Chapter - 1

Introduction

1.1 The Liquid State:

The liquid state exists within a very small temperature range. Amongst the four states of the matter, the solid and the gaseous states, have been extensively studied over a long time, firstly due to the simplicity of the microscopic behaviour and mainly due to the technological application. The liquid state has received a comparatively lesser attention and it is only in recent years that the study of the liquid state has received a real impetus due to the realization of a vanishing border lines between the solid-liquid or liquid-gas states.

It is usually said that Liquid state is intermediate in its properties between a solid and a gas. This statement should not be taken to consider that every property of a liquid is intermediate in value between those of the other two states. If the numerical values are compared, it is found that in a great majority of cases, the value of the coefficient representing a property of a liquid is quite close either to that of the solid or to that of the gas. The behavioural intermediateness then, is a statistical one. Liquid has some of the properties of a solid, and some others of the corresponding gas.

Forces between molecules are the short range forces which act through a distance of only 2 to 3 molecular diameters. In the gas these forces are of little importance. Any regular arrangement of the molecules is destroyed by thermal motion of the molecules and the usual assumption that the molecules of a gas are arranged in space at random is justified.

The theory of liquid state has not yet attained a respectibility of the theory of gases or the theory of crystalline solids on account of the intrinsic difficulty of an adequate description of liquids. In the theories of solid and gaseous states one property predominates, whether it be the kinetic energy of freely moving molecules in a gas or lattice vibrations in crystals, other factors like the finite size of molecules in gases
or the holes in crystals can then be treated as perturbations. In the theory of liquids by contrast free molecule and holes have both to be taken into account. This complication both the ideas and the calculations.

1.2 Molecular Packing In Liquids:
In a solid, the close packed arrangement of the molecules prevents any molecule from moving far from its original position, resulting in the rigidity of the crystal. The low compressibility of the solid is due to the fact that there is no free space between the molecules, so that any compression must be accomplished only by reducing molecular size themselves. If the liquid maintains the solid like molecular arrangement it is difficult to explain its fluidity. The molecules are packed so close together that an inside molecule may not change its position more than the molecule of the solid can does. The only conceivable way in which flow could take place would be by the simultaneous displacement of a whole plane of molecules. Such a motion requires simultaneous lengthening of a large number of intermolecular spaces and requires a large energy of activation for flow process to occur. To avoid this difficulty it is assumed that only a few molecules move at a time, and that it must be relatively easy for molecules to get displaced from the regular lattice.

1.3 Diffraction Of X-rays In Liquids:
The x-ray diffraction pattern of a liquid is a series of light and dark rings. This pattern, can be used to calculate the radial distribution of atoms surrounding a representative atom. The reassemblance between the liquid radial density curve and the solid structure is very striking and it is evident that the liquid structure must be a rather irregular version of the solid structure at least over distance of the order of a few atomic diameters.
1.4 Short-Range And Long-Range Order:

The regularity exhibited by atoms in a crystal is referred to as a long range order, wherein the positions of molecules, many diameters away from a central molecule, can be predicted from knowledge of the positions of the central molecule and the molecules immediately surrounding it. In a liquid, this long range order disappears. Nevertheless, since the arrangement of the molecules immediately surrounding the central atom is reasonably definite we can say that the liquid still possesses short range order. The crystal has a short range order as well as a long range order, but in the gas phase even the short range order disappears. The melting of a crystal therefore is accompanied by the disappearance of the long range order, and the evaporation of a liquid is accompanied by a disappearance of short range order.

1.5 The Loose Packing of Rigid Molecular Spheres:

The results of X-ray diffraction establish another important characteristic of the liquid structure. The area under the first peak in radial distribution function indicates the number of neighbours to be smaller than that in the crystal at or near this distance. There are thus definite gaps in the packing of the atoms. It is obvious that the fluidity of liquid depends directly on their presence. It should be noted that the decrease in density in the melting process is only partly accounted for by hole formation. The remainder arises from the increase in the average distance between nearest neighbours.

