

9 Superconductivity

9.1 Introduction

So far in this lecture we have considered materials as many-body “mix” of electrons and ions. The key approximations that we have made are

- the Born-Oppenheimer approximation that allowed us to separate electronic and ionic degrees of freedom and to concentrate on the solution of the electronic many-body Hamiltonian with the nuclei only entering parameterically.
- the independent-electron approximation, which greatly simplifies the theoretical description and facilitates our understanding of matter. For density-functional theory we have shown in Chapter 3 that the independent-electron approximation is always possible for the many-electron ground state.
- that the independent quasiparticle can be seen as a simple extension of the independent-electron approximation (e.g. photoemission, Fermi liquid theory for metals, etc.).

We have also considered cases in which these approximations break down. The treatment of electron-phonon (or electron-nuclei) coupling, for example, requires a more sophisticated approach, as we saw. Also most magnetic orderings are many-body phenomena. In Chapter 8 we studied, for example, how spin coupling is introduced through the many-body form of the wave function.

In 1911 H. Kamerlingh Onnes discovered superconductivity in Leiden. He observed that the electrical resistance of various metals such as mercury, lead and tin disappeared completely at low enough temperatures (see Fig. 9.1). Instead of dropping off as T^5 to a finite

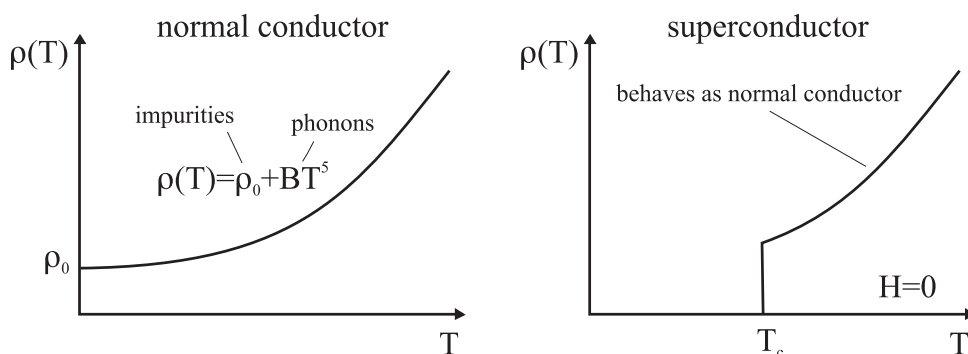


Figure 9.1: The resistivity of a normal (left) and a superconductor (right) as a function of temperature.

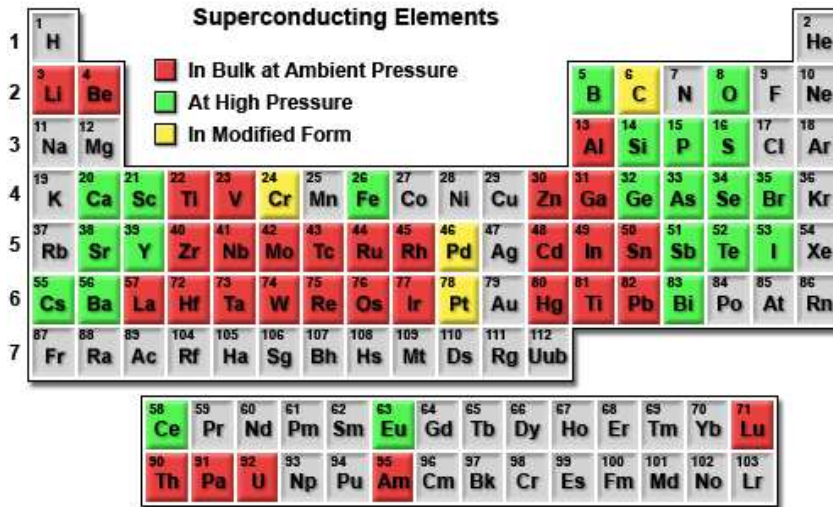


Figure 9.2: Superconducting elements in the periodic table. From *Center for Integrated Research & Learning*.

| element | Hg (α) | Sn | Pb | Nb |
|----------|-----------------|------|------|------|
| T_c /K | 4.15 | 3.72 | 7.19 | 9.26 |

Table 9.1: Critical temperatures in Kelvin for selected elemental superconductor.

resistivity that is given by impurity scattering in normal metals, the resistivity of superconductors drops sharply to zero at a critical temperature T_c . The record for the longest unstained current in a material is now 2 1/2 years. However, according to the theories for ordinary metals developed in this lecture, perfect conductivity should not exist at $T > 0$. Moreover, superconductivity is not an isolated phenomenon. Figure 9.2 shows the elements in the periodic table that exhibit superconductivity, which is surprisingly large. Much larger, in fact, than the number of ferromagnetic elements in Fig. 8.1. However, compared to the ferromagnetic transition temperatures discussed in the previous Chapter typical critical temperatures for elemental superconductors are very low (see Tab. 9.1).

The phenomenon of superconductivity eluded a proper understanding and theoretical description for many decades, which did not emerge until the 1950s and 1960s. Then in 1986 the picture that had been developed for “classical” superconductor was turned on its head by the discovery of high temperature superconductivity by Bednorz and Müller. This led to a sudden jump in achievable critical temperatures as Fig. 9.3 illustrates. The record now lies upwards of 150 Kelvin, but although this is significantly higher than what has so far been achieved with “conventional” superconductors (red symbols in Fig. 9.3), the dream of room temperature superconductivity still remains elusive. What also remains elusive is the mechanism that leads to high temperature superconductivity. In this Chapter we will therefore focus on “classical” or “conventional” superconductivity and recap the most important historic steps that led to the formulation of the BCS (Bardeen, Cooper, and Schrieffer) theory of superconductivity. Suggested reading for this Chapter are the books by A. S. Alexandrov *Theory of Superconductivity – From Weak to Strong Coupling*, M. Tinkham *Introduction to Superconductivity* and D. L. Goodstein *States of Matter*.

