

SUPERFLUIDS

VOLUME I

Macroscopic Theory of
Superconductivity

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INTRODUCTION

1. The "superfluids" or "quantum liquids" probably exhibit the most conspicuous phenomena of macroscopic physics which have not yet been integrated into molecular theory; this might be the reason why they are at present very much in the center of scientific interest. Two types of superfluids are known. One is represented by liquid helium (boiling point 4.2° abs) when cooled below 2.19° abs. The other type is represented by the superconducting state of the electrons. The latter occurs, at very low temperatures, in various pure metals (mercury, with which the phenomenon was discovered by Kamerlingh Onnes in 1911, lead, tin, etc.) and a great number of alloys. A characteristic feature of these peculiar states of matter is that they apparently allow a flow of matter without friction. In a superconductor electric charge is transferred without any measurable voltage difference between its ends. Superfluid helium, on the other hand, can pass with ease through extremely narrow capillaries or fine cracks which would be practically impassable for any ordinary liquid (Allen and Misener, 1938; Kapitza, 1938). Furthermore superfluid helium allows an extremely easy transfer of heat, which has occasionally been described as "heat-superconductivity."

These strange fluid states are a challenge to the theoretical physicist. The mere fact that they are non-solid states, presumably down to 0° abs, precludes an explanation of their structure on the basis of classical mechanics. According to the classical theory, at a sufficiently low temperature, any system composed of identical particles confined to a given volume should come to rest (vanishing kinetic energy) in the configuration of minimum potential energy. This obviously would be some structure such as a crystal lattice, which is ordered in space; in short, a solid and not a fluid state.

It is well known that classical Newtonian mechanics loses its competence in the domain of molecular and submolecular processes and has to be replaced by quantum or wave mechanics. According to quantum theory the most stable state of any system is *not* a state of *static equilibrium* in the configuration of lowest potential energy. It is rather a kind of *kinetic equilibrium* for the so-called zero point motion, which may roughly be characterized as defined by the minimum average total

(potential + kinetic) energy under the supplementary condition that each coordinate q has a mean range Δq for its motion, and its momentum p a corresponding range Δp such that the so-called uncertainty relation of Heisenberg

$$\Delta q \Delta p \geq \frac{h}{4\pi}$$

is fulfilled; where h is Planck's constant ($6.62 \cdot 10^{-27}$ erg/sec).

Quantum mechanics proved essential for the understanding of the structure of atoms and molecules and also for the determination of the interatomic (valence) and intermolecular (van der Waals) forces. However it is common practice, and it is, indeed, in general, a legitimate approximation to employ these forces within the framework of classical mechanics in order to determine the movements and rest positions of atoms and molecules. Thus it has been found possible to account for the structure of most molecules and, furthermore, of matter in bulk on a kind of "semi-classical" basis. This procedure finds justification in the fact that, for the heavier atoms and molecules, in the prevailing interatomic and intermolecular force fields Heisenberg's uncertainty relation entails in general a very small range Δq , which is, indeed, much smaller than the size of the atoms ($\Delta q < 10^{-9}$ cm). As a result at 0° abs the atoms or molecules frequent positions between their neighbors very close to the rest positions which would be expected from classical mechanics.

In fact, the differential equations of macroscopic physics betray no trace of the quantum character of the basic laws of nature. They were actually derived on an atomistic basis a long time before quantum mechanics was discovered. Thus it has become quite common to regard quantum mechanics as a "micro-mechanics," that is, as relevant *exclusively* to the understanding of the mechanisms of the submolecular world.

We should not, however, lose sight of the fact that this view is somewhat superficial, as it depends on the validity of certain approximations which are not always justified. The existence of the superfluids and in particular the strange transfer mechanisms they exhibit are direct indications that they represent macroscopic systems for which the classical theory is incompetent and that presumably quantum mechanics is relevant to their constitution *as a whole*. In recent years more and more convincing evidence has been brought forward to support the idea that these peculiar low temperature transfer mechanisms are *pure* quantum mechanisms. We mean that they are, although of macroscopic size, nevertheless withdrawn from the disorder of thermal agitation in essen-

tially the same manner as is the electronic motion within atoms and molecules, in short, that they are *quantum mechanisms of macroscopic scale*. Hence these low temperature phenomena are not to be considered as merely a special field of physics which is not yet explained by molecular theory. They seem to be of fundamental interest from a theoretical point of view because here quantum mechanics appears, so to speak, on a macroscopic plane.

2. This idea emerged quite incidentally when in 1934 H. London and F. London developed an electrodynamics of superconductivity in order to comprehend the Meissner effect. Meissner had found in 1933 that superconductors are not only ideal conductors but ideal diamagnetics as well. This discovery seemed to indicate that it might possibly be the *magnetic* field which sustains the electric current in superconductors. Accordingly in this electrodynamics superconductivity is characterized not by an infinite value of the electrical conductivity, but rather by a *new relation between magnetic field and electric current*. This relation is assumed, in superconductors, to replace Ohm's law, which in ordinary conductors relates the current to the *electric* field.

