

## Sixth and Seventh Virial Coefficients for the Parallel Hard-Cube Model\*

WILLIAM G. HOOVER† AND ANDREW G. DE ROCCO

Department of Chemistry, The University of Michigan, Ann Arbor, Michigan

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A procedure for calculating virial coefficients for parallel hard lines, squares, and cubes is outlined, and the sixth and seventh virial coefficients are computed for these models. The essential step in the evaluation of the star integrals lies in the recognition of the fact that only a few "subintegrals" contribute to each virial coefficient, relative to the total number of labeled star integrals. Both the sixth and seventh virial coefficients are negative for hard cubes, a fact interesting from the point of view of phase transitions. Approximations to the excess entropy are given for squares and cubes.

The procedure for the star integrals is extended to the calculation of approximations to the pair distribution function and the potential of the mean force. These functions are calculated through the fourth approximation for hard lines, squares, and cubes.

The topological graphs needed for the above investigations, together with the values of the related integrals in one dimension, are displayed.

## I. INTRODUCTION

STATISTICAL mechanics correlates the observed macroscopic properties of a system with the inferred microscopic properties of the system. The configurational integral

$$Q_N \equiv \frac{1}{N!} \int \exp[-\Phi(\mathbf{r}_1 \cdots \mathbf{r}_N)/kT] d\mathbf{r}_1 \cdots d\mathbf{r}_N \quad (1)$$

depends upon the intermolecular potential energy function  $\phi(\mathbf{r})$  and is related to the macroscopic equation of state by

$$P/kT = (\partial \ln Q_N / \partial V)_{N,T}. \quad (2)$$

$P$ ,  $V$ , and  $T$  have their usual thermodynamic meanings;  $N$  is the number of molecules;  $k$  is Boltzmann's constant; and  $\Phi(\mathbf{r}_1 \cdots \mathbf{r}_N)$  is the total potential energy of the system, which we will assume can be written

$$\Phi(\mathbf{r}_1 \cdots \mathbf{r}_N) = \sum_{i < j} \phi_{ij}(\mathbf{r}_{ij}). \quad (3)$$

The correlation of macroscopic with microscopic variables implicit in (2) is not very useful because the configurational integral is ordinarily too difficult to evaluate. Ursell and Mayer,<sup>1</sup> using a formalism heavily dependent on graph theory, were able to convert (1) into a form more useful from the point of view of the equation of state. Before giving these results we will

make a brief digression into the related theory of graphs.<sup>2</sup>

The graphs in which we are interested consist of a number of points (representing molecules) and lines [a line connecting the molecules  $i$  and  $j$  represents the function  $f_{ij} \equiv \exp(-\phi_{ij}/kT) - 1$ ]. If it is possible to trace a path of lines from any point in a graph to any other point in the graph the graph is called connected. If after removing a point from a connected graph, together with all of the lines adjacent to the missing point, the resulting graph is connected (no matter which point has been removed), the first graph is termed a star. Evidently the set of connected graphs includes the set of stars. We will denote the number of topologically different connected graphs of  $n$  unlabeled points by  $C(n)$  and the corresponding number for stars by  $S(n)$ . By way of orientation we give<sup>3</sup> in Table I  $C(n)$  and  $S(n)$  for  $n < 8$ . The stars of less than eight points are listed in Appendix I.

With any graph  $G_i$  is associated a number  $g_i$ , the number of topologically distinct ways in which the graph may be labeled. In Fig. 1 we display the six connected graphs of four points together with the  $g_i$  (which we call the degeneracy of the graph) for each graph.

The Ursell-Mayer formalism makes use of graph theory, finally obtaining the two Mayer equations

$$P/kT = \sum_{n=1}^N b_n z^n \quad (4)$$

† Based on a dissertation submitted in August, 1961, by William G. Hoover, in partial fulfillment of the requirements for the Ph.D. degree at The University of Michigan.

\* Present address: Department of Chemistry, Duke University, Durham, North Carolina.

<sup>1</sup> H. D. Ursell, Proc. Cambridge Phil. Soc. 23, 685 (1927); J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (John Wiley & Sons, Inc., New York, 1940).

<sup>2</sup> D. König, *Theorie der Endlichen und Unendlichen Graphen* (Chelsea Publishing Company, New York, 1950); C. Berge, *Théorie des graphes et ses applications* (Dunod, Paris, 1958); R. J. Riddell, dissertation, University of Michigan, 1951; G. W. Ford, dissertation, University of Michigan, 1954.

<sup>3</sup> R. J. Riddell, reference 2.

TABLE I. The number of topologically different connected graphs  $C(n)$  and star graphs  $S(n)$  for  $n < 8$ .

$n$ :	2	3	4	5	6	7
$C(n)$ :	1	2	6	21	112	853
$S(n)$ :	1	1	3	10	56	468

and

$$\rho \equiv N/V = \sum_{n=1}^{\infty} n b_n z^n, \quad (5)$$

where  $z$  is the thermodynamic fugacity, divided by  $kT$ , and the  $b_n$  are cluster integrals over the coordinates of  $n$  molecules:

$$b_n \equiv \frac{1}{n!V} \int \sum_{i=1}^{C(n)} g_i C_i(n) d\mathbf{r}_1 \cdots d\mathbf{r}_n. \quad (6)$$

If the  $b_n$  are known,  $z$  can be eliminated between the two Mayer equations, giving the well-known virial equation of state

$$P/kT = \rho + B_2\rho^2 + B_3\rho^3 + B_4\rho^4 + B_5\rho^5 + B_6\rho^6 + \cdots, \quad (7)$$

where  $B_n$  is the  $n$ th virial coefficient. Born and Fuchs<sup>4</sup> were able to show that only the star integrals contribute to the equation of state, getting finally,

$$P/kT = \rho + \sum_{n=2}^{\infty} \frac{1-n}{n!V} \rho^n \int \sum_{i=1}^{S(n)} g_i S_i(n) d\mathbf{r}_1 \cdots d\mathbf{r}_n. \quad (8)$$

As we can see from Table I, the number of integrals necessary to the calculation of successive terms in (8) increases rapidly with  $n$ . Furthermore the integrals become unmanageable, for realistic potentials, with  $n$  greater than 2 or 3. In the following section we will introduce a potential which is particularly useful because the necessary star integrals are easy to perform. Before going on, we stress the fact that the virial equation of state is useful only in the region where the convergence of the virial series is rapid, and that for the full equation of state an attack through the distribution functions or some other method is necessary.

