LECTURE 11
Superconducting Phase Transition

At $T_C$ there is a second order phase transition from a normal metal into a superconducting state that is much like the superfluid transition. Just as in Bose condensation, the electrons can be described by a coherent wavefunction or order parameter $\psi = |\psi|e^{i\phi}$. Gauge symmetry is broken and there is a coherent phase $\phi$ throughout the superconductor.

Superconducting Gap

The condensation energy that is gained upon forming the condensate results in a gap in the density of states. This can explain the absence of resistance. Recall that in the normal metal there were empty states just above the Fermi energy. Electrons which occupy states near or at the Fermi energy can easily make transitions into these empty states. Jumping into empty states is what happens when an electron scatters off some impurity or imperfection or sound vibration (phonon) in the metal. This results in inelastic scattering, dissipation, and electrical resistance. In the superconducting state, a gap in the electron density of states opens around the Fermi surface. By “gap” I mean that there are no states near the Fermi energy.

![Graphical representation of normal and superconducting states](image_url)

Normal State

![Graphical representation of normal and superconducting states](image_url)

Superconducting State

The states that used to be where the gap now is have been squished to either side. At $T = 0$, the states below the gap are filled and the states above the gap are empty. Now it is much harder for electrons to scatter off of impurities because they need a finite amount of energy to get to a state on the other side of the gap. If there isn’t enough energy in the scattering process to get to an unoccupied state, then the electron doesn’t change its state, there is no dissipation, and hence there is no electrical resistance. Forming the gap is analogous to the binding energy gained by forming a molecule from single atoms. The atoms gain energy by sharing their electrons. To break a chemical bond requires a minimum amount of energy just as to get across the superconducting gap requires a minimum amount of energy. The gap doesn’t appear suddenly at $T_C$; it opens up gradually as $T$ decreases below $T_C$, just like the order parameter. In fact the gap is basically the real part of the order parameter.
The presence of the gap in the density of states has been confirmed by tunneling experiments for which Ivar Giaver won the Nobel Prize. In these experiments a superconductor and a normal metal were juxtaposed with a thin (~ 20 Å) insulating barrier between them. This is a tunnel junction. (Classically electrons cannot go through an insulating barrier but quantum mechanically their wavefunction has a finite amplitude on the other side of the barrier, indicating that there is a finite probability for the electron to tunnel through the barrier.)

### NIS Tunnel Junction

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<tr>
<th>Superconductor</th>
<th>INS</th>
<th>Normal Metal</th>
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Then a voltage is applied across the junction and the current is measured. This provides a way of trying to inject electrons from the vicinity of the Fermi surface of the normal metal into the superconductor. The electrons can flow into the superconductor if there are empty states for them to jump into but they can’t flow if there are no states available in the superconductor.

For $T = 0$, current flows when $eV = \Delta$, where $V$ is the voltage across the junction and $2\Delta$ is the energy gap. Conventionally the "energy gap" refers to $2\Delta$.

At $T > 0$ there is finite probability that the states above the gap are populated. This is roughly given by the Boltzmann probability $e^{-\beta E}$ where the energy $E$ is measured from
the center of the gap. $E$ must be at least the size of the gap $\Delta$. The presence of a gap explains the exponential decrease of the specific heat and the thermal conductivity below $T_c$. The specific heat gives us some idea of how many more states can be populated as the temperature increases by a small amount $dT$. As the temperature increases, the only states available are those above the gap. The probability of occupying those states goes as $e^{-\beta\Delta}$. This is like the Arrhenius law. Exponential behavior usually signals the presence of a gap in the energy spectrum. Similarly the thermal conductivity decreases exponentially because the thermal conductivity $\kappa$ is proportional to the specific heat. ($\kappa = \frac{1}{3}C_v v_e \ell$ where $v_e$ is the electron drift velocity and $\ell$ is the electron mean free path, i.e., how far the electron gets before colliding with something.) In a metal it is primarily the electrons which are responsible for heat conduction. To carry heat, you must heat up the electrons on one side of the sample, have them run to the other side of the sample, and then dump their heat there. When we heat up electrons, we mean that we excite them into higher energy states. But the presence of a gap presents a barrier for the electrons to get into excited states. This is why the thermal conductivity of a superconductor is so poor.

