Chapter 1
Superconductivity

1.1 Introduction

The phenomenon of superconductivity was discovered in 1911 by Heike Kamerlingh Onnes (Onnes, 1911). He found the electritical resistivity vanishes at the temperature 4K of the liquid helium. Below a particular temperature, called the critical temperature or transition temperature, T_c a material becomes a perfect superconductor. Above the critical temperature it is a normal metal. A perfect superconductor has two characteristic properties, first the zero electrical resistance, secondly the perfect diamagnetism. Diamagnetism is the ability of a material to shield its interior from an applied magnetic field, on reaching its superconducting transition temperature, the magnetic flux is suddenly completely expelled from its interior . We know this effect as the Meissner effect which Meissner and Ochsenfeld found in 1933 (Meissner and Ochsenfeld, 1933). Both zero resistivity and perfect diamagnetism are fundamental properties of the superconducting state . Here we will summarize the basic experimental facts and the phenomenological theory of superconductivity.

1.2 Zero Resistivity

The d-c electrical resistivity of materials in the superconducting state is zero. This fact is established when the resistance of metallic elements suddenly drops at a critical temperature T_c and go to zero .

1.3 Meissner Effect

Although the first characteristic property of a superconductor is spectacular, the experiment shows that all magnetic flux is expelled from the interior

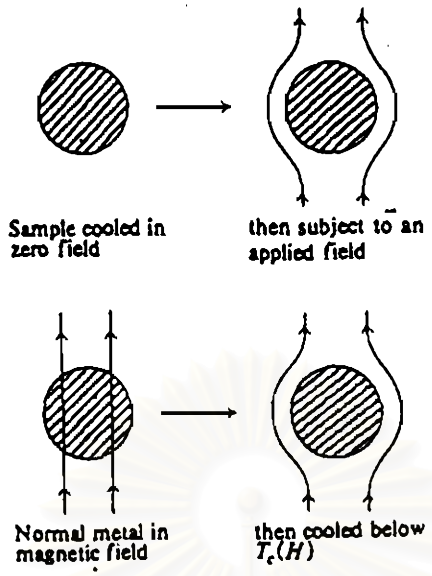

Figure 1.1: Meissner effect (Fetter and Walecka, 1995)

when the material is cooled through the superconducting transition temperature (Fig. 1.1). This result exhibits perfect diamagnetism which is an independent property of superconductors and involves a transition of thermodynamic state between the normal and superconducting states at sufficiently low magnetic fields. This transition is reversible and not a consequence of zero resistance and Lenz's law. Since there is no time rate change of the magnetic induction, Lenz's law does not apply. The magnetic field, at the absolute zero temperature, can destroy the superconducting state at some value which is called the critical magnetic field, $H_c(0)$. At any temperature T below T_c, the approximate expression of the critical field $H_c(T)$ for all superconductors is given by (Fig. 1.2)

$$H_c(T) = H_c(0)[1 - (\frac{T}{T_c})^2] \tag{1.1}$$

1.4 Flux Quantization

Another important property of the Meissner effect is the occurrence of the trapped flux when an applied magnetic field is removed. By considering the superconducing ring which magnetic flux can pass through it. The circulating

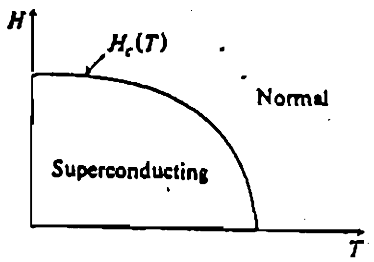

Figure 1.2: Phase diagram of the magnetic field vs. temperature, the seperation between the normal (N) and the superconducting (S) states represented by the curve $H_c(T)$ (Fetter and Walecka, 1995)

persistent current in the ring is related to the quantization of the flux enclosed, and the quantized flux value

$$\varphi = \frac{hc}{2e} = 2.07 \times 10^{-7} gauss.cm^2 \tag{1.2}$$

1.5 Specific Heat

Besides its magnetic property, the thermal property of a superconductor such as the specific heat provides a decisive evidence for the existence of an energy gap in the electronic excitation spectrum.

