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## A Study of Integral Equations for Computing Radial Distribution Functions

Robert C. Scherzer

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A STUDY OF INTEGRAL EQUATIONS FOR  
COMPUTING RADIAL DISTRIBUTION FUNCTIONS

by

Robert C Scherzer

A Thesis  
Submitted to the  
Faculty of The Graduate College  
in partial fulfillment of the  
requirements for the  
Degree of Master of Arts  
Department of Physics

Western Michigan University  
Kalamazoo, Michigan  
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# A STUDY OF INTEGRAL EQUATIONS FOR COMPUTING RADIAL DISTRIBUTION FUNCTIONS

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Western Michigan University, 1984

The use of integral equations to find radial distribution functions for computing thermodynamic properties is examined. The system considered is a simple classical fluid with interactions according to the Lennard-Jones (6-12) pair potential function. Two parametric integral equations (C and T) are studied in detail. Derivation of equation T and a power series solution are given. Computer solutions at several different temperatures, densities, and parameter values are obtained. Comparisons are made between these results and results from integral equation N, PY, and HNC, and results from Monte Carlo, molecular dynamics, and power series methods. Equations C and N are found to give nearly identical results with parameters chosen in a similar way. At the reduced temperature 2.74 equation T gives good agreement with "exact" results over a wide density range. Additional studies of equation T should be done at lower temperatures where previous integral equations have not worked well.

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Robert C Scherzer

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## CHAPTER I

### INTRODUCTION

A major goal in statistical mechanics is to relate the microscopic interaction of molecules to the macroscopic thermodynamic properties that are observed. This connection, which enables the calculation of macroscopic properties from a knowledge of the microscopic interaction, is the ultimate objective, but the process of getting there is often complicated and difficult. It is only in the cases of very dilute gases and nearly perfect crystals, that this connection is fairly well established. In the range of moderately dense gases to liquids the problem becomes very complex, and so far it has been necessary to use approximations to be able to make any significant progress.

On the one side of this problem are the intermolecular interactions which are very complex. The difficulty can be seen by considering a two particle system of spherically symmetric molecules. There are short-range repulsive forces due to electron interactions and nuclei electromagnetic interactions, which are both very complicated, and there are long-range attractive forces made up of electrostatic contributions, including induction contributions, and dispersion contributions, which are also very complicated. Because of these complexities and the resulting uncertainties,

the problem is made easier by using simplified potential energy functions. For one thing, they make the problem mathematically solvable and for another they remove the uncertainty from the problem of interpreting the results. Variation in results is then never due to a problem with the potential energy function, but only due to the theory being tested.

On the other side of the micro-macro connection problem is the equation of state. Theoretically it should be possible to obtain an equation of state for any substance, but in reality it is never that simple. The familiar ideal gas equation of state,

$$PV = NkT \quad (1)$$

is only good for very low density gases. The van der Waals equation is an improvement over the ideal gas equation, as it takes into account interactions with short-range and long-range terms, but it still falls short for any real system. It is the dense gases and the liquid state that present the problem. They do not have the long-range order of a solid nor do they have the simplicity of an ideal gas. Nor can properties be interpolated from solids or low density gases.

Anyone familiar with statistical mechanics might be tempted to seek the partition function as the solution to the problem, since once it is known it can be used to give a complete thermodynamic description of the equilibrium

system under study. The total phase partition function can be expressed as a cluster expansion and then the problem is just a matter of evaluating the cluster integrals. However, it is not that simple. Besides the difficulty of solving the cluster integrals, it is found at higher densities (densities still considerably below the liquid phase) that the series will not converge.

Therefore, a different direction is needed. Instead of seeking the partition function the distribution function is studied. The radial distribution function is related to the probability that if a reference particle is at the origin a second particle will be found at a location  $r$ . For an ideal gas  $g(r) = 1$ , which means that the distribution is uniform and no particular location is any more or less likely to contain a particle than any other. For a real fluid  $g(r) = 0$  at values of  $r$  less than the molecular diameter. The qualitative features of the structure of a substance are reflected in its radial distribution function. We see almost no structure in a gas, some short-range structure in a liquid, but no long-range order, and both short and long-range order in a solid. For a simple classical fluid once the radial distribution function is known the pressure, internal energy, and other properties can be calculated from it. The purpose of this study is to examine the integral equations from which radial distribution functions are calculated.

## CHAPTER II

### THEORY

#### The System

In this study only simple classical fluids are considered. This is a system of spherically symmetric particles with only radial forces between particles that can be described adequately by classical mechanics (quantum mechanics is not needed). By fluid is meant a substance in the liquid, vapor or gas phase. The potential energy of this system can be represented as a sum of pair interactions,

$$\phi_N = \sum_{i>j} \phi(r_{ij}) = \sum_{i>j} \phi_{ij} \quad (2)$$

where  $r_{ij}$  is the distance between particle  $i$  and  $j$ .

In reality this is not true. The potential energy of three particles is not just the sum of three separate pair potentials, but rather includes a term for the three body interaction. In the case of more particles in the system, more terms would have to be added to the energy expression,

$$\phi_N = \sum_{i>j} \phi_{ij} + \sum_{i>j>k} \phi_{ijk} + \dots \quad (3)$$

The two body terms are dominant, followed by the three body terms, then four body and so on. These higher order terms become significant only at higher densities and lower temperatures. However, pairwise additivity is assumed in this



study and these higher order terms are neglected.

Also, as was stated in the introduction, a simplified potential energy function is used to make the mathematics manageable and remove the potential energy function from the source of uncertainties. The potential energy function used is the Lennard-Jones (6-12) pair potential function<sup>1</sup> given by

$$\phi(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right], \quad (4)$$

where  $-\epsilon$  is the minimum energy and

$\sigma$  is the separation at which the energy equals zero.

There are two contributions to this potential function-- a short-range repulsive term (with no precise theoretical justification) and a long-range attractive term (theoretically from the dispersion energy contribution). The parameters  $\sigma$  and  $\epsilon$  are used to force agreement between experimental data and the calculated values. The typical shape of the Lennard-Jones potential is shown in figure 1.

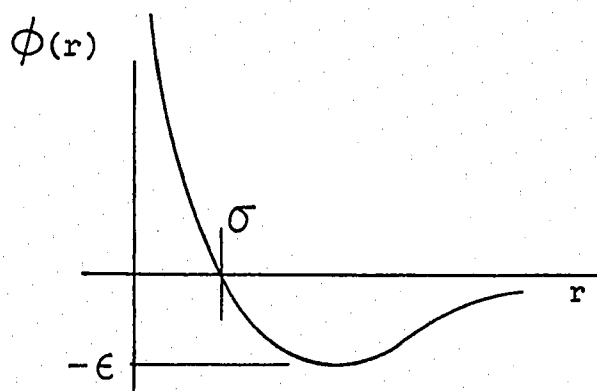


Figure 1. Lennard-Jones potential.

Although this potential function is more realistic than many of the simplified potential energy functions that are used, it must be kept in mind that it is not completely accurate in representing the potential for a real substance. Since the potential function has the general shape of real effective pair potentials, qualitative agreement between the thermodynamic properties of this theoretical fluid and real fluids can be expected, but not exact agreement. The Lennard-Jones potential is also useful because it has been extensively studied and thus considerable data are available for comparison.

#### Radial Distribution Function

If the average particle number density is  $n(r)$  at a distance of  $r$  from a selected particle and if  $\bar{n}$  is the particle number density of the system, then the radial distribution function is defined to be

$$g(r) = \frac{n(r)}{\bar{n}} \quad (5)$$

As can be seen, the radial distribution function is related to the molecular distribution, and therefore gives an indication of the structure as related to the origin. The structure in a dense gas or a liquid is correlated to the origin molecule only over a short distance. Beyond that point it is unaffected by the origin molecule. See figure 2.

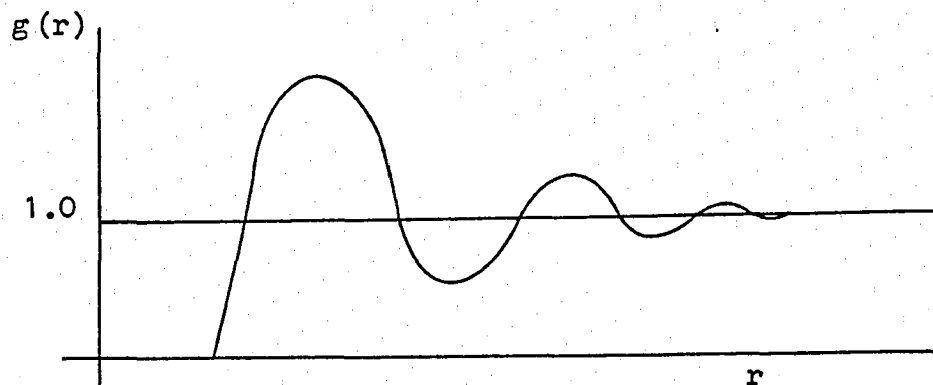


Figure 2. Radial distribution function.

The first peak occurs near the potential energy minima and peaks decrease in amplitude moving out from the origin, indicating the decrease in correlation.

The thermodynamic properties can be written in terms of the radial distribution function. For internal energy this is<sup>2</sup>

$$U = \frac{3}{2} NkT + \frac{2\pi N^2}{V} \int_0^{\infty} \phi(r) g(r) r^2 dr, \quad (6)$$

where  $N$  is the number of particles

$k$  is Boltzmann's constant

$V$  is the volume

and  $\phi(r)$  is the pair potential energy.

The first term,  $3/2 NkT$  is the kinetic energy (for an ideal gas) contribution. For pressure the expression is<sup>3</sup>

$$P = \bar{n}kT - \frac{2\pi\bar{n}^2}{3} \int_0^\infty g(r) \frac{d\phi(r)}{dr} r^3 dr. \quad (7)$$

At this time the total correlation function is introduced,

$$h(r) = g(r) - 1$$

This is a measure of the variation about the uniform density caused by the reference molecule at the origin. As  $r$  becomes large,  $g(r)$  goes to one and therefore  $h(r)$  goes to zero. The Ornstein-Zernike equation<sup>4</sup> relates the direct and indirect correlations to the total correlation,

$$\underset{\text{total}}{h(r_{12})} = \underset{\text{direct}}{c(r_{12})} + \bar{n} \underset{\text{indirect}}{\int c(r_{13})h(r_{23})d\vec{r}_3}, \quad (9)$$

which may be taken as the definition of the direct correlation function. This equation states that the total correlation between molecules 1 and 2 is the sum of two parts--the direct correlation of 1 on 2 and the indirect correlation which includes the direct correlation of 1 on 3 and the total correlation of 2 on 3. The direct correlation is valuable for two reasons--first, it is directly accessible experimentally and both  $g(r)$  and  $c(r)$  can be found from the same scattering data, and second, it and the pair potential, to which it is related, are of about the same range. The form of typical correlation functions can be seen in figure 3.

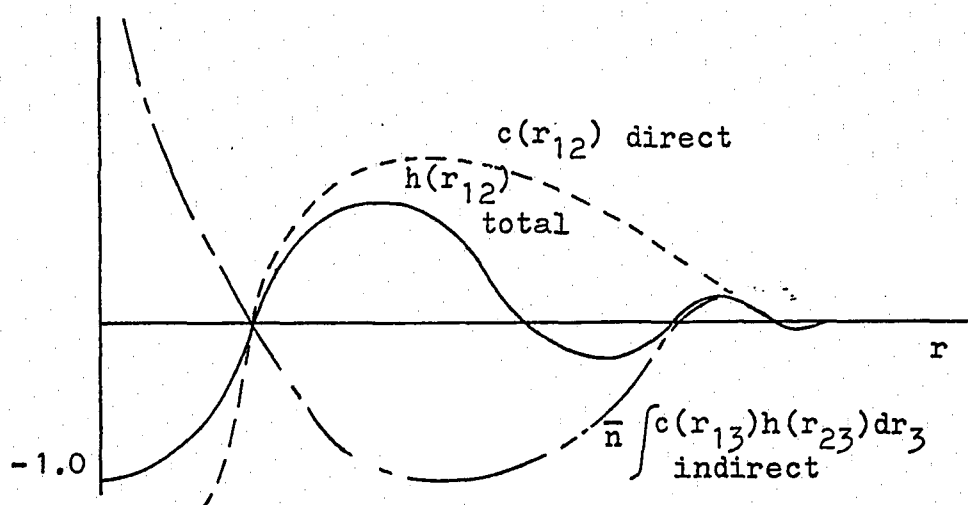


Figure 3. Correlation functions.

By finding  $c(r)$  and substituting it into the compressibility equation of Ornstein and Zernike, an equation of state can be obtained<sup>5</sup>,

$$\frac{1}{kT} \left( \frac{\partial P}{\partial \bar{n}} \right) = 1 - 4\pi \bar{n} \int_0^{\infty} c(r) r^2 dr. \quad (10)$$

Using the virial theorem of Clausius, another equation of state can be found,

$$\frac{PV}{NkT} = 1 - \frac{2\pi N}{3kTV} \int_0^{\infty} g(r) \frac{d\phi(r)}{dr} r^3 dr \quad (7)$$

Equations (7) and (10) will result in the same equation of state if exact values of  $c(r)$  and  $h(r)$  are used. However exact values of  $c(r)$  and  $h(r)$  are not available and approximations have to be used. Therefore inconsistent equations of state often result.

## Integral Equations

There have been several integral equations that have been developed to solve for approximate radial distribution functions. One class of equations, that is not considered in this study, is based upon the Kirkwood superposition approximation<sup>6</sup> (an approximation which equates the probability of seeing three molecules at specific locations to the product of the independent probabilities of seeing the three separate pairs of molecules). Using the total correlation and the Ornstein-Zernike equation to derive integral equations for  $g(r)$  leads to a more accurate radial distribution function.

