The rate of convergence of the virial series in confined systems

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Abstract

We examine cluster-series methods for the behavior of simple fluids under confinement, applying the Mayer-sampling Monte Carlo method to evaluate the necessary cluster integrals. We examine two series formulations, one based on the density of a bulk phase in equilibrium with the confined phase (effectively specifying the chemical potential), and another based on the density of the confined phase. The theory and methods are used to calculate the structure and properties of hard-sphere fluids confined between parallel planar hard walls. We present the effects of width of the confined region on the inhomogeneous virial coefficients, and through them, on the thermodynamics of the confined system.

Keyword: Mayer-sampling Monte Carlo; Confined fluids; Cluster expansions; Thermodynamic properties

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1. Introduction

The virial equation of state (VEOS) is an important and well-established theoretical approach in statistical mechanics for the description of bulk fluids [1,2]. For a homogeneous system, the virial expansion for the pressure $p$ is given by [1]:

$$\beta p = \rho + \sum_{n=2} B_n(T) \rho^n$$  \hspace{1cm} (1)

where $\beta = (k_B T)^{-1}$, $T$ is the temperature, $k_B$ is the Boltzmann constant, and $\rho$ is the number density. The $B_n$ are the virial coefficients, which are expressed as sums of integrals over the coordinates of $n$ molecules. The classical second virial coefficient is

$$B_2(T) = -\frac{1}{2} \int f_{i2} \, dr = -\frac{1}{2}$$ \hspace{1cm} (2)

where $f_{ij}$ in the integral is the Mayer function $f_{ij} = \exp(-\beta u_{ij})-1$, with $u_{ij}$ the pair potential between molecules labeled $i$ and $j$. As shown here, the integrals that give $B_n$ from the molecular model are often depicted with a graph notation in which $f_{ij}$ is drawn as a line (bond) between molecules $i$ and $j$, represented as points [3]. For homogeneous systems such as a bulk fluid, it is acceptable to consider molecule 1 fixed at the origin. Molecule 1 is represented with a white circle, as can be seen in Eq. (2) for $B_2$, and is referred to as a root point. The positions of other molecules $r_j$ are integration variables, and these molecules are represented with black circles. In this fashion, $B_3$ is, for a pairwise-additive potential,

$$B_3(T) = -\frac{1}{3} \int \int f_{12} f_{13} f_{23} \, dr_2 \, dr_3 = -\frac{1}{3}$$ \hspace{1cm} (3)

The number of graphs needed to represent the coefficients grows very quickly with order, so in practice a calculation of $B_n$ is limited to values of $n$ of about 5 to 10, depending on the molecular model. For sufficiently simple potentials of interaction, low-order coefficients can be calculated.
analytically, but the higher-order virials need to be calculated numerically [2]. General biased Monte Carlo methods are applied to evaluate the expansion coefficients for a given molecular model [4-6]. Although they may require significant computation, once the coefficients are determined they yield a simple explicit formula describing the behavior.

Formulations of the virial series applicable to inhomogeneous phases, such as found in fluids near a wall or under confinement, have been developed [7-9]. It is possible to do this by treating the inhomogeneous density as an independent variable [8], but it seems preferable to define the systems as one in the presence of an external field \( \phi(r) \) that couples to the particle position and thereby imposes the inhomogeneity. Although such treatments are now long-established [9,10], virial-based studies of non-uniform fluids are far less common than those for uniform, bulk fluids. Results are available for simple systems [7-9,11-14], but few calculations have been performed for coefficients above fourth order. The furthest this has been taken is calculation of first seven coefficients in the density expansion of the surface tension for hard spheres in contact with a hard wall [15], for which comparison to Monte Carlo simulations of these systems found very good agreement up to bulk densities approaching the freezing point.

In the present work we examine a system of hard spheres of diameter \( d \) bounded by two parallel hard walls separated by a distance \( H \), as depicted in Fig. 1. The hard-sphere potential for the fluid-fluid interaction is:

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

(4)

where \( r_{ij} \) is the separation between two spheres and \( d \) is the hard-sphere diameter; for the fluid-wall interaction we define:
\[ \phi(r) = \begin{cases} \infty & z \leq d/2, \ z > H - d/2 \\ 0 & z > d/2, \ z \leq H - d/2 \end{cases} \tag{5} \]

This is a planar potential of area \( A \) in the \( xy \) plane. The area \( A \) can be identified as the extent of the integrations in \( x \) and \( y \), across which all properties are homogeneous; hence, integrations over \( r \) can 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. To simplify notation, in what follows we express all lengths in units such that \( d = 1 \).

