The Hamiltonian operator in the second-quantization formalism is given by

$$H = \sum_{k'ks} \langle k's|H_1|ks\rangle c_{k's}{}^{+} c_{ks} + \tfrac{1}{2} \sum_{\substack{ijkl \\ ss'}} \langle ij|V|lk\rangle c_{is}{}^{+} c_{js'}{}^{+} c_{ks'} c_{ls} \quad \text{(A-29)}$$

where s and s' label the spin of the particle.

The wave fields are defined as

$$\psi(x) = \sum_{k} u_k(x) c_k$$

and they satisfy the anticommutation equations

$$\{\psi(x), \psi^{+}(x')\} = \delta(x - x')$$
$$\{\psi(x), \psi(x')\} = 0 = \{\psi^{+}(x), \psi^{+}(x')\}$$

Note that in (A-29) the order of the destruction operators with regard to the matrix-element indices is the inverse of that of the creation operators. The ν-body operator of Eq. (A-24) is

$$V_\nu = \frac{1}{\nu!} \sum_{k_\nu' s_\nu' \cdots k_1' s_1' k_\nu s_\nu \cdots k_1 s_1} \langle k_\nu' \cdots k_1' | V_\nu | k_\nu \cdots k_1 \rangle \times c_{k_\nu' s_\nu'}{}^{+} \cdots c_{k_1' s_1'}{}^{+} c_{k_1 s_1} \cdots c_{k_\nu s_\nu} \quad \text{(A-24')}$$

The ordering is not entirely arbitrary because of sign changes arising from anticommutation of fermion operators; that of (A-29), (A-24'), (A-24), and (A-22) gives the correct sign for either fermion or boson operators.

If one is dealing with particles of nonzero spin, the coordinate x represents both space and spin variables, as does the variable k. Integrals over x represent integrals over space and sums over spin variables.

MACROSCOPIC QUANTUM PHENOMENA FROM PAIRING IN SUPERCONDUCTORS

Nobel Lecture, December 11, 1972

by

J. R. SCHRIEFFER

University of Pennsylvania, Philadelphia, Pa.

I. INTRODUCTION

It gives me great pleasure to have the opportunity to join my colleagues John Bardeen and Leon Cooper in discussing with you the theory of superconductivity. Since the discovery of superconductivity by H. Kamerlingh Onnes in 1911, an enormous effort has been devoted by a spectrum of outstanding scientists to understanding this phenomenon. As in most developments in our branch of science, the accomplishments honored by this Nobel prize were made possible by a large number of developments preceding them. A general understanding of these developments is important as a backdrop for our own contribution.

On December 11, 1913, Kamerlingh Onnes discussed in his Nobel lecture (1) his striking discovery that on cooling mercury to near the absolute zero of temperature, the electrical resistance became vanishingly small, but this disappearance "did not take place gradually but *abruptly*." His Fig. 17 is reproduced as Fig. 1. He said, "Thus, mercury at 4.2 K has entered a new state

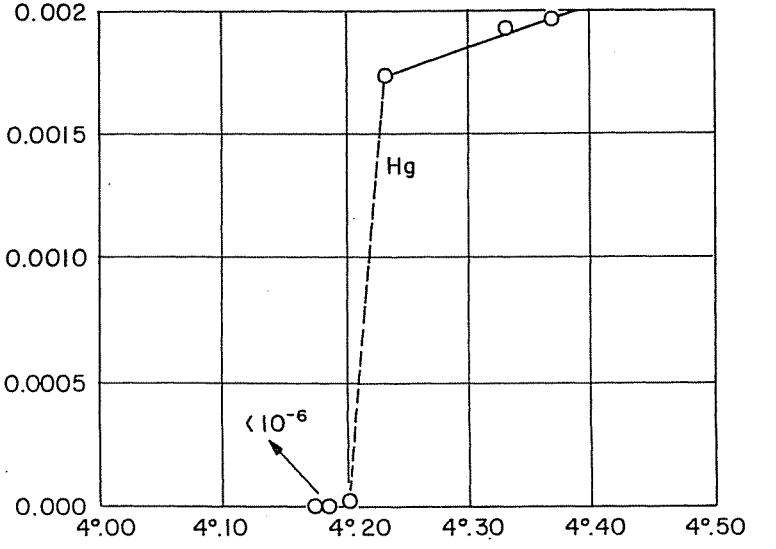


Fig. 1

which owing to its particular electrical properties can be called the state of superconductivity." He found this state could be destroyed by applying a sufficiently strong magnetic field, now called the critical field H_c. In April–June, 1914, Onnes discovered that a current, once induced in a closed loop of superconducting wire, persists for long periods without decay, as he later graphically demonstrated by carrying a loop of superconducting wire containing a persistent current from Leiden to Cambridge.

In 1933, W. Meissner and R. Ochsenfeld (2) discovered that a superconductor is a perfect diamagnet as well as a perfect conductor. The magnetic field vanishes in the interior of a bulk specimen, even when cooled down below the transition temperature in the presence of a magnetic field. The diamagnetic currents which flow in a thin penetration layer near the surface of a simply connected body to shield the interior from an externally applied field are stable rather than metastable. On the other hand, persistent currents flowing in a multiply connected body, e.g., a loop, are metastable.

An important advance in the understanding of superconductivity occurred in 1934, when C. J. Gorter and H. B. G. Casimir (3) advanced a two fluid model to account for the observed second order phase transition at T_c and other thermodynamic properties. They proposed that the total density of electrons ϱ could be divided into two components

$$\varrho = \varrho_s + \varrho_n \tag{1}$$

where a fraction ϱ_s/ϱ_n of the electrons can be viewed as being condensed into a "superfluid," which is primarily responsible for the remarkable properties of superconductors, while the remaining electrons form an interpenetrating fluid of "normal" electrons. The fraction ϱ_s/ϱ_n grows steadily from zero at T_c to unity at $T = 0$, where "all of the electrons" are in the superfluid condensate.

A second important theoretical advance came in the following year, when Fritz and Hans London set down their phenomenological theory of the electromagnetic properties of superconductors, in which the diamagnetic rather than electric aspects are assumed to be basic. They proposed that the electrical current density $\mathbf{j}_s$ carried by the superfluid is related to the magnetic vector potential $\mathbf{A}$ at each point in space by

$$\mathbf{j}_s = -\frac{1}{\Lambda c}\mathbf{A} \tag{2}$$

where Λ is a constant dependent on the material in question, which for a free electron gas model is given by $\Lambda = m/\varrho_s e^2$, m and e being the electronic mass and charge, respectively. A is to be chosen such that $\nabla \cdot \mathbf{A} = 0$ to ensure current conservation. From (2) it follows that a magnetic field is excluded from a superconductor except within a distance

$$\lambda_L = \sqrt{\Lambda c^2/4\pi}$$

which is of order 10^{-6} cm in typical superconductors for T well below T_c. Observed values of λ are generally several times the London value.

In the same year (1935) Fritz London (4) suggested how the diamagnetic

property (2) might follow from quantum mechanics, if there was a "rigidity" or stiffness of the wavefunction ψ of the superconducting state such that ψ was essentially unchanged by the presence of an externally applied magnetic field. This concept is basic to much of the theoretical development since that time, in that it sets the stage for the gap in the excitation spectrum of a superconductor which separates the energy of superfluid electrons from the energy of electrons in the normal fluid. As Leon Cooper will discuss, this gap plays a central role in the properties of superconductors.

In his book published in 1950, F. London extended his theoretical conjectures by suggesting that a superconductor is a "quantum structure on a macroscopic scale [which is a] kind of solidification or condensation of the average momentum distribution" of the electrons. This momentum space condensation locks the average momentum of each electron to a common value which extends over appreciable distance in space. A specific type of condensation in momentum space is central to the work Bardeen, Cooper and I did together. It is a great tribute to the insight of the early workers in this field that many of the important general concepts were correctly conceived before the microscopic theory was developed. Their insight was of significant aid in our own work.

The phenomenological London theory was extended in 1950 by Ginzburg and Landau (5) to include a spatial variation of ϱ_s. They suggested that ϱ_s/ϱ be written in terms of a phenomenological condensate wavefunction $\psi(r)$ as $\varrho_s(r)/\varrho = |\psi(r)|^2$ and that the free energy difference ΔF between the superconducting and normal states at temperature T be given by

$$\Delta F = \int \left\{ \frac{\hbar^2}{2\bar{m}} \left| \left(\nabla + \frac{\bar{e}}{c} A(r)\right) \psi(r) \right|^2 - a(T)|\psi(r)|^2 + \frac{b(T)}{2}|\psi(r)|^4 \right\} d^3r \tag{3}$$

where $\bar{e}$, $\bar{m}$, a and b are phenomenological constants, with $a(T_c) = 0$.

They applied this approach to the calculation of boundary energies between normal and superconducting phases and to other problems.

As John Bardeen will discuss, a significant step in understanding which forces cause the condensation into the superfluid came with the experimental discovery of the isotope effect by E. Maxwell and, independently, by Reynolds, et al. (6). Their work indicated that superconductivity arises from the interaction of electrons with lattice vibrations, or phonons. Quite independently, Herbert Fröhlich (7) developed a theory based on electron-phonon interactions which yielded the isotope effect but failed to predict other superconducting properties. A somewhat similar approach by Bardeen (8) stimulated by the isotope effect experiments also ran into difficulties. N. Bohr, W. Heisenberg and other distinguished theorists had continuing interest in the general problem, but met with similar difficulties.

An important concept was introduced by A. B. Pippard (9) in 1953. On the basis of a broad range of experimental facts he concluded that a coherence length ξ is associated with the superconducting state such that a perturbation of the superconductor at a point necessarily influences the superfluid within a distance ξ of that point. For pure metals, $\xi \sim 10^{-4}$ cm. for $T \ll T_c$. He gener-

alized the London equation (3) to a non-local form and accounted for the fact that the experimental value of the penetration depth is several times larger than the London value. Subsequently, Bardeen (10) showed that Pippard's non-local relation would likely follow from an energy gap model.

A major problem in constructing a first principles theory was the fact that the physically important condensation energy ΔF amounts typically to only 10^{-8} electron volts (e.V.) per electron, while the uncertainty in calculating the total energy of the electron-phonon system in even the normal state amounted to of order 1 e.V. per electron. Clearly, one had to isolate those correlations peculiar to the superconducting phase and treat them accurately, the remaining large effects presumably being the same in the two phases and therefore cancelling. Landau's theory of a Fermi liquid (11), developed to account for the properties of liquid He^3, formed a good starting point for such a scheme. Landau argued that as long as the interactions between the particles (He^3 atoms in his case, electrons in our case) do not lead to discontinuous changes in the microscopic properties of the system, a "quasi-particle" description of the low energy excitations is legitimate; that is, excitations of the fully interacting normal phase are in one-to-one correspondence with the excitations of a non-interacting fermi gas. The effective mass m and the Fermi velocity v_F of the quasi-particles differ from their free electron values, but aside from a weak decay rate which vanishes for states at the Fermi surface there is no essential change. It is the residual interaction between the quasi-particles which is responsible for the special correlations characterizing superconductivity. The ground state wavefunction of the superconductor ψ_0 is then represented by a particular superposition of these normal state configurations, Φ_n.

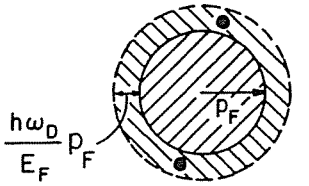
A clue to the nature of the states Φ_n entering strongly in ψ_0 is given by combining Pippard's coherence length ξ with Heisenberg's uncertainty principle

$$\Delta p \sim \hbar/\xi \sim 10^{-4} p_F \tag{4}$$

where p_F is the Fermi momentum. Thus, Ψ_0 is made up of states with quasi-particles (electrons) being excited above the normal ground state by a momentum of order Δp. Since electrons can only be excited to states which are initially empty, it is plausible that only electronic states within a momentum $10^{-4}\ p_F$ of the Fermi surface are involved significantly in the condensation, i.e., about 10^{-4} of the electrons are significantly affected. This view fits nicely with the fact that the condensation energy is observed to be of order $10^{-4} \varrho \cdot k_B T_c$. Thus, electrons within an energy $\sim v_F \Delta p \simeq k T_c$ of the Fermi surface have their energies lowered by of order kT_c in the condensation. In summary, the problem was how to account for the phase transition in which a condensation of electrons occurs in momentum space for electrons very near the Fermi surface. A proper theory should automatically account for the perfect conductivity and diamagnetism, as well as for the energy gap in the excitation spectrum.

II. The Pairing Concept

In 1955, stimulated by writing a review article on the status of the theory of superconductivity, John Bardeen decided to renew the attack on the problem.



He invited Leon Cooper, whose background was in elementary particle physics and who was at that time working with C. N. Yang at the Institute for Advanced Study to join in the effort starting in the fall of 1955. I had the good fortune to be a graduate student of Bardeen at that time, and, having finished my graduate preliminary work, I was delighted to accept an invitation to join them.

We focused on trying to understand how to construct a ground state Ψ_0 formed as a coherent superposition of normal state configurations Φ_n,

$$\Psi_0 = \sum_n a_n \Phi_n \tag{5}$$

such that the energy would be as low as possible. Since the energy is given in terms of the Hamiltonian H by

$$E_0 = (\Psi_0, H\psi_0) = \sum_{n,n'} a_{n'}{}^* a_n \, (\Phi_{n'}, H\Phi_n) \tag{6}$$

we attempted to make E_0 minimum by restricting the coefficients a_n so that only states which gave negative off-diagonal matrix elements would enter (6). In this case all terms would add in phase and E_0 would be low.

By studying the eigenvalue spectrum of a class of matrices with off-diagonal elements all of one sign (negative), Cooper discovered that frequently a single eigenvalue is split off from the bottom of the spectrum. He worked out the problem of two electrons interacting via an attractive potential-V above a quiescent Fermi sea, i.e., the electrons in the sea were not influenced by V and the extra pair was restricted to states within an energy $\hbar\omega_D$ above the Fermi surface, as illustrated in Fig. 2. As a consequence of the non-zero density of quasi-particle states $N(0)$ at the Fermi surface, he found the energy eigenvalue spectrum for two electrons having zero total momentum had a bound state split off from the continuum of scattering states, the binding energy being

$$E_B \cong \hbar\omega_D e^{-\frac{2}{N(0)V}} \tag{7}$$

if the matrix elements of the potential are constant equal to V in the region of interaction. This important result, published in 1956 (12), showed that, regardless of how weak the residual interaction between quasi-particles is, if the interaction is attractive the system is unstable with respect to the formation of bound pairs of electrons. Further, if E_B is taken to be of order $k_B T_c$, the uncertainty principle shows the average separation between electrons in the bound state is of order 10^{-4} cm.

While Cooper's result was highly suggestive, a major problem arose. If, as we discussed above, a fraction 10^{-4} of the electrons is significantly involved in the condensation, the average spacing between these condensed electrons

is roughly 10^{-6} cm. Therefore, within the volume occupied by the bound state of a given pair, the centers of approximately $(10^{-4}/10^{-6})^3 \cong 10^6$ other pairs will be found, on the average. Thus, rather than a picture of a dilute gas of strongly bound pairs, quite the opposite picture is true. The pairs overlap so strongly in space that the mechanism of condensation would appear to be destroyed due to the numerous pair-pair collisions interrupting the binding process of a given pair.

