STATES OF AGGREGATION

As gases condense into liquids and then solids, an order pattern develops in position space. Both superconductivity and superfluidity can be viewed as condensations in momentum space. Possibly life itself is an order pattern, perhaps in both spaces at once.

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SUPERFLUIDITY and superconductivity (figures 1 and 2) can be discussed in terms of a subject much older than either: states of aggregation.

In modern physics the concept of the three states of aggregation, solid, liquid and gas, has receded into the background of the elementary textbook. One of the reasons is that, thanks to the work of Thomas Andrews[1] on the critical point, exactly a century ago, the diagram of state has been well established. In it the phases have been allotted their respective regions of stability (figure 3). In fact the universal validity of this diagram has long been taken for granted, and one rarely becomes conscious of the remarkable fact that all simple substances obey the same pattern. Leaving out for the moment the rather special case of helium, we observe that the solid is always the stable condition at absolute zero. At finite temperatures it is in equilibrium with the fluid state at sharply defined pressures and temperatures, which represent the melting curve. The fluid state itself contains another sharp equilibrium line, the vapor-pressure curve, which separates this region into two mobile phases of different density, gas and liquid. This latter separation is not complete, however, because the equilibrium curve, which joins the melting line at the triple point, ends in the fluid phase itself at the critical point. Starting from a in figure 3 and going directly to b we pass the vapor-pressure curve, at which we can see the liquid evaporating through a meniscus into the gas phase of lower density. On the other hand we can now proceed along a circuitous route around the critical point back to a without ever observing a discontinuity in either the density or any other property.

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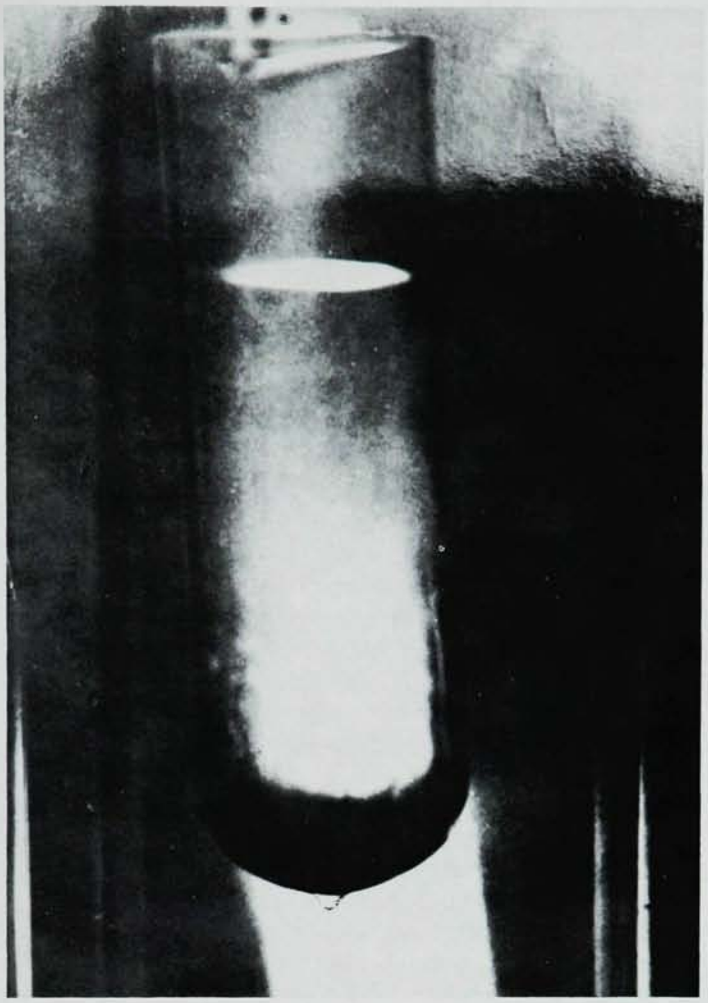
The next question, after establishing experimentally this universal pattern, was to find the reason for its existence. This led to an investigation of the attractive and repulsive forces between individual atoms, which had to wait for solution until the advent of quantum mechanics. Through this solution we now understand well the various mechanisms by which the Coulomb interaction creates bonding in the solid state. This understanding is the second reason why classification by aggregations has lost its appeal. In fact the enormous advances in solid-state physics have provided us with interpretations of a wide variety of phenomena, far beyond the aspects of bonding. One might therefore expect that the diagram of state should follow as one of the basic results from our knowledge of the cohesive forces. However, it does not.

