ADVANCES IN SUPERCONDUCTIVITY

Understanding has progressed from thermodynamic and phenomenological arguments to the pairing theory. Interest now is in problems of space and time variation of the pair potential and in theoretical prediction of relevant parameters.

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THE RAPID EXPANSION of the field of superconductivity in the past decade has been due to three factors: First, the microscopic theory provides a basis for interpretation of experimental data and prediction of new effects. Second, new superconducting materials have been discovered, some of which remain superconducting to very high magnetic fields. And third, applications are beginning to appear. These include superconducting magnets, linear accelerators, very sensitive detecting instruments and voltage standards. A comprehensive review has recently been published.[1]

John Bardeen received his MS and PhD from Princeton and since 1951 has been professor of electrical engineering and physics at the University of Illinois. In 1956 he shared a Nobel Prize with William Shockley and Walter H. Brattain for investigations of semiconductors and discovery of the transistor effect. This year, Bardeen was at the Institute for Pure and Applied Physical Sciences at the University of California, La Jolla.

Knowledge of the events leading to the development of the microscopic theory[2] is helpful for one who wants to acquire an understanding of superconductivity. An important variable describing superfluid electron flow is the phase of the complex order parameter, which can be taken to be the pair potential $\Delta(\mathbf{r},t)$ or the phenomenological Ginzburg-Landau condensate wave function. I will try to point out the meaning of the phase in terms of microscopic theory and as an example of its importance give the basis for the Josephson frequency condition.

Modern techniques of many-body theory, including Green's-function methods, have been applied successfully to superconductivity theory. To illustrate the power of the Green's-function method, I will trace the steps leading to our present understanding of strong-coupling superconductors with data from tunneling measurements. Another important application of Green's functions is to problems that involve space and time changes of the order parameter.

The theory is just beginning to give an understanding of the factors that determine the transition temperatures of real metals and so to be able to estimate transition temperatures from first principles. This is an important area for future superconductivity studies.

Early background

Development of our understanding of superconductivity can be divided into several periods. From its discovery by Heike Kamerlingh Onnes (figure 1) in 1911 until Walther Meissner's work in 1933, superconductivity was considered to be simply infinite conductivity, and attempts were made to try to understand the lack of scattering. Meissner had discovered that a superconductor excludes a magnetic field and that the state with the flux excluded is the thermodynamically stable state.

From 1933 until 1950 our understanding was based on thermodynamic and phenomenological arguments. Thermodynamics was applied successfully, for example, to relate critical fields with heat capacities. Phenomenological theories such as the Casimir-Gorter two-fluid model[3] (1933) and the London theory[4] for the electromagnetic properties (1935) were developed to describe various other aspects. The London theory included within its scope both infinite conductivity and the Meissner effect. This period culminated in 1950 with the appearance of the Ginzburg-Landau theory[5] and Fritz London's book.[6]

Vitali Ginzburg and Lev Landau generalized the London theory and introduced a complex order parameter with amplitude and phase to describe superfluid flow.

London, in his book, expanded on his earlier ideas of superconductivity as a quantum phenomenon. He suggested that superconductivity is "a quantum structure on a macroscopic scale" that requires "a kind of solidification or condensation of the average momentum distribution." We now know that these ideas are essentially correct. In a footnote, London suggested that the flux threading a superconducting ring is quantized in units of hc/e. It was not until 1962 that this prediction was verified experimentally[7] by Bascom Deaver, William Fairbank, Robert Doll and Martin Näbauer. They found that the flux unit is $hc/2e$ rather than hc/e, a result that can be accounted for by pairing.

Towards pairing theory

In 1950 Herbert Fröhlich[8] made a proposal that led eventually to the pairing theory of superconductivity. He based his theory on interactions between electrons and phonons, the quanta of the lattice vibrations. That year also two groups independently discovered that the superconducting transition temperature depends on isotopic mass. This discovery showed definitely that the motion of the ions in the metal is involved. Fröhlich's and other attempts at a theory, including my own, that were made at that time were unsuccessful. These attempts were based on the self-energy of the electrons in the field of the phonons rather than on true many-body interactions between the electrons that we now know are essential. present theory.

Advances in the period of 1950–57 were to provide experimental evidence for an energy gap[9] for quasi-particle excitations from the superconducting ground state and A. Brian Pippard's nonlocal revision[10] of the London electrodynamics. On the theoretical side was the idea of M. Roby Schafroth and others[11] that bound pairs may be involved. In 1956 Leon N. Cooper[12] showed that in the presence of an attractive interaction, a pair of electrons outside the normal Fermi sea will form a bound state no matter how weak the interaction. It had been shown by Fröhlich and more

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KAMERLINGH ONNES (above) in 1911 was first to observe the phenomenon of superconductivity. —FIG. 1

