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BY ANDREW M. SESSLER AT THE UNIVERSITY OF CALIFORNIA
DURING THE SPRING SEMESTER, 1960

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I. INTRODUCTION

Superconductivity was discovered by Kamerlingh-Onnes in 1911, who found that the resistivity of mercury vanished below 4.2°K. Since then, much effort has been expended in attempts to find a theoretical explanation for this and other properties of superconductors. Recently, a great measure of success has been achieved by Bardeen, Cooper, and Schrieffer, and independently by Bogoliubov. These notes begin with a discussion of experimental facts, and follow with a detailed discussion of the BCS-B theory. Also included are treatments of the thermodynamics and electromagnetic properties of superconductors.

II. EXPERIMENTAL FACTS

These can be outlined as follows:

A second-order phase transition occurs at critical temperature T_c; there is no latent heat (and hence no entropy change) in the transition, but the specific heats are discontinuous. The critical temperature T_c at which a material becomes superconducting is of the order of a few ^{o}K. Thermodynamics can be successfully applied for the superconducting transition. This implies that the transition is reversible, which was demonstrated by van Laer and Keesom in 1938. Superconductivity may be destroyed by the application of a sufficiently strong magnetic field; the critical value of the magnetic field H_c is zero at $T = T_c$, but increases as $T \longrightarrow 0$ to a value H_0 at $T = 0$.

There is evidence for the existence of an energy gap for individual particle-like excitations, notably in the dependence of specific heat on temperature, which goes as $\exp(-T_0/T)$. The gap width seems to be zero at T_c, increasing to around $3T_c$ or $4T_c$ at 0 degrees.

The Meissner effect, according to which the magnetic field $\underset{\sim}{B} = 0$ in the interior of a superconductor, cannot be explained on the basis of an assumed infinite conductivity. Since the current is finite, the electric field $\underset{\sim}{E}$ is zero, and hence $\nabla \times \underset{\sim}{E}$ is zero; thus by Maxwell's laws, $d\underset{\sim}{B}/dt = 0$, and flux lines would be frozen in a superconductor, if they ever existed there. But Meissner and Ochsenfeld showed in 1933 that flux lines are forced out of a metal as it passes through a superconducting transition. One may say, accordingly, that a superconductor then acts as a perfect diamagnet.

Because of the extremely low resistivity of superconductors (less than 10^{-17} of room-temperature resistivity), currents appear to be maintained indefinitely in them. But this result must also be interpreted in the light of the Bloch theorem; that the lowest state of a quantum-mechanical system, in the absence of a magnetic field, can carry no current.

It has been observed that there is a relationship of the form $T_c\sqrt{M} =$ a constant, where M is the mass of the ions in the crystal lattice. This is definitive evidence that lattice vibrations must be accounted for in a theory of superconductivity. The theory of electron-lattice interactions, first worked out by Fröhlich in 1950, does account in a general way for such a relationship.

Wave functions of electrons involved in superconductivity seem to be correlated over a length $\xi_0 \approx 10^{-4}$ cm.

III. A SURVEY OF OLD IDEAS

F. and H. London proposed an addition to Maxwell's equations as a phenomenological theory of superconductivity. It was postulated that the superconducting current obeyed the equation $\nabla \times (\Lambda \underset{\sim}{j}) = - \frac{1}{c} \underset{\sim}{B}$. The resulting theory has been very successful in macroscopic descriptions of superconductors; however, it will not be extensively described here.

Fröhlich, in 1950, proposed a theory of superconductivity based on electron-phonon interactions. This theory gives the correct isotope-effect dependence, but predicts a transition temperature in disagreement with experiment. The fundamental principle is that two electrons may interact by the exchange of a virtual phonon. Exactly which interactions are important is not obvious, especially when one considers the extremely small energy difference between normal and superconducting phases. By thermodynamic arguments, the energy difference is $- H_0^2/8\pi$, which is of the order of 10^{-8} ev/electron; this is to be compared to a kinetic energy of about 10 ev detection. Many terms in the Hamiltonian must be ignored which are large compared with the terms responsible for superconductivity; but it is assumed that the difference between these terms for the normal and superconducting states is small, compared with the superconducting interactions. Now, the condensation energy W_0 is of the order of kT_c per electron. Because this energy is small, only electrons near the Fermi surface possess it. The number of electrons above the surface, according to the well-known properties of the Fermi-Dirac distribution, is of the order of $N(0)kT_c$, where $N(0)$ is the density of states per unit energy at the Fermi surface. The total interaction energy is expected to be of the order $N(0)(kT_c)^2$. This indicates $T_c \approx H_0$, which has been confirmed experimentally.

Let N/V be the number of valence electrons per unit volume. The Fermi sphere is full (in momentum space) to the Fermi wave number k_f, so that $N/V = 2\,(4\pi/3h^3)\,(\hbar k_f)^3$, counting the spin multiplicity of 2. The number of states $d(N/V)/dE$ per unit energy interval at the Fermi energy E_f is $(3/2)\,(N/VE_f)$, and the number of states with a given spin $N(0)$ is just

half this number. N(0) is of the order of 10^{22} ev^{-1}cm^{-3}, and, as mentioned above, the energy width of the electrons above the surface is kT_c, or about 10^{-4} ev. This corresponds to a width in k-space of $\Delta k = k_f(kT_c/E_f) \approx 10^4 \text{cm}^{-1}$. The coherence length of electron wave packets ξ_0 is roughly $(\Delta k)^{-1}$, and ξ_0 is about 10^{-4} cm. This last relationship, of course, follows from application of the uncertainty principle to the correlated wave packet. The total number of electrons in such a wave packet is of the order of $\xi^3 kT_c N(0) \approx 10^6$. This is only a small fraction of the total number of electrons contained in such a volume, and is related to the fact that only electrons near the surface of the Fermi sea may contribute to a superconducting interaction, because of the exclusion principle. However, 10^6 electrons is still a very large number among which to combine correlations into a theory.

Before quantitative discussion of Fröhlich's arguments, a brief review of the theory of electrons in metals is in order, following the article by Sommerfeld and Bethe (1933) in the Handbuch der Physik. The crystal lattice is composed of positive ions surrounded by a core of bound electrons; outside these are the nearly free valence electrons. The crystal lattice is periodic; there are three vectors $\underset{\sim}{a}, \underset{\sim}{b}, \underset{\sim}{c}$, having the length and orientation of three sides of the unit cell. If a lattice point is at $\underset{\sim}{X}$, there is also a lattice point at $\underset{\sim}{X} + \underset{\sim}{a}, \underset{\sim}{b}, \underset{\sim}{c}$. The vectors $\underset{\sim}{a}, \underset{\sim}{b}, \underset{\sim}{c}$ need not be orthogonal, but we shall make the simplifying assumption that they are.

First, consider the motion of the lattice points alone. The heavy ions depart only slightly from their equilibrium positions under normal conditions, so it is convenient to expand the potential $V(\underset{\sim}{X}_m)$ of the ions about their equilibrium positions. Let m_i be the ith component of the equilibrium position of the mth ion, and X_{mi} the ith component of the position of the mth ion. The potential expanded about equilibrium is:

$$V = V_0 + \frac{1}{2} \sum_{\substack{i\,k \\ m\,n}} V_{mn}^{ik} (X_{mi} - m_i)(X_{nk} - m_k) + \cdots , \tag{1}$$

where V_0 is evaluated at the equilibrium positions m_i. The kinetic energy is, as usual,

$$T = \frac{M}{2} \sum_{mi} (\dot{X}_{mi} - \dot{m}_i)^2 . \tag{2}$$

The classical equations of motion can be derived from Eqs. (1) and (2), and lead to the following form for the displacement from equilibrium $\underset{\sim}{u}_m$ of the $\underline{m}$th atom:

$$\underset{\sim}{X}_m - \underset{\sim}{m} = \underset{\sim}{u}_m = \frac{1}{\sqrt{N}} \sum_{\underset{\sim}{w}j} \underset{\sim}{\epsilon}_{wj} \left[b_{wj} e^{i\underset{\sim}{w}\cdot\underset{\sim}{m} - i\omega_w t} + b_{wj}^* e^{-i\underset{\sim}{w}\cdot\underset{\sim}{m} + i\omega_w t} \right] \quad (3)$$

Here N is the total number of lattice ions for any wave number w; there are three independent polarization vectors $\underset{\sim}{\epsilon}_{wj}$. For our purposes, they may be taken as mutually perpendicular, with one polarization vector along the wave vector $\underset{\sim}{w}$, and the other two perpendicular to it. The * indicates a complex conjugate. The ω_w can be found as a function of the wave numbers w by substituting in the classical equations of motion. For long wave lengths, the sound velocity $S = \omega/w$ is independent of w, so $\omega_w = wS$.

The wave numbers w form a discrete set, when suitable boundary conditions on the displacement $\underset{\sim}{u}$ are assigned at the edges of the crystal containing N lattice ions. We may further restrict the values which w may have to lie inside the first Brillouin zone — that is, $-\pi/a < w_x < \pi/a$, etc., where a is the length of the side of the unit cell lying along the x direction. In the Debye approximation, the unit cell is considered to have a spherical shape, of the same volume as the actual unit cell. In this case, there is a maximum wave number w_0 satisfying $w_0 = 2\pi (3/4\pi\Omega_0)^{1/3}$, where Ω_0 is the volume of a unit cell.

By substituting Eq. (3) in Eqs. (1) and (2), we may express the total energy $E = T + V$ in terms of the numbers b and b^*:

$$E = m \sum_{\underset{\sim}{w}j} \omega_{wj}^2 (b_{wj} b_{wj}^* + b_{wj} b_{wj}^*), \quad (4)$$

where M is the ionic mass. This Hamiltonian may be quantized immediately, by analogy with the procedure used for quantizing the electromagnetic field. Upon quantization, b^* becomes $b^\dagger$, the Hermitian adjoint, and the b's and $b^\dagger$'s obey certain commutation rules. In order that the energy be expressible in the ordinary form

$$E = \sum \hbar\omega_{wj} (b_{wj}^\dagger b_{wj} + \tfrac{1}{2}), \quad (5)$$

it is convenient to redefine the quantities b, by multiplying them by the factor $(2m\omega_{wj}/\hbar)^{1/2}$. Then the usual boson commutation rules hold, and by applying them it is easy to see that Eq. (5) is equivalent to Eq. (4). It must be remembered that $\underset{\sim}{u}$, as given by Eq. (3), must also be multiplied by $(2m_{wj}/\hbar)^{1/2}$, since it involves the b's linearly.

So far, the ω_{wj} have been determined from the ion-ion interactions alone, without accounting for the valence electrons. The interaction will lead to a small change in every frequency; this will be discussed in detail later.

