CHAPTER 1
ARRANGEMENT OF ATOMS IN LIQUIDS

CHAPTER OVERVIEW

Section 1.1 gives an introduction to the arrangement of molecules in solids, gases and liquids. Section 1.2 gives a comparative study of X-ray scattering curves for the three phases of matter. Section 1.3 discusses various models proposed for the structure and dynamics of the liquid state. Section 1.4 introduces various intermolecular forces in liquids. Section 1.5 gives the importance of hydrogen bonding. Section 1.6 explains the various phase transitions in liquids. Section 1.7 introduces associated and un-associated liquids.

1.1 INTRODUCTION

Three different phases of matter are familiar to us – solid, liquid and gas. Liquids and gases flow while a solid under normal conditions does not. A solid retains its shape while a fluid (a collective name for gases and liquids) takes the shape of the containing vessel. In other words a solid is rigid while fluids do not possess the property of rigidity.

The same material can exist either as a solid, a liquid or a gas under different conditions of temperature and pressure. This is a matter of common observation. For example, when water, which is a liquid at room temperature, is cooled below 0°C at atmospheric pressure, it becomes solid ice. Heating water to 100°C at atmospheric pressure converts it to steam. Such a transition of matter is called a phase transition.
The kinetic theory explained the properties of gases in terms of molecular motions. The molecules in a gas are moving around randomly with velocities governed by the Maxwellian distribution. In this theory the pressure exerted by a gas is related to the average kinetic energy of a molecule, which is proportional to its temperature. If inter-molecular interactions are neglected and the molecules are taken as point particles, the kinetic theory of gases leads to the Boyle’s and Charles’ laws. To account for deviations from these laws one had to invoke inter-molecular attraction as well as the finite size of the molecules. Thus was born the Van der Waals equation, which, in a sense, represents the behaviour of actual gases over a wide range of pressure and temperature.

Because the molecules have a finite size the inter-molecular interaction must be a strong repulsion when the inter-molecular distance is of the order of the diameter of the molecule (a few Angstrom units). However when the molecules are far apart, one should postulate an attractive interaction to account for deviations from the ideal gas laws when the gases are compressed and cooled. Otherwise, one cannot account for liquefaction of gases.

Even in liquids molecules move in random directions with random velocities. This movement of molecules in a liquid gives rise to the phenomenon of Brownian motion. The botanist, Robert Brown, observed that pollen grains suspended in a liquid appear to move randomly. Brownian motion is a result of collisions of the grains with the molecules in the liquid. It was Einstein who first gave a satisfactory theory for this phenomenon. The kinetic theory of gases provides a satisfactory quantitative theory for the behaviour of gases. It is difficult to develop a similar quantitative theory for liquids, since the atoms are always close enough to be in constant interaction, while their spatial arrangement is scattered. Matter in the liquid state is important from the practical point of view. In the processing of metals one deals with molten metals like iron, aluminium, lead,
zinc, etc. Metals are cast into different shapes by pouring them in the molten state into moulds. One can control the grain size of many cast materials by dissolving specific elements in low concentration in the molten state before casting. Amorphous ribbons of many alloys are obtained by dropping molten liquid of the alloys on a rapidly spinning copper wheel. Many important applications of liquids depend on knowledge of their surface tension, wettability, viscosity and heat conductivity. A study of liquids to understand their behaviour is very important. [Rao, 1997]

1.2 STRUCTURE OF LIQUIDS FROM X-RAY DIFFRACTION

![Comparison of X-ray scattering curves for (A) crystal, (B) liquid and (C) mono atomic gas](image)

The liquid state of matter is of great practical importance. All biological processes depend crucially on the existence of the liquid phase. The arrangement of atoms in a liquid is more disordered than in a crystal, and can be studied by the scattering of X-ray. This disordered arrangement is described statistically by the pair correlation function \( g(r) \), which gives the relative probability of an atom having a neighbour at a distance \( r \). [Temperly & Trevana, 1978]
By 1912, X-ray diffraction from crystals had been discovered by Friedrich, Knipping and Laue. In a crystal atoms are arranged in a regular pattern. If X-ray of wavelength $\lambda$ is incident on a crystal, it is selectively diffracted at certain angles $2\theta$ to the incident direction, satisfying the equation discovered by Bragg $n\lambda = 2d \sin \theta$, where $d$ is the spacing of a family of planes responsible for the diffraction peak at the angle $2\theta$. The relation between constructive interference and structural periodicity can be well illustrated by a comparison of X-ray scattering by crystalline solids, liquids and gases as shown in fig.1.1. The curve of scattered intensity versus $2\theta$ for crystalline solid is nearly zero everywhere except at certain angle where sharp maxima occur - diffracted beams. Both amorphous solids and liquids have structures characterised by an almost complete lack of periodicity and tendency to order in the sense that the atoms are fairly tightly packed together. The atoms in amorphous structure show just statistical preference for a particular inter atomic distance; resulting X-ray diffractogram exhibits only one or two broad maxima. But in mono atomic gases there is no periodicity whatever, the atoms are arranged perfectly random and their relative positions change all the time. The corresponding scattering curve shows no maxima just a regular decrease of intensity with increasing scattering angle. [Temperly & Trevana, 1978]