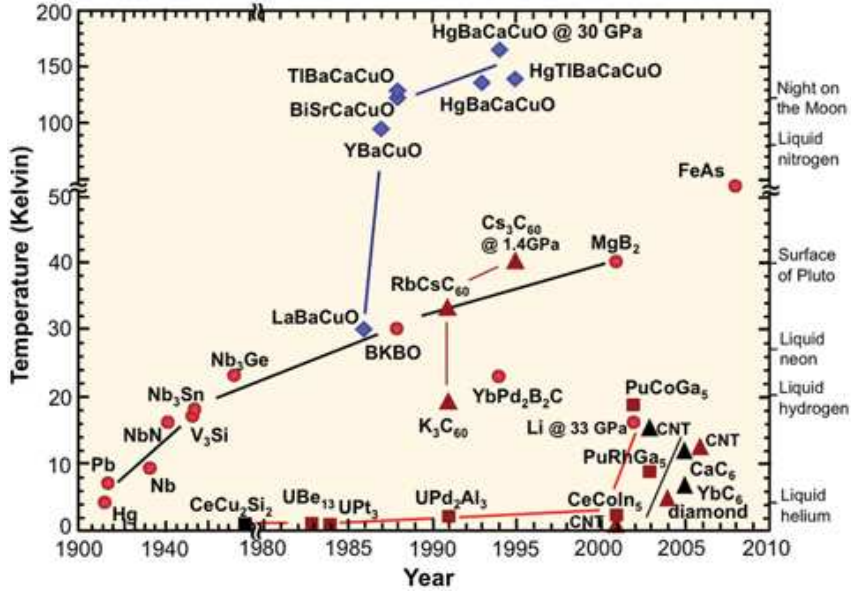


Figure 9.3: Timeline of superconducting materials and their critical temperature. Red symbols mark conventional superconductors and blue high temperature superconductors. From *Wikipedia*.

9.2 Meissner effect

Perfect conductivity is certainly the first hallmark of superconductivity. The next hallmark was discovered in 1933 by Meissner and Ochsenfeld. They observed that in the superconducting state the material behaves like a perfect *diamagnet*. Not only can an external field not enter the superconductor, which could still be explained by perfect conductivity, but also a field that was originally present in the normal state is expelled in the superconducting state (see Fig. 9.4). Expressed in the language of the previous Chapter this implies

$$\mathbf{B} = \mu_0 \mu \mathbf{H} = \mu_0 (1 + \chi) \mathbf{H} = 0 \quad (9.1)$$

and therefore $\chi = -1$, which is not only diamagnetic, but also very large. The expulsion of a magnetic field cannot be explained by perfect conductivity, which would tend to trap flux. The existence of such a reversible *Meissner effect* implies that superconductivity will be destroyed by a critical magnetic field H_c . The phase diagram of such a superconductor (denoted type I, as we will see in the following) is shown in Fig. 9.5.

To understand this odd behavior we first consider a perfect conductor. However, we assume that only a certain portion n_s of all electrons conduct perfectly. All others conduct dissipatively. In an electric field \mathbf{E} the electrons will be accelerated

$$m \frac{d\mathbf{v}_s}{dt} = -e\mathbf{E} \quad (9.2)$$

and the current density is given by $\mathbf{j} = -e\mathbf{v}_s n_s$. Inserting this into eq. 9.2 gives

$$\frac{d\mathbf{j}}{dt} = \frac{n_s e^2}{m} \mathbf{E} \quad (9.3)$$

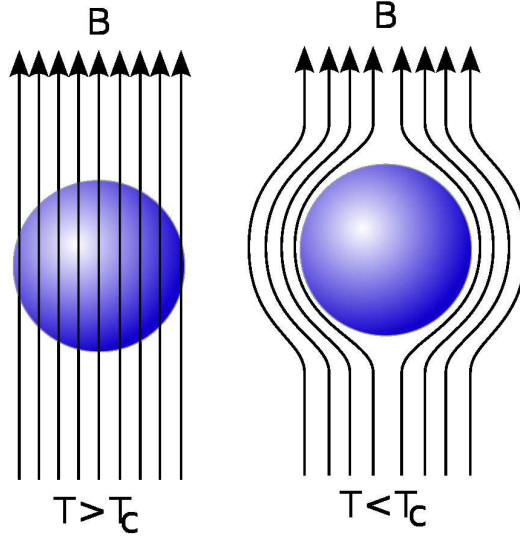


Figure 9.4: Diagram of the Meissner effect. Magnetic field lines, represented as arrows, are excluded from a superconductor when it is below its critical temperature.

Substituting this into Faraday's law of induction

$$\nabla \times \mathbf{E} = -\frac{1}{c} \frac{\partial B}{\partial t} \quad (9.4)$$

we obtain

$$\frac{\partial}{\partial t} \left(\nabla \times \mathbf{j} + \frac{n_s e^2}{mc} \mathbf{B} \right) = 0 \quad . \quad (9.5)$$

Together with Maxwell's equation

$$\nabla \times \mathbf{B} = \frac{4\pi}{c} \mathbf{j} \quad (9.6)$$

this determines the fields and currents that can exist in the superconductor. Eq. 9.5 tells us that any change in the magnetic field B will be screened immediately. This is consistent with Meissner's and Ochsensfeld's observation. However, there are static currents and magnetic fields that satisfy the two equations. This is inconsistent with the observation that fields are expelled from the superconducting region. Therefore perfect conductivity alone does not explain the Meissner effect.

To solve this conundrum F. and H. London proposed to restrict the solutions for superconductors to fields and currents that satisfy

$$\nabla \times \mathbf{j} + \frac{n_s e^2}{mc} \mathbf{B} = 0 \quad . \quad (9.7)$$

This equation is known as London equation and inserting it into Maxwell's equation yields

$$\nabla \times (\nabla \times \mathbf{B}) + \frac{4\pi n_s e^2}{mc^2} \mathbf{B} = 0 \quad . \quad (9.8)$$

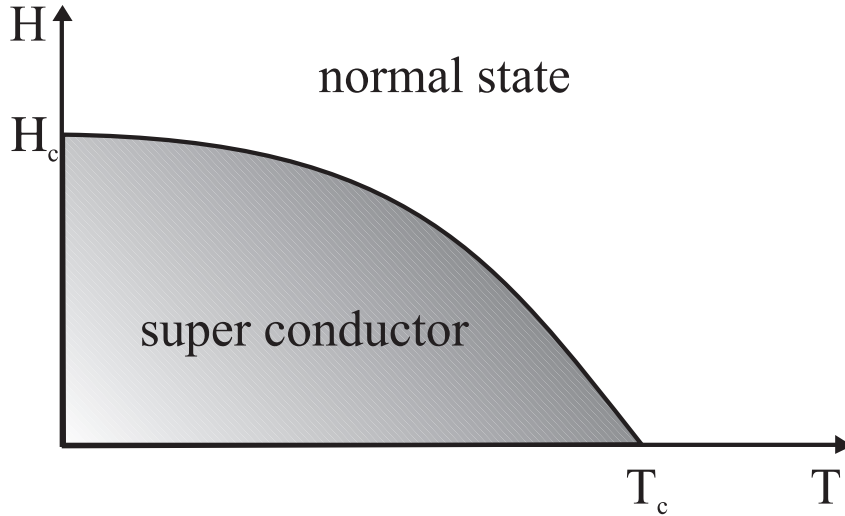


Figure 9.5: The phase diagram of a type I superconductor as a function temperature and the magnetic field H .

