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Overlap Graph Representation of B_6 and B_7

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The virial coefficients B_n of the pressure of a thermodynamic system can be represented in terms of graphs. The recently defined overlap graphs are studied in detail. Furthermore, the overlap graph representation of the sixth and seventh virial coefficients (B_6 and B_7) is determined.

KEY WORDS: Statistical mechanics; virial coefficients; cluster integrals; graph expansions; Mayer graphs; overlap graphs.

1. INTRODUCTION

A new type of graphs representing virial coefficients has been introduced recently.[1] The virial coefficients B_n are defined by

$$P/(\rho k_B T) = 1 + \sum_{n=2}^{\infty} B_n \rho^{n-1} \tag{1}$$

P is the pressure, ρ the number density, k_B Boltzmann's constant, and T the absolute temperature. The thermodynamic limit is considered. The overlap graphs contributing to B_2 and B_3 are the integrals

$$\begin{aligned} [1]_2 &= \int f_{12}\, d\mathbf{r}_2 \\ [1]_3 &= \int \tilde{f}_{12} f_{13} f_{23}\, d\mathbf{r}_2\, d\mathbf{r}_3 \end{aligned} \tag{2}$$

The expressions "clusters," "(cluster) integrals" and "graphs" are understood to be synonymous. f_{ij} is the usual Mayer f function, $\tilde{f}_{ij}$ the modified f

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Fig. 1. Overlap graphs up to five corners.

function,[2]

$$\tilde{f}_{ij} = f_{ij} + 1 = \exp[-u_{ij}/(k_B T)] \tag{3}$$

$u_{ij} = u(r_{ij})$ being the spherically symmetric pair interaction energy. Figure 1 displays the overlap graphs contributing to B_n, $n \leqslant 5$. The corners (circles) correspond to the integral variables [cf. (2)]. All circles but one are black. Over the black circles it is integrated. The white circle, without loss of generality variable 1, is held fixed. A solid bond between two corners i, j symbolizes f_{ij}, a dotted line $\tilde{f}_{ij}$. No bond between i and j just corresponds to the factor 1 in the integrand. Compare the two ways of presentation of $[1]_2$ and $[1]_3$ in Eq. (2) and Fig. 1. The term *overlap graph* comes from its geometrical interpretation for hard-core potentials.[1]

Definition 1.1. An overlap graph is a simple graph with l corners, $l \geqslant 2$. Corner 1 is a white circle, the others are black circles. If $l = 2$, an f-bond connects corners 1 and 2. If $l > 2$, there are two types of corners. Type A: $1, \ldots, k$; type B: $k+1, \ldots, l$ $(1 < k < l)$. Each pair of corners of type A is connected by an $\tilde{f}$ bond. The corners of type B are not connected among themselves. However, each of them is connected by f bonds with at least two corners of type A. Finally, no corner of type A is disconnected from all corners of type B.

The case $l = 2$ formally corresponds to $k = 1$ (cf. Fig. 1). The above definition will be discussed in Section 2. Since all corners of type A are connected with each other by $\tilde{f}$ bonds, the simplified representation chosen in Fig. 1 is possible, the corners $1, \ldots, k$ lying on a dotted line.

In the well-known Mayer graphs, no $\tilde{f}$ bonds occur. It follows from the definition of an overlap graph that it becomes a Mayer graph if all $\tilde{f}$ bonds are replaced by f bonds.[1] Moreover, only one overlap graph turns into a given Mayer graph. Thus, they correspond to each other. As to the designation, an overlap graph with l corners is called $[m]_l$ if the corresponding Mayer graph is $(m)_l$, the numbering of Mayer graphs being due to Ref. 3.

B_2 to B_5 can be represented via overlap graphs as follows[1]:

$$-2B_2 = [1]_2$$
$$-3B_3 = [1]_3$$
$$-8B_4 = 3[2]_4 + [3]_4 - 3[1]_2[1]_3 + 2[1]_2^3 \tag{4}$$
$$-30B_5 = 6[4]_5 + 12[5]_5 + 18[7]_5 + 4[9]_5 + [10]_5$$
$$- 18[1]_2[2]_4 - 4[1]_2[3]_4 - 15[1]_3^2 + 12[1]_2^2[1]_3 - 6[1]_2^4$$

Generally, B_n is represented by (products of) overlap graphs $[m]_l$, $l \leqslant n$. It is the aim of the present paper to find out the overlap graph representation of B_6 and B_7.

