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Reformulation of the Virial Series for Classical Fluids*

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The usual graphical representation of the virial coefficients is reformulated in terms of graphs containing not only Mayer f functions, but also $\tilde{f}$ functions $[\tilde{f}\equiv f+1\equiv\exp(-\phi/kT)]$.

This reformulation has three main advantages:

(1) The number of integrals of topological graphs contributing to the virial coefficients is reduced; this simplifies numerical calculations.

(2) In Mayer's formulation none of the star integrals contributing to the virial coefficients (for hard potentials, at least) could be ignored; each made a nonnegligible contribution. In the new formulation (again, for hard potentials) many integrals make negligible (or even zero) contributions; the extensive cancellation of positive and negative terms found in Mayer's formulation is reduced.

(3) Several new ways of summing the virial series by successive approximation are suggested by the new formulation. One such way is worked out, in the first three approximations, for gases of hard parallel squares and cubes; the third approximation reproduces the first five virial coefficients exactly.

The reformulation is not restricted to the virial series alone. We also generalize our treatment to the radial distribution function. It can be applied to any series whose coefficients are integrals of graphs.

I. INTRODUCTION

EXPERIMENTAL measurements of the pressure P of an N-particle system in a volume V and at a temperature T are conveniently expressed in virial form:

$$\frac{P}{kT}=\sum_{n=1}^{\infty}B_n\rho^n; \qquad \rho\equiv\frac{N}{V}. \tag{1}$$

The B_n are the virial coefficients and k is Boltzmann's constant. The first few virial coefficients can be determined from experimental compressibility data.

Mayer and others[1] were able to derive (1) for classical systems of particles with a pairwise-additive potential ϕ in the specific limit that N and V are infinite, with fixed ratio ρ. When the series converges, the nth virial coefficient B_n is proportional to a sum of integrals of all the labeled topological stars of n points,

$$\{S_i[\mathbf{r}^n]\mid 1\leq i\leq S^{n\dagger}\}.$$

(The notation used in this paper is found in the Glossary.) Using the notation $(\ )_n$ to indicate

$$\frac{1}{V}\int_V(\ )d\mathbf{r}^n,$$

B_n can be written in the following way:

$$B_n=\frac{(1-n)}{n!}\sum_{i=1}^{S^{n\dagger}}(S_i[\mathbf{r}^n])_n. \tag{2}$$

Each n-point star represents a complicated function of the coordinates of n particles $[\mathbf{r}^n]$. The lines in the stars join pairs of Points i and j, and the occurrence of such a line stands for the Mayer f function

$$f_{ij}\equiv\exp(-\phi_{ij}/kT)-1.$$

As an example, the 10 $S_i[\mathbf{r}^4]$ contributing to the fourth virial coefficient are shown in Fig. 1. They are of three different topological types (we indicate types of stars by $S_i[n]$), so that three different kinds of integrals need to be evaluated in the computation of the fourth

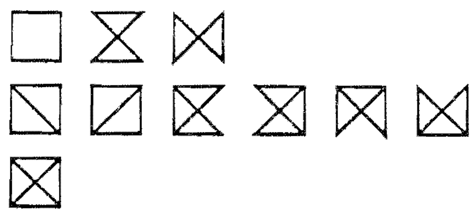

FIG. 1. The 10 labeled stars of four points. The numbering convention for the points is the same for each star

$$\begin{pmatrix}1 & 2\\ 3 & 4\end{pmatrix}$$

Notice that the stars are of three different types. $S^{4\dagger}=10$; $S^{4\ddagger}=3$.

virial coefficient for a given potential function ϕ. Introducing $\mathcal{S}_i[n]$ for the number of ways a star of the ith type can be labeled, we can write (2) in the following form:

$$B_n=\frac{(1-n)}{n!}\sum_{i=1}^{S^{n\ddagger}}\mathcal{S}_i[n](S_i[n])_n. \tag{3}$$

The number of types of star integrals in B_n according to Mayer's formulation is a rapidly increasing function[2] of n, which probably has the asymptotic n dependence

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[1] J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (John Wiley & Sons, Inc., New York, 1940); H. D. Ursell, Proc. Cambridge Phil. Soc. **23**, 685 (1927); M. Born and K. Fuchs, Proc. Roy. Soc. (London) **A166**, 391 (1938).

[2] R. J. Riddell, Jr. and G. E. Uhlenbeck, J. Chem. Phys. **21**, 2056 (1953).

$S^{n\ddagger} \approx 2^{n(n-1)/2}/n!$. The quantities $S^{2\ddagger}$, $S^{3\ddagger}$, $\cdots S^{7\ddagger}$ are 1, 1, 3, 10, 56, and 468, respectively.

Calculations for hard potentials show that the net contribution of positive integrals to $B_{n\geq 4}$ is roughly equal to that of negative integrals. Separating the positive and negative terms in (3) gives $B_5/(B_2)^4 = 7.902 - 7.793 = 0.110$ for hard spheres[3,4] and $6.364 - 6.352 = 0.012$ for hard cubes.[5] The final value of B_n is small in comparison to both the positive and negative contributions, being about the same order of magnitude as the contribution of the smallest star integral [0.024 for spheres and 0.020 for cubes in the case of $B_5/(B_2)^4$].

In the following section we introduce the $\tilde{f}$ function [$\tilde{f} \equiv f+1 \equiv \exp(-\phi/kT)$]. This "$f$ wiggle" function is indicated graphically by a wiggly line (as in Fig. 2). We then write B_n in terms of *modified star integrals* which contain both $\tilde{f}$ and f functions, with each n-point *modified star* containing $\binom{n}{2}$ $\tilde{f}$ and f functions in all. The number of integrals which must be evaluated for a particular B_n is considerably reduced, being 2, 5, 23, and 171[6] for n equal to 4, 5, 6, and 7, respectively. The excessive cancellation is also reduced. When $B_5/(B_2)^4$ is evaluated using modified star integrals, separating the positive and negative terms gives $0.158 - 0.048 = 0.110$ for hard spheres and $0.120 - 0.108 = 0.012$ for hard cubes.

