CHAPTER 1

The Liquid State

1.1 Introduction

Our universe contains matter, which has been subjected to an enormous range of conditions – from the very low temperature and pressure of space to the extremely high temperature and pressure found in the interior of stars. Liquids exist only as a small part of this range and are intermediate to the three states of matter. This domain is, however, of extraordinary importance for technology and life processes. Of the three states of matter, the properties of the liquid state are probably the least easy to calculate. Matter in the liquid state possesses a definite size, but has no definite shape. It is generally observed that some of the properties of liquids closely resemble those of gases while some other properties approach those of solids. A combination of the experiment and theory, together with computer simulations, provide a powerful means of extending the boundaries of our knowledge of this important state of matter. The direct measurement of the P, V, T properties of liquids leads to the following generalizations.

1. The isothermal compressibility $\beta_T$ decreases with increasing pressure, the rate of decrease being smaller as the pressure increases.
2. The isothermal compressibility \( \beta_T \) increases as the temperature increases, the effect being largest at low pressure and diminishing as the pressure increases.

3. At low temperatures, the coefficient of thermal expansion \( \alpha \) increases as the temperature increases. [1]

1.2 Liquids – A compromise between order and disorder

In the gaseous state, one can describe the system by the ideal gas equation. Effects of intermolecular interactions – departure from the ideal behaviour, are accounted by the virial expansion. The mobility of liquids shows that their molecules, like those of gases are free to move, but the limited volume of the liquid shows that the molecules must exert forces on one another, these preferably being the resultant of the attractive and repulsive short-range forces. In case the energy of interaction between the molecules become sufficiently large either due to the lowering of temperature or due to the increase in pressure, or both, resulting in the molecules being forced to be near each other. Then, these molecules are held so close together that the thermal energy is unable to break them apart and the gaseous state begins to disappear and liquefaction starts. These binding forces are not so strong as to counteract completely the thermal energy. The molecules still do move about, but their mean free path is very small and due to the net attractive forces, a new equilibrium is set up and the gas completely liquefies. [2 - 4]
1.3 Resemblance with solids

In the crystalline state, one can take advantage of the regular arrangement of molecular centres and use the harmonic perfect lattice to model its properties. It has all the difficulties of a high-density system without the benefits of long-range order in the form of a well-defined crystal structure. Nonetheless, one can still speak of the short-range structure of a liquid in a statistical sense. It was formerly supposed that liquid molecules executed random movements and their arrangement was disordered. It was found however that liquids give X-ray spectra indicating some degree of regularity and order in molecular arrangement, so that the liquid is more analogous to a crystalline solid than to a gas. [2,4, 5]

1.4 Resemblance with gases

In the light of the kinetic molecular theory, liquids may be considered as a continuation of gases to the region of small volumes and high intermolecular attraction. These intermolecular forces are not strong enough to eliminate the movements of the molecules in the liquid. Thus, the liquid state can be considered as the fluid state with a shorter mean free path. [2, 4]

1.5 Structure of liquid

The term structure of a liquid describes the arrangement of its molecules in space. For a simple liquid like argon, only the relative
positions of the centres of the atoms need to be specified while in the case of poly atomic molecules such as water, both the relative positions of the molecular centres of mass and the relative molecular orientations must be specified. There is generally no valid simple analytic equation of state for a liquid. Just as in the case of imperfect gases, empirical equations of state are used to represent observations in a compact form. The two most widely used equations are the Tait equation

\[
\frac{V_o - V}{V_o P} = \frac{A_1}{B_1 + P} \quad (1.1)
\]

and the Huddleston equation

\[
\ln \left( \frac{P V^{\frac{2}{3}}}{V_o^{1/3} - V^{1/3}} \right) = A_2 + B_2 (V_o^{1/3} - V^{1/3}) \quad (1.2)
\]

where V is the volume, P the pressure, \(V_o\) is the molar volume at 'zero' pressure, \(A_1, B_1, A_2,\) and \(B_2\) are positive constants. [1, 2, 6]