What can we deduce?

Let us assume for a moment that, being in possession of the complete lore of relevant particle interactions as revealed to us by quantum mechanics and by observations on the various types of crystalline solids, we knew nothing about the diagram of state itself. How much of it could we deduce? It is certain that one would predict a dissolution of the crystalline pattern with growing thermal motion. We could not expect, however, that, irrespective of the nature of bonding, this breakup would occur discontinuously. In other words, theory does not lead us in an easy manner to the strik-

SUPERCONDUCTIVITY. Lead ball cooled below transition temperature is held up by persistent currents. —FIG. 1



SUPERFLUIDITY. Helium cooled below lambda point flows over beaker wall and drips off at the bottom. —FIG. 2

ing phenomenon of a sharp melting point, the existence of which we would hardly postulate unless we knew it to be there. At best theory does not preclude a melting point.

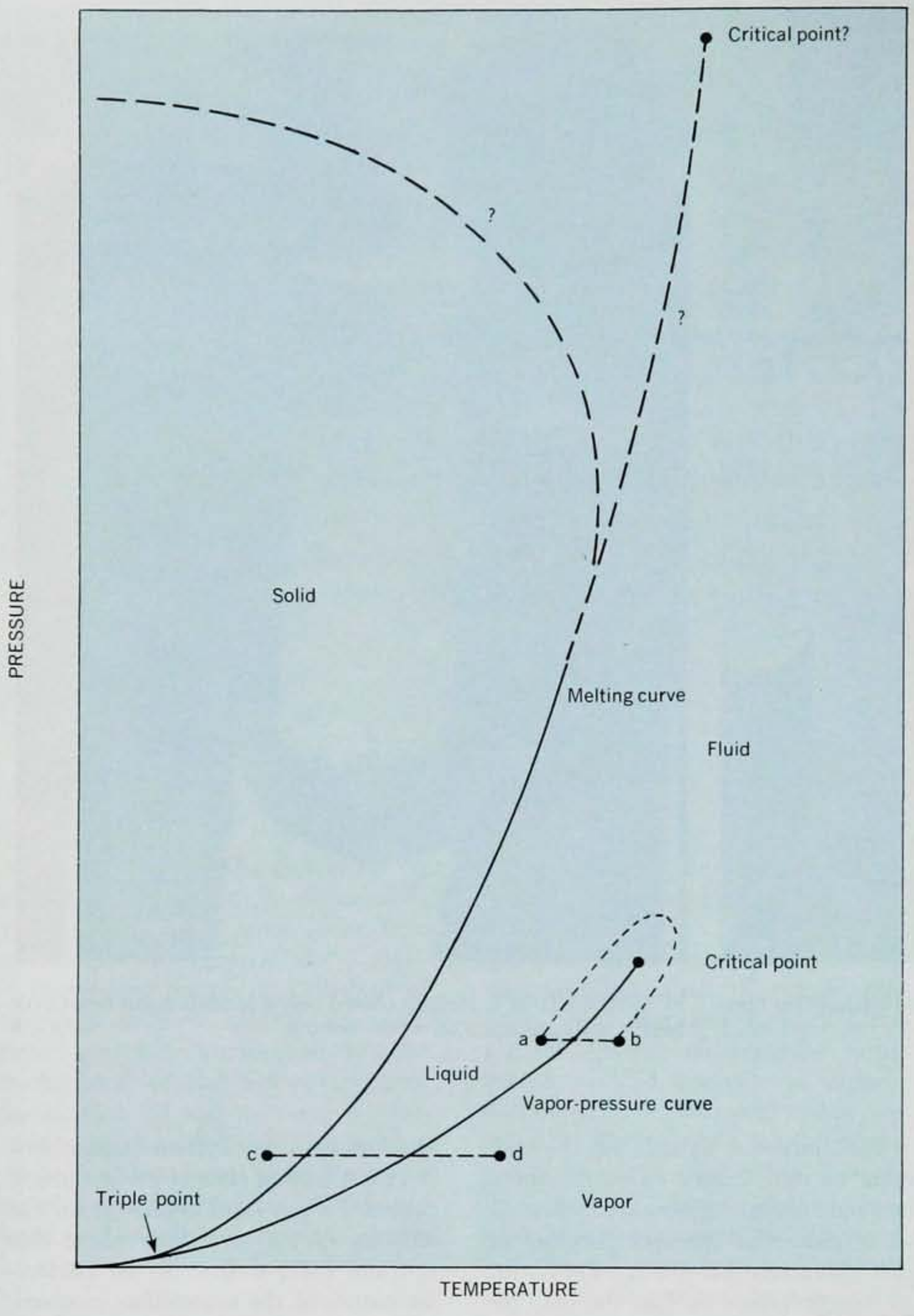
The position is no better when we come to the phase separation of the fluid state into liquid and gas. We should not suspect that a crystal of, say, molecular hydrogen, when heated at constant pressure (c to d in figure 3), will pass through not only one but two sharp transitions before approaching the state of a perfect gas. Such discontinuities appear particularly puzzling when we consider the case of a liquid metal. We know from its electrical properties that, close to its melting point, the liquid phase is still largely governed by the exchange interaction involving many particles and that this interaction is responsible for its cohesion in the solid state. Nevertheless, by raising pressure and temperature we can bring the substance to the state of an ideal gas without any discontinuity in its thermodynamic or electrical properties.