Starting out with the Ornstein-Zernike equation and making repeated substitutions for  $h(r)$  of  $(c(r) + \text{integral})$  will result in<sup>7</sup>

$$h(12) = c(12) + \bar{n} \int c(13)c(23)d\vec{r}_3 + \bar{n}^2 \iint c(13)c(34)c(42)d\vec{r}_3 d\vec{r}_4 + \dots \quad (11)$$

This is a simple series and if there were a means to close it the problem would be solved. The direct correlation can be expressed as a density expansion to give<sup>8</sup>

$$c(12) = \sum_{a \geq 1} \alpha_{a+1}(12) \bar{n}^{a-1}, \quad (12)$$

$$\text{where } \alpha_{a+1}(12) = \frac{1}{(a-1)!} \int \dots \int \sum \prod f(ij) d\vec{r}_3 \dots d\vec{r}_{N-1} \quad (13)$$

and  $f(ij) = \exp\left(-\frac{\phi_{ij}}{kT}\right) - 1$  --Mayer f-function (14)

(see reference 9 for a discussion of the terms included in equation 13). Using this and writing the direct correlation in diagram form gives,<sup>10</sup>

$$c(12) = \text{---} + \bar{n} \left[ \text{---} \right] + \frac{\bar{n}^2}{2} \left[ 2 \text{---} + 4 \text{---} \right] + \dots \quad (15)$$

where  $\bullet$ ---represent fixed points (fixed at separation  $r_{12}$ )

and  $\circ$ ---represent field points (free to range in accordance with the f-bonds)

and where the cluster integrals are defined as

$$\begin{aligned} \text{---} &= f_{12} \\ \text{---} &= \int f_{12} f_{13} f_{23} d\vec{r}_3 \\ \text{---} &= \int f_{12} f_{13} f_{34} f_{14} f_{23} d\vec{r}_3 d\vec{r}_4 \\ &\text{etc.} \end{aligned} \quad (16)$$

These diagrams can all be classified into one of three designations--

1. simple and netted chain clusters
2. parallel diagrams
3. bridge diagrams.

An expression for the direct correlation function can be found that is exact and closed,<sup>11</sup>

$$c(r) = g(r) - 1 - \ln g(r) - \frac{\phi(r)}{kT} + \text{sum of bridge diagrams} \quad (17)$$

If this last term is dropped the resulting expression is the hypernetted chain (HNC) approximation<sup>12</sup> for the direct correlation function, which can be written as

$$c_{\text{HNC}} = h(r) - \ln g(r) - \frac{\phi(r)}{kT} \quad (18)$$

A similar expression can be written for the Percus-Yevick (PY) approximation,<sup>13</sup> which leaves out other diagrams besides the bridge diagrams,

$$c_{\text{PY}} = h(r) - g(r) \exp \left( \frac{\phi(r)}{kT} \right) + 1 \quad (19)$$

Looking at the merits of these two equations, it is found that they both produce more accurate equations of state than the integral equations based on the Kirkwood superposition approximation. In the HNC equation only the bridge diagrams are left out, whereas in the PY equation these diagrams plus others are left out. Based on this, it would seem logical that the HNC equation, being more complete, should give better results than the PY. "Yet PY is nearly always more accurate than HNC.. It follows that whatever the full effects of the Bridge diagrams, part of their job must be to cancel at least partially the contributions of the other diagrams that are left out of PY."<sup>14</sup>

Looking at the diagrams dropped from the  $\bar{n}^2$  term in figure 4 it can be seen that the three terms that HNC includes, that PY does not, will actually produce a greater



error than totally leaving out all four of these diagrams like PY does.

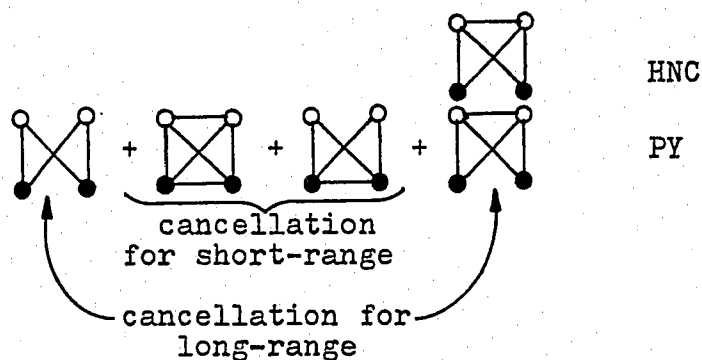


Figure 4. Terms dropped from  $\bar{n}^2$  term.

Using PY and HNC to obtain radial distribution functions and then using the resulting  $g(r)$  in the pressure equation of state and the compressibility equation of state results in inconsistent results for the two equations of state. This is, of course, because PY and HNC are approximations. For PY the pressure equation tends to be on the low side of the correct value and the compressibility equation tends to be on the high side. For HNC the results are just the opposite. Because of this, parametric equations (self-consistent approximations) have been tried which are usually linear combinations of PY and HNC. In a parametric integral equation a parameter is often used to attempt to force consistency.

#### Other Methods

There are two methods (other than integral equations) that are commonly used to determine macroscopic properties from microscopic behavior. These methods, molecular dynamics<sup>15</sup> and Monte Carlo,<sup>16</sup> are often considered to give "exact" results. There are several similarities between these two methods. Both molecular dynamics and Monte Carlo use a cell with a specified number of molecules in it (approximately 100 to 1000). The potential energy function is specified and is usually assumed to be pairwise additive, for simplicity. The coordinates of all the molecules are stored in the computer and the potential energy can be calculated for any configuration. Usually periodic boundary conditions are used to simulate an infinite system. The cell is surrounded by identical replicas of itself. When a molecule leaves the cell being studied, another identical molecule enters at the opposite face, therefore, the total number of molecules in the cell remains constant. It is necessary to assume truncation of the interaction to avoid a particle interacting with more than one image of a particle. Also, the truncation is necessary to make computation practical. The maximum time for an event must be limited to not more than about  $10^{-11}$  sec to keep computer time down (see above reference for explanation).

### Molecular Dynamics

In the molecular dynamics method some initial config-

uration is specified with defined potential and kinetic energies. Then Newton's equations of motion are solved numerically for the system of molecules, and integrated to get the position and velocity distributions. In this process the forces on each molecule resulting from all the others are summed (the minimum image convention is used--the shortest distance to molecules in the same or surrounding cells is used to calculate the energy). The new positions and velocities are then computed after the chosen time increment. From the stored positions and velocities, as a function of time, much information may be determined. The energy and pressure can be calculated, also the partition of energy into kinetic and potential, and transport properties can be determined. Molecular dynamics uses the microcanonical ensemble where total energy is held constant and the temperature is allowed to fluctuate.

#### Monte Carlo

The Monte Carlo method used in statistical mechanics was devised by Metropolis. The same setup is used as in the molecular dynamics method (fixed number of molecules in cells with periodic boundary conditions, etc., except now instead of using Newton's equations to calculate position and velocity distributions, probabilities are calculated). A particular distribution of molecules is started with. One molecule is chosen at random and a random

displacement is made for it. If this results in a decrease in the configurational energy then the move is accepted. If the new energy is higher than the original, then the move is accepted with the probability of

$$P_{ij} = \exp \left( - \frac{\Delta \phi_{ij}}{kT} \right) . \quad (20)$$

The computer selects, at random, a number from 0 to 1 and compares it to  $P_{ij}$ . If  $P_{ij}$  is greater than the random number, the move is accepted. If  $P_{ij}$  is less, it is rejected. If it is rejected, the previous move is counted again. After many such moves have been made, the thermodynamic properties of the system can be determined.

The energy is known for each configuration and the average energy can be determined. The pressure can be determined from the virial theorem. The radial distribution function can be determined from the distance between molecules and the number of pairs in various ranges. It is also possible, as it is in molecular dynamics, to obtain quantities which cannot be measured in real experiments.

It should be pointed out that the movement of these molecules in the Monte Carlo method has no physical significance, unlike the case for molecular dynamics. The movement of molecules is only to provide a sampling over which averages can be made. Monte Carlo uses the canonical ensemble which holds temperature constant and allows the energy to fluctuate. Other than the fact that molecular

dynamics can be used for transport properties, both methods are about equivalent in usefulness. The results of both methods are equally accurate and required computer time is similar.

These computer simulations are desirable because they are mathematically simpler to use than real experiments and eliminate much of the uncertainty in the pair potential, experimental scattering data, etc. The "exact" results that they provide are particularly valuable in evaluating the results of numerical solutions of integral equations. But there are some problems with them. The biggest limitation is the small number of degrees of freedom which can be considered, even on a large computer. The periodic boundary conditions and truncations that are found necessary to simulate an infinite system are not very realistic.

## CHAPTER III

### PARAMETRIC INTEGRAL EQUATIONS

All the integral equations give fairly good results at low densities. It is at the high densities that the discrepancy shows up. The parametric equation is of such a form that the parameter comes in at the higher terms, and therefore has little effect on the low density, but significant effect on the high density. The parameter is then chosen to give good high density results (results that agree with what is considered as exact).

In an effort to gain better insight into the relationships of the various integral equations, a function  $S$  can be introduced,

$$S = h - c. \quad (21)$$

Using this and the total correlation function  $h$  (equation 8), it is possible to write the Percus-Yevick equation (equation 18) in the following form

$$g = e^{-\beta\phi} (1 + S), \quad (22)$$

where

$$\beta = \frac{1}{kT}.$$

Also, the hypernetted chain equation (equation 17) can be written in the following form

$$g = e^{-\beta\phi} e^S = e^{-\beta\phi} (1 + S + \frac{1}{2}S^2 + \frac{1}{6}S^3 + \dots). \quad (23)$$

It can be seen from these that a general expression can be written for these equations of the form<sup>17</sup>

$$g = e^{-\beta\phi} (1 + s + b_2 s^2 + b_3 s^3 + b_4 s^4 + \dots). \quad (24)$$

In the case of the Percus-Yevick equation  $b_2 = b_3 = b_4 = \dots = 0$ , and for HNC the first two coefficients are  $b_2 = \frac{1}{2}$  and  $b_3 = \frac{1}{6}$ .

#### Equation C

One parametric integral equation which is considered in this study is equation C<sup>18</sup>,

$$c = g - 1 - \frac{1}{a} \ln [a g e^{\beta\phi} - a + 1]. \quad (25)$$

This can be written in the form of equation (24) as

$$\begin{aligned} g &= e^{-\beta\phi} \left[ 1 + \frac{1}{a} (e^{as} - 1) \right] \\ &= e^{-\beta\phi} (1 + s + \frac{1}{2} a s^2 + \frac{1}{6} a^2 s^3 + \dots). \end{aligned} \quad (26)$$

From examining equation 26 it can be seen that if "a" equals zero, equation C will be equivalent to PY and if "a" equals one, equation C will be equivalent to HNC. Parameter "a" can be taken as a constant or as a variable. It is found that "a" depends on temperature, and varies "...from 0.248 to 0.442 as  $T^*$  varies from 5.0 to 100.0 for a Lennard-Jones system."<sup>19</sup> It is found that very accurate and thermodynamically consistent results can be obtained with much less computer time than that required by the more exact methods by using equation C to calculate radial distribution

functions.

### Equation T

The other parametric integral equation that is considered in this study is equation T<sup>20</sup>,

$$c = e^{-\beta\phi}(1 + S + b_2 S^2 + b_3 S^3) - 1 - S. \quad (27)$$

This can be written in the form of equation 24 as,

$$g = e^{-\beta\phi}(1 + S + b_2 S^2 + b_3 S^3). \quad (28)$$

In this case  $b_4 = b_5 = b_6 = \dots = 0$ . This differs from equation C in that there are now two parameters rather than only one and the series is terminated.

It can be seen from examining equations 22 and 28 that if  $b_2 = b_3 = 0$  in equation T that it is equivalent to PY. From equations 23 and 28 it can be seen that if  $b_2 = \frac{1}{2}$  and  $b_3 = \frac{1}{6}$  equation T is equal to HNC through the  $S^3$  term. From equations 26 and 28 it can be seen that if  $b_2 = a/2$  and  $b_3 = a^2/6$  equation T equals equation C through the  $S^3$  term. Based upon this it would be expected that equation T should produce results close to equation C at low densities when  $b_2 = a/2$  and  $b_3 = a^2/6$ .

More insight into the relationship of these equations can be gained by examining the density expansion;

$$g e^{\beta\phi} = 1 + \bar{n} \left( \text{---} \circ \text{---} \right) + \bar{n}^2 \left( \text{---} \circ \text{---} \circ \text{---} \right) + 2 \left( \text{---} \circ \triangle \text{---} \right) + A \left( \text{---} \diamond \text{---} \right) + B \left( \text{---} \diamond \text{---} \right) + \dots, \quad (29)$$



where  $\overset{1}{\bullet} - \overset{3}{\circ} - \overset{2}{\bullet} = \int f(13)f(32)d\vec{r}_3$  etc.

The PY, HNC, equation C, and equation T are all exact through the  $\bar{n}$  term. Approximations begin with the  $\bar{n}^2$  term. The values of the parameters A and B are given in table one<sup>21</sup>.

TABLE 1  
Values of Parameters for Density Expansion

Equation	Parameters	
Exact	$A = \frac{1}{2}$	$B = \frac{1}{2}$
HNC	$A = \frac{1}{2}$	$B = 0$
PY	$A = 0$	$B = 0$
C	$A = \frac{a}{2}$	$B = 0$
T	$A = b_2$	$B = 0$

Parameter  $b_3$ , for equation T, does not appear until the  $\bar{n}^3$  term. From this it would be expected that parameter  $b_2$  would be more important at low densities, and that  $b_3$  would only come in at higher densities.