1.6 Bonding in molecules

The formation of bonds holding the atoms together to form molecules is explained quantum mechanically by considering the atom to be a cloud of electrons surrounding the positively charged core - nucleus. The electrons in the outermost shell of an atom are generally the ones concerned with bond formation, and from energy considerations molecules are formed only if each atom acquires a stable electronic configuration. A complete outer shell of eight electrons called an octet is the most stable configuration. This may be obtained in several ways: by losing, gaining or sharing electrons. The
bonds formed in these cases are termed as ionic, covalent and coordinate bonds respectively. But when the number of valence electrons is far too small to provide the complete outer shells for all the atoms, the metallic bond concept is used. [4, 5]

1.7 Hydrogen bonding

An unusual type of bonding, which is largely electrostatic in nature, is exhibited by hydrogen in certain circumstances. Hydrogen atom though possesses one electron and is normally univalent; it is capable of forming a bond or bridge between two atoms, provided these are small and strongly electronegative in character such as fluorine, oxygen and nitrogen. This bond or bridge, which is electrostatic in nature, is called hydrogen bond. It is indicated by dotted lines as illustrated in figure 1.1. Hydrogen bonding is also seen in water, ammonia, alcohols, phenols, carboxylic acid, amides etc. It occurs either intramolecularly giving rise to ring formation (chelation) or intermolecularly which gives rise to association. However hydrogen bond formation does not involve complete electron transfer. It is stronger than van der Waals’ forces but very much weaker than a covalent bond. It affects the physico-chemical properties such as melting point, boiling point, solubility, spectra etc. [7,8]

\[ \text{H} - \text{F} \quad \text{H} - \text{F} \quad \text{H} - \text{F} \]

Fig.1.1 Hydrogen bonding in hydrogen fluoride
The abnormal property of water molecules, which is due to intermolecular hydrogen bonding, is illustrated in figure 1.2. The cluster of water molecule may be described as \((\text{H}_2\text{O})_n\) [9]

\[
\cdots \text{O} - \text{H} \cdots \text{O} - \text{H} \cdots \text{O} - \text{H} \cdots \text{O} - \text{H}
\]

Fig. 1.2 Hydrogen bonding between water molecules

1.8 Hydrogen bonding in alcohols

The alcohols, which have the general formula ROH, behave like water in respect to hydrogen bond formation. The extent is less marked since it has only one hydrogen atom in the molecule and each ROH unit is attached to two other in the manner indicated in figure 1.3. The solubility of the long chain alcohols in water is less when compared to the lower alcohols. [10]

Fig. 1.3 Hydrogen bonding in alcohol
1.9 **Intermolecular forces**

There are certain identifiable intermolecular forces in liquids marked by certain characteristics. They can be classified as short-range and long-range forces. The former are due to the overlap of the electronic wave functions describing the separate molecules (anti-symmetrization) and decreases exponentially with increasing $r$. In the region of electron overlap, the identity of the interacting molecules is lost. The various intermolecular interactions in liquids lead to a peculiar compromise between order and disorder and in many theories of liquid state, these interactions are expressed as a potential. [5,7]

1.10 **Short-range interactions**

A liquid is characterized by a short-range order. In the immediate neighbourhood of a given molecule in a liquid some degree of order is noticeable in the packing. But the local structure is not repeated as the distance from the given point is increased. For certain purposes it is possible to look upon the molecule to possess a more or less rigid structure and correlated in position and orientation with its near neighbours, which diminishes rapidly with distance. Therefore it is convenient to assume that liquids have short-range order, which disappears at the boiling point of liquids. [2,5,11]

