THEORY OF SUPERCONDUCTIVITY

A Primer

by

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These lecture notes are dedicated, on the occassion of his eighties birthday on 4 July 2001,

to Musik Kaganov

who has done me the honor and delight of his friendship over decades and whom I owe a great part of an attitude towards Theoretical Physics.

Contents

1 INTRODUCTION

These lecture notes introduce into the *phenomenological and qualitative* theory of superconductivity. Nowhere any specific assumption on the microscopic mechanism of superconductivity is made although on a few occasions electron-phonon interaction is mentioned as an example. The theoretical presuppositions are exclusively guided by phenomena and kept to a minimum in order to arrive at results in a reasonably simple manner.

At present there are indications of non-phonon mechanisms of superconductivity, yet there is no hard proof up to now. The whole of this treatise would apply to any mechanism, possibly with indicated modifications, for instance a symmetry of the order parameter different from isotropy which has been chosen for the sake of simplicity.

This is a primer. For each considered phenomenon, only the simplest case is treated. References are given basically to the most important seminal original papers. Despite the above mentioned strict phenomenological approach the technical presentation is standard throughout, so that it readily compares to the existing literature.[1]

More advanced theoretical tools as field quantization and the quasi-particle concept are introduced to the needed level before they are used. Basic notions of Quantum Theory and of Thermodynamics (as well as of Statistical Physics in a few occasions) are presupposed as known.

In Chapter 2, after a short enumeration of the essential phenomena of superconductivity, the London theory is derived from the sole assumption that the supercurrent as an electrical current is a property of the quantum ground state. Thermoelectrics, electrodynamics and gauge properties are discussed.

With the help of simple thermodynamic relations, the condensation energy, the thermodynamic critical field and the specific heat are considered in Chapter 3.

In Chapter 4, the Ginsburg-Landau theory is introduced for spatially inhomogeneous situations, leading to Abrikosov's classification of all superconductors into types I and II. The simplest phase diagram of an isotropic type II superconductor is obtained in Chapter 5.

The Josephson effects are qualitatively considered on the basis of the Ginsburg-Landau theory in Chapter 6. Both, d.c. and a.c. effects are treated.

The remaining four chapters are devoted to the simplest phenomenological weak coupling theory of superconductivity on a microscopic level, the BCS theory, which provided the first quantum theoretical understanding of superconductivity, 46 years after the experimental discovery of the phenomenon. For this purpose, in Chapter 7 the Fock space and the concept of field quantization is introduced. Then, in Chapter 8, the Cooper theorem and the BCS model are treated with occupation number operators of quasi-particle states which latter are introduced as a working approximation in Solid State Physics. The nature of the charged bosonic condensate, phenomenologically introduced in Chapter 2, is derived in Chapter 9 as the condensate of Cooper pairs. The excitation gap as a function of temperature is here the essential result. The treatise is closed with a consideration of basic examples of the important notion of coherence factors.

By specifying more details as lower point symmetry, real structure features of the solid (for instance causing pinning of vortex lines) and many more, a lot of additional theoretical considerations would be possible without specifying the microscopic mechanism of the attractive interaction leading to superconductivity. However, these are just the notes of a one-term two-hours lecture to introduce into the spirit of this kind of theoretical approach, not only addressing theorists. In our days of lively speculations on possible causes of superconductivity it should provide the newcommer to the field (again not just the theorist) with a safe ground to start out.

[1] Two classics are recommended for more details: J. R. Schrieffer, *Theory of Superconductivity*, Benjamin, New York, 1964, and R. D. Parks (ed.), *Superconductivity, vol. I and II*, Dekker, New York, 1969.

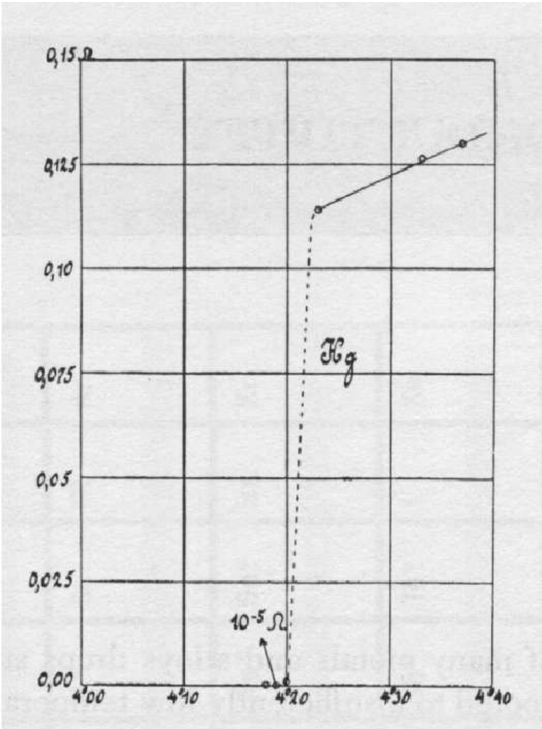

Figure 1: Resistance in ohms of a specimen of mercury versus absolute temperature. This plot by Kamerlingh Onnes marked the discovery of superconductivity. (Taken from: Ch. Kittel, *Introduction to Solid State Physics*, Wiley, New York, 1986, Chap. 12.)

2 PHENOMENA, LONDON THEORY

Helium was first liquefied by Kammerling Onnes at Leiden in 1908. By exhausting the helium vapor above the liquid the temperature could soon be lowered down to 1.5K.

Shortly afterwards, in the year 1911, it was found in the same laboratory[1] that in pure mercury the electrical resistance disappeared abruptly below a critical temperature, $T_c = 4.2$K.

Deliberately increasing electron scattering by making the mercury impure did not affect the phenomenon. Shortly thereafter, the same effect was found in indium (3.4K), tin (3.72K) and in lead (7.19K). In 1930, superconductivity was found in niobium ($T_c = 9.2$K) and in 1940 in the metallic compound NbN ($T_c = 17.3$K), and this remained the highest T_c until the 50's, when superconductivity in the A15 compounds was found and higher T_c-values appeared up to $T_c = 23.2$K in Nb_3Ge, in 1973.

These materials were all normal metals and more or less good conductors.

In 1964, Marvin L. Cohen made theoretical predictions of T_c-values as high as 0.1K for certain doped semiconductors, and in the same year and the following years, superconductivity was found in GeTe, SnTe ($T_c \sim 0.1$K, $n_e \sim 10^{21}\text{cm}^{-3}$) and in $SrTiO_3$ ($T_c = 0.38$K at $n_e \sim 10^{21}\text{cm}^{-3}$, $T_c \sim 0.1$K at $n_e \sim 10^{18}\text{cm}^{-3}$).

In 1979, Frank Steglich discovered superconductivity ($T_c \sim 0.6$ K) in $CeCu_2Si_2$, a magnetically highly correlated compound of a class of solids which later got the name "heavy fermion metals". In the early 80's, superconductivity was found in several conducting polymers as well as in other heavy fermion metals like UBe_{13} ($T_c \sim 1$K in both cases). The year 2000 Nobel price in Chemistry was dedicated tho the prediction and realization of conducting polymers (synthetic metals) in the late 70's.

[1] H. K. Onnes, Commun. Phys. Lab. Univ. Leiden, No124c (1911); H. K. Onnes, Akad. van Wetenschappen (Amsterdam) **14**, 818 (1911).

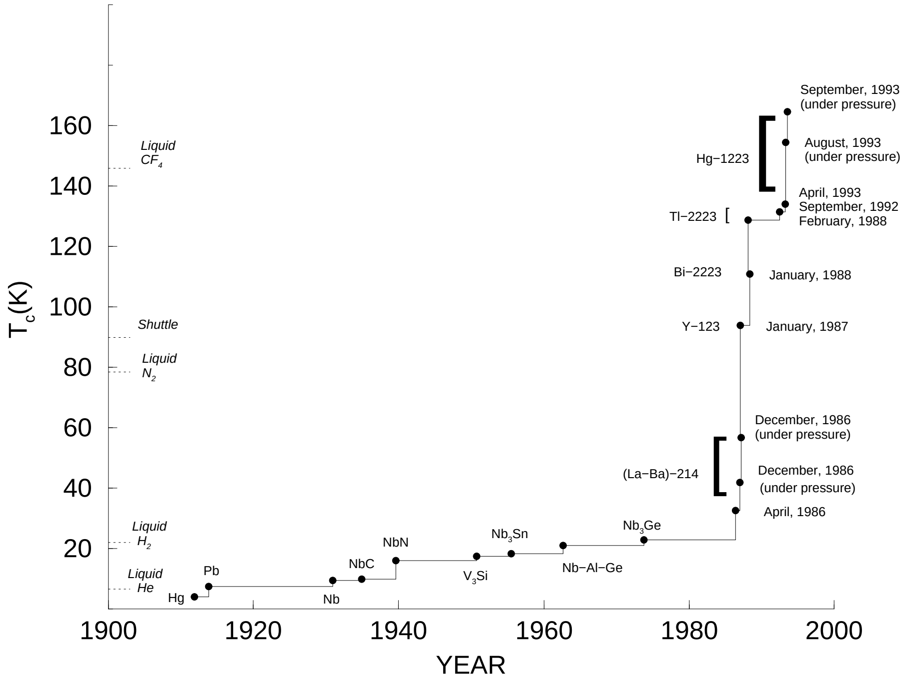

Figure 2: The evolution of T_c with time (from C. W. Chu, *Superconductivity Above 90K and Beyond* in: B. Batlogg, C. W. Chu, W. K. Chu D. U. Gubser and K. A. Müller (eds.) Proc. HTS Workshop on Physics, Materials and Applications, World Scientific, Singapore, 1996.).

In 1986, Georg Bednorz and Alex Müller found superconductivity in $(La,Sr)_2CuO_4$ with $T_c = 36$K, an incredible new record.[1]

Within months, T_c-values in cuprates were shooting up, and the record at ambient pressure is now at $T_c \sim 135$K.

In the spring of 2008, a new fascinating family of superconductors came into focus containing an iron pnictide/chalcogenide layer of anti-PbO structure as the superconducting component, so far with transition temperatures up to about 50 K.

2.1 Phenomena

(a) Zero resistance[2] No resistance is detectable even for high scattering rates of conduction electrons. Persistent currents magnetically induced in a coil of $Nb_{0.75}Zr_{0.25}$ and watched with NMR yielded an estimate of the decay time greater than 10^5 years! (From theoretical estimates the decay time may be as large as $10^{10^{10}}$ years!)

(b) Absence of thermoelectric effects[3] No Seebeck voltage, no Peltier heat, no Thomson heat is detectable (see next section).

(c) Ideal diamagnetism $\chi_m = -1$. Weak magnetic fields are completely screened away from the bulk of a superconductor.

(d) Meissner effect[4] If a superconductor is cooled down in the presence of a weak magnetic field, below T_c the field is completely expelled from the bulk of the superconductor.

[1] J. G. Bednorz and K. A. Müller, Z. Phys. **B64**, 189 (1986).
[2] J. File and R. G. Mills, Phys. Rev. Lett. **10**, 93 (1963).
[3] W. Meissner, Z. Ges. Kälteindustrie **34**, 197 (1927).
[4] W. Meissner and R. Ochsenfeld, Naturwiss. **21**, 787 (1933).

(e) Flux quantization[1] The magnetic flux through a superconducting ring is quantized and constant in time. This phenomenon was theoretically predicted by F. London in 1950 and experimentally verified 1961.

2.2 London theory[2]

Phenomena (a) and (b) clearly indicate that the supercurrent (at $T = 0$) is a property of the quantum ground state:

> There must be an electrically charged (charge quantum q), hence complex bosonic field which condenses in the ground state into a macroscopic amplitude:

$$n_B = |\Psi|^2, \tag{1}$$

where n_B means the bosonic density, and Ψ is the corresponding field amplitude.

Since the field is electrically charged, it is subject to electromagnetic fields $(\boldsymbol{E}, \boldsymbol{B})$ which are usually described by potentials $(U, \boldsymbol{A})$:

$$\boldsymbol{E} = -\frac{\partial \boldsymbol{A}}{\partial t} - \frac{\partial U}{\partial \boldsymbol{r}}, \tag{2a}$$

$$\boldsymbol{B} = \frac{\partial}{\partial \boldsymbol{r}} \times \boldsymbol{A}. \tag{2b}$$

In this chapter $\boldsymbol{E}$ *and* $\boldsymbol{B}$ *are the total fields locally seen.*

The field amplitude should obey a Schrödinger equation

$$\frac{1}{2m_B}\Big(\frac{\hbar}{i}\frac{\partial}{\partial \boldsymbol{r}} - q\boldsymbol{A}\Big)^2 \Psi + qU\Psi = \big(E - \mu_B\big)\Psi, \tag{3}$$

where the energy is reasonably measured from the chemical potential μ_B of the boson field, since what is measured in a voltmeter is rather the electrochemical potential

$$\phi = \mu_B + qU \tag{4}$$

than the external potential U, or the effective electric field

$$\boldsymbol{E}_{\text{eff}} = -\frac{\partial \boldsymbol{A}}{\partial t} - \frac{1}{q}\frac{\partial \phi}{\partial \boldsymbol{r}}. \tag{5}$$

As usual in Quantum Mechanics, $-i\hbar\partial/\partial\boldsymbol{r}$ is the canonical momentum and $(-i\hbar\partial/\partial\boldsymbol{r} - q\boldsymbol{A}) = \hat{\boldsymbol{p}}_m$ is the mechanical momentum.

