A VARIATIONAL APPROACH TO THE EQUILIBRIUM THERMODYNAMIC PROPERTIES OF SIMPLE LIQUIDS AND PHASE TRANSITIONS

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A VARIATIONAL APPROACH TO THE EQUILIBRIUM
THERMODYNAMIC PROPERTIES OF SIMPLE
LIQUIDS AND PHASE TRANSITIONS

APPROVED BY

[Signatures]

DISSERTATION COMMITTEE
TO

Professor Hossein Zad-Mard
University of Tehran

and

Professor Arthur J. Madden
University of Minnesota

My inspiring teachers
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A variational technique which is based on an inequality, first introduced by Feynman, is used to calculate the equilibrium thermodynamic properties of simple substances.

A system with hard-sphere potential function is used as the reference system. Helmholtz free energy of the original system is calculated by variation around the Helmholtz free energy of the reference system and the other thermodynamic properties are calculated from free energy. By the choice of the hard-sphere reference system, it is possible to calculate the equilibrium thermodynamic properties of fluids from very low densities to densities close to solid, and from high temperatures in the gas phase to low temperatures in the liquid phase, in the ranges where experimental and machine-calculated data are available. While the variational calculation based on a hard-sphere reference system does not predict the liquid-solid phase transition, it is argued that this might be due to the lack of some ordered characters in the formulation of the working inequality for fluids.
A system with molecules obeying cell model of Lennard-Jones and Devonshire, and having a harmonic oscillator type potential function inside their cells, is used for a reference system to produce an inequality for the Helmholtz free energy of the original system in the solid phase. Optimization upon this inequality indicates that a variational calculation based on a reference system with highly ordered structure, as the cell model, predicts the properties of the solid phase better than the liquid phase. Also, it shows that by an ordered structure reference model, it is possible to predict the liquid-solid phase transition. Equilibrium thermodynamic properties of the solid phase, and liquid-solid phase equilibria are calculated and are compared with machine-calculated and the experimental data of argon.

A system with a binary mixture of hard-spheres is used as the reference system to apply the basic inequality for the Helmholtz free energy of an original binary system. The formulation of the inequality is provided and the variational parameters are characterized.

Overall, it is shown that the present variational technique is a better approach to the prediction of the equilibrium thermodynamic properties of liquids, and phase transitions (both liquid-vapor and liquid-solid) than any other approach.
so far developed. Applicability of this variational technique to the broad range of gas-liquid-solid is remarkably unique.
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CHAPTER I

INTRODUCTION

The liquid state, in general, and the equation of state and other equilibrium properties of liquids, in particular, have been under investigation by scientists in different countries intensely during the last fifty years. With the rise of statistical physics, this interest increased more, and different people started to interpret or try to predict the macroscopic properties of liquids from their microscopic behavior and structure. These attempts always were barricaded by the complex molecular forms and behavior of the liquids in hand. Also, the intuitive idea that liquids should have properties intermediate between solids and gases paved two different ways for investigators to try to find at least the asymptotic behavior of liquids at the very low and
very high density limits where only a gas or a solid is present. It was probably at this stage where the predictive and interpretive approaches found their easiest ways to be applied. While the solid state was an ideal state to be used as a starting point for interpretive theories, the gaseous state was found to be the easier state in which to investigate into the predictive theories. Still, these limiting conditions were not easy to work on, because of the strange characters of ordinary substances at solid and gas phases. That is why the rare gases came into attention, particularly because of simple spherical shapes of their molecules and known functional forms of their intermolecular forces.

While there are other theories and approaches to the equation of state of simple fluids, such as the semi-empirical corresponding state principle and the significant structure theory of Eyring, in this work only those approaches which are free of empiricism will be discussed.

Interpretive Approaches

Theories of this class start from a description of the structure (usually a simplified and approximate description), leaving the question of how the structure is determined by the molecular properties to be answered after the fact. These
theories are called "lattice" theories because the proposed structure often bears some relation to the regular lattice structure of a crystalline solid. These approaches develop logically from methods found to be successful in the theory of solids. A lattice theory of the liquid state starts from a description or picture or model of the structure of liquids. It is clear that the word "structure" has different implications for solids on the one hand and for liquids on the other. A solid has a single, static crystal structure which is only slightly blurred by the thermal motions; in a liquid, the instantaneous structure changes continually and grossly, because of the random thermal motions of the molecules. In a solid the molecules vibrate about fixed equilibrium lattice sites, and jumps from one lattice site to another (or to an interstitial site) occur very rarely indeed; this is shown by the experimental fact that diffusion in solids is very slow. In liquids there are no fixed lattice sites and diffusion is much more rapid. But with the consideration of a static average or ideal structure (or structures) and to suppose that the molecules spend much of their time vibrating in regions defined by the structure or structures, the "lattice" theories might be satisfactory for liquid state. This is only true, if one could manipulate all the mathematical needs which
are, and have been, in the form of very difficult and complicated combinatorial problems [4].

Cell theory is the simplest lattice theory which involves considering one molecule per every cell in the system, or in other words each molecule in a liquid or a compressed gas which spends much of its time confined by its neighbors to a comparatively restricted region might follow the cell theory. Hole theory is another kind of lattice theory which is more sophisticated than the cell theory for the reason that existence of empty cells are permitted in the model. The introduction of holes in the model of the liquids is based on the fact that when most substances melt the density and the apparent number of nearest neighbors decrease which could be accounted for the production of empty cells, or holes, in the substance. To distinguish the properties of liquids from solids more than what cell and hole theories permit, Lennard-Jones and Devonshire proposed the Order-Disorder theory which involves the assumption of the existence of both solid and liquid phases within the framework of a lattice picture. After much work on the above mentioned approaches, it was found that the task of basing a satisfactory theory of liquids on a regular lattice model may prove at best difficult and at worst impossible. It was natural to ask whether one could imagine an irregular lattice
model, based on a model structure which has sufficient regularity or simplicity to permit a simple description but which is disordered in a more fundamental way than the cell or hole models permit. One such model is the "tunnel" model [3] which is one dimensionally disordered. The most sophisticated lattice theory of liquids is the cell cluster theory developed originally by DeBoer [17]. The basic idea in cell cluster theory is to divide the lattice of cells into clusters of cells. The cell cluster theory is formally satisfying, and there is no doubt that if one could solve the complicated combinatorial problems involved, it would give satisfactory results for liquids and solids. This is still a heavy task.

Predictive Approaches

Theories of this class place emphasis initially on the process by which the intermolecular forces determine the structure, in the hope that a correct mathematical description of this process will lead to equations whose solutions describe the actual structure. Theories of this class are called "distribution function" theories because the equations involve distribution functions specifying the probability of finding sets of molecules in particular configurations. This approach draws its ideas to some extent from the equally successful
kinetic theory of gases. Actually this decade coincides, rather precisely, with the start of the transition from the theories of interpretation to theories of prediction as regards the structure of simple fluids. Of course, there is still, and always will be, room for theories of interpretation. It would be foolish, for example, to attempt to predict the structure of water from the first principles. But for the really simple fluids, in particular (perhaps exclusively) for the inert gases, the last thirty years have seen increasingly successful attempts to predict scattering intensities, X-ray or neutron, directly from assumptions about the interatomic forces. And for liquid metals also, there is hope that the attempt will be profitable.

If we ignore multiple scattering, the scattering function \( i(s) \) is essentially the Fourier transform of the pair correlation function \( h(r) \), or \( g(r)^{-1} \), where \( g(r) \) is the radial distribution function.* For the customary assumption that the interatomic forces may be represented by additive pair potentials, all thermodynamic properties can be derived from this correlation function \( h(r) \), if it is known over an appropriate range

---

*The scattering function, \( i(s) \), for X-rays, is defined as \( i(s) = I(s)/f^2(s) - 1 \), where \( I(s) \) is the intensity of coherently scattered radiation, fully corrected for polarization, absorption, etc.; \( f(s) \) is the atomic scattering factor, and \( s = 4\pi \sin \theta /\lambda \) is the scattering variable.
of density and temperature. The theory of the structure of simple liquids is thus intimately enmeshed in the theory of the equation of state and, more particularly, in the theory of phase changes.

The three theories, customarily called Born-Green, hyperchain, and Percus-Yevick, [50] of which any discussion of the theory of fluids must take account, had very different origins: although the last two are sufficiently alike in structure to be classed together. It is the Born-Green theory which dates back to the mid-thirties. Its two equations,

$$kT \v_1 g(1,2) = -g(1,2) \v_1 u(1,2) - \rho \int g(1,2,3) \v_1 u(1,3) d3$$ (1)

and

$$g(1,2,3) = g(1,2)g(2,3)g(1,3)$$ (2)

having been given by Yvon [63] and Kirkwood [26] respectively, in 1935. The first, in which $g(1,2)$ and $g(1,2,3)$ denote the pair and triplet distribution functions and $u(1,2)$ the interatomic potential, is an exact equation: One of a hierarchy of equations linking successive distribution functions, it is a consequence of Boltzmann's distribution law.

The second is an approximation, the superposition approximation, expressing the additivity of potentials of mean force,
which can be argued on physical grounds. They were brought together by Yvon \cite{64} in 1937. Yvon also gave (1935) the pressure, or virial equation,

\[ P = \rho kT - \frac{1}{2} \rho^2 \int ru'(r)g(r)dr \quad (3) \]

enabling us to pass from the distribution function \( g(r) \) to the equation of state. Later (1946) the theory was redeveloped, independently of Yvon's work, both by Bogolyubov \cite{13} and by Born and Green \cite{14}.

Although quantitatively, the Born-Green theory is very much inferior to its later rivals, perhaps no theory has yet had greater consequences in predicting liquid-solid phase transition.

The most attractive feature of the two other theories is that both of them incorporate the Ornstein-Zernike \cite{40} equation

\[ h(1,2) = c(1,2) + \rho \int c(1,3)h(2,3) d3 \quad (4) \]

relating the total correlation function \( h(r) \), or \( g(r)-1 \) to the direct correlation function \( c(r) \). Essentially this equation provides the definition of one function in terms of another, and nothing more. It has the consequence, of course, that the compressibility equation of Zernike and Prins (1927) \cite{49}. 

\[ kT \frac{\partial \rho}{\partial P} = 1 + \rho \int h(1,2) d2 = I(0) \quad (5) \]
where $I(0)$ is the structure factor, $1 + i(s)$, for limitingly small scattering angles, and which is a second route to thermodynamic behavior, can be written in the alternative form,

$$\frac{1}{kT} \frac{\partial P}{\partial \rho} = 1 - \rho \int c(1,2) \, d2. \tag{6}$$

But whether we have gained anything, whether $c(r)$ is a useful physical concept, can be judged only by whether $c(r)$ is more simply, or transparently, related to the interatomic potential than is $h(r)$. A definition is not a theory.

The simplest possible theory, of hyperchain or Percus-Yevick type, is to assume that $c(r)$ is simply the Mayer f-function i.e., to write

$$c(r) = \exp[-u(r)/kT] - 1. \tag{7}$$

This assumption leads [49], essentially to the crudest form of the linearized Born-Green equations.

Hyperchain equation is originally the result obtained independently by many people some nine years ago [50], such that one retains the Ornstein-Zernike equation together with a second equation for $c(r)$, namely,

$$c(r) = h(r) - \ln[1 + h(r)] - u(r)/kT. \tag{8}$$
The Percus-Yevick theory [53], although of the same structure, had an entirely different origin. This theory joins the Ornstein-Zernike equation, the second prescription for $c(r)$,

$$c(r) = \left[ 1 - \exp\left(\frac{u(r)}{kT}\right) \right][1 + h(r)].$$

(9)

Extensive calculations [50] on the above mentioned theories have shown that none of them could satisfactorily predict the properties of real-simple liquids and phase-transitions. While Percus-Yevick theory has been successful in predicting an analytic and satisfactory equation of state for systems of hard spheres [60, 54], it is in need of improvement for more realistic models of intermolecular potential functions. Attempts to improve on the present theories of prediction usually bring us to the problem of the triplet distribution function $g(1,2,3)$. This is inevitably true of the Born-Green theory, where it must be the superposition approximation that is inadequate since the other, Yvon, equation is exact: and it is the very essence of Born-Green theory to use this exact equation. Rice and co-workers [62] have replaced the superposition approximation shown by Equation (2) by a more adequate approximation. But it is true also of the hyperchain and Percus-Yevick theories, which successfully by-pass the triplet distribution problem in their original forms. We are also faced with the triplet
distribution function if we attempt to bring three-body forces, or triplet potentials, into the theory of fluids. For although the compressibility Equation (5) or (6), is unmodified, the pressure Equation (3), must now include the virial of the three-body forces: which implies a term involving $g(1,2,3)$. Triplet distribution function $g(1,2,3)$ which is in reality a complicated and unknown function is a great barricade on the way of predictive approaches to the equation of state and other equilibrium properties of liquids.

**Variational and Perturbation Approaches to the Equilibrium Properties of Fluids**

Variational and perturbation approaches which are going to be considered in the next sections, and which the main purpose of this work is based upon, are neither predictive nor interpretive theories. They are mathematical means of expanding the configurational partition function of an original system around a relatively simple reference system in power series, and approximating, or truncating, the power series by some mathematical tools. The reference system which should be considered could be an ideal but exact. That is by defining a particular intermolecular potential function one must be able to calculate other properties of the reference system such as Helmholtz free energy, compressibility, and the radial distribution function, analytically, as functions of the molecular properties. Also, the reference system should be as close
to the original system as possible, which will help the convergence of the power series of the partition function of the original system to be more rapid. Consequently, the reference system could be the result of a predictive or an interpretive theory, which its macroscopic and microscopic properties are known analytically with respect to each other.
Originally the idea of variational and perturbation methods came from the observation that: at very high temperatures, the equation of state of a gas is determined largely by the forces of repulsion between its component molecules, and at somewhat lower temperatures, it should be possible to obtain the equation of state by considering the forces of attraction as variations or perturbations on the forces of repulsion. According to Zwanzig [65], who originally applied this idea, the experimentally available PVT data on the noble gases may be represented, at least at high temperatures, by the equation

\[ \frac{PV}{RT} = a_0(v) + \frac{a_1(v)}{RT} + \frac{a_2(v)}{(RT)^2} + \ldots \]  

(10)

The data on argon and nitrogen for the range of $0^\circ$ C to $150^\circ$ C temperature, and up to a density of six or seven hundred amagat units supported this idea. In his work, Zwanzig chose for the repulsion a rigid-sphere potential with an appropriate diameter, and for the attraction the Lennard-Jones potential. Since the
primary purpose was classical fluids, only the configurational
collection to the partition function was needed. For a sys-
tem consisting of $N$ molecules in a volume $v$, and total poten-
tial energy $U$, the configurational Helmholtz free energy $F$
will be given by

$$\exp (-\beta F) = Q = \frac{1}{N!} \int_v \ldots \int_v \exp (-\beta U) \, dx_1 \ldots \, dx_N; \quad (11)$$

$$\beta = 1/kT.$$

$U$ is a function of the configuration of each molecule, and
$$\int_v \, dx_i$$
is an integral over the entire configuration space of
the $i$th molecule. Also, one could assume that the potential
energy may be separated into two parts,

$$U = U^0 + U^1 \quad (12)$$

where $U^0$ is the potential energy of an unperturbed system,
and $U^1$ is the perturbation. With this assumption, Zwanzig
was able to expand $Q$ by a power series of inverse tempera-
ture around the unperturbed potential $U^0$ and get the follow-
ing relation

$$-kT \ln Q = F = F^0 + w_1 - w_2/kT + O(1/kT)^2 \quad (13)$$

where with the consideration of only two body forces he obtained

$$w_1 = \frac{1}{2} N(N - 1) \iint u(1,2) P^{(2)}_o (1,2) \, dx_1 \, dx_2, \quad (14)$$
and
\[ \begin{align*}
\mathcal{W}_2 &= \frac{1}{8} \left[ N^4 \int \cdots \int [P^{(4)}_o(1,2,3,4) - P^{(2)}_o(1,2)P^{(2)}_o(3,4)] u^{(1)}(1,2) u^{(1)}(3,4) \, dr_1 \cdots dr_4 \\
&+ N^3 \int \int \int \int P^{(3)}_o(1,2,3) u^{(1)}(1,2) u^{(1)}(2,3) \, dr_1 \, dr_2 \, dr_3 \\
&+ \frac{1}{2} N^2 \int \int P^{(2)}_o(1,2) [u^{(1)}(1,2)]^2 \, dr_1 \, dr_2 \right], \tag{15}
\end{align*} \]

where \( P^{(n)}_o \) is the probability distribution function, in the configuration space, of molecules 1, 2, ..., n.

Zwanzig applied this perturbation equation to the high temperature behavior of a gas of molecules which interact with the potential
\[ \begin{align*}
\mathbf{u}(r) &= \mathbf{u}^o(r) + \mathbf{u}^1(r), \\
\mathbf{u}^o(r) &= \begin{cases} 
\infty & (r \leq c\sigma) \\
0 & (r > c\sigma)
\end{cases}, \\
\mathbf{u}^1(r) &= 4\varepsilon[\left(\frac{\sigma}{r}\right)^{12} - (\frac{\sigma}{r})^6],
\end{align*} \tag{16} \]

where \( c \) was (a number) between zero and one. In fact, this is a modified Lennard-Jones potential. For the reference hard-sphere system, Zwanzig used the solution of Born-Green equation for the radial distribution function and the equation of state. While \( P^{(2)}_o(1,2) \) can be derived from radial distribution function
\[ P^{(2)}_o(1,2) = g_o(1,2)/v^2, \tag{17} \]
for higher distribution functions, there are no satisfactory
relations available; that was why Zwanzig truncated the series
(13) to the second term

\[ F = F^0 + \omega_1 + O(1/kT) \]  \hspace{1cm} (18)

By considering the definition of pressure with respect to
Helmholtz free energy, according to classical thermodynamics

\[ P = - \langle \partial F / \partial v \rangle_T \]  \hspace{1cm} (19)

We get from (18), by considering (14) and (17)

\[ \frac{Pv}{RT} = \left( \frac{Pv}{RT} \right)_0 - \frac{v(\partial F / \partial v)}{RT} \int_0^\infty r^2 g_0(r) u'(r) dr. \]  \hspace{1cm} (20)

This is the equation of state which is a result of the first-
order perturbation theory from the hard-sphere potential basis,
where \( (Pv/RT)_0 \) is the hard-sphere equation of state with the
diameter of hard-spheres equal to \( c\sigma \).

