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

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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,[1] 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.[2]

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[3] 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

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

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[1] 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).

[2] 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.

[3] 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

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

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

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

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

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

where B_n is the nth virial coefficient. Born and Fuchs[4] were able to show that only the star integrals contribute to the equation of state, getting finally,

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

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,[5] who calculated B_2 and B_3 for a hard-cube gas. Zwanzig[6]
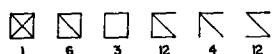

FIG. 1. The connected graphs of four points. The g_i indicate the number of ways each graph can be labeled.

[4] M. Born and K. Fuchs, Proc. Roy. Soc. (London) A166, 391 (1938).
[5] B. T. Geilikman, Proc. Acad. Sci. U.S.S.R. 70, 25 (1950).
[6] 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[7] to calculate virial coefficients through B_5 for cubes. Temperley[8] has extended these calculations to gases of more than three dimensions. As noted in an earlier communication,[9] 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
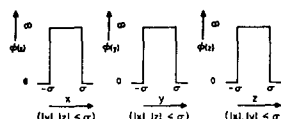

FIG. 2. The hard-cube potential. The molecular side length is σ.

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

$$\int \bigotimes d\mathbf{r}_1 \cdots d\mathbf{r}_5 = \int f_{12}f_{13}f_{14}f_{15}f_{23}f_{24}f_{25}f_{34}f_{35}f_{45} d\mathbf{r}_1 \cdots d\mathbf{r}_5,$$

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,[10] cluster integrals,[11] radial distribution function,[12] and thermodynamic properties of the hard-line gas are well known.

[7] R. J. Riddell and G. E. Uhlenbeck, J. Chem. Phys. 21, 2056 (1953).
[8] H. N. V. Temperley, Proc. Phys. Soc. (London) B70, 536 (1957).
[9] W. G. Hoover and A. G. DeRocco, J. Chem. Phys. 34, 1059 (1961).
[10] L. Tonks, Phys. Rev. 50, 955 (1936).
[11] R. J. Riddell, reference 2.
[12] 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 nth virial coefficient B_n is given by

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

This form applies in one, two, and three dimensions, keeping in mind that $d\mathbf{r}$ represents dx, $dxdy$, and $dxdydz$, respectively, in these cases. For convenience we assign the sign of each contributing star integral to the g_i for that star, so that all integrals are positive and $I_n = I_1{}^n$, where I is a star integral and we indicate dimensionality with a subscript. Using this convention we may write Eq. (9) for $n = 2 \cdots 4$:

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

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

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

We will now consider the evaluation of a typical star integral contributing to B_6 to illustrate our methods. Let

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

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^{-1}. Specializing to one dimension,

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

(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.
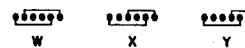
would be necessary to consider each of the 720 orderings.

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_{12} or f_{61}) 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

$$123456 = \int f_{12} f_{23} f_{34} f_{45} f_{56} f_{61} dx_2 dx_3 dx_4 dx_5 dx_6$$

$$(0 < x_2 < x_3 < x_4 < x_5 < x_6 < \sigma)$$

$$= \int_0^\sigma dw \int_w^\sigma dx \int_x^\sigma dy \int_y^\sigma dz \int_z^\sigma da = \sigma^5/5!. \qquad (15)$$

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-

TABLE II. Characteristics of the one-dimensional subintegrals contributing to $\int \bigcirc d\mathbf{r}_2 \cdots d\mathbf{r}_6$.

Ordering	Diagram	Subintegral	Name	Value× $5!/\sigma^5$
123456		$\int_0^\sigma dw \int_w^\sigma dx \int_x^\sigma dy \int_y^\sigma dz \int_z^\sigma da$	σ	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		$\int_0^\sigma dw \int_w^\sigma dx \int_x^\sigma dy \int_y^{\sigma+w} dz \int_z^{\sigma+x} da$	wx	5
126435		$\int_0^\sigma dw \int_w^\sigma dx \int_x^{\sigma+w} dy \int_y^{\sigma+w} dz \int_z^{\sigma+x} da$	wwx	7
126345		$\int_0^\sigma dw \int_w^\sigma dx \int_x^{\sigma+w} dy \int_y^{\sigma+x} dz \int_z^{\sigma+x} da$	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		$\int_0^\sigma dw \int_w^\sigma dx \int_x^{\sigma+w} dy \int_y^{\sigma+x} dz \int_z^{\sigma+y} da$	wxy	16
123564		$\int_0^\sigma dw \int_w^\sigma dx \int_x^\sigma dy \int_y^\sigma dz \int_z^{\sigma+x} da$	x	3

Table II (continued)

Ordering	Diagram	Subintegral	Name	Value× $5!/\sigma^5$
123654		$\int_0^\sigma dw \int_w^\sigma dx \int_x^\sigma dy \int_y^{\sigma+x} dz \int_z^{\sigma+x} da$	xx	6
123645		$\int_0^\sigma dw \int_w^\sigma dx \int_x^\sigma dy \int_y^{\sigma+x} dz \int_z^{\sigma+y} da$	xy	9
123465		$\int_0^\sigma dw \int_w^\sigma dx \int_x^\sigma dy \int_y^\sigma dz \int_z^{\sigma+y} da$	y	4

last molecule, but not to the last one. We know that the upper limits of the first four integration variables are σ, 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:

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

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

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

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

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

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

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 σ 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 σ integrals from $1\cdots2$ and $1\cdots6$ 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 $\int \bigcirc dr_2 \cdots dr_6$ for 72 representative linear orderings.

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

$681472\sigma^{15}/125$. In order to get the contributions of

$$g\int \bigcirc dr_2 \cdots dr_6$$

to B_6 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_n 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[13] are listed in Appendix I.

TABLE IV. Total subintegral contributions to $\int \bigcirc dr_2 \cdots dr_6$.

Subintegral:	σ	w	ww	www	wx	wwx	wxx
occurrences:	288	120	72	24	36	12	12

Subintegral:	wy	wwy	wxy	x	xx	xy	y
occurrences:	12	12	12	72	12	12	24

[13] 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 prepration.

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 ww subintegral on reversal of the ordering. There are three other such pairs in Table II: $www = y$, $wwx = wy$, 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 nth 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_1 as the number of different subintegrals with one-letter names other than σ (including $w, x, y, \cdots$); L_2 as the number with two-letter names; and L_3 as the number with three-letter names. One can easily show, by considering diagrams like those in Table II, that

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

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

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

We conjecture that the obvious generalization to L_n is valid for all n.

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 σ is taken as unit length. Second, the integral corresponding to an open ring ($\triangle$, $\square$, $\bigcirc$, $\cdots$) is known exactly[14]:

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

$$= \frac{(-1)^n}{(n-1)!}[n^{n-1} - n(n-2)^{n-1} + n(n-1)(n-4)^{n-1}/2$$

$$- n(n-1)(n-2)(n-6)^{n-1}/6 + \cdots], \quad (22)$$

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

[14] 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 $B_2 \cdots B_7$.

