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ON ANALYTIC SOLUTIONS FOR VIRIAL COEFFICIENTS
OF A HARD SPHERE GAS

by

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ABSTRACT

"ON ANALYTICAL SOLUTIONS FOR VIRIAL COEFFICIENTS OF A HARD SPHERE GAS"

By John H. Nairn

Various methods are considered for obtaining analytic solutions for the cluster integrals that contribute to the classical virial coefficients for a gas of hard spheres. Particular attention is given to the complete star graphs on four and five points. In Rowlinson's notation, these are the graphs $D_6$ and $E_{10}$.

The early work of Boltzmann, Van der Waals, and Van Laar is discussed extensively. Their methods are justified in terms of modern statistical thermodynamics and their results are translated into graph notation as introduced by Mayer. It is shown that their methods may be combined with a recently discovered connection between one-center and two-center graphs to give a direct geometrical verification of the Van Laar integration. The considerations necessary for extending this method to the graph $E_{10}$ are discussed. An integral expression for $E_{10}$ is given which involves the volume common to four spheres. The nature of this overlap volume and a method for calculating it are discussed.

Finally, a method used by Nijboer and Van Hove to evaluate the graph $\Delta \left( r_{12} \right)$ by the use of spherical Fourier transforms of the Mayer $f$-functions is discussed. A technique for extending this method to the evaluation of the graph $E_{10}$ is given.
I. INTRODUCTION

A. THE VIRIAL EQUATION OF STATE

In studying the behavior of gases, one is often interested in the relationship among the pressure (P), temperature (T), and the volume (V) of the system. A function relating these quantities is known as an equation of state. Such state equations also exist for solids and liquids, but their form is much more complex. As a result, considerably greater progress has been made toward understanding the gaseous state, and we shall confine our attention herein to gases.

The utility of an equation of state (for a system in any phase) stems from the fact that a knowledge of the exact form of such a state equation allows one to calculate many of the equilibrium properties of that system. If the exact function is not known (as it seldom is) the accuracy and range of validity of the calculated properties depend on how nearly the assumed equation of state approximates the true one.

The simplest model to study is the so-called ideal gas, for which the equation of state is \( PV = NkT \), where \( N \) is the number of particles and \( k \) is the Boltzmann constant. Point-mass particles with no interaction behave this way if the temperature is sufficiently high that quantum mechanical symmetry effects do not need to be taken into consideration. Quantum mechanical virial coefficients have been treated elsewhere (1,2) and we will assume classical statistics throughout this work. Real gases are found to obey this ideal gas law in the limit of zero density. At somewhat higher densities, corrections must be made for "gas imperfection", and it is the
nature of these corrections with which we will be concerned.

Historically, several empirical (and theoretical) attempts have been made to find approximate equations of state for real gases, the more famous of these resulting in the Van der Waals, the Berthelot, and the Dieterici equations. All of these depend on certain parameters which are different for each gas, and they are valid over a limited range of the variables.

Perhaps the most general equation of state is the virial equation, in which $P/kT$ is expanded as a power series in the density, $\rho = N/V$. This leads to

$$\frac{P}{kT} = \sum_{n=1}^{\infty} B_n(T) \rho^n$$  \hspace{1cm} (1-1)$$

where the $B_n(T)$'s are called the $n^{\text{th}}$ density virial coefficients per molecule. For all gases, $B_1 = 1$. In the limit of $\rho$ going to zero, the virial equation approaches the ideal-gas equation of state, $P/kT = \rho$.

From an experimental point of view, one may calculate the virial coefficients for each gas from measured $P$-$V$-$T$ data. From a theoretical viewpoint, one tries to calculate the virial coefficients based on a particular model for the particles in the system. Some of the properties of the virial coefficients are particular to the chosen model; and others are independent of the model, or have a known dependency. These latter properties may be studied by using a model which is non-trivial enough to exhibit the desired behavior, and yet simple enough to be mathematically treated with more or less exactness. One excellent model for such studies is the so-called hard sphere gas. This model takes into account the finite extent of
the repulsive core of the particles, and may be described mathematically by

\[ u(r) = \infty \quad \text{for} \quad 0 \leq r \leq \sigma \]
\[ u(r) = 0 \quad \text{for} \quad r > \sigma \]  \hspace{1cm} (1-2)

where \( u(r) \) is the "intermolecular" potential, \( r \) is the interparticle separation, and \( \sigma \) is the diameter of the hard spheres. It is this model, and the virial coefficients to which it gives rise, with which we shall be concerned in this work.

**B. MAYER CLUSTER THEORY**

In order to develop the virial coefficients for a hard sphere gas, we may make use of the general method of procedure as developed by Mayer (3) which gives a formal expression for the virial coefficients of all orders, for any system of classical particles with a pairwise additive potential.

Consider a system composed of \( N \) particles, each of which has associated with it a three-dimensional position vector, \( \vec{r}_j \), and let \( r_{ij} = |\vec{r}_i - \vec{r}_j| \). If \( u(r_{ij}) \) is the two-body potential, a function only of the distance between particles \( i \) and \( j \), then the total potential, \( U \), is pairwise additive iff

\[ U(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) = \sum u(r_{ij}) \]  \hspace{1cm} (1-3)

where the summation is over all \( i, j \) such that \( 1 \leq i < j \leq N \).

Under this assumption, Mayer shows that by the use of the classical partition function of the system, the virial coefficients

(3)
may be expressed as a weighted sum of certain multi-dimensional space integrals. The general result is

\[ B_n(T) = -\frac{B-1}{n!} \sum_{\mu} M_{n,\mu} \cdot \alpha_{n,\mu}(T) \] (1.4)

where the \( \alpha \)'s are the integrals mentioned and the \( M \)'s are integer weights. The details of the derivation of (1.4) have been treated extensively by Mayer (3) and others (4, 5, 6), and many of the properties of virial coefficients (both classical and quantum mechanical) have been discussed at length in a review article by Kiloatrick (2).

In this work we shall explore the nature of the \( \alpha \)'s and how they may be calculated for hard spheres.

Each of the \( \alpha \)'s is of the general form

\[ \alpha_{n,\mu} = V^{-1} \int \cdots \int TT_{i_1} d\mathbf{r}_1 \cdots d\mathbf{r}_n \] (1.5)

where \( f_{i_1} \) is the Mayer f-function defined by

\[ f_{i_1} = \exp \left[ -u(r_{i_1})/kT \right] - 1 \] (1.6)

Each \( \alpha_{n,\mu} \) involves \( n \) particles, and there is one three-dimensional integral over the volume of the container, \( V \), for each particle. The particular products of \( f_{i_1} \)'s which make up the integrand for a given \( \alpha_{n,\mu} \) is most easily understood by the use of a graphical representation of the integrals, and we shall digress briefly to introduce this terminology.

A collection of \( n \) labeled points, together with some subset of the \( n(n-1)/2 \) possible lines connecting these points, will be called an \( n \)-point graph. If a line exists between points \( i \) and \( j \), then we say that points \( i \) and \( j \) are connected, and symbolize this
by \( i \leftrightarrow j \). Furthermore, if \( i \leftrightarrow j \) and \( j \leftrightarrow k \), then \( i \leftrightarrow k \). Thus, when we say that two points are connected in this sense, we do not necessarily mean that a line exists between them, but that some path of lines connects them. If every point in a graph is connected to every other point in this way, the graph is said to be a connected graph. Finally, if the point \( i \) is necessary to an inductive establishment of the connectivity of the graph, then the point \( i \) is said to be an articulation point of the graph. A graph with no articulation points is called a star. A star may be thought of as a connected graph from which any one of its points may be removed without its becoming disconnected. Below are shown three six-point graphs which are: a) a disconnected graph; b) a non-star connected graph (articulation points shown as asterisks); c) a star graph.

![Graphs](image)

Every integral of the type shown in (1-5) may now be put into one-to-one correspondence with an \( n \)-point graph. The \( n \) particles to be integrated over correspond to the \( n \) labeled points of the graph, and any factors of \( f_{i,j} \) in the integrand correspond to the presence of a line in the graph between points \( i \) and \( j \). Even stronger, we shall say that an integral over \( n \) points in a volume \( V \) with argument a particular product of \( f \)-functions is represented by or is equal to the corresponding graph.

(5)
For example

\[ \mathcal{S} = V^{-1} \int f_{12} f_{23} f_{34} \, d\bar{r}_1 \, d\bar{r}_2 \, d\bar{r}_3 \, d\bar{r}_4 \, d\bar{r}_5 . \quad (1-8) \]

The integration may be carried out as indicated and then divided by the factor \( V \). Since the \( f_{ij} \)'s are in terms of the \( r_{ij} \)'s, it is often more convenient to carry out the integrations in a set of new coordinates relative to one of the points as an origin, say \( \mathbf{r}_k \). After integrating over the \( n-1 \) other points, we have

\[ \alpha_{n,m} = V^{-1} \int_{V} F(T) \, d\mathbf{r}_k . \quad (1-9) \]

If \( V \) is very large compared to the size of the particles, so that the "wall effects" are negligible, then \( F \) is independent of \( \mathbf{r}_k \) and

\[ \alpha_{n,m} = V^{-1} F(T) \int_{V} d\mathbf{r}_k = F(T) . \quad (1-10) \]

Thus we can eliminate the factor \( V^{-1} \) and the integration over \( \mathbf{r}_k \), and consider point \( k \) to be fixed. This results in a fixed-point or one-center graph. Because any point could have been chosen to be the reference origin, all one-center graphs which differ only by the point which is fixed are equal.* We may now reformulate (1-4) in terms of graphs, with the result

\[ B_n(T) = -\frac{n-1}{n!} \sum \{ \text{All distinct, labeled, one-center star graphs on } n \text{ points} \} . \quad (1-11) \]

* Some authors define a no-center graph as in (1-5), but without the factor \( V^{-1} \), and draw the one-center graphs with an open circle representing the fixed point. In this work, all one-center graphs will be drawn without the open circle in order to simplify the notation. Since we will not use any no-center graphs, and because the point chosen to be fixed in a one-center graph is immaterial, this should not lead to any confusion.
We may further observe that when a graph is evaluated, the labels on
the points are merely a set of dummy variables. Thus two graphs
having the same topological structure and differing only in the
numbering of their points have the same value. Using this, we may
interpret the summation in (1-4) to mean a sum over all topologically
distinct n-point star graphs, each weighted with the number of distinct
ways its points can be labeled.

We are now in a position to explicitly list the graphs which
contribute to a given virial coefficient. This is done for the first
five virial coefficients in Table 1-1. Below each graph is given the
symbol introduced by Rowlinson (7), and we shall make use of his
notation throughout the rest of this work.

Using Mayer's formalism, the problem of calculating virial
coefficients becomes a problem of evaluating the necessary star graphs
for the particular model of interest. For the case of hard spheres
where the potential is given by (1-2), the Mayer f-function becomes

\begin{align}
    f_{ij} &= -1 \quad \text{for} \quad 0 < r_{ij} < \sigma^- \\
    f_{ij} &= 0 \quad \text{for} \quad r_{ij} > \sigma^-.
\end{align} \quad (1-12)

In evaluating a star graph, the integrand is always a product
of specific $f_{ij}$'s. For every $f_{ij}$ that appears, any configuration of
the points for which the corresponding $r_{ij}$ is greater than $\sigma^-$ con-
tributes nothing to the integral, since the integrand is exactly zero.
Thus, the presence of the $f_{ij}$'s may be thought of as imposing bounding
conditions on the ranges of integration.

(7)
\begin{align*}
B_1 &= 1 \\
B_2 &= -\frac{1}{2} \left\{ \begin{array}{c}
\begin{array}{c}
\text{(B1)}
\end{array}
\end{array} \right\} \\
B_3 &= -\frac{1}{3} \left\{ \begin{array}{c}
\begin{array}{c}
\text{(C3)}
\end{array}
\end{array} \right\} \\
B_4 &= -\frac{1}{8} \left\{ \begin{array}{c}
\begin{array}{c}
3 \begin{array}{c}
\text{(D4)}
\end{array} \ + \ 6 \begin{array}{c}
\text{(D5)}
\end{array} \ + \ \begin{array}{c}
\text{(D6)}
\end{array}
\end{array} \right\} \\
B_5 &= -\frac{1}{30} \left\{ \begin{array}{c}
\begin{array}{c}
\begin{array}{c}
12 \begin{array}{c}
\text{(E5)}
\end{array} \ + \ 60 \begin{array}{c}
\text{(E6a)}
\end{array} \ + \ 10 \begin{array}{c}
\text{(E6b)}
\end{array} \ + \ 60 \begin{array}{c}
\text{(E7a)}
\end{array} \ + \ 30 \begin{array}{c}
\text{(E7b)}
\end{array}
\end{array} \right\} \\
&\quad + 10 \begin{array}{c}
\text{(E7c)}
\end{array} \ + \ 15 \begin{array}{c}
\text{(E8a)}
\end{array} \ + \ 30 \begin{array}{c}
\text{(E8b)}
\end{array} \ + \ 10 \begin{array}{c}
\text{(E9)}
\end{array} \ + \ \begin{array}{c}
\text{(E10)}
\end{array}
\end{array} \right\}
\end{align*}

\textbf{Table 1-1:} Star graphs contributing to the first five virial coefficients with their Mayer weights and alpha-numeric symbols introduced by Rowlinson.
As an example, let us evaluate the graph $B_{\gamma}$ which contributes to the second virial coefficient, $B_2$ (see Table 1-1).

$$B_{\gamma} = \int_{V} f_{12} \, d\vec{r}_2$$  \hspace{1cm} (1-13)

Recall that the integral in (1-13) is a three dimensional vector integral. We may rewrite (1-13) using spherical polar coordinates and simply writing $r$ for $r_{12}$.

$$B_{\gamma} = \int_{0}^{\pi} \int_{0}^{2\pi} \int_{0}^{\infty} f(r) \, r^2 \sin \varphi \, dr \, d\varphi \, d\varphi$$  \hspace{1cm} (1-14)

We may integrate over $\varphi$ and $\varphi$ since $f = f(r)$ only; and noting that $f(r) = 0$ for $r > \sigma$, we may absorb the $f(r)$ into the boundary conditions on $dr$, giving

$$B_{\gamma} = -4\pi \int_{0}^{\sigma} r^2 \, dr = -(4/3)\pi \sigma^3$$  \hspace{1cm} (1-15)

and the second virial coefficient is found to be

$$B_2 = -\frac{1}{2}(B_{\gamma}) = (2/3)\pi \sigma^3$$  \hspace{1cm} (1-16)

The same method extends in principle to the evaluation of more complicated graphs. The difficulty of expressing the $f_{ij}$'s as bounding conditions on the range of integrations, however, increases rapidly.
C. EVALUATION OF VIRIAL COEFFICIENTS

The graph \( C_3 \) which contributes to the third virial coefficient can be evaluated in a manner similar to that in which \( B_1 \) was treated in the last section. The details of this calculation are in Appendix I, with the result

\[ C_3 = -(15/8)b^2, \quad B_3 = (5/8)b^2 \quad (1-17) \]

where \( b = B_2 = (2/3)n^2 \).

Since the nature of the present work is an evaluation and an extension of certain techniques for calculating various four and five point graphs (particularly D6 and E10), a brief historical survey of the methods employed and results obtained to date will serve to place this work in perspective.

