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,[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

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

† 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.
[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

$$\rho\equiv N/V=\sum_{n=1}^{N} nb_n z^n, \tag{5}$$

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

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

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

$$P/kT=\rho+B_2\rho^2+B_3\rho^3+B_4\rho^4+B_5\rho^5+B_6\rho^6+\cdots, \tag{7}$$

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,

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

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] 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.

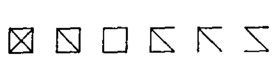

FIG. 1. The connected graphs of four points. The g_i indicate the number of ways each graph can be labeled.

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

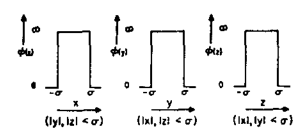

FIG. 2. The hard-cube potential. The molecular side length is σ.

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

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

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.

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[5] B. T. Geilikman, Proc. Acad. Sci. U.S.S.R. **70**, 25 (1950).
[6] R. W. Zwanzig, J. Chem. Phys. **24**, 855 (1956).
[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

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

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 $n = 2\cdots 4$:

$$B_2=\frac{1}{2V}\int\text{——}\,d\mathbf{r}_1d\mathbf{r}_2, \tag{10}$$

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

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

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

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

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,

$$I=\int f_{12}f_{23}f_{34}f_{45}f_{56}f_{61}dx_2dx_3dx_4dx_5dx_6 \tag{14}$$

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

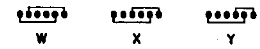


FIG. 3. The f functions characterizing w, x, and y subintegrals are indicated as lines connecting the molecules.

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

$$\begin{aligned}123456&=\int f_{12}f_{23}f_{34}f_{45}f_{56}f_{61}dx_2dx_3dx_4dx_5dx_6\\&\qquad(0<x_2<x_3<x_4<x_5<x_6<\sigma)\\&=\int_0^\sigma dw\int_w^\sigma dx\int_x^\sigma dy\int_y^\sigma dz\int_z^\sigma da=\sigma^5/5!.\end{aligned} \tag{15}$$

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 $\int \bigcirc\, dr_2 \cdots dr_6$.

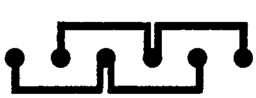
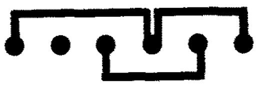
Ordering	Diagram	Subintegral	Name	Value$\times$ $5!/\sigma^5$
123456		$\int_0^\sigma dw \int_w^\sigma dx \int_x^\sigma dy \int_y^\sigma dz \int_z^\sigma da$	σ	1
124563		$\int_0^\sigma dw \int_w^\sigma dx \int_x^\sigma dy \int_y^\sigma dz \int_z^{\sigma+w} da$	w	2
124653		$\int_0^\sigma dw \int_w^\sigma dx \int_x^\sigma dy \int_y^{\sigma+w} dz \int_z^{\sigma+w} da$	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$\times$ $5!/\sigma^5$
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:

$$124563=\int f_{12}f_{23}f_{34}f_{45}f_{56}f_{61}dx_2dx_4dx_5dx_6dx_3$$

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

$$152463=\int f_{12}f_{23}f_{34}f_{45}f_{56}f_{61}dx_5dx_2dx_4dx_6dx_3$$

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

$$156423=\int f_{12}f_{23}f_{34}f_{45}f_{56}f_{61}dx_5dx_6dx_4dx_2dx_3$$

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

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

$$g\int \bigcirc\, d\mathbf{r}_2 \cdots d\mathbf{r}_6$$

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

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

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

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

We conjecture that the obvious generalization to L_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 (△, □, ⬠, $\cdots$) 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} and I_{2n}. Using this formula one finds $+88/5$ for the integral over ⬡, and $-5887/180$ for the integral over ⬡, 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

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

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

$n=2$ Subintegral	Value×1!
σ	1

$n=3$ Subintegral	Value×2!
σ	1

$n=4$ Subintegral	Value×3!
σ	1
w	2

$n=5$ Subintegral	Value×4!
σ	1
w	2
$ww=x$	3
wx	5

$n=6$ Subintegral	Value×5!
σ	1
w	2
$ww=x$	3
$www=y$	4
wx	5
$wwx=wy$	7
$wxx=xy$	9
wwy	11
wxy	16
xx	6

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

[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.