$n=2$		$n=3$	
Subintegral	Value$\times 1!$	Subintegral	Value$\times 2!$
σ	1	σ	1

$n=4$		$n=7$	
Subintegral	Value$\times 3!$	Subintegral	Value$\times 6!$
σ	1	σ	1
w	2	w	2
		$ww=x$	3
$n=5$		$wuw=y$	4
Subintegral	Value$\times 4!$	$wwww=z$	5
σ	1	wx	5
w	2	$wwx=wy$	7
$ww=x$	3	$wwwx=wz$	9
wx	5	xx	6
		$wxx=xy$	9
$n=6$		$wwxx=xz$	12
Subintegral	Value$\times 5!$	$xxx=yy$	10
σ	1	$wxxx=yz$	14
w	2	wwy	10
$ww=x$	3	$wwwy=wwz$	14
$www=y$	4	wxy	14
wx	5	$wwxy=wxz$	21
$wwx=wy$	7	$xxy=wyy$	16
$wxx=xy$	9	$wxxy=wyz$	26
wwy	11	$wwyy=xxz$	26
wxy	16	xyy	19
xx	6	$wxyy=xyz$	35
		$wwwz$	19
		$wwxz$	30
		$wxxz=wwyz$	40
		$wxyz$	61

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

Our results for the virial coefficients are given in Table VII, together with $B_1 \cdots B_5$ as calculated by earlier workers.[5,6] The virial coefficients are given first in terms of the edge length σ 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,[15] and those derived from a special

[15] 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_5 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 $B_2 \equiv 1$.

	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	$\dfrac{11}{3}$	$\dfrac{67}{18}$	$\dfrac{121}{40}$	$\dfrac{17827}{10800}$
Cubes	1	4	9	$\dfrac{34}{3}$	$\dfrac{455}{144}$	$\dfrac{-2039}{108}$	$\dfrac{-169149119}{3888000}$

	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[16] in which it is assumed that the f functions are Gaussian in form. These numbers are all given in terms of $B_2 \equiv$ 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,[9] negative virial coefficients for cubes do not imply such behavior for spheres, although these results are certainly suggestive. Alder and Wainwright[17] 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 β_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

	β_1	β_2	β_3	β_4	β_5	β_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

[16] G. W. Ford, dissertation, University of Michigan, 1954.
[17] B. J. Alder and T. E. Wainwright, J. Chem. Phys. **33**, 1447 (1960).

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

$$I(\square) = 16\sigma + 8w, \tag{23}$$

$$I(\boxslash) = 20\sigma + 4w, \tag{24}$$
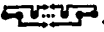
$$I(\boxtimes) = 24\sigma. \tag{25}$$

Taking the degeneracies into account one finds that only the σ 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[18] 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 $2[(n-2)!]$ σ subintegrals of value $1/(n-1)!$ each, gives for the net value of all σ subintegrals contributing to a given B_n,

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

This is the reciprocal of the factor appearing in Eq. (9), indicating that the σ 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. 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 σ subintegrals for the stars of n points is the same, except for a possible difference in sign, as the number of σ 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[19]

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

FIG. 4. Equation of state for hard spheres.

[18] R. J. Riddell, reference 2, p. 96.

[19] 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 $\times 1/2!$

Lines	σ
1	-1
Total	-1

B_3 Contributions $\times 1/3!$

Lines	σ
3	-1
Total	-1

B_4 Contributions $\times 1/4!$

Lines	σ	w
4	2	1
5	-5	-1
6	1	0
Totals	-2	0

B_5 Contributions $\times 1/5!$

Lines	σ	w	x+ww	wx
5	-6	-3	-2	-1
6	42	16	10	2
7	-70	-19	-10	-1
8	36	7	2	0
9	-9	-1	0	0
10	1	0	0	0
Totals	-6	0	0	0

B_6 Contributions $\times 1/6!$

Lines	σ	w	x+ww	y+www	wx	xx	wy+wwx	xy+wxx	wwy	wxy
6	24	10	12	4	3	1	2	2	1	1
7	-336	-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	σ	w	x+ww	y+www	z+wwww	wx	wy+wwx	wz+wwwx	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+wxx	xz+wwxx	yy+xxx	yz+wxxx	wwy	wwz+wwwy	wxy	wxz+wwxy	xxy+wyy
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+wxxy	xxz+wwyy	xyy	xyz+wxyy	wwwz	wwxz	wxxz+wwyz	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 used Eq. (27) to calculate excess entropies for hard squares and hard cubes. The results are displayed in Figs. 6 and 7. On the hard-cube plot we have included the molecular dynamical results of Alder and Wainwright[17] for hard spheres of diameter σ, recalculated for $V_0 \equiv \pi N \sigma^3/6$. It is interesting to note that at low densities the excess entropy depends upon the magnitude of the excluded volume V_0 and the results for cubes and spheres are approximately equal. At higher densities, where the geometry of the interacting molecules becomes important, large differences occur. All of the values for the excess entropy are negative, as one would expect, because the excluded volume of the molecules makes some configurations inaccessible for cubes and spheres which are accessible for ideal gas molecules.

4. CALCULATION OF THE RADIAL DISTRIBUTION FUNCTION

The Ursell-Mayer development of the pressure in powers of z may be generalized[20] to the calculation of pair, triplet, and higher distribution functions. To find, for example, the pair distribution function, one places two molecules at $\mathbf{r}_1$ and $\mathbf{r}_2$ and integrates over all of the other molecules to get the probability of the configuration as a function of $\mathbf{r}_1$ and $\mathbf{r}_2$. Using $n_2(\mathbf{r}_{12})$ to represent the pair distribution function, we have

$$n_2(\mathbf{r}_{12}) = \frac{\frac{1}{(N-2)!}\int \exp-\frac{\Phi(\mathbf{r}_1\cdots\mathbf{r}_N)}{kT}d\mathbf{r}_3\cdots d\mathbf{r}_N}{\frac{1}{N!}\int \exp-\frac{\Phi(\mathbf{r}_1\cdots\mathbf{r}_N)}{kT}d\mathbf{r}_1\cdots d\mathbf{r}_N}. \quad (28)$$
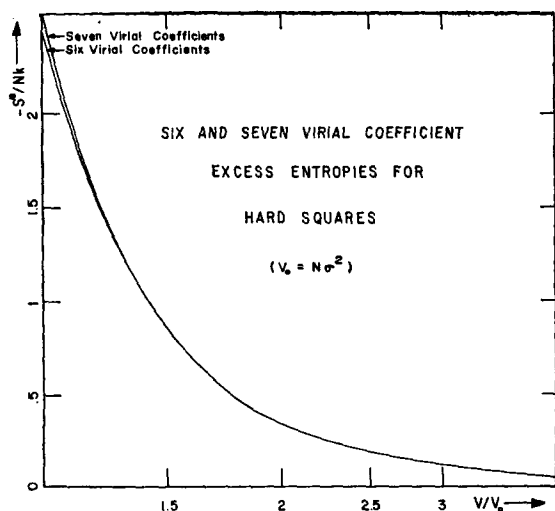
FIG. 6. Excess entropy for hard spheres.

[20] J. E. Mayer and E. W. Montroll, J. Chem. Phys. **9**, 2 (1941); see also J. de Boer, Repts. Progr. Phys. **12**, 305 (1949).
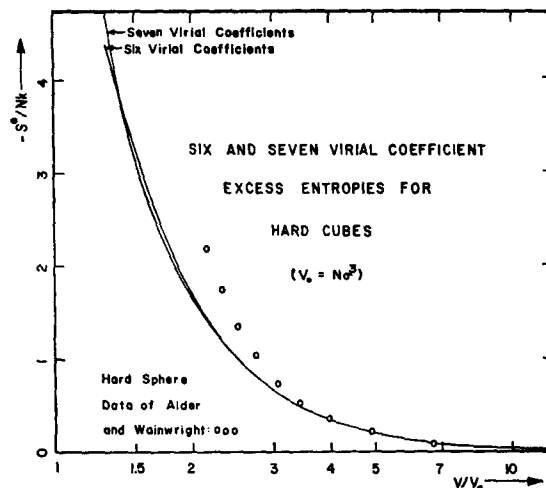
FIG. 7. Excess entropy for hard cubes.