We are now in a position to calculate the electron-ion interaction. The total Hamiltonian of the ion cores plus valence electrons is

$$H = \Sigma \frac{\rho_i^2}{2m} + \sum_{im} v(\underset{\sim}{x}_i - \underset{\sim}{X}_m) + H_{ion} + \sum_{ij} \frac{e^2}{|r_i - r_j|} , \tag{6}$$

where i, j run over valence electrons, m over ions, $v(\underset{\sim}{x}_i - \underset{\sim}{X}_m)$ represents the electron-ion interaction, H_{ion} is given by (5), and the last term is the electron-electron Coulomb interaction. In order to eliminate infinities which appear in the separate terms of Eq. (6) (but not in the sum), we suppose there is subtracted, from the electron-ion interaction, the interaction of each electron with a uniform positive charge, and from the electron-electron interaction the self-energy of a uniform negative charge, and from the ion-ion interaction the self-energy of a uniform positive charge. This does not change the Hamiltonian, since the sum of these energies is zero. The potential v is expanded around the equilibrium points m of the ions:

$$\Sigma v(\underset{\sim}{x}_i - \underset{\sim}{X}_m) = \Sigma v(\underset{\sim}{x}_i - \underset{\sim}{m}) - \Sigma \underset{\sim}{u}_m \cdot \nabla v(\underset{\sim}{x}_i - \underset{\sim}{m}) + \cdots . \tag{7}$$

In the absence of the interaction—second term in Eq. (7)—the electrons move in a potential $v(\underset{\sim}{x}_i - \underset{\sim}{m})$, plus the compensating uniform negative charge potential. We denote the sum of these potentials by $V(x_i)$. The Schrödinger equation for each electron (ignoring Coulomb effects) is

$$\left(\frac{p^2}{2m} + V(x) \right) \psi_k(\underset{\sim}{x}) = E_k \psi_k(\underset{\sim}{x}) . \tag{8}$$

The solutions are Bloch functions $\psi_k(\underset{\sim}{x}) = e^{i\underset{\sim}{k}\cdot\underset{\sim}{x}} \underset{\sim}{u}_k(\underset{\sim}{x})$, where $u_k(\underset{\sim}{x})$ has the periodicity of the crystal lattice. The electrons may be decribed by the occupation numbers of the states k; in other words, the electron

field may be second-quantized with the introduction of Fermi-Dirac operators C_{ks}, $C_{ks}^{\dagger}$ (s is a spin index) obeying the anticommutation rules

$$\left[C_{ks}^{+},\ C_{k's'}\right] = \delta_{kk'}\delta_{ss'} . \tag{9}$$

The matrix elements of the interaction — second term in Eq. (7)— may be reduced to a rather simple form, if one makes several assumptions: E_k depends only on the magnitude of $\underset{\sim}{k}$, not its direction; E_k is large compared with the energy $\hbar\omega_{wj}$ of the phonon involved. Under these assumptions, the only nonvanishing matrix elements are for longitudinal phonons, and momentum is conserved between phonons and electrons. The matrix elements are:

$$\begin{aligned}
\left\langle \underset{\sim}{k} \left| -\underset{\sim}{u}\cdot\nabla V \right| \underset{\sim}{k}+\underset{\sim}{w} \right\rangle &= \frac{2i}{3} C\left\{\frac{\hbar\omega_w}{NMS^2}\right\}^{1/2} b_w , \\
\left\langle \underset{\sim}{k} \left| -\underset{\sim}{u}\cdot\nabla V \right| \underset{\sim}{k}-\underset{\sim}{w} \right\rangle &= -\frac{2i}{3} C\left\{\frac{\hbar\omega_w}{NMS^2}\right\}^{1/2} b_w^{\dagger} , \\
C &= 3\int \frac{\hbar^2}{2m} \left|\nabla u_k\right|^2 dV .
\end{aligned} \tag{10}$$

S is, as above, the sound velocity of the crystal lattice. The quantity C is the expectation value of the electron kinetic energy, as can be seen by using Green's theorem, and is of the order of 10 ev. Since only longitudinal phonons are involved, the polarization index on b_w, $b_w^{\dagger}$ is dropped. If one knows the matrix elements of a perturbing energy in the Schrödinger picture, which we denote by $\left\langle k \left| U \right| k' \right\rangle$, the corresponding operator in the field theory is easily formed:

$$U_{op} = \sum_{kk'ss'} \left\langle k \left| U \right| k' \right\rangle C_{k's'}^{\dagger} C_{ks} . \tag{11}$$

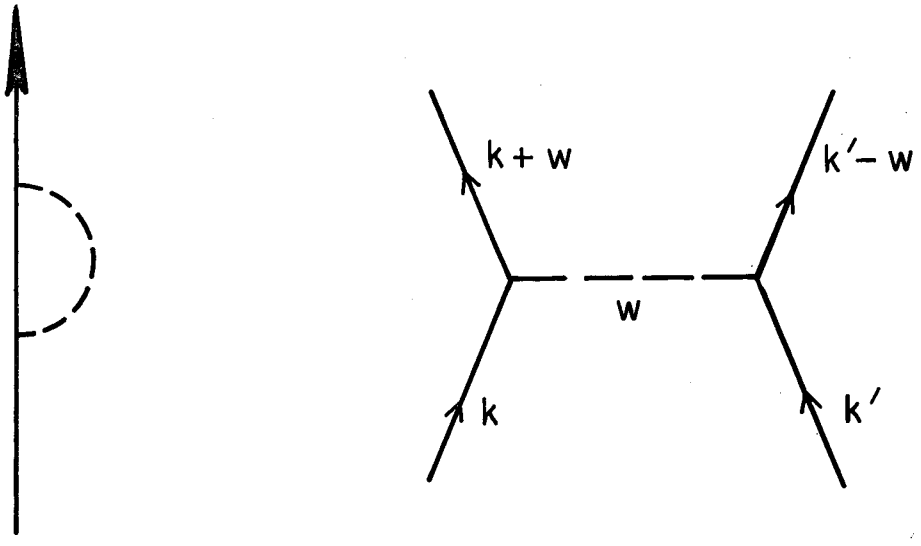
We can then write, for the interaction term between electrons and ions,

$$H_{int} = i \sum_{\underset{\sim}{w}} D_{\underset{\sim}{w}} \left[\rho_{\underset{\sim}{w}} b_{\underset{\sim}{w}}^{\dagger} - \text{H. A.}\right] \tag{12}$$

where H. A. is the Hermitian adjoint,

$$\rho_{\underset{\sim}{w}} = \sum_{\underset{\sim}{k}} C_{\underset{\sim}{k}-\underset{\sim}{w},s}^{\dagger} C_{\underset{\sim}{k}s} , \tag{13}$$

and



(a) Self-energy (b) Electron-electron interaction

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Fig. 1. Electron-phonon interactions.

$$D_w^2 = \frac{4C^2\hbar\omega_w}{9NMS^2} \quad . \tag{12}$$

This interaction term may be treated by the usual methods of perturbation theory. The first-order perturbation leads to the normal resistivity of a metal, caused by scattering of electrons by real phonons. The second-order terms, much smaller, lead to two different kinds of effects: self-energy effects, and electron-electron scattering via an intermediate virtual phonon. This is an interesting (but incomplete) analogy to quantum electrodynamics, in which the electron-photon interaction leads not only to Coulomb effects between electrons, but also to charge and mass renormalization of the electron. In Feynman graphs, the two types of interaction are as shown in Fig. 1, respectively (a) and (b).

The self-energy term is much the larger of the two second-order effects, but is also the less interesting.

The second-order perturbation energy shift is given by the usual Rayleigh-Schrödinger formula from (12):

$$\Delta E = \sum_{kqs} C_{ks}^{\dagger} C_{ks} C_{qs} C_{qs}^{\dagger} |D_w|^2/(E_k - E_q + \hbar\omega_w) , \tag{13}$$

for $w = k - q$. This can be further separated into the self-energy term ΔE_1 and the electron-electron interaction ΔE_2:

$$\Delta E_1 = -\sum_{kq\sigma} C_{ks}^{\dagger} C_{ks} |D_w|^2/(E_k - E_q + \hbar\omega_w) ; \tag{14}$$

$$\Delta E_2 = \sum_{kqs} C_{ks}^{\dagger} C_{ks} C_{qs}^{\dagger} C_{qs} |D_w|^2/(E_k - E_q + \hbar\omega_w) .$$

Fröhlich examined the values of ΔE_2 for various hypothetical ground states, and found the interesting result that there existed configurations of lower energy than the configuration in which all electron states are filled up to the Fermi level, and all others states are empty. In particular, there is a ground state with an energy gap at the Fermi level with lower energy than the above configuration. Excited states can occur for a number of electrons whose momentum vectors are strongly correlated—i. e., nearly the same in direction and magnitude. Both results are suggestive in view of the experimental results discussed in Sec. II. Notice that ΔE_2 is large only when the

energy denominator is small; since there is a maximum phonon frequency $\omega_0 = Sw_0$, the major contributions to E_2 occur when $|E_k - E_q| \lesssim \hbar\omega_0 = \hbar S w_0$; in fact, this is the criterion for an attractive potential ($\Delta E_2 < 0$). We may therefore approximate the sum in (14) by

$$\Delta E_2 \sim \sum_{kqs} |D_w|^2 / \hbar\omega_0 \quad \text{for } |E_k - E_F|, |E_q - E_F| < \hbar\omega_0) \tag{15}$$

$$\sim N(0)^2 V^2 (\hbar\omega_0)^2 C^2 / NMS^2 V$$

$$\sim V\left(\frac{N}{V}\right)\left(\frac{C^2}{E_F}\right)\left(\frac{m}{M}\right),$$

where we have used the fact that $w_0 \sim k_f$ (cf. pp. 7 , 9). Since $\Delta E_2 \sim 1/M \sim H_0^2$, and experimentally $H_c(T = 0) \sim T_c$, one finds that $T_c \sim 1/\sqrt{M}$ — the isotope effect. Unfortunately, the magnitude of the interaction is much larger than desired, since $\hbar k_f S \sim 10^4 kT_c$ for most materials.

A strong-coupling model ($kT_c >> \hbar k_f S$) has been worked out. The condensation energy turns out to be much smaller, but the isotope shift has vanished (since lattice recoil energy is ignored). By using Hartree-Fock techniques, Fröhlich showed that the condensation energy $W_0 \sim E_F e^{-3/F}$, where F is a coupling constant of the order of unity, is

$$F = \frac{C^2}{3E_F MS^2} \quad . \tag{16}$$

The exponential factor reduces the condensation energy to the right order of magnitude. Notice that, since $e^{-3/F}$ has an essential singularity at $F = 0$, the above result for W_0 cannot be achieved in any finite-order perturbation theory. Similar exponential terms appear in the BCS theory. These will be discussed below.