Returning to the variational approach, we noted that the matrix elements $(\Phi_{n'}, H\Phi_n)$ in (6) alternate randomly in sign as one randomly varies n and n' over the normal state configurations. Clearly this cannot be corrected to obtain a low value of E_0 by adjusting the sign of the a_n's since there are N^2 matrix elements to be corrected with only N parameters a_n. We noticed that if the sum in (6) is restricted to include only configurations in which, if any quasi-particle state, say k, s, is occupied ($s = \uparrow$ or $\downarrow$ is the spin index), its "mate" state $\bar{k}$, $\bar{s}$ is also occupied, then the matrix elements of H between such states would have a unique sign and a coherent lowering of the energy would be obtained. This correlated occupancy of pairs of states in momentum space is consonant with London's concept of a condensation in momentum.

In choosing the state $\bar{k}$, $\bar{s}$ to be paired with a given state k, s, it is important to note that in a perfect crystal lattice, the interaction between quasi-particles conserves total (crystal) momentum. Thus, as a given pair of quasi-particles interact, their center of mass momentum is conserved. To obtain the largest number of non-zero matrix elements, and hence the lowest energy, one must choose the total momentum of each pair to be the same, that is

$$k+\bar{k} = q. \tag{8}$$

States with $q \neq 0$ represent states with net current flow. The lowest energy state is for $q = 0$, that is, the pairing is such that if any state $k\uparrow$ is occupied in an admissible Φn, so is $-k\downarrow$ occupied. The choice of $\downarrow\uparrow$ spin pairing is not restrictive since it encompasses triplet and singlet paired states.

Through this reasoning, the problem was reduced to finding the ground state of the reduced Hamiltonian

$$H_{\text{red}} = \sum_{ks} \epsilon_k n_{ks} - \sum_{kk'} V_{k'k}\, b_{k'}^{+} b_k. \tag{9}$$

The first term in this equation gives the unperturbed energy of the quasi-particles forming the pairs, while the second term is the pairing interaction in which a pair of quasi-particles in $(k\uparrow, -k\downarrow)$ scatter to $(k'\uparrow, -k'\uparrow)$. The operators $b_k^{*} = c_{k\uparrow}^{*} c_{-k\downarrow}^{*}$, being a product of two fermion (quasi-particle) creation operators, do not satisfy Bose statistics, since $b_k^{+2} = 0$. This point is essential to the theory and leads to the energy gap being present not only for dissociating a pair but also for making a pair move with a total momentum different from the common momentum of the rest of the pairs. It is this feature which enforces long range order in the superfluid over macroscopic distances.

III. The Ground State

In constructing the ground state wavefunction, it seemed clear that the average occupancy of a pair state $(k\uparrow, -k\downarrow)$ should be unity for k far below the Fermi

surface and 0 for k far above it, the fall off occurring symmetrically about k_F over a range of momenta of order

$$\Delta k \sim \frac{1}{\xi} \sim 10^4 \text{ cm}^{-1}.$$

One could not use a trial Ψ_0 as one in which each pair state is definitely occupied or definitely empty since the pairs could not scatter and lower the energy in this case. Rather there had to be an amplitude, say v_k, that $(k\uparrow, -k\downarrow)$ is occupied in Ψ_0 and consequently an amplitude $u_k = \sqrt{1-v_k^2}$ that the pair state is empty. After we had made a number of unsuccessful attempts to construct a wavefunction sufficiently simple to allow calculations to be carried out, it occurred to me that since an enormous number ($\sim 10^{19}$) of pair states $(k'\uparrow, -k'\downarrow)$ are involved in scattering into and out of a given pair state $(k\uparrow, -k\downarrow)$, the "instantaneous" occupancy of this pair state should be essentially uncorrelated with the occupancy of the other pair states at that "instant". Rather, only the *average* occupancies of these pair states are related.

On this basis, I wrote down the trial ground state as a product of operators —one for each pair state—acting on the vacuum (state of no electrons),

$$\Psi_0 = \prod_k (u_k + v_k b_k^{+}) |0>, \tag{10}$$

where $u_k = \sqrt{1-v_k^2}$. Since the pair creation operators b_k^{+} commute for different k's, it is clear that Ψ_0 represents uncorrelated occupancy of the various pair states. I recall being quite concerned at the time that Ψ_0 was an admixture of states with different numbers of electrons, a wholly new concept to me, and as I later learned to others as well. Since by varying v_k the mean number of electrons varied, I used a Lagrange multiplier μ (the chemical potential) to make sure that the mean number of electrons (N_{op}) represented by Ψ_0 was the desired number N. Thus by minimizing

$$E_0 - \mu N = (\Psi_0, [H_{\text{red}} - \mu N_{\text{op}}]\Psi_0)$$

with respect to v_k, I found that v_k was given by

$$v_k^2 = \tfrac{1}{2}\left[1 - \frac{(\epsilon_k - \mu)}{E_k}\right] \tag{11}$$

where

$$E_k = \sqrt{(\epsilon_k - \mu)^2 + \Delta_k^2} \tag{12}$$

and the parameter Δ_k satisfied what is now called the energy gap equation:

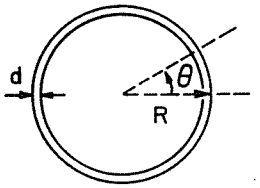
$$\Delta_k = -\sum V_{k'k} \frac{\Delta_{k'}}{2E_{k'}} \tag{13}$$

From this expression, it followed that for the simple model

$$V_{k'k} = \begin{cases} V, & |\epsilon_k - \mu| < \hbar\omega_D \text{ and } |\epsilon_{k'} - \mu| < \hbar\omega_D \\ 0, & \text{otherwise} \end{cases}$$

$$\Delta = \hbar\,\omega_D e^{-\frac{1}{N(0)V}} \tag{14}$$

İZMİR YÜKSEK TEKNOLOJİ ENSTİTÜSÜ
REKTÖRLÜĞÜ
Kütüphane ve Dokümantasyon Daire Bşk



and the condensation energy at zero temperature is

$$\Delta F = \tfrac{1}{2}N(0)\Delta^2 \qquad (15)$$

The idea occurred to me while I was in New York at the end of January, 1957, and I returned to Urbana a few days later where John Bardeen quickly recognized what he believed to be the essential validity of the scheme, much to my pleasure and amazement. Leon Cooper will pick up the story from here to describe our excitement in the weeks that followed, and our pleasure in unfolding the properties of the excited states.

IV. Quantum Phenomena on a Macroscopic Scale

Superconductors are remarkable in that they exhibit quantum effects on a broad range of scales. The persistence of current flow in a loop of wire many meters in diameter illustrates that the pairing condensation makes the superfluid wavefunction coherent over macroscopic distances. On the other hand, the absorption of short wavelength sound and light by a superconductor is sharply reduced from the normal state value, as Leon Cooper will discuss. I will concentrate on the large scale quantum effects here.

The stability of persistent currents is best understood by considering a circular loop of superconducting wire as shown in Fig. 3. For an ideal small diameter wire, one would use the eigenstates $e^{im\theta}$, $(m = 0,\pm1,\pm2, \ldots)$, of the angular momentum L_z about the symmetry axis to form the pairing. In the ground state no net current flows and one pairs $m\uparrow$ with $-m\downarrow$, instead of $k\uparrow$ with $-k\downarrow$ as in a bulk superconductor. In both cases, the paired states are time reversed conjugates, a general feature of the ground state. In a current carrying state, one pairs $(m+\nu)\uparrow$ with $(-m+\nu)\downarrow$, $(\nu = 0,\pm1,\pm2 \ldots)$, so that the total angular momentum of each pair is identical, $2\hbar\nu$. It is this commonality of the center of mass angular momentum of each pair which preserves the condensation energy and long range order even in states with current flow. Another set of flow states which interweave with these states is formed by pairing $(m+\nu)\uparrow$ with $(-m+\nu+1)\downarrow$, $(\nu = 0,\pm1,\pm2 \ldots)$, with the pair angular momentum being $(2\nu+1)\hbar$. The totality of states forms a set with all integer multiples n of $\hbar$ for allowed total angular momentum of pairs. Thus, even though the pairs greatly overlap in space, the system exhibits quantization effects as if the pairs were well defined.

There are two important consequences of the above discussion. First, the fact that the coherent condensate continues to exist in flow states shows that to scatter a pair out of the (rotating) condensate requires an increase of energy.

Crudely speaking, slowing down a given pair requires it ot give up its binding energy and hence this process will occur only as a fluctuation. These fluctuations average out to zero. The only way in which the flow can stop is if all pairs simultaneously change their pairing condition from, say, ν to $\nu-1$. In this process the system must fluctate to the normal state, at least in a section of the wire, in order to change the pairing. This requires an energy of order the condensation energy ΔF. A thermal fluctuation of this size is an exceedingly rare event and therefore the current persists.

The second striking consequence of the pair angular momentum quantization is that the magnetic flux Φ trapped within the loop is also quantized,

$$\Phi_n = n\cdot\frac{hc}{2e} \qquad (n = 0,\pm1,\pm2 \ldots). \qquad (16)$$

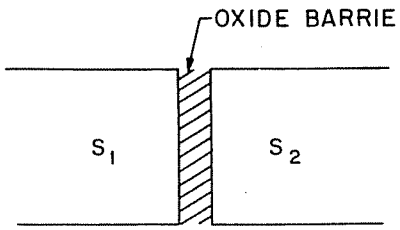
This result follows from the fact that if the wire diameter d is large compared to the penetration depth λ, the electric current in the center of the wire is essentially zero, so that the canonical angular momentum of a pair is

$$L_{\text{pair}} = \frac{2e}{c} r_{\text{pair}} \times A \qquad (17)$$

where r_{pair} is the center of mass coordinate of a pair and A is the magnetic vector potential. If one integrates L_{pair}, around the loop along a path in the center of the wire, the integral is nh, while the integral of the right hand side of (17) is $\frac{2e}{c}\Phi$.

A similar argument was given by F. London (4b) except that he considered only states in which the superfluid flows as a whole without a change in its internal strucutre, i.e., states analogous to the $(m+\nu)\uparrow, (-m+\nu)\downarrow$ set. He found $\Phi z = n\cdot hc/e$. The pairing $(m+\nu)\uparrow, (m+\nu+1)\downarrow$ cannot be obtained by adding ν to each state, yet this type of pairing gives an energy as low as the more conventional flow states and these states enter experimentally on the same basis as those considered by London. Experiments by Deaver and Fairbank (13), and independently by Doll and Näbauer (14) confirmed the flux quantization phenomenon and provided support for the pairing concept by showing that $2e$ rather than e enters the flux quantum. Following these experiments a clear discussion of flux quantization in the pairing scheme was given by Beyers and Yang (15).

The idea that electron pairs were somehow important in superconductivity has been considered for some time (16, 17). Since the superfluidity of liquid He^4 is qualitatively accounted for by Bose condensation, and since pairs of electrons behave in some respects as a boson, the idea is attractive. The essential point is that while a dilute gas of tightly bound pairs of electrons might behave like a Bose gas (18) this is not the case when the mean spacing between pairs is very small compared to the size of a given pair. In this case the inner structure of the pair, i.e., the fact that it is made of fermions, is essential; it is this which distinguishes the pairing condensation, with its energy gap for single pair translation as well as dissociation, from the spectrum of a Bose con-



densate, in which the low energy exictations are Bose-like rather than Fermi-like as occurs in acutal superconductors. As London emphasized, the condensation is an ordering in occupying momentum space, and not a space-like condensation of clusters which then undergo Bose condensation.

In 1960, Ivar Giaever (19) carried out pioneering experiments in which electrons in one superconductor (S_1) tunneled through a thin oxide layer ($\sim$ 20—30 Å) to a second superconductor (S_2) as shown in Fig. 4. Giaever's experiments were dramatic evidence of the energy gap for quasi-particle excitations. Subsequently, Brian Josephson made a highly significant contribution by showing theoretically that a superfluid current could flow between S_1 and S_2 with zero applied bias. Thus, the superfluid wavefunction is coherent not only in S_1 and S_2 separately, but throughout the entire system, S_1-0-S_2, under suitable circumstances. While the condensate amplitude is small in the oxide, it is sufficient to lock the phases of S_1 and S_2 together, as has been discussed in detail by Josephson (20) and by P. W. Anderson (21).

To understand the meaning of phase in this context, it is useful to go back to the ground state wavefunction Ψ_0, (10). Suppose we write the parameter v_k as $|v_k|$ exp $i\varphi$ and choose u_k to be real. If we expand out the k-product in Ψ_0, we note that the terms containing N pairs will have a phase factor exp (i $N\varphi$), that is, each occupied pair state contributes a phase φ to Ψ_0. Let this wavefunction, say $\Psi_0^{(1)}$ represent S_1, and have phase φ_1. Similarly, let $\Psi_0^{(2)}$ represent S_2 and have phase angle φ_2. If we write the state of the combined system as a product

$$\Psi_0^{(1,2)} = \Psi_0^{(1)}\,\Psi_0^{(2)} \tag{18}$$

then by expanding out the double product we see that the phase of that part of $\Psi_0^{(1,2)}$ which has N_1 pairs in S_1 and N_2 pairs in S_2 is $N_1\,\varphi_1+N_2\varphi_2$. For a truly isolated system, $2(N_1+N_2) = 2N$ is a fixed number of electrons; however N_1 and N_2 are not separately fixed and, as Josephson showed, the energy of the combined system is minimized when $\varphi_1 = \varphi_2$ due to tunneling of electrons between the superconductors. Furthermore, if $\varphi_1 = \varphi_2$, a current flows between S_1 and S_2

$$j = j_1 \sin(\varphi_1-\varphi_2) \tag{19}$$

If $\varphi_1-\varphi_2 = \varphi$ is constant in time, a constant current flows with no voltage applied across the junction. If a bias voltage is V applied between S_1 and S_2, then, according to quantum mechanics, the phase changes as

$$\frac{2eV}{\hbar} = \frac{d\varphi}{dt} \tag{20}$$

Hence a constant voltage applied across such a junction produces an alternating current of frequency

$$\nu = \frac{2eV}{\hbar} = 483\ \text{THz/V}. \tag{21}$$

These effects predicted by Josephson were observed experimentally in a series of beautiful experiments (22) by many scientists, which I cannot discuss in detail here for lack of time. I would mention, as an example, the work of Langenberg and his collaborators (23) at the University of Pennsylvania on the precision determination of the fundamental constant e/h using the frequency-voltage relation obeyed by the alternating Josephson supercurrent. These experiments have decreased the uncertainty in our experimental knowledge of this constant by several orders of magnitude and provide, in combination with other experiments, the most accurate available value of the Sommerfeld fine structure constant. They have resulted in the resolution of several discrepancies between theory and experiment in quantum electrodynamics and in the development of an "atomic" voltage standard which is now being used by the United States National Bureau of Standards to maintain the U.S. legal volt.