## 2. HARD-CUBE MODEL

The hard-cube model was introduced by Geilikman,<sup>5</sup> who calculated  $B_2$  and  $B_3$  for a hard-cube gas. Zwanzig<sup>6</sup>

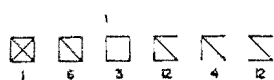


FIG. 1. The connected graphs of four points. The  $g_i$  indicate the number of ways each graph can be labeled.

<sup>4</sup> M. Born and K. Fuchs, Proc. Roy. Soc. (London) A166, 391 (1938).

<sup>5</sup> B. T. Geilikman, Proc. Acad. Sci. U.S.S.R. 70, 25 (1950).

<sup>6</sup> R. W. Zwanzig, J. Chem. Phys. 24, 855 (1956).

pointed out the intimate connection of the two- and three-dimensional cases (squares and cubes) with the one-dimensional case (lines), and used the one-dimensional results of Riddell and Uhlenbeck<sup>7</sup> to calculate virial coefficients through  $B_3$  for cubes. Temperley<sup>8</sup> has extended these calculations to gases of more than three dimensions. As noted in an earlier communication,<sup>9</sup> we have computed  $B_6$  for lines, squares, and cubes and will here present the method of calculation used together with our results for  $B_7$ , the excess entropy, the radial distribution function, and the potential of the mean force for such molecules.

The hard-cube potential is illustrated in Fig. 2. The least realistic property of this potential, which depends upon the fixed Cartesian coordinate system, is that the molecules cannot rotate, behaving as if their moments of inertia were infinite. This feature, together with the cubic, rather than spherical, symmetry is essential

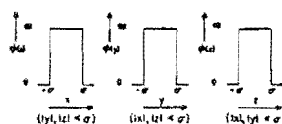


FIG. 2. The hard-cube potential. The molecular side length is  $\sigma$ .

in establishing the one-, two-, and three-dimensional correlation.

Let us consider a star integral contributing to one of the virial coefficients through Eq. (8), for instance

$$\int \int \int \int \int \int \int \int \int \int \int \int \int \int \int \int d\mathbf{r}_1 \cdots d\mathbf{r}_6 = \int f_{12} f_{13} f_{14} f_{15} f_{23} f_{24} f_{25} f_{34} f_{35} f_{45} d\mathbf{r}_1 \cdots d\mathbf{r}_6,$$

an integral which has not yet been evaluated analytically for hard spheres. Because an  $f$  function containing the coordinates of two hard cubes,  $f_{ij}(x_{ij}, y_{ij}, z_{ij})$ , may be written as the product  $f_{ij}(x_{ij})f_{ij}(y_{ij})f_{ij}(z_{ij})$ , it is clear that the complicated three-dimensional integral above may be factored into the product of three (equal) one-dimensional integrals, and, as we shall see, the one-dimensional integrals are easily evaluated. This property of factorization can also be used to advantage in calculations of the pair distribution function. The one-dimensional connection is also useful as a helpful check in calculations because the virial coefficients,<sup>10</sup> cluster integrals,<sup>11</sup> radial distribution function,<sup>12</sup> and thermodynamic properties of the hard-line gas are well known.

<sup>7</sup> R. J. Riddell and G. E. Uhlenbeck, J. Chem. Phys. 21, 2056 (1953).

<sup>8</sup> H. N. V. Temperley, Proc. Phys. Soc. (London) B70, 536 (1957).

<sup>9</sup> W. G. Hoover and A. G. DeRocco, J. Chem. Phys. 34, 1059 (1961).

<sup>10</sup> L. Tonks, Phys. Rev. 50, 955 (1936).

<sup>11</sup> R. J. Riddell, reference 2.

<sup>12</sup> Z. W. Salsburg, R. W. Zwanzig, and J. G. Kirkwood, J. Chem. Phys. 21, 1098 (1953).

3. CALCULATION OF VIRIAL COEFFICIENTS

As we see from Eqs. (7) and (8), the *n*th virial coefficient *B<sub>n</sub>* is given by

$$B_n = \frac{1-n}{n!V} \int \sum_{i=1}^{S(n)} g_i S_i(n) d\mathbf{r}_1 \cdots d\mathbf{r}_n. \quad (9)$$

This form applies in one, two, and three dimensions, keeping in mind that *d***r** represents *dx*, *dx dy*, and *dx dy dz*, respectively, in these cases. For convenience we assign the sign of each contributing star integral to the *g<sub>i</sub>*; for that star, so that all integrals are positive and *I<sub>n</sub>* = *I<sub>1</sub><sup>n</sup>*, where *I* is a star integral and we indicate dimensionality with a subscript. Using this convention we may write Eq. (9) for *n* = 2...4:

$$B_2 = \frac{1}{2V} \int \text{---} d\mathbf{r}_1 d\mathbf{r}_2, \quad (10)$$

$$B_3 = \frac{1}{3V} \int \Delta d\mathbf{r}_1 \cdots d\mathbf{r}_3, \quad (11)$$

$$B_4 = \frac{-1}{8V} \int (3 \square - 6 \nabla + \boxtimes) d\mathbf{r}_1 \cdots d\mathbf{r}_4. \quad (12)$$