[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 $\sigma\equiv 1$. 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	$\frac{11}{3}$	$\frac{67}{18}$	$\frac{121}{40}$	$\frac{17827}{10800}$
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[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: $\square$, $\boxbslash$, and $\boxtimes$. In terms of subintegrals,

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

$$I(\boxbslash)=20\sigma+4w, \tag{24}$$

$$I(\boxtimes)=24\sigma. \tag{25}$$

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 subintegral 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]

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

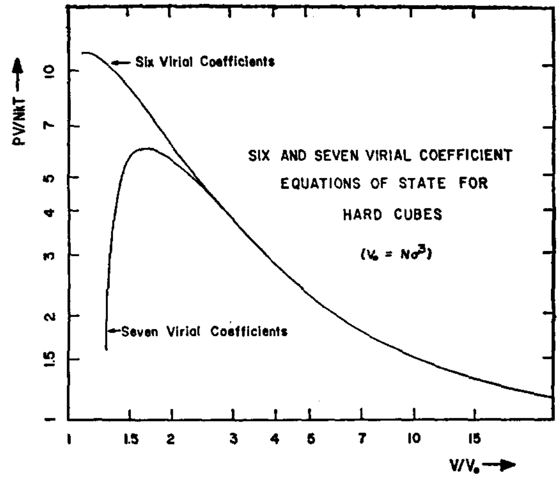


FIG. 5. Equation of state for hard cubes.

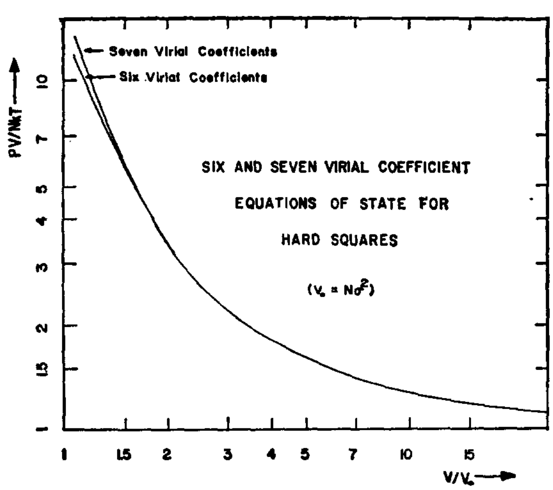


FIG. 4. Equation of state for hard spheres.

[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×1/2!

Lines	σ
1	−1
Total	−1

B_3 Contributions×1/3!

Lines	σ
3	−1
Total	−1

B_4 Contributions×1/4!

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

B_5 Contributions×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×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×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.

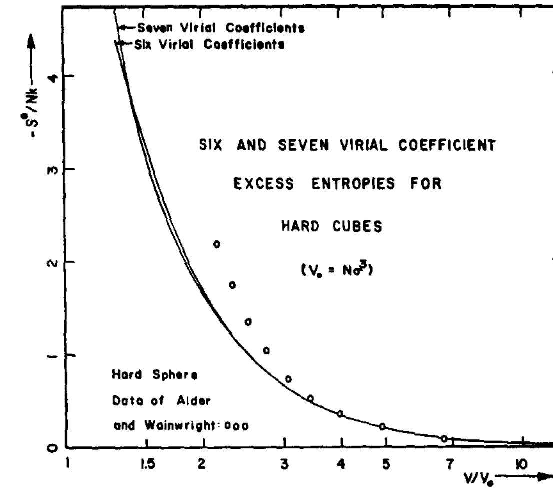


FIG. 7. Excess entropy for hard cubes.

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

$$n_2(\mathbf{r}_{12}) = \frac{\dfrac{1}{(N-2)!}\displaystyle\int \exp-\frac{\Phi(\mathbf{r}_1\cdots\mathbf{r}_N)}{kT}d\mathbf{r}_3\cdots d\mathbf{r}_N}{\dfrac{1}{N!}\displaystyle\int \exp-\frac{\Phi(\mathbf{r}_1\cdots\mathbf{r}_N)}{kT}d\mathbf{r}_1\cdots d\mathbf{r}_N}. \quad (28)$$