V. Conclusion

As I have attempted to sketch, the development of the theory of superconductivity was truly a collaborative effort, involving not only John Bardeen, Leon Cooper and myself, but also a host of outstanding scientists working over a period of half a century. As my colleagues will discuss, the theory opened up the field for many exciting new developments, both scientific and technological, many of which no doubt lie in the future. I feel highly honored to have played a role in this work and I deeply appreciate the honor you have bestowed on me in awarding us the Nobel prize.

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MICROSCOPIC QUANTUM INTERFERENCE EFFECTS IN THE THEORY OF SUPERCONDUCTIVITY

Nobel Lecture, December 11, 1972

by

LEON N COOPER

Physics Department, Brown University, Providence, Rhode Island

It is an honor and a pleasure to speak to you today about the theory of superconductivity. In a short lecture one can no more than touch on the long history of experimental and theoretical work on this subject before 1957. Nor can one hope to give an adequate account of how our understanding of superconductivity has evolved since that time. The theory (1) we presented in 1957, applied to uniform materials in the weak coupling limit so defining an ideal superconductor, has been extended in almost every imaginable direction. To these developments so many authors have contributed (2) that we can make no pretense of doing them justice. I will confine myself here to an outline of some of the main features of our 1957 theory, an indication of directions taken since and a discussion of quantum interference effects due to the singlet-spin pairing in superconductors which might be considered the microscopic analogue of the effects discussed by Professor Schrieffer.

NORMAL METAL

Although attempts to construct an electron theory of electrical conductivity date from the time of Drude and Lorentz, an understanding of normal metal conduction electrons in modern terms awaited the development of the quantum theory. Soon thereafter Sommerfeld and Bloch introduced what has evolved into the present description of the electron fluid. (3) There the conduction electrons of the normal metal are described by single particle wave functions. In the periodic potential produced by the fixed lattice and the conduction electrons themselves, according to Bloch's theorem, these are modulated plane waves:

$$\emptyset_K(r) = u_K(r)\, e^{ik\cdot r},$$

where $u_K(r)$ is a two component spinor with the lattice periodicity. We use K to designate simultaneously the wave vector k, and the spin state σ: $K \equiv k, \uparrow$; $-K \equiv -k, \downarrow$. The single particle Bloch functions satisfy a Schrödinger equation

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_0(r)\right]\emptyset_K = \varepsilon_K \emptyset_K$$

where $V_0(r)$ is the periodic potential and in general might be a linear operator to include exchange terms.

The Pauli exclusion principle requires that the many electron wave function be antisymmetric in all of its coordinates. As a result no two electrons can be

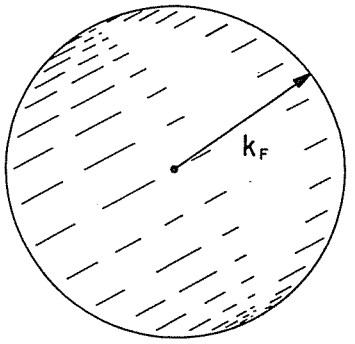


Fig. 1.
The normal ground state wavefunction, Φ_0, is a filled Fermi sphere for both spin directions.

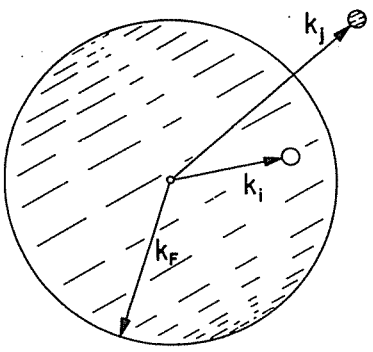


Fig. 2.
An excitation of the normal system.

in the same single particle Bloch state. The energy of the entire system is

$$W = \sum_{i=1}^{2N} \varepsilon_i$$

where ε_l is the Bloch energy of the i^{th} single electron state. The ground state of the system is obtained when the lowest N Bloch states of each spin are occupied by single electrons; this can be pictured in momentum space as the filling in of a Fermi sphere, Fig. 1. In the ground-state wave function there is no correlation between electrons of opposite spin and only a statistical correlation (through the general anti-symmetry requirement on the total wave function) of electrons of the same spin.

Single particle excitations are given by wave functions identical to the ground state except that one electron states $k_l < k_F$ are replaced by others $k_j < k_F$. This may be pictured in momentum space as opening vacancies below the Fermi surface and placing excited electrons above, Fig. 2. The energy difference between the ground state and the excited state with the particle excitation k_j and the hole excitation k_l is

$$\varepsilon_j - \varepsilon_l = \varepsilon_j - \varepsilon_F - (\varepsilon_l - \varepsilon_F) = \varepsilon_j - \varepsilon_l = |\varepsilon_j| + |\varepsilon_l|$$

where we define ε as the energy measured relative to the Fermi energy

$$\varepsilon_l = \varepsilon_l - \varepsilon_F.$$

When Coulomb, lattice-electron and other interactions, which have been omitted in constructing the independent particle Bloch model are taken into account, various modifications which have been discussed by Professor Schrieffer are introduced into both the ground state wave function and the excitations. These may be summarized as follows: The normal metal is described by a ground state Φ_0 and by an excitation spectrum which, in addition to the various collective excitations, consists of quasi-fermions which satisfy the usual anticommutation relations. It is defined by the sharpness of the Fermi surface, the finite density of excitations, and the continuous decline of the single particle excitation energy to zero as the Fermi surface is approached.

Electron Correlations that Produce Superconductivity

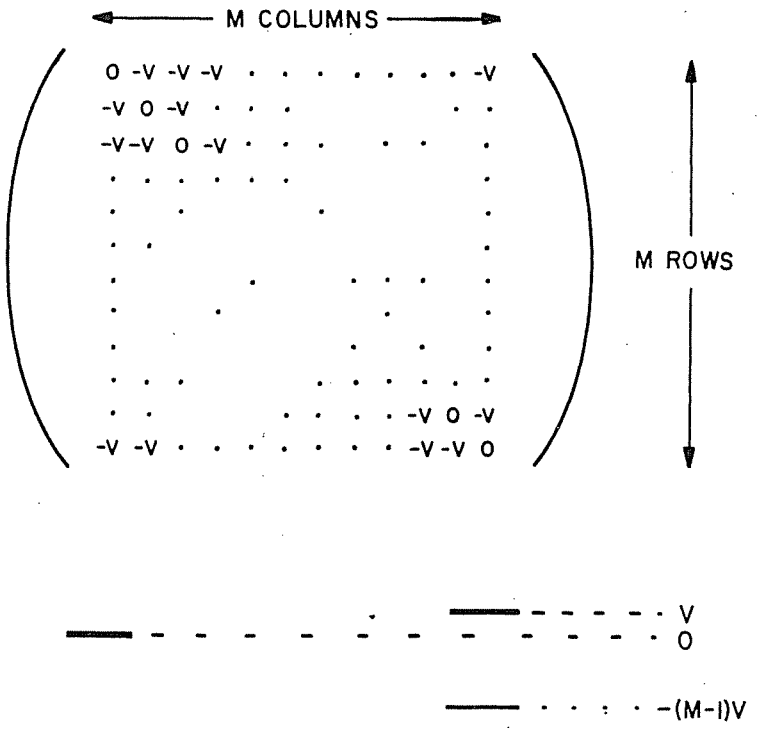
For a description of the superconducting phase we expect to include correlations that are not present in the normal metal. Professor Schrieffer has discussed the correlations introduced by an attractive electron-electron interaction and Professor Bardeen will discuss the role of the electron-phonon interaction in producing the electron-electron interaction which is responsible for superconductivity. It seems to be the case that any attractive interaction between the fermions in a many-fermion system can produce a superconducting-like state. This is believed at present to be the case in nuclei, in the interior of neutron stars and has possibly been observed (4) very recently in He^3. We will therefore develop the consequences of an attractive two-body interaction in a degenerate many-fermion system without enquiring further about its source.

The fundamental qualitative difference between the superconducting and normal ground state wave function is produced when the large degeneracy of the single particle electron levels in the normal state is removed. If we visualize the Hamiltonian matrix which results from an attractive two-body interaction in the basis of normal metal configurations, we find in this enormous matrix, sub-matrices in which all single-particle states except for one pair of electrons remain unchanged. These two electrons can scatter via the electron-electron interaction to all states of the same total momentum. We may envisage the pair wending its way (so to speak) over all states unoccupied by other electrons. [The electron-electron interaction in which we are interested is both weak and slowly varying over the Fermi surface. This and the fact that the energy involved in the transition into the superconducting state is small leads us to guess that only single particle excitations in a small shell near the Fermi surface play a role. It turns out, further, that due to exchange terms in the electron-electron matrix element, the effective interaction in metals between electrons of singlet spin is much stronger than that between electrons of triplet spin—thus our preoccupation with singlet spin correlations near the Fermi surface.] Since every such state is connected to every other, if the interaction is attractive and does not vary rapidly, we are presented with submatrices of the entire Hamiltonian of the form shown in Fig. 3. For purposes of illustration we have set all off diagonal matrix elements equal to the constant $-V$ and the diagonal terms equal to zero (the single particle excitation energy at the Fermi surface) as though all the initial electron levels were completely degenerate. Needless to say, these simplifications are not essential to the qualitative result.

Diagonalizing this matrix results in an energy level structure with $M-1$ levels raised in energy to $E = +V$ while one level (which is a superposition of all of the original levels and quite different in character) is lowered in energy to

$$E = -(M-1)V.$$

Since M, the number of unoccupied levels, is proportional to the volume of the container while V, the scattering matrix element, is proportional to 1/volume, the product is independent of the volume. Thus the removal of



For V = 0, M levels at E = 0

For V > 0, M −1 levels at E=V and one level at E=−(M−1) V

Fig. 3.

the degeneracy produces a single level separated from the others by a volume independent energy gap.

To incorporate this into a solution of the full Hamiltonian, one must devise a technique by which all of the electrons pairs can scatter while obeying the exclusion principle. The wave function which accomplishes this has been discussed by Professor Schrieffer. Each pair gains an energy due to the removal of the degeneracy as above and one obtains the maximum correlation of the entire wave function if the pairs all have the same total momentum. This gives a coherence to the wave function in which for a combination of dynamical and statistical reasons there is a strong preference for momentum zero, singlet spin correlations, while for statistical reasons alone there is an equally strong preference that all of the correlations have the same total momentum.

In what follows I shall present an outline of our 1957 theory modified by introducing the quasi-particles of Bogoliubov and Valatin. (5) This leads to a formulation which is generally applicable to a wide range of calculations

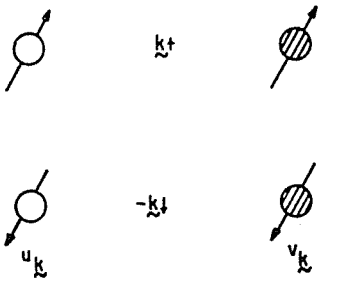


Fig. 4.
The ground state of the superconductor is a linear superposition of states in which pairs $(k\uparrow -k\downarrow)$ are occupied or unoccupied.

in a manner analogous to similar calculations in the theory of normal metals.

We limit the interactions to terms which scatter (and thus correlate) singlet zero-momentum pairs. To do this, it is convenient to introduce the pair operators:

$$b_k = c_{-K}c_K$$
$$b_k^* = c_K^* c_{-K}^*$$

and using these we extract from the full Hamiltonian the so-called reduced Hamiltonian

$$H_{\text{reduced}} = \sum_{k<k_f} 2|\varepsilon|\, b_k b_k^* + \sum_{k>k_f} 2\varepsilon b_k^* b_k + \sum_{kk'} V_{k'k} b_{k'}^* b_k$$

where $V_{k'k}$ is the scattering matrix element between the pair states k and k'.

Ground State

As Professor Schrieffer has explained, the ground state of the superconductor is a linear superposition of pair states in which the pairs $(k\uparrow, -k\downarrow)$ are occupied or unoccupied as indicated in Fig. 4. It can be decomposed into two disjoint vectors—one in which the pair state k is occupied, $\emptyset_k$ and one in which it is unoccupied, $\emptyset_{(k)}$:

$$\psi_0 = u_k \emptyset_{(k)} + v_k \emptyset_k.$$

The probability amplitude that the pair state k is (is not) occupied in the ground state is then $v_k(u_k)$. Normalization requires that $|u|^2+|v|^2 = 1$. The phase of the ground state wave function may be chosen so that with no loss o generality u_k is real. We can then write

$$u = (1-h)^{1/2}$$
$$v = h^{1/2}\, e^{i\varphi}$$

where

$$0 \leqslant h \leqslant 1.$$

A further decomposition of the ground state wave function of the superconductor in which the pair states k and k' are either occupied or unoccupied Fig. 5 is:

$$\psi_0 = u_k u_{k'} \emptyset_{(k),(k')} + u_k v_{k'} \emptyset_{(k),k'} + v_k u_{k'} \emptyset_{k,(k')} + v_k v_{k'} \emptyset_{k,k'}\ .$$

This is a Hartree-like approximation in the probability amplitudes for the occupation of pair states. It can be shown that for a fermion system the wave

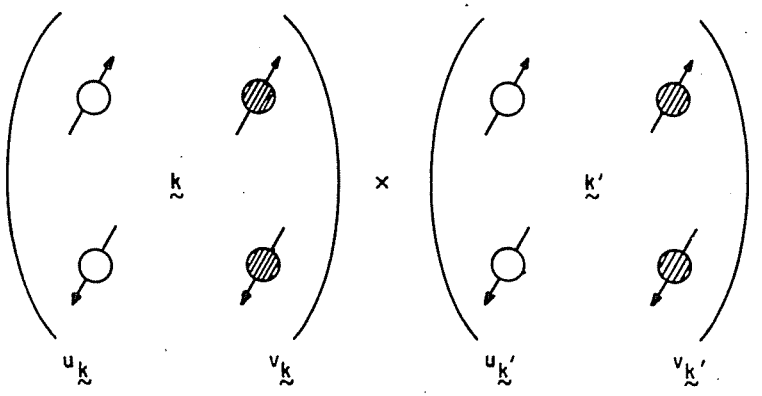


Fig. 5.
A decomposition of the ground state of the superconductor into states in which the pair states k and k' are either occupied or unoccupied.

function cannot have this property unless there are a variable number of particles. To terms of order $1/\mathcal{N}$, however, this decomposition is possible for a fixed number of particles; the errors introduced go to zero as the number of particles become infinite. (6)

The correlation energy, W_c, is the expectation value of H_{red} for the state ψ_0

$$W_c = (\psi_0, H_{red}\psi_0) = W_c\,[h,\varphi].$$

Setting the variation of W_c with respect to h and φ equal to zero in order to minimize the energy gives

$$h = 1/2\ (1-\varepsilon/E)$$
$$E = (\varepsilon^2+|\Delta|^2)^{1/2}$$

where

$$\Delta = |\Delta|e^{i\varphi}$$

satisfies the integral equation

$$\Delta(k) = -1/2 \sum_{k'} V_{kk'} \frac{\Delta(k')}{E(k')}.$$

If a non-zero solution of this integral equation exists, $W_c < 0$ and the "normal" Fermi sea is unstable under the formation of correlated pairs.

