THE UNIVERSITY OF OKLAHOMA

GRADUATE COLLEGE

A VARIATIONAL APPROACH TO THE EQUILIBRIUM

THERMODYNAMIC PROPERTIES OF SIMPLE

LIQUIDS AND PHASE TRANSITIONS

A DISSERTATION

SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the

degree of

DOCTOR OF PHILOSOPHY

IN

CHEMICAL ENGINEERING

BY

GHOLAM-ALI MANSOORI

Norman, Oklahoma

1969

A VARIATIONAL APPROACH TO THE EQUILIBRIUM

THERMODYNAMIC PROPERTIES OF SIMPLE

LIQUIDS AND PHASE TRANSITIONS

APPROVED BY

DISSERTATION COMMITTEE

TO

Professor Hossein Zad-Mard

University of Tehran

and

Professor Arthur J. Madden

University of Minnesota

My inspiring teachers

ACKNOWLEDGMENTS

iii

ABSTRACT

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.

v

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.

TABLE OF CONTENTS

TABLE OF CONTENTS (CONTINUED)

LIST OF TABLES

LIST OF ILLUSTRATIONS

Figure   Page

A VARIATIONAL APPROACH TO THE EQUILIBRIUM

THERMODYNAMIC PROPERTIES OF SIMPLE

LIQUIDS AND PHASE TRANSITIONS

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 barri-

caded 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 implica-
tions 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 diffu-
sion 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

4

are, and have been, in the form of very difficult and compli-
cated combinatory 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 com-
paratively 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 exis-
tence of empty cells are permitted in the model. The intro-
duction 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 assump-
tion 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 bas-
ing 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 combinatory 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,

$$kT \; \nabla_1 g(1,2) = -g(1,2) \nabla_1 u(1,2) - \rho \int g(1,2,3) \nabla_1 u(1,3) d3 \quad (1)$$

and

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

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 hirarchy 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 [64] in 1937.. Yvon also gave (1935) the

pressure, or virial equation,

$$P = \rho kT - \frac{1}{2} \rho^2 \int r u'(r) g(r) \, d\underline{r} \tag{3}$$

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 [13] and by

Born and Green [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 [40]

equation

$$h(1,2) = c(1,2) + \rho \int c(1,3) h(2,3) \, d3 \tag{4}$$

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) [49].

$$kT \frac{\partial \rho}{\partial P} = 1 + \rho \int h(1,2) \, d2 = I(0) \tag{5}$$

where I(0) is the structure factor, 1 + i(s), for limitingly

small scattering angles, and which is a second route to thermo-

dynamic 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 struc-
ture, had an entirely different origin. This theory joins the
Ornstein-Zernike equation, the second prescription for $c(r)$,

$$c(r) = [1 - \exp\{u(r)/kT\}][1 + h(r)]. \qquad (9)$$

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 ana-
lytic and satisfactory equation of state for systems of hard
spheres [60, 54], it is in need of improvement for more realis-
tic 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 approxima-
tion 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 pur-
pose of this work is based upon, are neither predictive nor
interpretive theories. They are mathematical means of expand-
ing 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 molecu-
lar 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.

CHAPTER II

HISTORICAL BACKGROUND AND PREVIOUS WORKS

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

$$\frac{Pv}{RT} = a_o(v) + \frac{a_1(v)}{RT} + \frac{a_2(v)}{(RT)^2} + \ldots \qquad (10)$$

The data on argon and nitrogen for the range of 0° C to 150° 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

13

primary purpose was classical fluids, only the configurational contribution to the partition function was needed. For a system consisting of N molecules in a volume v, and total potential energy U, the configurational Helmholtz free energy F will be given by

$$\exp(-\beta F) = Q = \frac{1}{N!} \int_v \ldots \int_v \exp(-\beta U)\, d\underline{r}_1 \ldots d\underline{r}_N; \tag{11}$$

$$\beta = 1/kT.$$

U is a function of the configuration of each molecule, and $\int_v d\underline{r}_i$ is an integral over the entire configuration space of the ith molecule. Also, one could assume that the potential energy may be separated into two parts,

$$U = U^o + U^1 \tag{12}$$

where U^o 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 temperature around the unperturbed potential U^o and get the following relation

$$-kT \ln Q = F = F^o + \omega_1 - \omega_2/kT + 0(1/kT)^2 \tag{13}$$

where with the consideration of only two body forces he obtained

$$\omega_1 = \frac{1}{2} N(N-1) \int\int u^{(1)}(1,2) P_o^{(2)}(1,2)\, d\underline{r}_1 d\underline{r}_2, \tag{14}$$

and

$$\omega_2 = \frac{1}{8}N^4\int[P_o^{(4)}(1,2,3,4)-P_o^{(2)}(1,2)P_o^{(2)}(3,4)]\,u^{(1)}(1,2)\,u^{(1)}(3,4)\,d\underline{r}_1\cdots d\underline{r}_4$$

$$+\ N^3\iiint P_o^{(3)}(1,2,3)\,u^{(1)}(1,2)\,u^{(1)}(2,3)\,d\underline{r}_1 d\underline{r}_2 d\underline{r}_3$$

$$+\ \frac{1}{2}N^2\iint P_o^{(2)}(1,2)\,[u^{(1)}(1,2)]^2\,d\underline{r}_1 d\underline{r}_2, \tag{15}$$

where $P_o^{(n)}$ 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

$$u(r) = u^o(r) + u^1(r),$$

$$u^o(r) = \begin{bmatrix} \infty & (r \leq c\sigma) \\ \\ o & (r > c\sigma) \end{bmatrix}, \tag{16}$$

$$u^1(r) = 4\epsilon[(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^6],$$

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 $P_o^{(2)}(1,2)$ can be derived from radial distribution function

$$P_o^{(2)}(1,2) = g_o(1,2)/v^2, \tag{17}$$

for higher distribution functions, there are no satisfactory relations available; that was why Zwanzig truncated the series (13) to the second term

$$F = F^O + \omega_1 + O(1/kT) \tag{18}$$

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

$$P = - (\partial F/\partial v)_T \tag{19}$$

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

$$\frac{Pv}{RT} = \left(\frac{Pv}{RT}\right)_O - \frac{v(\partial/\partial v)}{RT} \left[(2\pi N^2/v) \int_O^\infty r^2 g_O(r) u'(r) dr. \tag{20}$$

This is the equation of state which is a result of the first-order perturbation theory from the hard-sphere potential basis, where $(Pv/RT)_O$ 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

$$\frac{Pv}{RT} = 1 + B(T)/v + C(T)/v^2 + D(T)/v^3 + \ldots \tag{21}$$

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

$$g_O(r;v) = \exp(-u^O(r)/kT)[1 + \frac{g_{O,1}(r)}{v} + \frac{g_{O,2}(r)}{v^2} + \ldots] \tag{22}$$

were able to find the functional forms of the first few virial

coefficients with respect to $T^* = kT/\epsilon$ and c, the cutoff para-

meter as defined in (16),

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

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

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

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

For high densities, Smith and Alder [51] used the con-

figurational partition function due to free-volume theory of

Lennard-Jones and Devonshire [30]. For a Lennard-Jones poten-

tial with a hard sphere cutoff, the partition function is

$$Q = 2\pi a_0^* \int_0^q \sqrt{y} \exp[- \frac{12}{T^*} (\frac{l_1(y)}{v^{*4}} - \frac{2m_1(y)}{v^{*2}})] dy \qquad (26)$$

with

$$l_1(y) = \frac{1 + 12y + 25.2y^2 + 12y^3 + y^4}{(1-y)^{10}} - 1,$$

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

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

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

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

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

$$+ \frac{12}{T*} \left[(3 + q^{-\frac{1}{2}}) \frac{L_2(q)}{v*^4} - (1 + q^{-\frac{1}{2}}) \frac{2M_2(q)}{v*^2}\right] \quad (27)$$

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

$$l_2(q) = \frac{1 + 4.2q + 3q^2 + (1/3)q^3}{(1-q)^9} - 1,$$

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

$$\ddot{u}_n(r) = a \ [(\tfrac{\sigma}{r})^n - (\tfrac{\sigma}{r})^6] \qquad \qquad (28)$$
$$n \rightarrow \infty$$

with

$$a = [n/(n-6)](\tfrac{1}{6}n)^{6/(n-6)} \epsilon.$$

If we define $U_n(\sigma) \equiv \infty$, it will be evident that
$n \rightarrow \infty$

$$u_n(r) = 4\epsilon[(\tfrac{\sigma}{r})^{12} - (\tfrac{\sigma}{r})^6]$$
$$n \rightarrow 12$$

$$\qquad \qquad \qquad \qquad \qquad \qquad (29)$$

$$u_n(r) \equiv u_1(x) = \begin{bmatrix} \infty & (r \leq \sigma) \\ -\epsilon(\tfrac{\sigma}{r})^6 \ldots (r > \sigma) \end{bmatrix}$$
$$n \rightarrow \infty$$

Upon this character of $U_n(r)$ as defined by (29), McQuarrie and Katz rigorously expanded the partition function in powers of $1/n$

$$Q(n) = Q(n = \infty) + n^{-1} \left[\frac{\partial Q}{\partial 1/n} \right]_{n=\infty} + O(n^{-2}) \qquad (30)$$

Following Zwanzig and Rowlinson, they got

$$Q_n/Q_O = 1 - \frac{2\pi N^2 \beta \sigma^3}{V} \int_0^\infty x^2 u_1(x) g_O(x;\rho) dx$$

$$- \frac{2\pi N^2 \sigma^3 g_O(1;\rho)}{nV} (\gamma + \ln\beta a) \qquad (31)$$

$$+ O(1/n^2) + O(\beta/n) + O(\beta^2),$$

where

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

and Q_O, g_O are the partition function and the radial distribution function of hard-sphere system respectively, while $g_O(1;\rho)$ 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

$$\frac{Pv}{RT} = 1 + Z_O(\rho^*) + \frac{3}{n}(\gamma + \ln \frac{a}{\epsilon}) (\rho^* \frac{\partial Z_O}{\partial \rho^*})$$

$$- \frac{3 \ln(T^*)}{n} (\rho^* \frac{\partial Z_O}{\partial \rho^*}) - \frac{3(a/\epsilon)\rho^*}{T^*} \cdot \frac{\partial}{\partial \rho^*} [\rho^* \cdot J(\rho^*)], \qquad (33)$$

where

$$J(\rho^*) = \int_0^\infty x^{-4} g_O(x,\rho^*) dx,$$

and

$$Z_O = (\frac{Pv}{RT})_O - 1 = (2\pi N\sigma^3/3v) g_O(1;\rho) ,$$

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

$$Z_O = \frac{\rho^*(1 + 0.063507\rho^* + 0.017329\rho^{*2})}{1 - 0.561493\rho^* + 0.081313\rho^{*2}}. \qquad (34)$$

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, ω_2, the coefficient of $-\frac{1}{kT}$ in (13) which is shown by relation (15), is a complicated function of the second, third, and forth 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 per-
turbation treatments of the attractive forces or to the treat-
ment of the finite steepness of the repulsive potential. For
this purpose Barker and Henderson [6] decided to use the per-
turbation 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. Further-
more, 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 approxi-
mation: m.c.

$$w_2 = \frac{1}{4} \rho \int_V [u_1(r)]^2 kT \left(\frac{\partial \rho}{\partial P}\right)_0 g_0(r) \, d\underline{r},$$ (35)

and local compressibility approximation: l.c.

$$w_2' = \frac{1}{4} \rho \int_V [u_1(r)]^2 kT \left[\frac{\partial(\rho g)}{\partial P}\right]_0 d\underline{r}$$ (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

$$
\frac{F-F^0}{NkT} = -2\pi\rho \left(\frac{\epsilon}{kT}\right) \int_{\sigma}^{\lambda\sigma} r^2 g_0(r) \, dr
$$

$$
-\pi\rho \left(\frac{\epsilon}{kT}\right)^2 \frac{(1-\eta)^4}{1+4\eta+4\eta^2} \cdot \frac{\partial}{\partial\rho} \left[\rho \int_{\sigma}^{\lambda\sigma} r^2 g_0(r) \, dr\right] ,
$$

(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 $g_0(r)$ 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(d, σ, α, γ; r) by the relation

$$v(d, \sigma, \alpha, \gamma; r) = u[d+(r-d)/\alpha], \quad d + (r-d)/\alpha < \sigma$$

$$= 0, \quad \sigma < d + (r-d)/\alpha < d+(\sigma-d)/\alpha \qquad (39)$$

$$= \gamma u(r), \quad \sigma < r.$$

They assumed that u(r) rises to effectively infinite positive values for small values of r and that u(σ) 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 α varies the steepness of the modified potential in the repulsive region; this is inverse-steepness parameter. The parameter γ varies the depth of the potential in the attractive region. The procedure is to expand the configuration integral in a double Taylor series in α and γ about the point $\alpha = \gamma = 0$, which corresponds to the hard-sphere potential. The final result is shown by the following relation

$$\frac{F - F^O}{NkT} = - \alpha 2\pi\rho \ d^2 g_O(d) \left[d - \int_O^\sigma \{1-\exp[- \beta u(r)]\}dr \right]$$

$$+ \gamma 2\pi N\rho\beta \int_\sigma^\infty g_O(r) u(r) r^2 dr + \text{higher order terms.} \quad (40)$$

In Equation (40) F is the Helmholtz free energy corresponding to the potential v(r) and F^O 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 σ are still at disposal. As stated previously, they use for σ the value of r for which u(r) is zero. Also, they chose for d the value given by

$$d = \int_O^\sigma \{1 - \exp[-\beta u(r)]\}dr \quad (41)$$

This depends on temperature but not on density, and with this choice the term of order α 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 varia-

tional 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 poten-

tial. Even that in the method of Barker and Henderson these

two problems are solved completely for gas phase (because of

the fact that $T^*_{critical} \cong 1.35$ for Lennard-Jones fluid) they

can not 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

$$\langle f(x) \rangle = \int P(x) f(x) dx \qquad (42)$$

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

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

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

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

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

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

$$\langle f(x) \rangle \geq f(\langle x \rangle) \qquad (45)$$

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

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 $U(\underline{r}_1,\ldots,\underline{r}_N) = U$, of interaction of all the $\frac{N(N-1)}{2}$ pairs of particles in the system, in equilibrium, is [23]

$$Q = \frac{1}{N!\Lambda^{3N}} \int_V \cdots \int e^{-\beta U} d\underline{r}_1 \ldots d\underline{r}_N; \quad \Lambda = \frac{h}{(2\pi mkT)^{\frac{1}{2}}}. \quad (47)$$

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

$$\frac{Q}{Q_0} = \int \cdots \int \frac{e^{-\beta U_0}}{Z_0} \cdot e^{-\beta(U-U_0)} d\underline{r}_1 \ldots d\underline{r}_N; \quad Z_0 = N! \, \Lambda^{3N} Q_0 \quad (48)$$

where Z_0 is the configuration integral with U_0, the potential function of the system.

As we know from statistical mechanics $\dfrac{e^{-\beta U_O}}{Z_O}$ 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 $\dfrac{e^{-\beta U_O}}{Z_O}$, or

$$\frac{Q}{Q_O} = \langle\, e^{-\beta(U-U_O)}\,\rangle_O \,. \tag{49}$$

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

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

and

$$f^{IV}(x) = \exp(x) \geq 0 \,.$$

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

$$\frac{Q}{Q_O} \geq \exp[\langle -\beta(U-U_O)\rangle_O] \tag{50}$$

and

$$\frac{Q}{Q_O} \geq \exp[\langle -\beta(U-U_O)\rangle]\{1 + \frac{1}{2!}\langle[\,-\beta(U-U_O) - \langle -\beta(U-U_O)\rangle\,]^2\rangle$$

$$+ \frac{1}{3!}\langle[\,-\beta(U-U_O) - \langle -\beta(U-U_O)\rangle\,]^3\rangle\}. \tag{51}$$

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

$$F = -kT\ln Q$$

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)

$$F \leq F_o + \langle U-U_o \rangle_o \tag{52}$$

and from inequality (51)

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

where

$$\nu = + \beta^2 \{\frac{1}{2!} \langle (U-U_o - \langle U-U_o \rangle)^2 \rangle_o - \frac{\beta}{3!} \langle (U-U_o - \langle U-U_o \rangle)^3 \rangle_o \} \tag{54}$$

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:

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

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

$$F = F_o + \omega_1 - \frac{\omega_2}{2!} (\frac{1}{kT}) + \frac{\omega_3}{3!} (\frac{1}{kT})^2 - \frac{\omega_4(\xi)}{4!} (\frac{1}{kT})^3 \tag{56}$$

where ξ is a definite value and

$$\omega_1 = \langle U-U_o \rangle_o ,$$

$$\omega_2 = \langle (U-U_o - \langle U-U_o \rangle_o)^2 \rangle_o ,$$

$$\omega_3 = \langle (U-U_o - \langle U-U_o \rangle_o)^3 \rangle_o ,$$

$$\omega_4(\xi) = \langle (\xi - \langle \xi \rangle_o)^4 \rangle_o .$$

Now since $- \frac{\omega_4(\xi)}{4!} (\frac{1}{kT})^3$ is always negative, we could write

$$F \leq F_o + \omega_1 - \frac{\omega_2}{2!} (\frac{1}{kT}) + \frac{\omega_3}{3!} (\frac{1}{kT})^2$$

