Lecture notes: Superconductivity

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1 London's Theory

The first theory to explain the occurrence of superconductivity in metallic superconductors was given by London brothers (Fritz London and Heinz London) in 1935. London brothers started with the logic that if the electron in superconductor do not encounter resistance they will continue to accelerate in an applied electric field $\mathbf{E}$. Let n_{s} and $\mathbf{v}_{\mathrm{s}}$ be the number density (number/volume) and velocity of superconducting electrons in a superconductor respectively. The equation of motion of electrons in the superconducting state is given by

$$m\frac{\mathrm{d}\mathbf{v}_{\mathrm{s}}}{\mathrm{d}t} = -e\mathbf{E} \tag{1}$$

where m is the mass of the electron and $e = 1.6 \times 10^{-19}$ C. The current density (Am^{-2}) is given by

$$\mathbf{J}_{\mathrm{s}} = -en_{\mathrm{s}}\mathbf{v}_{\mathrm{s}}. \tag{2}$$

Differentiating it with respect to time we have,

$$\frac{\mathrm{d}\mathbf{J}_{\mathrm{s}}}{\mathrm{d}t} = -em\frac{\mathrm{d}\mathbf{v}_{\mathrm{s}}}{\mathrm{d}t}. \tag{3}$$

Combining eq. (1) and (3) we can write

$$\boxed{\frac{\mathrm{d}\mathbf{J}_{\mathrm{s}}}{\mathrm{d}t} = \frac{n_{\mathrm{s}}e^2}{m}\mathbf{E}.} \tag{4}$$

This is known as the *first London equation*:

> A supercurrent is freely accelerated by an applied voltage, or, in a bulk superconductor with no supercurrent or with a stationary supercurrent there is no effective electric field.

Taking curl on both sides of eq. (4) we have

$$\frac{\mathrm{d}}{\mathrm{d}t}(\boldsymbol{\nabla} \times \mathbf{J}_{\mathrm{s}}) = \frac{n_{\mathrm{s}}e^2}{m}\boldsymbol{\nabla} \times \mathbf{E}. \tag{5}$$

From third Maxwell's equation (Faradays law of electromagnetic induction) we know that

$$\boldsymbol{\nabla} \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \tag{6}$$

and combining eq. (5) and (6) we can have

$$\frac{\mathrm{d}}{\mathrm{d}t}(\boldsymbol{\nabla} \times \mathbf{J}_{\mathrm{s}}) = -\frac{n_{\mathrm{s}}e^2}{m}\frac{\partial \mathbf{B}}{\partial t}. \tag{7}$$

Integrating both sides of above equation

$$\boldsymbol{\nabla}\times\mathbf{J}_{\mathrm{s}}=-\frac{n_{\mathrm{s}}e^2}{m}\mathbf{B}+\mathcal{C}. \tag{8}$$

London brothers assumed the constant of integration, $\mathcal{C}$ to be zero so that eq. (8) takes into account the fact of zero resistivity in superconductors. Hence with $\mathcal{C}=0$ we get from above equation

$$\boxed{\boldsymbol{\nabla}\times\mathbf{J}_{\mathrm{s}}=-\frac{n_{\mathrm{s}}e^2}{m}\mathbf{B}.} \tag{9}$$

This is the *second London equation*. It yields the ideal diamagnetism, the Meissner effect, and the flux quantization.

1.1 Flux penetration from London equations

The integral form of Amperes' circuit law relates the magnetic field along a closed path to the total current following through any surface bounded by the path. In mathematical form:

$$\oint_{\mathrm{C}}\mathbf{B}\cdot\mathrm{d}\mathbf{l}=\mu_0 I_{\mathrm{encl}} \tag{10}$$

where C is the closed curve and I_{encl} is the total current flowing through any surface bounded by c. Again, form Stokes' theorem we can write

$$\int_{\mathrm{S}}(\boldsymbol{\nabla}\times\mathbf{B})\cdot\mathrm{d}\mathbf{s}=\oint_{\mathrm{C}}\mathbf{B}\cdot\mathrm{d}\mathbf{l} \tag{11}$$

where S is any surface bounded by C and d$\mathbf{s}$ is the differential surface area. We may express I_{encl} as the integral of the current density as follows:

$$I_{\mathrm{encl}}=\int_{\mathrm{S}}\mathbf{J}_{\mathrm{s}}\cdot\mathrm{d}\mathbf{s}. \tag{12}$$

Hence with help of eq. (11) and (12) we can rewrite eq. (10) as

$$\boldsymbol{\nabla}\times\mathbf{B}=\mu_0\mathbf{J}_{\mathrm{s}} \tag{13}$$

and taking curl on both sides yields

$$\boldsymbol{\nabla}\times(\boldsymbol{\nabla}\times\mathbf{B})=\mu_0\boldsymbol{\nabla}\times\mathbf{J}_{\mathrm{s}}. \tag{14}$$

However,

$$\boldsymbol{\nabla}\times(\boldsymbol{\nabla}\times\mathbf{B})=\boldsymbol{\nabla}(\boldsymbol{\nabla}\cdot\mathbf{B})-\boldsymbol{\nabla}^2\mathbf{B}=-\boldsymbol{\nabla}^2\mathbf{B} \tag{15}$$

since from second Maxwell's equation (Gauss's law for magnetism)

$$\boldsymbol{\nabla}\cdot\mathbf{B}=0. \tag{16}$$

Therefore, eq. (14) becomes

$$\nabla^2 \mathbf{B} = -\mu_0 \nabla \times \mathbf{J}_s. \tag{17}$$

Combining this with second London equation we get

$$\nabla^2 \mathbf{B} = \mu_0 \left(\frac{n_s e^2}{m} \right) \mathbf{B} = \frac{1}{\lambda_L^2} \mathbf{B} \tag{18}$$

where

$$\frac{1}{\lambda_L^2} = \mu_0 \left(\frac{n_s e^2}{m} \right) \tag{19}$$

and λ_L has dimension of length and is known as *Londons penetration depth*.

This eq. (18) is seen to account for the Meissner effect because it does not allow a solution uniform in space, so that a uniform magnetic field cannot exist in a superconductor. That is, $\mathbf{B}(\mathbf{r}) = \mathbf{B}_0 =$ constant is not a solution of eq. (18) unless the constant field $\mathbf{B}_0$ is identically zero. The result follows because $\nabla^2 \mathbf{B}_0$, is always zero, but $\mathbf{B}_0/\lambda_L^2$ is not zero unless $\mathbf{B}_0$ is zero. Note further that eq. (13) ensures that $\mathbf{J}_s = 0$ in a region where $\mathbf{B} = 0$.

In the pure superconducting state the only field allowed is exponentially damped as we go in from an external surface. Let a semi-infinite superconductor, placed in a magnetic field, occupy the space on the positive side of the x axis, as shown in Figure 1, such that $\mathbf{B} = \hat{z}B$, i.e., the field is only in the z-direction and can vary in space only in the x-direction inside the superconductor.

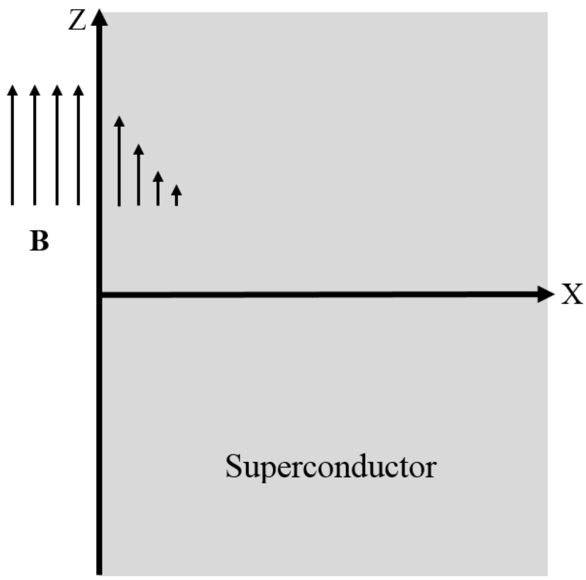

Figure 1: A superconducting slab in an external field.

Since $\nabla \times \mathbf{B} = \mu_0 \mathbf{J}_s$, the current in the y-direction. Hence from eq. (18) we get

$$\frac{\partial^2 B}{\partial x^2} = \frac{1}{\lambda_L^2} B \tag{20}$$

which has a solution of the type

$$\boxed{B(x) = B_0 \mathrm{e}^{-x/\lambda_\mathrm{L}}} \tag{21}$$

where B_0 is the field at the surface and x is the depth inside the superconductor.

> Any external field B_0 is screened to zero exponentially inside a bulk superconductor.

The eq. (21) shows that a uniform nonzero magnetic field can not exist in a superconductor, which is Meissner effect. In the pure superconducting state the only field allowed is the exponentially decreasing field as shown in Figure 2.

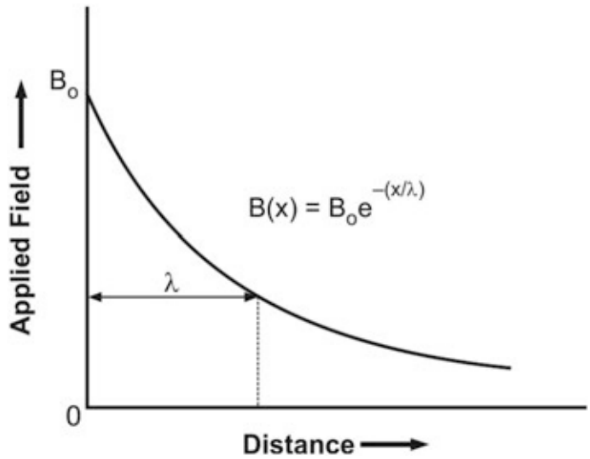

Figure 2: Field penetration in a superconductor. The magnetic flux drops exponentially inside the material. Penetration depth λ_L is defined as the depth at which the flux density drops to its eth value. [R.G. Sharma]

An applied magnetic field B will penetrate a thin film fairly uniformly if the thickness is much less than λ_L; thus in a thin film the Meissner effect is not complete. In a thin film the induced field is much less than B and there is little effect of B on the energy density of the superconducting state, so that eq. (13) does not apply. It follows that the critical field, that destroy the superconductivity, of thin films in parallel magnetic fields will be very high.

