Chapter1

Fundamental Properties of Superconductors

1.1 Introduction

Superconductivity was first observed in mercury by the Dutch physicist Heike Kamerlingh Onnes of Leiden University in 1911[1]. When he cooled it to the temperature of liquid helium - 4 K – its resistance suddenly disappeared. He called this extraordinary phenomenon *superconductivity* , and the temperature at which it appears *the critical temperature* , T_c . Thus *perfect conductivity* is the first characteristic property of superconductivity. The second property to be discovered was *perfect diamagnetism* , found in 1933 by Meissner and Ochsenfeld[2]. They found not only that a magnetic field is excluded from a superconductor (see Fig.1-1), as might appear to be explained by perfect conductivity, but also that a field is expelled from an originally normal sample as it is cooled through T_c. We will review some basic observed electrodynamic phenomena and their early phenomenological descriptions.

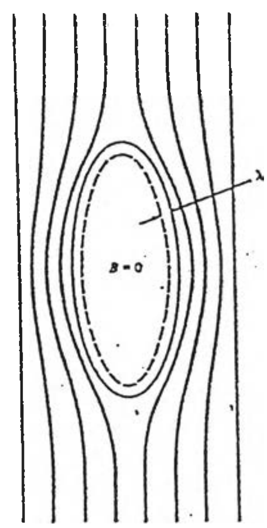

Figure 1-1: Schematic diagram of exclusion of magnetic flux from the interior of a massive superconductor. λ is the penetration depth, typically about 500 $\mathring{A}$. [3]

1.2 The Meissner effect

At any temperature T below T_c , the superconducting behavior can be quenched and normal conductivity be restored by the application of an external magnetic field. This field, H_c, is called the *critical* or *threshold magnetic field*, and, as shown in Figure 1-2, that at temperature near T = 0 it varies approximately as

$$H_c(T) \approx H_C(o)\left[1-\left(\frac{T}{T_c}\right)^2\right], \tag{1.1}$$

where $H_c(0) = H_c$ at T=0 K.

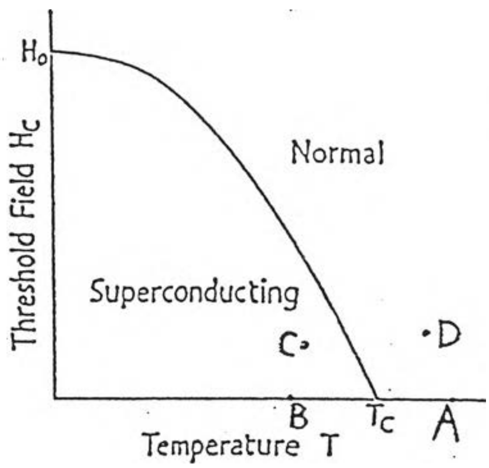

Figure1-2: Phase diagram of the critical magnetic field v.s. temperature, the separation between the normal and the superconducting states is represented by the curve.[4]

If a perfect conductor were placed in an external magnetic field, it was found that no magnetic flux could penetrate the specimen. Induced surface currents would maintain the internal flux, and would persist indefinitely. By the same token, if a *normal* conductor were in an external field before it became perfectly conducting, the internal flux would be locked in by induced persistent currents even if the external field were removed. Because of this, the transition of a merely perfectly conducting specimen from the normal to the superconducting state would not be reversible, and the final state of the specimen would depend on the path of the transition.

As an example, Figures 1-3 and 1-4 show the flux configuration for a perfectly conducting sphere taken from point *A* in Figure 1-2 to point *C* by the different paths *ABC* and *ADC*, respectively. The final field distribution at *C*, as well as that at *B* depends on whether one proceeds via B or via D, and the irreversibility of the transition is evident. Careful measurements of the field distribution around a spherical specimen by Meissner and Ochsenfeld [2] , however, indicated that regardless of the path of transition the situation at point C is always that shown in Figure 1-3c: the magnetic flux is expelled from the interior of the superconductor and the magnetic induction B vanishes. This is called the *Meissner effect*, and it shows that the superconducting transition is reversible.