We will now consider the evaluation of a typical star integral contributing to *B<sub>6</sub>* to illustrate our methods. Let

$$I \equiv \frac{1}{V} \int \bigcirc d\mathbf{r}_1 \cdots d\mathbf{r}_6. \quad (13)$$

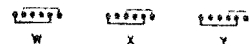
Because the integral in (13) is independent of the location of molecule 1 for large *V*, we place 1 at the origin and cancel the factor of *V*<sup>-1</sup>. Specializing to one dimension,

$$I = \int f_{12} f_{23} f_{34} f_{45} f_{56} f_{61} dx_2 dx_3 dx_4 dx_5 dx_6 \quad (14)$$

(molecule 1 at origin),

where we have assigned an arbitrary labeling to the star. We now note that the integral indicated in (14) can be written as the sum of 6! = 720 integrals in which a given molecular ordering, from left to right, is maintained, because there are 6! different ways of ordering the molecules on a line. We could evaluate the integral for each of these orderings, but because of the sixfold symmetry of the integrand it is sufficient to consider only those orderings in which the leftmost molecule is number 1, and then to multiply the results of these 120 integrals by 6 to obtain *I*. We will therefore consider orderings such as 123456 and 135246, but not 654321 or 531642. If the integrand had no symmetry it

FIG. 3. The *f* functions characterizing *w*, *x*, and *y* subintegrals are indicated as lines connecting the molecules.



would be necessary to consider each of the 720 orderings.

One could next list the 120 orderings, put in limits of integration with the help of the restrictions imposed by the ordering and by the *f* functions, and set out to evaluate the integrals. This is in fact the way in which we originally attacked the problem. It soon becomes obvious, while carrying out this procedure, that many of the integrals obtained are identical in form and value. Altogether only 14 distinct kinds of integrals are found, some occurring more often than others. We will now describe these fourteen "subintegrals" and show how to determine, from the form of the integrand of the star integral, how many times each occurs.




Let us first consider those orderings in which the last molecule is number 2 or number 6 (so that 134562 and 123456 are included in this category). Because an *f* function (*f<sub>12</sub>* or *f<sub>61</sub>*) connects the first and last molecules in these orderings it is clear that the upper limit of integration on the rightmost molecule is *σ*, the range of the intermolecular force. Because of the restriction that the ordering from left to right be maintained throughout the integration, all of the molecules are between the first (which is at the origin) and the last (which must be somewhere between the origin and *σ*). Thus all of the restrictions imposed by the *f* functions are automatically satisfied, and the *f* functions may be removed from the integrand. Using 123456 as an example of this type of integral we have

$$123456 = \int f_{12} f_{23} f_{34} f_{45} f_{56} f_{61} dx_2 dx_3 dx_4 dx_5 dx_6 \quad (0 < x_2 < x_3 < x_4 < x_5 < x_6 < \sigma) \\ = \int_0^\sigma dw \int_w^\sigma dx \int_x^\sigma dy \int_y^\sigma dz \int_z^\sigma da = \sigma^5/5!. \quad (15)$$

The use of *w*, *x*, *y*, *z*, and *a* as integration variables is convenient in deciding whether or not two different orderings give rise to the same subintegral. We use *w* to indicate the coordinate of the second molecule in the ordering, *x* for the third molecule, and so on. We will term an integral of the kind found in Eq. (15) a *σ* integral, because all of the upper limits of integration are *σ*. A *σ* integral will always result when an *f* function in the integrand connects the first and last molecules in the ordering under consideration.

Suppose we now consider an ordering in which molecule 1 is connected by an *f* function to the next-to-

Ordering	Diagram	Subintegral	Name	Value $\times$ $5!/\sigma^5$
123456		$\int_0^\sigma dw \int_w^\sigma dx \int_x^\sigma dy \int_y^\sigma dz \int_z^\sigma da$	$\sigma$	1
124563		$\int_0^\sigma dw \int_w^\sigma dx \int_x^\sigma dy \int_y^\sigma dz \int_z^{\sigma+w} da$	$w$	2
124653		$\int_0^\sigma dw \int_w^\sigma dx \int_x^\sigma dy \int_y^{\sigma+w} dz \int_z^{\sigma+w} da$	$ww$	3
126453		$\int_0^\sigma dw \int_w^\sigma dx \int_x^{\sigma+w} dy \int_y^{\sigma+w} dz \int_z^{\sigma+w} da$	$www$	4
125634		$\int_0^\sigma dw \int_w^\sigma dx \int_x^\sigma dy \int_y^{\sigma+w} dz \int_z^{\sigma+z} da$	$wx$	5
126435		$\int_0^\sigma dw \int_w^\sigma dx \int_x^{\sigma+w} dy \int_y^{\sigma+w} dz \int_z^{\sigma+z} da$	$wwx$	7
126345		$\int_0^\sigma dw \int_w^\sigma dx \int_x^{\sigma+w} dy \int_y^{\sigma+z} dz \int_z^{\sigma+z} da$	$wxx$	9
132645		$\int_0^\sigma dw \int_w^\sigma dx \int_x^\sigma dy \int_y^{\sigma+w} dz \int_z^{\sigma+y} da$	$wy$	7
126534		$\int_0^\sigma dw \int_w^\sigma dx \int_x^{\sigma+w} dy \int_y^{\sigma+w} dz \int_z^{\sigma+y} da$	$wwy$	11
126354		$\int_0^\sigma dw \int_w^\sigma dx \int_x^{\sigma+w} dy \int_y^{\sigma+z} dz \int_z^{\sigma+y} da$	$wxy$	16
123564		$\int_0^\sigma dw \int_w^\sigma dx \int_x^\sigma dy \int_y^\sigma dz \int_z^{\sigma+z} da$	$x$	3

