ON

THE THEORY OF SUPERCONDUCTIVITY AND SOME ELECTRON PAIRING MECHANISMS

by

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<u>CONTENTS</u>

ABSTRACT

The recent discovery of high-temperature superconductivity brought about the necessity of clarifying a set of questions. One of these is regarding the electron pairing mechanism. Upto now, we have a well-developed microscopic theory of the conventional superconductivity, the so-called BCS theory. As we know, the pairing of electrons in this theory is realized through the exchange of virtual phonons. This mechanism leads to the existence of energy gap in the spectrum of elementary excitations of low-temperature superconductivity. And, in the absence of magnetic field, it is known that the normal-superconducting transition is second-order phase transition. Thus, the BCS theory gives the recipe for calculating all physical quantities of conventional superconductors.

The situation with the high-temperature superconductivity is much more complex. The mechanism of high - T_C superconductivity is still unkonwn. This is the reason we decided to give in this paper the review of conventional phenomenological theories of superconductivity and give new formulation of BCS theory which is based on retarded thermal Green's function method. We also attempted to analyze the available experimental data on high - T_C and some of the pairing mechanisms discussed in the literature. We finally proposed a model which can execute high-temperature superconductivity where electrons are paired by the exchange of virtual plasmons which can be observed in some specially prepared thin films.

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INTRODUCTION

One of the great achievements of the twentieth century in physics is the discovery of the phenomenon of superconductivity. It is very pleasant to think of the generation of non-dissipative currents in this state. These superconducting materials can carry currents without any loss of energy or they can be used in lossless power transmission lines. Other applications are seen in magnetohydrodynamic generators, accelerators, nuclear fusion reactors, energy storage, ultra-fast computers, electronic devices, medical instruments, etc. This is of great advantage even to developing nations since one has pointed out that the preparation of these materials is simple.

With this in mind, the work is intended to present review of the theory of superconductivity from the phenomenological as well as from the microscopic points of view. Furthermore, it is to analize some of the theories proposed on the pairing mechanism of high-temperature superconductivity and, by far, to indicate the seemingly right mechanism responsible - the stimulated pairing by external longitudinal high frequency electric field applied on a thin film.

The formal approach to the work is to start with a survey of low - temperature superconductivity for it can serve as a basement for high temperature one. Accordingly, the first chapter deals with the main experimental data and phenomenological theories of low-temperature superconductivity. These encompass the electrical, magnetic and thermodynamic properties of superconductivity which are explained by the London and GL-equations. The GL-theory is a macroscopic one.

In 1957, Bardeen, Cooper, and Schrieffer (BCS) formulated the microscopic theory of superconductivity for which chapter two is devoted. Here, a comparatively simple technique is developed for the description of ground state of superconductivity and the spectrum of elementary excitations. In general, the microscopic BCS theory is treated using the reatrded thermal Green's function since, at present, this is the best mathematical tool in handling elementary excitations and, successfully, the necessary BCS results are obtained using this method. Besides its great beauty and power, the Green's function method is realtively simple and understandable.

In chapter three, the main physical features and the more plausible suggested theories of the newly discovered high-temperature superconductivity in the new ceramics are given. The stimulated pairing by external longitudinal high frequency electric field is indicated too. Nevertheless, to date, no one knows the actual pairing mechanism that can fully explain high-temperature superconductivity.

It is understandable that all the diverse views of the modern theory of superconductivity and possible applications, especially, the high-temperature superconducting devices cannot be covered in this paper since superconductivity has now become a hot cake of the time, meaning thereby, it is now a fastly developing and improving branch of physics with, as Nevil Mott said, as many theories as there are theorists active in this field.

CHAPTER I

PHENOMENOLOGICAL THEORIES OF SUPERCONDUCTIVITY

1. Experimental Data

Historically, the phenomenon of superconductivity was discovered by Kamerling Onnes in 1911 in Leiden. In his first observation, he found that several materials, especially metals such as mercury, lead, etc., showed quite unorthodox behaviour that their electrical resistance dropped to zero at which it was practically impossible for him to measure resistances below a certain critical temperature. Such a vanishing resistance made obvious that the sample underwent a change to a new state entirely different from the usual normal state. This phenomenon was called superconductivity.[1]

The temperature at which an abrupt transition from normal to superconducting state takes place is known as the critical temperature T_C of phase transition. Until recently, this temperature was supposed to range from below 1°K in pure metals to about 19°K in some alloys. But, nowadays, in the newly discovered rare-earth-copper oxides, the transition temperature is as high as 90°K.[2]

It is interesting to note that the value of the electrical resistivity is as small as $10^{-24}\ \Omega$ cm in the superconducting state.[3]

Experiments showed that a superconducting ring placed in a weak magnetic field set up persistent currents that sustained for years! In contrast, in a normal metal, the current would cease to flow in about 10^{-12}S. The idea of superconductivity seemed to be borrowed from perfect conductivity.

1.1 Magnetic Field and Superconductivity

1.1.1 The Critical Magnetic Field

Superconductivity can be destroyed by heating a sample to $T > T_c$ and thus the normal state is attained. Not only this, it disappears if the sample is exposed to a comparatively weak magnetic field. (In the past, these observations dashed the hopes of the first experimenters). Therefore, for superconductivity to occur, both the temperature and the external magnetic field must be kept below certain threshold values. Thus, it is useful to define the critical magnetic field H_c above which superconductivity is not observed. Experiments with different superconductors proved that H_c depends on temperature and the dependence is given by the empirical relation [3]

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

where $H_c(0)$ is defined as the critical magnetic field at absolute zero temperature. If $T>T_c$, then $H_c(T)$ is zero meaning the sample is no more a superconductor.

1.1.2 The Meissner-Ochsenfeld Effect

One of the important properties of superconductivity was diamagnetism of quite a new type discovered by Meissner and Ochsenfeld in 1933.[4] They discovered that the magnetic flux density $\vec{B}$ inside a superconductor was always zero. This means that magnetic field is expelled from an originally normal metal when the critical temperature is reached. It is also true that magnetic field never penetrates a superconducting sample.

The expulsion of the field may be interpreted by the generation of non-decaying (since $\rho = 0$) eddy currents on the superconducting surface, commonly called superconducting currents, which maintain the external field. This is simply Lenz's law.

The Meissner-Ochsenfeld effect is not a mere consequence of vanishing resistance but, a new kind of magnetic phenomenon which can be considered as an intrinsic property of superconductivity. Hence one can say that the superconducting state must satisfy the equations

$$\text{resistivity} \quad \rho = 0 \quad \text{and} \qquad \text{magnetic induction } \vec{B} = 0 \tag{1.2}$$

1.1.3 Quantization of Magnetic Flux

Suppose a metal ring is exposed to an external field where its plane is normal to the magnetic force lines. Decreasing the temperature to $T<T_C$ we see that the ring becomes a superconductor and if the field is switched off the changing flux will create non-dissipative currents. These currents set up magnetic field that happens to be quantized. More precisely, the flux Φ produced is an integral multiple of the quanta of magnetic flux $\Phi_0 = \pi\hbar c/e$. Mathematically[3],

$$\Phi = n\Phi_0 \tag{1.3}$$

where n is an integer and $\Phi_0 = 2.07 \times 10^{-7}$ Gcm².

1.2 Preliminary Thermodynamics of Superconductors

Now we come to the thermodynamic treatment of superconductivity from which we can understand the meaning of the critical field H_C and examine the type of transition. The Meissner effect exhibits the reversible superconducting transition and this gives a green light to the applicability of the well-known techniques of thermodynamics[1].

In electrodynamics, the magnetic field intensity $\vec{H}$ and the magnetic induction $\vec{B}$ are related by

$$\vec{B} = \vec{H} + 4\pi\ \vec{M} \tag{1.4}$$

where $\vec{M}$ is the magnetic moment per unit volume of the substance. If we consider a very long superconducting cylinder in a longitudinal external magnetic field $\vec{H}$, then $\vec{B} = 0$ inside as long as $H<H_c$ at $T<T_c$. If the magnetic field changes from 0 to $\vec{H}_0$, the work done on the system is

$$W = -\int_0^{H_0} \vec{M}.d\vec{H}_0 = \frac{H_0^2}{8\pi} \tag{1.5}$$

This energy is added to the free energy of the superconductor as

$$F_{sh} = F_{so} + \frac{H_0^2}{8\pi} \tag{1.6}$$

Here, F_{sh} is the density of free energy in the presence of field $\vec{H}$ and F_{so} is when $\vec{H} = 0$. The subscript s designates superconductivity. The thermodynamic transition at $H = H_c$ takes place when F_{sh} reaches the density of free energy of the normal state, F_n. Replacing F_{sh} by F_n[3]

$$F_n - F_{so} = \frac{H_c^2}{8\pi} \tag{1.7}$$

One can clearly see that the superconducting state is energetically more profitable than the normal one, provided that the magnetic field is below H_c. Equation (1.7) is regarded as the definition of H_c and for this reson H_c is most commonly called the thermodynamic critical field.

1.2.1 Entropy of the Superconductor

The entropy of a system is

$$S = \left(\frac{-\partial F}{\partial T}\right)_A \tag{1.8}$$

where F is the density of free energy, T is the temperature and A is the work of the system. Using the last two expressions, the difference in entropy between the normal and superconducting states is

$$S_s - S_n = \left(\frac{H_c(T)}{4\pi} \quad \frac{\partial H_c(t)}{\partial T}\right)_A \tag{1.9}$$

In statistical physics, entropy is identified with the "degree of disorder" of the system. Using equations (1.1) and (1.9) we can show that the entropy of the superconducting state is lower than that of the normal one and one can consider this like a state with more order.

It is useful to note that the difference in entropy vanishes at two extreme temperatures, namely, at zero temperature (Nernst's theorem) and at T_c and the latent heat of transition too. Because the normal-superconducting transition takes place with no discontinuity in entropy, at these two temperatures it is a second order phase transition. The transition shows itself clearly by a discontinuity in the specific heat.

1.2.2 Specific Heat of the Superconductor

The specific heat is given by

$$C = \frac{T\partial S}{\partial T} \tag{1.10}$$

Substituting for S from equation (1.9) we obtain

$$C_s - C_n = \frac{T}{4\pi}\left[\left(\frac{\partial H_c}{\partial T}\right)^2 + H_c \quad \frac{\partial^2 H_c}{\partial T^2}\right] \tag{1.11}$$

Since H_c vanishes at the critical temperature T_c, we have

$$C_s - C_n = \frac{T_c}{4\pi}\left(\frac{dH_c}{dT}\right)^2_{T_c} > 0 \qquad (1.12)$$

The specific heat of the superconductor has a discontinuity at T_c. Below T_c, experiments predict an exponential dependence while above T_c is the usual dependence, $C_n \sim T$, and the overall picture is plotted here.

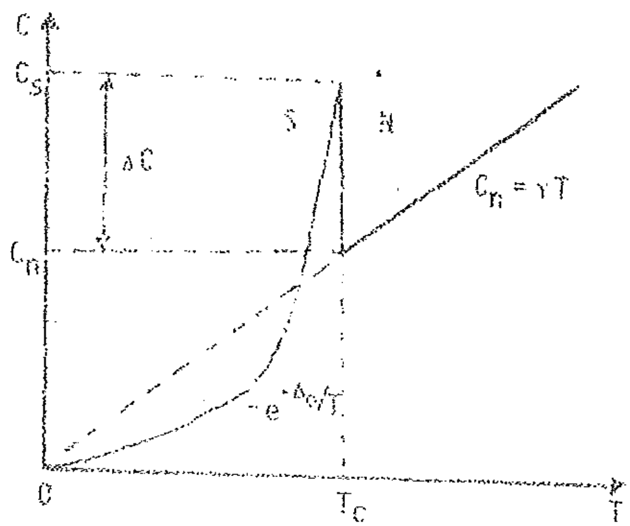


Fig.1. Schematic behaviour of the specific heat. It shows a sudden jump at T_c.

1.3 The London Equations[4]

London (1935) was the first to pay attention to the basic electrodynamic properties of a superconductor manifested by the Meissner-Ochsenfeld effect. Writing the equation of motion for superconducting electrons in an electric field $\vec{E}$ as

$$n_s m \frac{d\vec{v}_s}{dt} = n_s e\vec{E} \qquad (1.13)$$

where n_s is the density number of superconducting electrons, m and e are respectively the mass and charge of an electron and v_s is the velocity of superconducting electrons, and knowing that the superconducting current j_s is given by

$$j_s = en_s v_s \ , \tag{1.14}$$

London was able to develop two descriptive, phenomenological equations governing the microscopic electric and magnetic fields:

$$\vec{E} = \frac{d}{dt} (\Lambda \vec{j}_s) \tag{1.15}$$

and

$$\vec{H} + \lambda^2 \nabla \times \nabla \times \vec{H} = 0 \tag{1.16}$$

or

$$\vec{j}_s = \frac{-c}{4\pi\lambda^2} \vec{A}$$

where Λ was phenomenological parameter given by $\Lambda = m/n_s e^2$, λ was a characteristic length of penetration given by $\lambda^2 = \frac{mc^2}{4\pi n_s e^2}$ and $\vec{A}$ was the vector potential.