Figure 1. A schematic section of hard-spherical particles confined between slit hard walls.

In the next section we review the derivation of the virial-type series in the grand-canonical ensemble for confined fluids. In Sec. 3, we detail the Mayer-sampling Monte Carlo method [16] used to compute the cluster integrals for the confined hard-sphere fluid as well as the modifications to the approach required because of its interaction with walls. We present our results in Sec. 4, and conclude in Sec. 5.
2. Virial series

Assuming temperature is given, and assuming we use an external field to impose inhomogeneity, then there are two natural choices for the independent variable used to specify the state of a confined system. The first choice is the number of molecules in the confined region, which might be specified in the form of the pore density or a related quantity. For confined systems, the volume (and hence the pore density) is ambiguous, and its specification entails identifying (explicitly or implicitly) a dividing surface that defines the confined region. Alternatively, we can use a grand-canonical approach, specifying the state in terms of the chemical potential, or activity. This is often a natural choice because the state of the absorbed phase is determined by the activity of a bulk phase that is in equilibrium with it. In this case, it can be convenient to use the density of the bulk phase, \( \rho \), as the independent variable, serving as a surrogate for the activity. This is especially appropriate for systems in which the bulk phase is reached at a limit of the spatial coordinates of the inhomogeneous phase, such as in the case of molecules in the presence of a single wall, which approaches a homogeneous bulk at positions far from the wall.

The choice of independent variable of course affects the form of the series it defines. The necessary development has been performed by Rowlinson [9] for the pore-density approach, and by Bellemans [10] and Stecki and Sokolowski [11,12], for the bulk-density treatment. We will not repeat the development here, but provide only the key results. It should be noted that the two formulations are equivalent if taken to infinite order, but when the two series are truncated at the same order, they will produce different behavior.

2.1 Bulk density expansions

In previous work [15], we employed Bellemans’ series development to the study of hard spheres
near a single hard wall. The series for a confined system can be expressed in terms of the same type of cluster integrals that we used in that work. The key terms are labeled \( w_n(r) \), used for position-dependent quantities, and \( W_n \), used for position-averaged quantities. Specifically:

\[
-\sigma^+ A = \beta \sum_{n=3} W_n \rho^n
\]

(6)

\[
\Gamma^+ A = \left( 1 - \sum_{n=1} n \beta_n \rho^n \right)^{-1} \sum_{n=2} n W_n \rho^n
\]

(7)

\[
\rho(r) = g(r) \left( \rho + \sum_{n=2} n w_n(r) \rho^n \right)
\]

(8)

Here and in what follows, \( g(r) = \exp[-\beta \phi(r)] \), \( \beta_n \) are simply related to the bulk virial coefficients, and \( \sigma^+ \) and \( \Gamma^+ \) are the residual surface tension and adsorption, respectively, defined in excess of the Henry’s law limit (and thereby made independent of any definition of the dividing surface) [15].

The \( w_n(r) \) are defined in terms of sums of all simply connected clusters formed from \( n \) points joined by \( f \)-bonds. The difference between these for the present confined system versus the previous single-wall case is just the number of force fields (or alternatively, the shape of the force field). Each diagram still consists of a basic part, and zero or more terminal subparts as shown in Fig 1. in Ref. [11]; a typical diagram in the definition of \( w_3(r) \) is shown here:

![Diagram](image)

Open and filled circles represent the root point and field points, respectively, each with weight \( g(r) \), which precludes overlap with the walls. The black and shaded squares represent additional
field points with respective weights $g(r)-1$ (which then requires overlap with one of the confining walls) and $\left( \prod g(r) \right)^{-1}$ (which requires one or more wall overlaps among the points with this shading). Figure 2 presents a few of the relevant graphs in the context of the hard walls, in a way that is suggestive of the constraint that the field associated with each type of point restricts its position or range of integration.

Figure 2. A comparison of cluster diagrams (a) with one wall and (b) with two walls.