2. OVERLAP GRAPHS OF THE FIRST, SECOND, AND THIRD KIND

The starting point for using overlap graphs was an expansion of the canonical partition function,[1,4] the system being confined within a volume V. Assume that the partition function does not depend on the shape of the volume. Taking the thermodynamic limit, this results in virial coefficients[1] which are correct up to B_4 but false for higher B_n. The graphs occurring in this expansion are overlap graphs of the first kind.

Definition 2.1. Overlap graphs of the first kind are special overlap graphs. The last condition of Definition 1.1, "no corner of type A is disconnected from all corners of type B" has to be replaced by the stronger restriction. "At least one corner of type B is connected with all corners of type A."

All overlap graphs displayed in Fig. 1 are of first kind except for $[5]_5$. Thus, B_5 cannot be represented by overlap graphs of the first kind only. This was the reason to generalize the concept of overlap graphs. The last restriction of Definition 1.1 is necessary since an unique representation of B_n is intended. This restriction being dropped, a graph like g in Fig. 2 results. Using Eq. (3), i.e., replacing $\tilde{f}_{13}$ by $(f_{13} + 1)$ and $\tilde{f}_{23}$ by $(f_{23} + 1)$, a sum in terms of known overlap graphs results. Thus g can be replaced by

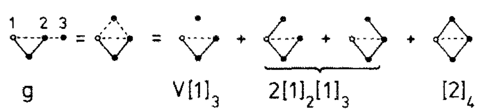

Fig. 2. Expansion of graph g in terms of overlap graphs.

overlap graphs. Additionally, g is infinite in the thermodynamic limit, which might be avoided by taking

$$g - V[1]_3 = 2[1]_2[1]_3 + [2]_4 \tag{5}$$

Figure 2 also explains the restriction of Definition 1.1 that each of the corners of type B is connected by f bonds with at least two corners of type A. If this is not the case, either clusters of infinite value ($V[1]_3 \to \infty$) or products of overlap graphs ($[1]_2[1]_3$) occur.

If $(f_{ij} + 1)$ is inserted instead of $\tilde{f}_{ij}$ for all $\tilde{f}$ bonds, the overlap graph $[m]_l$ changes into a sum of terms which are (products of) Mayer graphs. The first term in this expansion is the corresponding Mayer graph $(m)_l$, all $\tilde{f}$ turning into f. The last term is a graph G where all $\tilde{f}$ bonds of $[m]_l$ have been canceled. If $[m]_l$ is of first kind, G is automatically connected.

Definition 2.2. We consider an overlap graph which is not of first kind. Canceling all $\tilde{f}$ bonds results in a new graph G. If G is connected, the original graph is called an overlap graph of the second kind.

B_5 can be represented by overlap graphs of the first and second kind [cf. Eq. (4) and Fig. 1]. This is no longer the case from B_6 on. Thus, we are tempted to consider overlap graphs with G disconnected, which is possible for $n \geqslant 6$ corners. However, such graphs have the same disadvantage as graph g in Fig. 2: they are infinite in the thermodynamic limit. To avoid this, the "infinite part" of the original graph has to be subtracted (cf. Fig. 3). To avoid problems when considering $\infty - \infty$, the difference may be interpreted as a difference of the finite integrands [cf. (2)] and not of the infinite integrals.

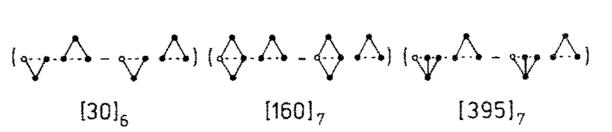

Fig. 3. Overlap graphs of the third kind with six and seven corners.

Definition 2.3. We assume that an overlap graph $[m]'_l$ is not of first or second kind. Thus, G is disconnected (cf. Definition 2.2). G_r is the graph which results when only those $\tilde{f}$ functions are reinserted which leave the graph disconnected. Then, $[m]_l = [m]'_l - G_r$ is called an overlap graph of the third kind.