The problem of calculating correction terms to the equation of state for a gas of hard spheres was first undertaken during the latter part of the nineteenth century. There was considerable disagreement among the researchers (notably Boltzmann and Van der Waals) as to the proper way to calculate these correction terms. None of the arguments put forward now seem to us completely convincing, and the subject of section II of this work deals in large part with resolving these difficulties and placing these early results on a firm thermodynamic foundation. Nevertheless, by about 1905 there was more or less general agreement that the values calculated by Boltzmann were correct. In terms

* It is convenient to express the value of an n-point graph in units of \( b \) to the \((n-1)\)th power, since this factor arises naturally during the course of the calculations and allows many graphs to be expressed as rational fractions.
of virial coefficients, his results were

\[ B_2 = b, \quad B_3 = (5/8)b^2, \quad B_4 = 0.2869\ldots b^3. \]

The value he obtained for \( B_4 \) is an exact analytical expression. It involves trigonometric functions, however, and it is not expressable as a rational fraction in units of \( b^3 \).

In the 1930's Ursell (10) and Mayer (3) developed the rigorous theory of the virial equation, and the expansion of the virial coefficients in terms of star graphs. Even so, because of the increasing difficulty in evaluating the required graphs, it was not until 1952 that Mijiboer and Van Hove (9) were able to confirm Boltzmann's value for \( B_4 \). We show in section II that not only can the final Boltzmann result for \( B_4 \) be verified, but that the individual terms contributing to \( B_4 \) can be correlated with the Mayer expansion.

In 1954 Rosenbluth and Rosenbluth (12) calculated a value for the fifth virial coefficient using a Monte Carlo integration system, and obtained the result

\[ B_5 = (0.115 \pm 0.010) b^4. \]

Values for five of the ten graphs that contribute to \( B_5 \) were determined analytically by Rushbrooke and Hutchinson (13) and later confirmed by Rowlinson (14) using a different technique. Their results are
\[
\frac{(E5)}{b^4} = -\frac{40949}{10752} = -3.808501 \\
\frac{(E6a)}{b^4} = \frac{68419}{26880} = 2.545350 \\
\frac{(E6b)}{b^4} = \frac{82}{35} = 2.342857 \\
\frac{(E7a)}{b^4} = -\frac{34133}{17920} = -1.904743 \\
\frac{(E7c)}{b^4} = -\frac{73491}{35840} = -2.050530
\]

Recently Kim and Henderson (11) have found exact closed expressions for the graphs E7b and E8b. They find

\[
\frac{(E7b)}{b^4} = -\frac{18583}{5376} + \frac{33291}{9800} \sqrt{3} = -1.58377
\]

The expression they give for E8b contains six terms, but can easily be transformed to the equivalent four-term form

\[
\frac{(E8b)}{b^4} = \frac{211283}{15360} + \frac{1458339}{627200} \frac{\sqrt{2}}{\pi} - \frac{33291}{9800} \frac{\sqrt{3}}{\pi} \\
- \frac{683559}{17920 \pi} \tan^{-1} \frac{\sqrt{2}}{\pi} = 1.32981\ldots
\]

Of the ten graphs on five points, then, three have not been evaluated analytically. These are E8a, E9, and E10. Several investigators have obtained approximate values for these graphs. The various techniques employed and results obtained are treated in detail in Kilpatrick's review article (2).

We will close this review with a note on the purpose of section IV of this work. Most of the techniques employed to evaluate the remaining five-point graphs use some modification of the Monte Carlo method. This method is basically a statistical form of numerical integration, and as such is not capable of yielding a unique analytical solution. Katsura (15) and Kilpatrick (16) have developed a method
known as the multiple summation or bond-face transformation technique for expanding the graphs in terms of Bessel functions and integrals over Legendre polynomials. This method also does not yield a closed analytical expression; and even when the problem of integrating over the Legendre polynomials is solved, the resulting summation (at least for the more complicated graphs) is not competitive with the Monte Carlo method as far as accuracy vs. total computational time.

Because of the topology of the graphs $E8a$, $E9$, and $E10$, the methods used to obtain analytic expressions for the simpler five-point graphs are not readily extended to these cases. In section III we show that the Boltzmann-Van der Waals method may be modified to yield analytic results for $D6$. But several mathematical complications arise in extending this method to the graph $E10$. Thus, it would appear that the most promising technique for evaluating the remaining graphs is an extension of a method introduced by Nijboer and Van Hove (9). In section IV we show how this extension is carried out, and we set up an expression for $E10$ which when integrated will yield the desired analytical result. While the actual integration appears tedious, there are no apparent problems that would make the integrations impractical.
II. INTERPRETATION OF BOLTZMANN'S WORK

A. THE EXCLUDED-VOLUME METHOD

In 1898 Boltzmann published the second volume of his "Lectures on Gas Theory" (17) in which he discusses the virial expansion of the pressure as a power series in the density*, \( \rho = N/V \). He considers a system of rigid spheres "for which the space filled by the molecules is not vanishingly small compared to the entire volume of the gas." The approach he takes is to consider a gas of \( N \) such hard spheres with a diameter \( \sigma \) in a Volume \( V \), and to define a quantity which he calls \( D(N) \) to be "the space left for the center of a molecule new added into the gas." It is apparent from his equations that he considers this available volume to be obtained by averaging over all positions of the \( N \) particles. We will postpone a discussion of the manner in which he obtains successive approximations to the available volume \( D \), and will consider it, for the moment, to be some known function of \( N \) and \( V \). We are interested in how the quantity \( D(N) \) may be used to calculate the pressure of the system.

Before we begin, let us define the quantities which we will need to establish the connection between pressure and available volume.

* Boltzmann's actual expansion was in powers of inverse volume. At this time, thermodynamics was just beginning to be well understood and systematized. Consequently, the literature of this period is difficult to read since the meaning of different symbols and concepts vary widely from one author to the next. Many of the equations which we quote from the early literature have been transformed into modern notation so that their relationship to later results may be more easily recognized.
If $S$ is the entropy of the real (in this case, hard sphere) gas, and $S^*$ the entropy of an ideal gas having the same $N$ and $V$, let

$$\hat{S}(N,V) = S(N,V) - S^*(N,V)$$  \hspace{1cm} (2-1)

so that $\hat{S}$ is the entropy of gas imperfection. Further, let

$$\hat{\sigma}(N,V) = \hat{S}(N+1,V) - \hat{S}(N,V)$$  \hspace{1cm} (2-2)

be the increase in entropy of gas imperfection when one more particle is added to a system of $N$ particles.

Boltzmann argues that a quantity $W$, which is the ratio of the probability that all $N$ molecules simultaneously are in the space $V$ to the probability that each of them lies in a separate space of volume $V$, is given by

$$W = \prod_{n=0}^{N-1} \frac{D(n)}{V}$$  \hspace{1cm} (2-3)

He further states that by setting $\hat{S} = k \ln(W)$, one may obtain

$$\hat{S}(N,V) = k \sum_{n=0}^{N-1} \ln \frac{D(n)}{V}$$  \hspace{1cm} (2-4)

Finally, he uses the relationship

$$\left( \frac{\partial (RTS)}{\partial V} \right)_T = P$$  \hspace{1cm} (2-5)

* Boltzmann's original equations are in terms of $S$ rather than $\hat{S}$, and his form of (2-4) contains a temperature dependent term which cancels out at a later stage in his derivation.
to give the result

\[ P = kT \left[ (\partial / \partial V) \sum_{n=0}^{N-1} \ln D(n) \right]_T \quad (2-6) \]

**B. JUSTIFICATION OF THE METHOD**

We would like to be able to derive equation (2-4) without using Boltzmann's assumptions about the nature of the probability function \( W \) and its relation to the entropy of the system. This equation can be placed on a firm thermodynamic foundation by the use of the properties of the canonical ensemble. The canonical partition function is given by

\[ Z_N = \frac{Q_N}{N! \Lambda^{3N}} \quad (2-7) \]

where \( \Lambda = h/(2\pi m kT)^\frac{1}{2} \), and \( Q_N \) is the classical configuration integral

\[ Q_N = \int \cdots \int \exp(-U/kT) \, d\vec{r}_1 \cdots d\vec{r}_N \quad (2-8) \]

the latter being equal to \( V^N \) for an ideal gas. From statistical thermodynamics we have

\[ \ln Z_N = -A/kT = \ln Q_N - 3N \ln \Lambda - \ln N! \quad (2-9) \]

and

\[ \left( \frac{\partial (-A/kT)}{\partial T} \right)_{N,V} = \frac{E}{kT^2} = \left( \frac{\partial \ln Q_N}{\partial T} \right)_{N,V} + \frac{3N}{2T\Lambda} \quad (2-10) \]

(16)
Thus

\[
\frac{S}{k} = \frac{E - A}{kT} = T \frac{\partial}{\partial T} \ln Q_N + \frac{3N}{2\Lambda} + \ln Q_N - 3N \ln \Lambda - \ln N! \quad (2-11)
\]

and for an ideal gas

\[
\frac{S^*}{k} = \frac{E^* - A^*}{kT} = \frac{3N}{2\Lambda} + N \ln V - 3N \ln \Lambda - \ln N! \quad . \quad (2-12)
\]

In general

\[
\hat{S}(N,V) = k \ln (Q_N/V^N) + kT \left( \frac{\partial \ln Q_N}{\partial T} \right)_{N,V} \quad . \quad (2-13)
\]

For a gas of hard spheres, \( Q_N \) is not a function of \( T \) and so

\[
\hat{S}(N,V) = k \ln (Q_N/V^N) \quad . \quad (2-14)
\]

Consider now a system composed of \( N \) hard spheres in a volume \( V \). For a given configuration of the \( N \) particles, let

\[
W_N(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) = \prod_{i<j} (1 + f_{ij}) \quad (2-15)
\]

where \( f_{ij} \) is defined by (1-12), and the product is over all \( i,j \) such that \( 1 \leq i < j \leq N \). We may then express \( D(N) \) as

\[
D(N) = \frac{\int \cdots \int W_{N+1} \, d\vec{r}_1 \cdots d\vec{r}_{N+1}}{\int \cdots \int W_N \, d\vec{r}_1 \cdots d\vec{r}_N} \quad . \quad (2-16)
\]

This definition makes \( D(N) \) the average volume available for the \( (N+1) \)th particle averaged over all configurations of the other \( N \) particles, and thereby identical to Boltzmann's \( D(N) \). Now for a pairwise additive potential (which we have already assumed) a comparison of the integrals
in (2-16) with the definition of $Q_N$ in (2-8) leads to

$$D(N) = \frac{Q_{N+1}}{Q_N}.$$  \hspace{1cm} (2-17)

Putting (2-14) into (2-2), combining the two logarithms, and using (2-17) to clear up we have

$$\hat{\sigma}(N, V) = k \ln \frac{D(N)}{V}.$$  \hspace{1cm} (2-18)

By the repeated use of (2-2) we may deduce

$$\hat{S}(N, V) = \sum_{n=0}^{N-1} \hat{\sigma}(n, V),$$  \hspace{1cm} (2-19)

which together with (2-18) gives

$$\hat{S}(N, V) = k \sum_{n=0}^{N-1} \ln \frac{D(N)}{V}.$$  \hspace{1cm} (2-20)

This last equation is identical to (2-4) which is the Boltzmann expression we wished to justify.
C. THE EVALUATION OF D(N)

In section II-D we will show how D(N) may be given as a power series in the density*, whose coefficients are expressable as sums of certain graphs. Before we do this, however, it is interesting to note the way in which Boltzmann and others arrived at an expression for D(N).

As a first approximation, D(N) is just the volume, V. This value is too large however, since all of V is not available to the center of a new sphere due to the size of the other N spheres. And since the center of the new sphere cannot approach another sphere closer than a distance $\sigma^{-}$, the other N spheres exclude a volume of $(4/3)\pi\sigma^{-3}N = 2Nb$. Thus

$$D(N) = V - 2Nb + \cdots .$$  \hspace{1cm} (2-21)

It is this imaginary sphere of radius $\sigma^{-}$ around each particle which Boltzmann calls the "Deckungssphere" or exclusion sphere.

When two spheres are at a distance between $\sigma$ and $2\sigma^{-}$ from each other, their exclusion spheres overlap. Consequently such a "pair" of spheres excludes a smaller volume than the simple sum of their exclusion volumes. Thus the term $2Nb$ is an over-correction and must be diminished by the volume $Z$, which is the volume common to two exclusion spheres averaged over all configurations of the N particles. Let $2K(x)$ be the volume common to two exclusion spheres whose centers

* In writing D(N) we are keeping Boltzmann's notation. Actually, the terms in D(N) evaluated in the limit of N and V going to infinity at a fixed ratio, $\rho$, and the quantity D(N)/V is a function of $\rho$ only.
are at a distance \( x \) apart. \( K(x) \) is readily determined to be given by \( \pi(16\sigma^{-3} - 12\sigma^{-1}x + x^3)/24 \). Further, let \( (dv)/N \) be the number of centers lying at a distance between \( x \) and \( x+dx \) from the center of a given sphere. Boltzmann shows that to a first approximation

\[
dv = 4\pi N^2 x^2 dx/V. \tag{2-22}
\]

Since \( \frac{1}{2}dv \) is the number of pairs of centers between \( x \) and \( x+dx \) apart, and \( 2K(x) \) is the overlap volume for such a pair, the total overlap volume \( Z \) is given by

\[
Z = \int_{x-\sigma}^{x+2\sigma} K(x) \, dv = (17/16) b^2 N^2 / V. \tag{2-23}
\]

Thus we now have

\[
D(N) = V \left( 1 - 2b\rho + (17/16)b^2 / \rho^2 + \cdots \right). \tag{2-24}
\]

Van der Waals (18) extended this reasoning to the volume common to three exclusion spheres and set up an expression to give the next correction term to \( D(N) \). The tedious calculations necessary to evaluate this expression were performed by Van Laar (19) who found this term to be \( -2\beta b^3 / \rho^3 \), where

\[
\beta = \frac{23\sqrt{2} + 1377(\tan^{-1}\sqrt{2} - \pi/4)}{1120\pi}. \tag{2-25}
\]

Boltzmann argued (20) that this was not the complete correction term to orders of \( \rho^3 \), but that the term \( (2357/6720)b^3 / \rho^3 \) must be added, so that

\[
(20)
\]
\[
\frac{D(N)}{V} = 1 - 2b + \frac{17}{16} b^2 \rho^2 + \left(\frac{2357}{6720} - 2b\right) b^3 \rho^3. \tag{2-26}
\]

The basis of his argument was that the value he used for \(dv'\) in (2-22) was only a first approximation, and is given more accurately by

\[
dv' = 4\pi N^2 x^2 dx \left(1 - 2b\rho + 2K\rho^2 - \frac{3K^2}{2}\rho^4\right)/V(1 - 2b\rho). \tag{2-27}
\]

When (2-27) is used for \(dv'\) in (2-23), \(Z\) is found to contain a term of order \(\rho^3\), which should be included in the expression for \(D(N)\) given to orders of \(\rho^3\).

There was much disagreement between Boltzmann and Van der Waals as to whether this additional correction term should be included in \(D(N)\). A running debate over this point finally led Van der Waals to make the following statement (21).

"So I pass by the question whether .... \(\beta\) must possibly be diminished by \(2357/13440\), as this is of minor interest. As our results differ so much, we cannot but have considered two different problems ... ."

In 1903, Van der Waals' son published a paper (22) upholding the Boltzmann value for \(D(N)\). His changes in notation and nebulous arguments appear to serve more to confuse the situation than to clarify it. The Nijboer and Van Hove paper (9) in 1952 finally confirmed Boltzmann's value for \(B_4\) but contributed little or nothing toward understanding the original source of discrepancy.