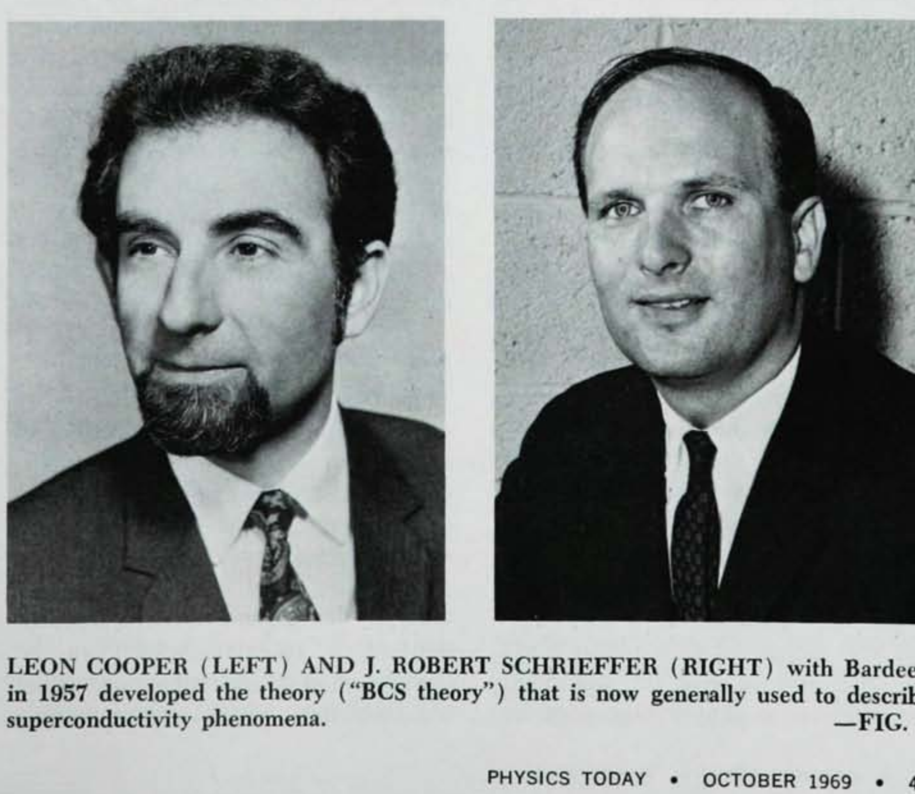
generally by David Pines and me[13] that an interaction between electrons by exchange of virtual phonons does provide such an attraction.

All of this work provided the background for the development of the pairing theory in 1957. If all electrons with energies within about $k_B T_c$ of the Fermi surface are involved in pairing, as should be true, the size of a pair wave function is much larger than average distance between neighboring pairs. Thus it could not be correct to think of the pairs as discrete entities. A true many-body approach was indicated. Cooper, J. Robert Schrieffer (figure 2) and I[2] collaborated closely to work out the form of the ground-state wave function and the spectrum of quasi-particle excitations and in applying the theory to a number of problems.

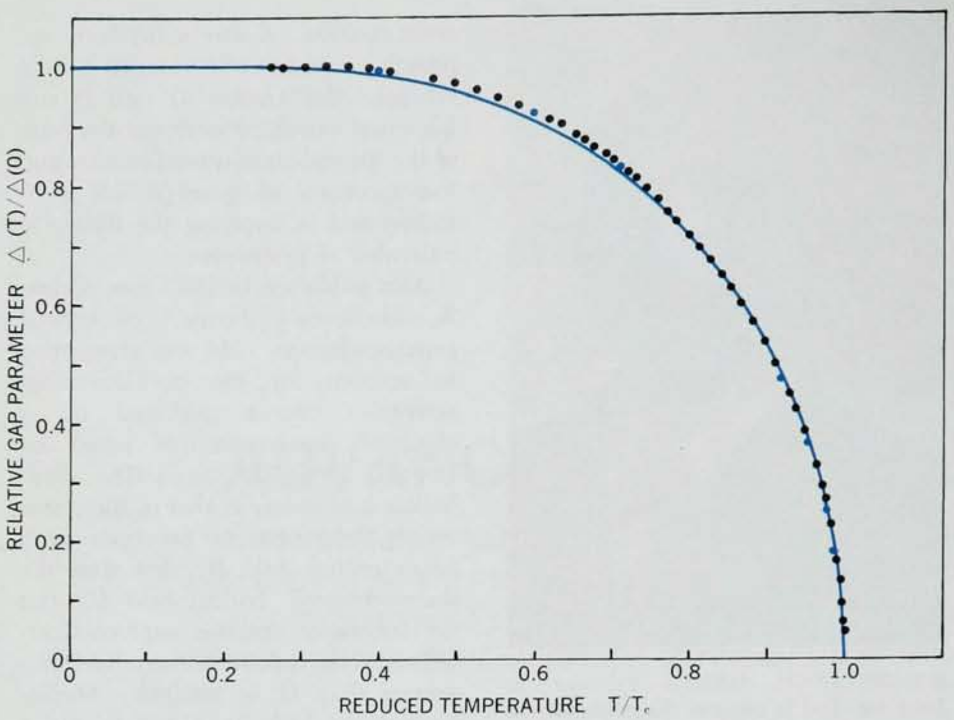
Also published in 1957 was Aleksei A. Abrikosov's theory[14] of type-II superconductors. He was attempting to account for the peculiar magnetization curves exhibited by a class of superconductors noted by Lev V. Shubnikov in 1937. Shubnikov had observed that in these materials flux starts to penetrate at a lower critical field H_{c1} less than the thermodynamic critical field H_c, but the substance remains superconducting until an upper critical field H_{c2} greater than H_c is reached. Abrikosov's paper, little noticed at the time, now forms the basis of our understanding of type-II superconductors. With the phenomenological Ginzburg-Landau theory he predicted that when $H_{c1} < H < H_{c2}$, flux penetrates in the form of an array of quantized vortex lines, each line carrying one flux quantum.

