Calculation of inhomogeneous-fluid cluster expansions with application to the hard-sphere/hard-wall system

Jung Ho Yang, Andrew J. Schultz, Jeffrey R. Errington, and David A. Kofke

Department of Chemical and Biological Engineering, University at Buffalo, The State University of New York, Buffalo, New York 14260-4200, USA

(Received 4 December 2012; accepted 7 March 2013; published online 4 April 2013)

We examine the suitability of cluster expansion methods for the description of inhomogeneous fluids. In particular, we apply these methods to characterize the density profile, surface tension, and excess adsorption for a hard-sphere fluid near a hard wall. Coefficients for these series up to seventh order are evaluated by the Mayer-sampling Monte Carlo method. Comparison of the series to Monte Carlo simulations of these systems finds very good agreement up to bulk densities approaching the freezing point. This work indicates that knowledge of surface cluster integrals of inhomogeneous systems can be at least as useful as the bulk-phase virial expansions. © 2013 American Institute of Physics.

[http://dx.doi.org/10.1063/1.4798456]

I. INTRODUCTION

A fluid with uniform properties throughout, say with constant density, is by definition a homogeneous fluid. In the real world such an idealized fluid exists only approximately, since any real fluid is exposed to external force fields. Such force fields, encountered in particular in confined and interfacial systems, disturb the homogeneity of a fluid. Consequently, its density and other properties vary with position, and key behaviors such as phase transitions can be significantly affected. Moreover, the homogeneity may break spontaneously, without the influence of an external field, such as when the fluid separates into phases of different density, freezes to form a crystal, or self-assembles into a mesoscopic structure. In the introduction of their 1962 paper, Stillinger and Buff outlined many compelling reasons for the study of the statistical mechanics of inhomogeneous fluids, and they all remain relevant today. Contemporary processes in chemical technology increasingly deal with fluids at interfaces or which are otherwise nanostructured, and in order to design and control such processes, knowledge of the statistical thermodynamic description of fluids in such environments is essential. Accordingly, over the past decades growing attention has been paid to the thermodynamics and structural properties of inhomogeneous fluids. In spite of these advances, the current state of knowledge of the properties of nonuniform fluids is still less developed in comparison to uniform fluids.

A major success in the treatment of inhomogeneous phases has come through the development of classical density functional theory (DFT). DFT is not so much a model as it is a general approach to treating inhomogeneous systems. It requires specification of a free-energy functional, such that a Helmholtz free energy can be computed for a given density distribution. In the general approach, the grand-canonical potential is represented in terms of this functional, and minimized upon specification of an imposed external field to arrive at the equilibrium density distribution. The modeling choice thus comes via specification of the free-energy functional, and many approaches to this problem have been developed over the years. A key advance came with the formulation of fundamental measure theory (FMT), which provides a very effective functional for the hard-sphere model. This functional opened the door to developments for more realistic systems, following a strategy in which other molecular features are introduced by adding appropriate terms to the FMT functional. In this manner, a rich variety of systems and phenomena have been studied using the DFT framework. Withstanding these successful applications, there are still many ways in which DFT using currently available functionals is inadequate, and further development is needed. For example, one might wish for DFT methods to handle multibody intermolecular interactions, non-rigid substrates, nuclear quantum effects, or more complex geometries. Also, the need to obtain the density function—which is not always of intrinsic interest—in the course of determining other properties may introduce an obstacle to applications when the density has a complex multivariate form. This is a limitation shared by integral-equation methods, which present a different set of advantages and disadvantages. A third general approach to the study of atomistic models of inhomogeneous fluids is molecular simulation, which has the advantage of providing an essentially exact description of the behavior for the given model. The disadvantages of simulation are, first, it is computationally expensive, and second, it does not provide an explicit mathematical description of the behavior; such a description is sometimes of value in developing a basic qualitative understanding of the behavior, and it is also useful when performing iterative procedures, such as in design of products or processes. On the other hand, molecular simulation can be applied to systems of arbitrary complexity and realism, with sufficient computational effort.
A fourth approach to studying model inhomogeneous systems is based on series expansions in terms of a density or activity,\textsuperscript{22,23} with Monte Carlo methods applied to evaluate the expansion coefficients for a given molecular model. Such techniques lie between the analytical theories and molecular simulation—they require significant computation, but they yield explicit formulas describing the behavior. They can be applied while incorporating a variety of complexities, including mixtures,\textsuperscript{24} non-rigid molecules,\textsuperscript{25-28} nuclear quantum effects,\textsuperscript{29} molecular association,\textsuperscript{30,31} and multibody interactions.\textsuperscript{31-33} At conditions where they are converged in density, they yield an exact description of the behavior (often more precisely than simulation), and they can be systematically improved, so it may be possible to identify convergence without requiring other information. They can be used to evaluate density distributions, but other properties of interest can be computed without doing this; thus, they are amenable to application in complex geometries where the density function may be hard to characterize. Important limitations are that high-order coefficients needed to describe behavior at high density grow exponentially difficult to compute with coefficient order, and the approach fails where the system undergoes a phase transition. There may be advantage in applying these methods in conjunction with other analytical techniques. For example, efforts have been made recently to apply systematic corrections to integral-equation theories via calculation of the lower-order neglected coefficients of the bridge function.\textsuperscript{34} Also, consideration of low-density behavior has proven useful as a guide in the development of density functionals, including FMT.\textsuperscript{11,15} Methods based on computation of cluster integrals have not received much attention, and the approach fails where the system boundary if needed, and he formulates his series in terms of either the activity or the bulk density. Formally, no system volume is identified, and accordingly no attempt is made to construct a pressure, but terms are defined that serve these roles in the homogeneous limit. Like Bellemans,\textsuperscript{35} Rowlinson\textsuperscript{36} focuses on the surface excess properties and generates cluster integrals that have net contributions to the free energy only in the presence of an external field. However, his clusters involve singly and even disconnected diagrams, which cancel when applied in a homogenous bulk phase. This formulation is reminiscent of the singly connected and disconnected clusters encountered for the virial coefficients of molecules having intramolecular degrees of freedom,\textsuperscript{25-27} which cancel in the case of rigid molecules.

Virial treatments for fluids have a long history.\textsuperscript{15} Most of the focus of these treatments has been on the bulk, homogeneous phase, but there also have been formulations applicable to inhomogeneous phases,\textsuperscript{6,35,36} such as found in fluids near a wall or under confinement. Depending on the property, virial coefficients for inhomogeneous phases can be position-dependent, making them significantly more complex than bulk-phase coefficients. The challenge to model such systems lies in obtaining the form of virial expansions and developing efficient methods to evaluate high virials for simple and complex fluids. From a theoretical point of view, exact virial coefficients of simple fluids can improve understanding of the behavior that emerges from the presence of the external forces and the competition between fluid-surface and fluid-fluid interactions.