123654		$\int_0^\sigma dw \int_w^\sigma dx \int_x^\sigma dy \int_y^{\sigma+z} dz \int_z^{\sigma+x} da$	<i>xx</i>	6
123645		$\int_0^\sigma dw \int_w^\sigma dx \int_x^\sigma dy \int_y^{\sigma+z} dz \int_z^{\sigma+y} da$	<i>xy</i>	9
123465		$\int_0^\sigma dw \int_w^\sigma dx \int_x^\sigma dy \int_y^{\sigma+z} dz \int_z^{\sigma+y} da$	<i>y</i>	4

last molecule, but not to the last one. We know that the upper limits of the first four integration variables are  $\sigma$ , but the last upper limit depends upon the details of the ordering. If the last molecule is connected to the second by an  $f$  function then the upper limit on the rightmost integration would be  $\sigma+w$ . Similarly, other orderings will give rise to integration limits of  $\sigma+x$  or  $\sigma+y$ . In Fig. 3 we indicate these possibilities pictorially, showing the  $f$  functions (as lines) which are used to determine the integration limits. The following orderings typify these kinds of subintegrals:

$$124563 = \int f_{12} f_{23} f_{34} f_{45} f_{56} f_{61} dx_2 dx_4 dx_5 dx_6 dx_3$$

$$= \int_0^\sigma dw \int_w^\sigma dx \int_x^\sigma dy \int_y^{\sigma+w} dz \int_z^{\sigma+x} da = 2\sigma^5/5! \quad (16)$$

$$152463 = \int f_{12} f_{23} f_{34} f_{45} f_{56} f_{61} dx_5 dx_2 dx_4 dx_6 dx_3$$

$$= \int_0^\sigma dw \int_w^\sigma dx \int_x^\sigma dy \int_y^{\sigma+z} dz \int_z^{\sigma+x} da = 3\sigma^5/5! \quad (17)$$

$$156423 = \int f_{12} f_{23} f_{34} f_{45} f_{56} f_{61} dx_6 dx_5 dx_4 dx_2 dx_3$$

$$= \int_0^\sigma dw \int_w^\sigma dx \int_x^\sigma dy \int_y^{\sigma+y} dz \int_z^{\sigma+y} da = 4\sigma^5/5! \quad (18)$$

We will term the three kinds of subintegrals appearing in (16)–(18) as  $w$ ,  $x$ , and  $y$  subintegrals, deriving the name from the rightmost integration limit. It is easy

to see that a  $z$  subintegral could not be obtained with six molecules, because if the last molecule is connected only to the next-to-last, the configuration could not be derived from a star. Thus we have disposed of all possible cases in which the first molecule is connected to the last, or to the next-to-last molecule.

One may go on to consider the other possibilities. In each case the lower integration limits are determined by the ordering, and the upper integration limits are determined by both the ordering and the  $f$  functions in the integrand. Rather than describe the individual cases, we list in Table II all of the possibilities found for six molecules, together with the integration limits, values, and names of the related subintegrals, and an ordering giving each type of subintegral.

Let us now calculate the integral  $I$  of Eq. (14) in terms of the subintegrals listed in Table II. We have already shown that all orderings with molecules 2 or 6 in the last position give rise to  $\sigma$  integrals. We will therefore list, in Table III, only those orderings in which one of the molecules 3, 4, or 5 occupies the last position. (By further use of symmetry we could avoid consideration of half of these cases, but for completeness each of the 72 permutations is included in the table.) Sorting these contributions to the integral by type, adding in the  $\sigma$  integrals from 1...2 and 1...6 orderings, and multiplying by six, we have  $I$  expressed in terms of the subintegrals. These totals are given in Table IV. The total number of occurrences is, of course, 720. From the values of the subintegrals listed in Table II we calculate the value of  $I$ . Adding all of the contributions we find  $I = 2112\sigma^5/5! = 88\sigma^5/5$ . The value of the integral in two dimensions is just  $(88\sigma^5/5)^2 = 7744\sigma^{10}/25$ ; the three-dimensional case gives  $(88\sigma^5/5)^3 =$

TABLE III. Subintegrals contributing to  $\int \bigcirc dr_1 \cdots dr_6$  for 72 representative linear orderings.

Ordering	Type	Ordering	Type	Ordering	Type	Ordering	Type
124563	w	142563	w	152463	x	162453	wxx
124653	wxw	142653	ww	152643	wx	162543	wxx
125463	w	145263	w	154263	x	164253	wx
125643	wxw	145623	w	154623	x	164523	x
126453	wxwx	146253	ww	156243	wy	165243	xy
126543	wxwx	146523	w	156423	y	165423	y
123564	x	132564	w	152364	w	162354	wxy
123654	xx	132654	wxw	152634	wxw	162534	wxy
125364	x	135264	w	153264	w	163254	wx
125634	wx	135624	w	153624	w	163524	x
126354	wxy	136254	wxw	156234	wxw	165234	xx
126534	wxy	136524	w	156324	w	165324	x
123465	y	132465	y	142365	w	162345	wxw
123645	xy	132645	wy	142635	wxw	162435	wxw
124365	x	134265	x	143265	w	163245	wxw
124635	wx	134625	x	143625	w	163425	w
126345	wxx	136245	wx	146235	wxw	164235	wxw
126435	wxx	136425	x	146325	w	164325	w

681472σ<sup>15</sup>/125. In order to get the contributions of

$$g \int \bigcirc dr_1 \cdots dr_6$$

to B<sub>6</sub> one must multiply these results by 60, the number of topologically distinct ways in which the points of a hexagon may be labeled.

