CHAPTER I

INTRODUCTION
Matter exists commonly in three different phases namely solid, liquid and gas. Solids are rigid and give sharp Bragg reflections in a diffraction experiment, demonstrating an ordered arrangement of atoms or molecules. Liquids and gases are fluids. They flow under a shear stress however small. Further in diffraction experiments they give no sharp Bragg reflections but diffuse rings. There is no long range ordered arrangement of molecules. Dense fluids exist in relatively small part of the enormous range of temperatures and pressures existing in the universe. To specify a liquid it is important to refer to a diagram of state that describes the relationship between pressure, volume and temperature. A diagram of this kind for a typical monatomic liquid namely argon is given in figure 1, part (a) being a P–T diagram while part (b) is a P–V diagram. The shaded regions in these diagrams indicate the liquid state.

The aim of physics of fluids is to understand why particular phases are stable in particular ranges of temperature and density, and to relate the stability, structure and dynamical properties of fluid phases to the size and shape of the molecules and atoms and to the nature of the forces between them. Clearly both the equilibrium and transport properties are extremely important for the study of the liquids. But this thesis contains only the study of their equilibrium properties.
FIG. 1

(a) Pressure vs. Temperature
- Solid
- Critical point
- Triple point
- Vapour

(b) Pressure vs. Volume
- Solid
- Triple point
- Vapour

FIG. 1
Dense fluids are difficult to deal with theoretically. Dilute gases and crystalline solids can be thought of as deviants from well understood ideal states like the ideal gas and the ideal harmonic crystal. But so far the dense fluid is far from any ideal model.

Nevertheless, in recent years, there have been some significant advances in the theory\textsuperscript{1,2}, particularly for very dense fluids. This progress has come about from the recognition that while there is no analytically simple reference system there does exist a practical reference system, it is a model fluid of hard space symmetric objects, hard rods, discs or spheres depending upon the number of dimensions considered. In three dimensions they have the same number density as the real fluid and diameter specified by density and temperature. The tractability of the hard sphere fluid and the realisation that it can serve as a quantitatively useful reference system owe a great deal to the availability of high speed computers\textsuperscript{3}.

By computer simulation one can at selected temperatures and densities solve 'exactly' the classical manybody problem with a given potential. The result of these computer experiment can then be compared with experiments on real fluids to test the adequacy of the classical description and of the assumed interparticle potential. Computer calculation on idealised test systems, such as
hard spheres play a very important role in comparing results from useful theories of real fluids.

I.A. 

\textbf{vander Waals Equation of State:}

The first and foremost theory on the liquid state of matter goes back over a century to vander Waals\textsuperscript{4}. According to him a simple fluid system consists of electrically neutral particles interacting through pair potentials that depend only on the distance $r$ between their centres. Moreover a microscopic system of such particles can be described by classical statistical mechanics. A rigorous deduction of the pair totalling would involve very complicated many body interactions between the atoms, so that the one usually considered is best thought of as an effective interaction. Remarkably enough, this potential can be adequately represented over a wide range of temperatures and densities by a simple analytic formula\textsuperscript{5}

\begin{equation}
    u(r) = 4\varepsilon \left[ (\sigma/r)^{12} - (\sigma/r)^{6} \right],
\end{equation}

due to Lennard–Jones. The appropriate values of $\varepsilon$ and $\sigma$ for different simple fluids are determined from the physical properties of the fluids.
The important feature of the pair potential reproducing physical properties of the fluid is the strong short range repulsion at small $r$ and the relatively weak long range attraction at large $r$. As a consequence, each particle in a dense fluid feels simultaneously the attractive part of the interaction of many other particles. This suggests that it is useful to separate $u(r)$ as to its effects on the different parts of the fluid. The short range part keeps the particles apart and is responsible for the local correlations while the long range part sees only the gross (macroscopic) density profile of the fluid and provides an attractive potential well for the fluid particles. The latter is also responsible for the condensation from the gas into the liquid below the critical temperature $T_c$. This separation can be implemented formally by writing $u(r)$ as a sum of two parts, a short range repulsive part, $u_o(r)$, and a long range attractive part $u_1(r)$ \cite{6,7,8} (Fig. 2)

$$u(r) = u_o(r) + u_1(r) \tag{1.2}$$

The different roles that $u_o(r)$ and $u_1(r)$ play in determining the physical properties of dense fluids are essential to useful approximation schemes.