Among the earliest attempts to formulate cluster methods for application to inhomogeneous systems is due to Stillinger and Buff.\textsuperscript{6} Their approach closely mirrors the formulation for bulk fluids. In it they develop expansions in terms of the activity, and then the singlet density. The external field giving rise to the inhomogeneity is arbitrary, so the approach is quite general. The treatment is formally elegant but difficult to apply because the position-dependent singlet density is not a natural independent variable. Another issue that arises for inhomogeneous systems is the treatment of the pressure, and Stillinger and Buff\textsuperscript{6} identify a position-dependent local pressure that integrates to the grand potential, while also reducing to the bulk pressure for the homogeneous case. They examine surface excess properties (e.g., surface tension), but they do not formulate their analysis in a way that attempts to isolate these features. Such a focus is a key element of the work by Bellemans,\textsuperscript{35} who developed cluster treatments for systems with hard, well-defined boundaries. He formulated series first in terms of the activity, and then in terms of the homogenous bulk density of a system in equilibrium with the inhomogeneous phase. With a focus on the surface excess properties, the cluster integrals in Bellemans\textsuperscript{35} formulation have particles integrating over positions inside the boundary while interacting with particles integrating over positions outside the boundary. Bellemans\textsuperscript{35} approach was later generalized by Sokolowski and Stecki\textsuperscript{37} to allow interactions of the adsorbing particles with the boundary (in addition to the hard-wall confinement). Finally, Rowlinson\textsuperscript{36} presented a formulation that captures some of the more appealing features of both Stillinger-Buff and Bellemans.\textsuperscript{35} His approach is developed for an arbitrary external field, which serves as the system boundary if needed, and he formulates his series in terms of either the activity or the bulk density. Formally, no system volume is identified, and accordingly no attempt is made to construct a pressure, but terms are defined that serve these roles in the homogeneous limit. Like Bellemans,\textsuperscript{35} Rowlinson\textsuperscript{36} focuses on the surface excess properties and generates cluster integrals that have net contributions to the free energy only in the presence of an external field. However, his clusters involve singly and even disconnected diagrams, which cancel when applied in a homogenous bulk phase. This formulation is reminiscent of the singly connected and disconnected clusters encountered for the virial coefficients of molecules having intramolecular degrees of freedom,\textsuperscript{25-27} which cancel in the case of rigid molecules.

Most of the fundamental work on cluster-integral descriptions of inhomogeneous systems has examined hard spheres in contact with a hard wall.\textsuperscript{38-40} The hard-sphere model considers only the repulsive forces among molecules,\textsuperscript{41} and as such it is among the simplest and most widely used models. Its simplicity enables analytic solution of its thermodynamic and structural properties for certain approximate theories, and its study by computer simulation can be done very efficiently. Perhaps most useful is the trivial dependence of all of its properties on temperature. The hard-sphere system is important as a reference for molecular systems with soft repulsive or attractive interactions, and in this manner it provides a platform for formulation of theories of complex fluids. However, even for hard-sphere systems, the calculation of inhomogeneous-phase cluster integrals is more difficult than the corresponding calculation of those in bulk fluids. Thus, only the first four coefficients in the density expansion of the surface tension are known for hard spheres in contact with a hard wall\textsuperscript{38,42} (in contrast to the bulk virial coefficients, which have been computed up to tenth order in density).\textsuperscript{43}

In the present study, we extend previous investigations by considering the system of hard spheres interacting with a hard wall, reporting the results of calculations of surface
cluster integrals up to seventh order, performed using the Mayer-sampling Monte Carlo (MSMC) method. This technique has been used to calculate the virial coefficients for a variety of potentials in bulk fluids but only much less frequently it has been applied to position-dependent cluster integrals that appear in treatments of inhomogeneous phases. In Sec. II, we define terms and review the cluster-expansion formulations for inhomogeneous systems. In Sec. III, we describe the computational methods we employ to compute the cluster integrals. Then in Sec. IV we present our results and compare them to analytic results and simulation data. We also formulate an approximant that gives an accurate representation of the dependence of the surface tension on density. We provide concluding remarks in Sec. V.

II. CLUSTER EXPANSION FOR BEHAVIOR NEAR A SURFACE

In this section, we review the formalism and theory for inhomogeneous fluids as developed by Bellemans and extended by Sokolowski and Stecki. Their formulation applies to a classical system of rigid molecules interacting via a pairwise-additive intermolecular potential \( u(r) \) and subject to a single-body external field \( \phi(r) \) that gives rise to the inhomogeneity, and is associated with an impenetrable boundary. Among other assumptions is the stipulation that the boundary is unaffected by its interactions with the molecules, so that there are no multibody molecule-molecule-wall behaviors in effect.

Dependent quantities of interest here are the surface tension \( \sigma \) (closely related to the spreading pressure), the specific adsorption \( \Gamma \), and the singlet density in the vicinity of the surface, \( \rho(r) \); higher-order structural quantities are sometimes of interest but will not be examined here. Each of these properties can be given as a series expansion in the activity \( \alpha \). While the activity expansions for inhomogeneous systems are relatively easy to develop, a more useful formulation is the series in terms of the bulk density \( \tilde{\rho} \) obtained for the same activity \( \alpha \) but without the external field. The density series has better convergence properties, and in instances in which the confined system approaches the bulk for some limiting value of the coordinates, it presents a natural variable for developing the properties. We present both bases for expansion in this summary.

A. Formalism

The starting point for this review is a description of the thermodynamic formalism for this ensemble. The governing fundamental equation is

\[
d(\beta \Omega) = Ud\beta - N d \ln \alpha + \beta \int d\rho(r) \delta \phi(r),
\]

where \( \Omega \) is the thermodynamic potential, \( U \) is the average configurational energy, \( N \) is the average number of molecules, and \( \beta = 1/kT \) with \( T \) the temperature and \( k \) the Boltzmann’s constant. The activity is \( \alpha = \exp[\beta \mu] \), with \( \mu \) the chemical potential. We also have \( \beta \Omega = -\ln \Xi \), where \( \Xi \) is the grand-canonical partition function. Notably, the volume \( V \) (and consequently, the pressure \( p \)) is not considered to be a relevant variable for the system. Instead the system is contained by the potential \( \phi \), which is defined to be infinite at points outside the contained region. Accordingly, the integral over \( r \) appearing in Eq. (1) and subsequent equations (except where indicated) can be taken over all of space, formally extending to infinity. This approach to defining the inhomogeneous system has the advantage of being physically meaningful regardless of the size of the system: it is appropriate to describing nanoscopic, molecularly confined phases, as well as those in which the inhomogeneity is a small feature in an otherwise macroscopic phase (such as that which forms the focus of the present work).

