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.

The author is working at Marburg

Further reading

Fluid Metals: The Liquid-Vapor Transition of Metals by F. Hensel and W.W. Warren Jr (Princeton University Press, 1999) • The Monoatomic-Molecular Transition in Expanded Rubidium by W.-C. Pilgrim, M. Ross, L.H. Yang and F. Hensel *Physical Review Letters* **78** 3685-3688 (1997)

John S. Rowlinson, England

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.

The author is working at Cambridge University