The recognition of different roles played by $u_o(r)$ and $u_1(r)$ dates back to van der Waals who used it in 1873.
to develop the equation of state that bears his name

\[ p(\rho, T) = \frac{\rho}{\beta}(1 - \rho b) - a\rho^2 \]  \hspace{1cm} (1.3)

In equation (1.3) the positive parameters \( a \) and \( b \) are related to the attractive and repulsive parts of the potential. \( \rho \) is the density and \( \beta = 1/k_B T \), where \( k_B \) is the Boltzmann constant.

The vander Waals equation gives a good qualitative representation of the isotherm of a real fluid at high temperature. For \( T \) less than the critical temperature \( T_C = 8a/27bk_B \), however, each isotherm contains a part that has a negative slope (Fig. 3). As such the equation predicts that a decrease in pressure results in a decrease in volume of the system. Such a situation is thermodynamically unstable and can be proved never to arise from a correct statistical mechanical computation of the equilibrium pressure of a macroscopic system whose particles interact via resonable potential. Maxwell who read and appreciated vander Waals paper, interpreted parts of the isotherm at low temperatures as representing metastable and unstable states of matter. He ammended the vander Waals equation of state for \( T < T_C \) by Maxwell's equal area construction (Fig. 3). This construction is designed to make the chemical potential equal in two phases. With this amendement the vander Waals equation, with suitably chosen constants
a and b, gives a qualitatively reasonable equation of state for many fluids. It was better than some purely empirical equations of state with many more adjustable parameters.

I.B. **Correlation Functions and Integral Equations** :

We now outline steps used in obtaining a good approximation to the properties of a classical fluid. First one has to calculate the pair correlation function of the system of particles. This function is also called the radial distribution function (RDF) $g(r)$. For systems having spherical symmetry it is so defined that the expression

$$dw(r) = g(r) \frac{4\pi r^2 dr}{V}, \quad (1.4)$$

(where $V$ is the volume of the system) is equal to the probability of observing the centres of two particles spaced $r$ apart within a range $dr$ at a given temperature $T$ and a particle number density $\rho$. It is also defined, formally in the form of a multiple integral of all the system particles in the coordinate space.

$$g(r) = \left[ \frac{(v^2/2)}{N^2} \right] \frac{(N!/(N-2)!)}{v} \left\{ e^{-\beta U} \int dN^Z N^{2} \right\} $$

$$\cdots (1.5)$$

where

$$z_N = \int \cdots \int e^{-\beta U} \int d\xi N^Z_1 \cdots \xi N^Z_N, \quad (1.6)$$

$U$ is the potential energy and $\xi N^Z$ denotes $(\vec{F}_1 \ldots \vec{F}_N)$. 

However, the estimation of the multiple integrals with a realistic potential poses a formidable problem. The function $g(r)$ is normalised here so that $g(r) \to 1$ as $r \to \infty$ in a single phase fluid. This pair correlation function is related to the total correlation function $h(r)$ by

$$h(r) = g(r) - 1$$  \hspace{1cm} (1.7)

So that $h(r) \to 0$ as $r \to \infty$.

If the function $g(r,T,\rho)$ is known, then we can find the thermodynamic functions for monatomic and single component systems. There are well known exact expressions for the pressure, energy density and compressibility $^9,^{10}$.

$$p(T,\rho) = \rho/\beta - 2\pi\rho^2/3 \int_0^\infty r u'(r) g(r,T,\rho) r^2 dr$$ \hspace{1cm} (1.8)

$$\mathcal{E}(T,\rho) = 3\rho/2\beta + 2\pi\rho^2 \int_0^\infty u(r) g(r,T,\rho) r^2 dr$$ \hspace{1cm} (1.9)

$$(1/\beta)(\partial p/\partial \rho)_T = 1 + 4\pi\rho \int_0^\infty [g(r,T,\rho) - 1] r^2 dr$$ \hspace{1cm} (1.10)