1.3 Modelling of liquids

The liquid state is more complicated than either the gaseous or the solid crystalline state. However, using X-ray and neutron diffraction on the one hand and computer simulation on the other, detailed information has been obtained on the structure and dynamics of the liquid state.

There are various models proposed in the literature for a liquid. These are (a) hard sphere model, (b) the lattice gas model, (c) the
defect solid state model and (d) Bernal's model of random close packed structure.

1.3.1 HARD SPHERE MODEL

In the hard sphere model, the particles of the liquid are taken to be hard spheres but with a long range attractive force. Such a model explains many of the properties of the liquid including the existence of a triple point at which the solid, liquid and gas phases coexist. This is a favourite model for computer experiments. [Croxton, 1974]

1.3.2 LATTICE GAS MODEL

In the lattice gas model, one assumes a network of periodic cells in a lattice as in a crystalline solid. However not all cells are occupied by a particle of the liquid. This model is mathematically attractive. [March & Tosi, 1976]

1.3.3 DEFECT SOLID STATE MODEL

The lattice gas model is an example of a defect solid state model in which one introduces vacancies at random in a lattice. One may introduce more complicated defects like random dislocation networks in the lattice to simulate a liquid. [March & Tosi, 1976]

1.3.4 RANDOM CLOSE PACKING MODEL

The random close packing model was obtained by a real life experiment. Bernal and co-workers filled a balloon with thousands of steel balls. After squeezing and shaking the balloon until they were satisfied that random close packing was achieved, they poured some paint inside. The balls had light coating of grease; hence the paint ran off the balls except in places where the balls actually touched or had a very small gap (about 5% of the diameter of the ball). When the paint was dry the balls were removed from the balloon and a
statistical count of the number of paint rings and dots were obtained. From this the coordination numbers and the radial distribution functions were obtained. One important conclusion was that in random close packing the coordination number was around eight with a statistical distribution. In the ideal close packed structure in a crystal this number is twelve. [Landau, 1988]

1.4 FORCES IN LIQUIDS

Molecules can attract each other at moderate distances and repel each other at close range. The attractive forces are collectively called "van der Waals forces". Van der Waals forces are much weaker than chemical bonds, and random thermal motion around room temperature (vibration, rotation and translation) can usually overcome or disrupt them. For example, the intermolecular bonds that hold the atoms in H₂O molecules together are almost 25 times as strong as the intermolecular bonds between water molecules. (It takes 464 kJ/mol to break the (H – O) bonds within a water molecule and only 19 kJ/mol to break the bonds between water molecules.)

Intermolecular forces are feeble; but without them, life as we know it would be impossible. Water would not condense from vapor into solid or liquid forms if its molecules didn't attract each other. Intermolecular forces are responsible for many properties of molecular compounds, including crystal structures, melting points, boiling points, heats of fusion and vaporization, surface tension and densities. Intermolecular forces pin gigantic molecules like enzymes, proteins, and DNA into the shapes required for biological activity. [Leighton, 1994]

The difference between solids and liquids or liquids and gases, is therefore based on a competition between the strength of intermolecular bonds and the thermal energy of the system. At a given temperature, substances that contain strong intermolecular
bonds are more likely to be solids. For a given intermolecular bond strength, the higher the temperature, the more likely the substance will be a gas.

Van der Waals' forces include all intermolecular forces that act between electrically neutral molecules.

Van der Walls' equation is

\[
\left( P + \frac{a}{V^2} \right) (V - b) = RT \tag{1.1}
\]

According to Lenard Jones, Potential energy (fig.1.2) is given by,

\[
W(r) = -\frac{A}{r^6} + \frac{B}{r^{12}} \tag{1.2}
\]

(Where, \(-A/r^6\) represents attraction and \(B/r^{12}\) represents repulsion)

Intermolecular force is given by [Richter, 1989]

\[
F(r) = -\frac{dW(r)}{dr} \tag{1.3}
\]

Fig.1.2 Schematic form of inter molecular potential energy \(W(r)\) as a function of separation
Van der Waals forces can be divided into six categories.

