

DEVELOPMENT OF CONCEPTS IN SUPERCONDUCTIVITY

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This is an excerpt from a talk that John Bardeen gave on the development of the theory of superconductivity in London, England on September 17, 1962 when he received the Fritz London award for his work developing the BCS theory of superconductivity. The talk was given at the *Eighth International Conference on Low Temperature Physics* at Queen Mary College in London and was reprinted in *Physics Today* in January of 1963.

My first attempt to construct a theory of superconductivity was made in the late '30s and was strongly influenced by London's picture I thought that it might be possible to extend the Bloch one-electron model to account for superconductivity. A periodic potential introduces Brillouin-zone boundaries in k space, with an energy gap at the boundary proportional to the Fourier coefficient of the potential. If one could produce zone boundaries at nearly all parts of the Fermi surface, one would get a lowering of energy of the electrons in states just inside the surface. No matter how complex the Fermi surface, it should be possible to accomplish this by introducing many small periodic distortions of the lattice corresponding to a very large complex unit cell. The attempt to construct a theory along these lines was not successful; various objections were raised. Further, more accurate estimates showed that this type of instability is unlikely to occur in real metals at low temperatures. The work was interrupted by the war and all that was published was an abstract of the talk. Much later, Fröhlich developed a far more complete theory for a one-dimensional model along similar lines.

After the war, my research interests turned to semiconductors, and it was not until May 1950, when I heard about the isotope effect from Serin, that I resumed work on superconductivity theory. Separated isotopes became available after the war, so that it was possible to determine whether

or not there was a dependence of critical temperature on isotopic mass. Experiments were undertaken independently by Reynolds, Serin *et al.* at Rutgers and by Maxwell at the National Bureau of Standards, first on mercury. These showed, surprisingly at the time, that T_c varies inversely with the square root of the isotopic mass. The mass would not be an important parameter unless the motion of the ions is involved, which suggested that superconductivity must arise from some sort of interaction between the electrons and zero-point vibrations of the lattice. I attempted to develop a theory in which I suggested that the effect of the interaction would be such as to lower the energy of electrons near the Fermi surface, but as a result of dynamic interactions with the zero-point motion rather than by periodic lattice distortions.

About a week after I sent in a letter to the editor outlining these ideas. Fröhlich visited the Bell Telephone Laboratories where I was working at the time. He told me about his own work on a theory of superconductivity



Fig. 1. John Bardeen.

based on electron-phonon interactions, which he had done at Purdue in the spring of 1950. Fröhlich's work was done without knowledge of the isotope effect. He was greatly encouraged when he learned, just about the time he was ready to send his manuscript to *The Physical Review*, about this strong experimental confirmation of his approach. Although there were mathematical difficulties in both his approach and mine, primarily because of a use of perturbation theory in a region where it is not justified, we were both convinced that at last we were on the road to an explanation of superconductivity.

It did not take long to discover that the difficulties with these theories were basic and not easy to overcome. This was shown perhaps most clearly by a calculation of Schafroth, who contributed much to superconductivity theory. His untimely death cut short a promising career. Schafroth showed that a theory based on treating the electron-phonon interaction by perturbation theory could not account for the Meissner effect, even though the expansion is carried to arbitrarily high order.

These theories of Fröhlich and myself were based essentially on the self-energy of the electrons in the phonon field rather than on a true interaction between electrons. It became evident that all or nearly all of the self-energy is included in the normal state and is not much changed by the transition.