The supercurrent density is then

$$\boldsymbol{j}_s = q\frac{\boldsymbol{p}_m}{m_B}n_B \;=\; \frac{q}{m_B}\Re\big(\Psi^*\hat{\boldsymbol{p}}_m\Psi\big) \;=\; -\frac{iq\hbar}{2m_B}\Big(\Psi^*\frac{\partial}{\partial \boldsymbol{r}}\Psi - \Psi\frac{\partial}{\partial \boldsymbol{r}}\Psi^*\Big) - \frac{q^2}{m_B}\Psi^*\Psi\boldsymbol{A}. \tag{6}$$

It consists as usual of a 'paramagnetic current' (first term) and a 'diamagnetic current' (second term).[3]

In a *homogeneous* superconductor, where $n_B = \text{const.}$, we may write

$$\Psi(\boldsymbol{r}, t) = \sqrt{n_B}e^{i\theta(\boldsymbol{r},t)}, \tag{7}$$

and have

$$\Lambda\boldsymbol{j}_s = \frac{\hbar}{q}\frac{\partial \theta}{\partial \boldsymbol{r}} - \boldsymbol{A}, \quad \Lambda = \frac{m_B}{n_B q^2}. \tag{8}$$

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[1] B. S. Deaver and W. M. Fairbank, Phys. Rev. Lett. **7**, 43 (1961); R. Doll and M. Näbauer, Phys. Rev. Lett. **7**, 51 (1961).

[2] F. London and H. London, Proc. Roy. Soc. **A149**, 71 (1935); F. London, Proc. Roy. Soc. **A152**, 24 (1935); F. London, *Superfluids*, Wiley, London, 1950.

[3] These are formal names: since the splitting into the two current contributions depends on the gauge, it has no deeper physical meaning. Physically, paramagnetic means a positive response on an external magnetic field (enhancing the field inside the material) and diamagnetic means a negative response.

Since in the ground state $E = \phi$, and $E\Psi = i\hbar\partial\Psi/\partial t$, we also have

$$\hbar\frac{\partial\theta}{\partial t} = -\phi. \tag{9}$$

The London theory derives from (8) and (9). It is valid in the *London limit*, where n_B = const. in space can be assumed.

The time derivative of (8) yields with (9)

$$\frac{\partial(\Lambda \boldsymbol{j}_s)}{\partial t} = -\frac{\partial \boldsymbol{A}}{\partial t} - \frac{1}{q}\frac{\partial\phi}{\partial \boldsymbol{r}},$$

or

$$\boxed{\frac{\partial(\Lambda \boldsymbol{j}_s)}{\partial t} = \boldsymbol{E}_{\text{eff}}} \tag{10}$$

This is 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 (constant electrochemical potential).

The first London equation yields the absence of thermoelectric effects, if the electrochemical potentials of conduction electrons, ϕ_{el}, and of the supercurrent, ϕ, are coupled. The thermoelectric effects are sketchy illustrated in Fig. 3. The first London equation causes the electrochemical potential of the supercurrent carrying field to be constant in every stationary situation. If the supercurrent carrying field reacts with the conduction electron field with n electrons forming a field quantum with charge q, then the electrochemical potentials must be related as $n\phi_{\text{el}} = \phi$. Hence the electrochemical potential of the conduction electrons must also be constant: no thermopower (Seebeck voltage) may develop in a superconductor. The thermoelectric current flowing due to the temperature difference is canceled by a back flowing supercurrent, with a continuous transformation of conduction electrons into supercurrent density at the one end of the sample and a back transformation at the other end.

If a loop of two different normal conductors is formed with the junctions kept at different temperatures, then a thermoelectric current develops together with a difference of the electrochemical potentials of the two junctions, and several forms of heat are produced, everything depending on the *combination* of the two metals. If there is no temperature difference at the beginning, but a current is maintained in the ring (by inserting a power supply into one of the metal halfs), then a temperature difference between the junctions will develop. This is how a Peltier cooler works. In a loop of two superconductors non of those phenomena can appear since a difference of electrochemical potentials cannot be maintained. Every normal current is *locally* short-circuited by supercurrents.

If, however, a normal metal A is combined with a superconductor B in a loop, a thermoelectric current will flow in the normal half *without* developing an electrochemical potential difference of the junctions because of the presence of the superconductor on the other side. This yields a direct absolute measurement of the thermoelectric coefficients of a single material A.

The curl of Eq. (8) yields (with $\frac{\partial}{\partial \boldsymbol{r}} \times \frac{\partial}{\partial \boldsymbol{r}} = 0$)

$$\boxed{\frac{\partial}{\partial \boldsymbol{r}} \times \left(\Lambda \boldsymbol{j}_s\right) = -\boldsymbol{B}.} \tag{11}$$

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

Take the curl of Maxwell's equation (Ampere's law) and consider $\frac{\partial}{\partial \boldsymbol{r}} \times \left(\frac{\partial}{\partial \boldsymbol{r}} \times \boldsymbol{B}\right) = \frac{\partial}{\partial \boldsymbol{r}}\left(\frac{\partial \boldsymbol{B}}{\partial \boldsymbol{r}}\right) - \frac{\partial^2}{\partial \boldsymbol{r}^2}\boldsymbol{B}$:

$$\frac{\partial}{\partial \boldsymbol{r}} \times \boldsymbol{B} = \mu_0(\boldsymbol{j}_s + \boldsymbol{j}), \quad \frac{\partial \boldsymbol{B}}{\partial \boldsymbol{r}} = 0, \tag{12}$$

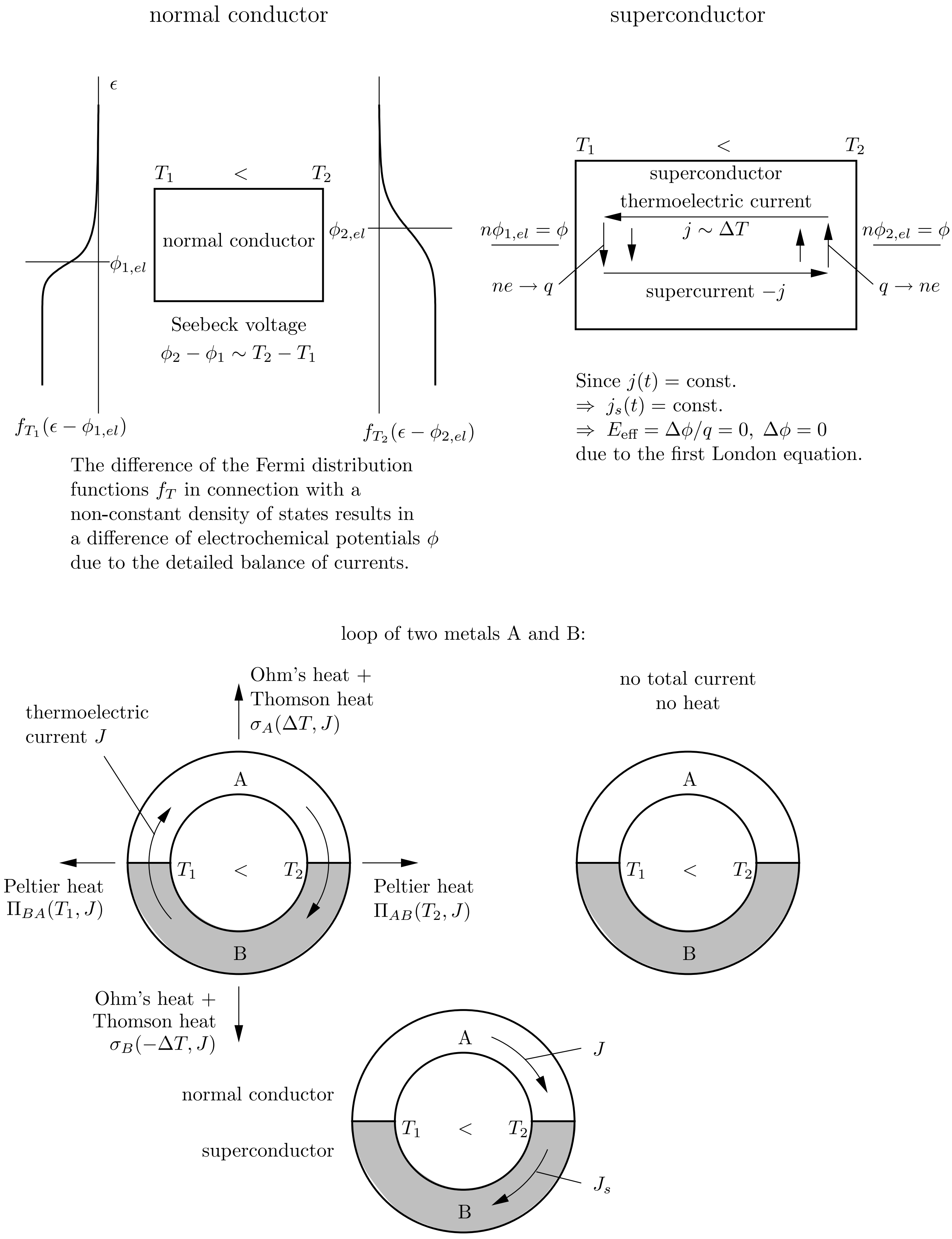


Figure 3: Thermoelectric phenomena in normal conductors and superconductors.

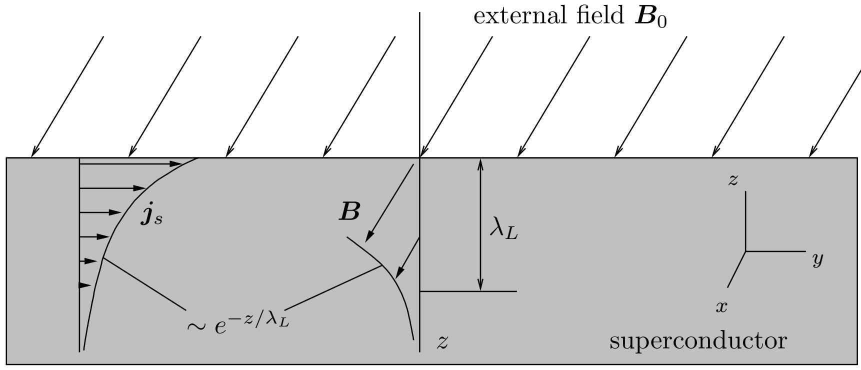


Figure 4: Penetration of an external magnetic field into a superconductor.

$$\begin{aligned}
\frac{\partial}{\partial \boldsymbol{r}} \times \left(\frac{\partial}{\partial \boldsymbol{r}} \times \boldsymbol{B}\right) &= \mu_0 \frac{\partial}{\partial \boldsymbol{r}} \times (\boldsymbol{j}_s + \boldsymbol{j}), \\
-\frac{\partial^2}{\partial \boldsymbol{r}^2} \boldsymbol{B} &= \mu_0 \frac{\partial}{\partial \boldsymbol{r}} \times (\boldsymbol{j}_s + \boldsymbol{j}), \\
\frac{\partial^2}{\partial \boldsymbol{r}^2} \boldsymbol{B} &= \frac{\mu_0}{\Lambda} \boldsymbol{B} - \mu_0 \frac{\partial}{\partial \boldsymbol{r}} \times \boldsymbol{j}.
\end{aligned}$$

If $\boldsymbol{j} = 0$ or $\frac{\partial}{\partial \boldsymbol{r}} \times \boldsymbol{j} = 0$ for the *normal* current inside the superconductor, then

$$\frac{\partial^2}{\partial \boldsymbol{r}^2} \boldsymbol{B} = \frac{\boldsymbol{B}}{\lambda_L^2}, \quad \lambda_L = \sqrt{\frac{\Lambda}{\mu_0}} = \sqrt{\frac{m_B}{n_B \mu_0 q^2}} \tag{13}$$

with solutions

$$\boldsymbol{B} = \boldsymbol{B}_0 e^{-\boldsymbol{n} \cdot \boldsymbol{r}/\lambda_L}, \quad \boldsymbol{n}^2 = 1, \quad \boldsymbol{n} \cdot \boldsymbol{B}_0 = 0 \tag{14}$$

several of which with appropriate unit vectors $\boldsymbol{n}$ may be superimposed to fulfill boundary conditions. λ_L is *London's penetration depth*.

Any external field $\boldsymbol{B}$ is screened to zero inside a bulk superconducting state within a surface layer of thickness λ_L. It is important that (11) does not contain time derivatives of the field but the field $\boldsymbol{B}$ itself: If a metal in an applied field $\boldsymbol{B}_0$ is cooled down below T_c, the field is expelled.

Consider a superconducting ring with magnetic flux Φ passing through it (Fig. 5). Because of (14) and (12), $\boldsymbol{j}_s = 0$ deep inside the ring on the contour C. Hence, from (10), $\boldsymbol{E}_{\text{eff}} = \boldsymbol{E} = 0$ there. From Faraday's law, $(\partial/\partial \boldsymbol{r}) \times \boldsymbol{E} = -\partial \boldsymbol{B}/\partial t$,

$$\frac{d\Phi}{dt} = \frac{d}{dt} \int_A \boldsymbol{B} d\boldsymbol{S} = -\oint_C \boldsymbol{E} d\boldsymbol{l} = 0, \tag{15}$$

where A is a surface with boundary C, and Φ is the magnetic flux through A.

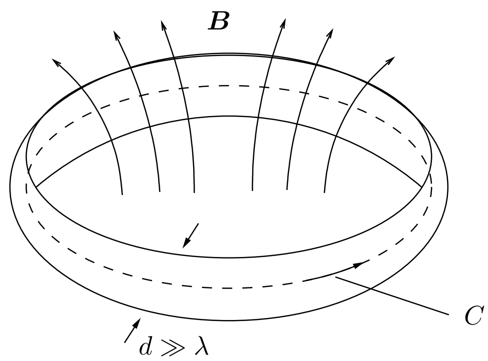


Figure 5: Flux through a superconducting ring.

