EVALUATION OF MAYER CLUSTER INTEGRALS FOR THREE-BODY INTERACTIONS AND SELECTED TOPICS IN NUMERICAL INTEGRATION OF TRIPLE INTEGRALS

by

Hugh Allan Reeder

Bachelor of Arts

Rice University

Houston, Texas

1960

Submitted to the faculty of the Graduate College of
the Oklahoma State University
in partial fulfillment of the requirements
for the degree of
MASTER OF SCIENCE
MAY, 1968

EVALUATION OF MAYER CLUSTER INTEGRALS FOR THREE-BODY INTERACTIONS AND SELECTED TOPICS IN NUMERICAL INTEGRATION OF TRIPLE INTEGRALS

Francis C. Todd
Thesis Adviser

E. K. McLachlan

N Durham
Dean of the Graduate College

PREFACE

When I was introduced to this problem by Dr. R. G. McIntyre, I found the cluster integral method most confusing. I have written the second chapter in this report in hopes of clarifying this method for someone else. The fifth chapter concerning numerical methods of triple integration should be of most interest to the mathematician. Although the formulae derived will be useful to the physicist when doing problems similar to the one discussed in this report.

It was not possible for me to attempt this project on my own. I am indebted to Dr. R. G. McIntyre for the introduction to this problem and for his patient guidance in the research, to Dr. F. C. Todd, the project director, for his continued encouragement, helpful suggestions, and the assumption of the chairmanship of my committee, and to Dr. Rufus Bruce whose dissertation proposed this problem and whose private communications proved very useful.

On the nonscholastic side, I should like to express my appreciation to my wife, Karen, for her patience, and to her mother, Mrs. Jim P. Wilkirson, and her father, Mr. Charles Walters, for their encouragement and financial aid in finishing my master's degree.

TABLE OF CONTENTS

Page

LIST OF TABLES

LIST OF FIGURES

CHAPTER I

INTRODUCTION

When a small hypervelocity particle strikes a stationary, plane, metallic target at normal incidence, several interesting phenomena are observed (3). A brief, but very intense, flash of light occurs in the first microsecond after impact. A hemispherical crater is formed about the center of impact which is many times larger than the projectile, and a small curled lip may be present about the crater. Ultra-highspeed photographs during crater formation reveal that a fine spray of material emanates from the circumferential region of the incipient crater. These phenomena are very different from subsonic velocity impact of a projectile which leaves a long, deep hole in the target which is only slightly larger than the projectile itself.

Such high speed projectiles occur naturally in the region above the earth's atmosphere and are given the name, micrometeroids.

Project NASr-7 responsible for the support of the research reported in this thesis began as an analytical study of micrometeoroid impact phenomena with particular interest on aluminum as a target material. Various theses have been written on the subject by Lake, Sodek, Wang, and Bruce. The particular concern of this report is an extension of one part of the work of Bruce (2).

There are several ways, involving various approximations, to obtain an equation of state during the time that a plasma is produced by hypervelocity impact. Bruce (2) discusses and compares different methods. One of the methods involves Mayer cluster integrals to calculate Helmholtz free energy of the system. From this, the thermodynamical properties of the system may be calculated. Bruce (2) used only two-body interactions for his work and obtained good results for some regions.

In order to extend his results, the present study was undertaken to include the three-body interaction terms to Mayer's cluster integral expansion of the Helmholtz free energy. As a preliminary study and to avoid the large number of ion species inherent with aluminum, the results for hydrogen were obtained in order to judge the order of magnitude of the correction. The values for the Mayer cluster integrals, which are associated with the three-body interactions, were applied to the calculation of the electron density as carried out by Bruce (2). The results are given in Chapter IV.

The cluster integral method is discussed in a simplified form and then generalized. The evaluation of the cluster integrals is discussed and the results applied to the calculation of the electron density in a hydrogen plasma. A general discussion of methods of numerical integration of triple integrals is given.

CHAPTER II

MAYER CLUSTER EXPANSION OF FREE ENERGY

In order to understand the general case better, a development of the Mayer cluster expansion of the free energy is developed for the case of a nonideal, monatomic gas. This will bring out most of the problems that are encountered in the classical many-body problem. The method of arriving at the expression for the free energy is from Brout (1).

Basic Equations

If one can find the free energy of a system, all thermodynamic quantities may then be calculated. The free energy is related to the partition function in a classical, canonical ensemble by the equation

$$F = -kT \log Z \tag{2-1}$$

where F is the free energy, k is Boltzmann's constant and T is the absolute temperature.

$$Z = \frac{1}{N!\,h^{3N}} \int dp\, dq \quad \mathrm{EXP}[-H(p,q)/kT] \tag{2-2}$$

for an N-particle system, h is Plank's constant and H(p, q) is the Hamiltonian. In H(p, q), p represents the 3N momenta components and q the 3N spatial coordinates, $\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N$. In equation 2-2,

$$dp = \prod_{j=1}^{N} d^3 p_j \qquad \text{and} \qquad dq = \prod_{j=1}^{N} d^3 \vec{r}_j \ .$$

Assuming that all particles have the same mass, and an ideal gas

$$H = \sum_{i=1}^{N} \frac{p_i^2}{2m}$$

i.e., there is no interaction between particles. Then

$$Z_{IDEAL} = \frac{1}{N!\,h^{3N}} \int dp\, dq \;\; EXP\left[-\sum_{i=1}^{N} \frac{p_i^2}{2mkT}\right] \ .$$

Carrying out the integration over the 3N spatial coordinates $\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N$,

$$Z_{IDEAL} = \frac{\Omega^N}{N!\,h^{3N}} \int dp \;\; EXP\left[-\sum_{i=1}^{N} \frac{p_i^2}{2mkT}\right]$$

where Ω is the volume of the system. Now the momentum is assumed to take on all values from $-\infty$ to $+\infty$

$$Z_{IDEAL} = \frac{\Omega^N}{N!\,h^{3N}} \prod_{i=1}^{N} \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} EXP\left[-\frac{(p_{x_i}^2 + p_{y_i}^2 + p_{z_i}^2)}{2mkT}\right] dp_{x_i}\, dp_{y_i}\, dp_{z_i}$$

since the momentum of each particle is independent of the others.

Now

$$\int_{-\infty}^{\infty} EXP\left[-\frac{p_{x_i}^2}{2mkT}\right] dp_{x_i} = \sqrt{2\pi mkT}\left(\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} EXP\left[-\frac{u^2}{2}\right] du\right)$$

where $\quad u = p_{x_i} / \sqrt{mkT} \quad ,$

The integral and the constant in parentheses is the normal distribution function over its range and, hence, must equal to 1.

Then

$$Z_{IDEAL} = \frac{\Omega^N}{N!\,h^{3N}} \prod_{i=1}^{N} (2\pi mkT)^{3/2} \ ,$$

Let $\quad \lambda = \dfrac{h}{(2\pi mkT)^{1/2}}$

$$Z_{IDEAL} = \frac{\Omega^N}{N!\,\lambda^{3N}} \ , \tag{2-3}$$

Where Ω is assumed to be of macroscopic dimensions and λ is the mean thermal, de Broglie wavelength.

Assuming that the potential energy, V, does not depend on the velocity of the particle, the kinetic energy in the Hamiltonian may be separated from the potential energy in (2-2).

$$Z = \frac{1}{N!h^{3N}} \int dp\, dq\, \mathrm{EXP}\left(-\sum_{i=1}^{N} \frac{p_i^2}{2mkT} - \frac{1}{kT} V(q)\right)$$
$$= \frac{Z_{IDEAL}}{\Omega^N} \int d\vec{r}_1\, d\vec{r}_2 \cdots d\vec{r}_N \quad \mathrm{EXP}(-V(q)/kT)$$

Note that $\frac{1}{\Omega^N}$ is non-negative and $\int \frac{1}{\Omega^N}\, d\vec{r}_1\, dr_2 \cdots dr_N = 1$.

Then, $\frac{1}{\Omega^N}$ is a uniform distribution function and Z may be expressed as an expected value

$$Z = Z_{IDEAL}\; E\,(\mathrm{EXP}[-V/kT]) \tag{2-4}$$

where E denotes the expected value.

Expansion of Free Energy

The free energy, ΔF, from the interactions between particles assumed a particularly simple form

$$\begin{aligned} \Delta F &= F - F_{IDEAL} \\ &= -\frac{1}{kT}\,(\log Z - \log Z_{IDEAL}) \\ &= -\frac{1}{kT}\,\log E\,(\mathrm{EXP}[-\tfrac{V}{kT}])\;. \end{aligned} \tag{2-5}$$

In this discussion, the principal of supposition is assumed; hence, the potential is the sum of pair interactions. If $V_{ij} = v(\vec{r}_i - \vec{r}_j)$ where $\vec{r}_i$ is the position of the i-th particle, then

$$V = \sum_{1 \le i < j < N} v_{ij} = \frac{1}{2} \sum_{i \neq j} V_{ij} \, . \tag{2-6}$$

Note that there are N(N-1)/2 terms in this sum.

The expression 2-5 is related to cumulants in statistical theory.

$$m(t) = E(e^{tx}) = \sum_{n=0}^{\infty} \frac{t^n \, E(x^n)}{n!} \tag{2-7}$$

is a moment generating function. In our equation $t = -\frac{1}{kT}$ and x is V. The cumulants of a distribution is given by log m(t) and it is this expression that is of interest in this discussion.

By expanding the logarithm by a Taylor series about t = 1 and substituting in the series for the moment generating function, the following series is derived

$$\log E(\exp[tx]) = \sum_{n=1}^{\infty} \frac{t^n M_n}{n!} \, . \tag{2-8}$$

The coefficients M_n are called cumulants. The first four are

$$M_1 = E(x) \tag{2-9}$$

$$M_2 = E(x^2) - (E(x))^2 \tag{2-10}$$

$$M_3 = E(x^3) - 3\,E(x^2)\,E(x) + 2(E(x))^2 \tag{2-11}$$

$$M_4 = E(x^4) - 4\,E(x^3)\,E(x) + 3(E(x^2))^2 + 12\,E(x^2)(E(x))^2 + 6(E(x))^4 \, . \tag{2-12}$$

Equation 2-5 becomes

$$\Delta F = -\frac{1}{kT} \sum_{n=1}^{\infty} \frac{\left(-\frac{1}{kT}\right)^n}{n!} M_n \, . \tag{2-13}$$

It would be more convenient to have the above equation in terms of the density, p = N/Ω. To convert the series, consider first

$$M_1 = E(v) = \frac{1}{\Omega^N} \int d\vec{r}_1 \, d\vec{r}_2 \cdots d\vec{r}_N \left(\sum_{i<j} v_{ij} \right), \tag{2-14}$$

Now each term in the sum gives the same contribution by the assumptions about potential energy

$$M_1 = \binom{N}{2} \frac{1}{\Omega^N} \int d\vec{r}_1 \, d\vec{r}_2 \cdots d\vec{r}_N \; v_{ij} ,$$

Without loss of generality, let $v_{ij} = v_{12} = v(\vec{r}_1 - \vec{r}_2)$. Since v_{12} is independent of $\vec{r}_3, \vec{r}_4, \cdots \vec{r}_N$, integration may be carried out over these 3(N-2) variables to yield

$$M_1 = \binom{N}{2} \frac{1}{\Omega^2} \int d\vec{r}_1 \, d\vec{r}_2 \; v(\vec{r}_{12}) .$$

For large N, $\binom{N}{2} = \frac{(N-1)N}{2} \approx \frac{N^2}{2}$.

Let $\vec{r} = \vec{r}_1 - \vec{r}_2$; $\vec{R} = \frac{1}{2} (\vec{r}_1 + \vec{r}_2)$.

The Jacobian of this transformation is

$$J = \frac{\partial(\vec{r}, \vec{R})}{\partial(\vec{r}_1, \vec{r}_2)} = \begin{vmatrix} 1 & 0 & 0 & \frac{1}{2} & 0 & 0 \\ 0 & 1 & 0 & 0 & \frac{1}{2} & 0 \\ 0 & 0 & 1 & 0 & 0 & \frac{1}{2} \\ -1 & 0 & 0 & \frac{1}{2} & 0 & 0 \\ 0 & -1 & 0 & 0 & \frac{1}{2} & 0 \\ 0 & 0 & -1 & 0 & 0 & \frac{1}{2} \end{vmatrix} = 1 .$$

$$M_1 = \frac{N^2}{2} \frac{1}{\Omega^2} \int v(\vec{r}) \, d\vec{r} \, d\vec{R}$$

Integrating over $\vec{R}$

$$M_1 = \frac{N^2}{2} \frac{1}{\Omega} \int v(\vec{r}) \, d\vec{r}$$

or

$$\frac{M_1}{N} = \frac{\rho}{2} \int v(\vec{r}) \, d\vec{r} . \tag{2-15}$$

Evaluation of M_2

For M_2 the procedure is somewhat more complicated.

$$M_2 = E(v^2) - (E(v))^2$$
$$M_2 = \sum_{i<j,\, k<l} \left(E(v_{ij} v_{kl}) - E(v_{ij}) E(v_{kl}) \right)$$

It is convenient to classify the terms in the above sum as to the indices that they have in common.

$E(v_{12}v_{34})$ (a) Unlinked $E(v_{12}v_{23})$ (b) Reducible $E(v_{12}^2)$ (c) Irreducible

Figure 1. Classes contributing to M_2.

Figure 1 gives the cluster graphs of configurations arising in the sum for M_2. The dots represent particles and the lines are bonds of interactions between particles.

In Figure 1(a), there are no indices in common. This implies that $\vec{r}_{12}$ and $\vec{r}_{34}$ can be varied independently of one another. Hence, v_{12} and v_{34} are, in essence, statistically independent and

$$E(v_{12} v_{34}) = E(v_{12}) E(v_{34})$$

(10). Therefore, considering indices of this type in the sum for M_2

$$E(v_{12} v_{34}) - E(v_{12}) E(v_{34}) = 0$$

and there is no contribution to M_2 by unlinked terms.

For the reducible terms, an example is $E(v_{12}\, v_{23})$. Since the medium is homogenous, choose $\vec{r}_2$ as the origin and integrate over $\vec{r}_1$ and $\vec{r}_3$.

$$E(v_{12}\; v_{23}) = \frac{1}{\Omega^N}\int v_{12}\, v_{23}\; d\vec{r}_1\; d\vec{r}_2 \cdots d\vec{r}_N$$

$$= \frac{1}{\Omega^N}\int v_{12}\, v_{23}\; d\vec{r}_1\; d\vec{r}_2\; d\vec{r}_3$$

Let $\vec{r}_{12} = \vec{r}_1 - \vec{r}_2$, $\vec{r}_{23} = \vec{r}_2 - \vec{r}_3$, $\vec{r}_2 = \vec{r}_2$,

then $|J| = 1$.

$$E(v_{12}\, v_{23}) = \frac{1}{\Omega^3}\int v_{12}\, v_{23}\; d\vec{r}_{12}\; d\vec{r}_{23}\; d\vec{r}_2$$

$$= \frac{1}{\Omega^2}\left(\int v_{12}\; dr_{12}\right)\left(\int v_{23}\; d\vec{r}_{23}\right)$$

$$E(v_{12}\, v_{23}) = E(v_{12})\; E(v_{23})$$

This last equation implies that the reducibly linked terms will contribute nothing to the sum of M_2.

The last case is given by $E(v_{12}^{\,2})$. No reduction is possible in this expected value, and

$$M_2 = \sum_{i<j}\left[E(v_{ij}^{\,2}) - (E(v_{ij}))^2\right]. \qquad (2\text{-}16)$$

If one compares the order of magnitude of the two types of terms in M_2.

$$E(v_{ij}^{\,2}) = \frac{1}{\Omega}\int v_{ij}^{\,2}\; d\vec{r}_{ij} = O\left(\frac{1}{N}\right)$$

$$(E(v_{ij}))^2 = \left(\frac{1}{\Omega}\int v_{ij}\; d\vec{r}_{ij}\right)^2 = O\left(\frac{1}{N^2}\right)$$

Hence, in equation 2-16, only the first term need be included. Again there are N(N-1)/2 identical contributions.

$$M_2 = \frac{N(N-1)}{2}\;\frac{1}{\Omega}\int v_{12}^{\,2}\; d\vec{r}_{12}$$

$$\lim_{\substack{N,\Omega \to \\ N/\Omega = \rho}} = \frac{1}{2} \rho \int v_{12}^{2} \, d\vec{r}_{12}$$

Evaluation of M_3

To carry out the analysis of higher order cumulants, it is convenient to expand on the graphs already introduced for M_2. The graph of the expectation corresponding to $E(v_{ij} v_{kl} \ldots v_{yz})$ is constructed by first drawing a vertex, or point, for each particle listed as a subscript and then drawing a bond, or line, between the pairs of subscripts. To generalize the terms that have already been used, an unlinked graph is two or more pieces which are not joined by any bond. A graph is reducibly linked, if it can be divided into two connected pieces by cutting the graph at one vertex. All remaining graphs are said to be irreducible.

