CHAPTER III

PHENOMENOLOGICAL THEORY OF SUPERCONDUCTIVITY

The macroscopic characteristics of a superconductor have been the subject of a number of phenomenological treatments of which the principle ones will be discussed in subsequent sections of this chapter. A thermodynamic treatment and an associated two-fluid model were worked out by Gorter and Casimir. F. and H. London developed a model for the magnetic behavior which is based on a point by point relation between the current density and the vector potential associated with a magnetic field. Pippard modified London theory and obtained a non-local integral relation between the current density at a point and the vector potential in a region surrounding the point. Ginzburg and Landau have used a thermodynamic approach to develop an alternate and even more useful method of treating the coherence of the superconducting wave functions. Their treatment explicitly allows for spatial variations in the superconducting order due to size and magnetic field effects.

A successful microscopic theory of superconductivity has been developed by Bardeen, Cooper, and Schrieffer. It is based on the fact, established by Cooper, that in the presence of an attractive interaction the electrons in the neighbourhood of the Fermi surface condense into a state of lower energy in which each electron is paired with one of opposite momentum and spin.

III.1 Two-Fluid Models of Superconductivity

The thermodynamics of a two-fluid model of superconductivity was worked out by Gorter and Casimir[1]. They assumed that below T_c the metallic electrons could be divided into two distinct groups. A fraction x were assumed to condense into a superconducting aggregate, while the remainder $(1 - x)$ remained normal. Since the phase transition at T_c is of second order, x is assumed to be unity at $T = 0$ and decreasing continuously to zero at $T = T_c$. They then assumed a free energy expression of the form

$$F(T) = xF_s(T) + (1-x)^r F_n(T) \tag{3.1}$$

where

$$F_n(T) = -\frac{1}{2}\gamma T^2 \tag{3.2}$$

as in the normal metal[2], and

$$F_s(T) = -H_0^2/8 \; ; \; H_0 = H_c (T = 0) \tag{3.3}$$

The last expression is based on the fact that supercurrents carry no entropy[3]. They found best agreement with experiment if the exponent r is $1/2$. Minimizing the free energy with respect to x, and using the condition that $x = 0$ at $T = T_c$, one gets the following relations

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[1] Gorter, C.J. and H.B.G. Casimir, Physica , 1 , 1934. quoted in Chandrasekkar, B.S., Superconductivity , Vol. I, Edited by R.D.Parks, Marcel Dekker, Inc, New York, 1969, p.24 .

[2] Tinkham, M., Superconductivity , Gordon and Breach science publishers, 1965. p. 4

[3] Ref. 2 p.4

$$x(t) = 1 - t^4 \quad ; \quad t = T/T_c$$

$$\gamma = H_0^2 / 2\pi T_c^2$$

$$c_{es} = 3\gamma T_c t^3 \qquad (3.4)$$

$$H_c = H_0 (1 - t^2)$$

which are in good agreement with experiment. The two-fluid model in superconductivity has had only limited success since this model was set up so as to have the observed thermodynamic properties. It did not provide information about the electrodynamic of superconductivity.

III.2 London Theory

To account for the electromagnetic properties of superconductors, in particular the Meissner effect and the existence of persistence current, F. and H. London[4] proposed that Ohm's law, which relates current density and impressed field in normal metals, be replaced by some other relations connecting the superconducting current with the fields in the superconductor. They also assumed that the current in a superconductor , J , is composed of a supercurrent J_s and a normal current J_n. The electrodynamics of the superconductor are then embodied in the following equations:

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[4]London, F. and H. London, " The electromagnetic equations of the supraconductor", Proc. Roy. Soc. London, A 149, 71(1935)

$$\mathrm{curl}\,(\Lambda \vec{j}_s) = -\hbar/c \qquad (3.5)$$

$$\frac{\partial}{\partial t}(\Lambda \vec{j}_s) = \vec{e} \qquad (3.6)$$

$$\vec{j} = \vec{j}_s + \vec{j}_n \qquad (3.7)$$

$$\vec{j}_n = \sigma \vec{e} \qquad (3.8)$$

$\Lambda = m/ne^2$, n is the density of electrons

along with the Maxwell equations,

$$\mathrm{curl}\,\hbar = \frac{4\pi}{c}\vec{j} + \frac{1}{c}\cdot\frac{\partial \vec{e}}{\partial t} \qquad (3.9)$$