In Fig. 2, we have reproduced a slide made in 1955 to illustrate the status of the theory up to that time. The thermal properties gave evidence for an energy gap for excitation of a quasi-particle from the superconducting ground state. Further, I showed that if one assumed a reasonable energy-gap model, one could account for the Meissner effect, but with a nonlocal theory similar to that proposed by Pippard. The "derivation of the Meissner effect" which I gave at that time has been criticized by Buckingham and others on the grounds that the calculation is not gauge invariant, but I believe that the argument as given is essentially correct and is in accord with the present microscopic theory. The energy-gap model was the unifying theme of my review article which appeared in 1956 in *Handbuch der Physik*, Vol. XV. At that time there was no way to derive an energy-gap model from microscopic theory. While the Heisenberg-Koppe theory based on Coulomb interactions could be interpreted in terms of an energy-gap, it did not yield the isotope effect and was also subject to other difficulties. Thus, at that time, it appeared that the main problem of the microscopic theory was to show how electron-phonon interactions might yield an energy gap.

That electron-phonon interactions lead to an effective attractive interaction between electrons by exchange of virtual phonons was shown by Fröhlich

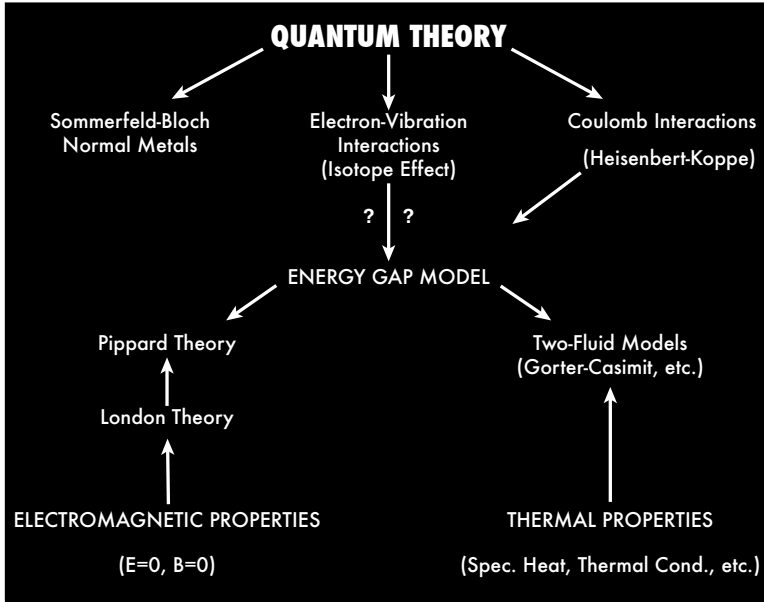


Fig. 2. Reproduction of a slide made in 1955 to illustrate the status of the theory at that time. Experiments on thermal properties gave evidence for an energy gap for excitation of electrons from the superconducting ground state. It was shown that a reasonable energy-gap model would most likely lead to Pippard's nonlocal modification of the phenomenological London equations to describe the electromagnetic properties. Thus, it seemed, the major problem was to see how an energy gap might follow from a microscopic theory based on interactions between electrons and phonons, as indicated by the isotope effect.

by use of field-theoretic techniques. His analysis was extended by Pines and myself to include Coulomb interactions. In second order, there is an effective interaction between the quasi-particle excitations of the normal state which is the sum of the attractive phonon-induced interaction and a screened Coulomb interaction. In the *Handbuch* article, I suggested that one should take the complete interaction, not just the diagonal self-energy terms, and use it as the basis for a theory of superconductivity.

The next major step was made by Cooper, who, following up this approach, showed that if there is an effective attractive interaction, a pair of quasi-particles above the Fermi sea will form a bound state no matter how weak the interaction. If the binding energy is of the order of kT_c , the size of the pair wave function is of the order of 10^{-5} to 10^{-4} cm. This calculation showed definitely that, in the presence of attractive interactions,

