The sixth virial coefficient of hard disc mixtures

RICHARD J. WHEATLEY*
Department of Chemistry, University of Nottingham, University Park, Nottingham NG7 2RD, UK

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New calculations of the sixth virial coefficient are presented for binary hard disc mixtures. For each diameter ratio considered, the calculations involve about 1600 9-dimensional integrals. The integrals are evaluated exactly in \(d\) dimensions, and approximately, using the Korobov–Conroy number theoretical method, in the other \((9-d)\) dimensions, where \(d\) is between 4 and 8 for each diagram. The results cover diameter ratios from 0.1 to 0.9, and are accurate to about 0.2%. A method for predicting the sixth virial coefficients for the binary mixture, based on interpolating the sixth virial coefficients for the pure components, gives results within 1% of the calculated values.

1. Introduction

Model hard sphere and hard disc systems have been used extensively as reference systems for estimating the thermodynamic and structural properties of atoms and molecules in the bulk and at interfaces. The recent interest in mixtures of hard spheres and hard discs (see, e.g., [1–10] and references therein) is based on the expectation that these will prove to be equally useful as reference systems for chemical mixtures. For a model system to be a useful reference system, its thermodynamic properties in the fluid phase should be known accurately; this is a more difficult problem for mixtures than for monodisperse systems, because thermodynamic functions depend on two additional variables (size ratio and mole fraction). The equation of state is known exactly only for 1-dimensional hard core potentials, so for hard discs and hard spheres the emphasis has been on obtaining reliable approximations, using either computer simulations, or direct calculations based on correlation functions or virial coefficients.

This paper presents, for the first time, calculations of the sixth virial coefficient of hard disc mixtures. Second and third virial coefficients are known analytically for hard discs, and high accuracy fourth and fifth virial coefficients have been published [1, 5, 6] so the present calculations are a logical continuation of this line of research. These high virial coefficients can be used in developing and testing equations of state, and the results suggest also that a knowledge of the virial coefficients of pure species can be used to estimate the virial coefficients of mixtures.

2. Calculations and results

The sixth virial coefficient \(B^6\) of a system of particles with a pairwise additive potential energy function is obtained from the equation

\[
B^6 = -\frac{1}{144} \sum_I I_m,
\]

where the integrals \(I_m\) include all connected, labelled diagrams with six nodes and no bridge points. Some of these are shown in figure 1. The integrands are products of Mayer \(f\) functions, each denoted by a line on the diagram. For example, a line connecting A and B corresponds to the function \(f_{AB}(r_{AB})\), which equals \(-1\) for hard discs when \(r_{AB} < \sigma_{AB}\) and 0 otherwise. Here \(r_{AB}\) is the separation of the centres of discs A and B, \(\sigma_A\) is the diameter of disc A, and \(\sigma_{AB} = (\sigma_A + \sigma_B)/2\). Integration is carried out over the positions of five of the six discs, the sixth being fixed. Unless otherwise stated, a quoted value of \(B^6\) in this work refers to \(B^6/\sigma_A^{10}\), and it is assumed that \(\sigma_A \geq \sigma_B\).

A total of 11 368 labelled diagrams contribute to the sixth virial coefficient if all six particles are different. For a pure substance, the particles are identical, and any diagram integrals related by permutation of the labels are equal. For example, \(I_2\) and \(I_8\) in figure 1 are related by exchanging particles B and D. There are then 56 distinct diagrams in equation (1), multiplied by symmetry factors between 1 and 720, which reflect the number of distinct ways of labelling each diagram.

*e-mail: Richard.Wheatley@nottingham.ac.uk
where $B^6$ is obtained from equation (1), if the same $n$ labels on each diagram (e.g., A and B if $n = 2$) always refer to small discs, and the other $6 - n$ labels always refer to large discs. Again, many of the diagrams are identical under exchange of small discs (A and B if $n = 2$) or large discs (C, D, E and F), although there are more distinct diagrams. For example, $I_2$ and $I_8$ in figure 1 are not identical if A and B are small discs and C, D, E and F are large discs. There are 178 distinct diagrams for $n = 1$ and $n = 2$, 7,548 diagrams for $n = 3$, 38,388 diagrams for $n = 2$ and $n = 4$, and 473 diagrams for $n = 3$. The remaining coefficients, $B^6_0$ and $B^6_6$, are the sixth virial coefficients for pure large and small discs, respectively.