In the wave function that results there are strong correlations between pairs of electrons with opposite spin and zero total momentum. These correlations are built from normal excitations near the Fermi surface and extend over spatial distances typically of the order of 10^{-4} cm. They can be constructed due to the large wave numbers available because of the exclusion principle. Thus with a small additional expenditure of kinetic energy there can be a greater gain in the potential energy term. Professor Schrieffer has discussed some of the properties of this state and the condensation energy associated with it.

Single-Particle Excitations

In considering the excited states of the superconductor it is useful, as for the

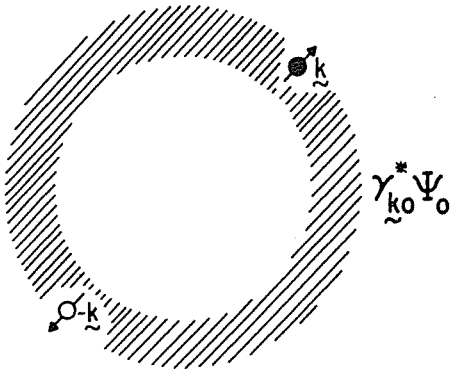


Fig. 6.
A single par icle excitation of the superconduc or in one-to-one correspondenc with an excitation of the normal fermion system.

normal metal, to make a distinction between single-particle and collective excitations; it is the single-particle excitation spectrum whose alteration is responsible for superfluid properties. For the superconductor excited (quasi-particle) states can be defined in one-to-one correspondence with the excitations of the normal metal. One finds, for example, that the expectation value of H_{red} for the excitation Fig. 6 is given by

$$E_k = \sqrt{\varepsilon_k^2 + |\Delta|^2}.$$

In contrast to the normal system, for the superconductor even as ε goes to zero E remains larger than zero, its lowest possible value being $E = |\Delta|$. One can therefore produce single particle excitations from the superconducting ground state only with the expenditure of a small but finite amount of energy. This is called the energy gap; its existence severely inhibits single particle processes and is in general responsible for the superfluid behavior of the electron gas. [In a gapless superconductor it is the finite value of $\Delta(r)$, the order parameter, rather than the energy gap as such that becomes responsible for the superfluid properties.] In the ideal superconductor, the energy gap appears because not a single pair can be broken nor can a single element of phase space be removed without a finite expenditure of energy. If a single pair is broken, one loses its correlation energy; if one removes an element of phase space from the system, the number of possible transitions of all the pairs is reduced resulting in both cases in an increase in the energy which does not go to zero as the volume of the system increases.

The ground state of the superconductor and the excitation spectrum described above can conveniently be treated by introducing a linear combination of c^* and c, the creation and annihilation operators of normal fermions. This is the transformation of Bogoliubov and Valatin (5):

$$\gamma^*_{k0} = u_k c^*_K - v_k c_{-K}$$
$$\gamma^*_{k1} = v_k c_K + u_k c^*_{-K}$$

It follows that

$$\gamma_{ki}\,\psi_0 = 0$$

so that the γ_{ki} play the role of annihilation operators, while the $\gamma^{\dagger}_{ki}$ create excitations

$$\gamma^{\dagger}_{ki} \cdots \gamma^{\dagger}_{mj} \psi_0 = \psi_{ki, \cdots mj}.$$

The γ operators satisfy Fermi anti-commutation relations so that with them we obtain a complete orthonormal set of excitations in one-to-one correspondence with the excitations of the normal metal.

We can sketch the following picture. In the ground state of the superconductor all the electrons are in singlet-pair correlated states of zero total momentum. In an m electron excited state the excited electrons are in "quasi-particle" states, very similar to the normal excitations and not strongly correlated with any of the other electrons. In the background, so to speak, the other electrons are still correlated much as they were in the ground state. The excited electrons behave in a manner similar to normal electrons; they can be easily scattered or excited further. But the background electrons—those which remain correlated—retain their special behavior; they are difficult to scatter or to excite.

Thus, one can identify two almost independent fluids. The correlated portion of the wave function shows the resistance to change and the very small specific heat characteristic of the superfluid, while the excitations behave very much like normal electrons, displaying an almost normal specific heat and resistance. When a steady electric field is applied to the metal, the superfluid electrons short out the normal ones, but with higher frequency fields the resistive properties of the excited electrons can be observed. [7]

Thermodynamic Properties, the Ideal Superconductor

We can obtain the thermodynamic properties of the superconductor using the ground state and excitation spectrum just described. The free energy of the system is given by

$$F[h, \varphi, f] = W_c(T) - TS,$$

where T is the absolute temperature and S is the entropy; f is the superconducting Fermi function which gives the probability of single-particle excitations. The entropy of the system comes entirely from the excitations as the correlated portion of the wave function is non-degenerate. The free energy becomes a function of $f(\boldsymbol{k})$ and $h(\boldsymbol{k})$, where $f(\boldsymbol{k})$ is the probability that the state $\boldsymbol{k}$ is occupied by an excitation or a quasi-particle, and $h(\boldsymbol{k})$ is the relative probability that the state $\boldsymbol{k}$ is occupied by a pair given that is not occupied by a quasi-particle. Thus some states are occupied by quasi-particles and the unoccupied phase space is available for the formation of the coherent background of the remaining electrons. Since a portion of phase space is occupied by excitations at finite temperatures, making it unavailable for the transitions of bound pairs, the correlation energy is a function of the temperature, $W_c(T)$. As T increases, $W_c(T)$ and at the same time Δ decrease until the critical temperature is reached and the system reverts to the normal phase.

Since the excitations of the superconductor are independent and in a one-to-one correspondence with those of the normal metal, the entropy of an

excited configuration is given by an expression identical with that for the normal metal except that the Fermi function, $f(\boldsymbol{k})$, refers to quasi-particle excitations. The correlation energy at finite temperature is given by an expression similar to that at $T = 0$ with the available phase space modified by the occupation functions $f(\boldsymbol{k})$. Setting the variation of F with respect to h, φ, and f equal to zero gives:

$$h = 1/2\ (1 - \varepsilon/E)$$
$$E = \sqrt{\varepsilon^2 + |\Delta|^2}$$

and

$$f = \frac{1}{1 + \exp(E/k_B T)}$$

where

$$\Delta = |\Delta| e^{i\varphi}$$

is now temperature-dependent and satisfies the fundamental integral equation of the theory

$$\Delta_k(T) = -1/2 \sum_{kk'} V_{kk'} \frac{\Delta_{k'}(T)}{E_{k'}(T)} \tanh\left(\frac{E_{k'}(T)}{2k_B T}\right).$$

The form of these equations is the same as that at $T = 0$ except that the energy gap varies with the temperature. The equation for the energy gap can be satisfied with non-zero values of Δ only in a restricted temperature range. The upper bound of this temperature range is defined as T_c, the critical temperature. For $T < T_c$, singlet spin zero momentum electrons are strongly correlated, there is an energy gap associated with exciting electrons from the correlated part of the wave function and $E(\boldsymbol{k})$ is bounded below by $|\Delta|$. In this region the system has properties qualitatively different from the normal metal.

In the region $T > T_c$, $\Delta = 0$ and we have in every respect the normal solution. In particular f, the distribution function for excitations, becomes just the Fermi function for excited electrons $k > k_F$, and for holes $k < k_F$

$$f = \frac{1}{1 + \exp(|\varepsilon|/k_B T)}.$$

If we make our simplifications of 1957, (defining in this way an 'ideal' superconductor)

$$V_{k'k} = -V \qquad |\varepsilon| < \hbar\omega_{av}$$
$$= 0 \qquad \text{otherwise}$$

and replace the energy dependent density of states by its value at the Fermi surface, $N(0)$, the integral equation for Δ becomes

$$1 = N(0)\, V \int_0^{\hbar\omega_{av}} \frac{d\varepsilon}{\sqrt{\varepsilon^2 + |\Delta|^2}} \tanh\left(\frac{\sqrt{\varepsilon^2 + |\Delta|^2}}{2k_B T}\right).$$

The solution of this equation, Fig. 7, gives $\Delta(T)$ and with this f and h. We can then calculate the free energy of the superconducting state and obtain the thermodynamic properties of the system.

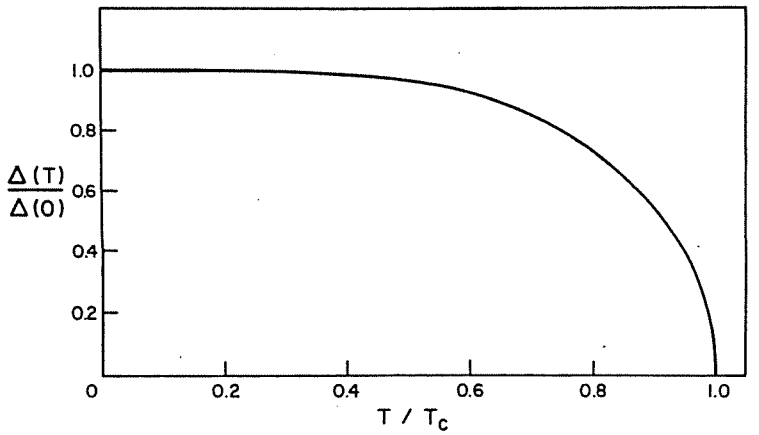


Fig. 7.
Variation of the energy gap with temperature for the ideal superconductor.

In particular one finds that at T_c (in the absence of a magnetic field) there is a second-order transition (no latent heat: $W_c = 0$ at T_c) and a discontinuity in the specific heat. At very low temperatures the specific heat goes to zero exponentially. For this ideal superconductor one also obtains a law of corresponding states in which the ratio

$$\frac{\gamma T_c^2}{H_0^2} = 0.170,$$

where

$$\gamma = 2/3\pi^2 N(0) k_B^2.$$

The experimental data scatter about the number 0.170. The ratio of Δ to $k_B T_c$ is given as a universal constant

$$\Delta/k_B T_c = 1.75.$$

There are no arbitrary parameters in the idealized theory. In the region of empirical interest all thermodynamic properties are determined by the quantities γ and $\hbar\omega_{av}\, e^{-1/N(0)V}$. The first, γ, is found by observation of the normal specific heat, while the second is found from the critical temperature, given by

$$k_B T_c = 1.14\, \hbar\omega_{av} e^{-1/N(0)V}.$$

At the absolute zero

$$\Delta = \hbar\omega_{av}/\sinh\left(\frac{1}{N(0)V}\right).$$

Further, defining a weak coupling limit [$N(0)V \ll 1$] which is one region of interest empirically, we obtain

$$\Delta \simeq 2\hbar\omega_{av} e^{-1/N(0)V}.$$

The energy difference between the normal and superconducting states becomes (again in the weak coupling limit)

$$W_s - W_n = W_c = -2N(0)(\hbar\omega_{av})^2\, e^{-2/N(0)V}.$$

The dependence of the correlation energy on $(\hbar\omega_{av})^2$ gives the isotope effect, while the exponential factor reduces the correlation energy from the dimensionally expected $N(0)(\hbar\omega_{av})^2$ to the much smaller observed value. This, however, is more a demonstration that the isotope effect is consistent with our model rather than a consequence of it, as will be discussed further by Professor Bardeen.

The thermodynamic properties calculated for the ideal superconductor are in qualitative agreement with experiment for weakly coupled superconductors. Very detailed comparison between experiment and theory has been made by many authors. A summary of the recent status may be found in reference (2). When one considers that in the theory of the ideal superconductor the existence of an actual metal is no more than hinted at (We have in fact done all the calculations considering weakly interacting fermions in a container.) so that in principle (with appropriate modifications) the calculations apply to neutron stars as well as metals, we must regard detailed quantitative agreement as a gift from above. We should be content if there is a single metal for which such agreement exists. [Pure single crystals of tin or vanadium are possible candidates.]

To make comparison between theory and experiments on actual metals, a plethora of detailed considerations must be made. Professor Bardeen will discuss developments in the theory of the electron-phonon interaction and the resulting dependence of the electron-electron interaction and superconducting properties on the phonon spectrum and the range of the Coulomb repulsion. Crystal symmetry, Brillouin zone structure and the actual wave function (S, P or D states) of the conduction electrons all play a role in determining real metal behavior. There is a fundamental distinction between superconductors w ich always show a Meissner effect and those (type II) which allow magnetic field penetration in units of the flux quantum.

When one considers, in addition, specimens with impurities (magnetic and otherwise) superimposed films, small samples, and so on, one obtains a variety of situations, developed in the years since 1957 by many authors, whose richness and detail takes volumes to discuss. The theory of the ideal superconductor has so far allowed the addition of those extensions and modifications necessary to describe, in what must be considered remarkable detail, all of the experience actually encountered.

Microscopic Interference Effects

In its interaction with external perturbations the superconductor displays remarkable interference effects which result from the paired nature of the wave function and are not at all present in similar normal metal interactions. Neither would they be present in any ordinary two-fluid model. These "coherence effects" are in a sense manifestations of interference in spin and momentum space on a microscopic scale, analogous to the macroscopic quantum effects due to interference in ordinary space which Professor Schrieffer discussed. They depend on the behavior under time reversal of the perturbing fields. (8) It is intriguing to speculate that if one could somehow amplify them

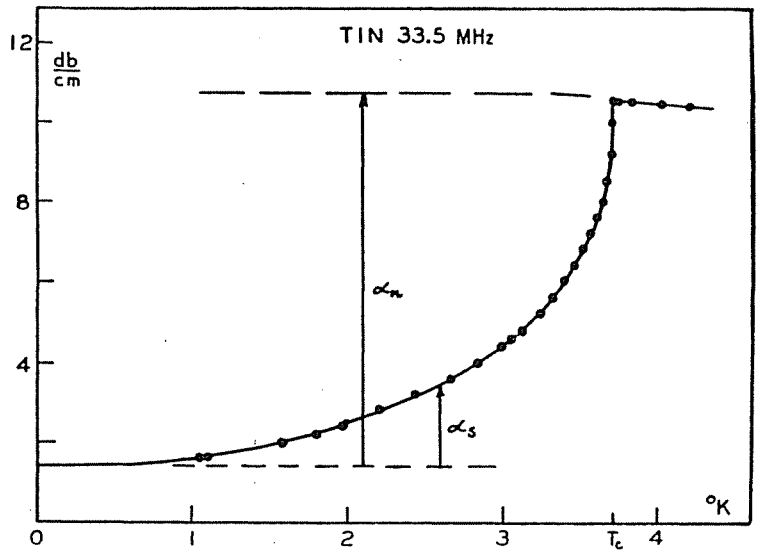


Fig. 8.
Ultrasonic attenuation as a function of temperature across the superconducting transition as measured by Morse and Bohm.

properly, the time reversal symmetry of a fundamental interaction might be tested. Further, if helium 3 does in fact display a phase transition analogous to the superconducting transition in metals as may be indicated by recent experiments (4) and this is a spin triplet state, the coherences effects would be greatly altered.

