

# Superconductivity and the BCS theory

PHY 313 - Statistical Mechanics

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## 1 Introduction

In this report we would discuss the evolution of the theories of superconductivity. We would discuss theories that explain superconducting phenomenon at both macroscopic and microscopic scales. Superconductors are materials that undergo a phase transition below a certain critical temperature in which the resistivity of the material suddenly drops to zero. This is a very interesting quantum mechanical phenomenon and offers great insights into the exciting and mind boggling quantum world.

We first motivate the need for a theory by studying the Drude model for metals and see how it does not cater for the superconducting phase shift. We also look at the evidences of superconducting behaviour like the Meissner effect and diamagnetism.

We discuss the distinction between the types of superconducting material and then derive the London Equation. This equation was the first time that the theory of superconductivity was modelled, we look into the limitations and assumptions of this theory and how it leaves space for a more complete theory.

We move on to the Ginzburg Landau model and see how superconductivity can be explained through thermodynamic parameters, this is a macroscopic model and BCS theory is a special case of it when we apply certain limits. We also solve an example and do some calculation for the GL model.

We look into macroscopic coherent states and motivate the microscopic theory for superconductivity, we then discuss the BCS theory which is the most complete microscopic theory of conductivity up till now. We highlight the main features of the theory and discuss Cooper pairs and energy gaps for a superconducting material. And finally we look at a couple of applications and examples related to the subject.

## 2 Superconductivity

### 2.1 Conduction in metals

The theory of conduction in metals was given by the Drude model around 1900, the wavefunction of crystalline solids obey the Bloch's theorem. The energy of these Bloch wave states give the energy bands,  $\epsilon_{nk}$  where  $\mathbf{n}$  counts the different electron bands. Electrons are fermions and so at temperature  $T$  a state with energy  $\epsilon$  is occupied according to the Fermi-Dirac distribution.

$$f(\epsilon) = \frac{1}{e^{\beta(\epsilon-\mu)}} \quad (1)$$

In all metals the temperature is such that this fermi gas is in a highly degenerate state, in which  $k_B T \ll \mu$ . In this case  $f(\epsilon)$  is nearly 1 inside the fermi surface and is 0 outside. In this Fermi gas description of metals the electrical conductivity,  $\sigma$  is given by the Drude theory:

$$\sigma = \frac{ne^2\tau}{m} \quad (2)$$

where  $m$  is the mass of electrons,  $e$  is the electron charge and  $\tau$  is the average lifetime. The resistivity  $\rho$  is the reciprocal of conductivity and is given by

$$\rho = \frac{m}{ne^2\tau^{-1}} \quad (3)$$

This scattering rate  $\tau^{-1}$  is a sum of many scattering rates due to the impurities and electron-electron, phonon-electron interactions. These scattering rates are proportional to different orders of Temperature and resistivity can be given in the form of.

$$\rho = \rho_0 + aT^2 + \dots \quad (4)$$

For most metals the resistivity does behave in this way, however in the case of superconductors below a certain critical temperature the resistivity suddenly drops to zero. This was quite different from the Drude model and in fact a new state of matter: superconductivity was discovered.

## 2.2 Zero Resistivity

The thermodynamic phase transition is very sudden, at this state the resistivity becomes exactly zero. But how can we be sure if the resistivity is exactly zero as there could be resistance due to the connecting leads and wires. A convincing evidence is the observation of persistent currents. Current can flow in superconductors without any impedance but above a certain critical current  $I_c$  the superconductivity is destroyed. Now we observe how a persistent current remains in a ring of superconducting material. The flux is given by:

$$\phi = \int B \cdot dS \quad (5)$$

By Maxwell equation

$$\nabla \times E = -\frac{\partial B}{\partial t} \quad (6)$$

and Stokes theorem

$$\int (\nabla \times E) \cdot dS = \oint E \cdot dr \quad (7)$$

$$-\frac{d\phi}{dt} = \oint E \cdot dr \quad (8)$$

The line integral is taken around a closed loop so it equals zero and it implies that

$$\frac{d\phi}{dt} = 0 \quad (9)$$

and hence the magnetic field remains constant as a function of time, Even when we close the external magnetic field  $B_{ext}$ , we know from equation (9) that the B field has to remain constant and so a B field would remain there to maintain constant flux and hence there would be a constant current in the ring. Experiments show that these currents can remain constant for over a period of years.

