10
Supercondcutor

10.1. Experimental phenomena

10.1.1. zero resistivity

The resistivity of some metals drops down to zero when the temperature is reduced below some critical value (T_C). Such a perfect conductor (at $T < T_c$) is known as a superconductor and T_C is known as the superconducting transition temperature.

This chapter focuses on "conventional superconductors", for which T_C typically ranges from mK to about 10K, depending on the compounds. In addition, there are other types of superconductor, known as unconventional superconductors. There, the mechanism of superconductivity is very different from that of conventional superconductors. For unconventional superconductors, the transition temperature could be much higher. For example, the high temperature superconductors has the T_C ~150K. The recently discovered Fe-based superconductors has $T_C \sim 50\,K$.

In this chapter, we will only focus on conventional superconductors and their T_c will not be very high.

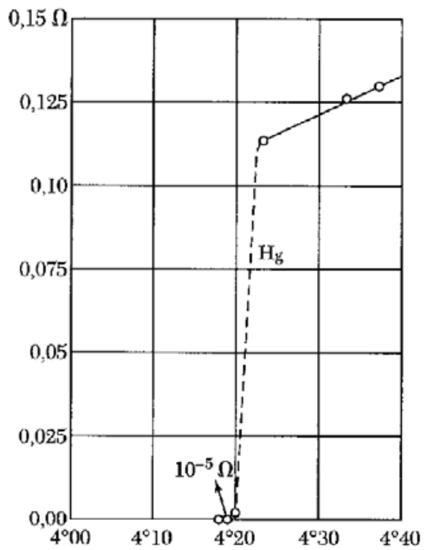

Fig. 1. The discovery of superconductivity. Resistance as a function temperature.

10.1.2. Meissner effect

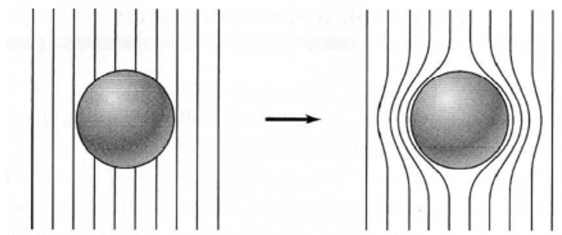

Fig. 2. The Meissner effect: magnetic field inside a superconductor (type I) is always zero.

If we apply some weak magnetic field, the superconductor will expel all the B field, such that the B field inside the superconductor is zero. This effect is known as the Meissner effect. It is important to notice that the Meissner effect is NOT a simple consequence of zero resistivity. For a perfect metal ($\rho = 0$), one can prove that the B field inside must be a constant independent of time, but the B field is not expected to be zero. In other words, superconductors are not just perfect metals. They are a special type of perfect metals which expel all B fields.

For a perfect metal, it is easy to show that since $\rho = 0$, the E field must be zero

$$\vec{E} = \rho\, \vec{j} = 0 \tag{10.1}$$

Then, the Maxwell's equation tells us that

$$\frac{1}{c} \frac{d\vec{B}}{dt} = -\nabla \times \vec{E} = 0 \tag{10.2}$$

Therefore, we find $d\vec{B} \big/ dt = 0$, which implies that the magnetic field is static and $\vec{B}$ can NOT vary as a function of t. For superconductors, $\vec{B} = 0$. This conclusions is stronger than just $\vec{B} =$ constant.

Another way to present the Meissner effect is by noticing that

$$\vec{B} = \vec{B}_a + \mu_0\, \vec{M} \tag{10.3}$$

Here, the total magnetic field B is separated into two parts: B_a is applied external field, M is the magnetization of the superconductor. The coefficient μ_0 is the magnetic susceptibility of the vacuum. The Meissner effect ($B = 0$) implies that if we apply an external field with strength B_a, the magnetization of the superconductor must be

$$\vec{M} = -\frac{1}{\mu_0}\, \vec{B}_a = -\epsilon_0\, c^2\, \vec{B}_a \tag{10.4}$$

This is exactly what one observes in experiments as shown in the figures below.