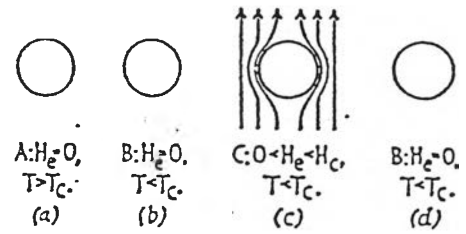

FIG. 1-3

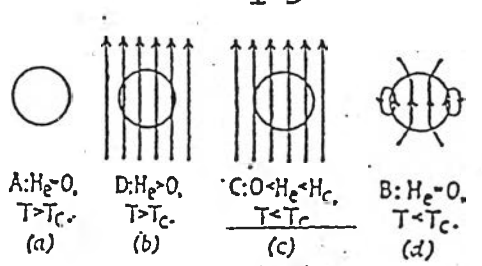

FIG. 1-4

Figures 1-3,1-4: The reversibility of the superconducting transition.[4]

1.3 Persistent currents and flux quantization

A different case of magnetic behavior is connected to the flux trapping in a superconductor ring. Suppose a normal metallic ring is placed in a magnetic field perpendicular on its plane. When the temperature is lowered, the metal becomes superconducting and the flux is expelled. If the external field is removed, no flux passes through the superconducting metal and the trapped flux must remain constant. This flux is maintained by the circulating supercurrent in the ring itself. The flux trapped in sufficiently thick rings is quantized in units of $\phi_o = \hbar c / 2e$.

The quantization of flux was verified experimentally in 1961 by Doll and Näbauer [8] and by Deaver and Fairbank [9]. These experiments have shown that the quantum of flux is given by

$$\phi_o = \hbar c / 2e \sim 2 \times 10^{-7} \quad \text{gauss - cm}^2$$

This quantity shows that q=2e, that is, the superconducting charge carriers are pairs of electrons.

1.4 Specific heat

The superconducting materials also have distinctive thermal properties. In the superconducting state, the specific heat C_s initially exceeds the specific heat of the normal state C_n and as $T \rightarrow 0$

$$C_s(T) \text{ varies as } \exp(-\frac{\Delta}{T}), \tag{1.2}$$

here Δ is an energy gap separating an excited state from the ground state.

This T dependence indicates the existence of a gap in the energy spectrum separating the excited states from the ground states by the energy Δ.

1.5 Isotope effect

In 1950, Frohlich [5] observed that the critical temperature of a superconductor varies with isotopic mass. In mercury, T_c varies from 4.185 K to 4.146 K as the average atomic mass M varies from 199.5 to 203..4 atomic mass units. The experimental results within each series of isotopes are fitted by a relation of the form

$$M^{\alpha}T_c = \text{constant}. \tag{1.3}$$

Observed values of α are given in Table1-1.

Substance	α	Substance	α
Zn	0.45 ± 0.05	Ru	0.00 ± 0.05
Cd	0.32 ± 0.07	Os	0.15 ± 0.05
Sn	0.47 ± 0.02	Mo	0.33
Hg	0.50 ± 0.03	Nb_3Sn	0.08 ± 0.02
Pb	0.49 ± 0.02	Zr	0.00 ± 0.05

Table1-1: Experimental values of α in $M^{\alpha}T_c$ = constant, where M is the isotopic mass.[6]

The isotope effect demonstrates the importance of the ionic lattice in superconductivtity.

1.6 The London equations for a superconductor

The two basic electrodynamic properties, which give superconductivity unique interest, were well described in 1935 by F. and H. London [7] with two equations governing the microscopic electric and magnetic fields:

$$\bar{E} = \frac{4\pi\lambda_L^2}{c^2}\frac{d\bar{j}}{dt} , \quad (1.4)$$

where $\bar{j} = ne\bar{v}$ is current density, n = number density of electrons, and

$$\frac{4\pi\lambda_L^2}{c^2}\nabla\times\bar{j} + \bar{H} = \mathbf{0} , \quad (1.5)$$

where

$$\lambda_L^2 = \frac{mc^2}{4\pi ne^2} . \quad (1.6)$$

The parameter λ_L has the dimension of length, and for an electron density corresponding to one electron per atom it has a value of the order of 10^{-6} cm.

