LIQUID THEORY

Random Configurations

from our Molecular Physics Correspondent

IF there is an orthodoxy in the theory of liquids—and recent conference proceedings suggest that there is—it has little place for notions which depart very far from the familiar, well founded and, regrettably, somewhat sterile formalism of Gibbsian statistical mechanics.

The Bernal "random geometric" approach to liquids, which is the subject of two new articles by J. L. Finney (*Proc. Roy. Soc., A*, **319**, 479, 495; 1970), is highly unorthodox. It cuts across most of the niceties of conventional many-body theory, appealing to crystallographic rather than mechanical insight and seeking to capture the essence of the liquid in the statistical properties of nearest-neighbour configurations reduced to units of the polyhedron. Although intuitively satisfying, this primarily visual approach proves to be of some mathematical sophistication, so much so that, to the dismay of the formalists, the theory cannot be placed in any recognizable chapter of geometry, far less reduced to a single set of equations. In fact, no method has been described within the theory to relate the polyhedron statistics either to the fundamental energy surfaces in configuration space or to the practical calculation of thermodynamic entropy. Thus, not surprisingly, its advocates have so far set greater store by its descriptive than its predictive powers, being chiefly concerned to check their statistics against measurements on mechanical or computer simulated random models. But if the Bernal theory lacks the formal virtues of conventional statistical mechanics, its informal ones are none the less compelling. The original articles (*Nature*, **183**, 141; 1959: **185**, 68; 1960) can hardly be read without the conviction that the author is at least talking about liquids as we know them — "homogeneous, coherent, essentially irregular

" and abounding in entropy—rather than about some discouraging cypher of configuration integrals.

In Finney's work, realistic computer-simulated liquids similar to those which appear in recent "Monte Carlo" thermodynamic studies are compared for the first time with the random sphere packings originally constructed by Bernal. A detailed analysis of the statistical distribution of configurational polyhedra confirms that Bernal's primitive ballbearing and ball-and-spoke models gave an essentially correct picture of the instantaneous geometry of a monatomic liquid, in which the principal structure-determining factor now seems certain to be the hard, repulsive potential rather than the soft attractive part. Finney also compares his results for liquids with those for simulated solids at their melting point and he demonstrates clearly the discontinuity in the polyhedron statistics at the melting point.

Unfortunately, important as these results are, they bring us little closer to a solution of the two central problems: what is the precise relationship between the statistical geometry and the configurational energy function for N atoms, and what are the essential determinants of the statistical geometry and how are they connected with the definition of thermodynamic entropy? It is not difficult to accept that the instantaneous geometry of a large enough sample of liquid contains all the information about its wanderings in phase-space sufficient for an accurate calculation of its

entropy. It is a plausible next step to maintain that this information resides in the statistics of polyhedral types related to nearest-neighbour arrangements. Beyond this, the trail disappears into the sand. Finney makes the tentative suggestion that the key to an algorithm for computing configurational entropy may lie somewhere in homology theory.

What is certain, however, is that there is little chance of an easy synthesis of Bernalian and Gibbsian statistical mechanics for, by insisting on the polyhedron as the descriptive unit, the geometrical theory seems to begin at the level of four and five-body angular correlations—several stages beyond the most refined predictions of ordinary statistical mechanics. This is both its strength and its weakness; it justifies itself as a truly structural theory of liquids, which can hardly be said of the conventional theories, but only at the risk of being over-determined and neglecting what plausible simplifications there are. For example, it seems to waste altogether the two-body force assumption, one of the few reasonable approximations which enter nicely into the ordinary theory.

Nevertheless, as Finney is careful to point out, the search for a formal relationship between statistical geometry and entropy is worth pursuing for reasons which go beyond the microscopic theory of liquids. There are many other disordered systems in nature and technology—powders, fluidized beds, biological aggregates—whose properties might well be elucidated through a deeper and imaginative understanding of what might be called the geometry of chaos.

QUANTUM ELECTRODYNAMICS

Gravity's Role in Removing Infinities

by our Cosmology Correspondent

THE infinities which occur both in classical and quantum electrodynamics have disturbed field and particle theorists for decades. The implication that there is some kind of physical limit, or critical length, associated with fundamental particles conflicts with basic dogma, but as the work of Feynman and that of Dyson has shown there is no way to remove the self-mass and self-charge infinities of lepton electrodynamics using the conventional techniques of expanding the mass and charge distributions by a polynomial solution about a point. But by using non-polynomial Lagrangians for small distances the self-mass and self-charge can be made finite.

A group working at Imperial College, London, have been investigating this problem for some time (see, for example, *Nuovo Cim. Let.*, **4**, 101; 1970). C. J. Isham, A. Salam and J. Strathdee have attempted to find a more general solution, modifying Dirac's Lagrangian to take account of gravity as well as electrons and photons, and using a non-polynomial solution. They have now found that the very small range of gravitational forces ($\sim 2.2 \times 10^{-22}$ m) does not, as traditionalists have assumed, make them insignificant. From the point of view of the critical length, gravity plays a vital part in quantum electrodynamics.

The crucial discovery by Isham and his colleagues is that their modification makes every Lagrangian in particle physics non-polynomial in character, with the gravitational length providing an inbuilt cutoff and preventing the occurrence of infinities. Conceivably,