As a means to isolate and characterize the surface effects, it can be helpful to view the behavior of the inhomogeneous system in relation to a bulk phase having the same activity and temperature. We view this as a true thermodynamic system, homogeneous, free of any fields, and with a volume so large that any surface effects are utterly insignificant. For such a system, the appropriate fundamental equation in the grand-canonical representation is

\[
d(\beta \Omega) = Ud\beta - \beta \rho dV - V \tilde{\rho} d\ln \alpha.
\]

We apply a tilde to indicate a quantity defined for the homogeneous field-free system of activity \( \alpha \), when needed to distinguish it from the corresponding quantity defined for the inhomogeneous system. From thermodynamics, we have \( \beta \Omega = -\beta p V \).

Between the two levels of characterization given by Eqs. (1) and (2) is one that adopts a bulk-phase thermodynamic perspective while accommodating the surface behavior. This picture inevitably leads to some ambiguity stemming from the incompatible levels of detail. Here, the fundamental equation may be written

\[
d(\beta \Omega) = Ud\beta - N d \ln \alpha - \beta \rho dV + \beta \sigma dA,
\]

where \( A \) is the area of the boundary defined by \( V \). We do not apply tildes to any variables because this formula still applies to the inhomogeneous system, and quantities in common with in Eq. (1) have the same meaning. Rather, we might view this formulation as an alternative (but less flexible) means to specify \( \phi \). The volume \( V \) is the same quantity as specified in Eq. (2), and at the same time the region defined by this volume should align with the contained region defined by \( \phi \); likewise, the area \( A \) in Eq. (3) should be consistent with the surface area implied by \( \phi \). It is in these connections that we encounter some ambiguity. The inexact relation between \( V \) (or \( A \)) and \( \phi \) is manifested in the notion of a Gibbs dividing surface, which exists simply to provide limits of integration on field-free configurational integrals that are generated when relating the inhomogeneous and homogeneous systems. Fortunately, the effects of this choice are trivial and can be isolated to some simple terms, or with appropriate definitions, removed entirely (thus, none of the properties calculated below depend on the location of the Gibbs dividing surface). The only stipulation is that the Gibbs surface be positioned in the region where \( \phi \) is infinite (or effectively so). Finally, in

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\( \Xi \) is the thermodynamic potential,

\( N \) is the average number of molecules,

\( \beta = 1/kT \) with \( T \) the temperature and \( k \) the Boltzmann’s constant.

\( \alpha = \exp[\beta \mu] \), with \( \mu \) the chemical potential.

\( \beta \Omega = -\ln \Xi \), where \( \Xi \) is the grand-canonical partition function.
this representation we have
\[ \beta \Omega = -\beta p V + \beta \sigma A. \] (4)

In Secs. II B and II C, we describe how the surface properties are expanded in terms of \( \alpha \) and \( \tilde{\alpha} \), respectively. We review in parallel expressions for both the inhomogeneous (no tilde) and homogeneous (with tilde) properties before combining them to isolate the surface effects.

**B. Activity expansions**

The series for the grand potential in terms of the activity \( \alpha \) is
\[ -\beta \Omega = \sum_{n=1}^{\infty} B_n \alpha^n, \quad -\beta \tilde{\Omega} = \sum_{n=1}^{\infty} \tilde{B}_n \tilde{\alpha}^n \] (5)

with the coefficients
\[ B_n = \int d\mathbf{r} g(\mathbf{r}) b_n(\mathbf{r}), \quad \tilde{B}_n = \int d\mathbf{r} \tilde{b}_n = V \tilde{b}_n. \] (6)

In the usual manner,\(^{22}\) the coefficients \( b_n \) can be written as a sum of all connected diagrams \( \gamma_{n,i} \) of \( n \) black circles joined by \( f \) bonds, with each black circle representing the integration of a molecule over its coordinates \( \mathbf{r} \). For the inhomogeneous system, each molecule’s integral is weighted by \( g(\mathbf{r}) = \exp(-\beta \phi(\mathbf{r})) \); for the homogeneous system, each integral is unweighted. Each \( f \) bond joining two circles represents a Mayer-function interaction between them, \( f(\mathbf{r}) = \exp(-\beta \mu(\mathbf{r})) - 1 \) (from here on we assume a spherically symmetric pair potential). In general, we write
\[ b_n(\mathbf{r}) = \int d\mathbf{r} r^{-1} \left( \sum_i Y_{n,i} \right) \prod_{m=2}^{n} g(\mathbf{r}_m), \] (7)
\[ \tilde{b}_n = \int d\mathbf{r} r^{-1} \left( \sum_i Y_{n,i} \right). \]

As an example, for \( n = 3 \)
\[ b_3(\mathbf{r}_1) = \frac{1}{3!} \int d\mathbf{r}_2 \int d\mathbf{r}_3 (f_1 f_{12} f_{23} + f_{12} f_{13} + f_{12} f_{23}) \]
\[ + f_{13} f_{23}) g(\mathbf{r}_2) g(\mathbf{r}_3), \]
\[ \tilde{b}_3 = \frac{1}{3!} \int d\mathbf{r}_2 \int d\mathbf{r}_3 (f_1 f_{12} f_{23} + f_{12} f_{13} + f_{12} f_{23}) \]
\[ + f_{13} f_{23} + f_{13} f_{23}), \] (8)

where \( f_{ij} = f(\mathbf{r}_i) \). The field-free integrals defining \( \tilde{b}_n \) can be taken over all of space, because the integrand goes to zero for configurations where any molecule is far from the (stationary) position of molecule 1, which is assumed to be a large distance from any boundaries in this case.

The singlet density is obtained by differentiation of Eq. (5) as indicated by Eq. (1) or Eq. (2)
\[ \rho(\mathbf{r}) = g(\mathbf{r}) \sum_{n=1}^{\infty} n b_n(\mathbf{r}) \alpha^n, \]
\[ \tilde{\rho} = \sum_{n=1}^{\infty} n \tilde{b}_n \tilde{\alpha}^n. \] (9)

For the activity expansion, it is a simple matter to isolate the surface effects by differencing the expressions with and without the external field. Accordingly, we define the excess singlet coefficients
\[ a_n(\mathbf{r}) = b_n(\mathbf{r}) - \tilde{b}_n. \] (10)
The coupling of the field with the position of the root particle is not included in the definition of \( a_n \), and consequently \( a_1 = 0 \). For larger \( n \), we have, for example,
\[ a_3(\mathbf{r}_1) = \frac{1}{3!} \int d\mathbf{r}_2 \int d\mathbf{r}_3 \left( f_{12} f_{13} f_{23} + f_{12} f_{13} + f_{12} f_{23} \right) \]
\[ + f_{13} f_{23} \left( g(\mathbf{r}_2) g(\mathbf{r}_3) - 1 \right). \] (11)
The last term in parentheses goes to zero if all of the molecules are outside the range of the potential (i.e., where \( \phi(\mathbf{r}) = 0 \) and thus \( g(\mathbf{r}) = 1 \)), and the term involving the Mayer functions is zero if any of the molecules is far from the others, so the integrand is non-negligible only where all of the molecules (including the root molecule, labeled 1) are in the vicinity of the surface.