The difficulty with the early methods is that all of the successive approximations to the desired quantities were based on physical considerations, and the number and nature of the terms to be included were supported by "hand-waving" arguments. Boltzmann showed
an amazing degree of insight in these considerations; and though he had no formalism to guide him, he made the proper choice at every turn. But even he (20) is led to the conclusion that due to the difficult integrals to be evaluated and the corrections on corrections which must be considered, "further correction terms are certainly not calculable" by this method.

In section II-D we show that all these quantities have reasonably simple expressions in terms of modern graph notation. In this notation, both the nature of the original discrepancy and the terms to be included in higher approximations become readily apparent.
D. **EARLY RESULTS EXPRESSED IN GRAPH NOTATION**

In this section we show how the early work of Boltzmann and Van der Waals can be put into graph notation. In particular, we seek an expansion of \( D(N) \) as a power series in the density.

From thermodynamics we have the relationship

\[
\left( \frac{\partial S}{\partial V} \right)_{N,T} = \left( \frac{\partial P}{\partial T} \right)_{N,V} = k \frac{\partial}{\partial T} T \sum_{n=1}^{\infty} R_n(T) \rho^n \tag{2-28}
\]

where the second equality is obtained from (1-1). For an ideal gas the right hand side of (2-28) is simply \( k \rho \). Recalling that \( \hat{S} = S - S^* \), and that \( S = S^* \) in the limit of \( V \) going to infinity, we have

\[
\hat{S} = \lim_{V \to \infty} \int_{V}^{V'} \left[ \left( \frac{\partial S}{\partial V} \right)_{N,T}^* - \left( \frac{\partial S}{\partial V} \right)_{N,T} \right] dV. \tag{2-29}
\]

Since \( B_1 = 1 \) for all gases, the \( n=1 \) term of (2-28) is \( k \rho \) and (2-29) becomes

\[
\hat{S} = -\frac{\partial}{\partial T} kT \sum_{n=2}^{\infty} R_n(T) \int_{V}^{V'} \rho^n dV. \tag{2-30}
\]

Carrying out the integration gives in general

\[
\hat{S} = -Nk \frac{\partial}{\partial T} T \sum_{n=1}^{\infty} n^{-1} B_{n+1}(T) \rho^n. \tag{2-31}
\]

For the particular case of hard spheres, the virial coefficients are independent of the temperature, and we have

\[
\hat{S} = -Nk \sum_{n=1}^{\infty} n^{-1} B_{n+1} \rho^n. \tag{2-32}
\]
Let us now digress for a moment to introduce some further definitions concerning graphs which will be useful. First we define

\[ Q_m = -\frac{(m+1)!}{m} R_{m+1} \]  \hspace{1cm} (2-33)

Reference to the discussion in section I-B and especially (1-11) shows that this definition makes \( Q_m \) equal to the sum of all distinct, labeled, one-center star graphs with \( m \) free points. We would like to extend this definition by allowing more than one fixed point.

Consider a graph having \( \ell \) (\( \ell \geq 2 \)) fixed points (denoted by open circles) and \( m \) free points, with no line (\( f_{i,j} \) factor) connecting any two fixed points, but otherwise unrestricted. Such a graph will be called an \( \ell \)-center star graph if the graph obtained by including \( \prod f_{i,j} \) over \( 1 \leq i < j \leq \ell \) is a star graph on \( \ell + m \) points. Let \( G_{\ell,m} \) be the sum of all distinct, labeled, \( \ell \)-center star graphs having \( m \) free points. In listing the graphs contributing to \( G_{\ell,m} \), one need only sum over topologically distinct graphs, each weighted with the number of distinct ways its fixed points can be labeled \((1,2,\cdots,\ell)\) and its free points labeled \((\ell+1,\ell+2,\cdots,\ell+m)\). Table 2-1 shows the graphs contributing to the first several \( G_{\ell,m} \)'s. The weights may also be obtained by dividing \( \ell!m! \) by the symmetry number of the graph, which is the number of permutations of the \( \ell \) fixed points among themselves and the \( m \) free points among themselves which keep the connectivity invariant. Rushbrooke (6) refers to topologically distinct graphs, each divided by its symmetry number, as unlabeled graphs. Using this terminology, we may express \( G_{\ell,m} \) as \( \ell!m! \) times the sum of all distinct, unlabeled, \( \ell \)-center star graphs with \( m \) free points.

(24)
\[
\begin{align*}
q_{2,0} &= \cdot \\
q_{2,1} &= \triangle \\
q_{2,2} &= 2 \bigcirc + 4 \bigtriangleup + \bigstar + \bigtriangleleft \\
q_{3,0} &= \cdot \\
q_{3,1} &= 3 \bigtriangleup + \bigstar \\
q_{3,2} &= 6 \bigcirc + 12 \bigtriangleup + 3 \bigstar + 3 \bigtriangleleft + 6 \bigtriangleleft + 6 \bigtriangleup + 6 \bigstar + 6 \bigtriangleleft + \bigstar + \bigtriangleleft \\
q_{4,0} &= \cdot \\
q_{4,1} &= 6 \bigcirc + 4 \bigtriangleup + \bigstar \\
q_{5,0} &= \cdot \cdot \cdot \\
\end{align*}
\]

**TABLE 2-1: The Graphs Contributing to \( G_{\ell, m} \).**

It should also be noted that while the value of a one-center graph is a pure number, multi-centered graphs are functions of the positions of the fixed points. Thus \( G_{\ell, m} = G_{\ell, m}(\bar{r}_1, \bar{r}_2, \ldots, \bar{r}_x) \).

Now let us define a quantity

\[
A_{\ell, m} = V^{-1} \int W_{\ell} \int G_{\ell, 1} G_{\ell, m} d \bar{r}_1 \cdots d \bar{r}_x , \quad (2-34)
\]

where \( W_{\ell} = W_{\ell}(\bar{r}_1, \ldots, \bar{r}_x) \) is defined by (2-15). The meaning of (2-34) can be best seen from a specific example. Consider the sequence of graphs listed below.

(a) \hspace{1cm} (b) \hspace{1cm} (c)

The graph (a) is a term from \( q_{2,2} \) (see Table 2-1). Its fixed points are 1 and 2, and it is a function of \( \bar{r}_{12} \). Since \( q_{2,1} = \triangle \) is also
a function of $F_{12}$, the fixed centers of the three factors in the
integrand of (2-34) coincide, and (b) is the graphical representation
of one term in the product $G_{2,1}G_{2,2}$. We now integrate over the
fixed points, with the restriction $W_2$ which is defined by (2-15). This
restriction makes the integrand zero if any two fixed points are less
than $\sigma$ apart. The term $G_{\ell,m}$ becomes zero if any two centers are more
than $2\sigma$ apart. Thus the range of integration in (2-34) may be con-
sidered to be over all relative configurations of the fixed points such
that every pair $i,j$ satisfies the condition $\sigma < r_{ij} < 2\sigma$. This
condition is represented in the graph by a dashed line as in (c). In
general, the graphs representing terms in $A_{\ell,m}$ will contain $\ell(\ell-1)/2$
such dashed lines.* Because of the factor $V^{-1}$ in (2-34), the graph (c)
is actually a one-center graph. As usual we will not mark the single
fixed point, and it should be recalled that any point of a one-center
graph may be considered to be the fixed point. It should be clear that
this is not true for the multi-centered graphs, for which the fixed
points will always be indicated by open circles. A list of the first
several $A_{\ell,m}$'s is found in Table 2-2.

* The notion of a graph containing dashed lines to represent the
factor $(1+f_{ij})$ was first introduced by Hoover (23). A Hoover type
graph is a Mayer graph in which any pairs of points not connected
by a solid line $(f_{ij})$ are connected by a dashed line. For this
reason, we shall refer to a graph like (c) in the example above as
an incomplete Hoover graph, or a mixed graph.
\[ A_{2,0} = \triangle \]
\[ A_{2,1} = \\
\[ A_{2,2} = 2 \bigstar + 4 \bigstar + \bigstar + \bigstar \]
\[ A_{3,0} = \\
\[ A_{3,1} = \bigstar + 3 \bigstar \]
\[ A_{4,0} = \\

**TABLE 2-2:** The Graphs Contributing to \( A_{\ell,m} \).

Let us now return to equation (2-32). Writing this in terms of the \( G_{m} \)'s, and using the relationship \( (\partial \tilde{S}/\partial N)_{\nu,T} = \hat{\varphi} \), we have

\[
\frac{\hat{\varphi}}{k} = \sum_{m,j} \frac{1}{m!} G_{m} \rho^{m/m!}.
\]  \( 2-35 \)

We may then use (2-18) to find \( D(N)/V \) as a power series in \( \rho \), with the result

\[
D(N)/V = 1 + G_{1} \rho + (G_{2} + G_{1}^{2})\rho^{2}/2! + (G_{3} + 3G_{2}G_{1} + G_{1}^{3})\rho^{3}/3! + (G_{4} + 4G_{3}G_{1} + 3G_{2}^{2} + 6G_{2}G_{1}^{2} + G_{1}^{4})\rho^{4}/4! + \cdots
\]

\( 2-36a \)

\[
= 1 + (I) \rho + (\bigstar + \Delta) \rho^{2}/2! + (\bigstar + 3 \bigstar + 3 \bigstar + 6 \bigstar + \bigstar \bigstar \bigstar \bigstar) \rho^{3}/3! + \cdots
\]

\( 2-36b \)

In general, the coefficient of \( \rho^{n}/n! \) in (2-36) is given by

\[
A_{n} = n! \sum_{\{m_{j}\}} \prod_{j=1}^{\infty} \frac{G_{m_{j}}}{(j!)^{m_{j}} (m_{j})!}
\]

\( 2-37 \)
where the sum is over all sets, \(\{m_j\}\), such that \(\sum j \cdot m_j = n\), with \(A_0 = 1\). Reference to (2-37) shows that the \(A_n\)'s are complicated to express in terms of Mayer graphs. The prescription for \(A_n\) is considerably simplified, however, when expressed as mixed Hoover graphs, that is in terms of the \(A_{\ell, m}\)'s. The result for \(n \geq 2\) is

\[
A_n = \sum_{m=0}^{n-2} \binom{n}{m} A_{n-m, m} \quad (2-38)
\]

where \(\binom{n}{m}\) is a binomial coefficient, \(n! / m!(n-m)!\). For \(n=1\), one cannot draw a mixed Hoover graph since there is but one fixed point, and \(A_1 = G_1\).

Table 2-3 shows the expansion (2-38) for \(n=2, 3, 4\). We may now write

\[
\frac{D(N)}{V} = 1 + A_1 \rho + (A_{2, 0}) \frac{\rho^2}{2!} + (A_{3, 0} + 3A_{2, 1}) \frac{\rho^3}{3!} \\
+ (A_{4, 0} + 4A_{3, 1} + 6A_{2, 2}) \frac{\rho^4}{4!} + \cdots \quad (2-39a)
\]

\[
= 1 + (\Box) \rho + (\square) \frac{\rho^2}{2!} + (\bigcirc + 3 \bigcirc) \frac{\rho^3}{3!} \\
+ (\bigstar + 4 \bigstar + 12 \bigstar + 6 \bigstar) \frac{\rho^4}{4!} + \cdots \quad (2-39b)
\]

* Equation (2-38) can be readily verified (see Table 2-3) by direct substitution for \(n \leq 4\). In Appendix II we prove that this relationship holds for all values of \(n\).
\[ A_2 = \binom{2}{0}A_{2,0} = \triangle = \triangle + \triangle = a_2 + a_1^2 \]

\[ A_3 = \binom{3}{0}A_{3,0} + \binom{3}{1}A_{2,1} = \square + 3 \quad \square \]

\[ \triangle + 3 \quad \triangle + 3 \quad \square + 6 \quad \square + \quad \square = a_3 + 3a_2a_1 + a_1^3 \]

\[ A_4 = \binom{4}{0}A_{4,0} + \binom{4}{1}A_{3,1} + \binom{4}{2}A_{2,2} \]

\[ = \quad \square + 4(\quad \square + 3 \quad \square) + 6(\quad \quad + \quad \quad + \quad \quad + \quad \quad )\]

\[ = 12 \quad \square + 60 \quad \square + 10 \quad \square + 60 \quad \square + 30 \quad \square + 10 \quad \quad + 15 \quad \quad + 30 \quad \quad \]

\[ + 10 \quad \quad + \quad \quad + 4 \quad \quad + 24 \quad \quad + 12 \quad \quad + 3 \quad \quad + 6 \quad \quad \]

\[ = a_4 + 4a_3a_1 + 3a_2^2 + 6a_2a_1^2 + a_1^4 \]

**Table 2-3:** Expansion of equation (2-38) for n=2,3,4 and correlation with the expansion of equations (2-36) and (2-37) in terms of the \(G_m\)'s.
The terms in (2-39) now bear a one-to-one correspondence to the integrals which Boltzmann, Van der Waals and Van Laar calculated to obtain successive approximations to $D(N)$.

The value of $A_1 = \int$ is just the integral in (2-13) which we found to be $-2b$. Let us consider the integral for $A_{2,0}$.

$$ A_{2,0} = \int_\sigma^{2\sigma} = 4\pi \int_\sigma^{2\sigma} \phi(x) x^2 dx = (17/8)b^2. \quad (2-40) $$

By noting that $\phi(x) = 2K(x)$, and comparing (2-40) with (2-22) and (2-23), we see that the term $A_{2,0}/2!$ is just Boltzmann's $Z/V$ correction term.

The next correction term which was evaluated by Van der Waals and Van Laar was found to be $-2\beta b^3/\rho^3$. To obtain this correction, they considered the volume common to three exclusion spheres ($\bigcap$) integrated over all relative positions of the three centers between $\sigma$ and $2\sigma$. From our discussion in section II-D, it should be clear that the integral they evaluated is equivalent to the graph

$$ \bigcap = A_{3,0} = -12\beta b^3. $$

The additional correction for which Boltzmann argued can best be seen from (2-27). Expressing $d\nu$ as a single power series in $\rho$, one has

$$ d\nu = 4\pi \rho^2 V x^2 dx \left( 1 + 2K(x) \rho + \cdots \right). \quad (2-41) $$

When this value for $d\nu$ is used in (2-23), a more exact value of $Z$ is obtained which contains a term of order $\rho^3$, which Boltzmann calls $\xi$. 

(30)
Thus

\[ \xi = \int_{x_o}^{x} k(x) \cdot 4\pi \rho^2 \psi x^2 dx = \frac{1}{2} V \Delta \rho^3. \quad (2.42) \]

One may readily evaluate the integral in (2.42) to obtain the result

\[ \frac{\xi}{V} = (2357/6720) b^2 \rho^3, \]

which is Boltzmann's correction. Equation (2.42) may also be evaluated by the relationship \( \Box = \Box + \Box \) with the same result.

We are now in a position to present a clear summary of precisely what Boltzmann and Van der Waals did to obtain their corrections through \( \rho^3 \), and to see what considerations would have been necessary to obtain one more correction term. To do this it is helpful to rewrite (2.39a) in the form*

\[ D(N)/V = 1 + A_1 \rho + \sum_{k=2}^{\infty} \alpha_k. \quad (2.43) \]

where

\[ \alpha_k = \frac{\rho^k}{k!} \sum_{m=0}^{\infty} A_{k,m} \frac{\rho^m}{m!}. \quad (2.44) \]

Notice that each term \( \alpha_k \) in (2.43) is a power series in \( \rho \) beginning with a term of order \( \rho^2 \). Thus to obtain \( D(N)/V \) correct to orders of \( \rho^2 \), only the terms involving \( A_{2,0} \) must be considered. This term was calculated both by Van der Waals (25) and by Boltzmann (17). Their results differed, with Boltzmann having the correct result of \( (17/8)b^2 \). Later, Van der Waals (13) outlined a method for calculating the next

* For a proof of the validity of this rearrangement, see Appendix II.

