the contact values, the positions of the peaks as well as the oscillatory profiles all in excellent agreement with simulation results. As indicated early, the PY theory underestimates the contact values of the radial distribution functions.

Figures 6 – 9 show the radial distribution functions \(g_{ij}(r)\) of a highly asymmetric binary hard-sphere mixture with the diameter ratio \(\sigma_2/\sigma_1 = 0.3\) and the overall packing fraction \(\eta = 0.49\) at the mole fraction of large spheres \(x_1 = 0.0625, 0.125, 0.5,\) and 0.9, respectively. For these calculations, the weighted densities and the integral in Eq. (21) are evaluated using a trapezoidal rule but with a mesh width equal to 0.002\(\sigma_1\). The agreement between the modified FMT and simulation results is particularly good at small separations, whereas the PY theory as well as other integral theories give poor results. Approximately, the minima and maxima values of the radial distributions functions correspond to the layering structure of hard spheres around a fixed particle. As the mole fraction of large hard spheres \(x_1\) increases while the total packing fraction \(\eta\) is kept at constant, the magnitudes of both peaks and troughs decline but their positions remain approximately the same. Figures 6 and 7 indicate that the trough and the peak positions in \(g_{ij}(r)\) appear approximately at distances \(r \sim (\sigma_1 + \sigma_2)/2 + \sigma_2\), suggesting the predominance of certain geometrical arrangements of the large and small hard spheres. At high mole fractions of large hard spheres (see Figs. 8 and 9), all radial distribution functions are smooth functions of the separation, and the radial distribution function between large particles resembles that for a one-component fluid.

Figure 10 shows the radial distribution functions for a binary hard-sphere mixture with the size ratio \(\sigma_2/\sigma_1 = 0.1\). Here the overall packing fraction of the mixture is \(\eta = 0.55\) and the mole fraction of large spheres is \(x_1 = 0.01\). For this system, several authors speculated that a thermodynamic de-mixing transition occurs at certain compositions of big spheres. Again, the radial distribution functions predicted from the modified FMT agree well with the results from molecular dynamics simulations. Figure 10 indicates that the radial distribution function between large particles, \(g_{11}(r)\), has an exceedingly high contact value in comparison with that for the hard-sphere reference system at the same packing fraction \(\eta_1\). The tendency of strong clustering is in qualitative agreement with previous simulations and with experiments on hard-sphere-like colloidal mixtures.

### V. CONCLUSIONS

We have demonstrated that the fundamental-measure theory of Rosenfeld can be systematically improved by using the excess Helmholtz energy density from the semiempirical Boublík–Mansoori–Carnahan–Starling–Leland equation of state for hard-sphere mixtures. Extensive comparison with Monte Carlo simulation indicates that the reformulated fundamental-measure theory provides more accurate density profiles of inhomogeneous hard-sphere fluids, particularly the contact densities. Besides, the pair and direct correlation functions derived from the new density functional theory are in very good agreement with simulation results for the uniform hard-sphere fluids, including those of highly asymmetric mixtures where demixing has been speculated. The original FMT underestimates the direct correlation function but overestimates the radial distribution function at small separations.

The modified fundamental-measure theory will be useful for the investigation of more complicated systems like adsorption and capillary condensation of realistic fluids. It provides an accurate reference system for complex fluids with additional inter-particle interactions such as those in charge stabilized colloids, associating colloids, and polymer-colloid mixtures.