The universal validity of the diagram of state leaves no doubt about its fundamental significance, but it also is clear that present theories of particle interaction are unsuitable for its interpretation. In fact the only indication for a critical point in the fluid phase is provided by the van der Waals equation. Although this merely provides an empirical correction to the ideal gas laws, which, moreover, does not lead directly to the liquid state, the additional terms represent attractive and repulsive potentials of the atoms. Accordingly the universal phenomenon of a phase separation at high fluid densities appears as a direct consequence of these potentials that is quite independent of any specific type of the Coulomb interaction.

A more meaningful approach than through theories of particle interaction seems to be provided by the statistical interpretation of the laws of thermodynamics, and particularly by Walther H. Nernst's heat theorem, often called "the Third Law of Thermodynamics." This postulate, that at absolute zero any system in equilibrium must be in a state of perfect order, provides a powerful argument for the stability of the crystalline phase that is quite independent of the particular nature of the interaction involved. Indeed it even holds if we go so far as to discard Coulomb interaction since, for instance, an assembly of hard, smooth and massive spheres must form an ordered crystalline pattern under its gravitational attraction. One is therefore led to the conclusion that, for an understanding of the nature and equilibrium of the states of aggregation, the concept of statistical order patterns is of greater relevance than that of interaction forces.

Helium as an exception

The only substance that does not obey the general diagram of state is helium. It has no triple point. The descending melting curve (figure 4), instead of approaching zero at absolute zero, becomes temperature independent near 1.5 K, leading to a finite melting pressure of 25 atmospheres at



UNIVERSAL DIAGRAM OF STATE applies to all simple substances except helium. Vapor-pressure curve ends in critical point. Melting curve at pressures greater than now available on earth may go to a second critical point or bend back to pressure axis. It can not go on indefinitely; high enough pressure will crush atomic structure. —FIG. 3

0 K. At any lower pressure helium is either gaseous or liquid and, since the vapor pressure at 0 K is zero, the liquid phase is the stable form at absolute zero. This departure of helium from the universal pattern is due to a quantum effect. Its zero-point energy is so high that it outweighs the weak interatomic forces which, without the application of external pressure, are not strong enough to bind the helium atoms into the crystalline state.