Equation (1.15) is known as the first London equation and it describes perfect conductivity that the electric field is to accelerate the superconducting electrons rather than sustaining their velocity against resistance. Equation (1.16) is London's second equation representing the distribution of $\vec{H}$ inside the superconductor.

As an example, consider half superconducting space: $x > 0$ in an external magnetic field H_0 along the z-axis perpendicular to the x-axis. The boundary conditions for such a problem are $H(0) = H_0$ and $H(\infty) = 0$- Meissner effect. The solution of eqn.(1.16) satisfying the boundary conditions is

$$H(x) = H_0 e^{-x/\lambda}$$

with

$$\lambda^2 = \frac{mc^2}{4\pi n_s e^2} \tag{1.17}$$

We can clearly see that the above example shows that magnetic field penetrates into a superconducting sample with a characteristics length of penetration λ which is typically of the order of 500°A. Thus, λ is called the London penetration depth. Using Maxwell's equation, we see the current will be

$$j_s = \frac{c}{4\pi\lambda} H_o \exp\{-x/\lambda\} \tag{1.18}$$

This current flows in a thin surface layer of order λ.

AT T = 0, n_s tends to n, the total number of conduction electrons ($n = n_s + n_n$) and at $T = T_c$, n_n tends to n or n_s tends to zero and λ tends to infinity. This shows that λ is a function of n_s as well as T. The dependence of λ on T is given by an empirical formula[3],

$$\lambda(T) = \lambda(0)[1 - (\frac{T}{T_c})^4]^{-\frac{1}{2}} \tag{1.19}$$

where $\lambda(0)$ is the value at T = 0 which is of the order of 600°A.

1.4 The Landau-Ginzburg Theory.

So far, we have studied that magnetic field could penetrate a superconductor, eventhough it was to a small extent. Consequently, inorder to minimize the Gibbs free energy alternating superconducting and normal regions must be formed and, eventually, the question that comes to our minds is what happens to the normal-superconducting interface? Such situations are explained by the macroscopic Ginzburg-Landau (GL) theory.

With remarkable intuition, in 1950, L.D. Landau and V.L. Ginzburg introduced a pseudo wave function of all superconducting electrtons as a complex order parameter in which the density of superconducting electrons was defined by [4]

$$|\psi(r)|^2 = n_s/2 \tag{1.20}$$

Despite its fruitfulness and boldness, the theory was given little attention until 1959 when Gorkov showed that it was a limiting case of microscopic BCS theory, a central idea of the next chapter.

Before the development of the BCS theory, Landau and Ginzburg proposed that, in the absence of external magnetic field, ψ did not appreciably vary in space and was small for T close to T_c resulting in an expansion of the free energy in powers of $|\Psi|^2$ as

$$F_{so} = F_n + \alpha|\Psi|^2 + \frac{\beta}{2}|\Psi|^4 \quad , T \leq T_c \tag{1.21}$$

Here F_{so} is the density of the superconducting free energy in zero field, F_n is the density of free energy in the normal state, and α and β are phenomenological coefficients. β is always positive but for α positive and negative, the values of $|\Psi|^2$ that minimize the free energy are, respectively,

$$|\Psi|^2 = 0 \tag{1.22}$$

and

$$|\Psi|^2 = |\Psi_o|^2 = \frac{-\alpha}{\beta} \tag{1.23}$$

The first solution corresponds to the normal state while the second one to superconducting state.

If we next consider the presence of magnetic field, we find that Ψ varies in space; $\nabla\Psi \neq 0$ which is associated with the kinetic energy of superconducting electrons. In this case, the appropriate thermodynamic function is the Gibbs free energy written as

$$G_{sh}=G_n + \int [\alpha|\psi|^2 + \frac{\beta}{2}|\psi|^4 + \frac{1}{2m^*}|(-i\hbar\nabla - \frac{e^*}{c}\vec{A})\psi|^2 + \frac{(\nabla \times A)^2}{8\pi} - \vec{H}_0\frac{(\nabla \times \vec{A})^2}{4\pi}]dV \qquad (1.24)$$

where $\vec{H}_0$ is the external magnetic field, $\vec{H} = \nabla \times \vec{A}$ is internal magnetic field, and integration is taken over the volume of the specimen. Notice that the additional terms are the kinetic energy of superconducting electrons and energy of fields.

We must now find equations for $\psi(r)$ and $\vec{A}(r)$ the solutions of which after substitution into equation (1.24) minimize the Gibbs free energy. Applying the calculus of variations, Landau and Ginzburg obtained two phenomenological equations (see Appendix A)

$$\alpha\,\psi + \beta\,\psi|\psi|^2 + \frac{1}{2m^*}(-i\hbar\nabla - \frac{e^*}{c}\vec{A})^2\,\psi = 0 \qquad \text{GL-I} \qquad (1.25)$$

$$j_s = \frac{-i\hbar e^*}{2m^*}(\psi^*\nabla\psi - \psi\nabla\psi^*)\frac{-e^*}{m^*c}|\psi|^2\,\vec{A} \qquad \text{GL-II} \qquad (1.26)$$

with the boundary condition

$$(i\hbar\,\nabla\psi + \frac{e^*}{c}\vec{A}\psi).\,\vec{n} = 0 \qquad (1.27)$$

where $\vec{n}$ was a unit normal to the surface of the superconductor.

The second GL equation is the usual QM expression for current density of particles with charge e^* and mass m^*. The BCS theory approves that $e^* = 2e$ exactly and it is natural to choose $m^* = 2m_e$.

1.4.1 The Two Characteristic Lengths

The GL theory introduces the dimensionless wave function

$$\psi'(r) = \frac{\psi}{|\psi_o|} \qquad (1.28)$$

where ψ_o is defined by (1.23), and it also introduces the natural unit of length $\xi(T)$ at temperature T for the variation of $\psi'(r)$ which is commonly called the coherence length,

$$\xi(T) = \frac{\hbar^2}{4m|\alpha|} \sim |\alpha|^{-1} \tag{1.29}$$

With the above dimensionless parameters, GL equations can be re-written as

$$\xi^2(i\nabla + \frac{2\pi}{\phi_0}\vec{A})^2\psi' - \psi' + \psi'|\psi'|^2 = 0 \tag{1.30}$$

$$\nabla\times\nabla\times\vec{A} = \frac{-i\phi_0}{4\pi\lambda^2}(\psi'^*\nabla\psi' - \psi'\nabla\psi'^*) - \frac{|\psi'|^2}{\lambda^2}\vec{A} \tag{1.31}$$

One can understand the physical significance of $\xi(T)$ by reducing (1.30) to its one dimensional case and applying it to a very thin film of normal metal doped onto a superconductor. The solution will have the form $\psi' \sim e^{-x/\xi}$ which describes that ψ' will decay in a characterstic length of order $\xi(T)$.

The second characteristic length is λ and both λ and $\xi \sim (T_c - T)^{-\frac{1}{2}}$. Therefore, it is important to define the ratio of two characteristic lengths, the so-called GL parameter by

$$\varkappa = \frac{\lambda}{\xi} \tag{1.32}$$

This parameter is approximately independent of temperature.

1.4.2 Determination of Surface Energy

In the intermediate state of a superconductor at which normal and superconducting states alternate, on the boundary between them one can introduce the surface energy

$$\tau_{ns} = \int_{-\infty}^{\infty} (G_{sh} - G_n)dx \tag{1.33}$$

Substituting the value of G_{sh} from (1.24), after much labor, one arrives at

$$\tau_{ns} = \frac{H_c^2}{2\pi} \int_{-\infty}^{\infty} \left[\xi^2 \left(\frac{d\Psi}{dx}\right)^2 + \frac{H(H-H_c)}{2H_c^2}\right] dx \qquad (1.34)$$

To a good approximation, the first integral is of the order of $\frac{H_c^2}{2\pi}\xi$ and the second is of the order of $-\frac{H_c^2}{2\pi}\lambda$ if $H < H_c$. Taking two limiting cases, one finds

a) when $\varkappa \ll 1$ or $\lambda \ll \xi$ then $\tau_{ns} > 0$, the material is of first kind;

b) when $\varkappa \gg 1$ or $\lambda \gg \xi$ then $\tau_{ns} < 0$, the material is of second kind.

Landau and Ginzburg found the value $\varkappa = 1/\sqrt{2}$ as the exact separation between the two types of behaviour.

1.5 Two Types of Superconductors

Depending on their admittance to external magnetic field, superconductors are classified into two catagories: type I and type II superconductors. Typé I superconductors manifest the Meissner-Ochsenfeld effect. As an illustration, if we consider a long type superconducting cylinder in a longitudinal weak magnetic field in the interval $0 < H < H_c$, then there is no penetration of field, that is, $\vec{B} = 0$ inside - complete Meissner effect. However, once $H \geq H_c$ superconductivity is completely destroyed as is shown below. We should keep in mind that $T \lesssim T_c$ in any case.

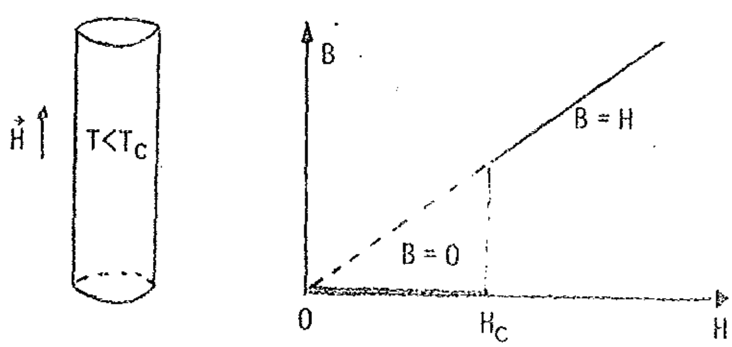


Fig.2. The induction $\vec{B}$ as a function of $\vec{H}$.

In relatively strong fields $H > H_c$ the system will be neither in the normal nor in the superconducting state but may probably break into alternating normal and superconducting states called the intermediate state.

For the same situations like that of type I, type II superconductors are characterized by the following macroscopic properties:

a) for $H<H_{c1}$, total field expulsion ($\vec{B} = 0$) - Meissner effect.

b) for $H_{c1} < H < H_{c2}$, we observe partial penetration of field and permanent superconducting current is generated.

c) for $H_{c2} < H < H_{c3}$, there is no Meissner effect but, we see superconducting sheath of typical thickness $10^3 A^0$. Above H_{c3} superconductivity is completely destroyed. H_{c1}, H_{c2}, H_{c3} are the first, second and third critical fields respectively. The above properties are displayed in Fig.3.

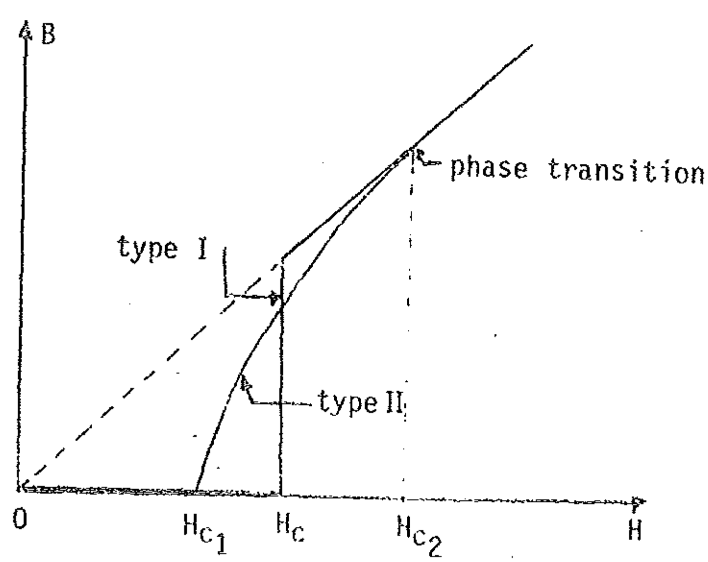


Fig.3. The dependence of $\vec{B}$ on $\vec{H}$ inside cylinder.

If the field is slightly greater than H_{c1}, filaments of small diameter ($\sim \xi$) appear and they are arranged in a triangular lattice to minimize the energy.[5] These filaments are sometimes called normal cores and each of them contains flux ϕ_o. To describe this, Abrikosov modified London's II equation as [6]

$$\vec{H} + \lambda^2 \nabla \times \nabla \times \vec{H} = \vec{\phi}_o \delta (r) \ , \tag{1.35}$$

where $\vec{\phi}_o$ is a vector along the line direction and the energy of each filament was found to be

$$J = \left(\frac{\phi_o}{4\pi\lambda}\right)^2 \ln \mathcal{X} \tag{1.36}$$

with this energy, the Gibb's function now becomes

$$G = n_L J + \sum_{i,j} U_{ij} - \frac{BH}{4\pi} \tag{1.37}$$

where n_L is the number of lines per cm² and hence $n_L J$ is the total energy of vortices per cm²; the second is the interaction term and the last one is the magnetic energy which is like pressure. For weak fields U_{ij} can be neglected and the Gibb's function is minimized if

$$H = H_{c_1} = \frac{\phi_o}{4\pi\lambda^2} \ln \mathcal{X} \tag{1.38}$$

We know that H_{c_1} is the first critical field.