Replacing the field by a vector potential $\nabla\times\bar{A} = \bar{H}$ and choosing a gauge such that $\nabla\bullet\bar{A} = 0$, Eq. (1.5) reduces to

$$\frac{4\pi\lambda_L^2}{c^2}\bar{j} + \bar{A} = \mathbf{0} . \quad (1.7)$$

The application of Maxwell's equations now leads to

$$\nabla^2\bar{H} = \bar{H}/\lambda_L^2 . \quad (1.8)$$

A solution of this equation for any geometry shows that H decays exponentially upon penetrating into a superconducting specimen. Eq. (1.8) has a solution

$$H(x) = H(0)\exp(-x/\lambda_L) , \quad (1.9)$$

which shows that for $x \gg \lambda_L$, $H(x) \approx 0$, in accordance with the Meissner effect.

The London equations (1.4) and (1.5) do not, in fact, yield the complete exclusion of a magnetic field from the interior of a superconductor. Instead, they predict the penetration of a field such that it decays to 1/e of its surface value in a distance λ_L, which is called the *London penetration length*.

1.7 Microscopic Theory of Superconductivity

The theory that can explain many properties of a superconductor was modeled successfully in 1957 by the efforts of John Bardeen, Leon Cooper, and Robert Schrieffer [10] in what is commonly called *the BCS theory*. A key conceptual element in this theory is the pairing of electrons close to the Fermi level into Cooper pairs through interaction with the crystal lattice. This pairing results from a slight attraction between the electrons is related to lattice vibrations; the coupling to the lattice is called a *phonon interaction*. Pairs of electrons can behave very differently from single electrons which are fermions and must obey the *Pauli exclusion principle*. The pairs of electrons act more like bosons which can condense into the same energy level. The electron pairs have a slightly lower energy and leave an energy gap above them on the order of 0.001 eV which inhibits the kind of collision interactions which lead to ordinary resistivity. For temperatures such that the thermal energy is less than the band gap, the material exhibits zero resistivity.

1.7.1 The electron-phonon interaction

In 1950, Fröhlich [5] pointed out that an electron moving through a crystal lattice has a self energy by being accompanied with virtual phonons. This contributes to the electron an amount of self-energy which, as was pointed out by Fröhlich and by Bardeen [11] is proportional to the square of the average phonon energy. It was only seven years later that Bardeen, Cooper, and Schrieffer succeeded in showing that the basic interaction responsible for superconductivity appears to be an interchange of virtual phonons between a pair of electrons. A second electron some distance away is affected when it is reached by the propagating fluctuation in the lattice charge distribution.

In Figure 1-5, an electron of wave vector $\vec{k}$ emits a virtual phonon $\vec{q}$ which is absorbed by an electron $\vec{k}'$. This scatters $\vec{k}$ into $\vec{k}-\vec{q}$ and $\vec{k}'$ into $\vec{k}'+\vec{q}$. The nature of the resulting electron – electron interaction depends on the relative magnitudes of the electronic energy change and the phonon energy $\hbar\omega_q$. If this latter exceeds the former, the interaction is attractive-the charge fluctuation of the lattice is then such as to surround one of the electrons by a positive screening charge greater than the electronic one, so that the second electron is attracted by a net positive charge.

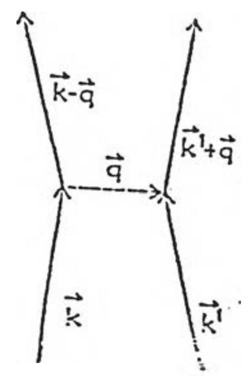

Figure 1-5: An electron of wave vector $\vec{k}$ emits a virtual phonon $\vec{q}$ which is absorbed by an electron $\vec{k}'$. [4]

The fundamental postulate of the BCS theory is that superconductivity occurs when such an attractive interaction between two electrons by means of phonon exchange dominates the usual repulsive screened Coulomb interaction.