For hard particles the two kinds of lines (f and $\tilde{f}$) restrict particles to be overlapping and nonoverlapping, respectively. In the Mayer stars some pairs of particles are restricted to overlap by f functions, but the overlap or nonoverlap of the other pairs (for which no lines appear) is unspecified. The removal of these degrees of freedom results in the reduced cancellation shown above for spheres and cubes.

All of the Mayer star integrals are generally nonzero, while many of the modified star integrals are identically zero for particular choices of potential function ϕ. The number of zero-valued modified star integrals contributing to B_n increases with n and decreases with dimensionality. For one-dimensional hard lines all but one of the contributing modified star integrals are zero.

In the Mayer representation the complete star integral gives the smallest contribution to the nth virial coefficient; in our reformulation, this integral gives the largest contribution of all the modified star integrals to the hard sphere and cube virial coefficients through B_7.

In addition to detailing the reformulation in Sec. III, we give a graphical interpretation of the coefficient associated with each kind of modified star appearing in B_n. In Sec. IV we cast our results in a more transparent series form. Truncating this series, we obtain approximate equations of state for gases of squares and cubes by summing over a small number of infinite sets of modified star integrals. A similar kind of summation appears in determinations of the equation of state from approximate integral equations for the radial distribution function. In Sec. V we show how to generalize our treatment to the number density expansion of the radial distribution function. Section VI is reserved for concluding remarks and a discussion of our results.

II. GLOSSARY

Meanings of symbols used, given in order of their introduction in the text.

- $\tilde{f}$ — f wiggle function, $\exp[-\phi/kT]$
- f — Mayer f function,
$$\tilde{f} - 1 \equiv [\exp(-\phi/kT)] - 1 \equiv f$$
- ϕ — pairwise-additive interparticle potential function
- kT — product of Boltzmann's constant and absolute temperature
- P — pressure of system
- N — number of particles in system
- V — volume of system
- B_n — coefficient of ρ^n in the number density expansion of P/kT; B_n is the nth virial coefficient
- ρ — number density, N/V
- $S_i[\mathbf{r}^n]$ — the ith labeled star of n points
- $S^{n\dagger}$ — the total number of different labeled stars of n points
- $(\ )_n$ — integral operator: $V^{-1}\int_V(\ )d\mathbf{r}^n$ for stars and modified stars, $\int_V(\ )d\mathbf{r}^n$ for doubly rooted graphs and modified doubly rooted graphs
- $\mathbf{r}^n$ — the coordinates of n particles
- $S_i[n]$ — the ith type of n-point star
- $\mathcal{S}_i[n]$ — the number of ways of labeling the ith type of n-point star
- $S^{n\ddagger}$ — the total number of different types of stars of n points
- $\tilde{S}_i[\mathbf{r}^n]$ — the ith labeled modified star of n points
- $\tilde{a}_i[n]$ — star content of an n-point modified star of the ith type
- $\tilde{S}_i[n]$ — the ith type of n-point modified star
- $\mathcal{S}_k[j, \mathbf{r}^n]$ — a Mayer star with f functions forming a subset of those in $\tilde{S}_j[\mathbf{r}^n]$
- ${}_n\mathcal{S}_j$ — the total number of Mayer stars with f functions forming a subset of those in $\tilde{S}_j[\mathbf{r}^n]$
- Δf_k — the number of f functions in $\tilde{S}_j[\mathbf{r}^n]$ which are not in $\mathcal{S}_k[j, \mathbf{r}^n]$
- η — number of $\tilde{f}$ functions in a wiggly-line graph
- p — the number of points connected by wiggly lines in a wiggly-line graph
- $(\varnothing)_n$ — the complete star integral,
$$V^{-1}\int_V \prod_{i<j}^{n} f_{ij} d\mathbf{r}^n;$$

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[3] S. Katsura and Y. Abe, J. Chem. Phys. **39**, 2068 (1963). The value of $B_5/(B_2)^4$, 0.1097 ± 0.002, found by these authors for hard spheres agrees with that found by us (Ref. 4), 0.1103 ± 0.0003.

[4] F. H. Ree and W. G. Hoover, J. Chem. Phys. **40**, 939 (1964).

[5] W. G. Hoover and A. G. De Rocco, J. Chem. Phys. **36**, 3141 (1962).

[6] We are calculating values of B_7 for hard spheres and disks using these modified stars.

$\varnothing$ is also used (in Fig. 8) to indicate

$$(f_{12})^{-1}\int_V \prod_{i<j}^{n+2} f_{ij}d\mathbf{r}_3\cdots d\mathbf{r}_{n+2}$$

h $\binom{n}{2}$

$B_n(1)$ first approximation to B_n, exact for $n<4$

$B_n(2)$ second approximation to B_n, exact for $n<5$

$B_n(3)$ third approximation to B_n, exact for $n<6$

y function of ρ,

$$\sum_{n=1}^{\infty}\rho^n n^{-2}\equiv y$$

$g(r)$ radial distribution function

$g_n(r)$ coefficient of ρ^n in the number density expansion of $g(r)\exp[\phi(r)/kT]$

$R_i[\mathbf{r}^{n+2}]$ the ith labeled doubly rooted graph of $n+2$ points with Rootpoints 1 and 2

$R_i[n+2]$ the ith type of doubly rooted graph of $n+2$ points with Rootpoints 1 and 2

$\tilde{R}_i[\mathbf{r}^{n+2}]$ the ith labeled modified doubly rooted graph of $n+2$ points with Rootpoints 1 and 2

$\tilde{R}_i[n+2]$ the ith type of modified doubly rooted graph of $n+2$ points with Rootpoints 1 and 2

$\mathfrak{r}_i[n]$ the number of ways of labeling the ith type of doubly rooted $n+2$ point graph

$R^{n\dagger}$ the total number of different labeled doubly rooted graphs of $n+2$ points with Rootpoints 1 and 2

$R^{n\ddagger}$ the total number of different types of doubly rooted graphs with Rootpoints 1 and 2

$\tilde{\alpha}_i[n]$ the doubly rooted graph content of an $n+2$ point doubly rooted graph of the ith type

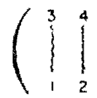
$\hat{f}$ the crossed-line function, $\hat{f}\equiv 1\equiv\tilde{f}-f$.