The next term in the series contains

$$M_3 = \sum_{\substack{i<j,\, k<l \\ m<n}} \Big(E(v_{ij} v_{kl} v_{mn}) - 3\, E(v_{ij} v_{kl}) E(v_{mn}) + 2\, E(v_{ij})\, E(v_{kl})\, E(v_{mn}) \Big)$$

The various difficulties of higher cumulants mostly occur in M_3, hence it is analyzed in detail

(a) (b) (c)

Figure 2. Unlinked Terms in M_3

An example of Figure 2(a) is $E(v_{12}\ v_{34}\ v_{56})$. Since

V_{12} , V_{34} , V_{56} have no indices in common, they are statistically independent and

$$E(V_{12} V_{34} V_{56}) = E(V_{12}) E(V_{34}) E(V_{56}) .$$

Accordingly, the sum

$$E(V_{12} V_{34} V_{56}) - 3E(V_{12} V_{34}) E(V_{56}) + 2E(V_{12}) E(V_{34}) E(V_{56}) = 0$$

and there is no contribution to the sum for this type of graph.

An example of Figure 2(b) is $E(V_{12} V_{23} V_{45})$. Since V_{45} is independent of the other terms,

$$E(V_{12} V_{23} V_{45}) = E(V_{12} V_{23}) E(V_{45})$$

By the same type arrangement as before $E(V_{12} V_{23}) = E(V_{12}) E(V_{23})$ and there will be no contribution to the sum for this type of graph.

For Figure 2(c), consider $E(V_{12}^2 V_{34}) = E(V_{12}^2) E(V_{34})$. The term $E(V_{12}^2 V_{34}) - 3E(V_{12}^2) E(V_{34}) + 2(E(V_{12}))^2 E(V_{34})$ does not equal to zero; but, these subscripts can occur in three different ways.

V_{12} V_{12} V_{34} as above,

V_{12} V_{34} V_{12} and

V_{34} V_{12} V_{12}

considering the total sum of these

$$\begin{aligned} &E(V_{12}^2 V_{34}) - 3E(V_{12}^2) E(V_{34}) + 2(E(V_{12})^2 E(V_{34}) + E(V_{12} V_{34} V_{12}) \\ &- 3E(V_{12} V_{34}) E(V_{12}) + 2(E(V_{12}))^2 E(V_{34}) + E(V_{34} V_{12}^2) - 3E(V_{34} V_{12}) E(V_{12}) \\ &+ 2(E(V_{12}))^2 E(V_{34}) = 3E(V_{12}^2) E(V_{34}) - 3(E(V_{12}^2) E(V_{34})) \\ &\qquad - 6(E(V_{12}))^2 E(V_{34}) + 6(E(V_{12}))^2 E(V_{34}) \\ &\qquad = 0 . \end{aligned}$$

Accordingly, there is no contribution for this type of graph.

(a) (b) (c)

Figure 3. Reducible graphs of M_3.

Consider the case for Figure 3(a).

$$E(V_{12}\, V_{23}\, V_{34}) = \frac{1}{\Omega^N}\int V_{12}\, V_{23}\, V_{34} \prod_{i=1}^{N} d\vec{r}_i$$

$$= \frac{1}{\Omega^4}\int V_{12}\, V_{23}\, V_{34} \prod_{i=1}^{4} d\vec{r}_i$$

$$\vec{r}_{12} = \vec{r}_1 - \vec{r}_2,\ \vec{r}_{23} = \vec{r}_2 - \vec{r}_3,\ \vec{r}_{34} = \vec{r}_3 - \vec{r}_4 = \vec{r}_2 - \vec{r}_{23} - \vec{r}_4$$

The absolute value of the Jacobian is 1. After integrating over $\vec{r}_2$,

$$E(V_{12}\, V_{23}\, V_{34}) = \frac{1}{\Omega^3}\left(\int V_{12}\, d\vec{r}_{12}\right)\left(\int V_{23}\, d\vec{r}_{23}\right)\left(\int V_{34}\, d\vec{r}_{34}\right)$$

$$= E(V_{12})\ E(V_{23})\ E(V_{34})$$

Similarly, for Figure 3(c) $E(V_{12}\, V_{32}\, V_{42}) = E(V_{12})\, E(V_{32})\, E(V_{42})$. Accordingly, there is no contribution to the sum from these terms.

In Figure 3(b), $E(V_{12}^2\, V_{23})$ will, upon passing to relative coordinates, become $E(V_{12}^2)\, E(V_{23})$. By considering, as with Figure 2(c), the three possible ways these subscripts arise, the contribution will be zero.

(a) (b)

Figure 4. Irreducible graphs of M_3.

The two remaining possible graphs are illustrated in Figure 4. Again by an order of magnitude argument, the terms in the sum, other than the first, have at least one more expectation value and, hence, are of an order 1/N times the leading term. Thus in the limit, as $N \to \infty$, only the irreducible clusters in the first term give a contribution to M_3/N.

Now there are N(N-1)/2 identical contributions of the type in Figure 4(a) and N(N-1)(N-2) of the type Figure 4(b); hence

$$\frac{M_3}{N} = \frac{N-1}{2\Omega} \int V^3(\vec{r})\, d\vec{r} + \frac{(N-1)(N-2)}{\Omega^2} \int V_{12} V_{23} V_{31}\, d\vec{r}_{12}\, d\vec{r}_{23}$$

$$\lim_{\substack{N,\Omega \to \infty \\ N/\Omega = \rho}} \frac{M_3}{N} = \frac{1}{2}\rho \int V^3(\vec{r})\, d\vec{r} + \rho^2 \int V_{12} V_{23} V_{31}\, d\vec{r}_{12}\, d\vec{r}_{23} \,, \qquad (2\text{-}17)$$

To summarize this discussion, the unlinked and reducibly linked graphs drop out of the sum for M_2 and M_3. The irreducible cluster integrals are the only important contributing factors to the sum. This may be generalized and, for higher order cumulants, only the irreducible clusters considered. This becomes plausible when it is realized that graphs of unlinked and irreducibly linked graphs represent essentially statistically independent variables and that terms, other than the leading irreducible terms, are at least an order of 1/N less (1).

From these considerations, the contributions to M_n consist of all, irreducibly linked diagrams which contain n bond among ν vertices, where $2 \leq \nu \leq n$. This combinatorial factor, that gives the number of ways that a given graph appears in sums over the indices, is $\binom{N}{\nu}$ times the number of diagrams which contain these ν particles in a particular topological arrangement. A further discussion of topological structure of the graph will be given below.

Expansion of Free Energy in Terms of Density

In converting equation 2-13 from powers of - 1/kT to density, a number of irreducible graphs contribute to M_n in each term of the sum. An irreducible graph of ν vertices has a factor of N^{ν} and all but $\nu - 1$ coordinates can be integrated, leaving a factor $\Omega^{-\nu+1}$. In the sum of $\Delta F/N$, a graph of ν vertices has a density dependence of $\frac{N^{\nu-1}}{\Omega^{\nu-1}} = \rho^{\nu-1}$. Examples of this are equation 2-15 and 2-17.

As a consequence, graphs which are classified according to vertices, correspond to powers of density; a classification according to bonds corresponds to expansion in terms of (- 1/kT). By summing over all graphs that have a given number of vertices, equation 2-13 can be converted into a power series in density. Figure 5 will serve to clarify these ideas. If the contributions of the graphs of column 1 are summed, it will give the coefficient of ρ; column 2 will give the ρ^2 terms, etc. This process gives the series

$$-\frac{1}{kT}\,\frac{\Delta F}{N} = \sum_{\nu=1}^{\infty} \frac{\beta_\nu \rho^\nu}{\nu+1} \tag{2-18}$$

as $N \to \infty$. The notation, to be defined below, is chosen to agree with Mayer's definition of "irreducible cluster integral" β_n(9)

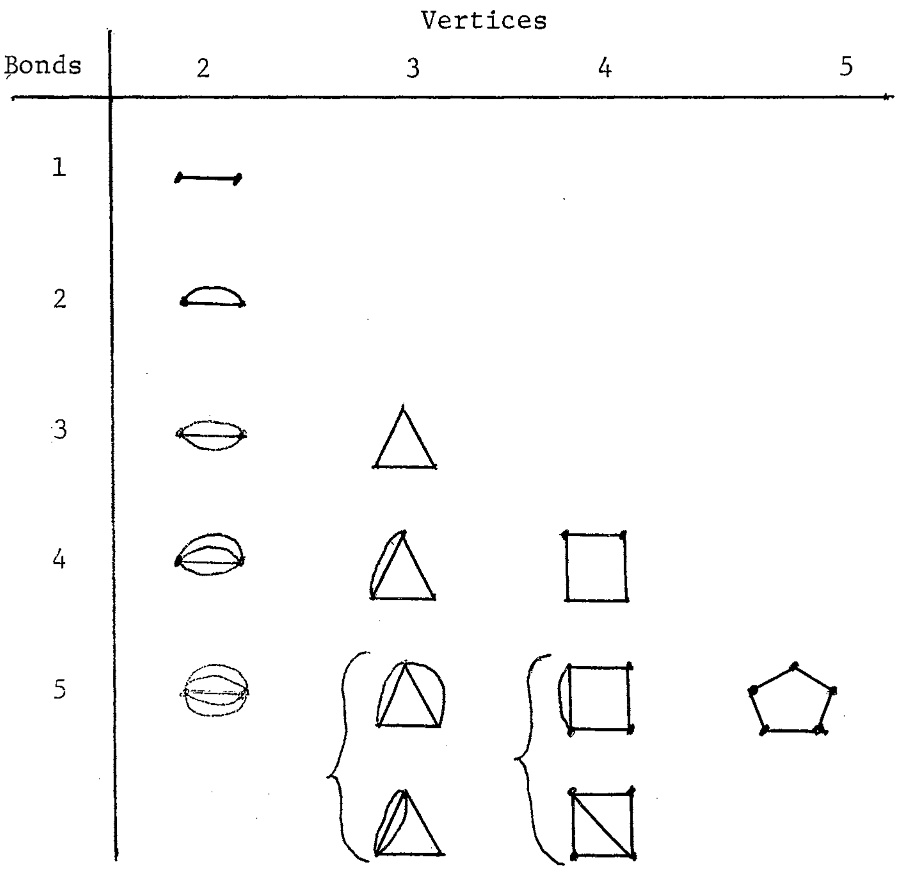

Figure 5. Classification of irreducible graphs according to bonds and vertices.

Consider the contribution of the graph in the first column of Figure 5 in the equation $-\frac{\Delta F}{kT} = \log Z$.

$$\frac{N}{2}\rho\sum_{n\geq 1}^{\infty}\frac{\left(-\frac{1}{kT}\right)^{n}}{n!}\int V^{n}(\vec{r})\,d\vec{r} = \frac{N}{2}\rho\int(e^{-\beta V}-1)\,d\vec{r}$$

The quantity $\beta_1 \equiv \int(e^{-\beta V}-1)\,d\vec{r}$

is the negative of the second virial coefficient in the expansion

$$\frac{pV}{NkT} = 1 + B_2\rho + B_3\rho^2 + \cdots \quad .$$

In general, the virial coefficient B_n is related to the irreducible cluster integral β_{n-1} by

$$B_n = -\frac{n-1}{n}\beta_{n-1} \qquad (1).$$

In summing the second column of Figure 5, the combinatorial problem is more complicated. Let the vertices be labeled 1, 2, 3 and the bonds (12), (23), and (31). The problem is to find how many graphs contribute to M_n such that there are l_{12} bonds of type (12), l_{23} of type (23) and l_{31} of type (31). There are $\binom{N}{3}$ ways of choosing three vertices out of N distinguishable vertices. The possible ordering of the factors $V_{12}^{l_{12}}\,V_{23}^{l_{23}}\,V_{31}^{l_{31}}$ which arise in $E\,(V^{l_{12}+l_{23}+l_{31}})$ must be taken into consideration. Since $l_{12} + l_{23} + l_{31} = n$ this is the number of arrangements of n things into three classes which is the multinomial coefficient

$$\frac{n!}{l_{12}!\,l_{23}!\,l_{31}!}$$

Consider Equation 2-13 for only those graphs with three vertices

$$\sum_{n=1}^{\infty}\frac{\left(-\frac{1}{kT}\right)^n}{n!}M_n \text{ (part from three irreducibly linked vertices)}$$

$$= \binom{N}{3}\sum_{n=3}^{\infty}\sum_{\substack{l_{12},l_{23},l_{31}=1\\ l_{12}+l_{23}\,l_{31}=n}}^{\infty}\left(-\frac{1}{kT}\right)^n\frac{1}{n!}\,\frac{n!}{l_{12}!\,l_{23}!\,l_{31}!}\,E(V_{12}^{\;l_{12}}V_{23}^{\;l_{23}}V_{31}^{\;l_{31}})$$

$$= \frac{N^3}{3!}E\left[\left(\sum_{l_{12}=1}^{\infty}\frac{\left(-\frac{V_{12}}{kT}\right)^{l_{12}}}{l_{12}!}\right)\left(\sum_{l_{23}=1}^{\infty}\frac{\left(-\frac{V_{23}}{kT}\right)^{l_{23}}}{l_{23}!}\right)\left(\sum_{l_{31}=1}^{\infty}\frac{\left(-\frac{V_{31}}{kT}\right)^{l_{31}}}{l_{31}!}\right)\right]$$

$$= \frac{N\rho^2}{3!}\int\left(e^{-\frac{V_{12}}{kT}}-1\right)\left(e^{-\frac{V_{23}}{kT}}-1\right)\left(e^{-\frac{V_{31}}{kT}}-1\right)dr_{12}\,dr_{23}$$

$$\equiv \frac{1}{3}N\rho^2\beta_2\,. \qquad (2\text{-}19)$$

The last equation defines β_2.

The summation of columns of Figure 5 may be continued. The coefficient of $\frac{\rho^{\nu-1}}{\nu+1}$ in the sum for $\frac{\log Z}{N}$ will be the sum of all reducible diagrams with ν vertices. Now each set of diagrams must further be divided into classes in which only certain bond types are permitted. To illustrate this, consider the case of four vertices. Figure 6 gives six possible arrangements of bonds among four vertices. Figures 6(a) and 6(d) are of the same bond type, the open square. Figures 6(b), 6(e), and 6(f) are of the same one diagonal bond type. Finally, Figure 6(c) has both diagonal bonds. The Figures 6(a), 6(b), and 6(c) determine the basic topologically distinct subsets of graphs for the four-vertex case.

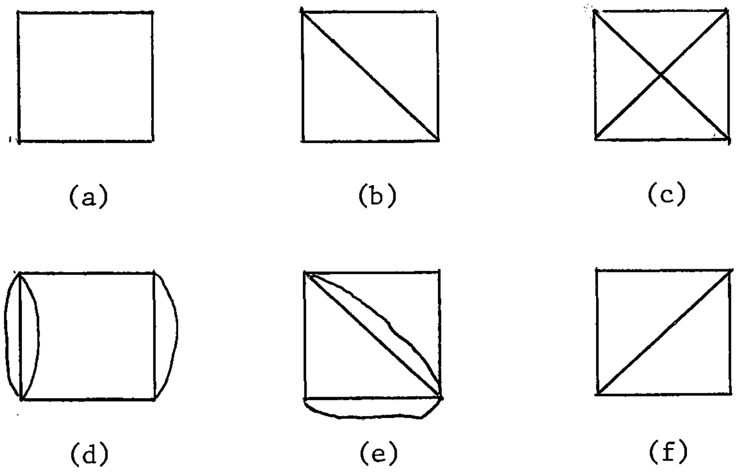

Figure 6. Various types of four-vertex diagrams.

To obtain the coefficient of ρ^3, sum over all possible distributions of bonds of a given subset and then over all subsets. Let (ij) label a bond type. Then a diagram with ν vertices and l_{ij} bonds of type ij contribute a factor to M_n of

$$\frac{N^{\nu}}{\nu!}\,\frac{n!}{\prod l_{ij}!}\;E\left(\prod v_{ij}^{\,l_{ij}}\right) \tag{2-20}$$

where

$$\sum_{1\le i<j\le n} l_{ij} = n \qquad \nu \le n \; .$$

If the summation is carried over all diagrams of this subset, it becomes

$$N\frac{1}{\nu!}\rho^{\nu-1}\int \underset{\substack{\text{Bonds in the}\\ \text{given subset}}}{\prod}\left(e^{-\frac{V_{ij}}{kT}}-1\right)\,d\vec{r}_1\,d\vec{r}_2\cdots d\vec{r}_{\nu-1} \tag{2-21}$$

by steps similar to those in equation 2-19.