(31)
correction term and set up an expression for what in our notation would be \( a_0 \). He was not able to carry out the integrations that were necessary to obtain \( A_{3,0} \). Van Laar (19) did succeed in integrating Van der Waals' expression and found \( A_{3,0} = -12/\theta \). It would appear that Van der Waals thought that this term was the entire contribution to orders of \( \rho^3 \). He apparently did not understand that Boltzmann's result of \( A_{2,0} \rho^2/2! \) is not the complete expression for \( \alpha_2 \), but is merely the first term of an infinite series. Boltzmann pointed out that \( \alpha_2 \) also contains a term of order \( \rho^3 \), namely

\[
A_{2,1} \rho^3/2! = (2357/6720)b^3 \rho^3
\]

which must also be included when giving \( D(N)/V \) to orders of \( \rho^3 \).

In general, if one wishes to express \( D(N)/V \) to orders of \( \rho^n \), there will be one term contributed from each \( \alpha_\ell \) for which \( 2 \leq \ell \leq n \), that is \((n-1)\) terms. (By a term here we mean \( A_{\ell,m} \rho^{\ell+m}/\ell!m! \), which itself may be composed of several graphs.) Thus if this method had been taken one step further to obtain \( D(N)/V \) to the \( \rho^4 \) term, the following contributions would be required from \( \alpha_2, \alpha_3, \) and \( \alpha_4 \):

\[
\begin{align*}
\alpha_2 & : \quad (1/4) \left( 2 \bigcirc \bigcirc + 4 \bigcirc \bigotimes + \bigcirc \bigotimes + \bigotimes \bigotimes \right) \rho^4 \\
\alpha_3 & : \quad (1/3) \left( 3 \bigcirc \bigotimes + \bigotimes \bigotimes \right) \rho^4 \\
\alpha_4 & : \quad (1/24) \left( \bigotimes \bigotimes \right) \rho^4
\end{align*}
\]

With this formalism, terms to any order may be expressed, albeit with difficulty, but nonetheless in a perfectly systematic manner. Based upon physical considerations alone, the job would be extremely difficult at best, and practically unconsiderable. Boltzmann must have sensed this when he stated that the next correction term was certainly not calculable.
Before leaving this section, we should make a few interesting observations concerning the \( \alpha_{\ell}'s \) in (2-43). Consider again Boltzmann's integral expression for \( Z \) in (2-23). Let us write \( dv' \) as \( dv'_2 \) to emphasize the fact that it pertains to the number of pairs of particles at a given separation. If \( dv'_2 \) were known exactly, then the integral of \( V^{-1}K(x)dv'_2 \) would give the complete \( \alpha_2 \). We can obtain an exact expression for \( dv'_2 \) from our knowledge of the radial distribution function, \( g(x) \). The average number of particles at a distance between \( x \) and \( x+dx \) from a specified particle is given by \( 4\pi \rho x^2 dx \cdot g(x) \). Since this is Boltzmann's definition of \( dv'_2/N \), we have

\[
dv'_2 = \frac{4\pi N^2 x^2 dx}{V} g(x). \quad (2-45)
\]

Uhlenbeck and Ford (24) define a quantity, \( \bar{n}_\ell \), which they call the \( \ell \)-particle distribution function. The definition of \( \bar{n}_\ell \) and its expansion in terms of the \( G_{\ell,m}'s \) is given in Appendix II. From their respective definitions, one can readily show that \( \bar{n}_2 = \rho^2 g(x) \).

Using this and (II-8), and recalling that \( K(x) = \frac{1}{\ell} \int x^2 dx \), we find

\[
\alpha_2 = \frac{\rho^2}{2!} \sum_{m=0}^{\infty} \int_0^{2\pi} w_2 G_{2,1} G_{2,m} \frac{\rho^m}{m!} x^2 dx
\]

\[
= \frac{\rho^2}{2!} \sum_{m=0}^{\infty} A_{2,m} \frac{\rho^m}{m!} . \quad (2-46)
\]

Notice that this agrees with the general expression for \( \alpha_{\ell} \) in (2-44) for \( \ell=2 \).

Let us extend the idea of \( dv'_2 \) to consider many particles at a time. In general, let

\[
dv'_\ell = \bar{n}_\ell dv'_\ell \quad (2-47)
\]
where $d\mathcal{T}_\ell$ is the differential volume element over all relative coordinates of the $\ell$ centers. The quantity $(1/2!)d\gamma_2$ is the number of pairs of centers in a given linear configuration (i.e., at a given separation); $(1/3!)d\gamma_3$ is the number of triplets in a given triangular configuration; etc. Since $G_{\ell,1}$ is the volume common to $\ell$ exclusion spheres whose centers are in a given $\ell$-configuration, then in general

$$\alpha_\ell = (1/2!) \int \cdots \int G_{\ell,1} \bar{\eta}_\ell d\mathcal{T}_\ell .$$

(2.48)

This last equation is the general extension of (2.23) for all $\ell$.

The ultimate use of $D(N)/V$ is to calculate the virial coefficients by the use of (2-6). Expansions for all of the virial coefficients are known both in terms of one-center (1-11) and in terms of two-center graphs. Boltzmann's method requires a knowledge of the $\ell$-particle distribution functions for all* values of $\ell$ in order to calculate $D(N)/V$, and thus the $R_\ell$'s, indefinitely. This fact points out one of the inherent inefficiencies of the method.

As a final note, consider the definition of $A_{\ell,m}$ as given in (2-34). Since $A_{\ell,m}$ is composed of one-center graphs, we may choose any point as the origin of our coordinate system. Let the one free point on $G_{\ell,1}$ be that origin. If any one of the $\ell$ fixed points is more than $\sigma$ from the origin, $G_{\ell,1} = 0$. If any two of the $\ell$ fixed points are less than $\sigma$ apart, $W_\ell = 0$. If a hard sphere of diameter

---

* As we shall see in the following discussion, there is an upper bound on the number of $\ell$-particle distribution functions that need be considered.
\( \sigma \) is at a distance \( \sigma \) from the origin, the point on that sphere farthest from the origin is at a distance \( 3\sigma/2 \). Thus we may consider the integration in (2-34) to be over all configurations of the centers of \( \ell \) hard spheres inside a hollow sphere of diameter \( 3\sigma \). It should be evident that only a finite number of small spheres can be packed into the larger sphere. Let \( n^* \) be the largest number of \( \sigma \)-diameter spheres that can be placed inside a \( 3\sigma \)-diameter sphere in any configuration. Then \( A_{\ell,m} \) is identically zero for all \( \ell > n^* \). Further, since \( \alpha_\ell \) involves only terms in \( A_{\ell,m} \), \( \alpha_\ell = 0 \) for \( \ell > n^* \). Thus there is a limit to the number of \( \alpha_\ell \)'s which must be considered in obtaining \( D(N)/V \) to a given power of \( \rho \). Of more interest, however, is the fact that \( G_{\ell,m} \) in (2-34) is a sum of graphs; and since the two factors which vanish (namely, \( W_\ell \) or \( V_{\ell,1} \)) multiply every term in \( G_{\ell,m} \), every graph in \( A_{\ell,m} \) is also identically zero for \( \ell > n^* \). Because the graphs in \( A_{\ell,m} \) are mixed Hoover graphs, each one can be expanded as a sum of Mayer graphs, giving a relation among them. Then at least for \( \ell > n^* \), all of the Mayer graphs are no longer independent. In particular, the complete star graph for \( \ell > n^* \) points need never be evaluated, since the expansion of \( A_{\ell,0} = 0 \) gives this graph in terms of non-complete \( \ell \)-point stars, and products of lower order star graphs. Because this phenomenon has been shown to occur only for \( \ell \) greater than about thirteen, there do not appear to be any immediate applications for

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We know \( n^* > 13 \), since this case can be easily demonstrated. We also know that \( n^* < 27 \), because the total volume of 27 small spheres is equal to the volume of the larger sphere. Much has been written on the problem of packing spheres, but no general results have yet been found. It seems highly probable, however, that if \( n^* \) is not identically 13, it is not very much greater than 13.
such a result.

It is interesting to note that some higher virial coefficients have been shown (12) to be necessarily negative, and most calculations (8, 23) place the first negative virial coefficient at about $B_{18}$. These calculations are based on extrapolations of the first seven virial coefficients. The values of $B_6$ and $B_7$ have only been approximated to within a few percent, and the extrapolation is very sensitive to these latter values. Thus the first negative $B_n$ could be several coefficients higher or lower than $B_{18}$. It may be coincidental that in this same range (i.e., $n$ about 13 and greater) a significant number of graphs that contribute to $B_n$ become interdependent through the expansion of the zero-value Hoover type graphs mentioned. Until a general formalism is developed to show the relative contributions of these dependent graphs to the virial coefficients for such large values of $n$, the possibility of a connection between these two phenomena remains a matter for speculation.
III. EXTENSION OF BOLTZMANN'S WORK

A. RELATIONSHIP OF ONE- AND TWO-CENTER GRAPHS.

In section II-D we defined multi-center graphs and showed that integrals over their fixed points, weighted with \( W_2 \), gave a Hoover type graph which could be expanded as a sum of Mayer graphs. It should also be clear that if we had used \( T \int f_{i,j} \) over \( 1 \leq i < j \leq \ell \) instead of \( W_\ell \) for the weighting factor in the integrand, we would have obtained the corresponding one-center Mayer graph with all \( \ell(\ell-1)/2 \) bonds between the "fixed" points. For the special case of \( \ell = 2 \), Yu (8) has shown a further correlation to one-center Mayer graphs. It is the nature of this correspondence between one-center and two-center graphs which we wish to discuss now and to make use of later in this section.

It is known that the pressure of the system may be related to the radial distribution function by the equation

\[
P/\rho kT = 1 - (\rho/6kT) \int r u'(r) g(r) \, dr
\]  

(3-1)

where \( u'(r) \) is the derivative of the two-body interaction potential. From the definition of \( f \) in (1-6) we find that \( u'(r) = -kT W_2 f'(r) \).

For a system of hard spheres with unit diameter,* \( f'(r) \) is a Dirac delta function, \( \delta(r-1) \). Using the relationship \( \bar{n}_2(r) = \rho^2 g(r) \),

---

* Throughout this section and the next we will use a system of reduced units in which the hard spheres have a diameter of one. Note that in this system of units \( b = (2\pi/3) \).

(37)
we may integrate (3-1) to obtain

$$P/kT = \rho + b \tilde{n}_2(1) \quad (3-2)$$

where $\tilde{n}_2(1)$ indicates that all two-center graphs in the expansion of $\tilde{n}_2$ are to be evaluated at unit separation of the fixed centers.

Recall that $P/kT$ can be expanded as a power series in $\rho$ whose coefficients involve the $G_m$'s. Also, $\tilde{n}_2$ can be given as a power series in $\rho$ (II-8) and put into (3-2). By equating the coefficients of matching powers of $\rho$, one obtains the relationship

$$q_{n-1} = -nb G_{2,n-2}(1) \quad (3-3)$$

This last equation, which relates the sum of one-center graphs on $n$ points to the sum of two-center, $n$-point graphs evaluated at unit separation, is a well-known result. Yu (8) has shown, however, that there also exists a relationship between each individual Mayer graph and certain two-center graphs evaluated at one. The nature of this relationship is treated by Kilpatrick (2) in his review article. The result of Yu's work in which we are mainly interested is the relation of the $n$-point Mayer graph having all $n(n-1)/2$ bonds, $M_n^*$, to the corresponding two-center graph without the line between the fixed centers, $M_{2,n}^*(1)$, evaluated at unit separation. For this particular case, the Yu result simplifies to

$$M_n^* = -nb M_{2,n}^*(1) \quad (3-4)$$
We will be especially interested in the case of $n=4,5$ for which

\[ D_6 = \quad = -4b \quad (1) \quad (3-5) \]

and

\[ E_{10} = \quad = -5b \quad (1) \quad (3-6) \]

B. EVALUATION OF $D_6$ USING THE VAN DER WAALS VOLUME.

In calculating the graphs contributing to $E_4$ (see Table 1-1), $D_4$ and $D_5$ can be readily evaluated by extending the method outlined in Appendix I, with the results

\[ D_4 = (272/105)b^3 \quad D_5 = (-6357/3360)b^3. \]

Evaluation of the graph $D_6$ is considerably more difficult. As we mentioned earlier, Van der Waals set up an expression for $A_{3,0} = \quad$ which Van Laar succeeded in integrating (with considerable difficulty) to give $-12\sigma b^3$. Because of the relationship

\[ \quad = \quad + 3 \quad + 3 \quad + \quad \quad (3-7) \]

and since all the graphs in (3-7) except $D_6$ are known analytically, we could solve this equation for $D_6$ to give

\[ D_6 = \left[ (2707/1120) - 12\sigma \right] b^3. \quad (3-8) \]

By making use of (3-5), we can evaluate $D_6$ directly, and with far less effort than was required of Van Laar. Van der Waals (18) gave an expression for a quantity which is related to the volume
common to three exclusion spheres whose centers are in a given triangular configuration, namely \( 0_{3,1} = \bigcap_0 \). Van Laar then integrated this expression over all relative configurations of the triangle for which each side was greater than one but less than two, to give \( A_{3,0} \).

Consider the relationship

\[
\bigcap_0 (1) = \int \Phi_{32} \Phi_{13} \bigcap_0 d\vec{r}_3
\]  

(3-9)

where \( r_{12} \) in the expression for \( \bigcap_0 \) is held fixed at one. Since the two-center graph in (3-9) is directly related to \( D_6 \) by (3-5), we may evaluate \( D_6 \) from Van der Waals' volume expression by integrating over \( \vec{r}_3 \) only.

Let us choose a set of spherical polar coordinate axes with point 1 at the origin, point 2 on the vertical \((\varphi=0)\) axis at a distance \( r_{12} \), and point 3 at \((r_{13}, \varphi, \varphi)\). Further, let \( x = |\vec{r}_{12}| \), \( y = |\vec{r}_{13}| \), and \( z = |\vec{r}_{12} - \vec{r}_{13}| \). Then we have

\[
d\vec{r}_3 = y^2 \sin \varphi \ dy \ d\varphi \ d\varphi
\]  

(3-10)

Since \( \bigcap_0 \) is only a function of \( x, y, \) and \( z \), we may integrate over \( \varphi \) to obtain \( 2\pi \) and transform (3-10) to a \( dy \) \( dz \) differential with the result

\[
y^2 \sin \varphi \ dy \ d\varphi = (yz/x) \ dy \ dz
\]  

(3-11)

Thus, (3-9) becomes

\[
\bigcap_0 (1) = 2\pi \int \int \bigcap_0 (y,z) \ y \ z \ dy \ dz
\]  

(3-12)

where the integrations are over all \( y \) and \( z \) between zero and one, and we have set \( x = 1 \). Let the integral in (3-12) be represented by \( -\tilde{f} \).
so that \[ \vec{\varphi}(1) = -2\pi \vec{\Phi} \]. Then from (3-5) we have

\[ (D6)/b^3 = (18/\pi) \vec{\Phi} \cdot \tag{3-13} \]

We now proceed to calculate \( \vec{\Phi} \).