A coefficient $W_n$ is defined as the integral of $w_n(r)$

$$W_n = \int dr g(r) w_n(r)$$  \hspace{1cm} (9)

and these are used to determine the surface virial coefficient, $W_n$ appearing in Eqs. (6) and (7), via the following relation:

$$W_n = \frac{1}{n} \sum_{\{p,q\}} pW_p \left( \sum_k n_k \right)! \prod_k \frac{(k\beta_k)^{n_k}}{n_k!}, \quad \left( \sum k n_k + p = n \right)$$  \hspace{1cm} (10)

which is inverted to give the $W_n$. The number of cluster integrals in $W_n$ is fewer than in $w_n(r)$, more so with increasing number of molecules. Consequently it is better to compute $W_n$ directly...
rather than via Eqs. (9) and (10). For example, for \( n = 2 \) and \( n = 3 \), the required cluster integrals are:

\[
2! w_2(r) = \int dr_2 \left( g(r_2) - 1 \right)f_{12} \\
= \begin{array}{c}
\text{Diagram 1}
\end{array}
\]

\[
2! W_2 = \int dr_1 dr_2 \left( g(r_2) - 1 \right)f_{12} \\
= \begin{array}{c}
\text{Diagram 2}
\end{array}
\]

\[
3! w_3(r) = \int dr_2 dr_3 \left( g(r_2) - 1 \right)\left( g(r_3) - 1 \right)f_{12} f_{13} \\
+ 2 \int dr_2 dr_3 g(r_2) \left( g(r_3) - 1 \right)f_{12} f_{13} \\
+ \int dr_2 dr_3 g(r_2) g(r_3) \left( g(r_3) - 1 \right)f_{12} f_{13} f_{23} \\
= \begin{array}{c}
\text{Diagram 3}
\end{array} + 2 \begin{array}{c}
\text{Diagram 4}
\end{array} + \begin{array}{c}
\text{Diagram 5}
\end{array}
\]

\[
3! W_3 = \int dr_1 dr_2 dr_3 \left\{ 3 \left( g(r_2) - 1 \right) \left( g(r_3) - 1 \right) f_{12} f_{13} f_{23} \right\} \\
+ (g(r_2)g(r_3) - 1) f_{12} f_{13} f_{23} \}
= \begin{array}{c}
\text{Diagram 6}
\end{array} + \begin{array}{c}
\text{Diagram 7}
\end{array}
\]

\[
\text{Table 1. Lists the number of diagrams needed for } n \text{ up to 5.}
\]

<table>
<thead>
<tr>
<th>( n )</th>
<th>( w_n(r) )</th>
<th>( W_n )</th>
</tr>
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<tr>
<td>2</td>
<td>1</td>
<td>1</td>
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<tr>
<td>3</td>
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<td>4</td>
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<td>6</td>
</tr>
<tr>
<td>5</td>
<td>58</td>
<td>21</td>
</tr>
</tbody>
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\[
2.2 \text{ Pore-density expansions}
\]

Rowlinson’s formulation of the virial series in terms of the pore density introduces a different set of expansion coefficients, which will be indicated with a ‘*’ superscript. The main formulas can be summarized as follows [9]
\[-\beta \Omega = \sum_{i} b^*_n z^n \quad (11)\]
\[\bar{N} = \sum_{i} n b^*_n z^n \quad (12)\]

where $\Omega$ is the grand-canonical thermodynamic potential, and $V = AH$. Rowlinson avoided defining a volume, preferring to use the integral of the external potential when a volume was needed. Such a choice can be reasonably interpreted as a volume if there are no attractive interactions between the particles and the confining walls. The definition of the volume used here ($V = AH$) to define pore density includes inaccessible regions, where the sphere center is between the walls but the sphere overlaps one of them, and so it differs from the form suggested by Rowlinson.