The excess singlet coefficients define a series that sums to the excess singlet density, which describes the deviation of the inhomogeneous density from the corresponding homogeneous bulk density
\[ \rho(\mathbf{r}) - \tilde{\rho} = g(\mathbf{r}) \sum_{n=1}^{\infty} n b_n(\mathbf{r}) \alpha^n - \sum_{n=1}^{\infty} n \tilde{b}_n \tilde{\alpha}^n \]
\[ = (g(\mathbf{r}) - 1) \sum_{n=1}^{\infty} n b_n \alpha^n + g(\mathbf{r}) \sum_{n=1}^{\infty} n(\tilde{b}_n - \tilde{b}_n) \alpha^n \]
\[ = (g(\mathbf{r}) - 1) \tilde{\rho} + g(\mathbf{r}) \sum_{n=2}^{\infty} n a_n \alpha^n. \] (12)

The specific adsorption \( \Gamma \) is obtained as the integral
\[ \Gamma = \int \int d\mathbf{r} (\rho(\mathbf{r}) - \tilde{\rho}) \]
\[ = \tilde{\rho} \int \int d\mathbf{r} (g(\mathbf{r}) - 1) + \sum_{n=2}^{\infty} n \left( \int \int d\mathbf{r} g(\mathbf{r}) a_n(\mathbf{r}) \alpha^n \right) \]
\[ = \tilde{\rho} K_H + \sum_{n=2}^{\infty} n A_n \alpha^n, \] (13)

which introduces the surface coefficients \( A_n \)
\[ A_n = \int d\mathbf{r} g(\mathbf{r}) a_n(\mathbf{r}). \] (14)

The integral here may be taken over all space, given that the Gibbs dividing surface (which in principle defines \( V \)) must extend into the region where \( g(\mathbf{r}) \) is effectively zero. Equation (13) also defines the Henry’s constant \( K_H \), which depends on where the Gibbs dividing surface is located; the coefficients \( A_n \) do not depend on the location of the dividing surface. It is helpful to define a residual adsorption\(^{46}\) \( \Gamma^* \equiv \Gamma - \tilde{\rho} K_H / A \), which does not depend on the definition of the dividing surface.

Finally, the surface excess for the grand potential gives the surface tension \( \sigma \), which is also expressed in terms
of the coefficients $A_n$

$$-\sigma A = -(\beta \Omega - \beta \tilde{\Omega})$$

$$= \sum_{n=1}^{\infty} (B_n - \tilde{B}_n) \alpha^n$$

$$= \sum_{n=1}^{\infty} \left( \int_{\infty}^{\omega} d\mathbf{r} \mathbf{g}(\mathbf{r}) b_n(\mathbf{r}) - \int_V d\mathbf{r} \tilde{b}_n \right) \alpha^n$$

$$= \sum_{n=1}^{\infty} \int_{\infty}^{\omega} d\mathbf{r} (\mathbf{g}(\mathbf{r}) \beta_n - \tilde{\mathbf{b}}_n) \alpha^n$$

$$+ \sum_{n=1}^{\infty} \int_{\infty}^{\omega} d\mathbf{r} \mathbf{g}(\mathbf{r})(b_n(\mathbf{r}) - \tilde{b}_n) \alpha^n$$

$$= pK_H + \sum_{n=2}^{\infty} A_n \alpha^n.$$  \hspace{1cm} (15)

Likewise, we define a residual surface tension $\sigma^+ \equiv \sigma + pK_H/\alpha$.

### C. Density expansions

The corresponding expressions for the surface properties as an expansion in the density $\bar{\rho}$ are not as easily developed, and this task was performed by Bellemans.\(^{35}\) The series can be expressed in terms of sums of clusters, labeled $w_n(\mathbf{r})$ or $W_n$, and explained below. The results are\(^{15,37}\)

$$-\sigma^+ A = \beta^{-1} \sum_{n=2}^{\infty} W_n \bar{\rho}^n,$$  \hspace{1cm} (16)

$$\Gamma^+ A = \left( 1 - \sum_{n=1}^{\infty} n\beta_n \bar{\rho}^n \right) \sum_{n=2}^{\infty} nW_n \bar{\rho}^n,$$  \hspace{1cm} (17)

$$\rho(\mathbf{r}) = \mathbf{g}(\mathbf{r}) \left( \bar{\rho} + \sum_{n=2}^{\infty} n w_n(\mathbf{r}) \bar{\rho}^n \right),$$

where $\beta_n$ are the usual irreducible Mayer clusters arising in the density expansion of the pressure for a field-free system. The $w_n(\mathbf{r})$ are, just like $b_n(\mathbf{r})$, defined as a sum of all simply connected clusters $\gamma_{n,\lambda}$ from $n$ points joined by $f$ bonds. The key difference between them is in how the weights are assigned to the points. For $b_n(\mathbf{r})$, all points except the root have weight $g(\mathbf{r})$; for $w_n(\mathbf{r})$, the prescription for the weights is more complex. For each diagram $\gamma_{n,\lambda}$ in $w_n(\mathbf{r})$, we identify a basic part, and zero or more terminal subparts. Each terminal subpart is doubly connected (i.e., contains no articulation points), and is joined to the basic part via a single point (which is not considered to be part of the terminal subpart, and may be the root point). The points $\lambda$ in each terminal subpart together have a weight $(\prod_{\lambda \in \lambda} g(\mathbf{r}_\lambda)) - 1$ and are integrated over all space. The basic part may itself be single or doubly connected, and contains an unweighted root point (not integrated upon) labeled 1; all other points in the basic part have weight $g(\mathbf{r}_1)$ and are integrated upon. The low-order graphs in $w_n(\mathbf{r})$ are listed in Fig. 1 and their example should make clear the definition of these terms. The symmetry number of the graph is defined in the same way as a homogeneous graph; the number of ways one can permute the field points without altering the connections between the points. The weight of each diagram of $w_n(\mathbf{r})$ is the inverse of the number divided by $n$. Analogous to Eq. (14), we define a coefficient $W_n$ as the integral of $w_n(\mathbf{r})$

$$W_n = \int_{\infty}^{\omega} d\mathbf{r} \mathbf{g}(\mathbf{r}) w_n(\mathbf{r}).$$  \hspace{1cm} (19)