Smith and Alder [51] by joining Equation (20) to the virial
expansion

\[ \frac{Pv}{RT} = 1 + B(T)/v + C(T)/v^2 + D(T)/v^3 + \ldots \]  \hspace{1cm} (21)

and the expansion of the hard-sphere radial distribution
function [39]

\[ g_0(r;v) = \exp(-u^0(r)/kT)[1 + \frac{g_{o,1}(r)}{v} + \frac{g_{o,2}(r)}{v^2} + \ldots] \]  \hspace{1cm} (22)
were able to find the functional forms of the first few virial coefficients with respect to \( T^* = kT/\epsilon \) and \( c \), the cutoff parameter as defined in (16),

\[
B^*/c^3 = B/b_0 c^3 = 1 + (1/T^*c^6)[-2.667 + 1.333[(1/c)^-1]], \quad (23)
\]

\[
C^*/c^6 = C/b_0^2 c^6 = 0.625 + (1/T^*c^6)[-1.247 + 1.333[(1/c^6)-1]], \quad (24)
\]

\[
D^*/c^9 = D/b_0^3 c^9 = 0.287 + (1/T^*c^6)[0.0899 + 0.637[(1/c^6)-1]], \quad (25)
\]

where \( b_0 = 2/3\pi N\sigma^3 \).

For high densities, Smith and Alder [51] used the configurational partition function due to free-volume theory of Lennard-Jones and Devonshire [30]. For a Lennard-Jones potential with a hard sphere cutoff, the partition function is

\[
Q = 2\pi a_0^* \int_0^q \sqrt{y} \exp\left[-12 \frac{1}{T^*} \frac{1(y)}{v^*4} - 2m_1(y)\right] dy \quad (26)
\]

where

\[
1_1(y) = \frac{1 + 12y + 25.2y^2 + 12y^3 + y^4}{(1-y)^{10}} - 1,
\]

\[
m_1(y) = [(1+y)/(1-y)^4] - 1,
\]

\[
a_0^* = a_0/\sigma = (\sqrt{2} v^*)^{1/3}, \quad v^* = v/\sigma^3,
\]

and

\[
q = [1 - (c/a_0^*)^2],
\]

where \( a_0^* \) is the reduced nearest-neighbor distance in a face-centered-cubic lattice. The series in powers of \( 1/T^* \) was
obtained by an expansion of the exponential in the partition function (26). The first perturbation term could be calculated analytically which then leads to the following equation of state

\[
Pv/RT = q^{-k} + \frac{24}{T^*} \left( \frac{1}{\nu^2} - \frac{1.2}{\nu^4} \right) + \frac{12}{T^*} (1 - q^{-k}) \left[ \frac{L_1(q)}{v^4} - \frac{2M_1(q)}{v^2} \right]
+ \frac{12}{T^*} \left[ (3 + q^{-k}) \frac{L_2(q)}{v^4} - (1 + q^{-k}) \frac{2M_2(q)}{v^2} \right]
\]

where \( L_i(q) = l_i(q) + (1/128)l_i(q/2) + (2/729)l_i(q/3) \),

\[
M_i(q) = m_i(q) + (1/16)m_i(q/2) + (2/27)m_i(q/3),
\]

and where

\[
l_2(q) = \frac{1 + 4.2q + 3q^2 + (1/3)q^3}{(1-q)^3} - 1,
\]

and \( m_2(q) = [1/(1-q)^3] - 1 \).

Even though the calculations by Zwanzig were not as successful as they were expected (probably because of the computational errors), Smith and Alder showed that it was possible to evaluate theoretically the thermodynamic quantities for a potential slightly different from the hard-sphere potential at all densities. Their calculations lead to an expansion of the thermodynamic quantities in powers of the reciprocal temperature. The convergence of the expansion on the equation of state was such that the first two terms were able to approximate \( Pv/RT \), for a reduced temperature greater than 2.0 to within 0.03 unit up to almost solid densities.
One disadvantage of the above perturbation methods comes from the fact that the repulsive part of a real intermolecular potential, though steep, is not infinitely steep as assumed in (16). This introduces complications in locating the hard-sphere cutoff, a parameter to which numerical results are extremely sensitive. To solve this problem, McQuarrie and Katz [36], following Rowlinson [47], considered a system with a pairwise-additive intermolecular potential

$$u_n(r) = a \left[ \left( \frac{\sigma}{r} \right)^n - \left( \frac{\sigma}{r} \right)^6 \right]$$  \hspace{1cm} (28)

with

$$a = \left[ \frac{n}{(n-6)} \right] \frac{1}{6}(n-6) \epsilon n.$$  \hspace{1cm} (29)

If we define $$U_\infty(n)$$, it will be evident that

$$u_n(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right]$$  \hspace{1cm} (29)

$$u_n(r) \equiv u_1(x) = \begin{cases} \infty & (r < \sigma) \\ -\epsilon \left( \frac{\sigma}{r} \right)^6 & (r \geq \sigma) \end{cases}$$

Upon this character of $$U_n(r)$$ as defined by (29), McQuarrie and Katz rigorously expanded the partition function in powers of $$1/n$$. 
\[ Q(n) = Q(n = \phi) + n^{-1} \left[ \frac{\partial Q}{\partial 1/n} \right]_{n=\infty} + O(n^{-2}) \] (30)

Following Zwanzig and Rowlinson, they got

\[
\frac{Q_n}{Q_o} = 1 - \frac{2\pi N^2 \beta \sigma^3}{V} \int_0^\infty x^2 u_1(x) g_o(x; \rho) \, dx
\]

\[
- \frac{2\pi N^2 \sigma^3 q_o(1; \rho)}{nV} (\gamma + \ln \beta a)
\]

\[ + O(1/n^2) + O(\beta/n) + O(\beta^2), \] (31)

where

\[
\gamma + \ln \beta a = - \beta a \int_0^\infty \ln Z \cdot \exp[-\beta a Z] \, dZ
\] (32)

and \( Q_o, g_o \) are the partition function and the radial distribution function of hard-sphere system respectively, while \( q_o(1; \rho) \) is the value of \( g_o \) at \( x = 1, x = r/\sigma \).

Finally for the equation of state by using (19), McQuarrie and Katz derived the following relation for Lennard-Jones \( n-6 \) potential

\[
\frac{PV}{RT} = 1 + Z_o(\rho^*) + \frac{3}{n} (\gamma + \ln \frac{\beta}{\sigma}) (\rho^* \frac{\partial Z_o}{\partial \rho^*})
\]

\[
- \frac{3}{n} \ln(T^*) (\rho^* \frac{\partial Z_o}{\partial \rho^*}) - \frac{3(a/\epsilon) \rho^*}{T^*} \frac{\partial}{\partial \rho^*} \left[ \rho^* J(\rho^*) \right],
\] (33)

where

\[
J(\rho^*) = \int_0^\infty x^4 g_o(x; \rho^*) \, dx.
\]
and

$$Z_0 = \left( \frac{PV}{RT_0} \right) - 1 = (2\pi N \sigma^3 / 3\nu) g_0 (1; \rho),$$

and for $Z_0$, they used the Padé approximant of Ree and Hoover [43]

$$Z_0 = \rho^* (1 + 0.063507 \rho^* + 0.017329 \rho^*^2) / (1 - 0.561493 \rho^* + 0.081313 \rho^*^2).$$

The equation of state (33), reliably produces PVT data up to $\rho^* = 0.95$ and reduced temperatures as low as $T^* = 3$. As could be seen, while the method due to McQuarrie and Katz (alike the previously mentioned perturbation methods) cannot predict the low temperature behavior, it is independent of any adjustable parameter:

As it was explained before, $\omega_2$, the coefficient of $-\frac{1}{kT}$ in (13) which is shown by relation (15), is a complicated function of the second, third, and fourth distribution functions. These distribution functions by themselves are very complicated and unknown functions. That was the reason why Zwanzig and the other investigators had to truncate the series (13) in the second term. Also, with the fact that all the above mentioned approaches suggested that the expansion in inverse powers of temperature provided by perturbation theory was useful only at high temperatures, and probably
not useful at the temperatures and densities characteristic of the liquid state: It was clearly important to know whether this apparent failure at low temperatures was due to the perturbation treatments of the attractive forces or to the treatment of the finite steepness of the repulsive potential. For this purpose Barker and Henderson [6] decided to use the perturbation theory of Zwanzig for the square-well potential function. In this case, the effect of the attractive forces is not complicated by the "softness" of the repulsive part of the potential, which is in fact infinitely steep. Furthermore, Monte Carlo [45] and molecular-dynamics [2] calculations provided them machine-calculated data with which the theory could be compared, without the uncertainty due to lack of knowledge of the true potential function which is inevitable in applications to real fluids. Also, they were able to find two different approximate but manageable relations for \( w_2 \) as defined by (15), to be able to check the convergence of the expansion (13) as follows: macroscopic compressibility approximation: m.c.

\[
\frac{1}{4} \rho \int_{V} \left[ u_1(r) \right]^2 kT \left( \frac{\partial \rho}{\partial P} \right)_o g_o(r) \, dr, \quad (35)
\]

and local compressibility approximation: l.c.

\[
\frac{1}{4} \rho \int_{V} \left[ u_1(r) \right]^2 kT \left[ \frac{\partial (\rho g)}{\partial P} \right]_o \, dr, \quad (36)
\]
The other advantage of choosing square-well potential was the fact that no adjustable parameter was needed.

\[
    u_{0}(r) = \begin{cases} 
    \infty & (r \leq \sigma) \\
    0 & (r > \sigma)
    \end{cases} \\
    u_{1}(r) = \begin{cases} 
    0 & (r < \sigma) \\
    -\epsilon & (\sigma < r < \lambda \sigma) \\
    0 & (r > \lambda \sigma)
    \end{cases}
\]

(37)

Then by using l.c. approximation, they got

\[
    \frac{F - F^{0}}{NkT} = -2\pi \rho \frac{\epsilon}{kT} \int_{0}^{\lambda \sigma} \frac{r^{2} g_{o}(r) dr}{\sigma}.
\]

Then

\[
    -\pi \rho \frac{\epsilon}{kT} \left( \frac{2}{1 + 4\eta} \right) \frac{(1 - \eta)^{4}}{4\eta^{5}} \frac{d}{d\rho} \left[ \sqrt{\lambda \sigma} \int_{0}^{\lambda \sigma} r^{2} g_{o}(r) dr \right].
\]

(38)

where

\[
    \eta = \pi \rho \sigma^{3}/6.
\]

In getting to this relation, the hard sphere compressibility from Percus-Yevick equation derived by Thiele [54] and Wertheim [60] was used. For \(\lambda < 2\), (which was the case of their calculation, \(\lambda = 1.5\)) analytic expressions [60] for \(g_{o}(r)\) were available. The equation of state can be obtained by straight-forward numerical differentiation of (38) by the use of relation (19). Relation (34) was used for the hard sphere pressure required for the zero order term

\[
    (Pv/RT)_{0} = 1 + Z_{0}.
\]
The difference between l.c. and m.c. approximations for the second term as shown by (35) and (36) was not that large to affect their graphical comparisons with machine-calculated data. Their results indicated that the useful convergence of the perturbation expansion extends to very low temperatures for the square-well potential, so that the truncated expansion with first- and second-order terms gives a good approximation to the correct pressures at all temperatures relevant for liquids and compressed gases. Also, their results suggested that their two approximations to the second order term were both reasonably accurate.

Later, Barker and Henderson applied the perturbation method to more realistic potentials [7, 8]. They considered an arbitrary potential function \( u(r) \) and defined a modified potential function \( v(\delta, \sigma, \alpha, \gamma; r) \) by the relation
\[
v(d, \sigma, \alpha, \gamma; r) = u[d+(r-d)/\alpha], \quad d+(r-d)/\alpha < \sigma
\]
\[
= 0, \quad \sigma < d + (r-d)/\alpha < d+(\sigma-d)/\alpha
\]
\[
= \gamma u(r), \quad \sigma < r.
\]
They assumed that \( u(r) \) rises to effectively infinite positive values for small values of \( r \) and that \( u(\sigma) \) is zero. For \( \alpha = \gamma = 0 \), the potential defined by Equation (39) becomes the
hard-sphere potential of diameter \( d \), for \( \alpha = \gamma = 1 \) the original potential is recovered. The parameter \( \alpha \) varies the steepness of the modified potential in the repulsive region; this is inverse-steepness parameter. The parameter \( \gamma \) varies the depth of the potential in the attractive region. The procedure is to expand the configuration integral in a double Taylor series in \( \alpha \) and \( \gamma \) about the point \( \alpha = \gamma = 0 \), which corresponds to the hard-sphere potential. The final result is shown by the following relation

\[
\frac{F - F^0}{NkT} = -2\pi \rho \int_0^\infty \left[ d - \int_0^\sigma \left( 1 - \exp[-\beta u(r)] \right) dr \right] dr + \gamma 2\pi \rho \beta \int_0^\infty g_o(r) u(r) r^2 dr + \text{higher order terms.} \tag{40}
\]

In Equation (40) \( F \) is the Helmholtz free energy corresponding to the potential \( v(r) \) and \( F^0 \) is that corresponding to the hard-sphere potential of diameter \( d \). For \( \alpha = \gamma = 1 \) one obtains an expression for the free energy corresponding to the original potential \( u(r) \). The values of \( d \) and \( \sigma \) are still at disposal. As stated previously, they use for \( \sigma \) the value of \( r \) for which \( u(r) \) is zero. Also, they chose for \( d \) the value given by

\[
d = \int_0^\sigma \left[ 1 - \exp[-\beta u(r)] \right] dr \tag{41}
\]

This depends on temperature but not on density, and with this choice the term of order \( \alpha \) in Equation (40) is zero at all densities.
With the choice of hard-sphere diameter $d$ as shown by (41) Barker and Henderson were able to extend the applicability of the perturbation equation of state (40) to reduced temperatures as low as 1.3 and reduced densities close to the solid phase. They also applied their perturbation approach to systems of fluids with two- and three-body forces [9,10] and also to quantum fluids [25].

Kozak and Rice [27] attempted to extend the perturbation equation of state which was derived by Smith and Alder [51] by using also higher order virial coefficients. Then they postulated that the cutoff parameter $c$ is an equilibrium property of the system. In other words, they required that at equilibrium the Helmholtz free energy should be minimum with respect to $c$. Even that they got satisfactory results at high temperatures, it is not expected that they could get good results at low temperatures. The cutoff parameter $c$ has only mathematical significance, and no physical meaning could be assigned to it. The reason for the success of the variational method of Kozak and Rice at high temperatures and its expected failure at low temperatures will be given in the later parts of this dissertation.

As was shown in the above review of the previous works, the main problem is still the choice of the cutoff parameter
and the infinite steepness of the repulsive part of the potential. Even that in the method of Barker and Henderson these two problems are solved completely for gas phase (because of the fact that $T^*_{\text{critical}} \approx 1.35$ for Lennard-Jones fluid) they cannot claim that their method is sufficient for liquid phase too. By the variational technique which will be introduced in the later parts of this dissertation, it is believed that the problem of the equation of state of simple liquids is solved at least, for the ranges of densities and temperatures where experimental and machine-calculated data are available.
CHAPTER III

THE BASIC INEQUALITIES

Consider a variable $x$ which is distributed according to a probability distribution $P(x)$. If, in the usual way, we define

$$\langle f(x) \rangle = \int P(x) f(x) \, dx$$  \hspace{1cm} (42)

a function $f(x)$ may be expanded about the value $\langle x \rangle$ by Taylor's theorem:

$$f(x) = f(\langle x \rangle) + (x-\langle x \rangle) f'(\langle x \rangle) + \frac{1}{2!} (x-\langle x \rangle)^2 f''(\xi)$$  \hspace{1cm} (43)

where $x < \xi < \langle x \rangle$.

If equation (43) is now averaged with probability distribution, $P(x)$, we have

$$\langle f(x) \rangle = f(\langle x \rangle) + \frac{1}{2!} \langle (x-\langle x \rangle)^2 f''(\xi) \rangle$$  \hspace{1cm} (44)

If one chooses $f(x)$ such that $f''(x)$ is always positive, then the following inequality holds

$$\langle f(x) \rangle \geq f(\langle x \rangle)$$  \hspace{1cm} (45)

when $f''(x) \geq 0$.  

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Similarly, if \( f(x) \) is chosen such that \( f^{IV}(x) \) is always positive, then the following inequality will also hold

\[
\langle f(x) \rangle \geq f(\langle x \rangle) + \frac{1}{2!} \langle (x-\langle x \rangle)^2 \rangle f''(\langle x \rangle) + \frac{1}{3!} \langle (x-\langle x \rangle)^3 \rangle f'''(\langle x \rangle) \quad (46)
\]

Equation (45) is essentially the variational principle used by Feynman \([18]\). According to Lukes and Jones \([33]\), we shall refer to (45) and (46) as the basic inequalities. It is quite evident that for \( f(x) = \exp(x) \), the above inequalities will hold.