1.7.2 The Cooper pairs

In 1956, Cooper [12] developed an important concept that if there is a net attraction, however weak, between a pair of electrons just above the Fermi surface, these electrons can form a bound state. The electrons for which this can occur as a result of the phonon interaction lie in a thin shell of width $\approx \hbar\omega_D$, where $\hbar\omega_D$ is of order of the average phonon energy of the metal. The pair of electrons have been chosen in such a way that from any set of values $(\vec{k}_1, \vec{k}_2)$ transitions into all other pairs are $(\vec{k}_1', \vec{k}_2')$ possible. As momenta are conserved, this means that

$$k_1 + k_2 \quad = \quad k_1' + k_2' \quad = \quad K \qquad (1.10)$$

That is , that all bound pairs have the same total momentum $\bar{K}$.[13]

The possible values of $\bar{k}_1$ and $\bar{k}_2$ which satisfy Eq.(1.10) lie in a narrow shell straddling the Fermi surface k_F, one can construct the diagram shown in Figure 1-6, drawing concentric circles of radii k_F-δ and k_F+δ from two points separated by K. All possible values of k_1 and k_2 satisfying Eq.(1.10) are restricted to the two shaded regions. This shows that the volume of phase space available for Cooper pairs has a very sharp maximum for K = 0. Thus the largest number of possible transitions yield the most appreciable lowering of energy is obtained by pairing all possible states such that their total momentum vanishes. It is also possible to show that exchange terms tend to reduce the interaction energy for pairs of parallel spin, to restrict the pairs to those of opposite spin. One can, therefore, summarize the basic hypothesis of the BCS theory as follows: *At 0 ^oK the superconducting ground state is a highly correlated one in which in momentum space the normal electron states in a thin shell near the Fermi surface are to the fullest extent possible occupied by pairs of opposite spin and momentum.*

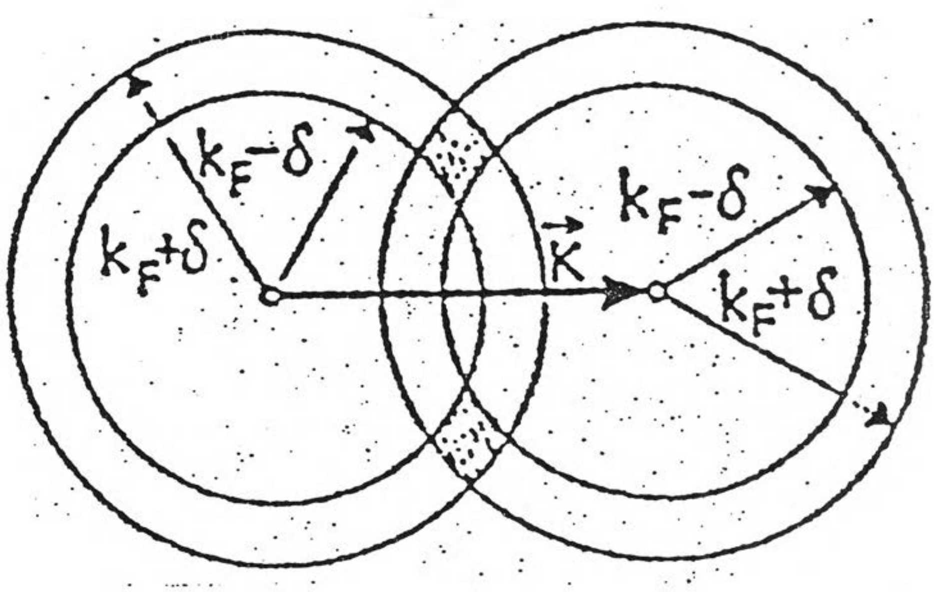

Figure1-6: Concentric circles of radii k_F-δ and k_F+δ from two points separated by K [4]

1.7.3 The ground state energy

BCS proceeded to calculate the superconducting ground state energy as being due uniquely to the correlation between Cooper pairs of electrons of opposite spin and momentum by phonon and screened Coulomb interactions.