The coefficients, $b^*_n$, are also given as sums of configurational integrals, and $z$ is a reduced activity defined as

\[z = \frac{\lambda V_1}{\Lambda^3}, \quad V_1 = \int g(r) \, dr \quad (13)\]

where $\lambda$ is the absolute activity as it appears in the grand-canonical partition function, and $\Lambda$ is the de Broglie wavelength. Elimination of $z$ between Eqs. (11) and (12) gives

\[-\beta \Omega / V = \sum_{i} B^*_n \rho^n_p \quad (14)\]

where

\[B^*_1 = 1\]
\[B^*_2 = -\frac{V}{2}\]
\[B^*_3 = -\frac{V^2}{3} \left[ \begin{array}{c}
\text{(triangle)} + 3 \left( \begin{array}{c}
\text{(link)} - \left( \begin{array}{c}
\text{(loop)}
\end{array} \right) \end{array} \right) \end{array} \right] \quad (15)\]
All points are weighted by a factor of $g(r)/V_1$; thus, unlike the Bellemans’ treatment, all points in this formulation are weighted to require that they lie inside the pore. The graphs in $B_n^*$ are not all irreducibly connected, unlike those in the virial expansion of a homogeneous system, and some are not even connected. Such graphs appear in the series because the integrals represented by the reducible graphs are not cancelled by those represented by their disconnected versions when each field point is weighted by a position-dependent factor. The effect is similar to that observed in virial series for flexible molecules [17,18], or for multibody potentials [19-21]: one molecule interacts (has an $f$-bond) with a second, and this influences its (conformation/electronic structure/position in pore), which in turn affects the way the second molecule interacts with a third, on average. Consequently, for example, the last two graphs in $B_3^*$ do not cancel, as they would for a (rigid molecule/pairwise potential/homogeneous) case.

3. Computation details

For the bulk-density expansions, separate Mayer-sampling Monte Carlo (MSMC) simulations are used to compute $w_n(r)$ and $W_n$. Details are as described in our previous work [15] with hard spheres and a single hard wall. As before, we can perform analytic integration over wall position to collect data for $W_n$ more efficiently, and also allow evaluation for different wall separations from a single MSMC run. At least 50 independent calculations were performed for each case, and each independent calculation sampled at least $10^{10}$ configurations.

For the pore-density expansions, we employ the overlap-sampling formulation of MSMC to compute $B_n^*$ and portions thereof. The method employs a hypothetical overlap system having
integrands intermediate between that of the target integral, evaluated with two hard walls, and that of the reference integral, evaluated with a field-free hard-sphere potential (in which only the root point interacts with walls). The working equation is

\[ \Gamma = (H - 1) b_n \frac{\langle \gamma / \pi \rangle_{\pi} / \langle \gamma_{OS} / \pi \rangle_{\pi}}{\langle \gamma_0 / \pi_0 \rangle_{\pi_0} / \langle \gamma_{OS} / \pi_0 \rangle_{\pi_0}} \]  

(16)

Here we use \( \Gamma \) to represent a general cluster integral, \( \gamma \) is the corresponding sum of integrands needed for its calculation, and \( \pi = |\gamma| \) is the sampling weight function. The subscript 0 indicates a value for the reference system, and angle brackets specify an ensemble average weighted by \( \pi \) or \( \pi_0 \). Also \( \gamma_{OS} \) is an overlap function, given by

\[ \gamma_{OS} = \frac{|\gamma_0||\gamma|}{\delta|\gamma_0| + |\gamma|} \]  

(17)

where \( \delta \) is an optimization parameter. In Eq. (16) \( b_n \) is the activity-series coefficient for the bulk pressure and is equal to the integral of \( \gamma_0 \).

We consider each pore-density expansion coefficient \( B_n^* \) into two parts: connected and disconnected diagrams. We define \( B_n^{*c} \) to refer to the connected diagrams of \( B_n^* \). For \( B_3^* \) the formulation is shown in Eq. (15). There are two connected diagrams consisting of all three molecules: one doubly and one singly, and one group of disconnected diagrams. We calculate the \( B_n^{*c} \) sum, and in the same MSMC calculation we also compute each individual diagram to use for higher order coefficients. We do not use the analytic integration over wall position described for calculation of \( W_n \). The total number of sample configurations varied considerably with the
size of the wall separation and the order \( n \). At least 100 independent calculations were performed for each case, and each independent calculation sampled at least \( 10^{10} \) configurations.