In conclusion, we give the operator form of the Coulomb interaction term in Eq. (6). We use the formula for two-particle operators,

$$U_{op} = \frac{1}{2} \sum_{k\ell k'\ell'} C_{k'}^\dagger C_{\ell'}^\dagger C_\ell C_k \langle k'\ell' | U | k\ell \rangle \, , \tag{17}$$

where U is a perturbation given in the Schrödinger picture. For the Coulomb matrix element, the free-electron states are taken as plane waves, $e^{i\mathbf{k}\cdot\mathbf{r}}$.

If one transforms to the center-of-mass coordinates of the two interacting electrons, the matrix element is easily evaluated, and it turns out that

$$H_{Coul} = \sum_k \frac{2\pi e^2}{k^2} \rho_k^\dagger \rho_k \quad . \tag{18}$$

The Coulomb term will be discussed more fully later on.

IV. EFFECTIVE ELECTRON-ELECTRON INTERACTION

In the section above, the influence of the valence electrons on the lattice was not taken into account. In order to treat the entire Hamiltonian consistently, one introduces a canonical transform of the type

$$H' = e^{-iS} H e^{iS} , \tag{19}$$

where S is Hermitian, and therefore e^{iS} is unitary. The purpose of the transformation is to decouple the electrons from the lattice as completely as possible. To this end, S is chosen with parameters adjustable so as to remove terms linear in the lattice variables $b, b^\dagger$. Following Nakajima (1953), and Bardeen and Pines, (1955), let

$$S = \sum_w S_w , \quad S_w = \sum_{ks} g_{kw} (C_{ks}^\dagger C_{k-w,s} b_w + H.A.) , \tag{20}$$

where the g_{kw} are the adjustable parameters.

The Hamiltonian to be transformed is (6), which, with the help of Eqs. (5), (7), (8), (12), and (18) may be written

$$H = \sum_{ks} E_k C_{ks}^\dagger C_{ks} + \sum_w \hbar\omega_w (b_w^\dagger b_w + \frac{1}{2}) + i \sum_w D_w (\rho_w b_w^\dagger - H.A.) + \sum_k \frac{2\pi e^2}{k^2} \rho_k^\dagger \rho_k . \tag{21}$$

The unitary transformation is expanded:

$$H' = H + i [H, S] - [[H, S], S]/2! + \cdots . \tag{22}$$

The commutators can be evaluated by use of the identity

$$\left[AB, CD\right]_- = A\left[B, C\right]_+ D - C\left[A, D\right]_+ B - \left[A, C\right]_+ BD + CA\left[D, B\right]_+ . \tag{23}$$

The following commutators are required:

$$\left[\sum_{ks} E_k C_{ks}^\dagger C_{ks}, S\right] = \sum_{kws} \left(E_k - E_{|k-w|}\right) g_{kw}\left[C_{ks}^\dagger C_{k-w,s} b_w - \text{H. A.}\right],$$

$$\left[\sum_w \hbar\omega_w (b_w^\dagger b_w + 1/2), S\right] = \sum_{kws} \hbar\omega_w g_{kw}\left[b_w^\dagger C_{k-w,s} C_{ks} - \text{H. A.}\right],$$

$$\left[\rho_w S\right] = \sum_{kws} \left(C_{k-w,s}^\dagger C_{k-w,s} - C_{ks}^\dagger C_{ks}\right)\left[g_{kw} b_w^\dagger + \text{H. A.}\right]$$

$$+ \text{nondiagonal terms.} \tag{24}$$

$$\left[D_w \rho_w b_w^\dagger - \text{H. A.}, S\right] = \sum_w D_w \left(b_w\left[\rho_w^\dagger, S\right] + \left[b_w^\dagger, S\right]\rho_w^\dagger - \text{H. A.}\right),$$

$$= \sum_{kws} D_w \left(C_{ks}^\dagger C_{ks} - C_{k-w,s}^\dagger C_{k-w,s}\right) g_{kw}\left(b_w^\dagger + b_w\right),$$

$$+ \sum_{kws} D_w g_{kw} \left(C_{k-ws}^\dagger C_{ks} \rho_w^\dagger + \text{H. A.}\right).$$

Then (22) gives:

$$H' = H - H_{int} + i \sum_{kws} \left\{D_w + g_{kw}\left(E_k - E_{|k-w|}\right) - \hbar\omega_w\right\}\left\{b_w C_{ks}^\dagger C_{k-w,s} - \text{H. A.}\right\}$$
$$+ \sum_{kws} \left\{D_w g_{kw} + \frac{1}{2} g_{kw}^2 \left(E_k - E_{|k-w|} - \hbar\omega_w\right)\right\}$$
$$\times \left\{\left(C_{ks}^\dagger C_{ks} - C_{k-w,s}^\dagger C_{k-w,s}\right)\left(b_w^\dagger b_w + b_w b_w^\dagger\right) - \right.$$
$$\left. - \left(\rho_w C_{k-w,s}^\dagger C_{ks} + \text{H. A.}\right)\right\} + \cdots \tag{25}$$

The coefficients g_{kw} are chosen to eliminate terms linear in $b, b^\dagger$:

$$g_{kw} = \frac{D_w}{E_{|k-w|} - E_k - \hbar\omega_w} . \tag{26}$$

The series expansion Eq. (22) is valid only if the g's remain finite. In order to assure this, we consider all sums to be replaced by principal-part integrations. With this understanding, (Eq. 25) can be rewritten as

$$H' = \sum_{ks} E_k C_{ks}^{\dagger} C_{ks} + \Sigma \hbar\bar{\omega}_w (b_w^{\dagger} b_w + \tfrac{1}{2})$$
$$- \tfrac{1}{2} \sum_{kws}' \frac{D_w^2}{E_{k-w} - E_k + \hbar\omega_w} (\rho_w C_{k-w,s}^{\dagger} C_{ks} + \text{H. A.}) + H_{\text{Coul}}' + \cdots , \tag{27}$$

where the terms neglected are at least quadratic and nondiagonal in the $b, b^{\dagger}$ and can be neglected, to within the validity of the harmonic approximation for the lattice waves (i.e., the validity of Eq. (5) as unperturbed lattice Hamiltonian). We have used in Eq. (27) the expression:

$$\bar{\omega}_w = \omega_w - \sum_{kws}' D_w g_{kw} (C_{ks}^{\dagger} C_{ks} - C_{k-w,s}^{\dagger} C_{k-w,s})$$
$$\simeq \omega_w - 2 \sum_{kws}' D_w^2 \langle C_{ks}^{\dagger} C_{ks} \rangle / (E_{|k-w|} - E_k) . \tag{28}$$

Thus we have arrived at a renormalized lattice frequency. To within the present approximation, we replace ω_w by $\bar{\omega}_w$ everywhere, and neglect $\hbar\omega_w$ entirely in the denominator of (28). We may also use the expectation values of $C_{ks}^{\dagger} C_{ks}$ in (28).

The Coulomb term in the transformed Hamiltonian also seems to present some difficulties, since it blows up at $k = 0$. However, as in most treatments of the electron gas, it is sufficient to cut off the sum at some critical value of k, roughly equal to the inverse of the interparticle spacing. The long-range effects (k very small) can be treated as plasma, or collective, oscillations (Bohm and Pines, 1953). For the present, the transformed Coulomb term will be dropped.

Finally, we rewrite the interaction term (renormalized) as

$$H_{\text{int}}' = \sum_{kws}' \frac{\bar{F}(\hbar\bar{\omega}_w)^2 C_{ks}^{\dagger} C_{k-w,s} \rho_w}{N(0) \left\{ (E_{|k-w|} - E_k)^2 - (\hbar\bar{\omega}_w)^2 \right\}} \tag{29}$$
$$= \frac{\bar{F}}{N(0)} \sum_{kws} G(E_k - E_{|k-w|}) C_{ks}^{\dagger} C_{k-w,s} \rho_w ,$$

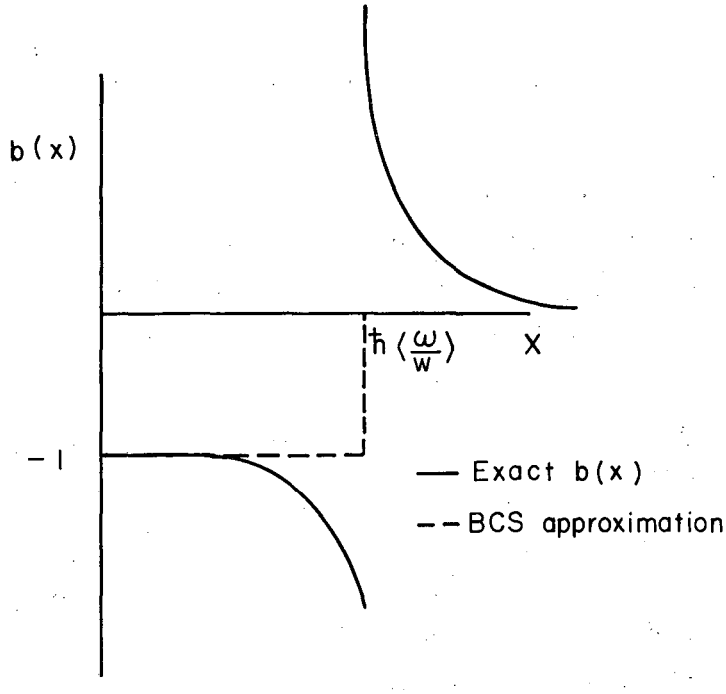


Fig. 2. Effective electron-electron potential b(x).

where

$$\overline{F}/F = \omega_w \,/\, \overline{\omega}_w \,, \quad G(x) = \frac{(\overline{k}\,\overline{\omega})^2}{x^2 - (\overline{k}\,\overline{\omega})^2} \,. \tag{30}$$

The BCS approach is to replace G(x) by

$$G = 1, \text{ for } x < \hbar \langle \omega_w \rangle, \tag{31}$$

$$G = 0, \text{ for } x > \hbar \langle \omega_w \rangle,$$

where $\langle \omega_w \rangle$ is an average wave number of the order of $\hbar k_f S$ (see Fig. 2). Before discussing the BCS theory in detail, we will introduce the concept of Cooper pairs.

V. MODERN THEORY OF THE GROUND STATE

A great advance in the understanding of mechanisms responsible for superconductivity was made by Cooper in 1956. Consider electrons at a temperature nearly zero, so that the electron gas is almost completely degenerate. The electrons are to be thought of as nearly free, but with an interaction potential whose effect we are to interpret. Only two-electron interactions will be considered—a rough approximation to the true state of affairs, in which all electrons interact. On the other hand, the effect of the exclusion principle is all-important, and this we shall be able to take into account. Electrons can interact with one another only above the Fermi level, because of this principle. According to Fröhlich, an attractive interaction occurs only when the difference in energy between two states is about $\hbar k_f S$ (p. 14) or less.