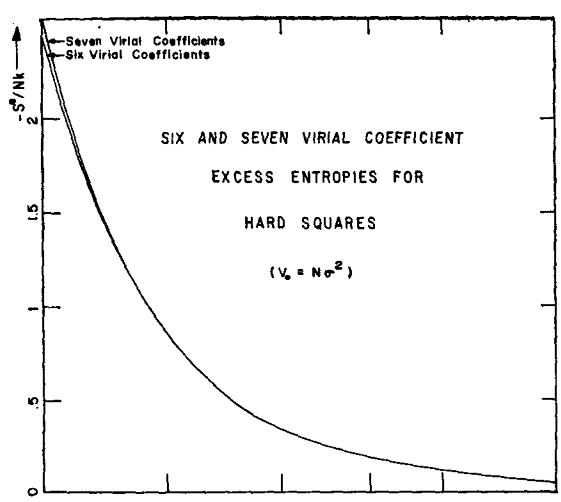


FIG. 6. Excess entropy for hard spheres.

[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).

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

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

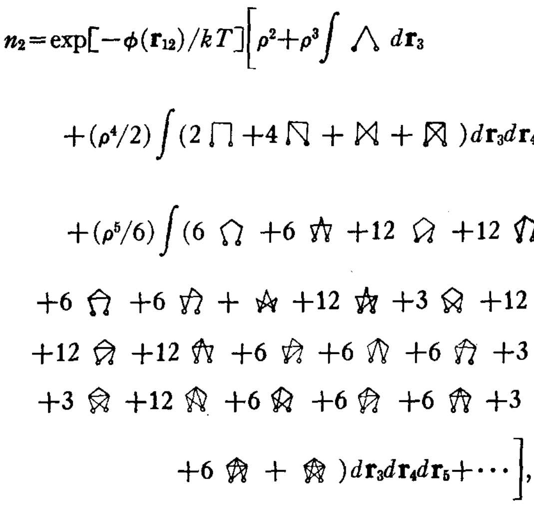
Using the fact that $z = Q_{N-1}/Q_N$ with the expansion of z in powers of ρ from inversion of Eq. (5),

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

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



(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.

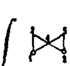
(2) Two kinds of molecules, not just one, are involved in distribution function calculations, the fixed molecules, 1 and 2 in the pair case, and the other molecules, whose coordinates are the integration variables. Thus, many different kinds of linear orderings are possible. For five molecules the orderings 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

$I\equiv\int$  $dx_3dx_4dx_5$, (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 $\int \bowtie \, dr_3dr_4dr_5$.

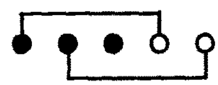
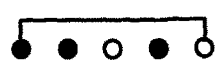
Ordering	Diagram	Integral for $0<r<1$	Integral for $1<r<2$
●●●12=12●●●:			
34512 35412		$2\int_{r-1}^{0}dw\int_{r-1}^{w}dx\int_{-1}^{x}dy$	Vanishes
43512 45312 53412 54312		$4\int_{r-1}^{0}dw\int_{r-1}^{w}dx\int_{r-1}^{x}dy$	Vanishes
Totals:		$(6-12r+6r^2)/6$	0
●●1●2=1●2●●:			
34152		$\int_{0}^{r}dw\int_{r-1}^{0}dx\int_{-1}^{x}dy$	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*)

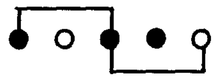
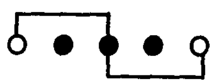
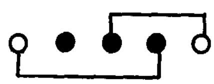
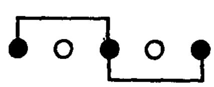
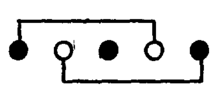
Ordering	Diagram	Integral for $0<r<1$	Integral for $1<r<2$
●1●●2=1●●2●:			
31452		$\int_0^r dw\int_0^w dx\int_{x-1}^0 dy$	$\int_{r-1}^1 dw\int_0^w dx\int_r^{w+1} dy$
31542		$\int_0^r dw\int_0^w dx\int_{w-1}^0 dy$	$\int_{r-1}^1 dw\int_{r-1}^w dx\int_{w-1}^0 dy$
41352 41532 51342 51432		$4\int_0^r dw\int_0^w dx\int_{r-1}^0 dy$	Vanishes
Totals:		$(18r^2-15r^3)/6$	$(12-12r+3r^2)/6$
1●●●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:		$(6r^3)/6$	$(12-6r)/6$
●1●2●:			
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 $x=0$(□□), as well as along $x=y$(◇◇); 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, ⋈ becomes ⧅ on setting $r=0$, and the value of