**BCS Theory of Superconductivity**

In 1957 John Bardeen, Leon Cooper, and Bob Schrieffer (BCS) developed a microscopic theory of superconductivity. They wrote down a wavefunction for the superconductor consisting of electron pairs ($\vec{k} \uparrow, -\vec{k} \downarrow$). Notice that these are time reversed states. These pairs are called Cooper pairs. The idea behind the pairing is that an electron goes whizzing through the lattice and creates a distortion of the positive ions (atoms) in the lattice. They are positive ions because they donated their outer shell electrons to be conduction electrons. The positive ions are attracted to the negative electron whizzing by, but they are much heavier than the electron, so by the time they move toward the electron, it’s long gone. But another electron is attracted to the increased concentration of positive charge. So the 2 electrons have interacted indirectly via a lattice distortion. Quanta of lattice distortions and vibrations are called phonons. So we say that phonons mediate the interaction between the electrons. Notice that the interaction between the electrons is attractive. Electrons also repel each other because of Coulomb interactions, but this attraction occurs because it is delayed in time. We say that the interaction is retarded.

So we can think of the Fermi sea below the superconducting gap as being filled with Cooper pairs. The gap represents the energy required to break one of these pairs and promote an electron into a state lying above the gap. The gap represents a pair binding energy. One should not necessarily think of tightly bound pairs. In an ordinary superconductor, the electrons in a Cooper pair may be 1 $\mu$m apart and have of order $10^6$ electrons between them. It’s like dancing in a crowded ballroom with your partner on the other side of the room from you.

Recall that when we talked about flux quantization, we said that the flux quantum was given by $\Phi_0 = \frac{hc}{2e}$. The denominator “2e” comes from having 2 electrons in a Cooper pair.
The BCS theory was very successful in explaining the properties of superconductivity such as the Meissner effect, zero electrical resistivity, flux quantization and the superconducting gap.

Flux Quantization

As we discussed earlier, the superconducting state can be described by an order parameter $\psi$:

$$\psi(r) = \sqrt{\rho} e^{i\theta(r)}$$  \hspace{1cm} (1)

where $\rho$ is the number density of superconducting electron pairs. Ginzburg and Landau used this order parameter to write down a phenomenological theory of superconductivity. In the superconducting state, the wavefunction acquires a certain rigidity in that there is a global phase $\theta$. This has important consequences. These consequences include the Meissner effect and flux quantization. Let’s see how this works.

In the presence of a magnetic field $\vec{B} = \nabla \times \vec{A}$, where $\vec{A}$ is the vector potential, the Hamiltonian has the form

$$H = \frac{1}{2m} \left( \vec{p} - \frac{q}{c} \vec{A} \right)^2$$  \hspace{1cm} (2)

where $q = 2e$ is the charge. The generalized momentum

$$\vec{p} = \left( \vec{p} - \frac{q}{c} \vec{A} \right)$$  \hspace{1cm} (3)

Using Hamilton’s equation for the velocity $\vec{v}$:

$$\vec{v} = \frac{\partial H}{\partial \vec{p}}$$  \hspace{1cm} (4)

we find

$$\vec{v} = \frac{1}{m} \left( \vec{p} - \frac{q}{c} \vec{A} \right) = \frac{1}{m} \left( -i\hbar \nabla - \frac{q}{c} \vec{A} \right)$$  \hspace{1cm} (5)

The particle flux is given by

$$\psi^* \vec{v} \psi = \frac{n_p}{m} \left( \hbar \nabla \theta - \frac{q}{c} \vec{A} \right)$$  \hspace{1cm} (6)

where $n_p$ is the number density of superconducting pairs. Here we used (1) for $\psi$. If we think of $n_p \sim \psi^* \psi$, then particle flux is $\sim n_p \vec{v}$. The electric current density is $\sim qn_p \vec{v}$ or, more correctly,

$$\vec{j} = q n_p \vec{v} = \frac{n_p}{m} \left( \hbar \nabla \theta - \frac{q}{c} \vec{A} \right)$$  \hspace{1cm} (7)

To show flux quantization, let us consider a superconducting ring or torus. Let us take a closed path $C$ through the interior of the ring or torus, well away from the surface. The Meissner effect tells us that $\vec{B}$ and $\vec{j}$ are zero in the interior. So if we plug $\vec{j} = 0$ into (7), we get

$$\hbar \nabla \theta = \frac{q}{c} \vec{A}$$  \hspace{1cm} (8)
Hit both sides of this equation with a closed line integral $\oint_C \dot{\mathbf{A}} \cdot d\ell$:

$$\oint_C \bar{\mathbf{A}} \cdot d\ell = \oint_C \frac{q}{c} \mathbf{A} \cdot d\ell$$  \hspace{1cm} (9)

The left hand side gives the change of phase on going once around the ring.

$$\oint_C \bar{\mathbf{A}} \cdot d\ell = \hbar (\theta_2 - \theta_1)$$  \hspace{1cm} (10)