We shall discuss the implications of this electrodynamics of the superconductor at greater length and see how it represents the facts. However, one point might be worth mentioning here. Although this theory originally was the outcome of entirely phenomenological considerations, aimed at bringing superconductivity and the Meissner effect under a common system of differential equations, it developed that the equations established in this way go so far as to suggest a quite specific interpretation of superconductivity in terms of quantum mechanics.

The theory in question describes the state of those electrons which become superconducting as a state of long range order with respect to the local mean value of the momentum vector \mathbf{p} —the same quantity whose components appear in Heisenberg's uncertainty relation.

At present it is not yet clear *how* at sufficiently low temperature this long range order of \mathbf{p} is established in superconductors. However, it is conceivable that something like this may happen if quantum mechanics is to play an essential role in determining the structure of a many-particle system of this kind. It is not necessarily a configuration close to the minimum of the potential energy (lattice order) which is the most advantageous one for the energy balance, since by virtue of the uncertainty relation the kinetic energy also comes into play. If the resultant forces are *sufficiently weak* and act between *sufficiently light particles*, then the structure possessing the smallest total energy would be characterized by a good economy of the kinetic energy (or any

other energy contribution depending on \mathbf{p}) rather than by a configuration which exploits the little potential energy gain possible by a particularly narrow choice of the q -coordinates (Δq small). In other words a small Δp would be more important in such a case than a small Δq . Under certain circumstances Δq could be quite large. This would then be a case of long range order of the momentum vector, as the electro-dynamics of the superconductor actually implies. It would be the outcome of a quantum mechanism of macroscopic scale.

The quantum mechanics of the electronic interactions in metals is a very difficult subject, and up to the present it has not been possible to derive the macroscopic electro-dynamics of the superconductor from electronic theory. This is still very much a matter for the future. Nevertheless this much can be said: The electrodynamic equations of the superconductor entail a *definite reduction* of the problem set for this future molecular theory. No longer does it seem necessary to explain why the electrons in superconductors apparently lose all vestige of resistance. The task will be to show that they prefer to "solidify" with respect to their momenta rather than with respect to their coordinates.

3. In the case of superfluid helium our knowledge of molecular theory seems to be somewhat more resourceful, since here we can refer to a mechanism which furnishes a remarkable example of a transition into an ordered state in momentum space.

In 1924, Einstein, generalizing ideas of the Indian physicist Bose, developed a very strange concept of a gas of identical molecules, which were assumed to be indistinguishable from each other in a new and very radical sense. He suggested that it should not only be impossible to distinguish a case (I) where molecule A is here and molecule B is there from another case (II) where molecule B is here and molecule A is there, but that these two undistinguishable cases, I and II, should not even be counted as two separate cases; they should be considered as *one single case*. Einstein remarked that this removal of the last vestige of individuality from the molecules of a species would imply a statistical preference of the molecules for having the same velocity, even if any interaction between them were disregarded, and this preference would lead, at a well-defined temperature, to a kind of change of state of aggregation; the molecules would "condense" into the lowest quantum state, the state of momentum zero. Einstein did not give a very detailed proof, and his remark received little attention at the time. Most people considered it a kind of oddity which had, at best, an academic interest, for at the extremely low temperatures or high pressures in question there are no gases, all matter being frozen or at least condensed by virtue of the intermolecular interaction forces. In addition doubt was

cast on the mathematical correctness of Einstein's remark, and hence the matter was disposed of as if there were no "Bose-Einstein condensation."

When the strange properties of superfluid helium were discovered, mostly in the years 1937 and 1938, it appeared to me that Einstein's remarks on the Bose-Einstein condensation might be of importance in this connection. Therefore I worked out his theory in greater detail. In the meantime, from spectroscopic observations with helium molecules, evidence had been found which could be interpreted in a very simple way on the assumption that permutations of helium atoms are, indeed, to be counted in the way suggested by Einstein. Thus it happened that only at that time was it ascertained that an ideal Bose-Einstein gas would actually show a peculiar discontinuity, manifested by a break in the specific heat curve $c_v(T)$ at a well-defined "critical" temperature T_0 . At this temperature the mean thermal (kinetic) energy becomes so small that the mean de Broglie wave length ($\lambda = h/p$) assumes a value of the order of the mean molecular distances. When the temperature is lowered below this critical temperature T_0 the velocity distribution becomes *inhomogeneous*. A *finite fraction* of all molecules is assembled in the lowest quantum state of momentum ($p = 0$) and accordingly has a *macroscopically large de Broglie wave length* while the rest of the molecules have a velocity distribution similar to that of a gas. The fraction of molecules in the lowest state ($p = 0$) increases with decreasing temperature until, at 0° abs, all molecules are assembled in this particular state. This is an example of a gradually progressing *condensation with respect to the momentum coordinates* quite comparable to an ordinary condensation, except that ordinarily the order refers to the space coordinates. Moreover, since for a finite fraction of all molecules the de Broglie wave length λ becomes infinite, the Bose-Einstein condensation represents a *quantum mechanism of macroscopic scale*.

