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A New Graph Expansion of Virial Coefficients

Karl W. Kratky[1]

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It is well known that the virial coefficients of the pressure of thermodynamic systems can be represented in terms of graphs. The existing graph expansions are compared with a new one, the overlap graph expansion. The merits of overlap graphs in general and especially for hard disks and spheres are discussed.

KEY WORDS: Statistical mechanics; virial coefficients; cluster integrals; graph expansions; hard disks; hard spheres.

1. INTRODUCTION

If the pressure of a real gas is expanded in powers of the density, the corresponding coefficients are called virial coefficients. They consist of cluster integrals which may be represented by graphs.[1] The expansion in so-called Mayer graphs or star graphs is well known.[2,3] Ree and Hoover[4,5] introduced the modified star graphs or Ree–Hoover (RH) graphs. This modification simplified the graph expansion and enabled Ree and Hoover to evaluate the sixth and seventh virial coefficients for hard disks and spheres. In the present paper, a further simplification will be investigated which leads to a new graph expansion of virial coefficients, the "overlap graph expansion." Throughout the paper, the expressions clusters, (cluster) integrals, and graphs will be regarded as synonymous words.

We assume that the potential energy U can be represented as the sum of pairwise interactions,

$$U = \sum_{i<j} u_{ij}, \qquad u_{ij} = u(r_{ij}) \tag{1}$$

the pair interaction being only a function of the distance r_{ij}. Furthermore,

[1] Institut für Experimentalphysik der Universität Wien, Boltzmanngasse 5, A-1090 Wien, Austria.

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we abbreviate the Boltzmann factor in the following way:

$$\tilde{f}_{ij} = 1 + f_{ij} = \exp(-u_{ij}/kT) \tag{2}$$

f_{ij} being the Mayer f function, $\tilde{f}_{ij}$ the modified $\tilde{f}$ function.[4] Then, the configurational partition function for a system of N identical molecules can be written as

$$\begin{aligned} Q_N[V] &= \int_V \cdots \int_V d\mathbf{r}_1 d\mathbf{r}_2 \cdots d\mathbf{r}_N \prod_{i<j} \tilde{f}_{ij} \\ &= \int_V \cdots \int_V d\mathbf{r}_1 d\mathbf{r}_2 \cdots d\mathbf{r}_N \prod_{i<j} (1 + f_{ij}) \end{aligned} \tag{3}$$

Expanding the product $\prod(1 + f_{ij})$ in products of f functions yields the deviation from the ideal gas where $f_{ij} = 0$. Since we are interested in systems with high N, we will neglect surface effects (at the boundary of the volume V). Thus, the integration over $\mathbf{r}_1$ in (3) yields just the factor V, and we assume in the following that molecule 1 is located at the origin. The pressure P follows from the knowledge of $Q_N[V]$:

$$\begin{aligned} \frac{P}{kT} &= \frac{1}{Q_N[V]} \left.\frac{\partial Q_N[V]}{\partial V}\right|_{N,T} \\ &= \frac{NV^{N-1} + \binom{N}{2}(N-1)V^{N-2}\int_V d\mathbf{r}_2 f_{12} + O(V^{N-3})}{V^N + \binom{N}{2}V^{N-1}\int_V d\mathbf{r}_2 f_{12} + O(V^{N-2})} \\ &= \frac{N}{V} - \binom{N}{2}\left(\frac{1}{V}\right)^2 \int_V d\mathbf{r}_2 f_{12} + O\left(\frac{1}{V}\right)^3 \end{aligned} \tag{4}$$

For symmetry reasons,

$$\int d\mathbf{r}_2 \cdots d\mathbf{r}_N \prod f_{ij} = \binom{N}{2} \int d\mathbf{r}_2 \cdots d\mathbf{r}_N f_{12} = \binom{N}{2} V^{N-2} \int d\mathbf{r}_2 f_{12}$$

Furthermore, the approximation

$$\frac{\partial}{\partial V} \int d\mathbf{r}_2 f_{12} = 0$$

has been used due to the neglect of surface effects. The full expansion in the number density $\rho = (N/V)$ yields the virial series

$$\frac{P}{\rho kT} = 1 + \sum_{n=2}^{\infty} B_n(N)\rho^{n-1} \tag{5a}$$

$$\frac{P}{\rho kT}(\text{thermodynamic limit}) = 1 + \sum_{n=2}^{\infty} B_n \rho^{n-1} \tag{5b}$$

The $B_n(N)$ are number dependent. The additional dependence on T has

been suppressed as in the cases f_{ij}, $\tilde{f}_{ij}$, and $Q_N[V]$. From (4) it follows that

$$B_2(N) = (1 - N^{-1})B_2, \qquad B_2 = -\frac{1}{2}\int_V d\mathbf{r}_2 f_{12} \tag{6}$$

Extending (4) to lower order of V, B_n can be obtained ($n \geqslant 2$) as a function of cluster integrals[2] like $\int d\mathbf{r}_2 f_{12}$. Deviations from the thermodynamic limit are twofold: First, the N dependence comes in which is independent of the shape of the volume, cf. (5a) and (6). This correction is included in (4) and is well known.[6] The second correction (due to the volume dependence of the cluster integrals) is much more complicated[7,8] and will be considered again in Section 5.

2. MAYER GRAPHS

Now we turn to the B_n which are valid in the thermodynamic limit. The Mayer cluster integrals occurring in B_n can be represented as graphs with n corners[1,3]; see Fig. 1. Each corner corresponds to a variable. Variables represented by black circles are integrated over; the white circle indicates an arbitrary but fixed location (e.g., of variable 1). A bond (straight line) between the corners i, j means f_{ij}; no bond between i and j corresponds just to the factor 1 in the integrand. Mayer graphs are characterized by the restriction that they are doubly connected, i.e., they do not have an articulation point.[1] In case of an articulation point, the cluster integrals would be equivalent to a product of Mayer graphs. Figure 1 shows the Mayer graphs up to $n = 5$ together with their designation.[3,9] The notation $(m)_n$ means that the Mayer graph has n corners, m being the graph number[2] due to Ref. 3. The numbering of the corners is irrelevant;

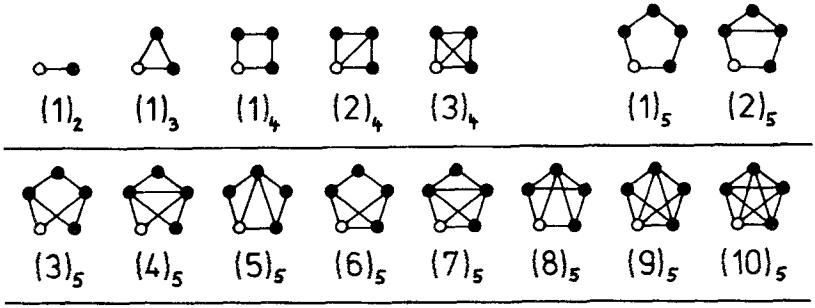

Fig. 1. The Mayer graphs up to 5 corners.