Using the relation $\nabla \times (\nabla \times \mathbf{B}) = \nabla(\nabla \cdot \mathbf{B}) - \nabla^2 \mathbf{B}$ and applying Gauss' law $\nabla \cdot \mathbf{B} = 0$ we obtain

$$\nabla^2 \mathbf{B} = \frac{4\pi n_s e^2}{mc^2} \mathbf{B} \quad . \quad (9.9)$$

For the solution of this differential equation we consider a half infinite superconductor ($x > 0$). The magnetic field then decays exponentially

$$\mathbf{B}(x) = \mathbf{B}(0)e^{-\frac{x}{\lambda_L}} \quad , \quad (9.10)$$

where the London penetration depth is given by

$$\lambda_L = \sqrt{\frac{mc^2}{4\pi n_s e^2}} = 41.9 \left(\frac{r_s}{a_0}\right)^{\frac{3}{2}} \left(\frac{n}{n_s}\right)^{\frac{1}{2}} \text{ \AA} \quad . \quad (9.11)$$

The magnetic field at the boarder between a normal material and a superconductor is shown schematically in Fig. 9.6. Inside the superconductor the field is expelled from the superconductor by eddy currents at its surface. The field subsequently decays exponentially fast. The decay length is given by the London penetration depth, which for typical superconductors is of the order of 10^2 to 10^3 \AA. Although London's explanation phenomenologically explains the Meissner effect it begs the question if we can create a microscopic theory (i.e. version of London's equation) that goes beyond standard electrodynamics. And how can we create a phase transition in the electronic structure that leads to the absence of all scattering.

9.3 London theory

F. London first noticed that a degenerate Bose-Einstein gas provides a good basis for a phenomenological model of superconductivity. F. and H. London then proposed a quantum mechanical analog of London's electrodynamic derivation shown in the previous section.

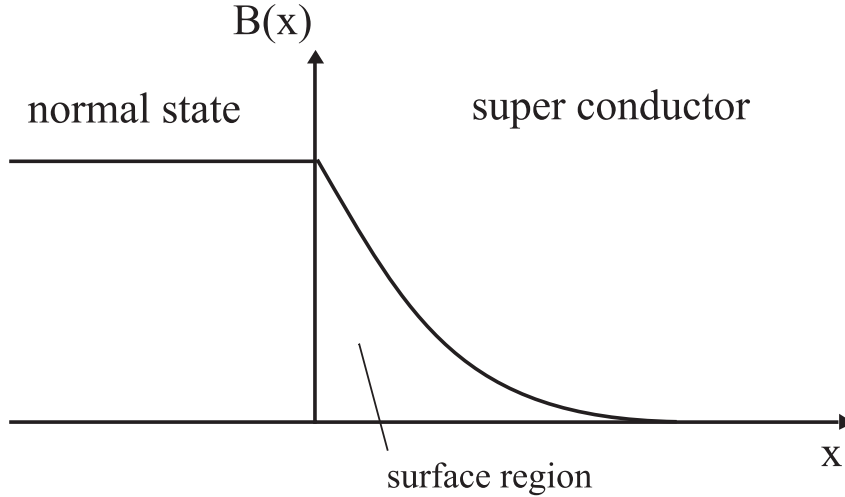


Figure 9.6: The magnetic field inside a type I superconductor drops off exponentially fast from its surface.

They showed that the Meissner effect could be interpreted very simply by a peculiar coupling in momentum space, as if there was something like a condensed phase of the Bose gas. The idea to replace Fermi statistics by Bose statistics in the theory of metals led them to an equation for the current, which turned out to be microscopically exact. The quantum mechanical current density is given by

$$\mathbf{j}(\mathbf{r}) = \frac{ie}{2m} (\psi^* \nabla \psi - \psi \nabla \psi^*) - \frac{e^2}{m} \mathbf{A} \psi^* \psi \quad (9.12)$$

where $\mathbf{A} \equiv \mathbf{A}(\mathbf{r})$ is a vector potential such that $\nabla \times \mathbf{A} = \mathbf{B}$. One should sum this expression over all electron states below the Fermi level of the normal metal. If the particles governed by the wave functions ψ in this expression were electrons we would only observe weak Landau diamagnetism (see previous Chapter). So let us instead assume bosons with charge e^* and mass m^* . They satisfy their Schrödinger equation

$$-\frac{1}{2m^*} (\nabla + ie^* \mathbf{A}) \phi(\mathbf{r}) = E \phi(\mathbf{r}) \quad . \quad (9.13)$$

Choosing the Maxwell gauge for the vector field ($\nabla \cdot \mathbf{A} = 0$) we obtain

$$\left(-\frac{1}{2m^*} \nabla^2 - \frac{ie^*}{m^*} \mathbf{A} \nabla + \frac{e^*}{2m^*} \mathbf{A}^2 \right) \phi(\mathbf{r}) = E \phi(\mathbf{r}) \quad . \quad (9.14)$$

Now we assume \mathbf{A} to be small so that we can apply perturbation theory

$$\phi(\mathbf{r}) = \phi_0(\mathbf{r}) + \phi_l(\mathbf{r}) \quad , \quad (9.15)$$

where $\phi_0(\mathbf{r})$ is the ground state wave function in the absence of the field and $\phi_l(\mathbf{r})$ the perturbation introduced by \mathbf{A} . We know from the theory of Bose condensates that at low temperatures the condensate wave function is a constant

$$\phi_0(\mathbf{r}) = \frac{1}{\sqrt{V}}, \quad \mathbf{k} = 0, E_0 = 0, \quad (9.16)$$

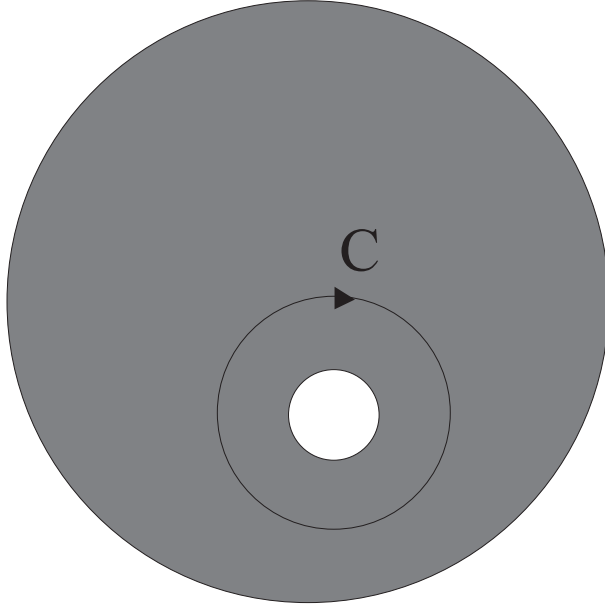


Figure 9.7: Flux trapped in a hole in a superconductor is quantized.