The critical field of a thin superconducting film of thickness "d" is given by [3]

$$H_{cF} \sim H_c \frac{\lambda}{d} \tag{1.39}$$

If $H > H_{c_1}$ the number of vortices increases and the regions among vortices can be imagined as thin films. Now, in our case replacing d by ξ we estimate the second critical field H_{c_2} as

$$H_{c_2} \sim H_c \frac{\lambda}{\xi} \tag{1.40}$$

Correct evaluations give

$$H_{c_2} = \sqrt{2}\varkappa H_c \ . \tag{1.41}$$

The third critical field is also given by

$$H_{c_3} = 1.69\ H_{c_2} \tag{1.42}$$

Notice that H_c has nothing to do with type II superconductors.

1.6 Josephson Effect and SQUIDS

As an application we will simply mention here the Josephson effect. This is an effect that occurs when there is a weak contact between two massive superconductors described by GL wave functions of the same amplitude (if they are kept at the same temperature), but the relation of the phases is not obvious. Weak enough non-dissipative current can pass through the junction (contact) which is given by [7]

$$I = I_s \sin(\theta_1 - \theta_2) = I_s \sin\gamma \tag{1.43}$$

where θ_1 and θ_2 are the phases of the two superconductors, $\gamma = \theta_1 - \theta_2$ is jump in these phases. The current density is determined by $\nabla\theta$ of ψ since $\psi = \psi_o\, e^{i\theta}$

Across the junction a voltage is developed given by the relation,if the current exceeds its critical value,which is

$$2e\bar{V} = \hbar\omega \tag{1.44}$$

where ω is the frequency of oscillation of the current, $\omega \sim 3\times10^{12}$ Hz-infrared region; $2e\bar{V}$ is the average energy difference between levels of Cooper pairs in the two superconductors.

It can also be shown that the maximum non-dissipative current through the junction is

$$I_{s\,max} = I_0 \left|\frac{\sin \pi\phi/\phi_0}{\phi/\phi_0}\right| \tag{1.45}$$

This suggests the possibility of constructing a device of sensitivity 10^{-15}Tm² for the ratio ϕ/ϕ_0 to be an integer. Based on this principle, superconducting Quantum Interference Devices (SQUIDS) are constructed which consist of two Josephson contacts connected in parallel that can register changes of magnetic fields as small as 10^{-10}- 10^{-11}G. For your comparison the earth's magnetic field is of the order of 0.5G. Moreover, equation (1.44) is useful for the measurement of h/e. It is also used for control and measurement of single quantized vortex lines as computer elements.

CHAPTER II

2. FOUNDATIONS OF THE MICROSCOPIC THEORY OF SUPERCONDUCTIVITY (BCS THEORY)

The phenomenological theory previously discussed could not explain what the superconducting state was. Even, it failed to describe some distinguishing characteristics of superconducting state. Among them were the exponential variations of specific heats at temperatures below T_C, or the existence of energy gap and the so-called isotope effect - different isotopes of the same material have different critical temperatures.

The energy difference between normal and superconducting states per one particle, $H_C^2/8\pi n$ which is of the order of 10^{-5}eV, is responsible for superconductivity eventhough it is very small in comparison with the Coulomb energy per electron in metals ~ leV. At this stage, it was necessary to find ordering behaviour of electrons in the superconducting state when the corresponding energy is much smaller than energies of other possible interactions.

The problem was solved in 1957 when Bardeen, Cooper, and Schrieffer formulated a fundamental microscopic theory (BCS theory) of superconductivity that gave an excellent account, especially, of the electron-lattice interaction at temperatures very near to zero. It was the isotope effect that gave a hint that some how lattice vibrational excitations or phonons were involved in the formation of superconductivity.

Before the development of BCS theory, Cooper (1956) introduced his pairing theory [8] that if two electrons near the Fermi surface interact, they form a bound pair, regardless of how weak the interaction is as long as it is attractive. In other words, if electrons are given some kinetic energy to be above the Fermi surface, they form pairs such tha their bound energy outweighs the kinetic energy. These pairs, commonly called Cooper pairs, have characteristic sizes of the order of ξ_o whic was introduced in the phenomenological theory. They are the supercondu ting charge carriers. Moreover, the pairs do not obey the Fermi-Dirac statistics, they are treated like bosons and a number of them can be described by the same wave functions as in the phenomenological GL theory.

2.1 Origin of the Attractive Interaction Between Electrons.

In a simple electron gas, the only interactions are Coulomb repulsions However, for attractive interaction the electron must be coupled to another system of particles. The general Hamiltonian for such a system of interacting particles is given by [9]

$$H = \sum_j H_j^{(1)} + \frac{1}{2} \sum_{j,\ell} V_{j\ell}^{(2)} \tag{2.1}$$

Introducting field operators

$$\psi = \sum_k C_{k\tau} \gamma_{k\tau} \; ; \; \psi^* = \sum_k C_{k\tau}^+ \gamma_{k\tau}^* \tag{2.2}$$

The Hamiltonian can be re-written as

$$H = \sum_{k\tau} \varepsilon(k) C_{k\tau}^+ C_{k\tau} + \frac{1}{2} \sum_{k_1 k_2 k_2' k_1' \tau\tau'} V_{k_1\tau k_2\tau'}^{k_2'\tau' k_1'\tau} C_{k_1\tau}^+ C_{k_2\tau'}^+ C_{k_2'\tau'} C_{k_1'\tau} \tag{2.3}$$

which is a typical example of second quantized Hamiltonian. The first term of (2.3) is the kinetic energy of electrons with respect to the Fermi level: $\varepsilon(k) = \hbar^2 k^2/2m - \varepsilon_F$, the second term is the interaction term which refers to the creation of two particles with opposite momenta

$(\vec{k}, -\vec{k})$ and spins (τ, τ') (τ stands for spin up and τ' for spin down) and annihilation of two particles simultaneously by the creation $C^{+}_{k\tau}$ and annihilation $C_{k\tau}$ operators respectively. The operators satisfy the usual Fermi commutation relation:

$$[C_{k\tau}, C^{+}_{k'\tau'}] = \delta_{kk'}\, \delta_{\tau\tau'}$$
$$[C_{k\tau}, C_{k'\tau'}] = [C^{+}_{k\tau}, C^{+}_{k'\tau'}] = 0 \tag{2.4}$$

In this section, we will attempt to examine how electrons interact through phonons and to determine the sign of the matrix element $V_{kk'}$ (eqn.2.3) of electron-electron interaction in transition from initial state I where the electrons are in $(\vec{k}_1, \vec{k}_2)$ to final state II where they are in $(\vec{k}_1', \vec{k}_2')$. We consider a metal at T = 0 when there are no phonons. If an electron passes through the medium of the metal it polarizes it by attracting ions which overscreen the negative charge of the electron such that the excess positive cloud inturn attracts another electron resulting in an effective attractive interaction between the two electrons. The effect of the electron on the lattice can be imagined as the emission of a (virtual) phonon of wave vector $\vec{q}$ and the electron attains a new state $\vec{k}_1'$, that is,

$$\vec{k}_1 = \vec{k}_1' + \vec{q} \tag{2.5}$$

assuming initial momentum of the electron to be $\vec{k}_1$. The emitted phonon will be absorbed by another electron of momentum $\vec{k}_2$ so that

$$\vec{k}_2 = \vec{k}_2' + \vec{q}\,' \tag{2.6}$$

The conservation of momentum:

$$\vec{k}_1 + \vec{k}_2 = \vec{k}_1' + \vec{k}_2' \tag{2.7}$$

leads to

$$\vec{q} = -\vec{q}\,' \tag{2.8}$$

Such scattering of two particles exhibits their interaction, electron-electron interaction via phonons which is displayed below:

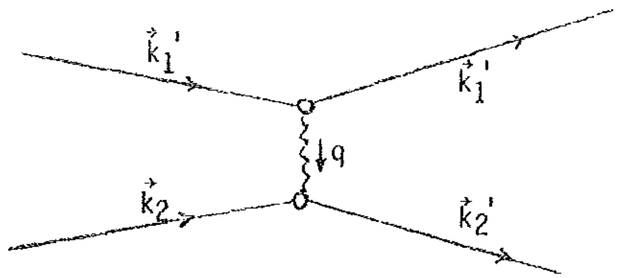


Fig.4. Phonon mediated electron-electron interaction

Next, we determine $V_{kk'}$. The initial state I has energy [6]

$$E_I = 2\varepsilon(k)$$

and the final state II has energy

$$E_{II} = 2\varepsilon(k')$$

Due to the conservation of momentum, there are two allowed intermediate states: electron 1 in state $\vec{k}'$ and electron 2 in $-\vec{k}$ or electron 1 in $\vec{k}$ and 2 in $-\vec{k}'$ with energies, respectively,

$$E_{i1} = \varepsilon(k') + \varepsilon(k) + \hbar\omega_q$$

$$E_{i2} = \varepsilon(k') + \varepsilon(k) + \hbar\omega_q = E_{i1}$$

One can show that the total matrix element coupling states I and II is

$$\langle I \,|V_{indirect}|\, II \rangle = U_q + \frac{2|W_q|^2}{\hbar} \quad \frac{\omega_q}{\omega^2 - \omega_q^2} \qquad (2.9)$$

where ω is defined by: $\hbar\omega = \varepsilon(k') - \varepsilon(k)$; $\hbar\omega$ and $\hbar\vec{q}$ are the energy and momentum change of electron 1 in transition $I \to II$, W_q is the matrix element of electron - phonon coupling and U_q is the matrix elment of Coulomb repulsion. From (2.9) we see that the second term is negative if $\omega < \omega_q$. Thus, there is an attractive interaction provided that the Coulomb part is not too large.

Similar expression can also be obtained using a simple model of two charged liquids: heavy charged liquid of ions and light charged liquid of electrons. Assume small charge density fluctuation $e\delta n$ caused by external means and proportional to $\exp(i\vec{k}.\vec{r} - i\omega t)$ is added to the system. The equations of motion for the two fluids are [10]

$$m\ddot{\vec{u}}_e = mv_F^2/3 \quad \nabla^2 \vec{u}_e - e\vec{E}$$

$$M\ddot{\vec{u}}_i = e\vec{E} \tag{2.10}$$

$$\operatorname{div} \vec{E} = 4\pi e[\delta n - n_0 \operatorname{div}(\vec{u}_i - \vec{u}_e)]$$

where M, $\vec{u}_i$ and m, $\vec{u}_e$ are the mass and displacement of ions and electrons respectively, $\vec{E}$ is the self consistent electric field, v_F is the velocity of an electron at the Fermi surface.

In the formation of superconductivity only longitudinal vibrtations play an important role, say k is along x-axis.

Now, let us seek solutions of the form

$$u_e = u_e^o \quad e^{i\vec{k}.\vec{r} - i\omega t}$$

$$u_i = u_i^o \quad e^{i\vec{k}.\vec{r} - i\omega t}$$

$$E = E_o \quad e^{i\vec{k}.\vec{r} - i\omega t}$$

$$\delta_n = \delta_{n_o} \quad e^{i\vec{k}.\vec{r} - i\omega t} \quad , \quad \delta n_o \text{ is given.}$$

Applying Cramer's rule, we get from (2.10)

$$E_o(k) = \frac{(\omega^2 - v_F^2k^2/3)\ \omega^2 \omega n_o/ikn_o^2}{(4\pi n_o e)^{-1}(\omega^2 - \omega_p^2(k))\ (\omega^2 - \omega_L^2(k))}$$

where the frequencies for free oscillations of the fluids are

$$\omega_p^2(k) = \omega_{p_o}^2 + \frac{v_F^2k^2}{3} \quad \text{and} \quad \omega_L^2(k) = \frac{v_S^2k^2}{1+v_F^2k^2/3\omega_{p_o}^2}$$

v_S is velocity of sound, and thus the potential energy will be

$$V_k = e\gamma_k = \frac{4\pi e^2}{k^2} \quad \frac{(\omega^2 - v_F^2k^2/3)}{(\omega^2 - \omega_p^2(k))} \quad \frac{\omega^2}{(\omega^2 - \omega_L^2(k))} \tag{2.11}$$

In the low frequency limit where ω is negligible compared to v_Fk and $\omega_p(k)$ but $\omega \leq \omega_L(k)$, we see that

$$V_k = \frac{4\pi e^2 \quad v_F^2k^2/3}{k^2(\frac{v_F^2k^2}{3} + \omega_{p_o}^2)} \left[1 + \frac{\omega_L^2(k)}{\omega^2 - \omega_L^2(k)}\right] \tag{2.12}$$

This is the expression we have been looking for. The first term is a screened Coulomb repulsion. The second term is due to the presence of ions and in the low ω limit there is a net negative potential in the model!

Cooper suggested a simple structure of the matrix element of transition:

$$V_{kk'} = \begin{cases} -V, & |\varepsilon_k - \varepsilon_F| \leq \hbar\omega_D \ ; \ |\varepsilon_{k'} - \varepsilon_F| \leq \hbar\omega_D \\ 0, & |\varepsilon_k - \varepsilon_F| \geq \hbar\omega_D \ ; \ |\varepsilon_{k'} - \varepsilon_F| \geq \hbar\omega_D \end{cases} \tag{2.13}$$

Here, ε_F is the Fermi energy, V is a positive constant.