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

$$F \leq F_o + \langle U-U_o \rangle - (kT)\nu \tag{57}$$

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:

$$F \leq F_o + \langle U-U_o \rangle_o , \tag{58}$$

and the second inequality:

$$F \leq F_o + \langle U-U_o \rangle_o - \beta \{ \frac{1}{2!} \langle (U-U_o - \langle U-U_o \rangle_o)^2 \rangle_o$$

$$+ \frac{\beta}{3!} \langle (U-U_o - \langle U-U_o \rangle_o)^3 \rangle_o \}. \tag{59}$$

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

$$U = \sum_{i>j=1}^{N} u_{ij}; \text{ and } U_o = \sum_{i>j=1}^{N} u^o_{ij} \tag{60}$$

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

$$F \leq F_o + \sum_{i>j=1}^{N} \langle u_{ij} - u^o_{ij} \rangle_o \tag{61}$$

and inequality (59) in the form of

$$F \leq F_o + \sum_{i>j=1}^{N} \langle u_{ij} - u^o_{ij} \rangle_o - \frac{\beta}{2!} \langle \{ \sum_{i>j=1}^{N} [(u_{ij}-u^o_{ij}) - \langle u_{ij} - u^o_{ij} \rangle_o]\}^2 \rangle_o \tag{62}$$

$$- \frac{\beta^2}{3!} \langle \{ \sum_{i>j=1}^{N} [(u_{ij} - u^o_{ij}) - \langle u_{ij} - u^o_{ij} \rangle_o]\}^3 \rangle_o.$$

For simplicity, let us define

$$X_{ij} = u_{ij} - u^o_{ij} - \langle u_{ij} - u^o_{ij} \rangle_o$$

Then,

$$\langle (\sum_{i>j=1}^{N} X_{ij})^2 \rangle_o = \sum_{ij}^{i \neq j} \langle X_{ij}^2 \rangle_o + 2 \sum_{ijk}^{i \neq j \neq k} \langle X_{ij} X_{jk} \rangle_o + \sum_{ijkl}^{i \neq j \neq k \neq l} \langle X_{ij} X_{kl} \rangle_o$$

(63)

In a similar way, an expansion could be produced for the coefficient of β^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:

$$\sum_{i>j=1}^{N} \langle u_{ij} - u_{ij}^o \rangle_o = \frac{N(N-1)}{2} \langle u_{12} - u_{12}^o \rangle_o$$

(64)

and

$$\langle (\sum_{i>j=1}^{N} X_{ij})^2 \rangle = \frac{1}{2} \frac{N!}{(N-2)!} \langle X_{12}^2 \rangle_o + \frac{N!}{(n-3)!} \langle X_{12} X_{23} \rangle_o$$

$$+ \frac{1}{4} \frac{N!}{(N-4)!} \langle X_{12} X_{34} \rangle_o .$$

(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 nth correlation function $g^{(n)}(\underline{r}_1, \ldots, \underline{r}_n)$

is defined as

$$g^{(n)}(\underline{r}_1 \cdots \underline{r}_n) = \frac{V^n \int \ldots \int e^{-\beta U} d\underline{r}_{n+1} \cdots d\underline{r}_n}{Z_o} \tag{66}$$

for $n = 2$, $g^{(2)}(\underline{r}_1, \underline{r}_2) = g^{(2)}(r_{12})$ is called the pair correla-

tion, or the radial distribution function. With this definition

of the correlation functions, relations (64) and (65) will be

as follows [65]:

$$\sum_{i>j=1}^{N} \langle u_{ij} - u_{ij}^o \rangle = \frac{N(N-1)}{2} \frac{1}{V^2} \iint_V (u_{12} - u_{12}^o) g_o^{(2)}(r_{12}) d\underline{r}_1 d\underline{r}_2 \tag{67}$$

and

$$\langle (\sum_{ij} X_{ij})^2 \rangle = \frac{1}{4V^4} \frac{N!}{(N-4)!} \iiiint_V g_o^{(4)} (\underline{r}_1 \cdots \underline{r}_4) \; X_{12} \; X_{34} d\underline{r}_1 \cdots d\underline{r}_4$$

$$+ \frac{1}{V^3} \frac{N!}{(N-3)!} \iiint_V g_o^{(3)} (\underline{r}_1 \cdot \underline{r}_2 \cdot \underline{r}_3) X_{12} \; X_{23} d\underline{r}_1 d\underline{r}_2 d\underline{r}_3$$

$$+ \frac{1}{2V^2} \frac{N!}{(N-2)!} \iint_V g_o^{(2)} (r_{12}) \; X_{12}^2 d\underline{r}_1 d\underline{r}_2 . \tag{68}$$

By a similar procedure as shown above, it is possible to find the relation between the coefficient of β^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:

$$F \leq F_o + \frac{N}{2} \rho \int_V (u_{12} - u_{12}^o) g_o^{(2)} (r_{12}) d\underline{r}_{12} \tag{69}$$

and the Second Inequality:

$$F \leq F_o + \frac{N}{2} \rho \int_V (u_{12} - u_{12}^o) g_o^{(2)} (r_{12}) d\underline{r}_{12} - \frac{\beta}{2} \langle (\sum_{ij} X_{ij})^2 \rangle_o - \frac{\beta^2}{6} \langle (\sum_{ij} X_{ij})^3 \rangle_o .$$

$$\tag{70}$$

In inequalities (69) and (70), $\frac{N}{V}$ is replaced by ρ, N-1 is approximated with N (which is a good approximation for $N \sim 0(10^{23})$), the

center of the coordinate is brought to the center of the parti-
cle number 1, and the integration over $d\underline{r}_2$ 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, $g^2(\underline{r}_1,\underline{r}_2)$,
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 β and β^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 formula-
tion 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 β
in inequality (70). In the present report, this formulation
is also extended for approximation of the coefficient of β^2 of
inequality (70).

According to Barker and Henderson [6], the partition func-
tion of a system can be expanded around the partition function

of a reference system in the following form

$$Q = Q_0 \exp(-\beta \sum_i \langle N_i \rangle u_1^i) \langle \exp[-\beta \sum_i (N_i - \langle N_i \rangle) u_1^i] \rangle \tag{71}$$

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 configu-

rations of the reference system", and $u_1^i = (u-u_0)^i$, is related

to the intermolecular distance R_i. Of course $\langle N_i \rangle$ is directly

related to the mean radial distribution function:

$$\langle N_i \rangle = 2\pi N \rho R_i^2 g_0(R_i) (R_{i+1} - R_i) \tag{72}$$

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

$$F = F_0 + \sum_i \langle N_i \rangle u_1^2 - \frac{1}{2}\beta \langle \sum_{ij} (N_i - \langle N_i \rangle)(N_j - \langle N_j \rangle) u_1^i u_1^j \rangle$$

$$+ \frac{1}{3!} \beta^2 \langle \sum_{ijk} (N_i - \langle N_i \rangle)(N_j - \langle N_j \rangle)(N_k - \langle N_k \rangle) u_1^i u_1^j j_1^k \rangle \tag{73}$$

$$+ 0(\beta^3).$$

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:

$$\langle N_i N_j \rangle - \langle N_i \rangle \langle N_j \rangle = 0 \qquad\qquad i \neq j,$$

$$\langle N_i N_j N_k \rangle - \langle N_i N_j \rangle \langle N_k \rangle = 0 \qquad\qquad k \neq i, j,$$

$$\langle N_i^2 N_j \rangle - \langle N_i^2 \rangle \langle N_j \rangle = 0 \qquad\qquad i \neq j,$$

and

$$\langle N_i \rangle^2 \langle N_j \rangle - \langle N_i N_j \rangle \langle N_i \rangle = 0 \qquad\qquad i \neq j. \qquad (74)$$

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

$$\langle (N_i - \langle N_i \rangle)^2 \rangle = \langle N_i \rangle \frac{1}{\beta} \frac{\partial \rho}{\partial P} \qquad (75)$$

and as is shown in the Appendix

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

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

$$F = F_0 + \frac{N}{2} \rho \int_V u_1(\underline{R}) \, g_0(\underline{R}) d\underline{R} - \frac{N}{4} \rho \beta \left[\frac{1}{\beta} \left(\frac{\partial \rho}{\partial P} \right) \right]_0 \int_V [u_1(\underline{R})]^2 g_0(\underline{R}) d\underline{R}$$

$$- \frac{N}{12} \rho \beta^2 \left[\frac{1}{\beta^2} \left\{ \left[\frac{\partial \rho}{\partial P} \right]_0^2 + \frac{\rho}{2} \frac{\partial}{\partial \rho} \left[\frac{\partial \rho}{\partial P} \right]_0^2 \right\} \right] \int_V [u_1(\underline{R})]^3 g_0(\underline{R}) d\underline{R}. \qquad (77)$$

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 β and β^2 in inequality (70) which otherwize would have been extremely difficult. Then, from (67), (68) and (77), we get

$$\left\langle \left(\sum_{ij} X_{ij} \right)^2 \right\rangle_0 \cong \frac{N}{2} \rho \left[\frac{1}{\beta} \frac{\partial \rho}{\partial P} \right]_0 \int_V [u_1(\underline{R})]^2 g_0(\underline{R}) d\underline{R} \qquad (78)$$

and

$$\left\langle \left(\sum_{ij} X_{ij} \right)^3 \right\rangle_0 \cong \frac{N}{2} \frac{\rho}{\beta^2} \left[\left[\frac{\partial \rho}{\partial P} \right]_0^2 + \frac{\rho}{2} \frac{\partial}{\partial \rho} \left[\frac{\partial \rho}{\partial P} \right]_0^2 \right] \int_V [u_1(\underline{R})]^3 g_0(\underline{R}) d\underline{R}. \qquad (79)$$

In the above relations, $\frac{1}{\beta}\left[\frac{\partial\rho}{\partial P}\right]_O$ 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

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

(80)

and

$$U_O = \sum_{i>j=1}^{N} u^O_{ij} + \sum_{i>j>k=1}^{N} w^O_{ijk}.$$

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*

$$F \le F_O + \sum_{i>j=1}^{N} \langle u_{ij} - u^O_{ij} \rangle_O + \sum_{i>j>k=1}^{N} \langle w_{ijk} - w^O_{ijk} \rangle_O$$

(81)

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

$$F \le F_O + \frac{N(N-1)}{2V^2} \iint\limits_V (u_{12} - u^O_{12}) g_O^{(2)}(r_{12}) d\underline{r}_1 d\underline{r}_2$$

(82)

$$+ \frac{N(N-1)(N-2)}{6V^3} \iiint\limits_V (w_{123} - w^O_{123}) g_O^{(3)}(\underline{r}_1, \underline{r}_2, \underline{r}_3) d\underline{r}_1 d\underline{r}_2 d\underline{r}_3.$$

---

*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 $N \sim 0(10^{23})$, the relation (82) becomes

$$F \leq F_o + \frac{N}{2} \rho \int_V (u_{12} - u^o_{12}) g^{(2)}_o (r_{12}) d\underline{r}_{12}$$

$$+ \frac{N}{6} \rho^2 \iint_V (w_{123} - w^o_{123}) g^{(3)}_o (\underline{r}_1, \underline{r}_2, \underline{r}_3) d\underline{r}_{12} d\underline{r}_{13} \qquad (83)$$

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

$u_{12}^0 \rightarrow u_{12}$, the inequality goes closer and closer to equality. 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.

$$u(r) = 4\epsilon [(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^{6}].$$ (84)

where ϵ is the depth of the minimum in the potential curve and σ 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 inter-
molecular potential function should be chosen such that the
analytic forms of Helmholtz free energy, and the radial distri-
bution function of the reference system can be calculated ana-
lytically 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

$$u^o(r) = \begin{cases} 0 & \text{for } r > d \\ \\ \infty & \text{for } r \leq d \end{cases} \tag{85}$$

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 $u^{\circ}(r)$ as defined by (84) and (85) and the fact that $d\underline{r}_{12} = 4\pi r_{12}^2 dr_{12}$, inequality (69) becomes

$$\frac{F}{NkT} \leq \frac{F_o}{NkT} + 2\pi\rho\beta \int_d^\infty 4\epsilon[(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^6]g_o(r)r^2 dr \qquad (86)$$

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

$$\frac{F}{NkT} \leq \frac{F_o}{NkT} + \frac{8\pi\rho d^3}{T^*} \int_1^\infty [(\frac{1}{xc})^{12} - (\frac{1}{xc})^6]g_o(x)x^2 dx \qquad (87)$$

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, $g_o(x)$, satisfying the Percus-Yevick integral equation

$$G(s) = \int_1^\infty e^{-sx}g_o(x)x\,dx. \qquad (88)$$

Let us consider $U_1(s)$ as the inverse Laplace transform of $xu*(x)$ where

$$xu*(x) = x \ [(\frac{1}{xc})^{12} - (\frac{1}{xc})^6] \tag{89}$$

Then

$$xu*(x) = \int_0^\infty e^{-sx} U_1(s) ds. \tag{90}$$

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

$$\int_1^\infty xu*(x) g_0(x) x dx = \int_0^\infty U_1(s) ds \int_1^\infty e^{-sx} g_0(x) x dx = \int_0^\infty U_1(s) G(s) ds. \tag{91}$$

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

$$U_1(s) = L^{-1}[xu*(x)] = (\frac{1}{c})^{12} \cdot \frac{s^{10}}{10!} - (\frac{1}{c})^6 \cdot \frac{s^4}{4!}, \tag{92}$$

and from reference [60]

$$G(s) = \frac{L(s)}{12\eta[L(s) + S(s)e^s]} \tag{93}$$

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

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

$$\eta = \frac{\pi}{6} \rho d^3 = \frac{\pi}{6} (\rho\sigma^3)c^3. \tag{94}$$

Finally, the first inequality as was shown by (87) can be written in the following form

$$\frac{F}{NkT} \leq \frac{F_o}{NkT} + \frac{48\eta}{T*} \int_o^\infty U_1(s)G(s)ds, \tag{95}$$

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

In a similar manner, the second inequality, (70) can be refomulated 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

$$\frac{F}{NkT} \leq \frac{F_o}{NkT} + \frac{48\eta}{T*} \int_o^\infty U_1(s)G(s)ds$$

$$- \frac{96\eta}{T*^2} \left[\frac{1}{\beta} \left[\frac{\partial \rho}{\partial P}\right]_o\right] \int_o^\infty U_2(s)G(s)ds \tag{96}$$

$$+ \frac{128\eta}{T*^3} \cdot \frac{1}{\beta^2} \left[- \left[\frac{\partial \rho}{\partial P}\right]_o^2 - \frac{\rho}{2} \cdot \frac{\partial}{\partial \rho}\left[\frac{\partial \rho}{\partial P}\right]_o^2 \right] \int_o^\infty U_3(s)G(s)ds,$$

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

$$U_2(s) = (\frac{1}{c})^{24} \frac{s^{22}}{22!} - 2(\frac{1}{c})^{18} \frac{s^{16}}{16!} + (\frac{1}{c})^{12} \frac{s^{10}}{10!}, \tag{97}$$

and

$$U_3(s) = (\frac{1}{c})^{36} \frac{s^{34}}{34!} - 3(\frac{1}{c})^{30} \frac{s^{28}}{28!} + 3(\frac{1}{c})^{24} \frac{s^{22}}{22!} - (\frac{1}{c})^{18} \frac{s^{16}}{16!}.$$

$$\tag{98}$$

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

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

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

$$\frac{F}{NkT} = \int \frac{1}{\rho} \frac{PV}{NkT} d\rho .$$

For a system obeying the ideal gas law, we have

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

Consequently,

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

Then by having the compressibility of a system in hand, we can calculate $\frac{F-F^{id}}{NkT}$ for that system. For the hard-sphere reference system in mind, there are several relations available for compressibility. The Pade 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

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

$$\left[\frac{PV}{NkT}\right]_O = \frac{1 + \eta + \eta^2}{(1-\eta)^3}.$$ (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.