where V is the volume of the condensate. Next we insert eq. 9.15 into eq. 9.14 and expand to first order in \mathbf{A} and ϕ_l

$$-\frac{1}{2m^*}\nabla^2\phi_0(\mathbf{r}) - \frac{1}{2m^*}\nabla^2\phi_l(\mathbf{r}) - \frac{ie^*}{m^*}\mathbf{A}\nabla\phi_0(\mathbf{r}) = E_0\phi_l(\mathbf{r}) + E_1\phi_0(\mathbf{r}) \quad . \quad (9.17)$$

The first and third term on the left hand side of this equation and the first term on the right hand side are zero. Since we are first order in \mathbf{A} , E_1 has to be proportional to \mathbf{A} and because E_1 is a scalar our only choice is for it to be proportional to $\nabla\mathbf{A}$. This means it vanishes in the Maxwell gauge and $\phi_l(\mathbf{r}) = 0$ to first order in \mathbf{A} . Inserting $\phi(\mathbf{r}) = \phi_0(\mathbf{r})$ into the equation for the current density (eq. 9.12) the term in brackets evaluates to zero and we are left with

$$\mathbf{j}(\mathbf{r}) = -\frac{e^{*2}}{2m^*}\frac{N_s}{V}\mathbf{A} = -\frac{e^{*2}n_s}{2m^*}\mathbf{A} \quad . \quad (9.18)$$

With $\nabla \times \mathbf{A} = \mathbf{B}$ and Maxwell's equation $\nabla \times \mathbf{B} = \frac{4\pi}{c}\mathbf{j}$ we finally arrive at

$$\mathbf{B} + \lambda_L\nabla \times \nabla\mathbf{B} = 0, \quad (9.19)$$

which is identical to the London equation derived from electrodynamics in the previous section (cf eq. 9.8). We now have a quantum mechanical derivation of the London equation and the London penetration depth and we have identified the carriers in the superconducting state to be bosons. However, this begs the question where these bosons come from?

9.4 Flux quantization

If the superconducting state is a condensate of Bosons, as proposed by London, then its wave function is of the form

$$\phi(\mathbf{r}) = \sqrt{n_s}e^{-i\varphi(\mathbf{r})} \quad . \quad (9.20)$$

n_s is the superconducting density, that we introduced in section 9.2 and which we assume to be constant throughout the superconducting region. $\varphi(\mathbf{r})$ is the phase factor of the wave function, which is yet undetermined. To pin down the phase let us consider a hole in our superconductor (cf Fig. 9.7) or alternatively a superconducting ring. The magnetic flux through this hole is

$$\Phi_B = \int_{surf} d\mathbf{s} \mathbf{B} = \int_{surf} d\mathbf{s} \nabla \times \mathbf{A}(\mathbf{r}) = \oint_C d\mathbf{l} \mathbf{A}(\mathbf{r}), \quad (9.21)$$

where we have used Stoke's theorem to convert the surface integral into the line integral over the contour C . But according to London's theory the magnetic field inside the superconductor falls off exponential so that we can find a contour on which \mathbf{B} and \mathbf{j} are zero. Using the equation for the current density (eq. 9.12) this yields

$$0 = \mathbf{j}(\mathbf{r}) = \frac{ie^*}{2m^*} (\psi^* \nabla \psi - \psi \nabla \psi^*) - \frac{e^{*2}}{m^*} \mathbf{A} \psi^* \psi. \quad (9.22)$$

Inserting our wave function (eq. 9.20) for the condensate gives the following equation for the phase

$$\frac{ie^*}{2m^*} (i\nabla\varphi\phi^*\phi + i\nabla\varphi\phi\phi^*) - \frac{e^{*2}}{m^*} \mathbf{A}\phi^*\phi = 0 \quad (9.23)$$

or

$$-\frac{e^*}{m^*} \phi^* \phi (\nabla\varphi + e^* \mathbf{A}) = 0. \quad (9.24)$$

This implies that there is a relation between the phase and the vector potential

$$\mathbf{A}(\mathbf{r}) = -\frac{\nabla\varphi(\mathbf{r})}{e^*}. \quad (9.25)$$

Inserting this result into our expression for the magnetic flux (eq. 9.21) we finally obtain

$$\Phi_B = -\oint_C d\mathbf{l} \frac{\nabla\varphi}{e^*} = \frac{\delta\varphi}{e^*}. \quad (9.26)$$

Here $\delta\varphi$ is the change of the phase in the round trip along the contour, which is only given up to modulo 2π : $\delta\varphi = 2\pi p$ with $p=0, 1, 2, \dots$. This means the magnetic flux is quantized

$$\Phi_B = \frac{2\pi\hbar c}{e^*} p. \quad (9.27)$$

Experimentally this was confirmed by Deaver and Fairbank in 1961 who found $e^* = 2e$!

9.5 Ogg's pairs

Recapping at this point, we have learned that the superconducting state is made up of bosons with twice the electron charge. This led Richard Ogg Jr to propose in 1946 that electrons might pair in real space. Like for the hydrogen molecule discussed in section 8.4.4.1 the two electrons could pair chemically and form a boson with spin $S=0$ or 1. Ogg suggested that an ensemble of such two-electron entities could, in principle, form a superconducting Bose-Einstein condensate. The idea was motivated by his demonstration

that electron pairs were a stable constituent of fairly dilute solutions of alkali metals in liquid ammonia. The theory was further developed by Schafroth, Butler and Blatt, but did not produce a quantitative description of superconductivity (e.g. the T_c of $\sim 10^4$ K is much too high). The theory could also not provide a microscopic force to explain the pairing of normally repulsive electrons. It was therefore concluded that electron pairing in real-space does not work and the theory was forgotten.

9.6 Microscopic theory - BCS theory

9.6.1 Cooper pairs

The basic idea behind the weak attraction between two electrons was presented by Cooper in 1956. He showed that the Fermi sea of electrons is unstable against the formation of at least one bound pair, regardless of how weak the interaction is, so long as it is attractive. This result is a consequence of Fermi statistics and of the existence of the Fermi-sea background, since it is well known that binding does not ordinarily occur in the two-body problem in three dimensions until the strength of the potential exceeds a finite threshold value.