In addition, the Fourier transform of the function $g(r)$ is directly connected with the intensity of the coherent scattering of X-rays or slow neutrons by the system. The scattering is, in fact, proportional to the 'structure factor' of the fluid $^9$, which is defined as

$$S(k) = 1 + (4\pi\rho/k) \int_0^\infty rh(r) \sin kr \, dr$$ \hspace{1cm} (1.11)
Thus, for simple liquids, the function $g(r,T,P)$ describes simultaneously their structure and thermodynamic properties. Therefore the main task of the theory of equilibrium properties of simple liquid is the calculation of the RDF from specified intermolecular potential $u(r)$ for all values of $T$ and $P$ from the region of existence of the liquid phase. The entire problem can be formulated in exactly the same manner for dense gases. So approximate integral equations, relating $u(r)$ and $g(r)$, have long been a corner-stone of modern theories of fluids.

It is seen that if the parameters $T$ and $P$, are specified, then the radial distribution function is uniquely determined by the function $u(r)$, and it is likely that there exists an integral equation in closed form, relating these two functions. Searches for such an equation have been going on since 1935. Kirkwood and Yvon first proposed a very simplified variant of an integral relation between $g(r)$ and $u(r)^{11,12}$. By now several such approximate equations are known, giving results with different degrees of accuracy. Integral equations in the theory of liquids are attractive as there is the possibility of obtaining analytical results concerning the structure and thermodynamic properties of simple liquids. The inverse problem, that of reconstructing the form of intermolecular potential $u(r)$ if the function $g(r)$ is known, can also be solved.
The first serious progress in the method of integral equations was made when Kirkwood\textsuperscript{13}, Bogolyubov\textsuperscript{14}, Born and Green\textsuperscript{15} proposed a nonlinear integral equation for the function $g(r)$ using Kirkwood's well known superposition approximation. The equation is

$$\ln g(r) + \beta u(r) + \int_v E(\vec{r}_1-\vec{r}) h(\vec{r}_1) d\vec{r}_1 = 0, \quad (1.12)$$

where

$$E(r) = \beta \int_\infty^r g(t) \frac{\partial u(t)}{\partial t} dt \quad (1.13)$$

An investigation of the solutions of this equation and of their thermodynamic consequences have shown that it is not accurate enough when it comes to numerical estimates of the properties of real simple liquids, but provides a correct qualitative description\textsuperscript{16,17} like the prediction of the YBG equation for critical region of a fluid. The YBG equation, however, has excited interest recently because numerical studies for three dimensions have suggested critical exponents agreeing well with experiment\textsuperscript{18,19,20}.

We discuss a second class of equations which have a somewhat more realistic basis. To do this we introduce the concept of total, direct and indirect correlation. The total correlation between two atoms may be considered to be comprised of two components: evidently there will also be direct correlation between the two particles, but
there will also be correlation on the relative position of 1 and 2 imposed via a third particle. The total correlation may therefore be written as the sum of the direct effect plus the indirect effect averaged over all possible positions of the third representative molecule, subject to its remaining directly correlated with 1. It was clearly shown through a classic paper by Ornstein and Zernike (OZ), known as OZ integral equation.

\[ h(r) = C(r) + \rho \int h(|\vec{x} - \vec{x}'|) C(\vec{x}') \, d\vec{x}', \]  

(1.14)

which may be regarded as a definition of the direct correlation function \( C(r) \). Regardless of the initially proposed meaning of the function \( C(r) \), we shall treat it as an auxiliary function. A virtue of the function is that, in many cases it is more short ranged than \( h(r) \).