[2] The value of a Mayer graph may be positive or negative now. Hoover and DeRocco[3] took always the absolute value for D-dimensional parallel hard cubes.

i.e., graphs which differ only in the numbering of corners will be identified in the following.

For $n = 5$, a comparison of several designations of the Mayer clusters has been given.[9] Unfortunately, there has been a misprint in the second column of Table I of that paper. The correct succession of numbers should be 1, 2, 3, 4, 5, 6, 8, 7, 9, 10. This means that the designation of Mayer clusters has been analogous to the present paper, except for an interchange of the numbers $(7)_5$ and $(8)_5$.

The virial coefficients up to B_5 are

$$B_2 = -\tfrac{1}{2}(1)_2 \tag{7a}$$

$$B_3 = -\tfrac{1}{3}(1)_3 \tag{7b}$$

$$B_4 = -\tfrac{1}{8}\{3(1)_4 + 6(2)_4 + (3)_4\} \tag{7c}$$

$$B_5 = -\tfrac{1}{30}\{12(1)_5 + 60(2)_5 + 10(3)_5 + 10(4)_5 + 60(5)_5 + 30(6)_5 + 30(7)_5 + 15(8)_5 + 10(9)_5 + (10)_5\} \tag{7d}$$

The number of integrals is a quickly increasing function of n. Moreover, experience shows that the contributions of the graphs almost cancel each other for several simple potentials if $n \geqslant 4$.[1,3,9] Therefore, the resulting virial coefficients are relatively small and thus inaccurate if the cluster values are not known very accurately. There have been early attempts to simplify the calculation of virial coefficients.[10] Using Eq. (2), one can evaluate for instance $[(6)_5 + (7)_5]$ at once (see Fig. 2, $\tilde{f}_{ij}$ being represented by a dotted line). This increased the accuracy of B_5 for hard spheres.[10]

3. REE–HOOVER GRAPHS

The integrand of $Q_N[V]$ is a product of $\tilde{f}$ functions, cf. (3). Using (2) yields virial coefficients with cluster integrals where two variables may have no bond or a f bond, cf. Fig. 1. Figure 2 shows an example where re-introducing a $\tilde{f}$ bond simplifies the calculation of a virial coefficient. Ree and Hoover[4,5] found a systematic simplification using f and $\tilde{f}$ bonds. The

Fig. 2. The interpretation of $(1 + f_{ij} = \tilde{f}_{ij})$ in terms of graphs, together with an application.

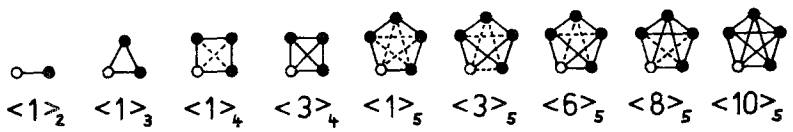

Fig. 3. The RH graphs occurring in the graph expansion of B_n up to $n = 5$.

resulting RH graphs are characterized by the fact that each pair i, j is connected in any case, but the bond may be either f or $\tilde{f}$. A RH graph is generated by inserting a $\tilde{f}$ bond between every pair i, j which is not connected in the corresponding Mayer graph. Thus the number of RH clusters and Mayer clusters is the same for any n. The RH graph corresponding to the Mayer graph $(m)_n$ may be called $\langle m \rangle_n$; see Fig. 3. Using Eq. (2), every RH graph may be written as a sum of Mayer graphs and vice versa. If this is done for the known Mayer graph representation of B_n, it follows for B_2 to B_5 that

$$B_2 = -\tfrac{1}{2}\langle 1\rangle_2 \tag{8a}$$

$$B_3 = -\tfrac{1}{3}\langle 1\rangle_3 \tag{8b}$$

$$B_4 = -\tfrac{1}{8}\{3\langle 1\rangle_4 - 2\langle 3\rangle_4\} \tag{8c}$$

$$B_5 = -\tfrac{1}{30}\{12\langle 1\rangle_5 + 10\langle 3\rangle_5 - 60\langle 6\rangle_5 + 45\langle 8\rangle_5 - 6\langle 10\rangle_5\} \tag{8d}$$

This means for B_4 and B_5 a simplification compared with (7). Not all of the RH graphs have a coefficient $\neq 0$ and do really occur in the RH graph expansion of B_n. The occurring RH clusters up to $n = 5$ are shown in Fig. 3. Using RH clusters is even more efficient[4,5] for B_6 and B_7.

Now we turn to the hard-sphere potential in D dimensions ($D = 1, 2, 3$). If the hard spheres have the diameter σ, it follows from (2) that

$$\tilde{f}_{ij} = \Theta(r_{ij} - \sigma) \geqslant 0, \qquad f_{ij} = -\Theta(\sigma - r_{ij}) \leqslant 0 \tag{9}$$

where Θ is the Heavyside step function. Thus, the sign of the value of any Mayer or RH cluster integral is given by the number of f functions. If the graph has an even (odd) number of f functions, the value is $\geqslant 0$ ($\leqslant 0$). The combination of f and $\tilde{f}$ bonds in RH clusters results in small absolute values. For example, $(10)_5 = \langle 10\rangle_5$ has the smallest absolute value of all Mayer clusters, but the largest one of all RH clusters ($D = 1, 2, 3$). Some of the RH graphs have zero value for hard-core potentials[4,5] which increases the accuracy of B_n further. From Eq. (9) follows a simple interpretation of the graphs shown in Fig. 4. $I(1, 2, \ldots, k)$ is the volume of intersection of k overlapping D-dimensional spheres of radius σ.[9,11] $I(1)$ is just the volume