For comparison purposes, standard Monte Carlo simulations were performed using grand canonical transition-matrix Monte Carlo (GC-TMMC) [22] to generate precise structure and thermodynamic properties for the equilibrium hard-sphere fluid confined between two hard walls. Histogram reweighting allows us to extract properties from the simulation data over an essentially continuous range of bulk density (i.e. \( \beta \mu \), chemical potentials). This technique provides particle number probability distribution at a chemical potential \( \beta \mu \) that is potentially different from the chemical potential \( \beta \mu_0 \) employed in the original simulation. Details are as described elsewhere [23]. We note that other very effective methods, such as Gibbs-Cahn integration [24], are also available for performing calculation of interfacial properties by molecular simulation.

**4. Results and Discussion**

**4.1. Density Profile – Bulk-density series**

We computed the virial coefficients from \( n = 2 \) to \( n = 6 \) for confined hard-sphere fluids between two hard walls, with \( H \) ranging from 1.1 to 3.5, via the MSMC method. In Fig. 3, we plot the position-dependent coefficients \( w_n(r) \), and examine the confinement dependence across the considered wall separation range.
Figure 3. The second- to sixth-order coefficients for the position-dependent pore density when expressed as a power series of bulk density (Eq. (8)) for wall separations ($H$) equal to (a) 1.1, (b) 1.5, (c) 2.0, and (d) 3.5. Confidence limits (68%) are indicated where larger than the line thickness. Number next to each line indicates the order $n$ of the coefficient.

The results obtained previously [15] for a single-wall system showed that the curves of the density profile coefficients are strictly zero for $z > (n-1)d$. This applies as well to the pore coefficients, but now for positions where the distance to the closer wall is greater than $(n-1)d$. For the cases studied here, this situation arises only for $n = 2$ and $H = 3.5$. Except for this case,
the bulk-density series coefficients in Fig. 3 are not zero at the center, and at all orders the walls affect the behavior across the entire pore. The coefficients show oscillations for larger pores, with increasing orders in \( n \) adding more oscillation cycles to the coefficient.

Figure 4. Plots of density distribution for hard-spheres in a flat slit pore, \( H = 1.1 \). The open squares correspond to MC data, the dashed-dot line is from density function theory, and the curves correspond to truncated virial expansions (numbers label order of truncation). The system is in equilibrium with a bulk hard-sphere fluid of density (a) 0.206, (b) 0.296. Confidence limits on all calculations are not visible on the scale of the figures.

Figure 4 presents the density profile \( \rho(z) \) for \( H = 1.1 \), comparing the results for increasing order of the virial series with data from Monte Carlo simulations. We also show results from classical density functional theory (DFT), implemented with the original fundamental measure theory (FMT) functional [25,26]. Profiles are presented for bulk densities
of $\rho = 0.206$ and 0.296. The virial expansion is seen to be accurate for all $z$, although the 6th-order virial expansion slightly overpredicts the density in comparison to MC simulation. For this pore width and at these densities, the profile from the DFT calculation underpredicts the local density at all positions.

**Figure 5.** Plots of density distribution for hard-spheres in a flat slit $H = 1.5$. Lines, symbols, and state conditions are as in Fig. 4.

In Fig. 5 we present the density profile $\rho(z)$ of a hard-sphere fluid in a flat slit with $H = 1.5$. The virial series again converges quite nicely at the lower density, but at the higher one the 6th-order series underpredicts the density profile by a non-negligible amount. However there is quite good qualitative agreement in the shape of the density profile between the virial series and simulation data. The qualitative behavior of the DFT-based profile is good as well, but again it underpredicts the pore-density profile at both bulk densities. At the lower density, the 6th-order virial series agrees better than DFT with simulation data, while at the higher density the performance is reversed.
Figure 6. Plots of density distribution for hard-spheres in a flat slit (a), (b) $H = 2.0$, (c), (d) $H = 3.5$. The system is in equilibrium with a bulk hard-sphere fluid of density of (a) 0.251, (b) 0.331, (c) 0.397, (d) 0.498. Lines and symbols are as in Fig. 4.

Figure 6 gives results for the density profiles for the larger pores. Both the virial series and the DFT calculations again show good agreement with the simulation data for all cases. The DFT calculation performs significantly better than seen for the lower-density and smaller-pore cases shown in Figs. 4 and 5, showing near-perfect agreement with simulation data. The $6^{th}$-order
virial series also performs quite well for these wider pores, even though the densities are higher than those in Figs. 4 and 5. However, the agreement with simulation data may be slightly fortuitous; the 6th-order series differs from the 5th, so we cannot be sure it is converged at these conditions.