The total specific heat C of a normal metal comes from the lattice and the conduction electrons, and can be expressed as

$$C = \gamma T + \beta T^3 \tag{1.3}$$

where the first term is due to the electrons and the second term is due to the lattice. Here T is the temperature, γ is the coefficient of the normal electronic specific heat, and β is the constant of the phonon part. Suppose the lattice has a property that is unchanged between the normal and the superconducting states. Then it is sufficient to consider only the electronic contribution to specific heat.

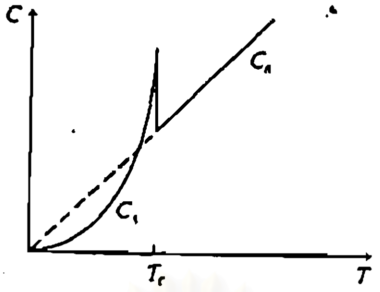

Figure 1.3: Diagram of specific heat as a function of temperature (Fetter and Walecka, 1995)

In zero applied magnetic field, the transition occurs with no latent heat which is a second-order phase change, i.e., the state of the system changes continuously from normal to superconducting states and vice versa. The specific heat shows a discontinuous jump at T_c, drops rapidly for $T < T_c$ and vanishes at $T = 0$. The specific heat in the superconducting states depends on temperature and is expressed in the form

$$C_s \propto exp(\frac{-\Delta}{k_B T}) \tag{1.4}$$

This formula suggests the existence of the energy gap Δ in the electronic excitation spectrum. If the transition occurs at $T < T_c$ in the presence of a magnetic field, the latent heat is associated with the transition which corresponds to the heat absorption of the sample to go to the normal phase.

1.6 Isotope Effect

An essential part of superconductivity is the discovery of the isotope effect, (Fröhlich, 1950), when different isotopes of metallic elements are substituted into superconductors, such as tin and mercury, the critical temperature varies with the mean atomic mass M as

$$T_c M^\alpha = constant \tag{1.5}$$

where T_c is the transition temperature, and $\alpha = 0.5$ for many superconductors. This result provides strong support for Fröhlich's suggestion that superconductivity might be associated with an electronic interaction mediated by movements of the lattice ions. This is the reason, why the lattice vibrations are important, since T_c should change as neutrons are added to the atomic nuclei to change the mass of vibrating ions.

1.7 London Theory

After the Meissner effect was established, F. and H. London introduced the first phenomenological theory of superconductivity (London and London, 1935). The London theory accounts for the observed properties of zero resistance and perfect diamagnetism which gives an essential description for all the electromagnetic properties of superconductors, and can explain the thermal properties of superconductors.

The central point of the London theory is that the supercurrent is always determined by the local magnetic field. The equations of this theory are postulated to satisfy

$$\frac{d\vec{j}_s}{dt} = \frac{n_s e^2}{m}\vec{E} \tag{1.6}$$

with $\vec{j}_s = -en_s\vec{v}_s$,

$$\nabla \times \vec{j}_s = -\frac{n_s e^2}{mc}\vec{B} \tag{1.7}$$

where -e is the electronic charge and n_s the electron density. The first equation is the Newton's law applied to the supercurrent density, $\vec{j}_s$. The latter equation leads to the Meissner effect. In order to see this, we take the curl of one of static Maxwell's equations

$$\nabla \times \nabla \times \vec{B} = \frac{4\pi}{c}\nabla \times \vec{j}_s \tag{1.8}$$