Near the transition temperature these coherence effects produce quite dramatic contrasts in the behavior of coefficients which measure interactions with the conduction electrons. Historically, the comparison with theory of the behavior of the relaxation rate of nuclear spins (9) and the attenuation of longitudinal ultrasonic waves in clean samples (10) as the temperature is decreased through T_c provided an early test of the detailed structure of the theory.

The attenuation of longitudinal acoustic waves due to their interaction with the conduction electrons in a metal undergoes a very rapid drop (10a) as the temperature drops below T_c. Since the scattering of phonons from "normal" electrons is responsible for most of the acoustic attenuation, a drop was to be expected; but the rapidity of the decrease measured by Morse and Bohm (10b) Fig. 8 was difficult to reconcile with estimates of the decrease in the normal electron component of a two-fluid model.

The rate of relaxation of nuclear spins was measured by Hebel and Slichter (9a) in zero magnetic field in superconducting aluminum from 0.94 K to 4.2 K just at the time of the development of our 1957 theory. Redfield and Anderson (9b) confirmed and extended their results. The dominant relaxation mechanism is provided by interaction with the conduction electrons so that one would expect, on the basis of a two-fluid model, that this rate should

decrease below the transition temperature due to the diminishing density of "normal" electrons. The experimental results however show just the reverse. The relaxation rate does not drop but increases by a factor of more than two just below the transition temperature. Fig 13. This observed increase in the nuclear spin relaxation rate and the very sharp drop in the acoustic attenuation coefficient as the temperature is decreased through T_c impose contradictory requirements on a conventional two-fluid model.

To illustrate how such effects come about in our theory, we consider the transition probability per unit time of a process involving electronic transitions from the excited state k to the state k' with the emission to or absorption of energy from the interacting field. What is to be calculated is the rate of transition between an initial state $|i>$ and a final state $|f>$ with the absorption or emission of the energy $\hbar\omega_{|k'-k|}$ (a phonon for example in the interaction of sound waves with the superconductor). All of this properly summed over final states and averaged with statistical factors over initial states may be written:

$$\omega = \frac{2\pi}{\hbar} \frac{\sum_{i,f} \exp(-W_i/k_B T) |<f|H_{\text{int}}|i>|^2 \delta(W_f - W_i)}{\sum_i \exp(-W_i/k_B T)}$$

We focus our attention on the matrix element $<f|H_{\text{int}}|i>$. This typically contains as one of its factors matrix elements between excited states of the superconductor of the operator

$$B = \sum_{K K'} B_{K'K} c^*_{K'} c_K$$

where $c^*_{K'}$ and c_K are the creation and annihilation operators for electrons in the states K' and K, and $B_{K'K}$ is the matrix element between the states K' and K of the configuration space operator $B(r)$

$$B_{K'K} = <K'|B(r)|K>.$$

The operator B is the electronic part of the matrix element between the full final and initial state

$$<f|H_{\text{int}}|i> = m_{fi} <f|B|i>.$$

In the normal system scattering from single-particle electron states K to K' is independent of scattering from $-K'$ to $-K$. But the superconducting states are linear superpositions of $(K, -K)$ occupied and unoccupied. Because of this states with excitations $k\uparrow$ and $k'\uparrow$ are connected not only by $c^*_{k'\uparrow} c_{k\uparrow}$ but also by $c^*_{-k\downarrow} c_{-k'\downarrow}$; if the state $|f>$ contains the single-particle excitation $k'\uparrow$ while the state $|i>$ contains $k\uparrow$, as a result of the superposition of occupied and unoccupied pair states in the coherent part of the wave function, these are connected not only by $B_{K'K} c^*_{K'} c_K$ but also by $B_{-K-K'} c^*_{-K} c_{-K'}$.

For operators which do not flip spins we therefore write:

$$B = \sum_{k k'} (B_{K'K} c^*_{K'} c_K + B_{-K-K'} c^*_{-K} c_{-K'}).$$

Many of the operators, B, we encounter (e.g., the electric current, or the charge density operator) have a well-defined behavior under the operation of time reversal so that

$$B_{K'K} = \pm B_{-K-K'} \equiv B_{k'k}.$$

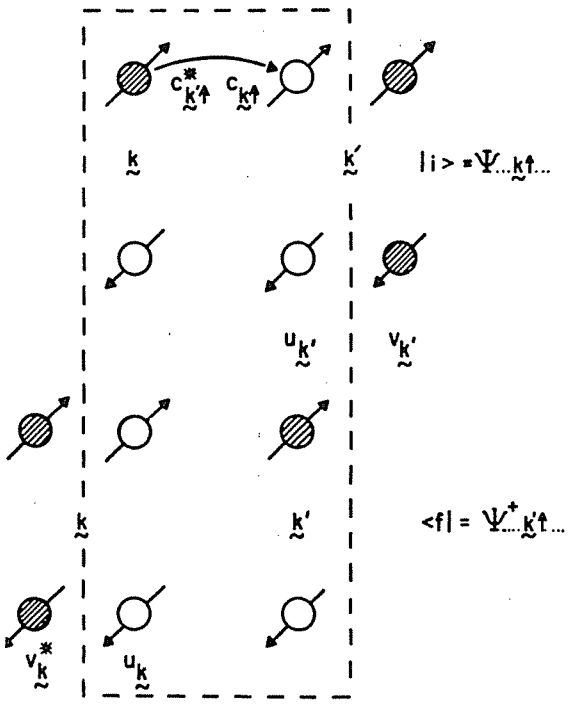


Fig. 9.
The two states $|i>$ and $<f|$ shown are connected by $c^*_{k'\uparrow}c_{k\uparrow}$ with the amplitude $u_{k'}u_k$.

Then B becomes

$$B = \sum_{kk'} B_{k'k}\,(c^*_{k'\uparrow}c_{k\uparrow} \pm c^*_{-k\downarrow}c_{-k'\downarrow})$$

where the upper (lower) sign results for operators even (odd) under time reversal.

The matrix element of B between the initial state, $\psi \ldots {}_{k\uparrow} \ldots$, and the final state $\psi \ldots {}_{k'\uparrow} \ldots$ contains contributions from $c^*_{k'\uparrow}c_{k\uparrow}$ Fig. 9 and unexpectedly from $c^*_{-k\downarrow}c_{-k'\downarrow}$ Fig. 10. As a result the matrix element squared $|<f|B|i>|^2$ contains terms of the form

$$|B_{k'k}|^2\ |(u_{k'}u_k \mp v_k v^*_k)|^2,$$

where the sign is determined by the behavior of B under time reversal:

upper sign B even under time reversal
lower sign B odd under time reversal.

Applied to processes involving the emission or absorption of boson quanta such as phonons or photons, the squared matrix element above is averaged with the appropriate statistical factors over initial and summed over final states; substracting emission from absorption probability per unit time, we obtain typically

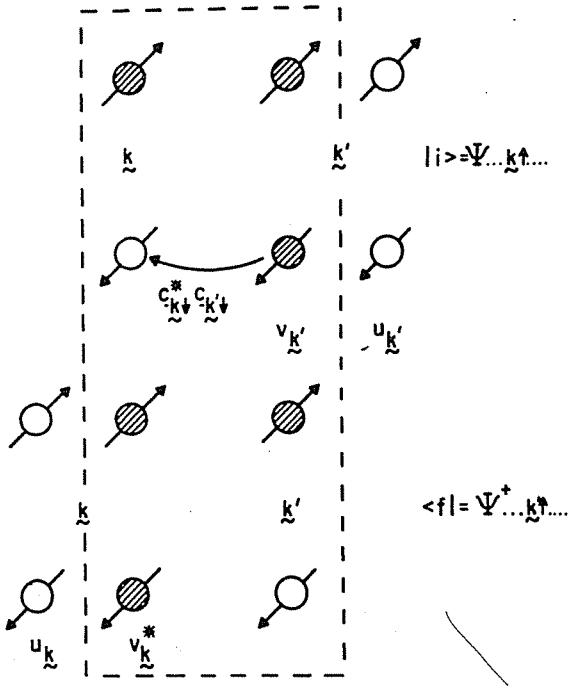


Fig. 10.
The two states $|i>$ and $<f|$ are also connected by $c^*_{k\downarrow}c_{-k'\downarrow}$ with the amplitude $-v_{k'}v^*_k$.

$$\alpha = \frac{4\pi}{\hbar}|m|^2 \sum_{kk'} |(u_{k'}u_k \mp v_{k'}v^*_k)|^2\ (f_{k'} - f_k)\ \delta(E_{k'} - E_k - \hbar\omega_{|k-k'|})$$

where f_k is the occupation probability in the superconductor for the excitation $k\uparrow$ or $k\downarrow$. [In the expression above we have considered only quasiparticle or quasi-hole scattering processes (not including processes in which a pair of excitations is created or annihilated from the coherent part of the wave function) since $\hbar\omega_{|k'-k|} < \Delta$, is the usual region of interest for the ultrasonic attenuation and nuclear spin relaxation we shall contrast.]

For the ideal superconductor, there is isotropy around the Fermi surface and symmetry between particles and holes; therefore sums of the form $\sum_k$ can be converted to integrals over the superconducting excitation energy, E:

$$\sum_k \to 2\mathcal{N}(0) \int_\Delta^\infty \frac{E}{\sqrt{E^2 - \Delta^2}}\,dE$$

where $\mathcal{N}(0)\dfrac{E}{\sqrt{E^2-\Delta^2}} = \mathcal{N}(0)\dfrac{E}{\varepsilon}$ is the density of excitations in the superconductor, Fig. 11.

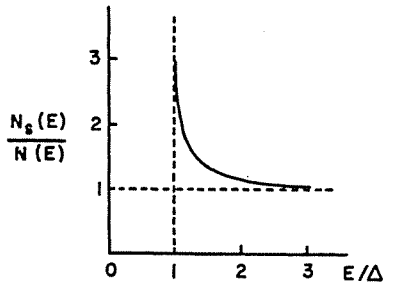


Fig. 11.
Ratio of superconducting to normal density of excitations as a function of E/Δ.

The appearance of this density of excitations is a surprise. Contrary to our intuitive expectations, the onset of superconductivity seems initially to enhance rather than diminish electronic transitions, as might be anticipated in a reasonable two-fluid model.

But the coherence factors $|(u'u \mp v'v^*)|^2$ are even more surprising; they behave in such a way as to sometimes completely negate the effect of the increased density of states. This can be seen using the expressions obtained above for u and v for the ideal superconductor to obtain

$$(u'u \mp v'v)^2 = \frac{1}{2}\left(1 + \frac{\varepsilon\varepsilon' \mp \Delta^2}{EE'}\right).$$

In the integration over $\boldsymbol{k}$ and $\boldsymbol{k}'$ the $\varepsilon\varepsilon'$ term vanishes. We thus define $(u'u \mp v'v)^2_s$; in usual limit where $\hbar\omega_{|\boldsymbol{k}'-\boldsymbol{k}|} \ll \Delta$, $\varepsilon \simeq \varepsilon'$ and $E \simeq E'$, this becomes

$$(u^2 - v^2)^2_s \to \frac{1}{2}\left(\frac{\varepsilon^2}{E^2}\right) \qquad \text{operators even under time reversal}$$

$$(u^2 + v^2)^2_s \to \frac{1}{2}\left(1 + \frac{E^2}{\Delta^2}\right) \qquad \text{operators odd under time reversal.}$$

For operators even under time reversal, therefore, the decrease of the coherence factors near $\varepsilon = 0$ just cancels the increase due to the density of states. For the operators odd under time reversal the effect of the increase of the density of states is not cancelled and should be observed as an increase in the rate of the corresponding process.

In general the interaction Hamiltonian for a field interacting with the superconductor (being basically an electromagnetic interaction) is invariant under the operation of time reversal. However, the operator B might be the electric current $\boldsymbol{j}(\boldsymbol{r})$ (for electromagnetic interactions) the electric charge density $\varrho(\boldsymbol{r})$ (for the electron-phonon interaction) or the z component of the electron spin operator, σ_z (for the nuclear spin relaxation interaction). Since under time-reversal

$\boldsymbol{j}(\boldsymbol{r}, t) \to -\boldsymbol{j}(\boldsymbol{r}, -t)$ (electromagnetic interaction)
$\varrho(\boldsymbol{r}, t) \to +\varrho(\boldsymbol{r}, -t)$ (electron-phonon interaction)
$\sigma_z(t) \to -\sigma_z(-t)$ (nuclear spin relaxation interaction)
these show strikingly different interference effects.

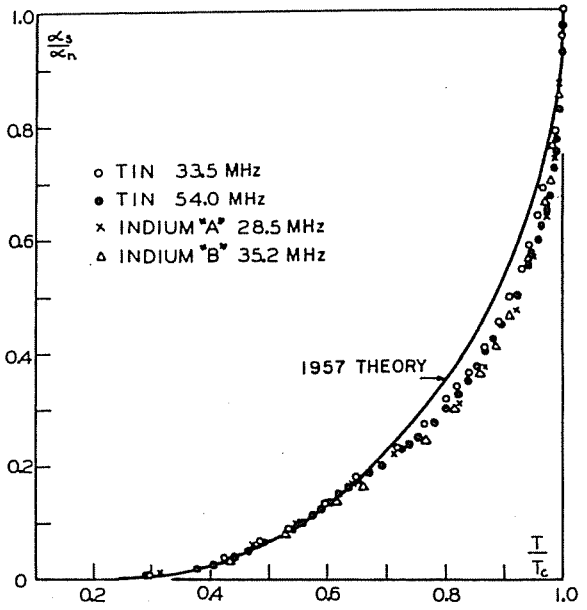


Fig. 12.
Comparison of observed ultrasonic attenuation with the ideal theory. The data are due to Morse and Bohm.

Ultrasonic attenuation in the ideal pure superconductor for $ql \gg 1$ (the product of the phonon wave number and the electron mean free path) depends in a fundamental way on the absorption and emission of phonons. Since the matrix elements have a very weak dependence on changes near the Fermi surface in occupation of states other than $\boldsymbol{k}$ or $\boldsymbol{k}'$ that occur in the normal to superconducting transition, calculations within the quasi-particle model can be compared in a very direct manner with similar calculations for the normal metal, as $B_{\boldsymbol{k}'\boldsymbol{k}}$ is the same in both states. The ratio of the attenuation in the normal and superconducting states becomes:

$$\frac{\alpha_s}{\alpha_n} = -4\int_{\Delta}^{\infty} dE (u^2 - v^2)^2_s \left(\frac{E}{\varepsilon}\right)^2 \frac{df(E)}{dE}.$$

Since $(u^2 - v^2)^2_s \to \frac{1}{2}\left(\frac{\varepsilon}{E}\right)^2$, the coherence factors cancel the density of states giving

$$\frac{\alpha_s}{\alpha_n} = 2f(\Delta(T)) = \frac{2}{1 + \exp\left(\frac{\Delta(T)}{k_B T}\right)}.$$

Morse and Bohm (10b) used this result to obtain a direct experimental determination of the variation of Δ with T. Comparison of their attenuation data with the theoretical curve is shown in Figure 12.

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REKTÖRLÜĞÜ
Kütüphane ve Dokümantasyon Daire Bşk.