the Fermi sea which describes the ground state of the normal metal is unstable against the formation of such bound pairs. However, one could not use this calculation immediately to construct a theory of superconductivity. If all of the electrons within $\sim kT_c$ of the Fermi surface form such bound pairs, the spacing between the pairs would be only $\sim 10^{-6}$ cm, a distance much smaller than the size of a pair. Because of the considerable overlap between the pairs, and because of the exclusion principle and required anti-symmetry of the wave functions, they cannot be regarded as moving independently. Thus, the picture proposed earlier by Schafroth (1955), and developed more completely in cooperation with Butler and Blatt of electron pairs as "localized entities (pseudo-molecules) whose center-of-gravity motion is essentially undisturbed", and which at low temperatures undergo an Einstein-Bose condensation is not valid. New methods were required to construct a theory of superconductivity, and this was first accomplished by the joint efforts of Cooper, Schrieffer, and myself. While the theory can be and has been developed by use of a variety of mathematical techniques, I believe that the variational method used in our original publications gives as good a picture as any of the ground-state wave functions and of the quasi-particle excitation spectrum with a gap.

One may describe the low-lying configurations for the normal phase of a metal by specifying the occupancy in k -space of the quasi-particles above the Fermi sea and of unoccupied states or holes below the sea. In accordance with the Landau Fermi-liquid model, the energy of one quasi-particle may depend on the distribution of the other quasi-particles. These quasi-particle configurations are not exact solutions of the Hamiltonian when Coulomb and phonon interactions are included, but are reasonably well defined if the excitation energies are not too high. The configurations are presumed to include correlation energies and quasi-particle self-energies characteristic of the normal phase. Superconductivity arises from residual attractive interactions between the normal quasi-particles.

Cooper, Schrieffer, and I took for the variational wave-function ground state of a superconductor a linear combination of normal configurations in which the quasi-particle states are occupied in pairs ($k_1 \uparrow, k_2 \downarrow$) of opposite spin and the same total momentum, $k_1 + k_2 = q$, common to all pairs. In any configuration, the two states of a pair are either both occupied or both empty. Values of q different from zero describe current flow in the ground state, that for $q = 0$ for zero current has the lowest energy. We also worked out a quasi-particle excitation spectrum for a superconductor in one-to-one correspondence with that for a normal metal with a temperature-

dependent energy gap for excitation of particles from the superconducting ground state.

A superconductor differs from a semiconductor in that the gap in the former is relative to the Fermi surface and is not fixed in k -space. The entire system with interactions can be displaced in momentum space to give a net current flow.^a If v_s is the velocity of flow, the mass of the flow at $T = 0^\circ \text{K}$ is ρv_s where $\rho = nm$ is the density of the electrons. At a finite temperature, quasi-particle excitations will reduce the current, but when a local equilibrium is established corresponding to a given v_s , a net flow $\rho_s v_s$ will remain. This defines the density of the superfluid component of the two-fluid model, ρ_s . With increasing temperature, ρ_s decreases from ρ at $T = 0^\circ \text{K}$ to zero as $T \rightarrow T_c$. When the Fermi sea of a normal metal is displaced in momentum space, quasi-particle excitations soon reduce the current to zero, so that $\rho_s = 0$. A superfluid is characterized by a value of ρ_s different from zero. These considerations are analogous to those Landau used to account for the superfluidity of liquid helium.

The theory has been applied to a wide variety of properties such as specific heats, electromagnetic properties, thermal conductivity, ultrasonic attenuation, nuclear spin relaxation times, the Knight shift and electron spin paramagnetism, electron tunneling, critical fields and currents, boundary effects, and other problems. In nearly all cases excellent agreement between theory and experiment is found when the parameters of the theory are evaluated empirically. Difficulties associated with thermal conductivity for phonon scattering and with the Knight shift appear to be on the way to resolution through a combination of experimental and theoretical work.

The metastability of persistent currents does not occur because of lack of scattering. Quasi-particles are readily scattered, but such scattering does not change the common momentum of the pairs and thus v_s . It only results in fluctuations about the current corresponding to local quasi-particle equilibrium, $\rho_s v_s$.

An unexpected feature of the theory is the marked effect of coherence on the matrix elements for scattering of quasi-particles in a superconductor. It accounts for phenomena which would be inexplicable on the basis of any simple two-fluid model. In the early spring of 1957, when Cooper, Schrieffer, and I were first working out the details of the theory, Hebel and Slichter, also working at Illinois, made the first measurements of nuclear spin relaxation times in a superconductor by use of ingenious experimental techniques.