Recently Kayser and Raveche have given a new derivation of OZ equation. Here the theory of inhomogeneous fluid is applied to a d dimensional system near its critical point to derive the probability of finding a particle at a distance \( r \) from a pair separated by a distance \( s \), given that \( r \gg \xi \gg s \), where \( \xi \) is the correlation length. When this result is used in the BGKY hierarchy, an approximation free equation is obtained from which it can be shown that the pair correlation for \( r \gg \xi \) satisfy the OZ equation.
In 1958, Percus and Yevic (PY)\textsuperscript{23,24} attempting to introduce collective co-ordinates proposed an important simplification to the auto-correlation function, that it can be approximated as

\[ C(r) \approx g(r) \left( 1 - e^{\beta u(r)} \right) \] (1.15)

A similar approximation frequently used is called hypernetted chain approximation is to take

\[ C(r) \approx g(r) - 1 - \ln g(r) - \beta u(r) \] (1.16)

Both approximations satisfy the general requirements with respect to the asymptotic behaviour of the functions \( g(r) \) and \( C(r) \) as \( r \to \infty \). Substituting equations (1.15) or (1.16) in the OZ equation (1.14) we obtain closed nonlinear integral equations for the function \( g(r) \), sometimes called the PY equation, and the equation of the hypernetted chain, respectively. The accuracy of the approximations can be verified and established only after solving the integral equation. In this approach, there is obviously no regular method for constructing approximations of the type (1.15) or (1.16). This arbitrariness is partially eliminated in Percus' method of functional expansions\textsuperscript{25}.

After approximate relations like PY and HNC have been proposed, interest in the OZ relation has been stimulated. Baxter\textsuperscript{26} has shown that when \( C(r) \) vanishes
Beyond a range $R$, OZ equation can be transformed so as to involve the equation for the function $h(r)$ only over the range $0$ to $R$. As an example of the utility of this result it is shown that the analytic solution of the PY approximation for hard spheres can be obtained very simply from the transformed equations. Since we have used Baxter formalism extensively it will not be out of place to give a brief review of his work.

The three dimensional Fourier transform of the OZ equation is given by

$$\tilde{h}(k) = \tilde{C}(k) + \rho \tilde{C}(k) \tilde{h}(k) \tag{1.17}$$

where $\tilde{h}(k)$ and $\tilde{C}(k)$ are the three dimensional Fourier transforms of $h(r)$ and $C(r)$ and are given by

$$\tilde{h}(k) = \int h(r) e^{i\mathbf{k} \cdot \mathbf{r}} \, d\mathbf{r} \tag{1.18}$$

and

$$\tilde{C}(k) = \int C(r) e^{i\mathbf{k} \cdot \mathbf{r}} \, d\mathbf{r} \tag{1.19}$$

From equation (1.17) it can be seen that

$$1 + \rho \tilde{h}(k) = \left[ \tilde{A}(k) \right]^{-1}, \tag{1.20}$$

where

$$\tilde{A}(k) = 1 - \rho \tilde{C}(k) \tag{1.21}$$

If the direct correlation function $C(r)$ vanishes beyond a range $R$, then the integration in equation (1.19) can be truncated at $R$. Integrating by parts and substituting the result in equation (1.21) gives

$$\tilde{A}(k) = 1 - 4\pi \rho \int_0^R \, dr \cos kr \, s(r) \tag{1.22}$$
where \( s(r) = \int_0^R dt \ t \ C(t) \) \hspace{1cm} (1.23)

For a disordered fluid the integral on the right hand side of equation (1.18) must be convergent for real \( k \).

Thus \( \tilde{h}(k) \) is finite and from equation (1.20) it follows that \( \tilde{A}(k) \) can have no zeros on the real \( k \) axis. When this is so \( \tilde{A}(k) \) can be factorised following Wiener-Hopf technique.

To outline Wiener-Hopf factorisation procedure, let us consider the behaviour of \( \tilde{A}(k) \) in the complex \( k \) plane and set \( k = k_R + ik_I \). \( \tilde{A}(k) \) is required to have no zeros on the real axis and it tends uniformly to unity as \( |k_R| \to \infty \) in any strip \( k_{10} \leq k_I \leq k_{11} \) (Fig. 4). Thus there exists a strip \( k_{1} \leq \epsilon \) about the real axis within which \( \tilde{A}(k) \) has no zeros.