#### Equation N

Another parametric integral equation can be introduced, equation N<sup>22</sup>,

$$c = \xi - 1 - \frac{1 - g e^{\beta \phi}}{g e^{\beta \phi} (a - 1) - a} \quad (30)$$

In this equation parameter "a" is introduced at the  $\bar{n}^2$  density term. It is found that this equation gives very similar results to equation C when the parameters are chosen in a similar way. This can be written in the form of equation 24 as

$$g = e^{-\beta \phi} (1 + S - (a - 1)S^2 + (a - 1)^2 S^3 - \dots) \quad (31)$$

Numerical solutions to equation N are not obtained in this study, but previously obtained results are used for the purpose of comparison.

## CHAPTER IV

### COMPUTATIONAL METHOD

#### Solution of Integral Equations

The only practical way to solve integral equations C (25) and T (27) is numerically on a digital computer. The method used in this study is a Fourier transform method and is essentially that of Broyles<sup>23</sup>. It is an iteration procedure in which each iteration moves closer to the correct answer. This procedure will be illustrated with equation C<sup>24</sup>.

The Fourier transform of the function S (21) is

$$\hat{S}(k) = \frac{1}{2\pi} \iiint s(\vec{r}) e^{i\vec{k} \cdot \vec{r}} d\vec{r} \quad (32)$$

In equation (26) g is written in terms of S

$$g = e^{-\beta\phi} \left[ 1 + \frac{1}{a}(e^{aS} - 1) \right], \quad (26)$$

and c can be written in terms of S as

$$c = e^{-\beta\phi} \left[ \frac{1}{a}(e^{aS} - 1) + 1 \right] - 1 - S \quad (33)$$

The Ornstein Zernike equation (7) can also be written as

$$h(r) = c(r) + \bar{n} \int h(\vec{s}) c(|\vec{s} - \vec{r}|) d\vec{s} \quad (34)$$

where  $\vec{s}$  is another position vector similar to  $\vec{r}$ .

The Fourier transform can be taken of both sides of

equation (34) and it can be combined with equation (21) to obtain

$$\bar{S} = \frac{(2\pi)^3 \bar{n} \bar{c}^2}{1 - (2\pi)^3 \bar{n} \bar{c}}. \quad (35)$$

The flow diagram shown in figure 5 illustrates the method used to find computer numerical solutions for equation C.

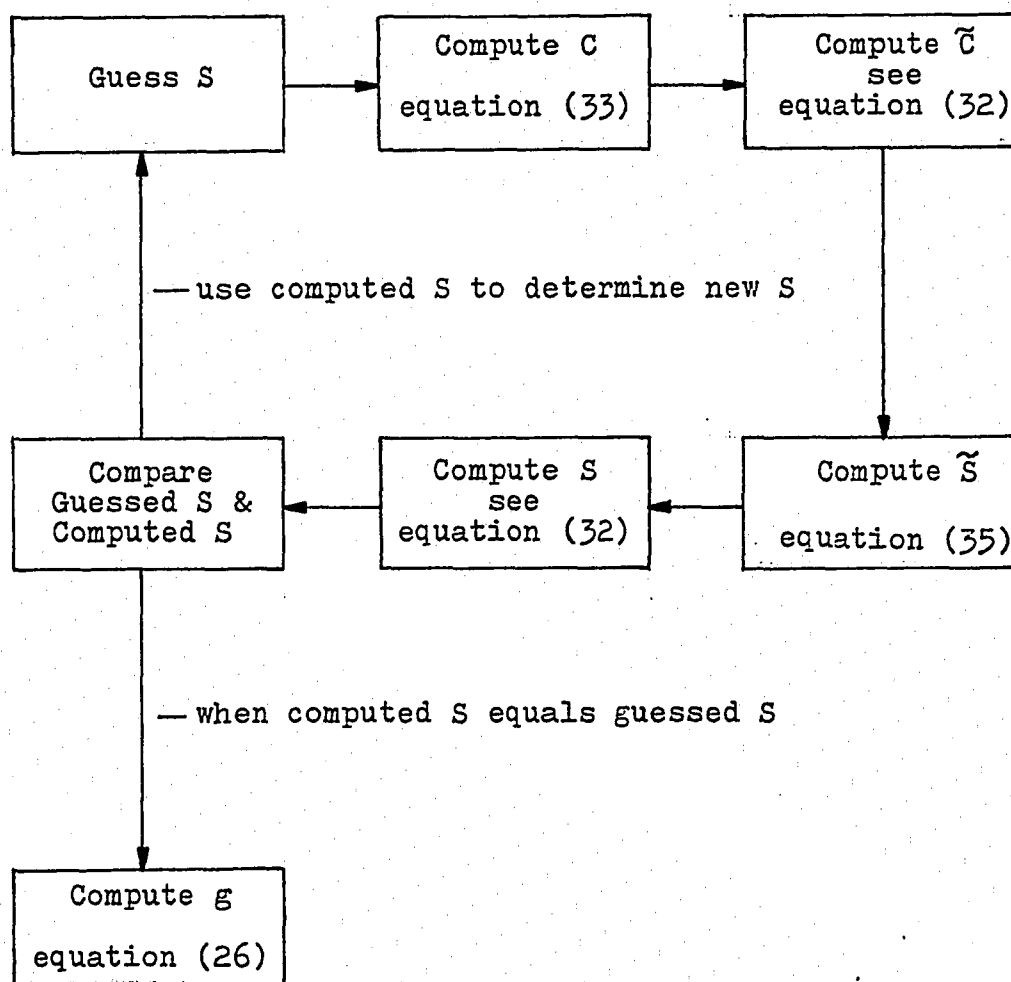


Figure 5. Flow diagram for computing  $g$ .

Using this method, radial distribution functions are computed for several different densities at several isotherms.

### Computing Pressures and Internal Energies

The radial distribution functions are used to calculate the pressure and internal energy using equations (7) and (6), respectively.

There are two interpolation formulas that can be used to extend the solutions to other densities without the need of solving the integral equations through the long iterative procedure. The results thus obtained are, of course, no more accurate than the original data used to obtain them, and may very likely be less accurate. But, the ease with which they may be obtained makes them very useful, and worth the effort. The interpolation formulas for pressure and internal energy<sup>25</sup> are, for constant temperature,

$$p^* = \frac{(1 + a_1 \bar{n}^* + a_2 \bar{n}^{*2} + a_3 \bar{n}^{*3})}{(1 + a_4 \bar{n}^* + a_5 \bar{n}^{*2} + a_6 \bar{n}^{*3})} \quad (36)$$

and

$$U^* = \frac{(a + a_1 \bar{n}^* + a_2 \bar{n}^{*2} + a_3 \bar{n}^{*3})}{(1 + a_4 \bar{n}^* + a_5 \bar{n}^{*2} + a_6 \bar{n}^{*3})} \quad (37)$$

where the dimensionless quantities<sup>26</sup>

$$\bar{n}^* = \bar{n} \sigma^3, \quad (38)$$

$$P^* = \frac{PV}{NkT}, \quad (39)$$

and  $U^* = 2U/3NkT \quad (40)$

are introduced. Also the dimensionless quantity

$$T^* = \frac{kT}{\epsilon} \quad (41)$$

will be introduced at this time, as it will be used later in this study. At low densities these interpolation formulas can be transformed into the virial series,

$$P^* = 1 + b_2 \bar{n}^* + b_3 \bar{n}^{*2} + b_4 \bar{n}^{*3} + \dots \quad (42)$$

$$U^* = 1 + b_2 \bar{n}^* + b_3 \bar{n}^{*2} + b_4 \bar{n}^{*3} + \dots \quad (43)$$

which require less effort to solve but are only useful at very low densities.

#### Determination of Exact Values

Before any progress can be made in work on parametric integral equations "exact" values must be established. Three sources were used to establish the "exact" values used in this study. Monte Carlo results from Wood and Parker<sup>27</sup> are used for the high density values. Extrapolated and interpolated Verlet<sup>28</sup> results were used for mid-range densities. For the low range densities results were used

from Barker<sup>29</sup> for the virial expansion.

Using the density expansion,

$$P^* = 1 + b_2 \bar{n}^* + b_3 \bar{n}^{*2} + b_4 \bar{n}^{*3} + b_5 \bar{n}^{*4} + \dots \quad (42)$$

and coefficients obtained from Carley<sup>30</sup> (which he computed from Barker's results), it was possible to interpolate coefficients for  $T^* = 2.74$ . These coefficients were then used to calculate the pressure, first using only  $b_2$ , then including the next term and so on up to  $b_5$  (the computer program to do this can be found in the appendix). This way it was possible to determine which calculated pressures could be accepted as reliable by noting how much they changed as more terms were included (the more terms included the more exact the result is). As the density increases, the importance of higher order terms increases and therefore this method is only useful at low densities.

All of the accepted values chosen as "exact" were then used with the interpolation formula, equation (36), to obtain "exact" pressures for densities from .05 to 1.00 (in .05 increments) and from .01 to .20 (in .01 increments).

The same thing was done for the internal energy to obtain "exact" values, except without the density expansion values, which were not available.

#### Method of Finding Parameters

Equation C

The parameter "a" in equation C is chosen to give good high density agreement with the "exact" values for each isotherm. Then, since integral equations give better results at lower densities, good results can be hoped for through the whole density range.

Equation T

In the case of equation T, with two parameters the method of choosing the parameters is more difficult. As a first check on the equation and the parameters, the parameters are chosen to give PY results, and also, HNC and equation C results to the  $S^3$  term.

In order to now find parameter values to give good agreement with the "exact" values, it might seem logical to choose parameter  $b_2$  from equation T to give agreement with low density and parameter  $b_3$  to give agreement with high density:

$$g = e^{-\beta\phi(1 + S + b_2 S^2 + b_3 S^3)} . \quad (28)$$

The problem with this is that  $b_2$  affects the high density result as well as low and  $b_3$  affects the low density result as well as high. There is an interaction that would require repeated readjustments of the parameters and repeated calculations. The method used in this study is a least



squares method, using the following equations for pressure and internal energy, at a fixed temperature and density,

$$P^* = P_0^* + c_1 b_2 + c_2 b_3 + c_3 b_2^2 + c_4 b_3^2 + c_5 b_2 b_3 \quad (44)$$

and

$$U^* = U_0^* + c_1 b_2 + c_2 b_3 + c_3 b_2^2 + c_4 b_3^2 + c_5 b_2 b_3, \quad (45)$$

where  $P_0^*$  and  $U_0^*$  are the pressure and internal energy values obtained when  $b_2 = b_3 = 0$ . Five or more combinations of parameters are used to find pressures and internal energies. A computer program (which can be found in the appendix) is then used to solve the resulting five simultaneous equations with five unknowns. The coefficients ( $c_1, c_2, c_3, c_4$ , and  $c_5$ ) that result can be used in these expressions (equations 44 and 45) along with an exact value of  $P^*$  to find values for the parameters  $b_2$  and  $b_3$  which will give the exact result. A graph is plotted of  $b_2$  versus  $b_3$  for several different densities. The range where the curves cross determines the best choice of parameters to use in equation T to give the best agreement with the "exact" results. Hopefully, of course, the best choice of parameters for pressure and internal energy would be in close agreement. The results for pressure are given precedence over the internal energy since pressure is more sensitive to changes in the parameters, and since more data are available for the "exact" pressure values.

After the best parameters are chosen, the computer program to solve the integral equations is used again with these parameters. The resulting pressures and internal energies are compared to the "exact" values and a graph is drawn comparing the resulting radial distribution functions to those given by Wood and Parker.

## CHAPTER V

### RESULTS AND COMPARISONS

#### Equation C

Equation C was solved for eight different densities at four different temperatures. Also, in each case the solution was found for 75 points (.075 interval) and for 297 points (.01875 interval). That is, the computer solutions of continuous functions, such as  $g(x)$ , are found at discrete values ( $x = 0$ ,  $x = \Delta$ ,  $x = 2\Delta$ , etc., where  $\Delta$  is the interval) the number of points (75 or 297) is the number of values at which  $g$ , etc., are found in the computer program. The results of using these radial distribution functions to compute pressure and internal energy are displayed in table 2 along with a comparison to results for equation  $N^{31}$ . The results given here are rounded off and only the 297 point results are given. More complete results can be found in the appendix.

As can be seen in table 2, equations C and N give almost identical results when the parameter for each equation is chosen at high density to agree with the exact values.

TABLE 2  
Comparison of Equation C results to Equation N

a(eq. C) = .10      a(eq. N) = .95      T* = 2.60				
n*	eq. C	P*	eq. N	U*
			eq. C	eq. N
.001	.99944	.99944	.998387	.998387
.01	.99459	.99459	.98390	.98390
.10	.9623	.9623	.8412	.8412
.20	.969	.969	.6867	.6867
.40	1.195	1.195	.3855	.3855
.60	1.94	1.94	.102	.102
.80	3.66		-.116	
.90	5.07	5.07	-.174	-.174
a(eq. C) = .07      a(eq. N) = .966      T* = 2.20				
n*	eq. C	P*	eq. N	U*
			eq. C	eq. N
.001	.99899	.99899	.997994	.997994
.01	.99009	.99009	.97998	.97998
.10	.9187	.9187	.8032	.8032
.20	.885	.885	.6135	.6135
.40	1.040	1.040	.246	.246
.60	1.75	1.75	-.1070	-.1070
.80	3.54	3.54	-.397	-.397
.90	5.04	5.04	-.489	-.489

$a(\text{eq. C}) = -.17 \quad a(\text{eq. N}) = 1.09 \quad T^* = 1.60$				
$n^*$	eq. C	$P^*$ eq. N	eq. C	$U^*$ eq. N
.001	.997799	.997799	.996920	.996920
.01	.978198	.978198	.969257	.969257
.10	.8047	.8047	.6988	.6988
.20	.670	.670	.4152	.4152
.40	.648	.648	-.108	-.108
.60	1.23	1.23	-.628	-.628
.80	3.01	3.01	-1.109	-1.110
.90	4.58	4.58	-1.303	-1.303
$a(\text{eq. C}) = -.34 \quad a(\text{eq. N}) = 1.18 \quad T^* = 1.35$				
$n^*$	eq. C	$P^*$ eq. N	eq. C	$U^*$ eq. N
.001	.99691	.99691	.996083	.996083
.01	.96936	.96936	.96086	.96086
.10	.7195	.7195	.6135	.6135
.20	.512	.512	.2487	.2488
.40	.386	.386	-.3666	-.3664
.60	.882	.881	-.9858	-.9860
.08	2.65	2.65	-1.596	-1.596

## Equation T

The first thing that was done with equation T was to choose the parameters to give agreement at low density with PY, HNC, and equation C, and compare the results to these equations<sup>32</sup>. With this done, the results given in table 3 are obtained. More complete results can be found in the appendix.