Many of the features of liquids are shown by a simple collection of rigid spheres. If the spheres are packed carefully to make the volume occupied, a minimum, then a regular crystal like lattice is formed. But if the volume available to the spheres is greater than that required for close packing, the regularity of structure will disappear. This has been demonstrated in two dimensions by Menke\(^2\) who studied distribution
of spheres and other objects distributed on a flat surface. The three dimensional problem has been studied experimentally by Morvel\textsuperscript{3} by suspending hard gelatin spheres in a solution of same density. These experiments gave radial distribution curves which were extremely close to those obtained by X-ray diffraction in liquids. Frenkel\textsuperscript{4} considered the problem in one dimension. It has not yet been possible to derive an exact form for the radial distribution function for three dimensional loose-packing of spheres. In spite of its approximate nature, Kirkwood\textsuperscript{5-6} has given results in good agreement with experiment.\textsuperscript{7,8}

1.6 Theoretical Work On Liquid State and Importance Of Model Approach :

Almost all the theoretical work on liquids has been done on simple idealized liquids, for example liquid rare gases and liquid metals. These ideal liquids consists of monoatomic molecules possessing radially statistically symmetric potentials, attractive at large and repulsive of homopolar or hydrogen bond nature, in a particular directions.

All theories of liquids developed so far make approximations at some stage of their development. The pair distribution method is essentially an extension of the statistic al mechanical theories of gases to liquids. These start of rigrously and then approximates in both mathematics and interatomic potentials are introduced in order to solve the complex integral equations which are deduced. The method works for low density fluids. The solid like theories (the cell, free volumes, or partition function methods) make their approximations at the beginning by postulating a particular solid like lattices and disordering it by introducing vacancies or dislocations. These fit best at high densities i.e. for small cell.

Until the theory based on distribution function reaches a form in which precise limits on the errors can be specified, there will always be role for adhoc models of liquid state. Such models are likely to be helpful for liquid with non-simple molecules.
Quite a number of such models have been proposed. The mathematics of some of these models are relatively simple as compared to that of the distribution function. The study of these models assists physical insight into the liquid state.

1.7 Hole Theory Of Liquids :

The Lattice theories of liquid state require a molecule to be more or less bound to one position in space. This is, in opposition to the view-point of the gas kinetic theories where the molecule has an almost complete freedom of motion. Once a molecule is restricted to a relatively small volume, the analysis can be simplified considerably, since in the first approximation, only the nearest neighbourhood be considered. However, the concept of 'holes' i.e. vacant sites in the lattice is required to account for the fluidity of liquids and the theory based on this model is usually referred to as the hole theory.\(^9\)\(^,\)\(^10\)

The hole theory treats a liquids as an imperfect solid. The previous theories of the liquid state considered liquid as an imperfect gas. The fact that a liquid can be converted reversibly into a gas without passing at any time through a region in which two phases are present, by simply heating the liquid under pressure to a temperature above its critical point and then allowing it to expand, is a cogent reason for believing that the liquid is somehow gaslike in structure. It seems difficult to reconcile such widely different models of liquid structure, and as a matter of fact, the reconciliation has been made only by modifying the theory of imperfect gases in a direction which gives even the gaseous state a resemblance to the solid.

Mayer\(^11\) has shown that in practically every respect the actual properties of a gas are those of an ideal gas composed of single molecule, double molecules, triple molecules, and so on. The total number of molecules in this equivalent ideal gas is a sum of all multiplets. The only extraordinary feature of the
equivalent ideal gas is that the number for some varieties of molecules are negative. It has also been shown that the clusters obey the mass action law, except, that negative values of the equilibrium constant are possible.

