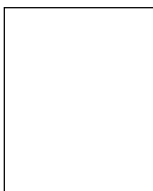


The Liquid State

1. The Arrangement of Atoms

K R Rao



K R Rao received his Ph.D. from Banaras Hindu University, Varanasi in 1969. He headed the Solid State Physics Division at BARC. His areas of work include neutron spectroscopy, phonon physics and neutron beam instrumentation. His contributions to the study of ionic molecular systems led to planning new experiments and the development of software for data analysis and interpretation.

The liquid state of matter is of great practical importance. The arrangement of atoms in a liquid is more disordered than in a crystal, and can be studied by the scattering of X-rays. This disordered arrangement is described statistically by the pair correlation function $g(r)$, which gives the relative probability of an atom having a neighbour at a distance r .

Introduction

Three different phases of matter are familiar to us – solid, liquid and gas. Liquids and gases flow while a solid under normal conditions does not. A solid retains its shape while a fluid (a collective name for gases and liquids) will take the shape of the containing vessel. In other words a solid is rigid while fluids do not possess the property of rigidity.

The same material can exist either as a solid, a liquid or a gas under different conditions of temperature and pressure. This is a matter of common observation. For example, when water, which is a liquid at room temperature, is cooled below 0°C at atmospheric pressure, it becomes solid ice. Heating water to 100°C at atmospheric pressure converts it to steam. Such a transition of matter is called a *phase transition*.

The Van der Waals equation in a sense, represents the behaviour of actual gases over a wide range of pressure and temperature.

The kinetic theory explained the properties of gases in terms of molecular motions. The molecules in a gas are moving around randomly with velocities governed by the Maxwellian distribution. In this theory the pressure exerted by a gas is related to the average kinetic energy of a molecule, which is proportional to its temperature. If inter-molecular interactions are neglected and the molecules are taken as point particles, the kinetic theory of gases leads to the Boyle's and Charles'

laws. To account for deviations from these laws one had to invoke inter-molecular attraction as well as the finite size of the molecules. Thus was born the Van der Waals equation, which, in a sense, represents the behaviour of actual gases over a wide range of pressure and temperature.

Because the molecules have a finite size the inter-molecular interaction must be a strong repulsion when the inter-molecular distance is of the order of the diameter of the molecule.¹ However when the molecules are far apart, one should postulate an attractive interaction to account for deviations from the ideal gas laws when the gases are compressed and cooled. Otherwise, one cannot account for liquefaction of gases. The picture of intermolecular interaction which emerged from the study of gases is shown in *Figure 1*.

Even in liquids molecules move in random directions with random velocities. This movement of molecules in a liquid gives rise to the phenomenon of *Brownian motion*. The botanist, Robert Brown, observed that pollen grains suspended in a liquid appear to move randomly. Brownian motion is a result of collisions of the grains with the molecules in the liquid. It was Einstein who first gave a satisfactory theory for this phenomenon.

The kinetic theory of gases provides a satisfactory quantitative theory for the behaviour of gases. It is difficult to develop a similar quantitative theory for liquids, since the atoms are always close enough to be in constant interaction, while their spatial arrangement is disordered.

Matter in the liquid state is important from the practical point of view. In the processing of metals one deals with molten metals like iron, aluminium, lead, zinc, etc.. Metals are cast into different shapes by pouring them in the molten state into moulds. One can control the grain size of many cast materials by dissolving specific elements in low concentration in the molten state before

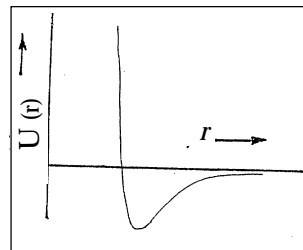


Figure 1 Interatomic potential as a function of distance between two atoms. Note that the potential is weakly attractive at large distance and strongly repulsive at short distance.

¹ This is typically a few Angstrom units i.e. a few times 10^{-8} cm.