In general, one follows the above procedure for each of the stars contributing to the B<sub>n</sub> of interest. One might expect that no two different star integrals would have the same representation in terms of subintegrals. We find two pairs of seven-point graphs with identical representations (numbers 380, 381 and 420, 421 in Appendix I) however, so that the corresponding set of subintegrals does not uniquely specify the star in question. The values found for all stars of less than eight points<sup>13</sup> are listed in Appendix I.

TABLE IV. Total subintegral contributions to  $\int \bigcirc dr_1 \cdots dr_6$ .

Subintegral:	σ	w	wxw	wxwx	wxx	wxy	y
occurrences:	288	120	72	24	36	12	12
Subintegral:	wy	wxy	wxy	x	xx	xy	y
occurrences:	12	12	12	72	12	12	24

<sup>13</sup> These stars, together with all other graphs of less than eight points may be found in "Diagrams of All Seven Point Graphs" by F. Harary and D. W. Crowe, Project R287, Horace H. Rackham School of Graduate Studies, University of Michigan (mimeographed; supplied to the authors, with many corrections, by G. W. Ford), 1953; a list of smaller graphs was prepared by F. Harary, also in 1953. F. Harary and R. Z. Norman plan to include a complete list of these graphs in a book now in preparation.

A slight further simplification arises because some pairs of subintegrals are equal. We note, for example, that any ordering giving rise to an x subintegral corresponds exactly to a wx subintegral on reversal of the ordering. There are three other such pairs in Table II: wwx = y, wxw = wy, and wxx = xy. The values of such pairs of subintegrals are clearly equal by symmetry. One would expect the number of such pairs to approach half the total number of subintegrals for n large, as the relative number of subintegrals with a center of symmetry must decrease. In Table V we list the number of subintegrals contributing to the n<sup>th</sup> virial coefficient for n < 8. Each pair is counted as only one subintegral in this table.

The number of different subintegrals increases rapidly with n. Let us define L<sub>1</sub> as the number of different subintegrals with one-letter names other than σ (including w, x, y, ...); L<sub>2</sub> as the number with two-letter names; and L<sub>3</sub> as the number with three-letter names. One can easily show, by considering diagrams like those in Table II, that

$$L_1 = \sum_{n>3}^n 1 = \frac{(n-3)}{1!}, \tag{19}$$

$$L_2 = \sum_{n>4}^n [\sum_{n>3}^n 1] = \frac{(n-4)(n-1)}{2!}, \tag{20}$$

$$L_3 = \sum_{n>5}^n (\sum_{n>4}^n [\sum_{n>3}^n 1]) = \frac{(n-5)(n-1)(n)}{3!}. \tag{21}$$

We conjecture that the obvious generalization to L<sub>n</sub> is valid for all n.

We encounter coefficient representations right-hand rows and an f further otherwise adjacentions.

We have coefficients of subintegral, star may. Although considerable of B<sub>7</sub>, we each integral was given.

For the into the the machine star, find contribution values of can then. Two in star integral all of the to be +1 integral c ... is kr

I(n ring)

$$= \frac{(-1)^{n-1}}{(n-1)}$$

where σ =

TABLE V. 2

Subintegrals Equal pairs:

<sup>14</sup> The integral belonging to G see E. T. Wh bridge Unive

We now list, in Table VI, all of the subintegrals encountered in the evaluation of the first seven virial coefficients. We note that the kind of subintegral represented by a given ordering follows from the upper right-hand corner of the so-called adjacency matrix in which the ordering is preserved in the labeling of the rows and columns. The adjacency matrix has  $a_{ij}=1$  if an  $f$  function connects molecules  $i$  and  $j$ , and  $a_{ij}=0$  otherwise. The relation of the subintegrals to the adjacency matrix is very useful for machine calculations.

We have seen that in order to find the virial coefficients one classifies each contributing star in terms of subintegrals, obtains the value of the related star integral, multiplies by the number of ways in which the star may be labeled, and adds, finding  $B_n$  by Eq. (9). Although the procedure is straightforward, a considerable amount of labor is involved, and in the case of  $B_7$ , which requires the evaluation of 468 integrals, each integral being the sum of 7! subintegrals, the task was given to an IBM 704 computer.

For the machine calculations, one reads each star into the computer in the form of an adjacency matrix; the machine then examines all of the orderings for each star, finding the number of times each subintegral contributes to the star integral in question. As the values of the subintegrals are known the computer can then calculate  $B_n$ .

Two important means of checking the results for the star integrals are available. First, as we have noted, all of the virial coefficients in one dimension are known to be  $+1$  where  $\sigma$  is taken as unit length. Second, the integral corresponding to an open ring ( $\triangle$ ,  $\square$ ,  $\circ$ ,  $\dots$ ) is known exactly<sup>14</sup>:

$$I(n \text{ ring}) = \frac{(-2)^n}{\pi} \int_0^\infty \left(\frac{\sin x}{x}\right)^n dx$$

$$= \frac{(-1)^n}{(n-1)!} [n^{n-1} - n(n-2)^{n-1} + n(n-1)(n-4)^{n-1}/2 - n(n-1)(n-2)(n-6)^{n-1}/6 + \dots], \quad (22)$$

where  $\sigma=1$  and the first  $n$  terms are taken for  $I_{2n-1}$

 TABLE V. Number of distinct subintegrals contributing to  $B_n$ .

$n$ :	2	3	4	5	6	7
Subintegrals:	1	1	2	4	10	26
Equal pairs:	0	0	0	1	4	16

<sup>14</sup> The integral appearing in (22) is taken from a notebook belonging to G. E. Uhlenbeck, who kindly lent it to the authors; see E. T. Whittaker and G. N. Watson, *Modern Analysis* (Cambridge University Press, London, 1958), 4th ed., p. 123.