To evaluate the diagram integrals, they are divided into seven different classes, which use the connectivity of the diagrams to simplify the integrals.

The fully connected diagram ($I_1$ in figure 1) contributes the least to the virial coefficient, since the associated integral is always numerically smallest, and its symmetry factor is only one. It is evaluated using a Monte Carlo method [1, 11] with $4 \times 10^6$ configurations, and its standard error is estimated by dividing these into 20 blocks of $2 \times 10^5$ configurations each.

Integral $I_2$ in figure 1 includes four discs (C, D, E and F) which are not directly connected to one another through $f$ functions. There are two different unlabelled diagrams of this type. To evaluate these integrals, it is convenient to use the $x^{(2)}$ function defined in [5] (which is similar to the Z function defined by Blaak [10]):

$$x^{(2)}_{C,AB}(r_{AB}) = f(r_{AC})f(r_{BC})dr_C.$$  \(3\)

Integral $I_2$ then reduces to a 1-dimensional integral:

$$I_2 = 2\pi \int_0^\infty x^{(2)}_{C,AB}(r_{AB})x^{(2)}_{D,AB}(r_{AB})x^{(2)}_{E,AB}(r_{AB}) \times x^{(2)}_{F,AB}(r_{AB})r_{AB}dr_{AB}.$$  \(4\)

The function $x^{(2)}_{C,AB}(r_{AB})$ can be interpreted geometrically as the area of overlap of two circles with radii $\sigma_{AC}$ and $\sigma_{BC}$, whose centres are separated by $r_{AB}$.

Integral $I_3$ has three discs (D, E and F) which are not directly connected through $f$ functions, and of the remaining three discs, two (B and C) are connected by an $f$ function which, if removed, would leave a bridge point at disc A. There are four unlabelled diagrams of this type. The connectivity allows analytical integration over the positions of D, E and F (giving $x$ functions as above), and the angle BAC [5]. This leaves a 2-dimensional integral over the AB and AC distances.

Integral $I_4$ has three discs (D, E and F) which are not directly connected through $f$ functions. There are 22 unlabelled diagrams which are of this type and not of any of the simpler types above. Analytical integration over the positions of D, E and F leaves a 3-dimensional integral in each case, which for integral $I_4$ is of the form:

$$I_4 = 4\pi \int_0^\infty \int_0^\infty \int_0^\infty x^{(3)}_{D,ABC}(r_{AB}, r_{AC}, r_{BC}) \times x^{(3)}_{E,ABC}(r_{AB}, r_{AC}, r_{BC}) \times x^{(3)}_{F,ABC}(r_{AB}, r_{AC}, r_{BC})f(r_{AB})f(r_{AC})f(r_{BC}) \times r_{AB}r_{AC}d\phi_{BAC}dr_{AB}dr_{AC}.$$  \(5\)

The function $x^{(3)}$ is analogous to $x^{(2)}$, but involves the overlap area of three circles rather than two [5]. Other integrals of this form have fewer $f$ functions in the integrand, or a lower connectivity for one or more of discs D, E and F, which means that the corresponding $x^{(3)}$ functions are replaced by $x^{(2)}$ functions.

Integral $I_5$ has two angles (ABC and BCD) over which analytical integration is possible, for the same reason as integral $I_3$, and two discs (E and F) which are not connected through an $f$ function. The two unlabelled diagrams of this type reduce to 3-dimensional integrals over the distances AB, BC and CD.
Integral \( I_6 \) has two discs (E and F) which are not connected, and one angle (BAC) which can be treated analytically. There are four unlabelled diagrams of this type, and they reduce to 4-dimensional integrals over the distances \( AB, AC \) and \( AD \) and the angle \( CAD \).