Mayer’s theory predicts the phenomenon of condensation. Its usefulness, however, depends on the possibility of evaluating the equilibrium constant. The calculation of those constants in terms of the intermolecular forces is a problem of great mathematical difficulty, but nevertheless much progress has been made towards its solution. In particular, the relationships are known between the \( b \) and the virial coefficient \( A_k \), in the equation,

\[
pV = RT \left( 1 + \frac{A_1}{V} + \frac{A_2}{V^2} + \frac{A_3}{V^3} + \ldots \right) \quad \ldots 1.1
\]

Which has been used as an empirical equation to describe the pressure-volume relationship, for gases at moderate pressures. It is also known that the phenomenon of condensation is not determined primarily by the early terms in this series, but by the later ones. There is no justification for trying to express the properties of liquids in terms of an equation of state extrapolated for low pressure. The failure of such equations of state as that of van der Waals’ to give good results for condensation phenomena is well known.

1.8 The Perturbation Theories of Liquids:

The perturbation theory of liquids considers the structure of a liquid in terms of hard core part of potential and that the main effect of the nonhard core part of the potential is assumed to provide a uniform background potential in which the molecules moves.

The concept has been used for some time. It is the basis of van der Waals’ equation of state,

\[
\left( p + \frac{N^2a}{V^2} \right) [V - Nb] = NkT \quad \ldots 1.2
\]
This gives results which are in poor agreement with the experimental data. The situation can be improved by regarding \('a'\) as a parameter chosen to fit some experimental data. However, the results are still unsatisfactory.

The application of Scaled Particle Theory to fluids with attractive forces indicates that liquids may be regarded as hard spheres in a uniform background potential\(^{12-14}\) and the main defect in the van der Waals' theory lies in the use of equation,

\[
\frac{A^0}{NkT} = 3 \log \lambda - 1 \log V_f + \log N \quad \ldots. 1.3
\]

where \(V_f = V - Nb\) \ldots. 1.4

for the hardsphere free energy. Thus, if equation 1.1 is replaced by

\[
\frac{p}{p_0} = \frac{N^2 a}{V^2} \quad \ldots. 1.5
\]

and some more reliable expression for \(p_0\) is used, then a good agreement with experimental results is obtained\(^{15}\). However, the LHW equation of state is fairly insensitive to the precise form of \(p_0\). In fact, good results could be obtained\(^{14}\) by replacing the van der Waals' expression,

\[
\frac{p_0 V}{NkT} = (1 - 4n)^{-1} \quad \ldots. 1.6
\]

\[
\frac{p_0 V}{NkT} = (1 - n)^4 \quad \ldots. 1.7
\]

where \(n = \left\lfloor \frac{n}{6} \right\rfloor \rho \, d^3\) \ldots. 1.8

\[
\frac{\pi d^3}{6} \quad \text{is the volume of a hard sphere and \textquoteleft}\textquoteleft a\textquoteright\textquoteleft\ is a parameter chosen arbitrarily. The value of \textquoteleft}\textquoteleft a\textquoteright\ results from equation 1.8.

\[
a = - 2\pi \int_0^\infty u_1(r) \, r^2 \, dr \quad \ldots. 1.9
\]
\( u(r) \) is the potential energy given by,
\[
    u(r) = \infty, \quad r > \sigma \\
    = u_{\perp}(r), \quad r < \sigma
\]
\[\text{......1.10}\]
which is quite different from that required to fit experimental data.

The work of LHW\textsuperscript{13}, Reiss\textsuperscript{12} and others\textsuperscript{14} indicates that hard-sphere fluid is an excellent reference system for the study of properties of liquids (even at the lowest temperatures).

1.9 Molecular Interaction Techniques For Study Of Liquids:

The role of intermolecular interactions in various theories of the liquid state is expressed as a potential. The aim of any approach to an understanding of the liquid state requires as much information as possible about the atomic or molecular interaction in a liquid as a first step towards the construction of a potential function. The molecular interactions manifest through a variety of phenomena e.g. molecular association, complex formation etc.