The expression for the total matrix element of such an interaction can also be obtained using a dielectric constant which is a macroscopic approach. The effective interaction will be the Fourier component of Coulomb interaction divided by the dielectric constant ε[6]:

$$V_k = \frac{4\pi e^2}{k^2 \varepsilon(\omega, k)} \qquad (2.14)$$

The jellium model with certain approximations leads to

$$V_k(\omega) = \frac{4\pi e^2}{k^2 + k_s^2} \left[1 + \frac{\omega_q^2}{\omega^2 - \omega_q^2}\right] \qquad (2.15)$$

where the phonon frequency

$$\omega_q^2 = \omega_i^2 \frac{q^2}{q^2 + k_s^2} \; ; \; k_s^2 = \frac{6\pi n e^2}{\varepsilon_F} \; ; \quad \omega_i \text{ - ion frequency.}$$

The equation (2.15) for V_k has the same form like (2.12). It is obvious that the first term is Coulomb repulsion (screened) while the second is phonon-mediated interaction and V_k is attractive for $\omega < \omega_q$ if the Coulomb repulsion is very small.

2.2 Green Functions: Connection with Elementary Excitations.

In this paper, we have applied the method of Green functions to determine the energy of quasi-particles or elementary excitations, a method which proved to be very powerful, transparent and elegant in treating elementary excitations. The starting point of an analysis of such excitation is to express the Hamiltonian in second quantized formalism as

$$H = \sum_{k\tau\tau'} \varepsilon(k) C^+_{k\tau} C_{k\tau'} - \frac{g}{V} \sum_{kk'\tau\tau'} C^+_{k'\tau} C^+_{-k'\tau'} C_{-k\tau'} C_{k\tau} \qquad (2.16)$$

where g is a coupling constant which is a measure of interaction and v is the volume of the system.

The Green function can be given in a number of ways. In statistical physics the thermal Green function is defined b y [11]

$$G_{AB}(t) = \frac{-i}{\hbar}\,\theta(t)\,\langle[A(t),\, B(0)]_{\pm}\rangle \qquad (2.17)$$

where A and B are operators of any physical observable, $\theta(t)$ is the Heviside step function, $[\quad]_-$ means commutator for Bose operators while $[\quad]_+$ is for Fermi operators and $\langle\quad\rangle$ is the thermal average

The equation of motion for the above Green function is

$$\dot{G}_{AB}(t) = \frac{-i}{\hbar}\,\theta(t)\,\langle[\dot{A}(t),B(0)]_{\pm}\rangle - \frac{i}{\hbar}\,\langle[A(t),B(0)]\rangle\,\delta(t) \qquad (2.18)$$

where $\dot{A}(t)$ can be found from the Heisenberg equation of motion

$$\dot{\hat{A}} = \frac{i}{\hbar}\,[\hat{H}\ ,\ \hat{A}] \qquad (2.19)$$

Next, taking Fourier transformation of $\dot{G}$, the solution we get has the form

$$G(\omega,k) = \frac{1}{\hbar\omega - E(k)} \qquad (2.20)$$

The ground state of a system is the one in which all states upto the Fermi level are occupied and the rest are empty. Application of C_k^{+} to the ground state will create one particle above the Fermi level and in such a process excited states of the system will be generated.

The pole of the Fourier component of Green function gives the spectrum of these elementary excitations which we will see soon.

The problem now is, finding

$$\dot{\hat{A}} = \frac{i}{\hbar}[\hat{H},\hat{A}] = \frac{i}{\hbar} \sum_{k\tau\tau'} \varepsilon(k)[\hat{C}^{+}_{k\tau}\hat{C}_{k\tau}, \hat{A}] - \frac{i}{\hbar}\frac{g}{V} \sum_{kk'\tau\tau'} [C^{+}_{k'\tau} C^{+}_{-k'\tau'} C_{-k\tau'} C_{k\tau}, A]$$

and substituting into eqn.(2.18) we get

$$\dot{G}_{AB}(t) = \frac{-i}{\hbar}\theta(t) < \sum_{k\tau\tau'} \frac{i}{\hbar}\varepsilon(k)[[C^{+}_{k\tau} C_{k\tau}, A], B] -$$

$$- \frac{i}{\hbar}\frac{g}{V} \sum_{kk'\tau\tau'} [[C^{+}_{k'\tau} C^{+}_{-k'\tau'} C_{-k\tau'} C_{k\tau}, A], B(0)]> - \frac{i}{\hbar} <[A(t), B(0)]\,\delta(t)$$

That is $\dot{G}(A,B) = G(CDE, A)$

and finding the equation of motion of G(CDE,A) we get higher and higher order Green functions which we can not terminate. For this reason, we transform the Hamiltonian of quartic form to the so-called model - Hamiltonian of quadratic form so that we will have the luxury to construct the Green function out of the creation and annihilation operators of eqn. (2.16) in the form of eqn. (2.17) where the Fourier transformation of its equation will automatically give the spectrum of elementary excitations.

2.3 Model Hamiltonian

We need to formulate the ground state of superconducting state which has lower energy than the normal Fermi sea state from the so-called model Hamiltonian.

We know that in a normal metal at $T = 0$ all states inside the Fermi surface are occupied while those outside are empty. If electrons are provided with some kinetic energy to come out of the Fermi surface, at the expense of this, the system has to lose some energy and attraction occurs which makes the net energy of the system in this state to be less than that of the normal state. One may say nature decides to increase the kinetic energy of the system hoping to outweigh this by attractive potential energy. This is also viewed as scattering of electrons from the state $\vec{k}, -\vec{k}$ to $\vec{k}', -\vec{k}'$. The minimum energy corresponds to the states with pairs $(\vec{k}'\tau, -\vec{k}'\tau')$ occupied and $(\vec{k}\tau, -\vec{k}\tau')$ unoccupied. The Hamiltonian that describes such a situation is the so-called "pairing Hamiltonian" or "reduced Hamiltonian" given by

$$H = \sum_{k\tau\tau'} \varepsilon(k)(C^{+}_{k\tau}C_{k\tau} + C^{+}_{k\tau'}C_{k\tau'}) - \frac{g}{V} \sum_{kk'\tau\tau'} C^{+}_{k'\tau} C^{+}_{-k'\tau'} C_{-k\tau'} C_{k\tau} \tag{2.21}$$

The first term is the kinetic energy of electrons that are assumed to lie above the Fermi surface ($\varepsilon(k) = \frac{\hbar^2 k^2}{2m} - \varepsilon_F$), the second is interaction term.

Inorder to fix the total number of particles N, use the Lagrange's undetermined multipliers that lead to the transition

$$\hat{H} \to \hat{H} - \mu\hat{N}$$

where μ is the chemical potential and $N = \sum_{k\tau\tau'} (C^{+}_{k\tau} C_{k\tau} + C^{+}_{k\tau'}C_{k\tau'})$ is the particle number operator. Thus, the pairing Hamiltonian is written as

$$H = \sum_{k\tau\tau'} \eta(k)(C^{+}_{k\tau}C_{k\tau} + C^{+}_{k\tau'}C_{k\tau'}) - \frac{g}{V} \sum_{kk'\tau\tau'} C^{+}_{k'\tau} C^{+}_{-k\tau'} C_{-k'\tau'} C_{k\tau} \tag{2.22}$$

where $\eta(k) = \varepsilon(k) - \mu$

The BCS theory permits operators such as $C_{-k\tau'}C_{k\tau}$ to have non-zero expectation values b_k. This may be due to coherent superposition or the large number of particles present that make fluctuations to be smal unlike the normal one where the phases are random. This explanation helps one to formally express $C_{-k\tau'}C_{k\tau}$ as [4]

$$C_{-k\tau'}C_{k\tau} = b_k + (C_{-k\tau'}C_{k\tau} - b_k) \tag{2.23}$$

As is stated above

$$b_k = \langle C_{-k\tau'}C_{k\tau} \rangle \quad ; \quad b_k^* = \langle C_{k\tau}^+ C_{-k\tau'}^+ \rangle \tag{2.24}$$

and define

$$\Delta = \frac{g}{V} \sum_k b_k \quad ; \quad \Delta^* = \frac{g}{V} \sum_k b_k^* \tag{2.25}$$

Actually, this is merely a denotation, nevertheless, Δ will soon turn out to be the BCS energy gap. Now, we re-write the model-Hamiltonian as

$$H_m = \sum_{k\tau\tau'} n(k)[C_{k\tau}^+ C_{k\tau} + C_{k\tau'}^+ C_{k\tau'}] - \Delta \sum_{k\tau\tau'} [C_{-k\tau'}C_{k\tau} + C_{k\tau}^+ C_{-k\tau'}^+] + \frac{\Delta^2 V}{g} \tag{2.26}$$

Note that Δ is real and operators such as $\frac{g}{V} \sum_{k\tau\tau'} C_{-k\tau'}C_{k\tau}$ are replaced by their average values.

We demand this Hamiltonian to be diagonalized so that it will consist of a ground state and spectrum of elementary excitations.

2.4 The Spectrum of Elementary Excitations

The spectrum of elementary excitations can be found using different methods. In this case, we use the method of Green functions to study the nature of these elementary excitations or quasi-particles. For this purpose, we define the retarded thermal Green function by

$$G_1(C^+_{k\tau}(t),\ C_{k'\tau},\ t) = \frac{-i}{\hbar}\ \theta(t) < [C^+_{k\tau}(t)\ ,\ C_{k'\tau}(0)] > \tag{2.27}$$

and

$$G_2(C_{-k\tau'}(t),\ C_{k'\tau},t) = \frac{-i}{\hbar}\ \theta(t) < [C_{-k\tau'}(t),\ C_{k'\tau}(0)] > \tag{2.28}$$

where [ ] means anti commutator in this situation.

The Heisenberg equation of motion for any operator A is

$$\dot{\hat{A}} = \frac{i}{\hbar}\ [\hat{H},\hat{A}] \tag{2.29}$$

thus, using the model Hamiltonian, we get

$$\begin{aligned}
\dot{C}^+_{k\tau} &= \frac{i}{\hbar}\ n(k)C^+_{k\tau} - \frac{i}{\hbar}\ \Delta^* C_{-k\tau'} \\
\dot{C}_{k\tau} &= \frac{-i}{\hbar}\ n(k)C_{k\tau} + \frac{i}{\hbar}\ \Delta\, C^+_{-k\tau'} \\
\dot{C}^+_{k\tau'} &= \frac{i}{\hbar}\ n(k)C^{+}_{k\tau'} + \frac{i}{\hbar}\,\Delta^* C_{-k\tau} \\
\dot{C}_{k\tau'} &= \frac{-i}{\hbar}\ n(k)C_{k\tau'} - \frac{i}{\hbar}\,\Delta\, C^+_{-k\tau}
\end{aligned} \tag{2.30}$$

Using (2.30), the equations of motion for (2.27) and (2.28) look like

$$i\hbar\ \dot{G}_1 = -n(k)G_1 + \Delta^* G_2 + \delta(t)\ \delta_{kk'} \tag{2.31}$$

$$i\hbar\ \dot{G}_2 = n(k)G_2 + G_1\Delta \tag{2.32}$$

Here $$\delta(t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-i\omega t}\ d\omega \tag{2.33}$$

Taking Fourier transformations

$$G(k,k',t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} G(k,k',\omega)\exp(-i\omega t)d\omega \tag{2.34}$$

We obtain a system of linear equations

$$\hbar\omega G_1(k,k',\omega) = -\eta(k)G_1(k,k',\omega) + \Delta^* G_2(k,k',\omega) + \delta_{kk'} \tag{2.35}$$

$$\hbar\omega G_2(k,k',\omega) = \Delta G_1(k,k',\omega) + \eta(k)G_2(k,k',\omega) \tag{2.36}$$

Solving for G_1 and G_2, we finally get

$$G_1(k,k',\omega) = \frac{\hbar\omega - \eta(k)}{\hbar^2\omega^2 - \eta^2(k) - \Delta^2} \tag{2.37}$$

$$G_2(k,k',\omega) = \frac{\Delta}{\hbar^2\omega^2 - \eta^2(k) - \Delta^2} \tag{2.38}$$

If we have Fourier components of Green functions, the spectrum of elementary excitations is $E(k) = \hbar\omega$ for ω which corresponds to poles of Fourier components of Green functions. More precisely,

$$E(k) = \sqrt{\eta^2(k) + \Delta^2} \tag{2.39}$$

We have obtained the energy of elementary excitations which is the same as that obtained in the BCS theory!

For electrons at the Fermi level $\eta(k) = 0$ and the minimum value $E(k)$ is Δ - energy gap.

2.5 The Equation for Energy Gap

Precise electronic specific heat measurements of superconductors revealed the existence of an energy gap between the ground state and elementary excitations of the system. Such measurements show that the electronic specific heat goes to zero exponentially below the critical temperature. We shall now obtain a self-consistent equation for the gap parameter using the method of Green functions which, from our point of view, is simpler than the others used so far.