u $[(n-1)!]^{-1}$

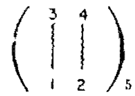
ν_k $(n-k)!$

III. REFORMULATION OF THE VIRIAL SERIES

In a previous publication[4] we described a new method for writing each virial coefficient in terms of modified star integrals. This method starts with Eq. (2), which expresses B_n in terms of labeled star integrals, and systematically introduces into each $S_i[\mathbf{r}^n]$ the identity $\tilde{f}-f$ ($\equiv 1$) for each pair of points which are not connected by f functions in that star. When these factors of $\tilde{f}-f$ are multiplied out, each Mayer star is expressed as a sum of modified stars, each of which has $\binom{n}{2}$ lines (counting both $\tilde{f}$ and f functions). We indicate the set of labeled modified stars by $\{\tilde{S}_i[\mathbf{r}^n] \mid 1\leq i\leq S^{n\dagger}\}$. There is an obvious one-to-one correspondence between $S_i[\mathbf{r}^n]$ and $\tilde{S}_i[\mathbf{r}^n]$, such that both have identical f functions. Combining the modified star expansions of all labeled Mayer stars of n points gives B_n in terms of modified star integrals. The results of this expansion are noteworthy; the number of integrals appearing in the new expression for B_n is considerably reduced from the number appearing in the Mayer expansions. The new expressions, for n less than 7, are given in Fig. 2. In this figure, and throughout this paper, we use the convention of drawing only the *wiggly-line graph* corresponding to a particular modified star. The wiggly-line graph consists only of the lines which represent $\tilde{f}$ functions in the modified star; the lines not drawn are understood to be Mayer f functions. This convention has the advantage that a single type of *wiggly-line integral* can be used to represent an infinite class of corresponding modified star integrals. For example,



$$\left(\ \right)_4 \equiv V^{-1}\int f_{12}\tilde{f}_{13}f_{14}f_{23}\tilde{f}_{24}f_{34}d\mathbf{r}^4,$$



$$\left(\ \right)_5 \equiv V^{-1}\int f_{12}\tilde{f}_{13}f_{14}f_{15}f_{23}\tilde{f}_{24}f_{25}f_{34}f_{35}f_{45}d\mathbf{r}^5.$$

The expansion of the Mayer stars by introducing products of the form $\prod[\tilde{f}-f]$ is somewhat unsatisfactory; in order to determine how many times a particular modified star $\tilde{S}_i[\mathbf{r}^n]$ contributes to B_n, it is necessary to expand all of the Mayer stars of n points. We have sought and found a more satisfactory way to determine the coefficient, $\tilde{a}_i[n]$, which multiplies each of the modified stars of type $\tilde{S}_i[n]$ in the full expansion. Notice that a particular modified star $\tilde{S}_j[\mathbf{r}^n]$, chosen to be of Type $\tilde{S}_i[n]$, is produced only by expanding those Mayer stars whose f functions form a subset of the f functions in $\tilde{S}_j[\mathbf{r}^n]$. Let us call this set of Mayer stars $\{\mathcal{S}_k[j,\mathbf{r}^n] \mid 1\leq k\leq {}_n\mathcal{S}_j\}$, and denote by $\Delta f_k(\geq 0)$ the number of functions in $\tilde{S}_j[\mathbf{r}^n]$ but not in $\mathcal{S}_k[j,\mathbf{r}^n]$. It is clear that the $\mathcal{S}_k[j,\mathbf{r}^n]$ are exactly those stars which can be formed by removing Δf_k f functions from those in $\tilde{S}_j[\mathbf{r}^n]$. We see that $\tilde{a}_i[n]$ is given by the expression

$$\tilde{a}_i[n]=\sum_{k=1}^{n\mathcal{S}_j}(-)^{\Delta f_k};\tag{4}$$

the minus sign appears because the expansion of $\prod(\tilde{f}-f)$ introduces f functions together with minus signs into $\mathcal{S}_k[j,\mathbf{r}^n]$. Equation (4) can be expressed by the following rule: *Count the number of labeled Mayer stars which can be formed by successively removing 0, 2, 4, $\cdots$ f functions from the f functions of any modified star $\tilde{S}_j[\mathbf{r}^n]$ of type $\tilde{S}_i[n]$; then substract the number of labeled Mayer stars which can be formed by removing 1, 3, 5, $\cdots$ f functions from the f functions of the same modified star. The resulting number (which can be positive, negative, or zero) is $\tilde{a}_i[n]$.* We call $\tilde{a}_i[n]$ the "star content" of the modified stars of type $\tilde{S}_i[n]$. Knowing the $\tilde{a}_i[n]$, we can express the nth virial coefficient in terms of modified star integrals:

$$B_n=\frac{(1-n)}{n!}\sum_{i=1}^{S^{n\ddagger}}\mathfrak{s}_i[n](S_i[n])_n$$

$$=\frac{(1-n)}{n!}\sum_{i=1}^{S^{n\ddagger}}\mathfrak{s}_i[n]\tilde{a}_i[n](\tilde{S}_i[n])_n.\tag{5}$$

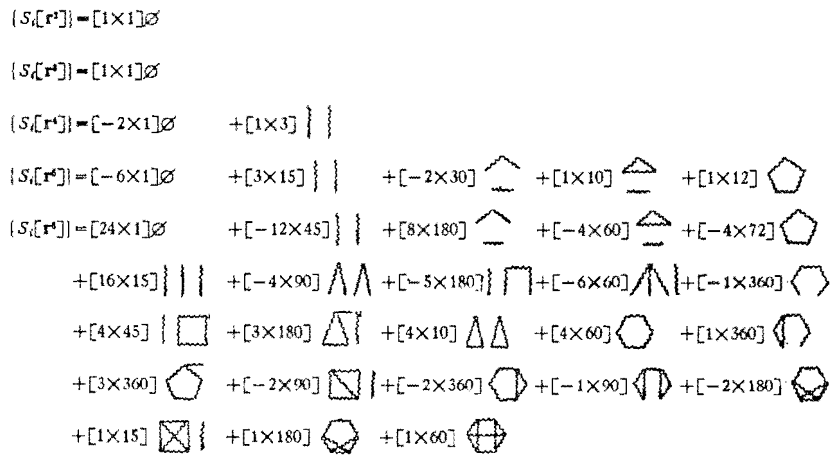


FIG. 2. The modified stars of 2, 3, 4, 5, and 6 points resulting from the expansion of $\{S_i[4]\}$, $\{S_i[5]\}$, and $\{S_i[6]\}$. $\{\tilde{S}_i[2]\}$ and $\{\tilde{S}_i[3]\}$ are identical with $\{S_i[2]\}$ and $\{S_i[3]\}$, respectively. The number of times a particular type of modified star appears in the full expansion, $\tilde{a}_i[n]\times\mathcal{S}_i[n]$, is prefixed to each topological type of modified star.