The radial distribution function $g(\mathbf{r}_{12})$ is just the ratio of the number of molecules separated by a distance $\mathbf{r}_{12}$ in the gas of interest to the number of molecules separated by $\mathbf{r}_{12}$ in an ideal gas at the same density. That is, $g(\mathbf{r}_{12}) = n_2$ (real gas)$/n_2$ (ideal gas).

In order to convert Eq. (28) for n_2 into a series in z, one introduces the modified cluster integrals $b_n^*(\mathbf{r}_{12})$:

$$b_n^*(\mathbf{r}_{12}) \equiv \frac{\exp[-\phi(\mathbf{r}_{12})/kT]}{n!}\int \sum_{i=1}^{C^{*(n+1)}} g_i C_i^*(n+1)$$
$$\times d\mathbf{r}_3\cdots d\mathbf{r}_{n+1}, \quad (29)$$

where the $C_i^*(n+1)$ are graphs of $n+1$ points, which would become (or remain) connected if the line linking molecules 1 and 2 were added. With the help of these modified cluster integrals one shows that

$$n_2(\mathbf{r}_{12}) = \sum_{n=1}^{N-1} n b_n^* Q_{N-n-1}/Q_N. \quad (30)$$

Using the fact that $z = Q_{N-1}/Q_N$ with the expansion of z in powers of ρ from inversion of Eq. (5),

$$z = \rho + (-2b_2)\rho^2 + (8b_2^2 - 3b_3)\rho^3$$
$$+ (-40b_2^3 + 30b_2b_3 - 4b_4)\rho^4$$
$$+ (224b_2^4 - 252b_2^2b_3 + 48b_2b_4 + 27b_3^2 - 5b_5)\rho^5 + \cdots, \quad (31)$$

we find

$$n_2(\mathbf{r}_{12}) = \rho^2 b_1^* + \rho^3(2b_2^* - 4b_1^*b_2)$$
$$+ \rho^4(3b_3^* - 12b_2^*b_2 - 6b_1^*b_3 + 20b_1^*b_2^2)$$
$$+ \rho^5(4b_4^* - 24b_3^*b_2 + 72b_2^*b_2^2 - 18b_2^*b_3$$
$$+ 72b_1^*b_2b_3 - 112b_1^*b_2^3 - 8b_1^*b_4) + \cdots. \quad (32)$$

[The coefficient of the ρ^4 term in Eq. (32) is given

incorrectly in at least two references.[21] On expanding the coefficients of each power of ρ in terms of $\exp[-\phi(\mathbf{r}_{12})/kT]$ and the f functions, a large amount of cancellation occurs, leaving

$$n_2 = \exp[-\phi(\mathbf{r}_{12})/kT]\Big[\rho^2 + \rho^3 \int \bigwedge d\mathbf{r}_3$$

$$+ (\rho^4/2) \int (2\ \square + 4\ \boxtimes + \bowtie + \boxtimes\ )d\mathbf{r}_3 d\mathbf{r}_4$$

$$+ (\rho^5/6) \int (6\ \circledast +6\ \circledast +12\ \circledast +12\ \circledast$$

$$+6\ \circledast +6\ \circledast + \circledast +12\ \circledast +3\ \circledast +12\ \circledast$$

$$+12\ \circledast +12\ \circledast +6\ \circledast +6\ \circledast +6\ \circledast +3\ \circledast$$

$$+3\ \circledast +12\ \circledast +6\ \circledast +6\ \circledast +6\ \circledast +3\ \circledast$$

$$+6\ \circledast + \circledast\ )d\mathbf{r}_3 d\mathbf{r}_4 d\mathbf{r}_5 + \cdots \Big], \quad (33)$$

where the coefficients prefixed to each graph indicate how many times the graph occurs in the full expansion. [In Eq. (33) we indicate molecules 1 and 2 by ○ ○.]

The integrals in (33) are closely related to the integrals for the virial coefficients. We see that all graphs which become stars when the line corresponding to f_{12} is added will appear in the expansion of n_2. The evaluation of the integrals is, as with the star integrals, straightforward. Again the one-dimensional integrals are simply related to the two- and three-dimensional integrals. If the value of a one-dimensional integral over a "doubly rooted" graph appearing in (33) is $P(x)$, where P is a polynomial, then in three dimensions the corresponding integral is $P(x)P(y)P(z)$. Because of the symmetry of the hard-cubes model, only the absolute values of x, y, and z will enter into the values of the integrals. We will delete the absolute value signs on all coordinates so that our equations, as written, will apply only to the region $0 < x, y, z$.

Before illustrating the procedure by evaluating one integral, let us list the principal complications which make the distribution function problem harder than the virial coefficient problem for hard lines, squares, and cubes.

(1) More types of graphs must be considered. To compute the fifth virial coefficient one evaluates 10 types of integrals. The corresponding term in the pair distribution function involves 24 types of integrals.

(2) Two kinds of molecules, not just one, are involved in distribution function calculations, the fixed

molecules, 1 and 2 in the pair case, and the other molecules, whose coordinates are the integration variables. Thus, many different kinds of linear orderings are possible. For five molecules the orderings 12●●●, 1●2●●, 1●●2●, 1●●●2, ●12●●, ●1●2●, ●1●●2, ●●12●, ●●1●2, and ●●●12 must all be considered; each of these possibilities gives rise to its own set of subintegrals.

(3) The polynomial in $r_{12} \equiv r$, which is the value of an integral over a doubly rooted graph, has a different form for different ranges of r. In general, different polynomials apply in each of the regions $0 < r < 1$, $1 < r < 2$, $\cdots$, where we are setting $\sigma \equiv 1$.

(4) More ingenuity is required in setting up the integration limits. It is no longer possible in all cases to write the integration limits by casual inspection.

Because of these difficulties we have calculated the pair distribution function through the fourth approximation only, including all terms appearing in Eq. (33). In principle one could evaluate any such integral in a straightforward way; in practice the labor involved soon becomes prohibitive.

We will now consider one example in detail to illustrate our methods. Let us take the one-dimensional integral

$$I \equiv \int \boxtimes dx_3 dx_4 dx_5, \quad (34)$$

which contributes to the fourth approximation to the pair distribution function. Because 1 and 2 are fixed, we need consider only $5!/2$ linear orderings, assuming that 1 is to the left of 2. We notice by symmetry that some of the classes of orderings must be equal. These are 12●●● and ●●●12, 1●2●● and ●●1●2, 1●●2● and ●1●●2, ●●12● and ●12●●. Further, the integral must vanish for $r > 2$ by inspection of (34).

In Table X we give the subintegrals for each of the 60 orderings contributing to (34) in the ranges $0 < r < 1$, and $1 < r < 2$, finally adding these contributions to obtain I. Diagrams indicating which f functions are used to set the integration limits are included with each kind of ordering. To find the total contribution of I to the pair distribution function we multiply the final total in Table X by $+6$, plus because the number of lines is even, and 6 because the doubly rooted graph can be labeled in six different ways. Proceeding in this way one can evaluate all of the integrals contributing to g_1, g_2, and g_3, where the radial distribution function is given by

$$g(x, y, z, \rho) = n_2/\rho^2 = \exp[-\phi(x, y, z)/kT]$$

$$\times [1 + \rho g_1 + \rho^2 g_2 + \rho^3 g_3 + \cdots]. \quad (35)$$

[21] J. de Boer, reference 20, p. 340; J. O. Hirschfelder *et al.*, reference 15, p. 147.