For molecules of molecular weight 4 and at the density of liquid helium, the Bose-Einstein condensation temperature T_0 is calculated to be 3.09° abs, relatively close to the temperature 2.19° abs, at which liquid helium transforms into superfluid helium. Furthermore the corresponding entropies, $1.28R$ and $0.8R$, respectively, are of comparable order of magnitude.

4. In view of this situation I advanced, in 1938, the hypothesis that the strange change of state in liquid helium at 2.19° abs, even though it occurs in the liquid and not in the gaseous state, is due to the condensation mechanism of the Bose-Einstein gas. The extension of the ideal gas theory to the liquid state was a somewhat unusual assumption, yet

not so unrealistic in helium as it would be in any other liquid. It was known that in helium the zero point motion (see above) is more important than in all other substances and is responsible for the fact that liquid helium has a quite extraordinarily "open structure" of a molar volume about three times as large as would correspond to the gas-kinetic diameter of the helium atoms. Under these circumstances it was not quite unjustified to try the hypothesis that the qualitative features of the condensing Bose-Einstein gas might be preserved in liquid helium—in particular the feature of an equilibrium between two interpenetrating fluids, of which one is in a macroscopic quantum state while the other is the carrier of the whole entropy of the liquid. On the basis of this so-called two-fluid model a macroscopic theory has been built up which covers a great number of the peculiar properties of liquid helium.

These ideas have been pursued with particular success by Tisza, who took the two-fluid model so literally as to attribute *two distinct velocity fields* to the two fluids. This assumption provided a simple framework for a qualitative interpretation of many of the paradoxical flow properties of liquid helium which had been quite unintelligible from the point of view of ordinary hydrodynamics. Moreover, the theory led to several predictions which were subsequently confirmed by experiments. Probably the most interesting of these conclusions was that heat would be able to go through superfluid helium by means of a new kind of wave propagation, by "thermal" waves, in which the two fluids vibrate relative to each other.

When Tisza made this prediction (1938), the theory was not taken seriously enough to be given an experimental test. However, in 1941 in Moscow Kapitza in a series of ingenious experiments gave a convincing quantitative corroboration of the two-fluid model. Thereupon this model was taken up again and considerably developed by Landau. He rejected the Bose-Einstein hypothesis and attempted to put the theory on a different quantum-mechanical basis, assuming a peculiar kind of excitation of the liquid, quantized vortices which he called "rotons."

At closer inspection, however, the roton theory did not prove to be more rigorous than the Bose-Einstein approach, and hence a decision between the two theories on purely theoretical grounds seems rather difficult. As far as the measurable phenomena are concerned the two theories seemed to be quite equivalent. In particular the new kind of wave propagation appears in Landau's theory also: Landau called the new waves "second sound," not quite appropriately, since it is heat rather than pressure which is being propagated by these waves.

Landau, being close to an excellent low temperature laboratory, now furnished the incentive to carry out experiments. They were conducted by Peshkov in Moscow between 1944 and 1946. These experiments brilliantly confirmed the existence of the predicted thermal waves and showed that the two-fluid model of liquid helium must be essentially correct, but they could not decide the issue between the Bose-Einstein and the roton theory.

Quite recently a new possibility has appeared which is likely to force a decision regarding the relevancy of the Bose-Einstein condensation for liquid helium. This method ought to settle the issue by experiment without having recourse to the obscurities of complicated and necessarily approximate calculations. Ordinary helium (He^4) has an extremely rare isotope, He^3 , which occurs in atmospheric helium only in a ratio of 1:1,200,000. There are very definite reasons for assuming for He^3 atoms a rule for counting their permutations entirely different from that for He^4 atoms. This rule, called "Fermi-Dirac statistics," entails *no condensation* of the kind derived for Bose-Einstein particles, at least as long as interaction forces are neglected. In fact, the rule of counting permutations of "Fermi-Dirac particles" does not imply individuality of the molecules either. However, the latter rule has a special feature in that several particles of the same kind are not allowed to have exactly the same velocity. It is this special feature of the Fermi-Dirac particles which excludes a condensation mechanism of the type encountered for the Bose-Einstein particles.

