CHAPTER - III
THEORIES OF DIFFUSION IN LIQUIDS.

In this chapter we shall briefly consider various theories which have been proposed to explain the phenomena of transport properties and indicate how the experimental findings can be correlated with their theoretical counterparts.

It is possible to approach the problem of liquid dynamics from two directions: (a) either the liquid is considered as a disordered solid and the solid state ideas are transferred to the liquid field or (b) the liquid is considered as a condensed gas and the gas aspects are supposed to be dominating. One or the other aspect dominates depending upon the temperature of the liquid and the time scale of observations. From the dynamical point of view, the liquids may be broadly divided into two classes: (a) monatomic liquids and (b) molecular liquids. From the theoretical point of view the molecular liquids present a manybody problem of formidable complexity, whereas the simpler monatomic liquids, such as liquefied noble gases and liquid metals are somewhat simpler to handle theoretically.

Most modern theories of liquids have been based upon a quasicrystalline structure of liquids. X-ray investigations have
shown that the structure of liquids in microscopic regions is similar to that of a crystal. There is a tendency for particles in the immediate vicinity of a central particle under consideration to occupy sites which correspond to those of a regular crystal lattice; this tendency, however, decreases rapidly with increasing distance from the central particle. For the statistical thermodynamical treatment of liquids this picture has been further simplified by replacing the quasicrystalline structure by that of an ordered crystal lattice.

We shall briefly review a few of the standard theories of liquid dynamics developed by Eyring, Born, Frenkel and others.

3.1. Eyring's theory.

Viscosity and diffusion are two closely related physical phenomena and both can be treated by means of the theory of absolute reaction rates, proposed by Eyring and his workers (1937). Just as a gas is assumed to consist of molecules moving about in space, so a liquid may be regarded as made up of 'holes' moving about in matter. The classical treatment of diffusion is solution is based on the assumption that Van't Hoff's equation \( P = CRT \), relating the osmotic pressure \( P \) to the concentration \( C \), is obeyed, that osmotic pressure is the driving force of diffusion and that stokes' law is applicable to the
Diffusion of large molecule (B) due to movement of small solvent molecule (A).  

Fig. 3. Eyring's treatment.
movement of solute molecules. The first two assumptions are probably justifiable only in extremely dilute solutions, and the last can hold only when the diffusing molecules are very much larger than those of the medium.

As in the case of viscosity, in order to diffuse in solution one molecule is to slip past another molecule. The distance between the two successive equilibrium positions is \( \lambda \) (fig. 3.1), so that this is the distance through which a molecule of solute is transported in each jump. It is assumed that the standard free energy is the same in the equilibrium positions that the molecule occupies in course of diffusion; since the concentrations at the initial and final positions must be different, as otherwise diffusion would not occur, this condition can hold only if the solutions are ideal. Hence the treatment given by Eyring and coworkers is applicable to ideal systems or to solutions which are so dilute that they behave virtually in an ideal manner. When a large molecule or ion diffuses or migrates electrically, in a solvent consisting of relatively small molecules, it is unlikely that the rate determining step will be the jump of the solute molecule from one equilibrium position to the next, since the work required to produce the necessary space would be very large. It is much
more probable therefore that the jump of the solvent in one direction is the rate determining process; the large molecule of solute then moves in the opposite direction into the space left vacant as a result of the motion of the solvent molecule. This conclusion is in agreement with the observation that the temperature coefficient of diffusion of large molecules is the same as the temperature coefficient of viscosity of the solvent. It is clearly the movement of the solvent molecules that determines the rate of diffusion of the solute in these instances. If the molecules are treated as hard spheres, it is evident that the solvent molecule must move through a distance of at least \( \pi \gamma \) where \( \gamma \) is the radius of the large diffusing molecule, in order that the latter may move from right to left a distance of approximately \( \lambda \), where \( \lambda \) is the distance between successive equilibrium positions of the solvent molecule.