TABLE X. Subintegrals contributing to $\int \bowtie dr_3 dr_4 dr_5$.

Ordering	Diagram	Integral for $0<r<1$	Integral for $1<r<2$
●●●12=12●●●:			
34512 35412		$2\int_{r-1}^{0}dw\int_{r-1}^{w}dx\int_{-1}^{x}dy$	Vanishes
43512 45312 53412 54312		$4\int_{r-1}^{0}dw\int_{r-1}^{w}dx\int_{r-1}^{x}dy$	Vanishes
Totals:		$(6-12r+6r^2)/6$	0
●●1●2=1●2●●:			
34152		$\int_{0}^{r}dw\int_{r-1}^{0}dx\int_{-1}^{x}dy$	Vanishes
35142		$\int_{0}^{r}dw\int_{r-1}^{0}dx\int_{w-1}^{x}dy$	Vanishes
43152 53142 45132 54132		$4\int_{0}^{r}dw\int_{r-1}^{0}dx\int_{r-1}^{x}dy$	Vanishes
Totals:		$(18r-27r^2+9r^3)/6$	0
●●12●=●12●●:			
34125		$\int_{r}^{1}dw\int_{w-1}^{0}dx\int_{-1}^{x}dy$	Vanishes
54123		$\int_{r}^{1}dw\int_{w-1}^{0}dx\int_{r-1}^{x}dy$	Vanishes
43125 35124 53124 45123		$4\int_{r}^{1}dw\int_{w-1}^{0}dx\int_{w-1}^{x}dy$	Vanishes
Totals:		$(8-21r+18r^2-5r^3)/6$	0

Table X (continued)

Ordering	Diagram	Integral for $0<r<1$	Integral for $1<r<2$
$\bullet 1\bullet\bullet 2 = 1\bullet\bullet 2\bullet$:			
31452		$\int_0^r dw \int_0^w dx \int_{x-1}^0 dy$	$\int_{r-1}^1 dw \int_0^w dx \int_r^{w+1} dy$
31542		$\int_0^r dw \int_0^w dx \int_{w-1}^0 dy$	$\int_{r-1}^1 dw \int_{r-1}^w dx \int_{w-1}^0 dy$
41352 41532 51342 51432		$4\int_0^r dw \int_0^w dx \int_{r-1}^0 dy$	Vanishes
Totals:		$(18r^2-15r^3)/6$	$(12-12r+3r^2)/6$
$1\bullet\bullet\bullet 2$:			
13452		$\int_0^r dw \int_w^r dx \int_x^r dy$	$\int_{r-1}^1 dw \int_0^w dx \int_w^r dy$
13542 14352		$2\int_0^r dw \int_w^r dx \int_x^r dy$	$2\int_{r-1}^1 dw \int_w^1 dx \int_x^r dy$
14532 15342 15432		$3\int_0^r dw \int_w^r dx \int_x^r dy$	$3\int_{r-1}^1 dw \int_w^1 dx \int_x^1 dy$
Totals:		$(6r^3)/6$	$(12-6r)/6$
$\bullet 1\bullet 2\bullet$:			
31425		$\int_0^r dw \int_{w-1}^0 dx \int_r^{w+1} dy$	$\int_{r-1}^1 dw \int_{w-1}^0 dx \int_r^{w+1} dy$
51423		$\int_{r-1}^0 dw \int_0^r dx \int_r^1 dy$	Vanishes
31524 41325 41523 51324		$\int_{r-1}^0 dw \int_0^r dx \int_r^{w+1} dy$	Vanishes
Totals:		$(24r-42r^2+19r^3)/6$	$(8-12r+6r^2-r^3)/6$

Table X (continued)

Ordering	Contribution to I for $0<r<1$	Contribution to I for $1<r<2$
●●●12	$(6-12r+6r^2)/6$	0
12●●●	$(6-12r+6r^2)/6$	0
●●1●2	$(18r-27r^2+9r^3)/6$	0
1●2●●	$(18r-27r^2+9r^3)/6$	0
●●12●	$(8-21r+18r^2-5r^3)/6$	0
●12●●	$(8-21r+18r^2-5r^3)/6$	0
●1●●2	$(18r^2-15r^3)/6$	$(12-12r+3r^2)/6$
1●●2●	$(18r^2-15r^3)/6$	$(12-12r+3r^2)/6$
1●●●2	$(6r^3)/6$	$(12-6r)/6$
●1●2●	$(24r-42r^2+19r^3)/6$	$(8-12r+6r^2-r^3)/6$
Total $=I$:	$(28-6r-12r^2+3r^3)/6$	$(44-42r+12r^2-r^3)/6$

The doubly rooted graphs of n points contribute to g_{n-2}. All of the graphs contributing to $g_1 \cdots g_3$, together with their values in one dimension are listed in Appendix II.

Because the radial distribution function has cubic rather than spherical symmetry, the locations of maxima and minima in the function depend upon direction as well as distance from the origin. In Table XI we have tabulated $g_1 \cdots g_3$ as calculated from the data in Appendix II for hard lines, squares, and cubes with $\sigma \equiv 1$. For squares we have tabulated these functions along the line $x=0(\square\square)$, as well as along $x=y(\diamondsuit\diamondsuit)$; for cubes we have tabulated $g_1 \cdots g_3$ along the lines $x=y=0$; $x=0$, $y=z$; and $x=y=z$. This serves to point out the angle dependence of the "radial" distribution function for these molecules.

It is worthwhile to list some of the ways in which these results can be checked. All but the first of the six checks listed could be applied to potentials other than the special cases with which we have been concerned.

(1) One may compare the one-dimensional radial distribution function with the well-known exact result[12]:

$$\exp(\phi/kT)g(r) = \rho^{-1}\sum_{k=1}^{\infty}\delta^+(r-k)(\rho/[1-\rho])^k(r-k)^{k-1}$$

$$\times \exp\{-(r-k)(\rho/[1-\rho])\}/(k-1)!, \quad (36)$$

where $\delta^+(r-k)=1$ for $r>k$ and 0 for $r<k$. Expanding the first few terms of (36) in powers of ρ we find that for $0<r<2$, $g_1=2-r$, $g_2=\frac{1}{2}(7-6r+r^2)$, $g_3=\frac{1}{6}(34-39r+12r^2-r^3)$; for $2<r<3$, $g_1=0$, $g_2=\frac{1}{2}(-9+6r-r^2)$,

$g_3=\frac{1}{6}(-98+87r-24r^2+2r^3)$; for $3<r<4$, $g_1=0$, $g_2=0$, $g_3=\frac{1}{6}(64-48r+12r^2-r^3)$, in agreement with the results we obtain using Appendix II.

(2) Setting $r=0$ in the expression for any doubly rooted graph integral gives the value of the corresponding star integral. For example, $\bowtie$ becomes $\boxtimes$ on setting $r=0$, and the value of

$$\int \bowtie dr_3 dr_4 dr_5$$

reduces to the proper value, 14/3, for $r=0$.

(3) The integral of the value of any doubly rooted graph from 0 to 1 will be equal to one-half the value of the corresponding star integral. For example,

$$\int_0^1 dr \left[\int \bowtie dr_3 dr_4 dr_5 \right]$$

gives 29/8, while from Appendix I the value of the corresponding star integral over $\bowtie$ is 29/4.

(4) In some cases doubly rooted graph integrals may be derived by inspection from simpler integrals. For example,

$$\int \bowtie dr_3 dr_4 dr_5 = \left[\int \wedge dr_3 \right]^3.$$

(5) The radial distribution function must satisfy the Ornstein-Zernicke relation,[22]

$$kT(\partial \rho/\partial P)_{N,T} = 1 + \rho \int_0^{\infty} d\mathbf{r}[g(\mathbf{r})-1].$$

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[22] J. de Boer, reference 20, p. 364.