At this point it is convinient to start with the definition

$$\Delta = \frac{g}{\hbar} \sum_{k\tau\tau'} \langle C_{-k\tau'}(t) C_{k\tau}(t) \rangle \tag{2.40}$$

which is like the time correlation function between the two operators $C_{-k\tau'}$ and $C_{k\tau}$. If we set the correlation function [11]

$$F(t) = \langle C_{-k\tau'}(t) C_{k\tau}(t) \rangle \tag{2.41}$$

then the Fourier transform of F(t), called the spectral density function $J(\omega)$, is, in this particular case, given by

$$J(\omega) = 2\pi \langle C_{-k\tau'}(t) C_{k\tau}(t) \rangle. \tag{2.42}$$

The spectral density function can also be expressed as

$$J(\omega) = \frac{-2\hbar}{1 \mp e^{\beta\hbar\omega}} \operatorname{Im} G_2 \tag{2.43}$$

The positive sign in the denominator refers to Fermi distribution whereas the negative one refers to Bose distribution; $\beta = \frac{1}{kT}$ as usual.

Since eqns. (2.37) and (2.38) can be re-written as

$$G_1(\omega,k) = \frac{\frac{1}{2}[1-\frac{\eta(k)}{E(k)}]}{\hbar\omega - E(k)} + \frac{\frac{1}{2}[1+\frac{\eta(k)}{E(k)}]}{\hbar\omega + E(k)} \tag{2.44}$$

and

$$G_2(\omega,k) = \frac{\Delta}{2E(k)}\left[\frac{1}{\hbar\omega - E(k)} - \frac{1}{\hbar\omega - E(k)}\right], \tag{2.45}$$

one can show that

$$I_m G_2(\omega,k) = \int_{-\infty}^{\infty} \frac{\Delta}{2E(k)}\,\pi\{\delta(\hbar\omega - E(k)) - \delta(\hbar\omega + E(k))\}\,d\omega \tag{2.46}$$

Now Δ becomes

$$\Delta = \frac{g}{V}\sum_{k\tau\tau'}\langle C_{-k\tau'}(t)C_{k\tau}(t)\rangle = \frac{g}{2\pi V}\Sigma\,J(\omega) \tag{2.47}$$

Using eqns. (2.46) and (2.47) we finally arrive at an equation for energy gap

$$1 = \frac{g}{2V}\sum_k \frac{1}{E(k)}\tanh\frac{\beta}{2}E(k) \tag{2.48}$$

which is again exactly the same as that obtained using conventional methods!

As a special case, at T = 0, the above equation reduces to

$$1 = \frac{g}{2V}\sum_k \frac{1}{\sqrt{\eta^2(k) + \Delta_0^2}} \tag{2.49}$$

where $\Delta_0 = \Delta(T = 0)$.

Evaluating its integral equivalent, we obtain an equation for Δ_o ;

$$\Delta_o = 2\hbar\,\omega_D \exp\,(-2v/N(0)g) \tag{2.50}$$

where N(0) is the number of states at the Fermi level, ω_D is the Debye frequency and v is the volume of the system.

Actually $\frac{N(0)g}{2v} \approx 0.3$ for most superconductors, $\hbar\omega_D \sim 100k$ and hence $\Delta_o \sim 4k$.

2.6 Ground State of Superconductor

We now formulate the ground state energy by performing canonical transformations on the Hamiltonian (2.26) of actual particles. This is done by specifying appropriate linear transformations as

$$\begin{aligned} C_{k\tau} &= u_k\, b_{k\tau} + v_k\, b^{+}_{-k\tau'} \\ C_{k\tau'} &= u_k\, b_{k\tau'} - v_k\, b^{+}_{-k\tau} \end{aligned} \tag{2.51}$$

where u_k, v_k are numerical coefficients; b_k are new operators. For Fermi character of the new operators we require that

$$u_k^{\,2} + v_k^{\,2} = 1 \tag{2.52}$$

Again, these coefficients can be evaluated using the Green functions method (see Appendix B) and the result is

$$v_k^{\,2} = \tfrac{1}{2}[1 - \frac{\eta(k)}{E(k)}] \;;\quad u_k^{\,2} = \tfrac{1}{2}[1 + \frac{\eta(k)}{E(k)}] \tag{2.53}$$

There is no lose of generality if we choose that all u_k are real and positive.

The model-Hamiltonian can be re-expressed interms of the new operators and replacing $b_{k\tau}^{+} b_{k\tau}$ by $n_{k\tau}$ and $b_{k\tau'}^{+} b_{k\tau'}$ by $n_{k\tau'}$ then the final diagonalized model-Hamiltonian (see Appendix C) we obtain looks like

$$H_M = \sum_k [\eta(k) - E(k) + \Delta b_k^*] + \sum_{k\tau\tau'} E(k)(n_{k\tau} + n_{k\tau'})$$

$$H_M = E_{so} + \sum_{k\tau\tau'} E(k)(n_{k\tau} + n_{k\tau'}) \qquad (2.54)$$

as required. Note that the occupation numbers $n_{k\tau}$ and $n_{k\tau'}$ are given by

$$n_{k\tau} = n_{k\tau'} = \frac{1}{e^{\beta E(k)} + 1} \quad ; \; \beta = \frac{1}{kT}, k \text{ -Boltzmann factor} \qquad (2.55)$$

since E(k) has received the justification of an energy of elementary excitations of momentum $\hbar k$.

Now let us see what the two terms of eqn.(2.54) are. The ground state energy of the transformed Hamiltonian is obtained when no particle is excited or no hole is created inside the Fermi surface. So it is given by the constant term of eqn.(2.54):

$$E_{so} = \sum_k [\eta(k) - E(k) + \Delta b_k^*] \qquad (2.56)$$

The second term refers to quasi-particles. Thanks to the Green functions method, we realized that E(k)has represented the energy of these quasi-particles. Moreover, the values of u_k^2 and v_k^2 obtained in this analysis (see Appendix C) are the same with those obtained by the Green functions method. Physically speaking, v_k^2 is the probability that the state $(k_\tau , -k_{\tau'})$ is occupied and u_k^2 is the probability that it is unoccupied.

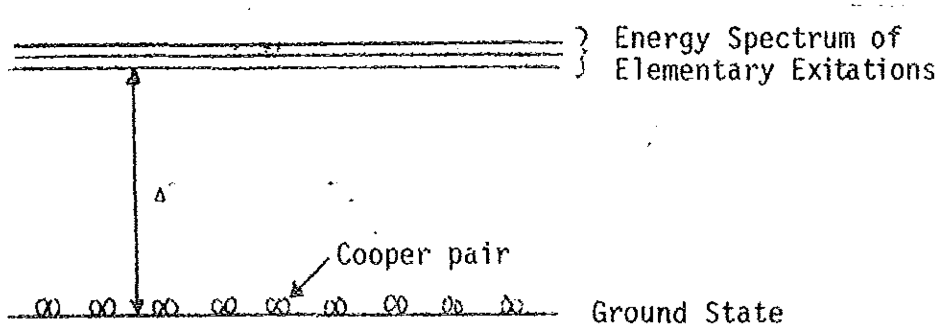
One can obtain an important relation that given the difference in energy between the ground state energy of superconductor and the normal Fermi sea state energy. In the weak coupling limit where $\Delta_o \ll h\omega_D$, at $T = 0$, it is [4]

$$E_{so} - E_n = -\tfrac{1}{2}N(0)\Delta_o^2 \qquad (2.57)$$

This difference is the condensation energy at $T = 0$ and it must, by definition, be the same as $H_c^2(0)/8\pi$, where $H_c(T)$ is the thermodynamic critical field.

To summarize, what we have done so far is, briefly, we obtained the ground state energy of Cooper pairs and if by some mechanism a pair is broken the two electrons will occupy higher state. The spectrum of these excitations have been studied and an expression for Δ is obtained.

The remaining thing may be to see what this Δ is and now, it is clear that, Δ is the minimum possible value of $E(k)$ since even if $\eta(k)$ is zero, that is at the Fermi surface, $E(k)$ will be equal to Δ which is positive. So, Δ plays an important role of energy gap - the gap between the ground state and spectrum of elementary excitations as sketched below.



In gneral, Δ is temperature dependent.

2.7 Temperature Dependence of Energy Gap

If the temperature of a given superconductor tends to zero, then we put $\Delta(0) = \Delta_o$ and

$$E(k) = \sqrt{\eta^2(k) + \Delta_o^2} \tag{2.58}$$

However, if $T \neq 0$ then Δ will be a function of T and

$$E(k) = \sqrt{\eta^2(k) + \Delta^2(T)} \tag{2.59}$$

The integral equivalent of (2.48) will then be

$$1 = \frac{g}{2V} \int_{-\hbar\omega_D}^{\hbar\omega_D} \frac{1}{\sqrt{\eta^2(k)+\Delta^2(T)}} \left[1 - \frac{2}{\exp(\sqrt{\eta^2(k)+\Delta^2(T)})}\right] \tag{2.60}$$

where the integral is taken over a thin layer of thickness $2\hbar\omega_D$ near the Fermi surface since electrons in this layer are the ones most strongly involved in superconductivity. This integral is not easily integrable, nevertheless, we can simplify it by taking limiting cases:

$$\begin{aligned} &\text{a)}\quad T \to 0 \ \text{ then } \ \Delta(T) = \Delta_o \ \text{which implies} \ \Delta_o/T \gg 1. \\ &\text{b)}\quad T \to T_c \ \text{ then } \ \Delta(T_c) \to 0 \ \text{ by definition.} \end{aligned} \tag{2.61}$$

We seek solution of the form

$$\Delta(T) = \Delta_o + \Delta_1 \tag{2.62}$$

If we also assume $\eta(k) \ll \Delta$ then, after much labor, we arrive at a final expression (see Appendix D1)

$$\Delta(T) = \Delta_o\left[1 - \left(\frac{2\pi T}{\Delta_o}\right)^{\frac{1}{2}} \exp(-\Delta_o/T)\right], \ T \ll \Delta_o \tag{2.63}$$

that expresses the temperature dependence of Δ and at $T = 0$ it reduces to $\Delta(T) = \Delta_o$.

2.7.1 Determination of T_c

The critical temperature T_c , in this respect can be defined as the temperature at which Δ tends to zero. Under this condition $E(k) = \eta(k)$ and equation (2.60) reduces to

$$1 = \frac{g}{2V} \int_{-\hbar\omega_D}^{\hbar\omega_D} \frac{1}{\eta(k)} N(\eta) \tanh \frac{\beta}{2} \eta(k) d\eta \quad (T=T_c) \tag{2.64}$$

Evaluating this integral

$$T_c = 0.57 \Delta_o \tag{2.65}$$

Δ_o is comparable in magnitude to KT_c . The numerical factor fairly agrees with the values obtained by many experiments. Experimental values of 2Δ , for many mateirlas, fall in the range 3 to 4.5 KT_c.

As a third case, we can consider temperatures very close but not equal to T_c, that is , $\frac{T_c - T}{T_c} \ll 1$. For this case, we get [12] (see Appendix D2).

$$\Delta(T) = 3.06\ T_c(1 - \frac{T}{T_c})^{\frac{1}{2}} \tag{2.66}$$

or using (2.65)

$$\frac{\Delta(T)}{\Delta_o} = 1.74(1 - \frac{T}{T_c})^{\frac{1}{2}} \ ,\ T \approx T_c \tag{2.67}$$

The variation of $\Delta(T)/\Delta_o$ with T/T_c is illustrated below that $\Delta(T)/\Delta_o$ decreases from 1 at $T = 0$ to zero at $T = T_c$.

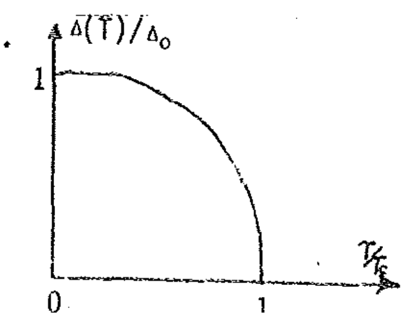


Fig.5. Temperature dependence of energy gap in the BCS theory.

2.7.2 The Isotope Effect

We would like to briefly present the isotope effect in relation to (2.65).

It was experimentally found that for different isotopes [4]

$$T_c M^a = \text{const.} \tag{2.68}$$

where M is the mass of an isotope, and the value of "a" for most materials is very close to 0.5. This effect confirmed Frölich's suggestion that superconductivity could be explained by electron-lattice interaction. And it is true that since $\Delta \sim \hbar\omega_D$ and $\omega_D \sim M^{\frac{1}{2}}$, it follows that $T_c M^{\frac{1}{2}} = \text{const}$ provided that $v, N(0), g$ are unchanged from one isotope to another.

2.8 Thermodynamics of Superconductors

Once $\Delta(T)$ is determined, the temperature dependent energy of quasi-particles can be found from (2.59), which inturn determines the electronic occupation numbers n_k and, by extension, the specific heat of the system. The first term of (2.54) does not contribute at all to the electronic specific heat while the second term contributes to the superconducting state electronic specific heat. The variation of the energy of the superconductor is

$$\delta E = \sum_{k\tau'} E(k)(\delta n_{k\tau} + \delta n_{k\tau'}) \tag{2.69}$$

On changing summation to integration we find the specific heat becomes

$$C = \frac{\delta E}{\delta T} = \int_{-\hbar\omega_D}^{\hbar\omega_D} 2N(\eta)E(\eta)\frac{dn}{dT}\,d\eta \tag{2.70}$$

If we restrict ourselves to low temperatures, we get

$$C = 2\sqrt{\pi 2}\;\; N(0)\;\; \Delta_o \left(\frac{\Delta_o}{T}\right)^{3/2} \exp(-\Delta_o/T)\;\;,\; T \ll \Delta_o \qquad (2.71)$$

One can clearly see that the specific heat of a superconductor decreases exponentially for small temperatures which is verified by experiments. Moreover, this exponential dependence vanishes at $T = 0$ which is in good agreement with Nernst's theorem which dictates that both the entropy and specific heat go to zero at this limit.