By taking the Fourier transform of the Schrödinger equation for two electrons, this equation is transformed into momentum space. Assume an attractive perturbing potential U, depending only on the interelectronic distance $\underset{\sim}{r}$, whose matrix elements in momentum space are, for simplicity, assumed constant:

$$\langle k' | U | k \rangle = - | G | = \text{constant, for } k_F < k, k' < k_m$$

$$\text{or} \quad = 0 \text{ otherwise.} \qquad \frac{\hbar^2}{m} (k_F^2 - k_m^2) \cong 2\hbar k_F S . \tag{32}$$

This is merely an expression of Eq. (31) again.

The Schrödinger equation is

$$(\mathcal{E}_K + \epsilon_K - E)\, a_k + \sum_{k'} a_{k'} (k | U | k') = 0 , \tag{33}$$

where

$$\mathcal{E}_K \approx \hbar^2 \frac{K^2}{4m} \quad \text{for } \underset{\sim}{R} = \tfrac{1}{2}(\underset{\sim}{r}_1 + \underset{\sim}{r}_2)\ \underset{\sim}{K} = \underset{\sim}{k}_1 + \underset{\sim}{k}_2$$

$$\epsilon_k = \frac{\hbar^2 k^2}{m} \qquad \underset{\sim}{r} = \underset{\sim}{r}_2 - \underset{\sim}{r}_1 \quad \underset{\sim}{k} = \frac{1}{2}(\underset{\sim}{k}_2 - \underset{\sim}{k}_1) \tag{34}$$

(Notice that the Fourier transform automatically leads to conservation of total momentum $\hbar \underset{\sim}{K}$.) The wave function is given by

$$\psi(\underset{\sim}{R}_1\underset{\sim}{r}) = \frac{1}{V} e^{i\underset{\sim}{K}\cdot\underset{\sim}{R}} \sum_k a_k e^{i\underset{\sim}{k}\cdot\underset{\sim}{r}} \quad . \tag{35}$$

V is the volume of quantization. By rearranging Eq. (33) and summing over k, we find

$$\sum_k a_k = \sum_k \frac{G}{\epsilon_k - \mathcal{E}_K - E} \sum_k a_{k'} \quad . \tag{36}$$

Cancel the terms in $\sum a_k$ on both sides, and introduce the density $N(K, \epsilon_k)$ of states of total momentum K, energy $\epsilon_k = (\hbar^2/m)k^2$. Since $\hbar k_f S$ is about 0.1 ev, compared with a Fermi energy of 10 ev, it is sufficient to replace $N(K, \epsilon_k)$ by $N(K, E_F)$. Replacing the sum in Eq. (36) by an integral over N, we get

$$1 = G \int_{E_F}^{E_f + 2\hbar k_F S} \frac{N(K, E_F)d\epsilon}{\epsilon - E_F + \Delta} = GN(K, E_F)\log\left[\frac{2\hbar k_F S + \Delta}{\Delta}\right] \quad . \tag{37}$$

Here the binding energy per electron is $\Delta = E_F + \mathcal{E}_K - E$. The actual condensation energy per electron is about 10^{-8} ev, much less than $\hbar k_f S$. As will be shown below, the important terms are those for which $\mathcal{E}_K = 0$. Then we may solve for Δ as

$$\Delta \cong 2\hbar k_F S\, e^{-1/GN} \quad . \tag{38}$$

This is to be compared with Fröhlich's strong-coupling model, which has the same exponential form (p. 14) but is multiplied by E_f, rather than $\hbar k_f S$. There is a difference of a factor of about 100 between the two models. The exponential factor serves to reduce the condensation energy to the order of magnitude observed experimentally. As mentioned above, this result cannot be achieved in any finite order of perturbation theory.

Of crucial interest is the variation of $N(K, E_F)$ with $\underset{\sim}{K}$. As a first approximation, assume that the ground state is a Fermi distribution. Then both $k_1, k_2 \leqslant k_f$. Solving Eq. (34) for $\underset{\sim}{k}_1, \underset{\sim}{k}_2$ in terms of K, k, one can write the limitations of k_1, k_2 as

$$\begin{aligned} &\frac{1}{2}\left|\underset{\sim}{K} \pm \underset{\sim}{k}\right|^2 \leqslant k_F^2 \; ; \quad \frac{K^2}{4} + k^2 \pm \frac{1}{8}\,\underset{\sim}{K}\cdot\underset{\sim}{k} \leqslant k_F^2 \\ &\pm\cos\theta \leqslant \frac{8}{Kk}\left(k_F^2 - \frac{K^2}{4} - k^2\right) . \end{aligned} \tag{39}$$

cos θ is the angle K-k. The total energy $(\hbar^2/m)(1/4\ K^2 + k^2)$ is roughly twice the Fermi energy, so we may write

$$\pm \text{Cos } \theta \leqslant - \frac{8k_F^2}{Kk} \quad . \tag{40}$$

The probability that two electrons have a given value of k^2 involves an integral over the solid angle of $\underset{\sim}{k}$, or over cos θ. Thus the wider the allowed range of values of cosθ, the more probable a given value of k^2. But this range, by Eq. (40), depends inversely on K. Another way of seeing this result is to observe that the sphere drawn with $\underset{\sim}{k}_1 - \underset{\sim}{k}_2 = \underset{\sim}{k}$ as a diameter has its greatest intersection with the Fermi sphere when $\underset{\sim}{k}_1 = - \underset{\sim}{k}_2$; this sphere then coincides with the Fermi sphere. We therefore expect most electron pairs in the superconducting state to have $\underset{\sim}{K} = 0$, or, in other words, the electrons have equal and opposite momenta. When exchange effects are taken into account, antiparallel spin orientations are favored over parallel spins.

The ground-state wave function represents a true bound state which for large values of r decreases about as $1/r^2$. The average extension of the pair is 10^{-4} cm for $\Delta \approx kT_c$.

Of course, this model leads to an energy gap Δ. The energy per unit volume is just the product of Δ with the number of electrons above the Fermi sea per unit volume; this is proportional to Δ/E_f. It is easily seen that the total condensation energy is proportional to S^2, but this is inversely proportional to the mass of the lattice ions. Since the condensation energy is proportional to H_0^2 (and thus T_c^2, by experiment), we find that the Cooper model yields an isotope effect.

The essential feature of the Cooper model is the formation of electron pairs with opposite momenta and spin. If each pair is considered as a quasi-molecule, the pairs have integral spin and hence obey Bose-Einstein statistics. A condensation into a ground state would be allowed, much as occurs in superfluidity. However, the quasimolecules have a very large spatial extension (of the order of 10^{-4} cm) and they overlap, so that we cannot treat the system as an ideal Bose-Einstein gas.

A more realistic analysis, involving interactions between all particles, has been worked out by Bogoliubov (1958). Consider the field-theoretic Hamiltonian for N_0 particles:

$$H_0' = \sum_k \epsilon_k C_k^\dagger C_k \quad (\epsilon_k = \epsilon_{-k}); \quad N = \sum_k C_k^\dagger C_k . \tag{41}$$

In contrast to the field theories of electromagnetism or elementary particles, we must arrange for conservation of the total number N_0 of particles. This is done by adding a term to the Hamiltonian involving a Lagrange multiplier, chosen so that the expectation value of the number of particles is equal to N_0:

$$H_0 = H_0' - \lambda N = \sum_k (\epsilon_k - \lambda) C_k^\dagger C_k ; \quad \langle N \rangle = N_0 . \tag{42}$$

This really involves only a redefinition of the energy scale, and, in fact, the parameter λ really represents the Fermi energy. To see this, let us define quasi-particle operators in terms of the ordinary Fermi operators as follows:

$$a_k = C_k \quad \epsilon_k > \lambda ; \quad \left[a_k^\dagger, a_{k'}\right]_+ = \delta_{k\,k'} ; \tag{43}$$

$$a_k = C_{-k}^\dagger \quad \epsilon_k < \lambda .$$

The number operators and the Hamiltonian become

$$N = \sum_{k(\epsilon_k > \lambda)} a_k^\dagger a_k + \sum_{k(\epsilon_k < \lambda)} a_{-k}\, a_{-k}^\dagger , \tag{44}$$

$$H_0 = \sum_{k(\epsilon_k < \lambda)} (\epsilon_k - \lambda)(1 - a_{-k}^\dagger a_{-k}) + \sum_{k(\epsilon_k > \lambda)} (\epsilon_k - \lambda)\, a_k^\dagger a_k$$

$$= \sum_{k(\epsilon_k < \lambda)} (\epsilon_k - \lambda) + \sum_k E_k\, a_k^\dagger a_k ; \quad E_k = \left| \epsilon_k - \lambda \right| .$$

The interpretation of the $a, a^\dagger$ variables is simple: $a^\dagger$ creates quasiparticles, i.e., a particle for energies $> \lambda$; a hole for energies $< \lambda$. The quasiparticle vacuum is defined as the state $\overline{\Phi}_0$ such that $a_k \overline{\Phi}_0 = 0$. This implies that there are no holes for energies $< \lambda$, and no particles for energies $> \lambda$, and that the vacuum represents a Fermi sea filled to energy λ. The energy of the Fermi sea is a solution of the Schrödinger equation $H_0 \overline{\Phi} = W_0 \overline{\Phi}_0$.