TABLE 3

Comparison of Equation T to Equation C, PY, and HNC

$b_2$	$b_3$	$a$	$n^*$	$T^*$	eq. T $P^*$	eq. C
.05	.00167	.10	.20	2.60	.969	.969
			.80		3.66	3.66
.035	.000817	.07	.20	2.20	.885	.885
			.80		3.54	3.54
-.085	.00482	-.17	.20	1.60	.670	.670
			.80		3.01	3.01
-.17	.01927	-.34	.20	1.35	.512	.512
$b_2$	$b_3$	$a$	$n^*$	$T^*$	eq. T $U^*$	eq. C
.05	.00167	.10	.20	2.60	.6867	.6867
			.80		-.116	-.116
.035	.000817	.07	.20	2.20	.6135	.6135

$b_2$	$b_3$	$a$	$n^*$	$T^*$	eq. T	$U^*$ eq. C
.035	.000817	.07	.80	2.20	-.397	-.397
-.085	.00482	-.17	.20	1.60	.4152	.4152
			.80		-1.109	-1.109
-.17	.01927	-.34	.20	1.35	.2487	.2487
$b_2$	$b_3$		$n^*$	$T^*$	eq. T	$P^*$ PY
0	0		.40	2.74	1.23	1.24
			.833		3.98	4.01
			1.00		6.65	6.8
$b_2$	$b_3$		$n^*$	$T^*$	eq. T	$U^*$ PY
0	0		.40	2.74	.4238	.423
			.833		-.073	-.073
			1.00		-.119	-.113
$b_2$	$b_3$		$n^*$	$T^*$	eq. T	$P^*$ HNC
.50	.167		.40	2.74	1.28	1.28
			.833		4.97	5.11
			1.00		8.70	9.1

$b_2$	$b_3$	$n^*$	$T^*$	eq. T	$U^*$ HNC
.50	.167	.40	2.74	4274	.427
		.833		.048	.067
		1.00		.148	.207

As can be seen from examining these results, when the parameters of equation T are chosen so as to give agreement with these other equations at high density, equation T agrees very well at all densities examined, with equation C but not as well with PY and HNC. The reason for this can be attributed to the fact that equations T and C were both solved using the same number of points, whereas PY and HNC were not. However, the agreement is still very good. Equation T agrees better with PY than with HNC because the expressions for equations T and PY are the same when equation T parameters are chosen to give PY results. However, in the case of HNC the agreement is only to the  $S^3$  term.

It was desired, in this study, to determine how the parameters in equation T affect the pressure and energy values, it was thus necessary to obtain many results relating the pressure and internal energy to the parameters in equation T. These can be found in table 4, all at  $T^* = 2.74$ .



TABLE 4  
Relation of  $P^*$  and  $U^*$  to the Parameters of Equation T

$b_2$	$b_3$	$n^*$	$P^*$	$U^*$
.167	.50	.001	.999567	.998493
.50	.167		.999567	.998493
.20	0		.999567	.998493
0	.20		.999567	.998493
.20	.20		.999567	.998493
.167	.50	.01	.99581	.98495
.50	.167		.99581	.98495
.20	0		.99581	.98495
0	.20		.99581	.98495
.20	.20		.99581	.98495
.167	.50	.10	.9742	.8515
.50	.167		.9743	.8515
.20	0		.9742	.8515
0	.20		.9741	.8515
.20	.20		.9742	.8515
.50	.167	.30	1.083	.5651
.15	0		1.073	.5644
.30	0		1.077	.5647
.40	0		1.079	.5648
0	.05		1.070	.5642

$b_2$	$b_3$	$n^*$	$P^*$	$U^*$
0	.10	.30	1.070	.5642
.10	.05		1.072	.5643
.30	.10		1.078	.5647
.60	0		1.084	.5651
0	.60		1.073	.5644
0	.40		1.072	.5643
0	.20		1.070	.5642
.167	.50		1.076	.5647
.20	.20		1.076	.5646
.20	0		1.074	.5645
.167	.50	.50	1.603	.2951
.50	.167		1.632	.2978
.20	0		1.559	.2909
0	.20		1.540	.2891
.20	.20		1.580	.2929
.167	.50		3.11	.096
.50	.167	.70	3.12	.097
.20	0		2.81	.062
0	.20		2.82	.064
.20	.20		2.96	.079
.167	.50		6.43	.085
.50	.167	.90	6.26	.062
.20	0		5.40	-.046

$b_2$	$b_3$	$n^*$	$P^*$	$U^*$
0	.20	.90	5.70	-.006
.20	.20		5.96	.025
.60	0	1.00	8.39	.108
.40	0		7.94	.048
.20	0		7.42	-.021
0	.20		8.06	.065
0	.40		8.64	.142
0	.60		9.05	.194
.20	.20		8.36	.103
.167	.50		9.00	.188

It was next necessary to determine what values of the parameters would give the "correct" pressures and energies. In order to do this the "exact" results had to be established first. It was therefore necessary to determine the low density results from the virial expansion,

$$P^* = 1 + b_2 \bar{n}^* + b_3 \bar{n}^{*2} + b_4 \bar{n}^{*3} + b_5 \bar{n}^{*4} + \dots \quad (42)$$

Table 5 gives the results of evaluating this equation including first only  $b_2$ , then  $b_2$  and  $b_3$ , and so on up to  $b_5$ .

Comparing the change in  $P^*$  as more terms are included, it was decided that densities up through .20 were stable enough to be considered as "exact."

TABLE 5  
Results of Virial Expansion at  $T^* = 2.74$

$n^*$	$P^*$ results with terms included up to			
	$b_2$	$b_3$	$b_4$	$b_5$
.001	.999564	.999565	.999565	.999565
.01	.99564	.99580	.99580	.99580
.10	.9564	.9724	.9735	.9736
.20	.9128	.9768	.9854	.9869
.30	.8691	1.0133	1.0422	1.0498
.40	.8255	1.0818	1.1502	1.1744

coefficients

$b_2 = -.436177$     $b_3 = 1.601900$     $b_4 = 1.067710$     $b_5 = .946957$

Using these results from table 5 and published results the "exact"  $P^*$  and  $U^*$  results found in table 6 were used to interpolate the "exact" results found in table 7.

TABLE 6  
"Exact" Results

$n^*$	$P^*$	$U^*$	Source
.001	.999565		
.01	.99580		Virial Expansion
.10	.9736		Results
.20	.9869		

$n^*$	$P^*$	$U^*$	Source
.5426	1.69	.229	
.65	2.23	.099	Verlet's
.75	3.06	-.006	Results <sup>33</sup>
.85	4.34	-.062	
.40		.4267	
.833	4.08	-.0467	Monte Carlo
1.00	6.97	-.0667	Results <sup>34</sup>
1.111	7.81	-.240	

The results in table 7 were interpolated from the interpolation formulas ( equations 36 and 37),

$$P^* = \frac{(1 + a_1 \bar{n}^* + a_2 \bar{n}^{*2} + a_3 \bar{n}^{*3})}{(1 + a_4 \bar{n}^* + a_5 \bar{n}^{*2} + a_6 \bar{n}^{*3})} \quad (36)$$

$$U^* = \frac{(1 + a_1 \bar{n}^* + a_2 \bar{n}^{*2} + a_3 \bar{n}^{*3})}{(1 + a_4 \bar{n}^* + a_5 \bar{n}^{*2} + a_6 \bar{n}^{*3})} \quad (37)$$

TABLE 7  
 "Exact" Interpolated Results

$n^*$	$P^*$	$U^*$
.01	.99580	.98566
.02	.99193	.97132
.03	.98839	.95698
.04	.98519	.94264
.05	.98233	.92829
.06	.97982	.91394
.07	.97768	.89958
.08	.97591	.88522
.09	.97454	.87086
.10	.9736	.8565
.11	.9730	.8421
.12	.9729	.8278
.13	.9732	.8134
.14	.9740	.7990
.15	.9753	.7847
.16	.9771	.7703
.17	.9794	.7559
.18	.9822	.7416
.19	.9856	.7272
.20	.990	.7128
.25	1.019	.6410

$n^*$	$P^*$	$U^*$
.30	1.067	.5693
.35	1.136	.4980
.40	1.231	.4267
.45	1.356	.3563
.50	1.518	.2869
.55	1.723	.2191
.60	1.98	.154
.65	2.29	.093
.70	2.68	.039
.75	3.14	-.006
.80	3.69	-.036
.85	4.34	-.049
.90	5.10	-.047
.95	5.98	-.044
1.00	6.97	-.067

## Coefficients for Interpolation Formulas

	$P^*$	$U^*$
$a_1$	12.8187	-3.41651
$a_2$	-20.8701	3.86607
$a_3$	33.8533	-3.45266
$a_4$	13.2554	-1.45266
$a_5$	-16.7658	1.04136
$a_6$	6.35569	-.011724

The values from table 4 were used with the least squares program to find the coefficients in equations (44) and (45),

$$P^* = P_0^* + c_1 b_2 + c_2 b_3 + c_3 b_2^2 + c_4 b_3^2 + c_5 b_2 b_3 \quad (44)$$

$$U^* = U_0^* + c_1 b_2 + c_2 b_3 + c_3 b_2^2 + c_4 b_3^2 + c_5 b_2 b_3. \quad (45)$$

These coefficients can be found in table 8.

TABLE 8  
Coefficients for Least Squares Equations

n*	P*				
	c <sub>1</sub>	c <sub>2</sub>	c <sub>3</sub>	c <sub>4</sub>	c <sub>5</sub>
.001	0	0	0	0	0
.01	0	0	0	0	0
.10	.0004	0	0	0	0
.30	.0259	.0059	-.0014	-.0001	-.0006
.50	.2178	.1157	-.0352	-.0131	-.0528
.70	.92068	.9841	-.2183	-.3481	-.9337
.90	2.6030	4.5549	-.5056	-2.6338	-6.0448
1.00	4.0530	7.6718	-1.9601	-6.1688	-7.0405

n*	U*				
	c <sub>1</sub>	c <sub>2</sub>	c <sub>3</sub>	c <sub>4</sub>	c <sub>5</sub>
.001	0	0	0	0	0
.01	0	0	0	0	0



$n^*$	$c_1$	$c_2$	$U^*$	$c_3$	$c_4$	$c_5$
.10	0	0	0	0	0	0
.30	.0017	.0005	-.0001	0	0	0
.50	.0201	.0111	-.0024	-.0013	-.0048	-.0048
.70	.1006	.1115	-.0200	-.0398	-.1034	-.1034
.90	.3188	.5747	-.0528	-.3360	-.7541	-.7541
1.00	.5186	1.0061	-.2389	-.8113	-.9183	-.9183

In figures 6 and 7 graphs of  $P^*$  versus  $n^*$  and  $U^*$  versus  $n^*$  are found that show the effect the parameters have on these curves. As can be seen from looking at these graphs, the parameters have little effect at low density. As the density increases the effect becomes more significant. The larger the parameters the greater the pressure or energy.

Using the "exact" values from table 7 and the coefficients from table 8 equations (44) and (45) were solved for the parameters  $b_2$  and  $b_3$  by choosing various values of  $b_2$  and computing the corresponding  $b_3$  values. The results of this are found in table 9.