Suppose $x = \lambda_\mathrm{L}$ then eq. (21) becomes

$$B(x) = \frac{B_0}{\mathrm{e}}. \tag{22}$$

From which we define London penetration depth:

> The London penetration depth is the distance inside the surface of a superconductor at which the magnetic field reduces to $1/\mathrm{e}$ times its value at the surface.

The equation for the London penetration depth is given by eq. (19) as:

$$\boxed{\lambda_{\mathrm{L}} = \sqrt{\frac{m}{\mu_0 n_{\mathrm{s}} e^2}}.} \tag{23}$$

The penetration depth thus turns out to be inversely proportional to the square root of n_{s}, the superelectron density which changes with temperature. As the temperature increases n_{s} decreases and the flux penetration increases. At the critical temperature T_{c}, n_{s} decreases to zero and the whole material is penetrated with magnetic field thus turning the superconductor into the normal state. The temperature dependent London penetration depth is mathematically written as

$$\lambda_{\mathrm{L}}(T) = \lambda_0 \left[1 - \left(\frac{T}{T_{\mathrm{c}}}\right)^4\right]^{-1/2} \tag{24}$$

where $\lambda_{\mathrm{L}}(T)$ and λ_0 are the London penetration depths at temperature T kelvin and 0 kelvin respectively.

Although Londons theory did explain the infinite electrical conductivity and the Meissner effect, yet the calculated values of λ_{L} differ from the experimentally determined values. This may be due to the uncertainty of the values of n_{s}, e and m taken for free electrons, which obviously cannot be justified. The parameters like the superelectron density, n_{s}, their effective charge and effective mass have to be taken into account. After all, a superconductor cannot be treated as a free electron metal. Instead, superelectrons in a superconductor, interact coherently.

1.2 Coherence Length

The London penetration depth λ_{L} is a fundamental length that characterizes a superconductor. An independent length is the coherence length ξ. The coherence length is a measure of the distance within which the superconducting electron concentration cannot change drastically in a spatially-varying magnetic field.

The London equation is a local equation: it relates the current density at a point $\mathbf{r}$ to the vector potential at the same point. So long as $\mathbf{J}_{\mathrm{s}}(\mathbf{r})$ is given as a constant time $\mathbf{A}(\mathbf{r})$, the current is required to follow exactly any variation in the vector potential. But the coherence length ξ is a measure of the range over which we should average $\mathbf{A}(\mathbf{r})$ to obtain $\mathbf{J}_{\mathrm{s}}(\mathbf{r})$. We present a plausibility argument for the energy required to modulate the superconducting electron concentration.

Any spatial variation in the state o r an electronic system requires extra kinetic energy. A modulation of an eigenfunction increases the kinetic energy. It is reasonable to restrict the spatial variation of $\mathbf{J}_{\mathrm{s}}(\mathbf{r})$ in such a way that the extra energy is less than the stabilization energy of the superconducting state.

We compare the plane wave $\psi(x) = \mathrm{e}^{ikx}$ with the strongly modulated wavefunction:

$$\varphi(x) = 2^{-1/2}(\mathrm{e}^{i(k+q)x} + \mathrm{e}^{ikx}). \tag{25}$$

The probability density associated with the plane wave is uniform in space:

$$\psi^*\psi = \mathrm{e}^{-ikx}\mathrm{e}^{ikx} = 1, \tag{26}$$

whereas $\varphi^*\varphi$ is modulated with the wavevector q:

$$\begin{aligned}\varphi^*\varphi &= \frac{1}{2}(\mathrm{e}^{-i(k+q)x} + \mathrm{e}^{-ikx})(\mathrm{e}^{i(k+q)x} + \mathrm{e}^{ikx}) \\ &= \frac{1}{2}(2 + \mathrm{e}^{iqx} + \mathrm{e}^{-iqx}) \\ &= 1 + \cos qx \end{aligned} \tag{27}$$

The kinetic energy of the wave $\psi(x)$ is $\hbar^2 k^2/(2m)$; the kinctic energy of the modulated density distribution is

$$\frac{1}{2}\left(\frac{\hbar^2}{2m}\right)[(k+q)^2 + k^2] \approx \frac{\hbar^2}{2m}k^2 + \frac{\hbar^2}{2m}kq,$$

where we neglected q^2 for $q \ll k$.

The increase of energy required to modulate is $\hbar^2 kq/(2m)$. If this increase exceeds the energy gap E_g, superconductivity will be destroyed. The critical value q_0 of the modulation wavevector is given by

$$\frac{\hbar^2}{2m}k_\mathrm{F} q_0 = E_\mathrm{g}, \tag{28}$$

We define an intrinsic coherence length ξ_0 related to the critical modulation by $\xi_0 = 1/q_0$. We wave

$$\boxed{\xi_0 = \frac{\hbar^2 k_\mathrm{F}}{2mE_\mathrm{g}} = \frac{\hbar v_\mathrm{F}}{2E_\mathrm{g}}} \tag{29}$$

where v_F is the electron velocity at the Fermi surface. On the BCS theory a similar result is found:

$$\boxed{\xi_0 = \frac{2\hbar v_\mathrm{F}}{\pi E_\mathrm{g}}} \tag{30}$$

The intrinsic coherence length ξ_0 to is characteristic of a pure superconductor. In impure materials and in alloys the coherence length ξ is shorter than ξ_0. This may be understood qualitatively as in impure material the electron eigenfunctions already have wiggles in them and we can construct a given localized variation of current density with less energy from wavefunctions with wiggles than from smooth wavefunctions.

The coherence length ξ and the actual penetration depth λ depend on the mean free path l_e of the electrons measured in the normal state. When the superconductor is very impure, with a very small l_e, then $\lambda \approx \lambda_\mathrm{L}(\xi_0/l_\mathrm{e})^{1/2}$ and $\xi \approx (\xi_0 l_\mathrm{e})^{1/2}$, so that $\lambda/\xi \approx \lambda_\mathrm{L}/l$. This is the "dirty superconductor" limit.

2 Ginzburg-Landau Theory

The Ginzburg-Landau theory of superconductivity or called just GL theory is a phenomenological theory and valid close to the transition temperature, T_c. Nevertheless, it accounts well for the main characteristic properties of the superconductors. Since superconductivity is caused by a second order phase transition, this theory draws an analogy with the similar second order ferromagnetic phase transition in metals like iron and nickel. The order parameter $\mathbf{M}$, the magnetization in ferromagnets has now been replaced by a macroscopic pseudowavefunction $\psi(\mathbf{r})$, a complex order parameter for superconductor such that

$$\boxed{n_s^* = |\psi(\mathbf{r})|^2 = \psi^*(\mathbf{r})\psi(\mathbf{r})} \tag{31}$$

where n_s^* is the effective number density of superelectrons in the superconductor. The theory was developed by applying a variational method to an assumed expansion of the free energy density in powers of $|\psi(\mathbf{r})|^2$ and $|\boldsymbol{\nabla}\psi(\mathbf{r})|^2$, leading to a pair of coupled differential equations for $\psi(\mathbf{r})$ and the vector potential $\mathbf{A}(\mathbf{r})$. The result was a generalization of the London theory to deal with situations in which n_s varied in space, and also to deal with the nonlinear response to fields that are strong enough to change n_s.

The GL theory expresses the free energy of a superconductor in terms of the expansion of $\psi(\mathbf{r})$. Ginzburg and Landau treated the order parameter $\psi(\mathbf{r})$ as the wave function of the superconducting state which can vary with the location $\mathbf{r}$. They expressed the order parameter as

$$\boxed{\psi(\mathbf{r}) = |\psi(\mathbf{r})|e^{i\phi(\mathbf{r})}} \tag{32}$$

where $\phi(\mathbf{r})$ is the phase. The gradient of the phase at $\mathbf{r}$ is related to the momentum, that is, the current flowing at the point $\mathbf{r}$.

2.1 The Ginzburg-Landau free energy

The basic postulate of GL theory is that if $\psi(\mathbf{r})$ is small and varies slowly in space, the Helmholtz free energy density F_s close to the transition temperature, T_c can be expanded in a series of the form

$$\boxed{F_s = F_n + \alpha|\psi(\mathbf{r})|^2 + \frac{\beta}{2}|\psi(\mathbf{r})|^4 + \frac{\hbar^2}{2m^*}\left|\left(\boldsymbol{\nabla} - \frac{ie^*}{\hbar c}\mathbf{A}(\mathbf{r})\right)\psi(\mathbf{r})\right|^2 + \frac{H^2}{8\pi}} \tag{33}$$

where F_n is the Helmholtz free energy density in normal state; α and β are material dependent phenomenological parameters to be determined experimentally (in the case of classic BCS superconductors, α and β can also be calculated from the microscopic theory); $\mathbf{A}(\mathbf{r})$ is the vector potential; H is the external magnetic field; e^* and m^* are the effective charge and mass of superelectron, respectively.

In right side of eq. (33) the second and third terms correspond to the condensation free energy density as superconducting state is more ordered than normal state. The fourth term represents the kinetic energy of a charge particle in a magnetic field. Magnetic field energy density is represented by the last term in eq. (33). The fourth term which is proportional to the square of the gradient of $\psi(\mathbf{r})$ indicates the uniform value of $\psi(\mathbf{r})$ at minimum energy. It is to be noticed that this square term also has the electromagnetic potential $\mathbf{A}(\mathbf{r})$ because $\boldsymbol{\nabla}\psi(\mathbf{r})$ is proportional to current which too depends upon $\mathbf{A}(\mathbf{r})$. The free energy expression above assumes a configuration $\psi(\mathbf{r})$, yielding minimum free energy condition controlled by external parameters like temperature and magnetic field. Quite a few solutions of eq. (33) are possible which yield various superconducting parameters.

