CHAPTER I

BULK SUPERCONDUCTIVITY

This chapter reviews the historical background and some of the essential concepts about superconductivity which we shall encounter.

1.1 Early Experiments and Macroscopic Theories

As is well known, many metals and alloys become superconducting below a certain temperature T_c - the temperature being different for different materials. In this state the d.c. electrical resistivity is zero. This was thought to be simply a case of infinite conductivity for more than twenty years after its discovery by Kammerlingh Onnes in 1911.

1.1.1 Meissner Effect

It was not until 1933 that Meissner and Oschenfeld (9) showed that a superconductor is a perfect diamagnet. Thus the magnetic field $\vec{B}$ penetrates only to a depth $\lambda \simeq 500$ Å and is excluded from the main body of the material. Even when cooled into the superconducting state in the presence of a magnetic field, the flux is expelled from the interior. If one (incorrectly) argues that the vanishing zero-frequency electrical resistance implies that there can be no electric field (of any frequency) in a superconductor, Maxwell's equation

$$\vec{\nabla} \times \vec{E} = -\frac{1}{c}\frac{\partial \vec{B}}{\partial t} \qquad (1.1)$$

shows that the magnetic field present in the normal metal will be

"frozen in" when the metal becomes superconducting. This is contrary to the Meissner effect, which states that the field is expelled in the superconducting phase.

1.1.2 Thermodynamic Properties

In zero magnetic field, there is a second-order phase transition at T_c. The jump in specific heat is generally about three times the electronic specific heat γT_c in the normal state just above the transition, where γ is a constant characteristic of the material. In well-annealed pure specimens the width of the transition can be as small as 10^{-4} K although this is not believed to be the intrinsic width of the transition. As $T / T_c \rightarrow 0$, the electronic specific heat generally falls as a $e^{-b/T}$, presumably due to the energy gap for creating elementary excitations. A plot of the specific heat of a superconductor is shown in Fig. 1. For $T \geqslant T_c / 2$, the curve is reasonably well fitted by αT^3, where α is a constant.

In the presence of a manetic field the N-S transition for a bulk specimen is first order, i.e., a latent heat is involved.

1.1.3 Gorter-Casimir Model

In 1934, Gorter and Casimir (10) advanced a phenomenological model to account for the thermal properties of a superconductor. Their general assumption is that a fraction of the electrons condensed into the ground state and take part in superfluid flow, while the rest behave normally and contribute to the specific heat.

If x represents the fraction of electrons which are in the "normal" fluid and (1 - x) the fraction condensed into the superfluid, Gorter and Casimir assumed that the free energy for the electrons is of

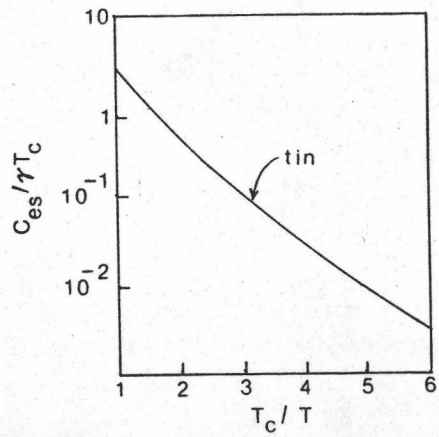

Fig. 1.1. The electronic specific heat of Sn.

the form

$$F(x,T) = X^{\frac{1}{2}} f_n(T) + (1-x) f_s(T) \tag{1.2}$$

where f_n and f_s were chosen to be

$$f_n(T) = -\tfrac{1}{2}\gamma T^2 \tag{1.3}$$

where γ is the usual coefficient defining the electronic specific heat, and

$$f_s(T) = -\beta = \text{const.} \tag{1.4}$$

In the normal metal the electronic free energy is just Eq. (1.3) so that the free energy of the S- and N-phases agree when $(1 - x) \rightarrow 0$, i.e., at T_c. The energy $-\beta$ represents the condensation energy associated with the superfluid. By minimizing F(x,T) with respect to x for fixed T, one finds that the fraction x of "normal" electrons at a temperature T is given by

