

Engineering Outline 152

Liquid structure theory

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Key words

atoms
liquids
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statistical mechanics

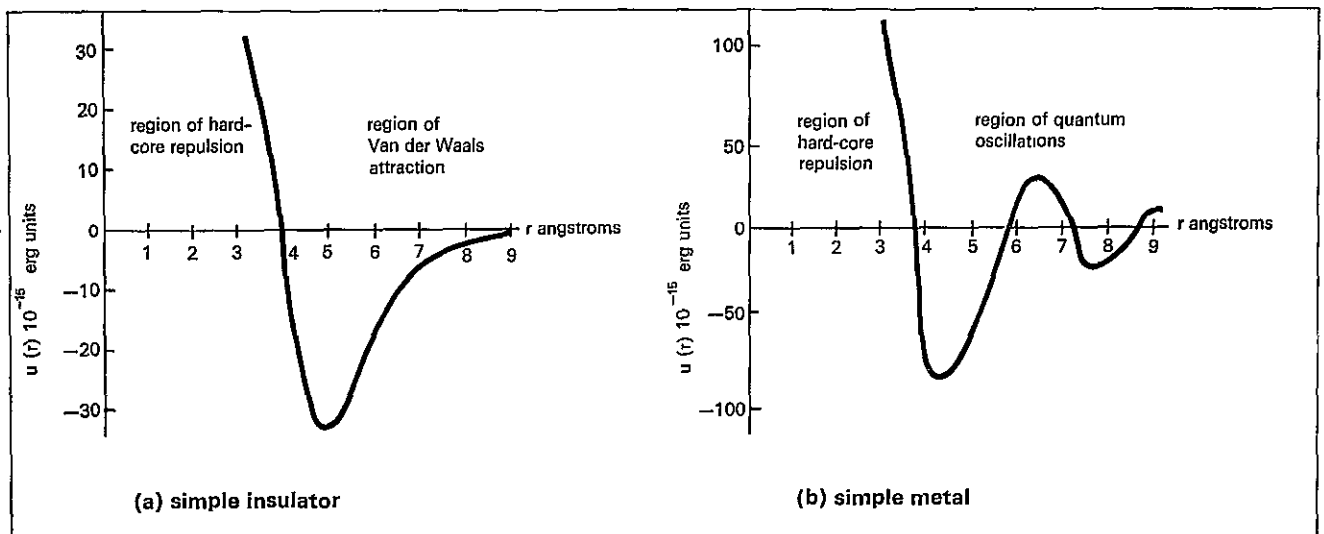
Basic facts

Liquids differ from solids, and resemble gases, in their flow properties. Solids do not deform under constant shearing stresses, but resist with elastic forces proportional to the strain; liquids and gases do deform, and resist with viscous forces proportional to the rate of strain. On the other hand, as in their thermodynamic properties (compressibility, entropy, energy, etc), liquids generally differ from gases and resemble solids. In extreme situations, these distinctions can disappear. For example, substances in the glassy state flow extremely slowly, and respond elastically to forces of short duration; and for temperatures above the critical point there is no phase transition between liquid and gas.

Microscopic model

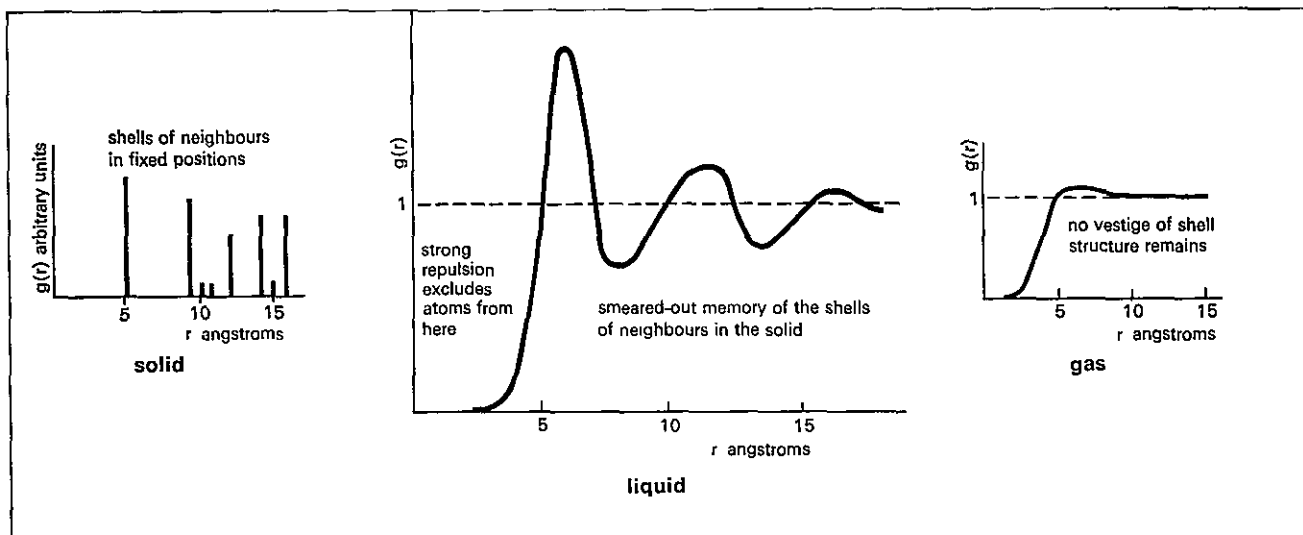
Liquids are envisaged as collections of mutually interacting microscopic units, which we shall call atoms although they may be molecules. An extensive body of theory exists only for so-called *simple liquids*, where the atoms are spherically symmetrical and the force between two atoms does not depend on the position of other atoms in their neighbourhood. Liquid argon and sodium are simple to a high degree of approximation, whereas water, because of the highly directional nature of the bonds between its molecules, is not.