Let us now focus our attention on the term in the GL free energy which leads to supercurrents, the kinetic energy part:

$$\begin{aligned}
F_{\text{kin}} &= \frac{\hbar^2}{2m^*}\left|\left(\boldsymbol{\nabla} - \frac{ie^*}{\hbar c}\mathbf{A}(\mathbf{r})\right)\psi(\mathbf{r})\right|^2 \\
&= \frac{\hbar^2}{2m^*}\left|\left(\boldsymbol{\nabla} - \frac{ie^*}{\hbar c}\mathbf{A}(\mathbf{r})\right)|\psi(\mathbf{r})|\mathrm{e}^{i\phi(\mathbf{r})}\right|^2 \\
&= \frac{\hbar^2}{2m^*}\left|(\boldsymbol{\nabla}|\psi|)\mathrm{e}^{i\phi(\mathbf{r})} + i|\psi|\mathrm{e}^{i\phi(\mathbf{r})}\boldsymbol{\nabla}\phi - \frac{ie^*}{\hbar c}\mathbf{A}(\mathbf{r})|\psi(\mathbf{r})|\mathrm{e}^{i\phi(\mathbf{r})}\right|^2 \\
&= \frac{\hbar^2}{2m^*}\left|\left\{\boldsymbol{\nabla}|\psi| + i|\psi|\left(\boldsymbol{\nabla}\phi - \frac{ie^*}{\hbar c}\mathbf{A}(\mathbf{r})\right)\right\}\mathrm{e}^{i\phi(\mathbf{r})}\right|^2 \\
&= \frac{\hbar^2}{2m^*}\left|\boldsymbol{\nabla}|\psi| + i|\psi|\left(\boldsymbol{\nabla}\phi - \frac{ie^*}{\hbar c}\mathbf{A}(\mathbf{r})\right)\right|^2 \times \left|\mathrm{e}^{i\phi(\mathbf{r})}\right|^2 \\
&= \frac{\hbar^2}{2m^*}\left\{(\boldsymbol{\nabla}|\psi|)^2 + |\psi|^2\left(\boldsymbol{\nabla}\phi - \frac{e^*}{\hbar c}\mathbf{A}\right)^2\right\} \times 1 \\
&= \frac{1}{2m^*}\left\{(\hbar\boldsymbol{\nabla}|\psi|)^2 + |\psi|^2\left(\hbar\boldsymbol{\nabla}\phi - \frac{e^*}{c}\mathbf{A}\right)^2\right\}
\end{aligned} \tag{34}$$

where in the second line eq. (32) is used. These expressions deserve several remarks. Firstly, note that the free energy is gauge invariant, if we make the transformation $\mathbf{A} \to \mathbf{A} + \boldsymbol{\nabla}\Lambda$ where Λ is any scalar function of position, while at the same time changing $\psi \to \psi \exp(-ie^*\Lambda/c)$. Secondly, eq. (34) shows explicitly the contributions in the kinetic energy density term. The first term gives the extra energy associated with gradients in the magnitude of the order parameter and will introduce new physics that are not included in the London theory. The second term gives the kinetic energy associated with supercurrents in a gauge-invariant form. In the London gauge, ϕ is constant, and this term is simply $e^{*2}A^2|\psi|^2/(2m^*c^2)$. Equating this to the kinetic energy density for a London superconductor based on eq. (2), namely, $A^2/(8\pi\lambda_{\text{eff}}^2)$, we get

$$\lambda_{\text{eff}}^2 = \frac{m^*c^2}{4\pi|\psi|^2 e^{*2}}. \tag{35}$$

With the identification $n_s^* = |\psi(\mathbf{r})|^2$, as in eq. (32), this agrees with the usual definition of the London penetration depth, except for the presence of the starred effective number density, mass, and charge values. As the order parameter decreases penetration length increases. The kinetic energy density term can then be written as $n_s^*(\frac{1}{2}m^*v_s^2)$, where the supercurrent velocity is given by

$$m^*\mathbf{v}_s = \mathbf{p}_s - \frac{e^*\mathbf{A}}{c} = \hbar\boldsymbol{\nabla}\phi - \frac{e^*\mathbf{A}}{c}. \tag{36}$$

It should be noted that by writing the energy associated with the vector potential in the simple form (34), we have restricted the theory to the approximation of local electrodynamics.

In the original formulation of the theory, it was thought that e^* and m^* would be the normal electronic values. However, experimental data turned out to be fitted better if $e^* \approx 2e$. The microscopic pairing theory (BCS theory) of superconductivity makes it unambiguous that $e^* = 2e$ exactly, the charge of a pair of electrons. In the free-electron approximation, it would then be natural to take $m^* = 2m$ and $n_s^* = \frac{1}{2}n_s$, where n_s is the number density of single electrons in the condensate. With these conventions, $n_s^* e^{*2}/m^* = n_s e^2/m$, so the London penetration depth is unchanged by the pairing.

2.2 Equilibrium value of order parameter

In the absence of fields and gradients (currents), e.g. deep inside of a bulk superconductor, we have from eq. (33)

$$F_s - F_n = \alpha|\psi(\mathbf{r})|^2 + \frac{\beta}{2}|\psi(\mathbf{r})|^4 \tag{37}$$

which can be viewed as a series expansion in powers of $|\psi(\mathbf{r})|^2$, in which only the first two terms are retained. An expansion in powers of $\psi(\mathbf{r})$ itself is excluded since F must be real. This difficulty cannot be avoided by taking the real part of $\psi(\mathbf{r})$ since F should not depend on the absolute phase of $\psi(\mathbf{r})$. Odd powers of $|\psi(\mathbf{r})|$ are excluded because they are not analytic at $\psi(\mathbf{r}) = 0$.

The two terms in the right side of eq. (37) should be adequate so long as one stays near the second-order phase transition at T_c, where the order parameter $|\psi(\mathbf{r})|^2 \to 0$. Inspection of eq. (37) shows that β must be positive if the theory is to be useful; otherwise the lowest free energy would occur for arbitrarily large values of $|\psi(\mathbf{r})|^2$, where the expansion is surely inadequate.

Minimizing F_s with respect to $|\psi|$ we obtain

$$\frac{\mathrm{d}F_s}{\mathrm{d}|\psi|} = 0 = 2\alpha|\psi| + 2\beta|\psi|^3 = 2(\alpha + \beta|\psi|^2)|\psi|$$

or

$$|\psi|^2 = |\psi_\infty|^2 = -\frac{\alpha}{\beta} \tag{38}$$

where the notation ψ_∞ is conventionally used because ψ approaches this value infinitely deep in the interior of the superconductor, where it is screened from any surface fields or currents. When this value of ψ is substituted back into eq. (37), one finds

$$F_{\rm s} - F_{\rm n} = -\frac{\alpha^2}{2\beta} = -\frac{H_{\rm c}^2}{8\pi} \tag{39}$$

using the definition of the thermodynamic critical field $H_{\rm c}$ as the stabilization free energy density of the superconducting state. Depending on whether α is positive or negative two cases can arise as illustrated in Figure 3. If α is positive, the minimum free energy occurs at $|\psi|^2 = 0$, corresponding to the normal state. On the other hand, if $\alpha < 0$, the minimum occurs when $|\psi|^2 = |\psi_\infty|^2$ as given by eq. (38).

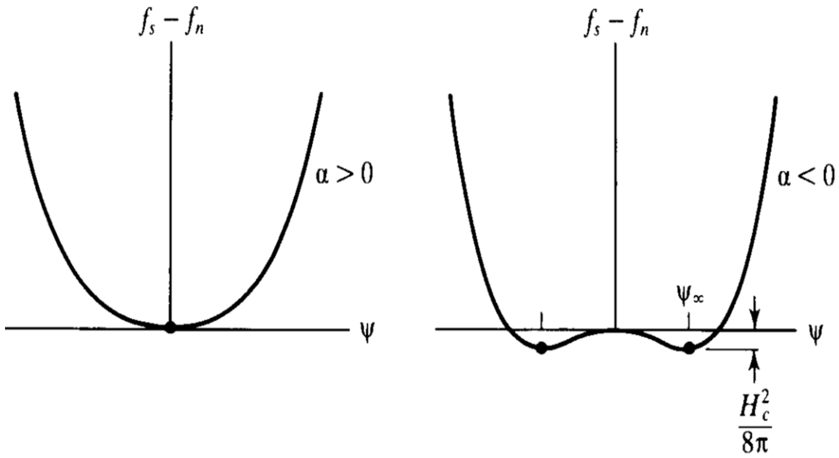

Figure 3: Ginzburg-Landau free-energy functions for $T > T_{\rm c}(\alpha > 0)$ and for $T < T_{\rm c}(\alpha < 0)$. Heavy dots indicate equilibrium positions. For simplicity, ψ has been taken to be real. [M. Tinkham]

Evidently, $\alpha(T)$ must change from positive to negative at $T_{\rm c}$, since by definition $T_{\rm c}$ is the highest temperature at which $|\psi|^2 \neq 0$ gives a lower free energy than $|\psi|^2 = 0$. Making a Taylor's series expansion of $\alpha(T)$ about $T_{\rm c}$, and keeping only the leading term, we have

$$\alpha(t) = \alpha'(t-1) \qquad\qquad \alpha' > 0 \tag{40}$$

where $t = T/T_{\rm c}$. Putting these temperature variations of α and β into eq. (38), we see that

$$|\psi|^2 \propto (1-t) \tag{41}$$

for T near, but below, $T_{\rm c}$. This is consistent with correlating $|\psi|^2$ with $n_{\rm s}$, the density of superconducting electrons in the London theory since $n_{\rm s} \propto \lambda_{\rm L}^{-2} \propto (1-t)$ near $T_{\rm c}$.

Having noted that $e^* = 2e$, and taking the convention that $m^* = 2m$, we can now evaluate the parameters of the GL theory by solving eq. (35), (38), and (39). The results are

$$|\psi_\infty|^2 \equiv n_s^* \equiv \frac{n_s}{2} = \frac{m^* c^2}{4\pi e^{*2}\lambda_{\text{eff}}^2} = \frac{mc^2}{8\pi e^2 \lambda_{\text{eff}}^2} \tag{42a}$$

$$\boxed{\alpha(T) = -\frac{e^{*2}}{m^* c^2} H_c^2(T)\lambda_{\text{eff}}^2 = -\frac{2e^2}{mc^2} H_c^2(T)\lambda_{\text{eff}}^2} \tag{42b}$$

$$\boxed{\beta(T) = \frac{4\pi e^{*4}}{m^{*2}c^4} H_c^2(T)\lambda_{\text{eff}}^4 = \frac{16\pi e^4}{m^2 c^4} H_c^2(T)\lambda_{\text{eff}}^4} \tag{42c}$$

where e and m are now the usual free-electron values and λ_{eff} and H_c are measured values, or those computed from the microscopic theory. Since the electrodynamics of some superconductors are significantly nonlocal, it is evident that this prescription in terms of an effective London penetration depth is straightforward only sufficiently near T_c at which condition the GL theory is really exact.