The next step is to sum over the subsets of a fixed ν .

$$\frac{N\rho^{\nu-1}}{\nu!}\sum\int\prod\left(e^{-\frac{V_{ij}}{kT}}-1\right)d\vec{r}_1\,d\vec{r}_2\cdots d\vec{r}_{\nu-1}$$

$$\equiv N\rho^{\nu-1}\beta_{\nu-1}/\nu \tag{2-22}$$

where the summation is over all topologically distinct diagrams among ν vertices. The identity defines the irreducible cluster integral $\beta_{\nu-1}$. It is necessary to include the phrase "topologically distinct" because, through the combinatorial factor in equation 2-20, the orderings of $\nu_{12}\;\nu_{23}\;\nu_{34}\;\nu_{41}$ have been included but not the type of $V_{12} V_{23} V_{34} V_{41}$ bonds. The final results may be expressed as

$$\left(-\frac{1}{kT}\right) \lim_{\substack{\Omega, N \to \infty \\ \frac{N}{\Omega} = \rho}} \frac{1}{N} \log\left(\frac{Z}{Z_{IDEAL}}\right) = \sum_{\nu=1}^{\infty} \frac{\beta_\nu \rho^\nu}{\nu+1} \, . \qquad (2\text{-}23)$$

Perhaps a further explanation of the subsets of graphs of a particular set of vertices is in order. Let the graph with only single bonds among ν vertices be defined as a "skeleton" graph. Let every bond, v_{ij}, of a skeleton be replaced by

$$f_{ij} \equiv EXP(-V_{ij}/kT - 1) \, , \qquad (2\text{-}24)$$

The contribution of an entire subset is the same as that of the skeleton of the subset; but, each skeleton can occur in several topologically distinct ways. As a consequence, the integral representing the contribution of a skeleton must be weighed with the number of ways that it may occur. To illustrate this, again consider the four-vertex case. The graphs of 6(a), 6(b), and 6(c) can occur in 3, 6, and 1 ways respectively. Hence, β_3 is given by

$$\beta_3 = \frac{1}{3!} \int (3 f_{12} f_{23} f_{34} f_{41} + 6 f_{12} f_{23} f_{34} f_{41} f_{13} + f_{12} f_{23} f_{34} f_{41} f_{13} f_{24}) \, d\vec{r}_2 \, d\vec{r}_3 \, d\vec{r}_4 \, .$$

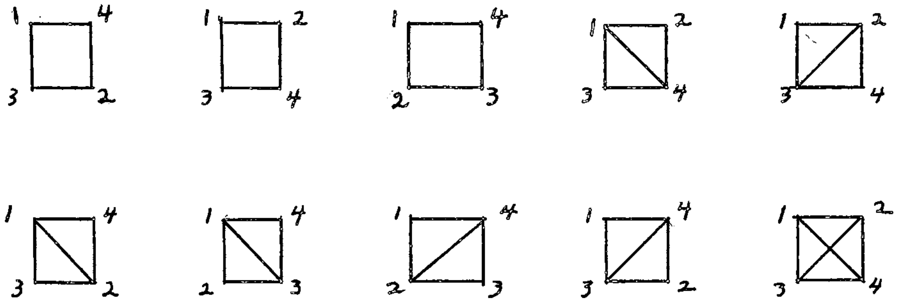

Figure 7. Skeleton graphs of four-vertex case with all possible different labelling.

The formal solution of the problem of a dilute, nonideal, classical gas is completed by the derivation of the Mayer cluster integral expansion since all thermodynamical quantities may be derived from the expression for the free energy of the system. The coefficient of the ν^{th} power of density is given by $\beta_\nu / \nu+1$ where β_ν is the irreducible cluster integral.

CHAPTER III

ANALYSIS OF CLUSTER INTEGRALS WITH COULOMB INTERACTIONS

The derivation of an expression for the free energy of a system in terms of cluster integrals and number density for systems of more than one ionic type is carried out in detail by Friedman (4).

Notation and Definitions

By establishing a rather complex notation for classifying sets of ionic types and bonds, the equations assume a simple form which is closely related to those that were derived in the previous chapter for a monotonic nonideal gas

$$-\frac{\Delta F}{VkT} = \mathcal{S} = \sum_{n=2}^{\infty} c^n B_n \qquad (3\text{-}1)$$

where $c_n = c_1^{n_1} c_2^{n_2} \cdots c_\sigma^{n_\sigma}$

V = volume

is the product of number densities of σ different species. The n_i are the number of the i^{th} species in the graph.

$$B_n = \frac{1}{VK}\int_V S_K \, d\{K\} \qquad (3\text{-}2)$$

is the cluster integral corresponding to a configuration. The rules of writing S_K will be given below. K is the configuration graph over which the integration is performed. For a coulomb potential, Friedman (4) finds that the cluster function of two particles is

$$f_{ij}(r_{ij}) = \mathrm{EXP}\left(-u_{ij}^{*}/kT - z_{ij}\lambda\ g(r_{ij})\right] - 1 \qquad (3\text{-}3)$$

where $\lambda = 4\pi\epsilon^{2}/kT$

is the coulomb length. The short range potential between the i^{th} and j^{th} particles is given by u_{ij}^{*}, and the distance dependence of coulomb potential by $4\pi g(r_{ij})$.

In order to understand the classification of terms in the sum, 3-1, it is necessary to repeat some definitions of terms that were used by Friedman. A g-bond is a coulomb bond between two particles. In a graph, if a vertex lies at the junction of exactly two g-bonds it is called a g-bond node. A g-bond chain is a sequence of g-bond nodes connected by g-bonds. A k-bond corresponds to a short range and a coulomb bond between two particles. A Y_m-bond is a bond connecting m vertices, e.g., Y_3 is a surface bounded by a triangle. A composition set, $n = n_1, n_2, \cdots n_\sigma$, is the number of each different species in a system. If brackets enclose the composition set, it is the set of coordinates of the species in the composition set.

Terms of the Expansion

With these definitions, equation 3-1 may be somewhat simplified. Let a graph of m vertices be given. The vertices, which are g-bond nodes, correspond to a subset of n of m. Let u be the remainder of m such that $m = n + u$. Then equation 3-1 becomes

$$S = S_k + S_c + \Sigma'' c^{u} B_u(X) \qquad (3\text{-}4)$$

where

S_ℓ' is the sum over all terms corresponding to two vertices connected only by a g -bond,

S_c' is the sum over all terms corresponding to simple cycles of g -bonds,

$c^{u} B_u(\chi)$ is the sum over all terms corresponding to graphs in which there are u vertices of the assigned composition set, u , that are not g -bond nodes. Note that, previously, the definition of the irreducible cluster integral did not depend on the Debye parameter χ , but this modified integral does. The symbol Σ'' indicates the terms corresponding to $u=0$ and $u=1$ are omitted in the summation.

The contributions to S_ℓ come only from m = 2; hence, from 3-1 we have

$$S_\ell = \sum_{i=1}^{\sigma}\sum_{j=1}^{\sigma} \frac{c_i c_j}{[i,j]!\,V} \int_V z_i z_j \, \lambda^2 g_{ij} \; d\{i,j\}$$

$$= \frac{1}{2}\left[\lambda \sum_{s=1}^{\sigma} c_s z_s\right]^2 \int_0^R g(r)\, 4\pi r^2 \, dr$$

where $[i,j]! = u!$ but $u = 1_i 1_j$; $2_i 0_j$; or $0_i 2_j$. Hence $[i,j]! = 2$ if $i = j$ but $= 1$ if $i \neq j$. Since the system is assumed to be electrically neutral, the sum $\sum_{s=1}^{\sigma} c_s z_s = 0$; hence

$$S_\ell = 0 \,,$$

Friedman evaluates the terms that contribute to S_c and obtains

$S_c = \frac{\varkappa^3}{12\pi}$ which corresponds to the Debye-Huckel, limiting-law expression for the thermodynamic function, S, Hill (6).

The General Cluster Integral

The terms in the integrand of $B_u(\varkappa)$ correspond to an indefinite number of expanded graphs of g-bonds, k-bonds, γ_3-bonds, $\ldots, \gamma_u$ bonds on a skeleton of u + n vertices. By considering the combinational problem and classifying graphs Friedman (4) reduces the problem of constructing the cluter integrals to

$$B_u(\varkappa) = \frac{1}{u!V} \int_V S_u(\varkappa, \{u\})\, d\{u\} .$$

Use the notation,

$$\begin{aligned}
\phi_{ab} &= \mathrm{EXP}\left[u^*_{ab}/kT - \lambda z_a z_b e^{-\varkappa r}/4\pi r \right] \\
\phi'_{ab} &= \phi_{ab} - 1 \\
\phi''_{ab} &= \phi_{ab} - 1 - q_{ab} \\
\phi'''_{ab} &= \phi_{ab} - 1 - q_{ab} - q_{ab}^2/2 ,
\end{aligned} \tag{3-5}$$

The graphs that enter into the integrand, $S_u(\varkappa, \{u\})$, are given by the rules

(1) Every vertex of the graphs is connected to every other vertex by at least two chains of bonds.

(2) There are no g-bond nodes.

(3) On a given pair of vertices there are at most one g-bond, or one ϕ'' bond, but not both. On any m vertices, there may be at most one V_m bond.

(4) In the case of u = 2

$$B_{ab}(\chi) = \frac{1}{V[a,b]!} \int_V \phi_{ab}''' \, d\{a,b\} \, . \tag{3-6}$$

Equation 3-4 now becomes

$$S = \frac{\chi^3}{12\pi} + \sum{}'' c^u B_u(\chi) \tag{3-7}$$

where the $B_u(\chi)$ terms are determined as stated above.

Hydrogen Gas Model

The evaluation of the cluster integrals becomes very difficult as u increases. The objective of this report is to evaluate the three body term in the sum for the case of hydrogen in order to gather some idea as to its importance. First, the two-body terms will be worked out, briefly. It is discussed in detail for aluminum by Bruce (2).

The general model that is chosen for a hydrogen plasma in this report is a collection of neutral atoms and an equal number of positively charged protons and negatively charged electrons. The net charge of the plasma is always zero. A hard-sphere, short-range potential is postulated

$$\begin{aligned} u^*(r_{ij}) &= \infty \qquad r_{ij} < a \\ &= 0 \qquad r_{ij} \geq a \, . \end{aligned} \tag{3-8}$$

It is particularly simplifying if the paramater a is chosen to be such that the coulomb potential at $r_{ij} = a$ is equal to the mean thermal energy

$$kT = \frac{|z_i z_j| \epsilon^2}{a}$$

$$a = \frac{|z_i z_j| \epsilon^2}{kT} \qquad (3\text{-}9)$$

where ϵ is the absolute charge of an electron,

T is the absolute temperature

z_i and z_j are the charge on the i^{th} and j^{th} particles.

Cluster Integrals for Two Bodies

According to rule 4, above, the cluster integral in the sum for the free energy is

$$B_{ij}(\chi) = \frac{4\pi}{[i,j]!} \int_0^\infty \phi'''(r)\, r^2 dr \qquad (3\text{-}10)$$

where

$$\phi''_{ij} = Exp\left(\frac{u^*_{ij}}{kT} + q_{ij}\right) - Q_{ij}$$

$$q_{ij} = -\frac{z_i z_j \lambda e^{-\chi r}}{4\pi r} \qquad (3\text{-}11)$$

$$Q_{ij} = 1 + q_{ij} + \frac{1}{2} q_{ij}^2 \qquad (3\text{-}12)$$

To simplify the integrals let

$$L = \frac{z_i z_j \lambda}{4\pi} \;; \quad k = \chi a \;; \quad x = \frac{r}{a}$$

$$q = L e^{-kx}/x \text{. Then,} \qquad (3\text{-}13)$$

$$B_{ij}(\chi) = \frac{4\pi}{[i,j]!} a^3 \left[\int_1^\infty (e^q - Q)\, x^2 dx - \int_0^1 Q\, x^2 dx \right]$$

The second integral can be evalute explicitly by integration by parts.

$$\int_0^1 Qx^2dx = \int_0^1 \left(1 - \frac{Le^{-kx}}{x} + \frac{L^2 e^{-2kx}}{x^2}\right) x^2 dx$$

$$= -\frac{L^2}{2k} e^{-2k} - L\left(\frac{k+1}{k^2}\right) e^{-k} + \frac{1}{3} + L^2/2k + L/k^2 \qquad (3\text{-}14)$$

The part of equation 3-7 that pertains to the two body terms may be written as

$$S_2 = C_+^2 B_{++} + C_+ C_- B_{+-} + C_-^2 B_{--} + C_0 C_+ B_{0+} + C_0 C_- B_{0-} + C_0^2 B_{00} \qquad (3\text{-}15)$$

where the subscripts $+$, $-$, and 0 stand for positive, negative, and neutral particles, respectively. Note, that since electrical neutrality is postulated $C_+ = C_- = C$.

If one, or both, of the particles are neutral then the product of charges $Z_i Z_j = 0$ then

$$L = 0$$
$$q = 0$$
$$e^q = 1$$
$$Q = 1 \,.$$

This implies that

$$\int_1^\infty [e^q - Q] x^2 dx = \int_1^\infty (1-1) \; x^2 dx = 0$$

but

$$\int_0^1 Q \; x^2 dx = \frac{1}{3} \,.$$

The factorial $[i,j]! = 0!1!1! = 1 \quad \text{or} = 0!2!0! = 2$

if a neutral and charged or two neutrals particles are considered, respectively.

Since $B_{ij}(K) = \frac{1}{[i,j]!}\frac{4\pi}{3}a^3$

$$B_{0+} = B_{0-} = \frac{4\pi}{3}a^3$$

$$B_{00} = \frac{2\pi}{3}a^3 .$$

Since the cluster integral depends on the product of the two charges considered, $B_{++} = B_{--}$. Doubly ionized hydrogen does not exist and electrons are singly charged, but this treatment is very necessary to discuss for the general case. With this consideration equation 3-15 becomes

$$S_2 = c^2(2B_{++} + B_{+-}) + \frac{4\pi}{3}a^3\left(2c_0c + \frac{c_0^2}{2}\right) . \quad (3\text{-}16)$$

The integrals B_{++} and B_{--} cannot be evaluated in closed form. Friedman gives limited tables of these integrals and Bruce (2) extends their range. The two body case is straight forward and the integral easy to evaluate, numerically. In the three body case, there are a number of complications and the number of integrals and cases increase considerably.

Cluster Integrals for Three Bodies

There are three different bond configurations possible for the three body terms of S as illustrated in figure 8.

(a) (b) (c)

Figure 8. Bond configuration for three bodies.

Considering the diagram in Figure 8(a) first, let

$$q_{ab} = \frac{-z_a z_b \lambda\, e^{-\varkappa r_{ab}}}{4\pi r_{ab}} \; ; \quad q_{bc} = \frac{-z_b z_c \lambda\, e^{-\varkappa r_{bc}}}{4\pi r_{bc}}$$

$$q_{ac} = \frac{-z_a z_c \lambda\, e^{-\varkappa r_{ac}}}{4\pi r_{ac}} \tag{3-17}$$

$$\phi''_{ab} = EXP\left[-\frac{u^*_{ab}}{kT} - q_{ab}\right] - 1 - q_{ab}$$

$$\phi''_{bc} = EXP\left[-\frac{u^*_{bc}}{kT} - q_{bc}\right] - 1 - q_{bc} \tag{3-18}$$

$$\phi''_{ac} = EXP\left[-\frac{u^*_{ac}}{kT} - q_{ac}\right] - 1 - q_{ac} .$$

The cluster integral, according to the rules above, becomes

$$B_{abc}(\varkappa) = \frac{1}{u!V} \int_V \phi''_{ab}\, \phi''_{bc}\, q_{ac}\, d\{a, b, c\} . \tag{3-19}$$

In order to simplify this integral let

$$\vec{r}_{ac} = \vec{a} - \vec{c} \; ; \quad \vec{r}_{bc} = \vec{r}_b - \vec{c} \; ; \quad \vec{r}_{ab} = \vec{r}_{bc} - \vec{r}_{ac} .$$

The absolute value of the Jacobian of this transformation is one, hence

$$B'_{abc}(\varkappa) = \frac{1}{u!V} \int_V \phi''_{ab}\, \phi''_{bc}\, q_{ac}\, d\vec{r}_{ac}\, d\vec{r}_{bc}\, d\vec{c} .$$

Carrying out the integration over $\vec{c}$ gives the volume of the space.

$$B'_{abc}(X) = \frac{1}{4!}\int_V \phi''_{ab}\,\phi''_{bc}\,q_{ac}\,d\vec{r}_{ac}\,d\vec{r}_{bc}$$

If $d\vec{r}_{ac}$ and $d\vec{r}_{bc}$ are expressed in spherical coordinates and if it is noted that ϕ''_{ab}, ϕ''_{bc}, and q_{ac} are functions of distance only, then

$$B'_{abc}(X) = \frac{1}{4!}\int_V \phi''_{ab}\,\phi''_{bc}\,q_{ac}\,r_{ac}^2\,r_{bc}^2\,\sin\gamma\,\sin\theta\,dr_{ac}\,dr_{bc}\,d\theta\,d\alpha_{ac}\,d\alpha_{bc}\,d\gamma$$

where $0 \leq \gamma \leq \pi$ is the polar angle associated with r_{bc}, $0 \leq \alpha_{ac} < 2\pi$, $0 \leq \alpha_{bc} < 2\pi$.

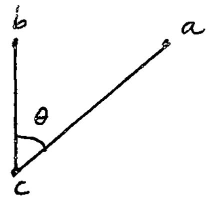

Figure 9. Particle geometry.