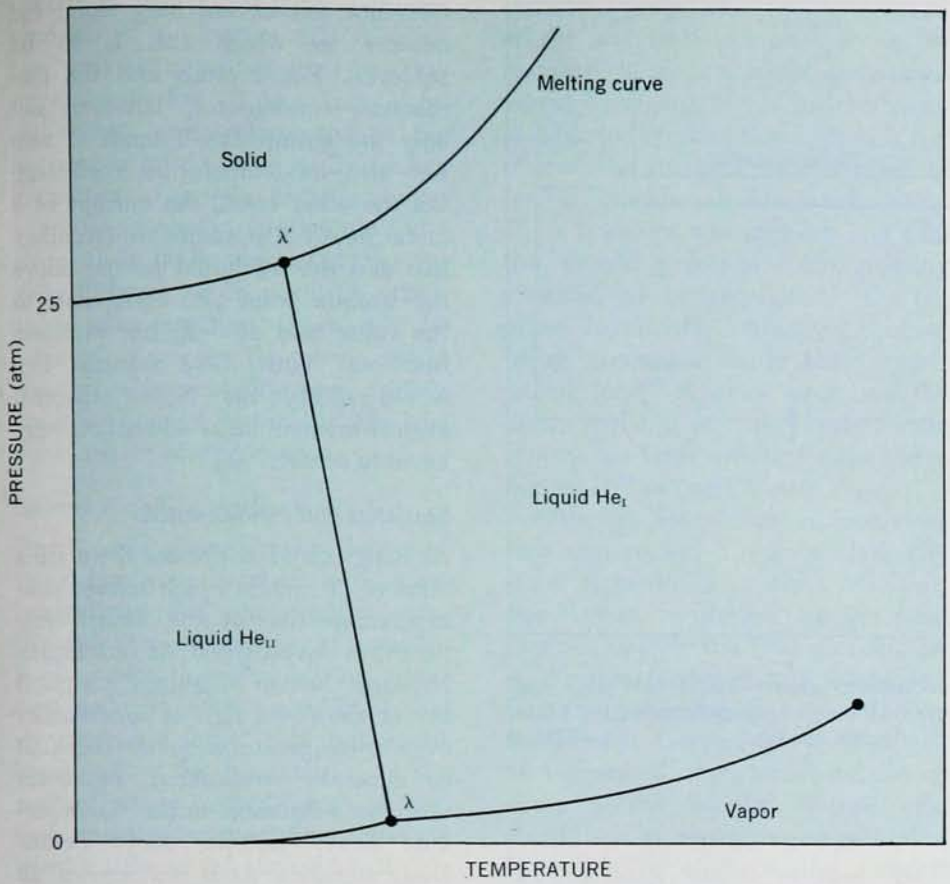
However, at 2.2 K a transition takes place in the liquid phase. It is marked by a large anomaly in the specific heat, which, owing to its shape, has been called the lambda point. At first it was suspected that this anomaly might indicate the establishment of some sort of spatial order as, for instance, of liquid crystals. X-ray investigation has shown beyond doubt, however, that helium below the lambda point is structurally a true liquid. The specific-heat anomaly corresponds to a rapid decrease in the entropy of the liquid towards lower temperature (figure 5), but this increase in statistical order is not reflected in a spatial pattern. Instead, the liquid now exhibits the strange phenomenon of superfluidity.

It is nowadays widely accepted that the superfluidity of liquid helium and electrical superconductivity are in some way connected. When I first suggested such a relation between the two phenomena 25 years ago,[2] however, it met with justified skepticism. It was felt that no basic similarity could exist between two such different assemblies as neutral helium atoms obeying Bose–Einstein statistics and charged electrons in a metal being subject to Fermi–Dirac statistics. Perhaps this suggestion would never have been made but for the accident that I was working at the same time in both fields so that the similarities appeared more striking. Admittedly the suggestion was also favored by the absence at the time of a microscopic theory that would have discouraged speculation.

The striking similarities are provided by the transport, in both cases, of part of the fluid without friction and the rapid drop in entropy that attends this phenomenon. The first task therefore was to try to find a link between these two features by determining the heat content of that fraction of the fluid that engages in frictionless flow. Opportunities for this search were provided by measuring the mechano–caloric effect in helium and the Thomson heat of a persistent supercurrent. Both experiments led to the same, at first surprising, result: namely that the thermal content of the superfluid component turned out to be zero.