Notice that whenever any $\tilde{a}_i[n]$ is zero, the corresponding modified stars of the ith type make no contribution to the nth virial coefficient. All of the types of modified stars of less than seven points which have nonzero star contents $\tilde{a}_i[n]$ are listed in Fig. 2. Five modified star types for which $\tilde{a}_i[6]$ is zero are illustrated in Fig. 3. Notice that the number of types of contributing six-point modified star integrals is 23, while Mayer's formulation gives B_6 as the sum of 56 different integrals.

A particularly useful result relates $\tilde{a}_i[n]$ to $\tilde{a}_j[n-1]$ when the modified star types $\tilde{S}_i[n]$ and $\tilde{S}_j[n-1]$ have the same type of wiggly-line graph. This result,

$$\tilde{a}_i[n]=(-)^{n-1}[n-2]\tilde{a}_j[n-1], \qquad (6)$$

can be established by generalizing the proof of a closely related theorem due to Hoover and Poirier.[7] Using (6) recursively, one has the further relation

$$\tilde{a}_i[n]=(-)^{\binom{n}{2}-\binom{m}{2}}\tilde{a}_j[m](n-2)!/(m-2)!, \qquad m<n; \qquad (7)$$

where m is the least number such that there exists a modified star $\tilde{S}_k[\mathbf{r}^m]$ which has a wiggly-line graph of the same type as $\tilde{S}_i[n]$. Examples of both (6) and (7) can be found in Fig. 2. From (7) we see that whenever an m-point modified star of the jth type has zero star content, then *all* higher-point modified stars with the same type of wiggly-line graph have zero star content and do not contribute to the virial coefficients.

FIG. 3. Five modified star types which have zero star content. $\tilde{a}_i[6]=0$.

[7] W. G. Hoover and J. C. Poirier, J. Chem. Phys. **38**, 327 (1963), Appendix III.

Figure 4 shows several general wiggly-line graphs which correspond to modified stars of zero star content. These modified stars all have nonzero integrals for one-dimensional hard lines. However, because their star content is zero, these integrals do not contribute to B_n. Other than $(\varnothing)_n$, no wiggly-line graph contributes to B_n for one-dimensional hard lines [see remarks following Eq. (10)]. We prove that the first of the wiggly-line graphs in Fig. 4 has zero star content, leaving proofs for the others to the reader. Accordingly, consider the labeled wiggly-line graph shown in Fig. 5. This type of graph appears in the modified star graphs of n or more points, so that according to (7), we need only to calculate the star content of that particular n-point modified star which has the wiggly-line graph shown in Fig. 5. Let us call that modified star $\tilde{S}_k[\mathbf{r}^n]$.

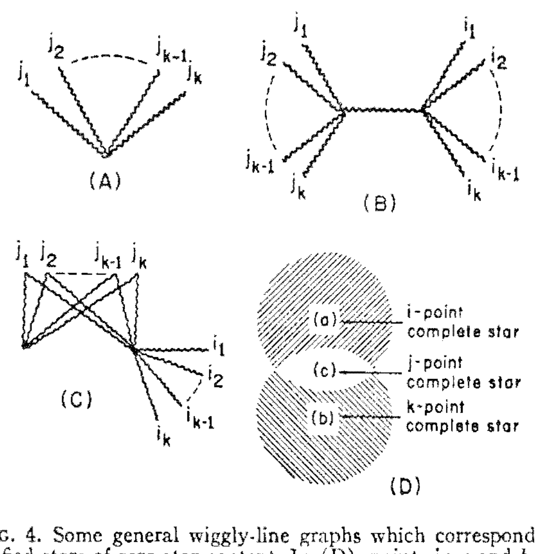


FIG. 4. Some general wiggly-line graphs which correspond to modified stars of zero star content. In (D), points in a and b are connected to those in c by f functions, but points in a are connected to those in b by $\bar{f}$ functions.

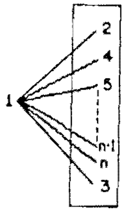


FIG. 5. A particular labeled $(n\text{-}2)$-point wiggly-line graph corresponding to an n-point modified star $\tilde{S}_k[n]$ with zero star content.

Each Mayer star that we can make by removing f functions from those of $\tilde{S}_k[\mathbf{r}^n]$ either contains or does not contain the f function f_{23}. Because each Mayer star that we make must contain both f_{12} and f_{13}, there is a one-to-one correspondence between stars with f_{23} and stars without f_{23}. Because corresponding stars contribute to (4) with opposite signs, the sum vanishes and the star content of $\tilde{S}_k[\mathbf{r}^n]$ is zero.

Using (7) we need to calculate the star content for only one member of each set of corresponding modified stars (those with the same type of wiggly-line graph), namely that member of the set with the least number of points, m. The contribution of this entire set of modified stars to all of the virial coefficients can then be written down immediately:

$$B_n=-\frac{1}{n}\sum_{i=1}^{S^{n\ddagger}}\frac{(-)^{\binom{n}{2}-\binom{m}{2}}\tilde{a}_j[m]\mathcal{S}_i[n](\tilde{S}_i[n])_n}{(m-2)!},\quad (8)$$

where j is chosen such that $\tilde{S}_j[m]$ and $\tilde{S}_i[n]$ have the same type of wiggly-line graph.

