The Liquid State
2. Its Structure and Dynamics

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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.

Modelling of Liquids

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.

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 mimics 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.

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 and can be handled in the same way as the Ising model for a ferromagnet.

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.

The random close packing model was obtained by a real life
experiment. Bernal and co-workers filled a balloon with thousands of steel ball bearings. 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.

Later Scott at Toronto created a computer replica of a heap. A detailed analysis of this replica showed that the radial distribution function for random close packing is essentially the radial distribution function for a liquid.

In the eighteenth and nineteenth centuries, mathematicians carried out the study of coordination numbers in terms of geometry of neighbours. This was done using the concept of Voronoi polyhedra. Take a point and bisect the line joining it to its neighbours with planes. The smallest polyhedron enclosed by the planes is called the Voronoi polyhedron for the given point. A set of all Voronoi polyhedra fill up space. One can make foam rubber models of these 'canonical' polyhedra and fill up space with them to make a model of a liquid.

**Multicomponent Liquids**

We have considered so far a single component liquid. But one often meets with liquid mixtures containing two, three or more components. In the simplest case of a binary (two component) mixture AB, one has to deal with three partial pair correlation functions $g_{AA}(r)$, $g_{AB}(r)$ and $g_{BB}(r)$. $g_{AB}(r)$ gives the neighbours of type B to an atom of type A. It will not be possible to derive the
three pair correlation functions using a single diffraction picture obtained with say X-rays. One should compliment this data by use of other radiations for obtaining diffraction pictures. Neutrons are suitable for this purpose as they have a large penetrative power. Also the scattering power of different atoms for neutrons is very different from the scattering power of the same atoms for X-rays. The scattering power of two isotopes of the same element can be very different for neutrons whereas for X-rays it is the same. One can therefore get two diffraction patterns with neutrons (on samples with and without substitution of isotopes) and one X-ray diffraction pattern. With three different diffraction patterns one can solve for the three pair correlation functions of a binary liquid. Figure 1 shows the partial structure factors obtained in this fashion in the case of liquid Cu$_6$–Sn$_5$ alloy.

It is obvious that the complexity increases when the number of components in the alloy is more than two.

**Dynamics of Liquids**

In a liquid the atoms are moving continuously. The structure of liquids that we have been discussing is a time-averaged structure. But it will be interesting to study the complicated molecular motions experimentally.

Glauber and Van Hove independently generalised the pair correlation function to take time dependence into account. This generalised function $G(r, t)$ has the following significance. Given an atom at the origin at time 0, $G(r, t)$ gives the probability of finding an atom at $r$ at time $t$. Since we are dealing with different instants of time, a contribution to $G(r, t)$ may come from a different atom at position $r$ at time $t$ or from the same atom moving from the origin to position $r$ at time $t$. Corresponding to this generalised pair correlation function, we have a generalised scattering factor $S(Q, \omega)$ defined by

$$S(Q, \omega) = \int \int dr \, dt \exp[i(Q \cdot r - \omega t)]G(r, t)$$
Just as $Q$ represents the change in the direction of the probe beam after scattering, $h\omega$ represents the change in energy of the probe particle after scattering. $\omega$ represents the angular frequency of the fluctuations associated with the dynamics of the atoms and molecules in the liquid.

Since the energy of the probe particle is changed in the scattering process, this is called inelastic scattering. The energies associated with the fluctuations are small. If one uses neutrons then the change in energy will be comparable to the original energy of the neutron. So one can measure the change in energy with good accuracy. This is not possible with X-rays. Inelastic neutron scattering is well suited for the study of dynamics of liquids. Figure 2 shows the dynamic structure factor $S(Q, \omega)$ measured in liquid argon. From this, using Fourier inversion techniques, one gets the self- and different-atom correlation functions, $G_s$ and $G_d$, as a function of $r$ at different times. This is shown for small, intermediate and large times in Figure 3. One sees that $G_s$...
is a Gaussian distribution in space which broadens out as time increases. From this, the self-diffusion coefficient of the atom in the liquid can be found. On the other hand, $G_d$ shows a structure at short times which gets washed out as time increases to approach the average density of the liquid.

Dynamics of liquids is characterised by two important types of motion – single particle modes like self-diffusion, and collective modes in which a large number of atoms partake collectively as in propagation of sound. Single particle motion is usually seen as a broadening of the elastic ($\omega=0$) peak, while collective modes appear as side bands at finite $\omega$ in the scattering function $S(Q, \omega)$. Thus using inelastic neutron scattering, one can probe dynamics in a liquid over microscopic time scales of $10^{-12}$ seconds.

Such studies have been carried out on a number of inert gas liquids including liquid helium, alkali metal liquids, liquid lead, water, etc. and these measurements have led to progress in liquid state theories.

**Computer Simulation Studies**

The dynamic behaviour of liquids is simulated on a computer using the molecular dynamic method. In this method the interatomic potential is assumed to be known. Starting with a box containing a reasonably large number of particles, with given initial positions and velocities, the subsequent motion is calculated on a computer sequentially at small intervals of time using Newton’s laws of motion. Various algorithms have been developed for carrying out such calculations. From these calculations one could arrive at various correlation functions, spectral functions, and microscopic and macroscopic properties. One may compare self-diffusion coefficients and frequencies of collective modes so computed with experimental results obtained by inelastic neutron scattering.

Such computer simulations have been carried out on a variety of
liquids including ionic systems, polymer melts, alloys, plasmas, etc. These studies have helped in unravelling phenomena on time scales ranging from a pico-second and upwards. Various phenomena like evaporation, clustering and surface effects in two dimensional thin film like systems have also been investigated.

Suggested Reading


and references cited in these publications.

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