Next, combining Eqs.(1.7) and (1.8) we obtain

$$\nabla^2\vec{B} = \frac{4\pi n_s e^2}{mc^2}\vec{B} = \frac{1}{\lambda_L^2}\vec{B} \tag{1.9}$$

where the London penetration depth, λ_L, is defined by

$$\lambda_L = \sqrt{\frac{mc^2}{4\pi n_s e^2.}} \tag{1.10}$$

The solution of Eq.(1.9) depends on geometry and boundary conditions of the material. For a semi-infinite superconductor ($z > 0$) in a parallel applied field $H_0\hat{x}$, the magnetic field $\vec{B}(z) = B(z)\hat{x}$ decreases into the superconductor according to

$$B(z) = H_0 e^{-\frac{z}{\lambda_L}} \tag{1.11}$$

Thus the magnetic field inside a superconductor vanishes exponentially for $z \gg \lambda_L$ and one obtains the Meissner effect, the perfect diamagnetism. The variation of λ_L with the temperature, as observed experimentally, is described by

$$\lambda_L(T) = \frac{\lambda_L(0)}{\sqrt{1 - (\frac{T}{T_c})^4}} \tag{1.12}$$

where $\lambda_L(0)$ is the London penetration depth, λ_L increases rapidly as T increases and λ_L tends to infinity when T approaches T_c so that the magnetic flux can penetrates the materials at T_c.

1.8 BCS Theory

The occurence of superconductivity at the microscopic level was a long time searching. A crucial point happened when Cooper (Cooper, 1956) developed an important concept that in the presence of an attractive interaction, two independent electrons above a Fermi sea are unstable toward the formation of a bound Cooper pair. The binding energy of one pair particles in the weak coupling limit [N(0)V $\ll$ 1] is found to be

$$E = -2\omega_D \exp\left[-\frac{2}{N(0)V}\right] \tag{1.13}$$

Here ω_D is the Debye cutoff energy, N(0) is the constant density of states per spin at the Fermi level due to the slow variation of the electronic states in an energy interval $0 < \epsilon < \omega_D$. V is the attractive interaction between electrons which comes from the phonon mediated interaction

$$V_{\vec{k}\vec{k}'} = \frac{|g^2_{\vec{k}-\vec{k}'}|\omega_{\vec{k}-\vec{k}'}}{(\epsilon_{\vec{k}} - \epsilon_{\vec{k}'})^2 - \omega^2_{\vec{k}-\vec{k}'}} \tag{1.14}$$

$g_{\vec{k}-\vec{k}'}$ is the coupling strength of an electron-phonon interaction matrix element, $\omega_{\vec{k}-\vec{k}'}$ is the phonon frequency and $\epsilon_{\vec{k}}$ is the excitation energy. When the interaction is weak, the difference between the excitation energies $\epsilon_{\vec{k}}$ and $\epsilon_{\vec{k}'}$ has a small value. Then the phonon interaction is attractive and reduced to

$$V_{\vec{k}\vec{k}'} = -\frac{|g^2_{\vec{k}-\vec{k}'}|}{\omega_{\vec{k}-\vec{k}'}} \tag{1.15}$$

which is approximately independent of $\vec{k}, \vec{k}'$. Thus the interaction can be taken to be a constant (-V) as stated before. The binding energy shows that an addition electron would like to form a state which is bound relative to the Fermi sea. However in the real system when the number of pairs are macroscopic, the interaction between pairs cannot be negligible. Bardeen, Cooper, and Schrieffer (BCS) (Bardeen, Cooper, and Schrieffer, 1957) developed further the Cooper's idea, they suggested that superconductivity arises from the presence of the Cooper pair mediated by the electron-phonon interaction. The ground state of the superconducting state with no supercurrent at the absolute zero of temperature may be written as

$$| BCS > = \prod_{\vec{k}} (u_{\vec{k}} + v_{\vec{k}} c^{\dagger}_{\vec{k}\uparrow} c^{\dagger}_{-\vec{k}\downarrow}) \mid 0 > \tag{1.16}$$