However, unlike the activity expansion, these coefficients do not appear directly in the density expansion given in Eqs. (16)–(18). Instead, we see there the coefficients $W_n$, which are related to the $W_n$ as\(^{33}\)

$$W_n = \frac{1}{n} \sum_{(p,n_k)} pW_p \left( \sum_{k} k! \frac{\prod_{k} (k^p \beta_k)^{n_k}}{n_k!} \right)^{\frac{1}{p}} \left( \sum_{p>1} kn_k + p = n \right).$$  \hspace{1cm} (20)

Inversion of this expression gives, for $n = 2$–7

$$W_2 = W_2,$$

$$W_3 = W_3 - \frac{2}{3} \beta_1 W_2,$$

$$W_4 = W_4 - \frac{3}{4} \beta_1 W_3 - \beta_2 W_2,$$

$$W_5 = W_5 - \frac{4}{5} \beta_1 W_4 - \frac{6}{5} \beta_2 W_3 - \frac{6}{5} \beta_3 W_2,$$

$$W_6 = W_6 - \frac{5}{6} \beta_1 W_5 - \frac{4}{5} \beta_2 W_4 - \frac{3}{2} \beta_3 W_3 - \frac{4}{3} \beta_4 W_2,$$

$$W_7 = W_7 - \frac{6}{7} \beta_1 W_6 - \frac{10}{7} \beta_2 W_5 - \frac{12}{7} \beta_3 W_4 - \frac{10}{7} \beta_4 W_3 - \frac{12}{7} \beta_5 W_2.$$
The graphs in $w_n(r)$ are very cleverly constructed. The nature of the weights is such that the integral receives contributions only where one or more of the molecules in each terminal subpart lies in the region where $g(r)$ is not unity, i.e., where the field is felt, including where $g(r) = 0$, which is outside of the volume $V$. At the same time, the molecules in the basic part are weighted to require that they lie inside $V$. Thus, the integrals straddle the boundary and in this manner capture the behavior that defines the surface properties. This is illustrated in Fig. 2. We refer to this definition of assigning weights to the diagrams as the Bellemans weighting scheme.

III. MODEL AND METHODS

In the present work, we study a system of hard spheres near a hard wall (Fig. 3). The potential for fluid-fluid and fluid-wall interactions are defined by, respectively,

$$u(r_{ij}) = \begin{cases} \infty & r \leq d \\ 0 & r > d \end{cases}$$

(21)

where $r_{ij}$ is the separation distance between two molecules and $d$ is the hard-sphere diameter,

$$\phi(r) = \begin{cases} \infty & z \leq \text{wall position} + d/2 \\ 0 & z > \text{wall position} + d/2 \end{cases}$$

(22)

This is a planar potential of area $A$ in the $xy$ plane.

The invariance of the system with respect to $x$ and $y$ implies that the position-dependent quantities $a_n(r)$ and $w_n(r)$ will be functions of $z$ only. The area $A$ can be identified as the extent of the integrations in $x$ and $y$, so integrations over $r$ can thus be given as $A$ times integrals over $z$, and in doing so one finds that the dependence on $A$ cancels for the quantities of interest.

A. Mayer-sampling algorithm

We employ the MSMC method for calculation of the cluster integrals. The basic idea of MSMC is to calculate the ratio of cluster-integral sum for the desired system (the target) to a known cluster sum having the same number of points (the reference). Importance sampling is used to generate configurations, and appropriate ensemble averages are recorded to calculate the ratio. In the present application, the target is a cluster sum for the inhomogeneous system, and the reference is a similar sum for a homogeneous (field-free) system.

We detail first how MSMC is applied to compute coefficients for the activity series ($a_n(z)$ and $A_n$) in the presence of the hard wall. As a reference system, we use $n$ hard spheres in the absence of an external potential, and the reference integral is the sum of clusters of the corresponding $n$-particle coefficient of the activity expansion (i.e., all connected Mayer clusters). One can easily reason that the target configuration space is a subset of reference configuration space—the configurations important to the target system are exactly those important to the reference, minus any configurations disallowed by the way the spheres overlap (or not) the wall—and in this circumstance direct sampling is favored.

The root particle is fixed at the origin, and configurations of the other spheres are generated via a Metropolis Monte Carlo process according to the distribution $\pi$. The integral over $r_1$ specified by Eq. (14) can be performed analytically for each configuration. It receives contributions when the wall overlaps at least one sphere without overlapping the root sphere, labeled 1. With the wall situated as shown in Fig. 4, it can be any distance from the root sphere between the point where it just begins to overlap the root, down to the point where it no longer overlaps at least one of the other spheres. All wall positions within this range of length $\ell$ have
the same weight, so the integral is just the value of $\gamma_n$ for the configuration, times $\ell$.

Thus, the working equation for evaluation of $A_n$ is

$$A_n = \frac{\bar{b}_n}{\bar{a}_n} A_n = \bar{b}_n \frac{\int \ell(r^n) \gamma_n(r^n) d\tau^n}{\int \gamma_n(r^n) d\tau^n} = \frac{\bar{b}_n \langle \gamma_n / \pi \rangle}{\langle \gamma_n / \pi \rangle}.$$  \hspace{1cm} (23)

The angle bracket indicates an ensemble average over all configurations, weighted by $\pi$. In this application, the reference system governs sampling so, $\pi = |\gamma_n|$, and the average in the denominator is just a sum of $+1$ and $-1$. Likewise, the function $a_n(z)$ is tabulated for a set of values of $z$, which we can write as the average

$$a_n(z) = \bar{b}_n \langle \frac{\bar{h}_n(z_1, r^n) \gamma_n(r^n) d\tau^n}{\gamma_n(r^n) d\tau^n} d\tau^n \rangle \delta_{z_1}.$$  \hspace{1cm} (24)

where $h_n(z)$ is 1 if the wall position $z$ is in the range $\ell$.