The interatomic forces are best described by the slope of the curve given the mutual potential energy u between two atoms as a function of the distance r separating their centres. At short distances, the electrostatic repulsion between the electrons in the outer shells of the atoms causes the force to be strongly repulsive, so that the atoms are virtually impenetrable in all but the most energetic collisions; for slightly greater



1 The forces between the atoms of a liquid are described by the pair potential function $u(r)$. The form of the long-range part of the force depends on the type of liquid

separations the force is zero (the $u(r)$ curve has a minimum). The long-range forces depend on the type of liquid being considered. In the case of *insulators*, 1a, they are attractive and fall off as r^{-7} , due to the Van der Waals forces between the partially polarised electron clouds surrounding the atoms. The case of *metals* is different. There, the free atoms have electrons in incomplete outer shells, and in the liquid state these electrons



2 Typical forms for the radial distribution function $g(r)$ which describes the correlation between pairs of atoms in a liquid. Using only this function and the interatomic potential, the thermodynamic properties of the liquid can be calculated.

become detached and form a gas. But the ions they leave behind are positively charged, so they neutralise themselves by attracting some of this gas into their neighbourhood, thus forming 'neutral pseudo-atoms' which are the microscopic units of the theory. Subtle quantum-mechanical arguments show that the force between two of these falls off fairly slowly in an oscillatory manner, **1b**.

Under normal conditions, the response of the atoms to their mutual interactions and external forces can be described by classical mechanics; quantum effects are negligible except in the lightest substances, where they are very small, and liquid helium, where they dominate. The concepts linking the microscopic structure of atomic motions with macroscopic observable quantities are provided by statistical mechanics, which predicts that such observables are certain *averages* over all the possible dynamical states of the whole assembly of atoms. The direct calculation of these averages for macroscopic systems is impossible at present, since it involves the evaluation of about as many integrals as there are atoms present. It is therefore necessary to find *physical pictures* of a liquid which make it possible to approximate to the correct expressions.

It is here that the peculiar difficulties associated with liquids arise. The density is so high that the atoms spend most of their time within the range of influence of several neighbours (in contrast to a gas where the interactions occur rarely, in clearly defined binary collisions), while at the same time the temperature is so high that considerable disordered thermal motion occurs (in contrast to a solid where the only motion is small vibrations about fixed lattice sites). The extreme difficulty of finding an approximate model which takes account both of the ordering effect of the potential energy and the disordering caused by the kinetic energy means that, while a fairly complete qualitative understanding of liquid properties has been achieved, numerical predictions with errors of less than a few per cent are rare.

Equilibrium properties

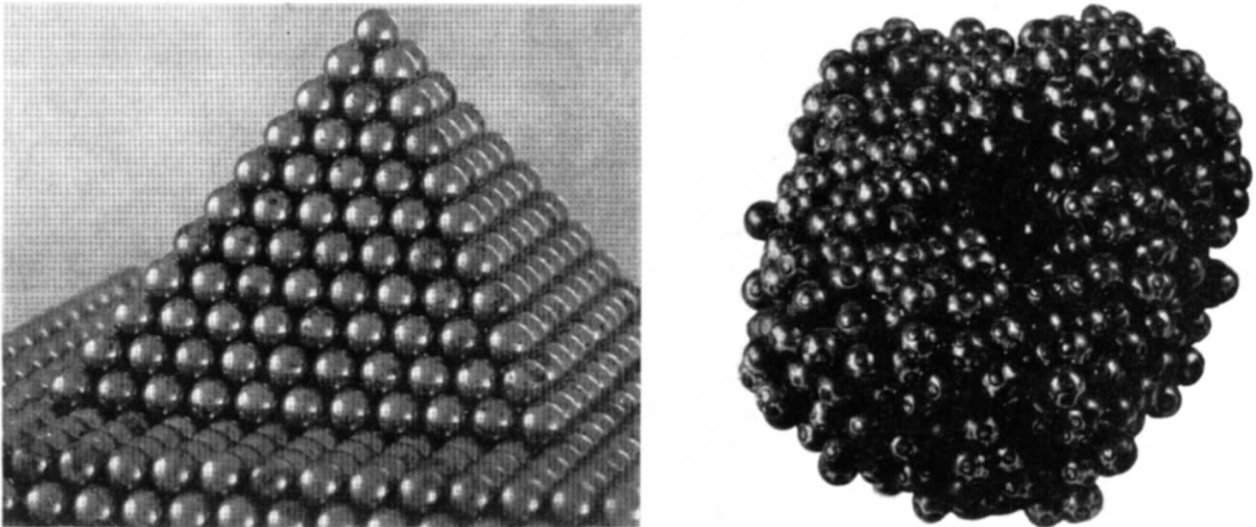
The high density in the liquid state, and the strong repulsive interatomic forces preventing interpenetration, imply (a) that the compressibility is low, as in the solid state; (b) that there is considerable short-range order, so that the entropy is not much greater than in the solid state; and (c) that it is difficult for the atoms, caged in by their neighbours, to move faster on being heated, so that the thermal capacity is high, as in the solid state.