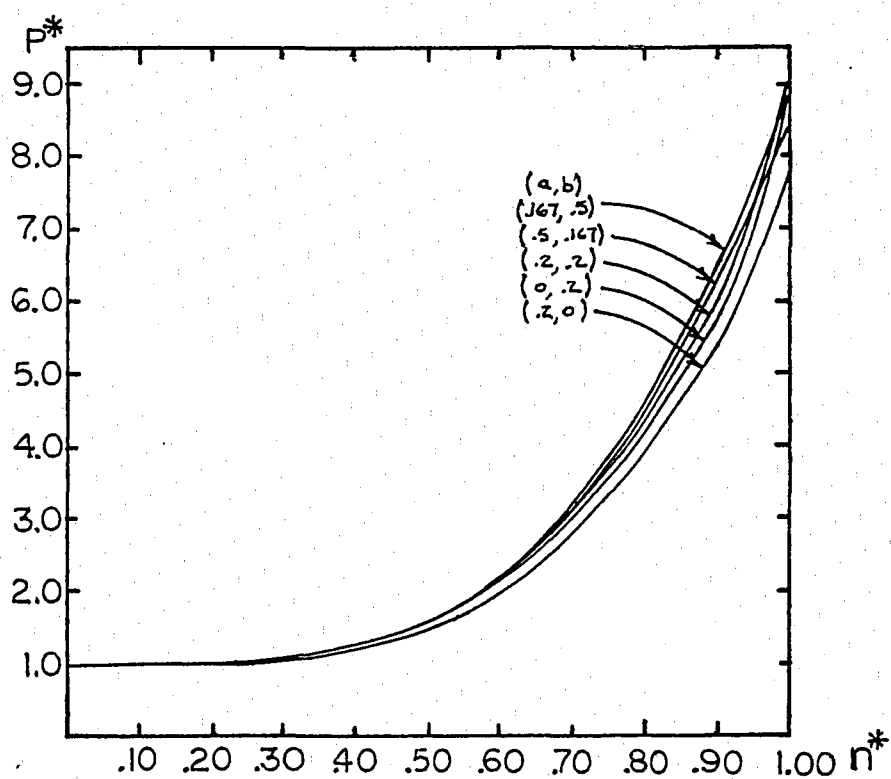


Figure 6.  $P^*$  vs.  $n^*$  for various parameters

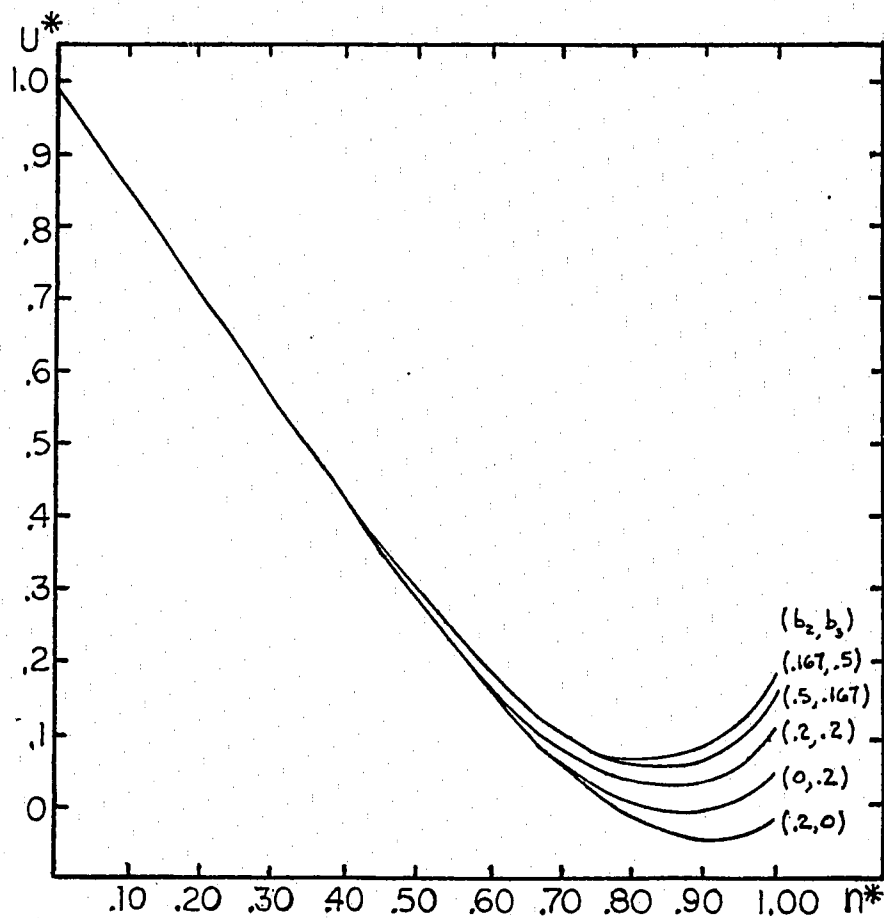


Figure 7.  $U^*$  vs.  $n^*$  for various parameters

TABLE 9  
 Combination of Parameters  $b_2$  and  $b_3$   
 That Produce "Exact" Results

$n^*$	$b_2$	$P^*$	$b_3$	$b_2$	$U^*$	$b_3$
.30	1.7352		-.50			
	1.5138		-.45			
	1.2927		-.40			
	1.0718		-.35			
	.8512		-.30			
	.6307		-.25			
	.4105		-.20			
	.1905		-.15			
	-.0293		-.10			
	-.2488		-.05			
	-.4681		0			
	-.6872		.05			
	-.9061		.10			
	-1.1248		.15			
	-1.3432		.20			
	-1.5614		.25			
	-1.7790		.30			
	-1.9972		.35			
	-2.2148		.40			
	-2.4321		.45			

$n^*$	$b_2$	$P^*$	$b_3$	$b_2$	$U^*$	$b_3$
.30	-2.6493		.50			
.50	.9139		-.50	.8455		-.50
	.8268		-.45	.7643		-.45
	.7390		-.40	.6822		-.40
	.6505		-.35	.5991		-.35
	.5613		-.30	.5151		-.30
	.4713		-.25	.4302		-.25
	.3806		-.20	.3442		-.20
	.2891		-.15	.2573		-.15
	.1969		-.10	.1694		-.10
	.1039		-.05	.0805		-.05
	.0101		0	-.0094		0
	-.0844		.05	-.1002		.05
	-.1797		.10	-.1921		.10
	-.2757		.15	-.2849		.15
	-.3726		.20	-.3788		.20
	-.4702		.25	-.4737		.25
	-.5686		.30	-.5695		.30
	-.6677		.35	-.6664		.35
	-.7677		.40	-.7643		.40
	-.8684		.45	-.8631		.45
	-.9699		.50	-.9630		.50
.70	.4257		-.50	.3406		-.50

$n^*$	$b_2$	$p^*$	$b_3$	$b_2$	$u^*$	$b_3$
.70	.3930		-.45	.3087		-.45
	.3593		-.40	.2756		-.40
	.3244		-.35	.2414		-.35
	.2882		-.30	.2059		-.30
	.2508		-.25	.1690		-.25
	.2119		-.20	.1307		-.20
	.1716		-.15	.0909		-.15
	.1297		-.10	.0495		-.10
	.0861		-.05	.0065		-.05
	.0409		0	-.0382		0
	-.0062		.05	-.0847		.05
	-.0552		.10	-.1331		.10
	-.1062		.15	-.1835		.15
	-.1592		.20	-.2358		.20
	-.2144		.25	-.2901		.25
	-.2717		.30	-.3466		.30
	-.3312		.35	-.4052		.35
	-.3930		.40	-.4660		.40
	-.4571		.45	-.5289		.45
	-.5235		.50	-.5941		.50
.90	.2341		-.50	.2717		-.50
	.2204		-.45	.2605		-.45
	.2059		-.40	.2486		-.40

n*	P*		U*	
	b <sub>2</sub>	b <sub>3</sub>	b <sub>2</sub>	b <sub>3</sub>
.90	.1904	-.35	.2360	-.35
	.1740	-.30	.2225	-.30
	.1564	-.25	.2079	-.25
	.1375	-.20	.1922	-.20
	.1171	-.15	.1751	-.15
	.0952	-.10	.1566	-.10
	.0714	-.05	.1363	-.05
	.0455	0	.1140	0
	.0173	.05	.0894	.05
	-.0134	.10	.0623	.10
	-.0470	.15	.0322	.15
	-.0837	.20	-.0012	.20
	-.1239	.25	-.0382	.25
	-.1676	.30	-.0793	.30
	-.2153	.35	-.1247	.35
	-.2671	.40	-.1746	.40
	-.3229	.45	-.2293	.45
	-.3830	.50	-.2887	.50
1.00	.3043	-.50	.3049	-.50
	.2783	-.45	.2803	-.45
	.2522	-.40	.2556	-.40
	.2262	-.35	.2307	-.35
	.2001	-.30	.2058	-.30

$n^*$	$b_2$	$P^*$	$b_3$	$b_2$	$U^*$	$b_3$
1.00	.1740		-.25	.1808		-.25
	.1478		-.20	.1557		-.20
	.1216		-.15	.1306		-.15
	.0954		-.10	.1053		-.10
	.0692		-.05	.0799		-.05
	.0430		0	.0544		0
	.0167		.05	.0288		.05
	-.0096		.10	.0032		.10
	-.0359		.15	-.0226		.15
	-.0623		.20	-.0485		.20
	-.0886		.25	-.0745		.25
	-.1150		.30	-.1006		.30
	-.1415		.35	-.1268		.35
	-.1679		.40	-.1531		.40
	-.1944		.45	-.1796		.45
	-.2209		.50	-.2061		.50

Plotting these results from table 9 in a graph of  $b_2$  versus  $b_3$  for each of the densities leads to the choice of  $b_2 = -.01$  and  $b_3 = .05$  as the best fit (see figures 8 and 9).



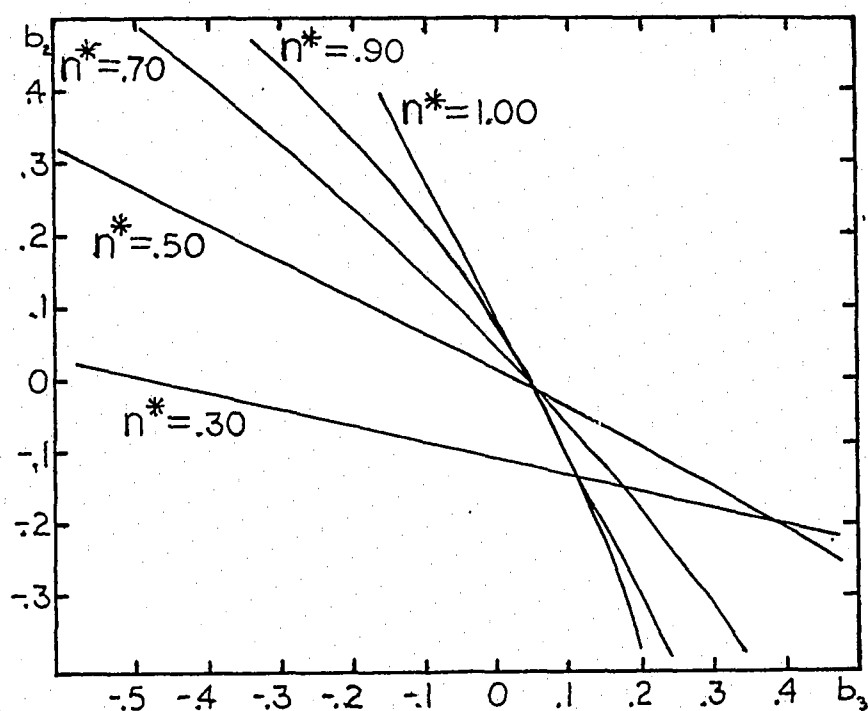


Figure 8. Parameters  $b_2$  vs.  $b_3$  for "exact" results-- $P^*$

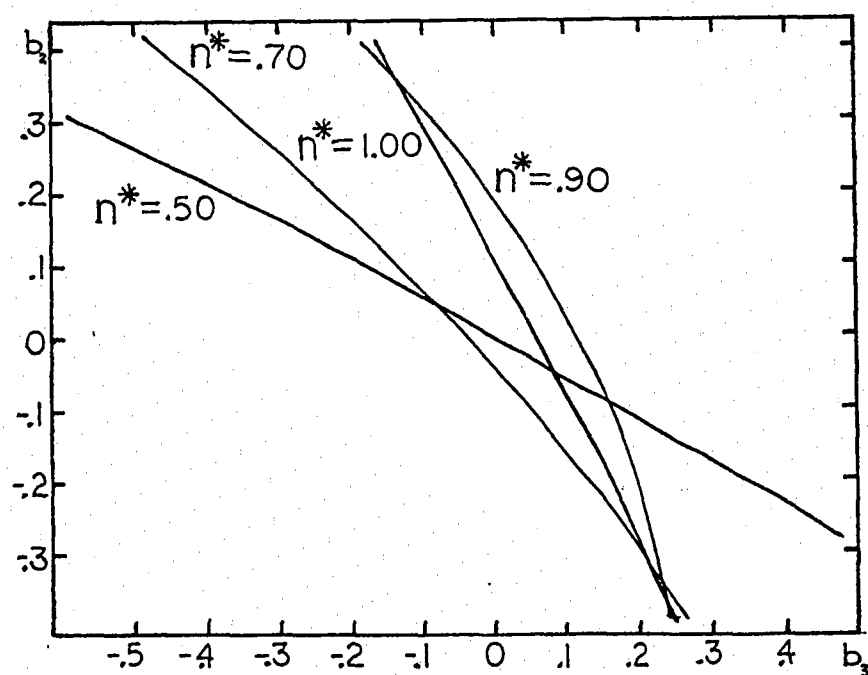


Figure 9. Parameters  $b_2$  vs.  $b_3$  for "exact" results-- $U^*$

In the graph for the pressure results, all the densities crossed close to the point  $b_2 = -.01$  and  $b_3 = .05$  except  $n^* = .30$ . Since the lower densities are less sensitive to the choice of parameters, the deviation of  $n^* = .30$  from the other parameters does not appear to be very significant. The fact that the results for  $U^*$  disagree significantly is not very surprising since less "exact" data were available and the internal energy is less sensitive to the parameter choice than is the pressure.

Using these parameters the radial distribution functions were recalculated and the pressures and internal energies were redetermined (see table 10 for results).

TABLE 10  
Comparison of Equation T Results to  
"Exact", Using Best Fit Parameters

$n^*$	Eq. T	$P^*$ "Exact"	Eq. T	$U^*$ "Exact"
1.00	7.17	6.97	-.050	-.067
.833	4.12	4.08	-.055	-.047
.75	3.14	3.14	.0015	-.0060
.50	1.52	1.52	.287	.287
.40	1.233	1.231	.4238	.4267
.30	1.069	1.067	.5642	.5693
.10	.9741	.9736	.8515	.8565

$n^*$	Eq. T	$P^*$ "Exact"	Eq. T	$U^*$ "Exact"
.01	.99581	.99580	.984953	.985664
.001	.99957	.99956	.998493	--
<hr/>				
	$T^* = 2.74$	$a = -.01$	$b = .05$	

Using the radial distribution functions found from equation T with the best fit parameters three graphs were drawn (figures 10, 11, and 12), comparing equation T to the "exact" Monte Carlo results<sup>35</sup>. From examining the results in table 10 and figures 10, 11, and 12, it can be seen that equation T produces very good results, but not exact agreement, with the present choice of parameters.