**Inequalities and Variational Principles for the Partition Function**

The partition function for a system with \( N \) particles and total potential energy \( U(x_1, \ldots, x_N) = U \), of interaction of all the \( \frac{N(N-1)}{2} \) pairs of particles in the system, in equilibrium, is \([23]\)

\[
Q = \frac{1}{N! \Lambda^{3N}} \int \cdots \int_{V} e^{-\beta U} \, dx_1 \cdots dx_N ; \quad \Lambda = \frac{\hbar}{(2\pi mkT)^{\frac{3}{2}}} \quad (47)
\]

Now let us consider a second system as a reference system with total potential energy function \( U_0 \). Then one can write

\[
\frac{Q}{Q_0} = \int \cdots \int \frac{e^{-\beta U_0}}{Z_0} \cdot e^{-\beta (U-U_0)} \, dx_1 \cdots dx_N ; \quad Z_0 = N! \Lambda^{3N} Q_0 \quad (48)
\]

where \( Z_0 \) is the configuration integral with \( U_0 \), the potential function of the system.
As we know from statistical mechanics $\frac{e^{-\beta U_o}}{Z_o}$ is the probability distribution function of the $N$ molecules in the reference system. Consequently, Equation (48) is, in fact, the expectation value of $\exp[-\beta(U-U_o)]$ over the probability distribution function $\frac{e^{-\beta U_o}}{Z_o}$, or

$$\frac{Q}{Q_o} = \langle e^{-\beta(U-U_o)} \rangle_o.$$  

Since for $f(x) = \exp(x)$ we always have

$$f''(x) = \exp(x) \geq 0$$

and

$$f''(x) = \exp(x) \geq 0.$$  

Then both of the basic inequalities (45) and (46) are correct here for $f(x) = \exp[-\beta(U-U_o)]$ and one could write

$$\frac{Q}{Q_o} \geq \exp[\langle -\beta(U-U_o) \rangle_o].$$

Then both of the basic inequalities (45) and (46) are correct here for $f(x) = \exp[-\beta(U-U_o)]$ and one could write

$$\frac{Q}{Q_o} \geq \exp[\langle -\beta(U-U_o) \rangle_o].$$

and

$$\frac{Q}{Q_o} \geq \exp[\langle -\beta(U-U_o) \rangle_o][1 + \frac{1}{2!} \langle [\beta(U-U_o) - \langle \beta(U-U_o) \rangle_o]^2 \rangle \rangle \rangle + \frac{1}{3!} \langle [\beta(U-U_o) - \langle \beta(U-U_o) \rangle_o]^3 \rangle].$$

According to statistical mechanics, the Helmholtz free energy of a system is defined in terms of the partition function of that system by

$$F = -kT \ln \Omega.$$
Also, after defining $\beta = \frac{1}{kT}$, the above inequalities could be written in terms of Helmholtz free energy in the following forms.

From inequality (50)

$$F \leq F_o + \langle U-U_o \rangle_o$$  \hspace{1cm} (52)

and from inequality (51)

$$F \leq F_o + \langle U-U_o \rangle_o - kT \ln(1 + \nu)$$  \hspace{1cm} (53)

where

$$\nu = + \beta^2 \left\{ \frac{1}{2!} \langle (U-U_o - \langle U-U_o \rangle_o)^2 \rangle_o - \frac{\beta}{3!} \langle (U-U_o - \langle U-U_o \rangle_o)^3 \rangle_o \right\}$$  \hspace{1cm} (54)

Because of the inapplicability of inequality (53), the following method is used to simplify it to a more rational form.

According to Zwanzig [65] the Helmholtz free energy of a system of $N$ molecules could be expanded with respect to the powers of $\frac{1}{kT}$ in the following form:

$$F = F_o + \sum_{n=1}^{\infty} \frac{w_n}{n!} (- \frac{1}{kT})^{n-1}.$$  \hspace{1cm} (55)

If we assume that the above series is convergent, we are able to truncate it to the following form

$$F = F_o + w_1 - \frac{w_2}{2!} \frac{1}{kT} + \frac{w_3}{3!} \left( \frac{1}{kT} \right)^2 - \frac{w_4(\xi)}{4!} \left( \frac{1}{kT} \right)^3$$  \hspace{1cm} (56)

where $\xi$ is a definite value and
\[ w_1 = \langle U_UO \rangle, \]
\[ w_2 = \langle (U-U_O - \langle U-U_O \rangle)^2 \rangle, \]
\[ w_3 = \langle (U-U_O - \langle U-U_O \rangle)^3 \rangle, \]
\[ w_4(\xi) = \langle (\xi - \langle \xi \rangle)^4 \rangle. \]

Now since \(-\frac{w_4(\xi)}{4!} \left(\frac{1}{kT}\right)^3\) is always negative, we could write

\[ F \leq F_O + w_1 - \frac{w_2}{2!} \left(\frac{1}{kT}\right) + \frac{w_3}{3!} \left(\frac{1}{kT}\right)^2 \]

By considering the definition of \(\nu\) as given by (54), the above inequality can be written in the following form

\[ F \leq F_O + \langle U_UO \rangle - (kT)\nu \quad (57) \]

Of course, inequality (52) could also be produced by a similar method as above, but the previous method is more rigorous.

From the above discussion, we see that we have produced two different inequalities for Helmholtz free energy as follows.

The first inequality:

\[ F \leq F_O + \langle U-U_O \rangle, \quad (58) \]

and the second inequality:
Consideration of Only the Two-Body Interactions

In the case where only the two-body interactions are considered, one can write for the potential energy functions, the following relations

\[ U = \sum_{i>j=1}^{N} u_{ij} \quad \text{and} \quad U_{o} = \sum_{i>j=1}^{N} u_{ij}^{o} \]  

(60)

where \( u_{ij} \) is the potential energy function of interaction between particles \( i \) and \( j \). In this case, inequality (58) could be written as

\[ F \leq F_{o} + \sum_{i>j=1}^{N} \langle u_{ij}^{o} \rangle \]  

(61)

and inequality (59) in the form of

\[ F \leq F_{o} + \sum_{i>j=1}^{N} \langle u_{ij}^{o} \rangle - \frac{\beta}{2!} \left\{ \sum_{i>j=1}^{N} \left[ \langle u_{ij}^{o} \rangle - \langle u_{ij} \rangle \right]\right\}^{2} \]  

\[ - \frac{\beta^{2}}{3!} \left\{ \sum_{i>j=1}^{N} \left[ \langle u_{ij}^{o} \rangle - \langle u_{ij} \rangle \right]\right\}^{3} \]  

(62)

For simplicity, let us define

\[ \chi_{ij} = u_{ij} - u_{ij}^{o} - \langle u_{ij} \rangle \]
Then,

\[
\langle (\sum_{i>j=1}^{N} x_{ij})^2 \rangle_0 = \sum_{ij}^{i\neq j} \langle x_{ij}^2 \rangle_0 + 2 \sum_{ijk}^{i\neq j \neq k} \langle x_{ij} x_{jk} \rangle_0 + \sum_{ijkl}^{i\neq j \neq k \neq l} \langle x_{ij} x_{kl} \rangle_0
\]

(63)

In a similar way, an expansion could be produced for the coefficient of \( \beta^2 \) in inequality (62) which is lengthy but straightforward. The above procedure is basically the same as Zwanzig's perturbation expansion of the partition function \([65]\).

By considering \( i \) and \( j \) as dummy indices, the summation signs in the above equations could be replaced by multipliers as follows:

\[
\sum_{i>j=1}^{N} \langle u_{ij} - u_{ij}^0 \rangle = \frac{N(N-1)}{2} \langle u_{12} - u_{12}^0 \rangle
\]

(64)

and

\[
\langle \left( \sum_{i>j=1}^{N} x_{ij} \right)^2 \rangle = \frac{1}{2} \frac{N!}{(N-2)!} \langle x_{12}^2 \rangle_0 + \frac{N!}{(N-3)!} \langle x_{12} x_{23} \rangle_0
\]

\[
+ \frac{1}{4} \frac{N!}{(N-4)!} \langle x_{12} x_{34} \rangle_0.
\]

(65)
CHAPTER IV

INEQUALITIES AND VARIATIONAL CALCULATIONS FOR FLUIDS

In this chapter, the inequalities (61) and (62) will be used to calculate the Helmholtz free energy and other thermodynamic properties of a fluid system by a variational technique which will be introduced.

Introduction of the Correlation Functions

In a fluid, the $n^{th}$ correlation function $g^{(n)}(\mathbf{r}_1, \ldots, \mathbf{r}_n)$ is defined as

$$g^{(n)}(\mathbf{r}_1, \ldots, \mathbf{r}_n) = \frac{v^n \int \ldots \int e^{-\beta U} d\mathbf{r}_{n+1} \ldots d\mathbf{r}_n}{z_0}$$

(66)

for $n = 2$, $g^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = g^{(2)}(r_{12})$ is called the pair correlation, or the radial distribution function. With this definition of the correlation functions, relations (64) and (65) will be as follows [65]:

$$\sum_{i>j=1}^{N} \langle u_{ij} - u_{ij}^o \rangle = \frac{N(N-1)}{2} \frac{1}{v^2} \int \int (u_{12} - u_{12}^o) g^{(2)}(r_{12}) d\mathbf{r}_1 d\mathbf{r}_2$$

(67)
and

$$
\langle \sum_{ij} x_{ij}^2 \rangle = \frac{1}{4V^4} \frac{N!}{(N-4)!} \int \int \int \int g^{(4)}_{ij} (x_1 \cdots x_4) x_{12} x_{34} dx_1 \cdots dx_4
$$

$$
+ \frac{1}{V^3} \frac{N!}{(N-3)!} \int \int g^{(3)}_{ij} (x_1, x_2, x_3) x_{12} x_{23} dx_1 dx_2 dx_3
$$

$$
+ \frac{1}{2V^2} \frac{N!}{(N-2)!} \int g^{(2)}_{ij} (r_{12}) x_{12}^2 dx_1 dx_2 .
$$

By a similar procedure as shown above, it is possible to find the relation between the coefficient of $\beta^2$ in inequality (62) and the correlation functions, but the result is a very lengthy equation.

Consequently, the two inequalities produced for the Helm­holtz free energy of the system will have the following forms.

**The First Inequality:**

$$
F \leq F_0 + \frac{N}{2} \rho \int (u_{12} - u_{12}^0) g^{(2)}_{ij} (r_{12}) dx_{12}
$$

(69)

and **the Second Inequality:**

$$
F \leq F_0 + \frac{N}{2} \rho \int (u_{12} - u_{12}^0) g^{(2)}_{ij} (r_{12}) dx_{12} - \frac{\beta}{2} \langle (\sum x_{ij})^2 \rangle_0 - \frac{\beta^2}{6} \langle (\sum x_{ij})^3 \rangle_0.
$$

(70)

In inequalities (69) and (70), $\frac{N}{V}$ is replaced by $\rho$, $N-1$ is approximated with $N$ (which is a good approximation for $N \approx O(10^{23})$), the
center of the coordinate is brought to the center of the particle number 1, and the integration over $d\mathbf{r}_2$ is performed which is equal to $V$, the total volume of the system.

**Approximations Introduced in the Second Inequality**

As is well known, the second correlation function, $g^2(\mathbf{r}_1, \mathbf{r}_2)$, is quite complicated and its analytic functional form is not available. For systems of particles with simple potential energy functions, such as hard-discs and hard-spheres, some satisfactory approximations are available for pair correlation functions. The coefficients of $\beta$ and $\beta^2$ in the inequality (70) involve also the third, fourth, fifth and sixth correlation functions for which also, no satisfactory approximations are available. Their direct evaluation from Monte Carlo or molecular dynamics calculations would be prohibitively difficult. For this reason, a formulation in terms of the higher moments of the second correlation function (which is actually the mean second correlation or the radial distribution function) will be used. This formulation is originally performed by Barker and Henderson [6] who used it for approximating a relation similar to the coefficient of $\beta$ in inequality (70). In the present report, this formulation is also extended for approximation of the coefficient of $\beta^2$ of inequality (70).

According to Barker and Henderson [6], the partition function of a system can be expanded around the partition function
of a reference system in the following form

\[ Q = Q_0 \exp(-\beta \sum_i \langle N_i \rangle u_i^i) \langle \exp[-\beta \sum_i (N_i - \langle N_i \rangle) u_i^i] \rangle \]  \hspace{1cm} (71)

where \( Q_0 \) is the partition function of the reference system. \( N_i \) is the number of intermolecular distances in the range of \( R_i \) to \( R_{i+1} \) for \( i = 0, \ldots \) etc., in the reference system. The angular brackets are defined as "the average over the configurations of the reference system", and \( u_i^i = (u-u_0)^i \), is related to the intermolecular distance \( R_i \). Of course \( \langle N_i \rangle \) is directly related to the mean radial distribution function:

\[ \langle N_i \rangle = 2\pi N_0 R_i^2 g_0 (R_i) (R_{i+1} - R_i) \]  \hspace{1cm} (72)

where the latter form is approximately valid if the interval width is sufficiently small. Expanding the exponential in (71) and introducing it in the form of Helmholtz free energy by the relation \( F = -kT \ln Q \), we get

\[ F = F_0 + \sum_i \langle N_i \rangle u_i^2 - \frac{1}{2} \beta \sum_{ij} \langle N_i - \langle N_i \rangle \rangle \langle N_j - \langle N_j \rangle \rangle u_i^i u_j^j \\
+ \frac{1}{3!} \beta^2 \sum_{ijk} \langle N_i - \langle N_i \rangle \rangle \langle N_j - \langle N_j \rangle \rangle \langle N_k - \langle N_k \rangle \rangle u_i^i u_j^j u_k^k \\
+ 0(\beta^3). \]  \hspace{1cm} (73)
We now proceed to derive an approximate expression based on semi-macroscopic considerations. The $N_i$ may be regarded as representing the numbers of molecules in spherical shells surrounding other central molecules. If these shells were large macroscopic volumes, the numbers of molecules in different shells would be uncorrelated, that is, the following relations would hold:

\[
\langle N_i N_j \rangle - \langle N_i \rangle \langle N_j \rangle = 0 \quad i \neq j,
\]
\[
\langle N_i N_j N_k \rangle - \langle N_i N_j \rangle \langle N_k \rangle = 0 \quad k \neq i, j,
\]
\[
\langle N_i^2 \rangle - \langle N_i \rangle^2 = 0 \quad i \neq j,
\]

and

\[
\langle N_i \rangle^2 \langle N_j \rangle - \langle N_i N_j \rangle \langle N_i \rangle = 0 \quad i \neq j. \quad (74)
\]

Then the fluctuations of the number in a given shell would be given by [23]

\[
\langle (N_i - \langle N_i \rangle)^2 \rangle = \langle N_i \rangle \frac{1}{\beta} \frac{\partial \rho}{\partial P} \quad (75)
\]

and as is shown in the Appendix

\[
\langle (N_i - \langle N_i \rangle)^3 \rangle = - \langle N_i \rangle \frac{1}{\beta^2} \left[ \left( \frac{\partial \rho}{\partial P} \right)^2 + \frac{\rho}{2} \frac{\partial}{\partial P} \left( \frac{\partial \rho}{\partial P} \right)^2 \right] \quad (76)
\]

where $P$ is the pressure and $\frac{1}{\beta} \frac{\partial \rho}{\partial P}$ is the macroscopic compressibility. If we substitute the known value of $\langle N_i \rangle$ as given by Equation (72) and consider relations (74), (75), and (76), Equation (73) becomes
As shown above, the formulation of Barker and Henderson, which is extended here, is basically the same as the variational expansion which ended up with the inequalities (69) and (70). But the advantage of inequalities (69) and (70) is the possibility of expressing their terms with respect to the correlation function. While it would have been possible to produce the same kind of inequalities as (69) and (70) with the perturbation expansion of Barker and Henderson as expressed above [6] (it could be shown that Equation (77) is an inequality), it has been also possible to find approximations for the coefficients of $\beta$ and $\beta^2$ in inequality (70) which otherwise would have been extremely difficult. Then, from (67), (68) and (77), we get

\[
\langle \Sigma_{ij} \chi_{ij} \rangle_O = \frac{N}{2} \rho \left[ \frac{1}{\beta} \frac{\partial \rho}{\partial \rho} \right]_O \int_V \left[ u_1(R) \right]^2 g_o(R) dR
\]

and

\[
\langle \Sigma_{ij} \chi_{ij} \rangle^3 O = \frac{N}{2} \rho \beta^2 \left[ \frac{\partial \rho}{\partial \rho} \right]^2 O + \frac{\rho \beta}{2} \left[ \frac{\partial \rho}{\partial \rho} \right]^2 \int_V \left[ u_1(R) \right]^3 g_o(R) dR.
\]
In the above relations, \( \frac{1}{\beta} \left[ \frac{\partial P}{\partial T} \right] \) is the macroscopic compressibility coefficient for the reference system.

**Consideration of Both Two- and Three-Body Forces**

In the case when both two- and three-body interactions are considered, the potential energy functions should be written as

\[
U = \sum_{i>j=1}^{N} u_{ij} + \sum_{i>j>k=1}^{N} w_{ijk},
\]

and

\[
U_0 = \sum_{i>j=1}^{N} u^0_{ij} + \sum_{i>j>k=1}^{N} w^0_{ijk}.
\]

The first terms in the above two relations describe pair interactions and the second terms, triplet interactions. In this case, the first inequality (69) becomes*

\[
F \leq F_0 + \sum_{i>j=1}^{N} \langle u_{ij} - u^0_{ij} \rangle + \sum_{i>j>k=1}^{N} \langle w_{ijk} - w^0_{ijk} \rangle
\]

By a similar procedure as in the case of only two-body forces, the above inequality becomes

\[
F \leq F_0 + \frac{N(N-1)}{2V^2} \iiint_V (u_{12} - u^0_{12}) g^{(2)} \frac{(r_{12})}{dr_1 dr_2} + \frac{N(N-1)(N-2)}{6V^3} \iiint_V (w_{123} - w^0_{123}) g^{(3)} (r_1, r_2, r_3) dr_1 dr_2 dr_3.
\]

*Inequality (81) is a general inequality and is not particularly for fluids.
By bringing the center of the coordinates to the center of the particle number 1, and approximating \((N-1)\) and \((N-1)(N-2)\) by \(N\) and \(N^2\) respectively, (which are satisfactory approximation for \(N \approx 0(10^{23})\), the relation (82) becomes

\[
F \leq F_o + \frac{N}{2} \rho \int \left(\sum_{12} (u_{12} - u_{12}^o) \right) g^{(2)}(r_{12}) \, dr_{12} \\
+ \frac{N}{6} \rho^2 \int \int \left(\sum_{123} (w_{123} - w_{123}^o) \right) g^{(3)}(r_1, r_2, r_3) \, dr_{12} \, dr_{13}
\]

The second inequality (70) also could be formulated, as above, for the case where three-body interactions are also considered. The formulation is straightforward and lengthy. It includes higher order correlation functions which are progressively difficult for use in any kind of calculation.

**Variational Technique**

The above mentioned inequalities suggest that by varying the properties of the reference system such that the right hand side of the inequalities go to a relative minimum, it may be possible to bring the inequalities to equality or, at least, closer to equality. Principles of variational calculus must be used to attack this problem. What is needed here is the properties of the reference system. In other words, we must know the Helmholtz free energy and the radial distribution function of the reference system as functions of intermolecular parameters of the reference system. Also, inequalities (69) and (70) suggest that, as
Consequently, if a reference system can be chosen such that its intermolecular potential function is close to the functional form of intermolecular potential function of the original system, then the inequalities will be closer to equality and the process of variational calculation will produce a better approximation of the original system.