Even if the supercurrent in a surface layer of the ring is changing with time (for instance, if an applied magnetic field is changing with time), the flux Φ is not:

The flux through a superconducting ring is trapped.

Integrate Eq. (8) along the contour C:

$$\oint_C \big(\boldsymbol{A} + \Lambda \boldsymbol{j}_s\big) \cdot d\boldsymbol{l} = \frac{\hbar}{q} \oint_C \frac{\partial \theta}{\partial \boldsymbol{r}} \cdot d\boldsymbol{l}.$$

The integral on the right hand side is the total change of the phase θ of the wavefunction (7) around the contour, which must be an integer multiple of 2π since the wavefunction itself must be unique. Hence,

$$\oint_C \big(\boldsymbol{A} + \Lambda \boldsymbol{j}_s\big) \cdot d\boldsymbol{l} = \frac{\hbar}{q} 2\pi n. \tag{16}$$

The left hand integral has been named the *fluxoid* by F. London. In the situation of our ring we find

$$\Phi = \frac{\hbar}{q} 2\pi n. \tag{17}$$

By directly measuring the *flux quantum* Φ_0 the absolute value of the superconducting charge was measured:

$$|q| = 2e, \qquad \boxed{\Phi_0 = \frac{h}{2e}.} \tag{18}$$

(The sign of the flux quantum may be defined arbitrarily; e is the proton charge.)

If the supercurrent $\boldsymbol{j}_s$ along the contour C is non-zero, then the flux Φ is not quantized any more, the fluxoid (16), however, is *always* quantized.

In order to determine the sign of q, consider a superconducting sample which rotates with the angular velocity $\boldsymbol{\omega}$. Since the sample is neutral, its superconducting charge density qn_B is neutralized by the charge density $-qn_B$ of the remainder of the material. Ampere's law (in the absence of a normal current density $\boldsymbol{j}$ inside the sample) yields now

$$\frac{\partial}{\partial \boldsymbol{r}} \times \boldsymbol{B} = \mu_0 \big(\boldsymbol{j}_s - qn_B \boldsymbol{v}\big),$$

where $\boldsymbol{v} = \boldsymbol{\omega} \times \boldsymbol{r}$ is the local velocity of the sample, and $\boldsymbol{j}_s$ is the supercurrent with respect to the rest coordinates. Taking again the curl and considering

$$\frac{\partial}{\partial \boldsymbol{r}} \times \boldsymbol{v} = \frac{\partial}{\partial \boldsymbol{r}} \times \big(\boldsymbol{\omega} \times \boldsymbol{r}\big) = \boldsymbol{\omega} \frac{\partial \boldsymbol{r}}{\partial \boldsymbol{r}} - \Big(\boldsymbol{\omega} \cdot \frac{\partial}{\partial \boldsymbol{r}}\Big) \boldsymbol{r} = 3\boldsymbol{\omega} - \boldsymbol{\omega} = 2\boldsymbol{\omega}$$

leads to

$$-\frac{\partial^2}{\partial \boldsymbol{r}^2} \boldsymbol{B} = \mu_0 \frac{\partial}{\partial \boldsymbol{r}} \times \boldsymbol{j}_s - 2\mu_0 q n_B \boldsymbol{\omega}.$$

We define the *London field*

$$\boldsymbol{B}_L \equiv -2\lambda_L^2 \mu_0 q n_B \boldsymbol{\omega} = -\frac{2m_B}{q} \boldsymbol{\omega} \tag{19}$$

and consider the second London equation (11) to obtain

$$\frac{\partial^2}{\partial \boldsymbol{r}^2} \boldsymbol{B} = \frac{\boldsymbol{B} - \boldsymbol{B}_L}{\lambda_L^2} : \tag{20}$$

Deep inside a rotating superconductor the magnetic field is not zero but equal to the homogeneous London field.

Independent measurements of the flux quantum and the London field result in

$$\boxed{q = -2e, \quad m_B = 2m_e.} \tag{21}$$

The bosonic field Ψ is composed of *pairs of electrons.*

2.3 Gauge symmetry, London gauge

If $\chi(\boldsymbol{r}, t)$ is an arbitrary differentiable single-valued function, then the electromagnetic field (2) is *invariant* under the *gauge transformation*

$$\begin{aligned} \boldsymbol{A} &\longrightarrow \boldsymbol{A} + \frac{\partial \chi}{\partial \boldsymbol{r}}, \\ U &\longrightarrow U - \frac{\partial \chi}{\partial t}. \end{aligned} \tag{22a}$$

Since potentials in electrodynamics can only indirectly be measured through fields, electrodynamics is *symmetric* with respect to gauge transformations (22a).

Eqs. (8, 9), and hence the London theory are *covariant* under local gauge transformations, if (22a) is supplemented by

$$\begin{aligned} \theta &\longrightarrow \theta - \frac{2e}{\hbar}\chi, \\ \phi &\longrightarrow \phi + 2e\frac{\partial \chi}{\partial t}. \end{aligned} \tag{22b}$$

From (8), the supercurrent $\boldsymbol{j}_s$ is still gauge invariant, and so are the electromagnetic properties of a superconductor. However, the electrochemical potential ϕ is directly observable in thermodynamics by making contact to a bath. The thermodynamic superconducting state breaks gauge symmetry.

For theoretical considerations a special gauge is often advantageous. The *London gauge* chooses χ in (22b) such that the phase $\theta \equiv 0$. Then, from (8),

$$\Lambda \boldsymbol{j}_s = -\boldsymbol{A}, \tag{23}$$

which is convenient for computing patterns of supercurrents and fields.

3 THE THERMODYNAMICS OF THE PHASE TRANSITION[1]

Up to here we considered superconductivity as a property of a bosonic condensate. From experiment we know, that the considered phenomena are present up to the *critical temperature*, T_c, of the transition from the superconducting state, indexed by s, into the normal conducting state, indexed by n, as temperature rises. The parameters of the theory, n_B and λ_L, are to be expected temperature dependent: n_B must vanish at T_c.

In this and the next chapters we consider the vicinity of the phase transition, $T - T_c \ll T_c$.

3.1 The Free Energy

Experiments are normally done at given temperature T, pressure p, and magnetic field $\boldsymbol{B}$ *produced by external sources.* Since according to the first London equation (10) there is no stationary state at $\boldsymbol{E} \neq 0$, we must keep $\boldsymbol{E} = 0$ in a thermodynamic equilibrium state. Hence, we consider the (Helmholtz) Free Energy

$$F_s(T, V, \boldsymbol{B}), \quad F_n(T, V, \boldsymbol{B}), \tag{24}$$

$$\frac{\partial F}{\partial T} = -S, \quad \frac{\partial F}{\partial V} = -p, \quad \frac{\partial F}{\partial \boldsymbol{B}} = -V\boldsymbol{m}, \tag{25}$$

where S is the entropy, and $\boldsymbol{m}$ is the magnetization density. First, the dependence of F_s on $\boldsymbol{B}$ is determined from the fact that in the bulk of a superconductor

$$\boldsymbol{B}_{\text{ext}} + \boldsymbol{B}_m = \boldsymbol{B} + \mu_0 \boldsymbol{m} = 0 \tag{26}$$

as it follows from the second London equation (11). Hence,

$$\frac{\partial F_s}{\partial \boldsymbol{B}} = +\frac{V\boldsymbol{B}}{\mu_0} \Longrightarrow F_s(\boldsymbol{B}) = F_s(0) + \frac{VB^2}{2\mu_0}. \tag{27}$$

The magnetic susceptibility of a normal (non-magnetic) metal is

$$|\chi_{m,n}| \ll 1 = |\chi_{m,s}|, \tag{28}$$

hence it may be neglected here:

$$F_n(\boldsymbol{B}) \approx F_n(0). \tag{29}$$

Eq. (27) implies (cf. (25))

$$\begin{aligned} F_s(T, V, \boldsymbol{B}) &= F_s(T, V, 0) + \frac{VB^2}{2\mu_0}, \\ p(T, V, \boldsymbol{B}) &= p(T, V, 0) - \frac{B^2}{2\mu_0}. \end{aligned} \tag{30}$$

The pressure a superconductor exerts on its surroundings reduces in an external field $\boldsymbol{B}$: The field $\boldsymbol{B}$ implies a force per area

$$\boldsymbol{F} = -\boldsymbol{n}\frac{B^2}{2\mu_0} \tag{31}$$

on the surface of the superconductor with normal $\boldsymbol{n}$.

[1] L. D. Landau and E. M. Lifshits, *Electrodynamics of Continuous Media*, Chap. VI, Pergamon, Oxford, 1960.

3.2 The Free Enthalpy

The relations between the Free Energy F and the Free Enthalpy (Gibbs Free Energy) G at $\boldsymbol{B} = 0$ and $\boldsymbol{B} \neq 0$ read

$$F_s(T, V, 0) = G_s(T, p(T, V, 0), 0) - p(T, V, 0)V$$

and

$$\begin{aligned} F_s(T, V, 0) + \frac{VB^2}{2\mu_0} &= F_s(T, V, \boldsymbol{B}) = \\ &= G_s(T, p(T, V, \boldsymbol{B}), \boldsymbol{B}) - p(T, V, \boldsymbol{B})V = \\ &= G_s(T, p(T, V, 0) - \frac{B^2}{2\mu_0}, \boldsymbol{B}) - p(T, V, 0)V + \frac{VB^2}{2\mu_0}. \end{aligned}$$

These relations combine to

$$G_s(T, p(T, V, 0), 0) = G_s(T, p(T, V, 0) - \frac{B^2}{2\mu_0}, \boldsymbol{B}),$$

or

$$G_s(T, p, \boldsymbol{B}) = G_s(T, p + \frac{B^2}{2\mu_0}, 0). \tag{32}$$

In accord with (31), the effect of an external magnetic field $\boldsymbol{B}$ on the Free Enthalpy is a reduction of the pressure exerted on the surroundings, by $B^2/2\mu_0$. In the normal state, from (29),

$$G_n(T, p, \boldsymbol{B}) = G_n(T, p, 0). \tag{33}$$

The critical temperature $T_c(p, \boldsymbol{B})$ is given by

$$G_s(T_c, p + \frac{B^2}{2\mu_0}, 0) = G_n(T_c, p, 0). \tag{34a}$$

Likewise $B_c(T, p)$ from

$$G_s(T, p + \frac{B_c^2}{2\mu_0}, 0) = G_n(T, p, 0). \tag{34b}$$

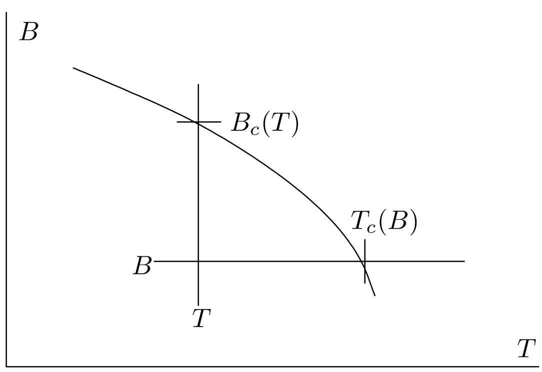


Figure 6: The critical temperature as a function of the applied magnetic field and the thermodynamic critical field as a function of temperature.

3.3 The thermodynamic critical field

The Free Enthalpy difference between the normal and superconducting states is usually small, so that at $T < T_c(\boldsymbol{B}=0)$ the thermodynamic critical field $B_c(T)$ for which (34) holds is also small. Taylor expansion of the left hand side of (34) yields

$$G_n(T,p) = G_s(T,p) + \frac{B_c^2}{2\mu_0}\frac{\partial G_s}{\partial p} \;=\; G_s(T,p) + \frac{B_c^2}{2\mu_0}V(T,p,\boldsymbol{B}=0). \tag{35}$$

Experiment shows that at $\boldsymbol{B}=0$ the phase transition is second order,

$$G_n(T,p) - G_s(T,p) = a\big(T_c(p) - T\big)^2. \tag{36}$$

Hence,

$$B_c(T,p) = b\big(T_c(p) - T\big), \tag{37}$$

where a is a constant, and $b = \sqrt{2\mu_0 a/V}$. $T_c(p)$ is meant for $\boldsymbol{B}=0$.

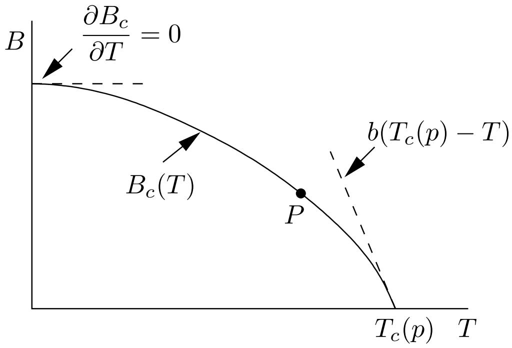


FIG. 7: The thermodynamic critical field.

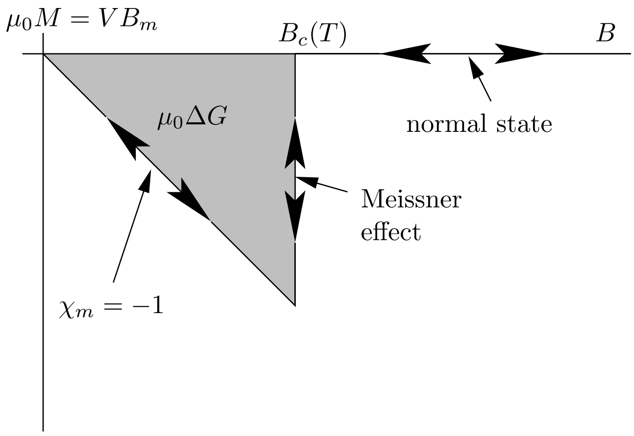


FIG. 8: The magnetization curve of a superconductor.