$$x = \left(\frac{T}{T_c}\right)^4 \tag{1.5}$$

From the thermodynamic relation

$$\frac{H_c^2(T)}{8\pi} = F_n(T) - F_s(T) \tag{1.6}$$

one finds from Eqs. (1.2) - (1.5) the expression

$$H_c(T) = H_o\left[1 - (T/T_c)^2\right] \tag{1.7}$$

For the temperature-dependent critical field. Thus, H_c is predicted to be a parabolic function of (T/T_c), in rough agreement with experiment, In addition, the free energy gives the electronic specific heat in the S-phase as

$$C_{es}(T) = 3\gamma T_c (T/T_c)^3 \tag{1.8}$$

so that the relative jump in the electronic specific heat at T_c is 3, again in general agreement with experiment.

1.1.4 The London Theory

In the year following Gorter and Casimir work (10), F. and H. London (11) developed a phenomenological theory of the electromagnetic behavior of superconductors. Their scheme is based on a two-fluid type concept with superfluid and normal fluid densities n_s and n_n plus the associated velocities v_s and v_n. Owing to local charge neutrality, the densities are restricted by $n_s + n_n = n$, where n is the average number of electrons per unit volume. The super and normal fluid current densities are postulated to satisfy

$$\frac{d\vec{J}_s}{dt} = n_s e^2 \vec{E} \quad (\vec{J}_s = -en_s \vec{v}_s) \tag{1.9a}$$

$$\vec{J}_n = \sigma_n \vec{E} \quad (\vec{J}_n = -en_n \vec{v}_n) \tag{1.9b}$$

The first of these equations is nothing more than $\vec{F} = m\vec{a}$ applied to a set of free particles of charge -e and density n_s. Apparently the superfluid is affected by the usual scattering mechanisms which produce the finite conductivity σ_n associated with normal fluid.

The second (and most famous) equation of the London theory is

$$\vec{\nabla} \times \vec{J}_s = -\frac{n_s e^2 \vec{B}}{mc} \tag{1.10}$$

This latter equation leads to the Meissner effect. One can see this by considering the curl of one of Maxwell's equations:

$$\vec{\nabla} \times \vec{\nabla} \times \vec{B} = \frac{4\pi}{c} \vec{\nabla} \times \vec{J}_s \tag{1.11}$$

where we have neglected the displacement current and the normal fluid current J_n since we are interested in the static Meissner effect. On combining Eqs. (1.10) and (1.11) one has

$$\vec{\nabla}^2\vec{B} = (4\pi n_s e^2 / mc^2)\,\vec{B} = (1/\lambda_L^2)\,\vec{B} \qquad (1.12)$$

where the London's penetration depth λ_L is defined by

$$\lambda_L = (mc^2 / 4\pi n_s e^2)^{\frac{1}{2}} \qquad (1.13)$$

If Eq.(1.12) is applied to a plane boundary located at x = 0, the magnetic field (parallel to the surface) decreases into the superconductor according to

$$B(x) = B(0)\, e^{-x/\lambda_L} \qquad (1.14)$$

Therefore the magnetic field vanishes in the bulk of the material and one obtains perfect diamagnetism as required.

To understand the relation between London's two equations (1.9), (1.10) we notice that the curl of Eq. (1.9a) is the time derivative of Eq. (1.10). Therefore, outside of a constant of integration, the Meissner effect follows from the "perfect" conductivity of the superfluid, i.e. Eq. (1.9a). By postulating Eq. (1.10), the Londons added the allimportant restriction that $\vec{B} = 0$ inside the superconductor regardless of its history, which is the essence of the Meissner effect.