Consideration of Only Two-Body Forces

In the case where the intermolecular forces between the particles of a system consist of only two-body forces, it is assumed that the intermolecular potential function of the original system is the Lennard-Jones, 12:6 potential.

\[ u(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right]. \]  

where \( \epsilon \) is the depth of the minimum in the potential curve and \( \sigma \) is the diameter of the particles. This choice of the potential function is due to the abundance of the so-called semi-experimental or Monte Carlo and molecular dynamics data for systems with Lennard-Jones potential function. Also, extensive use of the Lennard-Jones potential (see, for example, reference [24]) for real substances has indicated that this potential function is closer to reality than the most of the other analytic potential functions available.
Reference System

As was mentioned above, for the reference system, an intermolecular potential function should be chosen such that the analytic forms of Helmholtz free energy, and the radial distribution function of the reference system can be calculated analytically with respect to its parameters. Besides this, the reference system should be as close to the original system as possible. The only system with qualities as such available is a system consisting of hard spheres such that

\[ u^0(r) = \begin{cases} 
0 & \text{for } r > d \\
\infty & \text{for } r \leq d 
\end{cases} \quad (85) \]

where \( d \) is the diameter of the hard spheres. Wertheim [60] and Thiele [54], independently have calculated the properties of such a system by the solution of the Percus-Yevick equation for hard spheres. Even though the Percus-Yevick equation is an approximate equation, it is exact enough in the case of hard-sphere potential function [54]. While the equation of state of such a system is known analytically, [54, 60], its radial distribution function is not available in an analytic form. Wertheim [60] has introduced a Laplace transform of the radial distribution function in analytic form. Throop and Bearman [55] have done numerical inversion of Wertheim's Laplace transform of the radial distribution function of hard spheres and they
have introduced their results in a numerical table as a function of intermolecular distance and density. But in the variational calculation introduced in this work, it is of advantage to use the relations as analytic as possible. The elegant method of Frisch and coworkers [19] permits such a desire.

Reformulation of the First and Second Inequalities with Respect to the Laplace Transform of the Radial Distribution Function of The Hard-Sphere System

By inserting \( u(r) \) and \( u^0(r) \) as defined by (84) and (85) and the fact that \( dr_{12} = 4\pi r^2_{12} dr_{12} \), inequality (69) becomes

\[
\frac{F}{NkT} \leq \frac{F^0}{NkT} + 2\pi \rho \beta \int_0^\infty 4\epsilon\left[ \frac{(r)}{r} \right]^{12} - \left( \frac{r}{r} \right)^6 \right] g^0_\infty(r) r^2 dr
\]

where the dummy indices 12 in inequality (69) are discarded and \( g^{(2)}_\infty(r) \) is simply shown by \( g^0_\infty(r) \). By introducing \( x = r/d \), the integral in (86) can be shown in a dimensionless form as in the following relation.

\[
\frac{F}{NkT} \leq \frac{F^0}{NkT} + \frac{8\pi \rho d^3}{T^*} \int_1^\infty \left[ \frac{1}{x_\infty} \right]^{12} - \left( \frac{1}{x_\infty} \right)^6 \right] g^0_\infty(x) x^2 dx
\]

where \( T^* = \frac{1}{\beta \epsilon} \) is the dimensionless temperature, and \( c = d/\sigma \). Wertheim [60] has obtained an explicit Laplace transform, \( G(s) \), of the hard-sphere radial distribution function, \( g^0_\infty(x) \), satisfying the Percus-Yevick integral equation

\[
G(s) = \int_1^\infty e^{-sx} g^0_\infty(x) dx.
\]
Let us consider \( U_1(s) \) as the inverse Laplace transform of \( xu^*(x) \)

\[
xu^*(x) = x \left[ \frac{1}{xc} \right]^{12} - \left( \frac{1}{x_c} \right)^6
\]

Then

\[
xu^*(x) = \int_0^\infty e^{-sx} U_1(s) ds.
\]

Substituting (90) in the integral in (88) and rearranging the integral signs, we get

\[
\int_0^\infty xu^*(x) g_0(x) x dx = \int_0^\infty U_1(s) ds \int_0^\infty e^{-sx} g_0(x) x dx = \int_0^\infty U_1(s) G(s) ds.
\]

In deriving the final integral in (91), the definition of \( G(s) \) as introduced by (88), is used. From Laplace transform tables, it can easily be shown that

\[
U_1(s) = L^{-1}[xu^*(x)] = \left( \frac{1}{c} \right)^{12} \cdot \frac{s^{10}}{10!} - \left( \frac{1}{c} \right)^6 \cdot \frac{s^4}{4!}.
\]

and from reference [60]

\[
G(s) = \frac{L(s)}{12\eta[L(s) + S(s)e^s]}
\]

where \( L(s) = 12\eta[(1 + \frac{1}{2\eta})s + (1 + 2\eta)] \),

and \( S(s) = (1-\eta)^2s^3 + 6\eta(1-\eta)s^2 + 18\eta^2s - 12\eta(1+2\eta) \),

\[
\eta = \frac{\pi}{6} \rho d^3 = \frac{\pi}{6} (\rho \sigma^3) c^3.
\]
Finally, the first inequality as was shown by (87) can be written in the following form

\[
\frac{F}{NkT} \leq \frac{F_0}{NkT} + \frac{48n}{T^*} \int_0^\infty U_1(s)G(s)ds,
\]

where \( n, U_1(s), \) and \( G(s) \) are defined by (94), (92), and (93), respectively.

In a similar manner, the second inequality, (70) can be reformulated in an approximate way, with respect to the Laplace transform of the radial distribution function of the reference hard-sphere system. Inserting the approximations (78) and (79) in (70) and following the formulation discussed above, the second inequality (70) becomes

\[
\frac{F}{NkT} \leq \frac{F_0}{NkT} + \frac{48n}{T^*} \int_0^\infty U_1(s)G(s)ds
\]

\[\quad - \frac{96n}{T^*^2} \left[ \frac{1}{\beta} \left[ \frac{\partial \rho}{\partial \rho} \right] \right] \int_0^\infty U_2(s)G(s)ds
\]

\[\quad + \frac{128n}{T^*^3} \cdot \frac{1}{\beta^2} \left[ - \left[ \frac{\partial \rho}{\partial \rho} \right] \right] \int_0^\infty U_3(s)G(s)ds,
\]

where \( U_2(s) \) and \( U_3(s) \) are inverse Laplace transforms of \( xu^2(x) \) and \( xu^3(x) \), respectively

\[
U_2(s) = \left( \frac{1}{c} \right) 24 \frac{s^{22}}{22!} - 2 \left( \frac{1}{c} \right) 18 \frac{s^{16}}{16!} + \left( \frac{1}{c} \right) 12 \frac{s^{10}}{10!},
\]

and

\[
U_3(s) = \left( \frac{1}{c} \right) 36 \frac{s^{34}}{34!} - 3 \left( \frac{1}{c} \right) 30 \frac{s^{28}}{28!} + 3 \left( \frac{1}{c} \right) 24 \frac{s^{22}}{22!} - \left( \frac{1}{c} \right) 18 \frac{s^{16}}{16!}.
\]
Helmholtz Free Energy of the Reference Hard-Sphere System

According to thermodynamics, the following relation exists between the pressure and the Helmholtz free energy of a system

\[ P = \rho^2 \left( \frac{\partial F}{\partial \rho} \right)_{T,N} \]

or

\[ \frac{PV}{NkT} = Z = \rho \frac{\partial}{\partial \rho} \left[ \frac{F}{NkT} \right]_{T,N} \tag{99} \]

where \( Z \) is the compressibility. By integrating the equation (99) with respect to \( \rho \), one gets

\[ \frac{F}{NkT} = \int \frac{1}{\rho} \frac{PV}{NkT} \, d\rho. \]

For a system obeying the ideal gas law, we have

\[ Z^\text{id} = 1; \quad \frac{F^\text{id}}{NkT} = \int \frac{d\rho}{\rho}. \]

Consequently,

\[ \frac{F-F^\text{id}}{NkT} = \int_0^\rho \frac{1}{\rho} \left[ \frac{PV}{NkT} - 1 \right] \, d\rho. \tag{100} \]

Then by having the compressibility of a system in hand, we can calculate \( \frac{F-F^\text{id}}{NkT} \) for that system. For the hard-sphere reference system in mind, there are several relations available for compressibility. The Padé approximant of Ree and Hoover [43] is probably closer to the Monte Carlo and molecular dynamics calculations than other relations available. Solution of the
Percus-Yevick integral equation for the hard-sphere system produces two different equations of state whether for pressure the Ornstein-Zernike or virial theorem approximations are used [54], as the following

\[
\left[ \frac{PV}{NkT} \right]_0 = \frac{1 + 2\eta + 3\eta^2}{(1-\eta)^2}, \quad \text{(from virial theorem)}
\]

\[
\left[ \frac{PV}{NkT} \right]_0 = \frac{1 + \eta + \eta^2}{(1-\eta)^3}, \quad \text{(from Ornstein-Zernike Equation)}
\]

Thiele [54] has shown that the values of compressibility from virial equation is slightly less, and from Ornstein-Zernike equation is slightly more than the values calculated by Monte Carlo and molecular dynamic methods. This suggests that the arithmetic average of the above two equations should be better than either of the two.

\[
\left[ \frac{PV}{NkT} \right]_0 = \frac{1 + \eta + \eta^2 - 3\eta^3/2}{(1-\eta)^3} \quad (101)
\]

Figure 1 shows Equation (101) along with the machine-calculated points. As is evident, Equation (101) is in good fit with machine-calculated data and has the advantage over Padé approximant that its terms are in simple and rational forms. Insertion of Equation (101) in (100) and performing the integration, produces the following relation
\[
\frac{F_0 - F^{id}}{NkT} = \ln(1-\eta)^{\frac{1}{2}} + \frac{3}{(1-\eta)} + \frac{3}{4(1-\eta)^2} - \frac{15}{4},
\]

where

\[\eta = \frac{\pi}{6} \rho \sigma^3 = \frac{\pi}{6} (\rho \sigma^3) c^3.\]

Also, one can show that

\[
\frac{1}{\beta} \left[ \frac{\partial n}{\partial P} \right]_o = \frac{(1-\eta)^4}{(1+2\eta)^2 - 1.5\eta^3(4-\eta)},
\]

and

\[
-\frac{1}{\beta^2} \left[ \frac{\partial \rho}{\partial P} \right]_o^2 + \rho \frac{\partial}{\partial \rho} \left[ \frac{\partial \rho}{\partial P} \right]_o^2 = \frac{(1-\eta)^7 (1.5\eta^5 - 7.5\eta^4 + 20\eta^2 + 5n-1)}{[(1+2\eta)^2 - 1.5\eta^3(4-\eta)]^3}.
\]

Compressibility coefficient of the hard-sphere reference system, \( \frac{1}{\beta} \left[ \frac{\partial n}{\partial P} \right]_o \), as introduced by (103), and also relation (104) are parts of the coefficients of \( T^{*-2} \) and \( T^{*-3} \) in the inequality (96), respectively.

**Consideration of the Cutoff Parameter** *c*, as the Variational Parameter

For a single-component thermodynamic system, according to phase rule, if two of the intensive properties of the system are defined the other properties will be defined. Of course, at the phase transition points only one intensive

*Even that the parameter c in the variational technique, which is introduced in this work, does not have the characters as a cutoff parameter, this terminology is used for the sake of analogy with the perturbation methods.*
thermodynamic variable of the system will be enough to get the other variables. Then, in general, if we choose the two independent variable \( \rho \), the density and \( T \), the temperature, one could write

\[
F = F(\rho, T).
\]

Now if we define the reduced quantities \( \rho = \rho \sigma^3 \) and \( F^* = F/NkT \), one could write for the first inequality (95)

\[
F^*(\rho^*, T^*) \leq F^*(\rho^*, T^*, c) + \frac{\Gamma_1(\rho^*, c)}{T^*} \tag{105}
\]

and for the second inequality (96)

\[
F^*(\rho^*, T^*) \leq F^*(\rho^*, T^*, c) + \frac{\Gamma_1(\rho^*, c)}{T^*} + \frac{\Gamma_2(\rho^*, c)}{T^*^2}
+ \frac{\Gamma_3(\rho^*, c)}{T^*^3}, \tag{106}
\]

where \( \Gamma_1, \Gamma_2, \) and \( \Gamma_3 \) are the coefficients of the inverse 1\(^{st}\), 2\(^{nd}\), and the 3\(^{rd}\) powers of temperature as shown in (95) and (96).

The right hand sides of inequalities (105) and (106) are functions of \( \rho^*, T^* \), and \( c \), while the left hand side are only functions of \( \rho^* \) and \( T^* \). This suggests that, to bring the inequalities (105) and (106) closer to equality, their right hand sides should satisfy the following conditions, respectively.
\[
\frac{\partial F^*}{\partial c} + \frac{1}{T^*} \frac{\partial \Gamma_1}{\partial c} = 0;
\]
(107)

\[
\frac{\partial^2 F^*}{\partial c^2} + \frac{1}{T^*} \frac{\partial^2 \Gamma_1}{\partial c^2} \geq 0,
\]
and
\[
\frac{\partial F^*}{\partial c} + \frac{1}{T^*} \frac{\partial \Gamma_1}{\partial c} + \frac{1}{T^*} \frac{\partial \Gamma_2}{\partial c} + \frac{1}{T^*} \frac{\partial \Gamma_3}{\partial c} = 0;
\]
(108)

\[
\frac{\partial^2 F^*}{\partial c^2} + \frac{1}{T^*} \frac{\partial^2 \Gamma_1}{\partial c^2} + \frac{1}{T^*} \frac{\partial^2 \Gamma_2}{\partial c^2} + \frac{1}{T^*} \frac{\partial^2 \Gamma_3}{\partial c^2} \geq 0.
\]

If the conditions (107) and (108) are satisfied, there will be relative minimums for the right hand sides of the inequalities (95) and (96) with respect to \(c\), and one could write for the two inequalities, respectively

\[
F^* (\rho^*, T^*) \equiv F^*_o (\rho^*, T^*, c_{m1}) + \frac{\Gamma_1 (\rho^*, c_{m1})}{T^*},
\]
(109)

and

\[
F^* (\rho^*, T^*) \equiv F^*_o (\rho^*, T^*, c_{m2}) + \frac{\Gamma_1 (\rho^*, c_{m2})}{T^*} + \frac{\Gamma_2 (\rho^*, c_{m2})}{T^*} + \frac{\Gamma_3 (\rho^*, c_{m2})}{T^*}
\]
(110)

where \(c_{m1}\) and \(c_{m2}\) in relations (109) and (110) are the values of \(c\) which satisfy conditions (107) and (108) respectively.
Results

The variational calculations which are reported in this work were performed only on the inequality (95). Inequality (96) did not give satisfactory results. This was because of the approximations introduced in the coefficients of $T^*^{-2}$ and $T^*^{-3}$, which are critically effective on the process of variational calculations, at least at low densities, where their contributions are questionable.

For $E^N/NT$ in (95), the Equation (102) is used, and the integration in the second term of (95) is performed numerically by Simpson's rule. As is shown by relations (92), (93), and (94), the integrand of the integral in (95) is a complicated function of $c$. While the analytic first and second differentiations of the right-hand side of the inequality (95) are possible, they are very lengthy and cumbersome. For this reason the necessary first and second differentiations of (95) were done numerically and the usual optimization techniques were used to find the values of $c$ which could satisfy relations (107), the necessary constraints for the minimization of the right-hand side of the inequality (95).

For the ranges of density and temperature in which variational calculation is performed, the results showed that for every $T^*$ and $\rho^*$, there is only one $c = c_m$ that
satisfies conditions (107). In other words, the right hand side of (95) has only one relative minimum with respect to c. Figure 2 shows the values of $c^3$, which are calculated by the above mentioned procedures, as functions of $T^*$ and $\rho^*$. From the value of $c^3$ calculated by the variational calculation, it is possible to calculate $F^*_0(\rho^*, T^*, c_{ml})$ and $\Gamma_1(\rho^*, c_{ml})$ as given in Equation (109) for every temperature $T^*$ and density $\rho^*$. Even though the right hand side of inequality (95) is minimized with respect to c, it is not expected that the inequality is converted to an exact equality, but it can be claimed that the inequality is closer to equality for $c = c_{ml}$. That is why the relation (109) is not shown as an exact equation.

As was explained and shown in the previous parts of this dissertation, relations (105) and (106) are in fact Taylor expansions of the Helmholtz free energy of the original system, around the reference system. If the inequality signs are neglected in (105) and (106), the resulting two equalities are, in fact, two different approximations of the $F^*(\rho^*, T^*)$ which are the results of the truncations of the Taylor expansions. Consequently, one could also write

\[ F^*(\rho^*, T^*) \approx F^*_0(\rho^*, T^*, c_{ml}) + \frac{\Gamma_1(\rho^*, c_{ml})}{T^*} + \frac{\Gamma_2(\rho^*, c_{ml})}{T^{*2}} \]  \hspace{1cm} (111)
and also

\[ F^*(\rho^*, T^*) = F_0^*(\rho^*, T^*, c_{m1}) + \frac{\Gamma_1(\rho^*, c_{m1})}{T^*} + \frac{\Gamma_2(\rho^*, c_{m1})}{T^{*2}} + \frac{\Gamma_3(\rho^*, c_{m1})}{T^{*3}} \]  

(112)

where \(c_{m1}\) in Equations (111) and (112) are the result of the variational calculation on the inequality (105). If the terms \(\Gamma_2\) and \(\Gamma_3\) in (111) and (112) were exact functional forms, it would have been expected that these two equations be closer and closer to equality, respectively, than (109). But calculations show that \(\Gamma_3\) term gives erroneous and divergent contribution at low densities to the equation of state, while it is contributing little or nothing at high densities. This character of \(\Gamma_3\) is what is expected from the approximations introduced in it.

Figures 3 and 4 show the compressibility versus density for four isotherms for which experimental and machine-calculated data are available. Compressibilities are calculated from Helmholtz free energy by the thermodynamical relation (99). Figure 3 is made by the use of only the zeroth and the first order terms as shown by (109), while for Figure 4 the contribution of the second order term, \(\Gamma_2\), is also included, Equation (111). Because of the importance of the four isotherms
T* = 0.72, 1.00, 1.35, and 2.74, their related numerical values of the compressibilities are tabulated in Table II.