The study of molecular interactions in liquid provides valuable information about internal structure, molecular association, formation of macromolecules, internal pressure etc. The various experimental methods available to study these parameters are NMR, Microwave, U.V. and I.R. Spectroscopy, Neutron/X-ray scattering and Ultrasonics. The NMR technique reflects effect on the proton bearing molecules while microwave absorption provides information through dielectric constant. On the other hand Neutron/X-ray scattering help in the study of molecular motion. The spectroscopic techniques provide useful information of intermolecular interaction, when interaction energies involved are larger, as such weak molecular interactions can not be resolved from the observed spectra. The ultrasonic
techniques however, reveal weak intermolecular interaction. This is possible because of its useful wavelength range. The ultrasonic parameters are known to be directly related to a large number of molecular and thermodynamic parameters. Since various liquid state theories are based on thermodynamic considerations, the ultrasonic parameters provides a means to study them.

1.10 Some Important Ultrasonic Parameters In Liquids:

A. Ultrasonic Velocity \( (u) \) And Adiabatic Compressibility \( (\beta_a) \)

Ultrasonic studies have proved to be of immense utility in understanding the molecular behaviour in the liquid state. The two important parameters as regards ultrasonic waves are their velocities and absorption coefficients. The velocity of a ultrasonic wave in a liquid is given by,

\[
u^2 = \left[ \frac{\partial P}{\partial \rho} \right]_s \quad \ldots \ldots 1.11
\]

The adiabatic compressibility \( \beta_a \) therefore may be evaluated if density \( \rho \) and velocity \( u \) in the medium is measured as,

\[
\beta_a = \frac{1}{\rho u^2} \quad \ldots \ldots 1.12
\]

Beginning in 1938, Parthasarathy\(^{16}\) evolved number of empirical rules for the variation of u.s. velocity in different homologous series and different organic groupings. The ultrasonic velocity in aromatic compounds was found to be higher than in corresponding aliphatic compounds. The substitution of a heavier atom in a given organic molecule has been found to decrease the ultrasonic velocity. Since number of inconsistencies developed from some of these rules, no general quantitative formulation was possible.

B. Rao Constant: Rao\(^{17}\) in 1940 observed that the ratio of
the temperature coefficient of the velocity \( \left( \frac{du}{dT} \right) \) to the 
expansion coefficient \( \alpha = \left( \frac{dV}{dT} \right)/V \) is practically the same for 
all unassociated organic liquids and gave the following empirical rule,

\[
V \cdot u^{1/3} = R \tag{1.13}
\]

Where \( V \) is the molar volume, \( u \) is the molar sound velocity, \( R \) is a constant for a given liquid. Rao observed value of \( R \) to undergo regular increment among members of a homologous series of 
liquids. For a series, it was possible to express \( R \) as a linear 
function of the molecular weight i.e.

\[
R = a \cdot M + b \tag{1.14}
\]

where the constants \( a \) and \( b \) characterize a particular series.

C. **Wada Constant**: Wada\(^{18} \) has introduced, a quantity molecular 
compressibility or Wada Constant given by,

\[
W = \left( \frac{M}{\rho} \right)^{1/2} \beta_a^{-7} \tag{1.15}
\]

\( W \) being independent of temperature.

D. **Acoustic Impedance**: Impedance offered by a liquid to the 
propagation of ultrasonic wave is given by,

\[
Z = \rho \cdot u \tag{1.16}
\]

where \( \rho \) is the density and \( u \) is the u.s. velocity in the medium.

E. **Relative Association**: Relative association is given by,

\[
R.A. = \left( \frac{\rho}{\rho_0} \right) \left( \frac{u_0}{u} \right)^{1/3} \tag{1.17}
\]

where \( \rho \) and \( u \) are density and velocity at a given 
temperature and \( \rho_0 \) and \( u_0 \) are the density and velocity at \( 0^\circ \text{C} \).
1.11 Ultrasonic Velocity And Molecular Packing In Liquids:

If B is the effective volume occupied by the molecules in a mole of a liquid, then it can be related to the van der Waals' 'b' by the equation

\[ b = 4B \] ....1.18

Schaaffs introduced space filling factor \[ r = \frac{B}{V} \] i.e. the fraction of the total molar volume actually occupied by the molecules. Thus r is the same as the packing factor S. Debye pointed out that the quantity B is precisely equal to the molecular polarization, also known as molecular refraction \((M_R)\). This later quantity is obtainable independently from the law of Clausius-Mosotti as,

\[ M_R = \frac{M}{\rho} \left( \frac{a^2 + 1}{n^2 + 1} \right) \] ....1.19

where n is the index of refraction, usually for the sodium D line. Schaaffs then noted that the product \(u \cdot V\) was a simple function of \(M_R\) (or B) at least for substances formed from H, N, O and C. We therefore have,

\[ u = W \left( \frac{B}{V} \right) = W \cdot r \] ....1.20

Where W is a constant approximately equal to 5000 m.s. Physically, W represents the u.s. velocity when the entire volume of the space is filled with molecules. It is reasonable therefore that this number (W) is of the order of u.s. velocities in solids.

Analysing propagation of u.s. wave through loosely packed medium \((S < 1)\) in terms of a simple model which picturizes the molecules as rigid billard balls following expression for velocity in a liquid is obtained.

\[ u_{\text{liquid}} = \left( \frac{L}{L_f} \right) V_m = \left( \frac{L}{L_f} \right) \left( \frac{3P}{\rho} \right)^{1/2} \] ....1.21
\[ u_{\text{Liquid}} = \left( \frac{L}{L_f} \right) \left( \frac{3}{r \text{ gas}} \right)^{1/2} u_{\text{gas}} \quad \ldots \ldots 1.22 \]

Where \( L \) is average distance between the centres of the molecules, \( L_f \) the free path-length between their surfaces and \( V_m \) the gas kinetic velocity. The distances \( L \) and \( L_f \) are directly related to the free volume \( V_a \) and the molar volume \( V \). For relatively dense packing (\( L > L_f \))

\[ \left( \frac{L}{L_f} \right) = 3 \left( \frac{V}{V_a} \right) = \frac{3}{(1-S)} \quad \ldots \ldots 1.23 \]

using \( r = 1.4 \) equation 1.19 can be written as.

\[ u_{\text{Liquid}} = 4.3 \frac{u_{\text{gas}}}{(1-S)} \quad \ldots \ldots 1.24 \]

This establishes the importance of the packing factor for the ultrasonic propagation in liquids. Experimentaly it is found that \( u_{\text{Liquid}} \) is 5 to 10 times the velocity in the vapour at the same temperature. The magnitude of packing factor is thus found to be between 0.15 and 0.55. The measured u.s. velocities therefore reveals a large influence of the molecular shape on the degree of packing.

In an associated liquid, one may expect the ratio \( \left( \frac{dV}{dp} \right) \) in a u.s. wave to increase as the temperature is lowered. A compression will thus lead to a more orderly alignment of adjacent molecules. This would require less space than for a random packing. Since the adiabatic compressibility \( \beta_a \) is defined as \( \frac{d(\log V)}{dp} \), the u.s. velocity \( u = \frac{1}{(\beta_a \rho)^{1/2}} \) would become smaller as the temperature decreases. For non-associated liquid on the other hand, Rao’s empirical relationship holds over a wide temperature range.\(^{26,27}\)

The conclusions which can be drawn from the simple model of a liquid composed of rigid balls which are packed in a
characteristic way may be stated as follows. The time required for the transfer of momentum from molecule to molecule in a u.s. wave is directly proportional to the mass of the molecule, the distance \( L_f \) between the molecule, and is inversely proportional to the molecular volume. Among these three causes for a change in u.s. velocity, the later two are of primary importance.