$$\mathrm{curl}\,\vec{e} = -\frac{1}{c}\cdot\frac{\partial \hbar}{\partial t} \qquad (3.10)$$

$$\mathrm{div.}\,\hbar = 0 \qquad (3.11)$$

$$\mathrm{div}\,\vec{e} = 4\pi\rho \qquad (3.12)$$

where σ is the normal conductivity, ρ is the electric charge density, and $\vec{e}$ and $\hbar$ are the local fields. One can show that for the quasi-static case, these equations lead to perfect conductivity and the Meissner effect as follows.

Combining Eq. (3.5) - (3.8) yields

$$-c\,\mathrm{curl}\,\Lambda \vec{j} = \hbar + \sigma\Lambda \frac{\partial \hbar}{\partial t} \qquad (3.13)$$

$$\frac{\partial}{\partial t}(\Lambda \vec{j}) = \vec{e} + \sigma\Lambda \frac{\partial \vec{e}}{\partial t}\ ; \qquad (3.14)$$

$$c^2\,\mathrm{curl}\,\mathrm{curl}\,\hbar = -\left(\frac{4\pi}{\Lambda}\hbar + 4\pi\sigma\frac{\partial \hbar}{\partial t} + \frac{\partial^2 \hbar}{\partial t^2}\right) \qquad (3.15)$$

$$c^2\,\mathrm{curl}\,\mathrm{curl}\,\vec{e} = -\left(\frac{4\pi}{\Lambda}\vec{e} + 4\pi\sigma\frac{\partial \vec{e}}{\partial t} + \frac{\partial^2 \vec{e}}{\partial t^2}\right) \qquad (3.16)$$

$$c^2\,\mathrm{curl}\,\mathrm{curl}\,\vec{j} = -\left(\frac{4\pi}{\Lambda}\vec{j} + 4\pi\sigma\frac{\partial \vec{j}}{\partial t} + \frac{\partial^2 \vec{j}}{\partial t^2}\right) \qquad (3.17)$$

and

$$\frac{\partial^2 \rho}{\partial t^2} = -\left(\frac{4\pi\rho}{\Lambda} + 4\pi\sigma\frac{\partial \rho}{\partial t}\right) \qquad (3.18)$$

Assume that there is total charge neutrality leading to the vanishing of ρ, $\partial\rho/\partial t$, and $\operatorname{div}\vec{j}$; and static conditions, so that all time derivatives vanish. Using the cartesian identity

$$\text{curl curl} = \text{grad div} - \nabla^2$$

along with Eq. (3.9), one gets

$$\nabla^2\vec{h} = (4\pi/\Lambda c^2)\,\vec{h} \qquad (3.19)$$

From the Eq. (3.10) curl $\vec{e}$ = 0, and from the Eq. (3.16) $\vec{e}$ = 0 . Thus the electric field in a superconductor vanishes, even though the electric current may be nonzero. Thus the London equations imply perfect conductivity. The vanishing of the field $\vec{h}$ inside a macroscopic superconductor (Meissner effect) is contained in the Eq. (3.19), which along with (3.5), (3.6), (3.7), and (3.8) known as the London equations.

III.2.1 Solutions of the London Equations [5]

(a) Plane superconductor - vacuum interface : Let the plane be at the x- axis and positive x being the superconductor. Assume that $h_z = h_0$ at $x = 0$, and $h_x = h_y = 0$. Then the physically meaningful ($h_z \rightarrow 0$ as $x \rightarrow \infty$) solution of Eq. (3.19) is

$$h_z = h_0 \exp(-x/\lambda) \qquad (3.20)$$

where $\lambda = (\Lambda c^2/4\pi)^{1/2}$, showing an exponential decay of the field with a characteristic distance λ , the penetration depth.

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[5] Shoenberg, D., Superconductivity, Cambridge University Press, 1960, p. 234.