TABLE XI. g_1, g_2, and g_3 for hard lines, squares, and cubes.

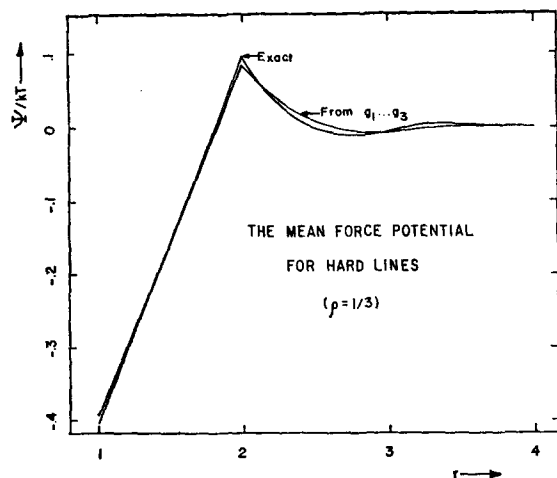|	Lines	Squares		Cubes		
d	$g_1(d)$	$g_1(0,d)$	$g_1(d,d)$	$g_1(0,0,d)$	$g_1(0,d,d)$	$g_1(d,d,d)$
1.00	1.0000	2.0000	1.0000	4.0000	2.0000	1.0000
1.10	0.9000	1.8000	0.8100	3.6000	1.6200	0.7290
1.20	0.8000	1.6000	0.6400	3.2000	1.2800	0.5120
1.30	0.7000	1.4000	0.4900	2.8000	0.9800	0.3430
1.40	0.6000	1.2000	0.3600	2.4000	0.7200	0.2160
1.50	0.5000	1.0000	0.2500	2.0000	0.5000	0.1250
1.60	0.4000	0.8000	0.1600	1.6000	0.3200	0.0640
1.70	0.3000	0.6000	0.0900	1.2000	0.1800	0.0270
1.80	0.2000	0.4000	0.0400	0.8000	0.0800	0.0080
1.90	0.1000	0.2000	0.0100	0.4000	0.0200	0.0010
2.00	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
d	$g_2(d)$	$g_2(0,d)$	$g_2(d,d)$	$g_2(0,0,d)$	$g_2(0,d,d,)$	$g_2(d,d,d)$
1.00	1.0000	3.5000	0.5000	12.5000	2.0000	−1.2500
1.10	0.8050	2.8200	0.1480	10.0800	0.7721	−1.4358
1.20	0.6200	2.1800	−0.1156	7.8200	−0.1420	−1.4417
1.30	0.4450	1.5800	−0.3020	5.7200	−0.7859	−1.3294
1.40	0.2800	1.0200	−0.4216	3.7800	−1.2000	−1.1481
1.50	0.1250	0.5000	−0.4844	2.0000	−1.4219	−0.9356
1.60	−0.0200	0.0200	−0.4996	0.3800	−1.4860	−0.7200
1.70	−0.1550	−0.4200	−0.4760	−1.0800	−1.4239	−0.5212
1.80	−0.2800	−0.8200	−0.4216	−2.3800	−1.2640	−0.3520
1.90	−0.3950	−1.1800	−0.3440	−3.5200	−1.0319	−0.2191
2.00	−0.5000	−1.5000	−0.2500	−4.5000	−0.7500	−0.1250
2.10	−0.4050	−1.2150	−0.1640	−3.6450	−0.4921	−0.0664
2.20	−0.3200	−0.9600	−0.1024	−2.8800	−0.3072	−0.0328
2.30	−0.2450	−0.7350	−0.0600	−2.2050	−0.1801	−0.0147
2.40	−0.1800	−0.5400	−0.0324	−1.6200	−0.0972	−0.0058
2.50	−0.1250	−0.3750	−0.0156	−1.1250	−0.0469	−0.0020
2.60	−0.0800	−0.2400	−0.0064	−0.7200	−0.0192	−0.0005
2.70	−0.0450	−0.1350	−0.0020	−0.4050	−0.0061	−0.0001
2.80	−0.0200	−0.0600	−0.0004	−0.1800	−0.0012	−0.0000
2.90	−0.0050	−0.0150	−0.0000	−0.0450	−0.0001	−0.0000
3.00	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
d	$g_3(d)$	$g_3(0,d)$	$g_3(d,d)$	$g_3(0,0,d)$	$g_3(0,d,d)$	$g_3(d,d,d)$
1.00	1.0000	5.5556	−0.3333	32.4444	0.0556	−3.4722
1.10	0.7148	3.9876	−0.5663	23.3804	−1.0834	−1.1508
1.20	0.4587	2.6116	−0.6344	15.6124	−1.3301	0.7241
1.30	0.2305	1.4196	−0.5855	9.0765	−0.9846	2.0718
1.40	0.0293	0.4036	−0.4599	3.7085	−0.2911	2.8943
1.50	−0.1458	−0.4444	−0.2912	−0.5556	0.5558	3.2495
1.60	−0.2960	−1.1324	−0.1065	−3.7796	1.4071	3.2292
1.70	−0.4222	−1.6684	0.0729	−6.0276	2.1535	2.9403
1.80	−0.5253	−2.0604	0.2312	−7.3636	2.7217	2.4907
1.90	−0.6065	−2.3164	0.3572	−7.8516	3.0702	1.9778
2.00	−0.6667	−2.4444	0.4444	−7.5556	3.1852	1.4815
2.10	−0.4363	−1.4361	0.4752	−3.2853	3.0496	1.0561
2.20	−0.2440	−0.6045	0.4519	0.1802	2.7193	0.7186
2.30	−0.0877	0.0606	0.3966	2.8891	2.2890	0.4663
2.40	0.0347	0.5689	0.3261	4.8901	1.8289	0.2879
2.50	0.1250	0.9306	0.2526	6.2315	1.3886	0.1687
2.60	0.1853	1.1556	0.1845	6.9618	1.0001	0.0934
2.70	0.2177	1.2539	0.1267	7.1294	0.6807	0.0487
2.80	0.2240	1.2356	0.0816	6.7828	0.4360	0.0239
2.90	0.2063	1.1106	0.0491	5.9704	0.2621	0.0109
3.00	0.1667	0.8889	0.0278	4.7407	0.1481	0.0046
3.10	0.1215	0.6480	0.0148	3.4560	0.0787	0.0018
3.20	0.0853	0.4551	0.0073	2.4273	0.0388	0.0006
3.30	0.0572	0.3049	0.0033	1.6261	0.0174	0.0002
3.40	0.0360	0.1920	0.0013	1.0240	0.0069	0.0001
3.50	0.0208	0.1111	0.0004	0.5926	0.0023	0.0000
3.60	0.0107	0.0569	0.0001	0.3034	0.0006	0.0000
3.70	0.0045	0.0240	0.0000	0.1280	0.0001	0.0000
3.80	0.0013	0.0071	0.0000	0.0379	0.0000	0.0000
3.90	0.0002	0.0009	0.0000	0.0047	0.0000	0.0000
4.00	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

FIG. 8. Potential of the mean force for hard lines.

(6) From the virial theorem one may derive, for hard cubes, the equation $PV/NkT = 1 + 4\rho g$(surface), where g(surface) is the average value of $g(x, y, z, \rho)$ on the surface of a cube of twice unit side length. This relation can be checked as can the analogous results for lines and squares.