^aTo simplify the argument, we omit effects of the magnetic field on current paths, which is not valid except for flow in very thin films.

They found, surprisingly, a marked *decrease* in the relaxation time as the temperature dropped below T_c in the superconducting state, followed by an increase at still lower temperatures. Relaxation of the nuclear spins occurs from interaction with the conduction electrons in which there is a spin flip of the electron as well as the nucleus. The experiments indicated a *larger* interaction in the superconducting than in the normal state, even though specific heats and other experiments showed that there must be a marked decrease in the number of quasi-particle excitations as the temperature drops below T_c . For example, the attenuation of ultrasonic waves drops abruptly at T_c . These apparently contradictory experiments are accounted for by coherence effects. In calculating matrix elements for quasi-particle transitions in a superconductor, we found that it is necessary to add coherently the contributions from electrons of opposite spin and momentum in the various normal configurations which make up the quasi-particle states of a superconductor. For the case of a spin flip, the two contributions to the matrix element add constructively, and the larger transition probability in the superconducting state is a result of the increased density of states in energy. For an ordinary interaction such as occurs in ultrasonic attenuation, the contributions add destructively, giving a drop with an infinite slope at T_c as observed. The experimental check of these very marked effects of coherence provides one of the best confirmations of pairing in the wave functions.

In working out the properties of our simplified model and comparing with experimental results on real metals, we were continually amazed at the excellent agreement obtained. If there was serious discrepancy, it was usually found on rechecking that an error was made in the calculations. Everything fitted together neatly like the pieces of a jigsaw puzzle. Accordingly, we were unprepared for the skepticism with which the theory was greeted in some quarters. Those most skeptical had generally worked long and hard on superconductivity theory themselves, and had their own ideas of what the theory should be like. Most of the criticism centered on our derivation of the Meissner effect, because it was not carried out in a manifestly gauge-invariant manner. While our derivation is not mathematically rigorous, we gave what we believe are good physical arguments for our use of a transverse gauge, and our procedure has been justified in subsequent work. As we have seen, our model is exactly of the sort which should account for superconductivity according to London's ideas.

At the opposite extreme were some who felt that the explanation of superconductivity would mark the end of what had long been a puzzling and challenging scientific problem. On the contrary, the theory has stimulated

much new experimental and theoretical work; it has helped put new life into the field. While some questions have been answered, many others have been raised as we probe more deeply, and plenty of problems remain, as is evident from the papers submitted to this meeting.

Since the original publications, the mathematical formulation of the theory has been developed considerably. Several different mathematical formulations have been given which have improved the rigor and have extended the theory so as to apply to a wider variety of problems. Particular mention should be made of the work of Bogoliubov and co-workers, who, along with Valatin, introduced the now famous transformation to quasi-particle variables, gave a much improved treatment of Coulomb interactions, provided a treatment of collective excitations, and made other noteworthy contributions. Independently of this work, Anderson gave a derivation based on an equation-of-motion approach which introduced collective excitations and allowed a manifestly gauge-invariant treatment of the Meissner effect. The approaches of Bogoliubov and of Anderson were extended by Rickayzen to give probably the most complete derivation of the Meissner effect to date. Green's-function methods, borrowed from quantum field theory, have been used widely and with great success, following the initial work of Gor'kov, Martin and Schwinger, Kadanoff, and others. Gor'kov, in particular, has used these methods to solve several difficult problems in superconductivity theory. Fröhlich was one of the pioneers in the use of field-theoretic methods in solid-state problems . . .

We have seen that the development of our understanding of superconductivity has resulted from a close interplay of theory and experiment. Physical insight into the nature of the superconducting state gained from a study of the experimental findings has been essential to make progress in the theory. Increased theoretical understanding has suggested new experiments, new paths to explore, and has helped to understand better such seemingly unrelated fields as nuclear structure and elementary particles.

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