Now, we are about to encounter overlap graphs of the third kind. In Fig. 3, the three overlap graphs of the third kind with 6 and 7 corners are displayed. The corresponding G_r are

$$
\begin{aligned}
[30]_6 &: G_r = V[1]_3^2 \\
[160]_7 &: G_r = V[1]_3[2]_4 \\
[395]_7 &: G_r = V[1]_3[3]_4
\end{aligned}
\tag{6}
$$

The above definitions have been chosen so as to be comprehensible. However, formally an overlap graph of the third kind turns out not to be an overlap graph in the sense of Definition 1.1. This may be corrected by defining $G_r = \emptyset$ (null graph, integral value zero) for overlap graphs of the first and second kind. The condition "leaving the graph disconnected" of Definition 2.3 cannot be fulfilled in these cases. If $[m]_l'$ is an overlap graph in the sense of Definition 1.1, the overlap graph $[m]_l$ is given by

$$[m]_l = [m]_l' - G_r \tag{7}$$

i.e., $[m]_l = [m]_l'$ for overlap graphs of the first and second kind.

Figure 1 displays all overlap graphs up to five corners, Fig. 3 the overlap graphs of the third kind with six and seven corners. For completion, Figs. 4 and 5 show the overlap graphs of the first and second kind with six and seven corners, respectively. Overlap graphs of the second kind are marked by a star. In Fig. 5, the subscript 7 of $[m]_7$ is omitted for simplicity. The numbering of the l corners is in all cases as follows. Corners $1, \ldots, k$ (type A) lie on a dotted line from left to right. Corners $k + 1, \ldots, l$ (type B) are numbered clockwise, starting from right below (cf. $[14]_6$ in Fig. 4). The numerical characterization of an overlap graph has only to take into account the f bonds since all corners of type A are connected with each other by $\tilde{f}$ bonds. For instance, the code for $[15]_6$, Fig. 4, is

$$[15]_6 : 414251526163 \text{ according to } f_{41} f_{42} f_{51} f_{52} f_{61} f_{63} \tag{8}$$

the code ij being used for f_{ij}, $i > j$. The i are in an ascending order. This is

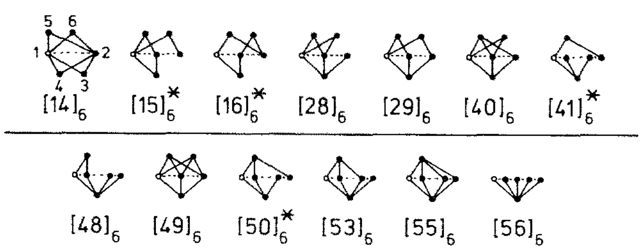

Fig. 4. Overlap graphs of the first and second kind with six corners. The latter graphs are marked by a star.

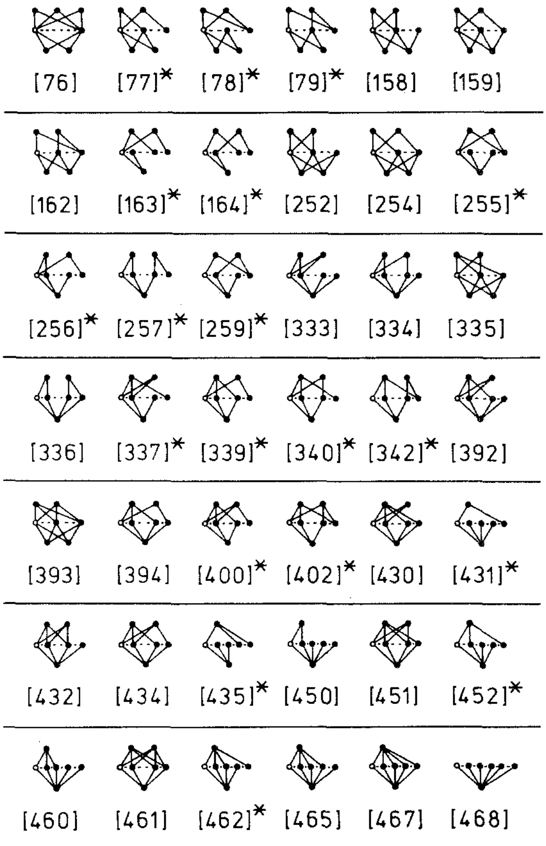

Fig. 5. Overlap graphs of the first and second kind with seven corners. The latter graphs are marked by a star.

also the case for j within the same i. The first number (4 for $[15]_6$) is $k+1$, the last but one (6 for $[15]_6$) is l. For overlap graphs of the third kind, $[m]'_l$ is encoded for simplicity instead of $[m]_l$ [cf. Eq. (7) and Fig. 3]. One may interpret the code 414251526163 for $[15]_6$ as decimal number d. On the other hand, the numbering of the corners is not essential. It follows that in general there are various equivalent representations of an overlap graph. In all cases, the representation yielding minimum d has been chosen (cf. Figs. 1, 3, 4, and 5).