 TABLE VI. Values and names of all subintegrals contributing to  $B_2 \dots B_7$ .

$n=2$		$n=3$	
Subintegral	Value $\times 1!$	Subintegral	Value $\times 2!$
$\sigma$	1	$\sigma$	1
$n=4$		$n=7$	
Subintegral	Value $\times 3!$	Subintegral	Value $\times 6!$
$\sigma$	1	$\sigma$	1
$w$	2	$w$	2
$n=5$		$wv=x$	3
Subintegral	Value $\times 4!$	$wvw=y$	4
$\sigma$	1	$wvwx=z$	5
$w$	2	$wvx$	5
$wv=x$	3	$wvx=wy$	7
$wvx$	5	$wvwx=wxz$	9
$n=6$		$xx$	6
Subintegral	Value $\times 5!$	$wxx=xy$	9
$\sigma$	1	$wvxxx=xz$	12
$w$	2	$xxx=yy$	10
$wv=x$	3	$wxxx=yz$	14
$wvw=y$	4	$wvwy$	10
$wvx$	5	$wvwy=vwz$	14
$wvwx=wy$	7	$wvxy$	14
$wvxx=xy$	9	$wvxy=wxz$	21
$wvwy$	11	$xyy=wy$	16
$wvxy$	16	$wvxy=wyz$	26
$xx$	6	$wvyy=xxz$	26
		$xyy$	19
		$wxyy=xyz$	35
		$wvwxz$	19
		$wvwxz$	30
		$wvwxz=wxvz$	40
		$wvxyz$	61

and  $I_{2n}$ . Using this formula one finds  $+88/5$  for the integral over  $\circ$ , and  $-5887/180$  for the integral over  $\circ$ , in agreement with the values appearing in Appendix I.

Our results for the virial coefficients are given in Table VII, together with  $B_1 \dots B_6$  as calculated by earlier workers.<sup>5,6</sup> The virial coefficients are given first in terms of the edge length  $\sigma$  as unit length, then in units of  $B_2$  as unit volume. Both sets of units are found in the literature. In Table VIII we list the cluster integrals and "irreducible cluster integrals,"  $\beta_n = -(n+1)B_n/n$ , together with the known values for hard spheres,<sup>15</sup> and those derived from a special

<sup>15</sup> See J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954), p. 157;  $B_6$  for hard spheres is known only approximately: A. W. Rosenbluth and M. N. Rosenbluth, *J. Chem. Phys.* **22**, 881 (1954).

TABLE VII. Virial coefficients for hard lines, squares, and cubes. First set of values is for  $\sigma=1$ . Second set is for  $B_2=1$ .

	$B_1$	$B_2$	$B_3$	$B_4$	$B_5$	$B_6$	$B_7$
Lines	1	1	1	1	1	1	1
Squares	1	2	3	$\frac{11}{3}$	$\frac{67}{18}$	$\frac{121}{40}$	$\frac{17827}{10800}$
Cubes	1	4	9	$\frac{34}{3}$	$\frac{455}{144}$	$-\frac{2039}{108}$	$-\frac{169149119}{3888000}$

	$B_1$	$B_2$	$B_3$	$B_4$	$B_5$	$B_6$	$B_7$
Lines	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
Squares	1.0000	1.0000	0.7500	0.4583	0.2326	0.0945	0.0258
Cubes	1.0000	1.0000	0.5625	0.1771	0.0123	-0.0184	-0.0106

"Gaussian" model used by Ford<sup>16</sup> in which it is assumed that the  $f$  functions are Gaussian in form. These numbers are all given in terms of  $B_2=$ unit volume. It is interesting to see the fairly close numerical agreement between the hard-cube and hard-sphere results, as contrasted with the poorer agreement between these and the Gaussian model.

The most interesting feature of these results is the fact that  $B_6$  and  $B_7$  are negative for parallel hard cubes. This is interesting from the point of view of phase transitions because negative virial coefficients are necessary to produce isotherms with flat portions or van der Waals loops. As previously pointed out,<sup>9</sup> negative virial coefficients for cubes do not imply such behavior for spheres, although these results are certainly suggestive. Alder and Wainwright<sup>17</sup> believe that  $B_6$  and  $B_7$  are both positive for hard spheres, although

they cannot estimate the magnitudes of these coefficients precisely. In Figs. 4 and 5 we have plotted the equation of state for hard parallel squares and cubes, with separate curves for six and seven virial coefficients to give an idea of the densities at which these coefficients become important in the two and three-dimensional cases. The closest-packed volume  $V_0$  is  $N\sigma^2$  for hard squares, and  $N\sigma^3$  for hard cubes.

Although the one-dimensional case is a solved problem, we think it is worthwhile to present the results of an investigation to determine which subintegrals contribute to the one-dimensional virial coefficients. Because each contributing star integral is expressible in terms of subintegrals, it is possible to calculate the net contribution of each kind of subintegral to each virial coefficient. We will illustrate this process for  $B_4$ ; the results for  $B_2 \cdots B_7$  are given in Table IX.

TABLE VIII. Cluster integrals  $b_n$  and irreducible cluster integrals  $\beta_n$  for five models. Unit volume is  $B_2$ .