The remaining thing is the contribution to the specific heat in the normal state. In this state, the specific heat linearly increases with temperature:

$$C_n = \gamma T \qquad (2.72)$$

γ being determined experimentally.

The above two results indicate that there is some sort of discontinuity at T_C. In order to understand such inconvenience we consider the following simple approach.

The electronic entropy for a Fermion gas is given by [4]

$$S_S = -2k \sum_k [(1-n_k)\ln(1-n_k)+n_k \ln n_k] \qquad (2.73)$$

and the specfic heat beocmes

$$C_S = \frac{TdS_S}{dT} = 2k\beta \sum_k \frac{-\partial n_k}{\partial E(k)} [E^2(k)+\frac{1}{2}\;\beta\,\frac{d\Delta^2}{d\beta}] \qquad (2.74)$$

where k is Boltzmann constant, $\beta = 1/kT$.

The first term is the contribution of the specific heat in the normal state and it can be shown that it is given by [13]

$$C_n = \gamma T = \frac{2\pi^2}{3} N(0)k^2T \qquad (2.75)$$

which is continuous at T_c, the interesting limit we are looking for. The second term shows the effect of the variation of the gap with temperature. It is finite below T_c and zero above indicating a discontinuity or a jump ΔC in the electronic specific heat at T_c. Equation (2.74) becomes

$$C_s = C_n + 2k\beta \sum_k \frac{-\partial n_k}{\partial E(k)} \frac{1}{2} \beta \frac{d\Delta^2}{d\beta} \qquad (2.76)$$

changing summation to integration

$$(C_s - C_n)|_{T_c} = \Delta C = k\beta^2 \int_{-\infty}^{\infty} N(\eta)\frac{d\Delta^2}{d\beta}\left(\frac{-\partial n_k}{\partial|\eta|}\right) d\eta \qquad (2.77)$$

Thus,

$$\Delta C = -k\beta^2 N(o)\left(\frac{d\Delta^2}{d\beta}\right)_{T_c} \qquad (2.78)$$

Since $\frac{d\Delta^2}{d\beta}$ is negative, ΔC is positive or $C_s > C_n$.

The overall behaviour of the electronic specific heat is depicted below.

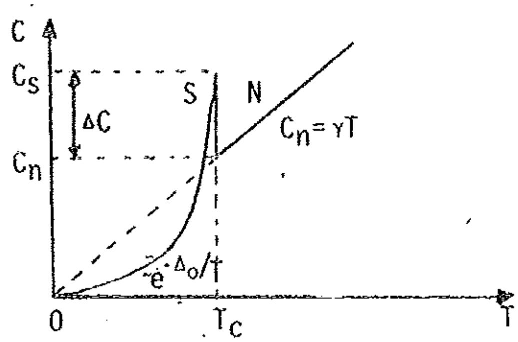


Fig.6 Variation of Specific heat with T and its jump at T_c.

The conclusion is that the jump in the specific heat was predicted by the phenomenological theories and the calculations are in good agreement with the predictions.

2.9 The Connection Between BCS Microscopic and GL Theories

As we know, GL theory is phenomenological one and it does not give the interpretations of ψ, ξ and λ on the microscopic level. After Bardeen, Cooper and Schrieffer had presented the complete microscopic theory of superconductivity, Gorkov succeeded in obtaining formulas that described the parameters ψ, ξ and λ on the basis of BCS theory. Here, we give only the final results. They are different for the so-called "pure" and "dirty" superconductors. All physical quantities are written with indices "p" and "d" which refer to the "pure" and "dirty" superconductors respectively. We call a material pure superconductor if the free path way of electron $\ell \gg \xi_o$, where ξ_o is a parameter of GL theory given by $\xi_o = 0.18\, \hbar v_F/k_B T_C$, k_B is the Boltzmann constant. The inequality $\ell \ll \xi_o$ is true for dirty superconductors.

As one may expect, the energy gap $\Delta(T)$ represents the order parameter in the superconductor and when T tends to T_C it should be proportional to the order parameter ψ of GL theory. The exact relation is [14]

$$\Psi_p = \left[\frac{7\xi(3) m v_F{}^2 N(0)}{2\pi^2 k_B{}^2 T_c{}^2}\right]^{\frac{1}{2}} \Delta(T) \tag{2.83}$$

$$\Psi_d = \left[\frac{\pi m v_F N(0)\ell}{12\hbar\, k_B T_C}\right]^{\frac{1}{2}} \Delta(T) \tag{2.84}$$

Further one can get (see Appendix D2)

$$\Delta(T) = \left(\frac{8\pi^2}{7\xi(3)}\right)^{\frac{1}{2}} k_B T_C \left(1 - \frac{T}{T_C}\right)^{\frac{1}{2}} \tag{2.85}$$

or

$$\Delta(T) \cong 3.1\, k_B T_C \left(1 - \frac{T}{T_C}\right)^{\frac{1}{2}} \tag{2.86}$$

and for the coherence length and penetration depth, the results are

$$\xi_p = 0.74\ \xi_o (1 - \frac{T}{T_c})^{-\frac{1}{2}} \tag{2.87}$$

$$\xi_d = 0.85\ \xi_o (1 - \frac{T}{T_c})^{-\frac{1}{2}} \tag{2.88}$$

$$\lambda_p = \frac{\lambda(0)}{\sqrt{2}} (1 - \frac{T}{T_c})^{-\frac{1}{2}} \tag{2.89}$$

$$\lambda_d = 0.615\,\lambda(0)(\xi_o/\ell)^{\frac{1}{2}}(1 - \frac{T}{T_c})^{-\frac{1}{2}}\ ;\ \lambda^2(0) = \frac{3c^2}{8\pi e^2 v_F^2 N(0)} \tag{2.90}$$

The coefficients α and β of expansion of the free energy interms of ψ are given by

$$\alpha_p = 1.83\ \frac{\hbar^2}{2m}\ \frac{1}{\xi_o^2}(\frac{T}{T_c} - 1) \tag{2.91}$$

$$\alpha_d = 1.36\ \frac{\hbar^2}{2m}\ \frac{1}{\xi_o \ell}(\frac{T}{T_c} - 1) \tag{2.92}$$

$$\beta_p = 0.35\ \frac{1}{N(0)}(\frac{\hbar^2}{2m\,\xi_o})^2\ \frac{1}{(k_B T_c)^2} \tag{2.93}$$

$$\beta_d = 0.2\ \frac{1}{N(0)}(\frac{\hbar^2}{2m\,\xi_o \ell})^2\ \frac{1}{(k_B T_c)^2} \tag{2.94}$$

and the GL parameters are

$$\varkappa_p = 0.96\ \frac{\lambda(0)}{\xi_o} \tag{2.95}$$

$$\varkappa_d = 0.725\ \frac{\lambda(0)}{\ell} \tag{2.96}$$

Now we shall establish the frame of application of GL theory. In the expansion of the density of Gibb's free energy with respect to powers of $|i\hbar\,\nabla\psi - \frac{2e}{c}\vec{A}\,\psi|^2$, we have to consider only the first term. This means that we want slow changes of ψ and $\vec{A}$ on the distance of order ξ_0 (the size of Cooper pair). In the case of pure superconductors where $\ell \gg \xi_0$, the condition for the application of GL theory is $\xi(T)$ and $\lambda(T) \gg \xi_0$. Since $\xi(T) \sim \xi_0 \ (1 - \frac{T}{T_C})^{-\frac{1}{2}}$, if T tends to T_C, then $\xi(T)$ is always larger than ξ_0 which implies that the condition $\xi(T) \gg \xi_0$ holds automatically. Now let us consider the second condition $\lambda(T) \gg \xi_0$. This is a condition for the application of local electrodynamics or this is condition for the superconductor to be London superconductor. We know that $\lambda(T) \sim \lambda(0)(1 - \frac{T}{T_C})^{-\frac{1}{2}}$ and $\varkappa \sim \lambda(0)/\xi_0$ and thus

$$\varkappa^2 \gg 1 - \frac{T}{T_C} \tag{2.97}$$

which is rather tough condition since in the first type superconductors $\varkappa$ may be small. For example, $\varkappa(A\ell) = 0.01$, $\varkappa(pb) = 0.23$.

In the case of dirty superconductors the domain of application of GL theory is much wider. In such a case the free path way serves as characteristic length of non-homogeneity and the conditions for validity of GL theory are $\xi(T)$ and $\lambda(T) \gg \ell$. Again, since $\xi(T) \sim (\xi_0 \ell)^{\frac{1}{2}}(1 - \frac{T}{T_C})^{-\frac{1}{2}}$ then condition $\xi(T) \gg \ell$ takes the form $\xi_0/\ell \gg (1 - \frac{T}{T_C})$ with $\xi_0 \gg \ell$. Therefore, this condition is much wider than the usual condition of the validity of Landau's thery of second order phase transition, $\frac{T_C - T}{T_C} \ll 1$. Refering to the second condition $\lambda(T) \gg \ell$, in the case of dirty superconductors $\lambda(T) \sim \lambda(0)(\xi_0 \ell)^{\frac{1}{2}}(1 - \frac{T}{T_C})^{-\frac{1}{2}}$ and $\varkappa \sim \lambda(0)/\ell$. This second condition can also be written in the form $\frac{\varkappa^2 \xi_0}{\ell} \gg (1 - \frac{T}{T_C})$. If $\varkappa \sim 1$, then this is again much wider than the common condition $\frac{T_C - T}{T_C} \ll 1$. The conclusion is that, in the case of dirty superconductors (alloys) the GL theory is true for the comparatively wide temperature range (at least qualitatively). The domain of quantitative application of GL theory again reduces to

$$\frac{T_c - T}{T_c} \ll 1 . \tag{2.98}$$

The phenomenological and microscopic theories can explain all phenomena of low-temperature superconductivity. But, recently, superconductivity was observed in relatively high temperatures (~ 90k). This cannot be explained by the conventional theories mentioned above and, so far, there is no theory to explain it. The next chapter is devoted to the experimental results of high-T_c and the explanations given to the data.

CHAPTER III

3. HIGH-TEMPERATURE SUPERCONDUCTIVITY

3.1 Discovery of High-T_c Superconductivity

High-temperature superconductivity was first observed by K.A. Müller and J.G. Bednorz of the IBM, Zurich, in January, 1986 in the new multi-phased oxides of barium, lanthanum and copper with transition temperatures upto 40k[15]. These new materials which are oxide ceramics are a completely new class of superconductors, the Cu-O Perovskite-type materials. This discovery became a break-through in the theoretical and experimental work on high-temperature superconductivity and a number of groups observed that T_c exceeded the boiling point of nitrogen (77k) in these new materials.

After Bednorz and Müller, Uchida et al.[16] at the University of Tokyo made a further step identifying $La_{2-x}Ba_xCuO_{4-y}$ with $x \sim 0.1$ as high-T_c phase, which has the layered perovskite k_2NiF_4 structure. Chu and co-workers at the University of Houston reported onset superconductivity near 70k in La-Ba-Cu-Oxide and they found that the transition can be enhanced by pressure[17]. In fact, when Wu et al. reported superconductivity above 90k in barium, yttrium and copper terniary oxides (YBa_2 - Cu_3O_{7-x}), there arose considerable excitement and interest and number of groups found comparable T_c's by replacing yttrium by trivalent rare-earths La-Lu[18]. These developments are promising that room-temperature superconductivity may be possible with these ceramics in the near future.

According to Tanaka of the University of Tokyo, high-T_c ceramics are grouped into three: $BaPb_{1-x}Bi_xO_3$ (a prototype of the newly discovered compounds) with T_c=14k, La-X-Cu-O (X=Ba,Sr,Ca) with $T_c \sim 40k$, and Y-Ba-Cu-O for which $T_c \sim 90k$[19].

There are several reports with different high T_c in substances of different compositions, but Tanaka insisted that these can be classified as real superconductors, if the structure of the material is clarified, the Meissner effect exists, the electrical resistance vanishes and the experiment is reproducible.

3.2 Main Experimental Data

Preparation and Structures

Since the discovery of the new materials, great efforts have been done in the preparation of quality materials with higher and higher T_c's from different compositions of rare-earth-copper-oxides. The preparation of these materials is simple. The Ba-La-Cu-O compound can be prepared [20] by mixing in the appropriate ratio nitrates of barium, lanthanum and copper, and precipitating the solid mixture with oxalic acid. The solid precipitate is heated at 900°C for five hours, pressed into pellets at 4k bar and sintered at 900°C.

X-ray diffraction studies revealed that samples prepared in this way consisted of three phases: $La_{1-x}Ba_xCuO_{3-y}$ with perovskite structure, $La_{2-x}Ba_xCuO_{4-y}$ with a layered perovskite structure of the K_2NiF_4 type and CuO.