Phenomenological theories

The parameters of the phenomenological two-fluid model and the Ginzburg-Landau[5] theory are related to microscopic theory. In the two-fluid model,[3] the particle and current densities ρ and j are given by the sum of superfluid (s) and normal (n)



LEON COOPER (LEFT) AND J. ROBERT SCHRIEFFER (RIGHT) with Bardeen in 1957 developed the theory ("BCS theory") that is now generally used to describe superconductivity phenomena. —FIG. 2



COMPARISON BETWEEN THEORY AND EXPERIMENT **of temperature dependence of Δ (T) in lead. Experimental values (black dots) are based on tunneling data of Richard F. Gasparovic, Barry N. Taylor and Robert E. Eck. Small departures from the BCS weak-coupling model (curve) are accounted for by detailed calculations of James C. Swihart, Douglas Scalapino and Yasuski Woda (colored dots) based on the strong-coupling theory. See reference 1, chapter 10, for details. —FIG. 3**

components $$\rho = \rho_s + \rho_n \qquad (1)$$

$$\mathbf{j} = \rho_s \mathbf{v}_s + \rho_n \mathbf{v}_n \qquad (2)$$

Here $\mathbf{v}_s$ and $\mathbf{v}_n$ are fluid velocities. The normal component of the current density $\rho_n \mathbf{v}_n$ results from a nonequilibrium distribution of quasi-particle excitations.

The Ginzburg-Landau theory describes superfluid flow $\rho_s \mathbf{v}_s$ in terms of an effective wave function with amplitude $|\psi|$ and phase χ

$$\psi(\mathbf{r}) = |\psi(\mathbf{r})| e^{i\chi(\mathbf{r})} \qquad (3)$$

The superfluid density ρ_s is assumed to be proportional to $|\psi(\mathbf{r})^2|$ and the velocity $\mathbf{v}$ is given by the usual expression from quantum mechanics. For $\rho_s = \text{const}$

$$m^* \mathbf{v}_s = \mathbf{p}_s - (e^*/c)\mathbf{A}(\mathbf{r}) \qquad (4)$$

where $\mathbf{p}_s = \hbar$ grad $\chi(\mathbf{r})$ is the canonical momentum determined by the gradient of the phase. We now interpret $\mathbf{p}_s$ as the momentum per pair of electrons in the condensate so that $m^* = 2m$ and $e^* = 2e$. The effective wave function $\psi(\mathbf{r})$ is determined from a nonlinear Schrödinger-like equation.

It can be noted that phase plays the same sort of role for superfluid flow of electrons that voltage does for flow in normal metals. In normal metals the current density is proportional to the voltage gradient, and in the absence of current flow the voltage is everywhere the same. Correspondingly, when the superfluid flow vanishes and there is no magnetic field, the phase is the same everywhere.

The wave function does not describe a single particle or the center of mass of a pair of particles but rather the motion of the superfluid condensate as a whole. Considerations based on the microscopic theory indicate that the Ginzburg-Landau theory is strictly valid only near T_c, but the Ginzburg-Landau theory does help to give a good qualitative understanding of superconductivity at all temperatures.

Microscopic theory

The microscopic theory has given an understanding, often quantitative, of many diverse properties of superconductors and has been used to predict new phenomena such as Josephson tunneling.

According to the microscopic theory,[2] the ground-state wave function of a superconductor can be thought of as a coherent superposition of low-lying normal many-particle configurations in which particles are excited out of the Fermi sea. A typical configuration $\psi_i(\mathbf{k}_1\sigma_1, \mathbf{k}_2\sigma_2 \ldots)$ can be designated by giving spin σ and wave vector $\mathbf{k}$ of the occupied states in $\mathbf{k}$ space. Even when interactions between particles are taken into account, low-lying quasi-particle states have a reasonably long lifetime. The superconducting ground state is given by the sum

$$\Psi_{sg} = \Sigma A_i \psi_i(\mathbf{k}_1\sigma_1, \mathbf{k}_2\sigma_2 \ldots) \qquad (5)$$

If the matrix elements of the attractive interaction between the ψ_i's are to add coherently to give a low-energy state, the quasi-particle states in the configurations ψ_i must be occupied in pairs $(\mathbf{k}_{1u}, \mathbf{k}_{2d})$, $(\mathbf{k}_{1d}{}', \mathbf{k}_{2u}{}')$ . . . (u stands for spin up and d for spin down). The occupation must be such that either both members of a pair are occupied or both are empty. Further, for any pair to be scattered into another pair, they must have the same momentum

$$\hbar(\mathbf{k}_1 + \mathbf{k}_2) = \hbar(\mathbf{k}_1{}' + \mathbf{k}_2{}') = \mathbf{p}_s \qquad (6)$$

For $\mathbf{p}_s = 0$, the pairs are of opposite spin and momentum.

Note that the pair momentum state $\mathbf{p}_s$ is macroscopically occupied. It is this feature that corresponds to London's idea of a condensation of the momentum distribution. The common momentum $\mathbf{p}_s$ of the pairs corresponds to the $\mathbf{p}_s$ of the Ginzburg-Landau theory.

There is a quasi-particle excitation spectrum of a superconductor in one-to-one correspondence with that of the normal state. If ϵ_k is the normal-state quasi-particle energy relative to the Fermi surface, the energy of the corresponding excitation in the superconducting state is $E_k = (\epsilon_k{}^2 + \Delta^2)^{1/2}$. ($\Delta$ is the gap parameter.) Because Δ is a measure of the pairing, it is also called the pair potential. With increasing temperature, Δ decreases and goes to zero at $T = T_c$. Quasi-particle excitations are created in pairs from the ground state; the minimal energy required to create a pair is the energy gap $E_g = 2\Delta$. As illustrated in figure 3, the temperature variation of Δ has been confirmed strikingly by experiment.