To conclude this section on the radial distribution function let us examine the potential of the mean force[23] for hard lines, squares, and cubes. This potential, $\Psi(\mathbf{r}_{12})$, is given by

$$g(\mathbf{r}_{12}) \equiv \exp[-\Psi(\mathbf{r}_{12})/kT], \qquad (37)$$

and is the potential energy of the average force on molecule 2 along $\mathbf{r}_{12}$ with molecule 1 (for convenience) at the origin. In Figs. 8–10 we have plotted Ψ/kT for hard lines, squares, and cubes at a volume of $3V_0$,
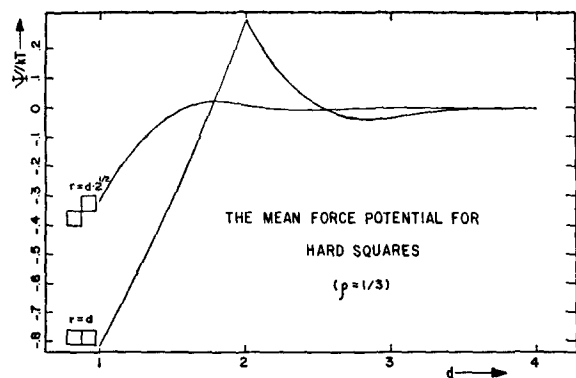

FIG. 9. Potential of the mean force for hard squares.
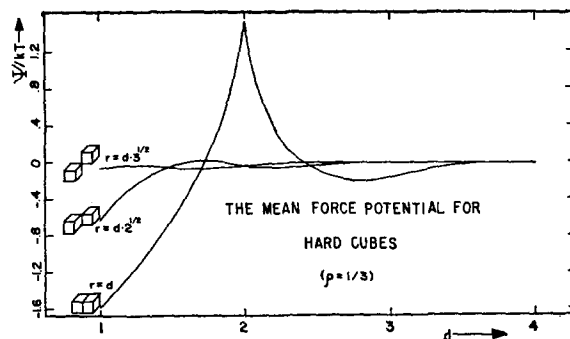
[23] J. de Boer, reference 20, p. 358.

FIG. 10. Potential of the mean force for hard cubes.

using the radial distribution function data from Table XI in Eq. (37). Because $g(x)$ is known exactly for hard lines [Eq. (36)], we include Ψ_{exact}/kT for comparison with $\Psi(g_1 \cdots g_3)/kT$ in Fig. 8. We do not mean to imply, by using $V = 3V_0$ for lines, squares, and cubes, that Ψ_{exact} will be equally close to $\Psi(g_1 \cdots g_3)$ in each case. It might, for example, be better to use equal values of $\rho^{1/n}$ for comparison, where n is the number of dimensions. As in the case of hard spheres,[23] we see that the mean force for lines, squares, and cubes is attractive for some values of the separation and number density. Again, the results for squares and cubes are strongly dependent upon angle as well as distance.

5. CONCLUSION AND REMARKS

The foregoing calculations for hard lines, squares, and cubes are interesting in illustrating the difficulties involved in using the exact cluster treatment of the configurational integral. The facts that (1) some virial coefficients are negative for hard cubes, and (2) that only a single kind of subintegral contributes to $B_2 \cdots B_7$ for hard lines, are both interesting and stimulating, because the physical basis of these results is not understood. The techniques used here are rather

TABLE XII. B_2 and B_3 for triangles, squares, equilateral hexagons, and circles. First set of values is for $V_0 \equiv N$. Second set is for $B_2 \equiv 1$.

	$\triangle$	$\square$	$\hexagon$	$\bigcirc$
B_2	3.0000	2.0000	2.0000	2.0000
B_3	7.0000	3.0000	3.1111	3.1280
B_2	1.0000	1.0000	1.0000	1.0000
B_3	0.7778	0.7500	0.7778	0.7820*

* $0.7820 = (4/3) - (\sqrt{3}/\pi)$.

specialized but may prove of value in suggesting treatments for more complicated potentials. Finally, the large amount of numerical data available from this investigation will permit rather exacting tests for any approximate theory of the configurational integral problem.

We note here that for other simple parallel molecules the integrations are more difficult. In Table XII we list for comparison B_2 and B_3 for parallel triangles, squares, equilateral hexagons, and circles,[24,10] first in units of V_0/N, then in units of B_2. It is interesting to see that in the latter units B_3 is the same for triangles and hexagons. A system which is particularly easy to study from the point of view of the virial equation of state is a mixture (two-dimensional) of hard lines, some pointing east-west and the rest north-south; for such a system one finds that B_2 is positive, B_3 is zero, and B_4 is negative.

Notes added in proof. It is clear that the equation of state for the two-dimensional mixture of hard lines (north-south, east-west) is identical with the equation of state for a corresponding mixture of hard parallel red and green squares, such that $\phi_{RR}=0$, $\phi_{GG}=0$, and $\phi_{RG}=\phi$ (hard parallel squares). The nonvanishing star integrals for north-south and east-west lines of length L are identical to the corresponding star integrals for squares of side length $L/2$.

Upon examination, it is found that most of the integrals vanish, and applying the expressions of Mayer[25] for the virial coefficients of mixtures, one finds for the case of an equimolar mixture, using the appropriate entries in our Appendix I, the results: $B_2=1/4$, $B_3=0$, $B_4=-1/48$, $B_5=-1/192$, where unit area is L^2. (2) We have noticed that the *net* number of points of degree $m \neq n-1$ is zero for the stars of $n<8$ points. The degree of a point is simply the number of points to which it is directly linked by lines. [Refer to Eqs. (23), (24), and (25) and the remarks that follow].

ACKNOWLEDGMENTS

[24] M. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller, and E. Teller, J. Chem. Phys. **21**, 1087 (1953).
[25] J. E. Mayer, J. Phys. Chem. **43**, 71 (1939).

APPENDIX I

Graphs and Integral Values for All Stars of Less than Eight Points

In this appendix we list all of the stars contributing to the first seven virial coefficients, together with the values of the one-dimensional integrals. The stars are numbered serially for each value of n, the number of points, and ordered according to (1) number of points, (2) number of lines, and (3) value of the one-dimensional integral. These values are derived from the following form of the integral

$$\frac{(n-1)!}{V_\sigma{}^{n-1}} \int S_i(n)\, dr_1 \cdots dr_n.$$

This form is chosen so as to make all values appear as integers.

Three numbers are associated with each star: first, the serial index; second, g, the number of ways in which a star may be labeled, positive if the number of lines is even, negative if odd; third, the value of the integral, which is always taken as positive.