Internal Energy and Internal Entropy

According to statistical mechanics [23] internal energy and internal entropy are defined by the following relations respectively

\[ U_i = kT^2 \left[ \frac{\partial \ln Q}{\partial T} \right]_{N,V} \]  \hspace{1cm} (113)

and

\[ S_i = k \ln Q + kT \left[ \frac{\partial \ln Q}{\partial T} \right]_{N,V} \]  \hspace{1cm} (114)

where \( Q \) is the partition function of the system. Using the relation \( F = -kT \ln Q \) in (113) and (114), we get

\[ U_i = F + TS_i \]  \hspace{1cm} (115)

and

\[ S_i = - \left( \frac{\partial F}{\partial T} \right)_{N,V} \]  \hspace{1cm} (116)

Of course, (115) and (116) are derived originally from classical thermodynamics. \( U_i \) and \( S_i \) can be calculated by relations (115) and (116) by having \( F \), the Helmholtz free energy of the system, as a function of temperature and density. Figures 5 and 6 show internal energy and internal entropy of Lennard-Jones fluid for three different isotherms which are compared
with experimental and machine-calculated data. $\Gamma_2$ and $\Gamma_3$ terms give erroneous contributions to the internal energy and internal entropy at low densities. What is reported by Figures 5 and 6 are based on the results of Equation (109).

**Calculation of Phase Equilibria Properties at Liquid-Vapor Phase Transition**

When two phases are at equilibrium, the temperatures, the pressures, and the chemical potentials of the two phases should be equal. Then to find the phase equilibria properties, it is necessary to solve the following two equations at a given temperature and find $\rho_\lambda$ and $\rho_v$ the densities of the coexisting liquid and vapor

$$
\begin{align*}
(F + PV)_\lambda &= (F + PV)_v \\
\rho_\lambda &= \rho_v
\end{align*}
$$

(117)

where $\lambda$ denotes liquid, and $v$ denotes the vapor phase. In the system of two equations which are shown by (117), the two unknowns are the two densities of the liquid and vapor phases. This system of the two equations is solved graphically and the results of coexisting phases are shown by Figures 7, 8, 9, and 10. Figure 7 shows the densities of the two coexisting phases for the 12:6 potential. Figure 8 shows the vapor
pressures for the 12:6 potential, while Figures 9 and 10 show the internal energy and internal entropy at saturated vapor pressures for the 12:6 potential. All these calculations are based on the Helmholtz free energy which is calculated by Equation (111).

Critical Properties

Critical properties are calculated from phase equilibria data as explained in the above paragraph. In the following table critical constants which are derived in the present study, the results of perturbation method of Barker and Henderson [7], experimental argon data, and machine calculations are shown.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$T^*_C$</td>
<td>1.36</td>
<td>1.35</td>
<td>1.32-1.36</td>
<td>1.26</td>
</tr>
<tr>
<td>$\rho^*_C$</td>
<td>0.325</td>
<td>0.30</td>
<td>0.32-0.36</td>
<td>0.316</td>
</tr>
<tr>
<td>$P^*_C$</td>
<td>0.165</td>
<td>0.14</td>
<td>0.13-0.17</td>
<td>0.117</td>
</tr>
<tr>
<td>$P_C V_C / NkT_C$</td>
<td>0.37</td>
<td>0.34</td>
<td>0.30-0.36</td>
<td>0.293</td>
</tr>
</tbody>
</table>
As is indicated in the descriptions of the graphs, the present variational calculations are compared with molecular dynamics results of Verlet [58], Monte Carlo results of Wood and Parker [61] and McDonald and Singer [35], and experimental results for liquid argon [46, 37, 38, 32, 56, 57, 20]. In reducing the experimental data for liquid argon, the parameters $\epsilon/k = 119.8^{\circ}K$, $\sigma = 3.405 \AA$ derived by Michels et al. [37] from second virial coefficients are used. In making the comparison with both liquid argon and machine-calculated data of Lennard-Jones 12:6 potential, it is not implied that the 12:6 potential with $\epsilon$ and $\sigma$ parameters as given above gives a close representation of the true pair potential for argon; evidence is now strong that it does not [48]. However, the good agreement between molecular dynamics [58], Monte Carlo [61, 35] calculations made with this potential and experimental data for liquid argon shows that it does represent a good effective pair potential for argon at high densities, apparently absorbing some many-body interactions into a pseudo-pair potential. It is on this basis that comparison of the variational calculation result for 12:6 potential with the properties of argon is regarded as meaningful.
Discussion

The above comparisons and results indicate that the present variational technique gives excellent results at all ranges of temperature from liquid state to gaseous state. This indicates that the present method is a more satisfactory approach to the theory of the equilibrium properties of liquids than the previous approaches reviewed and discussed before. As was shown, the perturbation theory of Barker and Henderson, even though it gives satisfactory results at high and moderate temperatures, it could not predict the properties of liquid state completely, while the present variational techniques is predicting the liquid state very satisfactorily.

As it was discussed in the historical background, Kozak and Rice [27] have used a variational technique based on the cutoff parameter $c$, as the variational parameter, to calculate the equilibrium properties of simple fluids. Their inequality for the Helmholtz free energy was based on a postulate that $c$ is an equilibrium property of the thermodynamic system and the free energy, at equilibrium, is supposed to be minimum with respect to $c$. But $c$ has only mathematical meaning and no physical significance. They got satisfactory results at high temperatures, and their prediction of low temperature data in
the liquid range was not reported. It is doubtful that they could get satisfactory predictions for fluids at low temperatures, because coefficients of $T^*^{-2}$, $T^*^{-3}$, ... at high temperatures are negligibly small, and they do not contribute to the variational results. Consequently, only the contribution of the zero-th and the first terms are of importance; which means they are using actually the inequality (105). At low temperatures, where the contributions of $T^*^{-2}$, $T^*^{-3}$, ... are important, while these coefficients are highly approximate (especially because of their rough approximations), it is doubtful that these coefficients are able to give any direction to the inequality on mathematical grounds and its consistency with respect to change of density and temperature.

While the present variational technique, based upon a hard-sphere system, as the reference system, predicts the properties of liquid state, gaseous state, and the liquid-vapor phase transition, it does not predict the liquid-solid phase transition and the solid state. This could be explained by the following remark: In solid state, the molecules of the system are in ordered positions with respect to each other, while in
liquid state, they are not. The transition from liquid phase to the solid phase is a transition from disorder to order. This transition can not be predicted unless the mathematical modeling or the approximations used for the configurational integral, and/or the distribution functions of the molecules in the system contain both ordered and disordered characters. In the present variational technique, the formulation was based upon a hard-sphere reference system which its radial distribution function was originally assumed to be free of orientation of the molecules in the system [54, 60], that is
\[ g_o(r_1 - r_2) \equiv g_o(|r_1 - r_2|) \]  
Consequently, the above variational calculation could not predict the liquid-solid phase transition.

The above remark is only an idea. It seems that the Kirkwood's Equation [23], which is also based on (118), does not negate this opinion, because it only diverges at high densities which could be interpreted in different ways.

Mathematical modelings or the approximations which are done for solid state, or are based on some ordered orientations of the molecules in the system, are more likely to be able to predict the liquid-solid phase transition.
In the next chapter, a variational technique formulation is introduced which is based upon a reference system that follows the cell theory of Lennard-Jones and Devonshire for a face-centered cubic crystal.
CHAPTER V

THE VARIATIONAL TECHNIQUE BASED ON
A REFERENCE SOLID SYSTEM

It was shown in Chapter III that for the ratio of the two partition functions of two different systems, the following inequality holds:

\[
\frac{Q}{Q_0} \geq \exp [-\beta (U-U_0)]
\]  

(119)

and by introducing Helmholtz free energies, we get

\[
F \leq F_0 + \langle U-U_0 \rangle_0
\]

(120)

where \(Q, F, U_0\) and \(Q_0, F_0, U\) are partition functions, Helmholtz free energy and total potential energy of a reference system while \(Q, F, U\) are properties of the original system. As was mentioned, and is clear, the more nearly the reference system approximates the original system, the more nearly the above inequality is to an equality.

The previous formulation was based upon the assumption that the original system is a fluid (liquid or gas). On this basis, the reference system was taken as a fluid of particles.
having only hard-core potential (because in the derivation of the Percus-Yevick equation, it was assumed that \( g(x) = g(|x|) \) which is only correct for fluids). In this part of the work, we are going to find the properties of the original system in solid phase. For this purpose, it is necessary to choose a reference system which resembles a solid phase. In other words, we should choose a reference system with its correlation functions which are dependent not only on the intermolecular distances, but the orientation of the molecules with respect to each other in the system too. For this purpose, the cell model of Lennard-Jones and Devonshire [30] will be used as the reference system.

The Cell Theory of Lennard-Jones and Devonshire

As the works of many investigators have shown [4] the cell model of Lennard-Jones and Devonshire [30, 31] which was originally designed to predict the liquid state is actually a model for solid state.

The fundamental assumptions of the cell model are: (i) that the available volume may be divided into identical cells, one for each molecule, and that only configurations in which every cell contains one molecule need be considered; (ii) that the cells can be chosen so that their centers form a regular
lattice; (iii) that the molecules can be regarded as moving independently in their cells. The second assumption is required in order that the distance between cell centers can be related to the density. The third assumption is required to make evaluation of the configuration integral practicable. It implies that the potential energy of the system can be approximated by a sum of terms each depending on the position of just one molecule. If this were not so, the force on one molecule would depend on the position of another and the motions of the molecules would not be independent. Thus, it is assumed that

\[ U = U' + \sum_i \Psi_i(\mathbf{r}_i) \]  \hfill (121)

where \( \mathbf{r}_i \) is the vector displacement of molecule \( i \) from the center of its cell and \( U' \) is a constant. If all the cells are identical, the functions \( \Psi_i \) must also be identical so that we can drop the subscript. If \( U_0 \) is the potential energy when all molecules are at their cell centers then

\[ U_0 = U'_0 + \sum_i \Psi(0) \]  \hfill (122)

so that (121) becomes

\[ U = U_0 + \sum_i [\Psi(\mathbf{r}_i) - \Psi(0)] \]  \hfill (123)

It is clear from (123) that \( [\Psi(\mathbf{r}_i) - \Psi(0)] \) is the change of potential energy when the molecule \( i \) moves from its cell center.
to the point $\mathbf{x}_1$, with all other molecules remaining at their cell centers.

With the potential energy approximated by (123), the configuration integral is given by

$$Q(N,V,T) = \frac{1}{N!} \sum \exp\left(-\frac{U_0}{kT}\right) v_f^N = \exp\left(-\frac{U_0}{kT}\right) v_f^N. \quad (124)$$

The summation $\sum$ in (124) is taken over all arrangements of the molecules with one in each cell, and the "free volume", $v_f$, is defined by

$$v_f = \int_{\Delta} \exp\left\{-\left[\Psi(\mathbf{x}_1) - \Psi(0)\right]/kT\right\} d\mathbf{x}_1. \quad (125)$$

The integration in (125) is to be taken throughout the interior of the cell. We have not so far specified the precise form of the cell, except that its volume must be equal to the volume per molecule. We shall assume that the lattice of cell centers is a face-centered cubic lattice. The most obvious choice for the cell shape is then the dodecahedron formed by the planes bisecting the lines drawn between nearest-neighbor lattice points. We shall see later that it is more convenient to replace this by a spherical cell.

**Cell Field, Free Volume and Lattice Energy**

Each molecule in its cell moves in a potential energy field defined by the function $[\Psi(\mathbf{r}) - \Psi(0)]$. If the potential energy function $u(\mathbf{r})$ for interaction of pairs of molecules is
known, this cell field can be calculated. In general, \( u(r) \) is a complicated function of the position of the molecule in the cell. Lennard-Jones and Devonshire proposed that this complicated function should be replaced by a spherically symmetrical function depending only on the distance \( r \) of the molecule from the center of its cell, and calculated by averaging the potential energy over a sphere of radius \( r \) centered at the cell center. The cell field derived in this way is identical with that derived by regarding the neighboring molecules as "smeared" with uniform probability distribution over the surfaces of concentric spheres of appropriate radius. This smearing approximation is quite accurate, particularly at high densities.

In calculating the free volume using smearing approximation, it is much more convenient to use a spherical cell than the dodecahedral cell described above. At sufficiently high densities (roughly speaking densities greater than the critical density \([59]\)), the integrand in relation (125) is effectively zero when \( x = r/a_0 \) (\( a_0 \) the radius of the dodecahedron) is equal to or greater than 0.5, so that the error involved in replacing the dodecahedral cell by a sphere of radius 0.5\( a_0 \) is negligible. With the latter value of the cell radius, the free volume will be given by
\[ v_f = 4\pi a_0^3 G = 4\sqrt{2\pi} \left(\frac{V}{N}\right) G \]

\[ G = \int_0^{0.5} x^2 \exp\left\{ -[\Psi(x) - \Psi(0)]/kT \right\} dx \]

Because for face-centered cubic crystal structure

\[ a_o = (\sqrt{2} N/V)^{1/3} \]  

If we define the potential of each atom in its cell, relative to the center, as \( W(r) \), then

\[ W(r) = \Psi(r) - \Psi(0) \]  

The average value of potential of each atom in its cell [30] is

\[ \langle \Psi(r) \rangle_\Delta = \langle W(r) \rangle_\Delta + \frac{U_0}{N}, \]  

where \( \frac{U_0}{N} = \Psi(0) \) and the averages are over cells such that

\[ \langle \chi \rangle_\Delta = \int_\Delta \chi P(r) \, dr \]  

and

\[ P(r) \, dr = \exp\left\{ -W(r)/kT \right\} dr / \int_\Delta \exp\left\{ -W(r)/kT \right\} dr \]  

where \( \chi \) could be any variable in the cell, and \( P(r) \, dr \) is the probability that a given molecule is at a distance between \( r \) and \( r + dr \) from the center of its cell.

The radial distribution function in a system following the cell theory of Lennard-Jones and Devonshire [4], [15] as
explained above is

$$g(r) = \frac{1}{16\pi} \sum_i N_i \int \frac{P(r')}{R'} \frac{1}{|y-a_i|} \int \frac{P(R)}{R} \frac{1}{|y-R|} dr'$$  \hspace{1cm} (132)$$

where $N_i$ is the number of the $i^{th}$ neighbors and $Z_i$ is the distance of the $i^{th}$ neighbors from the central molecules, $Z_i=a_o$, the summation in (132) is over the shells of the neighbors.

**Choice of Harmonic Field**

If the cell field, $W(r) = \psi(r) - \psi(0)$ be considered a harmonic field, that is

$$W(r) = A(r/a_o)^2 \cdot kT$$  \hspace{1cm} (133)$$

the relations for free volume, average potential, and radial distribution function can be evaluated analytically [15]. For this, it is also necessary to assume that the potential rises so steeply that the particle is effectively confined to a cell. This is like neglecting quantities involving $\exp(-\frac{A}{4})$, and this is only possible when the value of $A$ is very large. In the later sections of this work, we will see that the values of $A$ which are produced by variational calculations are so large that this is not any more an assumption or approximation but a reality.
Considering relation (133) in (126) we get

\[ G = \int_0^{0.5} x^2 \exp(-Ax^2) \, dx \]

for very large values of \( A \)

\[ G = \int_0^\infty x^2 \exp(-Ax^2) \, dx = \frac{\sqrt{\pi}}{4A} \, A^{-3/2} \]  \hspace{1cm} (134)

Then

\[ v_f = \sqrt{2\pi^3} \left( \frac{V}{N} \right) A^{-3/2} \]

and Helmholtz free energy

\[ F = -kT \ln Q = U_o - NkT \ln v_f \]

or

\[ F = U_o + NkT \left[ \ln \rho + \frac{3}{2} \ln A - \frac{1}{2} \ln(2\pi^3) \right]. \]  \hspace{1cm} (135)

Also, from relations (130) and (133) we get

\[ \langle W(r) \rangle = \int_0^{0.5} W(r) 4\pi r^2 \exp[-W(r)/kT] \, dr / \int_0^{0.5} 4\pi r^2 \exp[-W(r)/kT] \, dr \]

\[ = \int_0^{0.5} x^4 \exp(-Ax^2) \, dx / \int_0^{0.5} x^2 \exp(-Ax^2) \, dx. \]  \hspace{1cm} (136)

Now, again, considering the fact that \( A \) is very large, we can write

\[ \langle W(r) \rangle = \int_0^\infty x^4 \exp(-Ax^2) \, dx / \int_0^\infty x^2 \exp(-Ax^2) \, dx = \frac{3}{2} kT. \]  \hspace{1cm} (137)

Then from relations (137) and (129) we get for the average value of the potential energy of each atom the following relation
\[ \langle \Psi(r) \rangle_\Delta = \frac{3}{2} kT + \frac{U_0}{N} , \quad (138) \]

which is the classical value for the average potential energy of each atom.