3.2. Born's theory

The problem of formulating a rigorous mathematical description of the molecular motion in the liquids has always been regarded as much more difficult than that of the kinetic theory of gases or of the solids, because in the case of gases one has the simplifying features of low density and in the case of the solids a regular lattice structure.
Born realized the need of generalizing the conception of distribution function (used in statistical mechanics) by taking as arguments for each molecule, not only the position and the velocity vectors but also the accelerometer vectors. And the main point of his theory is that this mean acceleration can be expressed in a simple way with the help of Newton's equation of motion. These give the acceleration of one molecule in terms of forces due to all atoms. The resultant force may be regarded as due to two actions; first due to the remaining particles of the group to which the atom under question belongs and secondly that of all Rest.

The main general result obtained by Born's method is that all thermodynamical properties of the system can be expressed in terms of some mathematical functions, which express the probability of finding two particles at given positions. In the equilibrium condition, it depends obviously only on their distance $r$ and is identical with the radial distribution function determined by experimental investigations on the scattering of X-rays by monatomic liquids. Moreover all thermodynamical quantities can be expressed in terms of the Fourier transform of the aforesaid function, which is directly given by the intensity distribution of the scattered X-rays. Hence the thermodynamics of the liquid are reduced to the knowledge of
this experimental function. The function thus found can be used to obtain expressions for free energy, from which all thermodynamic quantities can be derived. The main object of Born's investigation is of course the derivation of the thermomechanical equations of motion and a determination of the coefficients of viscosity, thermal conductivity etc., in terms of atomic interaction. A feature of this theory is that one obtains not only the ordinary equations of hydrodynamics but also generalized ones describing simultaneously the motion of groups of molecules. All properties of a liquid in motion are compounded of two parts, due to thermal motion and the inter-molecular forces respectively. The first which is only considered in the cases of gas is quite insignificant in the case of liquids. When it is neglected, one obtains the coefficients of viscosity and thermal conduction as integrals involving the radial distribution function and its distortion by motion.

A different formula for the coefficient of viscosity has been given by Fürth. It is based on the theory of holes. The liquid is regarded as a continuum for small bubbles, the size and the apparent mass of which depend upon the surface tension. These bubbles perform a kind of Brownian movement and transfer energy and momentum; the coefficient of viscosity can thereby be
be expressed in terms of the surface tension. Fürth's formula contains an exponential factor of the same type as that of Born; the remaining factor cannot be compared with that of Born because of the entirely different assumptions made.

3.3. Frenkel's theory

Frenkel's theory emphasizes the facts that the similarity between liquids and solids is much closer than that between liquids and compressed gases, at least in the vicinity of the melting point. The volume increase on melting is of the order of magnitude of 10 percent only in most cases, in some cases it is less or may even become negative; the heat of fusion is of lower magnitude than the heat of evaporation. The conception of disorder in a crystal leads to a certain understanding of the properties of a liquid. The energy required for the production of a hole within a liquid, consisting of molecules is the same as that to be supplied for evaporation, provided that the size of the hole is equal to that of a molecule of the liquid.

The picture for diffusion in liquids does not differ essentially from that for solids, the only difference being a lower heat of activation in the case of liquids. In contrast to the case for solids, there exists a direct relationship between diffusion and viscosity in liquids. The coefficient of diffusion is given by,

\[ D = \frac{ukT}{3} \]  

(3.1)
where \( u \) is the mobility of the particle under consideration, i.e. the stationary velocity acquired under the influence of unit force. The mobility for a spherical particle moving in a continuous liquid is given by Stokes' formula,

\[
U = \frac{1}{6\pi\eta r} \quad (3.2)
\]

where \( \eta \) is the viscosity and \( r \) the radius of the particle. Though derived on the assumption of a continuous medium, equation (3.2) is a fairly good approximation for not too small values of \( r \). Therefore a satisfactory theory of diffusion in liquids should allow a calculation of viscosity and vice versa. It may be worthwhile to emphasize the fact that the relation between viscosity and diffusion in liquids is different from that for gases. In gases viscosity and diffusion constant are proportional to each other, while in liquids they are inversely proportional to each other.

