Chapter 10: Superconductivity

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1 Introduction

From what we have learned about transport, we know that there is no such thing as an ideal ($\rho = 0$) conventional conductor. All materials have defects and phonons (and to a lesser degree of importance, electron-electron interactions). As a result, from our basic understanding of metallic conduction $\rho$ must be finite, even at $T = 0$. Nevertheless many superconductors, for which $\rho = 0$, exist. The first one Hg was discovered by Onnes in 1911. It becomes superconducting for $T < 4.2^\circ K$. Clearly this superconducting state must be fundamentally different than the "normal" metallic state. I.e., the superconducting state must be a different phase, separated by a phase transition, from the normal state.

1.1 Evidence of a Phase Transition

Evidence of the phase transition can be seen in the specific heat (See Fig. 1). The jump in the superconducting specific heat $C_s$ indicates that there is a phase transition without a latent heat
Figure 1: The specific heat of a superconductor $C_S$ and normal metal $C_n$. Below the transition, the superconductor specific heat shows activated behavior, as if there is a minimum energy for thermal excitations. (i.e. the transition is continuous or second order). Furthermore, the activated nature of $C$ for $T < T_c$

$$C_s \sim e^{-\beta\Delta}$$

gives us a clue to the nature of the superconducting state. It is as if excitations require a minimum energy $\Delta$.

1.2 Meissner Effect

There is another, much more fundamental characteristic which distinguishes the superconductor from a normal, but ideal, con-
ductor. The superconductor expels magnetic flux, ie., \( B = 0 \) within the bulk of a superconductor. This is fundamentally different than an ideal conductor, for which \( \dot{B} = 0 \) since for any closed path

\[
0 = IR = V = \int \mathbf{E} \cdot d\mathbf{l} = \int_S \nabla \times \mathbf{E} \cdot d\mathbf{S} = -\frac{1}{c} \int_S \frac{\partial \mathbf{B}}{\partial t} \cdot d\mathbf{S}, \quad (2)
\]

or, since \( S \) and \( C \) are arbitrary

\[
0 = -\frac{1}{c} \mathbf{B} \cdot S \Rightarrow \dot{\mathbf{B}} = 0 \quad (3)
\]

Thus, for an ideal conductor, it matters if it is field cooled or zero field cooled. Where as for a superconductor, regardless of the external field and its history, if \( T < T_c \), then \( B = 0 \) inside the bulk. This effect, which uniquely distinguishes an
ideal conductor from a superconductor, is called the Meissner effect.

For this reason a superconductor is an ideal diamagnet. I.e.

$$ B = \mu H = 0 \Rightarrow \mu = 0 \quad M = \chi H = \frac{\mu - 1}{4\pi} H $$ (4)


\[ \chi_{SC} = -\frac{1}{4\pi} \]

I.e., the measured \( \chi \), Fig. 4, in a superconducting metal is very large and negative (diamagnetic). This can also be interpreted as the presence of persistent surface currents which maintain a magnetization of

\[ \mathbf{M} = -\frac{1}{4\pi} H_{\text{ext}} \]

in the interior of the superconductor in a direction opposite to the applied field. The energy associated with this currents

Figure 4: LEFT: A sketch of the magnetic susceptibility versus temperature of a superconductor. RIGHT: Surface currents on a superconductor are induced to expel the external flux. The diamagnetic response of a superconductor is orders of magnitude larger than the Pauli paramagnetic response of the normal metal at \( T > T_C \).
increases with $H_{\text{ext}}$. At some point it is then more favorable (ie., a lower free energy is obtained) if the system returns to a normal metallic state and these screening currents abate. Thus there exists an upper critical field $H_c$.

Figure 5: Superconductivity is destroyed by either raising the temperature or by applying a magnetic field.

2 The London Equations

London and London derived a phenomenological theory of superconductivity which correctly describes the Meissner effect. They assumed that the electrons move in a frictionless state, so that
m\dot{\mathbf{v}} = -e\mathbf{E} \tag{7}

or, since \( \frac{\partial j}{\partial t} = -en_s\dot{\mathbf{v}} \),

\[
\frac{\partial j_s}{\partial t} = \frac{e^2n_s}{m}\mathbf{E} \quad \text{(First London Eqn.)} \tag{8}
\]

Then, using the Maxwell equation

\[
\nabla \times \mathbf{E} = -\frac{1}{c} \frac{\partial \mathbf{B}}{\partial t} \Rightarrow \frac{m}{n_se^2} \nabla \times \frac{\partial j_s}{\partial t} + \frac{1}{c} \frac{\partial \mathbf{B}}{\partial t} = 0 \tag{9}
\]

or

\[
\frac{\partial}{\partial t} \left( \frac{m}{n_se^2} \nabla \times \mathbf{j}_s + \frac{1}{c} \mathbf{B} \right) = 0 \tag{10}
\]

This described the behavior of an ideal conductor (for which \( \rho = 0 \)), but not the Meissner effect. To describe this, the constant of integration must be chosen to be zero. Then

\[
\nabla \times \mathbf{j}_s = -\frac{n_se^2}{mc} \mathbf{B} \quad \text{(Second London Eqn.)} \tag{11}
\]

or defining \( \lambda_L = \frac{m}{n_se^2} \), the London Equations become

\[
\frac{\mathbf{B}}{c} = -\lambda_L \nabla \times \mathbf{j}_s \quad \mathbf{E} = \lambda_L \frac{\partial j_s}{\partial t} \tag{12}
\]
If we now apply the Maxwell equation \( \nabla \times \mathbf{H} = \frac{4\pi}{c} \mathbf{j} \Rightarrow \nabla \times \mathbf{B} = \frac{4\pi}{c} \mu \mathbf{j} \) then we get

\[
\nabla \times (\nabla \times \mathbf{B}) = \frac{4\pi}{c} \mu \nabla \times \mathbf{j} = -\frac{4\pi \mu}{c^2 \lambda_L} \mathbf{B}
\]

(13)

and

\[
\nabla \times (\nabla \times \mathbf{j}) = -\frac{1}{\lambda_L c} \nabla \times \mathbf{B} = -\frac{4\pi \mu}{c^2 \lambda_L} \mathbf{j}
\]