To see how the binding comes about, we consider the model of two quasiparticles with momentum \mathbf{k} and $-\mathbf{k}$ in a Fermi liquid (e.g. free-electron metal). The spatial part of the two-particle wave function of this pair is then

$$\psi_0(\mathbf{r}_1, \mathbf{r}_2) = \sum_{\mathbf{k}} g_{\mathbf{k}} e^{i\mathbf{k}\mathbf{r}_1} e^{-i\mathbf{k}\mathbf{r}_2} . \quad (9.28)$$

For the spin part we assume singlet pairing $|\chi_{\text{spin}} \rangle_S = 2^{-1/2} (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$ (see also section 8.4.4.1), which gives us $\mathbf{S}=0$, i.e. a boson. The triplet with $\mathbf{S}=1$ would also be possible, but is of higher energy for conventional superconductors (see e.g. unconventional superconductivity). $|\chi_{\text{spin}} \rangle_S$ is antisymmetric with respect to particle exchange and $\psi_0(\mathbf{r}_1, \mathbf{r}_2)$ therefore has to be symmetric:

$$\psi_0(\mathbf{r}_1, \mathbf{r}_2) = \sum_{\mathbf{k} > \mathbf{k}_F} g_{\mathbf{k}} \cos \mathbf{k}(\mathbf{r}_1 - \mathbf{r}_2) . \quad (9.29)$$

If we insert this wave function into our two-particle Schrödinger equation

$$\left[\sum_{i=1,2} \frac{\mathbf{p}_i^2}{2m} + V(\mathbf{r}_1, \mathbf{r}_2) \right] \psi_0 = E\psi_0 \quad (9.30)$$

we obtain

$$(E - 2\epsilon_{\mathbf{k}})g_{\mathbf{k}} = \sum_{\mathbf{k}' > \mathbf{k}_F} V_{\mathbf{k}\mathbf{k}'} g_{\mathbf{k}'} . \quad (9.31)$$

$V_{\mathbf{k}\mathbf{k}'}$ is the characteristic strength of the scattering potential and is given by the Fourier transform of the potential V

$$V_{\mathbf{k}\mathbf{k}'} = \frac{1}{\Omega} \int d\mathbf{r} V(\mathbf{r}) e^{-(\mathbf{k}-\mathbf{k}')\mathbf{r}} \quad (9.32)$$

with $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$ and Ω the normalized volume. The energies $\epsilon_{\mathbf{k}}$ in eq. 9.31 are the unperturbed plane-wave energies and are larger than ϵ_F , because the sum runs over $\mathbf{k} > \mathbf{k}_F$. If a set of $g_{\mathbf{k}}$ exists such that $E < 2\epsilon_F$ then we would have a bound state of two electrons.

But how can this be? Recall that the Fourier transform of the bare Coulomb potential (i.e. free electrons) is

$$V_{\mathbf{k}\mathbf{k}'} = V_{\mathbf{q}=\mathbf{k}-\mathbf{k}'} = \frac{4\pi^2}{\mathbf{q}^2} > 0. \quad (9.33)$$

This is always larger than zero and therefore not attractive, as expected. However, quasi-particles are not free electrons and are screened by the electron sea. Let us consider Thomas-Fermi screening introduced in Chapter 3. The dielectric function becomes

$$\varepsilon(\mathbf{k}) = \frac{\mathbf{k}^2 + \mathbf{k}_0^2}{\mathbf{k}^2} \neq 1. \quad (9.34)$$

The bare Coulomb potential is screened by ε

$$V(\mathbf{r}_1 - \mathbf{r}_2) = \frac{\varepsilon^{-1}(\mathbf{r}_1 - \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}. \quad (9.35)$$

Its Fourier transform

$$V_{\mathbf{q}} = \frac{4\pi^2}{\mathbf{q}^2 + \mathbf{k}_0^2} \quad (9.36)$$

is still positive, but now reduced compared to the bare Coulomb interaction. Building on the idea of screening we should also consider the ion cores. They are positively charged and also move to screen the negative charge of our electron pair. However, their “reaction speed” is much smaller than those of the electrons and of the order of typical phonon frequencies. A rough estimate (see e.g. Ashcroft Chapter 26) to further screen the Thomas-Fermi expression could look like

$$V_{\mathbf{q}} = \frac{4\pi^2}{\mathbf{q}^2 + \mathbf{k}_0^2} \left(1 + \frac{\omega^2}{\omega^2 - \omega_{\mathbf{q}}^2} \right), \quad (9.37)$$

where $\omega_{\mathbf{q}}$ is a phonon frequency of wave vector \mathbf{q} and $\omega = \frac{1}{\hbar}(\epsilon_{\mathbf{k}} - \epsilon'_{\mathbf{k}})$. If now $\omega < \omega_{\mathbf{q}}$ this (oversimplified) potential would be negative and therefore attractive. In other words, phonons could provide our attractive interaction that is schematically depicted in Fig. 9.8. At normal temperatures, the positive ions in a superconducting material vibrate away on the spot and constantly collide with the electron bath around them. It is these collisions that cause the electrical resistance that wastes energy and produces heat in any normal circuit. But the cooler the material gets, the less energy the ions have, so the less they vibrate. When the material reaches its critical temperature, the ions’ vibrations are incredibly weak and no longer the dominant form of motion in the lattice. The tiny attractive force of passing electrons that’s always been there is suddenly enough to drag the positive ions out of position towards them. And that dragging affects the behaviour of the solid as a whole. When positive ions are drawn towards a passing electron, they create an area that is more positive than their surroundings, so another nearby electron is drawn towards them. However, those electrons are on the move, so by the time the second one has arrived the first one has moved on and created a path of higher positivity that

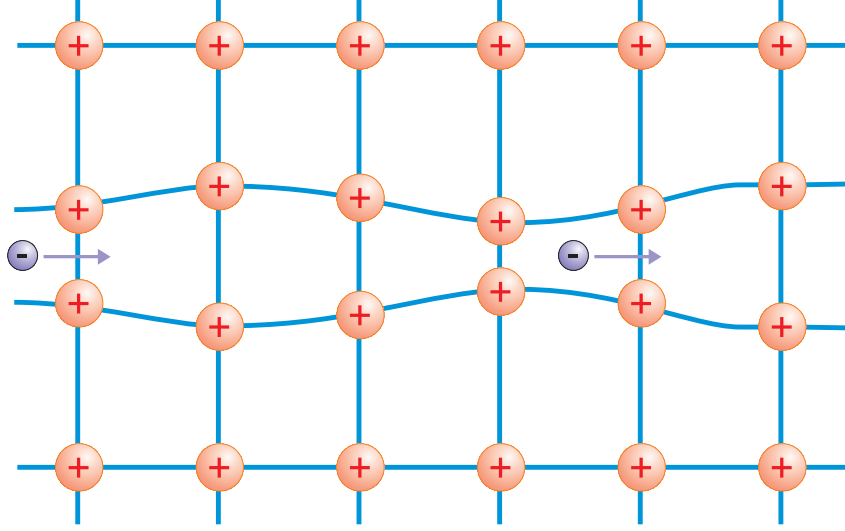


Figure 9.8: Cooper pair formation schematically: at extremely low temperatures, an electron can draw the positive ions in a superconductor towards it. This movement of the ions creates a more positive region that attracts another electron to the area.

the second electron keeps on following. The electrons are hitched in a game of catch-up that lasts as long as the temperature stays low.