Order in momentum space

This result means that this component has, even at finite temperatures, attained the condition of zero entropy. At the same time it has to be realized that the superfluid fraction is not spatially separated from the fluid as a whole, which, of course, retains finite entropy. However, a differentiation between the superfluid component and the rest of the substance is provided by the states of motion, and it was in this manner that its heat content could be separately determined. I therefore argued that the fundamental common feature of superconductivity and superfluidity is the appearance of a new phase not in coördinate but in momentum space. Moreover, because the new phase which had "fallen out" in the form of frictionless flow has maximal statistical order, it acquires the same significance as the conventional states of



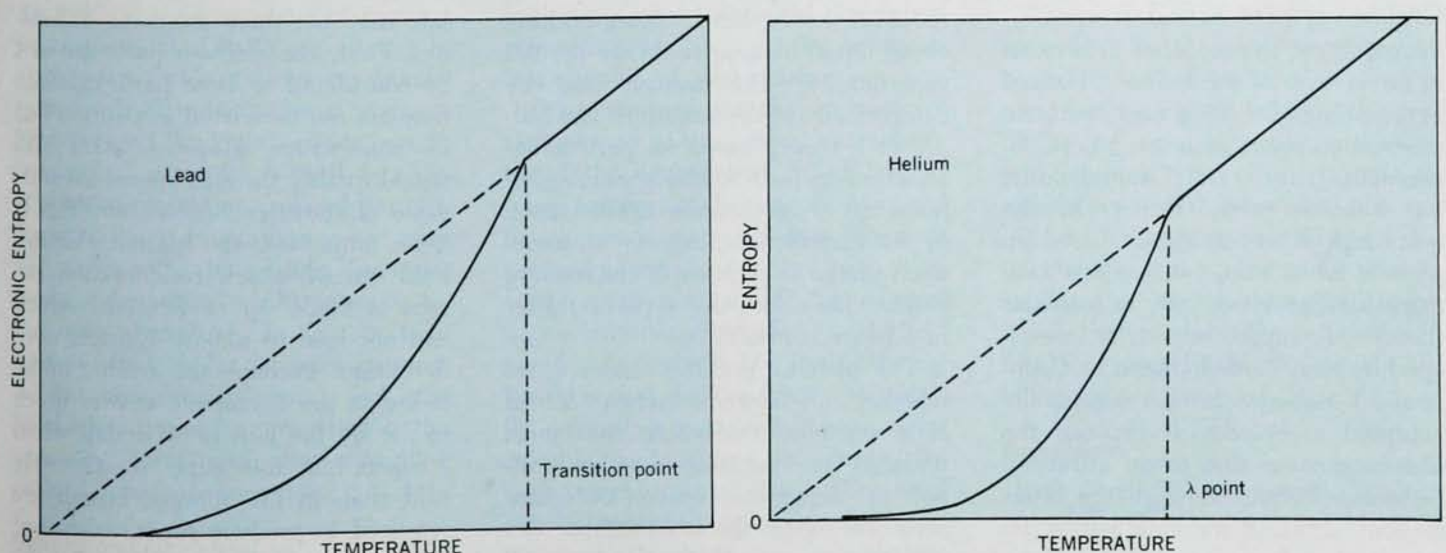
HELIUM is stable liquid at absolute zero. Departure from universal pattern is explained by zero-point energy that is high compared with interatomic forces. Anomaly in specific heat at lambda point corresponds to rapid decrease in entropy. —FIG. 4

aggregation. It differs from them in that the order is established not with regard to position but in momentum space.