The wavefunction must be single valued, so

$$\hbar (\theta_2 - \theta_1) = 2\pi \hbar s$$  \hspace{1cm} (11)

where $s$ is an integer. The right hand side (9) yields the flux $\Phi$:

$$\oint_C \bar{\mathbf{A}} \cdot d\ell = \oint_C \nabla \times \bar{\mathbf{A}} \cdot d\bar{a} = \oint_C \bar{\mathbf{B}} \cdot d\bar{a} = \frac{q}{c} \Phi$$  \hspace{1cm} (12)

$S_C$ is the surface bounded by the curve $C$. $\Phi$ is the magnetic flux through $S_C$. Putting all this together gives

$$2\pi \hbar s = \frac{q}{c} \Phi$$  \hspace{1cm} (13)

or

$$\Phi = \left( \frac{2\pi \hbar c}{q} \right) s = s \phi_o$$  \hspace{1cm} (14)

Thus the flux through the ring is quantized in integral multiples of the flux quantum:

$$\phi_o = \frac{2\pi \hbar c}{q} = \frac{2\pi \hbar c}{2e} = \frac{\hbar c}{2e} \approx 2.07 \times 10^{-7} \text{ gauss cm}^2$$  \hspace{1cm} (15)

**Type I and Type II Superconductors**

When we mentioned the Meissner effect, we said that a superconductor expels a magnetic field. But it costs energy to do this. So if the magnetic field is strong enough, it will destroy the superconductivity. Superconductors can behave in 2 ways as the field is increased. This results in classifying superconductors into 2 categories.

**Type I Superconductors:** As the magnetic field is increased, the system goes discontinuously from being perfectly superconducting and perfectly diamagnetic to normal with complete penetration of the magnetic field. The value of the field at which this transition takes place is called the critical field $H_c$:

$$\Delta G_{NS} = \frac{H_c^2}{8\pi}$$  \hspace{1cm} (16)

where $\Delta G_{NS}$ is the Gibbs free energy per unit volume that is gained by going from the normal state to the superconducting state in zero field. The right hand side is the energy density of the critical magnetic field. So

$$H_c = \sqrt{\frac{8\pi \Delta G_{NS}}{}}$$  \hspace{1cm} (17)
Type II Superconductors: For $H < H_{c1}$, the superconductor expels flux completely and behaves like a type I superconductor. For $H_{c1} < H < H_{c2}$, there is partial field penetration in the form of vortex lines of magnetic flux. They’re sort of like tornadoes with electric current instead of wind swirling around. Each vortex contains one flux quantum $\Phi_0$. The vortex cores contain normal (rather than superconducting) electrons. If the vortices move, one can get electrical resistance from the scattering of these normal electrons. $H_{c2}$ is typically of order tens of Tesla. For $H > H_{c2}$, the field penetrates uniformly and the system is a normal metal. Type II superconductors are used to construct high field magnets such as those used in MRI and in the big high energy accelerators like at Fermilab and CERN.

High Temperature Superconductors

Type II superconductors tend to have higher transition temperatures than type I superconductors. Indeed the high temperature superconductors are type II superconductors. It all began in 1986 when J. G. Bednorz and K. A. Müller published a somewhat obscure article in Z. Phys. B where they announced that a La–Ba–Cu–O compound began to go superconducting at 35 K. This broke the long standing ceiling of $T_C = 23$ K in intermetallic compounds. Their discovery was confirmed by workers at the University of Tokyo and Paul Chu’s group at the University of Houston. Early in 1987, it was found that replacing Ba with Sr raised $T_C$ to 40 K (La$_{2-x}$Sr$_x$CuO$_4$). It was soon found by Chu’s group that YBa$_2$Cu$_3$O$_{7-\delta}$ (“YBCO”) had a $T_C$ a few degrees above 90 K. This meant that it would be superconducting at liquid nitrogen temperatures (77 K), whereas previous values of $T_C$ required liquid $^4$He (4 K). A gallon of liquid nitrogen costs about the same as a gallon of milk while a gallon of liquid helium is the price of vodka.
So liquid nitrogen is much cheaper. So technological applications of superconductors would be more economically feasible with the high temperature superconductors. Other copper oxide superconductors have been found. Most notably Bi$_2$Sr$_2$CaCu$_2$O$_8$ (BSCCO, $T_C \sim 110$ K) is often studied experimentally. Tl$_2$Ba$_2$Ca$_2$Cu$_3$O$_{10}$ has $T_C \sim 125$ K and HgBa$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ has $T_C \sim 133$ K and under 30 GPa of pressure, its $T_C \sim 164$ K.