1.11 **Long-range interactions**

The long range Coulomb interaction energy of two ions varies as $r^{-1}$ and that of two dipoles as $r^{-3}$. Thus in general long-range interactions
vary as $r^{-m}$ at large $r$, where $m$ is a positive integer. At long range, intermolecular exchange is insignificant and it can be considered that the electrons are associated with one or the other of the molecules. Thus the long-range forces are related to the properties of the free molecules such as their charge distribution and polarizabilities. The long-range forces comprise of the electrostatic, inductive, dispersion, resonance and magnetic forces. Among these the most important one is the electrostatic energy which is additive and the total electrostatic energy is the sum of the pair energies. The relative importance of each contribution to the long-range interaction energy varies from system to system. The electrostatic and induction energies are zero in inert gases while in hydrogen-bonded systems the electrostatic energy is predominant. [1,5,11]

1.12 Dipole–dipole interactions

Distortion of electron clouds in molecules of dissimilar atoms constitutes a dipole and is affected by electric and magnetic fields. This leads to a dipole-dipole interaction and a dipole-induced dipole interaction. The interaction between two permanent dipoles depends on their relative orientation. At very low temperatures, molecules tend to take up the most favourable orientation, but at moderate temperatures, thermal agitation interferes with this orientation and dipole-dipole attraction will disappear at sufficiently high temperatures, where the molecules orient in a completely random manner. Dipole–dipole interaction or ion-dipole interaction leads to a stabilization and increase as the temperature decreases. Applying Boltzmann statistics, Keesom derived the potential resulting from dipole-dipole interactions
\[ U_{12} = \frac{-2 \mu_1^2 \mu_2^2}{r^6 k T} \] 1.3

where \( \mu \) is the dipole moment, \( r \) is the distance between the two dipoles, \( k \) is the Boltzmann constant and \( T \) the absolute temperature. [7]

1.13 London dispersive forces

Neutral molecules and atoms are known to have attractive forces. The attractions are brought out by the fluctuations in electron cloud producing instantaneous dipoles, which in turn polarise the electron cloud of the neighbouring molecules bringing about non-isotropic charge distribution inside the molecules. Such forces acting between non-polar molecules are the London dispersive forces. London has shown that the polarizability of the electron cloud induces a dispersion force and leads to an over all attraction. For completely symmetrical molecules London forces are the only attractive forces. The energy due to these forces is given by

\[ U_{12} = \frac{3 \alpha_1 \alpha_2 I_1 I_2}{2 r^6 (I_1 + I_2)} \] 1.4

where \( \alpha \) is the polarizability, \( r \) is the distance between the centre of the two molecules and \( I \) is the ionisation energy.

If the molecules have comparable ionisation energies the equation assumes the form

\[ U_{12} = \sqrt{|U_{11}|} \sqrt{|U_{22}|} \] 1.5

Thus the interaction energy \( U_{12} \) between two different molecules is close to the geometrical mean of the interaction energies \( U_{11} \) and \( U_{22} \).
of the respective molecules. Since geometric means are less than arithmetic means, large differences in intermolecular potentials of the components of a mixture lead to a weakening of cohesion, i.e. less stabilization, endothermic mixing and a positive heat of mixing. [4, 5, 7]

1.14 Need for a model

The experiments we perform and the theories we propose must be designed to serve our particular interest viz. properties of liquids, the properties of molecules or the relationship between them. We must also be concerned with the change in molecular property on transition from one phase to another. Because of the complexity of organic molecules and organic liquids simple models are considered which embody the essential chemistry or physics of the phenomena we are interested in. We may have to discard the model on progressing, if it is found to be incompatible with fact. Whatever be the model chosen for the liquid state the cohesive forces are of primary importance. To have a clear understanding of the structure of liquids, various models have been suggested, but no single model satisfies the properties of liquids over the whole composition range. The models worked out on the van der Waals idea of continuity between the gaseous and the liquid state satisfy only near about the critical point. The fact that liquids flow and diffuse suggests a random molecular structure like gases and on the other hand the cohesion and compactness displayed by them indicates a structure resembling that of a solid. The properties of liquids can only be understood by the time average of a large number of different arrangements brought about by molecular interaction due to attractive and repulsive forces. Steward and others feel that there are large
numbers of space arrangements and in each of them the molecules are arranged in a relatively ordered manner whereas the regions between them have random distribution. These groups of arranged molecules are not permanent but continuously shift in position and exchange partners with those in the random region. In each of these the number of different molecular configuration is so large and a mathematical treatment has become difficult. [1,5,7]