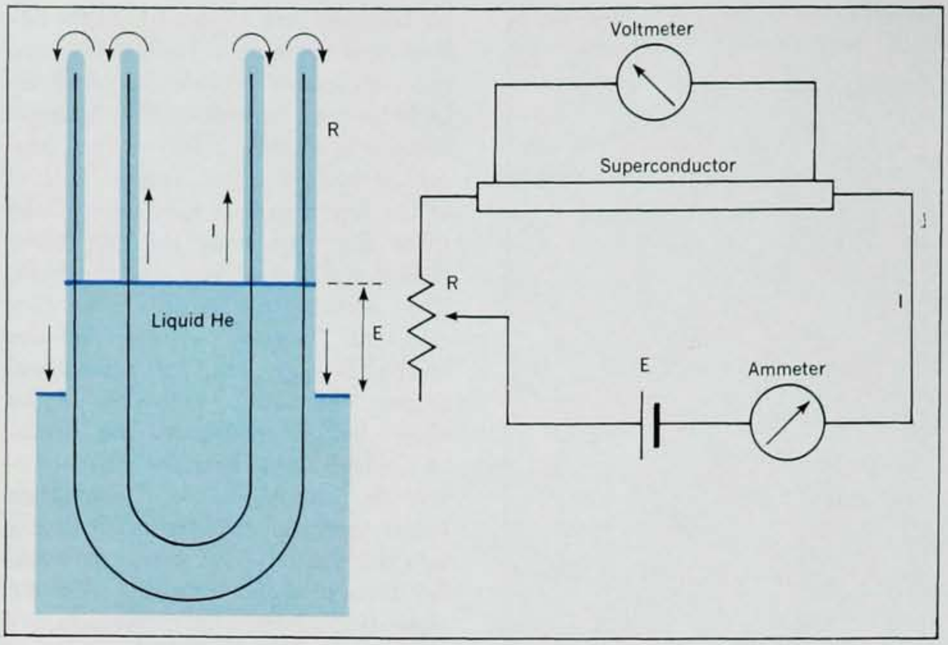
This initial success made it tempting to explore systematically the properties of this new "frictionless" state of aggregation. It is a line of research that, as yet, is by no means finished, but gradually a pattern emerges that is remarkably consistent in itself. Above all it seemed desirable to establish in superfluid helium a hydrodynamic analog to the basic experiment of electrical superconduction. The latter consists of the conventional current–potential measurement in which the voltage across the sample becomes zero (figure 6). In the helium case the mobile surface film was used because it provides an ideal vehicle for pure superflow. The arrangement was simply a set of two concentric beakers raised above the level of the liquid so that flow had to take place from the inner into the outer beaker and from there into the bath. The "current" was given by the flow rate, the "battery potential" by the level difference and, for geometrical reasons, the flow over the rim of the outer beaker simulated the "resistor," which has to keep the current below the critical value. It was then found that superflow from the inner into the outer beaker takes place under zero potential difference with no separation of the two meniscuses.

Several experiments have been made to simulate "persistent" currents by rotating superfluid helium. Although it is unfortunately impossible to measure angular momentum with the same accuracy as a magnetic field, rotation of the superfluid could be picked up many hours after it had been initiated.

The next question concerns the region of stability of the frictionless state. Being a momentum condensate, its boundaries have to be looked for in the states of motion, and indeed we observe well defined "critical" flow rates for both superconductivity and superfluidity at which frictionless flow breaks down. They correspond to melting curves, except that the "melting" of the momentum condensate takes place in the space of velocities and not of positions. This melting is quite sharp for the helium film and



SUDDEN DROP IN ENTROPY at the onset of both superconductivity and superfluidity. Ordering of momenta and not in space is explanation. —FIG. 5



ANALOGY between superfluidity and superconductivity shows liquid flow over wall with no height difference corresponds to current through a superconductor. Outer beaker corresponds to current-limiting resistor of electric analogy. —FIG. 6

pure superconductive metals (known as type I) whereas in superconductive alloys (type II) and in bulk helium there appears to exist an intermediate region between the pure frictionless state and the normal one. It is significant that in both cases this transitional region is marked by a state of vorticity within the superfluid component. Also, in both cases the vortex lines themselves correspond to single quanta of rotation, each involving an enormous number of particles. The parallelism extends further to the first onset of friction, which in helium as well as in superconductivity is sudden.