To proceed Cooper then further simplified the potential

$$V_{\mathbf{k}\mathbf{k}'} = \begin{cases} -V & \text{for } |\epsilon_{\mathbf{k}} - \epsilon_F|, |\epsilon_{\mathbf{k}'} - \epsilon_F| < \hbar\omega_c \\ 0 & \text{otherwise} \end{cases} \quad (9.38)$$

where ω_c is the Debye frequency. Now V pulls out of the sum on the right-hand side of eq. 9.31 and we can rearrange for $g_{\mathbf{k}}$:

$$g_{\mathbf{k}} = V \frac{\sum_{\mathbf{k}'} g_{\mathbf{k}'}}{E - 2\epsilon_{\mathbf{k}}}. \quad (9.39)$$

Applying $\sum_{\mathbf{k}}$ on both sides and canceling $\sum_{\mathbf{k}} g_{\mathbf{k}}$ we obtain

$$\frac{1}{V} = \sum_{\mathbf{k} > \mathbf{k}_F} (2\epsilon_{\mathbf{k}} - E)^{-1}. \quad (9.40)$$

Replacing the sum by an integral yields

$$\frac{1}{V} = \int_{\epsilon_F}^{\epsilon_F + \hbar\omega_c} d\epsilon N(\epsilon) \frac{1}{2\epsilon - E} \approx \frac{1}{2} N(\epsilon_F) \ln \frac{2\epsilon_F - E + 2\hbar\omega_c}{2\epsilon_F - E} \quad (9.41)$$

where we have made the assumption $N(\epsilon) \approx N(\epsilon_F)$. Solving this expression for E we obtain

$$E(e^{-\frac{2}{N\hbar\omega_c}} - 1) = 2\epsilon_F(e^{-\frac{2}{N\hbar\omega_c}} - 1) + 2\hbar\omega_c e^{-\frac{2}{N\hbar\omega_c}}. \quad (9.42)$$

Now we make the “weak coupling” approximation $N(\epsilon_F)V \ll 1$ such that $1 - e^{-\frac{2}{N\hbar\omega_c}} \approx 1$ to arrive at the final expression

$$E \approx 2\epsilon_F - 2\hbar\omega_c e^{-\frac{2}{N\hbar\omega_c}} < 2\epsilon_F. \quad (9.43)$$

We see that we indeed find a bound state, in which the binding outweighs the gain in kinetic energy for states above ϵ_F , regardless of how small V is. It is important to note that the binding energy is not analytic at $V = 0$, i.e. it cannot be expanded in powers of V . This means that perturbation theory is not applicable, which slowed down the development of the theory significantly. With view to the Ogg pairs discussed in section 9.5 we note that the Cooper pair is bound in reciprocal space:

$$\psi_0 = \sum_{\mathbf{k} > \mathbf{k}_F} g_{\mathbf{k}} \cos \mathbf{k}(\mathbf{r}_1 - \mathbf{r}_2) \quad (9.44)$$

$$\sim \sum_{\mathbf{k} > \mathbf{k}_F} \frac{V}{2(\epsilon_k - \epsilon_F) + 2\epsilon_F - E} \cos \mathbf{k}(\mathbf{r}_1 - \mathbf{r}_2) \quad (9.45)$$

The denominator assumes its maximum value for electrons at the Fermi level and falls off from there. Thus the electron states within a range $2\epsilon_F - E$ above ϵ_F are those most strongly involved in forming the bound states.

9.7 Bardeen-Cooper-Schrieffer (BCS) Theory

Having seen that the Fermi sea is unstable against formation of a bound Cooper pair when the net interaction is attractive, we then expect pairs to condense until an equilibrium point is reached. This will occur when the state of the system is so greatly changed from the Fermi sea due to the large number of pairs that the binding energy for an additional pair has gone to zero. The wave function for such a state appears to be quite complex and it was the ingenuity of Bardeen, Cooper and Schrieffer to develop it. The basic idea is to create the total many-electron wave function from the pair wave functions ϕ we discussed in the previous section

$$\Psi = \phi(\mathbf{r}_1\sigma_1, \mathbf{r}_2\sigma_2)\phi(\mathbf{r}_3\sigma_3, \mathbf{r}_4\sigma_4) \dots \phi(\mathbf{r}_{N-1}\sigma_{N-1}, \mathbf{r}_N\sigma_N) \quad (9.46)$$

and then to antisymmetrize ($\Psi_{\text{BCS}} = \hat{A}\Psi$). The coefficients of Ψ_{BCS} could then be found by minimizing the total energy of the many-body Hamiltonian. BCS introduced a simplified *pairing* Hamiltonian

$$H = \sum_{\mathbf{k}, \sigma} \xi_{\mathbf{k}} c_{\mathbf{k}\sigma}^\dagger c_{\mathbf{k}\sigma} \sum_{\mathbf{k}\mathbf{k}'} c_{\mathbf{k}\uparrow}^\dagger c_{-\mathbf{k}\downarrow}^\dagger V_{\mathbf{k}\mathbf{k}'} c_{-\mathbf{k}'\downarrow} c_{\mathbf{k}'\uparrow} \quad (9.47)$$

with $\xi = \epsilon_{\mathbf{k}} - \epsilon_F$ and the usual creation and annihilation operators $c_{\mathbf{k}\sigma}^\dagger$ and $c_{\mathbf{k}\sigma}$. $V_{\mathbf{k}\mathbf{k}'}$ is our attractive interaction, but it is restricted to $(\mathbf{k} \uparrow, -\mathbf{k} \downarrow)$ pairs. The minimization is doable, but maybe not too illustrative. Instead we will consider a mean-field approximation. We start with the observation that the characteristic BCS pairing Hamiltonian will lead to a ground state which is some phase-coherent superposition of many-body states with pairs of Bloch states $(\mathbf{k} \uparrow, -\mathbf{k} \downarrow)$ occupied or unoccupied units. Because of the coherence operators such as $-c_{-\mathbf{k}'\downarrow} c_{\mathbf{k}'\uparrow}$ can have nonzero expectation values $b_{\mathbf{k}} = \langle c_{-\mathbf{k}'\downarrow} c_{\mathbf{k}'\uparrow} \rangle_{\text{avg}}$ in such a state, rather than averaging to zero as in a normal metal, where the phases are random. Moreover, because of the large number of particles involved, the fluctuations about these expectation values should be small. This suggests that it will be useful to express such a product of operators formally as

$$c_{-\mathbf{k}'\downarrow} c_{\mathbf{k}'\uparrow} = b_{\mathbf{k}} + (c_{-\mathbf{k}'\downarrow} c_{\mathbf{k}'\uparrow} - b_{\mathbf{k}}) \quad (9.48)$$

and subsequently neglect quantities which are bilinear in the presumably small fluctuation term in parentheses. Making the following mean-field approximation for the potential term