In contrast the relaxation of nuclear spins which have been aligned in a magnetic field proceeds through their interaction with the magnetic moment of the conduction electrons. In an isotropic superconductor this can be shown to depend upon the z component of the electron spin operator

$$B_{K'K} = B(c^{\dagger}_{k'\uparrow}c_{k\uparrow} - c^{\dagger}_{-k\downarrow}c_{-k'\downarrow})$$

so that

$$B_{K'K} = -B_{-K-K'}.$$

This follows in general from the property of the spin operator under time reversal

$$\sigma_z(t) = -\sigma_z(-t).$$

The calculation of the nuclear spin relaxation rate proceeds in a manner not too different from that for ultrasonic attenuation resulting finally in a ratio of nuclear spin relaxation rates in superconducting and normal states in the same sample:

$$\frac{R_s}{R_n} = -4\int_{\Delta}^{\infty} dE(u^2+v^2)_s^2\left(\frac{E}{\varepsilon}\right)^2 \frac{df(E)}{dE}.$$

But $(u^2+v^2)_s^2$ does not go to zero at the lower limit so that the full effect of the increase in density of states at $E = \Delta$ is felt. Taken literally, in fact, this expression diverges logarithmically at the lower limit due to the infinite density of states. When the Zeeman energy difference between the spin up and spin down states is included, the integral is no longer divergent but the integrand is much too large. Hebel and Slichter, by putting in a broadening of levels phenomenologically, could produce agreement between theory and experiment. More recently Fibich (11) by including the effect of thermal phonons has obtained the agreement between theory and experiment shown in Fig. 13.

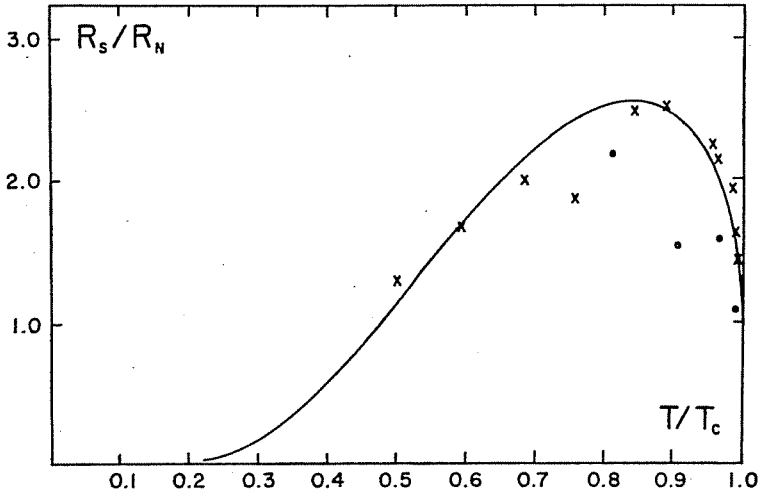

Fig. 13.
Comparison of observed nuclear spin relaxation rate with theory. The circles represent experimental data of Hebel and Slichter, the crosses data by Redfield and Anderson.

Interference effects manifest themselves in a similar manner in the interaction of electromagnetic radiation with the superconductor. Near T_c the absorption is dominated by quasi-particle scattering matrix elements of the type we have described. Near $T = 0$, the number of quasi-particle excitations goes to zero and the matrix elements that contribute are those in which quasi-particle pairs are created from ψ_0. For absorption these latter occur only when $\hbar\omega > 2\Delta$. For the linear response of the superconductor to a static magnetic field, the interference occurs in such a manner that the paramagnetic contribution goes to zero leaving the diamagnetic part which gives the Meissner effect.

The theory developed in 1957 and applied to the equilibrium properties of uniform materials in the weak coupling region has been extended in numerous directions by many authors. Professor Schrieffer has spoken of Josephson junctions and macroscopic quantum interference effects; Professor Bardeen will discuss the modifications of the theory when the electron-phonon interactions are strong. The treatment of ultrasonic attenuation, generalized to include situations in uniform superconductors in which $ql < 1$, gives a surprisingly similar result to that above. (12) There have been extensive developments using Green's function methods (13) appropriate for type II superconductors, materials with magnetic impurities and non-uniform materials or boundary regions where the order parameter is a function of the spatial coordinates. (14) With these methods formal problems of gauge invariance and/or current conservation have been resolved in a very elegant manner. (15) In addition, many calculations (16) of great complexity and detail for type II superconductors have treated ultrasonic attenuation, nuclear spin relaxation and other phenomena in the clean and dirty limits (few or large numbers of impurities). The results cited above are modified in various ways. For example, the average density of excitation levels is less sharply peaked at T_c in a type II superconductor; the coherence effects also change somewhat in these altered circumstances but nevertheless play an important role. Overall one can say that the theory has been amenable to these generalizations and that agreement with experiment is good.

It is now believed that the finite many-nucleon system that is the atomic nucleus enters a correlated state analogous to that of a superconductor. (17) Similar considerations have been applied to many-fermion systems as diverse as neutron stars, (18) liquid He^3, (19) and to elementary fermions. (20) In addition the idea of spontaneously broken symmetry of a degenerate vacuum has been applied widely in elementary particle theory and recently in the theory of weak interactions. (21) What the electron-phonon interaction has produced between electrons in metals may be produced by the van der Waals interaction between atoms in He^3, the nuclear interaction in nuclei and neutron stars, and the fundamental interactions in elementary fermions. Whatever the success of these attempts, for the theoretician the possible existence of this correlated paired state must in the future be considered for any degenerate many-fermion system where there is some kind of effective attraction between fermions for transitions near the Fermi surface.

In the past few weeks my colleagues and I have been asked many times: "What are the practical uses of your theory?" Although even a summary inspection of the proceedings of conferences on superconductivity and its applications would give an immediate sense of the experimental, theoretical and developmental work in this field as well as expectations, hopes and anticipations—from applications in heavy electrical machinery to measuring devices of extraordinary sensitivity and new elements with very rapid switching speeds for computers — I, personally, feel somewhat uneasy responding. The discovery of the phenomena and the development of the theory is a vast work to which many scientists have contributed. In addition there are numerous practical uses of the phenomena for which theory rightly should not take credit. A theory (though it may guide us in reaching them) does not produce the treasures the world holds. And the treasures themselves occasionally dazzle our attention; for we are not so wealthy that we may regard them as irrelevant.

But a theory is more. It is an ordering of experience that both makes experience meaningful and is a pleasure to regard in its own right. Henri Poincaré wrote (22):

> Le savant doit ordonner; on fait la science
> avec des faits comme une maison avec des
> pierres; mais une accumulation de faits
> n'est pas plus une science qu'un tas de
> pierres n'est une maison.

One can build from ordinary stone a humble house or the finest chateau. Either is constructed to enclose a space, to keep out the rain and the cold. They differ in the ambition and resources of their builder and the art by which he has achieved his end. A theory, built of ordinary materials, also may serve many a humble function. But when we enter and regard the relations in the space of ideas, we see columns of remarkable height and arches of daring breadth. They vault the fine structure constant, from the magnetic moment of the electron to the behavior of metallic junctions near the absolute zero; they span the distance from materials at the lowest temperatures to those in the interior of stars, from the properties of operators under time reversal to the behavior of attenuation coefficients just beyond the transition temperature.

I believe that I speak for my colleagues in theoretical science as well as myself when I say that our ultimate, our warmest pleasure in the midst of one of these incredible structures comes with the realization that what we have made is not only useful but is indeed a beautiful way to enclose a space.

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ELECTRON-PHONON INTERACTIONS AND SUPERCONDUCTIVITY

Nobel Lecture, December 11, 1972

By JOHN BARDEEN

Departments of Physics and of Electrical Engineering
University of Illinois

Urbana, Illinois

1
INTRODUCTION

Our present understanding of superconductivity has arisen from a close interplay of theory and experiment. It would have been very difficult to have arrived at the theory by purely deductive reasoning from the basic equations of quantum mechanics. Even if someone had done so, no one would have believed that such remarkable properties would really occur in nature. But, as you well know, that is not the way it happened, a great deal had been learned about the experimental properties of superconductors and phenomenological equations had been given to describe many aspects before the microscopic theory was developed. Some of these have been discussed by Schrieffer and by Cooper in their talks.

My first introduction to superconductivity came in the 1930's and I greatly profited from reading David Shoenberg's little book on superconductivity, [1] which gave an excellent summary of the experimental findings and of the phenomenological theories that had been developed. At that time it was known that superconductivity results from a phase change of the electronic structure and the Meissner effect showed that thermodynamics could be applied successfully to the superconductive equilibrium state. The two fluid Gorter—Casimir model was used to describe the thermal properties and the London brothers had given their famous phenomenological theory of the electrodynamic properties. Most impressive were Fritz London's speculations, given in 1935 at a meeting of the Royal Society in London, [2] that superconductivity is a quantum phenomenon on a macroscopic scale. He also gave what may be the first indication of an energy gap when he stated that "the electrons be coupled by some form of interaction in such a way that the lowest state may be separated by a finite interval from the excited ones." He strongly urged that, based on the Meissner effect, the diamagnetic aspects of superconductivity are the really basic property.

My first abortive attempt to construct a theory, [3] in 1940, was strongly influenced by London's ideas and the key idea was small energy gaps at the Fermi surface arising from small lattice displacements. However, this work was interrupted by several years of wartime research, and then after the war I joined the group at the Bell Telephone Laboratories where my work turned to semiconductors. It was not until 1950, as a result of the discovery of the

isotope effect, that I again began to become interested in superconductivity, and shortly after moved to the University of Illinois.

The year 1950 was notable in several respects for superconductivity theory. The experimental discovery of the isotope effect [4, 5] and the independent prediction of H. Fröhlich [6] that superconductivity arises from interaction between the electrons and phonons (the quanta of the lattice vibrations) gave the first clear indication of the directions along which a microscopic theory might be sought. Also in the same year appeared the phenomenological Ginzburg—Landau equations which give an excellent description of superconductivity near T_c in terms of a complex order parameter, as mentioned by Schrieffer in his talk. Finally, it was in 1950 that Fritz London's book [7] on superconductivity appeared. This book included very perceptive comments about the nature of the microscopic theory that have turned out to be remarkably accurate. He suggested that superconductivity requires "a kind of solidification or condensation of the average momentum distribution." He also predicted the phenomenon of flux quantization, which was not observed for another dozen years.

The field of superconductivity is a vast one with many ramifications. Even in a series of three talks, it is possible to touch on only a few highlights. In this talk, I thought that it might be interesting to trace the development of the role of electron-phonon interactions in superconductivity from its beginnings in 1950 up to the present day, both before and after the development of the microscopic theory in 1957. By concentrating on this one area, I hope to give some impression of the great progress that has been made in depth of understanding of the phenomena of superconductivity. Through developments by many people, [8] electron-phonon interactions have grown from a qualitative concept to such an extent that measurements on superconductors are now used to derive detailed quantitative information about the interaction and its energy dependence. Further, for many of the simpler metals and alloys, it is possible to derive the interaction from first principles and calculate the transition temperature and other superconducting properties.

The theoretical methods used make use of the methods of quantum field theory as adopted to the many-body problem, including Green's functions, Feynman diagrams, Dyson equations and renormalization concepts. Following Matsubara, temperature plays the role of an imaginary time. Even if you are not familiar with diagrammatic methods, I hope that you will be able to follow the physical arguments involved.

In 1950, diagrammatic methods were just being introduced into quantum field theory to account for the interaction of electrons with the field of photons. It was several years before they were developed with full power for application to the quantum statistical mechanics of many interacting particles. Following Matsubara, those prominent in the development of the theoretical methods include Kubo, Martin and Schwinger, and particularly the Soviet physicists, Migdal, Galitski, Abrikosov, Dzyaloshinski, and Gor'kov. The methods were first introduced to superconductivity theory by Gor'kov [9] and a little later in a somewhat different form by Kadanoff and Martin. [10] Problems of

superconductivity have provided many applications for the powerful Green's function methods of many-body theory and these applications have helped to further develop the theory.

Diagrammatic methods were first applied to discuss electron-phonon interactions in normal metals by Migdal [11] and his method was extended to superconductors by Eliashberg. [12] A similar approach was given by Nambu. [13] The theories are accurate to terms of order $(m/M)^{1/2}$, where m is the mass of the electron and M the mass of the ion, and so give quite accurate quantitative accounts of the properties of both normal metals and superconductors.

We will first give a brief discussion of the electron-phonon interactions as applied to superconductivity theory from 1950 to 1957, when the pairing theory was introduced, then discuss the Migdal theory as applied to normal metals, and finally discuss Eliashberg's extension to superconductors and subsequent developments. We will close by saying a few words about applications of the pairing theory to systems other than those involving electron-phonon interactions in metals.

2
Developments from 1950—1957

The isotope effect was discovered in the spring of 1950 by Reynolds, Serin, et al, [4] at Rutgers University and by E. Maxwell [5] at the U. S. National Bureau of Standards. Both groups measured the transition temperatures of separated mercury isotopes and found a positive result that could be interpreted as $T_c M^{1/2} \simeq$ constant, where M is the isotopic mass. If the mass of the ions is important, their motion and thus the lattice vibrations must be involved.

Independently, Fröhlich, [6] who was then spending the spring term at Purdue University, attempted to develop a theory of superconductivity based on the self-energy of the electrons in the field of phonons. He heard about the isotope effect in mid-May, shortly before he submitted his paper for publication and was delighted to find very strong experimental confirmation of his ideas. He used a Hamiltonian, now called the Fröhlich Hamiltonian, in which interactions between electrons and phonons are included but Coulomb interactions are omitted except as they can be included in the energies of the individual electrons and phonons. Fröhlich used a perturbation theory approach and found an instability of the Fermi surface if the electron-phonon interaction were sufficiently strong.

When I heard about the isotope effect in early May in a telephone call from Serin, I attempted to revive my earlier theory of energy gaps at the Fermi surface, with the gaps now arising from dynamic interactions with the phonons rather than from small static lattice displacements. [14] I used a variational method rather than a perturbation approach but the theory was also based on the electron self-energy in the field of phonons. While we were very hopeful at the time, it soon was found that both theories had grave difficulties, not easy to overcome. [15] It became evident that nearly all of the self-energy is included in the normal state and is little changed in the transition. A theory

involving a true many-body interaction between the electrons seemed to be required to account for superconductivity. Schafroth [16] showed that starting with the Fröhlich Hamiltonian, one cannot derive the Meissner effect in any order of perturbation theory. Migdal's theory, [11] supposedly correct to terms of order $(m/M)^{1/2}$, gave no gap or instability at the Fermi surface and no indication of superconductivity.