## 2.3 Meissner effect and Perfect diamagnetism

The Meissner effect is a fact that a superconductor expels a weak external magnetic field. This again follows from equation (9), we have a certain superconducting material inside a external magnetic field. Initially the temperature is above the critical temperature  $T_c$ , gradually we decrease the temperature and below the  $T_c$  the magnetic field is expelled.

In order to maintain  $B = 0$  inside the sample, screening currents flow around the edges of the sample. These currents produce a magnetic field which is equal and opposite to the applied external field, leaving zero field in total. The total current is a sum of the external applied currents  $j_{ext}$  and internal screening currents  $j_{int}$ ,

$$j = j_{ext} + j_{int} \quad (10)$$

the screening currents produce magnetisation  $M$  in the sample given by:

$$\nabla \times M = j_{int} \quad (11)$$

also there is the magnetic field  $H$  that causes the external currents:

$$\nabla \times H = j_{ext} \quad (12)$$

The vectors are related by equation

$$B = \mu_0(H + M) \quad (13)$$

By Maxwell equations

$$\nabla \cdot B = 0 \quad (14)$$

Hence we get that the applied field and the field due to the screening currents are equal and opposite in direction

$$M = -H \quad (15)$$

The magnetic susceptibility is given by

$$\chi = \frac{dM}{dH} \quad (16)$$

$$\chi = -1 \quad (17)$$

Solids with negative susceptibility are called diamagnets, superconductors are perfect diamagnets. They become magnetised oppositely to the applied field to create a net zero field.

## 2.4 Type I and Type II superconductivity

In type I superconductors, the  $B$  field remains zero inside the superconductor until the superconductivity is destroyed above a certain field  $H_c$ . However many superconductors are type II and behave differently, they have two different critical fields denoted by the lower critical field  $H_{c1}$  and upper critical field  $H_{c2}$ .

The region between  $H_{c1}$  and  $H_{c2}$  is the region in which the superconductor is a mixture of the superconducting and normal phase. This phenomenon can be explained with the help of vortices. Each vortex is a small region in a superconducting material which acts like a normal metal, this allows the bulk of the material to remain superconducting but allows a finite flux density to pass through hence the mixed behaviour.

## 2.5 London Equation

The first theory that explained the superconductivity model to a great extent was the London equation:

$$j = -\frac{n_s e^2}{m_e} A \quad (18)$$

where  $A$  is the magnetic vector potential and  $j$  is the electrical current density inside a superconductor. There were some limitations to this model as they assumed that the conductivity  $\sigma$  which is a function of frequency is a delta function centred at  $\omega = 0$ , but actually there is an additional term that is responsible for the energy gap. We would ignore that part for the derivation of the London equation and talk about it later in the report.

Now we derive the London equation, the current density  $j$  is given by:

$$j = \sigma E \quad (19)$$

taking curl on both sides, and plugging in the value of conductivity  $\sigma$  from the Drude model, equation(2)

$$\nabla \times j = -\frac{n_s e^2}{m_e} B \quad (20)$$

By Maxwell equation

$$\nabla \times B = \mu_0 j \quad (21)$$

Combining the above two equation

$$\nabla \times (\nabla \times B) = -\mu_0 \frac{n_s e^2}{m_e} B \quad (22)$$

$$\nabla \times (\nabla \times B) = -\frac{1}{\lambda^2} B \quad (23)$$

where  $\lambda$  is the penetration depth of the superconductor

$$\lambda = \left( \frac{m_e}{\mu_0 n_s e^2} \right)^{1/2} \quad (24)$$

## 3 Ginzburg Landau model

The theory of superconductivity introduced by Ginzburg and Landau is a macroscopic theory, and the BCS theory is a suitable limit to it at the microscopic scale. By the definition of magnetic work the first law of thermodynamics for a magnetic material becomes:

$$dU = TdS + \mu_0 V H.dM \quad (25)$$

The magnetic work is analogous to the work in a gas  $-PdV$ . Using Helmholtz free energy  $F(T,M)$  and Gibbs free energy  $G(T,M)$  we can further calculate the entropy and magnetisation of the system. We would skip the simple algebraic manipulation and jump to the result of getting the difference in Gibbs free energies for a superconducting and normal phase.

$$G_s(T, 0) - G_n(T, 0) = -\mu_0 V \frac{H_c^2}{2} \quad (26)$$

This quantity is the condensation energy, it is the measure of the gain in free energy per unit volume in superconducting phase compared to the normal state at the same temperature.

As an example we would calculate this condensation energy for a superconducting material niobium. Where  $T_c=9K$ , and  $H_c = 160kAm^{-1}$ . The condensation energy turns out to be  $16.5kJm^{-3}$ . Using the the volume per atom we can work out the condensation energy per atom which turns out to be  $2\mu eV/atom$ . Such tiny energies were a mystery until the BCS theory.

Landau and Ginzburg introduced a new parameter  $\psi$ , this characterised the superconducting state. It is zero for temperatures greater than the critical temperature and is non-zero for temperatures below the critical temperature. They proposed the free energy of a superconductor in terms of the order parameter  $\psi$ . By minimizing the free energy with respect to to fluctuations they arrived at the Ginzburg Landau equations:

$$\alpha\psi + \beta|\psi|^2\psi + \frac{1}{2m}(-i\hbar\nabla - 2eA)^2\psi = 0 \quad (27)$$

$$j = \frac{2e}{m}Re[\psi^*(-i\hbar\nabla - 2eA)\psi] \quad (28)$$

$\alpha$  and  $\beta$  are constants,  $j$  is the current density. Although the first equation is similar to the schrodinger equation but because of the  $\psi^2$  term it is a non linear equation and is solved using bessel functions. These equations can be used to calculate the coherence length (the length from the surface over which the order parameter recovers to its original value) and the penetration depth. This penetration depth is similar to that derived above using London equations but is in terms of the order parameter.

## 4 Macroscopic Coherent State

A macroscopic wavefunction arises from coherent states, many particles have the same wave function and no phase difference so you can observe the quantum mechanical properties at a macroscopic scale. Coherent states can be defined for Bosons but can not be defined for single fermions because of the pauli exclusion principle. So to explain superconductivity we define coherent states of pairs of fermions. I won't go into the details of the mathematics of these coherent states but qualitatively discuss some interesting aspects of these coherent states. We can treat them as Bose condensates of fermion pairs.

What we do is define a wavefunction for the coherent states and also define some ladder operators for the fermion pairs. Using commutator relationships we come up with a very interesting result relating the number of the states and the phase of the states. We find that the phase  $\theta$  and the number  $n$  are conjugate operators and follow a kind of uncertainty principle:

$$\Delta n \Delta \theta \geq \frac{1}{2} \quad (29)$$

Here  $\theta$  is the phase of the coherent state. This relation suggests that coherent states with a fixed phase, donot have a definitive values of number of states. And subsequently for well defined number  $n$  of the eigenstates we have a arbitrary phase. This is a beautiful mathematical property and is also applied to cooper pairs, which are the fermion pairs.

## 5 BCS theory of superconductivity

### 5.1 Introduction

One of the significant achievements of the BCS theory is explaining that the cooper pairs must have a definitive quantum mechanical phase  $\theta$  and consequently that we should not work with a fixed particle number  $N$ . This follows from the uncertainty principle we motivated above.