We consider all thermodynamic parameters T, p, B at the phase transition point P of Fig. 7. From (32),

$$\begin{aligned} S_s(T,p,B) &= -\frac{\partial G_s}{\partial T} \;=\; S_s(T, p + \frac{B^2}{2\mu_0}, 0), \\ V_s(T,p,B) &= \frac{\partial G_s}{\partial p} \;=\; V_s(T, p + \frac{B^2}{2\mu_0}, 0). \end{aligned} \tag{38}$$

Differentiating (34b) with respect to T yields, with (38),

$$\frac{\partial}{\partial T}G_s(T, p + \frac{B_c^2(T,p)}{2\mu_0}, 0) = \frac{\partial}{\partial T}G_n(T,p,0 \text{ or } B_c),$$

$$-S_s(T,p,B_c) + \frac{V_s(T,p,B_c)}{2\mu_0}\frac{\partial}{\partial T}B_c^2(T,p) = -S_n(T,p,B_c),$$

$$\Delta S(T,p,B_c) = S_s(T,p,B_c) - S_n(T,p,B_c) \;=\; \frac{V_s(T,p,B_c)}{\mu_0}B_c(T,p)\frac{\partial B_c(T,p)}{\partial T}. \tag{39}$$

According to (37) this difference is non-zero for $B_c \neq 0$ ($T < T_c(p)$): For $B \neq 0$ the phase transition is first order with a latent heat

$$Q = T\Delta S(T,p,B_c). \tag{40}$$

For $T \to 0$, Nernst's theorem demands $S_s = S_n = 0$, and hence

$$\lim_{T\to 0} \frac{\partial B_c(T,p)}{\partial T} = 0. \tag{41}$$

3.4 Heat capacity jump

For $B \approx 0$, $T \approx T_c(p)$ we can use (35). Applying $-T\partial^2/\partial T^2$ yields

$$\Delta C_p = C_{p,s} - C_{p,n} \;=\; -T\frac{\partial^2}{\partial T^2}\Big(G_s(T,p) - G_n(T,p)\Big) \;=\; \frac{TV(T,p)}{2\mu_0}\frac{\partial^2}{\partial T^2}B_c^2(T,p). \tag{42}$$

The thermal expansion $\partial V/\partial T$ gives a small contribution which has been neglected. With

$$\frac{\partial^2}{\partial T^2}B_c^2 = \frac{\partial}{\partial T}2B_c\frac{\partial B_c}{\partial T} = 2\left(\frac{\partial B_c}{\partial T}\right)^2 + 2B_c\frac{\partial^2 B_c}{\partial T^2}$$

we find

$$\Delta C_p = \frac{TV}{\mu_0}\left[\left(\frac{\partial B_c}{\partial T}\right)^2 + B_c\frac{\partial^2 B_c}{\partial T^2}\right] \tag{43}$$

For $T \to T_c(p)$, $B_c \to 0$ the jump in the specific heat is

$$\boxed{\Delta C_p = \frac{T_cV}{\mu_0}\left(\frac{\partial B_c}{\partial T}\right)^2 = \frac{T_cV}{\mu_0}b^2.} \tag{44}$$

It is given by the slope of $B_c(T)$ at $T_c(p)$.

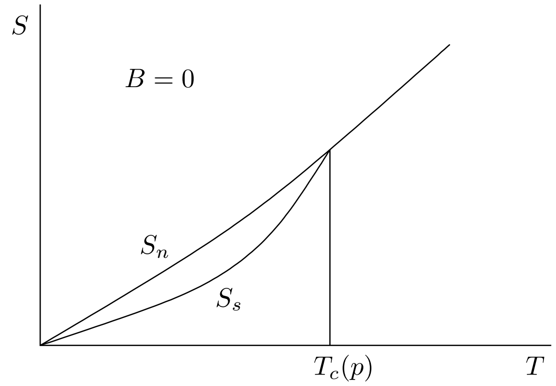


FIG. 9: The entropy of a superconductor.

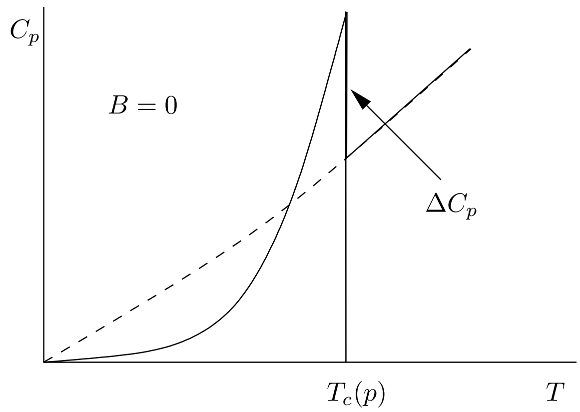


FIG. 10: The heat capacity of a superconductor.

4 THE GINSBURG-LANDAU THEORY;[1] TYPES OF SUPERCONDUCTORS

According to the Landau theory of second order phase transitions with symmetry reduction[2] there is a thermodynamic quantity, called an *order parameter*, which is zero in the symmetric (high temperature) phase, and becomes continuously non-zero in the less symmetric phase.

4.1 The Landau theory

The quantity which becomes non-zero in the superconducting state is

$$n_B = |\Psi|^2. \tag{45}$$

For $n_B > 0$, the electrochemical potential ϕ has a certain value which breaks the global gauge symmetry by fixing the time-derivative of the phase θ of Ψ (cf. (22b)). According to the Landau theory, the Free Energy is the minimum of a "Free Energy function" of the order parameter with respect to variations of the latter:

$$F(T,V) = \min_{\Psi} \mathcal{F}(T,V,|\Psi|^2). \tag{46}$$

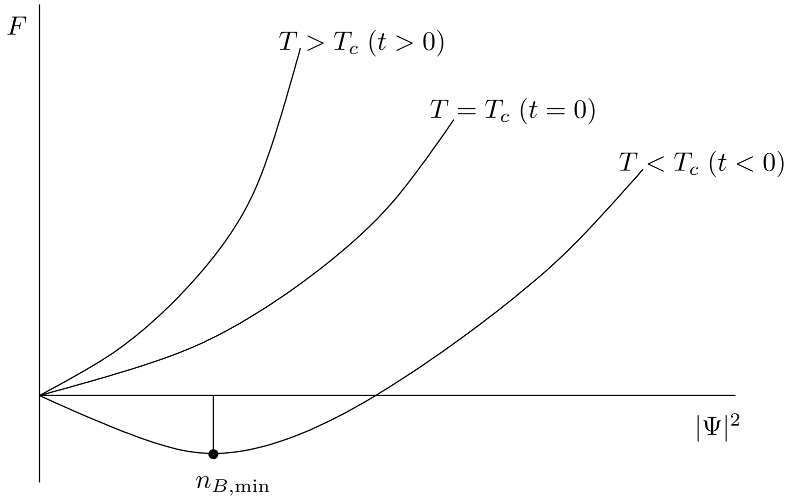


Figure 11: The Free Energy function.

Close to the transition, for

$$t = \frac{T - T_c}{T_c}, \quad |t| \ll 1, \tag{47}$$

the order parameter $|\Psi|^2$ is small, and $\mathcal{F}$ may be Taylor expanded (for fixed V):

$$\mathcal{F}(t,|\Psi|^2) = \mathcal{F}_n(t) + A(t)|\Psi|^2 + \frac{1}{2}B(t)|\Psi|^4 + \cdots \tag{48}$$

From the figure we see that

$$A(t) \gtreqless 0 \quad \text{for} \quad t \gtreqless 0, \quad B(t) > 0.$$

[1]V. L. Ginsburg and L. D. Landau, Zh. Eksp. Teor. Fiz. (Russ.) **20**, 1064 (1950).
[2]L. D. Landau, Zh. Eksp. Teor. Fiz. (Russ.) **7**, 627 (1937).

Since $|t| \ll 1$, we put

$$A(t) \approx \alpha t V, \quad B(t) \approx \beta V. \tag{49}$$

Then we have

$$F_n(t) = \mathcal{F}_n(t) \text{ for } t \geq 0, \tag{50}$$

and

$$\frac{1}{V}\frac{\partial \mathcal{F}}{\partial |\Psi|^2} = \alpha t + \beta |\Psi|^2 = 0, \text{ that is,}$$

$$|\Psi|^2 = -\frac{\alpha t}{\beta}, \quad F_s(t) = F_n(t) - \frac{\alpha^2 t^2}{2\beta} V \text{ for } t < 0. \tag{51}$$

Recalling that small changes in the Free Energy and Free Enthalpy are equal and comparing to (35) yields

$$\frac{\alpha^2 t^2}{2\beta} = \frac{B_c^2}{2\mu_0} \quad \Longrightarrow \quad B_c(t) = \alpha |t| \sqrt{\frac{\mu_0}{\beta}}. \tag{52}$$

From (43),

$$\Delta C_p = \frac{T_c V}{\mu_0}\left(\frac{\partial B_c}{T_c \partial t}\right)^2 = \frac{V}{T_c}\frac{\alpha^2}{\beta} \tag{53}$$

follows. While ΔC_p can be measured, this is not always the case for the thermodynamic critical field, B_c, as we will later see.

Eqs. (51) and (52) may be rewritten as

$$n_B(t) = \frac{\alpha}{\beta}|t|, \quad B_c^2(t) = \frac{\alpha^2 t^2 \mu_0}{\beta},$$

hence,

$$\beta = \frac{B_c^2(t)}{\mu_0 n_B^2(t)}, \quad \alpha = \frac{B_c^2(t)}{\mu_0 |t| n_B(t)}. \tag{54}$$

Since according to (37) $B_c \sim t$, it follows

$$n_B \sim t. \tag{55}$$

The bosonic density tends to zero linearly in $T_c - T$.

4.2 The Ginsburg-Landau equations

If we want to incorporate a magnetic field $\boldsymbol{B}$ into the "Free Energy function" (48), we have to realize that $\boldsymbol{B}$ causes supercurrents $\boldsymbol{j}_s \sim \partial\Psi/\partial\boldsymbol{r}$, and these create an internal field, which was called $\boldsymbol{B}_m$ in (26). The energy contribution of Ψ must be related to (3). Ginsburg and Landau wrote it in the form

$$\begin{aligned} \mathcal{F}(t, \boldsymbol{B}, \Psi) &= F_n(t) + \\ &+ \int^{\infty} d^3r \frac{B_m^2}{2\mu_0} + \int_V d^3r \left\{ \frac{\hbar^2}{4m}\left|\left(\frac{\partial}{\partial \boldsymbol{r}} + \frac{2ie}{\hbar}\boldsymbol{A}\right)\Psi\right|^2 + \alpha t |\Psi|^2 + \frac{\beta}{2}|\Psi|^4 \right\}, \end{aligned} \tag{56a}$$

where also (21) was considered. The first correction term is the field energy of the field $\boldsymbol{B}_m$ created by Ψ, including the stray field outside of the volume V while $\Psi \neq 0$ inside V only. $\boldsymbol{A}$ is the vector potential of the total field acting on Ψ:

$$\frac{\partial}{\partial \boldsymbol{r}} \times \boldsymbol{A} = \boldsymbol{B} + \boldsymbol{B}_m. \tag{56b}$$

The Free Energy is obtained by minimizing (56a) with respect to $\Psi(\boldsymbol{r})$ and $\Psi^*(\boldsymbol{r})$. To prepare for a variation of Ψ^*, the second integral in (56a) is integrated by parts:

$$\int_V d^3r\left[\left(\frac{\partial}{\partial\boldsymbol{r}}+\frac{2ie}{\hbar}\boldsymbol{A}\right)\Psi\right]\left[\left(\frac{\partial}{\partial\boldsymbol{r}}-\frac{2ie}{\hbar}\boldsymbol{A}\right)\Psi^*\right]=$$

$$= -\int_V d^3r\Psi^*\left(\frac{\partial}{\partial\boldsymbol{r}}+\frac{2ie}{\hbar}\boldsymbol{A}\right)^2\Psi+\int_{\partial V} d^2\boldsymbol{n}\Psi^*\left(\frac{\partial}{\partial\boldsymbol{r}}+\frac{2ie}{\hbar}\boldsymbol{A}\right)\Psi. \tag{56c}$$

From the first integral on the right we see that (56a) indeed corresponds to (3). The preference of the writing in (56a) derives from that kinetic energy expression being manifestly positive definite in any partial volume.