(b) Flat slab in parallel field : Let the slab be of thickness 2d along the x- axis, $h_z = h_0$ at $x = \pm d$; and $h_y = h_x = 0$. One then gets the solution

$$h_z = h_0 \frac{\cosh(x/\lambda)}{\cosh(d/\lambda)} \tag{3.21}$$

(c) Sphere and circular cylinder : For a cylinder of radius r_0, in an applied field h_0 parallel to its axis

$$h(r) = h_0 \frac{I_0(r/\lambda)}{I_0(r_0/\lambda)} \tag{3.22}$$

where I_0 is the Bessel function of imaginary argument.

III.2.2 London Kernel[6] : When one introduces a vector potential $\vec{A}$ for the magnetic field $\vec{h}$.

$$\vec{h} = \operatorname{curl} \vec{A} \tag{3.23}$$

then equation (3.5) is satisfied by

$$\vec{j}_s = -(1/\Lambda c)\vec{A} \tag{3.24}$$

The q^{th} Fourier component of $\vec{A}$ and $\vec{j}_s$ are therefore related by

$$\vec{j}_s(q) = -(1/\Lambda c)\vec{A}(q) \tag{3.25}$$

Suppose we now wish to obtain the magnetic field as a function of position, taking into account the distribution of shielding currents,

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[6] Chandrasekhar, B.S., Superconductivity, Vol.I., edited by R.D.Parks, Marcel Dekker, Inc., New York 1969 P.33

for a superconductor with a plane infinite surface in the yz - plane and extending in the x- direction. The simplest mathematical model is to consider the field h_a as produced by an external current sheet $\vec{j}_e$ in an infinite superconducting medium in the yz- plane and along the z-direction, producing a magnetic field h_a in the y- direction; let $\check{j}_s$ be the supercurrent response. We can write the Maxwell equation

$$\text{curl } \vec{h} = (4\pi/c)\, \vec{j}$$

for this case as

$$\nabla^2 \vec{A} = -(4\pi/c)\,(\check{j}_e + \check{j}_s) \qquad (3.26)$$

Then $\check{A}$ and $\check{j}_s$ will be in the z- direction. The quantities $\vec{A}$, $\check{j}_e$ and $\check{j}_s$ all vary along the x - axis, and each may be expressed as a Fourier integral like

$$\check{A}(x) = \int_{-\infty}^{\infty} \vec{A}(q) \exp\,(iqx)\, dq \qquad (3.27)$$

Equation (3.26) may therefore be rewritten

$$-q^2 \check{A}(q) = -(4\pi/c)\, \vec{j}_e(q) + k(q)\, \vec{A}(q) \qquad (3.28)$$

where we have defined $k(q)$ by

$$\check{j}_s(q) = -(4\pi/c)\, k(q)\, \check{A}(q) \qquad (3.29)$$

Note that for the London case, by comparing Eq. (3. 29) and (3.25), we get $k_L(q)$, the London kernel, as

$$k_L(q) = 4\pi/(\Lambda c^2) \qquad (3.30)$$

Thus the London kernel, as defined above, is independent of q. We shall see later that a more realistic description of the electrodynamic properties of superconductors is obtained by using the Pippard kernel, $K_P(q)$, which is a function of q .

III.3 Pippard Modification of London Theory

III.3.1 Pippard Coherence Length and Nonlocal Relation :

In 1953 Pippard[7] measured the penetration depth in a series of dilute alloys of indium in tin, and found that the decrease in the normal electronic mean free path of the metal was accompanied by an appreciable rise in the value of λ (Fig. 6)

The London relation for the penetration depth,

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

gives no indication at all that dilute alloying should give a significant change of λ , since m and n_s should change only slightly. We note that the rapid variation of λ begins at about where it is comparable to l , the mean free path.