If one combines the result Eq. (1.5) of the Gorter-Casimir model

$$(1 - x) = 1 = (T/T_c)^4 = n_s(T) / n \qquad (1.15)$$

for the temperature dependence of the superfluid density, with London's

expression Eq. (1.13) for the penetration depth, one finds

$$\lambda(T) = \lambda(0)/\left[1-(T/T_c)^4\right]^{\frac{1}{2}} \qquad (1.16)$$

Thus, for $T = T_c$, $\lambda = \infty$, so that no flux is excluded at T_c. As T drops infinitesimally below T_c, λ decreases rapidly, thereby establishing the Meissner effect in bulk specimens for all $T < T_c$. This temperature dependence is surprisingly close to that observed experimentally although the results of the microscopic theory are in some what better agreement with experiment than is Eq. (1.16).

1.1.5 Pippard's Nonlocal Generalization of the London Theory

The basic equations (1.9) and (1.10) of the London theory are "local" in the sense that they relate the current densities and the electromagnetic potentials at the same point in space. On the basis of numerous experimental results, Pippard (12) concluded that these local relations must be replaced by nonlocal relations giving the currents at a given point in space as a space average of the field strengths taken over a region of extent $\xi_o \sim 10^{-4}$ cm about the point in question. One of the most compelling arguments for this generalization is that the penetration depth λ increases appreciably if a sufficient amount of impurity is introduced into the material. This effect sets in when the mean free path ℓ of electrons in the normal state falls below a distance ξ_o, known as Pippard's "coherence" length. As we shall see, ξ_o is a measure of the pair bound state from which the superfluid wave function is constructed. In the microscopic theory it is related to the energy gap 2Δ by $\xi_o = hv_f/\pi\Delta$, where v_F is the Fermi velocity. On the other hand, in the London theory λ is not expected to be appreciably affected by impurities, particularly near T = 0, where all of the

electrons are condensed. In choosing a form for the nonlocal relations, Pippard was guided by Chambers' nonlocal expression (13) relating the current density and electric field strength in the normal metal

$$\vec{J}(r) = \frac{3\sigma}{4\pi\ell}\int \frac{\vec{R}\,[\vec{R}\cdot\vec{E}(r')]}{R^4}\, e^{-\vec{R}/\ell} d^3\vec{r}' \;;\; \vec{R} = \vec{r} - \vec{r}' \qquad (1.17)$$

where σ is the long wavelength electrical conductivity. Chambers' expression is a solution of Boltzmann's transport equation if the scattering mechanism is characterized by a mean free path ℓ. For field varying slowly over a mean free path ℓ, (1.17) reduces to Ohm's law $J = \sigma E$. With Chambers' expression in mind, Pippard assumed that London 's equation

$$\vec{J}_s(r) = -\frac{1}{c\Lambda(T)}\vec{A}(r) \;,\; \frac{1}{\Lambda(T)} = \frac{n_s(T)e^2}{m} \qquad (1.18)$$

should be replaced by

$$\vec{J}_s(r) = -\frac{3}{4\pi\xi_o\Lambda c}\int \frac{\vec{R}\,[\vec{R}\cdot\vec{A}(r)]}{R^4}\, e^{-\vec{R}/\xi} d^3\vec{r}' \qquad (1.19)$$

The effective coherence length ξ is given by

$$\frac{1}{\xi} = \frac{1}{\xi_o} + \frac{1}{\alpha\ell} \qquad (1.20)$$

where α is an empirical constant of order unity and ξ_o is a length characteristic of the material. For a pure material, Pippard's equation reduces to London's equation if A (r) varies slowly over a coherence length. For an impure material, Pippard's equation leads to an extra factor $\xi/\xi_o < 1$ multiplying $(1/c\Lambda)$ in London's equation in this long wavelength limit, thereby increasing the effective penetration depth. In most cases distances of order $\lambda \ll \xi$ are of importance in penetration phenomena so that the full reduction ξ/ξ_o is not effective. In highly impure specimens λ is of order or greater

than ξ and one has $\lambda \sim (\xi_0/\ell)^{1/2}$.