Until recently the extreme rarity of He^3 seemed to exclude experiments with pure samples of this isotope. However, now appreciable quantities of pure He^3 can be produced by employing the strong neutron beams of an atomic pile. In 1948 Sydoriak, Grilly, and Hammel, at Los Alamos, succeeded in liquefying pure He^3 ; they found a critical temperature of 3.34° abs and a critical pressure of 875 mm of mercury.

Thereupon Osborne, Weinstock, and Abraham, of the Argonne National Laboratory in Chicago, attacked the question whether or not liquid He^3 becomes superfluid like He^4 . They pressed liquid helium through a fine capillary and measured the flow velocity at different temperatures. Whereas for liquid He^4 this flow velocity, considered as a function of temperature, has a discontinuous tangent at 2.19° abs and for lower temperatures suddenly becomes extremely large, the experiments with He^3 showed no remarkable change in the flow properties from 3° abs down to 1.05° abs. The viscosity is of the same order of magnitude as that of liquid He^4 above 2.19° and shows *no discontinuity* in the whole temperature range measured. This is a negative result; still it appears quite decisive, as it is apt to settle a *qualitative* question.

If Bose-Einstein statistics were irrelevant for the occurrence of superfluidity in He^4 , then liquid He^3 would have about the same properties as liquid He^4 and would become superfluid in the neighborhood of 2° abs. Since this seems not to be the case, it is hard to suppress the feeling that the Bose-Einstein condensation mechanism is the essence of the transition into the superfluid state of He^4 . Nevertheless, an extension of these investigations with He^3 to still lower temperatures will, of course, be of great interest.

5. At present the theory of superfluids seems to be converging toward a relatively simple aspect. In superconductors as well as in superfluid helium, we encounter an equilibrium between two fluids which mutually interpenetrate in ordinary space but are in general separated in momentum space. One, the "superfluid proper," shows long range order of the mean momentum vector and does not contribute appreciably to the entropy. The other, the "normal fluid," is very much like the ordinary fluid above the transition point, except that its concentration is smaller and probably vanishes entirely at absolute zero. While in ordinary liquids each solution of the macroscopic hydrodynamical equations corresponds to a multitude of microscopically different states, it seems characteristic of a superfluid that its wave function is of macroscopic scale. For the superfluid proper the hydrodynamical boundary conditions apparently coincide with the wave-mechanical boundary conditions which determine the wave function of the whole superfluid. Thus, for the superfluid proper, each macro-state would correspond to one single quantum state.

6. One might wonder whether the study of the superfluids may have a bearing beyond the remote corner of the physics of lowest temperatures and the very limited number of substances to which it appears to be confined at the present time. Repeatedly has it been questioned whether the customary interpretation of organic chemistry is always justified in applying classical mechanics to additive chemical or other forces. It has been maintained that certain actions between macromolecules in biochemistry could not be understood unless they could be conceived as conditioned by some quantum mechanism involving the system as a whole. The author does not feel competent to take a position with respect to any of those suggestions. Of course it is conceivable that in some biological processes the concept of a fluid state of entropy zero could play a decisive role, for it combines the characteristic stability of quantum states with the possibility of motion (i.e., of matter transfer and of change of shape) without necessarily implying dissipation processes (i.e., transitions between quantum states).

Very little has been done in this direction so far. We may mention some theoretical investigations concerning the peculiar interatomic currents in the aromatic compounds and the extraordinary anisotropic diamagnetism they entail. Some calculations have been made concerning the possibility, in certain long chain molecules with conjugated double links, of electronic oscillators of large extension and their possible significance for the molecular forces between those molecules. These interatomic currents are examples of mechanisms in which a molecule acts as a single unit rather than as the sum of its parts. Naturally the reliability of the quantum-mechanical approximation methods which had to be applied in these calculations is very limited, and hence the results obtained so far have to be taken with some caution. In this light it appears plausible that an experimental and theoretical study, in inorganic isolation, of macroscopic quantum mechanisms as represented by the superfluids could provide information which might prove useful for an understanding of the macro-molecular systems of biophysics, which behave in many respects much more simply than would be expected in view of the apparent great complexity of their structure.

It is not our task to enter into a discussion of these unsolved problems. We have even to leave it to the future to substantiate the interpretation of the superfluids as quantum currents of macroscopic scale. In spite of various attempts in this respect, for the time being the quantum theory of the superfluids is a problem rather than an achievement. The theory as it is presented here is an attempt to interpret the most salient facts regarding the various superfluids from a consistent macroscopic point of view and, as far as this is possible at present, to locate the quantum-mechanical problem which has been left unsolved. The author believes that this step might be helpful preparing the way for the future molecular theory, since it seems that some prejudices are impeding progress in this direction. The present book is written from the standpoint of a theoretician. Accordingly we have not attempted to achieve complete coverage of the experiments performed with the superfluids, nor could justice be done to the amazing development in the difficult art of low temperature techniques.