1.12 Phase Change Phenomenon

The liquid in some respects resembles to a solid while in others it behaves more like a gas. These similarities will be most apparent for the liquid state in the neighbourhood of the respective phase transition point. At the temperatures at which a phase change occurs, there are discontinuities in the thermodynamic properties of a medium. Since ultrasonic propagation is also a function of these properties, it is expected that a ultrasonic investigation of a medium undergoing a phase change would yield useful information on its structural parameters and on the characteristics of the phase transition itself. Measurements of ultrasonic wave velocity and u.s wave absorption and its pressure and temperature coefficients may prove particularly useful for the analysis of phase transitions which take place during polymerization of plastics, in thixotropic changes of colloidal systems and in the crystallization of amorphous substances. Kor and Bahadur have done pioneering work in this field.

1.13 Concept of Free Length In Liquid:

Jacobson introduced the concept of intermolecular free lengths, to explain the ultrasonic velocity in pure liquids and liquid mixtures. He established a semiempirical relation for the intermolecular free lengths.

\[
L_f = 2 \frac{V_s}{Y}
\]

......1.25
Where $Y$ is the surface area per molecule and $V_s$, the available volume defined as $V_s = V_T - V_o$. $V_T$ and $V_o$ are the volume at a given temperature $T$ and $0^\circ$K respectively. $L_f$ for pure liquids can be calculated using Jacobson’s relation,

$$L_f = \frac{K}{(u_{\text{exp}} \rho_{\text{exp}})^{1/2}}$$

.....1.26

The concept of free length was extended to a liquid mixture and the free length $L_{mix}$ is expressed as

$$L_{mix} = 2 \left[ \frac{V_m - (X_A V_A^A + X_B V_B^B)}{X_A Y_A + X_B Y_B} \right]$$

.....1.27

$X$’s and $V_o$’s represents respectively the mole-fraction and volume at absolute zero respectively. $V_m$ stands for molar volume of the mixture, $Y_A$ and $Y_B$ are the surface area per mole of component $A$ and $B$ of the mixture and can be calculated from the relation,

$$Y = 36 \pi (M V_o^2)^{1/2}$$

.....1.28

$V_o$ can be evaluated using the expression,

$$V_o = V_T \left( 1 - \frac{T}{T_c} \right)^{0.3}$$

.....1.29

Where $V_T$ and $T_c$ are molar volume at temperature $T$ and critical temperature respectively. Thus u.s. velocity can be computed from relation 1.23.

Schaaffs on the basis of collision factor theory developed the following formula for u.s. velocity in pure liquids.

$$u = u_o \cdot S \cdot r = u_o \cdot \frac{B}{V}$$

.....1.30

Where $u_o = 1600$ m/s, $S$ = collision factor, $r = \frac{B}{V_m}$ i.e. space filling factor. For a mixture the u.s. velocity may be obtained as,
\[ u_{\text{mix}} = u_\infty \left( \frac{Y_A S_A + Y_B S_B}{V_M} \right) \left( \frac{Y_A B_A + Y_B B_B}{V_M} \right) \]  

......1.31

The volume occupied by the molecules per mole (B_A and B_B) for pure components may be calculated using the relation,

\[ B = \left( \frac{4\pi}{3} \right) r_m^3 N \]  

......1.32

where \( r_m \) stands for molecular radius and \( N \) is the avagadro number.

\( B \) can be calculated using the average value of \( r \) obtained from following expressions due to Schaaufs' and Gopala Rao\(^{16}\)

\[ \gamma_{(\text{Schaaff})} = \alpha \left[ 1 - B \left( \left( 1 + \frac{1}{3B} \right)^{1/2} - 1 \right) \right] \]  

......1.33

and

\[ \gamma_{(\text{Rao})} = \alpha \left[ 1 - B \left( \left( 1 + \frac{1}{B} \right)^{1/2} - 1 \right) \right]^{1/3} \]

where \( \alpha = \left( \frac{3V}{16\pi N} \right)^{1/3} \)

\[ B = \left( \frac{\gamma RT}{(MV^2)} \right) \]  

......1.34

\( \gamma, R, M \) and \( V \) stand for specific heat ratio, gas constant, molecular weight and molar volume respectively.