1.1.6 Isotope Effect

The isotope effect shows that lattice vibrations play an essential role in bringing about superconductivity. Experiments were undertaken independently by Reynolds, Serin et al.(14) at Rutgers and by Maxwell (15) at the National Bureau of Standards in 1950. In particular, one finds that the transition temperature T_c

$$T_c \propto \frac{1}{M^{\alpha}} \quad (\alpha \sim \tfrac{1}{2}) \tag{1.21}$$

where M is the isotope mass of the material. The mass would not be an important parameter unless the motion of the ions is involved, which suggested that superconductivity must arise from some sort of the lattice vibrations.

That the electron-phonon interactions lead to an effective attractive interaction between electrons by exchange of virtual phonons was shown by Fröhlich (16) by use of field-theoretical techniques. His analysis was extended by Pines and Bardeen to include Coulomb interactions.

1.2 Microscopic Theories

The next major step was made by Cooper (17), who showed that if there is an effective attractive interaction, a pair of quasiparticles above the Fermi sea will form a bound state no matter how weak the interaction. If the binding energy is of the order of $k_B T_c$, the size of the pair wavefunction is of the order of 10^{-5} to 10^{-4} cm. This calculation showed definitely that, in the presence of attractive interactions, the

Fermi sea which describes the ground state of the normal metal is unstable against the formation of such bound pairs.

However one could not use this calculation immediately to construct a theory of superconductivity. If all the electrons within $\sim k_B T_c$ of the Fermi surface form such bound pairs, the spacing between the pairs would be only $\sim 10^{-6}$ cm, a distance much smaller than the size of a pair. Because of the considerable overlap between the pairs, because of the exclusion principle and required antisymmetry of the wave functions, they cannot be regarded as moving independently Thus, the picture proposed earlier by Schafroth (18) , and developed more completely in cooperation with Butler and Blatt,(19) of electron pairs as "localized entities (pseudo-molecules) whose center-of-gravity motion is essentially undisturbed", and which at low temperatures undergo an Einstein-Bose condensation, is not valid. New methods were required to construct a theory of superconductivity, and this was first accomplished by the joint efforts of Bardeen, Cooper and Schrieffer.(20)

1.2.1 The BCS Theory (20)

One may describe the low-lying configurations for the normal phase of a metal by specifying the occupancy in k-space of the quasi-particles above the Fermi sea and of unoccupied states or holes below the sea. In accordance with the Landau Fermi liquid model, the energy of one quasi-particle may depend on the distribution of the other quasi-particles. These quasi-particle configurations are not exact solutions of the Hamiltonian when Coulomb and phonon interaction interaction energies are included, but are reasonably well defined if the excitation energies are not to high. The configurations are presumed

to include correlation energies and quasi-particle self-energies characteristic of the normal phase. Superconductivity arises from residual attractive interactions between the normal quasi-particles.

Bardeen, Cooper and Schrieffer (20) took for the variational wavefunction ground state of superconductor a linear combination of normal configurations in which the quasi-particle states are occupied in pairs $(k_1\uparrow, k_2\downarrow)$ of opposite spin and the same total momentum, $k_1 + k_2 = q$, common to all pairs. In any configuration, the two states of a pair are either both occupied or both empty, Values of q different from zero describe current flow in the ground state; that for $q = 0$ for zero current has the lowest energy. They also worked out a quasi-particle excitation spectrum for a superconductor in one-to-one correspondence with that for a normal metal, with a temperaturedependent energy gap for excitation of particles from the superconducting ground state.

1.2.2 The Bogoliubov-Valatin Transformation

Since the original publications of the BCS theory, the mathematical formulation of the theory has been developed considerably. Several different mathematical formulations (21,22,23) have been given which have improved the rigor and have extended the theory so as to apply to a wider variety of problems. Particular mention should be made of the work of Bogoliubov and co-workers(21), who, along with Valatin(22), introduced the now famous transformation to quasi-particle variables, gave much improved treatment of Coulomb interactions, provided a treatment of collective excitations, and made other noteworthy contributions. We would like to illustrate briefly their procedure below.

