Calculation of High-Order Virial Coefficients with Applications to Hard and Soft Spheres

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A virial expansion of fluid pressure in powers of the density can be used to calculate a wealth of thermodynamic information, but the Nth virial coefficient, which multiplies the Nth power of the density in the expansion, becomes rapidly more complicated with increasing N. This Letter shows that the Nth virial coefficient can be calculated using a method that scales exponentially with N in computer time and memory. This is orders of magnitude more efficient than any existing method for large N, and the method is simple and general. New results are presented for $N = 11$ and 12 for hard spheres, and $N = 9$ and 10 for soft spheres.

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Introduction.—The pressure P of a fluid at temperature T can be expanded in powers of the number density ρ using the virial series

$$\beta P = \rho + B_2(T)\rho^2 + B_3(T)\rho^3 \ldots \tag{1}$$

where $\beta = 1/(kT)$, k is the Boltzmann constant, and B_N is the virial coefficient of order N. The convergence is slow for dense fluids, and it is often more accurate to find an analytical representation of the pressure (such as a rational function) that agrees with the calculated virial coefficients [1]. High-order virial coefficients are extremely valuable, whether or not direct summation of the series is used, but they are difficult to calculate.

Calculation of the virial coefficient for hard spheres, in particular, is an important and long-studied problem in science. The hard-sphere potential is one of the simplest potentials that can be used to describe departures from the ideal gas law, and hard-sphere systems are structurally similar to assemblies of real spherical particles. Virial coefficients can be calculated more easily for hard spheres than for more realistic potentials. The second, third, and fourth virial coefficients are all known exactly. The fifth virial coefficient was first calculated numerically by Rosenbluth and Rosenbluth in 1954 [2]. In the 1960s the work of Ree and Hoover, who calculated the sixth [3] and seventh [4] virial coefficients, set out the methodology which has been adopted in most subsequent studies. The eighth virial coefficient was first calculated by van Rensburg in 1993 [5], the ninth by Labik, Kolafa, and Malijevsky in 2005 [6], and the tenth by Clisby and McCoy in 2006 [7]. In general, these calculations also improved on the precision of the lower-order virial coefficients. The convergence of the virial series is an important unsolved problem, which has also been considered recently by Maestre *et al.* [8]. Higher-order virial coefficients are needed to resolve alternative theories concerning the convergence of the virial series, but the enormous number of integrals that need to be evaluated to obtain eleventh and higher-order virial coefficients has prevented any such calculations until now.

Virial coefficients for a system of spherical particles, which interact through a pairwise potential U of their separation r, are formally calculated as integrals over products of Mayer f functions:

$$B_N = \frac{1-N}{N!}\int \ldots \int f_B(\mathbf{r}^N) d\mathbf{r}_{12} \ldots d\mathbf{r}_{1N}, \tag{2}$$

where the functions f_B are defined by

$$f_B(\mathbf{r}^N) = \sum_G \Big[\prod_{ij \in G} f(r_{ij}) \Big] \tag{3}$$

and $f(r_{ij})$ is the Mayer f function given by $f(r_{ij}) = \exp[-\beta U(r_{12})] - 1$. The sum is over all the biconnected graphs G on N vertices, where each vertex is associated with a different particle [9]. The pairs of particles ij in the product are all the pairs of vertices that are joined by edges in graph G. Hence, B_N is a sum of "diagram integrals", with one diagram integral for each biconnected graph G. In Fig. 1, (a) and (b) are biconnected graphs, (c) and (d) are not.

There are $2^{N(N-1)/2}$ possible graphs on N vertices, and most of these are biconnected for large N, so the time required for the direct evaluation of the f_B function using Eq. (3) increases very rapidly as a function of N. The computer memory needed to maintain a list of all the biconnected graphs G increases at a similar rate. Evaluation of B_N by performing the integrals in Eqs. (2) and (3) directly is not possible for $N > 10$ for hard spheres and $N > 8$ for soft spheres, even when the permutation symmetry of the graphs is taken into account for a 1-component system, which reduces the number of different graphs to approximately $2^{N(N-1)/2}/N!$ (that is, about 900 million for $N = 11$, and over 170 times more than this for $N = 12$).