Now, the variation $\Psi^*\to\Psi^*+\delta\Psi^*$ yields

$$0\overset{!}{=}\delta\mathcal{F} = \int_V d^3r\delta\Psi^*\left\{-\frac{\hbar^2}{4m}\left(\frac{\partial}{\partial\boldsymbol{r}}+\frac{2ie}{\hbar}\boldsymbol{A}\right)^2+\alpha t+\beta|\Psi|^2\right\}\Psi\ +$$
$$+\int_{\partial V} d^2\boldsymbol{n}\delta\Psi^*\frac{\hbar^2}{4m}\left(\frac{\partial}{\partial\boldsymbol{r}}+\frac{2ie}{\hbar}\boldsymbol{A}\right)\Psi.$$

$\mathcal{F}$ is stationary for any variation $\delta\Psi^*(\boldsymbol{r})$, if

$$\boxed{\frac{1}{4m}\left(\frac{\hbar}{i}\frac{\partial}{\partial\boldsymbol{r}}+2e\boldsymbol{A}\right)^2\Psi-\alpha|t|\Psi+\beta|\Psi|^2\Psi=0} \tag{57}$$

and

$$\boldsymbol{n}\left(\frac{\hbar}{i}\frac{\partial}{\partial\boldsymbol{r}}+2e\boldsymbol{A}\right)\Psi=0. \tag{58}$$

The connection of Ψ with $\boldsymbol{B}_m$ must be that of Ampere's law: $(\partial/\partial\boldsymbol{r})\times\boldsymbol{B}_m=\mu_0\boldsymbol{j}_s$ with $\boldsymbol{j}_s$ given by (6). Since in thermodynamic equilibrium there are no currents besides $\boldsymbol{j}_s$ in the superconductor, $(\partial/\partial\boldsymbol{r})\times\boldsymbol{B}=0$ there. Hence, we also have

$$\boxed{\begin{aligned}&\frac{\partial}{\partial\boldsymbol{r}}\times\boldsymbol{B}_{\text{tot}}=\mu_0\boldsymbol{j}_s,\qquad \boldsymbol{B}_{\text{tot}}=\boldsymbol{B}+\boldsymbol{B}_m=\frac{\partial}{\partial\boldsymbol{r}}\times\boldsymbol{A},\\ &\boldsymbol{j}_s=\frac{ie\hbar}{2m}\left(\Psi^*\frac{\partial}{\partial\boldsymbol{r}}\Psi-\Psi\frac{\partial}{\partial\boldsymbol{r}}\Psi^*\right)-\frac{2e^2}{m}\Psi^*\boldsymbol{A}\Psi.\end{aligned}} \tag{59}$$

It is interesting to see that (59) is also obtained from (56a), if Ψ^*, Ψ and $\boldsymbol{A}$ are varied independently: The variation of $\boldsymbol{A}$ on the left hand side of (56c) yields

$$\frac{2ie}{\hbar}\int_V d^3r\delta\boldsymbol{A}\cdot\left[\Psi\left(\frac{\partial}{\partial\boldsymbol{r}}-\frac{2ie}{\hbar}\boldsymbol{A}\right)\Psi^*-\Psi^*\left(\frac{\partial}{\partial\boldsymbol{r}}+\frac{2ie}{\hbar}\boldsymbol{A}\right)\Psi\right].$$

With $\delta\boldsymbol{B}_m=(\partial/\partial\boldsymbol{r})\times\delta\boldsymbol{A}$ the variation of the first integral of (56a) yields

$$\delta\int^\infty d^3rB_m^2=2\int^\infty d^3r\delta\boldsymbol{B}_m\cdot\boldsymbol{B}_m=2\int^\infty d^3r\left(\frac{\partial}{\partial\boldsymbol{r}}\times\delta\boldsymbol{A}\right)\cdot\boldsymbol{B}_m=$$
$$=2\int^\infty d^3r\overbrace{\frac{\partial}{\partial\boldsymbol{r}}\cdot\left(\delta\boldsymbol{A}\times\boldsymbol{B}_m\right.}\Big)=2\int^\infty d^3r\delta\boldsymbol{A}\cdot\left(\frac{\partial}{\partial\boldsymbol{r}}\times\boldsymbol{B}_m\right)=$$
$$=2\int_V d^3r\delta\boldsymbol{A}\cdot\left(\frac{\partial}{\partial\boldsymbol{r}}\times\boldsymbol{B}_{\text{tot}}\right)+\cdots. \tag{60}$$

In the fourth equality an integration per parts was performed, and $\boldsymbol{a}\cdot(\boldsymbol{b}\times\boldsymbol{c})=-\boldsymbol{b}\cdot(\boldsymbol{a}\times\boldsymbol{c})$ was used. (The over brace indicates the range of the differential operator.) Finally, the integral over the infinite space is split into an integral over the superconductor (volume V), where $(\partial/\partial \boldsymbol{r})\times\boldsymbol{B}_m = (\partial/\partial \boldsymbol{r})\times\boldsymbol{B}_{\text{tot}}$, and the integral over the volume outside of the superconductor, indicated by dots, since we do not need it. Now, after adding the prefactors from (56a) we see that stationarity of (56a) with respect to a variation $\delta\boldsymbol{A}$ inside the volume V again leeds to (59).

This situation is no accident. From a more general point of view the Ginsburg-Landau functional (56a) may be considered as an effective Hamiltonian for the fluctuations of the fields Ψ and $\boldsymbol{A}$ near the phase transition.[1] This is precisely the meaning of relating (56a) to (3).

Eqs. (57) and (59) form the complete system of the Ginsburg-Landau equations.

The boundary condition (58) comes about by the special writing of (56a) without additional surface terms. This is correct for a boundary superconductor/vacuum or superconductor/semiconductor. A careful analysis on a *microscopic* theory level yields the more general boundary condition

$$\boxed{\boldsymbol{n}\cdot\left(\frac{\hbar}{i}\frac{\partial}{\partial \boldsymbol{r}} + 2e\boldsymbol{A}\right)\Psi = \frac{i\Psi}{b},} \tag{61}$$

where b depends on the *outside* material: $b = \infty$ for vacuum or a non-metal, $b = 0$ for a ferromagnet, b finite and non-zero for a normal metal.[2]

In all cases, multiplying (61) by Ψ^* and taking the real part yields

$$\boldsymbol{n}\cdot\boldsymbol{j}_s = 0 \tag{62}$$

as it must: there is no supercurrent passing through the surface of a superconductor into the non-superconducting volume.

$\boldsymbol{B}_{\text{tot}}$ must be continuous on the boundary because, according to $\partial\boldsymbol{B}_{\text{tot}}/\partial\boldsymbol{r} = 0$ and (59), its derivatives are all finite.

4.3 The Ginsburg-Landau parameter

Taking the curl of (59) yields, like in (13),

$$\frac{\partial^2 B_{\text{tot}}}{\partial \boldsymbol{r}^2} = \frac{B_{\text{tot}}}{\lambda^2}, \quad \lambda^2 = \frac{m}{2\mu_0 e^2|\Psi|^2} = \frac{m\beta}{2\mu_0 e^2\alpha|t|}, \tag{63}$$

where (51) was taken into account in the last expression. λ is the *Ginsburg-Landau penetration depth;* it diverges at T_c like $\lambda \sim |t|^{-1}$: if T_c is approached from below, the external field penetrates more and more, and eventually, at T_c, the diamagnetism vanishes.

Eq. (57) contains a second length parameter: In the absence of an external field, $\boldsymbol{A} = 0$, and for small Ψ, $|\Psi|^2 \ll \alpha|t|/\beta$, one is left with

$$\frac{\partial^2\Psi}{\partial \boldsymbol{r}^2} = \frac{\Psi}{\xi^2}, \quad \xi^2 = \frac{\hbar^2}{4m\alpha|t|}. \tag{64}$$

This equation describes spatial modulations of the order parameter $|\Psi|^2$ close to T_c. ξ is the *Ginsburg-Landau coherence length* of such order parameter fluctuations. It has the same temperature dependence as λ, and their ratio,

$$\kappa = \frac{\lambda}{\xi} = \sqrt{\frac{2m^2\beta}{\hbar^2\mu_0 e^2}}, \tag{65}$$

is the celebrated *Ginsburg-Landau parameter.*

[1] L. D. Landau and E. M. Lifshits, *Statistical Physics, Part I*, §147, Pergamon, London, 1980.
[2] P. G. De Gennes, *Superconductivity in metals and alloys*, New York 1966, p. 225 ff.

Introduction of dimensionless quantities

$$
\boxed{\begin{aligned}
&\boldsymbol{x} = \boldsymbol{r}/\lambda,\\
&\psi = \Psi \Big/ \sqrt{\frac{\alpha|t|}{\beta}},\\
&\boldsymbol{b} = \boldsymbol{B}_{\rm tot}\Big/\sqrt{2}B_c(t) = \boldsymbol{B}_{\rm tot}\Big/\left(\alpha|t|\sqrt{\frac{2\mu_0}{\beta}}\right),\\
&\boldsymbol{i}_s = \boldsymbol{j}_s\left(\lambda\mu_0\Big/\sqrt{2}B_c(t)\right),\\
&\boldsymbol{a} = \boldsymbol{A}\Big/\left(\sqrt{2}\lambda B_c(t)\right)
\end{aligned}} \tag{66}
$$

yields the *dimensionless Ginsburg-Landau equations*

$$
\boxed{\begin{aligned}
&\left(\frac{1}{i\kappa}\frac{\partial}{\partial\boldsymbol{x}} + \boldsymbol{a}\right)^2\psi - \psi + |\psi|^2\psi = 0,\\
&\frac{\partial}{\partial\boldsymbol{x}}\times\boldsymbol{b} = \boldsymbol{i}_s, \quad \boldsymbol{i}_s = \frac{i}{2\kappa}\left(\psi^*\frac{\partial}{\partial\boldsymbol{x}}\psi - \psi\frac{\partial}{\partial\boldsymbol{x}}\psi^*\right) - \psi^*\boldsymbol{a}\psi
\end{aligned}} \tag{67}
$$

which contain the only parameter κ.

4.4 The phase boundary

We consider a homogeneous superconductor at $T \lesssim T_c$ in an homogeneous external field $B \approx B_c(T)$ in z-direction. We assume a plane phase boundary in the $y-z$-plane so that for $x \to -\infty$ the material is still superconducting, and the magnetic field is expelled, but for $x \to \infty$ the material is in the normal state with the field penetrating.

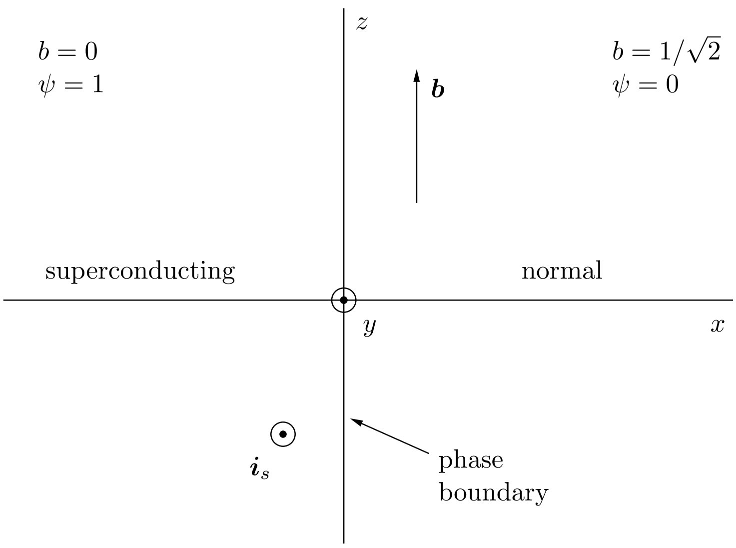


Figure 12: Geometry of a plane phase boundary.

We put

$$
\psi = \psi(x), \qquad b_z = b(x), \quad b_x = b_y = 0,
$$

$$a_y = a(x), \quad a_x = a_z = 0, \quad b(x) = a'(x).$$

Then, the supercurrent $\boldsymbol{i}_s$ flows in the y-direction, and hence the phase of ψ depends on y. We consider $y = 0$ and may then choose ψ real. Further, by fixing another gauge constant, we may choose $a(-\infty) = 0$.

Then, Eqs. (67) reduce to

$$-\frac{1}{\kappa^2}\psi'' + a^2\psi - \psi + \psi^3 = 0, \quad a'' = a\psi^2. \tag{68}$$

Let us first consider $\kappa \ll 1$. For large enough negative x we have $a \approx 0$ and $\psi \approx 1$. We put $\psi = 1-\epsilon(x)$, and get from the first equation (68)

$$\epsilon'' \approx \kappa^2\big(1 - \epsilon - 1 + 3\epsilon\big) = 2\kappa^2\epsilon, \quad \epsilon \sim e^{\sqrt{2}\kappa x}, \quad x \lesssim \kappa^{-1}.$$

On the other hand, for large enough positive x we have $b = 1/\sqrt{2}$, $a = x/\sqrt{2}$, $\psi \ll 1$, hence, again from the first equation (68),

$$\psi'' \approx \frac{\kappa^2 x^2}{2}\psi, \quad \psi \sim e^{-\kappa x^2/2\sqrt{2}}, \quad \kappa x^2 \gg 1.$$

The second Eq. (68) yields a penetration depth $\sim \psi_0^{-1}$, where ψ_0 denotes the value of $\psi(x)$ where the field drops:

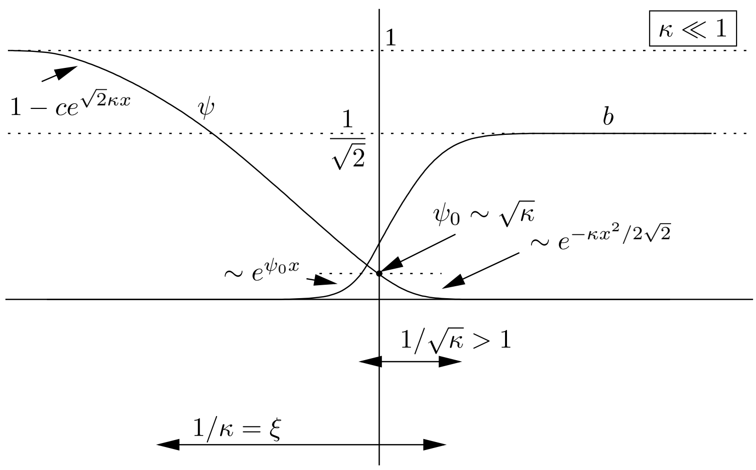


Figure 13: The phase boundary of a type I superconductor.