(14)

or since \( \nabla \cdot \mathbf{B} = 0, \nabla \cdot \mathbf{j} = \frac{1}{c} \frac{\partial \rho}{\partial t} = 0 \) and \( \nabla \times (\nabla \times \mathbf{a}) = \mathbf{0} \) we get

\[
\nabla^2 \mathbf{B} - \frac{4\pi \mu}{c^2 \lambda_L} \mathbf{B} = 0 \quad \nabla^2 \mathbf{j} - \frac{4\pi \mu}{c^2 \lambda_L} \mathbf{j} = 0
\]

(15)

Figure 6: A superconducting slab in an external field. The field penetrates into the slab a distance \( \Lambda_L = \sqrt{\frac{me^2}{4\pi ne^2 \mu}} \).
Now consider a the superconductor in an external field shown in Fig. 6. The field is only in the x-direction, and can vary in space only in the z-direction, then since $\nabla \times \mathbf{B} = \frac{4\pi}{c} \mu \mathbf{j}$, the current is in the y-direction, so

$$\frac{\partial^2 B_x}{\partial z^2} - \frac{4\pi \mu}{c^2 \lambda_L} B_x = 0 \quad \frac{\partial^2 j_{sy}}{\partial z^2} - \frac{4\pi \mu}{c^2 \lambda_L} j_{sy} = 0$$

(16)

with the solutions

$$B_x = B_x^0 e^{-\frac{z}{\Lambda_L}} \quad j_{sy} = j_{sy} e^{-\frac{z}{\Lambda_L}}$$

(17)

$$\Lambda_L = \sqrt{\frac{c^2 \lambda_L}{4\pi \mu}} = \sqrt{\frac{mc^2}{4\pi ne^2 \mu}}$$

is the penetration depth.

3 Cooper Pairing

The superconducting state is fundamentally different than any possible normal metallic state (ie a perfect metal at $T = 0$). Thus, the transition from the normal metal state to the superconducting state must be a phase transition. A phase transition is accompanied by an instability of the normal state. Cooper first quantified this instability as due to a small attractive(!?) interaction between two electrons above the Fermi surface.
3.1 The Retarded Pairing Potential

The attraction comes from the exchange of phonons. The lattice deforms slowly in the time scale of the electron. It reaches its maximum deformation at a time $\tau \sim \frac{2\pi}{\omega_D} \sim 10^{-13}s$ after the electron has passed. In this time the first electron has traveled

$$\sim v_F\tau \sim 10^8\frac{\text{cm}}{\text{s}} \cdot 10^{-13}\text{s} \sim 1000\ \AA.$$ 

The positive charge of the lattice deformation can then attract another electron without feeling the Coulomb repulsion of the first electron. Due to retardation, the electron-electron Coulomb repulsion may be neglected!
The net effect of the phonons is then to create an attractive interaction which tends to pair time-reversed quasiparticle states. They form an antisymmetric spin singlet so that the

\[ \xi \sim 1000 \Lambda \]

Figure 8: To take full advantage of the attractive potential illustrated in Fig. 7, the spatial part of the electronic pair wave function is symmetric and hence nodeless. To obey the Pauli principle, the spin part must then be antisymmetric or a singlet.

3.2 Scattering of Cooper Pairs

This latter point may be quantified a bit better by considering two electrons above a filled Fermi sphere. These two electrons
are attracted by the exchange of phonons. However, the maximum energy which may be exchanged in this way is $\sim \hbar \omega_D$. Thus the scattering in phase space is restricted to a narrow shell of energy width $\hbar \omega_D$. Furthermore, the momentum in this scattering process is also conserved

$$k_1 + k_2 = k'_1 + k'_2 = K$$  \hspace{1cm} (18)

Thus the scattering of $k_1$ and $k_2$ into $k'_1$ and $k'_2$ is restricted to the overlap of the two scattering shells, Clearly this is negligible unless $K \approx 0$. Thus the interaction is strongest (most likely) if $k_1 = -k_2$ and $\sigma_1 = -\sigma_2$; i.e., pairing is primarily between

![Figure 9: Pair states scattered by the exchange of phonons are restricted to a narrow scattering shell of width $\hbar \omega_D$ around the Fermi surface.](image)
time-reversed eigenstates.

Figure 10: *If the pair has a finite center of mass momentum, so that $k_1 + k_2 = K$, then there are few states which it can scatter into through the exchange of a phonon.*

### 3.3 The Cooper Instability of the Fermi Sea

Now consider these two electrons above the Fermi surface. They will obey the Schrödinger equation.

$$\frac{-\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2)\psi(r_1 r_2) + V(r_1 r_2)\psi(r_1 r_2) = (\epsilon + 2E_F)\psi(r_1 r_2)$$

If $V = 0$, then $\epsilon = 0$, and

$$\psi_{V=0} = \frac{1}{L^{3/2}}e^{ik_1 \cdot r_1} \frac{1}{L^{3/2}}e^{ik_2 \cdot r_2} = \frac{1}{L^3}e^{ik(r_1 - r_2)},$$
where we assume that $\mathbf{k}_1 = -\mathbf{k}_2 = \mathbf{k}$. For small $V$, we will perturb around the $V = 0$ state, so that

$$\psi(\mathbf{r}_1 \mathbf{r}_2) = \frac{1}{L^3} \sum_{\mathbf{k}} g(\mathbf{k}) e^{i\mathbf{k} \cdot (\mathbf{r}_1 - \mathbf{r}_2)}$$  \hspace{1cm} (21)

The sum must be restricted so that

$$E_F < \frac{\hbar^2 k^2}{2m} < E_F + \hbar \omega_D$$ \hspace{1cm} (22)

this may be imposed by $g(\mathbf{k})$, since $|g(\mathbf{k})|^2$ is the probability of finding an electron in a state $\mathbf{k}$ and the other in $-\mathbf{k}$. Thus we take

$$g(\mathbf{k}) = 0 \quad \text{for} \quad \begin{cases} \mathbf{k} < \mathbf{k}_F \\ \mathbf{k} > \frac{\sqrt{2m(E_F + \hbar \omega_D)}}{\hbar} \end{cases}$$ \hspace{1cm} (23)