$$\int \bowtie\, dr_3dr_4dr_5$$

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,

$$\int_0^1 dr\left[\int \bowtie\, dr_3dr_4dr_5\right]$$

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

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

$$\int ☆\; dr_3dr_4dr_5=\left[\int \wedge\; dr_3\right]^3.$$

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

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

[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

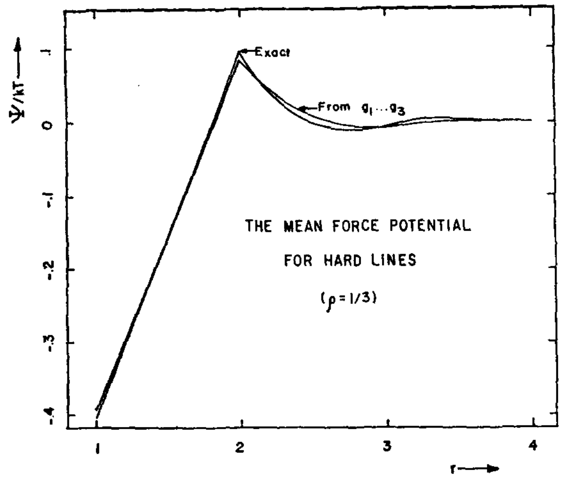


FIG. 8. Potential of the mean force for hard lines.

(6) From the virial theorem one may derive, for hard cubes, the equation $PV/NkT = 1 + 4\rho g(\text{surface})$, where $g(\text{surface})$ 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

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

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 $3V_0$,

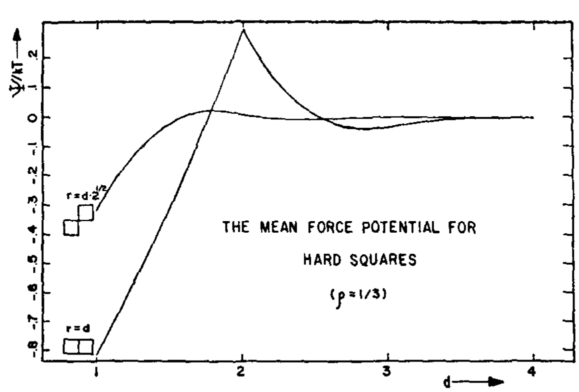


FIG. 9. Potential of the mean force for hard squares.

[23] J. de Boer, reference 20, p. 358.

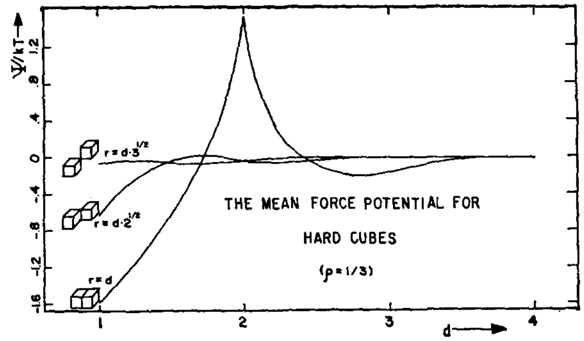


FIG. 10. Potential of the mean force for hard cubes.

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 $B_2 \equiv 1$.

	△	□	⬡	○
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[a]

[a] $0.7820 = (4/3) - (\sqrt{3}/\pi)$.

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].

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

I	Graph	g	Value
28		+90	1240
29		+360	1204
30		+90	1200
31		+360	1180
32		+360	1148
33		+360	1128
34		+360	1120
35		+180	1112
36		+72	1100
37		+45	1088
38		+360	1068
39		+60	1056
40		−180	1064
41		−360	1044

I	Graph	g	Value
42		−45	1040
43		−60	1008
44		−360	992
45		−60	984
46		−180	964
47		−90	960
48		+60	960
49		+20	936
50		+180	916
51		+180	888
52		+15	864
53		−60	840
54		−45	816
55		+15	768

I	Graph	g	Value
56		−1	720
1		−360	23548
2		+2520	19284
3		+2520	18596
4		+1260	18176
5		+1260	17724
6		−1260	16648
7		−5040	16384
8		−1260	16176
9		−2520	16098
10		−2520	16098
11		−2520	16008
12		−5040	15896
13		−2520	15896