1.2.2.1 Superconducting Ground State

We begin with the Hamiltonian of the system:

$$H = \sum_{k\sigma} \xi(k) b^{\dagger}_{k\sigma} b_{k\sigma} + \sum_{k_1, k_2, k} V(k) b^{\dagger}_{k_2 - K, \downarrow} b^{\dagger}_{k_1 + K, \uparrow} b_{k_1, \uparrow} b_{k_2 \downarrow} \quad (1.22)$$

where $b_{k\sigma}$, $b^{\dagger}_{k\sigma}$ are annihilation and creation operators for electrons. The first term represents the kinetic energy of the elctrons, measured from the Fermi level. It is often convenient to assume that this is variable — that the total number of the electrons N is not definitely fixed, by introducing the chemical potential, μ , of the electron gas, and writing the first term

$$\begin{aligned} H &= \sum_{k\sigma} n_{k\sigma} \left[\xi(k) - \mu \right] \\ &= \sum_{k\sigma} n_{k\sigma} \xi(k) - \mu N \end{aligned} \quad (1.23)$$

The second term in Eq. (1.22) represents the scattering whose effect is to "destroy" the electrons in k_1, and k_2, and then to "re-create" them in $k_1 + K$ and $k_2 - K$, with the matrix element $V(K)$. We assume here that only opposite spins interact.

Bogoliubov's method is to make a canonical transformation of the set, $b_{k\sigma}$ and $b^{\dagger}_{k\sigma}$ to new annihilation and creation operators having the same commutation relations. In particular, these must link the state $(k, \uparrow)$ with the state $(-k, \downarrow)$, as suggested by the Cooper effect.

For simplicity let us drop the spin indices, and write

$$\begin{aligned} \beta^{\dagger}_k &= u_k b^{\dagger}_k - v_k b_{-k}, \quad \beta_k = u_k b_k - v_k b^{\dagger}_{-k} \\ \beta^{\dagger}_{-k} &= u_k b^{\dagger}_{-k} + v_k b_k, \quad \beta_{-k} = u_k b_{-k} + v_k b^{\dagger}_k \end{aligned} \quad (1.24)$$

The operator β_k, $\beta_k^\dagger$ will have the proper anticommutation relations for fermions if

$$u_k^2 + v_k^2 = 1 . \tag{1.25}$$

When we solve Eq.(1.24) for the original operators, and substitute into the Hamiltonian Eq. (1.22), we get a variety of different terms containing products of the new operators β_k , $\beta_k^\dagger$. Now when any of these terms contains an annihilation operator b_k, we can use the anticommutator to shift to the right, e.g.

$$\beta_k \beta_{k'}^\dagger = \delta_{kk'} - \beta_{k'}^\dagger \beta_k \tag{1.26}$$

Suppose that our superconducting state is the "vacuum", $|0\rangle$, of these new operators. By definition, there are no objects in the vacuum that can be annihilated, so that

$$\beta_k |0\rangle = 0, \tag{1.27}$$

for all k. Such terms in the Hamiltonian do not contribute to the energy of the ground state, $|0\rangle$, which is thus an eigenstate of all this part of H.

But there remains terms which cannot be eliminated in this way- terms which contain only creation operators like $\beta_k^\dagger$. These arise from the kinetic energy part of Eq. (1.22), and also from the reduction of the interaction terms, as when k and k' in Eq.(1.26) happen to be equal. We find that our Hamiltonian can be written,

$$H = 2 \sum_k \xi(k)\ v_k^2 + \sum_{k,K} V(K)\ u_k v_k u_{k+K} v_{k+K}$$

$$+ \sum_k \left[2\, \xi(k) u_k v_k + (u_k^2 - v_k^2) \sum_k V(K)\ u_{k+K} v_{k+K} \right] \beta_k^\dagger\ \beta_{-k}^\dagger \tag{1.28}$$

The first term will give us the energy of our ground state — if only we could eliminate the creation operators in the final sum.