1. Ion – ion interactions
2. Ion - dipole interactions
3. Dipole - dipole interactions
4. Dipole - induced dipole interactions
5. Induced dipole - induced dipole interactions
6. Hydrogen bonding

1.4.1 Ion – ion interactions

The interactions between ions (ion - ion interactions) are the easiest to understand. These electrostatic forces operate over relatively long distances in the gas phase. The force depends on the product of the charges \( Z_1, Z_2 \) divided by the square of the distance of separation \( r^2 \). Two oppositely-charged particles flying about in a vacuum will be attracted toward each other, and the force becomes stronger and stronger as they approach until eventually they will stick together and a considerable amount of energy will be required to separate them. They form an ion-pair, a new particle which has a positively-charged area and a negatively-charged area. There are fairly strong interactions between these ion pairs and free ions, so that these the clusters tend to grow, and they will eventually fall out of the gas phase as a liquid or solid (depending on the temperature). [Henry & Gilman, 1980]

1.4.2 Ion - dipole interactions

Polar molecules can interact with ions as shown in fig.1.3. The potential energy of this type of interaction for the most stable arrangement is given by

\[
U = -\frac{eP}{r^2}
\]  

Where \( e \) = Charge of the ion
\[ P = \text{Dipole moment} \]
\[ r = \text{The distance of separation of the dipole and the ion} \]

\[ + \quad + \quad + \quad - \quad - \quad - \quad + \]

**Fig.1.3 Negative ends of the dipoles attracted towards the positive ion**

Ion dipole forces are important in the solvation process of a solute in a solvent. The solubility of ionic solids like Na\(^{+}\)Cl\(^{-}\), K\(^{+}\)Cl\(^{-}\) etc in H\(_2\)O is due to the fact that the energy resulting from the interaction between the dissolved ions and the dipolar H\(_2\)O molecules becomes comparable to that of the crystal lattice. In the case of Na\(^{+}\)Cl\(^{-}\) dissolved in water, the positive poles of H\(_2\)O is surrounded by Cl\(^{-}\) ions and the negative poles of H\(_2\)O by Na\(^{+}\) ions. Thus the ionic bonding between Na\(^{+}\) and Cl\(^{-}\) ions are broken and as a result Na\(^{+}\)Cl\(^{-}\) dissolves in H\(_2\)O. [Henry & Gilman, 1980]

**1.4.3 Dipole - Dipole Interactions**

Dipole-dipole interactions, also called Keesom interactions or Keesom forces after Willem Hendrik Keesom, who produced the first mathematical description in 1921, are the forces that occur between two molecules with permanent dipoles. They result from the dipole-
dipole interaction between two molecules. An example of this can be seen in hydrochloric acid (fig.1.4).

\[ \text{Fig.1.4 Dipole-dipole interaction of HCl molecules.} \]

Many molecules contain bonds that fall between the extremes of ionic and covalent bonds. The difference between the electro negativities of the atoms in these molecules is large enough that the electrons aren't shared equally, and yet small enough that the electrons aren't drawn exclusively to one of the atoms to form positive and negative ions. The bonds in these molecules are said to be polar, because they have positive and negative ends, or poles, and the molecules are often said to have a dipole moment.

The potential energy due to dipole-dipole interaction is given by,

\[ U = -\frac{2P^4}{3r^6k_BT} \]

Where \( P \) = Dipole moment  
\( r \) = distance of separation of dipoles  
\( T \) = absolute temperature  
\( k_B \) = Boltzmann constant
$HCl$ molecules, for example, have a dipole moment because the hydrogen atom has a slight positive charge and the chlorine atom has a slight negative charge. Because of the force of attraction between oppositely charged particles, there is a small dipole-dipole force of attraction between adjacent $HCl$ molecules. The dipole-dipole interaction in $HCl$ is relatively weak; only 3.3 kJ/mol. (The covalent bonds between the hydrogen and chlorine atoms in $HCl$ are 130 times as strong.) The force of attraction between $HCl$ molecules is so small that hydrogen chloride boils at $-85^\circ C$. [Henry & Gilman, 1980]

1.4.4 DIPOLE-INDUCED DIPOLE INTERACTIONS

Let us consider a mixture of $HCl$ and argon. Argon has no dipole moment. The electrons on an argon atom are distributed homogeneously around the nucleus of the atom. But these electrons are in constant motion. When an argon atom comes close to a polar $HCl$ molecule, the electrons can shift to one side of the nucleus to produce a very small dipole moment that lasts for only an instant. This is shown in fig.1.5.