I	Graph	g	Value
56		+5040	13264
57		+2520	13216
58		+2520	13168
59		+2520	13156
60		+2520	13116
61		+2520	13064
62		+2520	13016
63		+5040	12976
64		+5040	12976
65		+1260	12888
66		+2520	12868
67		+2520	12824
68		+1260	12760
69		+5040	12630

I	Graph	g	Value
70		+5040	12616
71		+1260	12544
72		+2520	12432
73		+1260	12236
74		+2520	12104
75		+630	11816
76		−21	15120
77		−840	13824
78		−630	13416
79		−1260	13088
80		−2520	13020
81		−2520	13020
82		−2520	12996
83		−2520	12996

I	Graph	g	Value
84		−630	12816
85		−1260	12744
86		−210	12696
87		−5040	12644
88		−5040	12606
89		−2520	12606
90		−2520	12606
91		−5040	12548
92		−1260	12520
93		−2520	12516
94		−2520	12408
95		−5040	12284
96		−630	12216
97		−2520	12196

I	Graph	g	Value
14		−420	15780
15		−1260	15700
16		−2520	15616
17		−5040	15498
18		−2520	15428
19		−1260	15428
20		−630	15032
21		−5040	14926
22		−1260	14852
23		−840	14592
24		−840	14508
25		−2520	14446
26		+21	15360
27		+420	15192

I	Graph	g	Value
28		+2520	14688
29		+5040	14460
30		+2520	14320
31		+1260	14320
32		+2520	14236
33		+840	14232
34		+5040	14208
35		+5040	14208
36		+1260	14172
37		+1260	14144
38		+5040	14032
39		+5040	14032
40		+5040	14032
41		+2520	13876

I	Graph	g	Value
42		+1260	13812
43		+2520	13808
44		+2520	13808
45		+1260	13776
46		+2520	13704
47		+2520	13704
48		+5040	13586
49		+1260	13560
50		+5040	13476
51		+2520	13336
52		+1260	13332
53		+630	13312
54		+2520	13276
55		+1260	13276

I	Graph	g	Value
98		−2520	12184
99		−2520	12168
100		−1260	12168
101		−2520	12156
102		−2520	12144
103		−2520	12120
104		−1260	12080
105		−2520	12052
106		−5040	12006
107		−5040	12006
108		−1260	12000
109		−2520	11940
110		−2520	11928
111		−5040	11926

I	Graph	g	Value
112		−5040	11926
113		−5040	11848
114		−2520	11828
115		−2520	11816
116		−2520	11792
117		−2520	11792
118		−1260	11740
119		−2520	11712
120		−5040	11710
121		−1260	11672
122		−5040	11622
123		−2520	11608
124		−5040	11598
125		−1260	11588

I	Graph	g	Value
126		−5040	11510
127		−1260	11460
128		−2520	11448
129		−1260	11444
130		−5040	11438
131		−5040	11418
132		−2520	11406
133		−2520	11388
134		−2520	11364
135		−2520	11332
136		−2520	11332
137		−5040	11298
138		−1260	11248
139		−630	11224

I	Graph	g	Value
140		−2520	11184
141		−2520	11112
142		−2520	11084
143		−2520	11082
144		−630	11056
145		−5040	11004
146		−1260	10960
147		−5040	10930
148		−5040	10910
149		−5040	10888
150		−1260	10872
151		−2520	10812
152		−630	10784
153		−420	10752

I	Graph	g	Value
154		−2520	10732
155		−2520	10604
156		−1260	10332
157		−1260	10244
158		+210	12476
159		+2520	11788
160		+630	11720
161		+2520	11532
162		+840	11496
163		+840	11448
164		+2520	11412
165		+1260	11352
166		+1260	11304
167		+5040	11218

I	Graph	g	Value
168		+5040	11218
169		+2520	11180
170		+1260	11052
171		+2520	11004
172		+2520	11004
173		+1260	11000
174		+1260	11000
175		+2520	10972
176		+1260	10936
177		+2520	10888
178		+2520	10868
179		+630	10816
180		+5040	10808
181		+5040	10780

I	Graph	g	Value
182		+5040	10750
183		+630	10728
184		+2520	10720
185		+2520	10692
186		+2520	10692
187		+5040	10638
188		+2520	10628
189		+2520	10624
190		+1260	10616
191		+1260	10576
192		+2520	10568
193		+5040	10566
194		+315	10560
195		+2520	10556