The remaining diagrams, such as integral \( I_7 \), all have two discs which are not connected. There are 21 unlabelled diagrams of this type. Using analytical integration over the coordinates of the unconnected discs, the diagrams reduce to 5-dimensional integrals with two \( X \) functions in the integrand. Integral \( I_7 \) has two \( X^{(4)} \) functions, which are defined as the overlap area of four circles, but other integrals of this type involve the \( X^{(3)} \) and \( X^{(2)} \) functions defined above. Since these diagram integrals are numerically larger than the fully connected diagram integral, with additional symmetry factors up to 720, and require numerical integration over more dimensions than all the other diagrams, their accuracy is expected to determine the accuracy of the calculated virial coefficients.

Apart from the integration method itself, there are three choices to be made when calculating integrals of the type \( I_7 \). If the diagram has fewer than 14 \( f \) functions, there may be a choice of unconnected discs to use for the analytical integrations. There is a choice of coordinates to use for the 5-dimensional numerical integration, and the way in which the five integrals are nested also can be chosen. These choices affect the accuracy of the integration method, and can become crucial as the diameter ratio approaches zero.

In this work, the two unconnected discs are chosen essentially at random. It is not known how much this affects the results, but the choice is usually quite limited. The remaining four discs are labelled A, B, C and D, in decreasing order with respect to their number of connections to the other three. If B and C (or C and D) have an equal number of connections, the disc connected to A is placed first. If equal under these criteria, discs are labelled in increasing order of size. One of three different sets of coordinates is then used for the integration. The first two coordinates are always the distances \( AB \) and \( AC \). If discs \( AB, AC, AD \) and \( BC \) are all connected, the third coordinate is the distance \( AD \), the fourth coordinate is the angle \( BAC \) and the fifth coordinate is the angle \( BAD \). Otherwise, if \( AB, AC \) and \( BD \) are connected, these coordinates are the distance \( BD \), the angle \( BAC \) and the angle \( CBD \). Finally, if only \( AB \) and \( CD \) are connected, the coordinates are the CD distance, the angle \( BAC \) and the angle \( ACD \). The coordinates are chosen to restrict the limits of integration as much as possible, while retaining the generality of the integration scheme.

Further restrictions on the limits of integration are achieved for discs of different sizes. For example, if disc A has diameter 1, and discs B and C have diameter 0.1, and \( AB, AC \) and \( BC \) are all connected in the diagram, then the limits for the ‘outer’ integration over \( r_{AB} \) are fixed (0 to 0.55), but the limits for the ‘inner’ integration over \( r_{AC} \) depend on the value of \( r_{AB} \), as discs B and C must overlap. The integration scheme finds the minimum and maximum allowed distances between each pair of discs, at each level of nesting, and uses the information to set limits for the ‘inner’ integrations, for both distance and angle coordinates.

Similar methods are used to integrate diagrams of the types \( I_2 \) to \( I_6 \). As expected, generally these are found to be more precise than integrals of type \( I_7 \), and less effort has to be expended in optimizing the integration strategy.