Electrical Resistance

Chu observed that the resistance of several Y-, Sc- and La- based multiphase Ba-Cu-Oxide samples at temperatures as high as 240k dropped by two orders of magnitude[21]. C.Y. Huang also found a sharp decrease in resistance of at least four orders of magnitude at ~ 230k in one annealed sample of $EuBa_2Cu_3O_{6+\delta}$[22]. Some argued that this could be a metallic transition to one with resistance smaller by three or four orders of magnitude. However, experiments showed the Meissner effect which proved that it is truly superconduction. For instance, $Y_{0.33}Ba_{0.67}CuO_{2.33\pm\delta}$ showed the onset of superconductivity at 120k, attaining zero resistance at 87k and the highest Meissner effect of all the high-T_C materials[23]. A highly conducting material will never show the Meissner effect. It is almost certain that persistent currents exist since the resistance of, say, $YBaCuO_4$ sample is less than $10^{-11}\Omega$. The value of the superconducting current density is about 10^6 A cm^{-2} in some materials.

Magnetic Behaviour

The fact that magnetic field is expelled from a superconductor indicates that the standard picture of a sea of conduction electrons is inappropriate. This behaviour has been called "perfect-diamagnetism", but it differs from conventional diamagnetism in that macroscopic surface currents are its deriving force[24].

The new oxides are type II superconductors with upper critical fields greater than 100 teslas. To obtain λ and ξ for these materials has so far been difficult due to their anisotropic structure.

Flux Quantization

One important observation is the quantization of magnetic flux in a high-T_c yttrium based ceramic superconductor. The value obtained for the flux quantum was 0.97±0.04(h/2e) where h is Planck's constant and e is the electron charge[23]. This serves as an indication that the charge carriers are electron pairs as in conventional BCS case. This implies the existence of coherent states in the newly discovered materials.

Josephson Effect

The a.c. Josephson effect in mixed-phase Y-Ba-Cu-Oxide sample below 240k, giving a very strong evidence for superconductivity, was detected[25].

3.3 Possible Mechanisms of High-Temperature Superconductivity

Since the recent discovery of high-T_c superconductivity, there has been a torrent of experimental and theoretical work both in finding quality materials with some concentration of oxygen for genuine superconducting properties and understanding the mechanism responsible for it. Of course, no one doubts that high-temperature superconductivity is related to the formation of condensate state where the charge carriers are electrons or ions whether paired or not remains to be seen. Accordingly, a number of possible pairing mechanisms are proposed by many researchers and here we shall mention some.

Refering to the pairing mechanism of low-temperature superconductivity which is the attractive interaction of electrons near the Fermi surface mediated by the exchange of phonons, we see that this cannot account for the properties of the new materials[26]. For example, in this frame T_C is of the order of a few degree kelvin. In addition, the isotope effect is absent in the new materials. Eventhough, the parameters of these new materials are somewhat unusual, the charge carriers are electron-pairs and it seems that many theorists agree that the possible high-temperature mechanism is pair formation but by some what stronger mechanism than that of Cooper[27].

Strongin et al.[16] pointed out that an exotic new mechanism such as excitonic or bipolaronic mechanism for the interaction between electrons might lead to the formation of Cooper pairs and hence superconductivity. The polaron is usually described as an electron (or a positive hole) which has trapped itself in the potential well of its interactions with the lattice; a bipolaron is merely a pair of polarons or localized electrons. It is questionable whether Bose condensation of bipolarons is possible and causes superconductivity. The answer to these questions was yes but not in the case of high-temperature superconductivity[28].

Vladmir Kresin[20] proposed that the pairing interaction in the oxides is mediated not only by low-frequency phonons but also by plasmons, the quanta of plasma oscillations of the electron gas. He argued that the plasma dispersion is that of a two dimensional system and these two dimensional plasmons give a significant contribution to the pairing interaction.

We can cite more and more suggested pairing mechanisms but, to date, we do not know which one is the actual mechanism responsible for high-T_c superconductivity. Any suggested mechanism may seem to be true. Hence, to elliminate the frustrating avalanch of theories, microscopic probes are being used. These are expected to elucidate the geometrical and electronic structure of the superconducting phase[16].

As Anderson[26] pointed out, the electron-phonon interaction mechanism in high-temperature superconductors $YBa_2Cu_3O_7$ and $EuBa_2Cu_3O_7$ seem to be effectively elliminated. There are two reasons for this. The first is the observation of atomic moments on Cu sites in La_2CuO_4 of at least 0.5 Bohr magneton. Magnetism in the d-transition series to which Cu belongs is invariably due to strong interelectronic repulsion. Therefore, theories such as BCS and bipolaron based entirely on electron-electron attractive interaction may not apply to high-temperature superconductivity. The other result arguing against strong phonon coupling is crystalographic (tetragonal to orthorhombic) transition in the lanthanum compounds. This transition is expected to be accompanied by the appearance of an electronic charge density wave, but this was observed to be irrelevant to the electronic structure. In this frame work, exchange mechanisms consistent with the repulsion such as the resonating valence bond (RVB) theory based entirely on short-range electron-electron repulsion are not elliminated. According to Anderson[20], in La_2CuO_4, pairs of nearest neighbour electrons are in a spin-singlet state, but there is no long-range anti-ferromagnetism. The bonds that bind pairs of electrons in a singlet configuration fluctuate: The spin of an electron may point up at one instant because its neighbour to the right points down; the next instant it may be down because that of its neighbour to the left is now up. Anderson called this a "resonating valence bond" state. The magnetic singlet pairs of the La_2CuO_4 insulating state become charged superconducting pairs when the insulator is doped sufficiently strongly[29]. The mechanism for superconductivity, according to this theory, is electronic and magnetic although weak phonon interactions may favour the state. Thus, if this is the right mechanism, phonons play no role but this cannot be verified experimentally until single crystals are available.

3.4 The Possibility of Stimulating Pairing in Thin Films in High Frequency Region.

The above discussed pairing mechanisms have limitations and, so far, we donot know which is the right one. We know that from BCS theory T_c depends on ω_D,N(0) and V. For increasing T_c, we need modifications of these variables by some mechanism. This led us to re-examine the two liquid model of sec. 2.1 and for simplicity we considered a very thin metallic film whose electrons and ions are imagined as two-charged liquids. We studied the possibility of attractive interaction between electrons in the low frequency limit, that is,

$$\omega < \omega_L(k) \tag{3.1}$$

Once more, in the high frequency region $\omega \leq \omega_{p_o}$; $\omega \gg \omega_L(k)$, one can get, from equation (2.12), negative sign of V_k if ω is in the interval

$$v_F^2k^2/3 < \omega^2 < \omega_{p_o}^2 + v_F^2k^2/3 \tag{3.2}$$

This produces limitation on k. Since $\omega \simeq \omega_{p_o}^2 > v_F^2k^2/3$, for typical values $v_F \sim 10^8$ cm/s, $\omega_{p_o} \sim 10^{16}$ then $k < 10^6 cm^{-1}$ and the corresponding wave length $\lambda \sim 100\mathring{A}$ so the inequality (3.2) is valid in the long wave limit. Now, let $\omega^2 = \alpha(\omega_{p_o}^2 + v_F^2k^2/3)$ where α is very close to 1 then equation (2.12) can be re-written as

$$V_k = \frac{4\pi e^2}{k^2}\left[1 - \frac{k^2}{k^2+3\omega_{p_o}^2/v_F^2}\right]\frac{1}{\alpha - 1} \qquad (3.3)$$

The first term is inverted Coulomb (negative) and the second is screened Coulomb interaction with screening radius $r_{sc} \sim v_F/\omega_{p_o}$. This interaction is attractive. In the BCS theory, the frequency ω arizes from vibrations of electron density: $\omega = \varepsilon_{k_1} - \varepsilon_{k_2}/\hbar$. Unfortunately, in our two-liquid model we donot have high frequency force which can stimulate the corresponding high frequency vibration of electron subsystem in the range of frequencies given by (3.2). However, we can create such a source of high frequency vibrations using external agent. One should keep in mind that longitudinal vibrations of electric field can penetrate into plasma only when $\omega^2 > \omega_{p_o}^2 + v_F^2k^2/3$. If $\omega^2 < \omega_{p_o}^2 + v_F^2k^2/3$ such vibrations can penetrate to a small extent only. This can be shown by solving (2.10).

$$E(Z) = \exp\left\{\frac{\sqrt{3(\omega_p^2(k) - \omega^2}}{v_F} Z\right\} \qquad (3.4)$$

where E(Z) is the longitudinal electric field in plasma from the external source.

For a thin film of thickness

$$d \sim \frac{v_F}{\sqrt{3(\omega_p^2(k) - \omega^2)}} \sim \frac{v_F}{\omega_{p_o}} \frac{1}{\sqrt{1-\alpha}} \tag{3.5}$$

electric field will practically completely penetrate into the film and can be considered as the driving force for electron sub-system. (For example, if $\alpha = 0.98$ we get $d \sim 10^3 \mathring{A}$ which is a reasonable thickness of films). This means that we can consider the fluctuating external source in (2.10) oscillating as $e^{ikx-i\omega t}$ with ω in the range given by (3.2). In such a system we can stimulate pairing of electrons in the high frequency range.

For typical metals, $\varepsilon_F \sim 10eV$ and $\hbar\omega_{p_o} \sim 0.1eV$ which shows that only electrons within a thin layer near the Fermi surface take part in pairing. Hence, it seems we can use the relation

$$T_c \sim 2\hbar\omega_{p_o} \exp\{-1/N(0)V\} \tag{3.6}$$

which was obtained in the BCS theory. If we leave the coupling constant V to be unaffected by the replacement of ω_D by ω_{p_o}, then we get $T_c > 40k$.

One can show that in a specially prepared thin film which consists of small metallic balls longitudinal high frequency collective vibrations of polarization $\omega \sim \omega_{p_o}/\sqrt{3}$ can occur. Thus, we can propose the experimental study of the possibility of stimulating pairing in the high frequency region using a thin film of small metallic balls doped onto a continuous thin film of the same metal as shown in Fig.7 below. The thickness of the films can be chosen according to (3.5) so that longitudinal high frequency electric field completely penetrates into the film.

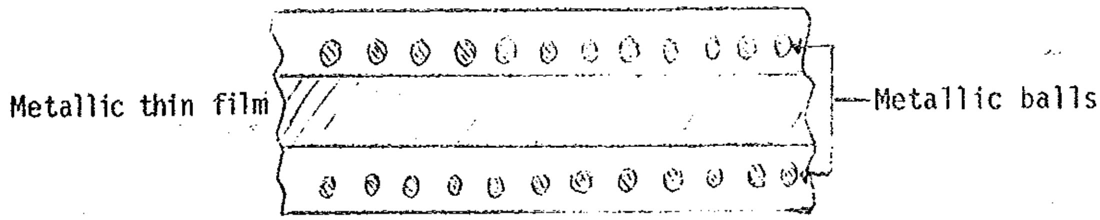


Fig.7 Metallic thin films

At sufficiently low temperatures, one can observe drop of resistance due to pairing of electrons that results from exchange of high frequency plasma vibrations in metallic balls. The idea of construction of such an experiment was proposed by V. Malnev*, Mulugeta Bekele and Salah Ahmed[30]. The final confirmation of this hypothesis can be done only experimentally.

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4. CONCLUSION

The theory of low-temperature superconductivity after the discovery of the pairing phenomenon by Cooper and formulation of the microscopic BCS theory can be, at present, considered as a well-developed branch of solid state physics. Nevertheless, for the description of different phenomena in conventional superconductivity, we have to enlist practically all branches of theoretical physics: quantum mechanics, field theory, statistical physics, etc. since the superconductivity problem can be studied as a many-body problem. We have also to use modern techniques, for example, Green's function method.

This work has started with the analysis of experimental data, particularly, the phenomenological theory, GL-equations, and Abrikosov's modified treatment of type II superconductors that can describe practically all phenomena in conventional superconductivity.

The BCS theory can be taken as a good example of one aspect of many-body problem, namely, the interaction between electron gas and vibrations of unique crystalline lattice, a problem that can be solved. The significant feature of such an interaction is that it results in a new ground state-superconducting state caused by attractive interaction between electrons mediated by phonons. At $T = 0$, this ground state possesses lower energy than the ground state of normal metal. The excited states or the spectrum of elementary excitations is separated from the ground state by an energy gap that depends on the coupling of electron-phonon interaction, density of electron states on the Fermi surface and on the limiting frequency ω_D of crystalline lattice.

The ground state can be considered as a system of Cooper pairs that forms the so-called condensate. In this state, current can exist which is non-dissipative upto the so-called critical current at which Cooper pairs are broken.

The further development of the conventional theory is now mostly connected with the prediction of the application of different superconductors as new physical devices.

The recent discovery of high-temperature superconductivity in ceramics drastically changed the direction of research in the physics of superconductivity. The crucial point at this time in the theory of superconductivity is the increase of the critical temperature and understanding its mechanism. Now, the common point of view is that the superconducting state in these new materials is also a state of paired electrons though the availability of energy gap in many cases is under question.