We choose our transformation coefficients u_k , v_k so as to make each "dangerous" term vanish. We let

$$2\,\xi(k)\,u_k v_k+(u_k^2-v_k^2)\sum_k V(K)\,u_{k+K}v_{k+K} = 0, \tag{1.29}$$

In general, this is a complicated integral equation for the unknown function u_k and v_k, which are subject also to the condition Eq. (1.25). But let us make the assumptions that V(K) is a constant, V, within an energy range + w, and zero beyond. The constant w is to be of the order of $k_B\,T_D$, where T_D is the Debye temperature. We let the sum over K in Eq. (1.29) be a parameter

$$\Delta_o = - V \sum_{-w}^{w} u_{k+K}\, v_{k+K} \tag{1.30}$$

and solve Eqs. (1.29) and (1.25) simultaneously. The result is

$$u_k^2 = \frac{1}{2}\left[1+\frac{\xi(k)}{\sqrt{\Delta_0^2+\xi^2(k)}}\right] \quad , v_k^2 = \frac{1}{2}\left[1-\frac{\xi(k)}{\sqrt{\Delta_0^2+\xi^2(k)}}\right], \tag{1.31}$$

which may be substituted back in Eq. (1.30) to give

$$1 = -\frac{1}{2} V \sum_{-w}^{w} \left[\Delta_o^2+\xi^2(k)\right]^{-1/2}$$

$$= - N(0)\, V \ln \frac{2w}{\Delta_o}, \tag{1.32}$$

where N(0) is the density of states at the Fermi level.

We can put this this back into the remainder of Eq. (1.28), from which all the operators have now been removed. We get

$$\mathcal{E}_0 = 2\sum_{\xi<0} \xi(k) - \frac{1}{2}\Delta_o^2 \sum \left[\Delta_o^2+\xi(k)\right]^{-\frac{1}{2}} \tag{1.33}$$

Thus, the state $|0\rangle$ is an eigenstate of H - but with lower energy than the full Fermi sphere of electrons, whose energy would just be the sum of the values of $\xi(k)$ for the occupied states, as in Eq. (1.23).

1.2.2.2 Quasi-Particles and the Energy Gap

It is very important to understand the significance of the operators $\beta_k^\dagger$ and β_k. We note that $\beta_k^\dagger$ always creates an excitation with net momentum k and spin up. Well aboye the Fermi surface, $u_k \sim 1$, $v_k \sim 0$, and the excitation is electron-like. Below the Fermi surface, $u_k < v_k$, and the excitation is predominantly a hole at $-k\downarrow$. Right at the Fermi surface, there is equal mixture but in all cases the net effect is to add $k\uparrow$ overall. The β_k excitation similarly always add $-k\downarrow$ to the momentum and spin of the system. The excitations of the superconducting state are thus rather peculiar quasi-particles which change from being "electrons" to be "holes" as they pass through the Fermi level.

The energy of an excitation can also be calculated. We look for the coefficient of terms containing the operator

$$n_k' = \beta_k^\dagger \beta_k \tag{1.34}$$

in the expansion of (1.22), since this measures the number of quasi-particles that have been excited in this mode. The result is

$$\epsilon(k) = \xi(k)\,(u_k^2 - v_k^2) - 2u_k v_k \sum_k V(K)\, u_{k+K} v_{k+K}$$

$$= \sqrt{\Delta_o^2 + \xi^2(k)} \qquad . \tag{1.35}$$

for our simplified interaction, using Eq. (1.30) and (1.31).

This is very important, for it demonstrates the existence of an energy gap Δ_o above the superconducting ground state. When $\xi(k) \gg \Delta_o$, then $\epsilon(k) \sim \xi(k)$ - the energy of the quasi-particle is the energy required to excite an ordinary electron above the Fermi level. But as k approaches the Fermi surface, where $\xi(k)$ is zero, the energy of the quasi-particle tends to the constant value Δ_o. Then, as k decreases still further, $\epsilon(k)$ increases again, until it becomes nearly equal to $|\xi(k)|$. This is of course, the energy required to remove an electron from the state of negative $\xi(k)$, just as we expect from our interpretation of the quasi-particle operators.