Figure 3-1 shows the region over which point 3, labeled P(y,z), must be integrated. Let 1 and 2 be unit distance apart, and let \( \overline{BC} \) and \( \overline{AC} \) be arcs of unit circles centered on 1 and 2 respectively. The area ABCA is the region over which point 3 is to be integrated, which we shall call region I, or \( \mathcal{K}_I \). Let the arc \( \overline{BEA} \) be an arc of a unit sphere centered at \( C' \). The area ADBEA will be called region II (\( \mathcal{K}_II \)) and the area AEBCA will be called region III (\( \mathcal{K}_III \)), so that \( \mathcal{K}_I = \mathcal{K}_II + \mathcal{K}_III \). Since all points that lie simultaneously within unit distance of 1 and 2 are in region I, \( \vec{\Phi} \) should be given by integrating \( \Delta \) over this region. There is, however, a discontinuity in the form of \( \Delta \) along the line AEB. For whenever \( P(y,z) \) is in region II, the exclusion sphere of point 3 completely covers the overlap volume of spheres 1 and 2. Thus for any location of \( P(y,z) \) in region II, the volume common to the three spheres is a constant which we shall call \( V_{II}^* \). For \( P(y,z) \) in region III, the overlap volume is \( V_{III}(y,z) \), a function of the location of \( P(y,z) \). Thus we

\[ \text{FIGURE 3-1} \]

* Recall that we have already integrated over \( \varphi \) from 0 to \( 2\pi \), and we are only considering \( P(y,z) \) in a half radial plane.
have \( \Phi = \Phi_{II} + \Phi_{III} \) where

\[
\Phi_{II} = \int \int_{\kappa} V_{II} y z \, dy \, dz,
\]

(3-14)

and

\[
\Phi_{III} = \int \int_{\kappa} V_{III} y z \, dy \, dz.
\]

(3-15)

\( V_{II} \) is merely the volume common to two exclusion spheres at unit separation, which is \( 5\pi/12 \). The equation of the boundary of region II (arc EEB) is found to be

\[
z^* = \frac{1}{4}(\sqrt{4-y^2} - \sqrt{3} y)
\]

(3-16)

where \( z^* \) is the value of \( z \) at the boundary for a given \( y \). Thus

\[
\Phi_{II} = \left(\frac{5\pi}{12}\right) \int_0^1 y \left[ \int_{z^*}^{y} z \, dz \right] \, dy
\]

\[
= \frac{5\pi}{12} \left[ \frac{11}{24} - \frac{\sqrt{3}\pi}{12} \right].
\]

(3-17)

\( \Phi_{III} \) is obtained in a similar manner by integrating \( V_{III}(y,z) \) over \( z \) running from \( z^*(y) \) to 1, and then over \( y \) from 0 to 1. As we shall see, though, the expression for \( V_{III}(y,z) \) is a complicated function of \( y \) and \( z \), and the actual integrations are not as straightforward as in (3-17).

Figure 3-2 shows a cross section of the volume \( V_{III} \) in the plane of the triangle of points 1, 2, and 3. This volume is symmetric to either side of this plane. It has the same shape for all cross sections parallel to the one shown, but decreases in size as one goes farther from the triangular plane until it becomes a single point. Van der Waals divides this volume into six segments (Figure 3-2b),
each bounded by two planes and one spherical surface. The division is made as follows. Let $G$ be the center of the circle circumscribed on the triangle formed by the three centers. The six dividing half-planes radiate from $G$, each perpendicular to the plane of the triangle. Three of these ($GA, GB, \text{and } GC$) pass through the points of intersection of the spheres, taken in pairs, in the triangular plane. Now continue the line from point 1 through $G$ until it intersects sphere 1 at $D$. Construct points $E$ and $F$ similarly from points 2 and 3 respectively. Points $D, E, \text{and } F$ determine the remaining three half-planes.

Van der Waals gives the volume of one of these segments as

$$V(\rho, \omega) = \frac{1}{3} (\rho \sin \omega)(\rho \cos \omega) \sqrt{1 - \rho^2}$$

$$+ \frac{2}{3} \tan^{-1} \left( \tan \omega \sqrt{1 - \rho^2} \right)$$

$$- \rho \sin \omega \left[ 1 - \frac{1}{3} (\rho \sin \omega)^2 \right] \tan^{-1} \left( \sqrt{1 - \rho^2} / \rho \cos \omega \right) \tag{3-18}$$

where $\rho$ is the radius of the circumscribed circle and $\omega$ is one of the angles of the triangle formed by the three centers. By congruency arguments, one can readily see that the volume DOA is equal to the volume EGA, and likewise for the other two pairs (see Figure 3-2b). Thus if the three angles of the triangle formed by the three centers are called $\omega_1, \omega_2, \text{and } \omega_3$, the total three-sphere overlap is given by

$$V_{\text{III}} = 2 \left[ V(\rho, \omega_1) + V(\rho, \omega_2) + V(\rho, \omega_3) \right]. \tag{3-19}$$

(43)
FIGURE 3-2. (a) Cross section of three-sphere overlap volume in the plane of triangle xyz. (b) Detail of overlap volume showing the Van der Waals sectioning.
We now wish to transform (3-19) into a function of* x, y, and z. In the general expression (3-18) we make the following substitutions.

\[
\rho \sin \omega = \frac{x}{2} \quad \rho \cos \omega = \left(\frac{x}{2W}\right)(y^2 + z^2 - x^2)
\]

\[
\tan \omega = \frac{W}{(y^2 + z^2 - x^2)}
\]

where

\[
\sqrt{1 - \rho^2} = \left(\frac{W^2 - x^2y^2z^2}{W^2 - x^2 - y^2 - z^2}\right)^{\frac{1}{2}}/W
\]

\[
W^2 = 4y^2z^2 - (y^2 + z^2 - x^2)^2.
\]

The quantity W is a symmetric function of x, y, and z, and is equal to four times the area of the xyz-triangle. Using these transforming equations on (3-18) we obtain

\[
V(x, y, z) = \frac{1}{12} \frac{x^2}{W^2} (y^2z^2 - x^2) \sqrt{W^2 - x^2y^2z^2}
\]

\[
+ \frac{2}{3} \tan^{-1} \left[ \sqrt{W^2 - x^2y^2z^2}/(y^2 + z^2 - x^2) \right]
\]

\[
- \frac{1}{2} x(1 - x^2/12) \tan^{-1} \left[ \frac{2\sqrt{W^2 - x^2y^2z^2}/x(y^2 + z^2 - x^2)}{W^2 - x^2 - y^2 - z^2} \right].
\]

The other two volume expressions in (3-19) are obtained from (3-22) by performing all even (in this case cyclic) permutations on x, y, and z, so that

\[
V_{III} = 2 \left[ V(x, y, z) + V(y, z, x) + V(z, x, y) \right].
\]

Notice that y and z appear symmetrically in (3-22). Thus

* The transformations are made by letting the value of x be a general undetermined quantity. We will set x = 1 just prior to carrying out the integrations.

(45)
V(x,y,z) = V(x,z,y), which reiterates the fact that the six volumes appear as three pairs of equal volumes. Because of this relation, we shall call the three volume terms in (3-23) V_x, V_y, and V_z, where the subscript gives the non-symmetric variable. (Even after we set x = 1, we shall continue to write V_x for V(1,y,z), since we will want to add numerical subscripts to the V's.) Let the three terms which contribute to each V be labeled 1, 2, and 3 in the order they are given in (3-22) so that \[ V_x = V_{x,1} + V_{x,2} + V_{x,3} \], and similarly for \( V_y \) and \( V_z \). We define

\[ \theta_{ij} = \int_0^1 2 V_{i,j} z \, dz \]  
(3-24)

and

\[ \xi_{ij} = \int_0^1 \theta_{ij} y \, dy \]

where \( i = x, y, z \) and \( j = 1, 2, 3 \). Thus, \( \xi_{ij} \) is given by the sum of the nine \( \xi_{ij} \) type terms. We will now show how these nine terms can be evaluated.

The three terms for which \( j = 1 \) are most easily integrated together, since their sum is a simpler expression. Letting

\[ V_1 = V_{x,1} + V_{y,1} + V_{z,1} \]

one may readily show that

\[ V_1 = (1/12) \sqrt{w^2 - y^2 z^2} \]  
(3-25)

* In general, any time we write a quantity \( V, \theta, \) or \( \xi \) with only an \( i \) or a \( j \) subscript, we will imply that this term is the sum of the three corresponding terms having the same \( i \) or \( j \).
From (3-24) and (3-25) we have
\[
\theta_i = \frac{1}{6} \int_{z^*}^t \left[ 3 y^2 z - (y^2 + z^2 - 1)^{1/2} \right] z \, dz.
\] (3-26)

Letting \( t = y^2 \) and \( s = z^2 \), we find
\[
\theta_i = \frac{1}{12} \int_s^t \left[ -(1-t)^2 + (2+t) s - s^2 \right] ds.
\] (3-27)

where
\[
S^* = 1 + \frac{1}{2} t - \frac{1}{2} \sqrt{3t(4-t)}.
\] (3-28)

Thus
\[
\theta_i = \frac{1}{72} \left[ 3t(4-t) \tan^{-1}(2\sqrt{\frac{3-t}{t}}) - 2t \sqrt{3-t} \right].
\] (3-29)

We may find \( \Phi_i \) by setting \( ydy = dt/2 \) and integrating \( \frac{1}{2} \theta_i \, dt \) from zero to one. The integration can be done by parts with
\[
u = \tan^{-1}(2\sqrt{\frac{3-t}{t}}), \quad dv = 3t(4-t) \, dt.
\] (3-30)

By letting \( u \) in the integration by parts (\( \int_a^b u dv = uv|_a^b - \int_a^b v du \)) be the arctangent term, and noticing that the differential of an arctangent is an algebraic expression, we convert a trigonometric integral into an algebraic one. We find
\[
 uv|_0^t = \frac{5}{192} \tan^{-1} 2\sqrt{2} = \frac{5}{192} (\pi - 2 \tan^{-1} \sqrt{2}).
\] (3-31)

Combining \( vdu \) with the second term of (3-29), and calling the result \( \xi \), so that \( \Phi_i = uv|_0^t + \xi \), we have
\[
\xi = \frac{1}{192} \int_0^t \left( 2t^3 - 5t^2 - 2t - 8 + \frac{3}{4t} \right) \frac{dt}{\sqrt{2} \sqrt{3-t}}.
\] (3-32)

\[
= \frac{1}{192} \left[ \frac{4}{3} \sqrt{2} - 11 \tan^{-1} 2\sqrt{2} + 16 \sin^{-1}(4\sqrt{2}/9) \right].
\] (47)
Since \( \sin^{-1}(4\sqrt{2}/9) = 4 \tan^{-1}\sqrt{2} - \pi \), we find as a final result

\[
\overline{F}_{x_2} = \frac{1}{144} \sqrt{2} - \frac{11}{72} \pi + \frac{17}{48} \tan^{-1}\sqrt{2} .
\]  

(3-33)

The method of obtaining the other \( \overline{F}_{x_2} \)'s is similar. We shall not show as much detail in their calculations, but we will indicate the steps which are not immediately obvious.

\[
\theta_{x_2} = \frac{2}{3} \int_{y}^{t} \tan^{-1}\left[\sqrt{3ts-(t+s-1)^2}/(t+s-1)\right] ds .
\]  

(3-34)

Integrating by parts with \( u \) being the entire integrand of (3-34) and \( dv = ds \), we have

\[
\theta_{x_2} = -\frac{2}{3} \tan^{-1}\left(\frac{\sqrt{3-t}}{3}\right) - \frac{27}{3} \left[ 2 + t - \sqrt{3t(y-t)} \right] + \mathcal{L}
\]  

(3-35)

where

\[
\mathcal{L} = -\frac{1}{3} \int_{3}^{\sqrt{3-t}} \left[ (t-s-1)/\sqrt{3ts-(t+s-1)^2} \right] ds
\]  

(3-36)

\[
= \frac{1}{6} (y-t) \tan^{-1}\left(2\sqrt{\frac{3-t}{t}}\right) - \frac{1}{3} \sqrt{t(3-t)} .
\]  

(3-37)

Thus

\[
\overline{F}_{x_2} = \frac{1}{12} \int_{2}^{\sqrt{3-t}} \left[ 4 \tan^{-1}\left(\frac{\sqrt{3-t}}{t}\right) + (y-t) \tan^{-1}\left(2\sqrt{\frac{3-t}{t}}\right) \right]
\]

\[
-2\sqrt{t(3-t)} - 2\pi \left[ 2 + t - \sqrt{3t(y-t)} \right] dt .
\]  

(3-38)

The arctangent terms may be integrated as in (3-29) and the other terms are simple algebraic integrals. When (3-38) is integrated and cleared up we have

\[
\overline{F}_{x_2} = \frac{2}{6} \tan^{-1}\sqrt{2} - \frac{1}{6} \sqrt{2} - \frac{3}{4} \pi + \frac{1}{4} \sqrt{3} \pi^2 .
\]  

(3-39)
We now calculate $\xi_{y,2}$ from

$$\theta_{y,2} = \frac{2}{3} \int_s^t \tan^{-1}\left[\frac{3ts-(t+s-1)^2}{(1-t+s)}\right] ds. \quad (3-40)$$

The initial steps are similar to those used in (3-34) with the result

$$\theta_{y,2} = \frac{2}{3} \tan^{-1}\left(\sqrt{t(3-t)}/(2-t)\right) + \frac{1}{2} t \tan^{-1}\left(2 \sqrt{\frac{3-t}{t}}\right)$$

$$- \frac{1}{3} \sqrt{t(3-t)} \ , \quad (3-41)$$

The usual method of integration yields

$$\xi_{y,2} = \frac{1}{3} \sqrt{2} - \pi + 3 \tan^{-1}\sqrt{2} \ . \quad (3-42)$$

Consider the volume $V_{z,2}$. If $y$ and $z$ are interchanged, the result is $V_{y,2}$. But since we are integrating over a range which is symmetric in $y$ and $z$, $\xi_{z,2} = \xi_{y,2}$. The same will be true for $j = 3$, so that $\xi_{y,3} = \xi_{z,3}$. Thus, only the terms $\xi_{x,3}$ and $\xi_{y,3}$ remain to be evaluated.

$$\theta_{x,3} = -\frac{u}{2y} \int_s^t \tan^{-1}\left[2 \frac{\sqrt{3ts-(t+s-1)^2}}{(t+s-1)}\right] ds. \quad (3-43)$$

Integration by parts as before gives

$$\theta_{x,3} = -\frac{u}{2y} \left[\tan^{-1}\left(2 \sqrt{\frac{3-t}{t}}\right) - \pi S(t) - t \mathcal{L}\right] \quad (3-44)$$

where

$$\mathcal{L} = \int_s^t [s(t-s-1), \sqrt{3ts-(t+s-1)^2}] ds \ . \quad (3-45)$$

To solve $\mathcal{L}$, we let $s = 1 + \frac{1}{2} t - \frac{1}{2} \sqrt{3t(4-t)} \omega$. The radical in (3-45) then becomes $\sqrt{1 - \omega^2}$, and the denominator factors so that the integrand can be broken into partial fractions giving

(49)
\[
\left[1 + \frac{(1-V_e)^{3} \tau^{-\frac{1}{2}}}{(\sqrt{\omega} + t - \sqrt{4V_e})} - \frac{(1+V_e)^{3} \tau^{-\frac{1}{2}}}{(\sqrt{\omega} + t + \sqrt{4V_e})}\right]/(1 - \omega^2)^{1/4}, \tag{3.46}
\]

where \( R = 3t(4-t) \). The integration of the separate terms is straightforward, and the integration over \( t \) by previous methods gives

\[
\bar{X}_{x,3} = -\frac{\pi}{12} \sqrt{2} + \frac{121}{72} \pi - \frac{209}{48} \tan^{-1}\sqrt{2} - \frac{11}{144} \sqrt{3} \pi^2. \tag{3.47}
\]

Finally

\[
\theta_{y,3} = -\frac{\sqrt{E}}{2} (1 - \frac{t}{12}) \int_{s}^{t} [2\sqrt{3-t-s}(t-s)/\sqrt{E}(t-s-t)] ds. \tag{3.48}
\]

Notice that by integrating over \( s \) and then \( t \), the factor \((1-t/12)\) can come out of the integral. The term \( \theta_{x,3} \) would have a corresponding term \((1-s/12)\) which would have to be included in the integral. Thus, even though \( \bar{X}_{y,3} = \bar{X}_{z,3} \), \( \theta_{y,3} \) is easier to calculate than \( \theta_{z,3} \) when we integrate over \( s \) and then \( t \).