Qualified success of BCS

Summing up, the evidence as it exists so far in favor of a frictionless state of aggregation, that is, a condensate in momentum space embracing both superconductivity and superfluidity, has become pretty strong. In the meantime, however, theory based on particle interaction, too, has made remarkable progress. A microscopic theory of superconductivity developed by John Bardeen, Leon N. Cooper and J. Robert Schrieffer is generally accepted as correct. It explains the phenomenon as due to an attraction between electrons through the intermediary action of the ionic lattice. Its success has been greeted by those working in the field with a sign of mingled relief and disappointment—relief, because at last a correct explanation had been given, and disappointment that with a double fanfare of the most spectacular effects, the Creator should have revealed nothing better than a little second-order interaction.

In fact, although the theory is doubtless correct in explaining the small energy gap that had been suggested by the Thomson heat experiment, it tells us nothing about a new form of aggregation. Again going through a similar exercise, as we did in the case of the position-order aggregates, makes this quite clear. Assuming our present knowledge of the superconductive phenomena and having the BCS theory, but knowing nothing about liquid helium, could we predict superfluidity? The answer must be categorically in the negative. The failure of a theory based on particle interaction to lead to the general phenomenon of momentum condensation in its macroscopic aspects is somewhat similar to the case of the melting point. There, too, this type of theory had proved unsuitable.

The obvious problem arises as to whether all systems when cooled close enough to absolute zero must undergo condensation, in either position or momentum space. Unfortunately for once thermodynamics can not help us to make a decision. All that the Nernst theorem does is to require the entropy to become zero. It does not tell us anything about the manner in which this is to be achieved. For crystals and the momentum condensates, however, not only the entropy itself tends to zero but also its temperature coefficient. On the other hand, the entropy of a metal before it becomes superconductive and that of liquid helium above the lambda point also extrapolate to the value zero at 0 K, but as linear functions. Thus these systems, too, would satisfy the Nernst theorem even if momentum condensation were never to occur.

Statistics and condensations

As things stand at present there are a number of metals which remain nonsuperconductive at the lowest temperatures investigated so far. Equally, liquid helium of isotopic weight 3 as yet shows no sign of superfluidity even at temperatures below 0.01 K. It is generally considered significant that this substance, unlike the superfluid heavy isotope, obeys Fermi–Dirac statistics. As is well known, an ideal Bose–Einstein gas, when cooled enough, will condense into a state of zero momentum, and it has been suggested that this type of phenomenon might account for superfluidity. This idea received a new impetus when it was discovered that the attractive term in BCS theory involved pairs of electrons of opposite spin and momentum. In fact their existence as carriers was shown experimentally in the quantization of persistent currents which turned out steps of $hc/2e$ and not, as had been expected, of hc/e.

Attractive as the idea of superconductivity as a Bose–Einstein condensate may be, there are some difficulties. First, the electron pairs can not be considered as Bose particles since they are not correlated in position but in momentum. However, this still would qualify them as bosons for purposes of statistics. Second, and this is more important, the normal electron fluid out of which condensation occurs is made up of fermions which can not lead to a Bose–Einstein condensation. Perhaps the truth can be found in the Solomonic answer given to me by the late Lev Landau when I asked him this same question. He said that, in his opinion, bosons are required to produce superfluidity but that he was equally convinced that the lambda point of helium is not a feature of Bose–Einstein condensation.

Perhaps the parallelism between condensates of position and momentum goes even further than one has suspected so far. It was mentioned earlier that, quite irrespective of the mechanism invoked for its formation, the pattern of position order is always a crystal. Equally, one might conclude that there can exist various quite different mechanisms in which order in momentum space can be achieved. Even so, the result would always be a condensate that exhibits the quite general features of the frictionless state of aggregation.