4.2. Surface Tension – Bulk-density series

The surface virial coefficients appearing in Eqs. (6) and (7) are presented in Fig 7, as a function of wall separation. As expected, they tend toward the values for single-wall virial coefficients as $H$ increases. Interestingly however, the higher-order coefficients show negative values for some of the narrow wall separations. This behavior is not seen in the single-wall case, and appears to be a feature of confinement. The effect is not strong enough though to produce a positive surface tension.

![Figure 7](image)

**Figure 7.** The second- to seventh-order coefficients $W_n$ of surface tension in a series in powers of bulk density. Coefficient order $n$ is indicated next each curve. Confidence limits are smaller than symbol size. The last point in each line is the result from a single-wall calculation [15].
In Fig. 8, we present results for the surface tension obtained by summing Eq. (6) using the coefficients plotted in Fig. 7, and compare them corresponding simulation data. To put the data on a common scale so that details may be visible, we subtract from all values the surface tension previously determined for the single-wall system by Monte Carlo simulation. The agreement between the virial series and the simulation data is excellent up to around $\rho = 0.4$ for all separations.

![Figure 8](image)

**Figure 8.** Residual surface tension of confined fluid, as a function of the density of the coexisting bulk phase. Plotted is the difference obtained by subtracting single-wall simulation data from the $7^{th}$-order virial series (solid lines) and confined-system simulation data (dashed-dot lines). The number next to each line indicates the wall separation $H$, showing values 1.1 (red), 1.5 (blue), 2.0 (green), 3.5 (magenta) 6.0 (gold) and semi-$\infty$ (single wall) (black).
4.3. Equation of State – Pore- and bulk-density series

We computed the virial coefficients $B_2^*$ via the MSMC method for confined hard sphere fluids between two hard walls, with separation $H$ ranging from 1.1 to 10. In Fig. 9, we plot $B_2^*$ and examine the confinement dependence across the considered wall width range. We provide for comparisons $B_n$ (bulk) for 2D and 3D limiting cases. The second cluster integral can be evaluated analytically:

$$
B_2^* = \begin{cases} 
\frac{\pi H}{2(H-1)^2}\left(\frac{5}{6} - \frac{4}{3}H + \frac{2}{3}H^3 - \frac{1}{6}H^4\right) & H \leq 2 \\
\frac{\pi H}{2(H-1)^2}\left(-\frac{11}{6} + \frac{4}{3}H\right) & H \geq 2 
\end{cases}
$$

The coefficient approaches the bulk values of $B_2$ for 2D ($\pi/2$) and 3D ($2\pi/3$) as $H \to 1$ and $H \to \infty$, respectively. The higher-order $B_n^*$ also approach their corresponding bulk values in the same limits, as shown in Fig. 9. However, except for $B_2^*$, for wall separations between these extremes, the coefficients do not simply interpolate limiting values. Instead, for separations slightly larger than the 2D limit, the coefficients take values that are two to three times larger than those found at the limits.
**Figure 9.** The second- to fifth-order coefficients $B_n^*$ for the power series in pore density. The numbers in the legend indicate the coefficient order, $n$. Values at $H = 1$ and $\infty$ (right axis) are those for the bulk 2D and 3D systems, respectively.

Having calculated the values $B_n^*$ for inhomogeneous fluids, we compute the grand potential density via Eq. (14), and compare with the results from the Bellemans bulk-density formulation and data for the same, as given by grand canonical transition-matrix Monte Carlo simulations. In order to calculate the grand potential density (or ‘pressure’) from the Bellemans formulation, we must combine surface virial series with bulk virial series. If one chooses the physical surface of the wall as the dividing surface, then the following expression results:
\[-\beta \Omega / V = p - \frac{\sigma^* + p}{H}\]

where \(p\) is a bulk pressure. Therefore the virial coefficient of confined fluids is calculated by

\[B_k^{**} = \left(1 - \frac{1}{H}\right) B_k + \frac{W_k}{H}\]