As \( \tilde{A}(k) \) is a Fourier transform over a finite interval it is regular throughout the complex plane. So the function \( \log \tilde{A}(k) \) is regular within the strip \( |k_I| \leq \epsilon \) and tends to zero as \( |k_R| \to \infty \). Integrating round the strip and applying Cauchy's theorem it follows that when \( |k_I| < \epsilon \)

\[
\log \tilde{A}(k) = \frac{1}{2\pi i} \int_{-\epsilon}^{\epsilon} dk' \frac{\log \tilde{A}(k')}{k'-k} - \frac{1}{2\pi i} \int_{\epsilon}^{\epsilon + \infty} dk' \frac{\log \tilde{A}(k')}{k'-k} \]

\[
\hspace{1cm} \cdots \hspace{1cm} (1.24)
\]
FIG. 4

$\text{Im}(k)$ Plane

$Q(k)$ Regular

$\epsilon$

$\text{Re}(k)$

$-\epsilon$

$Q(-k)$ Regular

$k_{I1}$

$k_{10}$
Identifying

\[ \frac{1}{2\pi i} \int_{-\infty}^{\infty} dk' \frac{\log \tilde{\Lambda}(k')}{k' - k} = \log \tilde{Q}(k) \quad (1.25) \]

and

\[ \frac{1}{2\pi i} \int_{-\infty}^{\infty} dk' \frac{\log \tilde{\Lambda}(k')}{k' - k} = \log \tilde{Q}_1(k) \quad , \quad (1.26) \]

one can write

\[ \log \tilde{\Lambda}(k) = \log \tilde{Q}(k) + \log \tilde{Q}_1(k) \quad (1.27) \]

From equation (1.27) it follows that

\[ \tilde{\Lambda}(k) = \tilde{Q}(k) \tilde{Q}_1(k) \quad (1.28) \]

Putting \( k' = -k' \) in equation (1.26) and using the fact that \( \tilde{\Lambda}(k) \) is an even function it can be seen that

\[ \log \tilde{Q}_1(k) = \log \tilde{Q}(-k) \quad (1.29) \]

The function \( \log \tilde{Q}(k) \) is regular in the domain \( k_1 > -\epsilon \), so when \( |k_1| < \epsilon \)

\[ \tilde{\Lambda}(k) = \tilde{Q}(k) \tilde{Q}(-k), \quad (1.30) \]

where \( \tilde{Q}(k) \) is regular and has no zeros in the domain \( k_1 > -\epsilon \).

When \( |k_R| \to \infty \) within the strip \( |k_1| < \epsilon \) it follows from equation (1.25) that \( \log \tilde{Q}(k) \sim O(k_R^{-1}) \). So that \( \tilde{Q}(k) \sim 1 + O(k_R^{-1}) \). The function \( 1 - \tilde{Q}(k) \) is therefore Fourier integrable along the real axis and a function \( Q(r) \) can be defined as

\[ 2\pi \rho Q(r) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dk \, e^{-ikr} \left[ 1 - \tilde{Q}(k) \right] \quad (1.31) \]

when \( k_1 \leq 0 \), \( \tilde{Q}(k) \) tends to unity as \( k \) tends to infinity.
If $r < 0$, the integration in equation (1.31) can therefore be closed round the upper half-plane, where $\tilde{\omega}(k)$ is regular, giving $\tilde{Q}(r) = 0$ for $r < 0$ (1.32)

The analytic continuation of the function $\tilde{Q}(k)$ into the lower half plane is given by equation (1.30), that is

$$
\tilde{Q}(k) = \tilde{A}(k)/\tilde{c}(-k)
$$

(1.33)

It follows from equations (1.22) and (1.33) that $\tilde{A}(k)$ and $\tilde{Q}(k)$ grow exponentially as $e^{kR}$ when $k_I$ becomes large and negative. When $r > R$ the integration in equation (1.31) can therefore be closed round the lower half plane, giving

$$
\tilde{C}(r) = 0 \text{ for } r > R
$$

(1.34)

Inverting the Fourier transform in equation (1.31), equations (1.32) and (1.34) give

$$
\tilde{A}(k) = 1 - 2\pi \rho \int_0^R dr e^{ikR} \tilde{Q}(r)
$$

(1.35)

Using this formalism the OZ equation can be transformed into two equations, one involving $C(r)$ and $q(r)$. The transformed equations can be used to solve a variety of problems.