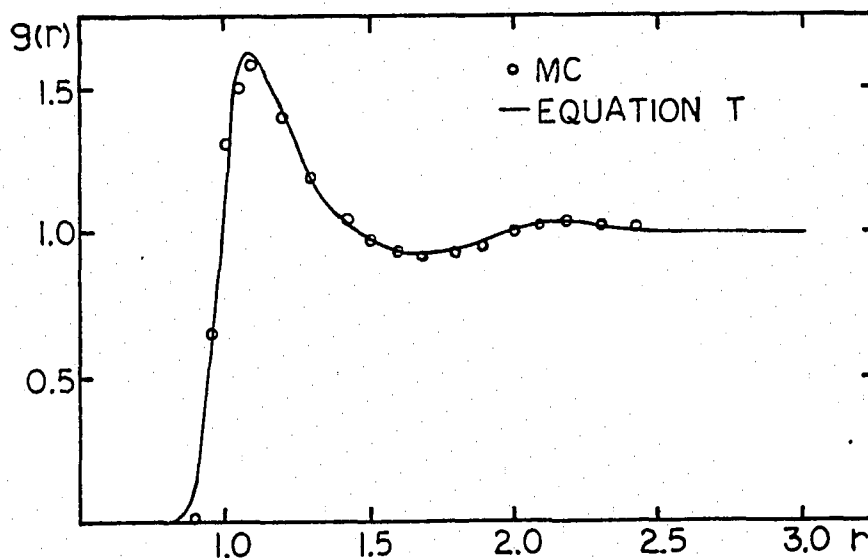


Figure 10. Radial distribution functions ( $n^* = .40$ )

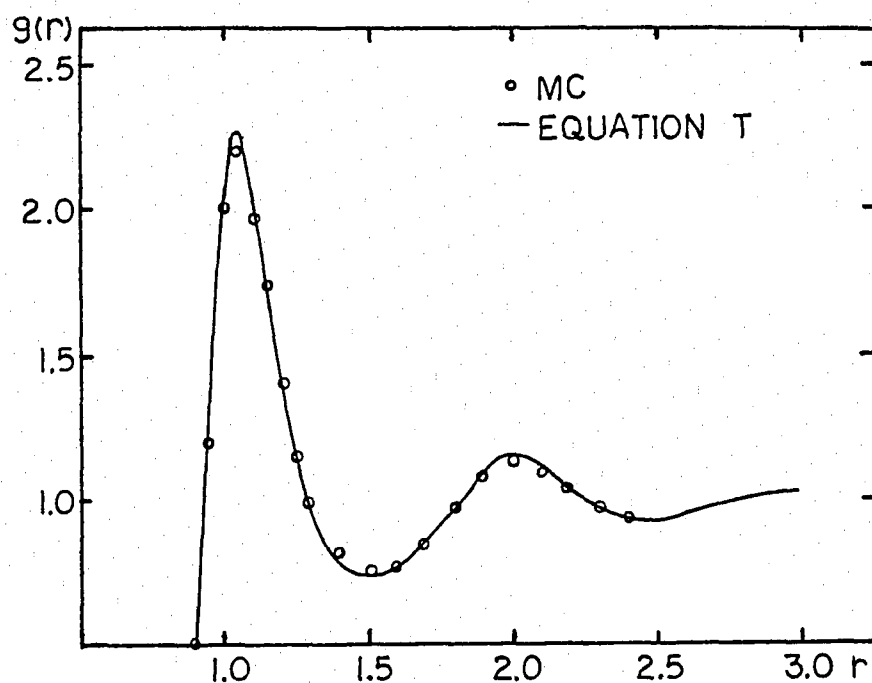


Figure 11. Radial distribution functions ( $n^* = .833$ )

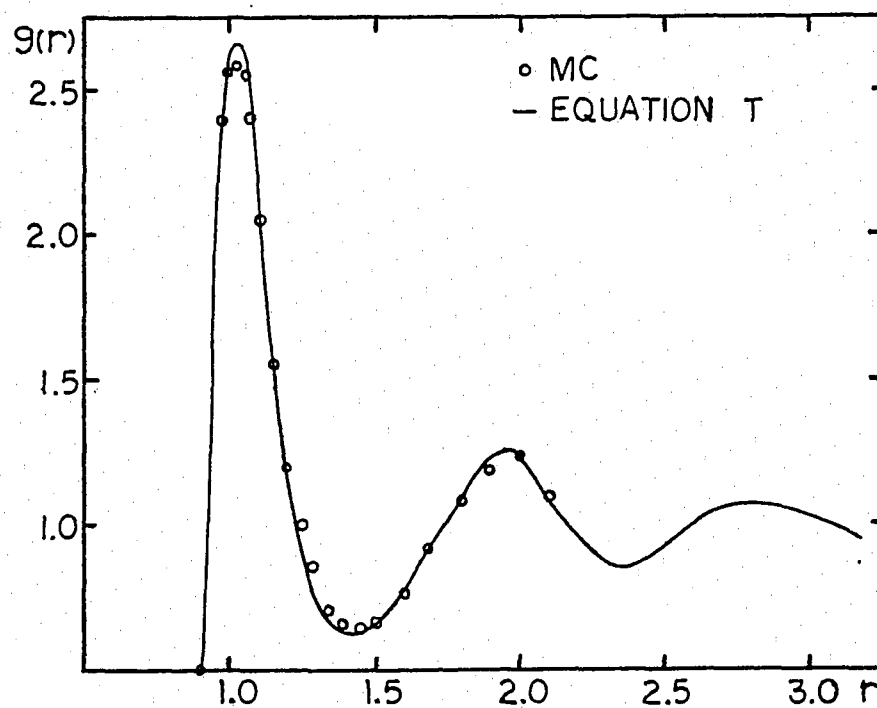


Figure 12. Radial distribution functions ( $n^* = 1.00$ )

## CHAPTER VI

### CONCLUSIONS

In this study two parametric integral equations were studied. Equation C was solved at densities from  $n^* = .001$  to  $n^* = 1.00$  and at temperatures from  $T^* = 2.60$  to  $T^* = 1.35$ , and was compared to equation N. This was done to see if there was any significant difference in the results obtained from parametric integral equations when the parameters were chosen at high density to give agreement. The results obtained were almost exactly the same and therefore it can be concluded, that over the studied density and temperature ranges there is no advantage of one equation over the other.

Equation T was introduced and first compared to equation C, PY, HNC by choosing parameters to agree with these equations. This was done to verify that the parameters in equation T do in fact affect the results as expected. Very good agreement was found.

"Exact" results were obtained from a combination of virial expansion, Verlet, and Monte Carlo results. These were used along with least squares results to obtain the best fit parameters (those values of the parameters that give the closest agreement of equation T with the "exact" results). The agreement was found to be good, but not as close as might be desired. However, since  $T^* = 2.74$  is a

"high" temperature, significant improvement over one parameter equations cannot be expected. Single parameter integral equations work very well at high temperatures, but are not as satisfactory at low temperatures. Also, the fact that the "exact" results are from three different methods and were interpolated between points would indicate that better agreement cannot be expected.

It was found in this study that the parameters in equation T become increasingly important as the density increases. As either parameter is increased both  $P^*$  and  $U^*$  increase. Also,  $b_3$  has more effect at high densities than does  $b_2$ , as might be expected, since  $b_3$  appears only in the higher density terms.

With the parameters occurring in different density terms in the power series, equation T is able to offer the flexibility of finding the importance of these various terms. Although equation T was not examined at low temperatures in this study, it is hoped that this could be done in a future study. Possibly equation T will provide information necessary to develop a simple integral equation which works well at low temperatures.

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## APPENDIX A

### DERIVATION OF EQUATION T

Numerous studies have shown that if an integral equation of the Ornstein-Zernike form is written and if a relationship between the direct correlation function and the radial distribution function is assumed which gives the correct density expansion for  $g \exp(\phi/kT)$  through the first power in density, an integral equation is obtained that works well for low densities. If the functional form of the relationship between  $c$  and  $g$  is well chosen, then good results are obtained even at high densities, at least for some potential functions and for some temperatures. Unfortunately, it has not appeared to be possible to predict if a good functional relationship between  $c$  and  $g$  has been chosen, without performing numerous calculations, and actually testing the results against Monte Carlo or molecular dynamics results. A major goal of this study is, indeed, to try to arrive at a good choice for the relationship between  $c$  and  $g$ . Many integral equations can be obtained which are of the Ornstein-Zernike form and which give the correct density expansion for  $g \exp(\phi/kT)$  through the first power in density. The following procedure generates such integral equations.

(1) Let  $G(x)$  be a function which can be written as a power series in  $x$ .  $G(x) = a_0 + a_1x + a_2x^2 \dots$

(2) Put the equation in the form:

$$A(x) = 1 + x + b_2x^2 + b_3x^3 + \dots$$

(3) Write,  $g \exp(\phi/kT) = A(x)$ .

(4) Solve for  $x$ :  $x = F(g, \beta\phi)$ .

(5) Let  $c = g - 1 - F$ .

(6) Define  $S = h - c = g - 1 - c$

(7) Find  $g(S)$  and  $c(S)$ .

The justification of this procedure lies in the power series solution of the integral equation thus obtained (see Appendix B).

Equation T can be derived by starting out with the partial power series,

$$A(x) = 1 + x + b_2x^2 + b_3x^3, \quad (45)$$

which is set equal to the quantity  $ge^{\beta\phi}$ . This can be written as

$$A(x) = ge^{\beta\phi} = 1 + x + b_2x^2 + b_3x^3. \quad (46)$$

It is now necessary to solve for  $x$ . To do this, an operator  $T$  is defined such that

$$T A(x) = x. \quad (47)$$

The inverse operator  $T^{-1}$  then results in

$$T^{-1} T A(x) = A(x) = T^{-1} x. \quad (48)$$

Applying this operator to equation (46) produces

$$TA(x) = x = T(ge^{\beta\phi}) = T(1 + x + b_2x^2 + b_3x^3). \quad (49)$$

It is then possible to write  $c$  as a function of  $x$  as

$$c = g - 1 - x = g - 1 - T(ge^{\beta\phi}). \quad (50)$$

From equations 21 and 22 the function  $S$  can be written as

$$S = h - c = g - 1 - c. \quad (51)$$

Substituting the expression from equation (50) into this, yields

$$S = g - 1 - g + 1 + T(ge^{\beta\phi}) = T(ge^{\beta\phi}). \quad (52)$$

If both sides of this expression are operated on by  $T^{-1}$ , the result is

$$T^{-1} S = T^{-1} T(ge^{\beta\phi}) = ge^{\beta\phi}, \quad (53)$$

which can be rearranged as

$$g = e^{-\beta\phi} T^{-1} S, \quad (54)$$

and by equation (48)

$$T^{-1} S = A(S) = 1 + S + b_2S^2 + b_3S^3. \quad (55)$$

Therefore equation T is found to be

$$g = e^{-\beta\phi}(1 + S + b_2 S^2 + b_3 S^3) . \quad (28)$$

This can be expressed in terms of the direct correlation function by going back to equation 50,

$$c = g - 1 - T(g e^{\beta\phi}) , \quad (50)$$

and substituting in the expression for  $g$  (equation 54),

$$c = e^{-\beta\phi} T^{-1} S - 1 - T \left[ e^{-\beta\phi} (T^{-1} S) e^{\beta\phi} \right] . \quad (56)$$

If equation 55 is substituted in for the first  $T^{-1} S$  on the right of equation 56 and if the last product on the right is rearranged, it can be seen that the result is,

$$c = e^{-\beta\phi}(1 + S + b_2 S^2 + b_3 S^3) - 1 - T T^{-1} S, \quad (57)$$

and finally this can be written as,

$$c = e^{-\beta\phi}(1 + S + b_2 S^2 + b_3 S^3) - 1 - S . \quad (27)$$

which is equation T in terms of the direct correlation function.