Persistent currents

One can see from this picture how to account for persistent current flow. To simplify the discussion, we take the vector potential $\mathbf{A} = 0$ so that

$\mathbf{p}_s = m^*\mathbf{v}_s$ is the common momentum of the pairs relative to the lattice or rest frame. We suppose that the quasi-particles scatter all they want and come to equilibrium with the rest frame, but with $\mathbf{p}_s$ fixed. Scattering of quasi-particles does not change $\mathbf{p}_s$. In a normal system, scattering reduces the current to zero, but in a superconductor, a net flow remains after the quasi-particle equilibrium is established, and it persists in time. This is the superfluid flow $\rho_s\mathbf{v}_s$ whose magnitude determines ρ_s. The heat flow vanishes; so a supercurrent carries no entropy.

Only macroscopic excitations, such as vortex lines, can cause $\mathbf{p}_s$ to change and the supercurrent to decay. This can occur in type-II superconductors in the mixed state and in thin films near T_c. The metastability of persistent currents has been discussed by Felix Bloch.[15]

Cooper, Schrieffer and I found it convenient to express the ground-state wave function of a superconductor mathematically in terms of products of creation operators acting on the vacuum state

$$\Psi_{sg} = \prod_k (u_k + v_k c_{ku}{}^* c_{kd}{}^*)\Psi_{vac} = \sum_N a_N \Psi_N \quad (7)$$

Here $|u_k|^2 + |v_k|^2 = 1$. The product $c_{ku}{}^* c_{kd}{}^*$ creates a pair in $(\mathbf{k}u, -\mathbf{k}d)$. The product over all $\mathbf{k}$ contains many configurations with varying numbers of pairs N. There is a probability amplitude v_k that the pair state $\mathbf{k}$ is occupied and u_k that it is unoccupied in any configuration. Written in this form Ψ_{sg} is a superposition of states Ψ_N with differing numbers of pairs N but with amplitudes a_N sharply peaked about an average number $N = N_0$.

The relative phase of u_k and v_k is arbitrary. Thus, if one changes v_k into $v_k\, e^{i\chi}$, Ψ_{sg} becomes[16]

$$\Psi_{sg} = \sum_N a_N e^{iN\chi}\, \Psi_N \quad (8)$$

It is χ that corresponds to the phase of the Ginzburg-Landau theory. If χ varies slowly in space one gets a state in which the local pair momentum is $\mathbf{p}_s = \hbar$ grad χ.

One could of course project the wave function Ψ_{sg} to get a state with definite N, but the resulting wave function is more complicated than the product state (equation 7). What was done originally for mathematical convenience turned out to make good physical sense; for it allows one to define the phase. In a quantum-mechanical sense N and $\hbar_\chi$ are conjugate variables like p and q (assuming that N is very large so that it can be considered as a continuous variable). For wave functions of the form of equation 8 the number operator N_{op} is given by the gradient in phase

$$N_{op} = -i\partial/\partial\chi \quad (9)$$

and the uncertainty relation is $\Delta N \Delta\chi \approx 1$. Because N is very large, in practice both N and χ can be specified with high precision ($\Delta N/N \ll 1$).

Calculations were made for a simplified model in which it is assumed that the matrix elements of the effective interaction for scattering a pair from $(\mathbf{k}_u, -\mathbf{k}_d)$ to $(\mathbf{k}_u', -\mathbf{k}_d')$ are attractive and equal to a constant $-V$ for quasi-particle states with energies within $\hbar\omega_c$ of the Fermi energy and vanish for $|\epsilon| > \hbar\omega_c$. The cutoff energy is a typical phonon energy of the order of $k_B\Theta_D$, where Θ_D is the Debye temperature. For this model, the energy difference between normal and superconducting states at $T = 0$ is

$$W_s - W_n = -N(0)\Delta(0)^2/2 \quad (10)$$

$\Delta(0)$ is the pair potential at zero temperature.

$$\Delta(0) = 2\hbar\omega_c \exp(-1/N(0)V) \quad (11)$$

$N(0)$ is the density of states of one spin at the Fermi surface. The transition temperature where Δ goes to zero is given by $k_B T_c = 1.14\ \hbar\omega_c \exp(-1/N(0)V)$.

Creation and destruction

In our 1957 paper we used a rather cumbersome scheme to describe the wave functions for quasi-particle excitations of a superconductor and their matrix elements. Shortly afterward Nikolai N. Bogoliubov and John G. Valatin[17] independently showed that the excitations could be expressed with quasi-particle operators that are linear combinations of creation and destruction operators

$$\gamma_{ku}{}^* = u_k c_{ku}{}^* - v_k c_{kd} \quad (12a)$$

$$\gamma_{-kd}{}^* = u_k c_{kd}{}^* + v_k c_{ku} \quad (12b)$$

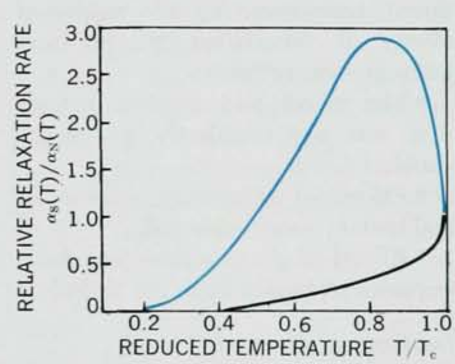
The ground state is the quasi-particle vacuum

$$\gamma_{ku}\Psi_{sg} = \gamma_{-kd}\Psi_{sg} = 0 \quad (13)$$

These operators are designed to operate on states of the form of equation 7 that are linear superpositions of states with varying numbers of pairs.