I	Graph	g	Value
196		+420	10548
197		+2520	10536
198		+5040	10516
199		+5040	10508
200		+2520	10368
201		+2520	10368
202		+630	10336
203		+2520	10312
204		+2520	10312
205		+2520	10304
206		+2520	10296
207		+420	10296
208		+1260	10248
209		+2520	10236

I	Graph	g	Value
210		+5040	10200
211		+630	10192
212		+420	10188
213		+1260	10164
214		+5040	10162
215		+5040	10138
216		+5040	10120
217		+5040	10078
218		+5040	10068
219		+2520	10056
220		+5040	10050
221		+5040	10022
222		+2520	10016
223		+2520	10012

I	Graph	g	Value
224		+2520	9980
225		+840	9972
226		+2520	9968
227		+1260	9960
228		+630	9928
229		+1260	9880
230		+2520	9848
231		+5040	9836
232		+1260	9824
233		+2520	9788
234		+1260	9776
235		+5040	9754
236		+1260	9744
237		+5040	9740

I	Graph	g	Value
238		+1260	9724
239		+2520	9684
240		+840	9612
241		+2520	9588
242		+2520	9544
243		+2520	9536
244		+2520	9496
245		+5040	9386
246		+1260	9372
247		+1260	9312
248		+840	9276
249		+1260	9248
250		+2520	9232
251		+35	9216

I	Graph	g	Value
252		−630	10576
253		−315	10320
254		−1260	10312
255		−1260	10208
256		−5040	10100
257		−2520	10072
258		−420	9960
259		−2520	9936
260		−1260	9916
261		−2520	9908
262		−2520	9904
263		−2520	9888
264		−630	9840
265		−2520	9728

I	Graph	g	Value
266		−2520	9728
267		−210	9720
268		−1260	9696
269		−5040	9654
270		−2520	9636
271		−840	9624
272		−630	9600
273		−2520	9508
274		−5040	9488
275		−1260	9464
276		−1260	9456
277		−420	9456
278		−2520	9428
279		−5040	9410

I	Graph	g	Value
280		−1260	9368
281		−2520	9352
282		−840	9348
283		−5040	9338
284		−2520	9320
285		−5040	9288
286		−1260	9288
287		−2520	9280
288		−1260	9280
289		−5040	9266
290		−1260	9244
291		−5040	9226
292		−1260	9216
293		−1260	9204

I	Graph	g	Value
294		−2520	9176
295		−2520	9176
296		−2520	9112
297		−5040	9106
298		−2520	9076
299		−2520	9068
300		−630	9048
301		−1260	9016
302		−1260	9004
303		−1260	8992
304		−630	8976
305		−5040	8964
306		−2520	8964
307		−1260	8964

I	Graph	g	Value
308		-1260	8936
309		-2520	8932
310		-2520	8922
311		-5040	8878
312		-2520	8824
313		-1260	8792
314		-5040	8786
315		-105	8784
316		-1260	8740
317		-2520	8720
318		-2520	8672
319		-5040	8662
320		-2520	8656
321		-2520	8580

I	Graph	g	Value
322		-2520	8572
323		-5040	8568
324		-2520	8532
325		-2520	8516
326		-2520	8478
327		-1260	8440
328		-1260	8416
329		-1260	8376
330		-2520	8336
331		-210	8280
332		-630	8272
333		+210	9480
334		+1260	9228
335		+420	9216

I	Graph	g	Value
336		+630	9200
337		+1260	9004
338		+840	8940
339		+1260	8872
340		+5040	8858
341		+630	8808
342		+1260	8708
343		+5040	8698
344		+2520	8680
345		+2520	8616
346		+1260	8568
347		+2520	8564
348		+1260	8536
349		+1260	8520

I	Graph	g	Value
392		-1260	8208
393		-35	8208
394		-2520	8068
395		-420	8040
396		-1260	7968
397		-315	7952
398		-210	7920
399		-2520	7864
400		-1260	7864
401		-1260	7776
402		-840	7716
403		-840	7716
404		-1260	7704
405		-630	7696

I	Graph	g	Value
406		-2520	7622
407		-1260	7584
408		-630	7512
409		-1260	7504
410		-5040	7500
411		-2520	7416
412		-2520	7400
413		-1260	7372
414		-630	7360
415		-2520	7324
416		-2520	7292
417		-1260	7272
418		-840	7224
419		-5040	7204