The basis of the high temperature superconductors are copper-oxygen planes. These planes are separated from other copper oxide planes by junk. The properties of the hiTc compounds are highly anisotropic. The conductivity in the planes is much higher than between the planes. The superconducting current flows more easily in the planes than between the planes.

\[
\begin{array}{c|c|c|c|c}
\text{Cu} & \text{O} & \text{Cu} & \text{O} \\
\hline
\text{O} & \text{Cu} & \text{O} & \text{Cu} \\
\hline
\text{Cu} & \text{O} & \text{Cu} & \text{O} \\
\hline
\text{O} & \text{Cu} & \text{O} & \text{Cu} \\
\end{array}
\]

. Copper Oxide Plane

**Josephson Effect**

Brian Josephson came up with idea for the Josephson effect while he was still a graduate student at Cambridge. It is one of those rare instances when theory predicted a completely new phenomenon and experiment later confirmed it. Usually experiment comes first and then the theorists figure it out. The Josephson effect is a remarkable consequence of the rigidity in phase of the superconducting wavefunction. If we put two superconductors next to each other separated by a thin insulating layer, the phase difference ($\theta_2 - \theta_1$) between the two superconductors will cause a current of superconducting Cooper pairs to flow between the superconductors. This is Josephson tunneling and the tunnel junction is called a Josephson junction or weak link. The effects of pair tunneling include the DC Josephson effect and the AC Josephson effect.

**Josephson Tunnel Junction**

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<tr>
<th>SC 1</th>
<th>INS</th>
<th>SC 2</th>
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. In the DC Josephson effect a DC current flows across the junction in the absence of any electric or magnetic field. Let $\psi_1$ be the superconducting order parameter on side 1:

\[
\psi_1 = \sqrt{n_1} e^{i\theta_1} \quad (18)
\]
\( n_1 \) is the density of superconducting pairs on side 1. Similarly

\[
\psi_2 = \sqrt{n_2} e^{i \theta_2} \tag{19}
\]

Assume that the superconductors are identical. Applying Schrodinger’s equation

\[
i \hbar \frac{\partial \psi}{\partial t} = H \psi \tag{20}
\]

yields

\[
i \hbar \frac{\partial \psi_1}{\partial t} = \hbar \psi_2 \quad i \hbar \frac{\partial \psi_2}{\partial t} = \hbar \psi_1 \tag{21}
\]

Here \( \hbar T \) represents the tunneling matrix element between the superconductors on the 2 sides. It represents the amplitude for a superconducting pair on one side to hop to the other side. \( T \) has units of frequency or rate. Plugging \( \psi_1 = \sqrt{n_1} e^{i \theta_1} \) and \( \psi_2 = \sqrt{n_2} e^{i \theta_2} \) into (21), we get

\[
\frac{\partial \psi_1}{\partial t} = \frac{1}{2 \sqrt{n_1}} e^{i \theta_1} \frac{\partial n_1}{\partial t} + i \psi_1 \frac{\partial \theta_1}{\partial t} = -i T \psi_2 \tag{22}
\]

Multiply through by \( \psi_1^* = \sqrt{n_1} e^{-i \theta_1} \). Let \( \delta = \theta_2 - \theta_1 \).

\[
\frac{1}{2} \frac{\partial n_1}{\partial t} + i n_1 \frac{\partial \theta_1}{\partial t} = -i T \sqrt{n_1 n_2} e^{i \delta} \tag{23}
\]

Take the real and imaginary parts

\[
\frac{\partial n_1}{\partial t} = 2 T \sqrt{n_1 n_2} \sin \delta \quad \frac{\partial \theta_1}{\partial t} = -T \sqrt{\frac{n_2}{n_1}} \cos \delta \tag{24}
\]

Similarly the equation for \( \frac{\partial n_2}{\partial t} \) yields

\[
\frac{\partial n_2}{\partial t} = -2 T \sqrt{n_1 n_2} \sin \delta \quad \frac{\partial \theta_2}{\partial t} = -T \sqrt{\frac{n_1}{n_2}} \cos \delta \tag{25}
\]

The current \( J \) flowing from side 1 to side 2 is proportional to \( \frac{\partial n_2}{\partial t} \), or equivalently, to \( -\frac{\partial n_1}{\partial t} \). Thus

\[
J = J_C \sin \delta = J_C \sin(\theta_2 - \theta_1) \tag{26}
\]

Thus the phase difference between the superconductors leads to current flow. Current flows without batteries or a power supply attached! \( J_C \) is the maximum zero voltage current that can be passed by the junction.