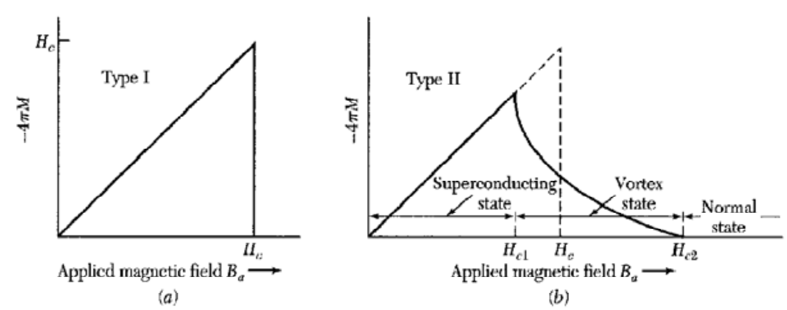

Fig. 3. M as a function of B_a for (a) type I and (b) type II superconductors

10.1.3. Critical field H_C and Type I/Type II superconductors

If one apply a very strong B field, the superconductivity will be destroyed, and the system turns back into a normal metal. In other words, two things will happen when B field is increased:

- The superconductivity is gone: the resistivity $\rho = 0$ when the field is weak, but when the field is larger than some critical value H_{C_2}, ρ turns into nonzero values.
- The Meissner effect is gone: $\vec{M} = -\vec{B}_a / \mu_0$ when the field is weak, but when the field is stronger than certain value H_{C_1}, $\vec{M} < -\vec{B}_a / \mu_0$ and the total B field inside the superconductor is no longer zero.

Since we can define two critical fields H_{C_1} and H_{C_2} by measuring the Meissner effect and the resistivity respectively, a natural question to ask is whether they take the same value of different ones?

- If $H_{C_1} = H_{C_2}$, we call the superconductor a type-I superconductor. For type I superconductors, we just have one critical field H_C. If external field is below H_C, we have a superconductor with $\rho = 0$ and $B = 0$. If the field is above H_C, the system turns into a normal metal and we lose the superconductivity and the Meissner effect.
- If $H_{C_1} < H_{C_2}$, we call the superconductor a type-II superconductor. For type II superconductors, when we increase external B fields, there are three regions (1) B less than H_{C_1}, (2) $H_{C_1} < B < H_{C_2}$ and (3) $B > H_{C_2}$. If the field is less than H_{C_1}, we have a superconductor with zero ρ and zero B. If the field is between H_{C_1} and H_{C_2}, the system is still a superconductor with $\rho = 0$, but it doesn't show Meissner effect ($B \neq 0$). Above H_{C_2}, the system is a normal metal with finite ρ and finite B.

10.1.4. Isotope effect

If we measure the T_c of the same compound made by different isotopes, one finds that T_c shows a strong connection to the isotopic mass M

$$M^\alpha T_c = \text{constant} \tag{10.5}$$

where α is some constant, typically close to 1/2.

This is a very strange observation, because transport phenomenon comes from the motion of electrons, instead of nucleons. Why does the superconductivity transition temperature depend on the mass of the nucleons?

Another way to put the question is that we can consider a metal as a gas made by electrons and phonons. Electrons carry electric charge (-e) but phonons are charge neutral. Therefore, for conductivity and superconductivity, it should comes from the motion of electrons instead of phonons. However, the mass of the nucleon is a parameter of phonon motions (Remember that the dispersion relation of the phonons relies on the mass of the nucleons). Why does phonons play a role in superconductivity? This question is actually very important and it offers a key hint for the mechanism of superconductivity, as will be discussed below.

10.2. Super Fluid and Bose-Einstein Condensate (BEC)

10.2.1. Experimental phenomena: by cooling down to low temperature (below some T_C), the viscosity of a quantum Bose gas drops down to zero.

10.2.2. reason: Bose-Einstein Condensate (BEC)

For weakly interacting bosons, at low enough temperature, most of the particles will go to the ground state. The phenomenon that large number of bosons occupies the ground state is known as a Bose-Einstein condensate.