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

Figure 1 shows Equation (101) along with the machine-caculated
points. As is evident, Equation (101) is in good fit with
machine-calculated data and has the advantage over Padé approxi-
mant that its terms are in simple and rational forms. Insertion
of Equation (101) in (100) and performing the integration, pro-
duces the following relation

$$\frac{F_O - F^{id}}{NkT} = \ln(1-\eta)^{\frac{1}{2}} + \frac{3}{(1-\eta)} + \frac{3}{4(1-\eta)^2} - \frac{15}{4}, \qquad (102)$$

where

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

Also, one can show that

$$\frac{1}{\beta}\left[\frac{\partial\rho}{\partial P}\right]_O = \frac{(1-\eta)^4}{(1+2\eta)^2 - 1.5\eta^3(4-\eta)}, \qquad (103)$$

and

$$-\frac{1}{\beta^2}\left[\left[\frac{\partial\rho}{\partial P}\right]_O^2 + \frac{\rho}{2}\frac{\partial}{\partial\rho}\left[\frac{\partial\rho}{\partial P}\right]_O^2\right] = \frac{(1-\eta)^7(1.5\eta^5 - 7.5\eta^4 + 20\eta^2 + 5\eta-1)}{[(1+2\eta)^2 - 1.5\eta^3(4-\eta)]^3}. \qquad (104)$$

Compressibility coefficient of the hard-sphere reference system,

$\frac{1}{\beta}\left[\frac{\partial\rho}{\partial P}\right]_O$, 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 ρ, 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)

$$F*(\rho*, T*) \leq F_0^*(\rho*, T*, c) + \frac{\Gamma_1(\rho*, c)}{T*} \qquad (105)$$

and for the second inequality (96)

$$F*(\rho*, T*) \leq F_0^*(\rho*, T*, c) + \frac{\Gamma_1(\rho*, c)}{T*} + \frac{\Gamma_2(\rho*, c)}{T*^2}$$

$$+ \frac{\Gamma_3(\rho*, c)}{T*^3}, \qquad (106)$$

where Γ_1, Γ_2, and Γ_3 are the coefficients of the inverse 1st, 2nd, and the 3rd 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.

$$\frac{\partial F_o^*}{\partial c} + \frac{1}{T^*} \frac{\partial \Gamma_1}{\partial c} = 0;$$

(107)

$$\frac{\partial^2 F_o^*}{\partial c^2} + \frac{1}{T^*} \frac{\partial^2 \Gamma_1}{\partial c^2} \geq 0,$$

and

$$\frac{\partial F_o^*}{\partial c} + \frac{1}{T^*} \frac{\partial \Gamma_1}{\partial c} + \frac{1}{T^{*2}} \frac{\partial \Gamma_2}{\partial c} + \frac{1}{T^{*3}} \frac{\partial \Gamma_3}{\partial c} = 0;$$

(108)

$$\frac{\partial^2 F_o}{\partial c^2} + \frac{1}{T^*} \frac{\partial^2 \Gamma_1}{\partial c^2} + \frac{1}{T^{*2}} \frac{\partial^2 \Gamma_2}{\partial c^2} + \frac{1}{T^{*3}} \frac{\partial^2 \Gamma_3}{\partial c^2} \geq 0.$$

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

$$F^*(\rho^*, T^*) \cong F_o^*(\rho^*, T^*, c_{m1}) + \frac{\Gamma_1(\rho^*, c_{m1})}{T^*},$$

(109)

and

$$F^*(\rho^*, T^*) \cong F_o^*(\rho^*, T^*, c_{m2}) + \frac{\Gamma_1(\rho^*, c_{m2})}{T^*} + \frac{\Gamma_2(\rho^*, c_{m2})}{T^{*2}}$$

$$+ \frac{\Gamma_3(\rho^*, c_{m2})}{T^{*3}},$$

(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 F_O/NkT 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 ρ^*. From the value of c^3 calculated by the variational calculation, it is possible to calculate $F_o^*(\rho^*, T^*, c_{ml})$ and $\Gamma_1(\rho^*, c_{ml})$ as given in Equation (109) for every temperature T^* and density ρ^*. 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

$$F^*(\rho^*, T^*) \simeq F_o^*(\rho^*, T^*, c_{ml}) + \frac{\Gamma_1(\rho^*, c_{ml})}{T^*} + \frac{\Gamma_2(\rho^*, c_{ml})}{T^{*2}} \qquad (111)$$

and also

$$F^*(\rho^*, T^*) \cong F_o^*(\rho^*, T^*, c_{ml}) + \frac{\Gamma_1(\rho^*, c_{ml})}{T^*} + \frac{\Gamma_2(\rho^*, c_{ml})}{T^{*2}}$$

$$+ \frac{\Gamma_3(\rho^*, c_{ml})}{T^{*3}} \tag{112}$$

where c_{ml} in Equations (111) and (112) are the result of the variational calculation on the inequality (105). If the terms Γ_2, and Γ_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 Γ_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 Γ_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 zero[th] and the first order terms as shown by (109), while for Figure 4 the contribution of the second order term, Γ_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

$$U_i = kT^2 \left[\frac{\partial \ln Q}{\partial T} \right]_{N,V} \tag{113}$$

and

$$S_i = k\ln Q + kT \left[\frac{\partial \ln Q}{\partial T} \right]_{N,V} \tag{114}$$

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

$$U_i = F + TS_i \tag{115}$$

and

$$S_i = - \left(\frac{\partial F}{\partial T} \right)_{N,V} \tag{116}$$

Of course, (115) and (116) are derived originally from classi-
cal 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. Γ_2 and Γ_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 ρ_ℓ and ρ_v the densities of the coexisting liquid and vapor

$$\begin{cases} (F + PV)_\ell = (F + PV)_v \\ \\ P_\ell = P_v \end{cases} \tag{117}$$

where ℓ 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 calcu-

lations are shown.

TABLE I

Critical Constants for 12:6 Potential

	Present Calculations	Barker and Henderson [7]	Verlet [58]	Experimental (Argon) [46]
T^*_c	1.36	1.35	1.32-1.36	1.26
ρ^*_c	0.325	0.30	0.32-0.36	0.316
P^*_c	0.165	0.14	0.13-0.17	0.117
$P_c V_c / N k T_c$	0.37	0.34	0.30-0.36	0.293

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 $\epsilon/k = 119.8^{\circ}K$, $\sigma = 3.405$ Å 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 ϵ and σ 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 tempera-

tures, because coefficients of $T*^{-2}$, $T*^{-3}$, ... at high tempera-

tures are negligibly small, and they do not contribute to the

variational results. Consequently, only the contribution of

the zeroth and the first terms are of importance; which means

they are using actually the inequality (105). At low tempera-

tures, 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 ine-

quality 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 transi-

tion 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

$$g_o(\underline{r}_1 - \underline{r}_2) \equiv g_o(|\underline{r}_1 - \underline{r}_2|) \tag{118}$$

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:

$$\frac{Q}{Q_0} \geq \exp[\langle -\beta(U-U_0)\rangle_0]$$ (119)

and by introducing Helmholtz free energies, we get

$$F \leq F_0 + \langle U-U_0\rangle_0$$ (120)

where Q_0, F_0, and U_0 are partition functions, Helmholtz free
energy and total potential energy of a reference system while
Q, F, and 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 $g(\underline{r}) = g(|\underline{r}|)$ 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

$$U = U_o' + \sum_i \Psi_i(\underline{r}_i) \tag{121}$$

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

$$U_o = U_o' + \sum_i \Psi(0) \tag{122}$$

so that (121) becomes

$$U = U_o + \sum_i [\Psi(\underline{r}_i) - \Psi(0)] \tag{123}$$

It is clear from (123) that $[\Psi(\underline{r}_i) - \Psi(0)]$ is the change of potential energy when the molecule i moves from its cell center

to the point $\underline{r}_i$, with all other molecules remaining at their cell centers.

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

$$Q(N,V,T) = \frac{1}{N!} \Sigma' \exp(-U_0/kT) v_f^N = \exp(-U_0'/kT) v_f^N. \qquad (124)$$

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

$$v_f = \int_\Delta \exp\{-[\Psi(\underline{r}_i) - \Psi(0)]/kT\} d\underline{r}_i \qquad (125)$$

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 $[\Psi(\underline{r}) - \Psi(0)]$. If the potential energy function $u(r)$ 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 sym-

metrical 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 neighbor-

ing molecules as "smeared" with uniform probability distribu-

tion over the surfaces of concentric spheres of appropriate

radius. This smearing approximation is quite accurate, parti-

cularly at high densities.

In calculating the free volume using smearing approxima-

tion, 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 criti-

cal density [59]), the integrand in relation (125) is effec-

tively 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 $0.5a_0$

is negligible. With the latter value of the cell radius, the

free volume will be given by

$$v_f = 4\pi a_o^3 G = 4\sqrt{2\pi} \ (V/N) G$$

$$G = \int_0^{0.5} x^2 \exp\{-[\Psi(\underline{r}) - \Psi(0)]/kT\}dx \qquad (126)$$

Because for face-centered cubic crystal structure

$$a_o = (\sqrt{2} \ N/V)^{1/3} \qquad (127)$$

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

$$W(\underline{r}) = \Psi(\underline{r}) - \Psi(0) \qquad (128)$$

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

$$\langle \Psi(\underline{r}) \rangle_\Delta = \langle W(\underline{r}) \rangle_\Delta + \frac{U_o}{N}, \qquad (129)$$

where $\dfrac{U_o}{N} = \Psi(0)$ and the averages are over cells such that

$$\langle \chi \rangle_\Delta = \int_\Delta \chi \ P(\underline{r}) \, d\underline{r} \qquad (130)$$

and

$$P(\underline{r}) \, d\underline{r} = \exp[-W(r)/kT]d\underline{r} / \int_\Delta \exp[-W(r)/kT]d\underline{r} \qquad (131)$$

where χ could be any variable in the cell, and $P(\underline{r}) \, d\underline{r}$ is the probability that a given molecule is at a distance between $\underline{r}$ and $\underline{r} + d\underline{r}$ 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

$$g(r) = \frac{1}{16\pi} \sum_i \frac{N_i}{Z_i r} \int_0^\infty dy \int_{|y-a_i|}^{\frac{1}{2}a_o} \frac{P(R')dR'}{R'} \int_{|y-r|}^{\frac{1}{2}a_o} \frac{P(R)dR}{R} \tag{132}$$

where N_i is the number of the ith neighbors and Z_i is the distance of the ith 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

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

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

$$G = \int_0^{\infty} x^2 \exp(-Ax^2)\, dx = \frac{\sqrt{\pi}}{4} A^{-3/2} \qquad (134)$$

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

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

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

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

$$= \int_o^{0.5} x^4 e^{-Ax^2}(AkT)\, dx / \int_0^{0.5} x^2 e^{-Ax^2}\, dx. \qquad (136)$$

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

$$\langle W(r) \rangle_\Delta = \int_0^{\infty} x^4 e^{-Ax^2}(AkT)\, dx / \int_0^{\infty} x^2 e^{-Ax^2}\, dx = \frac{3}{2} kT. \qquad (137)$$

Then from relations (137) and (129) we get for the average value

of the potential energy of each atom the following relation

$$\langle \Psi(r) \rangle_{\Delta} = \frac{3}{2} kT + \frac{U_o}{N} , \tag{138}$$

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 realtion (132) takes the following form

$$g(r) = \frac{\sqrt{A'}}{4\sqrt{2\pi}^{3/2} \rho a_o} \sum_i \frac{N_i}{Z_i} \cdot \frac{1}{r} \exp\left[- \frac{A}{2} \left[\frac{z_i - r}{a_o} \right]^2 \right] \tag{139}$$

with the following constraint for the contribution of each shell

of neighbors

$$z_i - a_o < r < z_i + a_o \tag{140}$$

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:

$$U = \sum_{i>j=1}^{N} u(r_{ij}) , \tag{141}$$

and the reference system following the cell model as expressed

above the total potential of the reference system is:

$$U_o = \sum_{i=1}^{N} \Psi\ (\underline{r}_i) . \tag{142}$$

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

$$F \leq F_o + 2\pi N\rho \int_o^{\infty} u(r) g_o(r) r^2 dr - N \langle \Psi(\underline{r}) \rangle_\Delta . \tag{143}$$

By replacing F_o in inequality (143) with F as given by (135), replacing $g_o(r)$ by $g(r)$ as given by (139) and considering the constraint (140), and by replacing $\langle \Psi(\underline{r}) \rangle_\Delta$ by its value as given by (138), the inequality (143) takes the following form

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

$$+ 2\pi N\rho \frac{A^{1/2}}{4\sqrt{2}^7 \pi^{3/2}\rho a_o} \sum_i \frac{N_i}{Z_i} \int_{\alpha_i}^{\beta_i} 4\epsilon[(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^6]r \ \cdot$$

$$\exp\left[-\frac{A}{2}\left[\frac{Z_i - r}{a_o}\right]^2 \right], \tag{144}$$

where

$$\alpha_i \ \rangle \ Z_i - a_o$$

and

$$\beta_i \ \langle \ Z_i + a_o$$

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

$$a_0 = (\sqrt{2}/\rho)^{1/3}$$

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

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

$$x = r/\sigma \tag{145}$$

$$Z_i^* = Z_i/a_0$$

and the dimensionless temperature

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

then inequality (144) takes the following form

$$\frac{F}{NkT} \leq \ln(\rho A^{3/2}) + \frac{1}{T^* \cdot a_0^{*2}} \left[\frac{2A}{\pi}\right]^{1/2} \sum_i \frac{N_i}{Z_i^*} \int_{\alpha_i^*}^{\beta_i^*} \left[\frac{1}{x^{12}} - \frac{1}{x^6}\right] \cdot$$

$$x \exp\left[-\frac{A}{2}(Z_i^* - x/a_0^*)^2\right] dx - \frac{3}{2} - \frac{1}{2}\ln(2\pi^3). \tag{146}$$

where

$$\alpha_i^* \langle (Z_i^* - 1)a_0^*, \tag{147}$$

and

$$\beta_i^* \rangle (Z_i^* + 1)a_0^*.$$

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 $i = 1 \to \infty$, 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,

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

we have

$$u(r) > 0 \text{ for } (r < \sigma)$$

$$u(r) > 0 \text{ for } (r > \sigma) \tag{148}$$

With the fact that $g_0(r)$, the radial distribution function, is
always positive or zero, the inequality (143) could be written
as

$$F \leq F_0 + 2\pi N\rho \int_0^\theta u(r)g_0(r)r^2dr - N \langle \Psi(\underline{r}) \rangle_\Delta \tag{149}$$

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

$$\alpha_i^* > 1,$$

or it is enough to have

$$(Z_i^* - 1) (\sqrt{2}/\rho*)^{1/2} \geq 1 \qquad (150)$$

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

$$\sqrt{i} - 1 \geq 1 \qquad \text{or} \qquad i \geq 4.$$

Then we can disregard the 4th, 5th, 6th, $\ldots$ 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

$$F/NkT \leq \ln(\rho A^{3/2}) + \frac{1}{T^* a_o^{*2}} \left[\frac{2A}{\pi}\right]^{1/2} \sum_{i=1}^{3} \frac{N_i}{Z_i^*} \int_{\alpha_i^*}^{\beta_i^*} \left[\frac{1}{x^{12}} - \frac{1}{x^6}\right] \cdot$$

$$x \exp\left[-\frac{A}{2}(Z_i^* - x/a_o^*)^2\right] dx - \frac{3}{2} - \frac{1}{2}\ln(2\pi^3), \qquad (151)$$

with

$$\alpha^*_i \, \langle \, (z^*_i - 1) a^*_o \; ; \qquad \beta^*_i \, \rangle \, (z^*_i + 1) a^*_o. \tag{152}$$

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 α_i^* and β_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 ρ^* 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 co-existing phase densities of the two liquid and solid phases versus temperature. There are two ways to calculate the co-existing 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

$$
\begin{cases}
(F + PV)_\ell = (F + PV)_s \\
\\
P_\ell = P_s
\end{cases}
\tag{153}
$$

for ρ_ℓ^* and ρ_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_{ℓ} 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 quanta-
tively 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 sys-
tem would be expected to yield better predictions of the thermo-
dynamic 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

$$F \leq F_O + \langle U_1 \rangle_O, \tag{154}$$

where F is the free energy of the crystal, F_O is the free energy corresponding to the energy U_O, and $\langle U_1 \rangle_O$ is the value of the energy $U_1 = U - U_O$ averaged over U_O. Bazarov [12] does not give any explanation for the mathematical significance or the physical meaning of F_O and U_O. 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:

$$F - F_o \leq \langle U-U_o \rangle_o \tag{155}$$

where F and F_o are the Helmholtz free energies of the original and reference systems respectively. U and U_o are the total potential energies of the two systems. The angled brackets mean the expectation over the reference system

$$\langle X \rangle_o = \int \ldots \int_V \frac{e^{-\beta U_o}}{Q_o} X \, d\underline{r}_1 \ldots d\underline{r}_N \tag{156}$$

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

$$U = \sum_{i>j=1}^{N_1} u_{11}(ij) + \sum_{i>j=N_1+1}^{N} u_{22}(ij) + \sum_{i=1}^{N_1} \sum_{j=N_1+1}^{N} u_{12}(ij)$$

$$\tag{157}$$

and

$$U_o = \sum_{i>j=1}^{N_1} u_{11}^o(ij) + \sum_{i>j=N_1+1}^{N} u_{22}^o(ij) + \sum_{i=1}^{N_1} \sum_{j=N_1+1}^{N} u_{12}^o(ij),$$

(158)

where

$$x_1 = \frac{N_1}{N}, \text{ and } \quad x_2 = \frac{N-N_1}{N} = \frac{N_2}{N}.$$

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

$$F \leq F_o = \int_{\Gamma} \left[\frac{N_1(N_1-1)}{2} u_{11}^1(r_{ij}) + \frac{N_2(N_2-1)}{2} u_{22}^1(r_{ij}) + N_1N_2u_{12}^1(r_{ij}) \right]$$

$$\frac{e^{-\beta U_o}}{Q_o} d\Gamma$$

(159)

where

$$d\Gamma = dr_1^1 \ldots dr_{N_1}^1 dr_1^2 \ldots dr_{N_2}^2 , \text{ and } u_{d\beta}^1(ij) = u_{\alpha\beta}(ij) - u_{\alpha\beta}^o(ij).$$

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]

$$g_{11}(|r_1^1 - r_2^1|) = v^2 \int \frac{e^{-\beta U}}{Q} d\underline{r}_3^1 \ldots d\underline{r}_{N_1}^1 d\underline{r}_1^2 \ldots d\underline{r}_{N_2}^2,$$

$$g_{22}(|\underline{r}_1^2 - \underline{r}_2^2|) = v^2 \int \frac{e^{-\beta U}}{Q} \, d\underline{r}_1^1 \ldots d\underline{r}_{N_1}^1 d\underline{r}_3^2 \ldots d\underline{r}_{N_2}^2, \tag{160}$$

and

$$g_{12}(|\underline{r}_1^1 - \underline{r}_1^2|) = v^2 \int \frac{e^{-\beta U}}{Q} \, d\underline{r}_2^1 \ldots d\underline{r}_{N_1}^1 d\underline{r}_2^2 \ldots d\underline{r}_{N_2}^2 = g_{21}(|\underline{r}_1^1 - \underline{r}_1^2|).$$