Using Eq. (44) and the definition of vacuum, we easily find

$$W_0 = \sum_{k(\epsilon_k < \lambda)} (\epsilon_k - \lambda) . \tag{45}$$

The Bogoliubov transformation operates on the Hamiltonian Eq. (27). We now add to Eq. (27) a term $-\lambda N$ to conserve fermions. The transformation itself involves replacing the fermion operators by the combinations

$$\left.\begin{aligned} \alpha_k &= u_k C_{k+} - v_k C_{-k-}^\dagger \\ \beta_k &= u_k C_{-k-} + v_k C_{k+}^\dagger \end{aligned}\right\} \text{ or } \left\{\begin{aligned} C_{k+} &= u_k \alpha_k + v_k \beta_k^\dagger \\ C_{-k-} &= u_k \beta_k - v_k \alpha_k^\dagger \end{aligned}\right. \tag{46}$$

The spin dependence is explicitly indicated: $u_k = u_{-k}$, $v_k = v_{-k}$. Let u_k, v_k be real c numbers; then the α, β obey Fermi commutation rules if $u_k^2 + v_k^2 = 1$. The transformation of variables is then canonical. Notice that the transformation involves exactly the pairing of electrons which was found to be important by Cooper. A particular choice of u_k and v_k which gives familiar results is

$$\begin{aligned} u_k &= 1 \quad \epsilon_k > \lambda \qquad & v_k &= 0 \quad \epsilon_k > \lambda \\ &\quad 0 \quad \epsilon_k < \lambda & &\quad 1 \quad \epsilon_k < \lambda \end{aligned} \tag{47}$$

With this choice, $\alpha_k^\dagger$ represents a creation operator for an electron $(k\ +)$ if $\epsilon_k > \lambda$, and for a hole $(-k\ -\ )$ if $\epsilon_k < \lambda$. Using Eq. (46), the transformation of the Hamiltonian Eq. (27) is straightforward, if tedious. For the time being, the Coulomb interaction term in Eq. (27) will be neglected. Now Eq. (27), minus the lattice Hamiltonian, simply represents a system of interacting fermions. For the time being, we simply rewrite the fermion terms in Eq. (27) in a very general fashion,

$$H' = \sum_{ks} (\epsilon_k - \lambda) C_{ks}^\dagger C_{ks} - \frac{1}{2} \sum \langle k_1 k_2 | G | k_1' k_2' \rangle C_{k_1}^\dagger C_{k_2}^\dagger C_{k_2'} C_{k_1'} , \tag{27a}$$

where it is understood that the interaction term $\langle k_1 k_2 | G | k_1' k_2' \rangle C_{k_1}^\dagger C_{k_1'}^\dagger C_{k_2'} C_{k_1'}$ will eventually be replaced by the BCS electron-electron interaction defined through Eq. (29), (30), and (31). With the

definitions

$$\xi_k = \epsilon_k - \lambda ,$$

$$\bar{\epsilon}_k = \epsilon_k - \sum_{k'} \left\langle k, k' \middle| \bar{G} \middle| k', k \right\rangle v_{k'}^2 , \tag{48}$$

$$\left\langle k, k' \middle| \bar{G} \middle| k', k \right\rangle = \left\langle k, -k' \middle| G \middle| -k', k \right\rangle + \left\langle k, k' \middle| G \middle| k', k \right\rangle - \left\langle k, k' \middle| G \middle| k, k' \right\rangle ,$$

$$\Delta_k = \sum_{k'} \left\langle k, -k \middle| G \middle| -k', k' \right\rangle u_{k'} v_{k'} ,$$

the Hamiltonian Eq. (27a) becomes

$$H' = u + H_{11} + H_{20} + H_{int} ,$$

$$u = \sum_k \left\{ 2 \xi_k v_k^2 - u_k v_k \Delta_k + \sum_{k'} \left\langle kk' \middle| \bar{G} \middle| k'k \right\rangle v_{k'}^2 \right\},$$

$$H_{11} = \sum_k \left[\xi_k (u_k^2 - v_k^2) + 2 u_k v_k \Delta_k \right] \left[\alpha_k^\dagger \alpha_k + \beta_k^\dagger \beta_k \right],$$

$$H_{20} = \sum_k \left[2 \xi_k u_k v_k - \Delta_k (u_k^2 - v_k^2) \right] \left[\alpha_k^\dagger \beta_k^\dagger + \beta_k \alpha_k \right], \tag{49}$$

where H_{int} contains terms of fourth order in the α, β and will be neglected. Since the u_k and v_k have not yet been determined, it is easy to diagonalize Eq. (49) by setting H_{20} equal to zero:

$$2 \xi_k u_k v_k - \Delta_k (u_k^2 - v_k^2) = 0 . \tag{50}$$

Using the normalization condition $u_k^2 + v_k^2 = 1$, it is easy to solve Eq. (50):

$$v_k^2 = \frac{1}{2} \left[1 - \frac{\xi_k}{\sqrt{\xi_k^2 + \Delta_k^2}} \right] \qquad j_k^2 = \frac{1}{2} \left[1 + \frac{\xi_k}{\sqrt{\xi_k^2 + \Delta_k^2}} \right] . \tag{51}$$

A determining equation for Δ_k can be obtained by substituting Eq. (51) in the definition for Δ_k:

$$\Delta_k = \frac{1}{2} \sum_{k'} \left\langle k, -k \middle| G \middle| -k', k' \right\rangle \frac{\Delta_{k'}}{\sqrt{\xi_k^2 + \Delta_k^2}} . \tag{52}$$

Now the Hamiltonian can be rewritten as

$$H' = \sum_k E_k (a_k^\dagger a_k + \beta_k^\dagger \beta_k) + U, \tag{53}$$

$$E_k = \xi_k (u_k^2 - v_k^2) + 2\Delta_k u_k v_k = \sqrt{\xi_k^2 + \Delta_k^2} .$$

This Hamiltonian represents a system of quasiparticles of energy E_k, plus a constant energy U.

We now determine Δ_k by using the BCS interaction Eq. (31)—replacing the sum by an integral in the usual fashion). Let

$$\langle k, -k | G | k', -k' \rangle = \frac{\overline{F}}{N(0)} , \quad |\xi_k|, |\xi_{k'}| \leq \hbar\overline{\omega} . \tag{54}$$

$$= 0 \qquad \text{otherwise.}$$

Then

$$\Delta_k \equiv \Delta = \widetilde{F} \int_0^{\hbar\overline{\omega}} \frac{\Delta}{\sqrt{\xi^2 + \Delta^2}} \, d\xi . \tag{55}$$

There are two solutions: $u_k v_k = 0$, leading to the representation (47) , (with $\overline{\epsilon}_k$ in place of ϵ_k) and representing a normal (nonsuperconducting) state. The other solution is found by evaluating the integral Eq. (55), and leads to

$$\Delta = \hbar\overline{\omega} \operatorname{cosech} \overline{F} \approx 2\hbar\overline{\omega} e^{-1/\overline{F}} . \tag{56}$$

The state represented by Eqs (51) and (56) is taken to be superconducting. We observe that the required ground state $\underline{\overline{\Phi}}_0$ such that $a_k \underline{\overline{\Phi}}_0 = \beta_k \underline{\overline{\Phi}}_0 = 0$, can be represented by

$$\underline{\overline{\Phi}}_0 = \prod_k (u_k + v_k C_{k+}^\dagger C_{-k-}^\dagger) |0\rangle . \tag{57}$$

This is easily verified by substituting the definitions (Eq.(46) of a_k, β_k in terms of the C, $C^\dagger$ in the above equation.

Having a ground state, we are in a position to evaluate energies of the normal and superconducting systems. Since the ground state is the quasiparticle vacuum, the only contribution to the energy comes from the term U in Eq. (49). It turns out that the energy difference between the superconducting and normal states is

$$E_s - E_N = -2\,N(0)\,(\hbar\bar{\omega})^2\; e^{-2/\overline{F}} \quad . \tag{58}$$

The superconducting state has a lower energy, and hence represents the stable ground state at temperature zero, as long as the net electron-electron interaction is attractive.

The probability that an electronic state is occupied is the expectation value of $C_{ks}^{\dagger} C_{ks}$, and is v_k^2. This probability, as a function of energy $\bar{\epsilon}_k$, looks something like a Fermi-Dirac distribution at a temperature slightly greater than zero.

For single quasiparticle excitations, the energy becomes $U + E_k$, where k is the quasiparticle in an excited state. This differs from the ground-state energy U by at least Δ, because of Eq. (53). Thus there is an energy gap for the elementary single quasiparticle excitations. We now turn to the BCS approach.

The BCS theory uses a variational technique on a Hartree-like trial wave function. In fact, the wave function used is exactly Eq. (57), the quasiparticle ground state designated in the section as ψ. Upon expansion of the operators, it is seen that this ground state represents a mixture of the electron vacuum with all possible combinations of occupied pair states. The trial function is chosen in this way to emphasize the importance of Cooper pairs. To ensure normalization, we choose $u_k^2 + v_k^2 = 1$; u_k, v_k real; $u_k = u_{-k}$, $v_k = v_{-k}$ (we could make the argument more general by allowing complex values, but variation of the phase factors leads only to the condition that these phases are arbitrary). The Hamiltonian again is Eq. (27a). We shall minimize the expectation value of this Hamiltonian as a function of the u_k, v_k, subject to the condition that the expectation value of the number of particles be fixed. This introduces the Lagrange multiplier λ again.

In order to perform the necessary algebra, it is useful to introduce the concept of a reduced ground state, defined as

$$\psi_k = \prod_{k'}{}' \; (u_{k'} + v_{k'}\, C_{k'+}^{\dagger} C_{-k'-}^{\dagger}) \; \Big| 0 \Big\rangle \, . \tag{59}$$

(term in k omitted)

This state is not occupied in the pair k. Ground states $\psi_{kk'}$ ··· reduced by more than one pair, are defined in an obvious extension of Eq. (59). Consider

the operations $C_{ks}^{\dagger}\psi$, $C_{ks}\psi$. The operators $C_{ks}^{\dagger}C_{ks}$ commute with all terms in ψ except the term $(u_k + v_k C_{k+}^{\dagger}C_{-k-}^{\dagger})$. Therefore consider

$$C_{k+}^{\dagger}(u_k + v_k C_{k+}^{\dagger}C_{-k-}^{\dagger})\psi_k : \tag{60a}$$

$$C_{k+}(u_k + v_k C_{k+}^{\dagger}C_{-k-}^{\dagger})\psi_k = \left[u_k C_{k+} + v_k (1 - C_{k+}^{\dagger}C_{k+})C_{-k-}^{\dagger}\right]\psi_k . \tag{60b}$$

In Eq. (60b), the destruction operator, commuted through the operators defining ψ_k, give the value zero operating on the electron vacuum $|0\rangle$. Therefore, the only nonzero part arises from the anticommutator,

$$C_{k+}\psi = v_k C_{-k-}^{\dagger}\psi_k . \tag{61}$$

Then the value of $C_{ks}^{\dagger}C_{ks}$ on ψ is easily found:

$$C_{ks}^{\dagger}C_{ks}\psi = v_k C_{ks}^{\dagger}C_{-k,-s}^{\dagger}\psi_k = \psi - u_k\psi_k . \tag{62}$$

Now,

$$\langle\psi \quad \psi_k\rangle = \langle\psi_k | (u_k + v_k C_{k+}C_{-k-})|\psi_k\rangle = u_k\langle\psi_k \quad \psi_k\rangle = u_k \tag{63}$$

(all ψ_k are normalized, as is easily seen); the expectation value of the number operator is

$$\langle\psi | C_{ks}^{\dagger}C_{ks} | \psi\rangle = \langle\psi | \psi - u_k\psi_k\rangle = 1 - u_k^2 = v_k^2 . \tag{64}$$