I	Graph	g	Value	I	Graph	g	Value	I	Graph	g	Value
1		−1	2	10		+1	120	14		−15	1488
1		−1	6	1		+60	2112	15		−360	1396
1		+3	32	2		−360	1756	16		−120	1356
2		−6	28	3		−180	1728	17		−360	1352
3		+1	24	4		−180	1676	18		−360	1352
1		−12	230	5		+180	1552	19		−180	1320
2		+60	196	6		+15	1536	20		−180	1304
3		+10	192	7		+720	1524	21		−720	1288
4		−10	180	8		+360	1504	22		−90	1288
5		−60	174	9		+180	1504	23		−360	1264
6		−30	164	10		+360	1480	24		−360	1236
7		+30	152	11		+180	1444	25		−360	1224
8		+15	144	12		+90	1408	26		−60	1176
9		−10	132	13		+360	1404	27		−10	1152

I	Graph	g	Value	I	Graph	g	Value	I	Graph	g	Value
28		+90	1240	42		−45	1040	56		−1	720
29		+360	1204	43		−60	1008	1		−360	23548
30		+90	1200	44		−360	992	2		+2520	19284
31		+360	1180	45		−60	984	3		+2520	18596
32		+360	1148	46		−180	964	4		+1260	18176
33		+360	1128	47		−90	960	5		+1260	17724
34		+360	1120	48		+60	960	6		−1260	16648
35		+180	1112	49		+20	936	7		−5040	16384
36		+72	1100	50		+180	916	8		−1260	16176
37		+45	1088	51		+180	888	9		−2520	16098
38		+360	1068	52		+15	864	10		−2520	16098
39		+60	1056	53		−60	840	11		−2520	16008
40		−180	1064	54		−45	816	12		−5040	15896
41		−360	1044	55		+15	768	13		−2520	15896

I	Graph	g	Value	I	Graph	g	Value	I	Graph	g	Value
56		+5040	13264	70		+5040	12616	84		−630	12816
57		+2520	13216	71		+1260	12544	85		−1260	12744
58		+2520	13168	72		+2520	12432	86		−210	12696
59		+2520	13156	73		+1260	12236	87		−5040	12644
60		+2520	13116	74		+2520	12104	88		−5040	12606
61		+2520	13064	75		+630	11816	89		−2520	12606
62		+2520	13016	76		−21	15120	90		−2520	12606
63		+5040	12976	77		−840	13824	91		−5040	12548
64		+5040	12976	78		−630	13416	92		−1260	12520
65		+1260	12888	79		−1260	13088	93		−2520	12516
66		+2520	12868	80		−2520	13020	94		−2520	12408
67		+2520	12824	81		−2520	13020	95		−5040	12284
68		+1260	12760	82		−2520	12996	96		−630	12216
69		+5040	12630	83		−2520	12996	97		−2520	12196

I	Graph	g	Value	I	Graph	g	Value	I	Graph	g	Value
14		−420	15780	28		+2520	14688	42		+1260	13812
15		−1260	15700	29		+5040	14460	43		+2520	13808
16		−2520	15616	30		+2520	14320	44		+2520	13808
17		−5040	15498	31		+1260	14320	45		+1260	13776
18		−2520	15428	32		+2520	14236	46		+2520	13704
19		−1260	15428	33		+840	14232	47		+2520	13704
20		−630	15032	34		+5040	14208	48		+5040	13586
21		−5040	14926	35		+5040	14208	49		+1260	13560
22		−1260	14852	36		+1260	14172	50		+5040	13476
23		−840	14592	37		+1260	14144	51		+2520	13336
24		−840	14508	38		+5040	14032	52		+1260	13332
25		−2520	14446	39		+5040	14032	53		+630	13312
26		+21	15360	40		+5040	14032	54		+2520	13276
27		+420	15192	41		+2520	13876	55		+1260	13276

I	Graph	g	Value	I	Graph	g	Value	I	Graph	g	Value
98		−2520	12184	112		−5040	11926	126		−5040	11510
99		−2520	12168	113		−5040	11848	127		−1260	11460
100		−1260	12168	114		−2520	11828	128		−2520	11448
101		−2520	12156	115		−2520	11816	129		−1260	11444
102		−2520	12144	116		−2520	11792	130		−5040	11438
103		−2520	12120	117		−2520	11792	131		−5040	11418
104		−1260	12080	118		−1260	11740	132		−2520	11406
105		−2520	12052	119		−2520	11712	133		−2520	11388
106		−5040	12006	120		−5040	11710	134		−2520	11364
107		−5040	12006	121		−1260	11672	135		−2520	11332
108		−1260	12000	122		−5040	11622	136		−2520	11332
109		−2520	11940	123		−2520	11608	137		−5040	11298
110		−2520	11928	124		−5040	11598	138		−1260	11248
111		−5040	11926	125		−1260	11588	139		−630	11224

I	g	Value	I	g	Value	I	g	Value
140	-2520	11184	154	-2520	10732	168	+5040	11218
141	-2520	11112	155	-2520	10604	169	+2520	11180
142	-2520	11084	156	-1260	10332	170	+1260	11052
143	-2520	11082	157	-1260	10244	171	+2520	11004
144	-630	11056	158	+210	12476	172	+2520	11004
145	-5040	11004	159	+2520	11788	173	+1260	11000
146	-1260	10960	160	+630	11720	174	+1260	11000
147	-5040	10930	161	+2520	11532	175	+2520	10972
148	-5040	10910	162	+840	11496	176	+1260	10936
149	-5040	10888	163	+840	11448	177	+2520	10888
150	-1260	10872	164	+2520	11412	178	+2520	10868
151	-2520	10812	165	+1260	11352	179	+630	10816
152	-630	10784	166	+1260	11304	180	+5040	10808
153	-420	10752	167	+5040	11218	181	+5040	10780

I	g	Value	I	g	Value	I	g	Value
224	+2520	9980	238	+1260	9724	252	-630	10576
225	+840	9972	239	+2520	9684	253	-315	10320
226	+2520	9968	240	+840	9612	254	-1260	10312
227	+1260	9960	241	+2520	9588	255	-1260	10208
228	+630	9928	242	+2520	9544	256	-5040	10100
229	+1260	9880	243	+2520	9536	257	-2520	10072
230	+2520	9848	244	+2520	9496	258	-420	9960
231	+5040	9836	245	+5040	9386	259	-2520	9936
232	+1260	9824	246	+1260	9372	260	-1260	9916
233	+2520	9788	247	+1260	9312	261	-2520	9908
234	+1260	9776	248	+840	9276	262	-2520	9904
235	+5040	9754	249	+1260	9248	263	-2520	9888
236	+1260	9744	250	+2520	9232	264	-630	9840
237	+5040	9740	251	+35	9216	265	-2520	9728

I	g	Value	I	g	Value	I	g	Value
182	+5040	10750	196	+420	10548	210	+5040	10200
183	+630	10728	197	+2520	10536	211	+630	10192
184	+2520	10720	198	+5040	10516	212	+420	10188
185	+2520	10692	199	+5040	10508	213	+1260	10164
186	+2520	10692	200	+2520	10368	214	+5040	10162
187	+5040	10638	201	+2520	10368	215	+5040	10138
188	+2520	10628	202	+630	10336	216	+5040	10120
189	+2520	10624	203	+2520	10312	217	+5040	10078
190	+1260	10616	204	+2520	10312	218	+5040	10068
191	+1260	10576	205	+2520	10304	219	+2520	10056
192	+2520	10568	206	+2520	10296	220	+5040	10050
193	+5040	10566	207	+420	10296	221	+5040	10022
194	+315	10560	208	+1260	10248	222	+2520	10016
195	+2520	10556	209	+2520	10236	223	+2520	10012

I	g	Value	I	g	Value	I	g	Value
266	-2520	9728	280	-1260	9368	294	-2520	9176
267	-210	9720	281	-2520	9352	295	-2520	9176
268	-1260	9696	282	-840	9348	296	-2520	9112
269	-5040	9654	283	-5040	9338	297	-5040	9106
270	-2520	9636	284	-2520	9320	298	-2520	9076
271	-840	9624	285	-5040	9288	299	-2520	9068
272	-630	9600	286	-1260	9288	300	-630	9048
273	-2520	9508	287	-2520	9280	301	-1260	9016
274	-5040	9488	288	-1260	9280	302	-1260	9004
275	-1260	9464	289	-5040	9266	303	-1260	8992
276	-1260	9456	290	-1260	9244	304	-630	8976
277	-420	9456	291	-5040	9226	305	-5040	8964
278	-2520	9428	292	-1260	9216	306	-2520	8964
279	-5040	9410	293	-1260	9204	307	-1260	8964