3. SIXTH AND SEVENTH VIRIAL COEFFICIENTS

Up to B_4, the overlap graph representation of B_n can be directly evaluated[1,4] (cf. Section 2). From B_5 on, an indirect way using Mayer graphs is necessary. One has to expand overlap graphs in terms of Mayer graphs via Eq. (3) and employ the Mayer graph representation[3] of B_n known for $n \leqslant 7$. As illustration, we consider B_4. The Mayer graph representation of B_4 is

$$-8B_4 = (3)_4 + 6(2)_4 + 3(1)_4 . \tag{9}$$

Expanding the overlap graphs yields[1]

$$\begin{bmatrix} [3]_4 \\ [2]_4 \\ [1]_2[1]_3 \\ [1]_2^3 \end{bmatrix} = \begin{bmatrix} 1 & 3 & 0 & 3 & 1 \\ 0 & 1 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 1 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} (3)_4 \\ (2)_4 \\ (1)_4 \\ (1)_2(1)_3 \\ (1)_2^3 \end{bmatrix} \tag{10}$$

The strange representation chosen in (9) and (10)—descending order of m in $[m]_l$ and $(m)_l$—corresponds to a descending number of bonds. This is adapted to the actual calculation of the overlap graph representation (cf. Table I).

Table I shows how the coefficients of $[3]_4, \ldots, [1]_2^3$ are determined successively from the known Mayer graph representation of B_4. As to the result, see (4). The number zero has been suppressed in Table I except where it occurs first in a sum. The order of determination according to descending number of bonds makes it possible to evaluate the coefficients uniquely step by step without changing the result in one of the next steps.

If a solution for the overlap graph representation of B_n exists, it is unique. However, the existence of a solution is by no means trivial: the problem can be formulated as a system of k_M linear equations with k_O unknown quantities, k_O and k_M being the number of (products of) overlap graphs and Mayer graphs, respectively. From B_4 on, $k_0 < k_M$ [cf. (10) and Tables I and II]. Thus not all linear equations can be independent for a

Table I. Evaluation of the Overlap Graph Representation of B_4

	$(3)_4$	$(2)_4$	$(1)_4$	$(1)_2(1)_3$	$(1)_2^3$
$-8B_4$	1	6	3		
$-[3]_4$	-1	-3		-3	-1
Sum	0	3	3	-3	-1
$-3[2]_4$		-3	-3		
Sum		0	0	-3	-1
$+3[1]_2^2[1]_3$				3	3
Sum				0	2
$-2[1]_2^3$					-2
Sum					0

Table II. Number of (Products of) Overlap Graphs Compared with Mayer Graphs, n Being the Total Number of Corners

n	Overlap graphs	Products of overlap graphs	Total (k_0)	Mayer graphs	Products of Mayer graphs	Total (k_M)
2	1	0	1	1	0	1
3	1	1	2	1	1	2
4	2	2	4	3	2	5
5	5	5	10	10	6	16
6	14	12	26	56	19	75
7	44	35	79	468	92	560

solution to exist. For instance, the second sum in Table I shows that two zeros occur at once, which reflects the above-mentioned dependency.

In Ref. 1, the assumption that a solution exists for any B_n was termed *overlap conjecture*. In that paper, the overlap graph representation of B_n, $n \leqslant 5$, was given. Table II displays how restrictive the overlap conjecture really is for B_6 and especially for B_7. However, explicit calculation for B_6 and B_7 shows that a solution exists for both virial coefficients. Using the expansion of overlap graphs in terms of Mayer graphs,[5-7] it follows that

$$\begin{aligned} -144B_6 = {} & \sum_m C_m[m]_6 - [1]_2\{60[4]_5 + 100[5]_5 + 140[7]_5 \\ & + 30[9]_5 + 5[10]_5\} - [1]_3\{180[2]_4 + 60[3]_4\} \\ & + [1]_2^2\{110[2]_4 + 20[3]_4\} + 90[1]_2[1]_3^2 \\ & - 60[1]_2^3[1]_3 + 24[1]_2^5 \end{aligned} \tag{11}$$