1.2.2.3 Temperature Dependence of the Energy Gap

The ground state is only appropiate at T = 0. At a finite temperature we expect quasi-particles to be excited according to the usual Fermi-Dirac function

$$f_k = \frac{1}{e^{\epsilon(k)/k_B T} + 1} \tag{1.36}$$

In the normal state such excitations, above or below the Fermi level, are independent of one another. In the superconducting state they tend to interact, co-operatively, and destroy the energy gap.

Let us suppose that we are dealing with the state $|f_k\rangle$, in which the average number of quasi-particles in the kth state is given by Eq. (1.36). The effect on this state of a destruction operator b_k is not zero. On the average, we can replace Eq. (1.34) by

$$b_k^\dagger b_k \; |f_k\rangle = f_k \; |f_k\rangle \quad . \tag{1.37}$$

The reduction of the Hamiltonian to diagonal form, when applied to the state $|0\rangle$, depended upon Eq. (1.27). If now we try to do the

same thing, applied to the state $|f_k\rangle$, there will be extra terms arising from the reduction of products of operators to standard order as in Eq. (1.26), multiplying the "dangerous" products $\beta_k^\dagger \beta_{-k}^\dagger$ in Eq. (1.28). To remove these "pairproduction" parts of the Hamiltonian, our condition Eq. (1.29) must be changed to read

$$2\xi(k)\, u_k v_k + (u_k^2 - v_k^2) \sum_k V(K)\, u_{k+k} v_{k+K} (1 - 2f_{k+K}) = 0 \qquad (1.38)$$

(allowing for the two possible spin states associated with each k).

This integral equation can be solved, for the simplified interaction V, by replacing Δ_o in Eqs. (1.30) and (1.31) by

$$\Delta = - V \sum_{-w}^{w} u_{k+k} v_{k+k} (1 - 2f_{k+k}). \qquad (1.39)$$

Instead of Eq. (1.32), we then get, using Eq. (1.36),

$$1 = -\tfrac{1}{2} V \sum_{-w}^{w} \frac{1}{\epsilon(k)} \tanh \frac{\epsilon(k)}{2k_B T} \qquad (1.40)$$

$$= - N(0)\, V \int_{-w}^{w} \frac{1}{\epsilon} \tanh \frac{\epsilon}{2k_B T}\, d\xi \quad , \qquad (1.41)$$

where, as before, ϵ is the energy of an excitation,

$$\epsilon(k) = \sqrt{\Delta^2 + \xi^2(k)} \quad . \qquad (1.42)$$

The two equations (1.41) and (1.42) yield an implicit relation between Δ and T. This relationship is rather untidy, but the main point is that Δ decreases from Δ_o at T = 0 as T increases, In other words, the energy gap, Δ, decreases as the temperature increases, and closes to zero at a well-defined temperature, T_c, where, by (1.42), $\epsilon(k) = |\xi(k)|$. Thus, we can find T by integrating

$$\frac{1}{N(o)V} = 2\int_0^w \frac{1}{\epsilon}\tanh\left(\frac{\epsilon}{2k_BT_c}\right)d\epsilon \ , \qquad (1.43)$$

whose solution is

$$\Delta_o \sim 1.76\, k_BT_c \qquad (1.44)$$

Above T_c there is no solution of the equations. Just below T_c the energy gap rises steeply from zero, varying as

$$\Delta(T) \sim 3.2\, k_BT_c \left(1 - \frac{T}{T_c}\right)^{\frac{1}{2}} , \qquad (1.45)$$

as may be verified by seeking an approximate solution of Eqs. (1.41) and (1.42) in the neighbourhood of the solution of Eq. (1.43). At lower temperatures it increases more slowly, and flattens off to below about $T \sim \frac{1}{2}\, T$.

1.2.3. Nambu-Gor'kov Formalism

As soon as impurities are introduced into the system, it becomes impossible to make direct use of the BCS procedure because one cannot find the single-particle states even in the normal metal. Fortunately, one neither wants nor needs these states. The only physical quantities are sums over all such states and in these sums the complexities of the individual states disappear. In order to make use of this simplification, we shall employ as our basic computational tool Green's functions, which are sums over all states of the products of creation and annihilation operators. These Green's functions are a standard computational tool in the analysis of doped normal and superconducting materials.