Pippard was much impressed by the resemblance of his results to those on the anomalous skin effect in normal metals. In the anomalous skin effect, as soon as the mean free path in metals becomes comparable with the skin depth, the skin depth varies rapidly with free path. This is accounted for in normal metals by the nonlocal relationship between the electric field, $E(\vec{r},t)$ (at low frequencies)

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[7] Pippard, A.B., " An Experimental and Theoretical Study for the Relation between Magnetic Field and Current in a Superconductor " Proc. Roy. Soc. London, A 216 , 547 (1953)

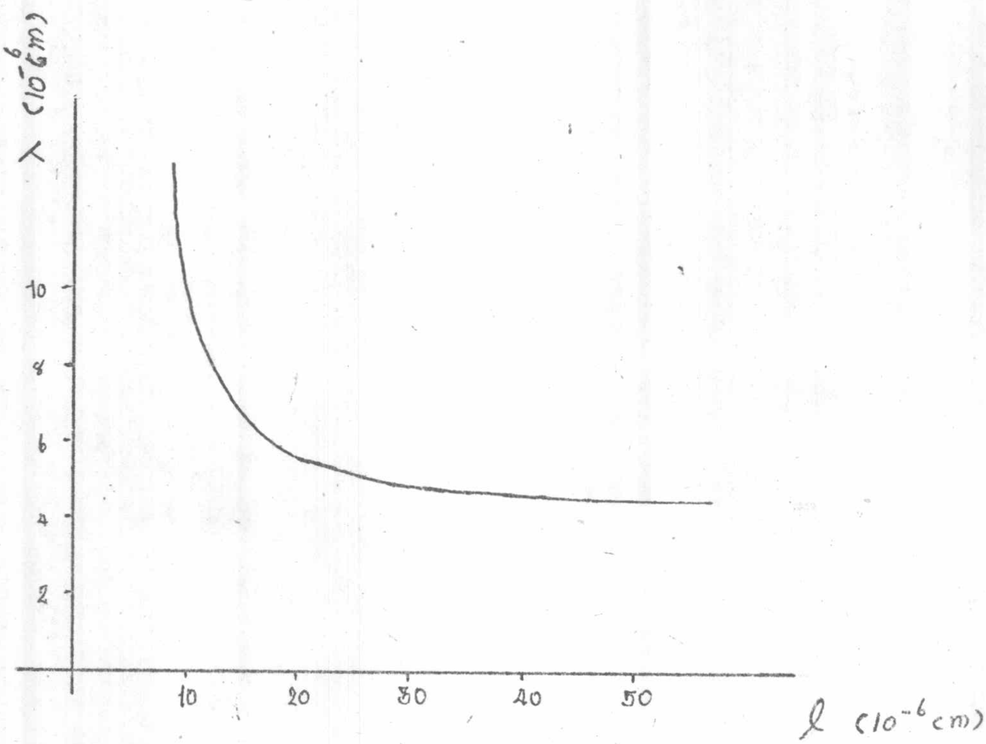

Fig. 6 Variation of penetration depth with mean free path in tin dilutely alloyed with indium.

and the current density it induces[8],

$$\vec{j}(\vec{r},t) = \frac{3\sigma}{4\pi l}\int d^3r' \frac{\vec{R}[\vec{R}\cdot\vec{E}(\vec{r}')]}{R^4} e^{-R/l} \qquad (3.31)$$

$$\vec{R} = \vec{r} - \vec{r}'$$

Here l denotes the electronic mean free path and σ the dc conductivity. Pippard[9] proposed that London's local relation between $\vec{j}$ and $\vec{A}$ should be replaced by a similar nonlocal relation of the form

$$\vec{j}_s(\vec{r},t) = \alpha\int d^3r' \frac{\vec{R}[\vec{R}\cdot\vec{A}(\vec{r}')]}{R^4} e^{-R/\xi} \qquad (3.32)$$

where α and ξ are new parameters. It is assumed that the vector potential is transverse. If in analogy with the equation between $\vec{j}$ and $\vec{E}$, we assume that parameter ξ depends on the mean free path and that, for slowly varying fields, in pure specimens, the equation should reduce to that of London, then we obtain

$$\frac{4}{3}\alpha\xi_0 = (C\Lambda)^{-1} \quad ;$$

here ξ_0 is the value of ξ for pure specimens. The equation for the current density is now

$$\vec{j}_s(\vec{r},t) = \frac{3}{4\pi\xi_0}(C\Lambda)^{-1}\int d^3r' \frac{\vec{R}[\vec{R}\cdot\vec{A}(\vec{r}')]}{R^4} e^{-R/\xi} \qquad (3.33)$$