	$b_1$	$b_2$	$b_3$	$b_4$	$b_5$	$b_6$	$b_7$
Lines	1.000	-1.000	1.500	-2.667	5.208	-10.800	23.343
Squares	1.000	-1.000	1.625	-3.236	7.214	-17.277	43.493
Cubes	1.000	-1.000	1.719	-3.705	9.054	-23.971	67.087
Spheres	1.000	-1.000	1.688	-3.554			
Gaussian	1.000	-1.000	1.872	-4.522	12.554	-38.045	122.706

	$\beta_1$	$\beta_2$	$\beta_3$	$\beta_4$	$\beta_5$	$\beta_6$
Lines	-2.000	-1.500	-1.333	-1.250	-1.200	-1.167
Squares	-2.000	-1.125	-0.611	-0.291	-0.113	-0.030
Cubes	-2.000	-0.844	-0.236	-0.015	+0.022	+0.012
Spheres	-2.000	-0.938	-0.383			
Gaussian	-2.000	-0.386	+0.167	-0.016	-0.046	+0.035

<sup>16</sup> G. W. Ford, dissertation, University of Michigan, 1954.<sup>17</sup> B. J. Alder and T. E. Wainwright, J. Chem. Phys. **33**, 1447 (1960).Three dif  
□, ▨, and

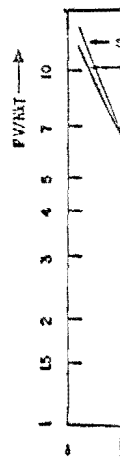
Taking the only the  $\sigma$  dimensional  $B_n$  for  $B_2 \cdots B_7$  relation general dimensions; however.

(1) Ridde in the stars  $c$  with odd number even number with the observed will give rise  $1/(n-1)!$  each integrals contribute

$$(-n!/2) \{2[$$

This is the (9), indicating sufficiently numerous one-dimensional therefore can

(2) In one it is possible a net one-dimensional subintegral diagram:



FIG

<sup>18</sup> R. J. Ridde



Three different types of stars contribute to  $B_4$ :  $\square$ ,  $\boxtimes$ , and  $\boxplus$ . In terms of subintegrals,

$$I(\square) = 16\sigma + 8w, \quad (23)$$

$$I(\boxtimes) = 20\sigma + 4w, \quad (24)$$

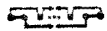
$$I(\boxplus) = 24\sigma. \quad (25)$$

Taking the degeneracies into account one finds that only the  $\sigma$  subintegrals contribute to the one-dimensional  $B_4$ . From Table IX we see that this is true for  $B_2 \cdots B_7$ . We have not been able to prove this relation generally or to find a parallel in two or more dimensions; the following three facts are relevant however.

(1) Riddell<sup>18</sup> has shown that the net number of lines in the stars of  $n$  points (calling lines negative for stars with odd numbers of lines and positive for stars with even numbers of lines) is  $-n!/2$ . This result, coupled with the observation that each line in a star of  $n$  points will give rise to  $2[(n-2)!]$   $\sigma$  subintegrals of value  $1/(n-1)!$  each, gives for the net value of all  $\sigma$  subintegrals contributing to a given  $B_n$ ,

$$(-n!/2) \{2[(n-2)!]\} (1/[n-1]!) = n!/(1-n). \quad (26)$$

This is the reciprocal of the factor appearing in Eq. (9), indicating that the  $\sigma$  subintegrals are just sufficiently numerous to give a virial coefficient of +1 in the one-dimensional case. The other subintegrals must therefore cancel out collectively, if not individually.

(2) In one individual case, for each value of  $n > 3$ , it is possible to point out a subintegral which will give a net one-dimensional contribution of zero. This is the subintegral corresponding to the following kind of diagram: . This corresponds to the  $w$  sub-

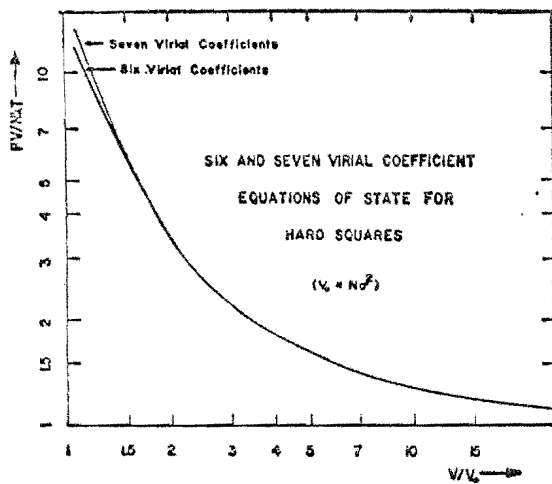


FIG. 4. Equation of state for hard spheres.

<sup>18</sup> R. J. Riddell, reference 2, p. 96.

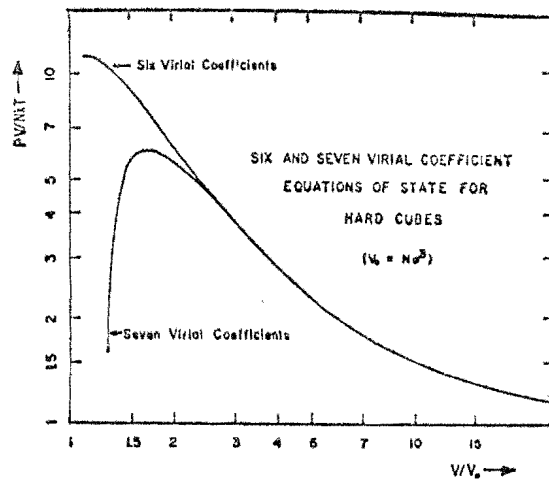


FIG. 5. Equation of state for hard cubes.

integral for  $B_4$ ,  $wx$  for  $B_5$ ,  $wxy$  for  $B_6$ , and so on. Because  $n-3$  lines may be added to the diagram above, without changing the type of subintegral involved, the number of times the subintegral will contribute to stars of  $n+m$  lines and  $n$  points is just

$$\binom{n-3}{m},$$

and the number of contributions to stars of odd numbers of lines must equal that to stars of even numbers of lines.