Integrate over γ, α_{ac}, and α_{bc} to obtain

$$B'_{abc}(X) = \frac{8\pi^2}{4!}\int_0^\infty\int_0^\infty\int_0^\pi \phi''_{ab}\,\phi''_{bc}\,q_{ac}\,r_{ac}^2\,r_{bc}^2\,\sin\theta\,d\theta\,dr_{ac}\,dr_{bc} \tag{3-20}$$

where $r_{ab} = \sqrt{r_{ac}^2 + r_{bc}^2 - 2\,r_{ac}r_{bc}\cos\theta}$ by the law of cosines. It is not possible to simplify the integral any further except in a few cases.

By similar transformations and integration the integral corresponding to Figure 8(b) may be reduced to

$$B''_{abc}(X) = \frac{8\pi^2}{4!}\int_0^\infty\int_0^\infty\int_0^\pi \phi''_{ab}\,\phi''_{bc}\,\phi''_{ac}\,r_{ac}^2\,r_{bc}^2\,\sin\theta\,d\theta\,dr_{ac}\,dr_{bc} \tag{3-21}$$

The nature and mathematical model for the r_3 bond is not clearly understood and will be discussed later in this report.

Since a hard sphere model of hydrogen is being considered, it is possible to simplify the integrals. By equation 3-9

$$a = \frac{|z_i z_j| \epsilon^2}{kT}$$

and for hydrogen $|z_i z_j| = 1$ hence

$$a = \frac{\epsilon^2}{kT}$$

The Coulomb length is $\lambda = \frac{4\pi\epsilon^2}{DkT}$ where D is the dielectric constant of the medium and is unity in the case under discussion.

Let

$$r_{ab} = x_{ab}\, a$$

$$r_{bc} = x_{bc}\, a$$

$$r_{ac} = x_{ac}\, a$$

and equation 3-17 assumes the form

$$\begin{aligned}
q_{ab} &= \frac{-z_a z_b \left(\frac{4\pi\epsilon^2}{kT}\right) e^{-K x_{ab}}}{4\pi \left(\frac{\epsilon^2}{kT}\right) x_{ab}} \\
&= -\frac{z_a z_b\, e^{-K x_{ab}}}{x_{ab}} \\
q_{bc} &= \frac{-z_b z_c\, e^{-K x_{bc}}}{x_{bc}} \\
q_{ac} &= \frac{-z_a z_c\, e^{-K x_{ac}}}{x_{ac}}
\end{aligned} \tag{3-22}$$

where $K = \varkappa a$

$$\varkappa = \left(\frac{4\pi\epsilon^2}{kT} \sum c_i z_i \right)^{1/2}$$

which is the reciprocal of the Debye length.

Since there are three possible states of charge for each of the three particles represented in each of the integrals, there are twenty-seven possible cases; however, only the products of two charges are of interest. There are only eleven different cases for these products. Table I lists these possibilities.

TABLE I

VARIOUS COMBINATIONS OF ION PRODUCTS FOR HYDROGEN

Product			Number of Configurations In Group
$Z_a Z_b$	$Z_b Z_c$	$Z_a Z_c$	
1	1	1	2
1	-1	-1	2
-1	-1	1	2
-1	1	-1	2
0	0	1	2
0	0	-1	2
0	1	0	2
0	-1	0	2
1	0	0	2
-1	0	0	2
0	0	0	7

Before taking up each of these eleven cases, it might be well to write, explicitly, the two cluster integrals with the change of variables of equation 3-21.

$$B'_{abc}(X) = \frac{8\pi^2}{u!} a^6 \int_0^\infty \int_0^\infty \int_0^\pi \Big[\Big(\mathrm{EXP}\Big[-\frac{u^*_{ab}}{kT} - \frac{z_{ab} e^{-kx_{ab}}}{x_{ab}}\Big] - 1 + \frac{z_{ab} e^{-kx_{ab}}}{x_{ab}}\Big)$$

$$\Big(\mathrm{EXP}\Big[-\frac{u^*_{bc}}{kT} - \frac{z_{bc} e^{-kx_{bc}}}{x_{bc}}\Big] - 1 + \frac{z_{bc} e^{-kx_{bc}}}{x_{bc}}\Big)\Big(-\frac{z_{ac} e^{-kx_{ac}}}{x_{ac}}\Big)$$

$$x_{bc}^2 \, x_{ac}^2 \, \sin\theta\Big] \, d\theta \, dx_{ac} \, x_{bc} \qquad (3\text{-}23)$$

$$B''_{abc}(X) = \frac{8\pi^2}{u!} a^6 \int_0^\infty \int_0^\infty \int_0^\pi \Big[\Big(\mathrm{EXP}\Big[-\frac{u^*_{ab}}{kT} - \frac{z_{ab} e^{-kx_{ab}}}{x_{ab}}\Big] - 1 + \frac{z_{ab} e^{-kx_{ab}}}{x_{ab}}\Big)$$

$$\Big(\mathrm{EXP}\Big[-\frac{u^*_{bc}}{kT} - \frac{z_{bc} e^{-kx_{bc}}}{x_{bc}}\Big] - 1 + \frac{z_{bc} e^{-kx_{bc}}}{x_{bc}}\Big)$$

$$\Big(\mathrm{EXP}\Big[-\frac{u^*_{ac}}{kT} - \frac{z_{ac} e^{-kx_{ac}}}{x_{ac}}\Big] - 1 + \frac{z_{ac} e^{-kx_{ac}}}{x_{ac}}\Big)$$

$$x_{bc}^2 \, x_{ac}^2 \, \sin\theta\Big] \, d\theta \, dx_{ac} \, d_{bc} \qquad (3\text{-}24)$$

where

$$z_{ab} = z_a z_b$$

$$z_{bc} = z_b z_c$$

$$z_{ac} = z_a z_c$$

$$x_{ab} = \sqrt{x_{bc}^2 + x_{ac}^2 - 2\, x_{ac} x_{bc} \cos\theta} \; .$$

Cluster Integrals for Three Bodies

Case I: $z_{ab} = z_{bc} = z_{ac} = 0$

This is the simplest case, and the integral can be evaluated explicitly.

Since the charge products are a coefficient of the q terms of equation 3-22,

$$q_{ab} = q_{bc} = q_{ac} = 0 . \qquad (3\text{-}25)$$

In every case that $Z_{ac} = 0$ and, hence, $q_{ac} = 0$

$$B'_{000}(\chi) = 0$$

since the q_{ac} term multiplies the integrand.

Using equation 3-25, equation 3-24 becomes

$$B''_{000}(\chi) = \frac{8\pi^2 a^6}{u!} \int_0^\infty \int_0^\infty \int_0^\pi \left[\left(EXP\left(-\frac{u^*_{ab}}{kT}\right) - 1 \right) \left(EXP\left(-\frac{u^*_{bc}}{kT}\right) - 1 \right) \right.$$
$$\left(EXP\left(-\frac{u^*_{ac}}{kT}\right) - 1 \right) x_{bc}^2 \, x_{ac}^2 \, SIN\,\theta \, d\theta \, dx_{bc} \, dx_{ac} \, . \qquad (3\text{-}26)$$

Now using the fact

$$\begin{aligned} u^*_{ij} &= \infty & 0 < x \le 1 \\ &= 0 & 1 < x < \infty . \end{aligned}$$

The integrand is zero if

$$1 < x_{ab} ; \quad 1 < x_{bc} ; \quad \text{or} \quad 1 < x_{ac} .$$

Now equation 3-25 becomes

$$B''_{000}(\chi) = \frac{8\pi^2 a^6}{u!} \int_0^1 \int_0^1 \int_0^\pi F(x_{ab}) \, x_{ac}^2 \, x_{bc}^2 \, SIN\,\theta \, d\theta \, dx_{ac} \, dx_{bc} \qquad (3\text{-}27)$$

where

$$\begin{aligned} F(x_{ab}) &= -1 & 0 < x_{ab} \le 1 \\ &= 0 & 1 < x_{ab} \end{aligned}$$

$0 < x_{ab} \le 1$ implies that

$$0 < x_{ac}^2 + x_{bc}^2 - 2 x_{ac} x_{bc} \cos\theta \le 1 .$$

To simplify the notation, let

$$X = x_{ac} \qquad Y = x_{bc}$$

The integrand is nonzero on the area

$$0 < x \le 1$$

$$0 < y \le 1$$

$$0 < x^2 + y^2 - 2xy\cos\theta \le 1 \; .$$

To find the expression for the bounding curve let

$$x^2 + y^2 - 2xy\cos\theta = 1 \qquad (3\text{-}28)$$

solving for y in terms of x and θ

$$y = \frac{2x\cos\theta \pm \sqrt{4x^2\cos^2\theta - (4x^2-1)}}{2}$$

$$y = x\cos\theta \pm \sqrt{1 - x^2\sin^2\theta} \; .$$

Consider x = 0; this implies that y = ± 1, since y > 0, this implies that the + sign must be used initially; hence

$$y = x\cos\theta + \sqrt{1 - x^2\sin^2\theta} \; , \qquad (3\text{-}29)$$

The question arises as to whether y becomes negative in the range of values. Since the above function for y is continuous, a negative value implies that y must have the value zero for some value of x. Let y = 0

$$0 = x\cos\theta + \sqrt{1 - x^2\sin^2\theta}$$

or $x^2 = 1$. This implies that x = 1, since x > 0. This means that for $0 < x \le 1$

$$y \ge x\cos\theta + \sqrt{1 - x^2\sin^2\theta} \; .$$

If y = 1, then equation 3-28 becomes $x^2 + 1 - 2\,x\,\mathrm{cox}\,\theta = 1$. This implies that x = 0, or $\theta = \cos^{-1}(\frac{x}{2})$

Now the integral 3-27 becomes

$$B''_{000}(X) = \frac{8\pi^2 a^6}{U!}\left(\int_0^1\int_0^{\cos^{-1}(\frac{x}{2})}\int_0^1 x^2y^2 \sin\theta \, dy\, d\theta\, dx \right.$$

$$\left. + \int_0^1\int_{\cos^{-1}(\frac{x}{2})}^{\pi}\int_0^{x\cos\theta+\sqrt{1-x^2\sin^2\theta}} x^2y^2 \sin\theta \, dy\, d\theta\, dx \right) , \qquad (3\text{-}30)$$

The integration of the above integral is tedious but straight forward and the details will not be reproduced. The result is

$$B''_{000}(X) = \frac{8\pi^2 a^6}{U!}\left(\frac{15}{144}\right) .$$

By numerical methods of triple integration which are outlined in Chapter 5, the coefficient was found to be .101684. This value compares favorably with .104166, that was found above, considering the rather crude grid that is used to cover the domain of the function.

The term U! = i! j! k!, where i, j, k, are the number of negative neutral, and positve particles, respectively, is summarized in Table II for this case.

TABLE II

VALUES OF U! FOR CASE I

Z_a	Z_b	Z_c	U!
0	0	0	0!3!0! = 6
0	0	1	0!2!1! = 2
0	0	-1	1!2!1! = 2
0	1	0	0!2!1! = 2
0	-1	0	0!2!0! = 2
1	0	0	0!2!1! = 2
-1	0	0	1!2!0! = 2

In case II let $Z_{ab} = 1 \quad Z_{ac} = Z_{bc} = 0$ This corresponds to the cases $Z_a = Z_b = 1,\ Z_c = 0,\ u\,! = 0!1!2! = 2$ and $Z_a = Z_b = -1,\ Z_c = 0$ $u! = 2!\,1!\,0! = 2.$ Since $Z_{ac} = 0$, $B'_{abc}(\chi) = 0$

$$B''_{abc}(\chi) = \frac{8\pi^2 a^6}{u!} \int_0^\infty \int_0^\infty \int_0^\pi \Big[\Big(\mathrm{EXP}\Big[-\frac{u^*_{ab}}{kT} - \frac{z_{ab}e^{-Kx_{ab}}}{x_{ab}}\Big] - 1 + Z_{ab}\frac{e^{-Kx_{ab}}}{x_{ab}}\Big)$$
$$= \Big(\mathrm{EXP}\Big[-\frac{u^*_{ab}}{kT}\Big] - 1\Big)\Big(\mathrm{EXP}\Big[-\frac{u^*_{ac}}{kT}\Big] - 1\Big) x_{ac}^2 x_{bc}^2 \sin\theta\, d\theta\, dx_{ac}\, dx_{bc}\,. \tag{3-31}$$

Now if $x_{bc} > 1$ or $x_{ac} > 1$

the integrand will be zero and equation 3-31 becomes

$$B''_{abc}(\chi) = \frac{8\pi^2 a^6}{u!} \int_0^1 \int_0^1 \int_0^\pi F(x_{ab})\, x_{ac}^2\, x_{bc}^2 \sin\theta\, d\theta\, dx_{ac}\, dx_{bc} \tag{3-32}$$

where

$$F = -1 + Z_{ab}\frac{e^{-Kx_{ab}}}{x_{ab}} \qquad 0 < x_{ab} \leq 1$$

$$= \mathrm{EXP}\Big(-\frac{Z_{ab}e^{-Kx_{ab}}}{x_{ab}}\Big) - 1 + Z_{ab}\frac{e^{-Kx_{ab}}}{x_{ab}} \qquad x_{ab} > 1\,.$$

The integrand is complicated by the fact that

$$x_{ab} = \sqrt{x_{ac}^2 + x_{bc}^2 - 2\,x_{ac}\,x_{bc}\cos\theta}\,.$$

After some investigation, there does not seem to be any profitable way to carry out further integrations. The integral was evaluated, numerically, for various values of the paramater K. The results are recorded in the Appendix.

In Case III, let $Z_{ab} = -1$, $Z_{ac} = Z_{bc} = 0$

This corresponds to $Z_a = -1$, $Z_b = 1$, $Z_c = 0$, u! = 1!1!1! = 1 and

$Z_a = 1$, $Z_b = -1$, $Z_c = 0$, u! = 1!0!1! = 1.

This case is very similar to Case II, except $Z_{ab} = -1$. With this understanding, equation 3-32 applies for case III.

For Case IV assume $Z_{ab} = Z_{ac} = 0$ and $Z_{bc} = 1$. Then $Z_a = 0$, $Z_b = Z_c = 1$, $u! = 0!1!2! = 2$; or $Z_a = 0$, $Z_b = Z_a = -1$ $u! = 2!1!0! = 2$.

Again $B'_{abc}(\chi) = 0$ since $z_{ac} = 0$.

Equation 3-24 becomes

$$B''_{abc}(\chi) = \frac{8\pi^2 a^6}{u!}\int_0^\infty\int_0^\infty\int_0^\pi \Big[\Big(\mathrm{EXP}\Big[-\frac{u^*_{bc}}{kT} - \frac{z_{bc}e^{-Kx_{bc}}}{x_{bc}}\Big] - 1 + \frac{z_{bc}e^{-Kx_{bc}}}{x_{bc}}\Big)$$

$$\Big(\mathrm{EXP}\Big[-\frac{u^*_{ab}}{kT}\Big]-1\Big)\Big(\mathrm{EXP}\Big[-\frac{u^*_{ac}}{kT}\Big]-1\Big)\, x_{ac}^2\, x_{bc}^2 \,\mathrm{SIN}\,\theta\Big]\, d\theta\, dx_{ac}\, dx_{bc} .$$

If $x_{ac} > 1$ or $x_{bc} > 1$, the integrand is zero if x_{bc} is greater than 2, x_{ab} must be greater than 1 since $x_{ac} \leqslant 1$. The limits of integration become:

$$B''_{abc}(\chi) = \frac{8\pi^2 a^6}{u!}\int_0^2\int_0^1\int_0^\pi F\, x_{ac}^2\, x_{bc}^2\,\mathrm{SIN}\,\theta\, d\theta\, dx_{ac}\, dx_{bc} \tag{3-33}$$

where

$$F = 0 \qquad 1 < x_{ab}$$

$$F = -1 + \frac{z_{bc}e^{-Kx_{bc}}}{x_{bc}} \qquad 0 < x_{ab} < 1,\ 0 < x_{bc} \leq 1$$

$$F = \mathrm{EXP}\Big[z_{bc}\frac{e^{-kx_b}}{x_{bc}}\Big] - 1 + \frac{z_{bc}e^{-kx_{bc}}}{x_{bc}} \qquad 0 < x_{ab} \leq 1,\ 1 < x_{bc} < 2 .$$

In Case V, $Z_{ab} = Z_{ac} = 0$ and $Z_{bc} = -1$. $Z_a = 0$, $Z_b = 1$, $Z_c = -1$, $u! = 1$; or $Z_a = 0$, $Z_b = -1$, $Z_c = 1$, $u! = 1$. Obviously this is the same as equation 3-33 except Z_{bc} is -1.

For Case VI, $Z_{ab} = Z_{bc} = 0$, $Z_{ac} = 1$ corresponding to $Z_a = Z_c = 1$ $Z_b = 0$, $u! = 2$ and $Z_a = Z_c = -1$, $Z_b = 0$, $u! = 2$.

In this case $B'_{abc}(\chi)$ is not zero.