$$\begin{aligned} -840B_7 = {} & \sum_m D_m[m]_7 - [1]_2 \sum_m \bar{C}_m[m]_6 \\ & - [1]_3\{630[4]_5 + 1260[5]_5 + 1890[7]_5 + 420[9]_5 + 105[10]_5\} \\ & + [1]_2^2\{525[4]_5 + 780[5]_5 + 1050[7]_5 + 220[9]_5 + 30[10]_5\} \\ & - \{630[2]_4^2 + 420[2]_4[3]_4 + 70[3]_4^2\} + [1]_2[1]_3 \\ & \times \{1890[2]_4 + 420[3]_4\} - [1]_2^3\{750[2]_4 + 120[3]_4\} \\ & + 840[1]_3^3 - 630[1]_2^2[1]_3^2 + 360[1]_2^4[1]_3 - 120[1]_2^6 \end{aligned} \tag{12}$$

The coefficients C_m, $\bar{C}_m$, and D_m are exhibited in Table III. As a first application, B_6 has been calculated for hard disks via direct Monte Carlo integration of $[m]_6$. The result is $B_6/B_2^5 = 0.19883 \pm 0.00001$ compared with the best value[8] up to now, 0.19893 ± 0.00024. This shows the merits of using overlap graphs. A table displaying the single values of $[m]_6$ for

Table III. Expansion coefficients C_m, $\bar{C}_m$ and D_m of the overlap graphs $[m]_6$ and $[m]_7$ [cf. Eqs. (11) and (12)]

$[m]_6$	C_m	$\bar{C}_m$	$[m]_7$	D_m	$[m]_7$	D_m	$[m]_7$	D_m
$[14]_6$	10	150	$[76]_7$	15	$[259]_7$	510	$[430]_7$	225
$[15]_6$	100	1290	$[77]_7$	270	$[333]_7$	150	$[431]_7$	90
$[16]_6$	40	510	$[78]_7$	240	$[334]_7$	630	$[432]_7$	120
$[28]_6$	60	750	$[79]_7$	510	$[335]_7$	225	$[434]_7$	420
$[29]_6$	140	1740	$[158]_7$	150	$[336]_7$	180	$[435]_7$	60
$[30]_6$	10	105	$[159]_7$	1110	$[337]_7$	225	$[450]_7$	75
$[40]_6$	80	975	$[160]_7$	105	$[339]_7$	270	$[451]_7$	160
$[41]_6$	50	510	$[162]_7$	390	$[340]_7$	1110	$[452]_7$	150
$[48]_6$	40	375	$[163]_7$	90	$[342]_7$	330	$[460]_7$	80
$[49]_6$	10	120	$[164]_7$	360	$[392]_7$	675	$[461]_7$	15
$[50]_6$	30	300	$[252]_7$	300	$[393]_7$	20	$[462]_7$	60
$[53]_6$	30	280	$[254]_7$	630	$[394]_7$	780	$[465]_7$	45
$[55]_6$	5	45	$[255]_7$	240	$[395]_7$	35	$[467]_7$	6
$[56]_6$	1	6	$[256]_7$	810	$[400]_7$	300	$[468]_7$	1
—			$[257]_7$	495	$[402]_7$	240	—	

hard disks can be obtained directly from the author. This is also the case for $[m]_6$ and $[m]_7$ in the parallel hard-cube model (in one, two, and three dimensions). The values of these overlap graphs have been calculated via the Mayer graph values exactly known up to seven corners for the hard-cube model.[3]

The overlap graph expansion turns out to be of advantage especially for B_6 and B_7, the number of graphs being relatively small. On the other hand, the roundabout way of determining the coefficients via the Mayer graph representation is tedious, especially if one would like to investigate further B_n. Nevertheless, some regularities of the result up to B_7 can be stated. For instance, every overlap graph (product) really contributes to B_n. In the Mayer graph expansion of B_n, all graphs occur, but no product. As can be seen from (4), (11) and (12), the sign of the coefficients is given by $-(-1)^p$, p being the number of products of overlap graphs. Furthermore, the absolute value of the coefficient of $[1]_2^{n-1}$ is $(n-2)!$ in all considered cases. The coefficient of $[m]_n$ with the largest m is 1. However, a general proof of the overlap conjecture is lacking. Such a proof together with a direct method of evaluating the coefficients of overlap graphs would be worthwhile.

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