Of course Coulomb interactions really are present. The effective direct Coulomb interaction between electrons is shielded by the other electrons and the electrons also shield the ions involved in the vibrational motion. Pines and I derived an effective electron-electron interaction starting from a Hamiltonian in which phonon and Coulomb terms are included from the start. [17] As is the case for the Fröhlich Hamiltonian, the matrix element for scattering of a pair of electrons near the Fermi surface from exchange of virtual phonons is negative (attractive) if the energy difference between the electron states involved is less than the phonon energy. As discussed by Schrieffer, the attractive nature of the interaction was a key factor in the development of the microscopic theory. In addition to the phonon induced interaction, there is the repulsive screened Coulomb interaction, and the criterion for superconductivity is that the attractive phonon interaction dominate the Coulomb interaction for states near the Fermi surface. [18]

During the early 1950's there was increasing evidence for an energy gap at the Fermi surface. [19] Also very important was Pippard's proposed non-local modification [20] of the London electrodynamics which introduced a new length the coherence distance, ξ_o, into the theory. In 1955 I wrote a review article [17] on the theory of superconductivity for the Handbuch der Physik, which was published in 1956. The central theme of the article was the energy gap, and it was shown that Pippard's version of the electrodynamics would likely follow from an energy gap model. Also included was a review of electron-phonon interactions. It was pointed out that the evidence suggested that all phonons are involved in the transition, not just the long wave length phonons, and that their frequencies are changed very little in the normal-superconducting transition. Thus one should be able to use the effective interaction between electrons as a basis for a true many-body theory of the superconducting state. Schrieffer and Cooper described in their talks how we were eventually able to accomplish this goal.

3
Green's Function Method for Normal Metals

By use of Green's function methods, Migdal [11] derived a solution of Fröhlich's Hamiltonian, $H = H_{el} + H_{ph} + H_{el\text{-}ph}$, for normal metals valid for abritrarily strong coupling and which involves errors only of order $(m/M)^{1/2}$. The Green's functions are defined by thermal average of time ordered operators for the electrons and phonons, respectively

$$G = -i\langle T\psi(1)\psi^+(2)\rangle \tag{1a}$$

$$D = -i\langle T\phi(1)\phi^+(2)\rangle \tag{1b}$$

Here $\psi(r,t)$ is the wave field operator for electron quasi-particles and $\phi(r,t)$ for the phonons, the symbols 1 and 2 represent the space-time points (r_1,t_1) and (r_2,t_2) and the brackets represent thermal averages over an ensemble.

Fourier transforms of the Green's functions for $H_0 = H_{el}+H_{ph}$ for non-interacting electrons and phonons are

$$G_0(P) = \frac{1}{\omega_n - \varepsilon_0(k) + i\delta_k} \tag{2a}$$

$$D_0(Q) = \left\{\frac{1}{\nu_n - \omega_0(q) + i\delta} - \frac{1}{\nu_n + \omega_0(q) - i\delta}\right\}, \tag{2b}$$

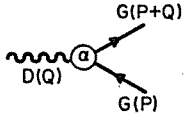
where $P = (k,\omega_n)$ and $Q = (q,\nu_n)$ are four vectors, $\varepsilon_0(k)$ is the bare electron quasiparticle energy referred to the Fermi surface, $\omega_0(q)$ the bare phonon frequency and ω_n and ν_n the Matsubara frequencies

$$\omega_n = (2n+1)\pi i k_B T; \quad \nu_n = 2n\pi i k_B T \tag{3}$$

for Fermi and Bose particles, respectively.

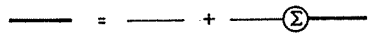
As a result of the electron-phonon interaction, $H_{el\text{-}ph}$, both electron and phonon energies are renormalized. The renormalized propagators, G and D, can be given by a sum over Feynman diagrams, each of which represents a term in the perturbation expansion. We shall use light lines to represent the bare propagators, G_0 and D_0, heavy lines for the renormalized propagators, G and D, straight lines for the electrons and curly lines for the phonons.

The electron-phonon interaction is described by the vertex



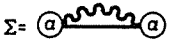
which represents scattering of an electron or hole by emission or absorption of a phonon or creation of an electron and hole by absorption of a phonon by an electron in the Fermi sea. Migdal showed that renormalization of the vertex represents only a small correction, of order $(m/M)^{1/2}$, a result in accord with the Born-Oppenheimer adiabatic-approximation. If terms of this order are neglected, the electron and phonon self-energy corrections are given by the lowest order diagrams provided that fully renormalized propagators are used in these diagrams.

The electron self-energy $\Sigma(P)$ in the Dyson equation:



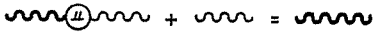
$$G(P) = G_0(P) + G_0(P)\Sigma(P)G(P) \tag{4}$$

is given by the diagram



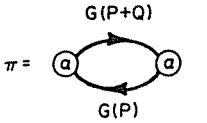
(5)

The phonon self-energy, $\pi(Q)$, defined by



(6)

is given by



Since to order $(m/M)^{1/2}$ one can use an unrenormalized vertex function $\alpha = \alpha_0$, the Dyson equations form a closed system such that both $\Sigma(P)$ and $\pi(Q)$ can be determined. The phonon self-energy, $\pi(Q)$, gives only a small renormalization of the phonon frequencies. As to the electrons, Migdal noted that we are interested in states k very close to k_F, so that to a close approximation $\Sigma(k,\omega)$ depends only on the frequency. For an isotropic system,

$$\Sigma(k,\omega) \simeq \Sigma(k_F,\omega) \equiv \Sigma(\omega) \tag{7}$$

The renormalized electron quasi-particle energy, ω_k, is then given by a root of

$$\varepsilon(k) = \omega_k = \varepsilon_0(k) + \Sigma(\omega_k) \tag{8}$$

In the thermal Green's function formalism, one may make an analytic continuation from the imaginary frequencies, ω_n, to the real ω axis to determine $\Sigma(\omega)$.

Although $\Sigma(\omega)$ is small compared with the Fermi energy, E_F, it changes rapidly with energy and so can affect the density of states at the Fermi surface and thus the low temperature electronic specific heat. The mass renormalization factor m^*/m, at the Fermi surface may be expressed in terms of a parameter λ:

$$m^*/m = Z(k_F) = 1+\lambda = (d\varepsilon_0/dk)_F/(d\varepsilon/dk)_F \tag{9}$$

In modern notation, the experession for λ is

$$\lambda = 2\int_0^\infty d\omega \frac{\alpha^2(\omega)F(\omega)}{\omega}, \tag{10}$$

where $F(\omega)$ is the density of phonon states in energy and $\alpha^2(\omega)$ is the square of the electron-phonon coupling constant averaged over polarization directions of the phonons. Note that λ is always positive so that the Fermi surface is stable if the lattice is stable. Values of λ for various metals range from about 0.5 to 1.5. The parameter λ corresponds roughly to the $N(0)V_{phonon}$ of the BCS theory.

4 Nambu-Eliashberg Theory for Superconductors

Migdal's theory has important consequences that have been verified experimentally for normal metals, but gave no clue as to the origin of superconductivity. Following the introduction of the BCS theory, Gor'kov showed that pairing could be introduced through the anomalous Green's function

$$F(P) = i < T\psi_\uparrow\psi_\downarrow >, \tag{11}$$

Nambu showed that both types of Green's functions can be conveniently included with use of a spinor notation

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$$\psi = \begin{pmatrix} \psi_\uparrow(r,t) \\ \psi_\downarrow^\dagger(r,t) \end{pmatrix} \tag{12}$$

where $\psi_\uparrow$ and $\psi_\downarrow$ are wave field operators for up and down spin electrons and a matrix Green's function with components

$$\check{G}_{\alpha\beta} = -\mathrm{i}\langle T\psi_\alpha\psi_\beta^\dagger\rangle \tag{13}$$

Thus G_{11} and G_{22} are the single particle Green's functions for up and down spin particles and $G_{12} = G_{21}^* = F(P)$ is the anomalous Green's function of Gor'kov.

There are two self-energies, Σ_1 and Σ_2, defined by the matrix

$$\check{\Sigma} = \begin{pmatrix} \Sigma_1 & \Sigma_2 \\ \Sigma_2 & \Sigma_1 \end{pmatrix} \tag{14}$$

Eliashberg noted that one can describe superconductors to the same accuracy as normal metals if one calculates the self-energies with the same diagrams that Migdal used, but with Nambu matrix propagators in place of the usual normal state Green's functions. The matrix equation for $\check{G}$ is

$$\check{G} = \check{G}_0 + \check{G}_0\check{\Sigma}\check{G} \tag{15}$$

The matrix equation for $\check{\Sigma}$ yields a pair of coupled integral equations for Σ_1 and Σ_2. Again Σ_1 and Σ_2 depend mainly on the frequency and are essentially independent of the momentum variables. Following Nambu, [13] one may define a renormalization factor $\mathcal{Z}_s(\omega)$ and a pair potential, $\Delta(\omega)$, for isotropic systems through the equations:

$$\omega\mathcal{Z}_s(\omega) = \omega + \Sigma_1(\omega) \tag{16}$$

$$\Delta(\omega) = \Sigma_2(\omega)/\mathcal{Z}(\omega). \tag{17}$$

Both $\mathcal{Z}_s$ and Δ can be complex and include quasi-particle life-time effects. Eliashberg derived coupled non-linear integral equations for $\mathcal{Z}_s(\omega)$ and $\Delta(\omega)$ which involve the electron-phonon interaction in the function $\alpha^2(\omega)F(\omega)$.

The Eliashberg equations have been used with great success to calculate the properties of strongly coupled superconductors for which the frequency dependence of $\mathcal{Z}$ and Δ is important. They reduce to the BCS theory and to the nearly equivalent theory of Bogoliubov [21] based on the principle of "compensation of dangerous diagrams" when the coupling is weak. By weak coupling is meant that the significant phonon frequencies are very large compared with $k_B T_c$, so that $\Delta(\omega)$ can be regarded as a constant independent of frequency in the important range of energies extending to at most a few $k_B T_c$. In weak coupling one may also neglect the difference in quasi-particle energy renormalization and assume that $\mathcal{Z}_s = \mathcal{Z}_n$.

The first solutions of the Eliashberg equations were obtained by Morel and Anderson [22] for an Einstein frequency spectrum. Coulomb interactions were included, following Bogoliubov, by introducing a parameter μ^* which renormalizes the screened Coulomb interaction to the same energy range as the phonon interaction, In weak coupling, $N(0)V = \lambda - \mu^*$. They estimated λ from electronic specific heat data and μ^* from the electron density and thus the transition temperatures, T_c, for a number of metals. Order-of-magnitude

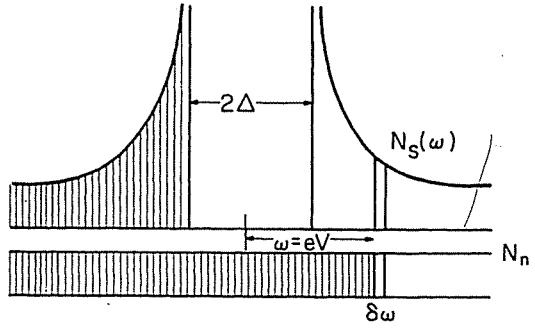
agreement with experiment was found. Later work, based in large part on tunneling data, has yielded precise information on the electron-phonon interaction for both weak and strongly-coupled superconductors.

4
Analysis of Tunneling Data

From the voltage dependence of the tunneling current between a normal metal and a superconductor one can derive $\Delta(\omega)$ and thus get direct information about the Green's function for electrons in the superconductor. It is possible to go further and derive empirically from tunneling data the electron-phonon coupling, $\alpha^2(\omega)F(\omega)$, as a function of energy. That electron tunneling should provide a powerful method for investigating the energy gap in superconductors was suggested by I. Giaever, [23] and he first observed the effect in the spring of 1960.

The principle of the method is illustrated in Fig. 1. At very low temperatures, the derivative of the tunneling current with respect to voltage is proportional to the density of states in energy in the superconductor. Thus the ratio of the density of states in the metal in the superconducting phase, N_S, to that of the same metal in the normal phase, N_n, at an energy eV above the Fermi surface is given by

$$\frac{N_s(eV)}{N_n} = \frac{(\mathrm{d}I/\mathrm{d}V)_{ns}}{(\mathrm{d}I/\mathrm{d}V)_{nn}} \tag{18}$$



$$\left(\frac{\mathrm{d}I}{\mathrm{d}V}\right)_{ns} \sim N_s(\omega) \sim \frac{\omega}{\sqrt{\omega^2 - \Delta^2}}$$

Tunneling from a normal metal into a superconductor

Fig. 1.

Schematic diagram illustrating tunneling from a normal metal into a superconductor near $T = 0°\mathrm{K}$. Shown in the lower part of the diagram is the uniform density of states in energy of electrons in the normal metal, with the occupied states shifted by an energy eV from an applied voltage V across the junction. The upper part of the diagram shows the density of states in energy in the superconductor, with an energy gap 2Δ. The effect of an increment of voltage δV giving an energy change $\delta\omega$ is to allow tunneling from states in the range $\delta\omega$. Since the tunneling probability is proportional to density of states $N_s(\omega)$, the increment in current δI is proportional to $N_s(\omega)\delta V$.

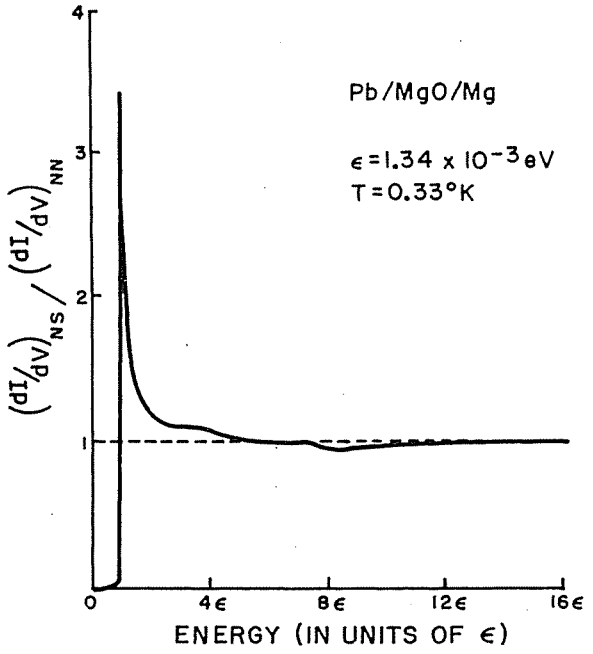


Fig. 2.
Conductance of a Pb-Mg junction as a function of applied voltage (from reference 24).

The normal density is essentially independent of energy in the range involved (a few meV). In weak coupling superconductors, for a voltage V and energy $\omega = eV$,

$$\frac{N_s(\omega)}{N_n} = \frac{\omega}{\sqrt{\omega^2 - \Delta^2}}. \tag{19}$$

As $T \to 0$ K, no current flows between the normal metal and the superconductor until the applied voltage reaches Δ/e, when there is a sharp rise in dI/dV followed by a drop. This is illustrated in Fig. 2 for the case of Pb.