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casting. Amorphous ribbons of many alloys are obtained by dropping molten liquid of the alloys on a rapidly spinning copper wheel. Many important applications of liquids depend on a knowledge of their surface tension, wettability, viscosity and heat conductivity. A study of liquids to understand their behaviour is very important.

In this two part article we shall confine ourself to a brief description of the structure and the dynamics of liquids, the arrangement and motion of the atoms.

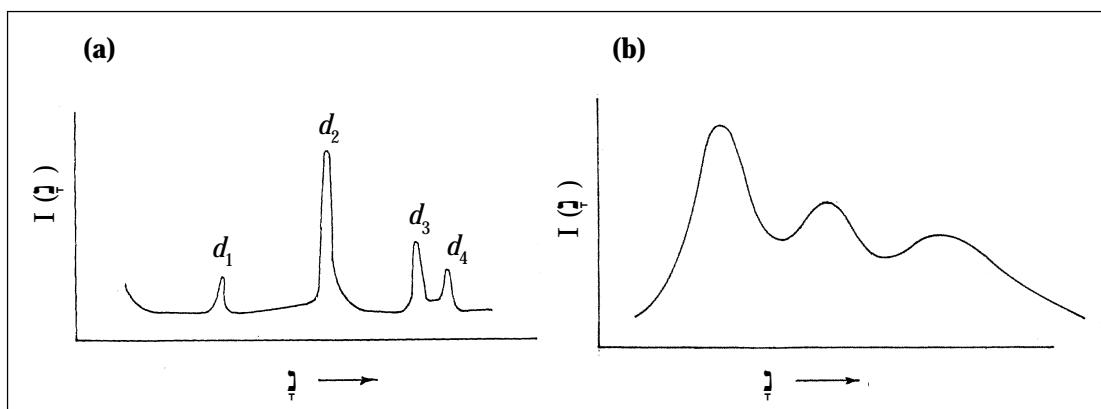
Structure of Liquids from X-ray Diffraction

By 1912, X-ray diffraction from crystals had been discovered by Friedrich, Knipping and Laue. In a crystal atoms are arranged in a regular pattern. If X-rays of wavelength λ are incident on a crystal, they are selectively diffracted at certain angles 2θ to the incident direction, satisfying the equation discovered by Bragg

$$\lambda = 2d \sin \theta ,$$

Figure 2 (a) A typical X-ray diffraction pattern from a crystal. Note the many sharp peaks. (b) A typical X-ray diffraction pattern from a liquid.

where d is the spacing of a family of planes responsible for the diffraction peak at the angle 2θ . Figure 2 shows such a diffraction pattern from a crystal. The intensity of the diffraction peak depends on the scattering power of the atoms and the way they are arranged in the crystal. One may 'invert' the diffraction



pattern to obtain structural information. This is the basis of X-ray crystallography – the study of the arrangement of atoms in solids by using measurements of X-ray scattering.

Zernicke and Prins studied X-ray diffraction from liquids. *Figure 2b* shows the diffraction pattern from a liquid. One sees it contains a few broad peaks in contrast to the large number of sharp peaks in a crystal. This arises because the atoms in a liquid are not arranged in a regular pattern as in a crystal.

The intensity of the diffraction peak depends on the scattering power of the atoms and the way they are arranged in the crystal.

The structure of the liquid is conveniently defined in terms of a pair correlation function, $g(r)$. For the sake of simplicity let us consider a monatomic liquid, say liquid xenon. *Around any given atom in the liquid*, we may draw a spherical shell of radius r and width dr . The number of atoms dn , on an average, in this shell is given by:

$$dn = 4\pi r^2 g(r) \nu dr.$$

This gives the definition of $g(r)$, the pair correlation function. Here, ν is the average number of atoms per unit volume.