1.15 Interaction between molecules

It is a well-known truth that molecules attract one another when they are far apart and repel one another when close. This is illustrated in the figure 1.4, which shows the interaction energy $U(r)$ of a pair of spherical molecules as a function of their separation $r$. [5,7,12]

![Interaction Energy Graph](image)

**Fig. 1.4** The interaction energy $U(r)$ of two spherical molecules as a function of their separation $r$
1.16 Theories of liquid state

A theory of liquid state is essential for many branches of Physics and Chemistry. The theory should be in a position to explain the thermodynamic behaviour of simple liquids, equilibrium and transport properties of liquids and the results of diffraction techniques. The characterization of molecular interaction and the statistical problem of relating the macroscopic properties of the system to the microscopic properties are the two major fundamental problems that are to be tackled by any liquid state theory. There are gross physical assumptions in such theories. [5,12,13]

1.17 The hole theory of liquids

Liquids have neither ordered arrangement like solids nor random arrangement as in gases. In reality, they have holes. The energy will increase due to the holes in the crystalline structure because of the loss of energy of attraction between molecules but it is limited by the total binding energy of the crystal. With the increase of holes, the energy will also increase and ultimately it will become constant. As holes increases, the number of arrangement of molecules and holes will also increase, so that the entropy of the system is bound to increase. X-ray diffraction pattern reveals that there are definite vacant spaces in the molecular arrangement of liquids. These are known as holes. The movement in the molecules of a liquid, or fluidity, is due to the presence of these holes. The decrease in density at the melting point is partially due to these holes and partially due to the increase in distance between the nearest neighbours. It has also been supposed that the
energy of activation is related to the latent heat of evaporation of the liquid, being the energy necessary to provide a vacant space or "hole" in the liquid, into which a molecule (or sometimes two molecules together) can roll by rotation. A hole is regarded as a statistical entity having four degrees of freedom, three of translation (defining its position) and one corresponding with a change of radius (defining its size). If "bonds" with a total energy $NE$ connect all the $N$ molecules forming the liquid, the energy to evaporate one molecule will be $\frac{1}{2} E$, if all the molecules associate to leave no hole. However, if a hole is left, the energy of evaporation of a single molecule is $E$. The return of a molecule from vapour to the hole in the liquid liberates the energy $\frac{1}{2} E$. Hence the energy required to produce a hole of molecular size with out evaporation is $E - \frac{1}{2} E = \frac{1}{2} E$. The energy required to make a hole of molecular size is the same as to evaporate a molecule with out leaving a hole. [1,2]

1.18 Theory of loose packing

The force of repulsion between the molecules of a liquid is more important than the force of attraction between them as it will decide about the packing of the molecules in the liquid. Lennard Jones and co-workers considered solids as an alloy of holes and molecules. At low temperatures, the atoms occupy all the sites of the crystal lattice and holes occupy all the sites of a perfect crystal interpenetrating the first like a sodium chloride crystal. The sites occupied by the atoms are known as $\alpha$ sites while those occupied by the holes are known as $\beta$ sites. If an atom moves from $\alpha$ site to $\beta$ site then some of the bonds holding the lattice are compressed because of the nearness of the neighbours and some of the bonds stretch themselves
because of longer distance. This will increase the energy of the system. If this increased energy becomes zero, then each atom will freely move from $\alpha$ site to $\beta$ site and vice versa. In this way the atoms and the holes both will be arranged at random on the two lattices with equal numbers of each. This will increase the entropy of the system and produce a disordered arrangement. In actual practice the attractive forces tend to produce an ordered arrangement while the entropy tries to produce a disorder. [3,5,7]