With a complete set of states, one can calculate the free energy. There is a second-order phase transition at $T = T_c$. The set of quasi-particle states can be used as a basis for a time-dependent perturbation expansion to calculate the various transport properties of superconductors with little more difficulty than for normal metals.

An unusual feature of the theory is a coherence between scattering of particles in the paired states $\mathbf{k}u$ and $-\mathbf{k}d$. This gives rise to constructive or destructive interference, depending on the nature of the scattering interaction. In this way, we were able to account for both a rapid drop in ultrasonic attenuation and an increase in nuclear-spin relaxation rate as temperature is lowered below the critical temperature. (See figure 4.) We showed that the response to static magnetic fields gives a Meissner effect with an expression for the current density in the penetration region similar to that proposed earlier by Pippard[10] on phenomenological grounds. We were able to account for the rise in absorption in thin films as $\hbar\omega$ becomes larger than the gap 2Δ. Rolfe E. Glover and Michael Tinkham[18] observed such a rise in lead



COHERENCE EFFECTS from scattering of electrons of opposite spin and momentum give a striking difference between nuclear spin-relaxation rate (color), which involves an electron-spin flip, and longitudinal ultrasonic-attenuation (black), which does not. Agreement of the theory with both experiments was an early confirmation of the pairing concept. The ratio of nuclear-spin relaxation rates in superconducting and normal states as a function of critical temperature was calculated by L. Charles Hebel to fit experimental data on aluminum, and the ultrasonic attenuation curve is based on data of Robert W. Morse and Henry Böhm and on the BCS theory. See reference 1, chapter 4. —FIG. 4

A NEW PERIODICITY IN SUPERCONDUCTIVITY?

Is there a periodic law relating superconductivity and American Physical Society presidents? Felix Bloch suggested the possibility in his 1966 retiring presidential address.[15] He spoke on superconductivity and reminded his listeners that it had been mentioned by William V. Houston[11] in 1963 and George Uhlenbeck[15] in 1960. At that time Bloch expressed his hope "that the tradition will be maintained and that the retiring president will favor us in 1969 with a comprehensive account of the insights achieved." While this is too large an order for me, I have tried to carry on the tradition. In the address on which this article is based, I discussed just a few of the insights achieved, picked from a rich grab bag to which many have contributed. For a true test of the periodic law, we will have to wait for Robert Serber's retiring presidential address in 1972.

films in the far infrared region.

Soon Daniel C. Mattis and I[19] extended the calculation of the electrodynamics response of superconductors to arbitrary wave vector and frequency, and Gerald Rickayzen, Ludwig Tewordt and I[20] derived an expression for thermal conductivity. Although there were a few discrepancies between theory and experiment, since largely resolved, the agreement in general was remarkably good for a wide range of phenomena.

Some of the limitations of the 1957 paper are the following:

- Only homogeneous systems, in which the pair potential Δ is independent of space and time, were considered.
- Quasi-particle lifetime effects were neglected for both normal and superconducting states.
- In taking an effective, phonon-induced interaction V, we neglected effects of retardation arising from finite phonon velocities.
- The theory was given in a form that was not manifestly gauge invariant.
- Effects of anisotropy, present in real metals, were neglected.
- Effects of a mean free path from impurity scattering were not included.

Subsequent advances

With modern techniques of many-body theory many physicists throughout the world have helped remove these and other limitations of the original theory. Philip W. Anderson[21] and later more completely Rickayzen[22] included collective excitations and gave a manifestly invariant theory. More general formulations of the theory were also given by Bogoliubov, Vladimir V. Tolmachev, Dmitri V. Shirkov[23] and Yoichiro Nambu.[24] The powerful method of thermal Green's functions was introduced to superconductivity theory by Lev P. Gor'kov[25] and others.[26] Gor'kov was able to show that the Ginzburg-Landau equations are valid just below T_c, with the effective wave function $\Psi(r)$ proportional to a complex space-dependent gap parameter $\Delta(r)$.

Bogoliubov[23] derived a generalized pairing scheme that also can be used to treat problems in which Δ varies in space. This method has been used by Pierre-Gilles deGennes[27] and others to treat the structure of vortex lines in type-II superconductors, surface superconductivity, proximity effects and other problems.

Anderson's theory[28] of dirty superconductors allows one to include a mean free path from scattering by nonmagnetic impurities. Independently Mattis and I[19] used similar methods to show that a scattering mean free path enters the theory of the electrodynamic properties in the way suggested earlier by Pippard on phenomenological grounds.

Abrikosov and Gor'kov[29] used Green's-functions methods in their treatment of spin-flip scattering by magnetic impurities. This scattering results in depairing and a large drop in transition temperature with increasing concentration of magnetic impurities. Before T_c goes to zero, there is a range of concentration in which the gap for quasi-particle excitations vanishes but the material remains superconducting.

Josephson tunneling

One of the most striking advances in the theory is Brian D. Josephson's prediction[30] of superfluid flow across a tunneling barrier. Because his theory brings out some basic features of superconductivity and emphasizes the importance of phase as a parameter, I will discuss it briefly. An understanding of tunneling has also been very important for an understanding of strong-coupling superconductors and the phonon-induced interaction.