10.3. BCS theory: superconductivity and pairing

10.3.1. Superconductor: a BEC state formed by pairs of electrons?

For superconductors, we have electrons, which are fermions (NOT bosons). For fermions, they cannot form a BEC state, because we cannot put all the fermions into the ground states. The Pauli's exclusive principle says that we can at most put one electron in a quantum state. However, if two electrons form a bound state (like two atoms form a molecule), then this pair of electrons is a boson. If we have large numbers of these pairs, they can form a condensate. Such a pair is called a Cooper pair, and they really exists in superconductors. The condensate of Cooper pairs is indeed the reason of superconductivity.

10.3.2. Why do two electrons want to bound together?

Q: Why do two electrons want to stay together? This is a very important question, because, naively speaking, electrons carry the same charge and thus typically they want to stay as far away as possible. It is easy to form a bound state for two particles with opposite charge, but how can two electrons form a bound state?

A: There is an attractive interactions between electrons in a metal.

10.3.3. Phonon mediated attraction

- An electron carries negative charge, and thus an electron will attract nearby nucleons. As a result, the spacing between the nucleons will be reduced around an electron (this is a lattice distortion). Because nucleons carrier positive charge, smaller lattice spacing means that there is a higher positive charge density in this region near an electron.
- Electron mass is much smaller than nucleons, so electrons move much faster than nucleons. When electron flies away, the lattice distortion will not recover immediately (because nucleons move much slower). Locally, there is a higher density of positive charges here, which will attract other electrons.
- Combining all the facts mentioned above, we found that an electron will attract other electrons via lattice distortions. Because lattice distortions are described by phonon, this effect is known as phonon mediated attractions between two electrons.

The rigorous theoretical description of this phenomenon requires quantum field theory, where two electrons exchange a virtue phonon and the exchange of virtue phonons induces an effective attractive interaction between electrons. This mechanism is in fact the same as what we used in the standard model to describe the interactions between fundamental particles. In quantum field theory, the interactions between two particles comes from the exchange of bosons (e.g. particle A emits a boson and particle B absorbs this boson). For examples, the origin of the E&M interaction is the exchange of photons. The weak interaction is caused by the exchange of W and Z bosons, while the strong interaction is mediated by gluons. Gravity force is probably induced by the exchange of gravitons (a boson with spin S=2). What we discussed here is exactly the same phenomenon, but in side a solid.

10.3.4.the BCS theory: Is this attraction strong enough to form a bound state?

An attractive interaction doesn't always result in a bound state. For two particles, if the attraction is not strong enough, it will not give us a bound state. But if the interaction is too weak, there may not be a bound state.

For Cooper pairs, it turns out that it is not just the bound state of two electrons, because there are many other electrons in the system. Other electrons turns out to help the formation of Cooper pairs. If we consider electrons near the Fermi surface, John Bardeen, Leon Neil Cooper, and John Robert Schrieffer found that no matter how weak the attraction is, there is always a bound state at low temperature. We will NOT present the detailed calculations here, but we will show two major conclusions:

At $T > T_c$, Cooper pairs break up and one just have a normal metal. This T_C is the transition temperature and the BCS theory says that

$$T_c = 1.13 \frac{\epsilon_D}{k_B} \exp\left[-\frac{1}{D(E_F)\,|\,V\,|}\right] \tag{10.6}$$

Here, $D(E_F)$ is the density of state of electrons at the Fermi energy E_F, V is the strength of the attractive interaction and ϵ_D is the Debye energy of the phonons.