Surface area \( Y \)'s and collision factor \( S \)'s of the molecules of pure liquids components are the two adjustable parameters in F.L.T. and C.F.T. respectively and these can be evaluated from experimental u.s. velocity using equations \([1.28, 1.29]\) and \([1.33]\).

### 1.14 Experimental And Theoretical Ultrasonic Work : A Review

Ultrasonic parameters are being extensively used to
study molecular interactions in pure liquids and liquid mixtures\textsuperscript{37,38}. Early work on the non linear behaviour of the ultrasonic velocity versus concentration curves in different liquid mixtures have been reported by a number of workers\textsuperscript{39-44}. The empirical relation due to Nomoto\textsuperscript{45} and the ideal mixing relation\textsuperscript{46,47} for ultrasonic velocity have been successfully used to investigate the thermodynamic and acoustical behaviour of binary liquid mixtures. Interactions in binary liquid mixtures have been studied by Rastogi\textsuperscript{48}, Jain\textsuperscript{49}, Hyderkhan\textsuperscript{50}, Hughes\textsuperscript{51}, Halzhauer\textsuperscript{52}, Delmos\textsuperscript{53}, Sheshadri\textsuperscript{54}, Naidu\textsuperscript{55}, Tabhane\textsuperscript{56-58} and others\textsuperscript{59} from the knowledge of excess thermodynamic functions and some acoustical parameters.

Westwater\textsuperscript{60} and Hildebrand\textsuperscript{61} pointed out that for a number of pure liquids the relation,

\[
a = V^2 \left( \frac{dE}{dV} \right)_T
\]

where 'a' is the van der waals' parameter which to a high degree of approximation be equated to TV\textsuperscript{2}, was almost constant over a limited range of temperature. This means that over this range the energy can be represented by the simple expression,

\[
E = -\frac{a}{V}
\]

\text{.....1.35}

The constancy of TV\textsuperscript{2} has been tested for extended range of temperature for pure liquids and their mixtures\textsuperscript{62}.

Adgaonkar\textsuperscript{63} studied the hydrogen bonded complex formation in a number of binary liquid mixtures. The formation of a complex is indicated by a peak in velocity versus concentration curve and a corresponding dip in the compressibility curve.

Many attempts\textsuperscript{64-69} have been made to evaluate the u.s. velocities in pure and binary liquid mixtures from Jacobson free length theory and Schaaffs' collision factor theory. While the discrepancy between the theoretical and experimental values of free length in case of pure liquids is large, it is less in case of liquid mixtures. Attempts have also been made\textsuperscript{70,71} to evaluate free lengths for ternary systems.
When the value of experimental and theoretical free lengths are compared, significant discrepancies between them are observed. An important reason for these discrepancies is that in calculating $Y$, the surface area, molecular association effects are not taken into account. Hence a comparison of $L_f$ (experimental) and $L_r$ (theoretical), would be of help in determining the association factor which for a pure liquid indicates the degree of self association. The associated molecular cluster is the result of a correlated behaviour of molecules in a liquid. The correlation being brought about mostly through hydrogen bond formation. In analogy with the quasiparticle behaviour of an electron gas exhibiting correlated motion of the electrons, an associated molecular cluster in a liquid may be called a quasi molecule or a pseudo molecule.

Study of ultrasonic absorption in pure liquids and liquid mixtures by interferometer method and applicability of Bauer-Sette theory has been studied by Rath. Ultrasonic absorption $\alpha/f^2$ studies in pure liquids dichloromethane, benzene, nitrobenzene, carbon tetrachloride, chloroform & 1,2-dichloroethane and liquid mixture like dichloromethane + benzene and dichloromethane trinitrobenzene at a fixed frequency 5 MHz has been measured. Recently Sabesan successfully described apparent molar volume obtained in molal and molar scale. The apparent molar volume has been computed from the values of volumes of the compressed water molecules that surround the solute ion. Values obtained by both the procedures are compared by them. The ultrasonic velocities have been calculated using the experimental surface tension and density data from Auerbach relation by Rajendran. The excess acoustic impedance, isentropic compressibility, free volume and internal pressure values have been used to discuss the existence of molecular interaction in the mixture of acetic acid with alkyl and benzyl alcohol.