It is worth noting that if we insert the empirical approximations $H_c \propto (1 - t^2)$ and $\lambda^{-2} \propto (1 - t^4)$ into eq. (42), we find

$$|\psi_\infty|^2 \propto 1 - t^4 \approx 4(1 - t) \tag{43a}$$

$$\alpha \propto \frac{1 - t^2}{1 + t^2} \approx 1 - t \tag{43b}$$

$$\beta \propto \frac{1}{(1 + t^2)^2} \approx \text{constant}. \tag{43c}$$

Since the theory is usually exactly valid only very near T_c, it is customary to carry only the leading dependence on temperature; i.e., $|\psi_\infty|^2$ and α are usually taken to vary as $(1-t)$ and β is taken to be constant, as anticipated in our preliminary discussion. Still, the more complete forms in eq. (43) give some idea of how the theory can be extended over a wider range of temperature, and they have a certain amount of experimental support.

Finally, we recall that although our discussion of eq. (34) has centered on the kinetic energy of the supercurrent, this term also describes the energy associated with gradients in the magnitude of $\psi(\mathbf{r})$. Moreover, no additional parameters are introduced since gauge invariance requires a particular combination of $\boldsymbol{\nabla}$ and $\mathbf{A}$ in eq. (33). Thus, the coefficients in the theory are completely determined by the values of $\lambda_{\text{eff}}(T)$ and $H_c(T)$.

2.3 The Ginzburg-Landau differential equations

In the absence of boundary conditions which impose fields, currents, or gradients, the free energy is minimized by having $\psi = \psi_\infty$ everywhere. On the other hand, when fields, currents, or gradients are imposed, $\psi(\mathbf{r}) = |\psi(\mathbf{r})|e^{i\phi(\mathbf{r})}$ adjusts itself to minimize the overall free energy, given by the eq. (33).

To derive the GL equations, let us first minimize the total free energy $\int \mathrm{d}V F_{\mathrm{s}}(\mathbf{r})$ with respect to variations in the function $\psi^*(\mathbf{r})$. We have

$$\int \mathrm{d}V \delta F_{\mathrm{s}} = \int \mathrm{d}V \Bigg[\alpha\psi\delta\psi^* + \beta|\psi|^2\psi\delta\psi^* + \frac{\hbar^2}{2m^*}\left(\boldsymbol{\nabla}\psi - \frac{ie^*}{\hbar c}\mathbf{A}\psi\right)\cdot\left(\boldsymbol{\nabla}\delta\psi^* + \frac{ie^*}{\hbar c}\mathbf{A}\delta\psi^*\right)\Bigg] \tag{44}$$

As all the terms are proportional to ψ, the integral may reduce to the volume of superconductivity only. In order to get rid of $\boldsymbol{\nabla}\delta\psi^*$ we integrate the term containing $\boldsymbol{\nabla}\delta\psi^*$ by parts and use Gauss' divergence theorem. In such a case, we obtain

$$\begin{aligned}
&\int \mathrm{d}V \left(\boldsymbol{\nabla}\psi - \frac{ie^*}{\hbar c}\mathbf{A}\psi\right)\cdot\boldsymbol{\nabla}\delta\psi^* + \int \mathrm{d}V \left(\boldsymbol{\nabla}\psi - \frac{ie^*}{\hbar c}\mathbf{A}\psi\right)\cdot\frac{ie^*}{\hbar c}\mathbf{A}\delta\psi^* \\
&= \int \mathrm{d}S\,\hat{n}\cdot\left(\boldsymbol{\nabla}\psi - \frac{ie^*}{\hbar c}\mathbf{A}\psi\right)\delta\psi^* - \int \mathrm{d}V\delta\psi^*\,\boldsymbol{\nabla}\cdot\left(\boldsymbol{\nabla}\psi - \frac{ie^*}{\hbar c}\mathbf{A}\psi\right) \\
&\qquad + \int \mathrm{d}V \left(\boldsymbol{\nabla}\psi - \frac{ie^*}{\hbar c}\mathbf{A}\psi\right)\cdot\frac{ie^*}{\hbar c}\mathbf{A}\delta\psi^* \\
&= \int \mathrm{d}S\,\hat{n}\cdot\left(\boldsymbol{\nabla}\psi - \frac{ie^*}{\hbar c}\mathbf{A}\psi\right)\delta\psi^* \\
&\qquad - \int \mathrm{d}V\delta\psi^*\left[\boldsymbol{\nabla}^2\psi - \frac{ie^*}{\hbar c}\boldsymbol{\nabla}(\mathbf{A}\psi) - \frac{ie^*}{\hbar c}\mathbf{A}\boldsymbol{\nabla}\psi + \left(\frac{ie^*}{\hbar c}\mathbf{A}\right)^2\right] \\
&= \int \mathrm{d}S\,\hat{n}\cdot\left(\boldsymbol{\nabla}\psi - \frac{ie^*}{\hbar c}\mathbf{A}\psi\right)\delta\psi^* - \int \mathrm{d}V\delta\psi^*\left(\boldsymbol{\nabla} - \frac{ie^*}{\hbar c}\mathbf{A}\right)^2\psi
\end{aligned}$$

where the integration in the first term runs over the surface of the superconductor ($\hat{n}$ is the unit vector of the normal). Now we substitute the result back into the previous expression (44) and get

$$\int \mathrm{d}V\delta F_{\mathrm{s}} = \int \mathrm{d}V\left[\alpha\psi\delta\psi^* + \beta|\psi|^2\psi\delta\psi^* - \frac{\hbar^2}{2m^*}\delta\psi^*\left(\boldsymbol{\nabla} - \frac{ie^*}{\hbar c}\mathbf{A}\right)^2\psi\right] + \frac{\hbar^2}{2m^*}\int \mathrm{d}S\,\hat{n}\cdot\left(\boldsymbol{\nabla}\psi - \frac{ie^*}{\hbar c}\mathbf{A}\psi\right)\delta\psi^*. \tag{45}$$

There are two contributions to the variation, the bulk term and the surface one. Taking into account that the superconducting specimens may have arbitrary sizes and shapes, one can hardly expect that any compensation of these two terms may ever happen. So each one must be set equal to zero independently of the other.

At the time being let us consider the volume integral. One can suppose it to be more important for a macroscopic body. The corresponding variation must be zero, and because $\delta\psi$ in the bulk is an arbitrary function, the following condition must take place in the equilibrium state to minimize the volume contribution to the free energy:

$$\boxed{\alpha\psi + \beta|\psi|^2\psi - \frac{\hbar^2}{2m^*}\left(\boldsymbol{\nabla} - \frac{ie^*}{\hbar c}\mathbf{A}\right)^2\psi = 0} \tag{46}$$

or

$$\boxed{\alpha\psi + \beta|\psi|^2\psi + \frac{1}{2m^*}\left(-i\hbar\boldsymbol{\nabla} - \frac{e^*}{c}\mathbf{A}\right)^2\psi = 0} \tag{46a}$$

This is known as the first Ginzburg-Landau differential equations. As one could see from the derivation, the equation is an equilibrium condition for the system with the free energy given by eq. (33).

Now let us continue the derivation of the second GinzburgLandau equation. A variation of the joint free energy of the superconductor and magnetic field is taken with respect to $\mathbf{A}$. Please remember that the volume integral is taken over the whole infinite space:

$$\begin{aligned}\int \mathrm{d}V\delta F_\mathrm{s} &= \int \mathrm{d}V\delta\left\{\frac{(\boldsymbol{\nabla}\times\mathbf{A})^2}{8\pi} + \frac{\hbar^2}{2m^*}\left(\boldsymbol{\nabla}\psi - \frac{ie^*}{\hbar c}\mathbf{A}\psi\right)\cdot\left(\boldsymbol{\nabla}\psi^* + \frac{ie^*}{\hbar c}\mathbf{A}\psi^*\right)\right\}\\ &= \int \mathrm{d}V\left\{\frac{(\boldsymbol{\nabla}\times\mathbf{A})\cdot(\boldsymbol{\nabla}\times\delta\mathbf{A})}{4\pi} + \frac{\hbar^2}{2m^*}\left[-\frac{ie^*}{\hbar c}\psi\left(\boldsymbol{\nabla}\psi^* + \frac{ie^*}{\hbar c}\mathbf{A}\psi^*\right)\right.\right.\\ &\qquad\left.\left. + \frac{ie^*}{\hbar c}\psi^*\left(\boldsymbol{\nabla}\psi - \frac{ie^*}{\hbar c}\mathbf{A}\psi\right)\right]\delta\mathbf{A}\right\}\end{aligned}$$

Using the formula

$$\boldsymbol{\nabla}\cdot(\mathbf{a}\times\mathbf{b}) = \mathbf{b}\cdot(\boldsymbol{\nabla}\times\mathbf{a}) - \mathbf{a}\cdot(\boldsymbol{\nabla}\times\mathbf{b})$$

with $\mathbf{a} = \boldsymbol{\nabla}\times\mathbf{A} = \mathbf{H}$ and $\mathbf{b} = \delta\mathbf{A}$ we get

$$\begin{aligned}\int \mathrm{d}V\delta F_\mathrm{s} = \int \mathrm{d}V&\left\{\frac{1}{4\pi}\Big[\delta\mathbf{A}\cdot(\boldsymbol{\nabla}\times\mathbf{H}) - \boldsymbol{\nabla}\cdot(\mathbf{H}\times\delta\mathbf{A})\Big]\right.\\ &\left. + \left[\frac{ie^*\hbar}{2m^*c}(\psi^*\boldsymbol{\nabla}\psi - \psi\boldsymbol{\nabla}\psi^*) + \frac{e^{*2}}{m^*c^2}|\psi|^2\mathbf{A}\right]\delta\mathbf{A}\right\}\end{aligned} \tag{47}$$

Here the integral of the second term in eq. (47) is transformed into a surface integral over an infinite surface and disappears. This is a consequence of the fact that the integration in the GinsburgLandau free energy is taken over the whole infinite space, and not over the superconducting specimen only.