In Nambu formalism (57) one works with matrix Green's functions, where the field operator is a two-component spinor

$$\Psi(x) = \begin{pmatrix} \psi_{\uparrow}(x) \\ \psi^{+}_{\downarrow}(x) \end{pmatrix} \tag{1.46}$$

and the Green's function is a 2 x 2 matrix defined by

$$G(x, x') = -i \langle 0 \mid T \left\{ \Psi(x)\, \Psi^{+}(x') \right\} \mid 0 \rangle \tag{1.47}$$

where x or x' denotes a set of four variables (the coordinate $\vec{r}$ and the time t), $|0\rangle$ is the ground state in the Heisenberg representation and T is the Wick time ordering operator. The 11 component of G is the ordinary electron Green's function and the 12 component is the Gor'kov's "anomalous" Green's function (55).

It is possible to prove (62) that G has the convenient Fourier series representation,

$$G(x-x') = \int e^{ipx}\, G(p)\, \frac{d^4p}{(2\pi)^4} \tag{1.48}$$

where

$$p \equiv (\vec{P}, p_o)$$

$$d^4p \equiv d^3p\, dp_o$$

$$px \equiv \vec{p} \cdot \vec{r} - p_o (t-t')$$

Using Nambu's Hamiltonian (57), in the absence of interactions we have

$$G_0(p) = \left[p_o \mathbf{1} - \xi_p \tau_3 \right]^{-1} \tag{1.49}$$

where $\xi_p = p^2/2m$ is the free-particle energy, $\mathbf{1}$ is the 2 x 2 unit matrix and τ_1, τ_2 and τ_3 are the Pauli matrices:

$$\tau_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \tau_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \qquad \tau_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{1.50}$$

To account for the workings of interactions we consider the most general form for the self-energy (p) according to

$$\Sigma(p) = \left[1 - Z(p)\right] p_o \mathbf{1} + \chi(p)\ \tau_3 + \phi(p)\ \tau_1 \tag{1.51}$$

From Dyson's equation

$$G^{-1}(p) = G_o^{-1}(p) - \Sigma(p) \tag{1.52}$$

and Eq.(1.51) we have

$$G(p) = \left[Z(p) p_o \mathbf{1} - \bar{\varepsilon}_p \tau_3 - \phi(p)\ \tau_1\right]^{-1} \tag{1.53}$$

where

$$\bar{\varepsilon}(p) = \varepsilon_p + \chi(p) \tag{1.54}$$

The advantage of the Nambu scheme lies in the fact that $\Sigma(p)$ may be expanded in almost the standard fashion in a power series in the interaction potential and G. In the general case, the Nambu formalism is equivalent to a self-consistent perturbation approach to determine the coefficients of the Pauli matrices in the expression for Σ [Eq.(1.51)]

The highly automatic nature of the zero-temperature perturbation series for G can be carried over to finite temperature by an elegantly simple procedure introduced by Abrikosov, Gor'kov and Dzyaloshinski(63), who extended the pioneering work of Matsubara (64) in this area. Similar techniques were advanced independently by Martin and Schwinger (65) in their fundamental work on Green's function techniques in the many-body problem. The basic result of their development is that $G(p,p_o)$ can be determined by the analytic continuation of a Green's function $\mathcal{G}(\vec{p}, iw_n)$ defined over a discrete set of pure imaginary frequencies

iw_n. The function $\mathcal{G}(p, iw_n)$ can be constructed by the usual Feynman-Dyson rules if all energy variable p_o associated with fermion lines occurring in the zero-temperature expansion are formally replaced by

$$p_o \to iw_n = i(2n + 1)\,\pi k_B T \quad (n = \text{integer}) \tag{1.55}$$

and the corresponding energy integrals are replaced by

$$\int \frac{dp_o}{2\pi} \longrightarrow ik_B T \sum_{n=-\infty}^{\infty} \tag{1.56}$$