The Schroedinger equations may be converted to a $k$-space equation by multiplying it by

$$\frac{1}{L^3} \int d^3 \mathbf{r} \ e^{-i\mathbf{k}' \cdot \mathbf{r}} \Rightarrow \text{S.E.}$$ \hspace{1cm} (24)

so that

$$\frac{\hbar^2 k^2}{m} g(\mathbf{k}) + \frac{1}{L^3} \sum_{\mathbf{k}'} g(\mathbf{k}') V_{\mathbf{k}\mathbf{k}'} = (\epsilon + 2E_F) g(\mathbf{k})$$ \hspace{1cm} (25)

where

$$V_{\mathbf{k}\mathbf{k}'} = \int V(\mathbf{r}) e^{-i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{r}} d^3 \mathbf{r}$$ \hspace{1cm} (26)
now describes the scattering from \((\mathbf{k}, -\mathbf{k})\) to \((\mathbf{k}', -\mathbf{k}')\). It is usually approximated as a constant for all \(\mathbf{k}\) and \(\mathbf{k}'\) which obey the Pauli-principle and scattering shell restrictions

\[
V_{kk'} = \begin{cases} 
-V_0 & \quad E_F < \frac{\hbar^2 k^2}{2m}, \frac{\hbar^2 k'^2}{2m} < E_F + \hbar \omega_D \\
0 & \quad \text{otherwise}
\end{cases}
\]  

(27)

so

\[
\left( -\frac{\hbar^2 k^2}{m} + \epsilon + 2E_F \right) g(\mathbf{k}) = -\frac{V_0}{L^3} \sum_{\mathbf{k}'} g(\mathbf{k}') \equiv -A \tag{28}
\]

or

\[
g(\mathbf{k}) = \frac{-A}{-\frac{\hbar^2 k^2}{m} + \epsilon + 2E_F} \quad \text{(i.e. for } E_F < \frac{\hbar^2 k^2}{2m} < E_F + \hbar \omega_D) \tag{29}
\]

Summing over \(\mathbf{k}\)

\[
\frac{V_0}{L^3} \sum_{\mathbf{k}} \frac{A}{\hbar^2 k^2/m - \epsilon - 2E_F} = +A \tag{30}
\]

or

\[
1 = \frac{V_0}{L^3} \sum_{\mathbf{k}} \frac{1}{\hbar^2 k^2/m - \epsilon - 2E_F} \tag{31}
\]

This may be converted to a density of states integral on \(E = \frac{\hbar^2 k^2}{2m}\)
4 The BCS Ground State

In the preceding section, we saw that the weak phonon-mediated attractive interaction was sufficient to destabilize the Fermi sea, and promote the formation of a Cooper pair \((k \uparrow, -k \downarrow)\). The scattering

\[
(k \uparrow, -k \downarrow) \rightarrow (k' \uparrow, -k' \downarrow)
\]

yields an energy \(V_0\) if \(k\) and \(k'\) are in the scattering shell \(E_F < E_k, E_{k'} < E_F + \hbar \omega_D\). Many electrons can participate in this process and many Cooper pairs are formed, yielding a new state (phase) of the system. The energy of this new state is not just
\[ \frac{N}{2} \epsilon \] less than that of the old state, since the Fermi surface is renormalized by the formation of each Cooper pair.

4.1 The Energy of the BCS Ground State

Of course, to study the thermodynamics of this new phase, it is necessary to determine its energy. It will have both kinetic and potential contributions. Since pairing only occurs for electrons above the Fermi surface, the kinetic energy actually increases: if \( w_k \) is the probability that a pair state \((\mathbf{k} \uparrow, -\mathbf{k} \downarrow)\) is occupied then

\[
E_{\text{kin}} = 2 \sum_k w_k \xi_k, \quad \xi_k = \frac{\hbar^2 k^2}{2m} - E_F \quad (36)
\]

The potential energy requires a bit more thought. It may be written in terms of annihilation and creation operators for the pair states labeled by \( \mathbf{k} \)

\[
|1\rangle_k \quad \text{\((\mathbf{k} \uparrow, -\mathbf{k} \downarrow)\) occupied} \quad (37)
\]

\[
|0\rangle_k \quad \text{\((\mathbf{k} \uparrow, -\mathbf{k} \downarrow)\) unoccupied} \quad (38)
\]

or

\[
|\psi_k\rangle = u_k |0\rangle_k + v_k |1\rangle_k \quad (39)
\]
where $v_k^2 = w_k$ and $u_k^2 = 1 - w_k$. Then the BCS state, which is a collection of these pairs, may be written as

$$|\phi_{BCS}\rangle \simeq \prod_k \{u_k |0\rangle_k + v_k |1\rangle_k\}.$$  \hfill (40)

We will assume that $u_k, v_k \in \mathbb{R}$. Physically this amounts to taking the phase of the order parameter to be zero (or $\pi$), so that it is real. However the validity of this assumption can only be verified for a more microscopically based theory.

By the Pauli principle, the state $(k \uparrow, -k \downarrow)$ can be, at most, singly occupied, thus a ($s = \frac{1}{2}$) Pauli representation is possible

$$|1\rangle_k = \begin{pmatrix} 1 \\ 0 \end{pmatrix}_k \quad |0\rangle_k = \begin{pmatrix} 0 \\ 1 \end{pmatrix}_k$$  \hfill (41)

Where $\sigma_k^+$ and $\sigma_k^-$, describe the creation and annihilation of the state $(k \uparrow, -k \downarrow)$

$$\sigma_k^+ = \frac{1}{2}(\sigma_k^1 + i\sigma_k^2) = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}$$  \hfill (42)

$$\sigma_k^- = \frac{1}{2}(\sigma_k^1 - i\sigma_k^2) = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$$  \hfill (43)

Of course $\sigma_k^+ |1\rangle_k = 0$ and $\sigma_k^+ |0\rangle_k = |1\rangle_k$  \hfill (44)
\[ \sigma_k^- |1\rangle_k = |0\rangle_k \quad \sigma_k^+ |0\rangle_k = 0 \quad (45) \]