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

$$\frac{F}{NkT} \leq \frac{F_o}{NkT} = \frac{\beta N}{v^2} \iint_V \left[\frac{x_1^2}{2} u_{11}^1(r_{12}) g_{11}^o(r_{12}) + \frac{x_2^2}{2} u_{22}^1(r_{12}) g_{22}^o(r_{12}) \right.$$

$$\left. + x_1 x_2 u_{12}^1(r_{12}) g_{12}^o(r_{12}) \right] d\underline{r}_1 d\underline{r}_2 \tag{161}$$

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

$$u_{11}^o = \begin{bmatrix} 0 \text{ for } r > d_{11} \\ \infty \text{ for } r \leq d_{11} \end{bmatrix}, \quad u_{22}^o = \begin{bmatrix} 0 \text{ for } r > d_{22} \\ \infty \text{ for } r \leq d_{22} \end{bmatrix}$$

and $\tag{162}$

$$u_{12}^o = \begin{bmatrix} 0 \text{ for } r > d_{12} \\ \infty \text{ for } r \leq d_{12} \end{bmatrix},$$

where $d_{12} = \dfrac{d_1 + d_2}{2}$, the above inequality takes the following form:

$$\frac{F}{NkT} \leq \frac{F_O}{NkT} + 4\pi\beta\rho\left[\frac{x_1^2}{2} \int_{d_{11}}^{\infty} u_{11}(r)g_{11}^O(r)r^2 dr + \frac{x_2^2}{2} \int_{d_{22}}^{\infty} u_{22}(r)g_{22}^O(r)r^2 dr \right.$$

$$\left. + x_1 x_2 \int_{d_{12}}^{\infty} u_{12}(r)g_{12}^O(r)r^2 dr \right] . \tag{163}$$

In deriving inequality (163) from inequality (161), the center of coordinates is transferred to the center of particle 1, and the integration over $d\underline{r}_1$ is performed, which gives V, while $d\underline{r}_{12} = 4\pi r_{12}^2 dr_{12}$, and the dummy indices 12 are dropped. By considering Lennard-Jones 12:6 potential energy function

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

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

$$\frac{F}{NkT} \leq \frac{F_O}{NkT} + 16\pi\beta\rho\left[\frac{d_{11}^3\epsilon_{11}}{2} x_1^2 \int_1^{\infty} u_{11}^*(t)g_{11}^O(t)t^2 dt \right.$$

$$+ \frac{d_{22}^3\epsilon_{22}}{2} x_2^2 \int_1^{\infty} u_{22}^*(t)g_{22}^O(t)t^2 dt + d_{12}^3\epsilon_{12}x_1 x_2 \int_1^{\infty}$$

$$\left. u_{12}^*(t)g_{12}^O(t)t^2 dt \right] , \tag{165}$$

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

and $c_{ij} = d_{ij}/\sigma_{ij} . \tag{167}$

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 avilable as follows: :

$$G_{ij}(s) = 12(\gamma_i\gamma_j)^{\frac{1}{2}} \int_{d_{ij}}^{\infty} e^{-sr} rg_{ij}(r)dr = G_{ji}(s) \qquad (168)$$

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

and $$G_{11}(s) = s[h-L_2(s)e^{sd_{22}}]/D(s), \qquad (169)$$

$$G_{22}(s) = s[h-L_1(s)e^{sd_{11}}]/D(s), \qquad (170)$$

$$G_{12}(s) = G_{21}(s) = 12(\gamma_1\gamma_2)^{\frac{1}{2}} s^2 e^{sd_{12}}\{[\frac{3}{4}(\gamma_2 d_{22}^3 - \gamma_1 d_{11}^3)(d_{22} - d_{11})$$

$$-d_{12}(1+ \frac{1}{2}\xi)]s - (1+2\xi)\}/D(s) \qquad (171)$$

where

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

and

$$h = 36\gamma_1\gamma_2(d_{22} - d_{11})^2,$$

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

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

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

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

$$-(1-\xi)^2 s^4,$$

and

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

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

$$\varphi_{ij}(s) = \int_1^\infty e^{-st} tg_{ij}(t)dt \tag{172}$$

and

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

or

$$tu_{ij}^*(t) = \int_0^\infty e^{-st} U_{ij}(s)ds.$$

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

$$\frac{F}{NkT} \le \frac{F_0}{NkT} + 16\pi\beta\rho\left[\frac{d_{11}^3 \epsilon_{11}}{2} x_1 \int_0^\infty U_{11}(s)\varphi_{11}(s)ds\right.$$

$$+ \frac{d_{22}^3 \epsilon_{22}}{2} x_2 \int_0^\infty U_{22}(s)\varphi_{22}(s)\,ds + d_{12}^3 \epsilon_{12} x_1 x_2 \int_0^\infty U_{12}(s)\varphi_{12}(s)\,ds \Bigg]$$

$$(173)$$

where from Laplace transform tables

$$U_{ij}(s) = \left[\frac{1}{c_{ij}}\right]^{12} \frac{s^{10}}{10!} - \left[\frac{1}{c_{ij}}\right]^6 \frac{s^4}{4!}. \qquad (174)$$

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

$$\varphi_{ii}(s) = \frac{1}{d_{ii}^2}\, \frac{G_{ii}(s/d_{ii})}{(12\eta_i)} \quad \text{for } i = 1,2 \text{ and,}$$

$$\varphi_{ij}(s) = \frac{1}{d_{ij}^2}\, \frac{G_{ij}(s/d_{ij})}{(\eta_i \eta_j)^{\frac{1}{2}}} \quad \text{for } i \neq j. \qquad (175)$$

Relations in Dimensionless Forms

Let us define

$$\alpha = \sigma_{11}/\sigma_{22},$$

$$\tau = \epsilon_{11}/\epsilon_{22},$$

$$\mu_1 = d_{11}/d_{22},$$

$$(176)$$

$$\mu_2 = d_{11}/d_{12},$$

$$\eta_{ii} = \frac{\pi}{6}\rho x_i d_{ii}^3; \quad \eta_{ij} = \frac{\pi}{3}\rho x_i x_j \;(i \neq j); \quad T_1^* = kT/\epsilon_{11}.$$

Then inequality (173) can be written in the following dimension-less form:

$$\frac{F}{NkT} \le \frac{F_o}{NkT} + \frac{48}{T_1^*} \; [x_1\eta_{11} \int_0^\infty U_{11}\varphi_{11}ds + \frac{x_2}{\tau} \eta_{22} \int_0^\infty U_{22}\varphi_{22}ds$$

$$+ \; \frac{\epsilon_{12}}{\epsilon_{11}} \; \eta_{12} \int_0^\infty U_{12}\varphi_{12}ds], \tag{177}$$

where U_{ij} is given in dimensionless form by relation (174).
Also, φ_{ij}'s could be given in dimensionless forms as follows:

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

$$\varphi_{22}(s) = \frac{S}{12\eta_{22}D^*(\mu_1 s)} \; [H - L_1^*(\,_1s)e^{\mu_1 s}] \tag{178}$$

$$\varphi_{12}(s) = \frac{s^2 e^s \mu_2^4}{D^*(\mu_2 s)} \; \{[\tfrac{3}{4}(\eta_{22} - \eta_{11}) (\tfrac{1}{\mu_1} - 1)\mu_2 - (1 + \tfrac{1}{2}\,\xi)] \; s$$

$$- (1 + 2\xi)\} \; = \varphi_{21}(s)$$

where

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

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

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

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

and

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

$$\xi = \eta_{11} + \eta_{22},$$

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

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

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

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

and

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

Since $d_{12} = \dfrac{d_{11}+d_{22}}{2}$

then,

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

In the present formulation for binary mixture, the following approximations for the collision terms ϵ_{12} and σ_{12} will be used:

$$\epsilon_{12} = (\epsilon_{11}\epsilon_{22})^{\frac{1}{2}} \qquad (179)$$

and

$$\sigma_{12} = (\sigma_{11} + \sigma_{22})/2$$

then

$$\epsilon_{12}/\epsilon_{11} = (1/\tau)^{\frac{1}{2}}.$$

We had also

$$c_{ij} = d_{ij}/\sigma_{ij}$$

and from the definition for α

$$c_{12} = \frac{\alpha c_{11} + c_{22}}{\alpha + 1} \tag{180}$$

Introduction of φ_{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

$$\frac{F-F^{id}}{NkT} = \int_0^\rho \frac{1}{\rho} \left[\frac{PV}{NkT} - 1\right] d\rho \tag{181}$$

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.

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

and

$$(\gamma_1 d_{11}^2 + \gamma_2 d_{22}^2]\}(1-\xi)^{-3} \tag{182}$$

$$\frac{P^V}{kT} = \frac{P}{KT} - \frac{18}{\pi} \frac{\xi}{(1-\xi)^3} (\gamma_1 d_{11}^2 + \gamma_2 d_{22}^2)^3 \tag{183}$$

where γ_i's and ξ 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 ξ. 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.

$$\frac{P^{av}V}{NkT} = \frac{PV}{NkT} - \frac{9}{\pi} \frac{\xi/\rho}{(1-\xi)^3} (\gamma_1 d_{11}^2 + \gamma_2 d_{22}^2)^3. \tag{184}$$

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

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

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

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 Paramets

Inequality (177) could be written in the following form

$$F*(\rho^*, T_1^*, x_1) \leq F_0^*(\rho^*, T_1^*, x_1; c_{11}, c_{22}) + \Gamma_1^*(\rho^*, x_1; c_{11}, c_{22})/T*$$

(186)

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 ρ^*, 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

$$\frac{\partial F_0^*}{\partial c_{11}} + \frac{\partial \Gamma_1^*}{\partial c_{11}} \frac{1}{T_1^*} = 0$$

$$\frac{\partial F_0^*}{\partial c_{22}} + \frac{\partial \Gamma_1^*}{\partial c_{22}} \frac{1}{T_1^*} = 0$$

(187)

with the conditions that

$$\frac{\partial^2 F_0^*}{\partial^2 c_{11}} + \frac{\partial^2 \Gamma_1^*}{\partial^2 c_{11}} \frac{1}{T_1^*} \geq 0$$

(188)

$$\frac{\partial^2 F_o^*}{\partial^2 c_{22}} + \frac{\partial^2 \Gamma_1^*}{\partial^2 c_{22}} \frac{1}{T_1^*} \geq 0 \qquad\qquad (188)$$

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 <u>first inequality</u> 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 ϵ_{12} and σ_{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 ϵ_{12} and σ_{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 a priorie definition of the interaction parameters in molecular dynamic and Monte Carlo calculations.

TABLES

TABLE II

COMPRESSIBILITIES OF LENNARD-JONES
FLUID FOR DIFFERENT ISOTHERMS

$(\frac{PV}{NkT})_{01}$, $(\frac{PV}{NkT})_{012}$, $(\frac{PV}{NkT})_{0123}$ 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 $(\frac{PV}{NkT})_{0123}$ are due to the divergent character of Γ_3^*, which was expected because of the inaccuracy of the approximations introduced in Γ_3^*.

TABLE II

COMPRESSIBILITIES OF LENNARD-JONES
FLUID FOR DIFFERENT ISOTHERMS

ρ^*	c^3	$T^* = 0.72$ $\left(\dfrac{PV}{NkT}\right)_{01}$	$\left(\dfrac{PV}{NkT}\right)_{012}$	$\left(\dfrac{PV}{NkT}\right)_{0123}$	c^3	$T^* = 1.00$ $\left(\dfrac{PV}{NkT}\right)_{01}$	$\left(\dfrac{PV}{NkT}\right)_{012}$	$\left(\dfrac{PV}{NkT}\right)_{0123}$
0.05	.94015	.70335	.79129		.91850	.81566	.86189	
0.10	.95013	.38908	.50867		.92670	.62373	.68687	
0.15	.96006	.06012	.17426		.93470	.42717	.48801	
0.20	.96985	-.27985	-.19419		.94242	.22985	.27635	
0.25	.97938	-.62467	-.58154		.94975	.036687	.06193	
0.30	.98853	-.96814	-.97364		.95659	-.14602	-.14535	
0.35	.99713	-1.3007	-1.3562		.96281	-.31030	-.33503	
0.40	1.00499	-1.6102	-1.7136		.96827	-.44618	-.49538	
0.45	1.01192	-1.8813	-2.0279		.97282	-.54135	-.61291	
0.50	1.01771	-2.0943	-2.2780		.97633	-.58059	-.67166	-.6476
0.55	1.02212	-2.2248	-2.4385	-2.5035	.97865	-.54563	-.65298	-.63842
0.60	1.02497	-2.2431	-2.4794	-2.5602	.97968	-.41469	-.53482	-.52568
0.65	1.02603	-2.1137	-2.3654	-2.4563	.97931	-.16217	-.29165	-.28572
0.70	1.02535	-1.7949	-2.0555	-2.1522	.97750	.24139	.10585	.10982
0.75	1.02272	-1.2390	-1.5025	-1.6020	.97422	.82959	.69112	.69378
0.80	1.01820	-.39216	-.65369	-.75339	.96950	1.6399	1.5014	1.5032
0.85	1.01188	.80496	.54957	.45162	.96339	2.7140	2.5780	2.5793
0.90	1.00387	2.4171	2.1713	2.0767	.95599	4.0969	3.9659	3.9668
0.95	.99436	4.5138	4.2807	4.1907	.94741	5.8376	5.7140	5.7147
1.00	.98354	7.1693	6.9517	6.8675	.93779	7.9885	7.8746	7.8751
1.05	.97161	10.462	10.263	10.186	.92727	10.605	10.504	10.504
1.10	.95878	14.475	14.297	14.228	.91599	13.746	13.659	13.660
1.15	.94523	19.296	19.142	19.082	.90409	17.475	17.405	17.405

TABLE II

COMPRESSIBILITIES OF LENNARD-JONES
FLUID FOR DIFFERENT ISOTHERMS
(Continued)

ρ^*	T* = 1.35				T* = 2.74			
	c^3	$\left(\dfrac{PV}{NkT}\right)_{01}$	$\left(\dfrac{PV}{NkT}\right)_{012}$	$\left(\dfrac{PV}{NkT}\right)_{0123}$	c^3	$\left(\dfrac{PV}{NkT}\right)_{01}$	$\left(\dfrac{PV}{NkT}\right)_{012}$	$\left(\dfrac{PV}{NkT}\right)_{0123}$
0.05	.89538	.88981	.91582		.82913	.99432	1.0020	
0.10	.90196	.77827	.81393		.83232	.99492	1.0057	
0.15	.90825	.66825	.70289		.83515	1.0041	1.0150	
0.20	.91418	.56331	.59027		.83760	1.0244	1.0336	
0.25	.91967	.46792	.48339		.83963	1.0592	1.0655	
0.30	.92462	.38753	.38966		.84118	1.1119	1.1150	
0.35	.92894	.32894	.31725		.84223	1.1871	1.1867	
0.40	.93254	.30034	.27531		.84273	1.2895	1.2860	
0.45	.93531	.31166	.27434		.84266	1.4251	1.4187	
0.50	.93717	.37481	.32668		.84198	1.6004	1.5915	
0.55	.93801	.50384	.44660	.47427	.84068	1.8229	1.8121	1.8311
0.60	.93779	.71515	.65063	.67562	.83873	2.1012	2.0890	2.1048
0.65	.93645	1.0278	.95792	.98148	.83612	2.4447	2.4320	2.4457
0.70	.93395	1.4634	1.3900	1.4128	.83287	2.8644	2.8516	2.8637
0.75	.93031	2.0464	1.9714	1.9934	.82898	3.3719	3.3599	3.3704
0.80	.92553	2.8041	2.7293	2.7505	.82445	3.9804	3.9699	3.9787
0.85	.91968	3.7666	3.6936	3.7139	.81933	4.7041	4.6958	4.7028
0.90	.91280	4.9665	4.8971	4.9161	.81364	5.5586	5.5534	5.5579
0.95	.90499	6.4394	6.3755	6.3928	.80741	6.5605	6.5594	6.5611
1.00	.89635	8.2232	8.1666	8.1818	.80069	7.7279	7.7318	7.7301
1.05	.88696	10.359	10.311	10.324	.79353	9.0800	9.0901	9.0844
1.10	.87695	12.888	12.852	12.862	.78596	10.637	10.654	10.644
1.15	.86640	15.858	15.836	15.842	.77805	12.421	12.447	12.431

TABLE III

NUMBER OF MOLECULES IN DIFFERENT SHELLS OF NEIGHBORS, N_i,

VERSUS THE SHELL NUMBERS, $i = z_i^{*2}$

FOR FACE-CENTERED CUBIC STRUCTURE

SHELL NUMBER z_i^{*2}	N_i	SHELL NUMBER z_i^{*2}	N_i	SHELL NUMBER z_i^{*2}	N_i
1	12	21	48	41	48
2	6	22	24	42	48
3	24	23	48	43	72
4	12	24	8	44	24
5	24	25	36	45	120
6	8	26	24	46	0
7	48	27	96	47	96
8	6	28	48	48	24
9	36	29	48	49	60
10	24	30	0	50	30
11	24	31	96	51	48
12	24	32	6	52	72
13	72	33	72	53	24
14	0	34	48	54	32
15	48	35	48	55	144
16	12	36	36	56	0
17	96	37	120	57	144
18	30	38	24	58	72
19	72	39	48	59	24
20	24	40	24	60	48