Extension and generalization

Such a wide generalization, however, would hardly be appropriate if superconductivity and superfluidity were the only representatives of momentum condensation. Possibly no others exist under terrestrial conditions, but we must not forget that nothing is known about the continuation of the melting curve towards higher pressures and temperatures than those accessible to us so far (figure 3). It may eventually lead to another critical point, one between solid and fluid. Such data as we have, however, do not seem to favor it since with rising pressure the entropy difference increases, indicating that the two states become increasingly dissimilar. It has been suggested that the melting curve may eventually bend over towards the pressure axis, making the crystal a closed region in the diagram of state. Again, present results show no tendency of this kind. The third possibility, that the melting curve might continue indefinitely, is clearly untenable since eventually, at high enough pressures, atomic structure and with it the crystalline state must be crushed out of existence. Matter in aggregation under these conditions, such as in the white dwarf stars, is likely to be a fluid, and, under certain conditions, its entropy will be low enough to require an ordered pattern. Since ordering in position space may be structurally impossible, momentum condensation would seem to be the only alternative. In fact, it may turn out that, as far as order patterns in the universe are concerned, the frictionless state of aggregation is the prevalent form and the crystalline pattern a rare phenomenon.

Biology and condensation

It is not necessary to reach into outer space in search for unexplained patterns of aggregation. They are with us all the time in the shape of living organisms. It may appear almost irreverent to regard life as another form of aggregation, but this approach has at least the virtue of being untried so far. Arguments can be advanced that life is transient and unstable and that this should preclude it from being classified as an aggregation. On the other hand, the individual human being presents a fairly steady state lasting for 70 years or more, and the helix spelling out the code *homo sapiens* has been with us for the better part of 10^{13} seconds.

Although for certain purposes we thus can regard life as a stationary state, it never is in thermodynamic equilibrium, and the conventional diagram of state has little meaning for it. We therefore must turn to the next best thing which is to look at the order pattern. Leaving out such aspects as biogenesis, replication and development, the salient feature that stands out is the immense statistical improbability of even the simplest living structures. Possibly the most generalized statement characterizing life is to say that it opposes randomness.

This, of course, does not mean that life is in contradiction with the second law of thermodynamics since its ordered structures are always created with an overall increase of entropy. Nevertheless, from the space occupied by life, randomness is always excluded to a remarkable extent. This feature is so general that it applies not only to the living organism itself but also to its works, from beehives to conurbations. An ocean liner requires for its proper functioning more individual parts arranged in a preselected order than a simple organism capable of propagation.

Once we concede the exclusion of randomness as the central characteristic of the aggregation called life, its other features such as replication and development may possibly follow as necessary corollaries. Like any other form of aggregation, life has to exist under external constraints, and these constraints include life itself. It may turn out that development into steadily increasing complexity becomes inevitable for survival in competition with other forms of life. It thus need not be regarded as a separate phenomenon requiring an independent explanation. Neither is "survival" itself a new concept because it denotes nothing more than the maintenance of the central feature of life. It simply is the name given to the steady state, mentioned earlier, which excludes randomness.

Physical basis of life

As yet we know almost nothing about the mechanism by which the exclusion of randomness is achieved. In the last decades the combination of x-ray analysis and the computer has led to rapid advances in molecular biology. A physical basis is being provided for the genetic code, and the process of replication has been reduced to an exercise in stereochemistry. Today most molecular biologists are convinced that the features and functions of life will eventually be explained by the geometric fitting of chemical bonds between individual atoms. The order pattern involved would be one according to positions or, as Schrödinger once called it, an aperiodic crystal.

This view certainly has the great advantage of simplicity, but one wonders whether it is not just a little too simple. According to it, living structures appear as a smooth extension of the crystalline state, and no account is taken of the hiatus that undeniably exists between the periodic and the aperiodic crystal. The limitation of the position order pattern lies in the short range of information that reaches essentially no further than the nearest atomic neighbor. This distance seems far too short to account for the large-scale aperiodic pattern required for excluding randomness. Whether large-scale geometrical fitting can bridge this gap must appear doubtful.

In our review of order patterns we have dealt with those operating with regard to *either* position *or* momentum, but we cannot exclude the possibility of mixed condensates embodying both types of order. Postulating them on first principles, one can expect these aggregates to have a distinct shape and at the same time to exhibit a coherence that goes far beyond the interatomic distance. In fact, they would look suspiciously like living matter.

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