The process \((k \uparrow, -k \downarrow) \rightarrow (k' \uparrow, -k' \downarrow)\), if allowed, is associated with an energy reduction \(V_0\). In our Pauli matrix representation this process is represented by operators \(\sigma_k^+ \sigma_k^-\), so

\[ V = -\frac{V_0}{L^3} \sum_{kk'} \sigma_k^+ \sigma_k^- \quad \text{(Note that this is Hermitian)} \quad (46) \]

Thus the reduction of the potential energy is given by \(\langle \phi_{BCS} | V | \phi_{BCS} \rangle\)

\[ \langle \phi_{BCS} | V | \phi_{BCS} \rangle = -\frac{V_0}{L^3} \left\{ \prod_p \left( u_p \langle 0 | + v_p \langle 1 | \right) \sum_{kk'} \sigma_k^+ \sigma_{k'}^- \right\} \prod_{p'} \left( u_{p'} \langle 0 |_{p'} + v_{p'} \langle 1 |_{p'} \right) \quad (47) \]

Then as \(k \langle 1 |_{k'} = \delta_{kk'}, k \langle 0 |_{k'} = \delta_{kk'}\) and \(k \langle 0 |_{1} = 0\)

\[ \langle \phi_{BCS} | V | \phi_{BCS} \rangle = -\frac{V_0}{L^3} \sum_{kk'} v_k u_k u_{k'} v_{k'} \quad (48) \]

Thus, the total energy (kinetic plus potential) of the system of Cooper pairs is

\[ W_{BCS} = 2 \sum_k v_k^2 \xi_k - \frac{V_0}{L^3} \sum_{kk'} v_k u_k u_{k'} v_{k'} \quad (49) \]

As yet \(v_k\) and \(u_k\) are unknown. They may be treated as variational parameters. Since \(w_k = v_k^2\) and \(1 - w_k = u_k^2\), we
may impose this constraint by choosing

\[ v_k = \cos \theta_k, \quad u_k = \sin \theta_k \quad (50) \]

At \( T = 0 \), we require \( W_{BCS} \) to be a minimum.

\[ W_{BCS} = \sum_k 2\xi_k \cos^2 \theta_k - \frac{V_0}{L^3} \sum_{kk'} \cos \theta_k \sin \theta_{k'} \cos \theta_{k'} \sin \theta_k \]

\[ = \sum_k 2\xi_k \cos^2 \theta_k - \frac{V_0}{L^3} \sum_{kk'} \frac{1}{4} \sin 2\theta_k \sin 2\theta_{k'} \quad (51) \]

\[ \frac{\partial W_{BCS}}{\partial \theta_k} = 0 = -4\xi_k \cos \theta_k \sin \theta_k - \frac{V_0}{L^3} \sum_{k'} \cos 2\theta_k \sin 2\theta_{k'} \quad (52) \]

\[ \xi_k \tan 2\theta_k = -\frac{1}{2} \frac{V_0}{L^3} \sum_{k'} \sin 2\theta_{k'} \quad (53) \]

Conventionally, one introduces the parameters \( E_k = \sqrt{\xi_k^2 + \Delta^2}, \Delta = \frac{V_0}{L^3} \sum_k u_k v_k = \frac{V_0}{L^3} \sum_k \cos \theta_k \sin \theta_k \). Then we get

\[ \xi_k \tan 2\theta_k = -\Delta \Rightarrow 2u_k v_k = \sin 2\theta_k = \frac{\Delta}{E_k} \quad (54) \]

\[ \cos 2\theta_k = \frac{-\xi_k}{E_k} = \cos^2 \theta_k - \sin^2 \theta_k = v_k^2 - u_k^2 = 2v_k^2 - 1 \quad (55) \]

\[ w_k = v_k^2 = \frac{1}{2} \left( 1 - \frac{-\xi_k}{E_k} \right) = \frac{1}{2} \left( 1 - \frac{\xi_k}{\sqrt{\xi_k^2 + \Delta^2}} \right) \quad (56) \]

If we now make these substitutions \( 2u_k v_k = \frac{\Delta}{E_k}, v_k^2 = \frac{1}{2} \left( 1 - \frac{\xi_k}{E_k} \right) \) into \( W_{BCS} \), then we get

\[ W_{BCS} = \sum_k \xi_k \left( 1 - \frac{\xi_k}{E_k} \right) - \frac{L^3}{V_0} \Delta^2. \quad (57) \]
Figure 11: Sketch of the ground state pair distribution function.

Compare this to the normal state energy, again measured relative to $E_F$

$$W_n = \sum_{k<k_F} 2\xi_k$$

or

$$\frac{W_{BCS} - W_n}{L^3} = -\frac{1}{L^3} \sum_k \xi_k \left(1 + \frac{\xi_k}{E_k}\right) - \frac{\Delta^2}{V_0}$$

$$\approx -\frac{1}{2} Z(E_F) \Delta^2 < 0.$$  

So the formation of superconductivity reduces the ground state energy. This can also be interpreted as $\Delta Z(E_F)$ electrons pairs per and volume condensed into a state $\Delta$ below $E_F$. The average energy gain per electron is $\frac{\Delta}{2}$.
4.2 The BCS Gap

The gap parameter $\Delta$ is fundamental to the BCS theory. It tells us both the energy gain of the BCS state, and about its excitations. Thus $\Delta$ is usually what is measured by experiments. To see this consider

\begin{equation}
W_{BCS} = \sum_{k} 2\xi_k \frac{1}{2} \left( 1 - \frac{\xi_k}{E_k} \right) - \frac{L^3 \Delta^2}{V_0} \tag{61}
\end{equation}

Lots of algebra (See I&L)

\begin{equation}
W_{BCS} = -\sum 2E_k v_k^4 \tag{62}
\end{equation}

Now recall that the probability that the Cooper state $(\mathbf{k} \uparrow, \mathbf{k} \downarrow)$ was occupied, is given by $w_k = v_k^2$. Thus the first pair breaking excitation takes $v_k^2 = 1$ to $v_k^2 = 0$, for a change in energy

\begin{equation}
\Delta E = -\sum_{k \neq k'} 2v_k^4 E_k + \sum_k 2v_k^4 E_k = 2E_{k'} = 2\sqrt{\xi_{k'}^2 + \Delta^2} \tag{63}
\end{equation}

Then since $\xi_{k'} = \frac{\hbar^2 k'^2}{2m} - E_F$, the smallest such excitation is just

\begin{equation}
\Delta E_{min} = 2\Delta \tag{64}
\end{equation}

This is the minimum energy required to break a pair, or create an excitation in the BCS ground state. It is what is measured by the specific heat $C \sim e^{-\beta^2 \Delta}$ for $T < T_c$. 