Now, setting $\int \mathrm{d}V\delta F_\mathrm{s}$ equal to zero within the superconductor, one obtains the second GinsburgLandau equation:

$$\boxed{\mathbf{J}_\mathrm{s} = \frac{c}{4\pi}\boldsymbol{\nabla}\times\mathbf{H} = \frac{e^*\hbar}{2im^*}(\psi^*\boldsymbol{\nabla}\psi - \psi\boldsymbol{\nabla}\psi^*) - \frac{e^{*2}}{m^*c}\psi^*\psi\mathbf{A}} \tag{48}$$

or

$$\mathbf{J}_\mathrm{s} = \frac{e^*}{m^*}|\psi|^2\left(\hbar\boldsymbol{\nabla}\phi - \frac{e^*}{c}\mathbf{A}\right) = e^*|\psi|^2\mathbf{v}_\mathrm{s} \tag{48a}$$

where in the last step we have repeated the identification (36). Note that the current expression (48) has exactly the form of the usual quantum-mechanical expression for particles of mass m^*, charge e^*, and wavefunction $\psi(\mathbf{r})$. Similarly, apart from the nonlinear term, the first equation has the form of Schrödinger equation for such particles, with energy eigenvalue $-\alpha$. The nonlinear term acts like a repulsive potential of $\psi(\mathbf{r})$ on itself, tending to favor wavefunctions $\psi(\mathbf{r})$ which are spread out as uniformly as possible in space.

In carrying through the variational procedure, one must provide boundary conditions. A possible choice, which assures that no current passes through the superconductor-vacuum interface, is

$$\left(\frac{\hbar}{i}\boldsymbol{\nabla} - \frac{e^*}{c}\mathbf{A}\right)\psi\bigg|_{\hat{n}} = 0 \tag{49}$$

which ensures that $\mathbf{J}_s \cdot \hat{n} = 0$ at the surface. This is the boundary condition used by GL, and it is appropriate at an insulating surface. This can easily be derived from the surface term in the free energy variation given by expression (45). If a media surrounding the superconductor does not influence superelectrons, which is true for the vacuum or a dielectric, then $\delta\psi$ may take arbitrary values at the surface. Then one can see that to eliminate the surface integral, the condensate wave function at the surface of the semiconductor must satisfy the boundary condition (49). Using the microscopic theory, de Gennes has shown that for a metal-superconductor interface with no current, eq. (49) must be generalized to

$$\left(\frac{\hbar}{i}\boldsymbol{\nabla} - \frac{e^*}{c}\mathbf{A}\right)\psi\bigg|_{\hat{n}} = \frac{i\hbar}{b}\psi \tag{49a}$$

where b is a real constant. As shown in Figure 4, if $A_n = 0$, b is the extrapolation length to the point outside the boundary at which ψ would go to zero if it maintained the slope it had at the surface. The value of b will depend on the nature of the material to which contact is made, approaching zero for a magnetic material and infinity for an insulator, with normal metals lying in between.

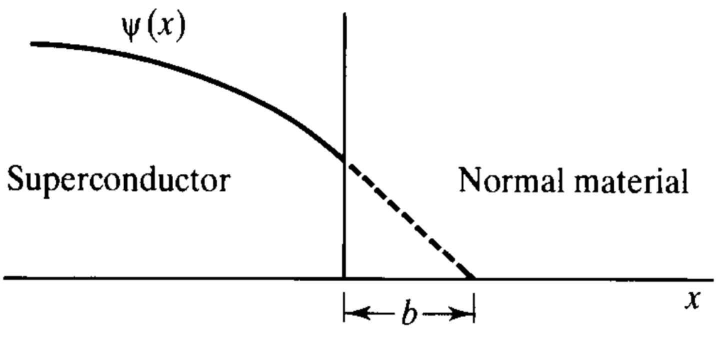

Figure 4: Schematic diagram illustrating the boundary condition (49a) at an interface characterized by an extrapolation length b. [M. Tinkham]

2.4 Flux exclusion and zero electrical resistance

The GL theory too leads to a London type relation between the electromagnetic vector potential $\mathbf{A}(\mathbf{r})$ and the electric current density $\mathbf{J}_s$. Taking the curl of the eq. (48a), the phase drops out, and we find the magnetic field:

$$\boldsymbol{\nabla} \times \mathbf{J}_\mathrm{s} = -\frac{e^{*2}}{m^* c} |\psi|^2 \, \boldsymbol{\nabla} \times \mathbf{A} = -\frac{e^{*2} n_\mathrm{s}^*}{m^* c} \, \mathbf{H} \tag{50}$$

which is the second London equation showing that in the absence of an external potential the current will flow indefinitely and charge carriers will accelerate in the presence of the potential. From the above expression it can easily shown that the London penetration depth will be

$$\begin{aligned} \lambda_\mathrm{eff} &= \left(\frac{m^* c^2}{4\pi n_\mathrm{s}^* e^{*2}} \right)^{1/2} \qquad \text{(CGS unit)} \\ &= \left(\frac{m^*}{\mu_0 n_\mathrm{s}^* e^{*2}} \right)^{1/2} \qquad \text{(SI unit)} \end{aligned}$$

same as eq. (23) except the presence of star marks. This has the same consequence as the London penetration depth i.e., the flux penetrates a superconductor a small depth λ_eff only and so does flow the screening current. Deep inside the bulk of a superconductor magnetic field can not penetrate unless the superconducting state is destroyed with a high enough magnetic field.

2.5 The Ginzburg-Landau coherence length

To help get a feeling for the differential equation eq. (46), we first consider a simplified case in which no fields are present. Then $\mathbf{A} = 0$, and we can take $\psi(\mathbf{r})$ to be real since the differential equation has only real coefficients. If we introduce a normalized wavefunction

$$f = \left(\frac{\beta}{|\alpha|} \right)^{1/2} \psi \tag{51}$$

where $\alpha = -|\alpha|$, the equation in one dimension becomes

$$\frac{\hbar^2}{2m^* |\alpha|} \frac{\mathrm{d}^2 f}{\mathrm{d}x^2} + f - f^3 = 0. \tag{52}$$

This makes it natural to define the characteristic length $\xi(T)$ known as the Ginzburg-Landau coherence length for the variation of $\psi(x)$ by

$$\boxed{\xi^2(T) = \frac{\hbar^2}{2m^* |\alpha(T)|} \propto \frac{1}{1-t}} \tag{53}$$

In terms of $\xi(T)$, eq. (52) becomes

$$\xi^2 f'' + f - f^3 = 0. \tag{54}$$

Now multiplying both side of the above equation by $f' = \frac{\mathrm{d}f}{\mathrm{d}x}$ we get

$$\frac{\mathrm{d}}{\mathrm{d}x} \left[\frac{1}{2} \xi^2 f'^2 + \frac{1}{2} f^2 - \frac{1}{4} f^4 \right] = 0$$

or

$$\xi^2 f'^2 + f^2 - \frac{1}{2} f^4 = \mathcal{C} \tag{55}$$

where $\mathcal{C}$ is the constant of integration. Far from the boundary in the superconducting state, where ψ does not vary in space, we have that $\frac{\mathrm{d}}{\mathrm{d}x}\psi = 0$ i.e., $f' = 0$ and $f^2 = 1$ (following eq. (38)). With these we find the value of integration constant as $\mathcal{C} = 1/2$. Therefore, from eq. (55) we get

$$\xi^2 \left(\frac{\mathrm{d}f}{\mathrm{d}x}\right)^2 = \frac{1}{2}(1 - f^2)^2 \tag{56}$$

which has a solution of the form

$$f(x) = \tanh\left(\frac{x}{\sqrt{2}\xi}\right). \tag{57}$$

These lead us to the solution of ψ in one dimension as

$$\boxed{\psi(x) = \left(\frac{|\alpha|}{\beta}\right)^{1/2} \tanh\left(\frac{x}{\sqrt{2}\xi}\right)} \tag{58}$$

which shows that a small disturbance of ψ from ψ_∞ will decay in a characteristic length of order $\xi(T)$.

Now that we have an idea of the significance of the length $\xi(T)$, let us see what its value is. Substituting the value of α from eq. (42b) into the definition (53), we find

$$\boxed{\xi(T) = \frac{\Phi_0}{2\sqrt{2}\pi H_c(T)\lambda_{\text{eff}}}} \tag{59}$$

where

$$\Phi_0 = \frac{hc}{e^*} = \frac{hc}{2e} = 2.0678 \times 10^{-15} \quad \text{tesla m}^2 \tag{60}$$

is the flux quantum and known as *fluxoid* or *fluxon*.

2.6 Ginzburg-Landau parameter

The ratio of London's penetration depth and the GL coherence length is called the GL parameter represented by κ, that is

$$\boxed{\kappa = \frac{\lambda_{\text{eff}}(T)}{\xi(T)}} \tag{61}$$

Since both the parameters λ and ξ diverge as $(1-t)^{1/2}$, the dimensionless GL parameter, κ remains temperature independent. For typical classical metallic superconductors λ is much smaller than ξ, the ratio κ is smaller than 1. In fact, the value of the GL parameter distinguishes between two class of superconductors type I and type II. For most metallic superconductor $\kappa < 1/\sqrt{2}$ and for type II superconductors (like alloy superconductors and high T_c superconductors) this ratio $\kappa > 1/\sqrt{2}$. Thus $\kappa = 1/\sqrt{2} \approx 0.707$ is the dividing line between the two classes of superconductors.

2.7 Flux quantization

London brothers postulated that the flux inside a superconducting ring is quantized, this also follows as a consequence of GL theory. We know that the flux penetrates a superconductor a small depth λ only and so does flow the screening current. Let us consider a ring made of a superconductor (toroid) as in Figure 5. The currents which lead to flux quantization will only flow in a small part of the cross section, a layer of thickness λ. Draw a contour C in the interior of the toroid, as shown in figure. Then $\mathbf{v}_s = 0$ everywhere on C. It follows from eq. (48a) that

$$0 = \oint_C \mathbf{v}_s \cdot \mathrm{d}\mathbf{l} = \frac{1}{m^*} \oint_C \left(\hbar \boldsymbol{\nabla} \phi - \frac{e^*}{c} \mathbf{A} \right) \cdot \mathrm{d}\mathbf{l}. \tag{62}$$

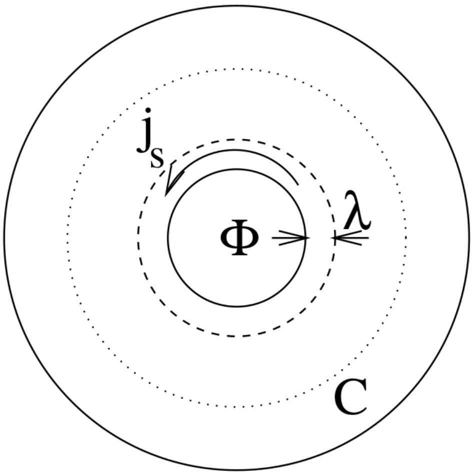

Figure 5: Quantization of flux in a superconducting toroid.