Equation 3-23 becomes

$$B'_{abc}(\chi) = \frac{8\pi^2 a^6}{u!} \int_0^{\infty}\int_0^{\infty}\int_0^{\pi} \left[\left(\mathrm{EXP}\left[-\frac{u^*_{ab}}{kT}\right] - 1 \right) \left(\mathrm{EXP}\left[\frac{u^*_{bc}}{kT}\right] - 1 \right) \left(\frac{z_{ac}\, e^{-k x_{ac}}}{x_{ac}} \right) x^2_{ac}\, x^2_{bc}\, \mathrm{SIN}\,\theta \right] d\theta\, dx_{bc}\, dx_{ac} \,,$$

If $x_{bc} > 1$ or $x_{ab} > 1$ the integral is zero.

This places the following restriction on x_{ac}.

$$0 \leq x_{ac} \leq 2$$

Hence,

$$B'_{abc}(\chi) = \frac{8\pi^2}{u!} a^6 \int_0^1\int_0^2\int_0^{\pi} F\, x_{ac}\, x^2_{bc}\, \mathrm{SIN}\,\theta\, d\theta\, dx_{ac}\, dx_{bc} \qquad (3\text{-}34)$$

where

$$\begin{aligned} F &= -z_{ac}\, e^{-k x_{ac}} && 0 < x_{ab} \leq 1 \\ &= 0 && 1 < x_{ab} \,. \end{aligned}$$

This integral can be evaluated explicitly. Let $x_{ac} = x$ and $x_{bc} = y$. F or $0 < x \leq 1$, the same region of integration is required as Case I. For $1 < x < 2$, the shaded area in Figure 10 is region for which the integrand is nonzero.

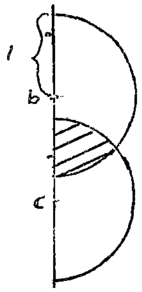

Figure 10. Domain of integration
Case VI

This region is defined by the following inequalities

$$1 < x < 2 \qquad 0 < y < 1$$

$$0 < x^2 + y^2 - 2xy\cos\theta < 1$$

$$0 < \theta < \pi$$

Let $y = 1$ and $x_{ab} = 1$. This implies $x^2 + 1 - 2x(1)\cos\theta = 1$ for which

$$x = 0 \qquad \text{or} \qquad \theta = \cos^{-1}\left(\frac{x}{2}\right)$$

hence, $0 < \cos^{-1}\left(\frac{x}{2}\right)$

and $y = x\cos\theta - \sqrt{1 - x^2\sin^2\theta}$

Equation 3-34 becomes

$$B'_{abc}(X) = \frac{8\pi^2 a^6}{u!}\Big[\int_0^1\int_0^1\int_0^{\cos^{-1}(\frac{x}{2})} -Z_{ac}\, e^{-KX}\, x y^2 \sin\theta \, d\theta \, dy \, dx$$

$$+ \int_0^1\int_{\cos^{-1}(\frac{x}{2})}^{\pi}\int_0^{x\cos\theta + \sqrt{1 - x^2\sin^2\theta}} -Z_{ac}\, e^{-KX}\, y^2 x \sin\theta \, dy \, d\theta \, dx$$

$$+ \int_1^2\int_0^{\cos^{-1}(\frac{x}{2})}\int_{x\cos\theta + \sqrt{1 - x^2\sin^2\theta}}^{1} -Z_{ac}\, e^{-KX}\, x y^2 \sin\theta \, dy \, d\theta \, dx\Big]$$

The evaluation of these integrals is straight forward but very long and tedious. The result is

$$B'_{abc}(X) = \frac{-Z_{ac}}{3}\,\frac{8\pi^2 a^6}{u!}\left(\frac{2}{K^2} - \frac{2}{K^3} + \frac{3}{K^5} - e^{-2K}\left(\frac{3}{K^3} + \frac{6}{K^4} + \frac{3}{K^5}\right)\right) \tag{3-35}$$

This formula, though explicitly true, is inconvenient to calculate on a computer of the parameter K is less than .3. Since it involves the difference of two large, nearly equal numbers, loss of significant digits can occur. In order to alleviate this situation for small K, the exponential was expanded in a Taylor's series about zero. After using the first nine terms of the series and carrying out the indicated algebraic operations equation 3-35 becomes

$$B'_{abc}(X) = -Z_{ac}\,\frac{8\pi^2 a^6}{u!}\left(\frac{4}{15} - \frac{2}{9}k + \frac{4}{35}k^2 - \frac{2}{45}\,k^3 + \frac{8}{567}\,k^4 - \cdots\right) \qquad (3\text{-}36)$$

The error in neglecting higher order terms should be 0 (10^{-3}), or less. At K = .3, four significant figures are obtained with equation 3-35 when nine significant figures are used. Since this is more significant figures than the IBM 7040 digital computer uses, without double precision programming, it is considered that for K < .3 equation 3-36 is better.

For the second integral $B''_{abc}(X)$ equation 3-24 becomes

$$B'_{abc}(X) = \frac{8\pi^2 a^6}{u!}\int_0^\infty\!\int_0^\infty\!\int_0^\pi \Big[\left(EXP\left[-\frac{u^*_{ab}}{kT}\right]-1\right)\left(EXP\left[-\frac{u^*_{bc}}{kT}\right]-1\right)\left(EXP\left[-\frac{u^*_{ac}}{kT} - \frac{Z_{ac}e^{-Kx_{ac}}}{x_{ac}}\right]\right.$$
$$\left. -1 + \frac{Z_{ac}\,e^{-Kx_{ac}}}{x_{ac}}\right) x^2_{ac}\; x^2_{bc}\; SIN\theta\Big]\; d\theta\; dx_{ac}\, dx_{bc}$$

If in the above equation x_{ac} and x_{bc} are interchanged, this is Case IV. It is unnecessary to evaluate both cases because of the symmetry of the integrand.

In Case VII, let $Z_{ab} = Z_{bc} = 0$, $Z_{ac} = -1$, then $Z_a = 1$, $Z_b = 0$, $Z_c = -1$, u! = 1, or $Z_a = -1$, $Z_b = 0$, $Z_c = 1$, u! = 1.

Equations 3-23 and 3-24 become

$$B'_{abc}(X) = \frac{8\pi^2 a^6}{u!}\int_0^\infty\!\int_0^\infty\!\int_0^\pi \Big[\left(EXP\left[-\frac{u^*_{ab}}{kT}\right]-1\right)\left(EXP\left[-\frac{u^*_{bc}}{kT}\right]-1\right)$$

$$\left(-Z_{ac}\;e^{-Kx_{ac}}\right)\; x_{ac}\; x^2_{bc}\;\; SIN\theta\Big]\; d\theta\; dx_{ac}\; dx_{bc}$$

and

$$B''_{abc}(\chi) = \frac{8\pi^2 a^6}{u!} \int_0^\infty \int_0^\infty \int_0^\pi \Big[\big(\mathrm{EXP}\big[-\frac{u^*_{ab}}{kT}\big] - 1\big)\big(\mathrm{EXP}\big[-\frac{u^*_{bc}}{kT}\big] - 1\big)$$

$$\Big(\mathrm{EXP}\Big[-\frac{u^*_{ac}}{kT} - \frac{Z_{ac} e^{-\kappa x_{ac}}}{x_{ac}}\Big] - 1 + \frac{Z_{ac} e^{-\kappa x_{ac}}}{x_{ac}}\Big)\Big] x_{ac}^2 x_{bc}^2 \sin\theta \, d\theta \, dx_{ac} \, dx_{bc}$$

These are obviously the same as the previous integrals. The only difference is that Z_{ac} is now -1. The regions of integration will be the same. The expression for $B'_{abc}(\chi)$ can be integrated and the result will be equation 3-35 with $Z_{ac} = -1$.

In the remaining four cases, it is not possible to limit the range of integration to certain values of the variables x_{ac}, x_{bc} and θ. For cases VIII through XI, the following general integrals pertain: It is necessary to substitute the proper values of the charge products, as listed in Table III, to evaluate the integrand for various values of the variables.

$$B'_{abc}(\chi) = \frac{8\pi^2 a^6}{u!} \int_0^\infty \int_0^\infty \int_0^\pi \Big[F_1(x_{ab})\, F_2(x_{bc})\, (-Z_{ac} e^{-\kappa x_{ac}})$$

$$x_{ac}\, x_{bc}^2 \sin\theta \Big] \, d\theta \, dx_{ac} \, dx_{bc} \qquad (3\text{-}37)$$

$$B''_{abc}(\chi) = \frac{8\pi^2 a^6}{u!} \int_0^\infty \int_0^\infty \int_0^\pi \Big[F_1(x_{ab})\, F(x_{bc})\, F_3(x_{ac})$$

$$x_{ac}^2\, x_{bc}^2 \sin\theta \Big] \, d\theta \, dx_{ac} \, d_{bc} \qquad (3\text{-}38)$$

where

$$F_1(x_{ab}) = -1 + Z_{ab} \frac{e^{-\kappa x_{ab}}}{x_{ab}} \qquad 0 < x_{ab} < 1$$

$$= \mathrm{EXP}\Big[- \frac{Z_{ab} e^{-\kappa x_{ab}}}{x_{ab}}\Big] - 1 + Z_{ab} \frac{e^{-\kappa x_{ab}}}{x_{ab}} \qquad 1 \leq x_{ab}$$

$$F_2(x_{bc}) = -1 + Z_{bc} \frac{e^{-\kappa x_{bc}}}{x_{bc}} \qquad 0 < x_{bc} < 1$$

$$F_2(x_{bc}) = EXP\left[-\frac{z_{bc}e^{-Kx_{bc}}}{x_{bc}}\right] - 1 + \frac{z_{bc}e^{-Kx_{bc}}}{x_{bc}} \qquad 1 \le x_{bc}$$

$$F_3(x_{ac}) = -1 + \frac{z_{ac}e^{-Kx_{ac}}}{x_{ac}} \qquad 0 < x_{ac} < 1$$

$$= EXP\left[-\frac{z_{ac}e^{-Kx_{ac}}}{x_{ac}}\right] - 1 + \frac{z_{ac}e^{-Kx_{ac}}}{x_{ac}} \qquad 1 \le x_{ac}$$

TABLE III

CHARGE PARAMETERS AND U! FOR CASES VIII THROUGH XI

Case	Z_{ab}	Z_{bc}	Z_{ac}	Z_a	Z_b	Z_c	U!
VIII	1	1	1	1	1	1	6
or				-1	-1	-1	6
IX	1	-1	-1	1	1	-1	2
or				-1	-1	1	2
X	-1	-1	1	1	-1	1	2
or				-1	1	-1	2
XI	-1	1	-1	-1	1	1	2
or				1	-1	-1	2

To evaluate the above integrals, it is necessary to use numerical analysis. The particular method used is discussed in Chapter 5. A set of tables for each case was constructed for various values of the parameter, K, ranging from 10^{-4} to 10.

Using the notation of equation 3-15 and equation 3-19, the three body terms of equation 3-7 become

$$S_3 = c_+^3 B_{+++} + c_+^2 c_- (B_{+++} + B_{+-+} + B_{-++}) + c_+ c_-^2 (B_{+--} + B_{-+-} + B_{--+}) + c_-^3 B_{---} + c_0 c_+^2 (B_{0++} + B_{+0+} + B_{++0}) + c_0 c_+ c_- (B_{+0-} + B_{+-0} + B_{0+-} + B_{0-+} + B_{-0+} \; B_{-+0}) + c_0 c_-^2 (B_{--0} + B_{-0-} + B_{0--}) + c_0^2 c_- (B_{00-} + B_{0-0} + B_{-00}) + c_0^2 c_+ (B_{00+} + B_{0+0} + B_{+00}) + c_0^3 B_{000} \qquad (3\text{-}39)$$

Since the g-bond of Figure 3-1(a) can appear between any two vertices, there are three different integrals contributing to $B'_{abc}\,(\mathcal{X})$

Let $$I_1' = \int_0^\infty \int_0^\infty \int_0^\pi \phi''_{ab} \phi''_{bc} \, q_{ac} \, x_{ac}^2 x_{bc}^2 \sin\theta \, d\theta \, dx_{ac} \, dx_{bc}$$

$$I_2' = \int_0^\infty \int_0^\infty \int_0^\pi \phi''_{ab} \phi''_{ac} \, q_{bc} \, x_{ac}^2 x_{bc}^2 \sin\theta \, d\theta \, dx_{ac} \, dx_{bc} \qquad (3\text{-}40)$$

$$I_3' = \int_0^\infty \int_0^\infty \int_0^\pi \phi''_{ac} \phi''_{bc} \, q_{ab} \, x_{ac}^2 x_{bc}^2 \sin\theta \, d\theta \, dx_{ac} \, dx_{bc}$$

and let $$I'' = \int_0^\infty \int_0^\infty \int_0^\pi \phi''_{ab} \phi''_{bc} \phi''_{ac} \, x_{ac}^2 x_{bc}^2 \sin\theta \, d\theta \, dx_{ac} \, dx_{bc}$$

Then $$B_u(\mathcal{X}) = \frac{8\pi^2 a^6}{4!} (I_1' + I_2' + I_3' + I'')$$

By appropriate transformations the integrals of 3-40 may be reduced to a form for integration. There are relations between the integrals for different charge product parameters.

Let

$$I' = \int_0^\infty \int_0^\infty \int_0^\pi \phi''_{ab} \phi''_{bc} \, q_{ac} \, x_{ac}^2 x_{bc}^2 \sin\theta \, d\theta \, dx_{ac} \, dx_{bc}$$

$$I'' = \int_0^\infty \int_0^\infty \int_0^\pi \phi''_{ab} \phi''_{bc} \phi''_{ac} \, x_{ac}^2 x_{bc}^2 \sin\theta \, d\theta \, dx_{ac} \, dx_{bc} \qquad (3\text{-}41)$$

The positive, negative and neutral signs on the nonsubscripted I's, above, refer to the charge products, not the individual charges on the particles. Examples are

$$I'_{+++} = I'_{1\,+++} = I'_{2\,+++} = I'_{3\,+++}$$

$$I'_{--+} = I'_{1\,-++} = I'_{1\,+--} = I'_{2\,-++} = I'_{2\,+--} = I'_{3\,++-} = I'_{3\,--+}$$

$$I'_{00+} = I'_{1\,+0+} = I'_{1\,-0-} = I_{2\,0++} = I'_{2\,0--} = I'_{3\,++0} = I'_{3\,--0}$$

By the use of the above relations, it is found that

$$B_{+++}(\chi) = \frac{8\pi^2}{6} a^6 (3 I'_{+++} + I''_{+++})$$

$$B_{++-}(\chi) = \frac{8\pi^2}{2} a^6 (I'_{+--} + I'_{--+} + I'_{-+-} + I''_{+--})$$

$$B_{+0+}(\chi) = \frac{8\pi^2}{2} a^6 (I'_{0+0} + I'_{00+} + I'_{+00} + I''_{00+})$$

Additional considerations simplify equation 3-39. $C_+ = C_- = C$ for hydrogen and $I'_{xx0} = 0$ where x is plus, minus or zero. The following symmetries have been discussed, also.

$$-I'_{00+} = I'_{00-}$$

$$I''_{--+} = I''_{-+-}$$

$$I''_{00+} = I''_{0+0}$$

and

$$I''_{00-} = I''_{0-0}$$

With the above properties and relations and after some algebraic manipulations, equation 2-39 becomes

$$\begin{aligned} S'_3 = 8\pi^2 a^6 \{ & C^3 (I'_{+++} + 3(I'_{+--} + I'_{-+-} + I'_{--+}) \\ & + \tfrac{1}{3} I''_{+++} + I''_{+--} + 2 I''_{--+}) + C_0 C^2 (-3 I'_{00+} + I''_{+00} \\ & + 2 I''_{-00} + 2 I''_{00+} + 4 I'_{00-}) + (3 C_0^2 + C_0^3/6) I''_{000} \} \end{aligned}$$

The I's in the above relations are, of course, the integrals of

Cases I through XI which were discussed above and evaluated by various means as a function of a parameter K.