I	Graph	g	Value
420		-2520	7184
421		-1260	7184
422		-1260	7152
423		-420	7128
424		-140	7128
425		-315	7056
426		-70	7056
427		-252	7020
428		-2520	7008
429		-420	6972
430		+630	7456
431		+840	7368
432		+210	7272
433		+105	7200

I	Graph	g	Value
350		+420	8496
351		+5040	8476
352		+1260	8464
353		+1260	8456
354		+1260	8448
355		+105	8448
356		+2520	8436
357		+2520	8376
358		+5040	8294
359		+2520	8288
360		+1260	8272
361		+1260	8244
362		+2520	8232
363		+2520	8212

I	Graph	g	Value
364		+2520	8212
365		+1260	8196
366		+315	8192
367		+210	8160
368		+1260	8104
369		+1260	8092
370		+2520	8084
371		+2520	8060
372		+5040	7990
373		+2520	7988
374		+1260	7960
375		+630	7960
376		+2520	7952
377		+1260	7944

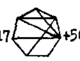
I	Graph	g	Value
378		+2520	7904
379		+2520	7872
380		+2520	7868
381		+2520	7868
382		+5040	7848
383		+630	7848
384		+1260	7816
385		+2520	7748
386		+2520	7692
387		+2520	7672
388		+2520	7640
389		+420	7584
390		+105	7488
391		+360	7476

I	Graph	g	Value
434		+1260	7132
435		+630	7048
436		+1260	7032
437		+1260	6944
438		+2520	6856
439		+2520	6836
440		+1260	6816
441		+252	6780
442		+1260	6728
443		+315	6720
444		+420	6696
445		+2520	6660

I	Graph	g	Value
446		+420	6624
447		+1260	6552
448		+1260	6540
449		+105	6528
450		-105	6960
451		-420	6576
452		-1260	6488
453		-105	6480
454		-420	6360
455		-1260	6312
456		-210	6288
457		-1260	6204

I	Graph	g	Value
458		-630	6192
459		-315	6096
460		+140	6120
461		+35	6048
462		+420	5964
463		+630	5856
464		+105	5760
465		-105	5616
466		-105	5520
467		+21	5280
468		-1	5040

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

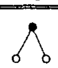
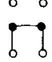
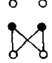
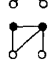
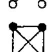
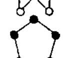
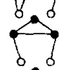
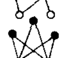
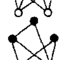
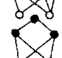
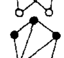
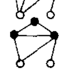
Doubly Rooted Graphs and Integral Values for Less than Six Points

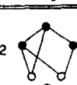
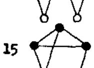
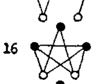
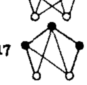
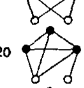
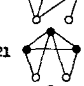
In this appendix we list all of the doubly rooted graphs contributing to the first four approximations to the radial distribution function, together with the values of the one-dimensional integrals. The graphs are numbered serially for each value of n, the number of points, and ordered according to (1) 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	$6-2r^2$	$9-6r+r^2$	$9-6r+r^2$
2		+1	$8-8r+2r^2$	$8-8r+2r^2$	0
3		+4	$6-2r-r^2$	$8-6r+r^2$	0
4		−1	$6-4r$	$8-8r+2r^2$	0
1		+6	$32-12r^2+3r^3$	$32-12r^2+3r^3$	$64-48r+12r^2-r^3$ (for $2<r<4$)
2		−6	$36-18r-12r^2+6r^3$	$54-63r+24r^2-3r^3$	0
3		−12	$32-12r-6r^2+2r^3$	$32-12r-6r^2+2r^3$	0
4		−12	$28-12r^2+2r^3$	$38-21r+r^3$	$54-45r+12r^2-r^3$
5		−6	$28-12r^2+2r^3$	$38-21r+r^3$	$54-45r+12r^2-r^3$
6		−6	$28-12r^2$	$54-54r+18r^2-2r^3$	$54-54r+18r^2-2r^3$
7		+1	$48-72r+36r^2-6r^3$	$48-72r+36r^2-6r^3$	0
8		+12	$36-30r+3r^3$	$48-60r+24r^2-3r^3$	0
9		+3	$32-24r+2r^3$	$32-24r+2r^3$	0
10		+12	$28-9r-6r^2+r^3$	$34-21r+r^3$	0
11		+12	$28-9r-6r^2+r^3$	$34-21r+r^3$	0

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