For the radial distribution function, by considering harmonic field, Corner and Lennard-Jones [15] have shown that the relation (132) takes the following form

\[ g(r) = \sqrt{\frac{A}{2\pi} \frac{3}{2}} \rho a_0 \sum_{i} \frac{N_i}{Z_i} \cdot \frac{1}{r} \exp \left[ - \frac{A}{2} \left( \frac{Z_i - r}{a_0} \right)^2 \right] \quad (139) \]

with the following constraint for the contribution of each shell of neighbors

\[ Z_i - a_0 < r < Z_i + a_0 \quad (140) \]

**The Basic Inequality in the Case of Solid Phase**

In the case of solid phase, the cell model with harmonic field as expressed in previous parts of this work is taken as the reference system. With the original system following Lennard-Jones potential function (considering only two body forces) the total potential of the original system is:

\[ U = \sum_{i>j=1}^{N} u(r_{ij}) , \quad (141) \]

and the reference system following the cell model as expressed above the total potential of the reference system is:
The summation in relation (141) is over the intermolecular distances while the summation in (142) is over the cells. By inserting relations (141) and (142) in inequality (120) we get

\[ F \leq F_0 + 2\pi N \rho \int_0^\infty u(r) g_\ast(r) r^2 dr - N \langle \Psi(x) \rangle_\Delta. \]  

(143)

By replacing \( F_0 \) in inequality (143) with \( F \) as given by (135), replacing \( g_\ast(r) \) by \( g(r) \) as given by (139) and considering the constraint (140), and by replacing \( \langle \Psi(x) \rangle_\Delta \) by its value as given by (138), the inequality (143) takes the following form

\[ F \leq NkT[\ln \rho + \frac{3}{2} \ln A - \frac{1}{2} \ln(2\pi^2)] - \frac{3}{2} NkT \]

\[ + 2\pi N \rho \frac{A^{1/2}}{4\sqrt{\pi}^{3/2} a_o} \sum_i N_i \int_0^\infty \frac{\beta_i}{Z_i} \left[ 4\epsilon \left[ \frac{\sigma_\ast}{r} \right]^{12} - \left[ \frac{\sigma_\ast}{r} \right]^{6} \right] \exp \left[ - \frac{A}{2} \left( \frac{Z_i - r}{a_o} \right)^2 \right]. \]  

(144)

where

\[ \alpha_i = Z_i - a_o \]

and

\[ \beta_i = Z_i + a_o \]

for every term of the summation which is related to each shell of neighbors. As is shown in inequality (144), for the original system, the Lennard-Jones 12:6 potential is considered.
As was shown before, for face-centered cubic (f.c.c) crystal structure one has

$$a_0 = \sqrt[3]{\sqrt{2/\rho}}$$

where $a_0$ is the diameter of the smeared cell, and $\rho$ is the number density. Now if we introduce all the variables in dimensionless forms as following

$$a^*_0 = a_0/\sigma = (\sqrt{2/\rho^*})^{1/3}; \quad \rho^* = \rho\sigma^3$$

$$x = r/\sigma$$

$$Z^*_i = Z_i/a_0$$

and the dimensionless temperature

$$T^* = kT/\xi$$

then inequality (144) takes the following form

$$\frac{F}{NkT} \leq \ln(\rho A^{3/2}) + \frac{1}{T^* \cdot a^*_0^2} \left[ \frac{2A}{\pi} \right]^{1/2} \sum_i \frac{N_i}{Z^*_i} \alpha^*_i \int \frac{1}{x^{12}} - \frac{1}{x^6} \right] \cdot x \exp \left[ -\frac{A}{2} \left( Z^*_i - x/a^*_0 \right)^2 \right] dx - \frac{3}{2} - \frac{1}{2} \ln(2\pi^3).$$

(146)

where

$$\alpha^*_i < (Z^*_i - 1)a^*_0,$$  \hspace{1cm} (147)

and

$$\beta^*_i > (Z^*_i + 1)a^*_0.$$
Inequality (146) is the basic inequality which will be dealt with in calculating the properties of the solid phase.

**Choice of the Proper Number of Shells of Neighbors**

In inequality (146) the summation sign is over the shells of the neighbors of a central molecule. This summation actually is for $i = 1^\infty$, like an infinite series. This series will be convergent if the terms of the series follow the convergent criteria of the infinite series. As was shown in previous parts of this work, Lennard-Jones and Devonshire considered the "smearing approximation" for deriving the cell theory relations as given before. This smearing approximation could only be close to reality when there are enough particles in every shell such that it be possible to claim that the potential inside every shell is homogenous. But actually, for any kind of crystal structure (including f.c.c. crystal), this is not the case. In other words, the number of molecules does not increase appreciably as the shell size increases in order to keep the shell filled with enough molecules that the smearing approximation is valid. Table III shows the number of molecules in different shells for a f.c.c. crystal structure. For other kinds of crystal structure, see reference [42]. Then for the reason of using the smearing approximation, it will be of
importance to consider the number of shells as small as possible. For this purpose, we must find out the smallest number of shells that can be used such that we do not disturb the sign of the inequality and the functional form of the variables involved.

For Lennard-Jones 12:6 potential, which is considered for the original system,

\[ u(r) = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right] \]

we have

\[ u(r) \geq 0 \text{ for } (r < \sigma) \]

\[ u(r) > 0 \text{ for } (r > \sigma) \] (148)

With the fact that \( g_o(r) \), the radial distribution function, is always positive or zero, the inequality (143) could be written as

\[ F \leq F_o + 2\pi N\rho \int_0^\theta u(r) g_o(r) r^2 dr - N \left\langle \Psi(r) \right\rangle_\Delta \]

(149)

for \( \theta > \sigma \).

This is because the contribution to the integral in inequality (143) for \( r > \theta \) is always negative, and when subtracted from the right hand side of the inequality (143), it does not change the direction of the inequality sign. Then in the case of the inequality (147) (which is a result of inequality (143)), the above condition takes the following form

\[ \sigma^*_1 \geq 1, \]
or it is enough to have
\[(Z^*_1 - 1) (\sqrt{2}/\rho^*)^{1/2} \geq 1 \quad (150)\]
to keep the inequality still valid, while the minimum number of the shell neighbors are used. Then condition (150) is for the first of the shells which we can disregard.

Since for a f.c.c. crystal \( Z^*_i = \sqrt{i}; \ i = 1, 2, 3, \ldots \), then we must have for \( i \), the index of the first of the shells to disregard,
\[\sqrt{i} - 1 \geq (\rho^*/\sqrt{2})^{1/2}\]
The largest value of \( \rho^* \) is the close-packed density, \( \rho^* = \sqrt{2} \), then in the extreme case
\[\sqrt{i} - 1 \geq 1 \quad \text{or} \quad i \geq 4.\]
Then we can disregard the 4\(^{th}\), 5\(^{th}\), 6\(^{th}\), \ldots shells. Consequently, if we consider only the first three shells, not only the sign of the inequality will not be disturbed, but the effect on the smearing approximation will be the least possible.

**Choice of the Variational Parameter**

With the consideration of only the first three shells, we have
\[
\frac{F}{NkT} \leq \ln(\rho A^{3/2}) + \frac{1}{T^* a^*_o} \left[ \frac{2A}{\pi} \right]^{1/2} \sum_{i=1}^{3} \frac{N_i}{Z_i^*} \int \frac{\beta^*_i}{\alpha^*_i} \left[ \frac{1}{x^{1/2}} - \frac{1}{x^{1/6}} \right] dx \exp \left[ - \frac{A}{2} (Z_i^* - x/a^*_o)^2 \right] dx - \frac{3}{2} - \frac{1}{2} \ln(2\pi^3), \quad (151)
\]
with
\[ \alpha_i^* \langle (Z_i^* - 1)a_o^* ; \beta_i^* \rangle (Z_i^* + 1)a_o^*. \] (152)

The only variable in the right hand side of the inequality (151) which does not appear in the left hand side of the inequality is A. A is proportional to the square of the frequency of the oscillation of the molecules in their cells. With a similar argument as given in the case of pure fluid, A could be considered as the variational parameter for the minimization of the right hand side of inequality (151).
Results

Inequality (151) with conditions (152) for $\alpha_i^*$ and $\beta_i^*$ is the working inequality, for the Helmholtz free energy. Minimization of the right hand side of the inequality (151) should be performed with respect to $A$. Numerical calculations by electronic computer shows that the right hand side of inequality (151) has always only one relative minimum with respect to $A$ for every temperature $T^*$ and density $\rho^*$ which was investigated.

The Helmholtz free energy, which is a result of the variational calculation on the right hand side of (151), is supposed to be more satisfactory for the solid state than for the fluid states. This is because the reference system which is chosen to produce the inequality (151), more nearly resembles a solid system.

Figure 11 shows the values of $A$ which are calculated for a range of densities for four different isotherms. The values of $A$ are always large which support the accuracy of relations (134), (137), and (139) for which the values of $A$, a priori, were assumed to be large.

Figure 12 indicates the compressibility of the solid phase of a system of molecules following Lennard-Jones 12:6 potential function. The compressibility is calculated from the Helmholtz free energy, which is a result of the variational calculation on inequality (151), and thermodynamic relation $\frac{PV}{NkT} = \rho \frac{\partial}{\partial \rho} \frac{F}{NkT}$. The compressibilities which are calculated by the present variational calculation for Lennard-Jones solid are compared with
machine-calculated data on Figure 12. As is clear in this figure, the compressibility has a discontinuity at a particular density for every isotherm. These discontinuities are related to the sharp changes of slopes of $A$ for each isotherm on Figure 11. The discontinuities in the isotherms on Figure 12 are clear indications of solid-liquid phase transitions. Even that the inequality (151) still has solutions for densities less than the solid-liquid phase transition densities, the resulting values for Helmholtz free energy and other thermodynamic properties are not expected to be correct. This is because the reference system on which the inequality (151) is based resembles a solid phase. In fact, comparison with machine-calculated data proves this argument. (Compare Figures 3 and 12). Figure 13 shows the coexisting phase densities of the two liquid and solid phases versus temperature. There are two ways to calculate the coexisting phase data. The first method is the predictive way which was discussed above and which is based upon the breaks of the compressibility curves or the sharp changes of the slopes on the graphs of $A$ versus density for different isotherms as shown on Figure 11. The second method is by solving the following system of two equations

$$
\begin{cases}
(F + PV)_L = (F + PV)_S \\
 p_L = p_S
\end{cases}
$$

(153)

for $\rho_L^*$ and $\rho_S^*$. This system of two equations and two unknowns are solved graphically as was explained before for the liquid-vapor
equilibria calculations. In these graphical calculations, the values of \( (F + PV)_{\ell} \) and \( P_{\ell} \) calculated from Equation (109) are used. In Figure 13 the results of the above two methods are compared with the coexisting liquid-solid experimental data of argon. Figure 13 indicates that the second method, based upon the solution of Equation (153) gives much better results than the first method. While the result of the first method quantitatively is not of significance, its predictive character of the solid-liquid phase transition is of importance.

**Discussion**

The above results indicate that a variational calculation based upon an ordered-structure reference system which resembles more the solid phase than a liquid is able to predict the liquid-solid phase transition. However, a more flexible reference system would be expected to yield better predictions of the thermodynamic properties of both phases and of the liquid-solid phase transition.

A similar, but more elementary, variational calculation for the prediction of the melting point of simple solids has been proposed by Bazarov [12]. The basic inequality which is used by Bazarov for the Helmholtz free energy of the system is in accordance with the Bogolyobov variational principle which is unfamiliar to this author. According to this principle, the free energy of a crystal structure is determined from the expression

\[
F \leq F_{0} + \langle U_{1} \rangle_{0},
\]

(154)
where $F$ is the free energy of the crystal, $F_0$ is the free energy corresponding to the energy $U_0$, and $\langle U_1 \rangle$ is the value of the energy $U_1 = U - U_0$ averaged over $U_0$. Bazarov [12] does not give any explanation for the mathematical significance or the physical meaning of $F_0$ and $U_0$. While the inequality (154) is apparently similar to the basic inequality (120) which was used in the present variational calculations, it seems to have less significance. This is because inequality (154), as Bazarov has indicated, holds only for crystals while inequality (120) holds for any state of the matter, in equilibrium conditions. Bazarov does not show how well his inequality for the Helmholtz free energy of the crystals predicts the thermodynamic properties of solids. But he indicates that the ratio of the melting point predicted by his method and the experimental melting point of simple substances (Ar, Ne, Kr, and Xe) is exactly the same, and is approximately equal to three. For the present method also, this ratio is approximately equal to 3 for the predictive approach which was related to the sharp change of slope of $A$ versus $\rho^*$ on Figure 11. But if the second approach which was based on the solution of Equations (153) be used, this ratio will be approximately equal to 1.3 which is much closer to unity. It is expected that if a reference system with more freedom for randomness of the relative positions of the molecules than the cell model be used, the liquid-solid phase transition be predicted more accurately.
CHAPTER VI

REFORMULATION OF THE FIRST INEQUALITY FOR
THE CASE OF A BINARY FLUID MIXTURE

According to Chapter III, it was shown that the following inequality exists for the difference between the Helmholtz free energy of two different systems, one original and the other a reference:

\[ F - F_0 \leq \langle U - U_0 \rangle_0 \]  \hspace{1cm} (155)

where \( F \) and \( F_0 \) are the Helmholtz free energies of the original and reference systems respectively. \( U \) and \( U_0 \) are the total potential energies of the two systems. The angled brackets mean the expectation over the reference system:

\[ \langle \chi \rangle_0 = \int \ldots \int \frac{e^{-\beta U_0}}{Q_0} \chi \, d\mathbf{r}_1 \ldots d\mathbf{r}_N \]  \hspace{1cm} (156)

In the case where the two systems, the original and the reference, are made of binary mixtures of two components 1 and 2 with only two body potential functions and mole fractions \( x_1 \) and \( x_2 = 1 - x_1 \), one can write

\[ U = \sum_{i>j=1}^{N_1} u_{11}(ij) + \sum_{i>j=N_1+1}^{N} u_{22}(ij) + \sum_{i=1}^{N_1} \sum_{j=N_1+1}^{N} u_{12}(ij) \]  \hspace{1cm} (157)
and
\[ U_o = \sum_{i>j=1}^{N_1} u_{11}^o(ij) + \sum_{i>j=N_1+1}^{N} u_{12}^o(ij) + \sum_{i=1}^{N_1} \sum_{j=N_1+1}^{N} u_{22}^o(ij), \]

where
\[ x_1 = \frac{N_1}{N}, \text{ and } x_2 = \frac{N-N_1}{N} = \frac{N_2}{N}. \]

Inserting relations of \( U \) and \( U_o \), as given above, in the inequality (155) and replacing the summation by the proper multipliers, as in the case of pure component system, we get
\[
F \leq F_o = \int \frac{e^{-\beta U_o}}{Q_o} d\Gamma
\]

where
\[ d\Gamma = dr_1^{1...} dr_1^{1...} dr_2^{2...} dr_2^{2...} , \text{ and } u_{11}^o(ij) = u_{\alpha\beta}(ij) - u_{\alpha\beta}^o(ij). \]

Again in this case, as in the case of pure component, because of the large values of \( N \) and \( N^2 \), one could write
\[
\frac{N_1(N_1-1)}{2} = \frac{N_1^2}{2} \text{ and } \frac{N_2(N_2-1)}{2} = \frac{N_2^2}{2}. \]

The pair correlation or the radial distribution functions of particles in a binary fluid system are defined as following [41]
\[
g_{11}(|r_1^1 - r_2^1|) = v^2 \int \frac{e^{-\beta U}}{Q} dr_3^{1...} dr_1^{1...} dr_2^{2...} dr_2^{2...},
\]
\[ g_{22}(|x_2^2 - x_2^2|) = v^2 \int \frac{e^{-\beta U}}{Q} \, dx_1^2 \ldots dx_{N_1}^2 \ldots dx_{N_2}^2, \quad (160) \]

and

\[ g_{12}(|x_1^1 - x_1^2|) = v^2 \int \frac{e^{-\beta U}}{Q} \, dx_1^1 \ldots dx_{N_1}^1 dx_2^2 \ldots dx_{N_2}^2 = g_{21}(|x_1^1 - x_1^2|). \]

By considering relations (160) in inequality (159), we get the following inequality with respect to the radial distribution functions:

\[
\frac{F}{NkT} \leq \frac{G}{NkT} = \frac{\beta N}{v^2} \int \left[ \frac{x_1^2}{2} u_{11}^1(r_{12}) g_{11}^0(r_{12}) + \frac{x_2^2}{2} u_{22}^1(r_{12}) g_{22}^0(r_{12}) + x_1 x_2 u_{12}^1(r_{12}) g_{12}^0(r_{12}) \right] \, dx_1 \, dx_2 \quad (161)
\]

Relation (161) is the first inequality for a binary mixture of particles with only pairwise-additive potential energy functions.

For the case where the system consists of mixture of hard spheres with diameters \( d_{11} \) and \( d_{22} \) such that

\[
u_{11}^0 = \begin{cases} 0 & \text{for } r > d_{11} \\ \infty & \text{for } r \leq d_{11} \end{cases}, \quad \nu_{22}^0 = \begin{cases} 0 & \text{for } r > d_{22} \\ \infty & \text{for } r \leq d_{22} \end{cases}
\]

and

\[
u_{12}^0 = \begin{cases} 0 & \text{for } r > d_{12} \\ \infty & \text{for } r \leq d_{12} \end{cases}
\]

(162)

where \( d_{12} = \frac{d_{11} + d_{22}}{2} \), the above inequality takes the following form:
\[
\frac{F}{NkT} \leq \frac{F_0}{NkT} + 4\pi \beta \rho \left[ \frac{x_1^2}{2} \int_{d_{11}}^{\infty} u_{11}(r) g_{11}^0 (r) r^2 dr + \frac{x_2^2}{2} \int_{d_{22}}^{\infty} u_{22}(r) g_{22}^0 (r) r^2 dr \right]
+ x_1 x_2 \int_{d_{12}}^{\infty} u_{12}(r) g_{12}^0 (r) r^2 dr \right] .
\] (163)

In deriving inequality (163) from inequality (161), the center of coordinates is transferred to the center of particle 1, and the integration over \(dr_1\) is performed, which gives \(V\), while \(dr_{12} = 4\pi r_{12}^2 dr_{12}\) and the dummy indices 12 are dropped. By considering Lennard-Jones 12:6 potential energy function

\[
u_{ij}(r) = 4\varepsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r} \right)^{12} - \left( \frac{\sigma_{ij}}{r} \right)^6 \right]
\] (164)

and defining \(t = r/d_{ij}\), the inequality (163) takes the following form

\[
\frac{F}{NkT} \leq \frac{F_0}{NkT} + 16\pi \beta \rho \left[ \frac{d_{11}^3 \varepsilon_{11}}{2} x_1^2 \int_{1}^{\infty} u_{11}^*(t) g_{11}^0 (t) t^2 dt \right]
+ \frac{d_{22}^3 \varepsilon_{22}}{2} x_2^2 \int_{1}^{\infty} u_{22}^*(t) g_{22}^0 (t) t^2 dt + d_{12}^3 \varepsilon_{12} x_1 x_2 \int_{1}^{\infty} u_{12}^*(t) g_{12}^0 (t) t^2 dt \right] ,
\] (165)

where \(u_{ij}^*(t) = (1/c_{ij} t)^{12} - (1/c_{ij} t)^6\) (166)

and \(c_{ij} = d_{ij}/\sigma_{ij}\). (167)
Reformulation of the Inequality for the Mixture with Respect to The Laplace Transforms of the Pair Correlation Functions