Method.—It is shown here that the function f_B for N particles can be evaluated using of order $3^N N$ calculations,

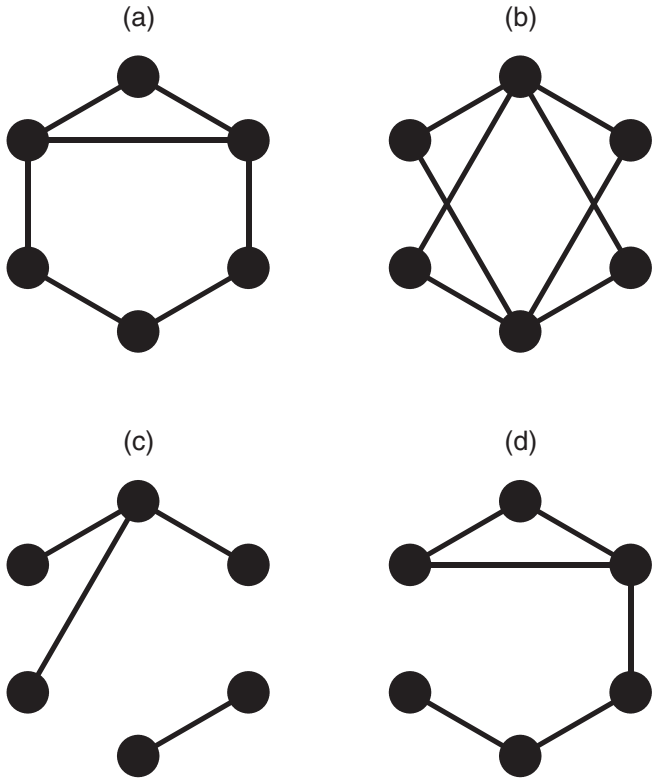

FIG. 1. Examples of graphs for $N = 6$. Graphs (a) and (b) are biconnected, (c) is disconnected, and (d) is articulated.

which means that the effort for $N = 12$ is less than 3.3 times that for $N = 11$, and similarly for other values of N. The saving in computer time relative to summing directly over graphs increases rapidly with N. Furthermore, the memory required is of order $2^N N$, which is available on modern computers for values of N in excess of 20.

The sum of all $2^{N(N-1)/2}$ diagram integrals, including graphs which are not biconnected or even connected, is denoted f_Q, and it can easily be calculated as a product over all $N(N-1)/2$ pairs of particles:

$$f_Q(\mathbf{r}^N) = \prod_{ij}[1 + f(r_{ij})]. \quad (4)$$

From this function f_Q, all diagram integrals corresponding to disconnected graphs [such as Fig. 1(c)] are removed to leave f_C, which is defined as the sum of diagram integrals of all connected graphs. This is done as follows. All disconnected diagram integrals on N vertices can be expressed uniquely as the product of a connected diagram on a proper subset S (size 1 to $N-1$) of the vertices, which contains the lowest-numbered vertex, and all diagrams (connected or not) on the complement of S, called S^*. Therefore,

$$f_C(\mathbf{r}^N) = f_Q(\mathbf{r}^N) - \sum_S f_C(S) f_Q(S^*), \quad (5)$$

where (S) denotes the coordinates of the vertices present in S, and (S^*) denotes the coordinates of the vertices not present in S. Since the sets S and S^* both have sizes less than N, the functions f_C can be calculated recursively, starting from all N sets of size one (for which $f_Q = f_C = 1$), then all $N(N-1)/2$ sets $\{ij\}$ of size two (for which $f_Q = f(r_{ij}) + 1$ and $f_C = f(r_{ij})$), and continuing the recursion up to size N. Overall, this requires of order 3^N mathematical operations and 2^N storage.

Finally, from f_C another recursive procedure is used to remove all the articulated (connected but not biconnected) diagram integrals (such as Fig. 1(d)), whose sum is called f_A, to leave the required function f_B. The function f_A is a sum of functions $f_{A,v}$, which are defined as the sum of all articulated diagram integrals with an articulation point at v (i.e., connected graphs which can be disconnected by removing vertex v), and with no articulation points at vertices numbered lower than v. All diagram integrals contained in $f_{A,v}$ can be expressed uniquely as the product of a two diagrams. The first is a connected diagram on a proper subset S (size 2 to $N-1$) of the vertices, which contains both v and the lowest-numbered vertex excluding v, and which does not have an articulation point at v or at any lower-numbered vertices. The second is a connected diagram on $S^* \cup v$ (the complement of S plus the vertex v), which does not have an articulation point at a lower-numbered vertex than v. Therefore,

$$f_{A,v}(\mathbf{r}^N) = \sum_S f_{B,v}(S)(f_{B,v}(S^* \cup v) + f_{A,v}(S^* \cup v)), \quad (6)$$