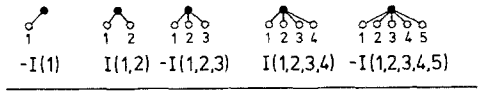

Fig. 4. The interpretation of several graphs in terms of intersections of overlapping spheres.

of one sphere. For instance, $(3)_4 = \langle 3 \rangle_4$ can be written as

$$\langle 3 \rangle_4 = \int\int\int d\mathbf{r}_2\, d\mathbf{r}_3\, d\mathbf{r}_4\, f_{12} f_{13} f_{14} f_{23} f_{24} f_{34}$$

$$= -\int\int d\mathbf{r}_2\, d\mathbf{r}_3\, I(1,2,3) f_{12} f_{13} f_{23} = \int_{r_2<\sigma}\int_{\substack{r_3<\sigma \\ r_{23}<\sigma}} d\mathbf{r}_2\, d\mathbf{r}_3\, I(1,2,3) \quad (10)$$

Expressing Mayer or RH cluster integrals in terms of overlaps made it possible to increase the accuracy of virial coefficients of hard disks and spheres.[9,12,13] The case $D = 1$ (hard rods) is already known exactly.[3,4,11] The problem of overlapping disks has been solved completely; the three-dimensional case can be solved in an analogous way.[11,14]

4. THE FORMALISM OF LESK

A completely different way of representing virial coefficients for D-dimensional hard spheres is due to Lesk.[15] Since the paper contains a few errors, a short corrected version shall be given now. From (3) and (9) it follows that

$$Q_N[V] = \int_V \cdots \int_V d\mathbf{r}_1 \cdots d\mathbf{r}_N \prod_{1 \leqslant i < j \leqslant N} \Theta(r_{ij} - \sigma) \quad (11a)$$

$$Q_{N+1}[V] = \int_V \cdots \int_V d\mathbf{r}_1 \cdots d\mathbf{r}_N$$

$$\times \left\{ \prod_{1 \leqslant i < j \leqslant N} \Theta(r_{ij} - \sigma) \left[\int_V d\mathbf{r}_{N+1} \prod_{k=1}^{N} \Theta(r_{k,N+1} - \sigma) \right] \right\}$$

$$= \int_V \cdots \int_V d\mathbf{r}_1 \cdots d\mathbf{r}_N \left\{ \prod_{1 \leqslant i < j \leqslant N} \Theta(r_{ij} - \sigma) V_a(1, \ldots, N) \right\} \quad (11b)$$

$V_a(1, \ldots, N)$ is the accessible volume, i.e., the volume accessible to another particle in the presence of N particles at the positions $\mathbf{r}_1, \ldots, \mathbf{r}_N$. $V_a(1, \ldots, N)$ may be written[11] in terms of intersections of spheres with

radius σ, cf. Fig. 4:

$$V_a(1,\ldots,N) = V - \sum_{i=1}^{N} I(i) + \sum\sum_{1\leqslant i<j\leqslant N} I(i,j) - \sum\sum\sum_{1\leqslant i<j<k\leqslant N} I(i,j,k) + \cdots \tag{12a}$$

$$V_a(1,2) = V - 2I(1) + I(1,2) \tag{12b}$$

$$V_a(1,2,3) = V - 3I(1) + I(1,2) + I(1,3) + I(2,3) - I(1,2,3) \tag{12c}$$

Since the volume of each sphere is the same, it follows that $\sum I(i) = NI(1)$ for any configuration. From (11b) it follows that

$$Q_{N+1}[V] = \{V - NI(1)\}\, Q_N[V] + \binom{N}{2} V \int_{r_{12}\geqslant\sigma} d\mathbf{r}_2\, I(1,2) Q_{N-2}[V_a(1,2)] - \binom{N}{3} V \int\int_{\substack{r_{ij}\geqslant\sigma \\ 1\leqslant i<j\leqslant 3}} d\mathbf{r}_2\, d\mathbf{r}_3\, I(1,2,3) Q_{N-3}[V_a(1,2,3)] + \cdots \tag{13}$$

To obtain (13), the same simplifications have been used as to get (4), i.e., symmetry arguments (change of variables) and the neglect of surface effects. If N is high, it follows that $V \gg I(1)$. Thus, it seems to be justified that $Q_{N-k}[V_a(1,\ldots,k)]$ can be substituted by $Q_{N-k}[V]$; compare Eqs. (12). This yields

$$Q_{N+1}[V] = \{V - NI(1)\}\, Q_N[V] + V\left\{\binom{N}{2} Q_{N-2}[V] \int_{r_{12}\geqslant\sigma} d\mathbf{r}_2\, I(1,2) - \binom{N}{3} Q_{N-3}[V] \int\int_{r_{ij}\geqslant\sigma} d\mathbf{r}_2\, d\mathbf{r}_3\, I(1,2,3) + \cdots\right\} \tag{14}$$

This is a recursion relation for $Q_N[V]$. To solve it, we assume that $Q_N[V]$ is only a function of V (the measure of the volume) and not of the shape of the volume. Then, from (14) $Q_N[V]$ can be determined as a double power series in N and V. Knowing $Q_N[V]$, it is possible to calculate the virial coefficients, cf. Eqs. (4) and (5). If this is done, it turns out that B_2 and B_3 are given correctly for hard disks and spheres, but that B_4 is wrong. Therefore, we have to go further than Lesk and start again with (13). It is possible to solve (13) directly without substituting $Q_{N-k}[V]$ for $Q_{N-k}[V_a(1,\ldots,k)]$. Again it is necessary to assume that $Q_N[V]$ is not a function of the shape of the volume (neglect of surface effects). Then, the structure of the recursion relation (13) induces that $Q_N[V]$ can be represented in the following way:

$$Q_N[V] = V^N \sum_{m=-\infty}^{\infty} G_m(N) V^{-m} = V^N \sum_{m=0}^{N} G_m(N) V^{-m} \tag{15}$$