By the same method as we used to calculate \( \theta_{x,3} \), we find

\[
\theta_{y,3} = -\frac{\sqrt{E}}{2}(1 - \frac{t}{12}) \left\{ \tan^{-1}[2\sqrt{3-t}/(t-s)] - \sqrt{E} \tan^{-1}[2\sqrt{3-t}/t] \right. \\
+ \frac{1}{2} (1+\sqrt{E}) \tan^{-1}[f(\sqrt{E})] - \frac{1}{2} (1-\sqrt{E}) \tan^{-1}[f(-\sqrt{E})] \right\} \tag{3.49}
\]

where

\[
f(\alpha) = 2(1+\alpha)\sqrt{3-\alpha}\sqrt{6 + 2\alpha - \alpha^2}. \tag{3.50}
\]

The usual integration by parts yields several complicated algebraic integrals, which finally reduce to

\[
\bar{X}_{y,3} = -\frac{2389}{10080} \sqrt{2} + \frac{13429}{20160} \pi - \frac{6767}{3360} \tan^{-1}\sqrt{2}. \tag{3.51}
\]

(50)
Summing all the values for $\Phi_{1j}$ we find

$$
\Phi_{\infty} = -\frac{73}{1680} \sqrt{2} + \frac{83}{560} \pi - \frac{459}{560} \tan^{-1} \sqrt{2} \\
+ \frac{5}{144} \sqrt{3} \pi^2 .
$$

(3-52)

Recalling that $\Phi = \Phi_{\infty} + \Phi_{\infty}$, and using $\Phi_{\infty}$ from (3-17) gives

$$
\Phi = -\frac{73}{1680} \sqrt{2} + \frac{2419}{10080} \pi - \frac{459}{560} \tan^{-1} \sqrt{2} .
$$

(3-53)

Using (3-13) we find

$$
\frac{D6}{b^3} = -\frac{219 \sqrt{2}}{280} \frac{3419}{560} - \frac{4131}{280} \frac{\tan^{-1} \sqrt{2}}{\pi} .
$$

(3-54)

Finally, putting (3-54) in terms of $\beta$ gives

$$
\frac{(D6)}{b^3} = (2707/1120) - 12/\beta ,
$$

(3-55)

which agrees with (3-8).

These calculations constitute the first geometrical verification of Van Laar's integrations, and show how two-center graphs can be used to significantly reduce the work involved in integrating overlap volumes.

Before continuing, we should make a few remarks concerning the Nijboer and Van Hove results (9). In their 1952 paper, they gave an expression for $\Phi$ as a function of $r$ which they obtained by introducing certain Fourier transform integrals. They recognized the fact that this expression (along with the graphs $\Omega$ and $\Lambda$ which they also found as functions of $r$) evaluated at $r=1$ could give the fourth virial
coefficient by using relations equivalent to (3-3) and (2-33). Doing this they verified Boltzmann's analytic result for $B_4$. They apparently did not realize that they could also verify the value of $D_6$ directly from $\mathcal{F}(1)$. When one evaluates their expression for $\mathcal{F}(r)$ at $r=1$, the result is

$$\mathcal{F}(1) = -\left( \frac{2707}{4480} - \gamma \beta \right) b^2,$$  \hspace{1cm} (3-56)

which when multiplied by $-4b$ gives a value for $D_6$ that agrees with (3-8).
C. EXTENSION TO THE GRAPH

We would now like to consider an extension of the methods used in the last section to the evaluation of the graph \( \mathcal{E}(1) \). The value of this graph, together with the relation (3-6), would give an expression for E10 (i.e., \( \mathcal{E} \)), which is one of the three remaining five point star graphs that are not yet analytically known.

We begin by writing the integral expression for the graph \( \mathcal{E} \) (which we shall call \( \mathcal{E} \)) as

\[
\mathcal{E}(r_{12}) = \int \int f_{13} f_{14} f_{23} f_{24} f_{34} \, d\mathbf{r}_3 \, d\mathbf{r}_4 
\]\n
where

\[
\mathcal{E} = \int f_{15} f_{25} f_{35} f_{45} \, d\mathbf{r}_5 .
\] (3-58)

If we again use a coordinate system as in section III-B, with points 1 and 2 at unit separation and the origin midway between these points, we have*

\[
\mathcal{E}(1) = \int \int f_{34} \, d\mathbf{r}_3 \, d\mathbf{r}_4 .
\] (3-59)

Geometrically the quantity \( \mathcal{E} \) represents the volume common to four unit-radius spheres whose centers are in a given tetrahedral configuration. It is the nature of this quantity which we shall now investigate.

* In this section, the regions \( \mathcal{E}_T, \mathcal{E}_R, \) and \( \mathcal{E}_M \) will be the three-dimensional regions of revolution obtained by rotating the corresponding regions described in section III-B through an angle of \( 2\pi \) about the axis which passes through points 1 and 2.
Depending upon the relative locations of points 1, 2, 3, and 4, the form of $\Delta$ is given by one of three different expressions. If points 3 and 4 are both located in $\mathcal{R}_x$, their spheres completely cover the volume common to spheres 1 and 2. In this case $\Delta = \Delta(1)$ which we found (see section III-B) to be $5\pi/12$.

As a second case, one of the points (say point 4) is in $\mathcal{R}_x$ and the other is in $\mathcal{R}_w$. Then the sphere of point 4 completely covers the volume common to spheres 1, 2, and 3. In this case, $\Delta = \Delta(3)$ which is the volume $V_{wi}$ given by (3-23).

Finally, let us consider the case for which point 3 and point 4 are both in $\mathcal{R}_w$. There are configurations of $\vec{F}_3$ and $\vec{F}_4$ both in $\mathcal{R}_w$ in which again one of the spheres completely covers the volume common to the other three, and for which $\Delta = V_{wi}$. For the remainder of the configurations of $\vec{F}_3$ and $\vec{F}_4$ in $\mathcal{R}_w$, $\Delta$ is a "true" four-sphere overlap volume which we shall call $V_{wi}$. Portions of the surfaces of each of the four spheres make up the boundary of this volume, and the volume itself is a function of the relative locations of all four centers. We will now look at how one might proceed to calculate $V_{wi}$.

Let us digress briefly to introduce some notation which will facilitate the description of the volume $V_{wi}$. Let a single number, $j$ ($j=1,2,3,4$), represent the point at which the center of a sphere is located. Let $\mathcal{F}$ represent the surface of a unit sphere centered at the point $j$. Let $\mathcal{F}_j$ be the circle common to $\mathcal{F}$ and $\mathcal{F}_i$, and let $ij$ be the plane determined by $\mathcal{F}_i$. Let $i\times\mathcal{F}$ be the points of intersection of the surfaces $\mathcal{F}_i$ and $\mathcal{F}$.

If $p$ and $q$ are two general points, let $pq$ represent the line segment between $p$ and $q$. If $\alpha$ is a general line (and the point $p$ is not on $\alpha$), let $\alpha / p$ be the plane
determined by $\alpha$ and $p$. Let $(\alpha/p)^+$ be the half-plane bounded by the line $\alpha$ and containing the point $p$; and let $(\alpha/p)^- = \alpha/p - (\alpha/p)^+$. In the following discussion, we will only be interested in those portions of the manifolds just described which lie within or on the surface of the particular overlap volume under consideration. That is, we will consider these manifolds to terminate at the boundary of the particular overlap volume.

Before attempting to describe $V_{\Pi}$, let us see how $V_{\Pi}$ and $V_{\Sigma}$ would be expressed in this notation. We will consider these expressions in general (i.e., without the restriction $r_{12} = 1$).

$V_{\Pi}(x)$ is the volume common to two unit-radius spheres whose centers are $x$ apart, and has the shape of a lens. This volume is most easily calculated by dividing $V_{\Pi}$ into two (=2!) regions by the plane $1:2$. A typical one of these regions is bounded by one plane, $1:2$, and one spherical surface, $\hat{1}$. Its volume is easily calculated and indeed is merely Boltzmann's $K(x)$. The volume of the other region is obtained by the permutation of the names of the points 1 and 2 in the expression for the typical region. Since $|\hat{1}_{12}| = |\hat{2}_{21}| = x$, both regions have the same volume.

$V_{\Sigma}$ (the volume common to three unit-radius spheres centered at 1, 2, and 3) presents a less-trivial case than does $V_{\Pi}$. Figure 3-2 shows a cross section of $V_{\Sigma}$ in the plane of the triangle formed by points 1, 2, and 3. Let $\alpha$ be the line determined by the two points $\hat{1} \times \hat{2} \times \hat{3}$. Construct the three planar sections bounded by $(\alpha/ \hat{1} \times \hat{2})^+, (\alpha/ \hat{1} \times \hat{3})^+, (\alpha/ \hat{2} \times \hat{3})^+$. These planes divide $V_{\Sigma}$ into three regions, each of which is bounded by two planes and one
spherical surface. The evaluation of these three volumes is simplified
by further subdividing them by the planes \((\alpha/1)^-,\ (\alpha/2)^-,\ \text{and}\ (\alpha/3)^-\).
We now have a total of six \((=3!)\) regions, each bounded by two planes
and one spherical surface. In addition, one of the bounding planes is
now a great-circle plane of the bounding sphere, which simplifies the
calculation of the volume expression.

Let us consider one of these typical regions bounded by the
planes \((\alpha/\hat{1}\times\hat{2})^+,\ (\alpha/1)^-,\ \text{and}\ \text{the spherical surface}\ \hat{1}\). The shape of
this region is that of a hemisphere
cut out by an arbitrary plane. Figure
3-3 shows a cross section of this
region in a plane which is perpen-
dicular to the two bounding planes.
Because of the cylindrical symmetry
of the hemisphere, the plane
\((\alpha/\hat{1}\times\hat{2})^+\) is given by two parameters.
We choose \(\omega\) (the angle between the
bounding planes) and \(\rho\) (the distance between point 1 and the line of
intersection of the bounding planes) since these are quantities which
are simply related to parameters of the original triangle of points 1,
2, and 3. (See equation (3-18) and the discussion which follows it.)
The descriptions for the remaining five regions are obtained from that
of the typical region by permuting the names of the three points in
all 3! ways. The volumes of these regions are obtained from the volume
expression of the typical region in the same way. However, instead of
six distinct volumes, we find three pairs of equivalent volumes. This
is because the volume of a region which can be described wholly in terms

(56)
of two points, i and j, and any number of points which lie in the perpendicular bisecting plane of the line i/j, is invariant to an interchange of i and j.

We now consider $V_{W}$ (the volume common to four unit spheres whose centers are in a given tetrahedral configuration). We would like to divide this volume into $4!$ regions so that each is bounded by a number of planes and one spherical surface. To obtain the maximum benefit from this sectioning, with regard to ease of evaluation of these volumes, we would like to have as many as possible of the bounding planes of the typical region pass through the center of the bounding sphere for that region. In the following discussion, we describe a method of sectioning $V_{W}$ in such a way that each region is bounded by one spherical surface and three planes (two of which pass through the center of the bounding sphere).

The shape of $V_{W}$ is that of an irregular spherical tetrahedron. The vertices of this tetrahedron are the points $p_{1} = \bar{2} \times \bar{3} \times \bar{4}$, $p_{2} = \bar{1} \times \bar{3} \times \bar{4}$, $p_{3} = \bar{1} \times \bar{2} \times \bar{4}$, and $p_{4} = \bar{1} \times \bar{2} \times \bar{3}$. Its edges are portions of the six circles $\bar{i} \times \bar{j}$ where $1 \leq i < j \leq 4$. Its faces are portions of the spheres $\bar{1}$, $\bar{2}$, $\bar{3}$, and $\bar{4}$.

Let point $\sigma$ be the circumcenter of the tetrahedron formed by points 1, 2, 3, and 4. It is readily shown that point $\sigma$ must lie within the volume $V_{W}$. Let the line $\alpha_{1}$ be given by $\sigma/ \bar{2} \times \bar{3} \times \bar{4}$, $\alpha_{2}$ by $\sigma/ \bar{1} \times \bar{3} \times \bar{4}$, $\alpha_{3}$ by $\sigma/ \bar{1} \times \bar{2} \times \bar{4}$, and $\alpha_{4}$ by $\sigma/ \bar{1} \times \bar{2} \times \bar{3}$. We now construct six partial planes as follows. Choose two points (say 1 and 2) from the set of points $\{1, 2, 3, 4\}$. Construct the portion of the plane bounded by $\alpha_{1}$, $\alpha_{2}$, and $\bar{3} \times \bar{4}$. The other five planes are obtained in
a similar manner by choosing other pairs from the set of four points. These six planes divide $V_{IV}$ into four regions, each bounded by three planes and one spherical surface. Consider a typical one of these which we will call $V_{IV}^{(i)}$ which is bounded by the following: plane $\alpha_i, \alpha_i', \hat{1} x \hat{4}$; plane $\alpha_i, \alpha_i', \hat{1} x \hat{3}$; plane $\alpha_i, \alpha_i', \hat{1} x \hat{2}$; spherical surface $\hat{1}$. The description of this section is symmetric in 2, 3, and 4. The other sections ($V_{IV}^{(j)}$ where $j = 2, 3, 4$) are obtained by letting, in turn, points 2, 3, and 4 be the special point. We now concentrate on the subdivision of $V_{IV}^{(i)}$.

For the purpose of this subdivision of $V_{IV}^{(i)}$, we will consider only the portions of those manifolds used herein which lie within or on the boundary of $V_{IV}^{(i)}$. Let us define the line segment $\beta$ by $(\partial/1)^-$, that is, the segment of the line determined by points $\partial'$ and 1 which lies between the circumcenter $\partial'$ and the point where this line intersects sphere 1. We will first divide $V_{IV}^{(i)}$ into three regions by the partial planes $(\beta/p_2)^+, (\beta/p_3)^+, (\beta/p_4)^+$, with the points $p_j$ as defined earlier. Each of these three regions is further divided into two pieces by the three planes $(\beta/2)^-, (\beta/3)^-, (\beta/4)^-$. We have now divided $V_{IV}^{(i)}$ into six regions, each bounded by three planes and one spherical surface. The complete description of a typical one of these regions is given by the following: plane $\alpha_i, \alpha_i', \hat{1} x \hat{2}$; plane $(\beta/p_2)^+$; plane $(\beta/2)^-$; spherical surface $\hat{1}$. The other five regions of $V_{IV}^{(i)}$ are given by renaming the points 2, 3, and 4 in the five remaining permutations. Furthermore, by choosing the special point to be 2, 3, and 4 in turn, we may obtain expressions for the regions into which the other $V_{IV}^{(j)}$'s (i.e., for $j = 2, 3, 4$) are to be divided.