1.15 Remarks:

The present theories of liquids are however inadequate to
comprehensively account for the experimental manifestations of molecular interactions in various ultrasonic processes. It is obvious that the intermolecular interaction potential for a liquid would require for its full description, the knowledge of at least dipole-dipole interactions, the collision factors, the hydrogen bond forces and the relative strengths of various interactions such as homomolecular (AA and BB) and heteromolecular (AB) interactions in a mixture of A and B liquids.

1.16 Orientation of The Present Work:

Many attempts\(^{39-44}\) have been made to investigate behaviour of pure liquids, binary and ternary\(^{75}\) liquid mixtures, liquid crystals\(^{76}\), polymers\(^{77}\), electrolytic solutions\(^{78}\) and wide range of thermodynamic data has been evolved. However, less attention has been given towards studying \(\alpha,\beta\)-unsaturated carbonyl compounds, which by themselves are interesting class of compounds with may applications in industry and bio-technology. It was in the recent years that ultrasonic investigation of these compounds has been taken up in this laboratory and attempts are being made to study their behaviour in different molecular environment. Study of representative carbonyl compounds viz. acrylonitrile, and methylmethacrylate in mixture with p-dioxane, cyclohexane and methyl alcohol was therefore proposed to be taken up for investigation.

Molecular interactions of the acrylonitrile and methylmethacrylate in mixture with a nonpolar liquid p-dioxane cyclohexane and a polar liquid methylalcohol has been studied. The binary liquid mixture systems investigated consisted of acrylonitrile + p-dioxane, acrylonitrile + cyclohexane, acrylonitrile + methyl alcohol, methylmethacrylate + p-dioxane, methylmethacrylate + cyclohexane and methylmethacrylate + methyl alcohol respectively. The relative orientation of molecular groups in a molecule containing different atoms, is expected to play an important role in the interaction of these molecules with other polar and non-polar molecules of a liquid. Earlier work has been
found to be directed in predicting ultrasonic velocities on a variety of liquids and compounds, using one or the other molecular interaction models employing some empirical constants. Among the various molecular interactions models the Flory’s theory\textsuperscript{79} and scaled particle theory\textsuperscript{12} have been most popular\textsuperscript{80,81}. While Flory theory is a solute-solvent interaction model the scaled particle theory is a single solute interaction model. Flory’s theory is known to be applicable to long chain molecules polymers and is a three parameter (pressure, volume and temperature) scaling theory while scaled particle theory is a single parameter (hard sphere diameter) scaling theory. The literature reveals\textsuperscript{83-92} various equation of state to predict thermodynamic parameters of variety of pure liquids and binary liquid mixtures. It was, therefore, thought worthwhile to apply single scaling parameter Scaled Particle theory to binary liquid mixture systems under investigation and compare the results with those derived from application of Khasare’s multiparameter scaling molecular interaction model\textsuperscript{82} (hard sphere diameter and minimum depth of Lennard - Jones potential).

The present study is an attempt to test Khasare’s molecular interaction model by applying it to the systems under investigation as regards its data reproducibility. The results are compared with Scaled Particle Theory, which is a theory based on molecular dimensions, in predicting u.s. velocity and the nature of molecular interaction in these pure liquids and their binary liquid mixtures. A software in Basic has been written to run on Computer Model PC/XT for evaluating theoretical thermodynamic data. The experimental data has been generated by measuring u.s. velocity at 2 MHz and density in these pure liquids and their binary liquid mixtures by employing ultrasonic interferferometer and hydrostatic plunger method respectively. The result of data investigation along with the relevant discussion is presented in this thesis.