

Liquids Special Issue

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A Varied Landscape

For many years the study of liquids was mainly pursued by chemists, probably because many physicists felt this to be a hopeless area for a microscopic treatment and understanding, and because it was not appreciated what new understanding of general interest could be gained. But things have changed and now the study of liquids has its own respected place among physicists. On the one hand, experimental techniques and the methods of statistical mechanics have developed to such a level that they give useful results and a rather complete description of a liquid. On the other hand, it has been recognized that the study of liquids is a paradigm of a system characterised by disorder and by strong correlations and as such is of quite general interest.

The presence of strong correlations means that many interesting effects arise such as local order, collective modes or even partial ordering of the molecules with the emergence of self-organization. The presence of disorder means that molecules move around and the system explores a huge number of microscopic configurations. It is not a coincidence that, as commonly believed, the origin of that very unlikely state of matter called life is so much connected with liquidity. In a solid only very few configurations are explored due to the small oscillations of the atoms and the fact that the diffusion processes are extremely slow. In a gas, diffusion is rapid but the low density makes it very unlikely that many particles will be found in the same place at the same time. Therefore, a liquid appears to be the most favourable situation where complex configurations can arise.

In many liquids can be found the spontaneous formation of supramolecular structures as in microemulsions or in liquid crystals. This possibility has enormous implications for interdisciplinary research and for applications. This justifies the large effort spent on the study of the so-called "complex liquids" and some of these aspects are discussed in some of the other articles in this issue. But liquidity is present not only on the large scale but also under strong confinement. For instance, in a living organism every cell contains a small pocket of confined liquid. The study of liquids under strong

confinement is another area of very active research.

When we look more closely at a liquid we immediately find that, strictly speaking, the liquid state is not a well-defined concept, or it is too narrow and we should really talk of the "fluid state". This makes sense given the continuity of the liquid and the gas phases, a consequence of the ending of the liquid-vapour phase transition at a critical point. But as a consequence, we face a big challenge because we have to develop appropriate tools to cover a system that can be at high density as well as at intermediate and at low densities, with no natural boundaries between them.

Our microscopic understanding of a liquid is based very much on the study of spatial and of spatio-temporal correlation functions. This is the main bequest by the liquid state to the whole of physics: think in terms of correlations, be these between molecules in water or between galaxies in the cosmos.

The study of correlations allows us to appreciate the local organization of one molecule around others, and to unravel the microscopic dynamics. Neutron diffraction and scattering have and continue to play a major role in these studies. X-ray diffraction is important as well, and very recently x-ray inelastic scattering has become available. We should add to these and to other laboratory experiments the computer experiments. Nowadays, computer experiments, like Monte Carlo or molecular dynamic simulations, pervade all areas of condensed matter. But the study of liquids was the first major area investigated in this way, and the methods have been instrumental to the development of simulation methods. In the liquid state, simulations have a fundamental role in validating theoretical schemes and models of interatomic interactions.

In any microscopic scheme we have to start by giving the interatomic forces. Often, we can represent this interaction by a suitable atom-atom or molecule-molecule interaction. In the case of a dense fluid a major role is played by the strong repulsion at short distance which prevents overlapping of particles (excluded volume effect) while the interaction at longer ranges usually has a smaller role in forming the structure of the liquid. The inter-

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atomic interaction is fairly well known in the case of monoatomic liquids like rare gases or simple metallic liquids like molten alkalis. Pair forces are dominant but thermodynamic properties and high precision measurements of the structure indicate that interactions beyond the pair level are non negligible even in a system as simple as liquid argon. The case of metals is very interesting because within the fluid phase there is a metal-insulator transition taking place around the density of the critical point and the interatomic forces have to change dramatically across the phase diagram.

Once we have the interatomic forces we have to apply statistical mechanics. The theory is mainly one of correlations from which scattering laws and thermodynamic properties can be deduced. In the case of spherical molecules the present theory for the static pair correlations (*ie* the function $g(r)$ giving the probability of finding two particles at a distance r apart) is very accurate. It is so accurate that we can use scattering data to obtain reliable information on the pair forces. And this theory of the liquid state is so good that it can be used to construct properties of the solid phase considered to be a liquid in which the density has a spatial modulation. The work of the last ten years has shown that this is the best way to study the liquid-solid phase transition.

In this short introduction I have not mentioned many things. For instance, when the end point of the liquid-vapour phase transition is approached a new series of phenomena takes place: as in a magnet at the Curie temperature, the fluctuations become enormous, correlations become long ranged and non analyticities pop up from everywhere.

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Further reading

[New Approaches to Old and to New Problems in Liquid State Theory](#) (a useful collection of lectures on problems of current interest) edited by C. Caccamo (Kluwer, Dordrecht, 1999) • [An Introduction to the Liquid State](#) by P.A. Egelstaff, Clarendon Press (Oxford, 1992) • [Theory of Simple Liquids](#) (the basic theory) by J.-P. Hansen and I. R. Mc Donald (Academic Press, London, 1986) • A. Parola and L. Reatto *Adv.* **44** 211 (1995)