In the next chapter, a thermodynamic relation is used that involves the partial derivative of S with respect to the ion concentration c. As a preliminary to the calculation, it is desirable to find $\frac{\partial K}{\partial c}$;

$$\frac{\partial K}{\partial c} = a\frac{\partial}{\partial c}\left[\frac{4\pi\epsilon^2}{kT}\sum c_i z_i^2\right]^{1/2}$$

$$= \frac{a\frac{4\pi\epsilon^2}{kT} z_i^2}{2\left[\frac{4\pi\epsilon^2}{kT}\sum c_i z_i^2\right]^{1/2}}.$$

For hydrogen, $z_i = \pm 1 \qquad c_+ = c_-$

$$\frac{\partial K}{\partial c} = \frac{a\left[\frac{4\pi\epsilon^2}{kT}\right]^{1/2}\left(\sum c_i z_i^2\right)^{1/2}}{2\sum c_i z_i^2}$$

$$= \frac{a\mathcal{K}}{2c} = \frac{K}{2c} \tag{3-43}$$

Using equation 3-16 for S_2,

$$\frac{\partial}{\partial c} S_2 = 2c(2B_{++} + B_{+-}) + \frac{8\pi a^3}{3}c_0 + c^2\frac{\partial}{\partial c}(2B_{++} + B_{+-})$$

$$= 2c(2B_{++} + B_{+-}) + \frac{8\pi a^3}{3}c_0 + c^2\frac{\partial K}{\partial c}\frac{\partial}{\partial K}(2B_{++} + B_{+-})$$

$$= 4\pi a^3\left\{2c(I_+ + 2I_-) + 4c_0 + \frac{Kc}{2}(DI_+ + 2DI_-)\right\} \tag{3-44}$$

where $B_{++} = B_{--} = \frac{1}{2}4\pi a^3 I_+$

$B_{+-} = B_{-+} = 4\pi a^3 I_-$

$DI_+ = \frac{\partial}{\partial K} I_+$

$DI_- = \frac{\partial}{\partial K} I_-$

Similar operations on S_3 as given in equations 3-42 yield

$$\begin{aligned}\frac{\partial S_3}{\partial c} = 8\pi^2 a^6 \Big\{ & 3c^2\big[I'_{+++} + 3(I'_{+--} + I'_{-+-} + I'_{--+}) \\ & + \tfrac{1}{3} I''_{+++} + I''_{+--} + 2I''_{--+}\big] + 2c_0 c(-3I'_{00+} + I''_{+00} \\ & + 2I_{-00} + 2I''_{00+} + 4I''_{00-}) + 3c_0^2\, I''_{000} \\ & + \tfrac{k}{2}\big[3c^2(DI'_{+++} + 3(DI'_{+--} + DI'_{-+-} + DI'_{--+}) \\ & + \tfrac{1}{3} DI''_{+++} + DI''_{+--} + 2DI''_{--+}) + 2c_0 c(-3DI'_{00+} \\ & + DI''_{+00} + 2DI''_{-00} + 2DI''_{00+} + 4DI''_{00-})\big]\Big\} \end{aligned} \qquad (3\text{-}45)$$

$\mathcal{V}_3$ Bond

The nature of the $\mathcal{V}_3$-bond has not yet been discussed. The potential associated with the $\mathcal{V}_3$-bond is defined as

$$\begin{aligned} u_{ijk}(\{i,j,k\}) = U_{ijk}(\{i,j,k\}) - u_{ij}(\{i,j\}) \\ - u_{ik}(\{i,k\}) - u_{jk}(\{j,k\}) \end{aligned} \qquad (3\text{-}46)$$

where U_{ijk} is the potential of average force between particles i, j, and k and u_{ij}, u_{ik}, and u_{jk} are the pairwise potentials between the appropriate particles. The formulation of potentials of average force is discussed by Hill (6). To define U_N for a composition set of N particles, let {N} be the spatial coordinates of the particles and $\{N_i\}_i$ be the internal coordinates. Then the probability of a particular configuration is proportional to

$$EXP[-U(\{N\},\{N_i\}_i)/kT]$$

The probability of a configuration that is specified by the spatial coordinates only is proportional to the relation,

$$\int \mathrm{EXP}[-U(\{N\},\{N_i\}_i)/kT]\, d\{N_i\}_i \equiv \mathrm{EXP}[-U(\{N\})/kT] \int d\{N\}_i \tag{3-47}$$

Equation 3-47 is to be considered as the definition of U ({N}). In general, this involves extremely difficult integrals. A special case has been considered by Sun (13) for three hydrogen atoms in a straight line. He found that the potential of the three atoms differed from the approximation that the potential is the sum of the pairwise potentials for distances less than 2.5 angstroms. Since this report has assumed a hardshell model with radius $a = 4\pi\epsilon^2/kT$, a will not be less than 2.5 angstroms for temperatures of less than 5 electron volts. If the approximation is used that the potential of average force is equal to the sum of the pairwise potentials, then u_{ijk} of equation 3-46 is zero. This approximation is called the principle of superposition and is widely used as a first approximation. It would then appear that as a first approximation that the integral associated with the Y_3-bond can be neglected in the summation of equation 3-7.

Summary

To summarize this chapter, an approximation has been found for S in terms of K and the Mayer cluster integrals for two and three body interactions by Coulomb potentials. Equation 3-7 becomes

$$S' = \frac{\kappa^3}{12\pi} + S'_2 + S'_3$$

where S_2 is given by equation 3-16 and S_3 by equation 3-42.

CHAPTER IV

ELECTRON DENSITY OF HYDROGEN PLASMA

As an application of the theory of Chapter 3 and to judge the relative importance of the three-body term, the expression for the free energy was applied to the calculation of electron number density in a hydrogen plasma. Bruce (2) reported on calculations similar to this with Mayer's cluster expansion for two-body terms only. The detailed plan for calculation was devised by Rouse (11). It involves the use of Saha's equation and iteration on the electron number density. The equations and theory will be presented briefly. For a more complete explanation, the references given should be consulted.

Theoretical Discussion and Programming Procedure

The Saha equation, as presented by Landau and Lipshitz (7), is derived from consideration of ionization equilibrium which is a special case of chemical equilibrium. The equations for the case of hydrogen are

$$\frac{c_0}{c_+ c_-} = P K_p^+ (T) \tag{4-1}$$

$$c_- = c_+ = c$$

$$1 = 2c + c_0 \tag{4-2}$$

In equation 4-1

$$K_p^+(T) = \frac{g_c}{g_+} \left(\frac{2\pi}{m_e}\right)^{3/2} \frac{\hbar}{(kT)^{5/2}} \quad EXP\left[I_n / kT \right] \tag{4-3}$$

where C_o = concentration of neutral atoms

C_- = concentration of electrons

C_+ = concentration of positive ions

g_o and g_+ = statistical weight of ion ground states

P = total pressure

P_e = electron pressure

m_e = electron mass

I_n = nth ionization potentail of the atom

T = temperature.

From the gas law in equation 4-1, the following relations are obtained

$$P = \frac{P_e}{C} = \frac{N_e}{C} kT$$

$$\frac{C_0}{C^2} = \frac{N_e}{C} kT \; K_p(T) = N kT \; K_p(T)$$

$$C_0 = C^2 \, N kT \, K_p(T)$$

Then, equation 4-2 becomes

$$1 = 2C + C^2 \, N kT \; K_p(T)$$

Since $C = N_e/N$,

where N_e = number of electrons

and N = total number of particles

$$1 = 2\frac{N_e}{N} + \frac{N_e^2}{N} N \, kT \, K_p(T)$$

It is more convenient to calculate with N_H, the number of heavy particles; hence, $N = N_e + N_H$

then

$$N_e^2(kT\ K_p(T)) + N_e - N_H = 0$$

By the quadratic formula

$$N_e = \frac{-1 \pm \sqrt{1 + 4kT K_p(T) N_H}}{2kT K_p(T)} \qquad (4\text{-}4)$$

The electron concentration cannot be negative so the positive square root must be taken.

The chemical potential is given by

$$\mu_e = \frac{\partial S}{\partial c} \qquad (4\text{-}5)$$

according to Friedman (4), and can be calculated from equations 3-44 and 3-45. This quantity permits the calculation of I_n in equation 4-3.

It is now possible to devise an iteration scheme to calculate the electron density of a hydrogen plasma. First, a trial concentration is assumed, then a chemical potential is calculated from the tabulated cluster integrals. Equation 4-3 is evaluated for $K_p(T)$. Finally, by again employing the assumed electron concentration, a new concentration is calculated from equation 4-4. This new concentration is used to start the cycle again. The iteration cycle is continued until the value for the electron concentration converges.

The iteration scheme was programmed in FORTRAN IV for the IBM 7040 digital computer. The methods of interpolation and representation of functions are discussed in Chapter 5.

Results of Program

The results of this program are represented as graphs and are given in Figures 11 through 13. The graphs for cluster integrals, with two-body interactions only, and for ideal gas are also given for comparison.

It will be noted that the three-body interactions tend to decrease the value calculated for the electron number density in the region of lower temperature and higher density. This extends, slightly, the region of applicability for the cluster integral method. As reported by Bruce (2), the Ecken and Kroll method appears to give as good a value, but these studies were necessary in order to establish the merit of their assumptions.

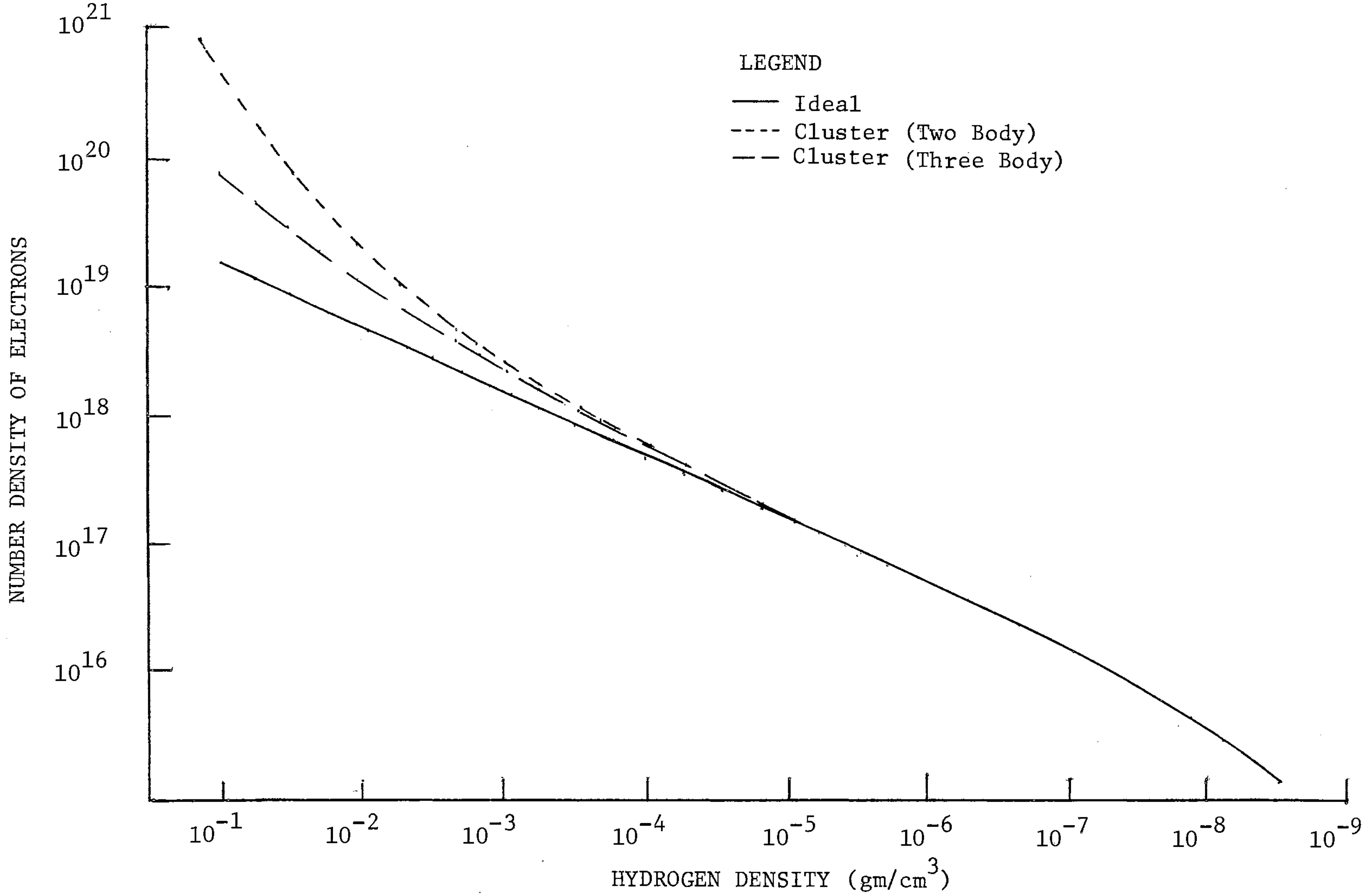

Figure 11.--Electron density of hydrogen vs. density at temperature of 1 ev.

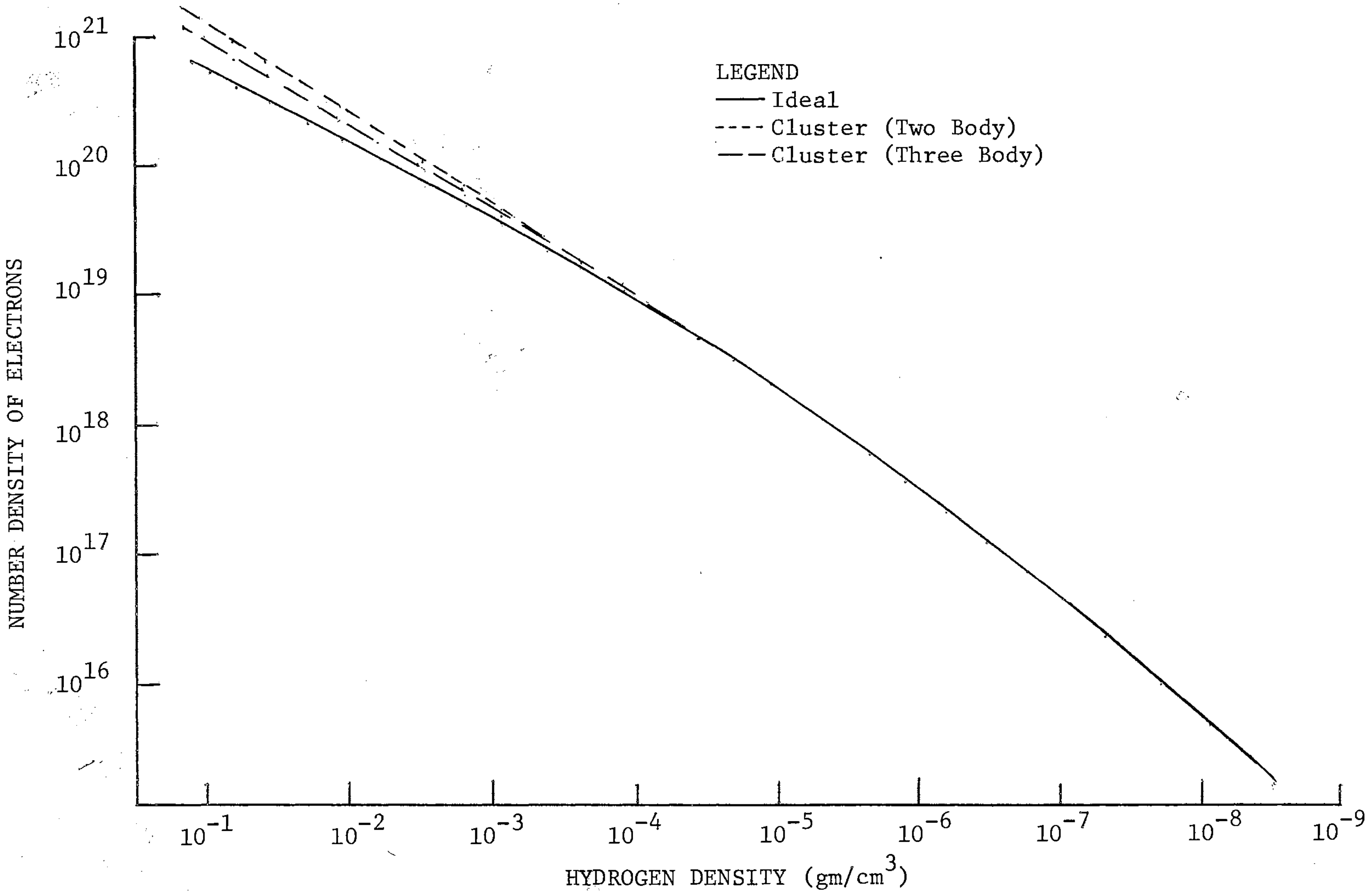

Figure 12.--Electron density of hydrogen vs. density at temperature of 2 ev.