I	Graph	g	Value	I	Graph	g	Value	I	Graph	g	Value
308		-1260	8936	322		-2520	8572	336		+630	9200
309		-2520	8932	323		-5040	8568	337		+1260	9004
310		-2520	8922	324		-2520	8532	338		+840	8940
311		-5040	8878	325		-2520	8516	339		+1260	8872
312		-2520	8824	326		-2520	8478	340		+5040	8858
313		-1260	8792	327		-1260	8440	341		+630	8808
314		-5040	8786	328		-1260	8416	342		+1260	8708
315		-105	8784	329		-1260	8376	343		+5040	8698
316		-1260	8740	330		-2520	8336	344		+2520	8680
317		-2520	8720	331		-210	8280	345		+2520	8616
318		-2520	8672	332		-630	8272	346		+1260	8568
319		-5040	8662	333		+210	9480	347		+2520	8564
320		-2520	8656	334		+1260	9228	348		+1260	8536
321		-2520	8580	335		+420	9216	349		+1260	8520

I	Graph	g	Value	I	Graph	g	Value	I	Graph	g	Value
392		-1260	8208	406		-2520	7622	420		-2520	7184
393		-35	8208	407		-1260	7584	421		-1260	7184
394		-2520	8068	408		-630	7512	422		-1260	7152
395		-420	8040	409		-1260	7504	423		-420	7128
396		-1260	7968	410		-5040	7500	424		-140	7128
397		-315	7952	411		-2520	7416	425		-315	7056
398		-210	7920	412		-2520	7400	426		-70	7056
399		-2520	7864	413		-1260	7372	427		-252	7020
400		-1260	7864	414		-630	7360	428		-2520	7008
401		-1260	7776	415		-2520	7324	429		-420	6972
402		-840	7716	416		-2520	7292	430		+630	7456
403		-840	7716	417		-1260	7272	431		+840	7368
404		-1260	7704	418		-840	7224	432		+210	7272
405		-630	7696	419		-5040	7204	433		+105	7200

I	Graph	g	Value	I	Graph	g	Value	I	Graph	g	Value
350		+420	8496	364		+2520	8212	378		+2520	7904
351		+5040	8476	365		+1260	8196	379		+2520	7872
352		+1260	8464	366		+315	8192	380		+2520	7868
353		+1260	8456	367		+210	8160	381		+2520	7868
354		+1260	8448	368		+1260	8104	382		+5040	7848
355		+105	8448	369		+1260	8092	383		+630	7848
356		+2520	8436	370		+2520	8084	384		+1260	7816
357		+2520	8376	371		+2520	8060	385		+2520	7748
358		+5040	8294	372		+5040	7990	386		+2520	7692
359		+2520	8288	373		+2520	7988	387		+2520	7672
360		+1260	8272	374		+1260	7960	388		+2520	7640
361		+1260	8244	375		+630	7960	389		+420	7584
362		+2520	8232	376		+2520	7952	390		+105	7488
363		+2520	8212	377		+1260	7944	391		+360	7476

I	Graph	g	Value	I	Graph	g	Value	I	Graph	g	Value
434		+1260	7132	446		+420	6624	458		-630	6192
435		+630	7048	447		+1260	6552	459		-315	6096
436		+1260	7032	448		+1260	6540	460		+140	6120
437		+1260	6944	449		+105	6528	461		+35	6048
438		+2520	6856	450		-105	6960	462		+420	5964
439		+2520	6836	451		-420	6576	463		+630	5856
440		+1260	6816	452		-1260	6488	464		+105	5760
441		+252	6780	453		-105	6480	465		-105	5616
442		+1260	6728	454		-420	6360	466		-105	5520
443		+315	6720	455		-1260	6312	467		+21	5280
444		+420	6696	456		-210	6288	468		-1	5040
445		+2520	6660	457		-1260	6204				

Errata

I	Graph	g	Value
158		+210	12456
217		+5040	10078
326		−2520	8478
327		−1260	8440
348		+1260	8536
360		+1260	8272
419		−5040	7204

APPENDIX II

Doubly Rooted Graphs and Integral Values for Less than Six Points

In this appendix we list all of the doubly rooted graphs contributing to the first four approximations to

the radial distribution function, together with the values of the one-dimensional integrals. The graphs are numbered serially for each value of n, the number of points, and ordered according to (1) number of points, (2) number of lines, and (3) value of the one-dimensional integral. These values are derived from the following form of the integral

$$(n-2)!\int S_i^*(n)\,dr_3\cdots dr_n.$$

This form is chosen so as to make all coefficients appear as integers.

Because the value of the integral is a function of $r_{12}\equiv r$, it is necessary to tabulate the values separately for $0<r<1$, $1<r<2$, $\cdots$, where we have assigned σ the value unity. The other numbers associated with each graph are the serial index and g, the number of ways the graph may be labeled with the root points being 1 and 2. Although the integral values for $0<r<1$ do not contribute to the one-dimensional radial distribution function, these values are needed for the distribution functions in two or more dimensions, and are included for that reason.

I	Graph	g	$0<r<1$	$1<r<2$	$2<r<3$
1		+1	2− r	2− r	0
1		−2	6 − 2r²	9− 6r+ r²	9− 6r+ r²
2		+1	8− 8r+ 2r²	8− 8r+ 2r²	0
3		+4	6− 2r− r²	8− 6r+ r²	0
4		−1	6− 4r	8− 8r+ 2r²	0
1		+6	32 −12r²+3r³	32 −12r²+3r³	64−48r+12r²− r³ (for 2<r<4)
2		−6	36−18r−12r²+6r³	54−63r+24r²−3r³	0
3		−12	32−12r− 6r²+2r³	32−12r− 6r²+2r³	0
4		−12	28 −12r²+2r³	38−21r + r³	54−45r+12r²− r³
5		−6	28 −12r²+2r³	38−21r + r³	54−45r+12r²− r³
6		−6	28 −12r²	54−54r+18r²−2r³	54−54r+18r²−2r³
7		+1	48−72r+36r²−6r³	48−72r+36r²−6r³	0
8		+12	36−30r +3r³	48−60r+24r²−3r³	0
9		+3	32−24r +2r³	32−24r +2r³	0
10		+12	28− 9r− 6r²+ r³	34−21r + r³	0
11		+12	28− 9r− 6r²+ r³	34−21r + r³	0

I	Graph	g	$0<r<1$	$1<r<2$	$2<r<3$
12		+12	28− 9r−12r²+4r³	46−51r+18r²−2r³	0
13		+6	28− 6r− 6r²−2r³	52−54r+18r²−2r³	0
14		+6	28− 6r−12r²+3r³	44−42r+12r²− r³	0
15		+6	24 −12r²+2r³	38−30r+ 6r²	54−54r+18r²−2r³
16		−3	36−42r+12r²	48−72r+36r²−6r³	0
17		−12	28−15r− 6r²+2r³	48−60r+24r²−3r³	0
18		−6	28−18r− 6r²+4r³	40−48r+18r²−2r³	0
19		−3	28−18r	32−24r +2r³	0
20		−6	24− 6r− 6r²	36−30r+ 6r²	0
21		−6	24− 6r−12r²+4r³	38−39r+12r²− r³	0
22		+3	28−24r +2r³	48−72r+36r²−6r³	0
23		+6	24−12r− 6r²+2r³	40−48r+18r²−2r³	0
24		−1	24−18r	48−72r+36r²−6r³	0