All the above integrals include \( X^{(n)} \) functions, which give the area of overlap of \( n \) circles, with \( n = 2, 3 \) and \( 4 \). An efficient method for calculating these functions is not trivial to find for \( n \geq 3 \) and the problem is considerably more difficult for \( n = 4 \), as the number of ways in which the boundaries of the circles can intersect increases rapidly with \( n \). Therefore a general program has been written to find the area of overlap of \( n \) circles of arbitrary size. The program is not as efficient as purpose-written routines for specific \( n \) would be, but its timescaling for increasing \( n \) is believed to be optimal, and it appears to be stable in the face of pathological examples, such as coincidence of three or more boundaries. The program begins by checking that all the circles overlap (otherwise the area is zero) and discarding any circles which entirely enclose other circles. The trivial example of only one remaining circle is dealt with. There are then \( m \) circles remaining, with \( 2 \leq m \leq n \), and the boundaries of each pair of circles intersect at two different points. A pair of circles (say 1 and 2) is chosen, and a single intersection of their boundaries is located. The number \( x \) of circles enclosing this intersection is found. The region just inside circles 1 and 2, and bounded by the chosen intersection and by the boundaries of circles 1 and 2, is inside \( x + 2 \) circles. The program conceptually moves along the boundary of this region, anticlockwise with respect to its centre (following the boundary of either circle 1 or 2 as appropriate) until the next intersection is reached, for example between circles 1 and 3, which become the new circles 1 and 2. This process is repeated, and it can be shown that \( x \) will increase monotonically, and if there is an area bounded by all \( m \) circles, then \( x \) will eventually reach \( m - 2 \). The same algorithm then causes the program to move round the entire boundary of this region, and its area is summed over the bounding arcs using Green’s theorem in the plane. When the program arrives at an intersection that it has reached before, it finishes. The algorithm is illustrated in figure 2.
The method chosen to perform the numerical integrations is important, and four candidates are considered: the NAG routine D01FDF (the Sag and Szekeres method [12]), the NAG routine D01GCF (the Korobov–Conroy method [13, 14]), a Monte Carlo algorithm, and the Gauss–Legendre method used for fifth virial coefficients [5]. The Gauss–Legendre method is found to give less accurate results than the D01GCF routine for several of the integrals used in calculating the fifth virial coefficients, and therefore it has not been extended to 5-dimensional integrals. Five different 5-dimensional integrals are evaluated using the other three methods, and in each case NAG routine D01GCF gives the best accuracy for a given computer time. The results for integral \( I_7 \) with discs A, B, C and D having diameter 0.1, and E and F having diameter 1, are used to calculate the area.

The actual value of the integral is \( 5.968 \times 10^{-6} \). The D01GCF routine therefore requires about 10 times less computer time, for a given accuracy, than the Monte Carlo method. The D01FDF routine, which has the disadvantage of not possessing any built-in error estimate, appears to be no better than the Monte Carlo method.

Calculated sixth virial coefficients, for diameter ratios from 0.1 to 0.9, are shown in Table 1. The calculations are performed in parallel using the MPI library on the DEC 8400 ‘Columbus’ machine, which is part of the facility for computational chemistry in the UK [15]. By running the calculations on 6 processors, a reduction in real time by a factor between 4 and 5 is achieved consistently. The virial coefficients are calculated in two stages. In the first stage, the D01GCF routine is used to evaluate each integral except the fully connected diagram integral, which is calculated by the Monte Carlo method as stated above. The integrals, and the corresponding standard errors, are estimated using 12 sets of 80,021 evaluations of the integrand for each diagram. The results are checked by evaluating each integral using the Monte Carlo method, with 20 sets of 10,000 configurations, and comparing the difference between the two calculations with the standard error in the Monte Carlo calculation (which is larger than the error in the D01GCF calculation). Results for \( B^6_3 \) with a diameter ratio of 0.5 are typical: the difference between the integrals calculated with the two methods