In the opposite case $\kappa \gg 1$, ψ falls off for $x \gtrsim 1$, where $b \approx 1/\sqrt{2}$, $a \approx x/\sqrt{2}$, and for $x \gg 1$, $\psi'' \approx \kappa^2 x^2 \psi/2$:

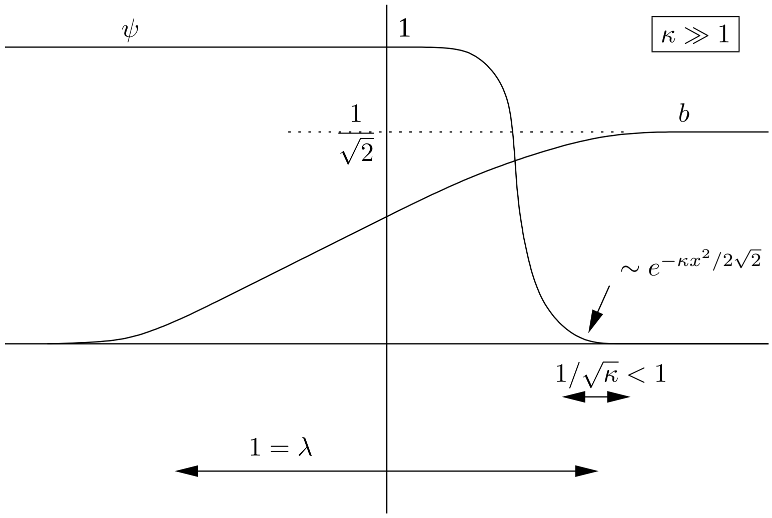


Figure 14: The phase boundary of a type II superconductor.

4.5 The energy of the phase boundary

For $B = B_c(T)$, $b = 1$ in our units, the Free Energy of the normal phase is just equal to the Free Energy of the superconducting phase in which $b = 0$, $\psi = 1$. If we integrate the Free Energy density variation (per unit area of the $y - z$-plane), we obtain the energy of the phase boundary per area:

$$\epsilon_{s/n} = \int_{-\infty}^{\infty} dx \left\{ \frac{(B - B_c)^2}{2\mu_0} + \frac{\hbar^2}{4m}\left(|\Psi'|^2 + \frac{4e^2}{\hbar^2} A^2 |\Psi|^2 \right) - \alpha|t||\Psi|^2 + \frac{\beta}{2}|\Psi|^4 \right\}. \tag{69}$$

Since the external field is B_c, we have used $\boldsymbol{B}_m = \boldsymbol{B}_{\text{tot}} - \boldsymbol{B}_{\text{ext}} = \boldsymbol{B} - \boldsymbol{B}_c$. In our dimensionless quantities this is (x is now measured in units of λ)

$$\begin{aligned} \epsilon_{s/n} &= \frac{\lambda B_c^2}{\mu_0} \int_{-\infty}^{\infty} dx \left\{ \big(b - \frac{1}{\sqrt{2}}\big)^2 + \frac{1}{\kappa^2}\psi'^2 + \big(a^2 - 1\big)\psi^2 + \frac{\psi^4}{2} \right\} = \\ &= \frac{\lambda B_c^2}{\mu_0} \int_{-\infty}^{\infty} dx \left\{ \big(a' - \frac{1}{\sqrt{2}}\big)^2 - \frac{1}{\kappa^2}\psi''\psi + \big(a^2 - 1\big)\psi^2 + \frac{\psi^4}{2} \right\} = \\ &= \frac{\lambda B_c^2}{\mu_0} \int_{-\infty}^{\infty} dx \left\{ \big(a' - \frac{1}{\sqrt{2}}\big)^2 - \frac{\psi^4}{2} \right\}. \end{aligned} \tag{70}$$

First an integration per parts of ψ'^2 was performed, and then (68) was inserted. We see that $\epsilon_{s/n}$ can have both signs:

$$\epsilon_{s/n} \gtrless 0 \quad \text{for} \quad \left(a' - \frac{1}{\sqrt{2}} \right)^2 \gtrless \frac{\psi^4}{2} \quad \text{or} \quad \frac{\psi^2}{\sqrt{2}} \lessgtr \big(\frac{1}{\sqrt{2}} - a' \big).$$

Since b must decrease if ψ^2 increases and $\psi = 0$ at $b = 1/\sqrt{2}$, $(b - 1/\sqrt{2}) = (a' - 1/\sqrt{2})$ and ψ^2 must have opposite signs which leads to the last condition. If

$$\frac{1}{\sqrt{2}} - a' = \frac{\psi^2}{\sqrt{2}}$$

would be a solution of (68), it would correspond to $\epsilon_{s/n} = 0$.

We now show that this is indeed the case for $\kappa^2 = 1/2$. First we find a first integral of (68):

$$\begin{aligned}
\psi'' &= \kappa^2\Big[\big(a^2-1\big)\psi + \psi^3\Big], \\
2\psi'\psi'' &= \kappa^2\Big[2\psi\psi' a^2 - 2\psi\psi' + 2\psi^3\psi'\Big] = \\
&= \kappa^2\Big[2\psi\psi' a^2 + \underbrace{2\psi^2 aa' - 2a'a''}_{=0 \text{ by the second Eq. (67)}} - 2\psi\psi' + 2\psi^3\psi'\Big] \\
{\psi'}^2 &= \kappa^2\Big[\psi^2 a^2 - {a'}^2 - \psi^2 + \frac{\psi^4}{2} + \text{const.}\Big] \qquad (71) \\
& \text{since } \psi' = \psi = 0 \text{ for } a' = \frac{1}{\sqrt{2}} \Longrightarrow \text{const.} = \frac{1}{2}.
\end{aligned}$$

Now we use

$$\kappa^2 = \frac{1}{2}, \quad \frac{1}{\sqrt{2}} - a' = \frac{\psi^2}{\sqrt{2}} \quad \Rightarrow \quad -a'' = \sqrt{2}\psi\psi' = -a\psi^2 \quad \Rightarrow \quad \psi' = -a\frac{\psi}{\sqrt{2}}$$

and have from (71)

$$ {\psi'}^2 = \frac{1}{2}\Big[2{\psi'}^2 - {a'}^2 - \big(1 - \sqrt{2}a'\big) + \big(\frac{1}{\sqrt{2}} - a'\big)^2 + \frac{1}{2}\Big],$$

which is indeed an identity.

Since ${\psi'}^2/\kappa^2 > 0$ enters the integral for $\epsilon_{s/n}$ in the first line of (70), it is clear that $\epsilon_{s/n}$ is positive for $\kappa^2 \to 0$. Therefore, the final result is

$$\boxed{\epsilon_{s/n} \gtrless 0 \quad \text{for} \quad \kappa \lessgtr \frac{1}{\sqrt{2}} \quad : \quad \text{type} \begin{array}{c} I \\ II \end{array}} \qquad (72)$$

The names "type I" and "type II" for superconductors were coined by Abrikosov,[1] and it was the existence of type II superconductors and a theoretical prediction by Abrikosov, which paved the way for technical applications of superconductivity.

[1]A. A. Abrikosov, Sov. Phys.–JETP **5**, 1174 (1957).

5 INTERMEDIATE STATE, MIXED STATE

In Chapter 2 we considered a superconductor in a sufficiently *weak* magnetic field, $B < B_c$, where we found the ideal diamagnetism, the Meissner effect, and the flux quantization.

In Chapter 3 we found that the difference between the thermodynamic potentials in the normal and the superconducting homogeneous phases per volume *without* magnetic fields may be expressed as (cf. (35))

$$\frac{1}{V}\Big[G_n(p,T) - G_s(p,T)\Big] = \frac{1}{V}\Big[F_n(V,T) - F_s(V,T)\Big] = \frac{B_c^2(T)}{2\mu_0} \tag{73}$$

by a *thermodynamic critical field* $B_c(T)$. (We neglect here again the effects of pressure or of corresponding volume changes on B_c.)

If a magnetic field $\boldsymbol{B}$ is applied to some volume part of a superconductor, it may be expelled (Meissner effect) by creating an internal field $\boldsymbol{B}_m = -\boldsymbol{B}$ through supercurrents, on the cost of an additional energy $\int d^3r B_m^2/2\mu_0$ for the superconducting phase (cf. (56a)) and of a kinetic energy density $(\hbar^2/4m)|(\partial/\partial\boldsymbol{r} + 2ie\boldsymbol{A}/\hbar)\Psi|^2$ in the surface where the supercurrents flow. If $B_m > B_c$, the Free Energy of the superconducting state becomes larger than that of the normal state *in a homogeneous situation.* However, $\boldsymbol{B}$ itself may contain a part created by currents in another volume of the superconductor, and phase boundary energies must also be considered. There are therefore long range interactions like in ferroelectrics and in ferromagnets, and corresponding domain patterns correspond to thermodynamic stable states. The external field $\boldsymbol{B}$ at which the phase transition appears depends on the geometry and on the phase boundary energy.

5.1 The intermediate state of a type I superconductor

Apply a homogeneous external field $\boldsymbol{B}_{\text{ext}}$ to a superconductor. $\boldsymbol{B} = \boldsymbol{B}_{\text{ext}} + \boldsymbol{B}_m$ depends on the shape of the superconductor. *Here and in all that follows $\boldsymbol{B}$ means $\boldsymbol{B}_{tot}$.* There is a certain point, at which $B = B_{\max} > B_{\text{ext}}$ (Fig. 15). If $B_{\max} > B_c$, the superconducting state becomes instable there. On could think of a normal-state concave island forming (Fig. 16).

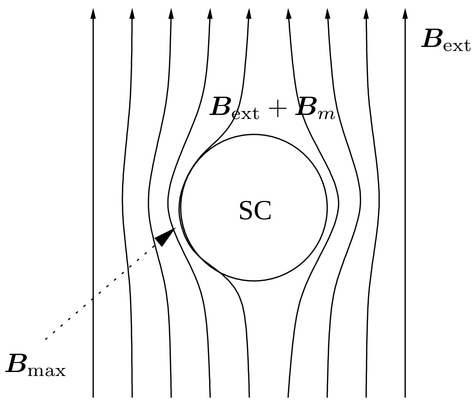


FIG. 15: Total (external plus induced) magnetic field around a type I superconductor.

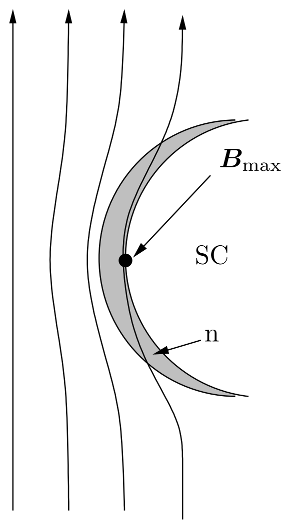


FIG. 16.

This, however, cannot be stable either: the point of $B_{\max} = B_c$ has now moved into the superconductor to a point of the phase boundary between the normal and superconducting phases, which means that in the shaded normal area $B < B_c$; this area must become superconducting again (Fig. 16). Forming of a convex island would cause the same problem (Fig. 17).

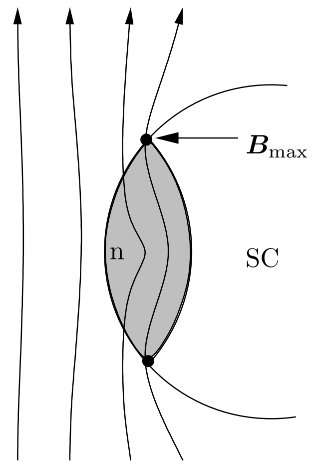


FIG. 17.

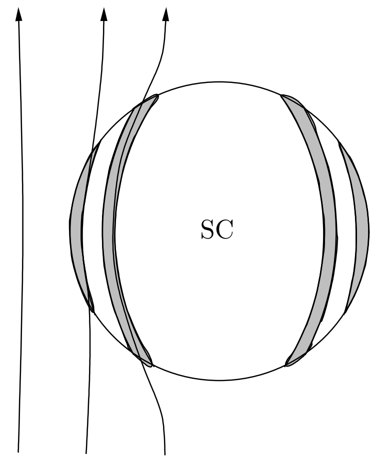


FIG. 18.

What really forms is a complicated lamellous or filamentous structure of alternating superconducting and normal phases through which the field penetrates (Fig. 18).

The true magnetization curve of a type I superconductor in different geometries is shown on Fig. 19. It depends on the geometry because the field created by the shielding supercurrents does. In Section 3.C, for $B \neq 0$ the phase transition was obtained to be first order. Generally, the movement of phase boundaries is hindered by defects, hence there is hysteresis around B_c.

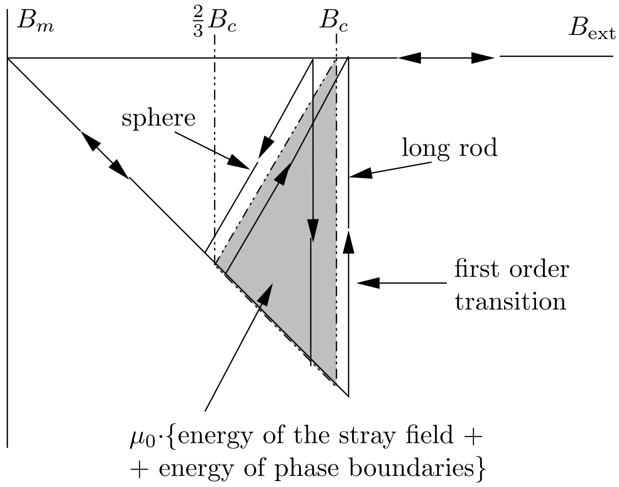


Figure 19:

5.2 Mixed state of a type II superconductor[1]

If the phase boundary energy is negative, germs of normal phase may form well below B_c, at the *lower critical field* B_{c1}, and germs of superconducting phase may form well above B_c, at the *upper critical field* B_{c2}, in both cases by gaining phase boundary energy.