The interaction term in Eq. (27a) is handled in a similar fashion:

$$\langle k_1 k_2 | G | k_1' k_2'\rangle C_{k_1 s_1}^{\dagger} C_{k_2 s_2}^{\dagger} C_{k_2' s_2'} C_{k_1' s_1'} | \psi\rangle \tag{65}$$

$$= v_{k_1'} v_{k_2'} \langle k_1 k_2 | G | k_1' k_2'\rangle C_{k_1 s_1}^{\dagger} C_{k_2 s_2}^{\dagger} C_{-k_1', -s_1'}^{\dagger}$$

$$C_{-k_1', -s_1'}^{\dagger}\psi_{k_1' k_2'}\rangle .$$

It is obvious that this has zero expectation value unless the four creation operators can be combined into pair-state operators such as appear in Eq. (57). If this can be done, the resulting state combines with the corresponding part of ψ, which is of the form $v_{k_1} v_{k_2} C_{k_1 s_1}^{\dagger} C_{-k_1 s_1}^{\dagger} C_{k_2 s_2}^{\dagger} C_{-k_2 s_2}^{\dagger} | \psi_{k_1 k_2})$. There are six ways of forming pair states in (65). The final result is

$$\langle H_{int} \rangle = \sum_{kk'} u_{kk'} v_k^2 v_{k'}^2 - 2 \sum_{kk'} u_k v_k u_{k'} v_{k'} V_{kk'} , \tag{66}$$

where

$$U_{kk'} = \langle k\uparrow\, k'\uparrow | G | k\uparrow\, k'\uparrow \rangle - \langle k\uparrow\, k'\uparrow | G | k'\uparrow\, k\uparrow \rangle + \langle k\uparrow\, -k'\downarrow | G | k\uparrow\, -k'\downarrow \rangle - \langle k\uparrow\, -k'\downarrow | G | -k'\downarrow\, k\uparrow \rangle$$

$$- V_{kk'} = \langle k\uparrow\, -k\downarrow | G | k'\uparrow\, -k'\downarrow \rangle - \langle k\uparrow\, -k\downarrow | G | -k'\downarrow\, k\uparrow \rangle . \tag{67}$$

Only $V_{kk'}$ involves matrix elements between Cooper pairs. In order to maintain the emphasis on these pairs, we define a new energy

$$e(k) = \epsilon_k + \sum_{k'} U_{kk'} v_{k'}^2 , \tag{68}$$

and we ignore the dependence of $e(k)$ on $v_{k'}^2$. In what follows, we use the term ϵ_k for $e(k) - \lambda$. The expression to be minimized is

$$W_0 = 2 \sum_k \epsilon_k v_k^2 - \sum_{kk'} u_k v_k u_{k'} v_{k'} V_{kk'} + \sum_k \lambda_k (u_k^2 + v_k^2) \tag{69}$$

(λ_k is a Lagrange multiplier to assure that $u_k^2 + v_k^2 = 1$). Taking the variation

$$-2 v_k \sum_{k'} u_{k'} v_{k'} V_{kk'} + 2 \lambda_k u_k = 0; \tag{70a}$$

$$4 \epsilon_k v_k - 2 u_k \sum_{k'} u_{k'} v_{k'} V_{kk'} + 2 \lambda_k v_k = 0: \tag{70b}$$

multiply (70a) by v_k, (70b) by u_k, and subtract:

$$-2(v_k^2 - u_k^2) \sum_{k'} u_{k'} v_{k'} V_{kk'} - 4 u_k v_k \epsilon_k = 0 . \tag{71}$$

With the following definitions:

$$\chi(k) = u_k v_k\ ,\quad E_k = \epsilon_k \Big/ (1-2v_k^2),\quad F(k) = \sum_{k'} V_{kk'}\,\chi(k')\ , \tag{72}$$

(71) becomes

$$\chi(k) = \frac{1}{2}\ F(k) \,/\, E_k\ ; \tag{73}$$

since

$$v_k^2 = \frac{1}{2}\ (1 - \epsilon_k/E_k),\ \chi^2(k) = \frac{1}{4}\ (1 - \epsilon_k^2/E_k^2) = \frac{1}{4}\ F(k)^2/E_k^2\ .$$

Then

$$E_k = \sqrt{\epsilon_k^2 + F(k)^2}\ , \tag{74}$$

$$\chi(k) = \frac{1}{2}\ F(k) \,/\, \sqrt{\epsilon_k^2 + F(k)^2}\ , \tag{75}$$

and Eq. (75) is the determining equation for $F(k)$, analogous to Eq. (52) for Δ.

At this point, it is interesting to take the Fourier transform of Eq. (75). This is

$$\chi(r) = -\ \frac{1}{2} \int G(r-r')\ V(r')\ \chi(r')dV';\quad G(r) = \frac{1}{(2\pi)^3} \int \frac{e^{(k\cdot r}\ d^3k}{\sqrt{\epsilon_k^2 + F(k)^2}}\ . \tag{76}$$

This bears a strong resemblance to the integral form of the Schrödinger equation. If $F(k) = 0$, and the $|\epsilon_k|$ is replaced with ϵ_k, it is in fact the Schrödinger equation. If the integral were restricted to $k > k_f$, one gets the Brueckner theory. The equation can be linearized by replacing $F(k)$ by $F(k_f)$, leading to an eigenvalue problem. The simplicity and strong resemblance of Eq. (76) to the Schrödinger equation suggest that it may be derivable from first principles, although this has not yet been accomplished.

As previously, replace $V_{kk'}$ by $\overline{F}/N(0)$, $|\epsilon_k|, |\epsilon_{k'}| < \hbar\overline{\omega}$; $V_{kk'}$ is zero otherwise. Then

$$\overline{F}(k) \equiv \epsilon_0 = (\overline{F}/N(0)) \sum_{|\epsilon_{k'}| < \hbar\overline{\omega}} u_{k'} v_{k'}\ , \tag{77}$$

$$v_k^2 = \frac{1}{2}\left[1 - \frac{\epsilon_k}{\sqrt{\epsilon_k^2+\epsilon_0^2}}\right], \tag{78}$$

and (78) is precisely the same as in the Bogoliubov theory. Also, (75) is exactly the same as (52), and leads to the solution

$$\epsilon_0 = \hbar\bar{\omega}\,\mathrm{cosech}(1/\bar{F}) \simeq 2\hbar\bar{\omega}\, e^{-1/\bar{F}}. \tag{79}$$

Equation (71) also admits the normal solution $u_k v_k = 0$. The energy difference between the normal and superconducting states is again given by Eq. (58).

So far we have only discussed the ground state at zero temperature. There is, of course, a complete set of excited states, orthogonal to ground state ψ. One such state involves the breaking up of Cooper pairs, and can be written

$$\psi_{k'k''}^{(\mathrm{exc})} = C_{-k'-}^{\dagger} C_{k''+}^{\dagger} \psi_{k'k''}. \tag{80}$$

This is obviously orthogonal to ψ, if $k'' \neq k'$. The energy difference between the excited state and the ground state is easy to find; we simply subtract the energy of the missing pairs k', k'' and add the energies of the single electrons $\epsilon_{k'}$, $\epsilon_{k''}$. This results in

$$W_{k'k''} - W_0 = \epsilon_{k'}(1 - 2v_{k'}^2) + \epsilon_{k''}(1-2v_{k''}^2) + 2\frac{\bar{F}}{N(0)}\sum_k u_k v_k (u_{k'}v_{k'}+u_{k''}v_{k''})$$

$$= E_{k'} + E_{k''} \geq 2\epsilon_0. \tag{81}$$

This illustrates the energy gap for single-particle excitations. This gap comes about only in the superconducting state ($\epsilon_0 > 0$). The existence of the gap is precisely the behavior we would expect in order for metastable current states to exist, since single-particle excitations extremely close to the ground state would provide a mechanism for dissipation of the currents. There are other types of excited states, notably excited pair states,

$$\psi_{k'}^{(\mathrm{exc})} = (u_{k'} C_{k'+}^{\dagger} C_{-k'-}^{\dagger} - v_{k'})\psi_{k'} = \frac{u_{k'}}{v_{k'}}\psi - \frac{1}{v_{k'}}\psi_{k'} \tag{82}$$

This is orthogonal to the ground state,

$$\left\langle \psi \left| \psi_{k'}^{(exc)} \right\rangle = \left\langle \psi \right| \frac{u_{k'}}{v_{k'}} \psi - \frac{1}{v_{k'}} \psi_{k'} \right\rangle = \frac{u_{k'}}{v_{k'}} - \frac{u_{k'}}{v_{k'}} = 0. \qquad (83)$$

The energy difference between this state and the ground state is $2E_{k'}$, again exhibiting the energy gap (this time for an excited pair).

We end this section with a brief word on Coulomb effects. At first sight, the Coulomb terms in the full Hamiltonian Eq. (21) appear to give troublesome divergences as $k \longrightarrow 0$. The removal of these divergences is extremely difficult, but has been accomplished in a rather satisfactory way (Bardeen and Pines; Sawada; Gell-Mann and Brueckner). The Coulomb interaction is assumed to be cut off below a certain wave number k_c (which is of the order of k_f). The long-range modes ($k < k_c$) correspond to collective plasma motion. The existence of superconductivity requires a net attractive interaction, and, since the Coulomb energy is repulsive, it tends to overcome the attractive interaction $\overline{F}/N(0)$. A simple criterion can be obtained, however, by averaging the Coulomb interaction, and using it as a constant term in the Hamiltonian. This averaging is accomplished sufficiently well by using k_f in the Coulomb term. Then the criterion for superconductivity (a net attractive interaction) can be written

$$\overline{F}/N(0) - \frac{2\pi e^2}{k_f^2} > 0 . \qquad (84)$$

VI. THERMODYNAMICS

So far, all our considerations have applied only to zero temperature. At temperatures different from zero, the entire problem must be solved anew, whether one uses the BCS or Bogoliubov method. This is because either the wave function, or the Hamiltonian, or both, are undetermined; they depend on a set of parameters u_k, v_k. In statistical mechanics, these parameters cannot be determined independently of the temperature and the chemical potential, both of which appear as Lagrange multipliers. We have already used the chemical potential as a Lagrange parameter in the zero-temperature problem. The temperature is now introduced, and we attempt to minimize the free energy $F = W - TS - \lambda N$. The steps involved are most easily conceived in the Bogoliubov theory, which is a theory of non interacting quasiparticles. However, we use the real-particle Hamiltonian Eq. (27a); the ground state is the electron vacuum; and excited states are generated by operating on the electron vacuum with $\alpha_k^\dagger, \alpha_k, \beta_k^\dagger, \beta_k$. These excited states form a complete orthonormal set. Notice, by the way, that the Hamiltonian Eq. (53) already contains the chemical potential λ.