The order parameter $\psi(\mathbf{r})$ should have a unique value with minimum energy at every point along the circular path. In going round the circular path phase $\phi(\mathbf{r})$ should change only by an integral multiple of 2π. Thus from eq. (62)

$$\oint_C \boldsymbol{\nabla} \phi \cdot \mathrm{d}\mathbf{l} = 2n\pi \tag{63}$$

where n is an integer. Having $n \neq 0$ requires that one not be able to shrink the contour to a point, i.e., the sample have to has a hole as in our superconducting ring. The line integral of the vector potential is

$$\begin{aligned} \oint_C \mathbf{A} \cdot \mathrm{d}\mathbf{l} &= \int_S \boldsymbol{\nabla} \times \mathbf{A} \cdot \mathrm{d}\mathbf{S} \\ &= \int_S \mathbf{B} \cdot \mathrm{d}\mathbf{S} \\ &= \Phi. \end{aligned} \tag{64}$$

Here S is a surface spanning the hole and Φ the flux through the hole. Combining these results,

$$\Phi = 2n\pi\frac{\hbar c}{e^*} = n\frac{hc}{2e} = n\Phi_0 \tag{65}$$

where Φ_0 is the flux quantum as in eq. (60). Thus the flux through the ring is quantized in integral multiples of $\Phi_0 = hc/(2e)$. Flux quantization indeed follows from the fact that the current is the result of a phase gradient. However, it is important to note that, a phase gradient does not guarantee that a current is flowing.

The flux through the ring is the sum of the flux Φ_{ext} from external sources and the flux Φ_{sc} from the persistent superconducting currents which flow in the surface of the ring: $\Phi = \Phi_{\text{sc}} + \Phi_{\text{ext}}$. The flux Φ is quantized. There is normally no quantization condition on the flux from external sources, so that Φ_{sc} must adjust itself appropriately in order that Φ assume a quantized value.

2.8 Duration of Persistent Currents

Consider a persistent current that flows in a ring of a type I superconductor of wire of length L and cross-sectional area A. The persistent current maintains a flux through the ring of some integral number of fluxoids as in eq. (60). A fluxoid can not leak out of the ring and thereby reduce the persistent current unless by a thermal fluctuation a minimum volume of the superconducting ring is momentarily in the normal state.

The probability per unit time that a fluxoid will leak out is the product

$$\begin{aligned} P &= (\text{attempt frequency}) \times (\text{activation harrier factor}) \\ &= (\text{attempt frequency}) \times \exp\left\{-\frac{\Delta F}{k_B T}\right\}, \end{aligned} \tag{66}$$

where the free energy of the barrier is

$$\Delta F \approx (\text{minimum volume}) \times (\text{excess free energy density of normal state}). \tag{67}$$

The minimum volume of the ring that must turn normal to allow a fluxoid to escape is of the order of $R\xi^2$, where ξ is the coherence length of the superconductor and R the wire thickness. The excess free energy density of the normal state is $H_c^2/(8\pi)$, whence the barrier free energy is

$$\Delta F \approx \frac{R\xi^2 H_c^2}{8\pi}. \tag{68}$$

Let the wire thickness be 10^{-4} cm, the coherence length $= 10^{-4}$ cm, and $H_c = 10^3$ G; then $\Delta F \approx 10^{-4}$ erg. As we approach the transition temperature from below, ΔF will decrease toward zero, but the value given is a fair estimate between absolute zero and $0.8T_c$. Thus the activation barrier factor is

$$\exp\left\{-\frac{\Delta F}{k_B T}\right\} \approx \exp\left(10^8\right) \approx 10^{-4.34\times10^7}.$$

The characteristic frequency with which the minimum volume can attempt to change its state must be of the order of $E_g/\hbar$. If $E_g \approx 10^{-15}$ erg, the attempt frequency is $\approx 10^{-15}/10^{-27} \approx 10^{12}$ s^{-1}. The leakage probability (66) becomes

$$\begin{aligned} P &\approx 10^{12} \times 10^{-4.34\times 10^7} \quad \mathrm{s}^{-1} \\ &\approx 10^{-4.34\times 10^7} \quad \mathrm{s}^{-1}. \end{aligned}$$

The reciprocal of this is a measure of the time required for a fluxoid to leak out, $T = 1/P = 10^{4.34\times 10^7}$ s. The age of the universe is only 10^8 s, so that a fluxoid will not leak out in the age of the universe, under our assumed conditions. Accordingly, the current is maintained.

There are two circumstances in which the activation energy is much lower and a fluxoid can be observed to leak out of a ring; either very close to the critical temperature, where H_c is very small, or when the material of the ring is a type II superconductor and already has fluxoids embedded in it. These special situations are discussed in the literature under the subject of fluctuations in superconductors.

2.9 Josephson effect

From the aforesaid discussion we understand now quite clearly that a superconductor is defined by an order parameter $\psi(\mathbf{r})$ with a phase which is constant within a superconductor. This phase can however be changed by an external electromagnetic field. Variation of phase causes a current to flow.

Consider a very thin weak link between two halfs of a superconductor as shown in Figure 6. The order parameter has its thermodynamic value on both sides $x < x_1$ and $x > x_2$, but is exponentially small at $x = 0$. Hence, any supercurrent through the weak link is small, and ψ may be considered constant in both bulks of superconductor. In the weak link, not only $|\psi|$ is small, also its phase may change rapidly, e.g. from $\phi_2 = \phi_1$ to $\phi_2 = \phi_1 + \pi$ by a very small perturbation. The current that tends to flow across the weak link or the junction is dependent on the phase difference $(\phi_2 - \phi_1)$.

Without the right half, the boundary condition (49) would hold at x_1 :

$$\left(\frac{\hbar}{i}\frac{\partial}{\partial x} - \frac{e^*}{c}A_x\right)\psi\bigg|_{x_1} = 0 \tag{69}$$

In the presence of the right half, this condition must be modified to slightly depending on the value ψ_2:

$$\left(\frac{\hbar}{i}\frac{\partial}{\partial x} - \frac{e^*}{c}A_x\right)\psi\bigg|_{x_1} = a\psi_2, \tag{70}$$

where a is a small number depending on the properties of the weak link. Time inversion symmetry demands that eq. (70) remains valid for $\psi \to \psi^*$, $\mathbf{A} \to -\mathbf{A}$, hence a must

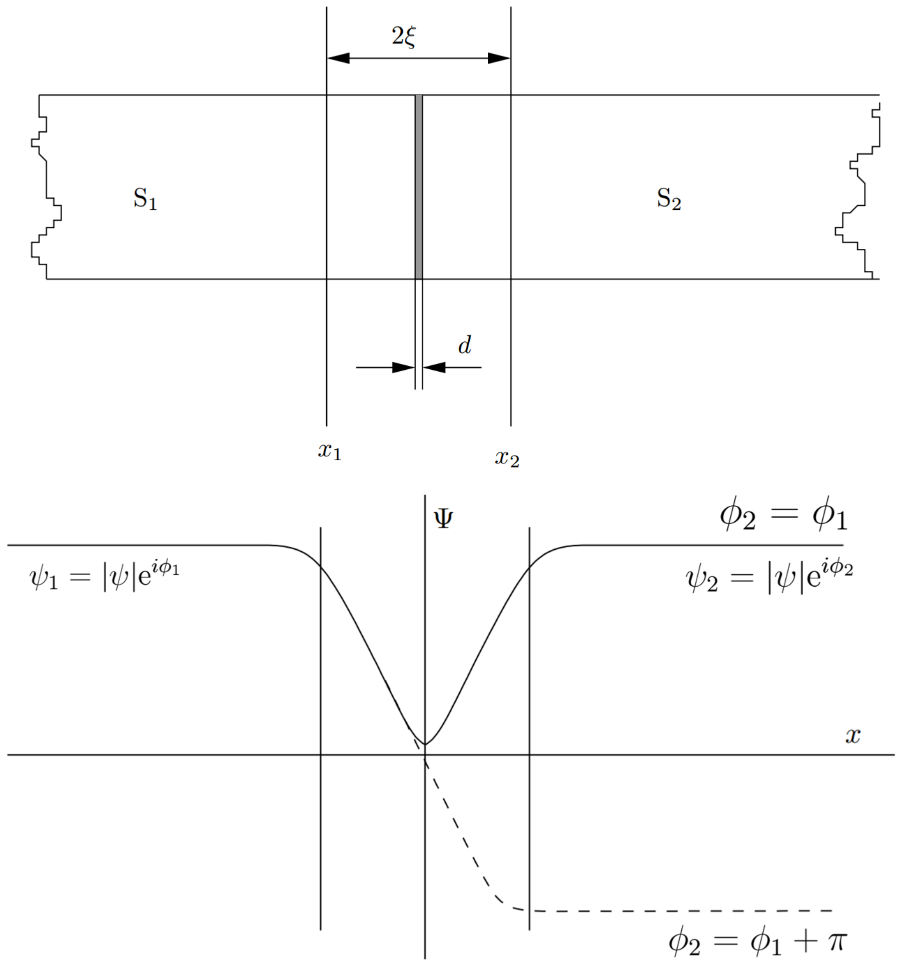

Figure 6: A weak link between two halfs of a superconductor (top) and the behavior of their order parameters (bottom).

be real as long as the phase of ψ does not depend on $\mathbf{A}$. For the moment we choose a gauge in which $A_x = 0$. Then, the supercurrent density at x_1 is

$$\begin{aligned} J_{\mathrm{s},x} &= \frac{\hbar e^*}{2im^*}\left[\psi_1^*\frac{\partial\psi}{\partial x}\bigg|_{x_1} - \psi_1\frac{\partial\psi^*}{\partial x}\bigg|_{x_1}\right] \\ &= \frac{a\hbar e^*}{2im^*}\left[\psi_1^*\psi_2 - \psi_1\psi_2^*\right] \\ &= \frac{a\hbar e^*}{2im^*}\left[\mathrm{e}^{i(\phi_2-\phi_1)} - \mathrm{e}^{-i(\phi_2-\phi_1)}\right] \\ &= \frac{a\hbar e^*}{m^*}\sin(\phi_2-\phi_1) \end{aligned} \tag{71}$$

Therefore, the expression for the current that flows through the weak link can be written as

$$I = I_\mathrm{c}\sin(\phi_2 - \phi_1). \tag{72}$$

No current will flow if the phase difference $(\phi_2 - \phi_1)$ is zero. I_c in the above equation is the critical current of the junction and depends upon the junction strength. This is DC Josephson effect. This current flows without a potential difference. In a geometry, like a superconducting ring, the phase difference will change with the flux in the ring which is quantized. Equation (72) will now take the form

$$I = I_c \sin\left[(\phi_2 - \phi_1) + 2\pi\frac{\Phi_{\text{junction}}}{\Phi_0}\right]. \tag{73}$$

In a Superconducting Quantum Interference Device (SQUID), shown in Figure 7 (left), the two arms acquire different phases equal to 2π times the number of unit quantum of flux depending on the enclosed flux. The current will be maximum when the phase difference is an even multiple of π and minimum when the phase difference is an odd multiple of π. The current pattern is thus oscillatory when plotted against the magnetic field passing through the SQUID as shown in Figure 7 (right).