The pair correlation function is related to the structure factor $S(Q)$ of the liquid. The parameter Q is called the wave number, and is a measure of periodicity in space. If we have a repetition over a period d in space, we define $Q = 2\pi/d$. The analogous and more familiar concept is the angular frequency ω , which measures periodicity in time, and is given by $2\pi/T$, where T is the period of repetition in time. $S(Q)$ is obtained from the diffraction pattern as follows. From the intensity of diffraction, $I(Q)$, where Q is given by

$$Q = 4\pi \sin \theta / \lambda,$$

the structure factor $S(Q)$ can be calculated using the relation

$$S(Q) = I(Q) / N \nu^2(Q),$$



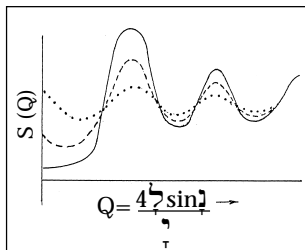


Figure 3 The variation of structure factor with density in a liquid. . . . low density, - - - intermediate density, — high density.

Suggested Reading

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- ◆ J P Hansen and I R Mac Donald. *Theory of simple liquids.* Academic Press, 1986.
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where N is the number of atoms and $f(Q)$ is the atomic scattering factor.

The structure factor $S(Q)$ is related to the density, ρ , of the liquid and the pair correlation function through

$$S(Q) = 1 + \rho \int \{g(r) - 1\} e^{iQ \cdot r} dr.$$

By ‘inverting’ the structure factor, one obtains information on the pair correlation function. *Figure 3* shows how $S(Q)$ changes with the density of the liquid. The fact that $S(Q)$ for a liquid is nonzero for a continuous range of Q means that unlike a solid, there are no sharply defined values of periodicity d . ($S(Q)$ for the crystal has sharp peaks). The two cases can be compared to a noise which has a continuous range of frequencies present, while a musical note has sharply defined frequencies.

The pair correlation function is strongly dependent on the interatomic potential, $U(r)$. Contributions to this potential $U(r)$ come from two-body, three-body, etc. potentials. From the pair correlation function one may obtain some information on the potential parameters i.e. the forces between atoms. The pair correlation function is also used to calculate the following properties of the liquid.

- The internal energy E of the liquid at temperature T can be written as

$$E = 3/2 Nk_B T + \langle \Phi \rangle .$$

Here k_B is the Boltzmann constant and $\langle \Phi \rangle$ is the average value of the two body interatomic potential energy. This last quantity can be related to the pair correlation function by the formula

$$\langle \Phi \rangle = (1/2) \rho^2 V \int U(r) 4\pi r^2 g(r) dr .$$

Here V is the volume of the fluid, and $\Phi(r)$ the potential energy

of two atoms separated by r .

- The equation of state of the liquid can be derived in the form

$$p = \frac{2}{3} k_B T - \frac{2}{3} \int_0^\infty r^2 \frac{dU(r)}{dr} g(r) dr.$$

Here p is the pressure and T the temperature of the liquid.

When we consider molecules with more than one atom, the definition of the pair correlation function becomes more complicated. It contains signatures of the centre of mass distribution of molecules, mass distribution of atoms within the molecules as well as the relative orientation of molecules. It is difficult to obtain these details from scattering data. However some understanding has emerged in the case of highly symmetric molecules like CCl_4 or CH_4 . *Figure 4* shows the X-ray diffraction pattern from CCl_4 . At small angles of diffraction the pattern is analogous to that seen with monatomic liquids. However there is a modulation seen at large angles. These two features can be understood in terms of inter-molecular distribution and intra-molecular distribution of atoms respectively.

We have so far considered molecular liquids containing neutral molecules. However there is a large class of ionic liquids containing negatively charged cations and positively charged anions. In such a liquid one will have to take into account the long range Coulomb interaction between the ions. The analysis of diffraction data is more complicated. One can obtain information about local number and charge density in such liquids.

In the next part of this article we will deal with multicomponent liquids, modelling of liquids and study of the dynamic behaviour of liquids using computer simulation.

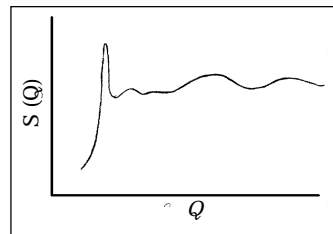


Figure 4 Typical structure factor for a molecular liquid such as CCl_4 .

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