We calculated \(-\beta \Omega / V\) using Eqs. (14) and (19). To compare the two virial series results without introducing error associated with converting bulk density \(\rho\) to pore density \(\rho_p\) using an approximate series (e.g., Eq. (7)), we perform this conversion using MC data. The results are shown in Fig. 10. The agreement between the virial series and simulation data is excellent for larger pores. Increasing the order of the virial series brings the curves closer and closer to simulation results. However, the virial series has not yet converged on simulation data for small pores, as shown in Fig. 10.
Figure 10. Plots of the equation of state of a confined HS fluid between hard walls with separation ($H$) equal to (a) $\infty$ (bulk); (b) 2.0; (c) 1.5; and (d) 1.1. The dashed lines correspond to the Bellemans bulk-density series based on Eq. (20) truncated at $B_5^{*\infty}$ (labeled 5B) and $B_7^{*\infty}$ (labeled 7B), the solid lines correspond to Rowlinson pore-density series, Eq. (14), truncated at $B_4^*$ (labeled 4R) and $B_5^*$ (labeled 5R), and the open squares correspond to simulation data.

For $H = 2$, the Rowlinson 5th-order series shows significant over-prediction compared to simulation data, while the 5th-order Bellemans series shows under-prediction, but not as much;
both 5th-order series depart from simulation data about the same pore density ($\rho_p = 0.35$, on the scale of the figure). The 7th-order Bellemans result suggests the series is converging to simulation data. On the other hand, for smaller pore widths (Figs. 10 (c) and (d)), the Bellemans series appears to be less converged while the Rowlinson series shows more consistent approach to the simulation data.

To summarize the behavior, we map convergence contours in wall-width/density plane, shown in Fig. 11. Specifically, we compute the “remainder” sum $r_n = \sum_{k=n+1}^{5} |B_k^* \rho_p^k|$ (note the absolute value) as well as the full sum $s = \sum_{k=1}^{5} |B_k^* \rho_p^k|$ (where $B_1^* = 1$); for all points to the left of a given line, the remainder is observed to be less than some small tolerance [27,28], taken to be 1% of the full sum: $r_n < 0.01s$. We interpret the line as indicating where the next coefficient $B_1^*$ +1 starts to have a significant contribution to the total potential $\beta \Omega / V$, meaning that all points to the left of it are well described by the pore-density series to the indicated order.
Figure 11. Lines showing approximate upper limits of applicability of pore-density series to various orders. 2D and 3D bulk results are provided for comparison.

For very narrow and very wide slit widths, convergence is reached at densities very similar to those seen for 2D and 3D bulk phases, respectively. For all case of slit widths, addition of higher coefficients yields continuous improvement to the range of the series.

5. Conclusions

Two different virial expansion methods have been used to calculate the structure and thermodynamic properties for a hard-sphere fluid confined between two hard walls. We investigated the effect of bulk density and slit width on the rate of convergence by calculating the density profile, surface tension, and equation of state. We have presented new comprehensive
virial series results for the hard-sphere fluid confined between hard walls. First, Bellemans’ virial expansion method, based on the coexisting bulk density as the expansion variable, has been used to calculate density profile for the confined hard sphere fluid. Also we compared the virial series results with classical density functional theory. We found that, at lower density and with a narrow pore, the virial series agrees better than DFT with simulation data, while at higher density the performance is reversed. The newly computed surface virial coefficients are used in the virial series to predict the surface tension for different pore sizes. The agreement between the virial series and the simulation data is excellent up to around $\rho = 0.4$ for all separations. For wider pores the simulation results differ little from the one-wall behavior. This is related to the observation that the second- to fourth-order coefficients $W_n$ quickly approach the values for $H = \text{semi-infinity}$ for $H > (n - 1)d$.

We also employed the overlap-sampling formulation of MSMC to compute the pore-density virial coefficients $B_2^* - B_5^*$ (based on Rowlinson’s method) for confined hard-sphere fluids between two hard walls, with separation $H$ ranging from 1.1 to 10. These coefficients approach corresponding values in 2D and 3D for the limits of very narrow and very wide pores, respectively. With the computed virial coefficients we calculated the equation of state.

Also a comparative study of the rate of convergence of different virial series is presented. One perhaps unexpected result is that, for the narrow-pore cases, the convergence behavior of the two bulk- and pore-density series differ, with the pore-density series showing better convergence for the narrower pores. The rate of convergence is also examined by mapping in wall width-density plane. For all considered cases, addition of higher coefficients provides improvement to the range of the pore-density virial series.

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References