TABLE IV

COMPRESSIBILITIES OF LENNARD-JONES SOLID

FOR DIFFERENT ISOTHERMS

ρ^*	T* = 0.72 A	PV/NkT	T* = 0.903 A	PV/NkT	T* = 1.00 A	PV/NkT	T*= 1.35 A	PV/NkT	T* = 2.74 A	PV/NkT
0.50	112.3	-6.1142	112.3	-4.6718	112.3	-4.1191	112.2	-2.7887	111.8	-.8575
0.55	112.4	-6.5450	112.3	-5.0151	112.3	-4.4289	112.2	-3.0176	111.9	-.9694
0.60	112.4	-6.6075	112.4	-5.0644	112.4	-4.4732	112.3	-3.0498	112.0	-.9841
0.65	112.5	-6.330	112.4	-4.7323	112.4	-4.1731	112.3	-2.8267	112.1	-.8729
0.70	120.1		112.5		112.5		112.4	-2.2850	112.1	-.6042
0.75	131.2	-4.155	121.7		120.6		112.5		112.2	-.1446
0.80	152.4	-3.6677	140.3	-1.9795	132.1	-1.2505	121.0		112.3	.5420
0.85	181.5	-2.7211	161.7	-1.1189	157.7	-.5254	137.8	.8010	112.4	.9488
0.90	218.6	-1.2900	190.8	.0888	180.7	.5976	157.8	1.7345	118.7	
0.95	259.5	0.7034	227.7	1.7490	211.2	2.1269	179.9	2.9540	128.6	3.8151
1.00	309.7	3.3710	268.1	3.9407	249.7	4.1334	208.9	4.5245	141.3	4.7273
1.05	369.8	6.8152	312.3	6.7384	291.7	6.6874	240.6	6.4888	160.2	5.8216
1.10	440.5	11.1546	371.0	10.2416	347.6	9.8708	280.1	8.9079	180.0	7.1419
1.15	522.3	16.5046	439.5	14.5434	407.9	13.7733	327.7	11.8525	202.0	8.7162
1.20	621.2	22.9861	518.5	19.7392	478.2	18.4789	379.0	15.3837	230.5	10.5595
1.25	732.4	30.7228	608.4	25.9306	558.8	24.0796	439.2	19.5696	260.8	12.7171
1.30	862.0	39.8425	709.9	33.2196	650.3	30.6694	508.7	24.4818	298.1	15.2224
1.35	937.6	50.4753	828.5	41.7115	758.2	38.3426	587.9	30.1901	337.7	18.1075

FIGURES 1-13

FIGURE 1

HARD-SPHERE COMPRESSIBILITY VERSUS V/V_O

Compressibility of the system of hard-spheres versus V/V_O, $(V_O = N\sigma^3/\sqrt{2})$, 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.
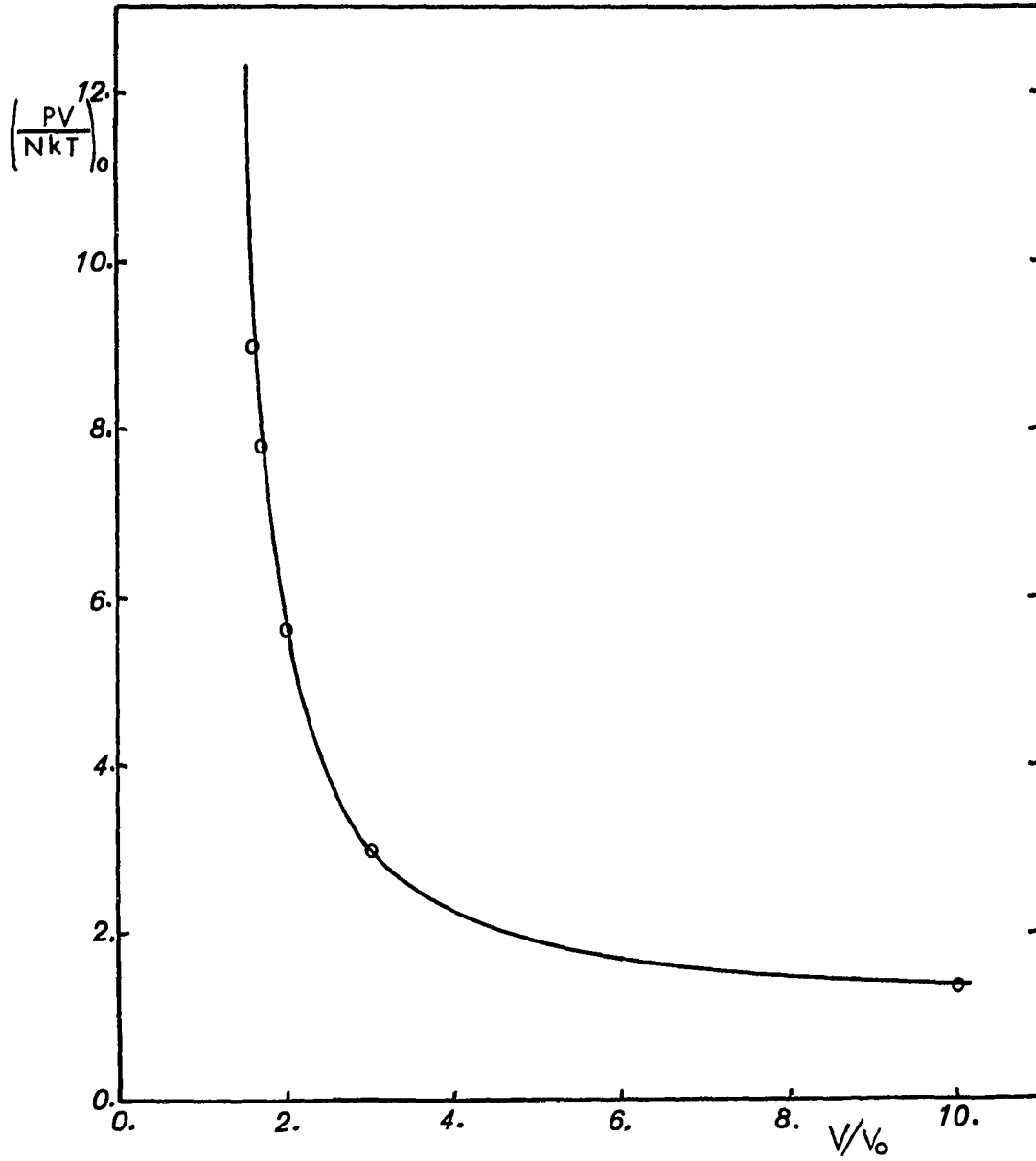
Figure 1.   Hard-sphere Compressibility vs. V/V_o.

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).
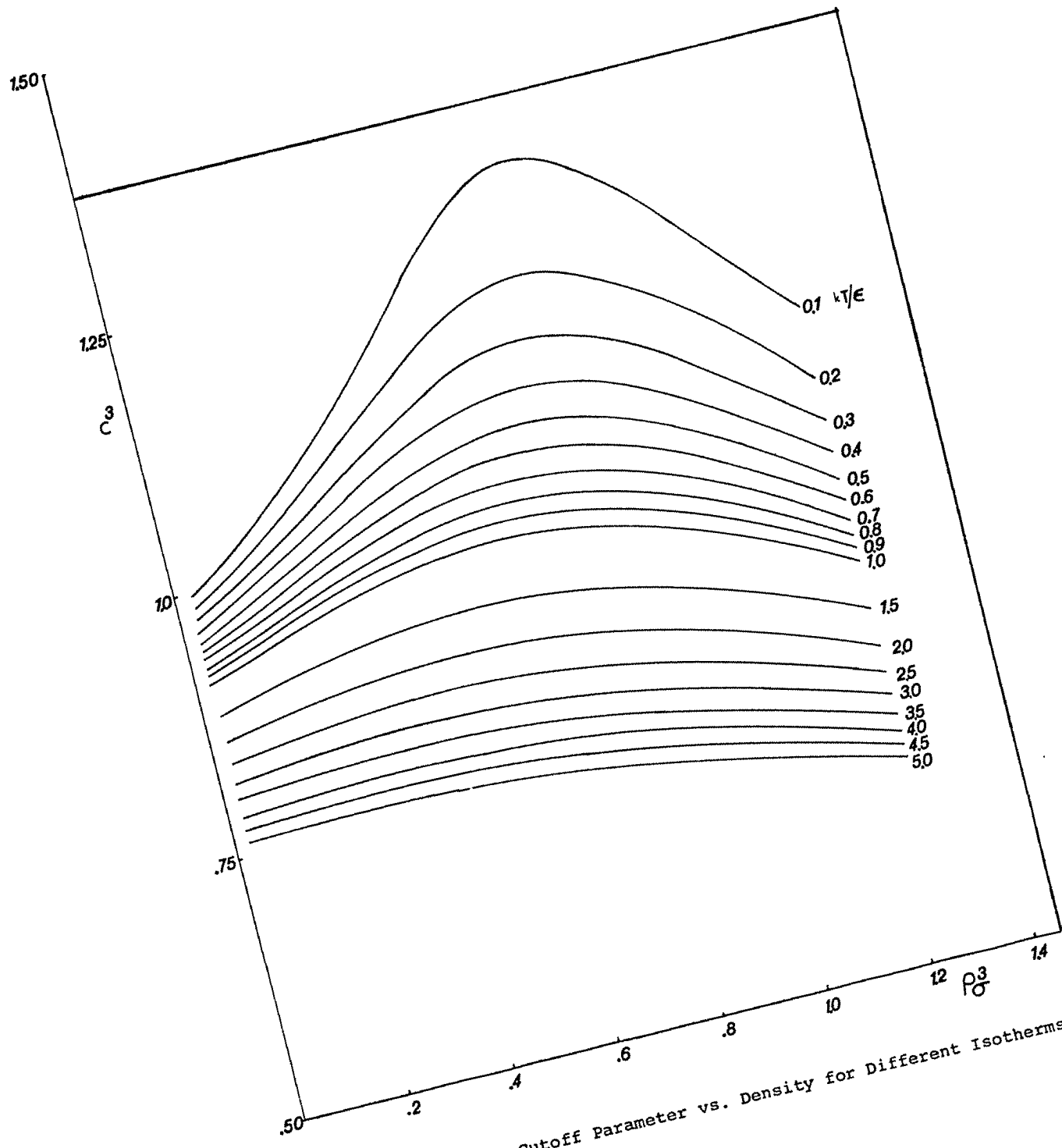
Figure 2. Cutoff Parameter vs. Density for Different Isotherms.

FIGURE 3

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

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

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

The points given by o, ϕ, and ● are machine-calculated values
which are taken from references [58, 61 and 35], respectively.
The points given by o were calculated using a five-term virial
expansion (reference [5]) and the points given by x, -o- and +
are experimental values and are taken from references [32, 56
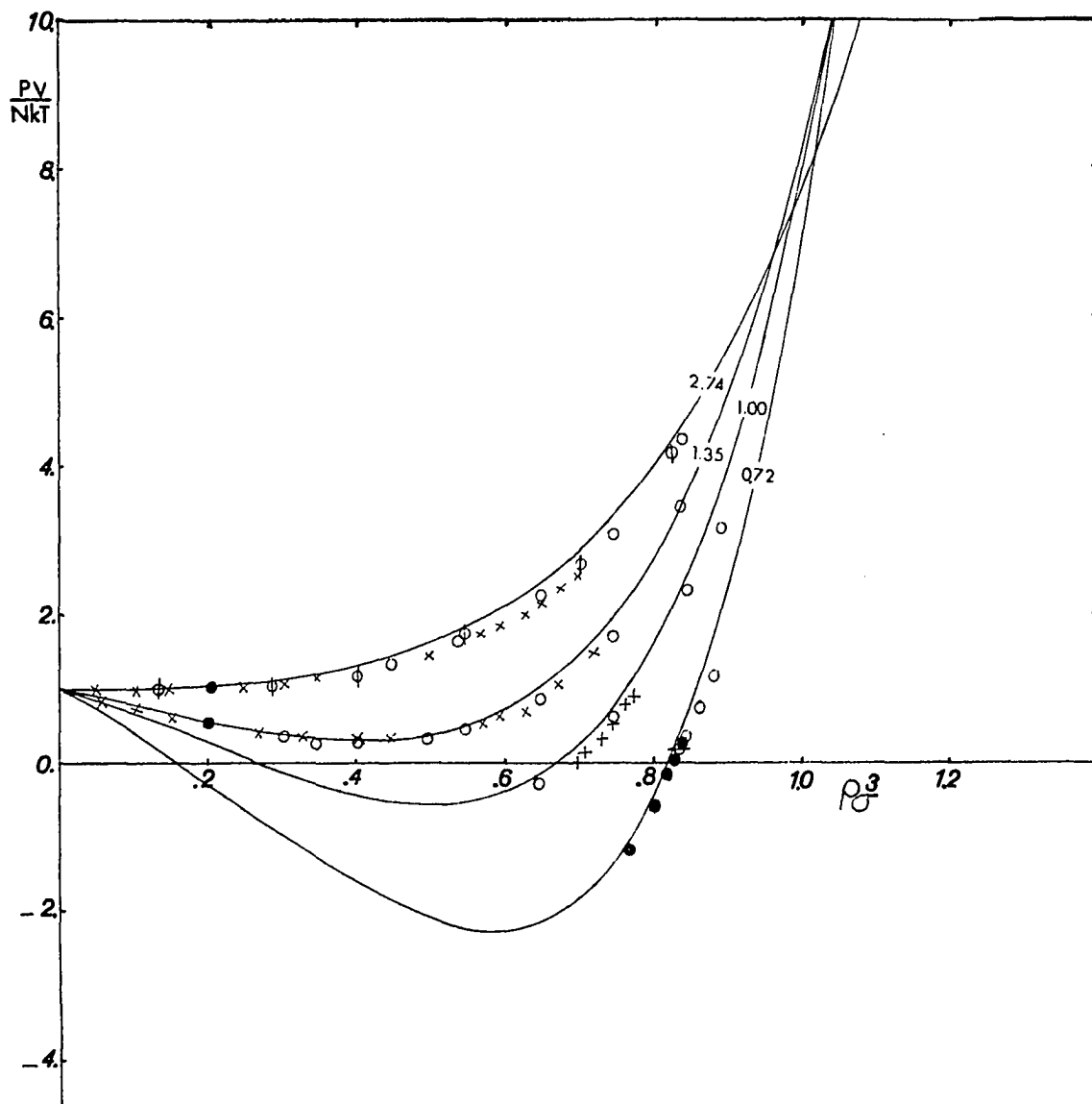and 57], respectively.

Figure 3. Equation of State of Lennard-Jones 12:6 Fluid for Different Isotherms.

FIGURE 4

EQUATION OF STATE OF LENNARD-JONES 12:6
FLUID VERSUS DENSITY 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 para-
meter the same values as used for Figure 3 are used. The
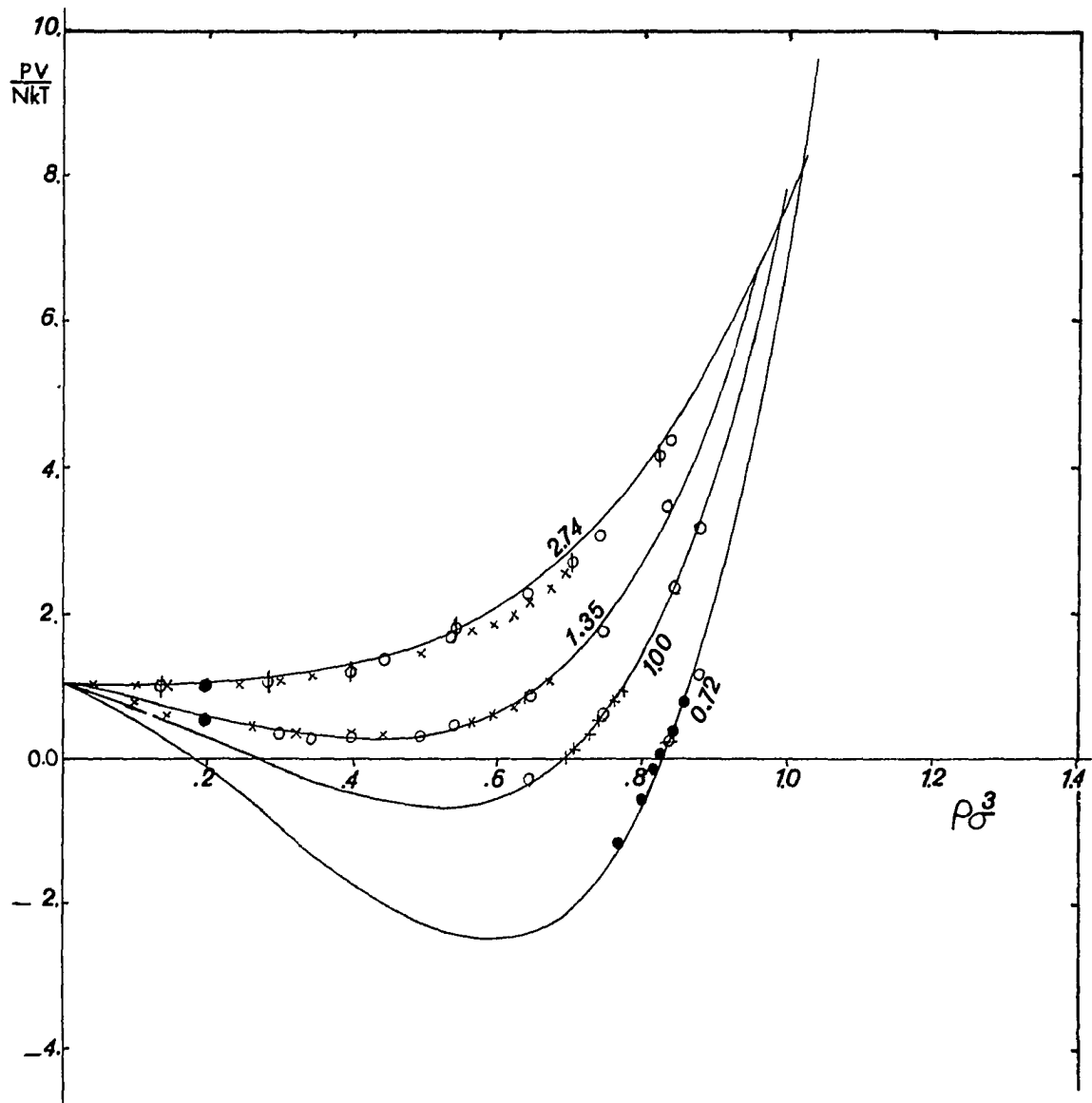experimental and machine-calculated points are the same as
in Figure 3.