From (8), we see that the contribution to B_n (for repulsive potentials) of a particular type of wiggly-line graph has the same sign for any $n\geq m$, since $\tilde{S}_i[n]$ has the sign

$$(-)^{\binom{n}{2}-\eta},$$

where η is the number of $\tilde{f}$ functions in the corresponding wiggly-line graph. The number of ways to label $\tilde{S}_i[n]$ can also be represented in terms of the number of points p connected by wiggly lines in the corresponding wiggly-line graph and the number of ways to label $\tilde{S}_i[m]$:

$$\mathcal{S}_i[n]=\binom{n}{p}\mathcal{S}_i[m].\quad (9)$$

We see from (8) and (9) that the n dependence of a particular type of wiggly-line integral in B_n is

$$-\frac{(-)^{\binom{n}{2}}(\tilde{S}_i[n])_n(n-1)!}{(n-p)!}$$

Thus the combinatorial aspects of the reformulation of the virial series are solved. In the next section we show how to cast our results (5)–(9) into a general form which can be summed (term by term) over n, giving a set of successive approximations not only to B_n, but to the equation of state itself.

IV. SUCCESSIVE APPROXIMATION TECHNIQUES

Using the results of Sec. III it is possible to formulate several successive approximation techniques for the equation of state and for the virial coefficients. We list the three most obvious of these, and apply the results derived in Sec. III to gases of hard parallel squares and cubes. From Fig. 2 we see that only the complete star integral in which all lines are f functions [denoted by $(\varnothing)_n$] contributes to B_2 and B_3, while B_4 includes the additional integral

and B_5 includes

  and 

as well. Therefore, a natural way of approximating the virial series is to include all wiggly-line integrals which contribute to a particular B_n. The lowest-order approximation (exact for B_2 and B_3) includes only the complete star integral $(\varnothing)_n$ in B_n and can be written

$$B_n(1)\equiv(-)^h(\varnothing)_n/n,\qquad h\equiv\binom{n}{2},\qquad n>1;\quad (10)$$

The factors multiplying $(\varnothing)_n$ arise because $\tilde{a}_i[n]$ is $-(-)^h(n-2)!$ for the complete star [from (7)], while $\mathcal{S}_i[n]$ is 1. For hard one-dimensional lines of unit length, $(\varnothing)_n$ is known to be $(-)^h n$, so that B_n is $+1$ for all n and the equation of state is

$$PV/NkT=(1-\rho)^{-1},\qquad 0<\rho<1,\quad (11)$$

as Herzfeld and Mayer showed[8] by a direct integration of the canonical partition function for this system. Equation (10) gives their derivation a graphical meaning. The second approximation, exact for B_2, B_3, and B_4, is

$$B_n(2)\equiv B_n(1)-(-)^h\frac{3}{8}\binom{n-1}{3}$$  $$n>1;\quad (12)$$

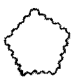
while the third approximation, exact for B_2 through B_5, is

$$B_n(3)\equiv B_n(2)-(-)^h\binom{n-1}{4}$$

$$\times\Big[-2$$  $$+\frac{1}{3}$$  $$+\frac{2}{5}$$  $$\Big],\qquad n>1.\quad (13)$$

[8] K. F. Herzfeld and M. G. Mayer, J. Chem. Phys. 2, 38 (1934).

TABLE I. Values of modified star integrals and contributions to B_n for hard parallel squares and cubes of unit side length.

Wiggly-line graphs	Corresponding modified star integrals $\times(-)^{\binom{n}{2}}$: Squares	Corresponding modified star integrals $\times(-)^{\binom{n}{2}}$: Cubes	Contributions to B_n: Squares	Contributions to B_n: Cubes
$\varnothing$ $(n\geq 2)$	n^2	n^3	n	n^3
 $(n\geq 4)$	$\frac{8}{(n-1)^2}$	$\frac{24(n^2-n+2)}{(n-1)^3}$	$-\frac{(n-2)(n-3)}{2(n-1)}$	$-\frac{3(n-2)(n-3)(n^2-n+2)}{2(n-1)^2}$
 $(n\geq 5)$	$\frac{16}{(n-1)^2(n-2)}$	$\frac{48(n^3-2n^2+3n-4)}{(n-1)^3(n-2)^2}$	$-\frac{4(n-3)(n-4)}{3(n-1)}$	$-\frac{4(n^3-2n^2+3n-4)(n-3)(n-4)}{(n-1)^2(n-2)}$
 $(n\geq 5)$	0	$\frac{288n}{(n-1)^3(n-2)^2}$	0	$-\frac{4n(n-3)(n-4)}{(n-1)^2(n-2)}$
 $(n\geq 5)$	$\frac{40(2n-5)}{(n-1)^2(n-2)^2(n-3)^2}$	$\frac{60}{(n-1)(n-2)(n-3)}\left\{-\frac{11}{n-1}+\frac{15}{n-3}-\frac{11}{(n-1)^2}+\frac{8}{(n-2)^2}+\frac{3}{(n-3)^2}\right\}$	$\frac{2(2n-5)(n-4)}{3(n-1)(n-2)(n-3)}$	$(n-4)\left\{-\frac{11}{n-1}+\frac{15}{n-3}-\frac{11}{(n-1)^2}+\frac{8}{(n-2)^2}+\frac{3}{(n-3)^2}\right\}$

In each of the Eqs. (10), (12), and (13), the $\tilde{a}_i[n]$ and $\mathfrak{B}_i[n]$ have been combined with $[(1-n)/n!]$ to give the numerical factors multiplying the wiggly-line integrals. Other successive approximation schemes can be based upon (i) the inclusion of all wiggly-line integrals containing fewer than a given number of $\tilde{f}$ functions, or (ii) the inclusion of all wiggly-line integrals whose $\tilde{f}$ functions connect less than a given number of points. All three of the successive approximations converge to the exact virial equation of state as the order of the approximation is increased. For particular potentials, still other kinds of approximations may be worthwhile. It appears possible to sort out those modified star integrals which make the most important contributions to the equation of state at high density. Combining the highest-order terms should give a reasonable approximation to the behavior of the high density virial equation of state.