where $f_{B,v}$ is the sum of all connected diagram integrals which do not have an articulation point at v or at any lower-numbered vertices. The function $f_{B,v}$ can easily be obtained from $f_{A,v}$; for example, in the final step of the recursion,

$$f_{B,1}(\mathbf{r}^N) = f_C(\mathbf{r}^N) - f_{A,1}(\mathbf{r}^N) \quad (7)$$

and for all v, $0 < v < N$,

$$f_{B,v+1}(\mathbf{r}^N) = f_{B,v}(\mathbf{r}^N) - f_{A,v+1}(\mathbf{r}^N). \quad (8)$$

Overall, this recursion requires of order $3^N N$ mathematical operations and $2^N N$ storage, but the evaluation of equation (6), which is the only step scaling as $3^N N$, can be implemented in an efficient manner, such that the time scaling in practice appears to be no slower than 3^N for the values of N considered here.

Results.—The inverse twelfth-power potential $U/\varepsilon = (\sigma/r)^{12}$ is a commonly-used soft sphere potential, which approximately represents short-ranged repulsion between atoms and molecules. The temperature scaling of the virial coefficients is trivial for inverse power potentials, and each virial coefficient can be calculated as a single reduced value in units of $\beta\varepsilon$ and σ. Hence, for simplicity, a reduced interaction energy and separation can be used, with $\beta U = r^{-12}$. The Mayer f function is negative; it is close to –1 for

small r, increases quickly around $r = 1$, and approaches zero with an asymptotic behavior of $-r^{-12}$ for large r.

The integrations to give the virial coefficients are done numerically, and the behavior of the Mayer f function motivates the use of a Monte Carlo integration scheme where interparticle distances are chosen based on a continuous, normalized probability function $P = (9/4)r^2$ for $r \leq 1$ and $P = (9/4)r^{-10}$ for $r > 1$. This includes the Jacobian factor of r^2 for a three-dimensional system. Particle 1 is fixed, then particle 2 is placed relative to 1 by choosing r_{12} randomly according to this probability function, and choosing a random orientation for the $\mathbf{r}_{12}$ vector. The remainder of the particles, $v = 3$ to N, are similarly placed relative to the previous particle $v - 1$. Once all N particles have been placed, the function f_B is calculated using the recursive scheme described above.

The integral of f_B is defined as a weighted sum over functions f_B calculated for a large number n of these N-particle configurations. In principle,

$$B_N \approx \frac{1 - N}{N!} \sum_{i=1}^{n} (f_B(\mathbf{r}^N)/P(\mathbf{r}^N)), \tag{9}$$

where $P(\mathbf{r}^N)$ is the product of all $N - 1$ probability functions for the interparticle distances, but this equation cannot be used in practice, as it is possible to have a diagram with significant f_B and very small P (such as a regular polygon with sides of unit length where the adjacent vertices are *not* sequentially numbered). Instead, for a 1-component system the permutation symmetry of f_B is used. The total probability of obtaining a particular N-particle configuration with any of the possible $N!$ labelings of the particles is given by $P(\mathbf{r}^N)$ averaged over all $N!$ permutations of the particles, and this average is used as the denominator in Eq. (9). The average over permutations of the particles is calculated recursively for each random configuration by considering chains of increasing length from 2 to N.

For the inverse twelfth-power potential, the calculation is numerically stable for almost all configurations, but occasionally a situation is encountered where particles are a long way apart, the average P is near zero, and f_B should also be near zero, but because of round-off errors it acquires a value close to the numerical precision of the computer ($\approx 10^{-14}$) and gives a significant contribution to B_N. In practice, this problem is avoided by setting all values of $|f_B|$ below this threshold to zero and checking that the choice of threshold does not affect the final result. Its effect is found to be negligible with respect to the quoted uncertainty in all results.

Results for the inverse twelfth-power potential are given in Table I. They agree with previous calculations within their standard errors, and improve on their precision. The longest calculations, for B_{10}, took approximately 440 h real time when run in parallel on 100 CPU cores. In the case of B_5, the increased accuracy is simply a result of using more sampling points, but for higher N the new calculation method rapidly becomes more efficient. The efficiency of the new method can be seen by comparing the computer time required per Monte Carlo point (which increases by about two orders of magnitude from $N = 5$ to $N = 10$) to the number of diagrams contributing to the integrand at each Monte Carlo point (which increases by about 6 orders of magnitude over the same range). The results will be valuable in constructing approximate equations of state for the important inverse twelfth-power potential. This is the "hardest" inverse power potential for which negative virial coefficients (here B_8 and B_9) are known in three dimensions, and the data in Table I suggest that the higher virial coefficients may oscillate around zero. Oscillations in the signs of virial coefficients of increasing order have been observed for other inverse power potentials [10], but it is not known from the existing data whether the oscillations will continue to infinite order, how they affect the convergence of the virial series, and whether they reflect the existence of poles in the complex plane.