24
Figure 12: Breaking a pair requires an energy $2\sqrt{\xi_k^2 + \Delta^2} \geq 2\Delta$

Now consider some experiment which adds a single electron, or perhaps a few unpaired electrons, to a superconductor (i.e., tunneling). This additional electron cannot find a partner for pairing. Thus it must enter one of the excited states discussed...
above. Since it is a single electron, its energy will be

\[ E_k = \sqrt{\xi_k^2 + \Delta^2} \]  

(65)

For \( \xi_k^2 \gg \Delta \), \( E_k = \xi_k = \frac{\hbar^2 k^2}{2m} - E_F \), which is just the energy of a normal metal state. Thus for energies well above the gap, the normal metal continuum is recovered for unpaired electrons.

To calculate the density of unpaired electron states, recall that the density of states was determined by counting \( k \)-states. These are unaffected by any phase transition. Thus it must be that the number of states in \( d^3 k \) is equal.

\[ D_s(E_k) dE_k = D_n(\xi_k) d\xi_k \]  

(66)

In the vicinity of \( \Delta \sim \xi_k \), \( D_n(\xi_k) \approx D_n(E_F) \) since \( |\Delta| \ll E_F \).
(we shall see that $\Delta \leq 2w_D$). Thus for $\xi_k \sim \Delta$

$$\frac{D_s(E_k)}{D_n(E_F)} = \frac{d\xi_x}{dE_k} = \frac{d}{dE_k} \sqrt{E_k^2 - \Delta^2} = \frac{E_k}{\sqrt{E_k^2 - \Delta^2}}$$

$E_k > \Delta$

(67)

Figure 15:

Given the experimental and theoretical importance of $\Delta$, it should be calculated.

$$\Delta = \frac{V_0}{L^3} \sum_k \sin \theta_k \cos \theta_k = \frac{V_0}{L^3} \sum_k u_k v_k = \frac{V_0}{L^3} \sum_k \frac{\Delta}{2E_k}$$

(68)

$$\Delta = \frac{1}{2} \frac{V_0}{L^3} \sum_k \frac{\Delta}{\sqrt{\xi_k^2 + \Delta^2}}$$

(69)

Convert this to sum over energy states (at $T = 0$ all states with
\( \xi < 0 \) are occupied since \( \xi_k = \frac{\hbar^2 k^2}{2m} - E_F \).

\[
\Delta = \frac{V_0 \Delta}{2} \int_{-\hbar \omega_D}^{\hbar \omega_D} \frac{Z(E_F + \xi) d\xi}{\sqrt{\xi^2 + \Delta^2}}
\]

(70)

\[
\frac{1}{V_0 Z(E_F)} = \int_{0}^{\hbar \omega_D} \frac{d\xi}{\sqrt{\xi^2 + \Delta^2}}
\]

(71)

\[
\frac{1}{V_0 Z(E_F)} = \sinh^{-1} \left( \frac{\hbar \omega_D}{\Delta} \right)
\]

(72)

For small \( \Delta \),

\[
\frac{\hbar \omega_D}{\Delta} \sim e^{\frac{1}{V_0 Z(E_F)}}
\]

(73)

\[
\Delta \simeq \hbar \omega_D e^{-\frac{1}{V_0 Z(E_F)}}
\]

(74)

Figure 16:
5 Consequences of BCS and Experiment

5.1 Specific Heat

As mentioned before, the gap $\Delta$ is fundamental to experiment. The simplest excitation which can be induced in a superconductor has energy $2\Delta$. Thus

\[
\Delta E \sim 2\Delta e^{-\beta \Delta} \quad T \ll T_c
\]  \hspace{1cm} (75)

\[
C \sim \frac{\partial \Delta E}{\partial \beta} \frac{\partial \beta}{\partial T} \sim \frac{\Delta^2}{T^2} e^{-\beta \Delta}
\]  \hspace{1cm} (76)

5.2 Microwave Absorption and Reflection

Another direct measurement of the gap is reflectivity/absorption. A phonon impacting a superconductor can either be reflected or absorbed. Unless $\hbar \omega > 2\Delta$, the phonon cannot create an excitation and is reflected. Only if $\hbar \omega > 2\Delta$ is there absorption. Consider a small cavity within a superconductor. The cavity has a small hole which allows microwave radiation to enter the cavity. If $\hbar \omega < 2\Delta$ and if $B < B_c$, then the microwave intensity is high $I = I_s$. On the other hand, if $\hbar \omega > 2\Delta$, or
Figure 17: If $B > B_c$ or $\hbar \omega > 2\Delta$, then absorption reduces the intensity to the normal-state value $I = I_n$. For $B = 0$ the microwave intensity within the cavity is large so long as $\hbar \omega < 2\Delta$.

$B > B_c$, then the intensity falls in the cavity $I = I_n$ due to absorption by the walls.