<table>
<thead>
<tr>
<th>( \alpha )</th>
<th>( B^6_1/\sigma^1 )</th>
<th>( B^6_2/\sigma^2 )</th>
<th>( B^6_3/\sigma^3 )</th>
<th>( B^6_4/\sigma^4 )</th>
<th>( B^6_5/\sigma^5 )</th>
</tr>
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<tr>
<td>0.1</td>
<td>0.1153[3]</td>
<td>((-)3)2.96[2])</td>
<td>((-)5)5.69[3])</td>
<td>((-)7)9.35[6])</td>
<td>((-)8)1.380[2])</td>
</tr>
<tr>
<td>0.2</td>
<td>0.20935[5]</td>
<td>((-)2)1.632[5])</td>
<td>((-)3)1.090[2])</td>
<td>((-)5)6.55[2])</td>
<td>((-)6)3.670[7])</td>
</tr>
<tr>
<td>0.3</td>
<td>0.3278[6]</td>
<td>((-)2)4.828[9])</td>
<td>((-)3)6.48[1])</td>
<td>((-)4)8.14[2])</td>
<td>((-)5)9.74[2])</td>
</tr>
<tr>
<td>0.4</td>
<td>0.474[1]</td>
<td>0.109[2]</td>
<td>((-)2)3.84[4])</td>
<td>((-)3)4.98[2])</td>
<td>((-)3)1.01[2])</td>
</tr>
<tr>
<td>0.5</td>
<td>0.64[1]</td>
<td>0.211[4]</td>
<td>((-)2)6.8[1])</td>
<td>((-)2)2.05[4])</td>
<td>((-)3)6.25[1])</td>
</tr>
<tr>
<td>0.6</td>
<td>0.842[2]</td>
<td>0.3678[7]</td>
<td>0.1574[2]</td>
<td>((-)2)6.67[1])</td>
<td>((-)2)2.778[5])</td>
</tr>
</tbody>
</table>

Figure 2. Illustration of an algorithm for finding the mutual overlap of \( m \) circles. The numbers in each region are two less than the number of bounding circles, denoted \( x \) in the text. The algorithm follows the path of the white line. In this (worst) case, where the starting intersection (the large white dot) is not inside any circles, the path comprises six arcs, of which the last three, around the \( x = 2 \) region, are used to calculate the area.

Table 1. Composition-independent components of the sixth virial coefficient of hard disc mixtures. The diameter ratio \( \alpha \) equals \( \sigma_B/\sigma_A \), and the coefficients \( B^6_n \) are defined in the text. The notation \((-)2)9.6[2]\) is used to abbreviate \((-)2)9.6\pm0.02) \times 10^{-3} \).
(D01GCF minus Monte Carlo) is from 3 to 4 times the Monte Carlo error for one integral; 17 differences between the integrals are 2 to 3 times the Monte Carlo error, 60 are between 1 and 2, 150 between 0 and 1, 154 between 0 and 1, 73 between 2 and 1, 17 between 3 and 2, and one between −4 and −3. This is close to a normal distribution of errors, and is a useful confirmation that the D01GCF method has been implemented correctly.

In the second stage, typically 10 to 20 integrals with the largest D01GCF standard errors are ‘improved’ using lengthier calculations. Based on the D01GCF and Monte Carlo standard errors, and the amount of CPU time required to use the two methods, the program decides which method is likely to be more efficient. Each of the 6 standard sets of points supplied by the D01GCF routine is compared in this way. The program then estimates how many sets of points, or Monte Carlo configurations, will be required to reduce the standard error to a user-specified value. Generally, this method is found to work well: usually the standard error is reduced by close to the estimated amount, and overall the calculation requires 60–70% of the time of the first stage, while reducing the overall standard error by a factor between 1.5 and 2. The overall standard error is estimated as the square root of the sum of the squares of the errors of the individual integrals. A typical example is the coefficient $B_1^6$ with a diameter ratio of 0.5: the first stage takes 43 min CPU and gives a result of $0.6477 \pm 0.0019$, with a maximum standard error of 0.12 in any integral (after taking symmetry factors into account, but before dividing by 144 from equation (1)). In the second stage, the 15 integrals with the largest errors are recalculated, and their errors are reduced to around 0.04 in 32 min CPU. This gives an overall error of 0.0012 in the recalculated virial coefficient, whose value changes to 0.646 7.

A final test of the method is carried out by computing the accurately known sixth virial coefficient for monodisperse hard discs. This is treated in the same way as a calculation of $B_1^6$, but with a diameter ratio of 1. The first stage produces $B_1^6 = 1.915 \pm 0.005$, and 18 integrals are considered in the second stage, which aims to reduce their errors to 0.1. The result is $B_1^6 = 1.901 \pm 0.003$, compared with the exact value of 1.9014 [16]. For comparison, a Monte Carlo integration, using $10^8$ configurations for each of the 56 unlabelled diagrams, uses more computer time and produces a worse result, $B_1^6 = 2.2 \pm 0.2$.