The interaction leading to the transition of a pair of electrons from the state $(k\uparrow,-k\downarrow)$ to $(k'\uparrow,-k'\downarrow)$ is characterized by a matrix element,

$$-V_{kk'} \quad = \quad 2\left\langle \vec{k}'\uparrow,-\vec{k}'\right|H_{\text{int}}\left|\vec{k}\uparrow,-\vec{k}\downarrow\right\rangle \ , \qquad (1.11)$$

where H_{int} is the truncated Hamiltonian from which all terms common to the normal and superconducting phases have been removed. $V_{kk'}$ is the difference between one term describing the interaction between the two electrons by means of a phonon, and a second one giving their screened Coulomb interaction. The basic similarity of the superconducting characteristics of widely different metals implies that the responsible interaction cannot crucially depend on details characteristic of individual substances. BCS therefore made the further simplifying assumption that $V_{kk'}$ is isotropic and constant for all electrons in a narrow shell, straddling the Fermi surface, of thickness less than the average energy of the lattice, and that $V_{kk'}$ vanishes elsewhere. Measuring electron energy from the Fermi surface, and calling ε_k the energy of an electron in state k , one can state this formally by the equations:

$$\left.\begin{array}{llll} & V_{kk'} = V & & \text{for} \left|\varepsilon_k\right|,\left|\varepsilon_{k'}\right| \leq \hbar\omega_q \\ \text{and} & V_{kk'} = 0 & & \text{elsewhere.} \end{array}\right\} . \qquad (1.12)$$

The basic BCS criterion for superconductivtity is equivalent to the condition $V<0$.

This simplification of the interaction parameter V necessarily leads to what can be called a law of corresponding states for all superconductors, that is, virtually identical predictions for the magnitudes of all characteristic quantities in terms of reduced co-ordinates. Any empirical deviation from such complete similarity is, therefore, no invalidation of the basic premise of the BCS theory, but merely an indication of the oversimplification inherent in Eq.(1.12).

Let h_k be the probability that states k and –k are occupied by a pair of electrons, and (1-h_k) the corresponding probability that the states are empty. $W(0)$, the ground state energy of the superconducting state at 0°K as compared to the energy of the normal metal, is then given by

$$W(0) = \sum_{k} 2\varepsilon_k h_k - \sum_{kk'} V_{kk'} \{h_k(1-h_{k'})h_{k'}(1-h_k)\}^{1/2}. \tag{1.13}$$

The summation is overall those k-values for which $V_{kk'} \neq 0$, so that using Eq. (1.12) one can simplify W(0) to

$$W(0) = \sum_{k} 2\varepsilon_k h_k - V\sum_{kk'} \{h_k(1-h_{k'})h_{k'}(1-h_k)\}^{1/2}. \tag{1.14}$$

The first term gives the difference of kinetic energy between the superconducting and normal phases at 0°K.The factors 2 arises because for every electron in state k of energy ε_k there is with an isotropic Fermi surface another electron of the same energy in –k. This first term can be either positive or negative, and gives the correlation energy for all possible transitions from a pair state (k , -k) to another (k',-k'). For such a transition to be possible, k must initially be occupied and k' empty. The simultaneous probability of this is given by $h_k(1-h_{k'})$. The final state must have k empty and k' occupied, and this has probability $h_{k'}(1-h_k)$. The square root of the product of these probabilities multiplied by the matrix element for the transition and summed over all possible values of k and k' gives the total correlation energy.

W(0) must be negative for the superconducting phase to exist, and to see whether this is possible Eq.(1.14) can be minimized with respect to $h_{k'}$. this leads to

$$\frac{[h_k(1-h_k)]^{1/2}}{1-2h_k} = V\frac{\sum_{k'}[h_{k'}(1-h_{k'})]^{1/2}}{2\varepsilon_k}. \tag{1.15}$$

By defining

$$\Delta(0) = V\sum_{k'}[h_{k'}(1-h_{k'})]^{1/2}, \tag{1.16}$$

Equation (1.15) simplifies to

$$h_k = \frac{1}{2}\left(1-\frac{\varepsilon_k}{E_k}\right), \tag{1.17}$$

where

$$E_k \equiv \left[\varepsilon_k^2 + \Delta^2(0)\right]^{1/2}. \tag{1.18}$$

Substituting Eq.(1.17) back into Eq.(1.16) one obtains a non-linear relation for $\Delta(0)$:

$$\Delta(0) = \frac{V}{2}\sum_k \frac{\Delta(0)}{\left[\varepsilon_k^2 + \Delta^2(0)\right]^{1/2}} . \tag{1.19}$$

This can be treated most readily by changing the summation to an integration and transforming the variable of integration from k to ε.