(58)
In summary, by permuting the names for the four points 
(1, 2, 3, and 4) in all $4!$ ways in the description given above for
the typical region, one obtains the descriptions of all 24 regions
which together make up all of $V_{IV}$. Notice that the description
of the typical region is symmetric in two of the points. Analogously
to the sectioning of $V_{III}$, in the case of $V_{IV}$ we do not obtain 24
different volume expressions, but rather 12 distinct pairs of
equivalent volumes.

Finally, let us consider the shape of the typical region of
$V_{IV}$. The two planes* $(\beta/p_2)^+$ and $(\beta/2)^-$ both contain the point 1.
Thus, the region bounded by plane $(\beta/p_2)^+$, plane $(\beta/2)^-$, and the
spherical surface $\tilde{r}$ is simply that portion of a unit sphere contained
between two half, great-circle planes. If this region is then cut by
an arbitrary plane, one is left with a region whose shape is that of
the typical region described above. Notice that the two great-circle
planes intersect along a line which is a diameter of the unit sphere.
Denote by $\rho$ the distance from the center of this sphere to the point
where the arbitrary plane intersects this diameter line. Let $\omega$ be the
angle between the two great-circle planes. Two more angular coordinates
(say $\varphi$ and $\phi$) are necessary to give the orientation of the arbitrary
plane. The best definitions for $\varphi$ and $\phi$ so that they are most
simply related to parameters of the original tetrahedron of the points
1, 2, 3, and 4 remains to be seen.

---

* For the purpose of evaluating the volume of the typical region,
we consider the full half-planes, and not just those portions within
a given set of boundaries.
The eventual goal is to express the volume of this typical region (and thus \( V_{\text{IV}} \)) as a function of the magnitudes of the six edges of the original tetrahedron of the points 1, 2, 3, and 4. Let us now consider how one could use such an expression in the evaluation of the graph \( \Phi(1) \).

Returning to equation (3-59), let us write \( \Phi(1) \) as

\[
\Phi(1) = \Phi'(1) = \Phi(1) + \Psi(1),
\]

where \( \Phi(1) \) is the value of (3-59) integrated over all positions of \( \Phi_3 \) and \( \Phi_4 \) such that \( \Phi_3 \) \( \Phi_4 \) \( V_{\text{IV}} \) (that is, over all configurations for which the expression for the four-sphere overlap volume degenerates into one of the lower cases). Note that configurations for which points 1, 2, 3, and 4 are coplanar are also a special form for the four-sphere overlap volume and are included in \( \Phi(1) \). For all other configurations we have

\[
\Psi(1) = \int \int V_{\text{IV}}(r_{12} = 1) \, d\Phi_3 \, d\Phi_4.
\]

Recall that in equations (3-9) through (3-12) we transformed the integral of \( V_{\text{IV}} \) over \( \Phi_3 \) to an integral over the edges of the triangle of points 1, 2, and 3. In a similar manner, we can transform (3-61) into an integral over the edges of the tetrahedron of points 1, 2, 3, and 4. The result (for \( r_{12} = 1 \)) is

\[
\Psi(1) = \frac{\pi}{3} \int \int V_{\text{IV}} \cdot V_T^{-1} \, r_1, r_2, r_3, r_4, dr_1, dr_2, dr_3, dr_4,
\]

where the integration is over all values of the \( r_{1,j} \)'s not covered in \( \Phi(1) \) and such that all of them are between zero and one. The factor \( V_T \) is the volume of the tetrahedron formed by the six edges in a given
configuration, and is most easily expressed as the determinant

\[
36 V_T^2 = \begin{vmatrix}
\mathbf{r}_{12} \cdot \mathbf{r}_{12} & \mathbf{r}_{12} \cdot \mathbf{r}_{13} & \mathbf{r}_{12} \cdot \mathbf{r}_{14} \\
\mathbf{r}_{13} \cdot \mathbf{r}_{12} & \mathbf{r}_{13} \cdot \mathbf{r}_{13} & \mathbf{r}_{13} \cdot \mathbf{r}_{14} \\
\mathbf{r}_{14} \cdot \mathbf{r}_{12} & \mathbf{r}_{14} \cdot \mathbf{r}_{13} & \mathbf{r}_{14} \cdot \mathbf{r}_{14}
\end{vmatrix}.
\]  

(3-63)

Since \( \mathbf{r}_{11} \cdot \mathbf{r}_{1j} = \frac{\left( r_{11}^2 + r_{1j}^2 - r_{1j}^2 \right)}{2} \), \( V_T \) can be written as a function of the six edges of the tetrahedron.

In order to evaluate \( \mathcal{V}(1) \), then, three problems must be faced. First, \( V_\text{IV} \) must be evaluated and expressed as a function of the \( r_{1j} \)'s. Second, the configurations of the \( r_{1j} \)'s for which \( \mathcal{A}_{\text{IV}} = V_\text{IV} \) must be expressed as bounding conditions on the integrations. (Note that we have already shown that \( \mathbf{r}_3 \) and \( \mathbf{r}_4 \) both in \( \mathcal{A}_\text{IV} \) is a necessary condition for \( \mathcal{A}_\text{IV} = V_\text{IV} \).) Third, the actual evaluation of the integrals must be performed.

In section IV, we will discuss an alternative method for evaluating the graph \( \mathcal{A}(1) \), based on a technique used by Nijboer and van Hove to obtain \( \mathcal{A}(r_{12}) \). It is difficult at this time to make a sound judgement as to which method will prove easier to carry out. If the expression for \( V_\text{IV} \) does not contain \( V_T \) as a factor, or if its form does not cause some simplification to occur in the denominator of the integrand in \( (3-62) \), it appears that the actual integration of \( (3-62) \) will be most difficult. In such an event, it may prove more practical to carry out the integrations in a set of coordinates other than those for the separations of the centers.
IV. EXTENSION OF THE NIJBOER AND VAN HOVE METHOD

A. DEFINITIONS AND NOTATION

In section III-B we mentioned that Nijboer and Van Hove (9) had obtained an expression for $\tilde{\Phi}$ as a function of $r$, the separation between the fixed centers. Their purpose in evaluating this quantity was to calculate an analytical expression for the radial distribution function through orders of $\rho^2$, which would then allow them to test the validity of the so-called superposition approximation proposed by Kirkwood in the theory of liquids. Since the value of the radial distribution function obtained from this approximation differed from their calculated value in the $\rho^3$ term, they had no need to continue their results to higher orders of $\rho$.

We now know that the complete, five-point Mayer graph ($E10 = \tilde{\Phi}$) can be obtained from the value of $\tilde{\Phi}(r)$ at $r=1$, which provides a renewed interest in any method that might lead to the evaluation of the latter graph. (We shall refer to the graph $\tilde{\Phi}$ as $\tilde{\Phi}(r)$.) The technique which Nijboer and Van Hove used to calculate $\tilde{\Phi}$ appears to be extendable to the evaluation of $\tilde{\Phi}(1)$. Because the method of extension does not appear to be immediately obvious, we shall proceed to outline our approach.

Nijboer and Van Hove define a function $F(h)$ as the spherical Fourier transform of the Mayer $f$-function, given by

$$F(h) = \int \hat{f}(r) \exp[2\pi i \hat{r} \cdot \hat{r}] \, d\hat{r} = -h^{-3/2} J_{3/2}(2\pi h), \quad (4-1)$$
where \( f(r) \) is the Mayer \( f \)-function and \( J_{3/2}(x) \) is the \( 3/2 \) order Bessel function. In addition, we define a new quantity, \( E \), by

\[
E(\vec{r}_1, \vec{r}_2) = \int_{\mathbb{V}} f_{1\gamma} f_{2\gamma} f_{3\gamma} \exp \left\{ 2\pi i \frac{1}{\hbar} \left[ \frac{\vec{r}_1}{2} \cdot \frac{\vec{r}_2}{2} \right] \right\} \, d\vec{r}_\gamma \quad (4.2)
\]

and a quantity \( E^* \) by

\[
E^*(\vec{r}_1, \vec{r}_2) = \int_{\mathbb{V}} f_{1\sigma} f_{2\sigma} f_{3\sigma} \exp \left\{ -2\pi i \frac{1}{\hbar} \left[ \frac{\vec{r}_1}{2} \cdot \frac{\vec{r}_2}{2} \right] \right\} \, d\vec{r}_\sigma. \quad (4.3)
\]

Notice that \( E \) and \( E^* \) are also functions of \( \vec{r}_1 \) and \( \vec{r}_2 \), but the product \( E^*E \) is only a function of \( \vec{r}_1 \) and \( \vec{r}_2 \). We have written (4-3) as \( E^*(\vec{r}_1, \vec{r}_2) \) because it is the complex conjugate of \( E(\vec{r}_1, \vec{r}_2) \).

Let us set up a cylindrical polar coordinate system with points 1 and 2 on the vertical axis with unit separation and locate the origin at a point midway between them (see Figure 4-1).

Let all angular coordinates be measured from the vector \( \vec{h} \), whose axial component is \( s \) and whose radial component is \( \sigma \). The points 3, 4, and 5 will be given by \( r_3(t, \rho, \varphi) \), \( r_4(a, \alpha, \nu) \), and \( r_5(b, \beta, \psi) \). In this section, the regions \( \mathcal{R}_1 \), \( \mathcal{R}_2 \), and \( \mathcal{R}_3 \) will be the three-dimensional regions of revolution obtained by rotating the corresponding regions described in section III-B through an angle of \( 2\pi \) about the cylindrical axis.

\[ \text{\textdagger} \text{ All vectors will be given in the order (axial coordinate, radial coordinate, angular coordinate).} \]

\( (63) \)
Consider the quantity

\[ T(\vec{r}_3) = \int F(h) \mathbb{E}(\vec{h}, \vec{r}_3) \mathbb{E}^*(\vec{h}, \vec{r}_3) \, dh. \]  

(4-4)

From the definitions in (4-1), (4-2), and (4-3) we have

\[ T(\vec{r}_3) = \int \int f(r) \mathcal{N} \exp[2\pi i \vec{h} \cdot (\vec{r} + \vec{r}_s - \vec{r}_3)] \, dh \, d\vec{r} \, d\vec{r}_s \]  

(4-5)

where \( \mathcal{N} = f_{14}^* f_{15}^* f_{24}^* f_{25}^* f_{34}^* f_{35} \). We can integrate over \( \vec{h} \) to obtain

\[ T(\vec{r}_3) = \int \int f(r) \mathcal{N} \delta(\vec{r} + \vec{r}_s - \vec{r}_3) \, d\vec{r} \, d\vec{r}_s \]  

(4-6)

where \( \delta(\vec{r} + \vec{r}_s - \vec{r}_3) \) is the Dirac delta function. We then integrate over \( r \) and notice that the integrand is zero except for \( \vec{r} = \vec{r}_s - \vec{r}_3 \).

In this case, \( f(r) \) becomes \( f(|\vec{r}_s - \vec{r}_3|) = f_{y5} \), and we have

\[ T(\vec{r}_3) = \int \int f_{14} f_{15} f_{24} f_{25} f_{34} f_{35} f_{45} \, d\vec{r}_s \, d\vec{r}_3. \]  

(4-7)

This last expression is equal to the graph \( \mathcal{R} \) which, in general, is a function of the locations of points 1, 2, and 3. Since we are considering points 1 and 2 to be fixed at unit separation and \( \vec{r}_3 \) to be measured from their midpoint, \( T \) is a function of \( \vec{r}_3 \) only.

Finally we may write \( \mathcal{E}(1) \) as

\[ \mathcal{E}(1) = \mathcal{R}(1) = \int f_{13} f_{23} T(\vec{r}_3) \, d\vec{r}_3. \]  

(4-8)

Since \( f_{13} f_{23} = 0 \) for point 3 outside of \( \mathcal{R} \), we will write an integral such as (4-8) without the \( f \)-factors and specify below the integral sign the region of integration for which these factors are non-zero.
We may summarize all of the foregoing results by the equation

$$\Omega^2(1) = \int_{\mathbb{R}^3} F(h) \ E(h, \vec{r}_3) \ E^*(h, \vec{r}_3) \, dh \, dr_3$$  \hspace{1cm} (4-9)$$

which is the main working equation for extending the Nijboer and Van Hove method to the evaluation of the graph \( \Omega^2 \). We now consider what must be done to evaluate the integrals in (4-9).
C. METHOD OF APPROACH.

Let point 3 be located somewhere in $\mathcal{R}_I$, and construct a sphere of unit radius about that point. The region which is common to this sphere and $\mathcal{R}_I$ will be called the region $\mathcal{R}$. Define $\tilde{\mathcal{R}}$ by $\tilde{\mathcal{R}} = \mathcal{R}_I - \mathcal{R}$. It should be clear that the region $\mathcal{R}$ is the locus of all points available to a point 3 such that $f_{1j}f_{2j}f_{3j} \neq 0$.

The definition of $E(\tilde{\mathbf{r}}, \mathbf{r}_3)$ in (4-2) is a general expression. For the particular coordinate origin which we are using (employing the terminology of the preceding paragraph), (4-2) may be given by

$$E(\tilde{\mathbf{r}}, \mathbf{r}_3) = \int_{\mathcal{R}} \exp[2\pi i \tilde{\mathbf{r}} \cdot \mathbf{r}_4] \, d\mathbf{r}_4$$

and similarly for $E^*$.

Again we find that $\tilde{\mathcal{F}}$ has different forms in region II and in region III. As we did in section III-B, we shall evaluate $\tilde{\mathcal{F}}$ over each of these regions and set $\tilde{\mathcal{F}} = \tilde{\mathcal{F}}_I + \tilde{\mathcal{F}}_II$. We find that $\tilde{\mathcal{F}}_II$ may be readily evaluated, and we shall consider this result first.

In evaluating $\Box (\mathbf{r}_{12})$, M. J. G. Boer and Van Hove derive an expression which, in our coordinate system, becomes

$$\Box (1) = \int F(h) G^2(h) \, dh$$

where

$$G(h) = \int_{\mathcal{R}_I} \exp[2\pi i \tilde{h} \cdot \mathbf{r}_j] \, d\mathbf{r}_j$$

Now, notice that whenever point 3 is in region II, $\mathcal{R} = \mathcal{R}_I$. For this case $E(\tilde{\mathbf{r}}, \mathbf{r}_3)$ is no longer a function of the location of point 3, and it becomes equivalent to $-G(\tilde{h})$. It can be shown that $G(\tilde{h})$ is a real
and symmetric function of $\vec{h}$, from which it follows that $E^*(\vec{h}, \vec{r}_3)$ is also equal to $-G(\vec{h})$. Thus for point 3 in region II, (4-9) becomes

$$\bar{F}_i = \int \int \mathcal{F}(h) \mathcal{C}^2 (\vec{h}) \, dh \, d\vec{r}_3 \, .$$ \hspace{1cm} (4-13)

The integral over $\vec{h}$ is identical to (4-11) and is independent of $\vec{r}_3$. The integral over $\vec{r}_3$ is just the volume of region II which is found to be $\pi (11 - 2 \sqrt{3} \pi)/12 \, . \quad \quad$ (4-14)

where $\mathcal{A}(1) = \frac{1}{6} (\frac{2707}{4480} - 3g_2)b^2$ as we found in (3-56).

The evaluation of $\bar{F}_i$ is considerably more difficult and we have not yet brought these calculations to an end. Several important observations serve to greatly reduce the complexity of the integrals to be evaluated, however, and we shall consider these at this time.