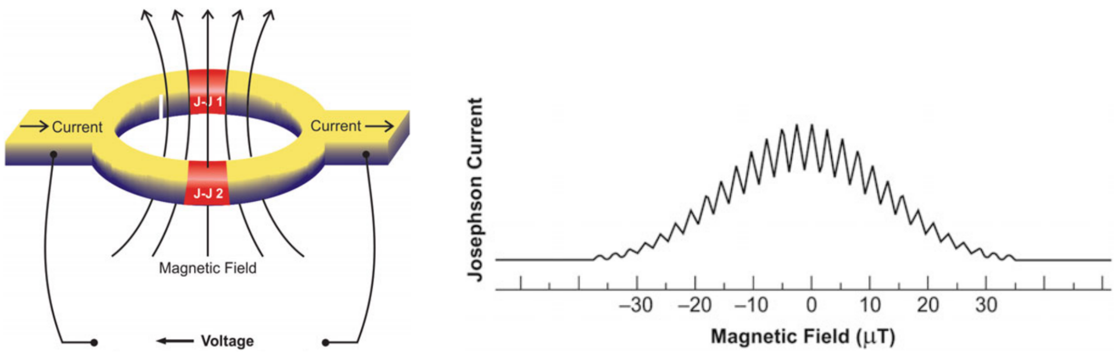

Figure 7: A dc SQUID with two Josephson-junctions (J-J1 and J-J2) mounted on a superconducting ring (left) and a typical Josephson current versus magnetic field pattern in a dc SQUID (right). [R.G. Sharma]

An expression for the ac Josephson effect can be driven from the eq. (62) by differentiating with respect to time, that is

$$\hbar\frac{\partial}{\partial t}\boldsymbol{\nabla}\phi = \frac{e^*}{c}\frac{\partial \mathbf{A}}{\partial t} = -e^*\mathbf{E}. \tag{74}$$

Since the electric field $\mathbf{E}$ i.e., the electro motive force V is determined by the rate of change of vector potential $\mathbf{A}$. Thus the phase difference between the two superconductors in a Josephson junction turns out to be,

$$\Delta\phi = \left[\frac{e^*V}{\hbar}\right]t = \left[\frac{2eV}{\hbar}\right]t. \tag{75}$$

Therefore,

$$I = I_c \sin\left[\frac{2eV}{\hbar}t + 2\pi\frac{\Phi_{\text{junction}}}{\Phi_0}\right]. \tag{76}$$

Hence if a voltage V is applied across the junction, an AC current with a frequency $2eV/\hbar$ will flow.

3 BCS Theory

The basis of a quantum theory of superconductivity was laid by the classic 1957 papers of Bardeen, Cooper, and Schrieffer. There is a "BCS theory of superconductivity" with a very wide range of applicability, from He^3 atoms in their condensed phase, to type I and type I1 metallic superconductors, and to high-temperature supercondnctors hased on planes of cuprate ions. Further, there is a "BCS wavefunction" composed of particle pairs $\mathbf{k}\uparrow$ and $-\mathbf{k}\downarrow$, which, when treated by the BCS theory, gives the familiar electronic superconductivity observed in metals and exhibits the energy gaps. This pairing is known as *s*-wave pairing. Some of the accomplishments of BCS theory with a BCS wavefunction are:

1. An attractive interaction between electrons can lead to a ground state separated from excited states by an energy gap. The critical field, the thermal properties, and most of the electromagnetic properties are consequences of the energy gap.

2. The electron-lattice-electron interaction leads to an energy gap of the observed magnitude. The indirect interaction proceeds when one electron interacts with the lattice and deforms it; a second electron sees the deformed lattice and adjusts itself to take advantage of the deformation to lower its energy. Thus the second electron interacts with the first electron via the lattice deformation.

3. The penetration depth and the coherence length emerge as natural consequences of the BCS theory. The London equation is obtained for magnetic fields that vary slowly in space. Thus the central phenomenon in superconductivity, the Meissner effect, is obtained in a natural way.

4. The criterion for the transition temperature of an element or alloy involves the electron density of orbitals $D(\epsilon_{\mathrm{F}})$ of one spin at the Fermi level and the electron-lattice interaction U, which can be estimated from the electrical resistivity because the resistivity at room temperature is a measure of the electron-phonon interaction. For $UD(\epsilon_{\mathrm{F}}) \ll 1$ the BCS theory predicts

$$T_{\mathrm{c}} = 1.14\theta \exp\left[-\frac{1}{UD(\epsilon_{\mathrm{F}})}\right] \tag{77}$$

where θ is the Debye temperature and U is an attractive interaction. The result for T_{c}, is satisfied at least qualitatively by the experimental data. There is an interesting apparent paradox: the higher the resistivity at room temperature the higher is U, and thus the more likely it is that the metal will be a superconductor when cooled.

5. Magnetic flux through a superconducting ring is quantized and the effective unit of charge is $2e$ rather than e. The BCS ground state involves pairs of electrons; thus flux quantization in terms of the pair charge $2e$ is a consequence of the theory.

3.1 BCS ground state

The filled Fermi sea is the ground state of a Fermi gas of noninteracting electrons. This state allows arbitrarily small excitations – we can form an excited state by taking an electron from the Fermi surface and raising it just above the Fermi surface. The BCS theory shows that with an appropriate attractive interaction between electrons the new ground state is superconducting and is separated by a finite energy $E_{\rm g}$ from its lowest excited state.

The formation of the BCS ground state is suggested by Figure 8. The BCS state in (b) contains admixtures of one-electron orbitals from above the Fermi energy $\epsilon_{\rm F}$. At first sight the BCS state appears to have a higher energy than the Fermi state: the comparison of (b) with (a) shows that the kinetic energy of the BCS state is higher than that of the Fermi state. But the attractive potential energy of the BCS state, although not represented in the figure, acts to lower the total energy of the BCS state with respect to the Fermi state.

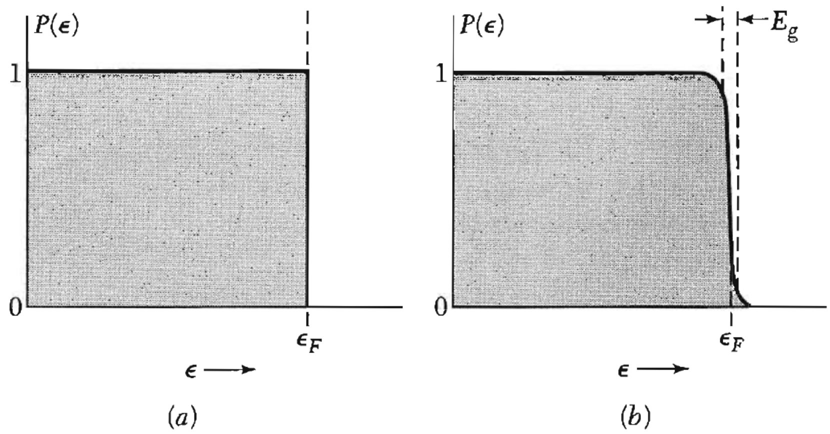

Figure 8: (a) Probability $P(\epsilon)$ that an orbital of kinetic energy ϵ is occupied in the ground state of the noninteracting Fermi gas; (b) the BCS ground state differs from the Fermi state in a region of width of the order of the energy gap $E_{\rm g}$. Both curves are for absolute zero. [C. Kittel]

When the BCS ground state of a many-electron system is described in terms of the occupancy of one-particle orbitals, those near $\epsilon_{\rm F}$ are filled some what like a Fermi-Dirac distribution for some finite temperature.

The central feature of the BCS state is that the one-particle orbitals are occupied in pairs: if an orbital with wavevector $\mathbf{k}$ and spin up is occupied, then the orbital with wavevector $-\mathbf{k}$ and spin down is also occupied. If $\mathbf{k}\uparrow$ is vacant, then $-\mathbf{k}\downarrow$ is also vacant. The pairs are called *Cooper pairs*. The binding energy is strongest when the electrons forming the pair have opposite moments and opposite spins. It follows, therefore, that if there is any attraction between them, then all the electrons in the neighborhood of the Fermi surface condense into a system of Cooper pairs. These pairs are, in fact, the superelectrons. The Cooper pair have spin zero and have many attributes of bosons.

3.2 Cooper pairs

Consider two electrons of opposite spin that interact with each other via an attractive potential, as shown in Figure 9. For a complete set of states of the two electron system that satisfy periodic boundary conditions in a cube of unit volume, we take plane wave product functions

$$\Psi(\mathbf{k}_1, \mathbf{k}_2; \mathbf{r}_1, \mathbf{r}_2) = \exp[i(\mathbf{k}_1 \cdot \mathbf{r}_1 + \mathbf{k}_2 \cdot \mathbf{r}_2)] \tag{78}$$

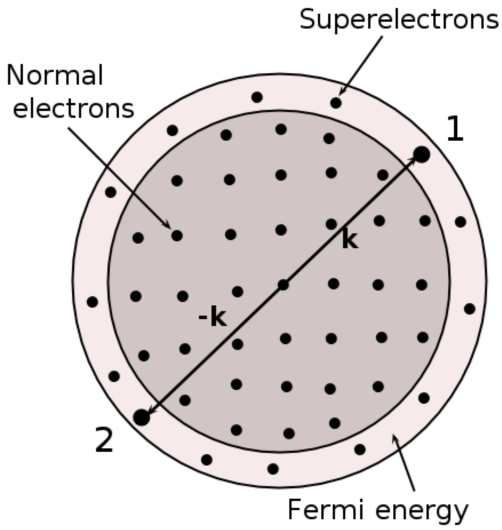

Figure 9: Interaction between two electrons, 1 and 2, near the Fermi surface in a metal.

