1.1. The liquid state – theories

It is quite-scientifically proven that the matter exists in solid, liquid, gaseous, plasma and Bose-Einstein condensate states. The existence of matter in low temperatures is solid form and in high temperatures as gaseous form. However, at intermediate temperatures, the large proportion of matter exists as liquid. A liquid possesses neither the rigidity of a solid nor the fluidity of a gas and exhibits properties intermediate to both the states. Solutions are homogeneous liquid phases consisting of more than one substance in variable ratios.

In the case of solid state, the arrangement of atoms, the force of interaction and many other properties are well defined and it well agrees with that of gaseous state. But, the state of liquid is rather complicated. Comparatively, both the liquids and gases possess similar properties and they are assumed as condensed matter jointly and in fact, as fluids.

The translational kinetic energy in a crystalline solid is usually negligible. The molecules, atoms or ions vibrate about the equilibrium position to which they are held by intermolecular, inter-atomic, inter-ionic forces with low potential energies. In this case, an adequate potential function can be obtained. On the other hand in a liquid, the cohesive forces are sufficiently strong to lead to a condensed state, but not strong enough to present a considerable to the individual molecules translational energy the thermal motions introduce a disorder into the
liquid without completely destroying the regularity of the structure. Hence, it is difficult to device an acceptable partition function for liquids.

The molecules of a liquid are close together much like a solid so that there would be only a small compressibility, the kinetic energy is sufficiently large to establish an ordered crystal structure. A liquid shows short range ordering in space. Experimental studies involving X-ray analysis and Neutron diffraction substantiate this nature. In view of the above complexities, the following theories try to explain the liquid state.

1.1. Theories of liquid state

(i) Lattice theories – Loosely Bound Crystalline model

Liquids are classified like crystals from a chemical point of view, based on the kind of cohesive forces that hold them together. Ionic liquids consist of ions and mobile electrons whereas liquids like water are held together mainly by hydrogen bonds. In molecular liquids, cohesion is due to Van der Waal’s forces between essentially saturated molecules. Many liquids fall into the last category and even when other forces are present, the Van der Waal’s contribution may be large [1].

The well-ordered arrangement of units in solids is the main difference between solids and liquids. The orderly arrangement extends over a short range only – five or six molecular diameter – in the case of liquids. This situation is called short range order and long range disorder. It is a reasonable model [2] since near the melting point, the densities of crystal and liquid the close together; the solid usually expands 10% in volume or only about 3% in intermolecular spacing, when it melts. Whatever order exists in a liquid, the structure is
continuously changing because of thermal motions of the individual molecules. The properties of liquids are determined by the time average of a large number of different arrangements.

(ii) Cell model

Lennard Jones [3] introduced the cell model for a liquid by considering varying potential field determined by the interactions of the cell molecule with the surrounding neighbours. Barker [4] distinguished a fluid from a solid in his tunnel model by constructing two dimensional lattice of tunnels in which molecules are confined to positions anywhere in the tunnels. Molecules are thus allowed more degrees of freedom as in fluids.

The lattice models assume that the variation of the number of nearest neighbours decreases with the decrease in density, while their distance remain constant.

(iii) Condensed Gas model

Liquid needs a container to contain itself. The walls exert pressure in the liquid in such a way that no resultant stress remains, so that the only stress, the liquid can experience, is a hydrostatic pressure. For this reason, the pressure is same in all directions. In this sense, the liquids can be considered as a condensed gas and the interaction between the neighbouring molecules may be calculated through pair potential function.

The Van der Waal’s forces both attractive and repulsive type come into play between molecules which are nearer enough to influence mutually and the behaviour molecules is largely determined by the balance between these two forces. The tendency of all the molecules to
aggregate at low temperature is a sufficient indication of the existence of cohesive forces between the molecules.

This model is also a reasonable one because in the critical region, the density of a fluid can be increased continuously from a low value appropriate to a gas to a high value close to that of a liquid.

A more direct approach to liquids would try to develop the theory directly from the fundamentals of intermolecular forces and statistical mechanics. This is a difficult task but a beginning has been made by Moore [2]. In Eyring and John’s [5] significant structure theory, the liquid is considered as a lattice in which these are large numbers of vacancies. Incorporating the above assumptions, Eyring has successfully accounted for the liquid properties.

(iv) Gel model

In this model, the liquid is viewed as an infinitely and randomly branched gel of rapidly interchanging hydrogen bonds in which closures of rings are present at random but in which there is no significant preference for an ordered array of small rings. This model satisfactorily explains the two-phase transitions (melting and boiling) that define the liquid phase.

1.2. Inadequacy of the theories

In describing the liquid, two fundamental problem that require to be tackled are

(i) Characterization of the molecular interactions and

(ii) the statistical problem of relating the macroscopic properties of the system to the microscopic properties.
Hildebrand [6] criticizes the unreality of the above two approaches which treat the liquid either as a disordered solid lattice or as a condensed gas. The disordered crystal theory is applicable near the melting (triple) point and the imperfect gas theory more valid, near the critical point. It is not possible to derive parameters from these two models in terms of which one can look at a liquid independently as a ‘liquid’.

Though there is great deal of an acceptable partition function for liquids, the gap between the physics of liquids and the mathematics of the existing theories is rather wide.