The coefficients $G_m(N)$ will be specified below. The equality of the two sums corresponds to the fact that $G_m(N) = 0$ if $m > N$ or $m < 0$. The ideal gas ($f_{ij} = 0$) yields $Q_N[V] = V^N$; see (3). Thus $G_0(N) = 1$ for any N, the other $G_m(N)$ vanish for the ideal gas. Combining (13) and (15) yields

$$\begin{aligned} G_m(N+1) = {} & G_m(N) - NI(1)G_{m-1}(N) \\ & + \binom{N}{2}\int_{r_{12}\geq\sigma} d\mathbf{r}_2 I(1,2) \sum_{h=0}^{m-2} \binom{N-2}{h} G_{m-h-2}(N-2) \\ & \times \left[-2I(1) + I(1,2)\right]^h \\ & - \binom{N}{3}\int\int_{r_{ij}\geq\sigma} d\mathbf{r}_2 d\mathbf{r}_3 I(1,2,3) \sum_{h=0}^{m-3} \binom{N-3}{h} G_{m-h-3}(N-3) \\ & \times \left[-3I(1) + I(1,2) + I(1,3) + I(2,3) - I(1,2,3)\right]^h \\ & + \cdots \end{aligned} \tag{16}$$

For any m, (16) contains only a finite number of terms. For instance,

$$G_0(N+1) - G_0(N) = 0 \tag{17a}$$

$$G_1(N+1) - G_1(N) = -NI(1)G_0(N) \tag{17b}$$

$$G_2(N+1) - G_2(N) = -NI(1)G_1(N) + \binom{N}{2}\int_{r_{12}\geq\sigma} d\mathbf{r}_2 I(1,2)G_0(N-2) \tag{17c}$$

$$\begin{aligned} G_3(N+1) - G_3(N) = {} & -NI(1)G_2(N) + \binom{N}{2}\int_{r_{12}\geq\sigma} d\mathbf{r}_2 I(1,2)F \\ & - \binom{N}{3}\int\int_{r_{ij}\geq\sigma} d\mathbf{r}_2 d\mathbf{r}_3 I(1,2,3)G_0(N-3) + \cdots \end{aligned} \tag{17d}$$

$$F \equiv (N-2)\left[-2I(1) + I(1,2)\right]G_0(N-2) + G_1(N-2)$$

Thus, $G_m(N+1) - G_m(N)$ is expressed as a function of $G_0(N)$, $\ldots, G_{m-1}(N)$. From (3) it follows that $Q_1[V] = \int d\mathbf{r}_1 = V$ for any potential, i.e., $G_0(1) = 1$ and $G_m(1) = 0$, $m > 0$. $G_0(1) = 1$ gives together with (17a) the result $G_0(N) = 1$ for any N. This is the starting point of the recursion. Furthermore, it is easy to obtain $G_m(N)$ from the knowledge of $G_m(N+1) - G_m(N)$:

$$m > 0 : \{G_m(1) = 0\} \Rightarrow \left\{ G_m(N) = \sum_{N'=1}^{N-1} \left[G_m(N'+1) - G_m(N')\right], N > 1 \right\} \tag{18}$$

$G_m(N)$ comes out as a power series in N (highest power: $2m$). Therefore, $Q_N[V]$ of D-dimensional hard spheres is represented at last by a double power series in N and V, the coefficients—apart from trivial numbers—being cluster integrals of the form $CI(k,l)$:

$$CI(k,l) = \int_{\substack{r_{ij} \geqslant \sigma \\ 1 \leqslant i < j \leqslant k}} \cdots \int d\mathbf{r}_2 \cdots d\mathbf{r}_k (-1)^k I(1,2,\ldots,k) \times \prod_{(l-k-1)} (-1)^{n_q} I(n_1,\ldots,n_q) \qquad (19)$$

$$1 \leqslant n_1 < \cdots < n_q \leqslant k, \qquad q > 1$$

or products of such integrals. $(l-k-1)$ beneath the product sign means that there are $(l-k-1)$ factors of the type $I(n_1,\ldots,n_q)$. The same $CI(k,l)$ also occur in the virial coefficients; cf. (4), (5). For D-dimensional hard spheres, it is easy to know whether $CI(k,l)$ vanishes or not. For instance, it is not possible that more than five disks have an intersection $\neq 0$ with $r_{ij} \geqslant \sigma$ for all pairs i,j.[11,15] Thus, $CI(k,l) = 0$ if and only if $k > 5$. The corresponding numbers[11] for rods ($D = 1$) and spheres ($D = 3$) are 2 and 12, respectively. This means for instance that for hard rods the expansion (16) stops with the term $\binom{N}{2}\int \cdots$ since the subsequent terms consist only of integrals of the type $CI(k,l), k > 2$, which are all zero. Equivalently, (16) stops with $-\binom{N}{5}\int \cdots$ for disks and with $+\binom{N}{12}\int \cdots$ for spheres.

Lesk tried to develop virial coefficients for hard disks and spheres. If one checks the derivation of his (corrected) results, one can see that it is a general formalism. If one uses f and $\tilde{f}$, Eq. (2), instead of Θ functions, Eq. (9), all steps remain valid. One has to insert the graphs shown in Fig. 4 instead of the hard-sphere interpretation $(-1)^q I(1,2,\ldots,q)$. The restriction $r_{ij} \geqslant \sigma$, $1 \leqslant i < j \leqslant k$, in the term $(-1)^k \binom{N}{k}\int \cdots$ of (16) turns into $\tilde{f}$ bonds between each pair of the variables $1,2,\ldots,k$. Thus the Lesk formalism gives at last a general graph expansion of virial coefficients which is different from the Mayer and RH graph expansions. The general graph theoretical description of $CI(k,l)$ is as follows: $CI(k,l)$ has l corners ($l \geqslant 2$), one of them (e.g., corner 1) being a white circle, the others are black circles. If $l = 2$, then $k = 1$. If $l > 2$, then $1 < k < l$. Each pair of the corners $1,\ldots,k$ is connected by a $\tilde{f}$ bond. The remaining $l-k$ corners are not connected among themselves, but are connected by f bonds with at least two (one if $k = 1$) corners out of the first k corners. At least one of the corners $k+1,\ldots,l$ is connected with all corners $1,2,\ldots,k$. Such a graph will be called an overlap graph of the first kind. "First kind" refers to the last restriction mentioned, "overlap graph" refers to the simple interpre-

tation in the case of overlapping spheres, Eq. (19). Explicit results of this graph expansion will be given in the next section.