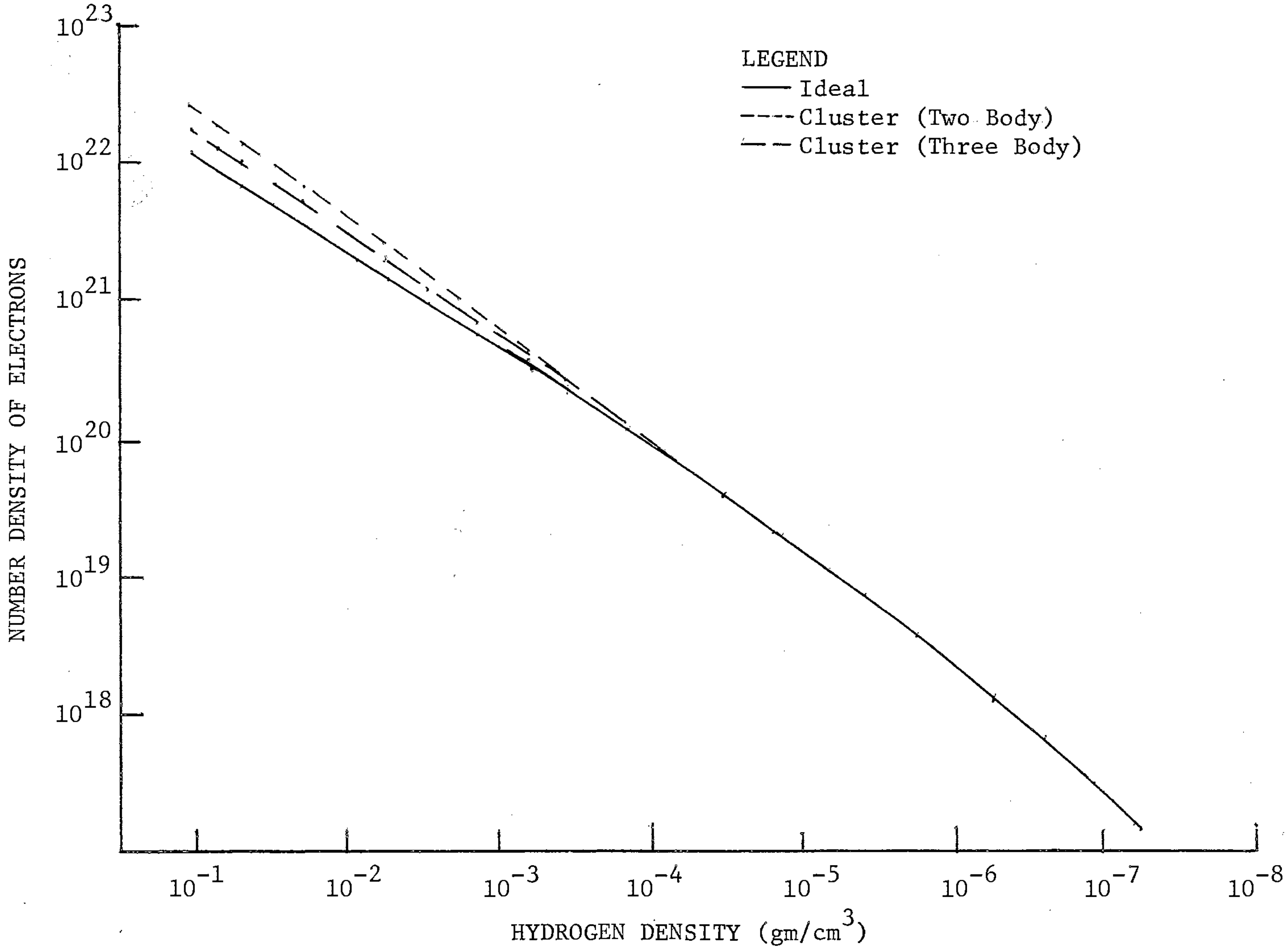

Figure 13.--Electron density of hydrogen vs. density at temperature of 5 ev.

CHAPTER V

NUMERICAL METHODS

The first problem to be considered is the evaluation of the cluster integrals as a function of the parameter K. This involves the triple integration of a rather complicated integrand. There are various methods that could be used in the integration; among them are the Monte Carlo procedures, special three-dimensional rules, or successive applications of one-dimensional formulas. These different approaches have various advantages.

Monte Carlo methods find, essentially, a statistical approximation of the true value of the integral. They are very good for a quick, rough value of an integral over a finite interval. Since the integrals in this report are over a semi-infinite range in two variables, the method is not attractive.

Special Formulas for Numerical Integration Over Three Dimensions

There are several, special three-dimensional formulas that are available. A few of them are derived from consideration of an approximation of the integrand as a polynomial over a finite cube. The derivations are based on a work by Tyler (14).

Let $F(x,y,z) = \sum_{i=0}^{n}\sum_{j=0}^{n}\sum_{k=0}^{n} A_{ijk}\, x^i y^j z^k \qquad i+j+k \le n$

and consider $I = \int_{-a_1}^{a_1}\int_{-a_2}^{a_2}\int_{-a_3}^{a_3} F(x,y,z)\, dx\, dy\, dz$.

After the integration is performed on the polynomial

$$I = \sum_{i=0}^{n}\sum_{j=0}^{n}\sum_{k=0}^{n} A_{ijk} \frac{(a_1^{i+1} - (-a_1)^{i+1})(a_2^{j+1} - (-a_2)^{j+1})(a_3^{k+1} - (-a_3)^{k+1})}{(i+1)(j+1)(k+1)} .$$

If any subscript is odd in the original sum, the integrated term will be equal to zero; and

$$I = 8 a_1 a_2 a_3 \sum_{i=0}^{n}\sum_{j=0}^{n}\sum_{k=0}^{n} A_{ijk} \frac{a_1^i a_2^j a_3^k}{(i+1)(j+1)(k+1)} \qquad \begin{matrix} i+j+k \le n \\ i, j, k \text{ even} \end{matrix} \; .$$

Approximate I by

$$I_1 = 8 a_1 a_2 a_3 \sum_{\alpha=1}^{m} R_\alpha F(x_\alpha, y_\alpha, z_\alpha)$$

where the R_α's are weights to be applied to the function values at the appropriate points.

If $I_1 - I$ is considered and the coefficients of A_{ijk} are set equal to zero, the following results

$$\begin{aligned} \sum_{\alpha=1}^{m} R_\alpha x_\alpha^i y_\alpha^j z_\alpha^k &= \frac{a_1^i a_2^j a_3^k}{(i+1)(j+1)(k+1)} && \begin{matrix} i, j, k \text{ even} \\ i+j+k \le n \end{matrix} \\ &= 0 && \text{otherwise} \end{aligned} \; .$$

The above formula gives a set of equations that must be satisfied if the integration formula I_1 is to be exact and if F(x,y,z) is a polynomial of degree n.

To derive an integration formula for six points and third degree accuracy, consider

$$\sum_{\alpha=1}^{6} R_\alpha = 1 \qquad \sum_{\alpha=1}^{6} R_\alpha y_\alpha = 0 \qquad \sum_{\alpha=1}^{6} R_\alpha z_\alpha = 0$$

$$\sum_{\alpha=1}^{6} R_\alpha x_\alpha = 0 \qquad \sum_{\alpha=1}^{6} R_\alpha y_\alpha^2 = \frac{a_2^2}{3} \qquad \sum_{\alpha=1}^{6} R_\alpha z_\alpha^2 = \frac{a_3^2}{3}$$

$$\sum_{\alpha=1}^{6} R_\alpha x_\alpha^2 = \frac{a_1^2}{3} \qquad \sum_{\alpha=1}^{6} R_\alpha y_\alpha^3 \qquad \sum_{\alpha=1}^{6} R_\alpha z_\alpha^3 = 0$$

$$\sum_{\alpha=1}^{6} R_\alpha x_\alpha^3 = 0$$

$$\sum_{\alpha=1}^{6} R_\alpha x_\alpha y_\alpha = 0 \qquad \sum_{\alpha=1}^{6} R_\alpha x_\alpha z_\alpha = 0 \qquad \sum_{\alpha=1}^{6} R_\alpha x_\alpha^2 y_\alpha = 0$$

$$\sum_{\alpha=1}^{6} R_\alpha x_\alpha^2 z_\alpha = 0 \qquad \sum_{\alpha=1}^{6} R_\alpha x_\alpha y_\alpha^2 = 0 \qquad \sum_{\alpha=1}^{6} R_\alpha x_\alpha z_\alpha^2 = 0$$

$$\sum_{\alpha=1}^{6} R_\alpha y_\alpha z_\alpha = 0 \qquad \sum_{\alpha=1}^{6} R_\alpha y_\alpha^2 z_\alpha \qquad \sum_{\alpha=1}^{6} R_\alpha y_\alpha z_\alpha^2 = 0$$

$$\sum_{\alpha=1}^{6} R_\alpha x_\alpha y_\alpha z_\alpha = 0 \quad .$$

If $R_\alpha = \frac{1}{6}$ $\alpha = 1, 2, \cdots, 6$ and the six points of integration are $(\pm a_1, 0, 0), (0, \pm a_2, 0)$ and $(0, 0, \pm a_3)$ all of the above twenty equations are satisfied. Hence,

$$I_1 = \frac{8}{6} a_1 a_2 a_3 \Big[\sum F(\pm a_1, 0, 0) + \sum F(0, \pm a_2, 0) + \sum F(0, 0, \pm a_3) \Big] .$$

An idea of the error can be obtained if one considers integrating a fourth order polynomial with the above formula and then subtracting the results from the true value. The result is

$$\Sigma' = \frac{8}{45} a_1 a_2 a_3 \Big[6 (A_{400} a_1^4 + A_{040} a_2^4 + A_{004} a_3^4) - 5 (A_{020} a_1^2 a_2^2 + A_{202} a_1^2 a_3^2 + A_{022} a_2^2 a_2^2) \Big] .$$

An alternate placement of points can be obtained with the eight points at each corner and the center of the parallelepiped.

$$I_1 = \frac{1}{3} a_1 a_2 a_3 \left[16 F(0,0,0) + \sum F(\pm a_1, \pm a_2, \pm a_3)\right]$$

with

$$E' = \frac{16}{45} a_1 a_2 a_3 \left[3(A_{400} a_1^4 + A_{040} a_2^4 + A_{004} a_3^4) + 5(A_{220} a_1^2 a_2^2 + A_{202} a_1^2 a_3^2 + A_{022} a_2^2 a_3^2)\right]$$

This method becomes very tedious as the degree of the polynomial increases. A slightly different approach is possible. If a fifth degree polynomial is integrated, the results are

$$\begin{aligned} I = 8 a_1 a_2 a_3 \Big(A_{000} &+ \frac{1}{3}(A_{200} a_1^2 + A_{020} a_2^2 + A_{002} a_3^2) \\ &+ \frac{1}{5}(A_{400} a_1^4 + A_{040} a_2^4 + A_{004} a_3^4) + \frac{1}{9}(A_{022} a_2^2 a_3^2 \\ &+ A_{202} a_1^2 a_3^2 + A_{220} a_1^2 a_2^2)\Big) \end{aligned}$$

$$= \frac{8}{45} a_1 a_2 a_3 (45M + 15N + 9N + 5Q)$$

where

$$M = A_{000} \qquad N = A_{200} a_1^2 + A_{020} a_2^2 + A_{002} a_3^2$$

$$P = A_{400} a_1^4 + A_{040} a_2^4 + A_{004} a_3^4$$

$$Q = A_{220} a_1^2 a_2^2 + A_{202} a_1^2 a_3^2 + A_{022} a_2^2 a_3^2 .$$

If the center of the parallelepiped (0, 0, 0) is chosen for one of the function values then F(0, 0, 0) = Aooo = M. If the six centers of the faces are considered, the sum of the function values is

$$\begin{aligned} \sum F(\pm a_1, 0, 0) + \sum F(0, \pm a_2, 0) + \sum F(0, 0, \pm a_3) &= 2(A_{200} a_1^2 \\ &+ A_{400} a_1^4 + A_{020} a_2^2 + A_{040} a_2^4 + A_{002} a_3^2 \\ &+ A_{004} a_3^4) + 6 A_{000} \\ &= 2N + 2P + 6M . \end{aligned}$$

Now consider the points located at the eight corners

$$\Sigma F(\pm a_1, \pm a_2, \pm a_3) = 8(A_{000} + A_{200} a_1^2 + A_{020} a_2^2 + A_{002} a_3^2 + A_{400} a_1^4 + A_{040} a_2^4$$
$$+ A_{004} a_3^4 + A_{220} a_1^2 a_2^2 + A_{202} a_1^2 a_3^2 + A_{022} a_2^2 a_3^2)$$
$$= 8(M + N + P + Q),$$

If these 15 points are to give the value of the integral, I, the three sets above must be properly weighted. Let

$$45M + 15N + 9P + 5Q = \alpha M + \beta(8M + 2N + 2P) + 8\gamma(M + N + P + Q).$$

Equating coefficients $8\gamma = 5$

$$2\beta + 8\gamma = 9$$
$$2\beta + 8\gamma = 15$$
$$\alpha + 8\beta + 8\gamma = 45 .$$

These equations are inconsistent and, hence, it is impossible to obtain a fifth degree accuracy by utilizing the chosen points.

If one adds the six midpoints of the segments that join the center of the parallelepiped to the centers of each face, it is possible to get a 21 point formula.

$$\Sigma F(\pm \tfrac{a_1}{2}, 0, 0) + \Sigma F(0, \pm \tfrac{a_2}{2}, 0) + \Sigma F(0, 0, \pm \tfrac{a_3}{2})$$
$$= 6A_{000} + 2(\tfrac{a_1^2}{4} A_{200} + \tfrac{a_2^2}{4} A_{020} + \tfrac{a_3^2}{4} A_{002} + \tfrac{a_1^4}{16} A_{400}$$
$$+ \tfrac{a_2^4}{16} A_{040} + \tfrac{a_3^4}{16} A_{004})$$

$$= 6M + \tfrac{1}{2} N + \tfrac{1}{8} P$$

Consider

$$45M + 15N + 9P + 5Q = \alpha M + \beta(6M + 2N + P)$$
$$+ 8\gamma(M + N + P + Q) + \delta(6M + \tfrac{1}{2} N + \tfrac{1}{8} P).$$

This yields

$$\begin{aligned} \alpha + 6\beta + 8\gamma + 6\delta &= 45 \\ 2\beta + 8\gamma + \tfrac{1}{2}\delta &= 15 \\ 2\beta + 8\gamma + \tfrac{1}{8}\delta &= 9 \\ 8\gamma &= 5 , \end{aligned}$$

With the solution $\alpha = -62, \beta = 1, \gamma = \frac{5}{8}, \delta = 16$.

With these values

$$I_1 = \frac{8}{45} a_1 a_2 a_3 \left(-62 F_1 + 16 \Sigma F_2 + \Sigma F_3 + \frac{5}{8} \Sigma F_4\right),$$

or $$I_1 = \frac{1}{45} a_1 a_2 a_3 \left(-496 F_1 + 128 \Sigma F_2 + 8 \Sigma F_3 + 5 \Sigma F_4\right)$$

where $F_1 = F(0, 0, 0)$,

ΣF_2 = the sum of the function values at the 6 points midway from the center of the parallelepiped to the six faces,

ΣF_3 = the sum of values of the function at the 6 centers of the faces,

ΣF_4 = the sum of values of the function at the 8 vertices.

It should be noted that the general ternary quintic has 56 terms that might contribute to error. The above formula provides fifth degree accuracy with only 21 points; hence, it controls polynomial error very well.

Another formula is of interest because all its points lie on the surface. It was derived by Sadowsky (12). This 42-point formula with fifth degree accuracy is

$$\int_{-1}^{1}\int_{-1}^{1}\int_{-1}^{1} \mu(x,y,z)\,dx\,dy\,dz = \frac{4}{225}\left[91 \Sigma \mu_6 - 4 \Sigma \mu_{12} + 16 \Sigma \mu_{24}\right].$$

where $\Sigma\mu_6$ denotes the sum of the six values of $\mu(x, y, z)$ at the centers of the six faces of the cube.

$\Sigma\mu_{12}$ denotes the sum of the values of $\mu(x, y, z,)$ at the midpoints of the twelve edges of the cube.

$\Sigma\mu_{24}$ denotes the sum of the values of $\mu(x, y, z)$ at the four points on the diagonals of each face at a distance of $1/2\sqrt{5}$ from the center of the face. Sadowsky also concludes that 42 is the minimum number of points that will give fifth degree accuracy with the restriction that all points lie on the surface of the cube.

Extended Simpson's Rule

For the present problem, the author felt that the best balance between accuracy, speed, ease of programming, and economy was obtained with the successive application of Simpson's rule to the integral over small cubes. Perhaps Gaussian quandrature would have given better accuracy; however, it was desired to be able to use the values of the integrand already evaluated in successively finer grids. The simpler trapezoid rule was judged to have too large an error. It must be realized that the primary purpose of this investigation was to determine the order of magnitude of the three-body terms. With this in mind, speed and economy of computation became important and evaluation of the integrals to two or three significant figures was acceptable.

If $f(x)$ is evaluated at points $x_o, x_1, \ldots, x_n$ when $x_i - x_{i-1} = h$ for $i = 1, 2, \ldots, n$, Simpson's rule for the interval (x_{i-1}, x_{i+1}) is

$$\int_{x_{i-1}}^{x_{i+1}} f(x)\,dx = \frac{h}{3}\left[f(x_{i-1}) + 4f(x_i) + f(x_{i+1})\right] - E$$

where $E = \frac{h^5}{90} f^{(iv)}(\xi) \qquad x_{i-1} \le \xi \le x_{i+1}$.

This formula and the error term may be derived by various considerations and is discussed in standard texts on numerical analysis, e.g., Hildebrand (5).