From our point of view, the theory of high-T_c superconductivity can be built only on the basis of the experimental data concerning the microscopic structure of these materials and their behaviour in different physical conditions. The agreement on the pairing of electrons in high-T_c reminds one the isotope effect that includes phonons into the theory. However, upto now, the existence of the isotope effect in high-T_c superconductors have not been established.

The main goals of this paper are, in the first place, review of the modern state of the theory of superconductivity in conventional case and secondly the relevant simplification of the description of the ground state and spectrum of elementary excitations the energy of which was found by the development of comparatively simple method of retarded thermal Green function. Despite the possession of the complete data of the modern state of high-T_c superconductivity, we decided to propose for discussion the possibility of stimulating pairing in thin metallic films that can result in $T_c > 40k$. The external longitudinal electric field in this model is still unspecified. This model regards the high frequency longitudianl optical phonons or excitones. Nevertheless, further investigation of this phenomenon lies beyond the scope of this thesis.

MATHEMATICAL APPENDICES

APPENDIX A

Derivation of the Landua-Ginzburg Equations

The expansion of the Gibb's free energy with respect to $\Psi(r)$ and $\vec{A}(r)$ is given by (1.24). Minimizing G with respect to ψ^*, keeping $\vec{A}$ and ψ constar we get

$$0 = \delta_{\psi^*} G_{sh} = \int dV[\alpha\psi\delta\psi^* + \beta\psi|\psi|^2\delta\psi^* + \frac{1}{2m^*}(i\hbar\nabla\delta\psi^* - \frac{e^*}{c}\vec{A}\delta\psi^*)(-i\hbar\nabla\psi - \frac{e^*}{c}\vec{A}\psi) \quad \text{(A.1}$$

Let $\vec{q} = -i\hbar\nabla\psi - \frac{e^*}{c}\vec{A}\psi$, then $\nabla.(\delta\psi^*\vec{q}) = \delta\psi^*\nabla.\vec{q} + \vec{q}.\nabla\delta\psi^*$ and

$$\delta_{\psi^*}G_{sh} = \int dV[\alpha\psi + \beta\psi|\psi|^2 + \frac{1}{2m^*}\{i\hbar\nabla.(-i\hbar\nabla\psi - \frac{e^*}{c}\vec{A}\psi) - \frac{e^*}{c}\vec{A}(-i\hbar\nabla\psi - \frac{e^*}{c}\vec{A}\psi)\}] \times$$

$$\times \; \delta\psi^* + \oint_S (-i\hbar\nabla\psi - \frac{e^*}{c}\vec{A}\psi).\, d\vec{s}\,\delta\psi^* = 0 \quad \text{(A.2}$$

where s encloses the volume V. Since $\delta\psi^*$ is arbitrary, the integral is zerc if the integrand vanishes. Hence, we obtain the first GL equation as

$$\alpha\psi + \beta\psi|\psi|^2 + \frac{1}{2m^*}(-i\hbar\nabla - \frac{e^*}{c}\vec{A})^2\psi = 0 \quad \text{GL-I} \quad \text{(A.3}$$

with its boundary condition

$$(i\hbar\nabla\psi + \frac{e^*}{c}\vec{A}\psi).\vec{n} = 0 \quad \text{(A.4}$$

Again we minimize G with respect to $\vec{A}$ so that

$$\delta_{\vec{A}} G_{sh} = 0 \quad \text{(A.5}$$

Applying similar procedures we obtain (for arbitrary $\delta\vec{A}$)

$$\frac{i\hbar e^*}{2m^*c}(\psi^*\nabla\psi - \psi\nabla\psi^*) + \frac{(e^*)^2}{m^*c^2}\vec{A}|\psi|^2 + \frac{1}{4\pi}\nabla\times\nabla\times\vec{A} = 0 \quad \text{(A.6}$$

Using the QM expression of the current density $\vec{j}$ and Maxwell's equations, we have

$$\vec{j}_s = \frac{-i\hbar\, e^*}{2m^*}[\psi^*\nabla\psi - \psi\nabla\psi^*] - \frac{(e^*)^2}{m^*c}|\psi|^2\,\vec{A} \quad - \text{GL-II} \tag{A.7}$$

APPENDIX B

Evaluation of u_k, v_k Using Green Function Method

The Green function we defined to obtain the spectrum of elementary excitations is given by (2.27). If we introduce the linear transformations

$$C^{+}_{k\tau} = v_k b^{+}_{k\tau} + u_k b_{-k\tau'}$$
$$C_{k\tau} = v_k b_{k\tau} + u_k b^{+}_{-k\tau'} \qquad (B.1)$$

then, for Fermi character of b_k

$$u_k^2 + v_k^2 = 1 \qquad (B.2)$$

Using (B.1) equation (2.27) can be given as

$$G_1 = -\frac{i}{\hbar}\,\theta(t)\langle v_k^2[b^{+}_{k\tau}, b_{k'\tau'}] + u_k^2[b_{-k\tau'}, b_{-k'\tau'}]\rangle \qquad (B.3)$$

Assume $\quad b^{+}_{k\tau}(t) = b^{+}_{k\tau}(0)\exp\left(-\frac{i}{\hbar}E(k)t\right)$

and $\quad b_{-k\tau'}(t) = b_{-k\tau'}(0)\exp\left(\frac{iE(k)}{\hbar}t\right) \qquad (B.4)$

Substituting these into (B.3) and taking its Fourier transformation we finally get

$$G_1 = \frac{v_k^2}{\hbar\omega - E(k)} + \frac{u_k^2}{\hbar\omega + E(k)} = \frac{\frac{1}{2}[1-n(k)/E(k)]}{\hbar\omega - E(k)} + \frac{\frac{1}{2}[1+n(k)/E(k)]}{\hbar\omega + E(k)}$$

Thus, one can write

$$u_k^2 = \frac{1}{2}\left[\frac{1+n(k)}{E(k)}\right] \quad \text{and} \quad v_k^2 = \frac{1}{2}\left[\frac{1-n(k)}{E(k)}\right] \qquad (B.5)$$

APPENDIX C

Diagonalization of Model-Hamiltonian by Canonical Transformations

We want to reduce the model-Hamiltonian (2.26) to the form

$$H_M = E_{so} + \sum_{k\tau\tau'} E(k)(b^{+}_{k\tau} b_{k\tau} + b^{+}_{k\tau'} b_{k\tau'}) \qquad (C.1)$$

where E_{so} is the ground state energy and $E(k)$ is the energy of quasi-particles. For this, substitute the transformations (B.1) into the Model-Hamiltonian (2.26) and diagonalize the Hamiltonian obtained after substituting by setting non-diagonal elements to zero. In other words, we choose u_k and v_k such that the coefficients of terms like $b_{k\tau'} b_{k\tau}$ & $b^{+}_{k\tau}\ b^{+}_{-k\tau'}$ will be zero. So we get

$$2\eta(k)u_k v_k - \Delta(u_k^2 - v_k^2) = 0 \qquad (C.2)$$

This relation and (B.2) yield the values of u_k and v_k the same as that obtained in Appendix B, that is,

$$u_k^2 = \tfrac{1}{2}\left[1+\frac{\eta(k)}{E(k)}\right] \ ; \quad v_k^2 = \tfrac{1}{2}\left[1-\frac{\eta(k)}{E(k)}\right] \qquad (C.3)$$

Again, using this result and replacing $b^{+}_{k\tau}\ b_{k\tau}$ by $n_{k\tau}$ and $b^{+}_{k\tau'} b_{k\tau'}$ by $n_{k\tau'}$, we write

$$H_M = \sum_k (\eta(k)-E(k)+ \Delta b_k^{*}) + \sum_{k\tau\tau'} E(k)(n_{k\tau} + n_{k\tau'})$$

or (C.4)

$$H_M = E_{so} + \sum_{k\tau\tau'} E(k)(n_{k\tau} + n_{k\tau'})$$

APPENDIX D1

Temperature Dependence of Δ

In the case $T \to 0$ or $\Delta(T) \to \Delta_0$ and taking $\eta(k) \ll \Delta$, we write (2.60) as

$$1 = V \int_{-\hbar\omega_D}^{\hbar\omega_D} \{\frac{1}{\sqrt{\eta^2(k)+\Delta^2(T)}} - \frac{2}{\Delta} \exp\left(-\sqrt{\eta^2(k)+\Delta^2(T)}\right)\} N(\eta) d\eta \qquad (D.1)$$

With the Binomial approximation

$$(\eta^2(k)+\Delta^2(T))^{\frac{1}{2}} = \Delta(1+\frac{\eta^2(k)}{\Delta^2})^{\frac{1}{2}} \cong \Delta(1+\frac{\eta^2(k)}{2\Delta^2}) = \Delta + \frac{\eta^2(k)}{2\Delta} \qquad (D.2)$$

the integral will be simplified as

$$\frac{1}{N(0)V} = \int_0^{\hbar\omega_D} \{\frac{1}{\sqrt{\eta^2(k)+\Delta^2(T)}} - \frac{2}{\Delta} \exp(\frac{-\Delta}{T} - \frac{\eta^2}{2\Delta T})\} \, d\eta \qquad (D.3)$$

where N(0), the number of states at the Fermi level, can be taken out of the integral sign. Now, Using the substitution $x = \eta/T$ for the last integral, we see the solution of (D.3) to be

$$\frac{\hbar\omega_D}{\Delta(T)} = \sin h(\frac{1}{N(0)V} + \sqrt{\frac{2\pi T}{\Delta}}\, e^{-\Delta/T}) = \tfrac{1}{2}[\exp(\frac{1}{N(0)V} + \sqrt{\frac{2\pi T}{\Delta}} e^{-\Delta/T} - \exp(\frac{-1}{N(0)V} - \sqrt{\frac{2\pi T}{\Delta}} e^{-\Delta/T} \qquad (D.4)$$

where the last term can be neglected.

Since $\quad e^x \cong 1 + x$

for small x, we see that

$$\frac{\hbar\omega_D}{\Delta(T)} = \tfrac{1}{2} \exp(\frac{1}{N(0)V})\exp(\sqrt{\frac{2\pi T}{\Delta}}\, e^{-\Delta/T}) = \tfrac{1}{2}\exp(\frac{1}{N(0)V})[1+\sqrt{\frac{2\pi T}{\Delta}}\, e^{-\Delta/T}] \qquad (D.5)$$

Since T is very small, to a good approximation Δ can be replaced by Δ_0 in the last term and we finally obtain

$$\Delta(T) = \Delta_0[1 - \sqrt{\frac{2\pi T}{\Delta}}\, e^{-\Delta_0/T}] \; , \; T \ll \Delta_0 \qquad (D.6)$$

This is an equation for energy gap as a function of temperature. At T = 0, $\Delta(T) = \Delta_0$ as expected.

APPENDIX D2

T Close to T_c

If $x = \eta/T$, then (2.60) becomes

$$\frac{1}{N(0)V} = \int_0^{\hbar\omega_D/T} \frac{1}{\sqrt{x^2+u^2}} \tanh \sqrt{\frac{x^2+u^2}{2}}\, dx \qquad \text{(D.7}$$

where $u^2 \equiv \Delta^2/T^2 \ll 1$. Since $\Delta(T) \to 0$ if $T \to T_c$, we can use the series expansion

$$\frac{1}{\sqrt{x^2+u^2}} \tanh \sqrt{\frac{x^2+u^2}{2}} = 4 \sum_{n=o}^{\infty} [\pi^2(2n+1)^2+(x^2+u^2)]^{-1}$$

and

$$\frac{1}{N(0)V} = 4 \sum_{n=o}^{\infty} \int_0^{\hbar\omega_D/T} \frac{dx}{[\pi^2(2n+1)^2+x^2]} \{1 - \frac{u^2}{\pi^2(2n+1)^2+x^2}\} \text{ since } u^2 \ll 1$$

or

$$\frac{1}{N(0)V} = \int_o^{\hbar\omega_D} \frac{1}{x} \tanh \frac{x}{2}\, dx - \frac{u^2 7\xi(3)}{8\pi^2} \qquad \text{(D.8)}$$

where $\xi(3)$ is the Riemann Zeta function ($\xi(3) \simeq 1.202$). The first term of (D.8) can be obtained by parts and we obtain

$$\frac{1}{N(0)V} = \ln(\frac{\hbar\omega_D}{T}) - \ln\frac{\pi}{2\gamma} - u^2\frac{7\xi(3)}{8\pi^2}$$

where γ is Euler's constant [12].

For T close to T_c,

$$\frac{\hbar\omega_D}{T} = \frac{\hbar\omega_D}{T-T_c+T_c} = \frac{\hbar\omega_D}{T_c}(1 + \frac{T_c-T}{T_c})$$

But we know that $\frac{1}{N(0)V} = \ln \frac{\hbar\omega_D}{T_c} - \ln\frac{\pi}{2\gamma}$ - definition of T_c: $T_c = 0.57\Delta_o$. For small x, $\ln(x+1) \simeq x$ and it follows that

$$\Delta(T) = \pi T_c[\frac{8}{7\xi(3)}(1-\frac{T}{T_c})]^{\frac{1}{2}} = 3.06\ T_c[1-\frac{T}{T_c}]^{\frac{1}{2}}\ . \qquad \text{(D.9)}$$

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