In this state the electrons are created in $(\vec{k}\uparrow, -\vec{k}\downarrow)$ pairs, all having the zero pair momentum and also the zero total spin. The parameters $u_{\vec{k}}$ and $v_{\vec{k}}$ are real with the normalization condition $u^2_{\vec{k}} + v^2_{\vec{k}} = 1$. $u^2_{\vec{k}}$ is the probability that the momentum pair state is empty while $v^2_{\vec{k}}$ the probability that it is occupied. BCS started from the wave function and found the coefficients $u_{\vec{k}}$ and $v_{\vec{k}}$ from the variational principle. The model Hamiltonian proposed by BCS is given by

$$H = \sum_{\vec{k}s} \epsilon_{\vec{k}} c^{\dagger}_{\vec{k}s} c_{\vec{k}s} + \sum_{\vec{k}\vec{k}'} V_{\vec{k}\vec{k}'} c^{\dagger}_{\vec{k}\uparrow} c^{\dagger}_{-\vec{k}\downarrow} c_{-\vec{k}'\downarrow} c_{\vec{k}'\uparrow} \tag{1.17}$$

where $\epsilon_{\vec{k}}$ is the energy of a conduction electron with respect to the chemical potential, μ. The creation and destruction operators for electrons of wave vector $\vec{k}$ and z component of spin s (up or down) are denoted by $c^{\dagger}_{ks}$ and c_{ks}, respectively. The interaction matrix element $V_{\vec{k}\vec{k}'}$ represents the scattering of one pair of states $(\vec{k}\uparrow, -\vec{k}\downarrow)$ into another pair of states $(\vec{k}'\uparrow, -\vec{k}'\downarrow)$. The solution of the Hamiltonian cannot be obtained by perturbation theory since the quasi particle picture of the normal state is insufficient to provide the superconducting phase. The important feature of the quasi particle picture is that the interaction between the quasi particles is neglected and absorbed into the effective mass of electrons.

Since the interaction term assumes that such electron pairs act as units, the ground state will be some coherent superposition of many-body states in which the states $(\vec{k}\uparrow, -\vec{k}\downarrow)$ are occupied or unoccupied in pairs. This means that the operator $c_{-\vec{k}\downarrow} c_{\vec{k}\uparrow}$ is equal to the thermal average $< c_{-\vec{k}\downarrow} c_{\vec{k}\uparrow} >$ and the fluctuation term, $c_{-\vec{k}\downarrow} c_{\vec{k}\uparrow} - < c_{-\vec{k}\downarrow} c_{\vec{k}\uparrow} >$, should be negligible. In general, the pair operators $c_{-\vec{k}\downarrow} c_{\vec{k}\uparrow}$ can be written in the form

$$c_{-\vec{k}\downarrow} c_{\vec{k}\uparrow} = < c_{-\vec{k}\downarrow} c_{\vec{k}\uparrow} > + (c_{-\vec{k}\downarrow} c_{\vec{k}\uparrow} - < c_{-\vec{k}\downarrow} c_{\vec{k}\uparrow} >) \tag{1.18}$$

The expectation value of this operator is now determined. A gap parameter is defined by

$$\Delta_{k'} = -\sum_{\vec{k}} V_{\vec{k}'\vec{k}} < c_{-\vec{k}\downarrow} c_{\vec{k}\uparrow} > \tag{1.19}$$

Δ_k is a new quantity and may be thought of as being like an internal field, it expresses the influence of the mixed occupation in all the other $(\vec{k}'\uparrow, -\vec{k}'\downarrow)$ pairs of the $(\vec{k}\uparrow, -\vec{k}\downarrow)$ pair through the attractive matrix elements. Using Eqs.(1.18) and (1.19), the model Hamiltonian becomes

$$H = \sum_{\vec{k}s} \epsilon_{\vec{k}} c^{\dagger}_{\vec{k}s} c_{\vec{k}s} - \sum_{\vec{k}} (\Delta_{\vec{k}} c^{\dagger}_{\vec{k}\uparrow} c^{\dagger}_{-\vec{k}\downarrow} + \Delta^{*}_{\vec{k}} c_{-\vec{k}\downarrow} c_{\vec{k}\uparrow} - \Delta^{*}_{\vec{k}} < c_{-\vec{k}\downarrow} c_{\vec{k}\uparrow} >) \tag{1.20}$$

since this Hamiltonian is now quadratic, it can be diagonalized by the canonical transformation