1.19 Significant structure theory

The density of a solid on melting decreases due to the addition of holes of molecular size to the crystal lattice. These holes move freely in bulk liquid. The molecules of the liquid in general have only vibrational degrees of freedom and vibrate about their mean position. The vacancies confer on adjacent molecules a translational degree of freedom. Thus there emerges a random fine-grained mixture of solid and gas-like regions with neither solid nor gas-like regions large enough to constitute nuclei for the formation of a solid or vapour phase. This picture is consistent with the observation that liquids can be super-cooled below the normal freezing point and super-heated above the normal boiling point. As the temperature of the liquid is increased, an increase in the number of molecules in the vapour is reflected by the increase in the number of vacancies in the liquid. A liquid molecule is acted upon by forces from about as many molecules as if it were part of a solid and these imprison it in a ‘cage’ from which it can only occasionally escape, “living a life of comparative freedom only in the very brief intervals between one term of imprisonment and the next”. In the scattered “cage”
theory, a liquid molecule is supposed to be surrounded by a cluster of about 12 other molecules, which act as a barrier in preventing its free translatory motion. [4]

1.20 Cell theory

The liquid state is characterised by the strong interaction of the molecules, which sets it apart from gases, and the state of disorder of molecular motion, which sets it apart from solids. The strong intermolecular energy in liquids is clearly reflected in the large internal energy deviation of the liquid from its ideal gas state. The molecules in a liquid is visualised to be bouncing around but confined to cells formed by the shell of the closest neighbours. Further more the X-ray diffraction studies of a liquid and the powdered solid of the same liquid reveal that the short-range orderliness is retained in a liquid form while the long-range orderliness is lost. The motion of a molecule in its cell can be described by a cell partition function

\[ \psi = \iiint_{\text{cell}} \exp \left( \frac{-\varepsilon}{kT} \right) \, dx \, dy \, dz \]  \hspace{1cm} (1.6)

and the configuration partition function is given by

\[ Q_{\text{conf}} = \left[ \frac{\psi}{V} \right]^N \]  \hspace{1cm} (1.7)

Evaluation of \( \psi \) is carried out by assuming the pair wise additivity of intermolecular potential. The energy \( \varepsilon \) can be determined as a function of position of the central molecule by assuming the neighbouring molecules to
be located on solid like lattice. For liquids at high densities, the potential energy $\varepsilon$ can be considered essentially as a constant $\varepsilon_0$ in the cell because of the averaging effect of the many neighbours. Under these conditions the partition function of a molecule in a liquid simplifies to

$$\psi = V_f \exp \left( -\frac{\varepsilon_0}{kT} \right)$$

where $V_f$ is the free volume defined by

$$V_f = \iiint_{\text{cell}} \exp \left( \frac{-(\varepsilon - \varepsilon_0)}{kT} \right) \, dx \, dy \, dz.$$  

and $\varepsilon_0$ denotes the value of $\varepsilon$ with the molecule at the centre of the cell. [4,14]

1.21 Repulsive forces and potential energy functions

Even with our increasing knowledge of interaction energies, we do not accurately know the kind of interaction potential to be employed in the theoretical study of liquids. So we are forced to use empirical or semi-empirical potentials. The relationship between the intermolecular potential and the various measurable properties are quite complex and the properties are usually sensitive to the exact form of potential. But it is customary to approximate the potential by some simple and mathematically traceable function with only a few adjustable parameters, capable of managing the experimental data. The important empirical potential functions in use are briefed below. [1,2,7]

a. Hard spheres

This is the simplest possible method, representing molecules as rigid spheres of diameter $\sigma$. Two such molecules will bounce off
each other elastically if their centres approach to a distance $\sigma$, but otherwise do not interact at all. The potential can be written in the form

\[
V(r) = \begin{cases} 
\alpha & \text{for } r < \sigma \\
0 & \text{for } r \geq \sigma 
\end{cases}
\]  