More accurate calculations demand a careful specification of the structure. It is a standard result of statistical mechanics that the thermodynamic properties can be calculated solely from the interatomic potential and a knowledge of correlations between pairs of atoms in the form of the *radial distribution function* $g(r)$. This is the mean density of atomic centres seen at a distance r from any selected centre, divided by the mean density of atomic centres. In a liquid, this function (which can be measured directly by diffraction from the liquid of X-rays or neutrons with wavelengths comparable with the mean interatomic spacing) shows for small r the peaks at the clearly defined shells of neighbours characteristic of a solid, which merge at large r into the uniform distribution characteristics of a gas, **2**.

One group of theories, then, attempts to calculate $g(r)$ from the basic interaction $u(r)$. Unfortunately, this demands a knowledge of the three-body distribution function, which in turn involves the four-body correlations, and so on. This infinite regression can be terminated in various ways, such as, for example, the superposition approximation in which the three-body distribution function is replaced by a product of radial distribution functions. However, although such methods give quite good representations of $g(r)$, the thermodynamic functions are extremely sensitive to such factors as the position of the first peak of $g(r)$ relative to the minimum in $u(r)$, and cannot be calculated reliably within this framework.

A formal expansion for thermodynamic quantities can be derived whose successive terms involve atoms interacting in clusters of one, two, three, etc. But this method at best describes a fairly dense gas, and must fail completely in a liquid where each atom always interacts with between four and twelve neighbours.

The fact that equilibrium liquid properties resemble those of solids has led to various *lattice theories* of liquid structure. In the *cell theory*, for instance, the atoms move independently of one another within cells which make up a regular lattice. The *hole theory* introduces disorder by allowing a random distribution of vacant sites. These theories predict thermodynamic quantities which agree with experiment quite well, but are not accurate enough to distinguish unambiguously between the liquid and solid states. The more elaborate *cell cluster theory* permits



3 Hard-sphere models illustrating the loss of long-range order in the transition from the solid to the liquid state. On the left is a regular close-packed pile (solid); on the right, a random close-packed heap (liquid)

multiple occupation of cells, and forms the basis of an exact formal expansion for quantities of interest; however, it presents formidable difficulties of calculation, centred basically on the need to treat large clusters.

It is clear that a numerically accurate theory should start from a model of the structure which includes correctly the short-range three-dimensional ordering characteristics of liquids, without smearing out the angular correlations as in a gas, or including the long-range type of solid order. This has not yet been done, but some progress has been made in setting up the required 'statistical geometry' by investigating in detail the arrangements of hard spheres in random-close packed heaps, 3. For example, the common occurrence of five-fold symmetry in the environments of atoms precludes any possibility of long-range order.

In addition to these models, computers have been used to simulate the detailed motion of assemblies of up to about a hundred atoms, in order to evaluate in a direct way the statistical-mechanical averages for observable quantities. The phase change from solid to dense gas has been examined in this way, and the resulting equation of state agrees well with experiment, but no results are available for liquids.

Transport properties

Viscosity, thermal conductivity and diffusion arise when liquids are disturbed from equilibrium, and to understand these processes it is not sufficient to know just the configurational structure. Exact expressions can be derived for the transport coefficients, and involve correlations between atomic motions at *different times*. These correlations can be measured by diffraction methods, but it is not possible to calculate them

accurately ab initio (ie from $u(r)$), and the theory is rudimentary compared with that for equilibrium properties.

Once again it is necessary to use models, this time for the detailed motion of the atoms. In gases, it is generally sufficient to use the *kinetic method*, which treats the atoms as moving freely except for rare binary collisions; thus, for example, viscosity arises from momentum being transferred by atoms in a fast layer moving into a slow layer. But in a liquid the transfer of momentum is affected directly by the interatomic forces, because the atoms are never free. The resulting conception, a form of Brownian motion through the long-range forces impeded by frequent collisions with the hard atomic cores, forms the basis of calculations agreeing with experiment to about 10%, and also explains, for example, why the viscosity of a liquid falls with temperature, in contrast to that of a gas.

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