In 1960 Ivar Giaever[31] made the first tunnel junctions and showed that they yield a powerful method for investigating superconductors. A thin oxide layer through which electrons can tunnel separates the metals on the two sides of the junction. If one metal is normal and the other superconducting, the current-voltage characteristic yields the density of energy states in the superconductor. In 1962 Josephson predicted that if metals on both sides of the junction are superconducting, a current can flow when no voltage is applied. The current is proportional to the sine of the difference in phase between the superconductors on the sides of the junction

$$J_s = J_1 \sin(\chi_1 - \chi_2) \qquad (14)$$

Many beautiful experiments have been done by John M. Rowell,[32] Robert C. Jaklevic, John J. Lambe, James E. Mercereau and Arnold H. Silver[33] to demonstrate phase-interference effects analogous to single- and double-slit diffraction in optics.

When a voltage is applied across the junction, the phase difference increases linearly with time

$$\chi_1(t) - \chi_2(t) = \chi_1(0) - \chi_2(0) + \omega t \qquad (15)$$

where ω is given by the Josephson frequency condition

$$\omega = 2e(V_1 - V_2)/\hbar \qquad (16)$$

This increase gives rise to an alternating current of frequency ω, which is in the microwave range for voltage differences of a few millivolts. If microwave radiation of frequency ω_a is applied to the junction, it beats against the ac Josephson current. In the direct current-voltage characteristic, steps of varying current at constant voltage occur when $V_1 - V_2$ is a multiple of $\hbar\omega_a/2e$. Such steps were first observed by Sidney Shapiro;[34] an example of the steps is shown in figure 5.

By measuring accurately the voltage at which the steps occur for a known frequency ω_a, William H. Parker, Barry N. Taylor and Donald N. Langenberg[35] have made a precise measurement of e/h. They find

$$2e/h = 4.835976(12) \times 10^{14}\ \mathrm{Hz/V(NBS)} \pm 2.4\ \mathrm{ppm} \qquad (17)$$

Taylor[36] has used this measurement

in a revision of the values of the fundamental constants.

Questions have been raised as to whether the Josephson frequency relation is exact or requires corrections from quantum electrodynamics or other origins. There is a slight frequency pulling of the emitted radiation. Theory indicates, however, that there should be no corrections to the voltage differences measured with the Shapiro steps. Following Anderson,[37] one can regard the coupling free energy F resulting from the fact that pairs can tunnel back and forth to depend on the phase difference $\chi_1 - \chi_2$ and the difference in numbers of pairs on the two sides, $N_1 - N_2$ as well as on the temperature. Taking $\hbar(\chi_1 - \chi_2)$ we have for the equation of motion

$$\hbar\frac{\partial(\chi_1 - \chi_2)}{\partial t} = -\frac{\partial F}{\partial(N_1 - N_2)} = 2e(V_1 - V_2) \quad (18)$$

The rate of change of free energy with respect to pair number is, by definition, equal to $2e\ (V_1 - V_2)$ the difference in electrochemical potential when a pair is transferred. Integration with respect to time yields equation 15.

With Josephson-junction techniques, one can detect extremely small voltage differences. By comparing junctions made of different materials to which the same frequency has been applied, John Clarke[38] has shown that the voltage steps are the same to within about one part in 10^8. This equality indicates that the relation between voltage and frequency is independent of material properties.

Strong coupling

Another important application of tunneling is to determine the density of energy states. One uses a junction between a normal metal A and the superconductor to be studied B. The ratio of the conductance when B is in the superconducting state to that when B is normal gives the tunneling density of states $N_T(E)$ at energy E relative to the Fermi energy ($E = eV$, and V is the applied voltage). As shown by Schrieffer,[26] in an isotropic material

$$\frac{(dI/dV)_s}{(dI/dV)_n} = \frac{N_T(E)}{N(0)} = \mathrm{Re}\left(\frac{E}{(E^2 - \Delta(E)^2)^{1/2}}\right) \quad (19)$$

Here $\Delta(E)$ is the complex energy-dependent pair potential. By use of Kramers–Kronig relations, one can obtain both real and imaginary parts of $\Delta(E)$ from the tunneling measurements. These together with the density of states $N(0)$ completely specify the Green's function. Then one can derive the various thermal and transport properties of the superconductor in excellent agreement with experiment. The most important application is to strong-coupling superconductors for which one must take into account the energy dependence of $\Delta(E)$.