The first experiments of Giaever were on aluminum, which is a weak coupling superconductor. Good agreement was found between theory and experiment. In later measurements on tunneling into Pb, a strongly coupled superconductor, Giaever, Hart and Megerle [24] observed anomalies in the density of states that appeared to be associated with phonons, as shown in Fig. 2. These results were confirmed by more complete and accurate tunneling data on Pb by J. M. Rowell et al. [25]

In the meantime, in the summer of 1961, Schrieffer had derived numerical solutions of the Eliashberg equations working with a group engaged in developing methods for computer control using graphical display methods. [26] He and co-workers calculated the complex $\Delta(\omega)$ for a Debye frequency

spectrum. Later, at the University of Pennsylvania, he together with J. W. Wilkins and D. J. Scalapino [27] continued work on the problem with a view to explaining the observed anomalies on Pb. They showed that for the general case of a complex $\Delta(\omega)$

$$\frac{(dI/dV)_{ns}}{(dI/dV)_{nn}} = \frac{N_s(\omega)}{N_n} = \mathrm{Re}\left\{\frac{\omega}{\sqrt{\omega^2 - \Delta^2(\omega)}}\right\} \tag{20}$$

where Re represents the real part. From measurements of the ratio over the complete range of voltages, one can use Kramers-Krönig relations to obtain both the real and imaginary parts of $\Delta(\omega) = \Delta_1(\omega) + i\Delta_2(\omega)$. From analysis of the data, one can obtain the Green's functions which in turn can be used to calculate the various thermal and transport properties of superconductors. This has been done with great success, even for such strongly-coupled superconductors as lead and mercury.

For lead, Schrieffer et al, used a phonon spectrum consisting of two Lorentzian peaks, one for transverse waves and one for longitudinal and obtained a good fit to the experimental data for $T << T_c$. The calculations were extended up to T_c for Pb, Hg, and Al by Swihart, Wada and Scalapino, [28] again finding good agreement with experiment.

In analysis of tunneling data, one would like to find a phonon interaction spectrum, $\alpha^2(\omega)F(\omega)$, and a Coulomb interaction parameter, μ^*, which when inserted into the Eliashberg equations will yield a solution consistent with the tunneling data. W. L. McMillan devised a computer program such that one could work backwards and derive $\alpha^2(\omega)F(\omega)$ and μ^* directly from the tunneling data. His program has been widely used since then and has been applied to a number of superconducting metals and alloys, including, Al, Pb, Sn, the transition elements Ta and Nb, a rare earth, La, and the compound Nb_3Sn. In all cases it has been found that the phonon mechanism is dominant with reasonable values of μ^*. Peaks in the phonon spectrum agree with peaks in the phonon density of states as found from neutron scattering data, as shown in Fig. 3 for the case of Pb. In Fig. 4 is shown the real and imaginary parts of $\Delta(\omega)$ for Pb as derived from tunneling data.

One can go further and calculate the various thermodynamic and other properties. Good agreement with experiment is found for strongly coupled superconductors even when there are significant deviations from the weak coupling limits. For example, the weak-coupling BCS expression for the condensation energy at $T = 0$ K is

$$E_{BCS} = \frac{1}{2} N(0) Z_n \Delta_0^2 \tag{21}$$

where $N(0)Z_n$ is the phonon enhanced density of states and Δ_0 is the gap parameter at $T = 0$ K. The theoretical expression with $Z_s(\omega)$ and $\Delta(\omega)$ derived from tunneling data, again for the case of Pb, gives [29, 30, 31]

$$E_{theor} = 0.78\, E_{BCS} \tag{22}$$

in excellent agreement with the experimental value

$$E_{exp} = (0.76 + 0.02)\, E_{BCS}. \tag{23}$$

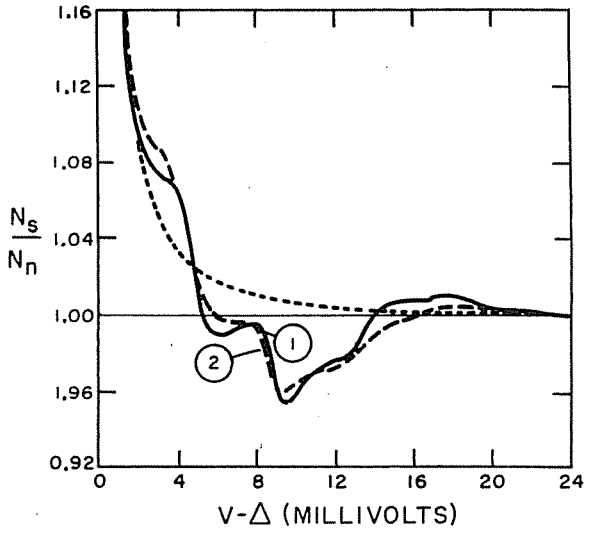
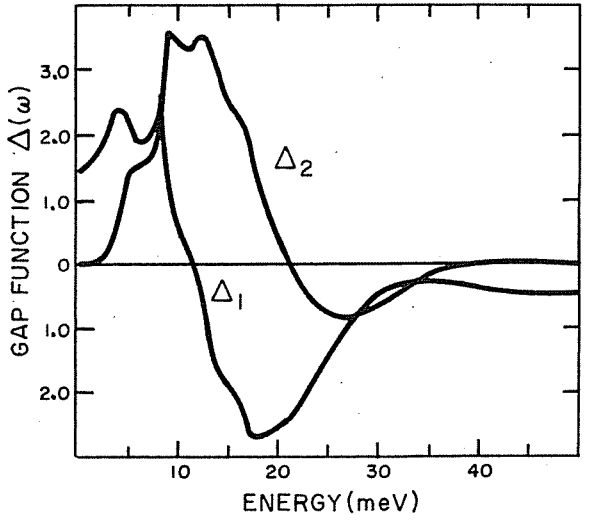
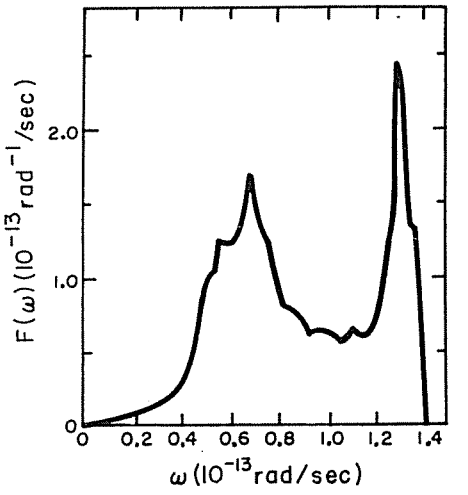


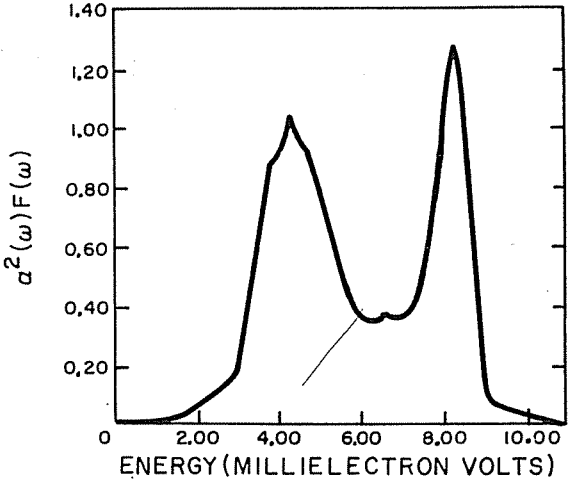
Fig. 3.
Density of states versus energy for Pb. Solid line, calculated by Schrieffer et al; long dashed ine, observed from tunneling; short dashed line, BCS weak coupling theory.



Real and imaginary parts of Δ versus $\omega-\Delta_0$ for Pb.

Fig. 4.
Real and imaginary parts of $\Delta(\omega) = \Delta_1(\omega) + i\Delta_2(\omega)$ versus energy for Pb. (After McMillan & Rowell).

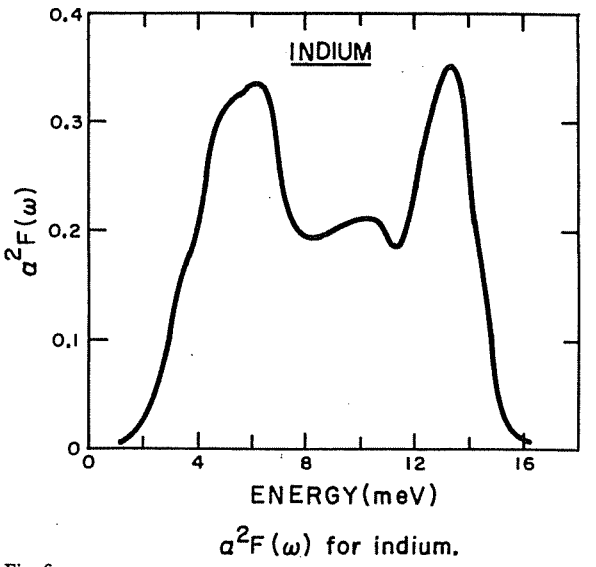




Comparison of $\alpha^2 F(\alpha)$ and $F(\omega)$ for Pb (after McMillan and Rowell)

Fig. 5.
Comparison of $\alpha^2 F$ for Pb derived from tunneling data with phonon density of states from neutron scattering data of Stedman et al. [8]

In Figs. 5, 6, 7, and 8 are shown other examples of $\alpha^2(\omega)F(\omega)$ derived from tunneling data for Pb, In, [31] La, [32] and Nb_3Sn. [33] In all cases the results are completely consistent with the phonon mechanism. Coulomb interactions play only a minor role, with μ^* varying only slowly from one metal to another, and generally in the range 0.1—02.



$\alpha^2F(\omega)$ for indium.

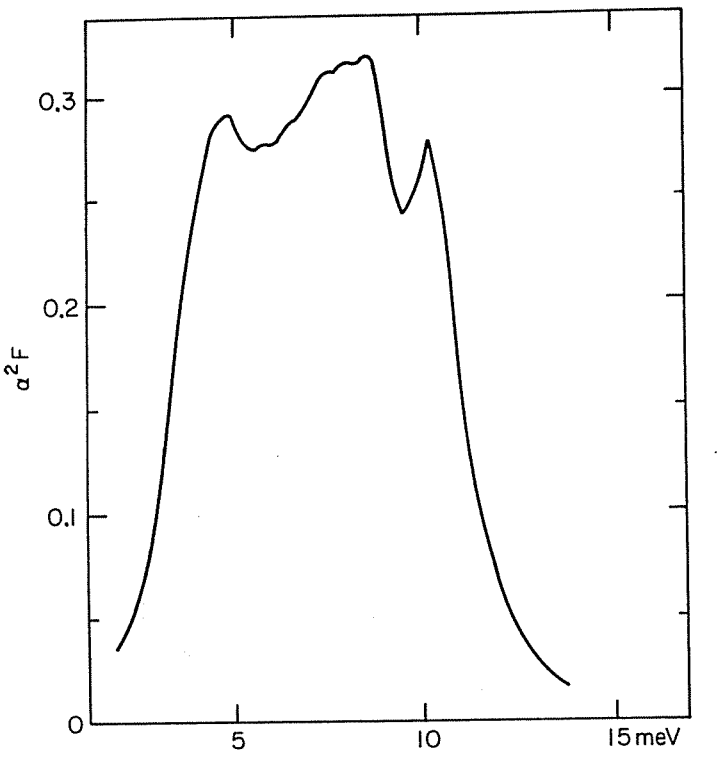
Fig. 6.
α^2F for In (after McMillan and Rowell).

As a further check, it is possible to derive the phonon density of states, $F(\omega)$ from neutron scattering data and use pseudo-potential theory to calculate the electron-phonon interaction parameter $\alpha_q(\omega)$. From these values, one can use the Eliashberg equations to calculate $Z_s(\omega)$ and $\Delta(\omega)$ and the various superconducting properties, including the transition temperature, T_c. Extensive calculations of this sort have been made by J. P. Carbotte and co-workers [34] for several of the simpler metals and alloys. For example, for the gap edge, Δ_0, in Al at $T = 0$ K they find 0.19 meV as compared with an experimental value of 0.17. The corresponding values for Pb are 1.49 meV from theory as compared with 1.35 meV from experiment. These are essentially first principles calculations and give convincing evidence that the theory as formulated is essentially correct. Calculations made for a number of other metals and alloys give similar good agreement.

Conclusions

In this talk we have traced how our understanding of the role of electron-phonon interactions in superconductivity has developed from a concept to a precise quantitative theory. The self-energy and pair potential, and thus the Green's functions, can be derived either empirically from tunneling data or directly from microscopic theory with use of the Eliashberg equations. Physicists, both experimental and theoretical, from different parts of the world have contributed importantly to these developments.

All evidence indicates that the electron-phonon interaction is the dominant mechanism in the cases studied so far, which include many simple metals,



α^2F for lanthanum (after Lou and Tomasch)

Fig. 7.
α^2F for La (after Lou and Tomasch).

transition metals, a rare earth, and various alloys and compounds. Except possibly for the metallic form of hydrogen, [35] which is presumed to exist at very high pressures, it is unlikely that the phonon mechanism will yield substantially higher transition temperatures than the present maximum of about 21 K for a compound of Nb, Al and Ge.

Other mechanisms have been suggested for obtaining higher transition temperatures. One of these is to get an effective attractive interaction between electrons from exchange of virtual excitons, or electron-hole pairs. This requires a semiconductor in close proximity to the metal in a layer or sandwich structure. At present, one can not say whether or not such structures are feasible and in no case has the exciton mechanism been shown to exist. As Ginzburg has emphasized, this problem (as well as other proposed mechanisms) deserves study until a definite answer can be found. [36]

The pairing theory has had wide application to Fermi systems other than electrons in metals. For example, the theory has been used to account for

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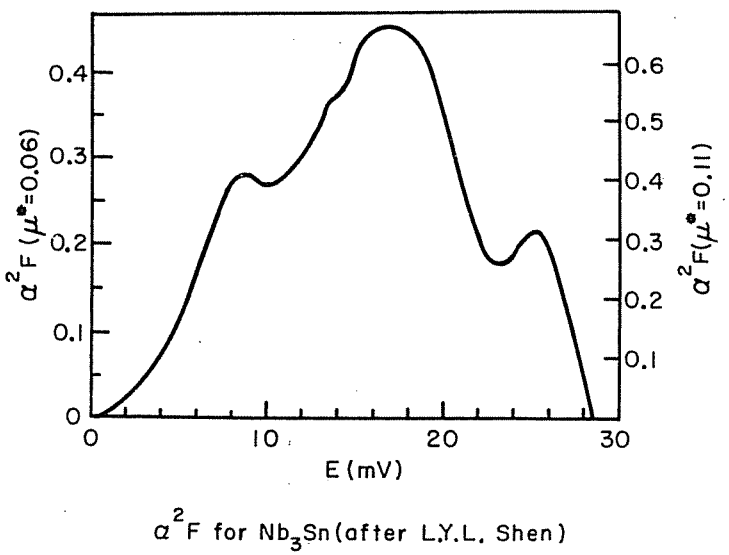

Fig. 8.
α^2F for Nb_3Sn (after Y. L. Y. Shen).

many aspects of nuclear structure. It is thought the nuclear matter in neutron stars is superfluid. Very recently, evidence has been found for a possible pairing transition in liquid He^3 at very low temperatures [37]. Some of the concepts, such as that of a degenerate vacuum, have been used in the theory of elementary particles. Thus pairing seems to be a general phenomenon in Fermi systems.

The field of superconductivity is still a very active one in both basic science and applications. I hope that these lectures have given you some feeling for the accomplishments and the methods used.

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