In the case of mixture, as in pure component, the pair correlation functions of particles of the system with respect to each other are also not available, while a kind of Laplace transform of them, as defined and derived by Lebowitz [28], are available as follows:

\[ G_{ij}(s) = 12(\gamma_i \gamma_j)^{1/2} \int_0^\infty e^{-sr} g_{ij}(r)dr = G_{ij}(s) \]  \hspace{1cm} (168)

where \( \gamma_i = \frac{\pi}{6} \rho x_i \),

and

\[ G_{11}(s) = s[h-L_2(s)e^{s d_{22}}]/D(s), \]  \hspace{1cm} (169)

\[ G_{22}(s) = s[h-L_1(s)e^{s d_{11}}]/D(s), \]  \hspace{1cm} (170)

\[ G_{12}(s) = G_{21}(s) = 12(\gamma_1 \gamma_2)^{1/2} s^2 e^{s d_{12}}\left[\frac{3}{4}(\gamma_2 d_{22}^3 - \gamma_1 d_{11}^3)(d_{22} - d_{11}) \right. \]

\[ \left. -d_{12}(1+\frac{1}{2} \xi)s -(1+2\xi)\right]/D(s) \]  \hspace{1cm} (171)

where

\[ D(s) = h-L_1(s)e^{s d_{11}} - L_2(s)e^{s d_{22}} + S(s)e^{s(d_{11}+d_{22})}/D(s) \]

and

\[ h = 36 \gamma_1 \gamma_2 (d_{22} - d_{11})^2, \]
\[ L_1(s) = 12\gamma_2 [(1 + \frac{1}{2}\xi) + \frac{3}{2} \gamma_1 d_{11}^2 (d_{11} - d_{11})] d_{22} s^2 + [12\gamma_2 (1 + 2\xi) - \h_1] s + h, \]

\[ L_2(s) = 12\gamma_1 [(1 + \frac{1}{2}\xi) + \frac{3}{2} \gamma_2 d_{22}^2 (d_{11} - d_{22})] d_{11} s^2 + [12\gamma_1 (1 + 2\xi) - \h_2] s + h, \]

\[ S(s) = h + [12(\gamma_1 + \gamma_2) (1 + 2\xi) - h (d_{11} + d_{22})] s \]

\[ - 18(\gamma_1 d_{11}^2 + \gamma_2 d_{22}^2) s^2 - 6(\gamma_1 d_{11}^2 + \gamma_2 d_{22}^2) (1 - \xi) s^3 \]

\[ -(1 - \xi) s^4, \]

and

\[ \xi = \gamma_1 d_{11}^3 + \gamma_2 d_{22}^3. \]

If we define \( \varphi_{ij}(s) \) and \( U_{ij}(s) \) as follows:

\[ \varphi_{ij}(s) = \int_1^\infty e^{-st} t g_{ij}(t) dt \quad \text{(172)} \]

and

\[ U_{ij}(s) = L^{-1} [t u_{ij}^*(t)] \]

or

\[ t u_{ij}^*(t) = \int_0^\infty e^{-st} U_{ij}(s) ds. \]

Then the inequality (165) takes the following form, the same way as for pure,

\[ \frac{F}{NkT} \leq \frac{F_0}{NkT} + 16\pi \beta_0 \left[ \frac{d_{11}^3 e_{11}}{2} x_1 \int_0^\infty U_{11}(s) \varphi_{11}(s) ds \right]. \]
\[ + \frac{d_2^3 \varepsilon_{22} x_2}{2} \int_0^\infty u_{22}(s) \varphi_{22}(s) ds + \frac{d_1^3 \varepsilon_{12} x_1 x_2}{2} \int_0^\infty u_{12}(s) \varphi_{12}(s) ds \]  

(173)

where from Laplace transform tables

\[ u_{ij}(s) = \left[ \frac{1}{c_{ij}} \right] \frac{12}{s^{12}} - \left[ \frac{1}{c_{ij}} \right] \frac{6}{s^4}. \]  

(174)

Also, by comparing relations (168) and (172), it can be shown that

\[ \varphi_{ii}(s) = \frac{1}{d_i^2} \frac{G_{ii}(s/d_i)}{12 \eta_i} \]  

for \( i = 1, 2 \) and,

\[ \varphi_{ij}(s) = \frac{1}{d_j^2} \frac{G_{ij}(s/d_j)}{(\eta_i \eta_j)^{1/2}} \]  

for \( i \neq j \).  

(175)

Relations in Dimensionless Forms

Let us define

\[ \alpha = \sigma_{11}/\sigma_{22}, \]

\[ \tau = \varepsilon_{11}/\varepsilon_{22}, \]  

\[ \mu_1 = d_{11}/d_{22}, \]

\[ \mu_2 = d_{11}/d_{12}, \]

\[ \eta_{ii} = \frac{\pi}{6} \rho x_i d_i^3; \quad \eta_{ij} = \frac{\pi}{3} \rho x_i x_j \quad (i \neq j); \]

\[ T_1 = kT/\varepsilon_{11}. \]  

(176)
Then inequality (173) can be written in the following dimensionless form:

\[
\frac{F}{NkT} \leq \frac{F^*}{NkT} + \frac{48}{T^*_1} \left[ x_1 \eta_{11} \int_0^\infty U_{11} \varphi_{11} ds + \frac{x_2}{\tau} \eta_{22} \int_0^\infty U_{22} \varphi_{22} ds \right] \\
+ \frac{\xi_{12}}{\xi_{11}} \eta_{12} \int_0^\infty U_{12} \varphi_{12} ds, \tag{177}
\]

where \( U_{ij} \) is given in dimensionless form by relation (174).

Also, \( \varphi_{ij} \)'s could be given in dimensionless forms as follows:

\[
\varphi_{11}(s) = \frac{s}{12\eta_{11}D^*_1(s)} [H - L_2^*(s) e^{s/\mu_1}],
\]

\[
\varphi_{22}(s) = \frac{s}{12\eta_{22}D^*_2(s)} [H - L_1^*(s) e^{-s/\mu_2}]. \tag{178}
\]

\[
\varphi_{12}(s) = \frac{s^2 e^{s/\mu_2}}{D^*_2(\mu_2 s)} \left[ \frac{3}{4} (\eta_{22} - \eta_{11}) (\frac{1}{\mu_2} - 1) \mu_2 - (1 + \frac{1}{2} \xi) \right] s \\
- (1 + 2 \xi) = \varphi_{21}(s)
\]

where

\[
D^*_1(s) = H - L_1^*(s) e^s - L_2^*(s) e^{s/\mu_1} + S^*_1(s) e^{(1+1/\mu_1)},
\]

\[
L_1^*(s) = 12\eta_{22}A_1 s^2 + B_1 s + H,
\]

\[
L_2^*(s) = 12\eta_{11}A_2 s^2 + B_2 s + H,
\]

\[
S^*_1(s) = H + A_3 s - 18(\eta_{11} + \eta_{22} \mu_1)^2 s^2 - 6(\eta_{11} + \eta_{22} \mu_1) (1-\xi) s^3 - (1-\xi)^2 s^4,
\]
and

\[ H = 36\eta_{11}\eta_{22}\mu_1(1-\mu_1)^2, \]

\[ \xi = \eta_{11} + \eta_{22}, \]

\[ A_1 = \mu_1^2[(1+\frac{1}{2}\xi) + \frac{3}{2}\eta_{11}(\frac{1}{\mu_1} - 1)], \]

\[ A_2 = [(1+\frac{1}{2}\xi) + \frac{3}{2}\eta_{22}(\mu_1-1)], \]

\[ A_3 = 12(\eta_{11} + \eta_{22}\mu_1^3)(1+2\xi) - H(1+1/\mu_1), \]

\[ B_1 = 12\eta_{22}(1+2\xi)\mu_1^3 - H, \]

and

\[ B_2 = 12\eta_{11}(1+2\xi) - H/\mu_1. \]

Since \[ d_{12} = \frac{d_{11}+d_{22}}{2} \]

then,

\[ \mu_2 = \frac{d_{11}}{d_{12}} = 2\mu_1/(1+\mu_1). \]

In the present formulation for binary mixture, the follow­ing approximations for the collision terms \( \xi_{12} \) and \( \sigma_{12} \) will be used:

\[ \xi_{12} = (\xi_{11}\xi_{22})^{\frac{1}{2}} \quad (179) \]

and

\[ \sigma_{12} = (\sigma_{11} + \sigma_{22})/2 \]
then
\[ \epsilon_{12}/\epsilon_{11} = (1/\tau)^{1/2}. \]

We had also
\[ c_{ij} = d_{ij}/\sigma_{ij} \]

and from the definition for \( \alpha \)
\[ c_{12} = \frac{\alpha c_{11} + c_{22}}{\alpha + 1} \quad (180) \]

Introduction of \( \phi_{ij} \)'s in the above dimensionless forms is a lengthy process which is not included here.

**Helmholtz Free Energy of the Reference Hard-Sphere Mixture System**

As we showed in the previous parts for the pure system one can write the following relation between the Helmholtz free energy and compressibility of a system
\[ \frac{F - F^{id}}{NkT} = \int_0^\rho \frac{1}{\rho} \left[ \frac{PV}{NkT} - 1 \right] \, d\rho \quad (181) \]

Solution of Percus-Yevick integral equation for a system consisting of a mixture of hard spheres produces two different equations of state whether for pressure the Ornstein-Zernike or virial theorem approximations are used [28] as follows.

\[ \frac{P}{kT} = \rho\left[1+\xi+\xi^2\right] - \frac{18}{\pi} \gamma_1\gamma_2 (d_{22}-d_{11})^2 \left[ (d_{11}+d_{22}) + d_{11}d_{22} \right]. \]

and
\[ (\gamma_1 d_{11}^2 + \gamma_2 d_{22}^2)^{-3} (1-\xi)^{-3} \quad (182) \]

\[ \frac{P^V}{kT} = \frac{P}{kT} - \frac{18}{\pi} \frac{\xi}{(1-\xi)^3} \left( \gamma_1 d_{11}^2 + \gamma_2 d_{22}^2 \right)^{-3} \quad (183) \]
where $\gamma_i$'s and $\xi$ are as defined already. Alder [1] has found that both $P$ and $P^V$ from Equations (182) and (183) are in very good agreement (with $P$ slightly above and $P^V$ slightly below) with Monte Carlo computations carried out by himself for several values of $d_{11}/d_{22}$ and $x_1/x_2$, and a large range of $\xi$. This indicates that the arithmetic average of the two equations (182) and (183) will be a better approximation to the equation of state than either.

$$\frac{P^{av}}{NkT} = \frac{P}{NkT} - \frac{9}{\pi} \frac{\xi}{(1-\xi)^3} \left(\gamma_1 \frac{d_{11}^2}{d_{22}} + \gamma_2 \frac{d_{22}^2}{d_{22}}\right)^3. \quad (184)$$

By inserting (184) into (181), performing the integration and introducing the result in a dimensionless form, one gets for the mixture of hard spheres

$$\frac{P^0-P^\text{id}}{NkT} = \left[\frac{3}{2} \frac{Y^3}{Z^2} - 1\right] \ln(1-\xi) + 3 \frac{V}{Z^2} \left(\frac{Y^2 + W \mu_1}{1-\xi}\right)$$

$$+ \frac{3}{2} \left[1 - \frac{1}{Z} \left(\frac{Y^3}{Z} + W (1+\mu_1 + \mu_1 \frac{Y_1}{Z})\right)\right] (1-\xi)^{-2} \quad (185)$$

where

$Y = x_1 \mu_1^2 + x_2$,

$Z = x_1 \mu_1^3 + x_2$,

$W = x_1 x_2 (1-\mu_1)^2$. 
Derivation of Equation (185) from (184) and (181) involves a lengthy algebraic calculation which is not included here.

Choice of the Variational Parameters

Inequality (177) could be written in the following form

\[ F^*(\rho^*, T_1^*, x_1) \leq F^*_o(\rho^*, T_1^*, x_1, c_{11}, c_{22}) + \Gamma^*_1(\rho^*, x_1; c_{11}, c_{22})/T^* \]

where \[ c_{12} = (\alpha c_{11} + c_{22})/(\alpha + 1) \].

Then it is clear that the right hand side of the above inequality, besides being a function of \( \rho^*, T^*, x_1 \) as the left hand side, is also a function of the two other independent variables \( c_{11} \) and \( c_{22} \).

To bring the inequality (186) closer to equality, it is necessary to choose \( c_{11} \) and \( c_{22} \) such that

\[ \frac{\partial F^*_o}{\partial c_{11}} + \frac{\partial \Gamma^*_1}{\partial c_{11}} \frac{1}{T^*} = 0 \]

(187)

\[ \frac{\partial F^*_o}{\partial c_{22}} + \frac{\partial \Gamma^*_1}{\partial c_{22}} \frac{1}{T^*} = 0 \]

with the conditions that

\[ \frac{\partial^2 F^*_o}{\partial^2 c_{11}} + \frac{\partial^2 \Gamma^*_1}{\partial^2 c_{11}} \frac{1}{T^*} \geq 0 \]

(188)
Relations (187) and (188) are the necessary and sufficient conditions for the minimization of the right hand side of inequality (186) with respect to the independent variables $c_{11}$ and $c_{22}$.

**Discussion**

Variational calculation on inequality (186), with the variational parameters $c_{11}$ and $c_{22}$, is supposed to predict the properties of binary mixtures as well as the pure component which was shown in Chapter IV (by putting $\sigma_{11} = \sigma_{22}$ and $d_{11} = d_{22}$, inequality (177) will be the same as the first inequality which was produced in Chapter IV for pure component). However, no machine-calculated data are available for the mixture of Lennard-Jones fluids or for any other kind except hard-spheres. Also, experimental data for mixtures of such simple fluids as argon, krypton, and xenon are very rare, especially in the liquid phase, where the present variational technique might show some superiority to other approaches. Alder is doing some calculations for the binary mixture of hard-sphere and square-well fluids by the method of molecular dynamics which are not published yet.

The choice of the interaction parameters $\epsilon_{12}$ and $\sigma_{12}$ might be critical in comparing the results of the binary mixture as calculated by the present variational technique and the experimental data of the mixture of real-simple fluids. While the
approximate relations for \( \xi_{12} \) and \( \sigma_{12} \), as shown by (179), are satisfactory for the corresponding state approach, their accuracy for the variational calculations, especially in the liquid range, can not be trusted. This problem will not rise in the comparison with the machine-calculated data. This is because of the necessity for \textit{a priori} definition of the interaction parameters in molecular dynamic and Monte Carlo calculations.
TABLES
TABLE II
COMPRESSIBILITIES OF LENNARD-JONES FLUID FOR DIFFERENT ISOTHERMS

\[
\left( \frac{PV}{NkT} \right)_{01}, \left( \frac{PV}{NkT} \right)_{02}, \left( \frac{PV}{NkT} \right)_{0123}
\]
are the values of compressibility as calculated by the thermodynamic relation (99), based on the Helmholtz free energy calculated from relation (105), (111) and (112), respectively. The places which are left blank for \( \left( \frac{PV}{NkT} \right)_{0123} \) are due to the divergent character of \( \Gamma^*_3 \), which was expected because of the inaccuracy of the approximations introduced in \( \Gamma^*_3 \).
### TABLE II

**COMPRESSIBILITIES OF LENNARD-JONES FLUID FOR DIFFERENT ISOTHERMS**

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### TABLE II

**COMPRESSIBILITIES OF LENNARD-JONES FLUID FOR DIFFERENT ISOTHERMS**

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TABLE III

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FOR FACE-CENTERED CUBIC STRUCTURE

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### TABLE IV

**COMPRESSIBILITIES OF LENNARD-JONES SOLID FOR DIFFERENT ISOOTHERMS**

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FIGURES 1-13
Compressibility of the system of hard-spheres versus \( V/V_0 \), \( (V_0 = N_0^3/\sqrt{2}) \), as calculated from the average Percus-Yevick Equation (101), points shown by o are the molecular dynamic calculations of Alder and Wainwright [43]. As it is clear from Figure 1 and also from Figure 1 of reference [54] the average Percus-Yevick equation as shown by (101) is in better agreement with machine-calculated data than either of the two, virial and Ornstein-Zernike equations.
Figure 1. Hard-sphere Compressibility vs. $V/V_0$. 
FIGURE 2

CUTOFF PARAMETER VERSUS DENSITY FOR DIFFERENT ISOTHERMS

Cube of cutoff parameter as a function of density and temperature. The values of cutoff parameter in Figure 1 are those values which satisfy conditions (107) which are the necessary and sufficient conditions for the minimization of the right hand side of the first inequality (105).
Figure 2. Cutoff Parameter vs. Density for Different Isotherms.
FIGURE 3

EQUATION OF STATE OF LENNARD-JONES 12:6 FLUID FOR DIFFERENT ISOTHERMS

Equation of state for 12:6 potential. The curves are isotherms labeled with the appropriate values of $T^* = kT/\epsilon$. They are calculated from Equation (109) with consideration of the thermodynamic relation

$$\frac{PV}{NkT} = \rho \frac{\partial^2 F}{\partial \rho^2} \frac{F}{NkT}$$

The points given by $\circ$, $\phi$, and $\bullet$ are machine-calculated values which are taken from references [58, 61 and 35], respectively. The points given by $\circ$ were calculated using a five-term virial expansion (reference [5]) and the points given by $x$, $\Theta$ and $+$ are experimental values and are taken from references [32, 56 and 57], respectively.
Figure 3. Equation of State of Lennard-Jones 12:6 Fluid for Different Isotherms.
Equation of state for 12:6 potential. The difference between this figure and Figure 3 is that the coefficient of $T^*_2$ in the variational expansion of the free energy is also used which is shown by Equation (111). For the cutoff parameter the same values as used for Figure 3 are used. The experimental and machine-calculated points are the same as in Figure 3.
Figure 4. Equation of State of Lennard-Jones 12:6 fluid vs. Density for Different Isotherms.
Internal energy for the 12:6 potential. The curves are isotherms calculated from Equation (115) and are labeled with appropriate values of $T^*$. For the Helmholtz free energy in Equation (115), the values calculated from Equation (109) are used. Equation (111) gives divergent results for internal energy at low densities while it is giving good results at high densities. This might be due to the approximations introduced in $\Gamma_2^*$ which actually is not expected to be correct at low densities.