The BCS theory also tells us that at $T = 0$, the binding energy for a Cooper pair is:

$$E_B = 2\,\Delta_0 = 4\,\epsilon_D \exp\left(-\frac{1}{N(0)\,|\,V\,|}\right) \tag{10.7}$$

10.3.5. Experimental evidence of the BCS theory I: energy gap

Half of the binding energy Δ is known as the BCS gap. The physical meaning of this gap is: how much energy it cost to add one electron to the system. If we shoot one Cooper pair into a superconductor, it wouldn't cost any energy, because we can put the pair into the ground state (zero energy). If we shoot two unpaired electrons into the superconductor, we need at least energy 2Δ, because unpaired electrons has a higher energy than the paired ones, and this energy difference is the binding energy $E_B = 2\,\Delta$. Since adding two unpaired electrons needs energy 2Δ, if we shoot one electron into the superconductor, the energy cost is $\Delta = E_B/2$. This Δ is known as the BCS gap.

Experimentally, Δ can be measured via tunneling experiments. Let's put a metal and a superconductor together and apply a voltage between them (V). If $|\text{eV}| < \Delta$, a single electron cannot move from the metal into the superconductor (or vice versa), because the energy gain |eV| is smaller than the energy cost (Δ). If we increase the voltage, the current increases dramatically as $|\text{eV}|$ becomes larger than Δ, because now a single electron can tunnel through.

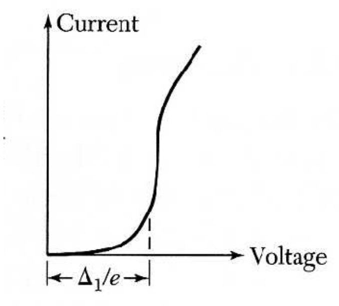

Fig. 4. Tunneling experiments and the energy gap.

10.3.6. Experimental evidence of the BCS theory II: energy gap/T_C

In the BCS theory,

$$\frac{\Delta_0}{k_B\,T} = \frac{2}{1.13} = 1.764 \tag{10.8}$$

This is indeed what one observes experimentally for convectional superconductors.

10.3.7. Experimental evidence of the BCS theory III: isotope effect

Because the attraction is mediated by phonons in the BCS theory, the transition temperature should depend on the mass of nucleons. As shown above, for the BCS theory, $T_c \propto \epsilon_D$, where ϵ_D is the Debye energy. For an isotropic elastic medium, it is

$$\epsilon_D = \hbar\omega_D = \hbar \left(\frac{6\,\pi^2}{V_C}\right)^{1/3} v \tag{10.9}$$

Here, V_C is the volume of a unit cell and v is the sound velocity. The sound velocity is typically proportional to $M^{-1/2}$, where M is the mass of the nucleons. For example, in Chapter 3, we calculated before the sound velocity for a 1D crystal, which has

$$v = \sqrt{\frac{K}{M}}\; a \tag{10.10}$$

Here, a is the lattice spacing, K is the spring constant of the bond and M is the mass of the atom.

Therefore, we found that $T_c \propto \epsilon_D \propto v \propto M^{-1/2}$, so the BCS theory predicts that $\alpha = 1/2$ in the isotope effect, which is indeed what observed in experiments.

10.3.8. Experimental evidence of the BCS theory IV (the direct evidence): charge are carried by particles with charge $-2\,e$, instead of $-e$

Q: How to measure the charge of the carriers?

A: the Aharonov–Bohm effect. Aharonove and Bohm told us that if we move a charged particle around a closed loop, the quantum wave function will pick up a phase $\Delta\phi$

$$\Delta\phi = q\,\Phi_B/\hbar \tag{10.11}$$

where q is the charge of the particle and Φ_B is the magnetic flux

$$\Phi_B = \int\int_S \vec{B}\cdot d\vec{S} = \oint \vec{A}\cdot d\vec{r} \tag{10.12}$$

We know that in quantum physics, particles are waves and thus they have interference phenomenon. For interference, the phase of a wave plays the crucial role, and thus one can detect this phase $\Delta\phi$ using interferometers. By measuring $\Delta\phi$ as a function of B, one can determine the charge of the particle. For superconductors, it is found to be $q = -2\,e$ (or $+2\,e$ for paring of holes).

We will come back to this point later with more details.