5. EXPLICIT RESULTS

The (products of) overlap graphs of the first kind which contribute to B_n, $n \leqslant 4$, are exhibited in Fig. 5. They are of the type $CI(k,n)$, $k \leqslant n-1$, or products of $CI(k_i,n_i)$ with $k_i \leqslant n_i - 1$, $\sum(n_i - 1) = n - 1$. Since all pairs of corners $1, \ldots, k$ are connected by $\tilde{f}$ bonds (dotted lines), a simplified drawing (the points $1, \ldots, k$ lying on one dotted line) is possible and will be used in the following. The cluster integrals $CI(k,n)$ are denoted $[m]_n$ if $(m)_n$ is the Mayer graphs with n corners which is generated by replacing all $\tilde{f}$ bonds in $CI(k,n)$ by f bonds. The designation of products, e.g., $[1]_2^2 = [1]_2[1]_2$, is analogous.

Graph $[2]_4$ is not obtained using the recursion relation (14) instead of (16). Thus, (14) yields an incorrect B_4 as mentioned above. Relation (16), however, yields all overlap graphs of the first kind and leads to a correct fourth virial coefficient. The number dependence $B_4(N)$ is also given correctly, see below. All (products of) overlap clusters with n corners really contribute to B_n.

The expansion of the graphs shown in Fig. 5 in terms of Mayer graphs yields:

$$\underline{n=2}: \quad [1]_2 = (1)_2 \tag{20}$$

$$\underline{n=3}: \quad [1]_3 = (1)_3 \tag{21a}$$

$$[1]_2^2 = (1)_2^2 \tag{21b}$$

$$\underline{n=4}: \quad [2]_4 = (1)_4 + (2)_4 \tag{22a}$$

$$[3]_4 = 3(2)_4 + (3)_4 + 3(1)_2(1)_3 + (1)_2^3 \tag{22b}$$

$$[1]_2[1]_3 = (1)_2(1)_3 + (1)_2^3 \tag{22c}$$

$$[1]_2^3 = (1)_2^3 \tag{22d}$$

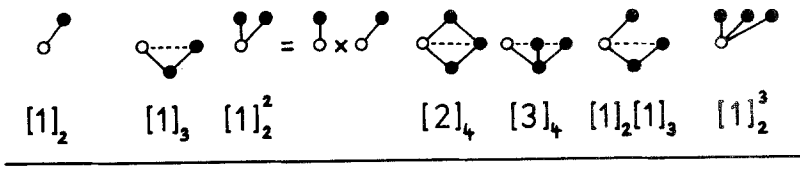

Fig. 5. Overlap graphs of the first kind (and their products) which contribute to B_2, B_3, and B_4.

Table I. Cluster Values of D-Dimensional Parallel Hard Cubes. The (Products of) Overlap Graphs up to $n = 4$ are Exhibited

		Rods	Squares	Cubes
n	(Products of) Overlap Graphs	$3\times$ value$/B_2^{n-1}$	$12\times$ value$/B_2^{n-1}$	$432\times$ value$/B_2^{n-1}$
2	$[1]_2$	-6	-24	-864
3	$[1]_3$	3	21	999
	$[1]_2^2$	12	48	1 728
4	$[2]_4$	2	10	338
	$[3]_4$	0	-8	-708
	$[1]_2[1]_3$	-6	-42	$-1\,998$
	$[1]_2^3$	-24	-96	$-3\,456$

The explicit values for these graphs in the case of D-dimensional parallel hard cubes are shown in Table I. They are based on the Mayer graph values which are known analytically up to $n = 7$.[3] Now we turn to the explicit representation of $B_n(N)$, $n \leqslant 4$, via overlap graphs of the first kind. To do this, we start with $G_m(N)$, Eq. (15). Combination of (17) and (18) yields

$$G_0(N) = 1 \tag{23a}$$

$$G_1(N) = \tfrac{1}{2}[1]_2(N^2 - N) \tag{23b}$$

$$G_2(N) = \tfrac{1}{6}[1]_3(N^3 - 3N^2 + 2N) + \tfrac{1}{24}[1]_2^2(3N^4 - 10N^3 + 9N^2 - 2N) \tag{23c}$$

$$G_3(N) = \tfrac{1}{8}[2]_4(N^4 - 6N^3 + 11N^2 - 6N) + \tfrac{1}{24}[3]_4(N^4 - 6N^3 + 11N^2 - 6N) + \tfrac{1}{24}[1]_2[1]_3(2N^5 - 11N^4 + 16N^3 - N^2 - 6N) + \tfrac{1}{48}[1]_2^3(N^6 - 7N^5 + 17N^4 - 17N^3 + 6N^2) \tag{23d}$$

Comparison of the expansion of $Q_N[V]$ in powers of V, Eq. (15), with the virial expansion, Eq. (5a), results in relations between the $G_m(N)$ and the $B_n(N)$, cf. (4):

$$B_2(N) = -G_1(N)/N^2 \tag{24a}$$

$$B_3(N) = -\{G_2(N) - G_1^2(N)\}/N^3 \tag{24b}$$

$$B_4(N) = -\{G_3(N) - 3G_1(N)G_2(N) + G_1^3(N)\}/N^4 \tag{24c}$$

Thus, from the known $G_m(N)$, Eqs. (23), it follows that

$$B_2 = -\tfrac{1}{2}[1]_2, \qquad B_2(N) = (1-w)B_2 \tag{25a}$$

$$B_3 = -\tfrac{1}{3}[1]_3, \qquad B_3(N) = (1-w)(1-2w)B_3 + 2w(1-w)B_2^2 \tag{25b}$$

$$B_4 = -\tfrac{1}{8}\{3[2]_4 + [3]_4 - 3[1]_2[1]_3 + 2[1]_2^3\}$$

$$B_4(N) = (1-w)(1-2w)(1-3w)B_4 + 9w(1-w)(1-2w)B_2B_3 - 4w(1-w)(1-3w)B_2^3 \tag{25c}$$

w being $(1/N)$. Developing the overlap graphs of the first kind in Mayer graphs, Eqs. (20)–(22), confirms the correct representation[3] of B_2, B_3, and B_4. The $B_n(N)$ are also given correctly[6] up to $n = 4$. The (products of) overlap graphs of the first kind yielding B_5 are shown in Fig. 6. The graph $[5]_5$ is not an overlap graph of the first kind and will be treated later. As to $[7]_5$, the first of three equivalent representations (Fig. 6) is chosen from now on. $G_4(N)$ and $B_5(N)$ can be evaluated in the same manner as above, Eqs. (23)–(25). The result is that $B_5(N)$ does not come out correctly:

$$B_5^{\text{Lesk}}(N) - B_5^{\text{exact}}(N) = \tfrac{1}{5}(1-w)(1-2w)(1-3w)(1-4w) \times \{2(1)_5 + 6(2)_5 + 4(5)_5 + (6)_5 + (7)_5 + 2(1)_2^2(1)_3 + 2(1)_3^2\} \tag{26}$$