Figure 4. Equation of State of Lennard-Jones 12:6 fluid
vs. Density for Different Isotherms.

FIGURE 5

INTERNAL ENERGY OF LENNARD-JONES 12:6
FLUID VERSUS DENSITY FOR DIFFERENT ISOTHERMS

Internal energy for the 12:6 potential. The curves are isotherms calculated from Equation (115) and are labled 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 Γ_2^* which actually is not expected to be correct at low densities.

The points given by o, □ , Δ are machine-calculated values for T^* = 2.74, 1.35, 0.72, respectively, taken from reference [58]. The points given by Φ and ● are machine-calculated values for T^* = 2.74 from reference [61] and for T^* = 0.72 from reference [35], respectively. The points given by x, + are experimental values taken from reference [32] for T^* = 2.74 and 1.35 respectively, and the point given by ⊖ was taken from experimental data in references [46 and 7].
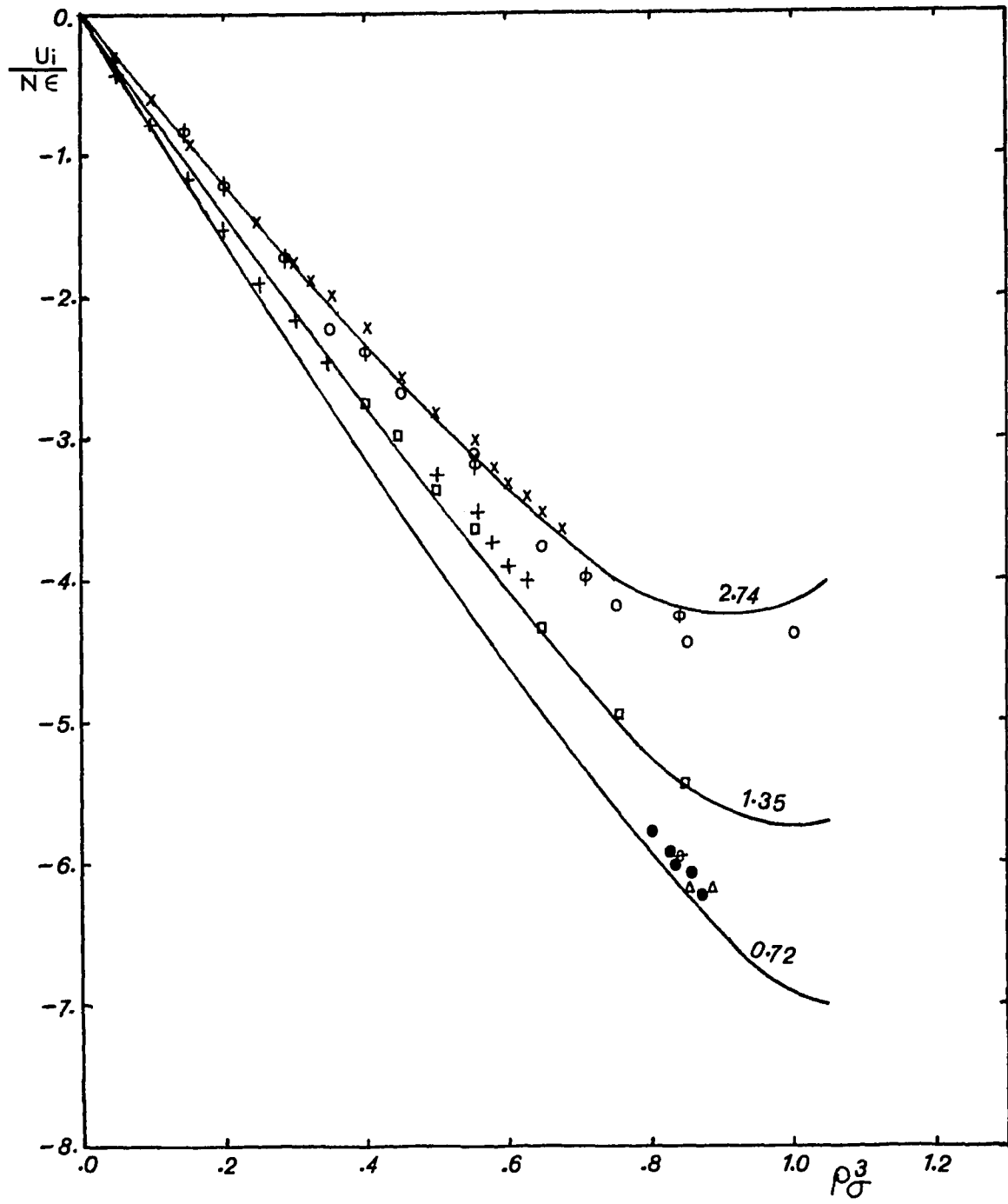
Figure 5. Internal Energy of Lennard-Jones 12:6 Fluid vs.
Density for Different Isotherms.

FIGURE 6

INTERNAL ENTROPY OF LENNARD-JONES 12:6
FLUID VERSUS 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 Γ_2^* which actually is not expected to be correct at low densities.

The points given by x, $+$ are experimental values taken from reference [32] for $T^* = 2.74$ and 1.35, respectively, and the point given by $\ominus$ was calculated from experimental data given in references [46 and 7].
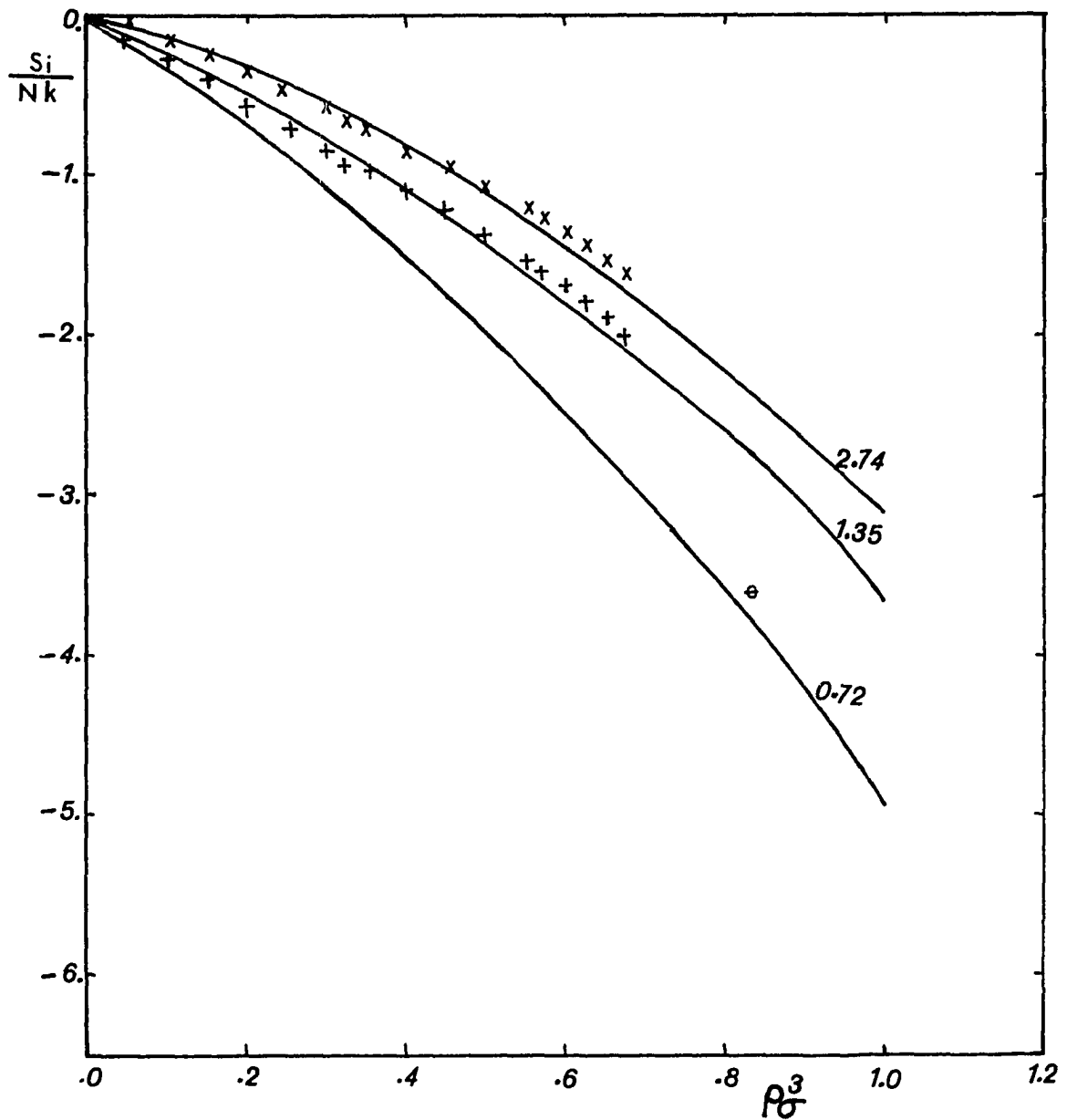
Figure 6.   Internal Entropy of Lennard-Jones 12:6 fluid vs.
Density for Different Isotherms.

FIGURE 7

DENSITIES OF COEXISTING VAPOR AND LIQUID PHASES
FOR LENNARD-JONES 12:6 FLUID VERSUS TEMPERATURE

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 ϕ and $\ominus$ are machine-
calculated values and are taken from references [58 and 35],
respectively. The points given by o and ● are experimental
values for liquid and solid argon and are taken from refer-
ences [20 and 7], respectively.

Figure 7. Densities of Coexisting Vapor and Liquid Phases for
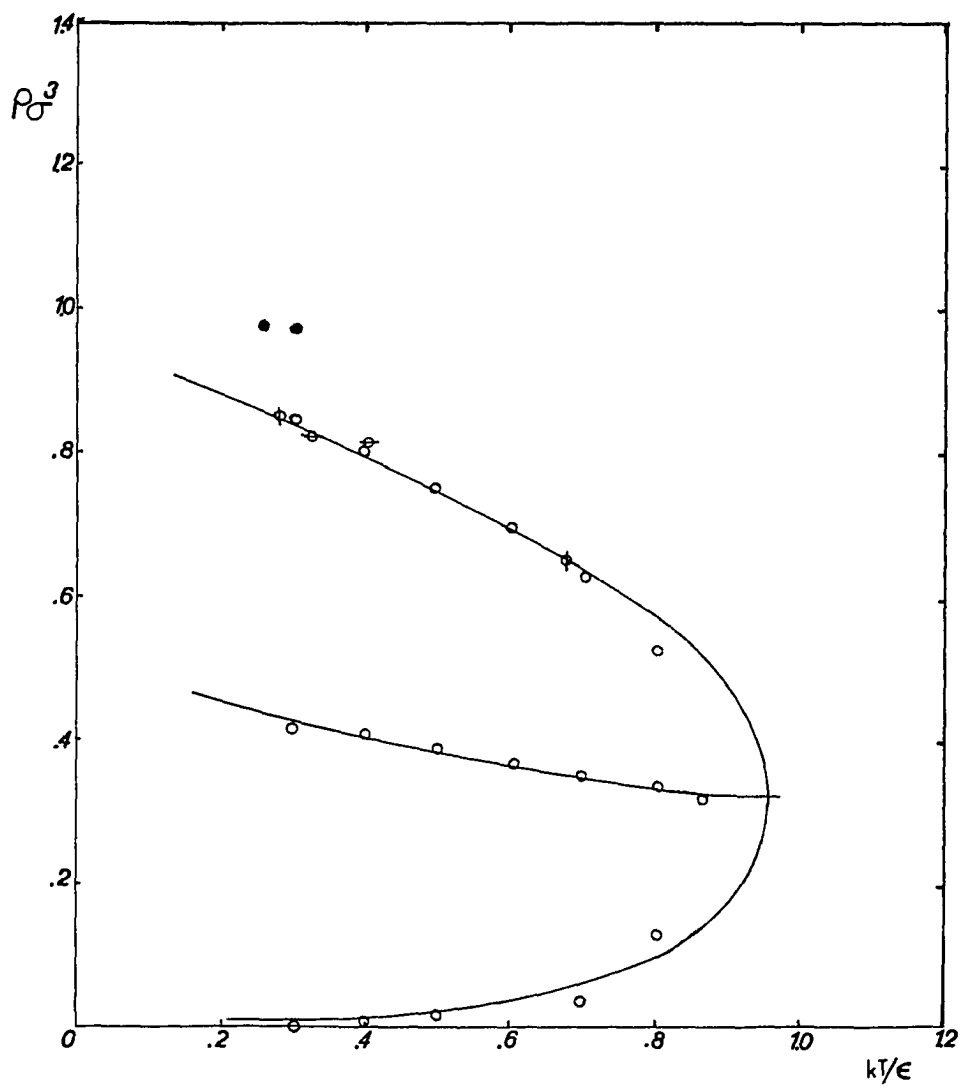Lennard-Jones 12:6 Fluid vs. Temperature.

FIGURE 8

REDUCED VAPOR PRESSURES FOR LENNARD-JONES 12:6
LIQUID VERSUS INVERSE 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 experi-
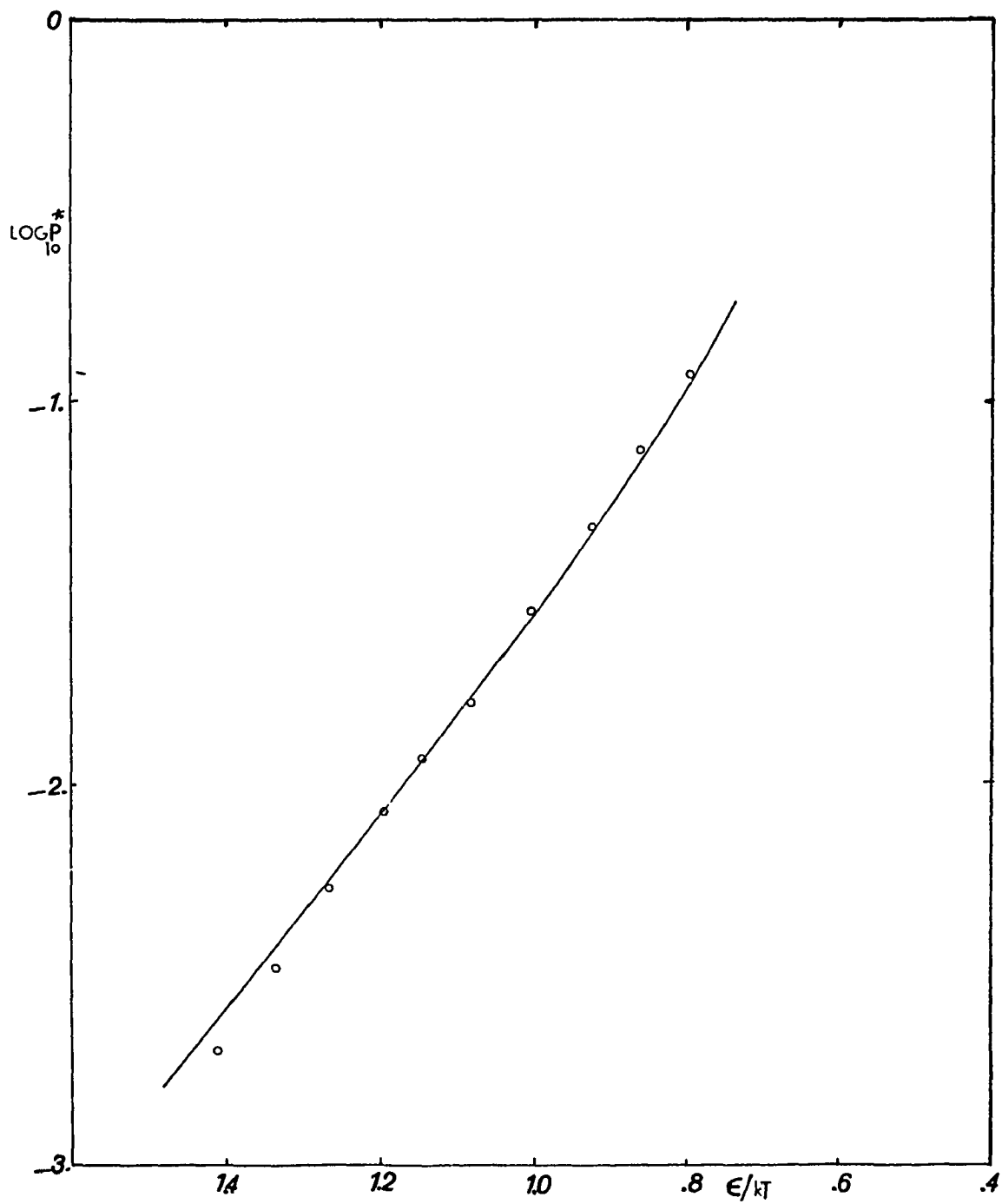mental values taken from reference [48].