The mathematical simplicity of the hard square and cube potentials makes it possible to evaluate the modified star integrals as functions of n. Details of the evaluation appear in the Appendix. The results, for the five kinds of wiggly-line integrals contributing to the first five virial coefficients, are given in Table I. Tables II and III also include the contribution of each kind of wiggly-line integral to B_n for $n<8$; notice that the third approximation (13) gives reasonably accurate values for B_6 (where 18 integrals are omitted from the exact equation by the approximation) and B_7 (where 166 integrals are omitted). Because, in each of the approximations (10), (12), and (13), *all* virial coefficients are given explicity as functions of n, it is possible to obtain corresponding approximations to the virial equation of state. For hard squares and cubes the resulting equations of state are plotted in Figs. 6 and 7 [the seven-term virial expansion is shown for comparison] and given analytically below:

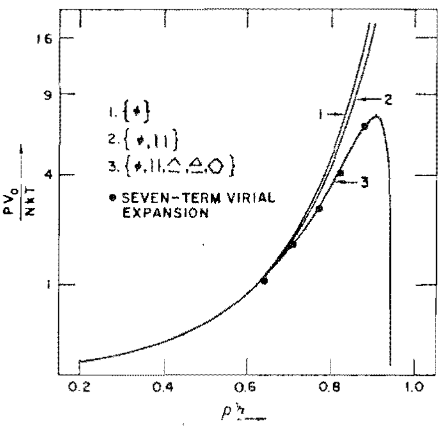


FIG. 6. Equations of state for hard parallel squares of unit side length, using modified star integrals. The curves labeled 1, 2, and 3 are based upon approximations (discussed in the text) which reproduce the first three, four, and five virial coefficients, respectively. The seven-term virial equation of state from Ref. 5 is included for comparison. The number density is 1 at the close-packed volume V_0.

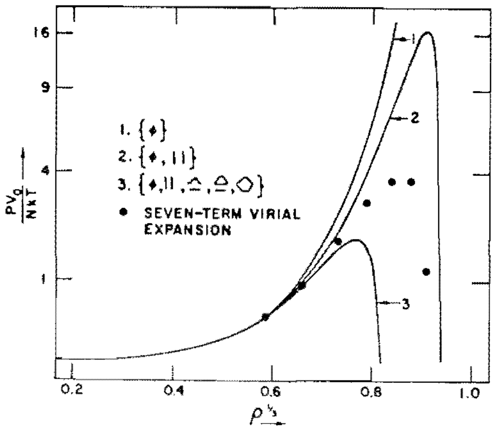


FIG. 7. Equations of state for hard parallel cubes of unit side length, using modified star integrals. The curves labeled 1, 2, and 3 are based upon approximations discussed in the text which reproduce the first three, four, and five virial coefficients, respectively. The seven-term virial equation of state from Ref. 5 is included for comparison. The number density is 1 at the close-packed volume V_0.

(1) $$P/kT(\text{squares})=\rho(1-\rho)^{-2}, \quad (14a)$$

$$P/kT(\text{cubes})=\rho(1+\rho)(1-\rho)^{-3}; \quad (14b)$$

(2) $$P/kT(\text{squares})=\rho(1+\rho-1\tfrac{1}{2}\rho^2)(1-\rho)^{-2}+\rho\ln(1-\rho), \quad (15a)$$

$$P/kT(\text{cubes})=\rho(1+\rho-1\tfrac{1}{2}\rho^2-1\tfrac{1}{2}\rho^3)(1-\rho)^{-3}-6\rho\ln(1-\rho)-6\rho y; \quad (15b)$$

(3) $$P/kT(\text{squares})=\rho(1+6\rho-7\tfrac{2}{3}\rho^2-\tfrac{1}{6}\rho^4)(1-\rho)^{-2}+\rho(6+1\tfrac{1}{3}\rho+\tfrac{1}{3}\rho^2)\ln(1-\rho), \quad (16a)$$

$$P/kT(\text{cubes})=\rho(1-98\rho+288\tfrac{1}{4}\rho^2-276\tfrac{3}{4}\rho^3+61\tfrac{1}{4}\rho^4+15\tfrac{1}{4}\rho^5)\times(1-\rho)^{-3}+4\rho(-24+6\rho+3\rho^2)\ln(1-\rho)+\rho(3-16\rho-3\rho^2)y; \quad (16b)$$

where y is defined by the expression

$$y\equiv\sum_{n=1}^{\infty}\rho^n n^{-2}=\int_{\rho}^{0}\ln(1-\rho)\,d\ln\rho. \quad (17)$$

For both squares and cubes the third approximation (16) to the equation of state (exact for the first five virial coefficients) exhibits a maximum in pressure, and predicts negative pressures at higher densities. It may be that this represents the true behavior of the virial expansion of such systems; another possibility is that higher approximations will contain large positive terms, so that taking these into account gives either (i) a van der Waals wiggle, or (ii) an isotherm which is monotone increasing with density.

TABLE II. Contribution of various wiggly-line integrals to B_n for hard squares. $B_n(1)$ reproduces exact values of B_n up to $n=3$. $B_n(2)$ reproduces exact values of B_n up to $n=4$. The expression in the next-to-last column, $B_n(3)$ reproduces exact values of B_n (Ref. 5) up to $n=5$.

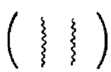
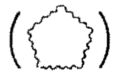
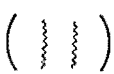
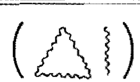
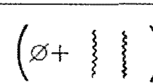
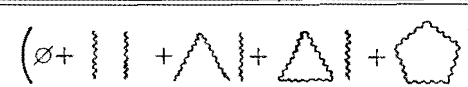
	(∅)						
n	$B_n(1)$				$B_n(2)$	$B_n(3)$	Exact
2	**2**	**0**	0	0	2	**2**	**2**
3	3	0	0	0	3	**3**	**3**
4	4	−1/3	0	0	3.6667	3.6667	3.6667
5	5	−27/36	−24/36	5/36	4.2500	3.7222	3.7222
6	6	−54/45	−72/45	7/45	4.8000	3.3556	3.0250
7	7	−100/60	−160/60	9/60	5.3333	2.8167	1.6506

TABLE III. Contributions of various wiggly-line graphs to B_n for hard cubes. $B_n(1)$ reproduces exact values of B_n up to $n=3$. $B_n(2)$ reproduces exact values of B_n up to $n=4$. The expression in the next-to-last column reproduces exact values of B_n (Ref. 5) up to $n=5$.