To derive a formula for triple integration over a cube, consider points with spacing h, l, and n in the x, y, and z directions, respectively. Let (x_i, y_j, z_k) be the center of the cube. Use a notation similar to above and $f(x_i, y_j, z_k) = f_{ijk}$ to obtain

$$I = \int_{z_{k-1}}^{z_{k+1}} \int_{y_{j-1}}^{y_{j+1}} \int_{x_{i-1}}^{x_{i+1}} f(x, y, z)\, dx\,dy\,dz \; .$$

The successive application of Simpson's rule gives

$$\begin{aligned} I = \frac{h\ell n}{27} \big(& f_{i-1,j-1,k-1} + f_{i-1,j-1,k+1} + f_{i-1,j+1,k-1} + f_{i-1,j+1,k+1} \\ & + f_{i+1,j-1,k-1} + f_{i+1,j-1,k+1} + f_{i+1,j+1,k-1} + f_{i+1,j+1,k+1} \\ & + 4[f_{i-1,j-1,k} + f_{i-1,j+1,k} + f_{i-1,j,k-1} + f_{i-1,j,k+1} + f_{i,j-1,k+1} \\ & + f_{i,j+1,k-1} + f_{i,j+1,k+1} + f_{i,j-1,k-1} + f_{i+1,j+1,k} + f_{i,j-1,k-1} \\ & + f_{i+1,j,k-1} + f_{i+1,j,k+1}] + 16[f_{i-1,j,k} + f_{i,j,k-1} + f_{i,j,k+1} \\ & + f_{i,j-1,k} + f_{i,j+1,k} + f_{i+1,j,k}] + 64 f_{i,j,k} \end{aligned} \qquad (5\text{-}1)$$

with an error term of

$$E = \frac{-2h\ell n}{45}\left[h^4 \frac{\partial^4 f(x_1', y_1', z_1')}{\partial x^4} + \ell^4 \frac{\partial^4 f(x_2', y_2', z_2')}{\partial y^4} + n \frac{\partial^4 f(x_3', y_3', z_3')}{\partial z^4}\right]$$

$$x_{i-1} \le x_m' \le x_{i+1} \; ; \quad y_{j-1} \le y_m' \le y_{j+1} \; ; \quad z_{k-1} \le z_m' \le z_{k+1} \; ; \quad m = 1, 2, 3 \; .$$

The above formula, though formidable, is relatively easy to program in FORTRAN IV.

The integrals in question were evaluated by dividing the region of integration into cells and then applying this formula to each cell. The error term becomes

$$E = -\frac{h\ell n}{90}\left(ph^4\,\frac{\partial^4 f(\bar{x}_1',\bar{y}_1',\bar{z}_1')}{\partial x^4} + q\ell^4\,\frac{\partial^4 f(\bar{x}_2',\bar{y}_2',\bar{z}_2')}{\partial y^4} + rh^4\,\frac{\partial f(\bar{x}_3',\bar{y}_3',\bar{z}_3')}{\partial z^4}\right)$$

where p, q, and r are the number of steps in the x, y, and z, directions, respectively.

The integrals extend over a semi-infinite region for two of the variables; however, the integrand goes to zero rather rapidly for most values of the parameter K. As a consequence, the integrals over the semi-infinite range may be truncated with a small error. The actual integration was performed by stepping x_{ac} and x_{bc} by a unit distance, by integrating over the added region, and by adding this result to the previous value. Then a comparison was made to determine the amount of change. If this change was sufficiently small, the integration was stopped. In most of the integrations, this value was chosen as .0001. For values of K greater than .05, the integration was stopped with x_{ac} and x_{bc} less than 20. All other integrals where terminated at $x_{ac} = x_{bc} = 20$. The greatest change between $x_{ac} = x_{bc} = 19$ and $x_{ac} = x_{bc} = 20$ was 4%, which is considered acceptable. To extend the integral to $x_{ac} = x_{bc} = 21$ would require the calculation of 1640 cells, even with rather crude spacing. This becomes expensive in terms of machine time.

The main calculation of integrals was obtained on an IBM 7094 at Goddard Space Flight Center in about 66 minutes. Supplemental calculations were obtained with the IBM 1620 computer at the Engineering Computing Laboratory. The values of the integrals for various cases are tabulating in Table IV. Note that the values do not include the coefficient $8\pi^2 a^6$.

Differentiation Formula

The second numerical problem is to determine the derivation with respect to K of the functions that are tabulated above. The spacing of the values of K are not uniform. Most differentiation formulas require equal spacing of the variable. To devise a differentiation formula, it was decided to pass a parabola through three adjacent points and then calculate the derivative at the middle-point.

Let f_{i-1}, f_i and f_{i+1} be the function values at x_{i-1}, x_i, and x_{i+1}, respectively. Let

$$f(x) = A_1 (x - x_i)^2 + A_2 (x - x_i) + A_3 , \tag{5-2}$$

If

$$x_i - x_{i-1} = c_1$$

$$x_{i+1} - x_i = c_2$$

$$x_{i+1} - x_{i-1} = c_1 + c_2 = c_3 ,$$

then

$$x = x_i \Rightarrow f(x) = f(x_i) = f_i = A_3$$

$$x = x_{i-1} \Rightarrow f_{i-1} = A_1 c_1^2 - A_2 c_1 + f_i \tag{5-3}$$

$$x = x_{i+1} \Rightarrow f_{i+1} = A_1 c_2^2 + A_2 c_2 + f_i \, . \qquad (5\text{-}4)$$

Equations 5-3 and 5-4 can be solved simultaneously for A_1 and A_2 with the results

$$A_1 = \frac{f_{i-1}}{c_1 c_3} + \frac{f_{i+1}}{c_2 c_3} - \frac{f_i}{c_1 c_2}$$

and

$$A_2 = \frac{1}{c_3}\left(\frac{c_2}{c_1}(f_i - f_{i-1}) + \frac{c_1}{c_2}(f_{i+1} - f_i)\right) .$$

If equation 5-2 is differentiated with respect to x,

$$f'(x) = 2A_1(x - x_1) + A_2$$

$$x = x_i \Rightarrow f'(x) = A_2 \quad .$$

At the left end point

$$x = x_0 \qquad i = 1$$

$$f'(x_0) = -2A_1 c_1 + A_2 \; .$$

At the right end point

$$x = x_{i+1} \qquad i = n-1$$

$$f'(x_n) = 2 c_2 A_1 + A_2 \; .$$

From these formulas it is easy to generate a table of derivatives for use in the ionization program.

Langrangian Interpolation

In the program to use the theory that was discussed in Chapter 4, it is necessary to calculate a value for K and then find the value of the derivative of the free energy with respect to K at that point. Since it is impractical to evaluate the cluster integrals each time in that program, interpolation between tabulated values is used. There are various ways to perform such interpolations and, again, the unequal spacing of the values of K complicates matters. Linear interpolation was rejected because large inaccuracies may occur. It was decided that a six point, Lagrangian interpolation would be performed. The polynomial coefficients may be conveniently calculated in a computer program. Lagrangian polynomial interpolation is discussed in McCormick and Salvadori (8). Briefly, the fifth degree polynomial may be passed through six points.

$$P_j(x) = A_j (x-x_0)(x-x_1)\cdots(x-x_{j-1})(x-x_{j+1})\cdots(x-x_5)$$

where

$$A_j = \frac{1}{(x_j-x_0)(x_j-x_1)\cdots(x_j-x_{j-1})(x_j-x_{j+1})\cdots(x-x_5)}$$

which is equal to zero for all x_i, except i equals j.

Now consider the linear combination

$$P_5(x) = \sum_{i=0}^{5} f_i P_i(x).$$

Note that

$$\begin{aligned} P_5(x_i) &= f_0 P_0(x_i) + \cdots + f_i P_i(x_i) + \cdots + f_5 P_5(x_i) \\ &= 0 \cdot f_0 + \cdots + f_i \cdot 1 + \cdots + f_5 \cdot 0 \\ &= f_i . \end{aligned}$$

Hence, the polynomial $P_5(x)$ passes through the six given points regardless of the uneven spacing.

Approximations

Throughout the calculations, approximations were employed for the functions in order to obtain greater accuracy, or speed. For example, the ionization program involves a square root of a number that is sometimes very near 1. Then 1 is subtracted from the results. All significance can be lost in some cases. This can be prevented by expanding the square root of 1 + δ by a Taylor series about $\delta = 0$

$$\sqrt{1+\delta} = 1 + \frac{1}{\sqrt{1+0}} \cdot \delta - \frac{1}{4(\sqrt{1+0})^2} \frac{\delta^2}{2!} + \frac{3}{8} \frac{\delta^3}{3!} - \frac{15}{16} \frac{\delta^4}{4!} + \cdots$$

$$= 1 + \frac{1}{2}\delta - \frac{1}{8}\delta^2 + \frac{3}{48}\delta^3 - \frac{15}{384}\delta^4$$

so that

$$\sqrt{1+\delta} - 1 = \frac{1}{2}\delta - \frac{1}{8}\delta^2 + \frac{3}{48}\delta^3 .$$

If δ is less than 10^{-4} this will give at least eight significant digits; whereas a calculation of $\sqrt{1+\delta} - 1$ with eight digits in each operation will generate a number with three significant figures at the most.

Another case similar to this arises in the evaluation of the integrand of the cluster integrals.

Consider $e^{-\delta} - 1 + \delta$

expanding $e^{-\delta}$ in a Taylor's series about $\delta = 0$

$$e^{-\delta} - 1 + \delta = \frac{\delta^2}{2!} - \frac{\delta^3}{3!} + \frac{\delta^4}{4!} - \frac{\delta^5}{5!} + \cdots ,$$

For δ less than 10^{-3}, the retention of the first three terms of this expansion will give more than six significant digits.

CHAPTER VI

SUMMARY AND CONCLUSIONS

An acceptable expression for the Helmholtz Free Energy can be very useful in the quanitative analysis of a plasma. If it is desired to work only within the framework of the classical, many-body problem, the Mayer, cluster integral expansion of the free energy in terms of density is promising. This leads, however, to an infinite series containing progressively more complicated terms. The cluster expansion, using only two-body interactions is relatively simple to handle. In some applications, such as in the regions of high density and low temperature, this simple approach breaks down. In the hope of extending the range of usefulness of the cluster approach and in order to judge the order of magnitude of the next term in the series, the evaluation of the cluster terms which correspond to three-body interactions was carried out for a hydrogen model.

The resulting expression for the free energy was used to calculate the electron number density in a hydrogen plasma. The results were compared to previous calculations which used only two body interactions. From this comparison, it appears that the three body interactions do indeed contribute to the calculation. They do extend the Mayer theory by a significant amount in the case of this hydrogen model.

It is interesting to note that the integrals evaluated and, in fact, the expression for the free energy can be applied to ionic solution of single binary solute and solvent. This may be of interest to the physical chemist in his quantitative investigation of solutions.

The primary interest of the NASA project which supported this work is, of course, the hyperveolicity impact on a metallic target, such as aluminum. In trying to calculate the cluster integrals for this case, many problems arise or intensify over the hydrogen case. Aluminum can take on 15 different charge states. If all different charge products are considered, an enormous number of integrals must be evaluated. The actual distribution of ion states should be investigated to eliminate many of the charge products. For example, if the average energy of the system were such that the aluminum atom was stripped of all but one, or two, of its electrons it is unlikely that one exists with all its electrons. Further study may allow the calculation to be performed easily; however, at the present stage, the problem appears formidable and relatively expensive in terms of computer time.

The applicability of the principal of superposition to the case of aluminum must receive very careful consideration. This, in turn, raises the problem of the γ_3-bond that is discussed in Chapter 3.

If future triple integrations are performed in the evaluation of cluster integrals, it is recommended that the six-point integration formula which is derived in Chapter 5, be given very serious consideration. The 21 point formula should give better accuracy, but would be more cumbersome to employ.

SELECTED BIBLIOGRAPHY

(1) Brout, R. Lecture on the Many-Electron Problem. New York: Interscience Publishers, 1963.

(2) Bruce, R. "A Model and Calculations for the Properties of an Exploding Plasma Sphere" (unpub. Ph.D. Thesis, Oklahoma State University, 1966).

(3) Charters, A. C. "High Speed Impact." Scientific American, 203 (October, 1960), 128-140.

(4) Friedman, Harold L. Ionic Solution Theory. New York: Interscience Publishers, 1962.

(5) Hidebrand, F. B. Introduction to Numerical Analysis. New York: McGraw-Hill Book Company, 1956.

(6) Hill, T. L. Statistical Mechanics. New York: McGraw-Hill Book Company, 1956.

(7) Landau, L. D. and E. M. Lifshitz, Statistical Physics, Vol. 5, Course of Theoretical Physics. Reading, Massachusetts: Addison-Wesley Publishers, 1958.

(8) McCormick, John M. and Mario G. Salvadori. Numerical Methods in FORTRAN. Englewood Cliffs, New Jersey: Prentice-Hall, 1964.

(9) Mayer, J. E. and M. G. Mayer. Statistical Mechanics. New York: John Wiley and Sons, 1940.

(10) Mood, Alexander M. and Franklin A. Graybill. Introduction to the Theory of Statistics. New York: McGraw-Hill Book Company, 1963.

(11) Rouse, Carl A. "Ionization Equilibrium Equation of State." Astrophysical Journal, 134, 435-446. (1961).

(12) Sadowsky, M. "A Formula for Approximate Computation of a Triple Integral." Amer. Math. Monthly, 47, 539-543. (1940).

(13) Sun, C. E., H. Eyring, and H. Sershinowitz. J. Chem. Phys. 3 (1935), 786.

(14) Tyler, G. W. "Numerical Integration of Functions of Several Variables." Canadian Journal of Mathematics, 5 (1953), 353-412.

APPENDIX

EXPLANATION OF TABLE

The values of the cluster integrals, which are discussed in Chapter III, are listed in Table 1. Note that the tabulated entries must be multiplied by $8\pi^2a^6$ to give the true value of the cluster integral for the appropriate value of the parameter K.

TABLE IV

VALUES OF CLUSTER INTEGRALS

K	Case										
	II-2	III-2	IV-2	V-2	VIII-1	VIII-2	IX-1	IX-2	X-1	XI-1	XI-2
10.0	-.0972	-.105	-.124	-.112	-.00308	-.0601	.00321	-.0738	-.00356	.00329	-.0732
8.75	-.189	-.215	-.125	-.111	-.00546	-.0548	.00569	-.118	-.00657	.00588	-.114
7.5	-.116	-.108	-.128	-.109	-.00632	-.0890	.00662	-.120	-.00840	.00697	-.111
6.25	-.279	-.326	-.131	-.105	-.0106	-.0794	.0115	-.124	-.0152	.0118	-.118
5.0	-.182	-.222	-.0644	-.0981	-.0111	-.0342	.0131	-.0791	-.0204	.0129	-.0765
2.5	-.237	-.369	-.0374	-.125	-.0173	-.00129	.0291	-.0748	-.0907	.0252	-.0699
1.0	-.238	-.563	.0100	-.165	-.0102	+.0116	.00504	.0227	-.363	-.0180	+.0354
.75	-.223	-.768	.0243	-.173	-.0126	.0124	-.0298	.0743	-.470	-.0609	.0748
.5	-.187	-.983	.0423	-.181	-.0342	.0172	-.0964	.145	-.597	-.133	.144
.25	-.124	-1.21	.0655	-.184	-.185	.0500	-.167	.250	-.760	-.155	.266
.1	-.413	-1.43	.0829	-.182	-.969	.155	.338	.351	-1.26	.587	.364
.075	-.0836	-1.65	.0861	-.181	-1.49	.213	.807	.403	-1.78	1.16	.410
.05	+.177	-1.87	.0894	-.180	-2.55	.303	1.84	.493	-2.93	2.35	.509
.025	.271	-2.09	.0928	-.179	-5.168	.494	4.51	.662	-5.95	5.16	.725
.01	.368	-2.32	.0949	-.178	-8.81	.742	7.25	.778	-10.12	9.14	1.00
.005	.466	-2.54	.0956	-.178	-10.77	.869	10.42	.904	-12.41	11.29	1.15
.001	.564	-2.76	.0962	-.178	-12.75	.998	12.54	1.12	-14.75	13.46	1.30
.0005	.663	-2.98	.0963	-.178	-13.04	1.02	12.84	1.33	-15.08	13.77	1.32
.0001	.761	-3.20	.0963	-.178	-13.27	1.03	13.09	1.55	-15.35	14.02	1.34

VITA

Hugh Allan Reeder

Candidate for the Degree of

Master of Science

Thesis: EVALUATION OF MAYER CLUSTER INTEGRALS FOR THREE-BODY INTERACTIONS AND SELECTED TOPICS IN NUMERICAL INTEGRATION OF TRIPLE INTEGRALS

Major Field: Mathematics

Biographical:

Personal Data: Born in Corsicana, Texas, January 20, 1938, the son of Robert C. and Anna Mae Reeder.

Education: Attended grade school and high school in Corsicana and Waco, Texas; graduated from Waco High School in 1956; received Bachelor of Arts degree from Rice University, with majors in Mathematics and Physics, in June, 1960; completed requirements for Master of Science degree in May, 1968.

Professional Experience: Entered United States Navy in 1960 and has extensive experience in electronics, communications, and operations; member of the Society of Industrial and Applied Mathematics.