hard spheres is also a sphere with a radius twice as large). The earlier versions of this approach could not be used in the study of freezing because of strong divergences of geometrical origin, which have been removed using the "zero-dimension" limit of the equation of state: the free energy of small cavities which can only contain one hard sphere. These are the first theories of freezing in which the crystal is described as the global minimum of the free energy with respect to the density distribution, giving the correct occupation of the unit cell; they allow the study of problems for which the restricted variational approach was not valid.
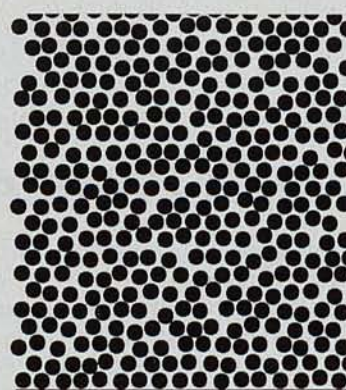
The author is working at Madrid

Further reading
Fundamentals of Inhomogeneous Fluids by R. Evans (editor D. Henderson, Dekker, New York, 1992) · M. Baus *Journal of Physics of Condensed Matter* 2 2241 (1990) · Y. Rosenfeld, M. Schmidt, H. Löwen and P. Tarazona *Journal of Physics of Condensed Matter* 8 L577 (1997) · P. Tarazona, Y. Rosenfeld *Physical Review E* 55 R4873 (1997)
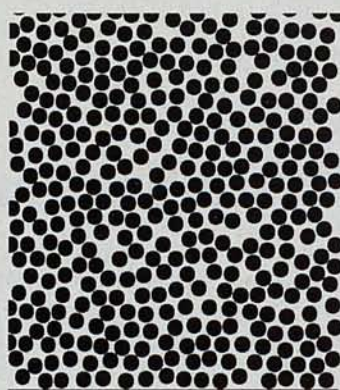
Fluid   Solid

Sketch of hard molecules in fluid and solid phases. The mean density and the local structure around each molecule are similar—but viewing the figure with small angle over the paper (*try it*) shows that the molecules in the solid keep the overall alignment along the main crystalline directions. Which phase has the larger entropy? The answer comes with the walls represented by the bottom lines: its effect in the fluid phase is limited to a few molecular layers and the density distribution averaged over the statistical configurations goes to a homogeneous bulk. In the solid the walls fix the crystalline lattice over the whole system and give a strongly inhomogeneous density distribution, with narrow peaks for the distribution of each molecule
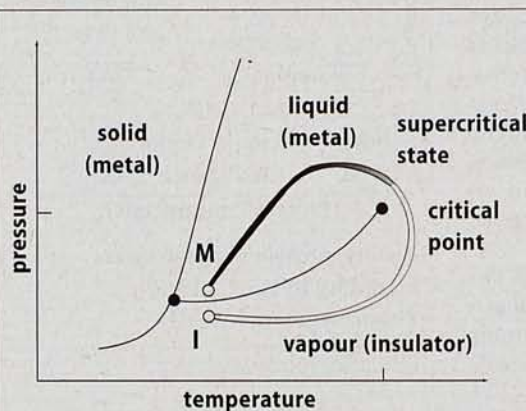
Metal or insulator?

Friedrich Hensel

hot topic

Fluid Metals

Nearly four fifths of the elements in the periodic table are metals. These elements remain metallic when they are heated trough their melting points at normal (1 bar) pressure. In contrast to melting, however, there are substantial changes in the electronic structure when the dense metallic liquid vaporizes. The liquid conducts electricity while the vapour does not. There is therefore a metal (M) insulator (I) transition that coincides exactly with the liquid-vapour transition, with the implication that both the density and the interparticle forces change.

However, this state of affairs applies only to conditions far below the critical point terminating the liquid-vapour phase line (see *figure*). Near the critical point, the liquid density is much less and the vapour density much greater. At what density does the vapour become a metallic fluid, or the liquid an insulator, along a line (see *figure*) going around the critical point starting from the ordinary liquid metal (point M) to the low density insu-

lating vapour (point I)?

The problem that throughout the fluid range of metals the interparticle interaction must change from metallic to nonmetallic binding has been a primary motivation for experiment. Most of this experimental effort has focused on mercury, caesium and rubidium because they have critical points that lie within current limits of static temperatures ($T_c < 2200$ K) and pressures ($p_c < 2000$ bar). Electrical, optical, magnetic, structural, thermodynamic and interfacial properties have been studied as functions of temperature and pressure up to and beyond the critical point. Each of these properties exhibits noteworthy variations with density. For example, the density dependence of the dynamic structure of liquid rubidium reveals that a monoatomic-molecular transition occurs in the metal-

A typical metal in the pressure temperature plane. Below the critical point the liquid is in equilibrium with a low-density vapour phase. Above the critical temperature, where the liquid and vapour no longer coexist, the fluid is said to be in the supercritical state

non-metal transition region of the expanded liquid analogous to that suggested to occur in shock compressed hydrogen. This is a direct demonstration of the interplay between electronic structure and the atomic arrangement of the liquid. It supports the view that the transition to a metallic state in hydrogen and the alkali metals evolves from the diatomic system.