Thus, even the corrected and improved Lesk formalism fails, and it fails for an interesting reason: The only approximation used was the assumption that $Q_N[V]$ is only a function of V and not of the shape of the volume; see Section 4. This is a problem closely related to the volume-dependent correction of virial coefficients[7] mentioned in Section 1. However, this

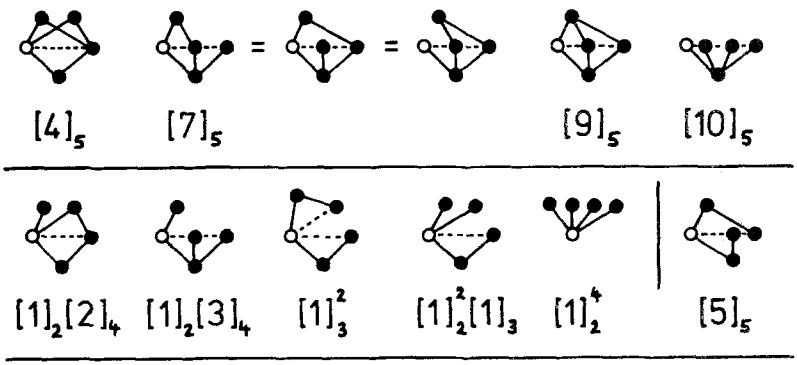

Fig. 6. Overlap graphs and their products contributing to B_5.

latter correction vanishes in the thermodynamic limit, while the discrepancy between B_5^{Lesk} and B_5^{exact} does not. Even if V goes to infinity, the shape of the volume excluded, e.g., by particles 1, 2, and 3 remains a function of the actual locations of these particles. It is well conceivable that the differences between B_n^{Lesk} and B_n^{exact} will throw more light on the volume dependence of virial coefficients which is not yet well known.

The fact that B_5^{Lesk} is the first incorrect virial coefficient can be explained for hard spheres as follows: The shape of the volume common to two intersecting spheres (radius σ) is determined by its measure $[V - V_a(1,2)] = [2I(1) - I(1,2)]$. On the other hand, it is possible to locate three spheres in different ways yielding the same volume $[V - V_a(1,2,3)]$. Thus, neglecting the shapes of volumes starts to be crucial with the term $-\binom{N}{3}V\int \cdots$ in Eq. (13), which contains $Q_{N-3}[V_q(1,2,3)]$. However, the first approximation to $Q_{N-3}[V_a(1,2,3)]$ is $Q_N[V]$. Thus, the coefficients $G_m(N)$ up to $G_3(N)$, Eqs. (16) and (17), are not affected by the above-mentioned neglect. Equations (24) show that this induces B_n^{Lesk} to be correct up to $n = 4$. This is no longer the case from B_5^{Lesk} on.

6. THE CORRECT OVERLAP GRAPH REPRESENTATION OF B_5

The result of Section 5 concerning B_5 seems to be discouraging. However, it is possible to obtain the correct fifth virial coefficient by generalizing the definition of overlap graphs. B_6 and B_7 will be considered in the next section.

First, we analyze the discrepancy between B_5^{Lesk} and B_5^{exact} further. That B_5^{Lesk} is not correct can be seen from a simple fact (cf. Fig. 6): None of the four overlap graphs of the first kind $[4]_5, [7]_5, [9]_5$, and $[10]_5$ yield $(1)_5$ if they are expanded in Mayer graphs. Since $(1)_5$ occurs in B_5, Eq. (7d), B_5^{Lesk} cannot be correct except for the hypothetical existence of a relation among the $(m)_5$ valid for any potential.

The restriction which specified the "first kind" of an overlap graph was the requirement that at least one corner out of $k+1, \ldots, n$ is connected with all corners $1, \ldots, k$ by f bonds. In the following, we define a (generalized) overlap graph by replacing the above restriction by a weaker one. It is now only required that each of the corners $1, \ldots, k$ has a f bond to one or more of the corners $k+1, \ldots, n$. A check of the overlap graphs up to $n = 4$ yields that they are automatically of first kind. For $n = 5$, however, there exists one overlap graph which is not of first kind, see Fig. 6. It is called $[5]_5$ using the same numbering rule as for overlap graphs of the first kind, Section 5. Expansion in Mayer graphs yields

$$[5]_5 = (1)_5 + 2(2)_5 + (5)_5 + (1)_3^2 + 2(1)_2^2(1)_3 + (1)_2^4 \tag{27}$$

Table II. Cluster Values of D-Dimensional Hard Cubes, $n = 5$

(Products of) Overlap Graphs	Rods $6 \times$ value$/B_2^4$	Squares $1152 \times$ value$/B_2^4$	Cubes $221\,184 \times$ value$/B_2^4$
$[4]_5$	3	558	77 868
$[5]_5$	3	2 735	1 034 319
$[7]_5$	0	− 359	− 119 619
$[9]_5$	0	120	31 440
$[10]_5$	0	102	160 878
$[1]_2[2]_4$	− 8	− 1 920	− 346 112
$[1]_2[3]_4$	0	1 534	724 992
$[1]_3^2$	6	3 528	1 182 816
$[1]_2^2[1]_3$	24	8 064	2 045 952
$[1]_2^4$	96	18 432	3 538 944