$$\begin{aligned} c_{\vec{k}\uparrow} &= u_{\vec{k}} a_{\vec{k}1} + v^{*}_{\vec{k}} a^{\dagger}_{\vec{k}2}, \\ c^{\dagger}_{-\vec{k}\downarrow} &= -v_{\vec{k}} a_{\vec{k}1} + u^{*}_{\vec{k}} a^{\dagger}_{\vec{k}2} \end{aligned} \tag{1.21}$$

where the new operators $a_{\vec{k}1}$ and $a_{\vec{k}2}$ are Fermion annihilation operators. The parameters $u_{\vec{k}}$ and $v_{\vec{k}}$ are chosen such that the coefficients of the mixed terms such as $c^{\dagger}_{\vec{k}1} c^{\dagger}_{\vec{k}2}$ in the Hamiltonian vanish. This can be satisfied if

$$2\epsilon_{\vec{k}} u_{\vec{k}} v_{\vec{k}} + \Delta_{\vec{k}} v^2_{\vec{k}} - \Delta^{*}_{\vec{k}} u^2_{\vec{k}} = 0. \tag{1.22}$$

From the canonical transformation, the important property is that the anticommutation relations between a's being the same as those between the c's, and the constraints is that

$$|u_{\vec{k}}|^2 + |v_{\vec{k}}|^2 = 1. \tag{1.23}$$

Since there is no external field associated with the system, the parameters $u_{\vec{k}}, v_{\vec{k}}$ are real and if we also introduce the quantity

$$E_{\vec{k}} = \sqrt{\epsilon^2_{\vec{k}} + |\Delta_{\vec{k}}|^2} \tag{1.24}$$

We thus obtain the coefficients $u_{\vec{k}}, v_{\vec{k}}$ from Eqs.(1.22) and (1.23) as

$$\begin{aligned} u^2_{\vec{k}} &= \frac{1}{2}(1 + \frac{\epsilon_{\vec{k}}}{E_{\vec{k}}}), \\ v^2_{\vec{k}} &= \frac{1}{2}(1 - \frac{\epsilon_{\vec{k}}}{E_{\vec{k}}}) \end{aligned} \tag{1.25}$$

The model Hamiltonian is now diagonalized, the result is

$$H = \sum_{\vec{k}} E_{\vec{k}}(a^{\dagger}_{\vec{k}1}a_{\vec{k}1} + a^{\dagger}_{\vec{k}2}a_{\vec{k}2}) + \sum_{\vec{k}}(\epsilon_{\vec{k}} - E_{\vec{k}} + \Delta^{\dagger}_{\vec{k}} < c_{-\vec{k}\downarrow}c_{\vec{k}\uparrow} >) \tag{1.26}$$

this Hamiltonian requires the average of the operators $c_{-\vec{k}\downarrow}c_{\vec{k}\uparrow}$. The expectation value of this operator is given by

$$\begin{aligned} < c_{-\vec{k}\downarrow}c_{\vec{k}\uparrow} > &= Tr[\exp(-\beta H)c_{-\vec{k}\downarrow}c_{\vec{k}\uparrow}]/Tr[\exp(-\beta H)] \\ &= u_{\vec{k}}v^{*}_{\vec{k}}Tr[\exp(-\beta H)(-a^{\dagger}_{\vec{k}1}a_{\vec{k}1} + a_{\vec{k}2}a^{\dagger}_{\vec{k}2})]/Tr\exp(-\beta H) \\ &= u_{\vec{k}}v^{*}_{\vec{k}}[1 - 2f(E_{\vec{k}})] \end{aligned} \tag{1.27}$$

where Tr represents the trace in the occupation number Hilbert space, β is the inverse of temperature T, and f(E) is the Fermi function,

$$f(E) = \frac{1}{\exp(\beta E) + 1} \tag{1.28}$$

Using Eqs.(1.19), (1.25), and (1.27) the gap parameter is determined to be

$$\Delta_{\vec{k}} = -\sum_{\vec{k}'} V_{\vec{k}\vec{k}'}\frac{\Delta_{\vec{k}'}}{2E_{\vec{k}'}}\tanh(E_{\vec{k}'}/2T) \tag{1.29}$$