One can further use a mean spherical approximation (MSA) to solve OZ equation in the PY approximation. We recall that equation (1.15) is the PY approximation. For large $r$, (1.15) becomes

$$
C(r) = -\beta u(r)
$$

(1.36)
Lebowitz and Percus\textsuperscript{28} have suggested using equation \textup{(1.36)} not just for large $r$, but for all $r$ in the region where the potential is attractive. This approximation called MSA has been applied almost exclusively to potentials with hard core of diameter $R$. For such potentials, the MSA is specified by equation \textup{(1.36)} and
\begin{equation}
    h(r) = -1, \quad r < R
\end{equation}

\textup{(1.37)}
together with \textup{OZ} equation. One advantage of MSA is that it can be solved analytically for a wide variety of systems.

The term generalised mean spherical approximation (GMSA) was coined by Hoye\textsuperscript{29} et al. However, the earliest work of this type was that of Waisman\textsuperscript{30} who solved the MSA for hard spheres with a Yukawa tail and applied the solution to the hard sphere system. In the GMSA, the Yukawa tail is not a pair potential but an assumed form for the direct correlation function outside the core. The parameters are chosen to give thermodynamic consistency between the pressure and compressibility equations.

We have examined in detail four theories for the correlation functions. The \textit{PY} theory gives an analytic solution for the hard sphere problem. But the disadvantage of the \textit{PY} theory is that the equations of state obtained from virial and compressibility equations are not unique. The discrepancy becomes much more at the liquid state densities.
To give the thermodynamic consistency between the virial and compressibility equations is one of the main objectives of the present work. We will deal with this point further at appropriate places. We have also seen that the PY theory does not work well for systems with attractive forces. However, even for repulsive soft spheres, the PY theory is not satisfactory. The HNC theory, and possibly BG theory also, seem to be complement of the PY theory. It is unsatisfactory for hard spheres but accounts satisfactorily for the effect of attractive forces and nonhard core forces.

I.C. Perturbation Theories:

We shall examine some of the perturbation theories which have been developed and have received much attention in the past few years. The method which we will discuss are quite general, and can be applied to any system which is, in some sense, slightly perturbed from some reference system whose properties are known. In practice, the reference system is usually taken to be the hard sphere system. This is both because hard spheres are a good reference fluid for many liquids of interest and because there is already much data available from machine simulations for the RDF and thermodynamic properties of hard spheres.

We must mention the perturbation theory by Weeks, Chandler and Andersen which is more refined. They have
obtained a nonlinear integral equation for a normalised potential \( \xi(r) \) that is very similar in structure to the integral equation in the PY approximation for hard sphere. In the simplest version of their scheme, called the exponential approximation, \( g(r) \) is obtained from \( \xi(r) \) through

\[
g(r) = g_0(r) \xi(r) \tag{1.38}
\]

At low densities \( \xi(r) \) goes to \( u_1(r) \), but at large fluid densities it is smaller and has a shorter range than \( u_1(r) \). In particular, if \( g(r) \propto g_0(r) \), which is true for large fluid densities, then \( \xi(r) \) vanishes. The exponential approximation and the corresponding thermodynamic functions, are found to give an accurate description of the dense single phase Lennard–Jones fluid. In fact, for \( \rho R^3 \gtrsim 0.65 \) the radial distribution function is within the experimental accuracy of computer experiments.