	(∅)							
n	$B_n(1)$					$B_n(2)$	$B_n(3)$	Exact
2	4	0	0	0	0	4	4	**4**
3	9	0	0	0	0	9	9	**9**
4	16	−14/3	0	0	0	11.3333	11.3333	11.3333
5	25	−1782/144	−2064/144	−120/144	821/144	12.6250	3.1597	3.1597
6	36	−1728/75	−2844/75	−108/75	479/75	12.9600	−20.0133	−18.8796
7	49	−44000/1200	−83840/1200	−2240/1200	7627/1200	12.3333	−53.0442	−43.5054

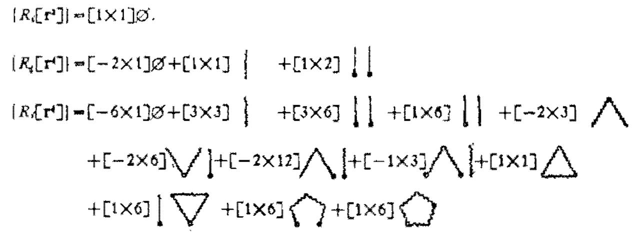


FIG. 8. The modified doubly rooted graphs of three, four, and five points resulting from the expansion of $\{R_i[3]\}$, $\{R_i[4]\}$, and $\{R_i[5]\}$. The number of times a particular type of modified doubly rooted graph appears in the full expansion $a_i[n]\times \mathfrak{r}_i[n]$ is prefixed to each topological type of doubly-rooted modified graph. Open circles indicate Rootpoints (Points 1 and 2). Whether or not open circles appear in the doubly rooted modified graphs, Points 1 and 2 are not connected by an f function.

Equations (14) through (16) show that the partial summations of wiggly-line integrals converge up to the close-packed density ($\rho=1$). For squares the difference between (14a) and (16a) is less than 10% for all densities less than half the close-packed density.

V. REFORMULATION OF OTHER SERIES

As pointed out in the introduction, our reformulation can easily be generalized to the radial distribution function. Any series expansion in the fugacity or number density whose coefficients are integrals of products of f functions can be so treated.[9] We will quote some results for the radial distribution function $g(r)$, defined by

$$g(r)\ \exp\left(\frac{\phi(r)}{kT}\right)=1+\sum_{n=1}^{\infty}g_n(r)\rho^n. \qquad (18)$$

Mayer and Montroll[10] showed that each $g_n(r)$ can be written as a sum of integrals (over the coordinates of the n particles 3, 4, $\cdots n+2$) of labeled doubly rooted (Rootpoints 1 and 2) graphs of $n+2$ points. Each of these graphs will become or remain a star if the f function joining the rootpoints, f_{12}, is added to the graphs. We denote the graphs by $\{R_i[\mathbf{r}^{n+2}]\mid 1\leq i\leq R^{n\dagger}\}$, types of topologically different graphs by

$$\{R_i[n+2]\mid 1\leq i\leq R^{n\ddagger}\},$$

and the number of ways to label $R_i[\mathbf{r}^{n+2}]$ by $\mathfrak{r}_i[n]$. Then we have the relations

$$g_n(r)=(n!)^{-1}\sum_{i=1}^{R^{n\dagger}}\int R_i[\mathbf{r}^{n+2}]d\mathbf{r}_3\cdots d\mathbf{r}_{n+2},$$

$$\equiv(n!)^{-1}\sum_{i=1}^{R^{n\dagger}}\mathfrak{r}_i[n](R_i[n+2])_n. \qquad (19)$$

By introducing $\tilde{f}-f$ for each pair of unconnected points in $R_i[\mathbf{r}^{n+2}]$(omitting the term $\tilde{f}_{12}-f_{12}$) we have a result for $g_n(r)$ analogous to (5) for B_n:

$$g_n(r)=(n!)^{-1}\sum_{i=1}^{R^{n\dagger}}\mathfrak{r}_i[n]\tilde{\alpha}_i[n](\tilde{R}_i[n+2])_n. \qquad (20)$$

The *modified doubly rooted graph integrals* $\tilde{R}i[n+2]$ and the *doubly rooted graph contents* $\tilde{\alpha}_i[n]$ are defined by analogy with the virial coefficient treatment. The recursion relation for $\tilde{\alpha}_i[n]$, analogous to (6) for $\tilde{a}_i[n]$, becomes

$$\tilde{\alpha}_i[n]=(-)^{n-1}n\tilde{\alpha}_i[n-1]. \qquad (21)$$

As examples of the reformulation of the radial distribution function, the modified doubly rooted graph integrals contributing to $g_1(r)$, $g_2(r)$, and $g_3(r)$ are listed[11] in Fig. 8. Again the number of integrals to be evaluated is reduced; a similar reduction occurs if the potential of mean force rather than $g(r)$ is reformulated.

VI. CONCLUDING REMARKS AND SUMMARY

In the preceding sections we have presented a general method for reformulating the virial series and the radial distribution function in terms of graphs containing not only f functions, but also $\tilde{f}$ functions. The original motivation for this work was to simplify the Monte Carlo calculation of virial coefficients for hard spheres.[4] Besides reducing the number of integrals to be evaluated, the reformulation produces a set of integrals of widely different values, some being much larger than others. For hard disks, for example,[4] 8 of the 23 modified star integrals contributing to the sixth virial coefficient are identically zero. Our reformulation is also of value for more realistic potentials, such as the Lennard-Jones-Mie or exponential-six potentials, except at low temperatures. At very low temperatures neither the Mayer formulation nor our own promises accurate virial coefficients by numerical techniques.[12]

Equation (5) has a form adaptable to Monte Carlo calculation of virial coefficients for gases interacting with hard potentials. This can be done with a high speed computer by placing Particles 2, $\cdots$ n at random (1 at the origin) in a sufficiently large volume [large enough to accommodate all geometrically accessible configurations in $(\tilde{S}_i[n])_n$]. Each configuration corresponds to many Mayer stars but to at most one modified star. The star content of a randomly selected modified star can be found by using the adjacency matrix.[12]

[9] Specific functions that can be treated include the fugacity series for the pressure and the number density, series for the surface tension [A. Bellemans, Physica 28, 493 (1962)], series for s-particle distribution functions, and series for s-particle potentials of mean force.

[10] J. E. Mayer and E. W. Montroll, J. Chem. Phys. 9, 2 (1941).

[11] N. Keeler and F. H. Ree are currently working on the calculation of $g_3(r)$ for hard spheres and disks using our reformulation.

[12] Unpublished work.