## APPENDIX B

### POWER SERIES SOLUTION OF EQUATION T

Starting out with the Ornstein-Zernike equation (equation 9) and equation T (equation 27), it is possible to derive the power series solution of equation T;

$$h(12) = c(12) + \bar{n} \int h(13)c(32)d3 \quad (58)$$

$$c = e^{-\beta\phi} (1 + s + b_2 s^2 + b_3 s^3) - 1 - s. \quad (27)$$

The Mayer f function was defined as

$$f = e^{-\beta\phi} - 1,$$

and a function Y can be introduced as

$$Y = g e^{\beta\phi} - 1. \quad (59)$$

Also, the total correlation function was defined as

$$h = g - 1 \quad (9)$$

Then equation (58) can be written as

$$s = h - c = \bar{n} \int h(13)c(32)d3 = \bar{n}x, \quad (60)$$

where

$$x = \int h(13)c(32)d3.$$

Rearranging terms the direct correlation function can be written as

$$c = h - s = e^{-\beta\phi} (1 + s + b_2 s^2 + b_3 s^3) - 1 - s, \quad (61)$$

and it can be seen that the total correlation function is

$$h = e^{-\beta\phi} (1 + S + b_2 S^2 + b_3 S^3) - 1. \quad (62)$$

The radial distribution function is then

$$g = h + 1 = e^{-\beta\phi} (1 + S + b_2 S^2 + b_3 S^3) \quad (28)$$

Substituting this into the expression for Y results in

$$\begin{aligned} Y = g e^{\beta\phi} - 1 &= e^{-\beta\phi} (1 + S + b_2 S^2 + b_3 S^3) e^{\beta\phi} - 1 \\ &= S + b_2 S^2 + b_3 S^3 \end{aligned} \quad (63)$$

By using the reversion of series, it is possible to express S in terms of Y as,

$$S = Y - b_2 Y^2 + (2b_2^2 - b_3) Y^3 + \dots \quad (64)$$

Since  $S = \bar{n}x$ , from equation (60), it is possible to write equation (63) as,

$$Y = \bar{n}x + b_2 \bar{n}^2 x^2 + b_3 \bar{n}^3 x^3. \quad (65)$$

Equation (9) can be rewritten as

$$h = g - 1 = g e^{\beta\phi} e^{-\beta\phi} - 1 = g e^{\beta\phi} (f + 1) - 1, \quad (66)$$

and, from equation (59), this can be written as

$$h = (Y + 1) (f + 1) - 1, \quad (67)$$

and expanding this

$$h = Y + Yf + f. \quad (68)$$

Now  $C$  can be written in terms of  $Y$  by substituting equations (64) and (68) into equation (61)

$$\begin{aligned} C = h - S &= Y + Yf + f - Y + b_2 Y^2 - (2b_2^2 - b_3)Y^3 \\ &= Yf + f + b_2 Y^2 - (2b_2^2 - b_3)Y^3 \end{aligned} \quad (69)$$

From equation (60)

$$x(12) = \int h(13)c(32)d3. \quad (70)$$

Now  $h$  from equation (67) and  $C$  from equation (69) can be substituted into equation (70),

$$x(12) = \int \left[ Y(13) + Y(13)f(13) + f(13) \right] \left[ Y(32)f(32) + f(32) + b_2 Y(32)^2 - (2b_2^2 - b_3)Y(32)^3 \right] d3. \quad (71)$$

Now the first approximation of the density expansion can be obtained, correct to order  $\bar{n}^0$ , by setting  $Y = 0$ ,

$$Y = 0 = g e^{\beta\phi} - 1. \quad (72)$$

To obtain the second approximation, correct to order  $\bar{n}^1$ , zero is substituted into equation (71) for  $Y$ ,

$$x(12) = \int f(13)f(32)d3. \quad (73)$$

Then from equation (65)

$$Y(12) = \bar{n}x(12) + b_2 \bar{n}^2 x(12)^2 + b_3 \bar{n}^3 x(12)^3. \quad (65)$$

The terms from  $\bar{n}^2$  and above are dropped in the second approximation, so equation (65) becomes

$$Y(12) = \bar{n} \int f(13)f(32)d3 = \bar{n} \bullet \text{---} \circ \text{---} \bullet \quad (74)$$

The third approximation, correct to order  $\bar{n}^2$ , is obtained by dropping YY terms from equation (71),

$$x(12) = \int \left[ Y(13)f(32) + Y(13)f(13)f(32) + f(13)Y(32) + f(32) + f(13)f(32) \right] d3. \quad (75)$$

Then substituting equation (74) for Y will result in

$$x(12) = \int \bar{n}f(14)f(43)f(32)d3d4 + \int \bar{n}f(14)f(43)f(13)f(32)d3d4 + \int \bar{n}f(13)f(34)f(42)f(32)d3d4 + \int f(13)f(32)d3 \quad (76)$$

For the third approximation equation (65) becomes

$$Y(12) = \bar{n}x(12) + b_2\bar{n}^2 x(12)^2, \quad (77)$$

$$\text{where } x(12)^2 = \int f(13)f(32)f(14)f(42)d3d4. \quad (78)$$

Substituting equation (76) into equation (77) results in

$$Y(12) = \bar{n}^2 \int f(14)f(43)f(32)d3d4 + \bar{n}^2 \int f(14)f(43)f(13)f(32)d3d4 + \bar{n}^2 \int f(13)f(34)f(42)f(32)d3d4 + \bar{n} \int f(13)f(32)d3 + b_2\bar{n}^2 \int f(13)f(32)f(14)f(42)d3d4, \quad (79)$$

or in terms of diagrams this is

$$Y = \bar{n} \bullet \text{---} \circ \text{---} \bullet + \bar{n}^2 \bullet \text{---} \circ \text{---} \circ \text{---} \bullet + 2\bar{n}^2 \bullet \text{---} \triangle \text{---} \bullet + b_2\bar{n}^2 \bullet \text{---} \diamond \text{---} \bullet \quad (80)$$



And the density expansion of equation T, correct to order  $\bar{n}^2$  is

$$\xi e^{\beta\phi} - 1 = \bar{n} \text{ (diagram: two dots connected by a line)} + \bar{n}^2 \left( \text{diagram: three dots in a line with two internal lines} + 2 \text{ (diagram: triangle)} + b_2 \text{ (diagram: diamond)} \right) \quad (81)$$

## APPENDIX C

### EQUATION C RESULTS

This table shows the results of numerical solutions to equation C. The following notation is used.

- No. This is the number assigned to this particular solution for identification purposes.
- a This is the value of the parameter in equation C.
- $n^*$  This is the value of the reduced number density.
- $T^*$  This is the value of the reduced temperature.
- N An A in this column indicates 75 points were used to specify the functions and an interval of .075.  
A B in this column indicates 297 points were used to specify the function and an interval of .01875.
- SDSS This is a measure of the difference between the final guessed value for S and computed value of S. The smaller the value of SDSS, the better is the convergence.
- $P^*$  This is the value of the reduced pressure as calculated from the radial distribution function obtained through the iteration process.
- $U^*$  This is the value of the reduced internal energy.

TABLE 11  
Equation C Results

No.	a	n*	T*	N	SDSS	P*	U*
1	.10	.90	2.60	A	.86E-4	4.9579526	-.18309727
2				B	.16E-4	5.0677024	-.17431441
3		.001		A	O	.99943645	.99838657
4				B	O	.99944425	.99838734
5		.01		A	O	.99451140	.98388868
6				B	O	.99459103	.98389662
7		.10		A	.10E-8	.96126486	.84109788
8				B	.25E-8	.96226364	.84120014
9		.20		A	.51E-8	.96616109	.68642848
10				B	.41E-8	.96880986	.68666857
11		.40		A	.11E-6	1.1846432	.38489509
12				B	.14E-6	1.1948910	.38548284
13		.60		A	.83E-6	1.9127022	.10046657
14				B	.83E-6	1.9434037	.10216124
15		.80		A	.24E-4	3.5822703	.12158379
16				B	.60E-5	3.6585101	-.11617078
17	.07	.90	2.20	A	.13E-3	4.8864843	-.50258468
18				B	.22E-4	5.0433804	-.48859991
19		.001		A	O	.99897924	.99799265
20				B	O	.99899291	.99799447
21		.01		A	O	.98995296	.97996011

No.	a	n*	T*	N	SDSS	P*	U*
22				B	.25E-9	.99009191	.97997870
23		.10		A	.16E-8	.91707937	.80299328
24				B	.15E-8	.91873793	.80322141
25		.20		A	.62E-8	.88074612	.61299051
26				B	.59E-8	.88489048	.61352598
27		.40		A	.37E-7	1.0255103	.24490363
28				B	.36E-7	1.0399904	.24616751
29		.60		A	.66E-6	1.7125801	-.11002097
30				B	.64E-6	1.7542962	-.10702582
31		.80		A	.22E-4	3.4322476	-.40584975
32				B	.93E-5	3.5359055	-.39736103
33	-.17	.90	1.60	A	.15E-3	4.4282210	-1.3142541
34				B	.28E-4	4.5848814	-1.3025447
35		.001		A	0	.99779940	.99691955
36				B	0	.99779915	.99692039
37		.01		A	0	.97819742	.96924778
38				B	0	.97819763	.96925689
39		.10		A	.38E-8	.80442209	.69862548
40				B	.28E-8	.80474691	.69880352
41		.20		A	.51E-8	.66794543	.41462686
42				B	.44E-8	.66952321	.41523305
43		.40		A	.30E-7	.63882468	-.10936885
44				B	.32E-7	.64792615	-.10806179

No.	a	n*	T*	N	SDSS	P*	U*
45	-.17	.60	1.60	A	.39E-6	1.1963696	-.62960330
46				B	.54E-6	1.2311601	-.62763359
47		.80		A	.89E-5	2.9113566	-1.1159320
48				B	.16E-4	3.0102510	-1.1094353
49	-.34	.80	1.35	A	.43E-4	2.5760873	-1.5967888
50				B	.34E-4	2.6462697	-1.5955839
51		.001		A	0	.99693195	.99608435
52				B	0	.99691277	.99608279
53		.01		A	0	.96954841	.96087992
54				B	0	.96935852	.96086475
55		.10		A	.19E-8	.72116286	.61360673
56				B	.28E-8	.71952268	.61353609
57		.20		A	.13E-7	.51413307	.24831934
58				B	.87E-8	.51182213	.24874938
59		.40		A	.61E-7	.38537690	-.36778322
60				B	.42E-7	.38554713	-.36656800
61		.60		A	.71E-6	.86406671	-.98549464
62				B	.69E-6	.88224557	-.98579620

TABLE 12

Results of Interpolation Formulas for Equation C  
(Results for  $P^*$ --see Equations 36 and 42)

	$T^* = 2.60$ $a = .10$	$T^* = 2.20$ $a = .07$	$T^* = 1.60$ $a = -.17$	$T^* = 1.35$ $a = -.34$
$b_2$	-.557341	-1.00885	-2.20311	-3.08969
$b_3$	1.59259	1.75804	2.25795	2.45431
$b_4$	2.07178	2.0423	2.45431	3.94844
$a_1$	6.4419	-1.09804	-2.33845	15.0505
$a_2$	-11.3385	.904972	1.83971	-66.1774
$a_3$	20.3771	2.74121	2.73418	92.9351
$a_4$	6.99997	-.0891914	-.132471	18.1402
$a_5$	-9.15132	-.978609	-1.02519	-12.5948
$a_6$	3.52946	.571818	.642601	-1.06873

TABLE 13

Results of Interpolation Formulas for Equation C  
(Results for  $U^*$  --see Equations 37 and 43)

	$T^* = 2.60$ $a = .10$	$T^* = 2.20$ $a = .07$	$T^* = 1.60$ $a = -.17$	$T^* = 1.35$ $a = -.34$
$b_2$	-1.61293	-2.00593	-3.0802	-3.91746
$b_3$	.267268	.395042	.582867	.250428
$b_4$	-.179512	-.136285	.994776	2.7781
$a_1$	-2.62555	-3.2747	-6.00944	-8.46407
$a_2$	2.02214	3.28251	11.5773	26.1621
$a_3$	-.472305	-1.21054	-7.26013	-13.2004
$a_4$	-1.01228	-1.26247	-2.92693	-4.54612
$a_5$	.0947275	.25093	1.73272	7.91333
$a_6$	.318634	.38775	.657158	1.38153

## APPENDIX D

### EQUATION T RESULTS

This table shows the results of numerical solutions to equation T. The following notation is used.

- No. This is the number assigned to this particular solution for identification purposes.
- $b_2, b_3$  These are the values of the parameters in equation T.
- $n^*$  This is the value of the reduced number density.
- $T^*$  This is the value of the reduced temperature.
- N An A in this column indicates 75 points were used to specify the functions and an interval of .075.  
A B in this column indicates 297 points were used to specify the function and an interval of .01875.
- SDSS This is a measure of the difference between the final guessed value for S and computed value of S. The smaller the value of SDSS, the better is the convergence.
- $P^*$  This is the value of the reduced pressure as calculated from the radial distribution function obtained through the iteration process.
- $U^*$  This is the value of the reduced internal energy.



TABLE 14

## Equation T Results

(For No. 43-46  $T^* = 2.60$ , for No. 47-50  $T^* = 2.20$ , for No. 51-54  $T^* = 1.60$ , for No. 55-56  $T^* = 1.35$ , for No. 57-206  $T^* = 2.74$ )

No.	$b_2$	$b_3$	$n^*$	N	SDSS	$P^*$	$U^*$
43	.05	.00167	.20	A	.32E-8	.96616109	.68642848
44				B	.25E-8	.96880987	.68666857
45			.80	A	.45E-4	3.5817642	-.12162274
46				B	.16E-4	3.6583895	-.11619015
47	.035	.000817	.20	A	.88E-8	.88074611	.61299050
48				B	.20E-8	.88489050	.61352598
49			.80	A	.48E-4	3.4317554	-.40587768
50				B	.43E-5	3.5358910	-.39736402
51	-.085	.00482	.20	A	.38E-8	.66794542	.41462687
52				B	.47E-8	.6695321	.41523305
53			.80	A	.33E-4	2.9112153	-1.1158596
54				B	.19E-4	3.0108665	-1.1093542
55	-.17	.01927	.20	A	.43E-8	.51413304	.24831926
56				B	.66E-8	.51182211	.24874932
57	0	0	.40	A	.93E-7	1.2243946	.42341521
58				B	.38E-7	1.2327493	.42375050
59			.833	A	.47E-4	3.9036408	-.077768549

No.	$b_2$	$b_3$	$n^*$	N	SDSS	$P^*$	$U^*$
60	0	0	.833	B	.93E-5	3.9779964	-.072804138
61			1.00	A	.68E-4	6.5161843	-.13023844
62				B	.17E-4	6.6518030	-.11901079
63	.50	.167	.40	A	.66E-7	1.2676679	.42700865
64				B	.28E-7	1.2771572	.42743923
65			.833	A	.20E-4	4.8853133	.041306958
66				B	.52E-4	4.9727429	.047785304
67			1.00	A	.41E-3	8.5454572	.13483206
68				B	.20E-3	8.7017792	.14792611
69	0	0	.001	A	0	.99956184	.99849287
70				B	0	.99956688	.99849325
71			.01	A	0	.99576199	.98494901
72				B	0	.99581391	.98495288
73			.10	A	.13E-8	.97342650	.85141498
74				B	.12E-8	.97412516	.85147130
75			.30	A	.62E-7	1.0649968	.56393383
76				B	.27E-7	1.0692888	.56415403
77			.50	A	.55E-6	1.5019789	.28637326
78				B	.50E-6	1.5171300	.28695902
79			.70	A	.83E-5	2.5951587	.040668108
80				B	.64E-5	2.6370114	.042900316
81			.90	A	.65E-4	4.8013348	-.11472981
82				B	.21E-4	4.8978758	-.10765207