The reason for this partial success of the perturbation theory of liquids is that the structure of the simple liquid is determined primarily by the hard core part of the potential. The nonhard core part of the potential is supposed to provide a weak perturbation, which is treated either in a straightforward expansion or in some self consistent scheme.
I.D. **Cell and Cell Cluster Theory:**

Among the earliest theories of liquids were 'cell' or free volume theories which were based on the intuitive idea that a molecule in a liquid is essentially confined to a cell or a cage formed by its neighbours. If the molecules were regarded as moving independently in their cells this led, for hard spheres, to an expansion for the canonical configuration integral of the form

\[ C_N = v_f^N, \]  

(1.39)

where \( v_f \) is the free volume available to a single molecule moving in its cell. Much of the early development of these ideas, including the inclusion of the effect of attractive forces and of empty cell or vacancies, was done by Eyring and his collaborators. Since that time, Eyring and a number of collaborators have developed these ideas into the 'significant structures theory of liquids' in which the liquid is regarded as a mixture of solid like and gas like degrees of freedom. The aim of this theory is to predict the properties of liquids on the basis of the known properties of the corresponding solids and gases, without explicit reference to intermolecular forces. The theory correlates a very wide range of properties of wide range of liquids.

Because of additional freedom, gas molecules are said to have 'communal entropy' not possessed by molecules in a
crystal. The liquid state is intermediate in nature, and it is not at all obvious to what extent the liquid state possesses communal entropy. Originally, Hirschfelder, Stevenson and Eyring\textsuperscript{34} assumed that the liquid state had essentially the complete communal entropy and that the communal entropy therefore appeared on melting as a large part of the entropy of fusion. This view was later criticized by O.K. Rice\textsuperscript{35}. So the situation with regard to communal entropy in the liquid state still remains obscure. Nalk and Mishra\textsuperscript{36} have used the "significant structures theory of liquids" and have made an effort to solve the problem of communal entropy of liquids. Their result shows that the communal entropy gradually appears in the liquid state and satisfies the limiting cases nicely.

There have been a number of attempts, until recently relatively unsuccessful, to use the cell concept as a basis of the theory relating dense fluid properties directly to intermolecular forces. Most of this work was based on the formulation of the cell model by Lennard-Jones and Devonshire\textsuperscript{37,38}. The most important formal development was the idea of a cell cluster expansion, introduced independently and in somewhat different forms by de Boer\textsuperscript{39}, Barker\textsuperscript{40} and Taylor\textsuperscript{41}. There was one difficulty in the LJD theory to explain the equilibrium properties of simple liquids. It was because of the fact that it only employed 6-12 potential.
It was later suggested to use a deeper and steeper potential for better correspondence with experiment. Naik and Mishra\textsuperscript{42} used a temperature and density dependent potential in the LJD theory which works quite well for the equilibrium properties of liquid hydrogen.

The recent work of G. Stell\textsuperscript{43} points up the fact that even the most successful theories are incapable of yielding the correct equation of state of simple liquid via the compressibility relation or virial theorem. It confirms that we still do not have reliable insight into the equilibrium state of a simple fluid.

The plan of the thesis is now as follows. In chapter II, entitled, "Statistical Mechanics of one Dimensional fluid" we have solved OZ equation in one dimension using PY approximation. The theoretical technique essentially consists of Wiener-Hopf factorization procedure. The Laplace transform of the RDF is obtained. In the vander Waals limit it agrees nicely with the classical results of Kac et al\textsuperscript{6}, as well as with the results of Lebowitz et al\textsuperscript{7}, to the desired order. The striking feature of our deduction is its unusual simplicity and elegance.

In chapter III a novel approximation scheme is formulated in which the intermediate function $Q(r)$ is extended beyond
the hard core instead of the direct correlation function $C(r)$ in three dimensions. This formulation has the advantage that the pair correlation functions of hard sphere are evaluated in an exact way and the discrepancy of the virial and compressibility equation of state is removed.

The structure function of simple dense fluids like neon and argon are evaluated following the suggested method of calculation in chapter IV. The results agree nicely with the X-ray diffraction data of Aisenstein and Gingrich for liquid argon and neutron diffraction data of de Graaf and Moser for liquid neon. The significant result is the nice agreement with experiment both in the low as well as high $k$ region. The direct correlation function and shape of the potential are illustrated.

We conclude in chapter V where we mention some of the merits of the proposed formalism. It can be applied to the calculation of correlation functions, structure and potentials of polyatomic liquids and one component plasma as well.