The approximate expression for the coefficient of diffusion in a liquid on the basis of the 'hole' theory of liquids is the exact analogue of the formula derived for diffusion in solids,

\[
D \approx f \frac{d^2}{t} \exp\left(-\frac{E}{RT}\right) \approx fdv \exp\left(-\frac{E}{RT}\right) \quad (3.3)
\]

where the exponential term is essentially the number of holes in the liquid (given as the fraction of the number of particles present), \( d \) is the average distance travelled by a migrating particle.
hole i.e. by a neighbouring particle, jumping into the position of the hole, \( t \) is the time necessary for a particle in the vicinity of a hole to move over the distance \( d \). Thus \( d/t \) may be interpreted as the velocity \( v \) of the diffusing particle. It we identify \( v \) with the average thermal velocity of a particle of the order of magnitude of \( 10^4 \) cm per sec. then with \( d \approx 10^{-8} \) cm, \( t = 10^{-12} \) sec, of the order of magnitude of time necessary for one oscillation of a particle about its instantaneous equilibrium position. The numerical \( f \) would have to be derived from a more rigorous theory. Frenkel chooses \( f = 1/6 \) equivalent to the factor entering the expression for the mean square displacement for motion in three dimensions.

Frenkel emphasizes the fact that the diffusion coefficients in liquids, in contrast to those in crystal, are all of about the same order of magnitude, \( 10^{-5} \) cm\(^2\) sec\(^{-1}\) or smaller. This holds even for different solvents and over a considerable range of temperature. Since the energies of activation, found empirically for diffusion in liquids are much smaller than those for solid crystal, the variation of this energy, consequently must smaller, also, as must be the influence of temperature on the coefficient of diffusion. These facts are readily understood in the cases where Stokes' law holds good. Variation of the coefficient of diffusion due to variation of radius are not larger
Unless colloidal particles are considered.

According to Sutherland, for a small molecule diffusing through a solvent of comparable molecular diameter one has

\[ D = \frac{kT}{4\pi\eta r^4} \]  

(3.4)

In this case it is no longer possible to regard the solute molecule as moving in a continuum. Except in the case of self-diffusion coefficients, it is not certain whether the bulk viscosity of the solvent or of the solution should be used in (3.4). In addition, other theories of viscosity give values of the numerical coefficient which differ from both 4 and 6. Lamm found it to be 1.64 using Andrade's theory of viscosity. Collins and Raffel made a kinetic calculation of the self-diffusion coefficient of a liquid consisting of perfectly elastic cubically packed spheres, with a Boltzmann distribution of energy leading to the conclusion that

\[ D = \frac{kT}{2.77 \pi d_c \eta} \]  

(3.5)

where \( d_c \) is the collision diameter and \( \eta \) the collisional contribution to viscosity.

A 'Stokes law' radius can be calculated for a solute molecule from its measured diffusion coefficient, especially if the uncertainty about the viscosity value to be used is minimised.
Fig. 3.2. Swalin's picture of liquid metals.
by measuring the mutual diffusion coefficient of a dilute
solution or a tracer diffusion coefficient of the pure solute.
It can be identified with the true dimensions of the solute
molecule only if this is spherical, unsolvated, and large
compared with the molecules of the solvent in which it is
moving. For a nonspherical molecule it is necessary to introduce
three frictional coefficients.

3.4. Swalin's treatment

Swalin (1958) considered the theory of diffusion in liquids
from the standpoint of fluctuation theory. It is postulated
that diffusion results from the movements of atoms through
small and variable distances as a result of local density
fluctuations (fig. 3.2). From geometrical considerations it
is deduced that about four atoms besides the diffusing atom
are involved in such a fluctuation. The theory results in
there being no activation energy for the diffusion process but
a plot of log D vs. 1/T yields an apparent straight line over
a small temperature interval. The slope of the straight line
is not a function of the properties of the element but only a
function of the temperature of measurement.

In the present series of experiments we have measured
the diffusion coefficient of liquid mercury at various temperature
These diffusion coefficient data together with the viscosity data of mercury were analysed by the theory of Eyring, the radius of mercury atoms was calculated by the Eyring equation and also the Stokes-Einstein equation and was compared with the experimentally measured values. The data has been analysed in the light of Swalin's treatment also.