No.	$b_2$	$b_3$	$n^*$	N	SDSS	$P^*$	$U^*$
83	.50	.167	.30	A	.36E-7	1.0781906	.56480739
84				B	.12E-7	1.0828177	.56505074
85	.15	0		A	.31E-7	1.0687555	.56417789
86				B	.10E-7	1.0731434	.56440478
87	.30	0		A	.29E-7	1.0724517	.56441864
88				B	.98E-8	1.0769323	.56465200
89	.40	0		A	.39E-7	1.0748822	.56457731
90				B	.49E-8	1.0794226	.56481490
91	0	.05		A	.42E-7	1.0652820	.56395652
92				B	.27E-7	1.0695835	.56417727
93	0	.10		A	.42E-7	1.0655667	.56397919
94				B	.88E-8	1.0698777	.56420049
95	.10	.05		A	.31E-7	1.0677918	.56411944
96				B	.15E-7	1.0721575	.56434462
97	.30	.10		A	.35E-7	1.0730041	.56446295
98				B	.27E-7	1.0775024	.56469731
99	.60	0		A	.33E-7	1.0796657	.56489036
100				B	.18E-7	1.0843217	.56513619
101	0	.60		A	.41E-7	1.0683941	.56420436
102				B	.41E-7	1.0727986	.56443106
103	0	.40		A	.61E-7	1.0672675	.56411462
104				B	.28E-7	1.0716351	.56433921
105	0	.20		A	.40E-7	1.0661351	.56402446

No.	$b_2$	$b_3$	$n^*$	N	SDSS	$P^*$	$U^*$
106				B	.22E-7	1.0704651	.56424686
107	.167	.50		A	.61E-7	1.0719632	.56442807
108				B	.31E-7	1.0764524	.56466088
109	.20	.20		A	.19E-7	1.0711091	.56434769
110				B	.19E-7	1.0755647	.56457882
111	.20	0		A	.29E-7	1.0699943	.56425851
112				B	.95E-8	1.0744136	.56448757
113	.60	0	1.00	A	.13E-3	8.2420491	.095022105
114				B	.55E-4	8.3887675	.10777602
115	.40	0		A	.23E-3	7.7837237	.034402445
116				B	.12E-3	7.9431582	.047998719
117	.20	0		A	.13E-3	7.2807423	-.032152176
118				B	.31E-4	7.4178628	-.020452395
119	0	.20		A	.24E-3	7.9138060	.053171851
120				B	.51E-4	8.0586591	.065192133
121	0	.40	1.00	A	.38E-3	8.5191420	.13250809
122				B	.34E-3	8.6409165	.14172798
123	0	.60		A	.48E-3	8.9230909	.18505474
124				B	.52E-3	9.0494902	.19429141
125	.20	.20		A	.39E-3	8.2129010	.091136768
126				B	.35E-3	8.3550334	.10262901
127	.167	.50		A	.39E-3	8.8756968	.17859095
128				B	.48E-3	9.0042911	.18797401

No.	$b_2$	$b_3$	$n^*$	N	SDSS	$P^*$	$U^*$
129	.167	.50	.001	A	O	.99956184	.99849287
130				B	O	.99956688	.99849325
131	.50	.167		A	O	.99956184	.99849287
132				B	O	.99956688	.99849325
133	.20	0		A	O	.99956184	.99849287
134				B	O	.99956688	.99849325
135	0	.20		A	O	.99956184	.99849287
136				B	O	.99956688	.99849325
137	.20	.20		A	O	.99956184	.99849287
138				B	O	.99956688	.99849325
139	.167	.50	.01	A	O	.99576204	.98494900
140				B	O	.99581395	.98495287
141	.50	.167		A	O	.99576216	.98494899
142				B	O	.99581404	.98495287
143	.20	0		A	O	.99576204	.98494900
144				B	O	.99581396	.98495287
145	0	.20		A	O	.99576199	.98494901
146				B	O	.99581391	.98495288
147	.20	.20		A	O	.99576204	.98494900
148				B	O	.99581396	.98495287
149	.167	.50	.10	A	.18E-8	.97351252	.85141448
150				B	.11E-8	.97421294	.85147076
151	.50	.167		A	.17E-8	.97364365	.85140957

No.	$b_2$	$b_3$	$n^*$	N	SDSS	$P^*$	$U^*$
152				B	.21E-8	.97434656	.85146571
153	.20	0		A	.13E-8	.97351150	.85141265
154				B	.12E-8	.97421183	.85146891
155	0	.20		A	.20E-8	.97343252	.85141556
156				B	.14E-8	.97413132	.85147189
157	.20	.20		A	.20E-8	.97351752	.85141323
158				B	.16E-8	.97421799	.85146949
159	.167	.50	.50	A	.46E-6	1.5849687	.29426629
160				B	.22E-6	1.6026544	.29507966
161	.50	.167		A	.52E-6	1.6137724	.29696170
162				B	.35E-6	1.6317740	.29781922
163	.20	0		A	.38E-6	1.5430455	.29018907
164				B	.34E-6	1.5592823	.29087832
165	0	.20		A	.50E-6	1.5237609	.28847106
166				B	.48E-6	1.5397368	.28912970
167	.20	.20		A	.40E-7	1.5628560	.29210752
168				B	.34E-6	1.5797760	.29285631
169	.167	.50	.70	A	.57E-5	3.0598441	.093029261
170				B	.25E-5	3.1117231	.096316800
171	.50	.167		A	.57E-5	3.0683199	.093804270
172				B	.44E-5	3.1194481	.097073302
173	.20	0		A	.59E-5	2.7666067	.059537202
174				B	.24E-5	2.8124172	.062218092

No.	$b_2$	$b_3$	$n^*$	N	SDSS	$P^*$	$U^*$
175	0	.20		A	.57E-5	2.7724257	.060781665
176				B	.54E-5	2.8199010	.063615456
177	.20	.20		A	.61E-5	2.9085795	.075745307
178				B	.12E-5	2.9579573	.078796692
179	.167	.50	.90	A	.60E-4	6.3281232	.076732613
180				B	.63E-4	6.4327401	.084501140
181	.50	.167		A	.56E-4	6.1487035	.053925887
182				B	.28E-4	6.2554447	.062182017
183	.20	0		A	.63E-4	5.2939959	-.054051340
184				B	.52E-4	5.3982496	-.046002343
185	0	.20		A	.62E-4	5.5951909	-.014546469
186				B	.20E-4	5.7035068	-.0061521828
187	.20	.20		A	.27E-4	5.8549351	.017065287
188				B	.38E-4	5.9620907	.025333092
189	-.01	.05	1.00	A	.39E-3	7.0125673	-.064062253
190				B	.12E-3	7.1726527	-.050443873
191			.833	A	.38E-4	4.0459023	-.06253441
192				B	.90E-5	4.1248392	-.054753944
193			.75	A	.18E-4	3.0879017	-.0018205345
194				B	.70E-5	3.1428263	.0015187114
195			.50	A	.13E-6	1.5054245	.28671416
196				B	.72E-7	1.5207360	.28731371
197			.40	A	.57E-7	1.2250127	.42347383

No.	$b_2$	$b_3$	$n^*$	N	SDSS	$P^*$	$U^*$
198				B	.25E-7	1.2333992	.42381126
199			.30	A	.63E-7	1.0650294	.56394015
200				B	.12E-7	1.0693244	.56416046
201			.10	A	.76E-9	.97342376	.85141524
202				B	.90E-9	.97412237	.85147157
203			.01	A	0	.99576199	.98494901
204				B	0	.99581390	.98495288
205			.001	A	0	.99956184	.99849287
206				B	0	.99956688	.99849325



## APPENDIX E

### COMPUTER PROGRAMS

The following programs were written for this study.

The least squares program was used to find the coefficients in equations (42) and (43),

$$P^* = P_0^* + c_1 b_2 + c_2 b_3 + c_3 b_2^2 + c_4 b_3^2 + c_5 b_2 b_3, \quad (42)$$

$$U^* = U_0^* + c_1 b_2 + c_2 b_3 + c_3 b_2^2 + c_4 b_3^2 + c_5 b_2 b_3. \quad (43)$$

```
10 DIM A(20), B(20), Y(20), X(5,5), C(5), Z(5)
15 MAT Z = ZER
20 MAT X = ZER
30 PRINT "TYPE THE NO. OF POINTS"
40 INPUT N
50 PRINT "TYPE THE PY VALUE"
60 INPUT P
70 PRINT "TYPE THE N VALUES OF P"
80 FOR J = 1 TO N
90     INPUT P1
100    Y(J) = P1 - P
110 NEXT J
120 PRINT "TYPE THE N VALUES OF A"
130 FOR J = 1 TO N
140     INPUT A(J)
```

```
150  NEXT J
160  PRINT "TYPE THE N VALUES OF B"
170  FOR J = 1 TO N
180    INPUT B(J)
190  NEXT J
200  FOR J = 1 TO N
210    X(1,1) = X(1,1) + A(J) * A(J)
220    X(1,2) = X(1,2) + A(J) * B(J)
230    X(1,3) = X(1,3) + A(J)3
240    X(1,4) = X(1,4) + A(J) * B(J) * B(J)
250    X(1,5) = X(1,5) + A(J) * A(J) * B(J)
260    X(2,2) = B(J) * B(J)
270    X(3,3) = X(3,3) + A(J)4
290    X(3,4) = X(3,4) + A(J) * A(J) * B(J) * B(J)
300    X(3,5) = X(3,5) + (A(J)3) * B(J)
310    X(4,4) = X(4,4) + B(J)4
320    X(4,5) = A(J) * (B(J)3)
330    X(2,1) = X(1,2)
340    X(2,3) = X(1,5)
350    X(2,5) = X(1,4)
360    X(3,1) = X(1,3)
370    X(3,2) = X(2,3)
380    X(4,1) = X(1,4)
390    X(4,2) = X(2,4)
400    X(4,3) = X(3,4)
410    X(5,1) = X(1,5)
```

```
420    X(5,2) = X(2,5)
430    X(5,3) = X(3,5)
440    X(5,4) = X(4,5)
450    Z(1) = Z(1) + A(J) * Y(J)
460    Z(2) = Z(2) + B(J) * Y(J)
470    Z(3) = Z(3) + A(J) * A(J) * Y(J)
480    Z(4) = Z(4) + B(J) * B(J) * Y(J)
490    Z(5) = Z(5) + A(J) * B(J) * Y(J)
495  NEXT J
500  MAT D = INV(X)
510  MAT C = D*Z
520  PRINT
530  PRINT "C1 =" ; C(1)
540  PRINT "C2 =" ; C(2)
550  PRINT "C3 =" ; C(3)
560  PRINT "C4 =" ; C(4)
570  PRINT "C5 =" ; C(5)
580  PRINT
590  PRINT "A","B","P", "P-CALC"
600  PRINT
610  FOR J = 1 TO N
620    P1 = P + Y(J)
630    P2 = P + C(1) * A(J) + C(2) * B(J) + C(3) * A(J) * A(J)
        + C(4) * B(J) * B(J) + C(5) * A(J) * B(J)
640    PRINT A(J), B(J), P1, P2
```

```

650 NEXT J
660 PRINT "DETERMINANT OF X = " DET
670 END

```

The virial expansion program was used to compute the pressure by first including only  $b_2$  then  $b_3$  and so on up to  $b_5$ ,

$$P^* = 1 + b_2 \bar{n} + b_3 \bar{n}^2 + b_4 \bar{n}^3 + b_5 \bar{n}^4 + \dots \quad (41)$$

```

10 DIM X(4)
20 PRINT "TYPE THE 4 VALUES OF B"
30 INPUT X(1), X(2), X(3), X(4)
40 PRINT "TYPE THE DENSITY"
50 INPUT N
60 P = 0
70 FOR J = 1 TO 4
80   P = P + X(J) * N * * J
90   P1 = P + 1
100  PRINT "P = ", P1
110 NEXT J
120 END

```

The last program that was written for this study was used to solve the quadratic equations (42) and (43) for  $b_3$  when  $b_2$  was given and the exact values were substituted in for  $P^*$  and  $U^*$ .

$$P^* + P_0^* + c_1 b_2 + c_2 b_3 + c_3 b_2^2 + c_4 b_3^2 + c_5 b_2 b_3 \quad (42)$$

$$U^* + U_0^* + c_1 b_2 + c_2 b_3 + c_3 b_2^2 + c_4 b_3^2 + c_5 b_2 b_3 \quad (43)$$

```

REAL B1, B2, C1, C2, C3, C4, C5, A, PO, P, E, F
5  READ (20, 100, END = 20) PO, P
   READ (20, 200) C1, C2, C3, C4, C5
   WRITE (21, 300) PO, P
   WRITE (21, 350) C1, C2, C3, C4, C5
   A = -.55
10  A = A + .05
   E = C2 + C5 * A
   F = C1 * A + C3 * A * A + PO - P
   B1 = -(E + E/ABS(E) * SQRT (E*E - 4. * C4 * F))
        /(2. * C4)
   B2 = F/(C4 * B1)
   WRITE (21, 400) B1, B2, A
   IF (A.GT.0.5) GO TO 5
   GO TO 10
20  CONTINUE
100 FORMAT (2F)
200 FORMAT (5F)
300 FORMAT ('/', ' PY PRESSURE = ', 1F, ' EXACT PRESSURE = ', 1F)
350 FORMAT ('/', ' C1 = ', 1F, ' C2 = ', 1F, ' C3 = ', 1F, '
        C4 = ', 1F, ' C5 = ', 1F)

```

```
400  FORMAT (' ', 'B1 = ',1F,' B2 = ',1F,' A = ',1F)
```

```
END
```

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