Since we are dealing with noninteracting quasifermions, the usual Fermi-Dirac distribution functions can be introduced at one. Let f_k be the average number of quasiparticles in state k (using the grand canonical ensemble); then the entropy is

$$S = -2k \sum_{k'} f_{k'} \log f_{k'} + (1-f_{k'}) \log (1-f_{k'}) . \tag{85}$$

If there is no quasiparticle in a state k, s, then the electron expectation kinetic energy contains the term $v_k^2 \left(\frac{\hbar k}{2m}\right)^2$, since the wave function $\Pi \alpha_k |0\rangle$ or $\Pi \beta_k |0\rangle$ contains the factor $\pm v_k C_{\pm k\pm}^\dagger$ —see (46)— which means that the probability of a real electron in k, s is v_k^2. Likewise, if a quasiparticle state is occupied, the wave function contains the factor $u_k C_{\pm k\pm}^\dagger$ and the probability for a real electron is u_k^2. These two configurations occur respectively with statistical weights $(1 - f_k)$, f_k, and the total expectation kinetic energy is

$$2\Sigma \left(\frac{\hbar k}{2m}\right)^2 \left[u_k^2 f_k + v_k^2 (1 - f_k)\right] . \tag{86}$$

The interaction terms Eq. (67) are handled similarly. If there is no quasiparticle in a state k, s, the probability that there is a Cooper pair in the states $k, s; -k, -s$ is $u_k v_k$. If there is a quasiparticle, the probability is $-u_k v_k$; and again the statistical weights are respectively $(1 - f_k)$, f_k. The interaction $V_{kk'}$ in Eq. (67) which connects Cooper pairs thus yields a contribution

$$\sum_{kk'} V_{kk'}\, u_k v_k u_{k'} v_{k'}\, (1 - 2 f_k)(1 - 2f_{k'}) . \tag{87}$$

Similarly, the interaction $U_{kk'}$ leads to a contribution

$$\sum_{kk'} U_{kk'} \left[u_k^2 f_k + v_k^2 (1-f_k)\right] \left[u_{k'}^2 f_{k'} + v_{k'}^2 (1 - f_{k'})\right]. \tag{88}$$

The total free energy takes the form

$$F = 2 \sum_k \left[(\hbar^2 k^2/2m) - \lambda\right]\left[f_k + (1 - 2 f_k) h_k\right] + \sum_{kk'} U_{kk'} \left[f_k + (1-2 f_k) h_k\right] \cdot \left[f_{k'} + (1 - 2 f_{k'}) h_{k'}\right] + \sum_{kk'} V_{kk'} \left[h_k (1-h_k) h_{k'} (1-h_{k'})\right]^{1/2} (1-2f_k)(1-2f_{k'}) - TS, \tag{89}$$

where we have replaced v_k^2 by h_k, u_k^2 by $(1 - h_k)^{1/2}$. Define

$$\chi(k) = \left[h_k(1-h_k)\right]^{1/2} (1-2f_k); \quad F(k) = \sum_{k'} V_{kk'} \chi(k'); \tag{90}$$

$$\epsilon(k) = \frac{\hbar^2 k^2}{2m} - \lambda + \sum_{k'} U_{kk'} \left[f_{k'} + (1-2f_{k'}) h_{k'}\right],$$

$$E_k = \sqrt{\epsilon(k)^2 + F(k)^2},$$

Then upon varying with respect to h_k, f_k we find

$$f_k = (e^{\beta E_k} + 1)^{-1}; \tag{91}$$

$$\chi(k) = -\frac{1}{2}\,\frac{\tanh\frac{1}{2}\beta E_k}{E_k}\sum_{k'} V_{kk'}\,\chi(k') \quad . \tag{92}$$

This differs from Eq. (75) by the temperature-dependent multiplier, and the definitions Eq. (90), which differ from Eq. (72) somewhat. As usual, replace $V_{kk'}$ by a constant $\overline{F}/N(0)$ for $|\epsilon(k)|$, $|\epsilon(k')| \leq \hbar\bar{\omega}$. Calling $F(k) = \epsilon_0(T)$, we replace the sum by an integral to get

$$\frac{1}{\overline{F}} = \int_0^{\hbar\bar{\omega}} \frac{d\epsilon}{\sqrt{\epsilon^2 + \epsilon_0^2}} \tanh\left(\frac{\beta}{2}\sqrt{\epsilon^2 + \epsilon_0^2}\right) \quad . \tag{93}$$

$\epsilon_0(T)$ is half the energy gap. There is a temperature T_c at which $\epsilon_0(T_c)$ vanishes; this is identified with the transition temperature. Above this temperature, Eq. (93) has no real positive solution for ϵ_0. Setting $\epsilon_0 = 0$, we get

$$\frac{1}{\overline{F}} = \int_0^{\hbar\bar{\omega}} \frac{d\epsilon}{\epsilon} \tanh\left(\frac{\beta_c \epsilon}{2}\right), \tag{94}$$

which is solved by

$$kT_c = 1.14\,\hbar\bar{\omega}\; e^{-1/\overline{F}} \quad , \quad kT_c << \hbar\bar{\omega} \quad . \tag{95}$$

This can be related to the energy gap at zero temperature:

$$2\,\epsilon_0(0)/k\,T_c = 3.50 \quad . \tag{96}$$

This value of 3.5 is in reasonably good agreement with experimental data. Note that Eq. (95) yields the isotope effect, since $\hbar\bar{\omega} \approx M^{-1/2}$.

The critical field $H_c(T)$ may also be found from the above thermodynamics. One need only evaluate the free energy for the normal state. The details of the calculation will not be gone through here. We quote the BCS results:

$$H_c(T)^2/8\pi = N(0)\,(\hbar\bar{\omega})^2\left\{\left[1 + (\hbar\bar{\omega})^{-2}\,\epsilon_0^2(T)\right]^{1/2} - 1\right\} \tag{97}$$
$$-(\pi^2/3)\,N(0)\,(kT)^2\left\{1 - \beta^2\int_0^{\infty} d\epsilon\left[\frac{2\epsilon^2 + \epsilon_0^2}{(\epsilon^2+\epsilon_0^2)^{1/2}}\right] f\left(\beta\sqrt{\epsilon^2+\epsilon_0^2}\right)\right\}.$$

It is also possible to find the specific heats. The electronic specific heat is given by the formula

$$C_e = T \frac{dS}{dT} = - \beta \frac{dS}{d\beta} . \tag{98}$$

Using Eqs. (85) and (91), we get

$$C_{es} = - 4k\beta \sum_{k>k_F} \beta (\epsilon_k^2 + \epsilon_0^2(T))^{1/2} \frac{df_k}{d\beta} \tag{99}$$

$$= 4k\beta^2 \sum_{k>k_F} f_k (1-f_k) \left\{ \epsilon_k^2 + \epsilon_0^2(T) + \frac{\beta}{2} \frac{d\epsilon_0^2(T)}{d\beta} \right\} .$$

The normal specific heat C_{en} is just Eq. (99) with $\epsilon_0(T)$ set equal to zero. At T_c, where $\epsilon_0(T_c)$ is zero, we may subtract the two specific heats to get

$$C_{es} - C_{en} \Big|_{T_c} = 2k\beta_c^3 \sum_{k>k_F} f_k (1-f_k) \frac{d\epsilon_0^2(T)}{d\beta} \Big|_{T_c}$$

$$= kN(0) \beta_c^2 \frac{d\epsilon_0^2(T_c)}{d\beta} . \tag{100}$$

Numerical evaluation leads to

$$\frac{d\epsilon_0^2(T_c)}{d\beta} = 10.2 \beta_c^{-3} ; \quad (C_{es}-C_{en}) / C_{en} = 1.52 . \tag{101}$$

For $T << T_c$, the specific heat has an exponential form, as observed experimentally, which indicates the single-particle energy gap,

$$\frac{C_{es}}{C_{en}} = 8.5 e^{-1.44 T_c/T} \tag{102}$$

The first experimental knowledge about superconductors was that they could sustain currents for indefinite periods of time. According to the Bloch theorem, the ground state of a quantum-mechanical system cannot carry

current; if a state carries current, there is another state with lower energy. For current is a macroscopic phenomenon, involving the correlation of many electrons. Since this current must be carried by an excited state, we shall assume that excited states of non-zero total momentum carry the current, and to exhibit the macroscopic correlation, we assume that all excited states carry the same net momentum. The excited states are of the type Eq. (80),

$$\psi^{(\mathrm{exc})} = \left(\prod_{i=1}^{J} C_{q-k_i-}^{\dagger} C_{k_i+}^{\dagger} \right) \psi_{k_1 k_2 \cdots k_J}, \tag{103}$$

where q is the net momentum of the excited states.

This can be interpreted in another way. Suppose we observe the superconductor from a frame of reference moving at velocity v. Then Cooper pair states, of zero momentum in the rest frame, all assume the same non-zero momentum in the moving frame. The situation in the rest frame would correspond to pair excitations of the type of Eq. (82). These excitations have an energy gap from the ground state. In the moving frame, for sufficiently slow velocities, this gap will remain essentially unchanged. However, the Bloch energies determined by the lattice interaction will change, since the lattice now appears (in the moving frame) to be moving. Under the transformation $\underset{\sim}{x}' = \underset{\sim}{x} - \underset{\sim}{v}t$, the time operator $ih\,\partial/\partial t$ becomes $ih\left(\frac{\partial}{\partial t} - \underset{\sim}{v}_0 \nabla'\right)$ or $ih\,\frac{\partial}{\partial t} + \underset{\sim}{v}_0 \underset{\sim}{p}$. This last term appears as an additional energy in the Schrödinger equation for the interaction. If the lattice-electron interaction energy is E_k in the rest frame, it is $E_k + \hbar \underset{\sim}{k} \cdot \underset{\sim}{v}$ in the moving frame. The lower this energy is, the more probable it is that an electron will interact with the lattice, giving up energy. The extreme case is when $\underset{\sim}{k}$ is opposite to $\underset{\sim}{v}$. If the total interaction energy $E_k - \hbar kv$ is less than zero, interactions will surely take place. These interactions, just as in the theory of metals at normal temperatures, constitute the resistance of the metal to electric current. A superconductor, therefore, should not partake in such interactions, which means that $E_k > \hbar kv$. In the superconducting state, the minimum pair excitation energy is $2\epsilon_0$, so that E_k/k is never zero, and in fact is never extremely small. It is therefore possible to sustain excited states of net momentum $\hbar q$ (corresponding to moving the entire system at velocity v) if q is less than some critical

wave number. This corresponds, in a way, to the criterion for Čerenkov radiation. An electron can radiate Čerenkov radiation only if its velocity exceeds the phase velocity of light in the medium (not the group velocity). The phase velocity for electrons in superconductors is $E_k/\hbar k$; the criterion that this is greater than v implies that there are no "Čerenkov" processes in the superconductor.

VII. ELECTRODYNAMICS

In this section, we establish the existence of the Meissner effect. The considerations below are not entirely rigorous, since they are not gauge-invariant. On the other hand, a completely gauge-invariant theory (involving the full Coulomb interaction, including plasma modes) leads to the same conclusion.