1.10

The model takes into account of the short-range repulsion only, and even that is in ideal form, since the real repulsive force cannot be infinitely large. But it has the great advantage of mathematical simplicity, and calculations with this model can be carried out with relative ease. [1,7]

b. Point centres of repulsion

A somewhat more realistic representation of the repulsive energy is given by the potential $V(r) = d r^{-\delta}$ where $d$ is a constant and the index of repulsion $\delta$ must be larger than 3. (values are in between 9 and 15). This model recognises the fact that molecules that are more energetic can approach each other more closely before being repelled, and thus can represent temperature dependence of some of the properties. But it neglects the attractive part of molecular interaction. [1,5,7]

c. Square well

The simplest potential model that includes the attractive and repulsive contributions is the square well potential – a hard sphere core surrounded by an attractive well of constant depth. It is defined by the equations
\[
\begin{align*}
V(r) &= \alpha \quad \text{for } r \leq \sigma_1 \\
V(r) &= -\varepsilon \quad \text{for } \sigma_1 < r < \sigma_2 \\
V(r) &= 0 \quad \text{for } r \geq \sigma_2
\end{align*}
\]
with three adjustable parameters \(\sigma_1, \sigma_2\) and \(\varepsilon\). This model is a great compromise between mathematical simplicity and realism. [1, 5]

d. Lennard-Jones potential

The empirical potential most widely used in analyzing the properties of gases is Lennard-Jones potential. It is the simplest of the models considered here which gives a potential energy curve similar to the correct one.

The L.J potential is

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

where \(\varepsilon\) is the well depth and \(\sigma\) is the distance at which \(V(r) = 0\). One can easily show that the minimum energy \(V(r) = -\varepsilon\), occurs at a distance of \(r = 2^{1/6}\sigma\). The attractive term represented by \(r^{-6}\) indicates the long-range dependence of the dispersion energy. The repulsive term is more arbitrary, in that wide range of exponents would fit the available data and it is chosen for convenience as the square of \(r^{-6}\). Most determinations of intermolecular potentials derive from measurement of one component systems, and gain information only on the interaction between molecules of the same kind. For unlike molecules, one often intimates the L. J parameters by the empirical combining laws. [1]

\[
\sigma_{AB} = \frac{1}{2} \left( \sigma_{AA} + \sigma_{BB} \right)
\]
e. Atom-atom interaction potential

Another popular empirical potential is the atom-atom interaction model. In this, the interaction energy is assumed to be a sum of interactions of all pairs of atoms in different molecules. In addition to changes in the potential energy, molecular interactions can have important effect on optical, electric and magnetic properties. At small intermolecular distance, a repulsive potential abruptly sets in. This potential has been represented by an exponential function of the distance of separation ‘r’, but it is more frequently represented by a high inverse power $r^{-n}$. The repulsion rise so quickly with diminishing separation such that using $n = 12$ does not result in a serious discrepancy. [1,5]

1.22 Solutions

Solutions are mixtures of molecules comprising two or more substances between which there are physical or chemical interactions. When two liquids with similar physical and chemical properties are mixed, it is observed that the volume and energy change of mixing are practically zero. Dissolution has been considered mainly as a chemical process. But the physical theory of solutions considers it as the summary result of molecular motion and mutual cohesion of molecules. The intricate nature and the diversity of the laws covering the properties of solutions of various substances make the theory of solutions a very difficult problem. [3,5,7]
1.23 Raoult’s law

The simple theory of solutions is that due to Raoult and it often provides a reasonable approximation for liquid solutions whose components are chemically similar such as n-hexane and heptane, benzene and toluene etc. The law states that the partial pressure of any component is equal to the product of its own vapour pressure and mole fraction in the liquid phase, at modest pressures. The relation is exact only if the components of the mixture are identical and its failure to represent the behaviour of actual solutions is due to the difference in molecular size and intermolecular forces of the pure components. Thus Raoult’s relation is used as a reference to express observed behaviour of real solutions, namely alcohol and chloroform, acetone and chloroform, as deviations from the behaviour calculated using Raoult’s law. [12]

1.24 The Theory of van Laar

An attempt to describe quantitatively the properties of fluid mixtures was first made by van der Waals and his coworkers. Later J. J van Laar one of van der Waals students put forward a theory of solutions, which though inadequate underwent advancement to give a useful theory of regular solutions.