(3) One can easily show that the net number of  $\sigma$  subintegrals for the stars of  $n$  points is the same, except for a possible difference in sign, as the number of  $\sigma$  subintegrals derived from the star corresponding to an open ring, being  $\pm n!(n-2)!$ . This result indicates the hopelessness of trying to find approximations for the star integrals in order to sum the virial series exactly. The total contribution of all stars to  $B_n$  (in one, two, or three dimensions) is, for those potentials which we are considering at least, of the order of magnitude of the contribution of a single type of star, and the error in an excellent approximation would undoubtedly exceed this for large  $n$ .

Using the virial coefficients in Table VII one can calculate approximations to the thermodynamic properties of hard square and hard cube gases. For such gases the entropy in excess of the ideal gas value is given by<sup>19</sup>

$$\frac{S^e}{Nk} = \ln \left( \sum_{n=1}^N B_n \rho^{n-1} \right) - \sum_{n=2}^N B_n \rho^{n-1} / (n-1). \quad (27)$$

<sup>19</sup> For a derivation see T. L. Hill, *Statistical Mechanics* (McGraw-Hill Book Company, Inc., New York, 1956), p. 221.

TABLE IX. Subintegral contributions to the one-dimensional virial coefficients.

$B_2$ Contributions $\times 1/2!$		$B_4$ Contributions $\times 1/4!$			$B_6$ Contributions $\times 1/5!$				
Lines	$\sigma$	Lines	$\sigma$	$w$	Lines	$\sigma$	$w$	$x+ww$	$wx$
1	-1	4	2	1	5	-6	-3	-2	-1
Total	-1	5	-5	-1	6	42	16	10	2
		6	1	0	7	-70	-19	-10	-1
					8	36	7	2	0
					9	-9	-1	0	0
					10	1	0	0	0
		Totals	-2	0	Totals	-6	0	0	0

$B_3$ Contributions $\times 1/3!$		$B_6$ Contributions $\times 1/6!$										
Lines	$\sigma$	Lines	$\sigma$	$w$	$x+ww$	$y+www$	$wx$	$xx$	$wy+www$	$xy+www$	$wwy$	$wxy$
3	-1	6	24	10	12	4	3	1	2	2	1	1
Total	-1	7	-356	-127	-132	-46	-28	-9	-22	-12	-5	-3
		8	1304	437	398	134	67	26	48	20	8	3
		9	-2121	-622	-492	-148	-68	-26	-40	-12	-5	-1
		10	1798	465	302	72	34	9	14	2	1	0
		11	-979	-218	-108	-18	-9	-1	-2	0	0	0
		12	364	66	22	2	1	0	0	0	0	0
		13	-91	-12	-2	0	0	0	0	0	0	0
		14	14	1	0	0	0	0	0	0	0	0
		15	-1	0	0	0	0	0	0	0	0	0
		Totals	-24	0	0	0	0	0	0	0	0	0

$B_7$ Contributions $\times 1/7!$									
Lines	$\sigma$	$w$	$x+ww$	$y+www$	$z+www$	$wx$	$wy+www$	$wz+www$	$xx$
7	-120	-42	-60	-36	-12	-13	-14	-4	-9
8	2880	978	1268	700	252	249	260	94	171
9	-20070	-6528	-7704	-3954	-1442	-1363	-1364	-516	-943
10	63610	19642	21128	10062	3560	3375	3174	1150	2313
11	-113641	-33243	-32448	-14124	-4650	-4756	-4086	-1346	-3023
12	133040	36900	32256	12538	3688	4372	3316	950	2386
13	-113620	-29702	-22856	-7738	-1968	-2841	-1834	-438	-1249
14	74510	18137	12018	3436	728	1339	702	132	445
15	-38305	-8520	-4720	-1092	-182	-453	-180	-24	-105
16	15472	3058	1358	238	28	105	28	2	15
17	-4845	-816	-272	-32	-2	-15	-2	0	-1
18	1140	153	34	2	0	1	0	0	0
19	-190	-18	-2	0	0	0	0	0	0
20	20	1	0	0	0	0	0	0	0
21	-1	0	0	0	0	0	0	0	0
Totals	-120	0	0	0	0	0	0	0	0

Lines	$xy+www$	$xz+www$	$yy+xxx$	$yz+www$	$wwy$	$wwz+www$	$wxy$	$wwx+www$	$xyy+www$
7	-10	-4	-4	-4	-4	-6	-1	-4	-2
8	162	72	62	50	75	82	31	42	30
9	-742	-314	-322	-180	-363	-322	-132	-130	-138
10	1538	586	730	282	762	574	243	190	254
11	-1744	-570	-798	-220	-862	-550	-243	-152	-222
12	1204	320	454	90	592	310	145	70	98
13	-538	-110	-146	-20	-264	-108	-53	-18	-22
14	154	22	26	2	76	22	11	2	2
15	-26	-2	-2	0	-13	-2	-1	0	0
16	2	0	0	0	1	0	0	0	0
Totals	0	0	0	0	0	0	0	0	0

Lines	$wyz+www$	$xzz+www$	$xyy$	$xyz+www$	$wwwz$	$wwxz$	$wwwz+www$	$wxyz$
7	-2	-2	-1	-2	-1	0	-2	-1
8	24	18	10	14	14	6	12	4
9	-70	-58	-35	-32	-54	-22	-26	-6
10	88	84	52	32	91	31	26	4
11	-54	-58	-35	-14	-78	-21	-12	-1
12	16	18	10	2	36	7	2	0
13	-2	-2	-1	0	-9	-1	0	0
14	0	0	0	0	1	0	0	0
Totals	0	0	0	0	0	0	0	0

We have a hard square in Figs. 6 included the Wainwright related for low density magnitude for cubes higher density molecules. All of the as one would the molecules for cubes molecules.

4. CALCULATION

The upper powers of pair, trip find, for places two all of the configurat to represent

$$n_2(\Gamma_{12}) =$$