BCS is the first theory that explained superconductivity at a microscopic scale. It also correctly predicts the energy gap  $2\Delta$  at the fermi level. The BCS theory gives us some major insights into the world of superconductivity. Firstly it turns out that the effective forces between electrons can sometimes be attractive, this is due to the phonon electron coupling. Cooper considered a single electron pair outside a occupied fermi surface and found that the fermions formed a stable pair bound state no matter how weak the attractive force. Finally Schreiffer constructed a many particle wave function in which all electrons near the fermi surface are paired up, this is a form of coherent states and the energy gap arises from it's analysis. This energy gap  $2\Delta$  is the energy required to breakup a pair into two free electrons.

## 5.2 Electron-phonon interaction and Cooper pairs

The first key idea is attraction between the electron pairs, this is surprising as there is usually coulomb repulsion between bare electrons. But in a metal we should think of them as quasiparticles rather than bare electrons. A quasiparticle is an excitation of a solid consisting of a moving electron together with a surrounding exchange correlation hole. An electron moving through a conductor will attract nearby positive charges in the lattice. This deformation of the lattice causes another electron, with opposite "spin", to move into the region of higher positive charge density. The two electrons then become correlated. There are a lot of such electron pairs in a superconductor, so that they overlap very strongly, forming a highly collective "condensate". So electrons which lie within  $\pm k_B T$  of the fermi energy and  $\hbar\omega_D \geq k_B T$ , there is superconductivity.

In the normal state of a metal, electrons move independently, whereas in the BCS state, they are bound into "Cooper pairs" by the attractive interaction. The BCS formalism is based on the "reduced" potential for the electrons attraction.

## 5.3 Energy gap and quasiparticle state

You have to provide energy equal to the 'energy gap' to break a pair, to break one pair you have to change energies of all other pairs. This is unlike the normal metal, in which the state of an electron can be changed by adding a arbitrary small amount of energy. The energy gap is highest at low temperatures but does not exist at temperatures higher than the transition temperature. The BCS theory gives an expression of how the gap grows with the strength of attractive interaction and density of states.

The BCS theory gives the expression of the energy gap that depends on the Temperature  $T$  and the Critical Temperature  $T_c$  and is independent of the material:

$$E = 3.52k_B T_c (1 - (T/T_c))^{1/2} \quad (30)$$

# 6 Examples and Applications

## 6.1 Josephson Effect

The Josephson effect is an example of quantum coherence and BCS theory. It is a demonstration of tunneling between two superconductors. We have performed this experiment in our junior physics lab using SQUIDS (Superconducting Quantum Interference Devices). The superconductors are weakly coupled and the current that flows through one junction is:

$$I = I_c \sin(\theta_L - \theta_R) \quad (31)$$

Where  $I_c$  is the critical current. What we do is have two such superconductor junctions in a ring, as a result the two components of the input current pass through two junctions and add, after some simple

algebraic manipulation we get the following expression:

$$I_c(\phi) = I_o \left| \cos\left(\frac{\pi\phi}{\phi_o}\right) \right| \quad (32)$$

Here the two Josephson junctions play the role of two slits and there is interference between the supercurrents passing through the two halves of the ring. These SQUIDS can be used to measure very small magnetic fields, we can also measure the flux quantum  $\phi_o$  which is the smallest quantity of quantised flux.

## 6.2 Quantum Computing

Another interesting application of microscopic quantum coherence is in quantum computing. The macroscopic wave function does not obey the fundamental principle of superposition. There is the idea of decoherence in which the interactions with the environment lead to entanglement between the quantum states of the system and the environment and 'quantum information' is lost. But if we keep making the SQUID ring smaller and smaller, we would have bits so small that they behave as quantum mechanically and not classically. For such a quantum bit or 'qubit' information is carried by its full quantum state and not just 0 or 1.

## References

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