At $B \lessapprox B_{c2}$, in small germs $\psi \ll 1$ and $b \approx$ const. The dimensionless Ginsburg-Landau equations (67) may be linearized:

$$\left(\frac{1}{i\kappa}\frac{\partial}{\partial \boldsymbol{x}} + \boldsymbol{a}\right)^2 \psi = \psi. \tag{74}$$

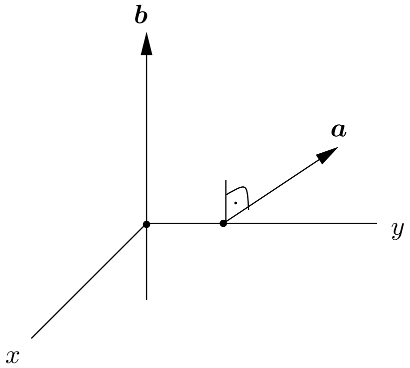


Figure 20:

We apply the external $\boldsymbol{B}$-field in z-direction (Fig. 20),

$$b_x = b_y = 0, \quad b_z = b, \quad a_x = -by, \quad a_y = a_z = 0,$$

and assume germ filaments along the field lines:

$$\psi = \psi(x, y).$$

Then, (74) is cast into

$$\left[\left(\frac{1}{i\kappa}\frac{\partial}{\partial x} - by\right)^2 - \frac{1}{\kappa^2}\frac{\partial^2}{\partial y^2}\right]\psi = \psi.$$

With $\psi(x, y) = e^{ipx}\phi(y)$, $p/(b\kappa) = y_0$ this equation simplifies to $[-(1/\kappa^2)(d^2/dy^2) + b^2(y - y_0)^2]\phi = \phi$, or, after multiplying with $\kappa/2$ and by defining $u^2 \equiv \kappa(y - y_0)^2$:

$$\left[-\frac{1}{2}\frac{d^2}{du^2} + \frac{1}{2}b^2u^2\right]\phi = \frac{\kappa}{2}\phi. \tag{75}$$

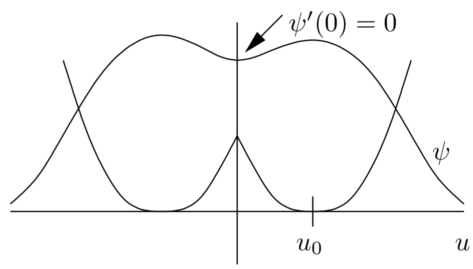
This is the Schrödinger equation for the ground state of a harmonic oscillator with

$$\omega = b = \kappa \quad \Longrightarrow \quad B = \sqrt{2}\kappa B_c.$$

Hence,

$$\boxed{B_{c2}(T) = \sqrt{2}\kappa B_c(T).} \tag{76}$$

If a germ close to the surface of a superconductor at y=const. is considered, then the u-coordinate must be cut at some finite value. There, the boundary condition (58) yields $d\phi/du = 0$ (since $\boldsymbol{n}\cdot\boldsymbol{a} = 0$). Therefore, instead of the boundary problem, the symmetric ground state in a double oscillator with a mirror plane may be considered (Fig. 21).



$$\min_{u_0} E_0 = 0.59\frac{\hbar\omega}{2}$$

FIG. 21: The ground state of a double oscillator.

[1] A. A. Abrikosov, unpublished 1955; Sov. Phys.–JETP **5**, 1174 (1957).

Hence, at

$$\boxed{B_{c3} = \frac{B_{c2}}{0.59} = 1.7B_{c2} = 2.4\kappa B_c} \tag{77}$$

superconductivity may set in in a surface layer of thickness $\sim \xi$.

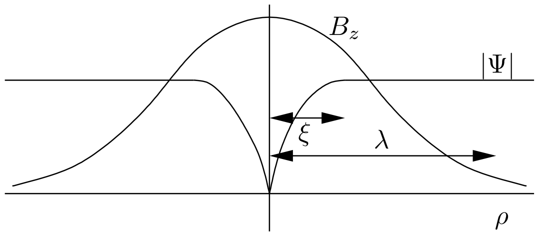
In a type I superconductor, $B_{c2} < B_c$. However, only below B_{c2} germs with arbitrarily small ψ-values could form where the superconducting phase is already absolutely stable in a type I superconductor. Here, for $B_{c2} < B < B_c$ germs can only form with a non-zero minimal ψ-value, which is inhibited by positive surface energy. In this region the supercooled normal phase is metastable. For $\kappa > 0.59/\sqrt{2}$, $B_{c3} > B_c$, and surface superconductivity may exist above B_c.

5.3 The flux line in a type II superconductor

To determine B_{c1}, the opposite situation is considered. In the homogeneous superconducting state with $\psi = 1$, the external magnetic field is tuned up until the first normal state germ is forming. Again we may suppose that the germ is forming along a field line in z-direction. Since the phase boundary energy is negative, there must be a tendency to form many face boundaries. However, the normal germs cannot form arbitrarily small since we know from (17) that the flux connected with a normal germ in a superconductor is quantized and cannot be smaller than

$$\Phi_0 = \frac{2\pi\hbar}{2e} = 2\pi\sqrt{2}B_c\lambda\xi = 2\pi\sqrt{2}B_c\frac{\lambda^2}{\kappa}, \tag{78}$$

where additionally the definition of λ, ξ and κ by (63–65) was used. We consider a flux line of total flux Φ_0 along the z-direction (Fig. 22):



$$\Psi = |\Psi|e^{i\theta},\ \boldsymbol{B} = \boldsymbol{e}_z B(\rho),\ \rho^2 = x^2 + y^2$$

FIG. 22: An isolated flux line.

One could try to solve the Ginsburg-Landau equations for that case. However, there is no general analytic solution, and the equations are valid close to T_c only, where $|\Psi|$ is small. Instead we assume $\kappa \gg 1$, that is, $\lambda \gg \xi$, and consider only the region $\rho \gg \xi$, where $|\Psi|$ =const. Then, from Ampere's law and (6),

$$\begin{aligned}\frac{\partial}{\partial \boldsymbol{r}} \times \boldsymbol{B} &= \mu_0 \boldsymbol{j}_s = \frac{\mu_0 e\hbar}{m}|\Psi|^2\frac{\partial\theta}{\partial\boldsymbol{r}} - \frac{2\mu_0 e^2}{m}|\Psi|^2\boldsymbol{A} = \\ &= \frac{2\mu_0 e^2|\Psi|^2}{m}\left(\frac{\hbar}{2e}\frac{\partial\theta}{\partial\boldsymbol{r}} - \boldsymbol{A}\right) = \frac{1}{\lambda^2}\left(\frac{\Phi_0}{2\pi}\frac{\partial\theta}{\partial\boldsymbol{r}} - \boldsymbol{A}\right),\end{aligned}$$

hence,

$$\boldsymbol{A} + \lambda^2\frac{\partial}{\partial\boldsymbol{r}} \times \boldsymbol{B} = \frac{\Phi_0}{2\pi}\frac{\partial\theta}{\partial\boldsymbol{r}}.$$

We integrate this equation along a circle around the flux line with radius $\rho \gg \xi$ and use Stokes' theorem, $\oint d\boldsymbol{s}\boldsymbol{A} = \int d^2\boldsymbol{n} \cdot (\frac{\partial}{\partial\boldsymbol{r}} \times \boldsymbol{A})$:

$$\int d^2\boldsymbol{n} \cdot \boldsymbol{B} + \lambda^2 \oint d\boldsymbol{s} \cdot \left(\frac{\partial}{\partial\boldsymbol{r}} \times \boldsymbol{B}\right) = \Phi_0. \tag{79}$$

The phase θ must increase by 2π on a circle around one fluxoid.

Now, we take $\xi \ll \rho \ll \lambda$. Then, the first term in (79) may be neglected. We find

$$-2\pi\rho\lambda^2 \frac{dB}{d\rho} = \Phi_0 \tag{80}$$

or

$$B(\rho) = \frac{\Phi_0}{2\pi\lambda^2} \ln\left(\frac{\rho_0}{\rho}\right), \qquad \rho_0 \approx \lambda. \tag{81}$$

The integration constant ρ_0 was chosen such that (81) vanishes for $\rho \gtrsim \lambda$, where a more accurate analysis of (79) is necessary to get the correct asymptotics.

By applying Stokes' theorem also to the second integral of (79), we have for all $\rho \gg \xi$

$$\int d^2\boldsymbol{n} \cdot \left(\boldsymbol{B} + \lambda^2 \frac{\partial}{\partial \boldsymbol{r}} \times \left(\frac{\partial}{\partial \boldsymbol{r}} \times \boldsymbol{B}\right)\right) = \int d^2\boldsymbol{n} \cdot \left(\boldsymbol{B} - \lambda^2 \frac{\partial^2}{\partial \boldsymbol{r}^2} \boldsymbol{B}\right) = \Phi_0.$$

Since the right hand side does not change if we vary the area of integration,

$$\boldsymbol{B} - \lambda^2 \frac{\partial^2}{\partial \boldsymbol{r}^2} \boldsymbol{B} = 0$$

must hold. In cylindric coordinates,

$$\frac{\partial^2}{\partial \boldsymbol{r}^2} = \frac{1}{\rho}\frac{\partial}{\partial \rho}\rho\frac{\partial}{\partial \rho} + \frac{1}{\rho^2}\frac{\partial^2}{\partial \phi^2} + \frac{\partial^2}{\partial z^2},$$

hence,

$$B - \lambda^2 \frac{1}{\rho}\frac{\partial}{\partial \rho}\rho\frac{\partial}{\partial \rho} B = 0$$

or

$$B'' + \frac{1}{\rho} B' - \frac{1}{\lambda^2} B = 0. \tag{82}$$

This equation is of the Bessel type. Its for large ρ decaying solution is

$$B(\rho) = \frac{\Phi_0}{2\pi\lambda^2} K_0\left(\frac{\rho}{\lambda}\right) \xrightarrow[\rho\to\infty]{} \frac{\Phi_0}{\sqrt{8\pi\rho\lambda^2}} e^{-\rho/\lambda}, \tag{83}$$

where K_0 is McDonald's function (Hankel's function with imaginary argument), and the coefficient has been chosen to meet (80) for $\rho \ll \lambda$.

The energy per length ϵ of the flux line consists of field energy and kinetic energy of the supercurrent:

$$\begin{aligned}
\epsilon &= \int d^2\boldsymbol{r}\left(\frac{B^2}{2\mu_0} + \frac{m_B}{2} n_B v^2\right), \quad \boldsymbol{j}_s = -2en_B v, \quad n_B = |\Psi|^2, \\
\epsilon &= \int d^2\boldsymbol{r}\left(\frac{B^2}{2\mu_0} + \frac{m}{4e^2 n_B} j_s^2\right) = \\
&= \int d^2\boldsymbol{r}\left[\frac{B^2}{2\mu_0} + \frac{m}{4\mu_0^2 e^2 |\Psi|^2}\left(\frac{\partial}{\partial \boldsymbol{r}} \times \boldsymbol{B}\right)^2\right] = \\
&= \int d^2\boldsymbol{r}\left[\frac{B^2}{2\mu_0} + \frac{\lambda^2}{2\mu_0}\left(\frac{\partial}{\partial \boldsymbol{r}} \times \boldsymbol{B}\right) \cdot \left(\frac{\partial}{\partial \boldsymbol{r}} \times \boldsymbol{B}\right)\right] = \\
&= \frac{1}{2\mu_0}\int d^2\boldsymbol{r}\boldsymbol{B} \cdot \left[\boldsymbol{B} + \lambda^2 \frac{\partial}{\partial \boldsymbol{r}} \times \left(\frac{\partial}{\partial \boldsymbol{r}} \times \boldsymbol{B}\right)\right] - \\
&\quad -\frac{\lambda^2}{2\mu_0}\left(\oint_{\rho\approx\xi} - \oint_{\rho\to\infty}\right) d\boldsymbol{s} \cdot \left[\boldsymbol{B} \times \left(\frac{\partial}{\partial \boldsymbol{r}} \times \boldsymbol{B}\right)\right].
\end{aligned}$$

The first integrand was shown to vanish for $\rho \gg \xi$, and the last contour integral vanishes for $\rho \to \infty$. We neglect the contribution from $\rho \lesssim \xi$, and find with (80))

$$\epsilon \approx -\frac{\lambda^2}{2\mu_0} 2\pi\xi B \frac{dB}{d\rho} \approx \frac{\Phi_0 B(\xi)}{2\mu_0} \approx \frac{\Phi_0 B(0)}{2\mu_0}. \tag{84}$$

With (81), the final result with logarithmic accuracy ($\ln(\xi/\lambda) \ll 1$) is

$$\epsilon \approx \frac{\Phi_0^2}{4\pi\mu_0\lambda^2} \ln\left(\frac{\lambda}{\xi}\right) = \frac{\Phi_0^2}{4\pi\mu_0\lambda^2} \ln\kappa. \tag{85}$$

This result also proves that the total energy is minimum for flux lines containing one fluxoid each: For a flux line containing n fluxoids the energy would be $n^2\epsilon$ while for n flux lines it would only be $n\epsilon$ ($\epsilon > 0$).