We change variables to the relative coordinates: $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$, $\mathbf{k} = \frac{1}{2}(\mathbf{k}_1 - \mathbf{k}_2)$ and to the coordinates of the center of mass: $\mathbf{R} = \frac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2)$, $\mathbf{K} = \mathbf{k}_1 + \mathbf{k}_2$ so that

$$\mathbf{k}_1 \cdot \mathbf{r}_1 + \mathbf{k}_2 \cdot \mathbf{r}_2 = \mathbf{K} \cdot \mathbf{R} + \mathbf{k} \cdot \mathbf{r} \tag{79}$$

Thus eq. (78) becomes

$$\Psi(\mathbf{K}, \mathbf{k}; \mathbf{R}, \mathbf{r}) = \mathrm{e}^{i(\mathbf{K} \cdot \mathbf{R})} \times \mathrm{e}^{i(\mathbf{k} \cdot \mathbf{r})}, \tag{80}$$

and the kinetic energy of the two-electron system is

$$\epsilon_{\mathbf{K}} + E_{\mathbf{k}} = \frac{\hbar^2}{m}\left(\frac{1}{4}K^2 + k^2\right) \tag{81}$$

We give special attention to the product functions for which the center of mass wavevector $\mathbf{K} = 0$, so that $\mathbf{k}_1 = -\mathbf{k}_2$. With an interaction H_1 between the two electrons, we set up the eigenvalue problem in terms of the expansion

$$\chi(\mathbf{r}) = \sum g_{\mathbf{k}}\, \mathrm{e}^{i(\mathbf{k} \cdot \mathbf{r})}. \tag{82}$$

The Schrödinger equation is

$$(H_0 + H_1 - \epsilon) = 0 = \sum_{\mathbf{k}'} [(E_{\mathbf{k}'} - \epsilon) g_{\mathbf{k}'} + H_1\, g_{\mathbf{k}'}\, \mathrm{e}^{i(\mathbf{k}'\cdot\mathbf{r})} \tag{83}$$

where ϵ is the eigenvalue. We take the scalar product with $\exp(i\mathbf{k}\cdot\mathbf{r})$ to obtain

$$(E_{\mathbf{k}} - \epsilon) g_{\mathbf{k}} + \sum_{\mathbf{k}} g_{\mathbf{k}'} \langle \mathbf{k}|H_1|\mathbf{k}'\rangle = 0, \tag{84}$$

the sacular equation of the problem. Transforming the sum to an integral we have

$$(E - \epsilon) g(E) + \int \mathrm{d}E'\, g(E') H_1(E, E') N(E') = 0, \tag{85}$$

where $N(E')$ is the number of two electron state with total momentum $\mathbf{K} = 0$ and with kinetic energy in $\mathrm{d}E'$ at E'.

Now consider the matrix elements $H_1(E, E') = \langle \mathbf{k}|H_1|\mathbf{k}'\rangle$. Studies of these by Bardeen suggest that they are important when the two electrons are confined to a thin energy shell near the Fermi surface within a shell of thickness $\hbar\omega_{\mathrm{D}}$ above E_{F}, where ω_{D} is the Debye phonon cutoff frequency. We assume that

$$H_1(E, E') = -V \tag{86}$$

for E, E' within the shell and zero otherwise. Here V is assumed to be positive. Thus eq. (85) becomes

$$(E - \epsilon) g(E) = V \int_{2\epsilon_{\mathrm{F}}}^{2\epsilon_{\mathrm{m}}} \mathrm{d}E'\, g(E') N(E') = \mathcal{C}, \tag{87}$$

where $\epsilon_{\mathrm{m}} = \epsilon_{\mathrm{F}} + \hbar\omega_{\mathrm{D}}$. Here $\mathcal{C}$ is a constant, independent of E. From eq. (87) we have

$$g(E) = \frac{\mathcal{C}}{E - \epsilon} \tag{88}$$

and

$$1 = V \int_{2\epsilon_{\mathrm{F}}}^{2\epsilon_{\mathrm{m}}} \mathrm{d}E'\, \frac{N(E')}{E' - \epsilon}. \tag{89}$$

With $N(E')$ approximately constant and equal to N_{F}, over the small energy range between $2\epsilon_{\mathrm{m}}$ and $2\epsilon_{\mathrm{F}}$, we take it out of the integral to obtain

$$1 = N_{\mathrm{F}} V \int_{2\epsilon_{\mathrm{F}}}^{2\epsilon_{\mathrm{m}}} \mathrm{d}E'\, \frac{1}{E' - \epsilon} = N_{\mathrm{F}} V \ln \frac{2\epsilon_{\mathrm{m}} - \epsilon}{2\epsilon_{\mathrm{F}} - \epsilon}. \tag{90}$$

Let the eigenvalue ϵ of eq. (90) be written as

$$\epsilon = 2\epsilon_{\mathrm{F}} - E_{\mathrm{b}}, \tag{91}$$

which defines the binding energy E_{b} of the electron pair, relative to the free electrons at the Fermi surface. Then eq. (90) becomes

$$1 = N_{\mathrm{F}} V \ln \frac{2\epsilon_{\mathrm{m}} - 2\epsilon_{\mathrm{F}} + E_{\mathrm{b}}}{E_{\mathrm{b}}} = N_{\mathrm{F}} V \ln \frac{2\hbar\omega_{\mathrm{D}} + E_{\mathrm{b}}}{E_{\mathrm{b}}} \tag{92}$$

or

$$\frac{1}{N_{\mathrm{F}} V} = \ln \left(1 + \frac{2\hbar\omega_{\mathrm{D}}}{E_{\mathrm{b}}} \right). \tag{93}$$

Hence the binding energy of a Cooper pair may be written as

$$E_{\mathrm{b}} = \frac{2\hbar\omega_{\mathrm{D}}}{\exp\left(\frac{1}{N_{\mathrm{F}} V} - 1\right)}. \tag{94}$$

For V positive (attractive interaction) the energy of the system is lowered by excitation of a pair of electrons above the Fermi level. Therefore the Fermi gas is unstable in an important way. The binding energy (94) is closely related to the superconducting energy gap E_{g}. The BCS calculations show that a high density of Cooper pairs may form in a metal.

3.3 Transition temperature

In the weak coupling limit $k_{\mathrm{B}} T_{\mathrm{c}} \ll \hbar\omega_{\mathrm{D}}$ the expression for the transition temperature has been obtained by solving ground state energy equations and is given by the expression

$$k_{\mathrm{B}} T_{\mathrm{c}} \approx 1.14\, \hbar\omega_{\mathrm{D}} \exp\left(-\frac{1}{N(0)V} \right) \tag{95}$$

where $N(0)$ is the density of electron states of one spin per unit energy at the Fermi level, V the electron-phonon interaction parameter and k_{B} is the Boltzmann constant. Here we find that T_{c} is proportional to the phonon frequency ω_{D} which is consistent with the observation of the isotope effect in superconductors. We also notice in eq. (95) that T_{c} is a strong function of the electron concentration as the density of state enters in the exponential term. It is thus possible for one to make calculations for the change in T_{c} as a result of alloying or applying pressure.

3.4 The energy gap

Another remarkable finding of the BCS theory is that it predicts a relationship of T_{c} with the energy gap E_{g}, also denoted by 2Δ in some literature, which is given by

$$E_{\mathrm{g}}(0) \approx 3.5\, k_{\mathrm{B}} T_{\mathrm{c}}. \tag{96}$$

It is interesting to note that the energy gap normalized to the zero temperature value when plotted for various superconductors against the reduced temperature, T/T_{c} lie on a

Table 1: Measured energy gap ratio $E_{\mathrm{g}}(0)/(k_{\mathrm{B}}T_{\mathrm{c}})$ for metal superconductors at zero temperature.

Metal	$E_{\mathrm{g}}(0)/(k_{\mathrm{B}}T_{\mathrm{c}})$	Metal	$E_{\mathrm{g}}(0)/(k_{\mathrm{B}}T_{\mathrm{c}})$
Aluminum	3.3	Tin	3.5
Zinc	3.2	Mercury	4.6
Gallium	3.5	Vanadium	3.4
Cadmium	3.2	Molybdenum	3.4
Indium	3.6	Lanthanum	3.7

single universal curve. Experimental values of $E_{\mathrm{g}}(0)$ for different materials and different directions in k space generally fall in the range from $3.0\,k_{\mathrm{B}}T_{\mathrm{c}}$ to $4.5\,k_{\mathrm{B}}T_{\mathrm{c}}$ with most clustered near the BCS value $3.5\,k_{\mathrm{B}}T_{\mathrm{c}}$ (Figure 10). The energy gap at $T = 0$ is almost independent of temperature. Close to T_{c}, gap versus temperature relationship is given by

$$E_{\mathrm{g}}(T) \approx 3.2\,k_{\mathrm{B}}T_{\mathrm{c}} \left(1 - \frac{T}{T_{\mathrm{c}}}\right)^{1/2}. \tag{97}$$

Strictly speaking, this universal curve holds only in a weak coupling limit, but it is a good approximation in most cases.

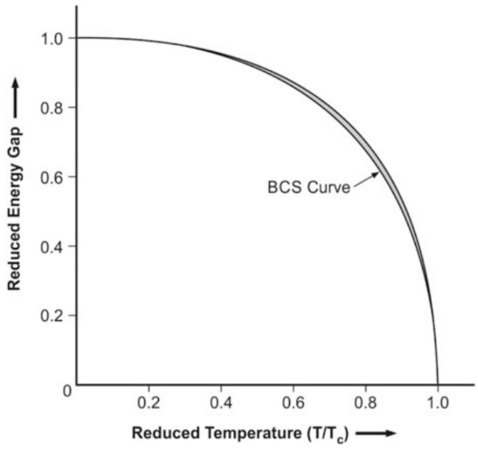

Figure 10: Reduced energy gap $E_{\mathrm{g}}(T)/E_{\mathrm{g}}(0)$ plotted against the reduced temperature T/T_{c} for most metal superconductors lie on a universal curve and fit well with BCS theory within the width in the curve. [R.G. Sharma]

References

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