10.4. the Ginzburg–Landau theory

The BCS theory answered the question why electrons pair up. However, to understand why these pairs lead to the interesting phenomena of superconductivity and the Meissner effect, one needs to do something more. This task will be address in this section via investigating the Ginzburg–Landau theory of superconductivity. This theory is actually developed before the BCS theory, but in this lecture, we will use the BCS theory to guide us to write down this Ginzburg-Landau theory. Please keep in mind that when Ginzburg and Landau wrote down this theory, they didn't know the microscopic mechanism of superconductivity and they didn't know the existence of the Cooper pair. However, they still successfully developed the correct phenomenological theory, based on their physics intuitions.

10.4.1. Wave function and super fluid density

Let's first write down the wave function for the ground state of a Cooper pair $\psi_G(\vec{r})$. Because this ground state have many Cooper pairs (at low T, a large portion of Cooper pairs are on this ground state), we can combine all these Cooper pairs together and describe them with one wave function

$$\psi(\vec{r}) = \sqrt{N_S}\;\psi_G(\vec{r}) \tag{10.13}$$

Here, N_S is the number of Cooper pairs in the ground state. With this normalization factor, the mode square of $\psi(\vec{r})$ has a simple physical meaning

$$\rho(\vec{r}) = \psi(\vec{r})^*\,\psi(\vec{r}) = N_S\,\psi_G(\vec{r})^*\,\psi_G(\vec{r}) \tag{10.14}$$

Here, $\psi_G(\vec{r})^*\,\psi_G(\vec{r})$ is the probability density of finding a Cooper pair at position $\vec{r}$ if we just have one Cooper pair in the ground state. Therefore, $\rho(\vec{r}) = N_S\,\psi_G(\vec{r})^*\,\psi_G(\vec{r})$ is the probability density to find one Cooper pair at this position when we have a condensate (here N_S Cooper pairs is in the ground state). In other words, $\rho(\vec{r})$ is the density of Cooper pairs in the ground states. Because these Cooper pairs result in superconductivity, $\rho(\vec{r})$ is called the super fluid density.

The integer of ρ give us the total number of particles in the ground state, which is just N_S

$$\int d\vec{r}\;\rho(\vec{r}) = N_S \tag{10.15}$$

Notice that $\psi(\vec{r})$ is a complex function, we can write it in terms of absolute value and a complex phase

$$\psi(\vec{r}) = \sqrt{\rho(\vec{r})}\;e^{i\,\phi(\vec{r})} \tag{10.16}$$

The amplitude here is just the square root of the super fluid density, because $|\psi|^2 = \rho$.

Deep inside the superconductor, we assume that $\rho(\vec{r})$ is a constant, so that we can write

$$\psi(\vec{r}) = \rho\, e^{i\,\phi(\vec{r})} \tag{10.17}$$

10.4.2. Ginzburg–Landau free energy

For such a wavefunciton, one can write down the energy of this quantum state and this energy is known as the Ginzburg–Landau free energy. It is NOT the free energy we used in thermal dynamics, but it is similar. Very typically, the system want to go to the state which minimize the GL free energy.

The energy of this state relies on the detailed properties of the materials, which we don't know here. For Ginzburg and Landau, they didn't know the BCS theory when they developed this theory, so they didn't even know the clear physical meaning of ψ, and therefore, there is no way that they can obtain the accurate form of the enregy. However, they are smart enough to identify the "structure" of the energy, which is enough to explain many important phenomena. We know that the energy must relies on the wavefunction $\psi(\vec{r})$ and its derivatives $\nabla\psi(\vec{r})$, so we can write it down as

$$F = F\left(\psi(\vec{r}),\ \nabla\psi(\vec{r})\right) \tag{10.18}$$

Then, we expand the GL free energy as a power series of ψ and $\nabla\psi$

$$F = F_0 + \int d\vec{r}\left[\frac{\hbar^2}{2M}\nabla\psi^*(\vec{r})\nabla\psi(\vec{r}) + a\,\psi^*(\vec{r})\,\psi(\vec{r})\right] + \int d\vec{r}\, b\left[\psi^*(\vec{r})\,\psi(\vec{r})\right]^2 \tag{10.19}$$

Here the first term is the zeroth order term. The second and third terms are of the order ψ^2 and ψ^4 respectively. Because F must be real, we cannot have other terms up to $O(\psi^4)$.