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[8] Reuter, G.E.H., and E.H. Sondheimer "The Theory of the Anomalous Skin Effect in Metals" <u>Proc. Roy. Soc. London</u>, <u>A 195</u>, 336 (1948)

[9] see Ref. 7

Even in pure metals there is a nonlocal relation between current density and vector potential which depends on a new parameter ξ_0 . According to equation (3.33), any local disturbance is spread out over a distance of the order of ξ . This was interpreted by Pippard as meaning that any disturbance of the wave function would spread over this distance and that electrons tend to cohere over distances of the order of ξ . For this reason he called the length ξ the coherence length.

III.3.2 Pippard Kernel[10] : If we consider a semi-infinite superconductor bounded by the yz-plane, with a current $\check{j}_s$ flowing in the z- direction, h in the y-direction, and $\vec{A}$ in the z-direction, then in terms of the q^{th} Fourier components of the field quantities $\check{j}_s$ and $\check{A}$, we have , from Eq. (3.33)

$$\check{j}_s(q) = -\frac{3\check{A}(q)}{4\pi c\,\xi_0\Lambda}\int\frac{x^2\exp(-r/\xi)\exp(iqx)}{r^4}\,d\tau \qquad (3.34)$$

The intergration in spherical coordinates leads to an expression for the kernel $K_p(q)$ defined in terms of Eq. (3.29)

$$K_p(q) = \frac{\xi}{\xi_0\lambda_L^2}\cdot\frac{3}{2(q\xi)^3}\left[(1-q^2\xi^2)\tan^{-1}q\xi - q\xi\cdots\right] \qquad (3.35)$$

From this expression for $K_p(q)$, we get the following limiting forms of $\check{j}_s(q)$:

$$\check{j}_s(q) = -\frac{\xi}{\xi_0}\cdot\frac{\vec{A}(q)}{c\Lambda}\left\{1-\frac{q^2\xi^2}{5}+\cdots\right\}, \qquad (3.36)$$

$$q \to 0$$

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[10] see Ref. 6 p. 39

$$\check{j}_s(q) = -\frac{3\pi}{4q\xi_0}\cdot\frac{\check{A}(q)}{c\Lambda}\left\{1-\frac{4}{4q\xi}+\cdots\right\}, \quad q\to\infty \qquad (3.37)$$

and the penetration depth

$$\lambda = \lambda_L(\xi_0/\xi)^{1/2} \; ; \; \xi \ll \lambda_L \qquad (3.38)$$

$$\lambda = \lambda_L\frac{3^{1/6}}{(2\pi)^{1/3}}\left(\frac{\xi_0}{\lambda_L}\right)^{1/3} \; ; \; \xi \gg \lambda_L \qquad (3.39)$$

Now we have the expressions for the kernels:

$$K_L(q) = \frac{1}{\lambda_L^2} \qquad (3.40)$$

$$K_p(q) = \frac{1}{\lambda_L^2}\cdot\frac{\xi}{\xi_0}\left\{1-\frac{q^2\xi^2}{5}+\cdots\right\} \; ; \; q\xi \ll 1 \qquad (.341)$$

$$K_p(q) = \frac{1}{\lambda_L^2}\cdot\frac{\xi}{4q\xi_0}\left\{1-\frac{4}{4q\xi}+\cdots\right\} \; ; \; q\xi \gg 1 \qquad (3.42)$$

The magnetic behavior is markedly different according to whether $\lambda_L \gg \xi$ or $\lambda_L \ll \xi$. In the former case, the connection between $\vec{j}$ and $\vec{A}$ is local and, although the penetration depth can depend on the mean free path, the behavior is given essentially by the London equations. Superconductors of this type are referred to as London superconductors or type-II superconductors. They include many alloys and transition metals. At the other extreme of $\xi > \lambda$, we have to use the nonlocal relationship between $\check{j}$ and $\check{A}$. These superconductors are Pippard superconductors or type-I superconductors. The common, pure superconductors belong to this class.