$$\sum_{\mathbf{k}'} V_{\mathbf{k}\mathbf{k}'} c_{-\mathbf{k}'\downarrow} c_{\mathbf{k}'\uparrow} \approx -V \Theta(\hbar\omega_c - |\xi_{\mathbf{k}}|) \sum_{\mathbf{k}'} \Theta(\hbar\omega_c - |\xi_{\mathbf{k}'}|) \langle c_{-\mathbf{k}'\downarrow} c_{\mathbf{k}'\uparrow} \rangle_{\text{avg}} \quad (9.49)$$

$$=: \Delta_{\mathbf{k}} = \begin{cases} \Delta & \text{for } |\epsilon_{\mathbf{k}} - \epsilon_F|, |\epsilon_{\mathbf{k}'} - \epsilon_F| < \hbar\omega_c \\ 0 & \text{otherwise} \end{cases}, \quad (9.50)$$

inserting all into the BCS Hamiltonian we write and expanding to first order yields

$$H_{\text{MF}} = \sum_{\mathbf{k},\sigma} \xi_{\mathbf{k}} c_{\mathbf{k}\sigma}^\dagger c_{\mathbf{k}\sigma} + \sum_{\mathbf{k}\mathbf{k}'} V_{\mathbf{k}\mathbf{k}'} \left(c_{\mathbf{k}\uparrow}^\dagger c_{-\mathbf{k}\downarrow}^\dagger b_{\mathbf{k}'} + b_{\mathbf{k}}^\dagger c_{-\mathbf{k}'\downarrow} c_{\mathbf{k}'\uparrow} - b_{\mathbf{k}}^\dagger b_{\mathbf{k}'} \right) \quad (9.51)$$

$$= \sum_{\mathbf{k},\sigma} \xi_{\mathbf{k}} c_{\mathbf{k}\sigma}^\dagger c_{\mathbf{k}\sigma} - \sum_{\mathbf{k}} \left(\Delta_{\mathbf{k}} c_{\mathbf{k}\uparrow}^\dagger c_{-\mathbf{k}\downarrow}^\dagger + \Delta_{\mathbf{k}}^* c_{-\mathbf{k}'\downarrow} c_{\mathbf{k}'\uparrow} - \Delta_{\mathbf{k}} b_{\mathbf{k}}^\dagger \right). \quad (9.52)$$

This is an effective single pair Hamiltonian (two c-operators instead of four), which we can solve.

To diagonalize this mean-field Hamiltonian we define a suitable linear transformation onto a new set of Fermi operators

$$c_{\mathbf{k}\uparrow} = u_{\mathbf{k}} \alpha_{\mathbf{k}} + v_{\mathbf{k}} \beta_{\mathbf{k}}^\dagger \quad (9.53)$$

$$c_{-\mathbf{k}\downarrow} = u_{\mathbf{k}} \beta_{\mathbf{k}} - v_{\mathbf{k}} \alpha_{\mathbf{k}}^\dagger, \quad (9.54)$$

where $\alpha_{\mathbf{k}}$ and $\beta_{\mathbf{k}}$ are two types of new non-interacting Fermions (i.e. quasiparticles). The expansion coefficients are

$$u_{\mathbf{k}}^2 = \frac{1}{2} \left(1 + \frac{\xi_{\mathbf{k}}}{\tilde{\epsilon}_{\mathbf{k}}} \right) \quad (9.55)$$

$$v_{\mathbf{k}}^2 = \frac{1}{2} \left(1 - \frac{\xi_{\mathbf{k}}}{\tilde{\epsilon}_{\mathbf{k}}} \right) \quad (9.56)$$

$$u_{\mathbf{k}} v_{\mathbf{k}} = -\frac{\Delta_{\mathbf{k}}}{2\tilde{\epsilon}_{\mathbf{k}}} \quad (9.57)$$

and

$$\tilde{\epsilon}_{\mathbf{k}} = \sqrt{\xi_{\mathbf{k}}^2 + |\Delta_{\mathbf{k}}|^2}. \quad (9.58)$$

With this the transformed Hamiltonian becomes diagonal

$$H_{\text{MF}} = E_0 + \sum_{\mathbf{k}} \tilde{\epsilon}_{\mathbf{k}} (\alpha_{\mathbf{k}}^\dagger \alpha_{\mathbf{k}} + \beta_{\mathbf{k}}^\dagger \beta_{\mathbf{k}}) \quad (9.59)$$

with

$$E_0 = 2 \sum_{\mathbf{k}} (\xi_{\mathbf{k}} v_{\mathbf{k}} + \Delta_{\mathbf{k}} u_{\mathbf{k}} v_{\mathbf{k}}) + \frac{|\Delta|^2}{V}. \quad (9.60)$$

The order parameter Δ is given as before by

$$\Delta = -V \sum_{\mathbf{k}'} \Theta(\hbar\omega_c - |\xi_{\mathbf{k}'}|) \langle c_{-\mathbf{k}'\downarrow} c_{\mathbf{k}'\uparrow} \rangle_{\text{avg}}. \quad (9.61)$$

If we now replace $\langle c_{-\mathbf{k}'\downarrow}c_{\mathbf{k}'\uparrow} \rangle_{\text{avg}}$ by $\alpha_{\mathbf{k}}$ and $\beta_{\mathbf{k}}$ as given in eq. 9.53 and 9.54 we obtain the following relation

$$\Delta = V \sum_{\mathbf{k}'} \frac{\Delta}{\tilde{\epsilon}_{\mathbf{k}}} (1 - 2f_{\mathbf{k}'}) . \quad (9.62)$$

$f_{\mathbf{k}}$ is the quasiparticle distribution function $f_{\mathbf{k}} = \langle \alpha_{\mathbf{k}}^\dagger \alpha_{\mathbf{k}} \rangle = \langle \beta_{\mathbf{k}}^\dagger \beta_{\mathbf{k}} \rangle$. Unlike in the case of bare electrons the total average number of quasi-particles is not fixed. Therefore, their chemical potential is zero in thermal equilibrium. They do not interact so that

$$f_{\mathbf{k}} = \frac{1}{e^{\frac{\tilde{\epsilon}_{\mathbf{k}}}{k_B T}} + 1} . \quad (9.63)$$

We see that at $T=0$ $f_{\mathbf{k}} = 0$, so there are no quasiparticles in the ground state. This implies that E_0 is the ground state energy of the BCS superconductor at $T=0$.