A similar approach can be taken to compute the density-expansion cluster integrals $w_n(z)$ and $W_n$, but there are important differences in comparison to the activity-coefficient calculation. First, as described above, we do not compute $W_n$ directly, but instead evaluate it via the coefficients $W_n$. This is nevertheless a minor issue. A more significant complication is that we need for more sophisticated averaging to obtain these quantities. An important feature of the activity-series diagrams is that all diagrams in the sum forming $\gamma_n$ have the same weights associated with each point. This means that for a given wall position, either all diagrams contribute (and in the same amount they do in the reference), or none do. Thus, any diagram cancellation that occurs in the reference-system sum will occur also in the contributing diagrams of the target-system sum, and we are assured that the phase-space subset relation holds, i.e., all configurations important to the target can be sampled by the reference system. This contrasts with the situation for the density coefficients. Here, the weights assigned to the sphere coordinates differ from one diagram to the next, so that for a given wall position and configuration of spheres, some diagrams may be zero while others are not. This can cause some configurations important to the target system to be unimportant (not sampled) by the reference—two diagrams that cancel in a configuration for the reference (causing that configuration to not be sampled) might not cancel in the target because the wall position leads one of them to be weighted zero while the other is not.

This is a routine problem for MSMC, and the remedy is to use overlap sampling. In this manner, we evaluate the target-system integral using two simulations, one in which sampling is governed by the target-system integrand, and the other by the reference-system integrand. We have one more complication, however, in that $w_n(z)$ defines many target systems, one for each value $z$ that we tabulate. To avoid having to perform an overlap-sampling calculation for each $z$, we introduce an umbrella potential $^5$ that encompasses configurations important to the target across all relevant values of $z$. Thus, we define

$$\gamma_n^{US} = \sum_i \ell_{n,i} |\gamma_{n,i}|.$$  \hspace{1cm} (25)

Here, we introduce $\ell_{n,i}$ which is the length of the range of values of the wall placement that gives a nonzero Bellemans$^5$ weight for diagram $i$ in sum for $\gamma_n$. The wall may be as far away as allowed by the position of the spheres that are required to overlap the wall, and as near as allowed by the position of spheres that cannot overlap the wall.

The overall strategy is depicted in Fig. 5(b). In the overlap-sampling method, an intermediate system (system B in the figure) is formulated to be a subset of both the target (which in this case is the umbrella potential, system C) and reference (system A). The overlap system given by Bennett’s optimization$^5$ is

$$\gamma_n^{OS} = \frac{|\gamma_n| \gamma_n^{US}}{\delta |\gamma_n| + \gamma_n^{US}},$$  \hspace{1cm} (26)

where $\delta$ is an optimization parameter. The averages of interest are given by

$$\mathcal{W}_n = \bar{b}_n \frac{\langle \sum_i \ell_{n,i} \gamma_{n,i} \rangle / \gamma_n^{US} |\gamma_n^{OS} / \gamma_n^{US} |\gamma_n^{OS} / \gamma_n | / |\gamma_n| \rangle}{\langle \gamma_n / |\gamma_n| \rangle / |\gamma_n^{OS} / \gamma_n^{US} |\gamma_n^{OS} / \gamma_n | / |\gamma_n| \rangle},$$  \hspace{1cm} (27)

$$w_n(z) = \bar{b}_n \langle \sum_i h_{n,i}(z) \gamma_{n,i} \rangle / \gamma_n^{US} |\gamma_n^{OS} / \gamma_n^{US} |\gamma_n^{OS} / |\gamma_n| \rangle / |\gamma_n| \rangle,$$  \hspace{1cm} (28)

where $h_{n,i}(z)$ is 1 if $z$ is in the range $\ell_{n,i}$, and is zero otherwise.

B. Simulation details

MSMC simulations are performed in an infinite volume with no periodic boundaries. Particle 1 is fixed at the origin and the other particles are constrained to be in its vicinity via the $f$-bonds that tie them together. For the evaluation of $n$th order corresponding cluster, $a_n(z)$ and $A_n$, we employ $n$
spheres and generate configurations importance-sampled according to the unweighted (homogeneous) cluster sum integrand $|\gamma_n|$. For each configuration, we compute $\ell$ (for $A_n$) as the distance from the farthest to the nearest contributing wall positions, and we accumulate contributions to $a_n(z)$ in increments of $0.01d$ for tabulation of the $z$ dependence. This approach allows us to collect all data in a single simulation. For the calculation of second to sixth order corresponding clusters, we performed 10 separate simulations of $10^9$ steps. For $n = 7$, we ran 100 simulations of $10^8$ steps.

For the calculation of $w_n(z)$ and $W_n$, we ran simulations of $10^6$ MC steps to collect the results for each $n$ from $n = 2$ to $n = 6$. For $n = 2$ and 3, we ran 50 simulations; for $n = 4$ and 5, we performed 100 simulations; for $n = 6$, 1500 simulations were run. We ran 1500 simulations of $5 \times 10^6$ steps for the seventh-order coefficient. The reported values and uncertainties are one standard deviation of the mean as determined from the independent simulations. We also ran the same simulation for $v_n(z)$ (defined below) from $n = 2$ to $n = 7$.

For comparison purposes, standard Monte Carlo simulations were performed using grand canonical transition-matrix Monte Carlo (GC-TMMC) to generate precise structure and thermodynamic properties for the equilibrium hard-spheres fluids near a hard wall. Details are as described in Refs. 53 and 54.

### IV. RESULTS AND DISCUSSION

#### A. Density profile

First, we examine the excess singlet coefficients, $a_n(z)$, for hard spheres near a hard wall; results are shown in Figure 6 for $n = 2$–7. Uncertainties of each coefficient are less than 0.1%. Wall-contact values range over several orders of magnitude and alternate with $n$ between positive and negative signs, and each curve is strictly zero where $z > (n - 1)d$. A sinh$^{-1}$ scale is employed, which is similar to a log scale for large magnitudes while allowing both positive and negative values to be displayed; near zero the scale is linear.

Figure 7 gives a characterization of the difficulty of these calculations, and how it depends on $n$ and $z$. Plotted is the product of the standard error in each $a_n(z)$ times the square-root of the total cpu time required for the calculation. For large computation times, this product approaches a constant that characterizes the difficulty of the calculation. As expected, the calculation becomes more difficult with increasing $n$ and, perhaps less obviously, for values of $z$ near but not contacting the wall.

We now turn to the cluster integrals for the density expansion, $w_n(z)$, which are displayed for $n = 2$–7 in Figure 8. The results obtained using the MSMC methods are smooth and precise for $n$ from 2 to 6, and deteriorate noticeably for $n = 7$. The curves again are strictly zero for $z > (n - 1)d$. 

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**FIG. 5.** The phase space schematic of appropriate intermediate system: (a) direct-sampling and (b) umbrella and overlap-sampling. The arrows indicate perturbing from one system to another.