Thus, $(1)_5$ is occurring now. In fact, the difference between B_5^{Lesk} and B_5^{exact}, Eq. (26), can be represented in overlap graphs when including $[5]_5$:

$$B_5^{\text{Lesk}} - B_5^{\text{exact}} = \tfrac{1}{5}\{2[5]_5 + [7]_5 - [1]_2[2]_4 - 2[1]_2^2[1]_3\} \tag{28}$$

By the way, the lack of $[5]_5$ in the Lesk formalism does not change $B_5(N)$ as long as $N \leqslant 4$, see Eq. (26). This is consistent with the fact that clusters with five variables do not come in as long as there are not more than four particles. The correct B_5 expressed in overlap graphs is

$$B_5 = -\tfrac{1}{30}\{6[4]_5 + 12[5]_5 + 18[7]_5 + 4[9]_5 + [10]_5 - 18[1]_2[2]_4 - 4[1]_2[3]_4 - 15[1]_3^2 + 12[1]_2^2[1]_3 - 6[1]_2^4\} \tag{29}$$

The analytical values of the (products of) overlap clusters contributing to B_5 are exhibited in Table II for D-dimensional parallel hard cubes.[3] Furthermore, the numerical values of all (products of) overlap clusters up to $n = 5$ are shown in Table III for D-dimensional hard cubes and spheres.[3,9,12] To facilitate the comparison, all values are exhibited in the units $(2B_2)^{n-1}$ in Table III. Thus, $[1]_2^{n-1}$ has the absolute value 1 for all n and potentials. All numbers are exact within the given digits apart from $[10]_5$, spheres, which has an uncertainty of ± 0.0000025. In most cases, the small difference between the results for spheres and cubes of the same dimension is remarkable. For rods, the clusters with zero value are of the type $CI(k,l), k > 2$; compare (19). These graphs have small absolute values for the other potentials included in Table III.

Table III. (Products of) Overlap Graphs up to $n = 5$. Comparison of the Cluster Values of D-dimensional Hard Cubes and Spheres in Units of $(2B_2)^{n-1}$

n	(Products of) Overlap Graphs	Rods	Squares	Disks	Cubes	Spheres
2	$[1]_2$	−1	−1	−1	−1	−1
3	$[1]_3$	0.2500 000	0.4375 000	0.4134 967	0.5781 250	0.5312 500
	$[1]_2^2$	1	1	1	1	1
4	$[2]_4$	0.0833 333	0.1041 667	0.0953 836	0.0978 009	0.0876 860
	$[3]_4$	0	−0.0833 333	−0.0588 725	−0.2048 611	−0.1437 575
	$[1]_2[1]_3$	−0.2500 000	−0.4375 000	−0.4134 967	−0.5781 250	−0.5312 500
	$[1]_2^3$	−1	−1	−1	−1	−1
5	$[4]_5$	0.0312 500	0.0302 734	0.0262 356	0.0220 032	0.0182 704
	$[5]_5$	0.0312 500	0.1483 833	0.1302 261	0.2922 677	0.2433 175
	$[7]_5$	0	−0.0194 770	−0.0134 584	−0.0338 008	−0.0234 830
	$[9]_5$	0	0.0065 104	0.0041 804	0.0088 840	0.0059 230
	$[10]_5$	0	0.0055 339	0.0013 037	0.0454 593	0.0179 273
	$[1]_2[2]_4$	−0.0833 333	−0.1041 667	−0.0953 836	−0.0978 009	−0.0876 860
	$[1]_2[3]_4$	0	0.0833 333	0.0588 725	0.2048 611	0.1437 575
	$[1]_3^2$	0.0625 000	0.1914 063	0.1709 795	0.3342 285	0.2822 266
	$[1]_2^2[1]_3$	0.2500 000	0.4375 000	0.4134 967	0.5781 250	0.5312 500
	$[1]_2^4$	1	1	1	1	1

Table IV. Hard-Disk Values of the Overlap Clusters Contributing to B_5

Cluster	Value/B_2^{n-1}	Cluster	Value/B_2^4
$[1]_2$	−2	$[4]_5$	0.4197 6985 76
$[1]_3$	1.6539 8686 63	$[5]_5$	2.0836 1785 3(2)[a]
$[2]_4$	0.7630 6855 23	$[7]_5$	−0.2153 3487 (2)
$[3]_4$	−0.4709 8023 05	$[9]_5$	0.0668 8661 6(2)
		$[10]_5$	0.0208 59(1)

[a]The number in parentheses denotes the uncertainty of the last digit.

The overlap graph representation makes it possible to determine for instance B_5 (hard disks) with an improved accuracy. The five products occurring in (29) are known analytically since this is the case for all Mayer clusters[16] up to $n = 4$. $[4]_5$ is also known analytically since $[4]_5 = (3)_5 + (4)_5$, the values of both Mayer graphs being known.[9] Using simplifications analogous to Ref. 9, $[5]_5$, $[7]_5$, and $[9]_5$ can be evaluated directly by at most threefold numerical integration, the integrand being for instance $I^2(1,2,3)$ for $[9]_5$. $[10]_5$ is a fivefold integral with the integrand $I(1,2,3,4)$. However, a more accurate estimate follows from the fact[4] that $\langle 3 \rangle_5 = 0$ for hard disks, cf. Fig. 3. Inserting the best values for the Mayer graphs[9] yields $[10]_5$. Table IV shows the resulting values of the overlap clusters contributing to B_5 for hard disks. It follows that B_5/B_2^4 is $0.33355604 \pm 0.00000004$. This may be compared with the best value up to now,[9] 0.3335561, the last digit being uncertain. The improvement in accuracy comes from the direct calculation of $[5]_5$, $[7]_5$, and $[9]_5$. The main error of B_5 is due to $[10]_5$.

7. DISCUSSION

We will compare now several properties of Mayer graphs $S_i(n)$, RH graphs $\tilde{S}_j(n)$, and (products of) overlap graphs with n corners. The properties of overlap clusters have only been confirmed up to $n = 5$ so far. As for B_6 and B_7, see below.

All Mayer and overlap graphs with n corners contribute to B_n. This is not the case for the $\tilde{S}_j(n)$. No products of clusters occur in the graph expansion of B_n: This is true for $S_i(n)$ and $\tilde{S}_j(n)$, but not for the overlap clusters where all possible products occur. All three graph expansions can represent the virial coefficients. The number of $S_i(n)$ and $\tilde{S}_j(n)$ is the same, the number of overlap clusters is smaller for $n > 3$.