This equation is non-linear because $E_{\vec{k}}$ depends on $\Delta_{\vec{k}}$ and it cannot be solved exactly except by the numerically method or the approximation one. In order to determine the critical temperature T_c , we put $E_{\vec{k}} = \epsilon_{\vec{k}}$ in Eq.(1.29) and obtain

$$\Delta_{\vec{k}} = -\sum_{\vec{k}'} V_{\vec{k}\vec{k}'}\frac{\Delta_{\vec{k}'}}{2\epsilon_{\vec{k}'}}\tanh(\epsilon_{\vec{k}'}/2T_c) \tag{1.30}$$

where the pair-excitation spectrum is taken at the temperature T_c. To solve Eq.(1.30) we assume a constant gap for $|\epsilon_{\vec{k}}| \leq \omega_D$, i.e. $\Delta_{\vec{k}} = \Delta$, we, furthermore, assume the approximation for $V_{\vec{k}\vec{k}'}$ as

$$V_{\vec{k}\vec{k}'} = -V, \tag{1.31}$$

for $|\epsilon_k|, |\epsilon_{k'}| \leq \omega_D$, and zero otherwise. This model is valid only for the weakly coupled superconductors (e.g., aluminium and tin) for which N(0)V is very much less than unity, and not for strongly coupled superconductors (e.g., lead and mercury). By virtue of this approximation, the equation for T_c is determined from the equation

$$\frac{1}{N(0)V} = \int_0^{\omega_D} \frac{d\epsilon}{\epsilon} \tanh \frac{\epsilon}{2T_c} \tag{1.32}$$

Introducing the dimensionless variable $x = \epsilon/2T_c$, with the integration by parts, we have

$$\begin{aligned} \frac{1}{N(0)V} &= \ln(\frac{\omega_D}{2T_c}) \tanh(\frac{\omega_D}{2T_c}) - \int_0^{\frac{\omega_D}{2T_c}} dx \frac{\ln x}{\cosh^2 x} \\ &\cong \ln(\frac{2e^{\gamma}\omega_D}{\pi T_c}) \end{aligned} \tag{1.33}$$

where the upper limit of the last integral is extended to infinity and it value is equal to, $-\ln(4e^{\gamma}/\pi)$ with the Euler constant, $\gamma = 0.5772$. Thus the equation for T_c is given by

$$T_c = 1.13\omega_D \exp(-\frac{1}{N(0)V}). \tag{1.34}$$

To find the solution for the gap parameter $\Delta_{\vec{k}}$, we consider only the interaction of the form Eq.(1.31) and consequently the gap parameter satisfies the equation

$$\Delta = N(0)V\Delta \int_0^{\omega_D} \frac{d\epsilon}{E} \tanh(E/2T) \tag{1.35}$$

where

$$E = \sqrt{\epsilon^2 + |\Delta|^2}. \tag{1.36}$$

At the absolute zero of temperature Eq.(1.35) becomes

$$\begin{aligned} \frac{1}{N(0)V} &= \int_0^{\omega_D} \frac{d\epsilon}{\sqrt{\epsilon^2 + \Delta^2(0)}} \\ &= \sinh^{-1}(\frac{\omega_D}{\Delta(0)}) \end{aligned} \tag{1.37}$$

In the weak coupling limit $\omega_D \gg \Delta(0)$, we can approximate $\sinh^{-1} x \cong \ln(2x)$ in Eq.(1.37). Hence, the solution for the gap parameter at the absolute zero of temperature is

$$\Delta(0) = 2\omega_D \exp(-\frac{1}{N(0)V}). \tag{1.38}$$

Combining Eqs.(1.34)and (1.38),the ratio of the gap parameter at the absolute zero temperature to the critical temperature is

$$\Delta(0)/T_c = 1.76. \tag{1.39}$$

According to BCS, this ratio is expected to be the same for all superconductors.