THE VARENNA CONFERENCE ON SIMPLE LIQUIDS

a report

By Joseph E. Mayer

AN international conference on the condensed state of simple systems was held at Varenna sul Lago di Como, Italy, on the 11th to the 14th of September, 1957. The subject of discussion concerned primarily simple liquids and the melting of crystals. The meeting was at the invitation of the Italian Physical Society and was held in the charming Villa Monastero on the shores of Lake Como. Approximately eighty scientists from over eleven different countries attended. Both experimental papers and theoretical papers on statistical mechanical theory composed the formal part of the program.

The arrangements for the conference were made by its efficient secretary, Professor Giorgio Careri of the University of Padua. In addition to the official host organization, the Italian Physical Society, the conference was sponsored by IUPAP, through the Commission of Thermodynamics and Statistical Mechanics of the Union.

Varenna is a small Italian town on the east shore of beautiful Lake Como. As the letters of direction to those arriving by private car explained, it has only one drivable street and one town square. Most of the members of the conference were quartered in one of the two hotels adjacent to the square; the official banquet on Saturday evening at the end of the conference was held in the larger of the two, the very pleasant Hotel Victoria. A few fortunate members enjoyed the luxury of rooms in the Villa itself, where the scientific meetings were held, only a few hundred yards from the hotel.

The Villa Monastero is the site of an old eleventh century monastery, and the Italian Physical Society has obtained its use for conferences and summer schools. The buildings of the Villa are less ancient, however, and hardly monastic in the character of their decorations. The garden of the Villa has the area of one linear mile, being squeezed for that distance on the steep banks of the lake between the highway, which runs some fifty feet above the lake, and the shore of the lake itself. The garden has the quality of a botanical garden to visitors from a more rigorous climate, and the American visitor cannot fail to be impressed by palms and ripening oranges at the latitude of northern Maine.

The secretary of the conference was cognizant of the charms of the location, and the scientific sessions were scheduled between nine in the morning and noon, and between three-thirty and six. With due sternness the chairmen managed to hold them to these limits, in spite of the enthusiasm of the speakers, so that ample time was allowed for a leisurely swim in the lake before midday meal, and for a visit to the Bistro across from the hotel before dinner. Indeed recollections of the meeting give equal importance to the hydrodynamic properties of the flow of Lake Como around the human body, and to the gustatory joys of good Italian Grappa, as to the more simple, but less enticing, liquids discussed at the scientific meetings.

THE larger delegations of foreign scientists came from the USA, Great Britain, Holland, and Belgium. The hoped for participants from the USSR did not arrive. One scientist from Poland attended, Professor Piekara from Poznan. Two came from Japan, Professors Ono and Toda. There were several each from Canada, France, Germany, and Sweden. In the four days of the meeting a little more than half of the papers presented dealt with theories or theoretical methods, and somewhat less than half presented the results of experiments. Three half-days of the meeting were devoted to liquid helium, one of these to papers on He^3 or He^3-He^4 mixtures.

Since clearly in a subject of the complexity of liquid behavior and the theory of liquids most of the papers do not lend themselves easily to a brief description, the writer will content himself with comments on only a very few subjects which can readily be so described.

In most theories of classical liquids one makes the starting assumption that the total potential energy is the sum of the pair interactions of the molecules only. Although the simple derivations of the quantum mechanical origin of this potential always give the pair interactions as the leading terms, there is no compelling reason for assuming that the specific three-body interactions can actually be neglected, especially in view of the greatly increased number of these over the pair interactions in a condensed system. One method of investigating this assumption is to compute with it the equation of state of a simple crystal from the pair interaction potential derived from second virial coefficients of the gas. G. O. Jones of London presented new data on the equation of state of one of the simplest materials expected to obey the largely classical equations, namely argon. The values differ rather considerably from the older data. With the new data the pair potential required to fit the solid data and the second virial data are almost identical, indicating indeed that the neglect of the three-body potential is actually justified.

G. Careri of Padua, the secretary of the conference, discussed the use of isotopic tracers in measuring diffusion and self-diffusion in liquids. In particular he presented evidence that the self-diffusion near to the

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Group photograph of the Varenna Conference on Condensed-State Physics (*photo by G. R. Valsecchi*).

wall of the capillaries used is less than in the bulk of the liquid. The remarkable feature is that this hindering of diffusion appears to extend hundreds of molecular diameters away from the wall. If substantiated, this would require a somewhat different picture of the process of self-diffusion than that customarily used, possibly one involving microvortices of turbulence in thermal equilibrium. In addition he described the use of ions produced by radioactive bombardment of liquid helium, to measure transport and flow properties in He II.

The problems of whether a hypothetical gas composed of rigid spheres could ever show a phase transition on compression is one which has led to enumerable fruitless arguments in the past. The fact that helium still crystallizes under sufficient compression at some sixteen fold its critical temperature, where the attractive potential divided by kT is negligibly small, has given sufficient experimental evidence to convince most sceptics that a *soft* sphere gas can show a gas-crystal transition without requiring an attractive potential. The argument against the same phenomenon in a rigid sphere gas follows a line which may be sketched as follows: Since the equations depend on the pair potential, $u(r)$, divided by kT, the rigid sphere gas for which this is infinity for r less than r_0, and zero otherwise, can be considered as a gas at infinite temperature for which the potential has the normal form for values of $u(r)/kT$ at ordinary temperatures, but rises infinitely steeply at a potential not reached at ordinary T. The transition, if it occurs, must be between the crystalline and gas phase, since T is far above the critical temperature of the liquid-gas transition. Now on the other hand we are accustomed to thinking of the crystal as a state of long-range order. However, an assembly of very many rigid spheres will not retain long-range order if the fractional volume is increased by only a negligible amount above the minimum close-packed volume, since then there will be slip planes along which the spheres can glide with no energy of interaction. Hence the transition will occur at zero volume above the close-packing volume, or in short it just isn't there!

Kirkwood has shown that his integral equations lead to a transition for hard spheres, but one was able to discount this by the fact that a nonrigorous assumption entered the solution. W. W. Wood of Los Alamos and B. Alder of Livermore show now that by two rather independent methods, using electronic computers, a transition starts at almost twice the close packing volume, and goes to a condensed phase of volume apparently appreciably higher than that of close packing. The surprising thing about the result is that the condensed phase can hardly retain much long-range order, and its properties must resemble those of a liquid rather than of a conventional low-temperature crystal.

Isotopic liquid mixtures of molecules of the same chemical species normally form almost completely "perfect solutions", which is another way of saying that they show random mixing with no tendency to separate into two phases. Theoretical predictions have long been made that this would no longer be true at 0°K, and that a two-phase liquid should result, namely the two isotopic species should not be mutually soluble. Fairbanks showed the phase diagram for He^3-He^4 liquid mixtures observed below 1°K. They do indeed separate into two phases. It appears probable that the He^3-rich phase has no superfluid properties.

Only a few theoretical papers concerned the treatment of transport properties, largely since that was the topic of last year's conference in Brussels. The use of statistical mechanical methods in the treatment of transport is by no means as clean as in the evaluation of equilibrium properties for which a universal algorithm exists, even if sometimes difficult to apply. The treatments of transport cases, other than in the very dilute gas, have been arduous and more or less special to the particular problem. However, some progress toward simplicity is appearing, and one begins to hope that a more satisfactory and more general method may evolve.