![Fig.1.5 Dipole induced dipole interaction of HCl molecule and Ar atom.](image)

The potential energy due to dipole-induced dipole interaction is given by,

$$U = -\frac{2\alpha P^2}{r^6}$$

(1.6)
Where \( P \) = Permanent dipole moment  
\( a \) = Polarisation of the permanent dipole  
\( r \) = Distance of separation of dipoles

By distorting the distribution of electrons around the argon atom, the polar \( HCl \) molecule induces a small dipole moment on this atom, which creates a weak dipole-induced dipole force of attraction between the \( HCl \) molecule and the \( Ar \) atom. This force is very weak, with bond energy of about 1 kJ/mol. As a result polar and non-polar liquids are often immiscible. [Henry & Gilman, 1980]

### 1.4.5 Induced Dipole - Induced Dipole Interactions (London Force)

Non-polar molecules also exert attractive force on each other. Neither dipole-dipole nor dipole-induced forces can explain the fact that helium becomes a liquid at temperatures below 4.2 K. By itself, a helium atom is perfectly symmetrical. But movement of the electrons around the nuclei of a pair of neighboring helium atoms can become synchronized so that each atom simultaneously obtains an induced dipole moment. This is represented in fig.1.6.

![Fig.1.6 Induced dipole induced dipole interaction of He atoms.](image)

The potential energy due to dispersion force is given by the equation

\[
U = -\frac{3\hbar \alpha^2}{4r^6}
\] (1.7)
Where $n = \text{Frequency of oscillations of the charge cloud}$

$a = \text{polarisation of the molecule or atoms}$

$h = \text{Planck's constant}$

$r = \text{Distance of separation of the dipoles}$

These fluctuations in electron density occur constantly, creating an induced dipole-induced dipole force of attraction between pairs of atoms. As might be expected, this force is relatively weak in helium (0.076 kJ/mol). But atoms or molecules become more polarisable as they become larger because there are more electrons to be polarized. It has been argued that the primary force of attraction between molecules in solid $I_2$ and in frozen $CCl_4$ is induced dipole-induced dipole attraction. [Henry & Gilman, 1980]

1.5 **Hydrogen Bonding**

Hydrogen bonds are abnormally strong dipole-dipole attractions that involve molecules with $-OH$, $-NH$, or $FH$ groups. Hydrogen atoms are very small. When a bonded electronegative atom (oxygen, nitrogen, or fluorine) pulls electrons away from the hydrogen atom, the positive charge which results is highly concentrated. The hydrogen is intensely attracted to small, electron-rich $O$, $N$, and $F$ atoms on other molecules. (Larger electron-rich groups and atoms (like $-Cl$, for example) will also attract the hydrogen, but because their electrons aren't as tightly concentrated, the resulting dipole-dipole attraction is too weak to be considered a "real" hydrogen bond.) Hydrogen bonds are essential for building biological systems: they are strong enough to bind biomolecules together but weak enough to be broken, when necessary, at the temperatures that typically exist inside living cells.

Hydrogen bonding is an intermolecular interaction with a hydrogen atom being present in the intermolecular bond. This hydrogen is covalently (chemically) bound in one molecule, which
acts as the proton donor. The other molecule acts as the proton acceptor. The simplest example of a hydrogen bond is one between water molecules. In a discrete water molecule, water has two hydrogen atoms and one oxygen atom. Two molecules of water can form a hydrogen bond between them; the simplest case, when only two molecules are present, is called the water dimer and is often used as a model system. The water dimer is shown in fig. 1.7. The water molecule on the right is the proton donor, while the one on the left is the proton acceptor. [Bahl et al., 1996]

![Fig. 1.7 Hydrogen bond - H₂O dimer.](image)

Hydrogen bonds are found throughout nature. In water the dynamics of these bonds produce unique properties essential to all known life forms. Hydrogen bonds, between hydrogen atoms and nitrogen atoms, of adjacent DNA base pairs generate intermolecular forces that improve binding between the strands of the molecule.

The energy of a hydrogen bond (typically 5 to 30 kJ/mole) is comparable to that of weak covalent bonds (155 kJ/mole), and a typical covalent bond is only 20 times stronger than an intermolecular hydrogen bond.