Note that this also allows us to measure $\Delta$ as a function of $T$. At $T = T_c$, $\Delta = 0$, since thermal excitations reduce the number of Cooper pairs and increase the number of unpaired electrons, which obey Fermi-statistics. The size of (Eqn. 71) is only effected by the presence of a Cooper pair. The probability that an electron is unpaired is $f \left( \sqrt{\xi^2 + \Delta^2} + E_F, T \right) = \frac{1}{\exp \beta \sqrt{\xi^2 + \Delta^2} + 1}$ so, the probability that a Cooper pair exists is...
1 - 2 f \left( \sqrt{\xi^2 + \Delta^2} + E_F, T \right). \text{ Thus for } T \neq 0
\frac{1}{V_0 Z(E_F)} = \int_0^{\hbar \omega_D} \frac{d\xi}{\sqrt{\xi^2 + \Delta^2}} \left\{ 1 - 2 f \left( \sqrt{\xi^2 + \Delta^2} + E_F, T \right) \right\}
(77)

Note that as \sqrt{\xi^2 + \Delta^2} \geq 0, when \beta \to \infty \text{ we recover the } T = 0 \text{ result.}

This equation may be solved for \Delta(T) \text{ and for } T_c. \text{ To find } T_c

Figure 18:

\[ \Delta(T) \]
\[ \Delta(0) \]
\[ \ln \text{ Pb/Sn} \]
\[ \text{Real SC data (reflectivity)} \]

Figure 19: \textit{The evolution of the gap (as measured by reflectivity) as a function of temperature. The BCS approximation is in reasonably good agreement with experiment.}
consider this equation as \( \frac{T}{T_c} \rightarrow 1 \), the first solution to the gap equation, with \( \Delta = 0^+ \), occurs at \( T = T_c \). Here

\[
\frac{1}{V_0 Z(E_F)} = \int_0^{\hbar \omega_D} d\xi \frac{\xi}{\xi} \tanh \left( \frac{\xi}{2k_B T_c} \right)
\]  

which may be solved numerically to yield

\[
1 = V_0 Z(E_F) \ln \frac{1.14 \hbar \omega_D}{k_B T_c}
\]  

\( k_B T_c = 1.14 \hbar \omega_D e^{-1/\{V_0 Z(E_F)\}} \)  

but recall that \( \Delta = 2 \hbar \omega_D e^{-1/\{V_0 Z(E_F)\}} \), so

\[
\frac{\Delta(0)}{k_B T_c} = \frac{2}{1.14} = 1.764
\]

\[
\begin{array}{|c|c|c|c|}
\hline
\text{metal} & T_c ^\circ K & Z(E_F)V_0 & \Delta(0)/k_B T_c \\
\hline
\text{Zn} & 0.9 & 0.18 & 1.6 \\
\text{Al} & 1.2 & 0.18 & 1.7 \\
\text{Pb} & 7.22 & 0.39 & 2.15 \\
\hline
\end{array}
\]

Table 1: Note that the value 2.15 for \( \Delta(0)/k_B T_c \) for Pb is higher than BCS predicts. Such systems are labeled strong coupling superconductors and are better described by the Eliashberg-Migdal theory.
5.3 The Isotope Effect

Finally, one should discuss the isotope effect. We know that $V_{kk'}$, results from phonon exchange. If we change the mass of one of the vibrating members but not its charge, then $V_0 N(E_F)$ etc are unchanged but

$$\omega_D \sim \sqrt{\frac{k}{M}} \sim M^{-\frac{1}{2}}.$$  \hspace{1cm} (82)

Thus $T_c \sim M^{-\frac{1}{2}}$. This has been confirmed for most normal superconductors, and is considered a ”smoking gun” for phonon mediated superconductivity.

6 BCS ⇒ Superconducting Phenomenology

Using Maxwell’s equations, we may establish a relation between the critical current and the critical field necessary to destroy the superconducting state. Consider a long thick wire (with radius $r_0 \gg \Lambda_L$) and integrate the equation

$$\nabla \times \mathbf{H} = \frac{4\pi}{c} \mathbf{j}$$ \hspace{1cm} (83)
Figure 20: Integration contour within a long thick superconducting wire perpendicular to a circulating magnetic field. The field only penetrates into the wire a distance \( \Lambda_L \).

along the contour shown in Fig. 20.

\[
\int \nabla \times \mathbf{H} dS = \int \mathbf{H} \cdot d\mathbf{l} = \frac{4\pi}{c} \int \mathbf{j} \cdot ds \tag{84}
\]

\[
2\pi r_0 H = \frac{4\pi}{c} 2\pi r_0 \Lambda_L j_0 \tag{85}
\]

If \( j_0 = j_c \) (\( j_c \) is the critical current), then

\[
H_c = \frac{4\pi}{c} \Lambda_L j_c \tag{86}
\]

Since both \( H_c \) and \( j_c \propto \Delta \), they will share the temperature-dependence of \( \Delta \).

At \( T = 0 \), we could also get an expression for \( H_c \) by noting
that, since the superconducting state excludes all flux,

\[ \frac{1}{L^3} (W_n - W_{BCS}) = \frac{1}{8\pi} H_c^2 \]  

(87)

However, since we have earlier

\[ \frac{1}{L^3} (W_n - W_{BCS}) = \frac{1}{2} N(0) \Delta^2, \]  

(88)

we get

\[ H_c = 2\Delta \sqrt{\pi N(0)} \]  

(89)

We can use this, and the relation derived above \( j_c = \frac{c}{4\pi \Lambda_L} H_c \), to get a (properly derived) relationship for \( j_c \).

\[ j_c = \frac{c}{4\pi \Lambda_L} 2\Delta \sqrt{\pi N(0)} \]  

(90)

However, for most metals

\[ N(0) \approx \frac{n}{E_F} \]  

(91)

\[ \Lambda_L = \sqrt{\frac{mc^2}{4\pi ne^2 \mu}} \]  

(92)

taking \( \mu = 1 \)

\[ j_c = \frac{c}{4\pi} \sqrt{\frac{4\pi ne^2}{mc^2}} 2\Delta \sqrt{\frac{\pi n 2m}{\hbar^2 k_F^2}} = \sqrt{2\Delta} \frac{ne}{\hbar k_F} \]  

(93)
This gives a similar result to what Ibach and Lüth get, but for a completely different reason. Their argument is similar to one originally proposed by Landau. Imagine that you have a fluid which must flow around an obstacle of mass $M$. From the perspective of the fluid, this is the same as an obstacle moving in it. Suppose the obstacle makes an excitation of energy $\epsilon$ and momentum $p$ in the fluid, then

$$E' = E - \epsilon \quad P' = P - p$$

(94)

or from squaring the second equation and dividing by $2M$

Figure 21: A superconducting fluid which must flow around an obstacle of mass $M$. From the perspective of the fluid, this is the same as an obstacle, with a velocity equal and opposite the fluids, moving in it.