### 3. Discussion

The calculations presented in this paper required somewhat more computer time than analogous calculations of the fifth virial coefficients, and employed a more efficient integration strategy, yet the present results for sixth virial coefficients are relatively 40 or 50 times less precise. This is because the number of diagram integrals contributing to the virial coefficient $B_1^N$ increases faster than factorially with $N$, and the cancellation between positive and negative diagram integrals becomes closer for larger $N$. The cancellation is also closer for smaller diameter ratios, which explains why generally the results are the least accurate for $\alpha = 0.1$.

Therefore it is useful to investigate methods where the virial coefficients for hard disc mixtures are estimated from their values for the pure substances. One possibility [6] is the interpolating function

$$B_1^N = \sigma_A^{2N-2a} \sigma_B^{-2} (a_0 + a_1a + a_2a^2), \quad (6)$$

where $a = \sigma_B/\sigma_A$. The $a_i$ coefficients are fixed by the value of $B_1^N$ at $\alpha = 0$, $\alpha = 1$ and $\alpha = \infty$, which are all known in terms of virial coefficients for the pure substances [6]. The current calculations can be used to test this interpolation for $N = 6$. Figure 3 shows the percentage difference $(100B_0^N \text{[calculated]} - B_0^N \text{[equation (6)]})/B_0^N$ as a function of diameter ratio for $N = 6$, and also $N = 4$ and $N = 5$ for comparison, using previously published results [5, 6].

The errors introduced by the interpolating formula (6) appear to be quite small, especially when $\alpha$ is not too near zero. For $N = 6$, the maximum error is 1%. Overall, the error also does not appear to increase greatly as $N$ increases. In fact, the largest deviation from equation (6) occurs for $N = 4$. The evidence from the accurate calculations for $N = 4$ and $N = 5$ suggests that the ratio of calculated and interpolated values should be a smooth function of $\alpha$. This is not obviously the case for $N = 6$, but the fluctuations seen on the graph are within the estimated uncertainty of the calculated points. In fact, for the coefficient $B_1^5$ the error in the interpolation is probably no larger than the uncertainty in the calculations.

The relatively poor agreement between the interpolated and calculated coefficients $B_1^6$ can be attributed to the difference between the derivatives $(\partial B/\partial \alpha)$ at $\alpha = 0$. The true behaviour of this virial coefficient for small $\alpha$ can be shown to be $B_1^6 = 0.1211\sigma_0^6(1 + 6\alpha + \ldots)$, whereas the interpolating function gives $B_1^6 = 0.1211\sigma_0^6(1 + 6.65\alpha + \ldots)$. Truncating these expansions at the $\alpha^4$ term gives a 4% error in $B_1^6$ for $\alpha = 0.1$, but this is seen in figure 3 to be reduced to 2.26% by higher terms in the series. The behaviour of virial coefficients for small diameter ratios is discussed further in a separate paper [17].

Several equations of state, for both hard discs and spheres, have been extended to multicomponent mixtures by Santos et al. [18]. They used published calculations of virial coefficients, up to the fifth, as a basis for comparison. The present results give extra information which is important in this type of study. In particular,
the extension denoted eH [18] of the Henderson equation of state [19] gives composition-independent sixth virial coefficients within 3% of almost all the values in table 1.

In conclusion, new calculations of sixth virial coefficients for hard disc mixtures have been reported. These will be useful in their own right as well as for testing proposed equations of state. An interpolating formula predicts the virial coefficients accurately, as long as the diameter ratio is not too small.

Figure 3. The percentage difference between the calculated and interpolated virial coefficients $B_i^N$, for (a) $N = 4$, (b) $N = 5$ and (c) $N = 6$. On each graph, the largest dots denote $n = 1$ and the smallest $n = N - 1$. Lines are guides to the eye.

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References