Figure 8. Reduced Vapor Pressures for Lennard-Jones 12:6
Liquid vs. Inverse Temperature.

FIGURE 9

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 ϕ and $\ominus$ 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 o 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 o were calculated from
experimental data as reported in reference [7].

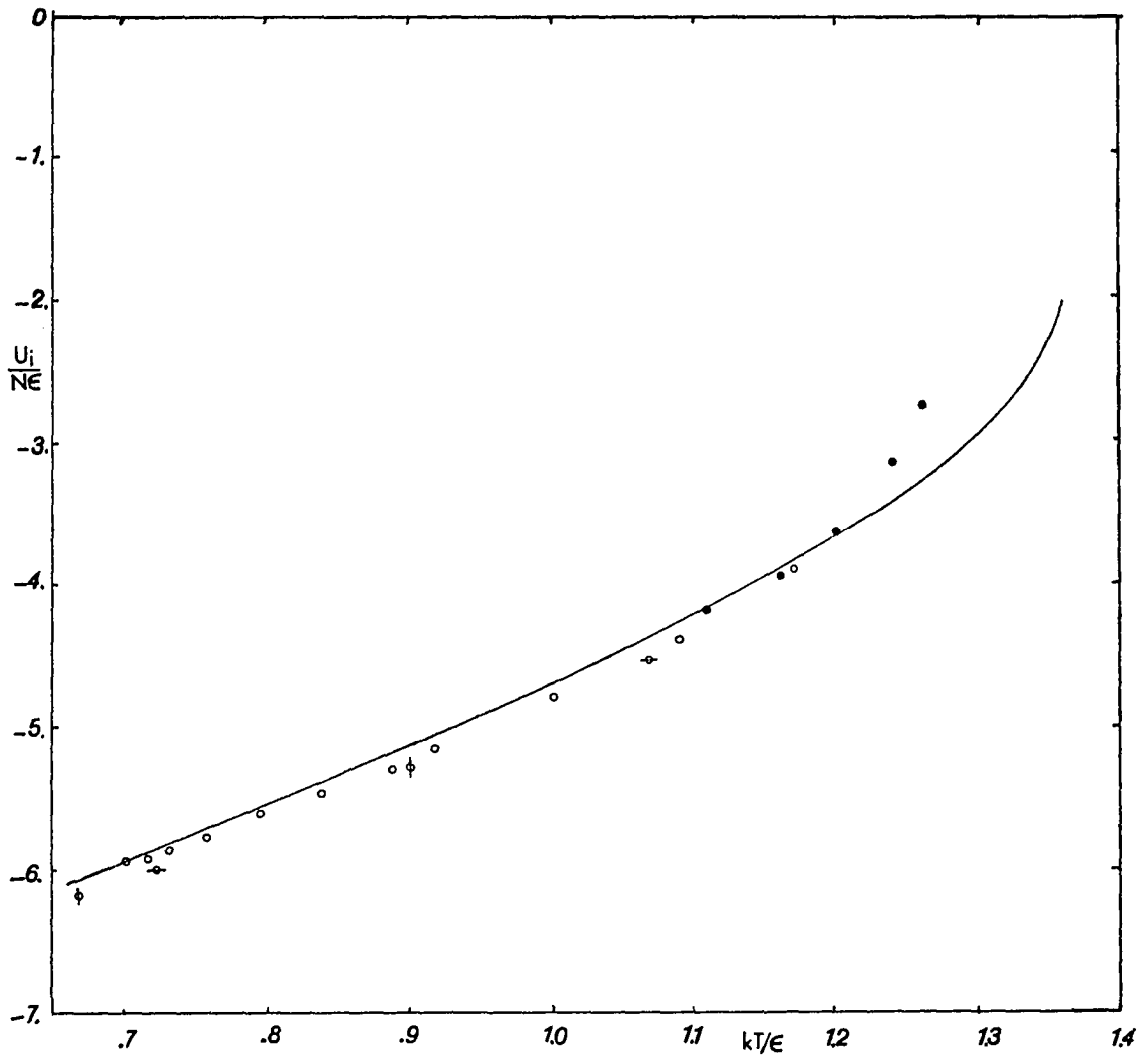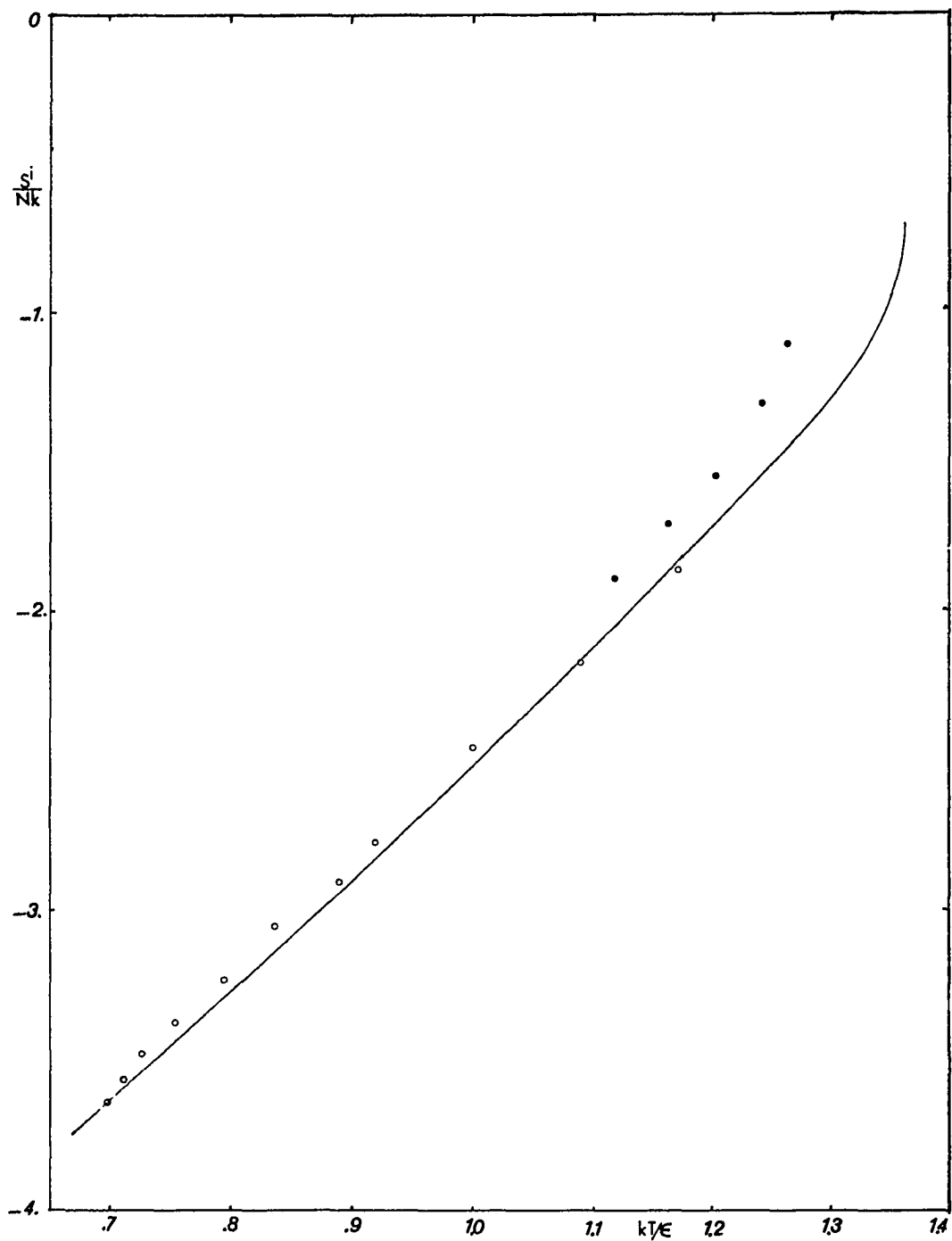Figure 10. Internal Entropy at Saturated Vapor Pressure for
Lennard-Jones 12:6 Liquid vs. Temperature.

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 calcu-
lated 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

$$A = m\omega^2 / (kT)$$

where ω is the harmonic oscillation frequency.
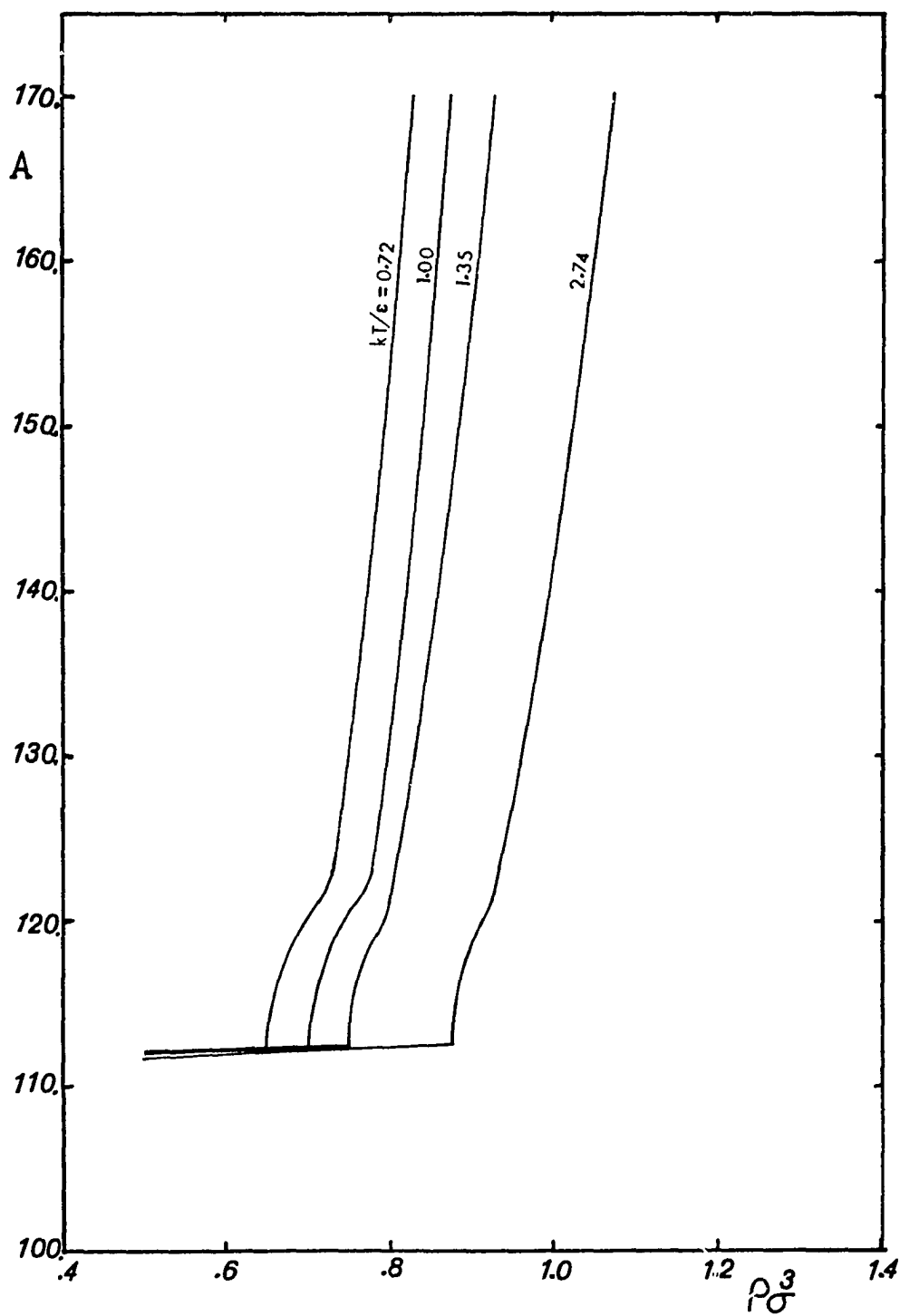
Figure 11.   Values of A vs. Density for Lennard-Jones 12:6
             Potential vs. Density for Different Isotherms.

FIGURE 12

EQUATION OF STATE OF LENNARD-JONES 12:6 SOLID
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 ϕ, ●, and ■ are taken from references [44, 35, and 61] respectively.
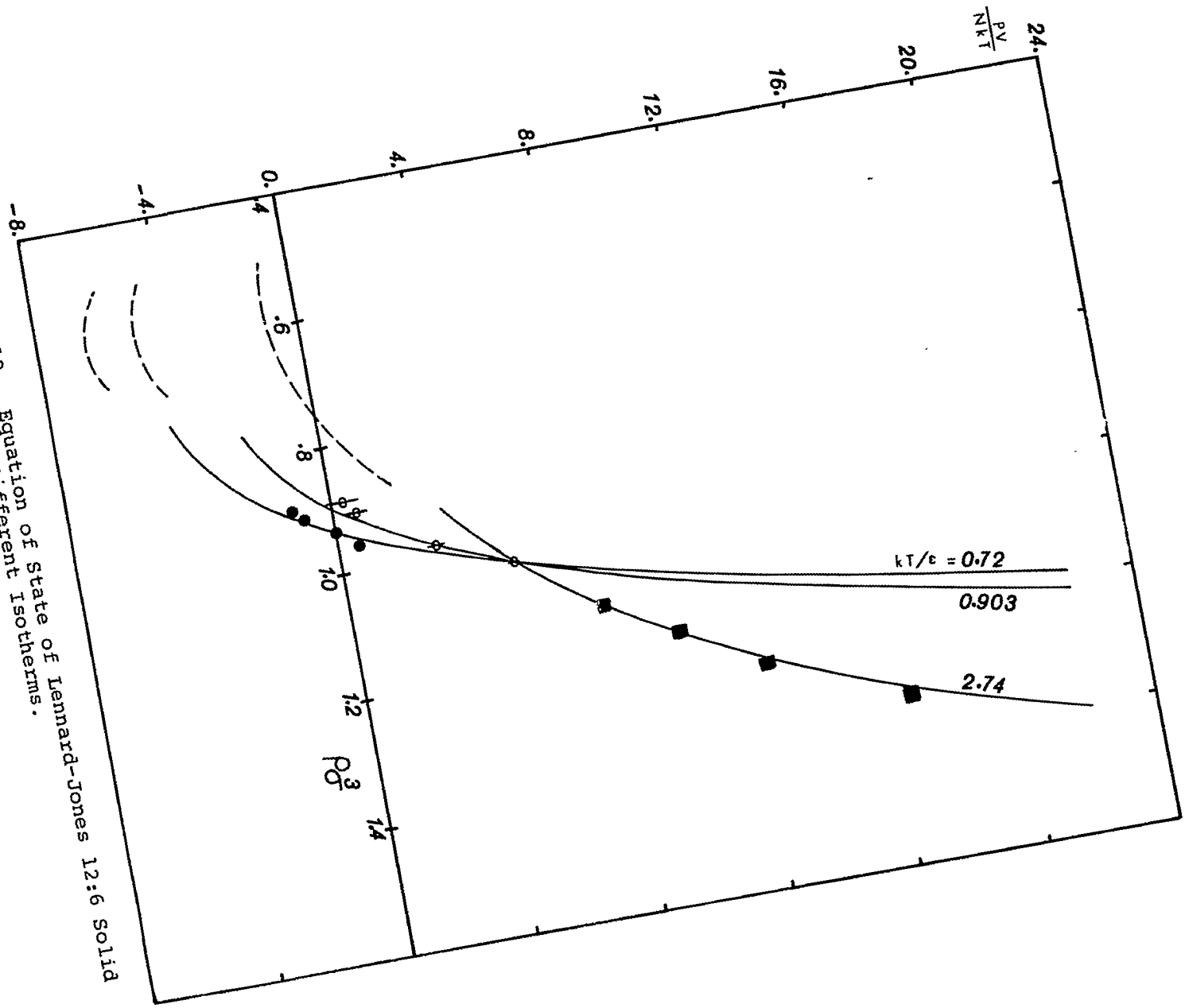
Figure 12. Equation of State of Lennard-Jones 12:6 Solid
for Different Isotherms.