**FIG. 6.** The second- to seventh-order coefficients of the excess singlet density in a series in powers of activity.

**FIG. 7.** Et$^{1/2}$ presents the difficulty of calculation for each coefficient, $a_n(z)$ and $w_n(z)$. Curves proceed in sequence from $n = 2$ to 7 as indicated on plot.
The density-series coefficients show oscillations, with each increase in order \( n \) adding another oscillation cycle to the coefficient (the number of nodes in the oscillation is \( n - 1 \)). This contrasts with the activity-series coefficients \( a_n(z) \), which apparently introduce oscillations in the sum for \( \rho(r) \) via alternation of the sign of the coefficient with each order \( n \).

The difficulty \( E_{1/2}t \) of calculating each curve is shown in Fig. 7. Again the calculation becomes more difficult with increasing \( n \) and for values of \( z \) next to the wall. The comparison provided in Figs. 7 finds that the difficulty of \( a_n(z) \) and \( w_n(z) \) are about the same for a given \( n \).

One potential way to improve the efficiency of the calculation of \( w_n(z) \) is through a diagrammatic reduction, and in particular the application of the exponentiation theorem. If we identify

\[
v_n(r) = \left[ \text{sum of all diagrams in } w_n(r) \text{ in which the root point is not itself an articulation point} \right],
\]

then, in place of Eq. (18) we have

\[
\rho(r) = \tilde{\rho}g(r)\exp \left[ \sum_{n=2}^\infty v_n(r)\tilde{\rho}^{n-1} \right].
\]

The exponential function generates the diagrams in \( w_n(r) \) having root articulation points as products of those in \( v_n(r) \). The coefficients \( v_n(r) \) may be advantageous because for a given \( n \) they require computation of fewer and tighter (more highly connected) clusters. Another potential advantage is that the sum to order \( n \) in \( v_n(r) \) represents all those clusters in the sum up to \( n \) in \( w_n(r) \), plus higher-order terms formed from higher products of the diagrams in \( v_n(r) \). On the other hand, the diagrams eliminated from \( w_n(r) \) to yield \( v_n(r) \) will die off quickly with separation from the wall. According to the Bellemans weighting, the subcomponents joined by the root articulation point in \( w_n(r) \) will each require that at least one of its spheres be in contact with the wall, thereby greatly restricting the distance that the root point can be from the wall, for a given \( n \).

The coefficients \( v_n(z) \) and their corresponding difficulty of calculation are presented in Figures 9 and 10. The exponential-form coefficients \( v_n(z) \), which correspond to the expansion of \( \ln(\rho(r)) \), also shows oscillations. The same observations for the difficulty of the calculations of \( w_n(z) \) from

FIG. 8. (a) and (b) The second- to seventh-order coefficients of the density distribution when expressed as a series in powers of the bulk density.

FIG. 9. (a) and (b) The second- to seventh-order coefficients, \( v_n(z) \), of density distribution when expressed as a series in powers of the bulk density.

FIG. 10. \( E_{1/2}t \) presents effort needed for each coefficient, \( v_n(z) \). Curves proceed in sequence from \( v_2(z) \) to \( v_7(z) \) as indicated on plot.
Fig. 7 also apply here. Two conclusions may be drawn from comparison between \( w_n(z) \) and \( v_n(z) \). First, the contribution of the second-order term of the exponential form is much bigger than the contribution made by \( w_2(z) \). It is because the \( v_2(z) \) contains one diagram of \( w_3(z) \) plus all diagrams which contain articulation points at the root point. Thus, we may consider that the exponential form has a better starting point. Second, it requires more CPU time to evaluate \( v_n(z) \) over almost the whole range.

Having calculated the values of cluster integrals for inhomogeneous fluids, we now turn our attention to calculating their sum, the singlet distribution function. We use the results above to calculate the density profile of inhomogeneous fluids and compare with data for the same, but given by grand canonical transition-matrix Monte Carlo simulations.

First, the rate of convergence of the \( w_n(z) \) and \( v_n(z) \) series are compared in Fig. 11. As expected, the primary effect of working with the \( v_n(z) \) series rather than \( w_n(z) \) is seen as an improved description for \( n = 2 \) in the vicinity of the wall. Except for this benefit, there is no additional effect of the exponentiation theorem to describe better the singlet density. Addition of higher terms to the virial expansion diminishes the significant difference of second order terms of \( w_n(z) \) and \( w_n(z) \). Finally, this makes the expansion of \( \ln(\rho(z)) \) increasingly like the virial expansion itself (see Fig. 11(b)). We also tested the contribution of second-order term by adding one of the diagrams of \( w_3(z) \) to \( w_2(z) \). As shown in Fig. 12, one may conclude that the significant difference of the contribution of the second-order term is made by a product of \( w_2(z) \). This is somewhat obvious because the product of \( w_2(z) \) is shown in \( w_3(z) \) and exponential of \( v_2(z) \) but not in \( v_3(z) \). We may say that the contribution of any other product of \( w_2(z) \) is very small even very near a wall. Although not shown in Fig. 11, we have also compared with the activity expansion of the density distribution, Eq. (9). The series in powers of activity converges much more slowly than the other two series—even in the low-density case of \( \bar{\rho} = 0.0897 \) the series has not yet converged at seventh order.

In Fig. 13, we present the density profile \( \rho(z) \) of a hard-sphere fluid near a wall in equilibrium with a bulk density for \( \bar{\rho} = 0.206, 0.296, 0.397, 0.498, 0.608, \) and 0.699, corresponding to activities \( \ln(\alpha) = -0.5, 0.5, 1.7, 3.1, 5, \) and 7, respectively. Figure 13 displays the results of only the \( w_n(z) \) series because the \( v_n(z) \) series does not show any significant improvement. Data are compared to molecular simulation results, and inset figures are used to highlight the difference between the theory and the simulation data; the insets use a fixed scale across all figures to permit a better comparison.

The agreement between the cluster series and the simulation data is excellent at the lower densities, and remains satisfactory through the moderate densities presented here. In general, the agreement near the wall is best, and differences are observed mainly at about the third layer of spheres from the wall. At the lowest bulk density shown, \( \bar{\rho} = 0.206 \), the fourth-order expansion of the density profile gives a good agreement with simulation results at all separations, and convergence of the cluster series is rapid. Convergence is achieved by about the fifth-order term for the next higher density (Fig. 13(b)), while the seventh-order series captures the behavior at all separations for the density of 0.397. At a density of 0.498, shown in Fig. 13(d), the seventh-order cluster expansion has not quite converged on the simulation data at larger distances from the wall, but it still agrees well (within its confidence limits) with simulation data for the first and second sphere layers. This behavior continues into the two highest densities studied, shown in Figs. 13(e) and 13(f), where good agreement is still found near the wall, while further from the wall, the phase as well of the amplitude of the oscillations departs from the simulation behavior. One way to appreciate the difficulties in capturing the behavior away from the wall is as follows. As the density increases, the structure of the layers not adjacent to the wall shifts to a tighter packing, leading...
FIG. 13. Plots of density distribution for hard-spheres near a hard wall. The open squares correspond to MC data and the curves labeled 2, 3, 4, etc., correspond to truncated virial expansions, truncated after $w_2(z)$ (black), $w_3(z)$ (red), $w_4(z)$ (blue), $w_5(z)$ (cyan), $w_6(z)$ (magenta), and $w_7(z)$ (gold) terms, respectively. The system is in equilibrium with a bulk hard-sphere fluid of density of (a) $\rho = 0.206$, (b) $\rho = 0.296$, (c) $\rho = 0.397$, (d) $\rho = 0.498$, (e) $\rho = 0.608$, (f) $\rho = 0.699$. Dashed-dotted lines are from lower-order series, and solid lines from highest-order plotted in each case. Inset figures indicate the difference obtained upon subtracting each truncated virial series from MC data.