For the normal phase ($N_S = 0$ and thus $\rho_S = 0$), we have $\psi(r) = 0$. Therefore, $F = F_0$. This tells us that the zeroth order term F_0 is just the GL free energy for the normal state. Therefore, we will now rename F_0 as F_n, where n stands for the normal state

$$F = F_n + \int d\vec{r}\left[\frac{1}{2M}(-i\hbar\nabla\psi)^*(-i\hbar\nabla\psi) + a\,\psi^*\psi + b\,(\psi^*\psi)^2\right] \tag{10.20}$$

The first term in the integral is just the kinetic energy $\left(p^2/2M\right)$, and therefore the value of M should be the mass of the particles (cooper pairs). In other words, M should be twice of the effective mass of electrons (or holes)

$$M = 2\,m^* \tag{10.21}$$

This is something Ginzburg and Landau didn't know when they develop this theory.

Because Cooper pairs are charged, the wave function should couple to E and M field. We have discussed before how to couple a wavefunction to E and M field before in quantum mechanics (the minimal coupling). Basically, we just need to substitute momentum p into

$$\vec{p} \to \vec{p} + \frac{q}{c}\vec{A} \tag{10.22}$$

Here we don't need to consider electric potential , because E=0 inside a perfect metal.

$$F = F_n + \int d\vec{r}\left[\frac{1}{2M}\left[\left(-i\hbar\nabla + \frac{q}{c}\vec{A}\right)\psi\right]^*\left[\left(-i\hbar\nabla + \frac{q}{c}\vec{A}\right)\psi\right] + a\,\psi^*\psi + b\,(\psi^*\psi)^2\right] \tag{10.23}$$

Now, we use the fact

$$\psi(\vec{r}) = \sqrt{\rho}\; e^{i\,\phi(\vec{r})} \tag{10.24}$$

So the free energy can be rewrite as

$$F = F_n + \int d\vec{r} \left[\frac{\rho}{2M} \left(\hbar \nabla\phi + \frac{q}{c} \vec{A}\right)^2 + a\,\rho + b\,\rho^2\right] \tag{10.25}$$

10.4.3. The superconductor transition

We need to minimize the GL free energy to find the proper quantum state.

$$F = F_n + \int d\vec{r} \left[\frac{\hbar^2 \rho}{2M} \left(\nabla\phi + \frac{q}{\hbar c} \vec{A}\right)^2 + a\,\rho^2 + b\,\rho^4\right] \tag{10.26}$$

The first term inside the integer is no negative. So its minimum value is zero. This minimum is reached when

$$\nabla\phi + \frac{q}{\hbar c} \vec{A} = 0. \tag{10.27}$$

This result has very important impact and we will revisit it in the next section.

$$F = F_n + \int d\vec{r} \left[a\,\rho + b\,\rho^2\right] \tag{10.28}$$

The problem here is to minimize the function $a\,\rho + b\,\rho^2$ for $\rho \geq 0$. For stability reasons, we assume $b > 0$ (if $b < 0$, the minimum of the free energy is $-\infty$ at $\rho = \pm\infty$, which is unphysical).

If $a > 0$, the function $a\,\rho + b\,\rho^2$ reaches its minimum at $\rho = 0$. In other words, the system has zero super fluid density, so this is the normal state.

If $a < 0$, the function $a\,\rho + b\,\rho^2$ reaches its minimum at $\rho = -a/2\,b$, and the minimum value is $-a^2 \big/ 4\,b$. In other words, this is the superconductor state with super fluid density $\rho = -a/2\,b$.

With this intuition, we know that the coefficient a must depend on temperature $a(T)$.

At $T > T_C$, $a(T)$ is positive, so the normal state has the lowest GL free energy

At $T < T_C$, $a(T)$ is negative, so the superconductor state has the lowest GL free energy.