Figure 22: A large mass $M$ moving with momentum $P$ in a superfluid (a), creates an excitation (b) of the fluid of energy $\epsilon$ and momentum $p$
\[
\frac{P'^2}{2M} - \frac{P^2}{2M} = -\frac{\mathbf{P} \cdot \mathbf{p}}{M} + \frac{p^2}{2M} = E' - E = \epsilon
\] (95)

\[\epsilon = \frac{pP \cos \theta}{M} - \frac{p^2}{2M} \quad (96)\]

\[\epsilon = pv \cos \theta - \frac{p^2}{2M} \quad (97)\]

If \( M \to \infty \) (a defect in the tube which carries the fluid could have essentially an infinite mass) then

\[\frac{\epsilon}{p} = v \cos \theta \quad (98)\]

Then since \( \cos \theta \leq 1 \)

\[v \geq \frac{\epsilon}{p} \quad (99)\]

Thus, if there is some minimum \( \epsilon \), then there is also a minimum velocity below which such excitations of the fluid cannot
happen. For the superconductor

\[ v_c = \frac{\epsilon_{\text{min}}}{p} = \frac{2\Delta}{2h\kappa_F} \]  \hspace{1cm} (100)

Or

\[ j_c = env_c = \Delta \frac{ne}{\hbar \kappa_F} \] \hspace{1cm} (101)

This is the same relation as we obtained with the previous thermodynamic argument (within a factor \( \sqrt{2} \)). However, the former argument is more proper, since it would apply even for \textit{gapless} superconductors, and it takes into account the fact that the S.C. state is a collective phenomena ie., a minuet, not a waltz of electric pairs.

7 \textbf{Coherence of the Superconductor }\Rightarrow \textit{Meisner effects}

Superconductivity \textit{is} the Meissner effect, but thus far, we have not yet shown that the BCS theory leads to the second London equation which describes flux exclusion. In this subsection, we will see that this requires an additional assumption: the rigidity of the BCS wave function.
In the BCS approximation, the superconducting wave function is taken to be composed of products of Cooper pairs. One can estimate the size of the pairs from the uncertainty principle

\[ 2\Delta = \delta \left( \frac{p^2}{2m} \right) \sim \frac{p_F}{m} \delta p \Rightarrow \delta p \sim 2m \frac{\Delta}{p_F} \]  

(102)

\[ \xi_{cp} \sim \delta x \sim \frac{\hbar}{\delta p} \sim \frac{\hbar p_F}{2m\Delta} = \frac{\hbar^2 k_F}{2m\Delta} = \frac{E_F}{k_F\Delta} \]  

(103)

\[ \xi_{cp} \sim 10^3 - 10^4 \text{ Å} \sim \text{size of Cooper pair wave function} \]  

(104)

Thus in the radius of the Cooper pair, about

\[ \frac{4\pi n}{3} \left( \frac{\xi_{cp}}{2} \right)^3 \sim 10^8 \]  

(105)

other pairs have their center of mass.

Figure 24: Many electron pairs fall within the volume of a Cooper wavefunction. This leads to a degree of correlation between the pairs and to rigidity of the pair wavefunction.
The pairs are thus *not* independent of each other (regardless of the BCS wave function approximation). In fact they are specifically anchored to each other; i.e., they maintain coherence over a length scale of at least $\xi_{cp}$.

![Image of a graph showing the transition between SC and Normal Metal, with $|\phi_{BCS}|^2$, $\xi_{coh} > \xi_{cp}$, and an arrow indicating the coherence length.](image)

Figure 25:

In light of this coherence, let’s reconsider the supercurrent

$$j = -\frac{2e}{4m} \left\{ \psi p^* \psi^* + \psi^* p \psi \right\}$$  \hspace{1cm} (106)

where pair mass = $2m$ and pair charge = $-2e$.

$$p = -i\hbar \nabla - \frac{2e}{c} A$$  \hspace{1cm} (107)

A current, or a CM momentum $\mathbf{K}$, modifies the single pair state

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{L^3} \sum_k g(k) e^{i\mathbf{K} \cdot (\mathbf{r}_1 + \mathbf{r}_2)/2} e^{ik \cdot (\mathbf{r}_1 - \mathbf{r}_2)}$$  \hspace{1cm} (108)

$$\psi(\mathbf{K}, \mathbf{r}_1, \mathbf{r}_2) = \psi(\mathbf{K} = 0, \mathbf{r}_1, \mathbf{r}_2) e^{i\mathbf{K} \cdot \mathbf{R}}$$  \hspace{1cm} (109)
where $\mathbf{R} = \frac{\mathbf{r}_1 + \mathbf{r}_2}{2}$ is the cm coordinate and $\hbar \mathbf{K}$ is the cm momentum. Thus

$$
\Phi_{BCS} \simeq e^{i\phi} \Phi_{BCS}(\mathbf{K} = 0) = e^{i\phi} \Phi(0) \quad (110)
$$

$$
\phi = \mathbf{K} \cdot (\mathbf{R}_1 + \mathbf{R}_2 + \cdots) \quad (111)
$$

(In principle, we should also antisymmetrize this wave function; however, we will see soon that this effect is negligible). Due to the rigidity of the BCS state it is valid to approximate

$$
\nabla = \nabla_R + \nabla_r \approx \nabla_R \quad (112)
$$

Thus

$$
\mathbf{j}_s \approx \frac{2e}{4m} \sum_{\nu} \left\{ \Phi_{BCS}^* \left( -i\hbar \nabla_{R\nu} + \frac{2eA}{c} \right) \Phi_{BCS} \\
+ \Phi_{BCS} \left( i\hbar \nabla_{R\nu} + \frac{2eA}{c} \right)^* \Phi_{BCS}^* \right\} \quad (113)
$$

or

$$
\mathbf{j}_s = -\frac{2e}{2m} \left\{ |\Phi(0)|^2 \frac{4eA}{c} + 2\hbar |\Phi(0)|^2 \sum_{\nu} \nabla_{R\nu} \phi \right\} \quad (114)
$$

Then since for any $\psi$, $\nabla \times \nabla \psi = 0$

$$
\nabla \times \mathbf{j}_s = -\frac{2e^2}{mc} |\Phi(0)|^2 \nabla \times A \quad (115)
$$
or since $|\Phi(0)|^2 = \frac{n_s}{2}$

$$\nabla \times \mathbf{j} = -\frac{ne^2}{mc} \mathbf{B}$$

(116)

which is the second London equation which as we saw in Sec.?? leads to the Meissner effect. Thus the second London equation can only be derived from the BCS theory by assuming that the BCS state is spatially homogeneous.