To evaluate E_0 we need to know Δ . The trivial solution to eq. 9.61 is $\Delta = 0$. It corresponds to the normal state and gives

$$E_0 = 2 \sum_{\mathbf{k}} \xi_{\mathbf{k}} v_{\mathbf{k}}^2 = 2 \sum_{\mathbf{k}} \frac{1}{2} \left(1 - \frac{\xi_{\mathbf{k}}}{\tilde{\epsilon}_{\mathbf{k}}} \right) . \quad (9.64)$$

At $\Delta=0$ we have $\tilde{\epsilon}_{\mathbf{k}} = |\xi_{\mathbf{k}}|$ and therefore

$$E_0 = 2 \sum_{\xi_{\mathbf{k}} < 0} \xi_{\mathbf{k}} \quad (9.65)$$

as expected (the term for $|\mathbf{k}| > k_F$ gives zero since $\tilde{\epsilon}_{\mathbf{k}} = \xi_{\mathbf{k}}$). The non-trivial solution is obtained by canceling the obvious Δ from eq. 9.62:

$$1 = V \sum_{\mathbf{k}'} \frac{1}{\tilde{\epsilon}_{\mathbf{k}}} . \quad (9.66)$$

Since $\tilde{\epsilon}_{\mathbf{k}}$ still depends on Δ we solve for it, by replacing the sum ($\sum_{\mathbf{k}}$) by an integral ($\int d\mathbf{k}$) and then \mathbf{k} by energy ($\int d\epsilon N(\epsilon)$). We again approximate the density of states by its value at the Fermi level ($N(\epsilon) = N(\epsilon_F)$). This then yields

$$\frac{1}{N(\epsilon_F)V} = \int_0^{\hbar\omega_c} \frac{d\xi}{\sqrt{\Delta^2 + \xi^2}} = \sinh^{-1} \left(\frac{\hbar\omega_c}{\Delta} \right) . \quad (9.67)$$

Solving for Δ in the weak coupling limit $N(\epsilon_F)V \ll 1$ finally gives

$$\Delta = \frac{\hbar\omega_c}{\sinh \left(\frac{1}{N(\epsilon_F)V} \right)} \approx 2\hbar\omega_c e^{-\frac{1}{N(\epsilon_F)V}} . \quad (9.68)$$

Inserting everything into the equation for the ground state energy (eq. 9.60) we obtain for the condensation energy

$$E_c = E_0(\Delta \neq 0) - E_0(\Delta = 0) \quad (9.69)$$

$$\approx 2 \sum_{\xi_{\mathbf{k}} < 0} \xi_{\mathbf{k}} - \frac{1}{2} N(\epsilon_F) \Delta^2 - 2 \sum_{\xi_{\mathbf{k}} < 0} \xi_{\mathbf{k}} \quad (9.70)$$

$$= -\frac{1}{2} N(\epsilon_F) \Delta^2 < 0 . \quad (9.71)$$

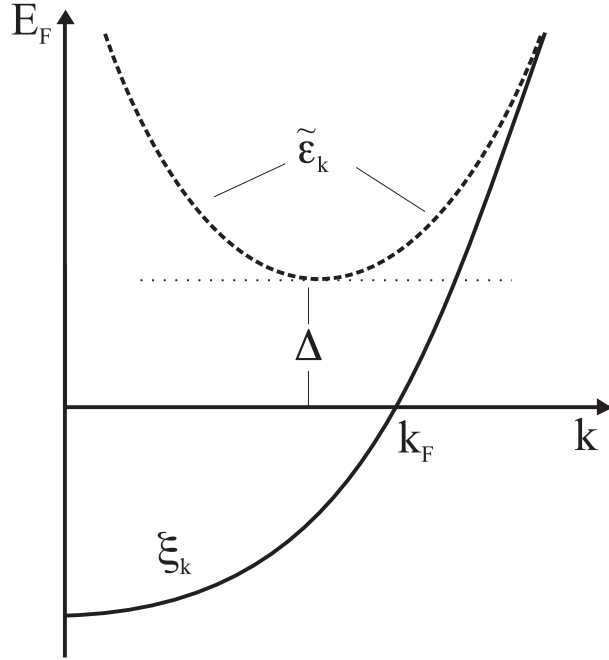


Figure 9.9: The dispersion of the Cooper pairs ($\tilde{\epsilon}_k$) is gapped and differs from that of the free electrons (ξ_k).

We see that the condensation energy is indeed smaller than zero at $T=0$ and therefore favors Cooper pair formation. $\Delta = \Delta(T)$ is called the order parameter that determines when superconductivity sets in. The order parameter also affects the dispersion of the quasiparticles. Recall eq. 9.58 ($\tilde{\epsilon}_k = \sqrt{\xi_k^2 + |\Delta_k|^2}$). Away from the Fermi surface, the quasiparticles α and β are electrons with up and down spin. In the vicinity of the Fermi surface they are a mixture of both and their energy dispersion is remarkably different from that of the non-interacting electrons and holes (see Fig. 9.9). Most importantly the dispersion now exhibits an energy gap. This is the energy to create a Cooper pair. The existence of an energy gap in the superconducting state was confirmed by the optical experiments of Glover and Tinkham in 1956/1957 and is seen as the first, decisive early verification of the BCS theory.

The second strong evidence for the existence of an energy gap is given by the temperature dependence of the heat capacity (shown in Fig. 9.10). Corak and co-workers had determined in 1954 and 1956 that the electronic specific heat in the superconducting state was dominated by an exponential dependence ($e^{-\frac{\Delta}{k_B T}}$), whereas in the normal state it followed the expected linear dependence with temperature expected for the conduction electrons of an ordinary metal.

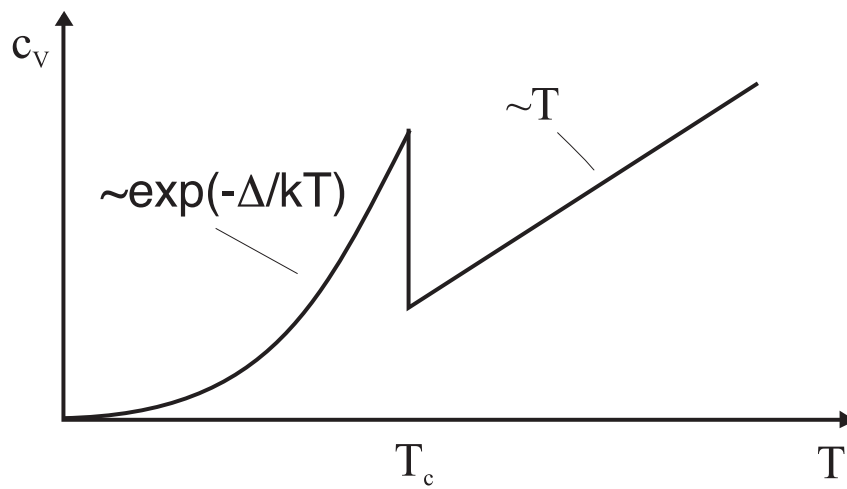


Figure 9.10: The heat capacity in the superconducting state exhibits an Einstein-like exponential behavior with temperature and assumes the linear behavior of a metal in the normal state.