

## P R E F A C E

It is well known that matter exists in three different phases ( solid, liquid and gaseous phase ). Solids are rigid and give sharp Bragg reflection in a diffraction experiment, demonstrating an ordered arrangement of atoms or molecules. Liquids and gases are fluid. Although there is a clear distinction between solid and fluid, there is no qualitative distinction between liquid and gas. Van der Waals pointed out explicitly the continuity of the liquid and gaseous states. At temperatures below the critical temperature two fluid phases can co-exist in equilibrium : the denser phase is called liquid and the less dense phase is called gas. Above the critical temperature co-existence of fluid phases is not observed. One can pass continuously from low temperature gas to low temperature liquid by heating above the critical temperature, compressing and cooling. The difference between liquid and gas is essentially a difference in density  $[1,2,3,4]$ .

However, liquids and dense fluids are distinguished from dilute gases by the importance of collisional processes and short range interaction and from solids by the lack of long range order. In the case of low density gases disorder due to thermal motion predominates over the ordering imposed

by the intermolecular forces. On the other hand a crystal has a regular arrangement. Here the amplitudes of the vibrations of the atoms and molecules about their mean position of rest is small compared to their diameters. Any one molecule is always interacting with many neighbours. Thus long range ordering predominates and at low temperature these ordered solids have their mean potential energy (P.E.) greater than the mean kinetic energy (K.E.). Contrary to this, dilute gases have their mean K.E. much greater than the mean P.E. resulting in complete disorder in their molecular arrangement.

Unlike that of the dilute gases and crystalline solids which can be thought of as deviants from well understood ideal states, the ideal gas and the ideal harmonic crystal (both of which can be treated exactly), the structure of liquids is a bit difficult to visualize on a molecular scale. Liquid structure is a compromise between order and disorder. It is therefore tempting to treat liquids as an intermediate state between gas and solid. Cell or lattice theories have been developed basing upon these considerations. However, such theories tend to overemphasize the solid like character of liquids and for that reason have fallen largely out of favour. Liquids and solids resemble each other in their degree of packing and in their property of cohesion. But in a

liquid the cohesive forces are not strong enough to prevent the translational movement of molecules.

The first fundamental problem in describing the structure of liquids is the understanding of the nature of the intermolecular forces. ( Here the word molecule refers to atoms, molecules and ions ). It has been established that the forces are harshly repulsive for small molecular separations and attractive for large separations. The effect of these strongly repulsive forces is to create the short range order characteristic of the liquid state. The structure of simple liquids is primarily determined by these repulsive forces. The attractive forces acting at long distances vary much more smoothly with the distance between particles and play a minor role in determining the structure of the liquid. Their main effect is to constitute an essentially uniform background potential which provides the cohesive energy required to stabilize the liquid. This separation of the effects of repulsive and attractive forces is a very old-established concept originated by Van der Waals in the last century and this forms the basis of the very successful perturbation theories of liquid state  $\llbracket 1 \rrbracket$ . The second fundamental problem is that of relating the bulk or macroscopic properties of a system to the microscopic or molecular properties and in particular to the potential energy function which describes the way in which an

isolated pair of molecules interact. This link is now provided by statistical mechanics through the introduction of equilibrium probability densities and molecular distribution functions. A number of integral equation approaches for distribution function theories have been developed over the last two decades.

It should be emphasized that for a liquid there are two types of descriptions ( static - time independent and dynamic - time dependent ). The static description refers to thermodynamic or equilibrium properties and to the steady state transport coefficients measured overtimes and distances long compared on a molecular scale and these properties do not change with time. The dynamic description refers to properties whose measured values depend on the time scale or frequency of observation. This time and distance scale has special significance in the discussion of liquids. Crystalline solids have an ordered and time - independent structure. At short times a liquid behaves as a solid with elastic properties and at some short distance a liquid has some degree of order. A gas has none of these at any time and distance. Barton [2] has described the above features succinctly but in a rather oversimplified way through the following words :

Solids are always 'solid'. Gases are always 'fluid'  
Liquids are 'solid like' at short times and short distances but 'fluid like' at long times and long distances.