Phenomenologically, the Meissner effect follows from the London equation,

$$\underset{\sim}{J}(\underset{\sim}{r}) = - \frac{n e^2}{m c} \underset{\sim}{A}(\underset{\sim}{r}) , \quad m = \frac{n}{v} . \tag{104}$$

Therefore, we need only establish Eq. (104) to establish the Meissner effect. We use the Fourier transform of Eq. (104), and prove that, in the limit $|q| \longrightarrow 0$,

$$\underset{\sim}{j}(\underset{\sim}{q}) \longrightarrow \text{const. } \underset{\sim}{a}(\underset{\sim}{q}) \left[\underset{\sim}{a}(\underset{\sim}{q}) = \frac{1}{(2\pi)^{3/2}} \int \underset{\sim}{A}(\underset{\sim}{r}) \, e^{-i\underset{\sim}{q}\cdot\underset{\sim}{r}} \, d^3\underset{\sim}{r} \right] . \tag{105}$$

The gauge $\nabla \cdot \underset{\sim}{A} = 0$ will be used. In the field-theoretic formulation, the current operator $\underset{\sim}{J}(\underset{\sim}{r})$ is given by

$$\underset{\sim}{J}(\underset{\sim}{r}) = \frac{e\hbar}{2\,i m} \left\{ \psi^*(\underset{\sim}{r}) \, \nabla\psi(\underset{\sim}{r}) - \left[\nabla\psi^*(\underset{\sim}{r}) \right] \psi(\underset{\sim}{r}) \right\} \tag{106}$$

$$- \frac{e^2}{mc} \psi^*(\underset{\sim}{r}) \, \underset{\sim}{A}(\underset{\sim}{r}) \psi(\underset{\sim}{r}) = \underset{\sim}{J}_p(\underset{\sim}{r}) + \underset{\sim}{J}_d(\underset{\sim}{r}) ,$$

where

$$\psi(\underset{\sim}{r}) = \frac{1}{\sqrt{v}} \sum_{ks} C_{ks} \, u_s \, e^{i\underset{\sim}{k}\cdot\underset{\sim}{r}} . \tag{107}$$

Here u_s is a basis spinor and V is the volume of quantization. If $\underset{\sim}{A} = 0$, both $\underset{\sim}{J}_p$ and $\underset{\sim}{J}_d$ are zero. In proposing their phenomenological theory, the Londons mentioned that if the wave function ψ were rigid, that is, unaffected by the perturbation $\underset{\sim}{A}$, the $\underset{\sim}{J}_p$ would still be zero, and $\underset{\sim}{J}_d$ would be proportional to $\underset{\sim}{A}$, thus establishing the London equations.

The perturbing interaction, in a gauge in which $\nabla \cdot \underset{\sim}{A} = 0$, is

$$H_I = \frac{1}{c}\int d^3\underset{\sim}{r}\ \underset{\sim}{J}(\underset{\sim}{r}) \cdot \underset{\sim}{A}(\underset{\sim}{r}) = H_I' + 0\,(\underset{\sim}{A}^2);$$

$$H_I' = \frac{e\hbar}{mcV}\int d^3\underset{\sim}{r} \sum_{kqs} C_{k+q,s}^{\dagger} C_{ks}\, e^{-i\underset{\sim}{q}\cdot\underset{\sim}{r}}\, \underset{\sim}{k}\cdot\underset{\sim}{A}(r) \qquad (108)$$

$$= \frac{(2\pi)^3 e\hbar}{mcV} \sum_{kqs} C_{k+q,s}^{\dagger} C_{ks}\, \underset{\sim}{a}(q)\cdot\underset{\sim}{k}.$$

To first order of perturbation theory, the perturbed wave function $\underline{\Phi}'$ is given by

$$\underline{\Phi}^1 = \sum_{i\neq 0} \frac{\langle \psi_i | H_I' | \psi_0 \rangle}{E_0 - E_i}\, \psi_i + \psi_0 = \underline{\Phi}_1 + \psi_0\,, \qquad (109)$$

where ψ_0 is the BCS ground state; ψ_i is an excited state. To first order in A, the diamagnetic current expectation value is

$$\left\langle \underset{\sim}{J}_d(\underset{\sim}{r}) \right\rangle = -\frac{e^2 \underset{\sim}{A}(r)}{mcV} \left\langle \psi_0 \left| \sum_{kqs} C_{k+q,s}^{\dagger} C_{k,s}\, e^{-i\underset{\sim}{q}\cdot\underset{\sim}{r}} \right| \psi_0 \right\rangle. \qquad (110)$$

The operator in Eq. (110) has no diagonal terms unless $\underset{\sim}{q} = 0$, in which case the operator becomes the number operator $N = \Sigma\, C_{ks}^{\dagger} c_{ks}$. Then the diamagnetic current is

$$\underset{\sim}{J}_d(\underset{\sim}{r}) = -\frac{e^2}{mc}\left(\frac{N}{V}\right) \underset{\sim}{A}(\underset{\sim}{r})\,, \qquad (111)$$

which is just the London equation. It still remains to be shown that $\lim_{q\to 0} \underset{\sim}{j}_p(\underset{\sim}{q}) = 0$. We must now use the perturbed wave function (109). Using the first part of the current operator Eq. (106) we get

$$\left\langle \underset{\sim}{J}_p(\underset{\sim}{r}) \right\rangle = \left\langle \psi_0 \left| \frac{e\hbar}{2mV} \sum_{kqs} C_{k+q,s}^{\dagger} C_{ks} \, e^{-i\underset{\sim}{q}\cdot\underset{\sim}{r}} (2\underset{\sim}{k}+\underset{\sim}{q}) \right| \underline{\Phi}_1 \right\rangle$$

$$+ \left\langle \underline{\Phi}_1 \left| \frac{e\hbar}{2mV} \sum_{kqs} C_{k+q,s}^{\dagger} C_{ks} \, e^{-i\underset{\sim}{q}\cdot\underset{\sim}{r}} (2\underset{\sim}{k}+\underset{\sim}{q}) \right| \psi_0 \right\rangle$$

$$= \frac{e^2\hbar^2}{2m^2c^2V^2} (2\pi)^{3/2} \sum_{i\neq 0} \sum_{kqs} \sum_{k'q's'} (2\underset{\sim}{k}+\underset{\sim}{q}) (\underset{\sim}{k}'\cdot\underset{\sim}{a}(q') \, e^{-i\underset{\sim}{q}\cdot\underset{\sim}{r}}$$

$$\times \left\langle \psi_0 \left| C_{k'+q',s'}^{\dagger} C_{k's'} \right| \psi_i \right\rangle \left\langle \psi_i \left| C_{k+q,s}^{\dagger} C_{ks} \right| \psi_0 \right\rangle (E_0 - E_i)^{-1} + \text{C.C.} \tag{112}$$

Take the Fourier transform:

$$\underset{\sim}{j}_p(\underset{\sim}{q}) = \frac{e^2\hbar^2}{2m^2c^2V^2} \sum_{i\neq 0} \sum_{ks} \sum_{k'q's'} (2\underset{\sim}{k}+\underset{\sim}{q}) \, \underset{\sim}{k}'\cdot\underset{\sim}{a}(\underset{\sim}{q}')$$

$$\times \left\langle \psi_0 \left| C_{k'+q',s'}^{\dagger} C_{k's'} \right| \psi_i \right\rangle \left\langle \psi_i \left| C_{k+q,s}^{\dagger} C_{ks} \right| \psi_0 \right\rangle (E_0 - E_i)^{-1} + \text{C.C.} \tag{113}$$

At this point, notice that the vanishing of this quantity in the limit $q \longrightarrow 0$ depends crucially on the behavior of the energy denominators. None of these denominators vanishes in the superconducting state, because of the excited single-particle energy gap.

For the excited states ψ_i, we obviously must use the single-particle excited states Eq. (80). It is, however, somewhat simpler to use Bogoliubov excited states. At a temperature other than zero, the population of these excited states f_k is known from the previous thermodynamic considerations. Then the sum in (113) can be replaced by an integral. It turns out that

$$\underset{\sim}{j}_p(\underset{\sim}{q}) = \frac{e^2\hbar^2}{m^2C} \left(\frac{1}{2\pi^3} \right) \int d^3\underset{\sim}{k} (\underset{\sim}{k}+\underset{\sim}{q}) \, (\underset{\sim}{k}\cdot\underset{\sim}{a}(\underset{\sim}{q})) \, L(\epsilon_k, \epsilon_{k+q}) , \tag{114}$$

where

$$\lim_{q \longrightarrow 0} L = \beta \, e^{\beta\epsilon_k} \left(1 + e^{\beta\epsilon_k} \right)^{-2} \left(\beta = \frac{1}{kT} \right) . \tag{115}$$

Then

$$\lim_{q \to 0} \underset{\sim}{j}_p(\underset{\sim}{q}) = \frac{n e^2}{mc} \left(1 - \frac{\Lambda}{\Lambda_T}\right) \underset{\sim}{a}(\underset{\sim}{q}) , \tag{116}$$

where

$$\Lambda = m/n e^2 ;$$

$$\Lambda_T = \Lambda \left(1 + \frac{\beta}{\epsilon_0} \frac{d\epsilon_0}{d\beta}\right) , \tag{117}$$

and

$$\Lambda/\Lambda_T = 1 - 2 \int_0^\infty e^{(y^2 + \beta^2 \epsilon_0^2)} \left[1 + e^{(y^2 + \beta^2 \epsilon_0^2)}\right]^{-2} dy . \tag{118}$$

At $T = 0$, $\lim_{q \to 0} \underset{\sim}{j}_p(\underset{\sim}{q}) = 0$. For $T < T_c$, $\underset{\sim}{j}_p(\underset{\sim}{q})$ does not approach zero, but it is still proportional to $\underset{\sim}{a}(q)$, so that the London equations are still valid (with a slightly different penetration depth). For finite $\underset{\sim}{q}$, it can be shown that the total superconducting current is

$$\underset{\sim}{J}_s(\underset{\sim}{r}) = - (4\pi c \Lambda_T \hbar v_0)^{-1} 3\pi \epsilon_0(0) \int d^3\underset{\sim}{r}' \, J(\underset{\sim}{R}, T) \, \underset{\sim}{R} \, \underset{\sim}{R} \cdot \underset{\sim}{A}(\underset{\sim}{r}') \, R^{-4} , \tag{119}$$

similar to the Pippard equation, if $J(R, T) = e^{-R/\xi_0}$. In (119), $\underset{\sim}{R} = \underset{\sim}{r} - \underset{\sim}{r}'$; v_0 is the velocity of an electron at the top of the Fermi sphere.

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