III.4 Ginzburg Landau Theory

In 1950 Ginzburg and Landau[11] introduced a phenological approach to superconductivity which modifies the absolute rigidity of the superconducting order parameter or wave function which is implicit in the London model. They defined a parameter $\psi(r)$ which is a measure of the order in the superconducting phase, so that it is zero for $T > T_c$ and increases smoothly as T is reduced below T_c in zero field. Then the free energy density $F_{s0}(P, T, \psi)$ of the superconducting phase in zero field near T_c can be expanded as

$$F_{s0} = F_{n0} + \alpha |\psi|^2 + \beta |\psi|^4 \cdots\cdots \qquad (3.43)$$

where α, β are functions of P and T. This equation leads to the result

$$H_c^2 = \frac{4\pi}{\beta(T_c)} (T_c - T)^2 \left(\frac{d\alpha}{dT}\right)^2_{T_c} \qquad (3.44)$$

which agrees with experiment.

This is the first success of the GL theory. The second step that GL took was to state that, if there was a spatial variation of ψ, as well as a magnetic field $\vec{H}$ derived from a potential $\vec{A}$, then the energy density in the superconducting phase, F_{SH}, was given by

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[11] Ginzburg, V.L. and L.D. Landau, JETP (USSR), 20, 1064 (1950); quoted in Ref. 6 p. 42

$$F_{sH} = F_{s0} + \frac{H^2}{8\pi} + \frac{1}{2m}\left|(-i\hbar\vec{\nabla} + \frac{e^*}{c}\vec{A})\psi\right|^2 \qquad (3.45)$$

m = electronic mass

e^* = effective charge ,

which led to the results

$$\frac{1}{2m}\left|-i\hbar\vec{\nabla} - \frac{e^*}{c}\vec{A}\right|^2\psi + \frac{\partial F_{s0}}{\partial \psi^*} = 0 \qquad (3.46)$$

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

$$= \frac{2\pi i e^* \hbar}{mc}(\psi^*\nabla\psi - \psi\nabla\psi^*) + \frac{4\pi e^{*2}}{mc^2}|\psi|^2\vec{A} \qquad (3.47)$$

With the subsidiary conditions

$$\operatorname{div}\vec{A} = 0 \qquad (3.48)$$

$$\vec{n}\cdot(-i\hbar\vec{\nabla} - \frac{e^*}{c}\vec{A})\,\psi = 0 \qquad (3.49)$$

where $\vec{n}$ is the unit vector normal to the superconducting boundary.

The application of the GL equations to a planar boundary leads to the following results. One can define parameters λ_0 (of the dimension of length) and k (dimensionless) such that

$$\lambda_0 = (mc^2/4\pi e^{*2}\psi_0^2)^{1/2} \qquad (3.50)$$

$$k = (2e^{*2}H_c^2\lambda_0^4/\hbar^2c^2)^{1/2} \qquad (3.51)$$

so that the GL equations are formally reduced to the London equations if $k \to 0$ and $\psi_0 = n_s$. Thus λ_0 becomes the penetration depth for a macroscopic sample.

But for a thin sample it turns out that the penetration depth becomes a function of the sample thickness, because the $\psi(x)$ needed to minimize the free energy depends on sample dimension.

A second important result that GL obtained was that, for $k \ll 1$, the interphase surface energy density σ_{ns} between normal and superconducting phases is

$$\sigma_{ns} = \delta \, (H_c^2/8\pi)$$

$$\delta = 1.89 \, \lambda_o / k$$

Thus explaining the very large positive energy $(\gg \lambda_o H_c^2/8\pi)$ needed to explain the Meissner effect, and the structure in the intermediate state. Physically, the significance of this result was that while the magnetic field decayed over a characteristic distance λ_o to a vanishingly small value in the superconductors, $|\psi|^2$ decayed to zero toward the normal region over a much longer distance $\sim \lambda_o/k$.

GL made the further observation that for $k > 1/\sqrt{2}$, σ_{ns} becomes negative. This was subsequently recognized as defining the difference between type-I ($k < 1/\sqrt{2}$) and type-II ($k > \frac{1}{\sqrt{2}}$) superconductors.