Van Laar assumed that liquids mix at constant temperature and pressure in such a manner that there is no volume change and the entropy of mixing is given by that corresponding to ideal solution. For evaluation of the energy change of mixing a three-step, isothermal, thermodynamic cycle was formulated wherein the pure liquids are first vapourised to some
arbitrarily low pressure, mixed and then recompressed to the original pressure. The energy change is calculated for each step and the total energy \( (\Delta u) \) of mixing is given by the sum of the three energy changes. [15]

1.25 The Scatchard–Hildebrand theory

Hildebrand defined regular solutions as one in which the components mix with no excess entropy at constant temperature and volume. Scatchard and Hildebrand realized that van Laar’s theory could be greatly improved if it can be freed from limitation of van der Waals equation of state. This is achieved by introduction of a new parameter ‘cohesive energy density \( (c) \), which is defined by the expression

\[
c = \frac{\Delta u^v}{V^L} \tag{1.21}
\]

where \( \Delta u^v \) is the energy change during the isothermal vapourisation of saturated liquid to ideal gas and \( V^L \) is the volume in liquid state. The positive root of \( c \) denoted by \( \delta \) is called as the solubility parameter. The difference in solubility parameters of the mixture components provides a measure of the solution non-ideality. [15]

1.26 Corresponding-states theory

The theory asserts that when residual properties of two different liquids are expressed in the reduced form they should coincide when plotted upon the same non dimensional coordinates. This theory can be extended to liquid mixtures, which can be considered as a hypothetical pure fluid. Accordingly if the residual properties of two liquids can be made to coincide
on the same dimensionless plot, then the residual properties of any mixture of these two fluids should also coincide on the same plot. In the case of a pure liquid, the reducing parameters are constants, which characterize molecular size and intermolecular forces in the pure fluid. For a mixture, the reducing parameters are composition dependent because they characterize average molecular size and average intermolecular force in the mixture. [15]

1.27 Two liquid theory

Scott’s “Two liquid theory” was developed in connection with the corresponding state treatment. The theory states that the properties of a binary mixture are equivalent to those obtained by averaging the properties of two hypothetical fluids. [6,15]

1.28 Interaction between molecules in solutions

The interaction between molecules in pure liquids is mainly the van der Walls interaction comprising orientational attraction between molecules with a constant dipole, induction attraction between molecules with a constant dipole and with an induced dipole, and dispersion attraction between mutually induced dipoles of molecules whose moments fluctuates near zero. The attraction of molecules is counteracted by repulsion, which is of importance for small distances and is mainly due to the interaction of the electron shells. This repulsion combined with thermal motion balances the attraction and establishes a mean equilibrium between the moving molecules of a liquid. In addition to the interaction between the molecules of one of the components, interaction between the molecules of
different components also occurs in a solution. The molecules of the solute, however, by changing the surroundings of a molecule of the solvent, can appreciably change the intensity of interaction between the molecules of the latter and they themselves interact with one another in a different way than in a pure second component. The observed positive or negative deviations in liquid mixtures are due to various factors. If the different kinds of molecules in the solution are mutually attracted with a smaller force than molecules of the same kind, then this facilitates the transition of molecules from the liquid phase to the gaseous one producing positive deviations from Raoult's law. An increase in the mutual attraction of molecules of different kinds in a solution hinders the transition of the molecules to the gaseous phase forming negative deviations from Raoult's law. It should be remembered that the factors causing positive and negative deviations may act in a solution simultaneously, and for this reason the deviations observed are often the result of superposition of deviations that are opposite in sign. This simultaneous action of opposite factors is clearly seen in solutions in which the sign of the deviations changes from the Raoult's law with a change in the concentration. Thus, it follows that the absence of deviation from Raoult's law upon the formation of a solution of a definite composition are not necessarily indications of the fact that the given components form ideal solutions when mixed. [15,16]