The coefficient of a Mayer graph in the expansion of B_n follows directly from the symmetry[1,3] of the graph. On the other hand, the coefficients of $\tilde{S}_j(n)$ have to be evaluated indirectly[4,5] from the known

coefficients of $S_i(n)$ and the transformation $S_i(n) \rightarrow \tilde{S}_j(n)$. Using a simple criterion,[1] however, one can determine most of the RH clusters that are not occurring in B_n, i.e., with a coefficient $= 0$. As to overlap clusters, the direct way from $Q_N[V]$ to the B_n via the Lesk formalism is no longer valid from B_5 on. Therefore, one has to choose also the indirect way for overlap graphs as in the case of $\tilde{S}_j(n)$. The expansion of overlap graphs in terms of Mayer graphs up to $n = 4$ is exhibited in Eqs. (20) to (22); the transformation tables up to $n = 6$ are given in Ref. 17.

Table V shows the number of Mayer, RH, and (products of) overlap graphs with n corners up to $n = 7$. It is by no means evident that the relatively small number of overlap clusters makes it possible to express B_6 and B_7 properly. However, we will formulate the following conjecture: It is possible to express B_n for any n in terms of overlap graphs, and also the other above-mentioned properties of overlap graphs are valid for any n. This conjecture was the starting point to determine the coefficients of the overlap graphs for B_6 and B_7 in the described indirect way. This will be treated in another publication; the main result is: The above conjecture turns out to be true for $n = 6$ and 7. For $n \leqslant 5$, it is known to be valid from the present paper. Table V shows that the graph expansion in terms of overlap graphs is the simplest one. The occurring products do not matter since they are already known from the knowledge of lower virial coefficients. Apart from the number, the structure of the overlap graphs is advantageous. It is easy to write down all overlap graphs up to $n = 7$ without much meditation, which would be impossible for Mayer or RH graphs. For example, Fig. 7 shows all overlap graphs of the first kind $CI(3, n)$, cf. Eq. (19), up to $n = 7$. Finally, we will discuss the merits of the overlap graph expansion for hard disks and spheres. The smaller number of graphs helps to improve the accuracy of B_n. In RH graphs, each pair of corners is connected by a f or $\tilde{f}$ bond which makes Monte Carlo integration necessary for any $\tilde{S}_j(n)$ with $n \geqslant 5$.[4,5] The simpler structure of overlap

Table V. Comparison of the Number of Overlap, Mayer, and RH Graphs Occurring in B_n

n	Overlap graphs	Products of overlap graphs	Total	Mayer graphs	RH graphs
2	1	0	1	1	1
3	1	1	2	1	1
4	2	2	4	3	2
5	5	5	10	10	5
6	14	12	26	56	23
7	44	35	79	468	171

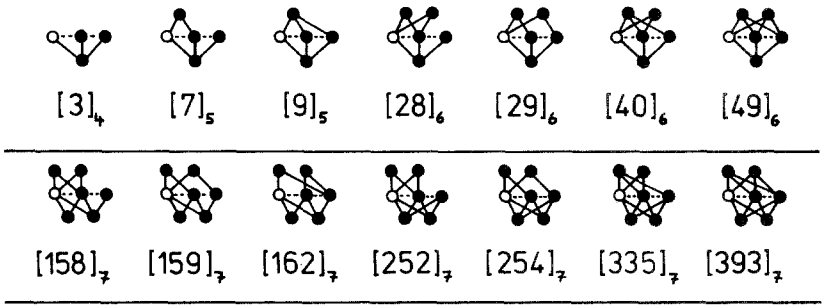

Fig. 7. Overlap graphs of the first kind $CI(3,n)$ up to $n = 7$; cf. Eq. (19).

graphs makes it possible to interpret any of them as the integral over (products of) intersections. The graphs shown in Fig. 7 contain intersections of at most three disks or spheres. These clusters can be evaluated by threefold numerical integration. Since the integral regions[11] of variable 3 are only determined by $I(1,2,3)$, all integrals shown in Fig. 7 can be calculated at once. The validity of the corresponding computer program can easily be checked since the first graph, $[7]_5$, is known accurately; see Table IV. Furthermore, it is of advantage that the most complicated overlap graphs have small absolute values. For instance, all graphs $CI(3,n)$ shown in Fig. 7 are of zero value for hard rods since $k > 2$, cf. Eq. (19). Correspondingly, all $CI(k,n)$ with $k > 5$ vanish for hard disks, and all $CI(5,n)$ which necessitate Monte Carlo integration are very small. Thus, the overlap graph expansion seems to be promising not only from a general point of view, but also for specific potentials.

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REFERENCES

1. J. E. Kilpatrick, *Adv. Chem. Phys.* **20**:39 (1971).
2. N. G. van Kampen, *Physica* **27**:783 (1961).
3. W. G. Hoover and A. G. De Rocco, *J. Chem. Phys.* **36**:3141 (1962).
4. F. H. Ree and W. G. Hoover, *J. Chem. Phys.* **40**:939 (1964).
5. F. H. Ree and W. G. Hoover, *J. Chem. Phys.* **46**:4181 (1967).
6. J. B. Hubbard, *J. Comput. Phys.* **7**:502 (1971).

7. J. L. Lebowitz and J. K. Percus, *Phys. Rev.* **124**:1673 (1961).
8. K. W. Kratky, *J. Comput. Phys.* **37**:205 (1980).
9. K. W. Kratky, *Physica* **85A**:607 (1976).
10. J. S. Rowlinson, *Proc. R. Soc. (London) Ser. A* **279**:147 (1964).
11. K. W. Kratky, *J. Stat. Phys.* **25**:619 (1981).
12. K. W. Kratky, *Physica* **87A**:584 (1977).
13. K. W. Kratky, *J. Chem. Phys.* **69**:2251 (1978).
14. K. W. Kratky, *J. Phys. A* **11**:1017 (1978).
15. A. M. Lesk, *J. Chem. Phys.* **63**:5048 (1975).
16. J. S. Rowlinson, *Mol. Phys.* **7**:593 (1964).
17. K. W. Kratky, *Sitzungsber. Österr. Akad. Wiss., Abt. II*, **190**:231 (1981).