The points given by $\circ$, $\square$, $\Delta$ are machine-calculated values for $T^* = 2.74$, 1.35, 0.72, respectively, taken from reference [58]. The points given by $\bigcirc$ and $\bullet$ are machine-calculated values for $T^* = 2.74$ from reference [61] and for $T^* = 0.72$ from reference [35], respectively. The points given by $\times$, $+$ are experimental values taken from reference [32] for $T^* = 2.74$ and 1.35, respectively, and the point given by $\bigast$ was taken from experimental data in references [46 and 7].
Figure 5. Internal Energy of Lennard-Jones 12:6 Fluid vs. Density for Different Isotherms.
Internal entropy for the 12:6 potential. The curves are isotherms calculated from Equation (116) and are labeled with the appropriate values of $T^*$. For the Helmholtz free energy in Equation (116) the values from Equation (109) are used. Helmholtz free energies calculated from Equation (111) give divergent results for the internal entropy at low densities, while they give good results at high densities. This might be due to the approximations introduced in $\Gamma_2^*$ which actually is not expected to be correct at low densities.

The points given by $\times$, $+$ are experimental values taken from reference [32] for $T^* = 2.74$ and 1.35, respectively, and the point given by $\Theta$ was calculated from experimental data given in references [46 and 7].
Figure 6. Internal Entropy of Lennard-Jones 12:6 fluid vs. Density for Different Isotherms.
Densities of the coexisting vapor and liquid phases for 12:6 potential. The curve gives the results of the system of Equation (117) based upon the Helmholtz free energy calculated from Equation (111). The points given by \( \phi \) and \( \psi \) are machine-calculated values and are taken from references [58 and 35], respectively. The points given by \( o \) and \( \bullet \) are experimental values for liquid and solid argon and are taken from references [20 and 7], respectively.
Figure 7. Densities of Coexisting Vapor and Liquid Phases for Lennard-Jones 12:6 Fluid vs. Temperature.
Reduced vapor pressures for the 12:6 potential. The curves are calculated from Equation (117) based on the Helmholtz free energy as calculated by Equation (111). The points are the experimental values taken from reference [48].
Figure 8. Reduced Vapor Pressures for Lennard-Jones 12:6 Liquid vs. Inverse Temperature.
INTERNAL ENERGY AT SATURATED VAPOR PRESSURES FOR LENNARD-JONES 12:6 LIQUID VERSUS TEMPERATURE

Internal energy at saturated vapor pressures for the 12:6 potential. The curve gives the results of Equation (115) when the theoretical liquid densities as calculated from Equation (117) are used. For the Helmholtz free energy relation (111) is used.

The points given by $\phi$ and $\varphi$ are machine-calculated values and are taken from references [58 and 35] respectively. The points given by $\bullet$ are experimental values taken from reference [38] and the points given by $\circ$ were calculated from experimental data as reported by reference [7].
Figure 9. Internal Energy at Saturated Vapor Pressures for Lennard-Jones 12:6 Liquid vs. Temperature.
FIGURE 10

INTERNAL ENTROPY AT SATURATED VAPOR PRESSURE FOR LENNARD-JONES 12:6 LIQUID VERSUS TEMPERATURE

Internal entropy at saturated vapor pressures for the 12:6 potential. The curve gives the results of Equation (116) when the theoretical liquid densities as calculated from Equation (117) are used. For the Helmholtz free energy relation (111) is used.

The points given by ● are experimental values taken from reference [38] and the points given by ○ were calculated from experimental data as reported in reference [7].
Figure 10. Internal Entropy at Saturated Vapor Pressure for Lennard-Jones 12:6 Liquid vs. Temperature.
FIGURE 11

VALUES OF A VERSUS DENSITY FOR LENNARD-JONES 12:6 POTENTIAL VERSUS DENSITY FOR DIFFERENT ISOTHERMS

Values of A versus density for different isotherms as calculated by variational calculation on inequality (151). The sharp change of A in each isotherm is the indication of liquid-solid phase transition. A has the following relation with the frequency of harmonic oscillation of the molecules of the reference system in their cells

\[ A = \frac{m\omega^2}{kT} \]

where \( \omega \) is the harmonic oscillation frequency.
Figure 11. Values of $A$ vs. Density for Lennard-Jones 12:6
Potential vs. Density for Different Isotherms.
Equation of state for the solid 12:6 potential. The curves are isotherms each labeled with the appropriate $T^*$. They are calculated by the thermodynamic relation (99) using variational results based on inequality (151) for the free energy.

The points shown by $\phi$, $\bullet$, and $\blacksquare$ are taken from references [44, 35, and 61] respectively.
Figure 12. Equation of State of Lennard-Jones 12-6 Solid for Different Isotherms.
FIGURE 13

DENSITIES OF COEXISTING LIQUID AND SOLID PHASES FOR LENNARD-JONES 12:6 POTENTIAL VERSUS TEMPERATURE

Densities of the coexisting liquid-solid phases for the 12:6 potential. The solid lines are the experimental values for argon taken from reference [16]. The dashed lines are calculated by the system of Equation (153). The dot-dashed lines are the values related to the sharp changes of the slope of $A$ versus $\rho^*$ for different isotherms in Figure 11.
Figure 13. Densities of Coexisting Liquid and Solid Phases for Lennard-Jones 12:6 Potential vs. Temperature.
LITERATURE CITED


NOMENCLATURE

\( a \) = depth of the n:6 potential curve

\( a_0 \) = \((\sqrt{2}/\rho)^{1/3}\) nearest-neighbors distance in f.c.c. crystal

\( a^* \) = \(a_0/\sigma\)

\( a_1(v) \) = coefficient of \((\frac{1}{RT})^i\) in the perturbation equation of state

\( A \) = \(kTW(r)/(r/a_0)^2\)

\( b_0 \) = \(2/3\pi N\sigma^3\)

\( B \) = second virial coefficient

\( B^* \) = \(B/b_0\)

\( c \) = \(d/\sigma\) = cutoff parameter

\( c_{11}, c_{m2} \) = cutoff parameters produced by the variational calculation on the first and second inequalities, respectively

\( c_{11} \) = \(d_{11}/\sigma_{11}\)

\( c_{22} \) = \(d_{22}/\sigma_{22}\)

\( c_{12} \) = \((\alpha c_{11} + c_{22})/(\alpha+1)\)

\( c(i,j) \) = direct correlation function

\( c(r) \) = direct correlation function

\( C \) = third virial coefficient

\( C^* \) = \(C/b_0^2\)

\( d \) = hard-sphere diameter
\[ d_{11} = \text{first component hard-sphere diameter} \]
\[ d_{22} = \text{second component hard-sphere diameter} \]
\[ d_{12} = (d_{11} + d_{22})/2 \]
\[ D = \text{fourth virial coefficient} \]
\[ D^{*} = D/b_{0}^{3} \]
\[ F = \text{Helmholtz free energy (original system)} \]
\[ F^{*} = F/NkT \]
\[ g(r), g^{(2)}(r), g(i,j), g_{i}^{(r_{ij})} = \text{radial distribution function} \]
\[ g_{\alpha\beta} = \text{radial distribution function in the binary mixture} \]
\[ g_{\alpha,i} = \text{coefficient of } \left(\frac{1}{v}\right)^{i} \text{ in the expansion of } g_{\alpha}(r,v) \]
\[ g^{(n)}(x_{1}, \ldots, x_{n}) = n^{th} \text{ distribution function} \]
\[ G = v_{f}/4\pi a_{0}^{3} \]
\[ G(s) = L^{-1}[g_{\alpha}(x)x] \]
\[ h = \text{Planck's Constant} \]
\[ h(r) = g(r) - 1 = \text{total correlation function} \]
\[ h(i,j) = \text{total correlation function} \]
\[ I(0) = \text{structure factor} \]
\[ i = \text{shell number} \]
\[ i = \text{particle number} \]
\[ i(s) = \text{scattering function} \]
\[ k = \text{Boltzmann's Constant} \]
\[ m = \text{particle's mass} \]
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>n</td>
<td>= particle number</td>
</tr>
<tr>
<td>n</td>
<td>= power in n:6 potential function</td>
</tr>
<tr>
<td>N</td>
<td>= total number of particles in the system</td>
</tr>
<tr>
<td>$N_i$</td>
<td>= number of the particles in the shell $R_i \rightarrow R_i + dR_i$</td>
</tr>
<tr>
<td>$N_1$</td>
<td>= total number of the particles of component 1 in binary mixture.</td>
</tr>
<tr>
<td>$N_2$</td>
<td>= $N - N_1$</td>
</tr>
<tr>
<td>$p(x)$</td>
<td>= probability of x</td>
</tr>
<tr>
<td>P</td>
<td>= pressure</td>
</tr>
<tr>
<td>$P^v$</td>
<td>= pressure from virial theorem</td>
</tr>
<tr>
<td>$P_c$</td>
<td>= $P \sigma^3 / \epsilon = \text{reduced critical pressure}$</td>
</tr>
<tr>
<td>$p(n)$</td>
<td>= probability distribution function of particles 1, ..., n</td>
</tr>
<tr>
<td>Q</td>
<td>= partition function</td>
</tr>
<tr>
<td>$r$</td>
<td>= intermolecular distance = $</td>
</tr>
<tr>
<td>$R$</td>
<td>= vectorial distance</td>
</tr>
<tr>
<td>$X_i$</td>
<td>= vector position of particle $i$</td>
</tr>
<tr>
<td>$X_i$</td>
<td>= vector displacement of particle $i$ from the cell center</td>
</tr>
<tr>
<td>$R$</td>
<td>= intermolecular distance = $</td>
</tr>
<tr>
<td>$R$</td>
<td>= vectorial distance</td>
</tr>
<tr>
<td>$R$</td>
<td>= gas constant</td>
</tr>
<tr>
<td>$S_i$</td>
<td>= internal entropy</td>
</tr>
<tr>
<td>t</td>
<td>= $r / d_{ij}$</td>
</tr>
</tbody>
</table>
\( T \) = temperature

\( T^* \) = \( kT/\epsilon \) = reduced temperature

\( T^*_c \) = \( kT/\epsilon_1 \)

\( T^*_c \) = reduced critical temperature

\( u_{ij}, u(r), u(ij) \) = two-body intermolecular potential function

\( u^1, u^1 \)

\( u_n \)

\( u^* \) = \( u/4\epsilon \)

\( U \) = total potential energy

\( U^1 \) = \( U-U^0 \)

\( U_i \) = \( L[xu^i(x)] \)

\( v \) = specific volume

\( v^* \) = \( v/\sigma^3 \)

\( v(d, \sigma, \alpha, \gamma; r) \) = generalized two-body potential energy function

\( v_f \) = free volume

\( V \) = total volume of the system

\( w_{ijk} \) = three-body potential energy function

\( W(r) \) = \( \Psi(r) - \Psi(0) \)

\( x \) = \( r/\sigma \)

\( x_1 \) = mole fraction of component 1 in binary mixture

\( x_2 \) = \( 1 - x_1 \)

\( Z \) = \( \frac{PV}{NkT} = \frac{Pv}{RT} \) = compressibility

\( Z \) = configuration integral
\( z_i \) = distance of the \( i \)th neighbor from the central molecule

\( z_i^* \) = \( z_i/a_0 \)

**Greek Letters**

\( \alpha \) = steepness parameter

\( \alpha = \sigma_{11}/\sigma_{22} \)

\( \alpha_i \) = lower bound for \( z_i - a_0 \)

\( \alpha_i^* \) = \( \alpha_i/a_0 \)

\( \beta \) = \( 1/kT \)

\( \beta_i \) = upper bound for \( z_i + a_0 \)

\( \beta_i^* \) = \( \beta_i/a_0 \)

\( \gamma \) = depth parameter

\( \gamma_i = \pi \rho x_i \)

\( \Gamma_i \) = coefficient of \( \left( \frac{1}{T^*} \right)^i \) in variational expansion of Helmholtz free energy

\( \epsilon \) = depth of the Lennard-Jones potential curve

\( \epsilon_{11} \) = depth of the Lennard-Jones potential curve

\( \epsilon_{12} = \left( \epsilon_{11} \epsilon_{22} \right)^{\frac{1}{2}} \)

\( \eta \) = \( \frac{\pi}{6} (\rho \sigma^3) \) for perturbation of Barker and Henderson

\( \eta = \frac{\pi}{6} (\rho \sigma^3) c^3 \) for the variational technique

\( \eta_{11} = \frac{\pi}{6} \rho x_1 d_{11}^3 \)
\[ \eta_{22} = \frac{\pi}{6} \rho x_2 d_{22}^3 \]
\[ \eta_{12} = \frac{\pi}{3} x_1 x_2 d_{12}^3 \]
\[ \lambda = \text{square-well potential function parameter} \]
\[ \Lambda = \frac{\hbar}{(2\pi mkT)^{1/2}} \]
\[ \mu_1 = \frac{d_{11}}{d_{22}} \]
\[ \mu_2 = \frac{d_{11}}{d_{12}} \]
\[ \xi = \text{truncation parameter in the Taylor expansion} \]
\[ \xi = \gamma_1 d_{11}^3 + \gamma_2 d_{22}^3 \]
\[ \pi = 3.1415926... \]
\[ \rho = \frac{N}{v} = \text{number density} \]
\[ \rho^* = \rho \sigma^3 \]
\[ \rho^*_c = \text{reduced critical density} \]
\[ \sigma = \text{Lennard-Jones length parameter} \]
\[ \sigma_{ii} = \text{Lennard-Jones length parameter for component } i \text{ in binary mixture} \]
\[ \sigma_{12} = \frac{(\sigma_{11} + \sigma_{22})}{2} \]
\[ \tau = \frac{\epsilon_{11}}{\epsilon_{22}} \]
\[ \phi_{ij}(s) = L[tg_{ij}(t)] \]
\[ \chi = \text{a general undefined variable} \]
\[ \chi_{ij} = u_{ij} - u_{ij}^0 - (u_{ij} - u_{ij}^0) \]
\[ \Psi(r_1), \Psi(r), \Psi(r) = \text{potential energy function inside cell} \]
\[ \omega_i = \text{coefficient of } \left(\frac{1}{kT}\right)^{i-1} \text{ in the perturbation expansion of free energy} \]
### Superscripts
- $o$: reference system
- $id$: ideal gas
- $v$: virial theorem
- $*$: dimensionless

### Subscripts
- $o$: reference system (except for $a_o$ and $U'_o$)
- $l$: liquid
- $s$: solid
- $v$: vapor
- $V$: volume
- $ij$: particles $i$ and $j$
- $i$: shell number
- $\Delta$: cell

### Mathematical Operators
- $\nabla_i$: the "del" or "nohla" operator with respect to particle $i$
- $dr, di, dr_i$: differential volume (with respect to particle $i$)
- $d\Gamma$: differential phase volume
- $\partial[\ ]$, $\partial[\ ]$: partial derivative
- $\exp(x)$: $e^x$ = the exponential of $x$
- $\ln(x)$: natural logarithm of $x$
- $\int_V$: triplet (volume) integral
\[ \int_{\Delta}^{\ldots} \quad = \text{integral over cell volume} \]

\[ \langle x \rangle \quad = \text{expectation value of } x \]

\[ \langle x \rangle_0 \quad = \text{expectation value of } x \text{ over the reference system} \]

\[ \langle x \rangle_\Delta \quad = \text{expectation value of } x \text{ over the cell} \]

\[ |r_i - r_j| \quad = \text{intermolecular distance of molecules } i \text{ and } j. \]

\[ f(x) \quad = \text{a function of } x \]

\[ f^{(n)}(x) \quad = \text{n}^{\text{th}} \text{ derivative of } f(x) \]

\[ \sum_{i=1}^{N} \quad = \text{summation over } N \text{ molecules (or cells)} \]

\[ \sum_{i>\ldots>k=1}^{N} \quad \sum_{i=1}^{N} \ldots \sum_{k=1}^{N} \quad = \sum_{i>\ldots>k=1}^{X} \quad = \text{summation over all the arrangements of molecules with one in each cell} \]

\[ 0(\ldots) \quad = \text{in the order magnitude of} \]
APPENDIX

In a grand canonical ensemble, g.c.e., we have [23]

\[
\langle N^3 \rangle = \sum_N N^3 P_N = \frac{\sum_N N^3 \exp(\beta N \mu) Q_N(T,V)}{\Xi} = \frac{1}{\beta^3 \Xi} \left( \frac{\partial^2 \Xi}{\partial \mu^2} \right)_{T,V}
\]

(A-1)

where \( \Xi \) is the partition function of g.c.e., \( \mu \) is the activity coefficient, and \( Q_N \) is the canonical ensemble partition function.

For g.c.e. we also have

\[
\left( \frac{\partial^2 \Xi}{\partial \mu^2} \right)_{T,V} = [\langle N^2 \rangle + kT \left( \frac{\partial \langle N \rangle}{\partial \mu} \right)_{T,V} \beta^2 \Xi].
\]

(A-2)

Then

\[
\langle N^3 \rangle = \frac{1}{\beta^3} \frac{\partial}{\partial \mu} \left[ \frac{\partial^2 \Xi}{\partial \mu^2} \right]_{T,V}
\]

(A-3)

By inserting (A-2) in (A-3) and performing the necessary differentiations, we get

\[
\langle N^3 \rangle = 3 \langle N \rangle \langle N^2 \rangle - 3 \langle N^3 \rangle + \langle N \rangle^3 + \frac{1}{\beta^2} \left( \frac{\partial^2 \langle N \rangle}{\partial \mu^2} \right)_{T,V}
\]

or

\[
\langle (N-\langle N \rangle)^3 \rangle = \frac{1}{\beta^2} \left( \frac{\partial^2 \langle N \rangle}{\partial \mu^2} \right)_{T,V}
\]

(A-4)
Also for g.c.e., we have

\[ \left( \frac{\partial \langle N \rangle}{\partial \mu} \right)_{T,V} = \langle N \rangle \left( \frac{\partial \rho}{\partial P} \right)_{T,V} \]  \hspace{1cm} (A-5)

From (A-4) and (A-5), it can be shown that

\[ \langle (N - \langle N \rangle)^3 \rangle = -\langle N \rangle \frac{1}{\beta^2} \left[ \left( \frac{\partial \rho}{\partial P} \right)^2 + \frac{\partial}{\partial \rho} \frac{\partial}{\partial \rho} \left( \frac{\partial \rho}{\partial P} \right)^2 \right]. \] \hspace{1cm} (A-6)

Relation (A-6) which is an exact macroscopic equation is the same as Equation (76) which is actually an approximation derived from (A-6).