B. Surface tension and adsorption

The coefficients for the residual surface tension $\sigma^*$ and adsorption $\Gamma^*$ are tabulated in Table I. These are used to compute $\sigma^*$ as a function of density, and the results are presented in Fig. 14. The plot extends up to the freezing density of the
TABLE I. Expansion coefficients $A_n$, $W_n$, and $W_n/A$.

<table>
<thead>
<tr>
<th>$n$</th>
<th>$A_n/A$</th>
<th>$W_n/A$</th>
<th>$W_n/A$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.39269(1)</td>
<td>0.39267(2)</td>
<td>0.39267(2)</td>
</tr>
<tr>
<td>3</td>
<td>-2.4146(1)</td>
<td>-0.2208(2)</td>
<td>0.8757(2)</td>
</tr>
<tr>
<td>4</td>
<td>14.354(2)</td>
<td>0.1103(6)</td>
<td>1.0312(9)</td>
</tr>
<tr>
<td>5</td>
<td>-87.60(3)</td>
<td>-0.053(2)</td>
<td>0.882(3)</td>
</tr>
<tr>
<td>6</td>
<td>548.9(3)</td>
<td>0.027(4)</td>
<td>0.670(9)</td>
</tr>
<tr>
<td>7</td>
<td>-3530(3)</td>
<td>0.20(18)</td>
<td>0.70(18)</td>
</tr>
</tbody>
</table>

homogeneous hard-sphere system, and good convergence is demonstrated over the entire density range. The seventh-order series shows deviation from the MC data at the highest bulk-phase densities, at about $\bar{\rho} = 0.7$ and above. In contrast, the activity series does very poorly, with the seventh-order expansion being accurate only to about $\bar{\rho} = 0.1$.

Recently, it was demonstrated\textsuperscript{55} that an exponential approximant arises as a natural limit for hard spheres in a sequence of asymptotically consistent approximants for the family of inverse-power potentials, and it performs remarkably well in accelerating the convergence of the virial series for the pressure of a bulk-phase hard-sphere system. It is of interest then to examine the performance of such an approximant for the surface tension. We write the approximant as

$$[J/0]^{\infty} = \exp(N_2 \bar{\rho} + N_3 \bar{\rho}^2 + \cdots + N_J \bar{\rho}^{J-2})$$ \hspace{1cm} (31)

with coefficients $N_n$ that are independent of density and temperature, and are selected such that the Taylor expansion of the approximant at $\bar{\rho} = 0$ agrees with the series given by modified Eq. (16)

$$\frac{-\beta \sigma^* A}{W_2 \bar{\rho}^2} = 1 + \frac{W_3}{W_2} \bar{\rho} + \frac{W_4}{W_2} \bar{\rho}^2 + \frac{W_5}{W_2} \bar{\rho}^3 + \frac{W_6}{W_2} \bar{\rho}^4.$$ \hspace{1cm} (32)

Comparison between the exponential approximant, surface virial expansion, and molecular simulation data is shown in Fig. 15. The same observations from Fig. 11 also apply here. Again, the exponential approximants show better convergence than the original virial expansions (we ignore seventh-order term due to its low precision). For inhomogeneous fluids, the exponential approximant method seems to provide improvement over the surface virial expansion over the whole range. It is shown that $[6/0]^{\infty}$ agrees well with the simulation data.

Another quantity studied in simulations is the residual adsorption at the planar wall, which is defined as the number of adsorbed particles per unit surface, relative to the bulk density, and in excess of the Henry’s law limit. In this case, the denominator in the second term on the right side of Eq. (17) is first calculated with the first ten bulk virial coefficients.\textsuperscript{43} Figure 16 displays the results of virial series of the $\Gamma^*$ truncated from the second to seventh terms, respectively. For the case of a planar hard wall, $\Gamma^*$ can be calculated from the Gibbs adsorption equation $-\Gamma^* = \partial \gamma^*/\partial \mu$. Again, good convergence to the simulation data is observed.
V. CONCLUSIONS

In conclusion, we have applied Mayer-sampling methods to the computation of the series coefficients for inhomogeneous systems. We evaluated the cluster coefficients of the density profile, surface tension, and adsorption to seventh order in both the activity and bulk-density series for hard spheres interacting with a hard wall. Calculation of the bulk-density coefficients is complicated by the need to use overlap and umbrella sampling methods, but precise results can be obtained and the resulting series converges much more quickly than the activity series. Using the recently developed MSMC methods, we were able to go significantly beyond previous calculations, which extended only to order \( n = 4 \), obtaining precise results up to \( n = 6 \), and less-precise but still useful results for \( n = 7 \).

The sixth-order results compare well with simulation data up to moderate densities. At high densities, the theory with higher-order coefficients predicts the general behavior particularly well near a surface, while there are noticeable differences from simulation data further from the surface. The surface virial coefficients are used in the virial series to predict the surface tension. In this study, we did not directly evaluate the surface virial coefficients. However, it was possible to indirectly calculate the coefficients based on the connection between \( W_n \) and \( w_n(r) \). Also a comparative study of the rate of convergence of different cluster-integral series is presented. Similar to the bulk virial series, the series in powers of density or exponential forms show better convergence characteristics than the series in powers of activity. On the other hand, the series expansion of the logarithm of the density distribution does not converge faster than the conventional cluster expansions.

The cluster-series treatment is a severely underutilized approach for understanding surface behavior and inhomogeneous systems in general. While most applications have been to hard-sphere systems in simple geometries, the advent of the Mayer-sampling methods demonstrated here opens the door to application to more realistic molecular models, and more complex surfaces and adsorption media.

ACKNOWLEDGMENTS

This work is financially supported by the U.S. National Science Foundation (NSF), Grant Nos. CBET-0854340, CHE-0626305, and CHE-1012356.