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.
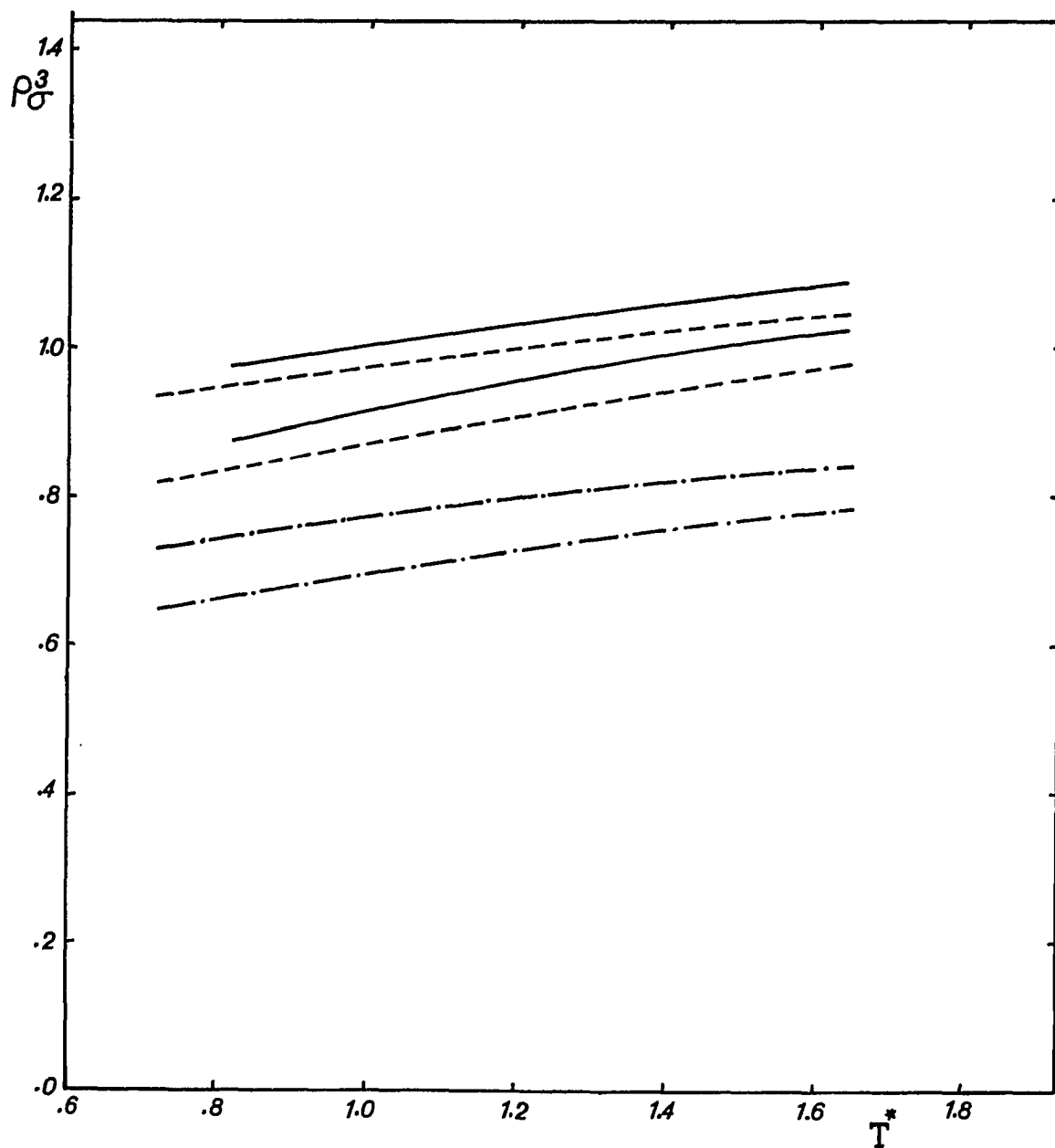
Figure 13.   Densities of Coexisting Liquid and Solid Phases
             for Lennard-Jones 12:6 Potential vs. Temperature.

LITERATURE CITED

1. Alder, B. J., _J. Chem. Phys._, 40, 2724 (1964).

2. Alder, B. J., (unpublished results).

3. Barker, J. A., _Australian J. Chem._, 13, 187 (1960).

4. Barker, J. A., _Lattice Theories of Liquid State_, Pergamon Press (1963).

5. Barker, J. A., P. J. Leonard and A. Pompe, _J. Chem. Phys._, 44, 4206 (1966).

6. Barker, J. A. and D. Henderson, _J. Chem. Phys._, 47, 2856 (1967).

7. Barker, J. A. and D. Henderson, _J. Chem. Phys._, 47, 4714 (1967).

8. Barker, J. A. and D. Henderson, _J. Chem. Education_, 45, 2 (1968).

9. Barker, J. A., and D. Henderson, _Phys. Rev. Lett._, 21, 3, 134 (1968).

10. Barker, J. A., D. Henderson and W. R. Smith, Proceeding of the Fourth Symposium on Thermodynamic Properties, _ASME_, p. 30.

11. Barker, J. A., D. Henderson and W. R. Smith, _J. Phys. Soc. of Japan_, 26, 284, Supplement (1969).

12. Bazarov, I. P., _Soviet Physics-Doklady_, 135, 6, 1293 (1960).

13. Bogolyubov, N. N., _J. Phys. U. R. S. S._, 10, 257, 265 (1946).

14. Born, M. and M. S. Green, "A General Kinetic Theory of Liquids." (Cambridge University Press, 1949).

15. Corner, J. and J. E. Lennard-Jones, Proc. Roy. Soc., A178, 401 (1941).

16. Crawford, R. K., Thesis, Princeton University (1968); See also, R. K. Crawford and W. B. Daniels, Phys. Rev. Lett., 21, 6, 367 (1968).

17. DeBoer, J., Physica, 20, 655 (1954).

18. Feynman, R. P., Phys. Rev., 47, 3, 660 (1955).

19. Frisch, H. L., J. L. Katz, E. Praestgaard and J. L. Lebowitz, J. Phys. Chem., 70, 6, 2016 (1966).

20. Guggenheim, E. A., J. Chem. Phys., 13, 253 (1945).

21. Henderson, D. and J. A. Barker, J. Chem. Phys., 49, 3377 (1968).

22. Henderson, D. and J. A. Barker, Mol. Phys., 14, 6, 587 (1968).

23. Hill, T. L., "Statistical Mechanics", McGraw Hill (1956).

24. Hirschfelder, J. O., C. F. Curtiss and R. B. Bird, "Molecular Theory of Gases and Liquids", Wiley, (1967).

25. Kim, S., D. Henderson and J. A. Barker, Canadian J. Phys., 47, 99 (1969).

26. Kirkwood, J. G., J. Chem. Phys., 3, 300 (1935).

27. Kozak, J. J. and S. A. Rice, J. Chem. Phys., 48, 1226 (1968).

28. Lebowitz, J. L., Phys. Rev., 2nd, Ser., 133, 4A, A895 (1964).

29. Lebowitz, J. L. and J. S. Rowlinson, J. Chem. Phys., 41, 133 (1964).

30. Lennard-Jones, J. E. and A. F. Devonshire, <u>Proc. Roy. Soc.</u>, A163, 53 (1937).

31. Lennard-Jones, J. E. and A. F. Devonshire, <u>Proc. Roy. Soc.</u>, A165, 1 (1938).

32. Levelt, J. M. H., Physica, 26, 361 (1960).

33. Lukes, T. and R. Jones, <u>J. Phys. A (Proc. Phys. Soc.)</u>, Ser. 2, 1, 29 (1968).

34. Layer, J. E. and M. G. Mayer, "Statistical Mechanics", Wiley, New York (1940).

35. McDonald, I. R. and K. Singer, <u>Disc. Fara. Soc.</u>, 43, 40 (1967).

36. McQuarrie, D. A. and J. L. Katz, <u>J. Chem. Phys.</u>, 44, 2393 (1966).

37. Michels, A. and H. Wijker, <u>Physica</u>, 15, 627 (1949).

38. Michels, A., J. M. Levelt and G. J. Wolkers, <u>Physica</u>, 24, 769 (1958).

39. Nijboer, B. R. A. and L. Van Hove, <u>Phys. Rev.</u>, 85, 777, (1952).

40. Ornstein, L. S. and F. Zernike, <u>Proc. Acad. Sci. Amst.</u>, 17, 793 (1914); and F. Zernike, <u>Proc. Acad. Sci. Amst.</u>, 19. 1520 (1916).

41. Prigogine, I., "Molecular Theory of Solutions", North-Holland Pub. Co., Amsterdam (1957).

42. Prins, J. A. and H. Peterson, <u>Physica</u>, 3, 147 (1936).

43. Ree, F. H. and W. G. Hoover, <u>J. Chem. Phys</u>. 40, 939, (1964).

44. Ross, M. and B. J. Alder, <u>Phys. Rev. Lett.</u>, 16, 24, 1077 (1966).

45. Rotenberg, A., _J. Chem. Phys._, 43, 1198 (1965).

46. Rowlinson, J. S., "Liquids and Liquid Mixture", Butterworth, London (1959).

47. (a) Rowlinson, J. S., _Mol. Phys._, 7, 349 (1964); (b) 8, 107 (1964).

48. Rowlinson, J. S., _Disc. Fara. Soc._, 40, 19 (1965).

49. Rushbrooke, G. S. and H. I. Scoins, _Proc. Roy. Soc. A_, 216, 203 (1953).

50. Rushbrooke, G. S., _Disc. Fara. Soc._, 43, 7 (1967).

51. Smith, E. B. and B. J. Alder, _J. Chem. Phys._, 30, 1190 (1959).

52. Smith, W. R., D. Henderson and J. A. Barker, _Canadian J. Phys._, 46, 1725 (1968).

53. Stell, G., _Physica_, 29, 517 (1963).

54. Thiele, E., _J. Chem. Phys._, 30, 474 (1963).

55. Throop, G. J. and R. J. Bearman, _J. Chem. Phys._, 42, 2408, (1964).

56. Van Itterbeck, A. and O. Verbeke, _Physica_, 26, 931 (1960).

57. Van Itterbeck, A., O. Verbeke and K. Staes, _Physica_, 29 742 (1963).

58. Verlet, L., _Phys. Rev._, 159, 98 (1967).

59. Wentorf, R. H., Jr., Buehler, R. J., Hirschfelder, J. O. and Curtiss, C. F., _J. Chem. Phys._, 18, 1484 (1950).

60. Wertheim, M. S., _Phys. Rev. Lett._, 10, 8, 321 (1963).

61. Wood, W. W. and F. R. Parker, _J. Chem. Phys._, 27, 720 (1957).

62. Young, D. A. and S. A. Rice, <u>J. Chem. Phys.</u>, 47, 5061 (1967), Look also for the references 8, 9, 10, and 11 in this reference.

63. Yvon, J., <u>Actualities Sci. Ind.</u>, (Hermann et.cie, Paris, 1935), p. 203.

64. Yvon, J., <u>Actualities Sci. Ind.</u>, (Hermann et.cie, Paris, 1937), 542, 543.

65. Zwanzig, R. W., <u>J. Chem. Phys.</u>, 22, 1420 (1954).

a	= depth of the n:6 potential curve
a_o	= $(\sqrt{2}/\rho)^{1/3}$ = nearest-neighbors distance in f.c.c. crystal
a_o^*	= a_o/σ
$a_i(v)$	= coefficient of $(\frac{1}{RT})^i$ in the perturbation equation of state
A	= $kTW(r)/(r/a_o)^2$
b_o	= $2/3\pi N\sigma^3$
B	= second virial coefficient
B*	= B/b_o
c	= d/σ = cutoff parameter
c_{m1}, c_{m2}	= cutoff parameters produced by the variational calculation on the first and second inequalities, respectively
c_{11}	= d_{11}/σ_{11}
c_{22}	= d_{22}/σ_{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_o^2
d	= hard-sphere diameter

d_{11} = first component hard-sphere diameter

d_{22} = second component hard-sphere diameter

d_{12} = $(d_{11} + d_{22})/2$

D = fourth virial coefficient

D* = D/b_o^3

F = Helmholtz free energy (original system)

F* = F/NkT

$g(r)$, $g^{(2)}(r)$, $g(i,j)$, $g(r_{ij})$ = radial distribution function

$g_{\alpha\beta}$ = radial distribution function in the binary mixture

$g_{o,i}$ = coefficient of $(\frac{1}{v})^i$ in the expansion of $g_c(r,v)$

$g^{(n)}(\underline{r}_1, \ldots, \underline{r}_n)$ = n^{th} distribution function

G = $v_f/4\pi a_o^3$

G(s) = $L^{-1}[g_o(x)x]$

h = Planck's Constant

$h(r)$ = $g(r)-1$ = total correlation function

$h(i,j)$ = total correlation function

I(0) = structure factor

i = shell number

i = particle number

i(s) = scattering function

k = Boltzmann's Constant

m = particle's mass

n	= particle number
n	= power in n:6 potential function
N	= total number of particles in the system
N_i	= number of the particles in the shell $R_i \to R_i + dR_i$
N_1	= total number of the particles of component 1 in binary mixture.
N_2	= $N - N_1$
$p(x)$	= probability of x
P	= pressure
P^V	= pressure from virial theorem
P_c^*	= $P_c \sigma^3 / \epsilon$ = reduced critical pressure
$P^{(n)}$	= probability distribution function of particles 1, ..., n
Q	= partition function
r	= intermolecular distance = $\|\underline{r}\|$
$\underline{r}$	= vectorial distance
$\underline{r}_i$	= vector position of particle i
$\underline{r}_i$	= vector displacement of particle i from the cell center
R	= intermolecular distance = $\|\underline{R}\|$
$\underline{R}$	= vectorial distance
R	= gas constant
S_i	= internal entropy
t	= r/d_{ij}

T	$=$ temperature
T^*	$= kT/\epsilon =$ reduced temperature
T_1^*	$= kT/\epsilon_{11}$
T_c^*	$=$ reduced critical temperature
u_{ij}, $u(r)$, $u(ij)$	$=$ two-body intermolecular potential function
u^1, $\dot{u}_1$	$= u - u^o$
u_n	$=$ Lennard-Jones $n{:}6$ potential function
u^*	$= u/4\epsilon$
U	$=$ total potential energy
U^1	$= U{-}U^o$
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	$= \dfrac{PV}{NkT} = \dfrac{Pv}{RT} =$ compressibility
Z	$=$ configuration integral

z_i = distance of the ith neighbors from the central molecule

z_i^* = z_i/a_o

Greek Letters

α = steepness parameter

α = σ_{11}/σ_{22}

α_i = lower bound for $z_i - a_o$

α_i^* = α_i/a_o

β = $1/kT$

β_i = upper bound for $Z_i + a_o$

β_i^* = β_i/a_o

γ = depth parameter

γ_i = $\frac{\pi}{6}\rho x_i$

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

ϵ = depth of the Lennard-Jones potential curve

ϵ_{ii} = depth of the Lennard-Jones potential curve

ϵ_{12} = $(\epsilon_{11}\epsilon_{22})^{\frac{1}{2}}$

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

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

η_{11} = $\frac{\pi}{6}\rho x_1 d_{11}^3$

η_{22} $= \frac{\pi}{6} \rho x_2 d_{22}^3$

η_{12} $= \frac{\pi}{3} x_1 x_2 d_{12}^3$

λ = square-well potential function parameter

Λ $= h/(2\pi mkT)^{\frac{1}{2}}$

μ_1 $= d_{11}/d_{22}$

μ_2 $= d_{11}/d_{12}$

ξ = truncation parameter in the Taylor expansion

ξ $= \gamma_1 d_{11}^3 + \gamma_2 d_{22}^3$

π = 3.1415926...

ρ = N/v = number density

ρ^* $= \rho \sigma^3$

ρ^*_c = reduced critical density

σ = Lennard-Jones length parameter

σ_{ii} = Lennard-Jones length parameter for component i in binary mixture

σ_{12} $= (\sigma_{11} + \sigma_{22})/2$

τ $= \epsilon_{11}/\epsilon_{22}$

$\varphi_{ij}(s)$ $= L[tg_{ij}(t)]$

χ = a general undefined variable

χ_{ij} $= u_{ij} - u_{ij}^o - \langle u_{ij} - u_{ij}^o \rangle_o$

$\Psi(\underline{r}_i), \Psi(\underline{r}), \Psi(r)$ = potential energy function inside cell

ω_i = coefficient of $(\frac{1}{kT})^{i-1}$ 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
Δ	= cell

Mathematical Operators

∇_i	= the "del" or "nohla" operator with respect to particle i
$d\underline{r}$, di, $d\underline{r}_i$	= differential volume (with respect to particle i)
$d\Gamma$	= differential phase volume
$\dfrac{\partial(\ )}{\partial(\ )}$	= partial derivative
$\exp(x)$	= e^x = the exponential of x
$\ln(x)$	= natural logarithm of x
$\int_V$	= triplet (volume) integral

$\int_\Delta$ = integral over cell volume

$\langle x \rangle$ = expectation value of x

$\langle x \rangle_o$ = expectation value of x over the reference system

$\langle x \rangle_\Delta$ = expectation value of x over the cell

$|\underline{r}_i - \underline{r}_j|$ = intermolecular distance of molecules i and j.

$f(x)$ = a function of x

$f^{(n)}_{(x)}$ = n^{th} derivative of $f(x)$

$\sum\limits_{i=1}^{N}$ = summation over N molecules (or cells)

$\sum\limits_{\substack{i>\ldots>\ell=1}}^{N} = \sum\limits_{i=1}^{N} \ldots \sum\limits_{\ell=1}^{N} ; \sum\limits_{\substack{i\ldots\ell \\ i\neq\ldots\neq\ell}}$ = $\sum\limits_{i>\ldots>\ell=1}^{N}$

$\sum{}'$ = summation over all the arrangements of molecules with one in each cell

$0(\ )$ = in the order magnitude of

APPENDIX

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

$$\langle N^3 \rangle = \sum_N N^3 P_N = \frac{\sum_N N^3 e^{\beta N \mu} Q_N(T,V)}{\Xi} = \frac{1}{\beta^3 \Xi} \left(\frac{\partial^3 \Xi}{\partial \mu^3}\right)_{T,V} \qquad (A-1)$$

where Ξ is the partition function of g.c.e., μ is the activity coefficient, and Q_N is the canonical ensemble partition function. For g.c.e. we also have

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

Then

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

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

$$\langle (N - \langle N \rangle)^3 \rangle = \frac{1}{\beta^2} \left(\frac{\partial^2 \langle N \rangle}{\partial \mu^2}\right)_{T,V} \qquad (A-4)$$

142

Also for g.c.e., we have

$$\left(\frac{\partial \langle N \rangle}{\partial \mu}\right)_{T,V} = \langle N \rangle \left(\frac{\partial \rho}{\partial P}\right)_{T,V} \tag{A-5}$$

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

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

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