Many other unique properties of water are due to the hydrogen bonds. For example, ice floats because hydrogen bonds hold water molecules further apart in a solid than in a liquid, where there is one
less hydrogen bond per molecule. The unique physical properties, including a high heat of vaporization, strong surface tension, high specific heat, and nearly universal solvent properties of water are also due to hydrogen bonding.

The hydrophobic effect or the exclusion of compounds containing carbon and hydrogen (non-polar compounds) is another unique property of water caused by the hydrogen bonds. The hydrophobic effect is particularly important in the formation of cell membranes. The best description is to say that water "squeezes" non-polar molecules together.

The ability of ions and other molecules to dissolve in water is due to polarity. For example, in the illustration fig.1.8, sodium chloride is shown in its crystal form and dissolved in water. Liquids that display hydrogen bonding are called associated liquids. The hydrogen bonding in methanol is given in fig.1.9.[Emsley, 1980]
1.6 PHASE TRANSITIONS IN LIQUIDS

Theoretical studies have shown that thermodynamically different phases can be associated with a pure liquid. One distinguishes between a ‘two-state’ model and a ‘two-phase’ model in liquids. In the ‘two-state’ model, low and high density states coexist within a liquid and the high density state grows relative to the low density state as a function of pressure. The two-state behaviour can go over into the two-phase behaviour below a certain temperature, the two-phases being characterized by different thermodynamic properties like energy or entropy. Just as there is a liquid–gas critical point in the pressure–temperature phase space, a second liquid–liquid critical point is hypothesized to exist below this critical temperature at some lower temperature. Below such a critical temperature, a first order liquid–liquid phase transition can occur as a function of pressure. Sudden jumps in properties like electrical conductivity can occur within the two-state domain within a single liquid phase or it could happen in two-phase regime of a liquid when liquid–liquid phase transition occurs. An unequivocal proof of occurrence of a liquid–liquid phase transition has to come from other techniques. The diffraction technique can provide such evidence.
However, phase transitions across the liquid–liquid coexistence boundary may not be easily observable in experiments. Several candidate liquids are expected to exhibit liquid–liquid phase transitions. These include liquids having open molecular coordination at low pressure; liquids having locally tetrahedral molecular structures for example, Si, Ge, C, SiO$_2$, GeO$_2$ and H$_2$O are some of them. Stephen Hanington reported results of molecular dynamics simulation of a one-component model system, namely, that of ST2 model of water. By evaluating the pressure–density isotherms above and below a critical temperature, they found presence of two coexisting phases differing by 15% in density. According to this model 'liquid is not homogeneous and in any liquid there exist locally favoured structures which are frustrated with normal structure'. This concept has led to a new possibility that ‘even in an ordinary molecular liquid there could be a hidden liquid–liquid phase transition’. [Mitus, 1985; Stephen Hanington, 1997]

1.7 ASSOCIATED AND UNASSOCIATED LIQUIDS

An associated liquid consists of groups of attached molecules. Examples of associated molecules are water, formic acid, methanol, methyl amine etc. An unassociated liquid is one which consists only of individual molecules. Examples of unassociated liquids are benzene, carbon tetra chloride etc.

Liquids whose molecules are held together by hydrogen bonding are associated liquids. Hydrogen bonding is an especially strong kind of attraction between a hydrogen atom (that is bound to a highly electro negative atom) and another highly electronegative atom. This type of bond is formed by purely electrostatic forces between the positive end of one polar molecule and the negative end of another polar molecule. For hydrogen bonding to be important, the electronegative atoms must be F, O or N. Thus, once the structure of
the species is known, one can tell if they are associated liquids. Some examples are given below.

1. CH$_3$OH, Methanol

   It is an associated liquid because oxygen is bounded to the hydrogen atom and the hydrogen atom can form bonds with oxygen atoms of other methanol molecules.

2. CH$_3$-O-CH$_3$ (dimethyl ether)

   It is not an associated liquid. The oxygen is not bonded directly to any hydrogen atom and therefore cannot form any hydrogen bonds.

3. Liquid CH$_3$Cl, (Methyl chloride)

   This is not an associated liquid because Chlorine is not electronegative enough to form a stable hydrogen bond.

4. CH$_3$HN$_2$, (Methyl amine)

   It is an associated liquid. Nitrogen is highly electronegative and the hydrogen can form hydrogen bonds with nitrogen atoms of other $CH_3NH_2$ molecules. [Kundu & Jain, 1984]