8 Quantization of Magnetic Flux

The rigidity of the wave function (superconducting coherence) also guarantees that the flux penetrating a superconducting loop is quantized. This may be seen by integrating Eq. 114 along a contour within the superconducting bulk (at least a distance $\Lambda_L$ from the surface).

$$\mathbf{j}_s = -\frac{e^2n_s}{mc} \mathbf{A} - \frac{ehn_s}{2m} \sum_\nu \mathbf{\nabla}_{R_\nu} \phi$$

(117)

$$\oint \mathbf{j}_s \cdot dl = -\frac{e^2n_s}{ms} \oint \mathbf{A} \cdot dl - \frac{ehn_s}{2m} \sum_\nu \oint \mathbf{\nabla}_{R_\nu} \phi \cdot dl$$

(118)

Presumably the phase of the BCS state $\Phi_{BCS} = e^{i\phi}\Phi(0)$ is
Figure 26: Magnetic flux penetrating a superconducting loop is quantized. This may be seen by integrating Eq. 114 along a contour within the superconducting bulk (a distance $\Lambda_L$ from the surface).

Also since the path $l$ may be taken inside the superconductor by a depth of more than $\Lambda_L$, where $j_s = 0$, we have that

$$\int j_s \cdot dl = 0$$  \hspace{1cm} (120)$$

I.e., the flux in the loop is quantized.
9 Tunnel Junctions

Imagine that we have an insulating gap between two metals, and that a plane wave (electronic Block State) is propagating towards this barrier from the left.

\[
\psi_a = A_1 e^{ikx} + B_1 e^{-ikx} \quad \psi_b = A_2 e^{ik'x} + B_2 e^{-ik'x} \quad \psi_c = B_3 e^{-ikx}
\]

These are solutions to the S.E. if

\[
k = \frac{\sqrt{2mE}}{\hbar} \quad \text{in a & c} \quad (123)
\]

\[
k' = \frac{\sqrt{2m(E - V_0)}}{\hbar} \quad \text{in b} \quad (124)
\]
The coefficients are determined by the BC of continuity of $\psi$ and $\psi'$ at the barriers $x = 0$ and $x = d$. If we take $B_3 = 1$ and $E < V_0$, so that

$$k' = i\kappa = \frac{\sqrt{2m(E - V_0)}}{\hbar}$$

(125)

then, the probability of having a particle tunnel from left to right is

$$P_{l\rightarrow r} \propto \frac{|B_3|^2}{|B_1|^2} = \frac{1}{|B_1|^2} = \left\{ \frac{1}{2} - \frac{1}{8} \left( \frac{k}{\kappa} - \frac{\kappa}{k} \right)^2 + \frac{1}{8} \left( \frac{k}{\kappa} + \frac{\kappa}{k} \right)^2 \cosh 2\kappa d \right\}^{-1}$$

(126)

For large $\kappa d$

$$P_{l\rightarrow r} \propto 8 \left( \frac{k}{\kappa} + \frac{\kappa}{k} \right)^{-2} e^{-2\kappa d}$$

(127)

$$\propto 8 \left( \frac{k}{\kappa} + \frac{\kappa}{k} \right)^{-2} \exp \left\{ -\frac{2d\sqrt{2m(V_0 - E)}}{\hbar} \right\}$$

(128)

Ie, the tunneling probability falls exponentially with distance.

Of course, this explains the physics of a single electron tunneling across a barrier, assuming that an appropriate state is
filled on the left-hand side and available on the right-hand side. This, as can be seen in Fig. 28, is not always the case, especially in a conductor. Here, we must take into account the densities of states and their occupation probabilities \( f \). We will be interested in applied voltages \( V \) which will shift the chemical potential \( eV \). To study the gap we will apply

\[
eV \sim \Delta
\]  

(129)

We know that \( \frac{2\Delta}{k_B T_c} \sim 4, \Delta \sim \frac{4k_B T_c}{2} \sim 10^5 K \). However typical metallic densities of states have features on the scale of electron-

Figure 28: Electrons cannot tunnel across the barrier since no unoccupied states are available on the left with correspond in energy to occupied states on the right (and vice-versa). However, the application of an appropriate bias voltage will promote the state on the right in energy, inducing a current.
volts $\sim 10^{4^\circ}K$. Thus, on this energy scale we may approximate the metallic density of states as featureless.

$$N_r(\epsilon) = N_{metal}(\epsilon) \approx N_{metal}(E_F)$$  \hspace{1cm} (130)

The tunneling current is then, roughly,

$$I \propto P \int d\epsilon f(\epsilon - eV)N_r(E_F)N_l(\epsilon)(1 - f(\epsilon))$$

$$- P \int d\epsilon f(\epsilon)N_l(\epsilon)N_r(E_F)(1 - f(\epsilon - eV))$$  \hspace{1cm} (131)

For $eV = 0$, clearly $I = 0$ i.e. a balance is achieved. For $eV \neq 0$ a current may occur. Let’s assume that $eV > 0$ and $k_B T \ll \Delta$. Then the rightward motion of electrons is
suppressed. Then

\[ I \sim PN_r(E_F) \int d\epsilon f(\epsilon - eV)N_l(\epsilon) \]  

(132)

and

\[ \frac{dI}{dV} \sim PN_r(E_F) \int d\epsilon \frac{\partial f(\epsilon - eV)}{\partial V}N_l(\epsilon) \]  

(133)

\[ \frac{\partial f}{\partial V} \sim e\delta(\epsilon - eV - E_F) \quad (T \ll E_F) \]  

(134)

\[ \frac{dI}{dV} \sim PN_r(E_F)N_l(eV + E_F) \]  

(135)

Thus the low temperature differential conductance \( \frac{dI}{dV} \) is a measure of the superconducting density of states.

Figure 30: At low temperatures, the differential conductance in a normal metal–superconductor tunnel junction is a measure of the quasiparticle density of states.