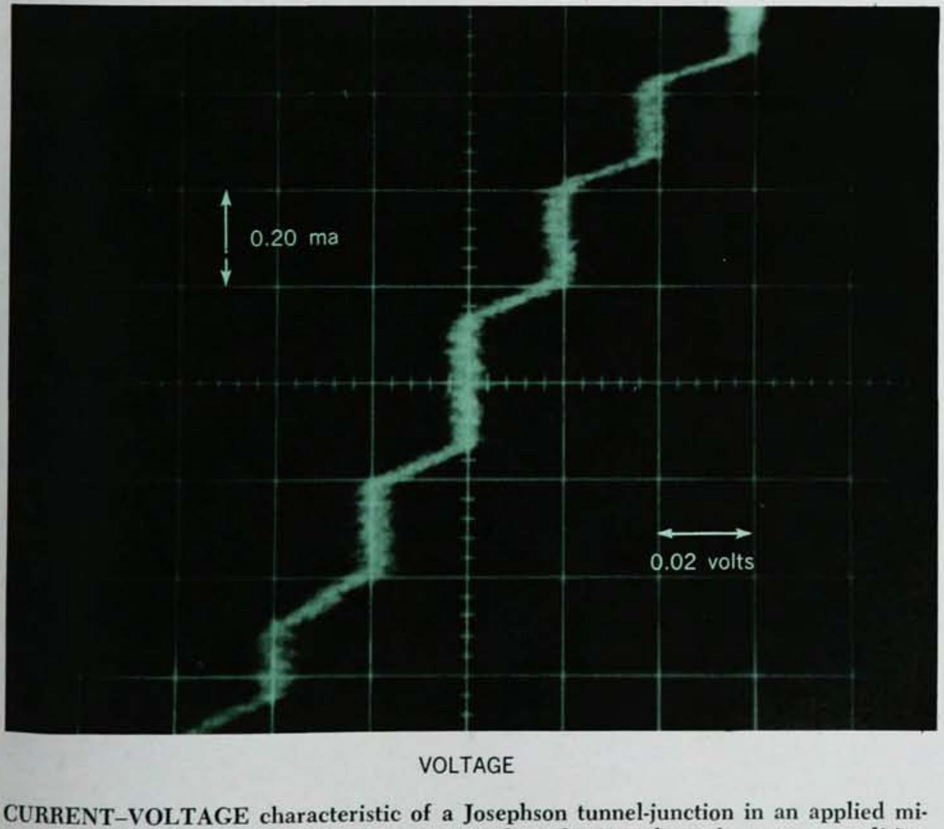
Nambu[24] and Gerasim M. Eliashberg[39] have given coupled integral equations to determine $\Delta(E)$ from the electron-phonon interaction α_q and the phonon density of states $F(\omega_q)$. Here $\mathbf{q}$ is the phonon wave vector and $\hbar\omega_q$ the phonon energy. Schrieffer, Douglas J. Scalapino and John W. Wilkins[40] have obtained solutions of the integral equations for application to lead. William L. McMillan[41] has worked out a computer program to derive $\alpha_q{}^2F(\omega)_q$ directly from the tunneling data and has applied it to a number of cases. This work has been extremely valuable for an understanding of the origin of superconductivity in real metals.

Present problems

Some of the most active areas of research interest now are problems dependent on space and time variations of the pair potential $\Delta(\mathbf{r},t)$. Among these are:

- the energy and motion of the boundary between normal and superconducting regions in the intermediate state of type-I superconductors
- the proximity effect
- the Tomasch effect in tunneling resulting from quasi-particle scattering by a pair potential
- the free energy, quasi-particle excitations and motion of vortex lines in type-II superconductors
- surface superconductivity, calculations of H_{c3} and electrodynamic response
- fluctuations, particularly in thin films, resulting in shifts in T_c and a reduction in normal resistance above T_c.

Green's-function methods are frequently used for such problems. Progress has been made for T near or above T_c and for H near H_{c2} when Δ can be treated as a small parameter. To solve problems for which Δ is not small, some colleagues and I have been attempting to solve the Bogoliubov equations for quasi-particle excitations with the WKBJ approximation. Reiner Kümmell, Allan Jacobs, Tewordt and I[42] have made calcula-



CURRENT–VOLTAGE characteristic of a Josephson tunnel-junction in an applied microwave field. Constant-voltage steps occur when the Josephson frequency condition $n\hbar\omega = 2eV$ is satisfied. The experimental data, from Sidney Shapiro, are for a niobium–oxide–lead junction at 4.2K in a microwave field of 9.75 GHz/sec. —FIG. 5

tions of the free energy of vortex lines at low temperatures and H near H_{c1} by this method.

In comparisons of theory and experiment, relevant parameters have usually been measured experimentally. Ultimately, one would like to be able to predict the values of superconductance parameters in advance of measurements and to understand how they vary from one substance to another.

Bernd Matthias, who has obtained well deserved recognition for his role in discovering a great many new superconducting compounds and alloys, complains that the theorists have not helped him in his search through the periodic table for new superconducting materials with unusual properties. Getting a better understanding of the microscopic basis for various material parameters, such as the transition temperature, is a very important task for the future. Progress is being made: The transition temperatures of simple metals such as aluminum and lead have been calculated essentially from first principles.

Probably the most challenging problem in superconductivity is whether or not there are ways for getting an attractive interaction between electrons other than through phonons. A number of mechanisms involving only electron excitations have been suggested. These include virtual excitation of excitons (bound electron-hole pairs), excitation to low-lying f levels (suggested for lanthanum) and excitation of low-lying electronic states in side chains of organic polymer chains (suggested by William A. Little). The hope is that if such mechanisms are established and understood, it may be possible to design superconducting materials to operate at higher temperatures, perhaps as high as liquid nitrogen or even room temperature. Although such non-phonon mechanisms for superconductivity appear possible, they have not yet been established either theoretically or experimentally in a convincing manner.

After more than a decade of development of the microscopic theory, there are still many challenging problems, and one can look forward to continual development of the field in the years to come. Much of this is likely to be focused on the problems of specific materials.

This discussion has been confined to superconductivity in metals. Closely related phenomena occur in superfluidity in liquid helium.[43] The concepts and mathematical methods of the theory have been applied successfully to pairing effects in nuclei. Neutron stars (pulsars) may be superfluid. Some of the ideas, particularly those relating to the degenerate ground state, have been used in theories of particle physics. It can be expected that these related subjects will also be further developed as time goes on and that superconductivity theory will benefit from these interactions with neighboring disciplines.