Recall that

$$\bar{F}_i = \int \mathcal{T}(\vec{r}_3) \, d\vec{r}_3 \, ,$$ \hspace{1cm} (4-15)

where

$$\mathcal{T}(r_3) = \int \mathcal{F}(h) \mathcal{E}(\vec{h}, \vec{r}_3) \mathcal{E}^*(\vec{h}, \vec{r}_3) \, dh \, .$$ \hspace{1cm} (4-16)

Using the region that we defined as $\mathcal{R}$ at the beginning of this section we may write

$$E^*E = \int \int \exp [2\pi i \mathcal{I} \cdot (\vec{r}_4 - \vec{r}_5)] \, d\vec{r}_4 \, d\vec{r}_5 \, .$$ \hspace{1cm} (4-17)

The vector dot product can be expanded in terms of the cylindrical

(67)
polar coordinates of the vectors to give

\[
\begin{align*}
\vec{h} \cdot \vec{r}_4 &= sa + s\alpha \cos \nu, \\
\vec{h} \cdot \vec{r}_5 &= sb + s\beta \cos \psi.
\end{align*}
\] (4-18)

Let the integrand in (4-17) be given by \( \vec{X} \). Using (4-18) and Euler's formula for the exponential, we have \( \vec{X} = \vec{A} \vec{B} \), where

\[
A = \cos[2\pi s(a-b)] + i \sin[2\pi s(a-b)] \tag{4-19}
\]

and

\[
B = \cos[2\pi s(\alpha \cos \nu - \beta \cos \psi)] \\
+ i \sin[2\pi s(\alpha \cos \nu - \beta \cos \psi)]. \tag{4-20}
\]

Notice that the real part of \( A \) is symmetric in \( s \), the imaginary part of \( A \) is antisymmetric in \( s \), and \( B \) is independent of \( s \). Since the region \( \mathcal{R} \) is independent of \( \vec{h} \) (and therefore of \( s \)), and because \( s \) is integrated over a symmetric range \(( -\infty \text{ to } \infty )\), the second term in (4-19) will make a zero contribution to \( \mathcal{I}(r_3) \).

Consider now the term in the integrand formed by the product of the remaining term in \( A \) (i.e., the real part of \( A \)) and the imaginary term from \( B \). We note that \( \vec{r}_4 \) and \( \vec{r}_5 \) are integrated over the same range (i.e., \( \mathcal{R} \)), which is a function of \( \vec{r}_3 \) only. Thus during the course of the integrations over \( \vec{r}_4 \) and \( \vec{r}_5 \), for every configuration such that \( \vec{r}_4 = \vec{v}_1 \) and \( \vec{r}_5 = \vec{v}_2 \) (\( \vec{v}_1 \) and \( \vec{v}_2 \) being general locations in \( \mathcal{R} \)) we will also have a configuration for which \( \vec{r}_4 = \vec{v}_2 \) and \( \vec{r}_5 = \vec{v}_1 \). These two configurations will make equal and opposite contributions to the term under consideration. Therefore, the total contribution of this term to \( \mathcal{I}(r_3) \) is zero.
As a result of these considerations, the total non-zero contribution of (4-16) to $T(\vec{r}_3)$ is given by

$$T(\vec{r}_3) = \int \int F(h) \cos \left[ 2\pi s(a-b) \right]$$

$$\cos \left[ 2\pi \sigma(\alpha \cos \nu - \beta \cos \psi) \right] \, d\vec{r}_4 \, d\vec{r}_5 \, dh. \tag{4-21}$$

For the purpose of abbreviation in writing the following expansions, let us introduce the following symbols:

$$2\pi sa = \gamma_1, \quad 2\pi \sigma \alpha \cos \nu = \gamma_3$$

$$2\pi sb = \gamma_2, \quad 2\pi \sigma \beta \cos \psi = \gamma_4. \tag{4-22}$$

Also, let us represent by $\mathcal{A}$ the double integral over $\vec{r}_4$ and $\vec{r}_5$ in (4-21). Using the trigonometric identity for the cosine of a sum, we expand the integrand of $\mathcal{A}$ to obtain the following four terms:

$$\cos(\gamma_1) \cos(\gamma_3) \cos(\gamma_4)$$

$$+ \cos(\gamma_1) \cos(\gamma_2) \sin(\gamma_3) \sin(\gamma_4)$$

$$+ \sin(\gamma_1) \sin(\gamma_3) \cos(\gamma_4)$$

$$+ \sin(\gamma_1) \sin(\gamma_2) \sin(\gamma_3) \sin(\gamma_4). \tag{4-23}$$

Let us consider the contribution of the first term in (4-23) to $\mathcal{A}$, which we will denote by $\mathcal{A}_1$. Thus,

$$\mathcal{A}_1 = \int \int \cos(\gamma_1) \cos(\gamma_3) \cos(\gamma_4) \, d\vec{r}_4 \, d\vec{r}_5. \tag{4-24}$$

Since $\gamma_1$ and $\gamma_3$ are functions of $\vec{r}_4$ only, and $\gamma_2$ and $\gamma_4$ are functions of $\vec{r}_5$ only, $\mathcal{A}_1$ is a product of the separate integrals. In addition, since both integrals are of the same form, we may write

(69)
\[ \mathcal{E}_I = \left\{ \int_R \cos(2\pi sa) \cos(2\pi \sigma \alpha \cos \nu) \, dr \right\}^2. \tag{4-25} \]

Let us now transform \( \hat{r}_4 \) into Cartesian coordinates \((x, y, z)\) where
\[ x = \alpha \cos \nu, \quad y = \alpha \sin \nu, \quad z = a. \tag{4-26} \]

The integral in (4-25), which we shall call \( I_1 \), is given by
\[ I_1 = \int_R \cos(2\pi sz) \cos(2\pi \sigma x) \, dx \, dy \, dz. \tag{4-27} \]

The analogous operations may be performed on the other three terms in (4-23) to give
\[ \begin{align*}
I_2 &= \int_R \cos(2\pi sz) \sin(2\pi \sigma x) \, dx \, dy \, dz, \\
I_3 &= \int_R \sin(2\pi sz) \cos(2\pi \sigma x) \, dx \, dy \, dz, \tag{4-28} \\
I_4 &= \int_R \sin(2\pi sz) \sin(2\pi \sigma x) \, dx \, dy \, dz.
\end{align*} \]

Collecting all of these results we finally have
\[ \mathcal{F}_{III} = \int \int_{\mathcal{R}} \mathcal{F}(h) \sum_{j=1}^{4} I_j^2 \, dh \, dr. \tag{4-29} \]

At this point we can observe that (4-29) is a general expression of which \( \mathcal{F}_x \) is a special case. For if we let the \( r_3 \) integration in (4-29) be over \( \mathcal{R}_x \) instead of \( \mathcal{R}_{III} \), then as we saw before \( \mathcal{R} = \mathcal{R}_x \).

Since \( \mathcal{R}_x \) is symmetric in \( x, y, \) and \( z \), all the integrals in (4-28) vanish and we are left with
\[ \mathcal{F}_x = \int \int_{\mathcal{R}_x} \mathcal{F}(h) I_1^2(\hat{n}, \hat{r}_3) \, dh \, dr. \tag{4-30} \]
The integral \( I_1 \) can be solved for this case (i.e., \( \mathcal{R} = \mathcal{R}_I \)) by a moderately straightforward method to give

\[
I_1(\hat{h}) = \left( \frac{2}{\sigma'} \right) \int_0^{\chi} \cos(2\pi sz) \sqrt{1 - \left( \frac{\hat{h}}{\sigma} + z \right)^2} \\
\times J_1(2\pi \sigma' \sqrt{1 - \left( \frac{\hat{h}}{\sigma} + z \right)^2}) \, dz
\]  

which is identical with the Nijboer and Van Hove representation of \( G(\hat{h}) \). Thus (4-30) becomes identical with (4-13).

Returning to equation (4-29), it would appear that since \( F(h) \) is a function of the magnitude \( |\hat{h}| \) only, and all of the \( I_j \)'s occur only as squares, further arguments to provide cancellation or zero contribution are not available. At this point one must confront the evaluation of the integrals themselves. Although such an evaluation appears to be lengthy and tedious, no insurmountable difficulties are readily apparent. The author personally believes that the method outlined in this section is the most promising one to date for finding an analytical solution to the complete five-point Mayer graph.
APPENDIX I: EVALUATION OF THE GRAPH C3.

We will evaluate the graph C3 by the method used to calculate E1 in section I-C, in order to show how the presence of more than one f-function may be absorbed into the integration limits. This example also serves to show how the difficulty of calculation of the graphs increases with the number of points. We begin with

\[ C3 = \int \int f_{12} f_{13} f_{23} \, d\vec{r}_2 \, d\vec{r}_3. \quad (I-1) \]

Recall that point one is fixed in space and is the origin of our coordinate system. Let point 2 be located at some arbitrary position with polar coordinates \((r, \nu, \varphi)\). Since \(f_{12} = 0\) for \(r > \sigma^\prime\), we need only consider \(r\) in the range \(0 < r < \sigma^\prime\).

Construct spheres of radius \(\sigma^\prime\) about points 1 and 2 (see Figure I-1). The product \(f_{13} f_{23}\) will be non-zero iff point 3 is located within the volume that the two spheres have in common.

Within this region, \(f_{13} f_{23} = 1\). The volume of this region is a function of \(r\) only (depending parametrically on \(\sigma^\prime\)) and may be readily calculated to be

\[ V(r) = \pi(16\sigma^3 - 12\sigma^2 r + r^3)/12. \quad (I-2) \]
Thus, after integrating over \( \vec{r}_2 \) we have

\[
C_3 = \int_{\gamma} f_{12} V(|\vec{r}_2|) \, d\vec{r}_2 .
\]  
(I-3)

We may now rewrite (I-3) in spherical polar coordinates, integrate over \( z^2 \) and \( \varphi \), and absorb \( f_{12} \) into the limits on \( r \), giving

\[
C_3 = -4\pi \int_0^\infty V(r) \, r^2 \, dr .
\]  
(I-4)

Substituting (I-2) into (I-4) and carrying out the integration gives

\[
C_3 = -(15/18)\pi^2 = -(15/8)b^2 .
\]  
(I-5)

From this we may calculate \( B_3 \) (see Table 1-1) which is

\[
B_3 = (5/8)b^2 .
\]  
(I-6)
APPENDIX II: A GENERAL PROOF FOR EQUATION (2-38).

In section II-D we expanded \( D(N)/V \) as a power series in \( \phi \), with \( A_n \) as the coefficient of \( \phi^n/n! \). Equation (2-37) gives the \( A_n \)'s in terms of the \( \gamma_m \)'s. Because the expansion for \( A_n \) is simpler in terms of the \( A_{\ell,m} \)'s, as shown in (2-38), we seek to prove this relationship in general.

The available volume, \( D(N) \), is given exactly by

\[
D(N) = V - 2Nb + \overline{V} \tag{II-1}
\]

so that \( \overline{V} \) is the total volume common to all of the exclusion spheres, averaged over all configurations. Let \( \mathcal{V}_N(\vec{r}_1, \ldots, \vec{r}_N) \) be the total common volume for a particular configuration of the \( N \) particles and \( P_N(\vec{r}_1, \ldots, \vec{r}_N) \) be the probability of that configuration, given by

\[
P_N(\vec{r}_1, \ldots, \vec{r}_N) = \exp \left[ -U(\vec{r}_1, \ldots, \vec{r}_N)/kT \right] / Q_N. \tag{II-2}
\]

Further, let \( \mathcal{L} \) be an operator which extracts the limit for \( N \) and \( V \) going to infinity at a fixed ratio, \( \rho \). Then

\[
\overline{V} = \mathcal{L} \int_v \cdots \int_v \mathcal{V}_N \cdot P_N \, d\vec{r}_1 \cdots d\vec{r}_N. \tag{II-3}
\]

Recall that \( \mathcal{G}_{\ell,1} \) is the volume common to \( \ell \) exclusion spheres and is a function of their relative positions. Then

\[
\mathcal{V}_N = \sum_{\ell=2}^{\infty} \sum_{\{n_j\}} \mathcal{G}_{\ell,1}(\{\vec{r}_j\}_\ell) \tag{II-4}
\]

where the second summation is over all distinct subsets of \( \{\vec{r}_1, \ldots, \vec{r}_N\} \) which contain exactly \( \ell \) elements. Thus we are considering the volume common to two spheres, \( \mathcal{G}_{2,1} \), for all pairs; a term \( \mathcal{G}_{3,1} \) for all
triplets; etc. Notice that when (II-4) is put into (II-3) and integrated over all $N$ particles, the contribution from every term having a given value of $\ell$ will be the same. Thus, we can choose a typical term, $G_{\ell,1}\left(\{\bar{r}_j\}_\ell\right)$, weighted with $\binom{N}{\ell}$, the number of $\ell$-order subsets of $\{\bar{r}_1, \ldots, \bar{r}_N\}$. The typical term we will choose will be the canonical form we have been using, namely the one in which the fixed points are labeled $1, 2, \ldots, \ell$. Thus we have

$$\bar{U} = \mathcal{L} \int \cdots \int \sum_{\ell=2}^N \binom{N}{\ell} G_{\ell,1} \, P_N \, d\bar{r}_1 \cdots d\bar{r}_N \quad . \quad (II-5)$$

Uhlenbeck and Ford (24) define the $\ell$-particle distribution function, $\bar{n}_\ell$, by

$$\bar{n}_\ell = \mathcal{L} \frac{N!}{(N-\ell)!} \int \cdots \int P_N \, d\bar{r}_{\ell+1} \cdots d\bar{r}_N \quad , \quad (II-6)$$

which we use to obtain

$$\bar{U} = \sum_{\ell=2}^\infty \int \cdots \int \frac{1}{\ell!} G_{\ell,1} \, \bar{n}_\ell \, d\bar{r}_1 \cdots d\bar{r}_\ell \quad . \quad (II-7)$$

They expand $\bar{n}_\ell$ as a power series in $\rho$, which in our notation becomes

$$\bar{n}_\ell = \rho^{\mathcal{W}_\ell} \sum_{m=0}^{\infty} G_{\ell,m} \rho^m / m! \quad . \quad (II-8)$$

Using this result in (II-7) gives

$$\bar{U} = \sum_{\ell=2}^\infty \sum_{m=0}^{\infty} \int \cdots \int \mathcal{W}_\ell \, G_{\ell,1} \, G_{\ell,m} \rho^{\ell+m} / \ell! m! \, d\bar{r}_1 \cdots d\bar{r}_\ell \quad . \quad (II-9)$$

From the definition of $A_{\ell,m}$ in (2-34) we have

$$\bar{U} = V \sum_{\ell=2}^\infty \sum_{m=0}^{\infty} A_{\ell,m} \rho^{\ell+m} / \ell! m! \quad . \quad (II-10)$$

(75)
Letting $n = \ell + m$ and eliminating $\ell$ gives

$$\overline{V} = V \sum_{\ell=0}^{\infty} \sum_{m=0}^{\ell} \binom{n}{m} A_{n-m,m} \rho^{n}/n!.$$  \hspace{1cm} (II-11)

Putting this result into (II-1), dividing by $V$, and recalling that $A_0 = 1$ and $A_1 = -2b$, we have

$$D(N)/V = \sum_{n>0}^{\infty} A_n \rho^{n}/n!$$  \hspace{1cm} (II-12)

where

$$A_n = \sum_{m=0}^{n-2} \binom{n}{m} A_{n-m,m} \hspace{1cm} \text{(for } n > 2\text{)}. \hspace{1cm} (II-13)$$

This last result is identical to (2-38) which is the relationship we wished to prove in general.
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