The same sampling scheme and probability distribution are used for hard spheres as for the inverse power potential; each sphere is placed relative to the previous one in exactly the same way as described above. More optimal sampling schemes have been devised for $N \leq 10$ for hard spheres [7], but the general-purpose sampling scheme used here does not increase the uncertainty greatly (see Table II), and it can be used without modification for $N > 10$. Since f_B is always an integer, there are no round-off problems in the

TABLE I. Reduced virial coefficients B_N for the inverse twelfth-power potential. Standard errors in the last 1–2 digits are in parentheses. The number of Monte Carlo points is n, the relative computer time required per point is t_{rel}, and the relative number of biconnected graphs not related by permutation symmetry is $N(G)_{\text{rel}}$. Literature values are from [10] ($N = 5$) and [11] ($N > 5$).

N	5	6	7	8	9	10
B_N	2.11494(2)	0.76953(4)	0.09043(12)	−0.0742(6)	−0.035(3)	0.040(9)
$n/10^{11}$	20	20	20	10	4	6
t_{rel}	1	2.3	5.4	13	35	97
$N(G)_{\text{rel}}$	1	5.6	47	710	19 000	970 000
Literature	2.1150(1)	0.7695(2)	0.0908(5)	−0.074(2)	...	...

TABLE II. Reduced virial coefficients B_N for hard spheres with unit diameter. The notation is the same as in Table I. The literature value is from [7].

N	10	11	12
B_N	0.314(3)	0.198(7)	0.090(24)
$n/10^{13}$	1	2	3
t_{rel}	1	1.5	2.7
$N(G)_{\mathrm{rel}}$	1	92	16 000
Literature	0.313(1)	...	...

calculation for hard spheres. For hard spheres, f_B is zero for almost all of the random configurations, and the procedure can be made more efficient by identifying as many zero values as possible without doing the full recursive calculation of f_B. A graph G_n is created for each configuration n, with edges between all ij pairs with $r_{ij} \leq 1$ (hence $f = -1$). No edge is present for pairs separated by more than 1 ($f = 0$). Then, if the graph G_n is not biconnected, f_B is zero. This is tested using a standard Depth-First Search algorithm. However, even if graph G_n is biconnected, f_B is still zero in more than 90% of cases. All biconnected graphs are therefore tested for the presence of a simple clique separator, which would cause f_B to be zero. A simple clique separator is defined as a single vertex v connected by edges to $m < N - 1$ other vertices, where all m vertices connected to v are also connected to one another. [Figure 1(a) has a clique separator with $m = 2$.] Graphs having clique separators with $m = 2$, 3, 4, and 5 are identified and their values are set to zero, then f_B is calculated recursively for all remaining graphs. In practice, the remaining graphs are roughly equally divided between zero and nonzero f_B, so further efforts to screen graphs for zero f_B would give relatively little improvement in computer time.

Tenth, eleventh, and twelfth reduced virial coefficients for hard spheres with unit diameter are given in Table II. Calculation of B_{12} took approximately 640 h real time when run in parallel on 100 CPU cores. The efficiency of the new method is again shown by the small increase in computer time per point with increasing N, compared to the rapid increase in the number of graphs. The tenth virial coefficient agrees with more precise literature calculations, the eleventh virial coefficient agrees well with estimates of 0.198, 0.203(2), and 0.202(2) obtained by extrapolating lower-order virial coefficients ([7,12,13], respectively), and the twelfth virial coefficient agrees reasonably well with similar estimates [7,12,13] of 0.124, 0.128(3), and 0.128(3), respectively, given its relatively large uncertainty. The current calculations therefore lend support to the extrapolation techniques used in the literature.

The recursive method developed in this work is directly applicable to any two-body potentials, to mixtures, and to systems of different dimensionality such as hard disks. The method may also be adapted for calculating correlation functions. Extensions to non-pair-additive potentials (using a formulation related to that of Hellmann and Bich [14]), to flexible molecules, and to quantum statistics, should also be considered.

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