The feasibility of making successive approximations to the virial coefficients, radial distribution function, and equation of state, through the neglect of certain wiggly-line integrals has been demonstrated in the case of parallel hard squares and cubes. Such calculations can also be made for various lattice gases; for particular choices of lattice gas interparticle potentials, a great number of the modified star integrals vanish. For example, in the case of a two-dimensional lattice gas of hard particles covering four sites on a plane square lattice, the sixth virial coefficient has only six nonvanishing modified star sums (analogs of modified star integrals) in addition to the complete star sum $(\varnothing)_6$, and five of these star sums have the same value.[12]

The equations of state given for squares and cubes in Figs. 6 and 7 are almost certainly better approximations to the virial equation of state than are the corresponding (same number of exact virial coefficients) truncated virial expansions. The density range over which the virial expansion converges to the true equation of state remains unknown; in this connection Monte Carlo or molecular dynamics measurements of the equations of state for finite systems of hard squares and cubes would be useful, and yield interesting results. For these potentials one has the low-density seven-term virial expansion,[5] the approximate equations of state (14), (15), and (16), and knowledge of the exact finite-system high-density equation of state.[13] "Experimental" equations of state would be useful in determining the applicability of these theoretical results.

For squares and cubes, it may be possible to sort out those modified star integrals which make the most important contributions to the equation of state at high density. In two dimensions, for example, the contributions of the five wiggly-line integrals contributing to B_6 (see Fig. 2) to B_n are, respectively, of order n, n, n, 0, and $1/n$ for n large.

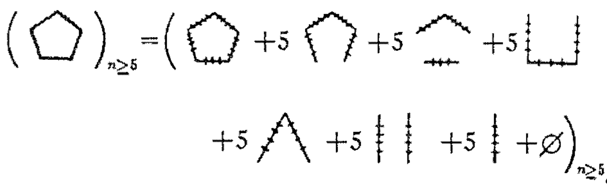
ACKNOWLEDGMENT

We wish to thank Dr. Theodore Einwohner for illuminating discussions related to the present work.

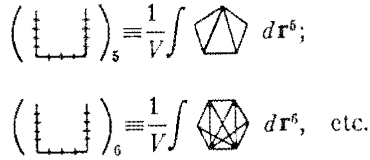
APPENDIX

In this Appendix we list some intermediate results necessary to the calculation of the wiggly-line integrals for hard lines, squares, and cubes. The calculation itself consists of many trivial steps not easy to describe in a formal way, so that we quote results rather than taking the considerable space necessary to give a complete proof.

We introduce the *crossed line* $\hat{f}$ to indicate that the two particles connected by such a line are independent, $\hat{f}\equiv 1$. This definition makes it possible to adhere to our convention of writing explicitly only those lines in a graph which are not Mayer f functions. Then, using the identity $\tilde{f}\equiv\hat{f}+f$, any wiggly-line integral over the coordinates of n points can be written as a finite sum of *crossed-graph integrals*:



The crossed-graph integrals are just the usual Mayer stars, where the crossed lines make up the complementary graph of the star in question:



In one dimension each crossed-graph integral can be expressed in terms of $n!$ subintegrals (as defined in Ref. 5) corresponding to the $n!$ ways of ordering n particles on a line. In this Appendix we evaluate only those wiggly-line integrals which contribute to B_5. The only kinds of subintegrals which occur in the related crossed-graph integrals are those called σ, w, ww, x, and wx by Hoover and De Rocco.[5] It can be shown that the values of these subintegrals are, respectively, u, $2u$, $3u$, $3u$, and $5u$, where u is $[(n-1)!]^{-1}$. For the ten Mayer stars contributing to B_5, there are ten corresponding crossed line integrals. Their decomposition into $n!$ subintegrals is as follows [where $\nu_k=(n-k)!$]:

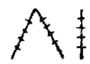
$$(-)^h(\varnothing)_n=\nu_0\sigma,$$

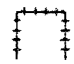
$-(-)^h\Big($  $\Big)_n=(\nu_0-2\nu_2)\sigma+2\nu_2 w,$

$(-)^h\Big($  $\Big)_n=(\nu_0-4\nu_2)\sigma+4\nu_2 w,$

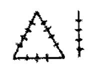
$(-)^h\Big($  $\Big)_n=(\nu_0-4\nu_2)\sigma+(4\nu_2-4\nu_3)w+2\nu_3(ww+x),$

[13] W. G. Hoover, J. Chem. Phys. **40**, 937 (1964).

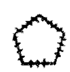
$-(-)^h\Big($  $\Big)_n = (\nu_0-6\nu_2)\sigma+(6\nu_2-4\nu_3)w+2\nu_3(ww+x),$

$-(-)^h\Big($  $\Big)_n = (\nu_0-6\nu_2)\sigma+(6\nu_2-8\nu_3+2\nu_4)w+(4\nu_3-2\nu_4)(ww+x)+2\nu_4wx,$

$-(-)^h\Big($  $\Big)_n = (\nu_0-6\nu_2)\sigma+(6\nu_2-12\nu_3)w+6\nu_3(ww+x),$

$(-)^h\Big($  $\Big)_n = (\nu_0-8\nu_2)\sigma+(8\nu_2-12\nu_3)w+6\nu_3(ww+x),$

$(-)^h\Big($  $\Big)_n = (\nu_0-8\nu_2)\sigma+(8\nu_2-12\nu_3+4\nu_4)w+(6\nu_3-4\nu_4)(ww+x)+4\nu_4wx,$

$-(-)^h\Big($  $\Big)_n = (\nu_0-10\nu_2)\sigma+(10\nu_2-20\nu_3+10\nu_4)w+(10\nu_3-10\nu_4)(ww+x)+10\nu_4wx.$

Substituting the values of the subintegrals into the above expressions gives explicity the values of the 10 one-dimensional hard-line star integrals. As an example, the last crossed-graph integral shown corresponds to

$\frac{1}{V}\int$  $d\mathbf{r}^7$

for $n=7$. With $\nu_0=5040$, $\nu_2=120$, $\nu_3=24$, $\nu_4=6$, the above integral for $n=7$ is 6780/720, in agreement with Ref. 5 (seven-point star Number 441 in Appendix I). Using the results just given, the crossed-line integrals can be combined to give the values listed in Tables II and III of the text.