Assuming symmetry of states on either side of the Fermi surface (ε=0), and introducing the constant density of single electron states of one spin in the normal state N(0) at ε = 0: Eq.(1.19) becomes

$$\frac{1}{N(0)V} = \int_0^{\hbar\omega_D} \frac{d\varepsilon}{\left[\varepsilon^2 + \Delta^2(0)\right]^{1/2}} . \tag{1.20}$$

The limit of integration is the phonon energy above which, according to Eq. (1.12), V = 0. The solution of Eq.(1.20) is

$$\Delta(0) = \hbar\omega_D / \sinh[1/N(0)V] . \tag{1.21}$$

Putting this back into Eq.(1.18) and Eq.(1.16) and finally into Eq.(1.14), one finds that the ground state energy of the superconducting state is given by

$$W(0) = -\frac{2N(0)(\hbar\omega_D)^2}{\exp[2/N(0)V]-1} . \tag{1.22}$$

The numerator of this quantity follows from dimensional reasoning from any theory which postulates an interaction between electrons and phonons and allows this interaction to be cut off at some averages phonon energy $\hbar\omega_D \approx k_B\Theta$ where Θ is Debye cutoff-temperature beyond which the interaction becomes repulsive. A term like this had been contained in the earlier attempts of Fröhlich and of Bardeen, and, as mentioned before, is much too large. The success of the BCS theory lies in the appearance of the exponential denominator which reduces W(0) by many orders of magnitude. Although a precise calculation of the average interaction parameter V for a specific metal continues to be among the most important questions still to be solved, various estimates [12-14] indicate that the values of N(0)V $\approx$ 0.3, derived form a knowledge of H_o, are reasonable. Thus the denominator has a value of about e^7.

1.7.4 The energy gap at 0 K

From Eq.(1.14) one can see that the contribution of a single pair state $(\vec{k},-\vec{k}')$ to this total condensation energy is

$$W_k \quad = \quad 2\varepsilon_k h_k - 2V\sum_{k'}\{(1-h_{k'})h_{k'}\}^{1/2} . \qquad (1.23)$$

The first term represents the kinetic energy of both electrons in the pair state $\vec{k}$, and the second term is the total interaction energy due to ali possible transitions into or out of the state.

At 0 K the lowest excited state of the superconductor must correspond to breaking up a single pair by transferring an electron from a state $\vec{k}$ to another, leaving an unpaired electron in $-\vec{k}$. The condensation energy is then reduced by W_k. The first term of this can be made arbitrarily small, and is analogous to the excitation energy in a normal metal, for which there is a quasi-continuous energy spectrum above the ground state. The second term of W_k, however, is finite for all values of $\vec{k}$, which is why in the superconducting phase the lowest excited state is separated from the ground state by an energy gap.

Comparing Eq.(1.23) with Eq.(1.16) one sees that this energy gap has the value of $2\varepsilon(0)$, which according to Eq.(1.21) equals

$$2\varepsilon(0) \quad = \quad 2\hbar\omega_D / \sinh[1/N(0)V] . \qquad (1.24)$$

As $1/N(0)V \approx 3-4$, this can be approximated by

$$2\varepsilon(0) \quad = \quad 4\hbar\omega_D \exp[1/N(0)V] . \qquad (1.25)$$

1.7.5 The superconductor at finite temperatures

As the temperatures of the superconductor is raised above 0 K, an increasing number of electrons find themselves thermally excited into single quasi-particle states.

These excitations behave like those of a normal metal; they are readily scattered and can gain or lose further energy in arbitrarily small quantities. In what follows they are simply called normal electrons. At the same time there continues to exist the configuration of all electrons still correlated into Cooper pairs, and displaying superconducting properties, being very difficult to scatter or to excite. One is thus led again to a two-fluid point of view.

As at 0 K, one can write down an analytic expression for the ground state energy $W(T)$ containing a kinetic energy term and an interaction term. In both, the presence of the normal electrons must be accounted for, which is done by introducing a suitable probability factor f_k.

Letting f_k = a probability of occupation of $\vec{k}$ or of $-\vec{k}$ by a single normal electron, then ,

$1-2f_k$ = probability that neither $\vec{k}$ nor $-\vec{k}$ is occupied by a normal electron.