The transition temperature T_C is determined by the equation $\alpha(T) = 0$. [or say, $a(T_C) = 0$]

If we expand $a(T)$ near the transition point,

$$a(T) = a(T_C) + a'\,(T = T_C)\,(T - T_C) + \ldots \tag{10.29}$$

If we ignore higher order term, we find that

$$a(T) = a_0(T - T_C) \tag{10.30}$$

Here we used the fact that $a(T_C) = 0$ and we defined $a_0 = a'\,(T = T_C)$.

Because $\rho = -a/2\,b$, near the transition temperature (T close but slightly smaller than T_C)

$$\rho = -a/2\,b \approx -a_0(T - T_C)/2\,b = a_0/2\,b(T_C - T) \tag{10.31}$$

Therefore, the super fluid density creases as $T_C - T$ for $T \sim T_C$.

10.4.4. The Meissner effect

Now, let's consider the superconducting phase where $\rho = -a/2\,b > 0$.

$$F = F_n + \int d\vec{r} \left[\frac{\hbar^2 \rho}{2M} \left(\nabla\phi + \frac{q}{\hbar c} \vec{A}\right)^2 - \frac{a^2}{4\,b}\right] \tag{10.32}$$

To minimize the free energy, the first term must be zero

$$\nabla\phi + \frac{q}{\hbar c} \vec{A} = 0 \tag{10.33}$$

If we take a curl on both sides, we find that

$$0 = \nabla \times \nabla \phi + \frac{q}{\hbar c} \nabla \times \vec{A} = -\frac{q}{\hbar c} \vec{B} \tag{10.34}$$

Therefore, B=0 inside a superconductor. This is the Meissner effect.

10.4.5. Quantization of magnetic flux

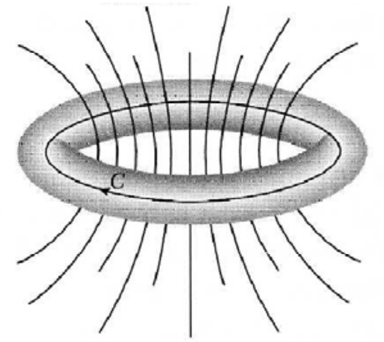

Fig. 5. Magnetic flux through a superconducting ring

Consider a superconducting ring and we draw a loop around the ring. We can compute the loop integral around this loop

$$\oint d\vec{r} \cdot \left(\nabla \phi + \frac{q}{\hbar c} \vec{A}\right) = \oint d\vec{r}\, 0 = 0 \tag{10.35}$$

Therefore,

$$\oint d\vec{r} \cdot \nabla \phi = -\oint d\vec{r} \cdot \frac{q}{\hbar c} \vec{A} \tag{10.36}$$

$$\oint d\vec{r} \cdot \nabla \phi = \phi_{\theta=2\pi} - \phi_{\theta=0} \tag{10.37}$$

Here, $\oint d\vec{r} \cdot \nabla \phi$ measures the change of the phase ϕ when we go around the loop. Because the final point and the initial point are the same point in real space, the phase must differ by $2 \pi n$.

$$\oint d\vec{r} \cdot \nabla \phi = 2 \pi n = -\oint d\vec{r} \cdot \frac{q}{\hbar c} \vec{A} = -\frac{q}{\hbar c} \oint d\vec{r} \cdot \vec{A} = -\frac{q}{\hbar c} \int\int d\vec{r}\, \nabla \times \vec{A} = -\frac{q}{\hbar c} \int\int d\vec{r}\, \vec{B} = -\frac{q}{\hbar c} \Phi_B \tag{10.38}$$

where Φ_B is the magnetic flux inside the ring.

$$\Phi_B = 2 n \pi \frac{\hbar c}{q} = n \frac{h c}{q}. \tag{10.39}$$

Notice that this quantization has the charge of the particle q invovled. Here, the charge q is ±2e, instead of e because electrons pairs up. This is the direct evidence of the existence of Cooper pairs.

10.4.6. London equation