Another interesting feature is provided by the behaviour of mercury in the vicinity of a non-metallic substrate. Indeed, the most familiar example from everyday experience of a non-wetting substance is metallic liquid mercury on a non-metallic solid. However, when mercury in contact with sapphire is heated near to its liquid vapour critical point a first order wetting transition occurs at a wetting temperature T_w. This transition is accompanied

by a line of prewetting transitions. These are transitions from a thin to a thick liquid layer. At high temperatures the prewetting line terminates at the prewetting critical point where the distinction between thin and thick films disappears. It is very significant that the wetting transition temperature T_w lies in the range where the gradual metal-non-metal transition occurs in liquid mercury at coexistence. The coincidence of these two transitions is again a striking example of the intimate interplay between changes in interparticle forces and changes in the electronic structure associated with the metal-non-metal transition.

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The History

Our understanding of liquids has been linked to our understanding of the cohesion of matter generally, or to what we now call the study of intermolecular forces. Early experiments under Newton's direction at the Royal Society in London early in the eighteenth century established the laws of capillarity, and the mathematician Brook Taylor (of Taylor's expansion) studied cohesion by measuring the force needed to lift a piece of wood off the surface of water. Such experiments were repeated throughout the century with different solids and liquids, but all this work led nowhere until Laplace brought the subject to life again with his successful theory of capillarity of 1806. He had intended to use the theory to study the inter-particle forces but found that all he could learn was that the forces were strong but of short range, "sensible only at insensible distances" in his phrase. His was a static view of matter and little progress could be made until the codification of the laws of heat and work into thermodynamics, and the development of the kinetic theory of matter in the middle of the nineteenth century. The synthesis of this work and Laplace's into a theory of liquids was the achievement of van der Waals in the last quarter of the century. His work, in turn, inspired that of Kamerlingh Onnes and his school at Leiden who studied liquids and liquid mixtures up to high pressures, and so laid the foundations of our knowledge of phase equilibria and critical phenomena. The move to high pressures was followed by one to low temperatures, to the liquefaction of helium and so to the quantal phenomena of superfluidity and superconductivity. On the theoretical side the culmination of the work of the Dutch school was L.S. Ornstein's adaptation of Gibbs's statistical mechanics to the study of liquids and his introduction, with F. Zernike, of their eponymous equation for the direct correlation function.

"Everything has its fashions, even science has its own," wrote R.A.F. Réaumur in 1749, and this was equally true around 1914. Quantum theory and the study of the atom were the exciting parts of physics and the theory of liquids was put to one side. Indeed, it is hard to see how more progress could have been made when little more was known about intermolecular forces than was set out in Laplace's dictum of a hundred years earlier. J.E. Lennard-Jones and others struggled throughout the 1920s to find the functional form of the intermolecular forces from the equilibrium and transport properties of gases but without coming to any satisfactory conclusions. Only when F. London showed in 1929 that the attractive potential comprised terms in r^{-6} (the dominant one), r^{-8}, r^{-10} *etc*, where r is the interatomic separation, was there an adequate basis for further advance.

The study of liquids did not, however, revive along the lines mapped out by Ornstein. Why this was so is hard to say, but of influence were the successes of solid-state physics in the 1930s. P. Debye and P. Scherrer had shown that the x-ray diffraction pattern of liquids implied a structure that seemed to be close to that of a solid and so, notwithstanding the "continuity" of the liquid and gaseous states, the study of liquids became assimilated into solid-state theory. Lennard-Jones and A.F. Devonshire in Britain, and H. Eyring and J.O. Hirschfelder in America were active in devising lattice theories of liquids. A second reason for the neglect of the work of the Dutch school may have been the feeling that physics had started anew in 1925 with the development of quantum mechanics, and that there was no need to study what had been done earlier. Some remained free from the attraction to lattice theories, notably J.G. Kirkwood who obtained an integral equation for the total correlation function in 1935, but made little progress in solving it.

The resurrection of the Ornstein-Zernike equation and the direct correlation function by G.S. Rushbrooke and H.I. Scoins in 1953 marked the opening of a new era: the slow abandonment of lattice theories and a return to continuum theories in which the spherically symmetrical environment of any given (spherical) molecule was recognized. There followed the era of integral equations, the prototype of which was Kirkwood's equation of 1935, but the most successful of which led to the equation of state of hard spheres of J.K. Percus and G.J. Yevick in 1959. The new technique of computer simulation emphasised the point that the structure of a liquid (or of a realistic model of a liquid) resembled closely that of a hard-sphere fluid. W.W. Wood showed by the Monte Carlo method that a system of hard spheres could crystallise, a result that B.J. Alder at once confirmed with his newly discovered technique of molecular dynamic simulation. The theoretical implication was that perturbation theory was the way to add an attractive intermolecular potential to the accurately solvable model of the hard-sphere fluid. How to do this was not at first clear but practicable routes were found, first by J.A. Barker and D. Henderson in 1967 and then by J.D. Weeks, D. Chandler and H.C. Andersen from 1971. Their work was a vindication of van der Waals's ideas.

One problem remained obstinately outside this line of progress and that was the unusual behaviour of fluids near their gas-liquid critical points. Here, lattice models proved their worth by the establishment, notably by L. Onsager from 1942, that the free energy was not an analytic function of its natural variables at a critical point, thus showing the limitations of the van der Waals model. It was not surprising that no enlightenment came from the newly established liquid-state theories. Only when a wholly different approach was adopted, in which the details of the intermolecular potential were ignored and attention was directed to structure on a larger scale, was a breakthrough achieved. This culminated in the use of the renormalisation group by K.G. Wilson in 1971 to give us a quantitative representation of critical phenomena. Thus both for normal simple liquids, on a molecular scale, and for critical fluids, on a larger scale, the key to successful theories has been to start from an accurate assessment of the important structural features. This generalization is again shown to be true for the more complex fluids discussed in this issue.