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References

1. *Superconductivity*, (R. D. Parks, ed.) vols. 1 and 2, Marcel Dekker, Inc., New York (1969).
2. J. Bardeen, L. N. Cooper, J. R. Schrieffer, Phys. Rev. **106**, 162 (1957); **108**, 1175 (1957).
3. C. J. Gorter, H. B. G. Casimir, Phys. Z. **35**, 963 (1934); Z. techn. Phys. **15**, 539 (1934).
4. H. London, F. London, Proc. Roy. Soc. (London) **A149**, 71 (1935).
5. V. L. Ginzburg, L. D. Landau, Zh. Eksp. Teor. Fiz. **20**, 1064 (1950).
6. F. London, *Superfluids*, vol. 1, John Wiley & Sons, New York (1950).
7. B. S. Deaver Jr, W. M. Fairbank, Phys. Rev. Lett. **7**, 43 (1961); R. Doll, M. Näbauer, Phys. Rev. Lett. **7**, 51 (1961).
8. H. Fröhlich, Phys. Rev. **79**, 845 (1950).
9. M. A. Biondi, A. T. Forrester, M. P. Garfunkel, C. B. Satterthwaite, Rev. Mod. Phys. **30**, 1109 (1958).
10. A. B. Pippard, Proc. Roy. Soc. (London) **A216**, 547 (1953).
11. V. L. Ginzburg, Usp. Fiz. Nauk **48**, 25 (1952); M. R. Schafroth, Phys. Rev. **100**, 463 (1955).
12. L. N. Cooper, Phys. Rev. **104**, 1189 (1956).
13. J. Bardeen, D. Pines, Phys. Rev. **99**, 1104 (1955).
14. A. A. Abrikosov, Zh. Eksp. Teor. Fiz. **32**, 1442 (1957) [English transl.: Sov. Phys.–JETP **5**, 1174 (1957)].
15. F. Bloch, PHYSICS TODAY **19**, no. 5, 27 (1966).
16. P. W. Anderson, Phys. Rev. **110**, 827 (1958).
17. N. N. Bogoliubov, Nuovo Cimento **7**, 794 (1958); J. G. Valatin, Nuovo Cimento **7**, 843 (1958).
18. R. E. Glover III, M. Tinkham, Phys. Rev. **108**, 243 (1957).
19. D. C. Mattis, J. Bardeen, Phys. Rev. **111**, 412 (1958).
20. J. Bardeen, G. Rickayzen, L. Tewordt, Phys. Rev. **113**, 982 (1959).
21. P. W. Anderson, Phys. Rev. **112**, 1900 (1958).
22. G. Rickayzen, Phys. Rev. **115**, 795 (1959).
23. N. N. Bogoliubov, V. V. Tolmachev, D. V. Shirkov, *A New Method in the Theory of Superconductivity*, Consultants Bureau, New York (1959).
24. Y. Nambu, Phys. Rev. **117**, 648 (1960).
25. L. P. Gor'kov, Zh. Eksp. Teor. Fiz. **34**, 735 (1958) [English transl.: Sov. Phys.–JETP **7**, 505 (1958)].
26. J. R. Schrieffer, *Theory of Superconductivity*, W. A. Benjamin, New York (1964).
27. P-G. deGennes, *Superconductivity in Metals and Alloys*, W. A. Benjamin, New York (1966).
28. P. W. Anderson, J. Phys. Chem. Solids **11**, 26 (1959).
29. A. A. Abrikosov, L. P. Gor'kov, Zh. Eksp. Teor. Fiz. **39**, 1781 (1960) [English transl.: Sov. Phys.–JETP **12**, 1243 (1961)].
30. B. D. Josephson, Phys. Rev. Lett. **1**, 251 (1962); *Advances in Physics* **14**, 419 (1965).
31. I. Giaever, Phys. Rev. Lett. **5**, 147 and 464 (1960).
32. J. M. Rowell, Phys. Rev. Lett. **11**, 200 (1963).
33. R. C. Jaklevic, J. Lambe, J. E. Mercereau, A. H. Silver, Phys. Rev. Lett. **12**, 159 (1964); Phys. Rev. **A140**, 1628 (1965).
34. S. Shapiro, Phys. Rev. Lett. **11**, 80 (1963).
35. W. H. Parker, B. N. Taylor, D. N. Langenberg, Phys. Rev. Lett. **18**, 287 (1967).
36. B. N. Taylor, W. H. Parker, D. N. Langenberg, Rev. Mod. Phys. **41**, 375 (1969) (to be published also by Academic Press as a monograph); PHYSICS TODAY **22**, no. 8, 66 (1969).
37. P. W. Anderson, chap. I in *Progress in Low Temperature Physics*, vol. 5, (C. J. Gorter, ed.) North-Holland, Amsterdam (1967).
38. J. Clarke, Phys. Rev. Lett. **21**, 1566 (1968).
39. G. M. Eliashberg, Zh. Eksp. Teor. Fiz. **38**, 966 (1960) [English transl.: Sov. Phys.–JETP **11**, 696 (1960)].
40. J. R. Schrieffer, D. J. Scalapino, J. W. Wilkins, Phys. Rev. Lett. **10**, 336 (1963); Phys. Rev. **148**, 263 (1966).
41. W. L. McMillan, Phys. Rev. **167**, 331 (1968).
42. J. Bardeen, R. Kümmel, A. Jacobs, L. Tewordt, Phys. Rev. (to be published).
43. K. Mendelssohn, PHYSICS TODAY **22**, no. 4, 46 (1969).
44. W. V. Houston, PHYSICS TODAY **16**, no. 9, 36 (1963).
45. G. Uhlenbeck, PHYSICS TODAY **13**, no. 7, (1960). □