This leads to a kinetic energy term

$$[W(T)]_{K.E.} = 2\sum_{k}|\varepsilon_k|[f_k + (1-2f_k)h_k] \quad , \tag{1.26}$$

where the summation is over the same range as at 0 K, and h_k retains the same definition, though no longer the same value. The second term in the brackets clearly gives the probability that the pair state $(\vec{k},-\vec{k})$ not be occupied by normal electrons but by a correlated pair. The correlation energy at a finite temperature is

$$[W(T)]_{corr} = -V\sum_{kk'}\{h_k(1-h_{k'})h_{k'}(1-h_k)\}^{1/2} \times (1-2f_k)(1-2f_{k'}) . \tag{1.27}$$

The last two terms ensure that the correlated pair states not be occupied by normal electrons. It is obvious that the presence of these terms decreases the pairing energy.

The thermal properties of the superconductors can now be found quite readily by writing down the free energy of the system and requiring this to be at a minimum. The free energy is

$$G = W(T) - TS = [W(T)]_{K.E.} + [W(T)]_{corr} - TS \,, \qquad (1.28)$$

where T is the temperature and S the entropy. This last term is due entirely to the normal electrons; the electrons which are still paired are in a state of highest possible order and do not contribute at all. Thus the entropy is given by the usual expression for particles obeying Fermi-Dirac statistics:

$$TS = -2k_B T \sum_k \{f_k \ln f_k + (1 - f_k)\ln(1 - f_k)\} \,. \qquad (1.29)$$

Substituting Eq.(1.26), Eq.(1.27) and Eq.(1.29) into Eq.(1.28), and minimizing this free energy with respect to h_k, one now obtains

$$\frac{[h_k(1 - h_k)]^{1/2}}{1 - 2h_k} = V \frac{\sum_{k'} [h_{k'}(1 - h_{k'})]^{1/2}(1 - 2f_{k'})}{2\varepsilon_k} \,. \qquad (1.30)$$

This time one defines

$$\Delta(T) \equiv V \sum_{k'} [h_{k'}(1 - h_{k'})]^{1/2}(1 - 2f_{k'}) \,, \qquad (1.31)$$

and one obtains

$$h_k = \frac{1}{2}\left[1 - \frac{\varepsilon_k}{E_k}\right] \,, \qquad (1.32)$$

where E_k is now defined as $E_k \equiv \left[\varepsilon_k^2 + \Delta^2(T)\right]^{1/2}$.

One see that, as at 0 K, $2\varepsilon\,(T)$ represents the contribution of a single pair state to the total correlation energy, and that to break up one such pair at any finite temperature removes from the superconducting energy at least this amount. In other words, the superconducting state continues to contain an energy gap $2\varepsilon\,(T)$ separating the lowest energy configuration at any given temperature from that with one less correlated pair.

To evaluate the magnitude of the energy gap one must first find an expression for f_k , which one obtains by minimizing the free energy with respect to f_k. This yields

$$f_k = [\exp(E_k / k_B T) + 1]^{-1} \,. \qquad (1.33)$$

Eq.(1.33), Eq.(1.25), and Eq.(1.31) yield for $\varepsilon\,(T)$ a non-linear relation which, by changing as before from a summation over $\vec{k}$ to an integration over ε, becomes

$$\frac{1}{N(0)V} = \int_0^{\hbar\omega_D} \frac{d\varepsilon}{\left[\varepsilon^2+\Delta^2(T)\right]^{1/2}} \tanh\left\{\frac{\left[\varepsilon^2+\Delta^2(T)\right]^{1/2}}{2k_B T}\right\}. \tag{1.34}$$

The critical temperature T_c is reached when all pair states are broken up so that

$$\frac{1}{N(0)V} = \int_0^{\hbar\omega_D} \frac{d\varepsilon}{\varepsilon} \tanh\left\{\frac{\varepsilon}{2k_B T_c}\right\}, \tag{1.35}$$

because $\Delta(T_c)=0$, hence.

As long as $k_B T_c << \hbar\omega_D$ the solution of this equation can be written as

$$k_B T_c = 1.14\hbar\omega_D \exp\left[-1/N(0)V\right]. \tag{1.36}$$