In this analysis, $\boldsymbol{B}$ was the field created by the supercurrent around the vertex line. Its interaction energy per length with a homogeneous external field in the same direction is

$$-\int d^2r \frac{BB_{\text{ext}}}{\mu_0} = -\frac{\Phi_0 B_{\text{ext}}}{\mu_0}. \tag{86}$$

(85) and (86) are equal at the lower critical field $B_{\text{ext}} = B_{c1}$:

$$\boxed{B_{c1} = \frac{\Phi_0}{4\pi\lambda^2} \ln\kappa = B_c \frac{\ln\kappa}{\sqrt{2}\kappa}, \quad \kappa \gg 1.} \tag{87}$$

The phase diagram of a type II superconductor is shown in Fig. 23. (There might be another phase with spatially modulated order parameter under certain conditions, theoretically predicted independently by Fulde and Ferell and by Larkin and Ovshinnikov; this FFLO phase has not yet been clearly observed experimentally.)

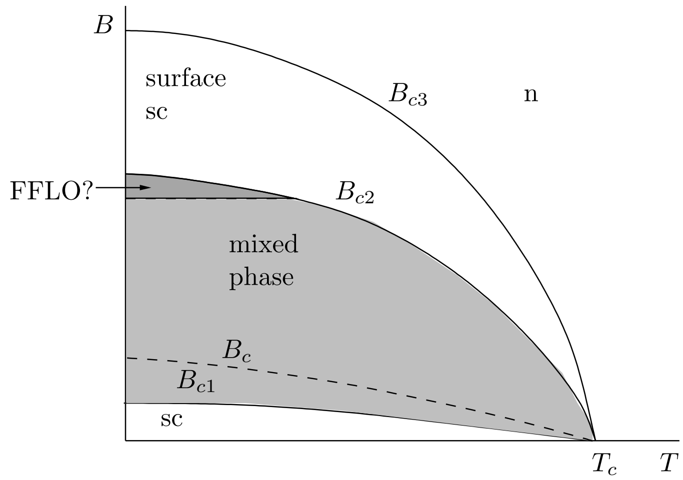


Figure 23: The phase diagram of a type II superconductor.

A more detailed numerical calculation shows that in an isotropic material the energy is minimum for a regular triangular lattice of the flux lines in the plane perpendicular to them. From (87), at $B = B_{c1}$ the density of flux lines is $\ln\kappa/4\pi\lambda^2$, that is, the lattice constant a_1 is obtained from $a_1^2\sqrt{3}/2 = 4\pi\lambda^2/\ln\kappa$:

$$a_1 = \sqrt{\frac{8\pi}{\sqrt{3}\ln\kappa}}\,\lambda \gtrsim \lambda. \tag{88}$$

The lines (of thickness λ) indeed form nearly individually (Fig. 24). Since $B_{c2} = B_{c1}2\kappa^2/\ln\kappa$, the lattice constant a_2 at B_{c2} is

$$a_2 = a_1\sqrt{\frac{\ln\kappa}{2\kappa^2}} = \sqrt{\frac{4\pi}{\sqrt{3}}\,\frac{\lambda}{\kappa}} = \sqrt{\frac{4\pi}{\sqrt{3}}}\,\xi \gtrsim \xi. \tag{89}$$

The cores of the flux lines (of thickness ξ) touch each other while the field is already quite homogeneous (Fig. 25). Since $|\Psi| \ll 1$ in the core, the Ginsburg-Landau equations apply, and $|\Psi|$ may rise continuously from zero: the *phase transition at B_{c2} is second order.*

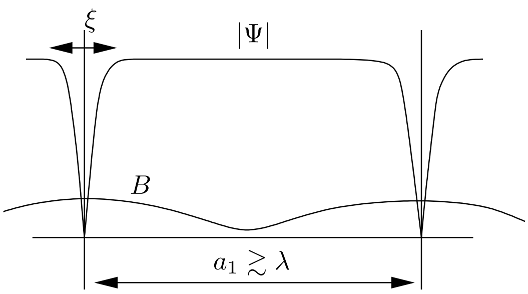


FIG. 24: Mixed phase for $B_{\text{ext}} \approx B_{c1}$.

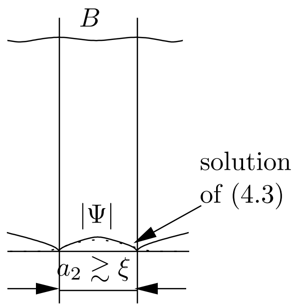


FIG. 25: Mixed phase for $B_{\text{ext}} \approx B_{c2}$.

For a long cylindric rod the stray field created by supercurrents outside of the rod may be neglected, and one may express the field inside the rod as

$$B = B_{\text{ext}} - \mu_0 M$$

by a magnetization density M. The change in Free Energy at fixed T and V by tuning up the external magnetic field is

$$dF = M dB_{\text{ext}}$$

$$F_n - F_s = \int_0^{B_{c2}} dB_{\text{ext}} M = \frac{B_c^2}{2\mu_0}.$$

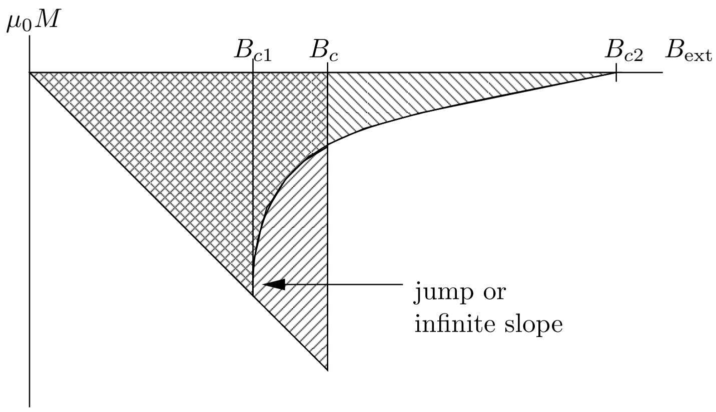


Figure 26: Magnetization curve of a type II superconductor.

The differently dashed areas in Fig. 26 are equal. For type II superconductors, B_c is only a theoretical quantity.

6 JOSEPHSON EFFECTS[1]

The quantitative description of Josephson effects at $T \ll T_c$ (the usual case in applications) needs a microscopic treatment. However, *qualitatively* they are the same at all temperatures $T < T_c$, hence qualitatively they may be treated within the Ginsburg-Landau theory.

Consider a very thin weak link between two halfs of a superconductor (Fig. 27).

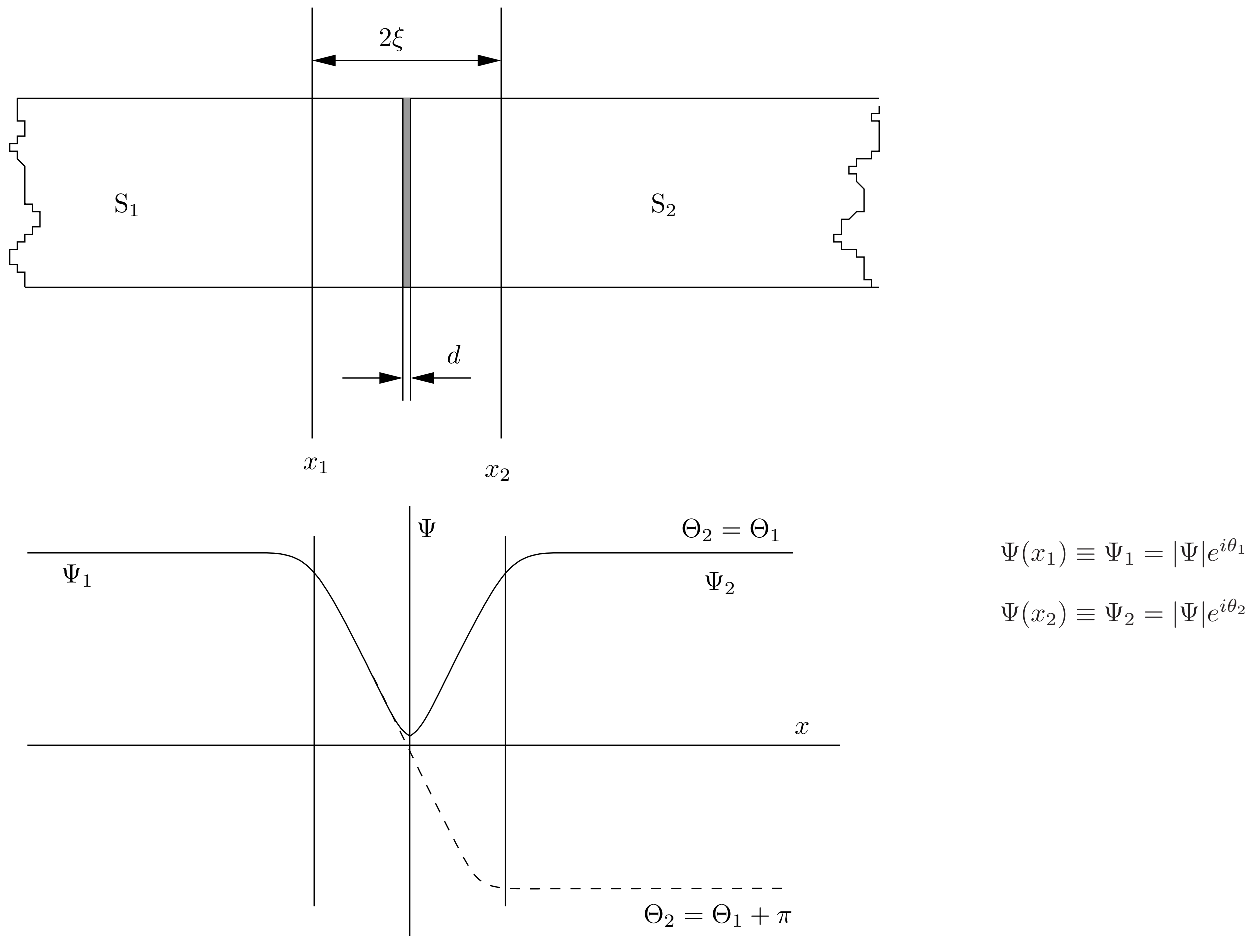


FIG. 27: A weak link between two halfs of a superconductor.

The order parameter has its thermodynamic value on both sides $x < x_1$, $x > x_2$, 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 $\theta_2 = \theta_1$ to $\theta_2 = \theta_1 + \pi$ by a very small perturbation).

Without the right half, the boundary condition (58) would hold at x_1 :

$$\left(\frac{\partial}{\partial x} + \frac{2ie}{\hbar} A_x\right)\Psi\bigg|_{x_1} = 0.$$

In the presence of the right half, this condition must be modified to slightly depending on the value Ψ_2 :

$$\left(\frac{\partial}{\partial x} + \frac{2ie}{\hbar} A_x\right)\Psi\bigg|_{x_1} = c\Psi_2, \tag{90}$$

[1]B. D. Josephson, Phys. Lett. **1**, 251 (1962).

where c is a small number depending on the properties of the weak link. Time inversion symmetry demands that (90) remains valid for $\Psi \to \Psi^*$, $\boldsymbol{A} \to -\boldsymbol{A}$, hence c must be real as long as the phase of Ψ does not depend on $\boldsymbol{A}$. For the moment we choose a gauge in which $A_x = 0$. Then, the supercurrent density at x_1 is

$$\begin{aligned} j_{s,x}(x_1) &= \frac{ie\hbar}{2m}\left[\Psi_1^*\frac{\partial\Psi}{\partial x}\bigg|_{x_1} - \Psi_1\frac{\partial\Psi^*}{\partial x}\bigg|_{x_1}\right] = \\ &= \frac{ie\hbar}{2m}c\Big[\Psi_1^*\Psi_2 - \Psi_1\Psi_2^*\Big] = \\ &= \frac{j_m}{2}\left[e^{i(\theta_2-\theta_1)} - e^{i(\theta_1-\theta_2)}\right] = j_m\sin\big(\theta_2-\theta_1\big). \end{aligned} \tag{91}$$

We generalize the argument of the sine function by a general gauge transformation (22):

$$\begin{aligned} \theta &\longrightarrow \theta - \frac{2e}{\hbar}\chi, \\ \boldsymbol{A} &\longrightarrow \boldsymbol{A} + \frac{\partial\chi}{\partial\boldsymbol{r}}, \quad \left(A_x = 0 \to A_x = -\frac{\partial\chi}{\partial x}\right), \\ \phi &\longrightarrow \phi + 2e\frac{\partial\chi}{\partial t} \end{aligned}$$

$$\theta_2 - \theta_1 \longrightarrow \gamma = \theta_2 - \theta_1 - \frac{2e}{\hbar}\big(\chi_2 - \chi_1\big) = \theta_2 - \theta_1 + \frac{2e}{\hbar}\int_1^2 dx A_x, \tag{92}$$

$$\frac{d\gamma}{dt} = \frac{2e}{\hbar}\big(\phi_2 - \phi_1\big). \tag{93}$$

Recall that ϕ is the electrochemical potential measured by a voltmeter.

Now, the general *Josephson equation* reads

$$\boxed{j_s = j_m \sin\gamma.} \tag{94}$$

6.1 The d.c. Josephson effect, quantum interference

According to (94), a d.c. supercurrent of any value between $-j_m$ and j_m may flow through the junction, and according to (93) the potential difference $\phi_2 - \phi_1$ is zero in that case.

Now, consider a junction in the $y-z$-plane with a magnetic field applied in z-direction. There are supercurrents screening the field away from the bulks of the superconducting halfs.

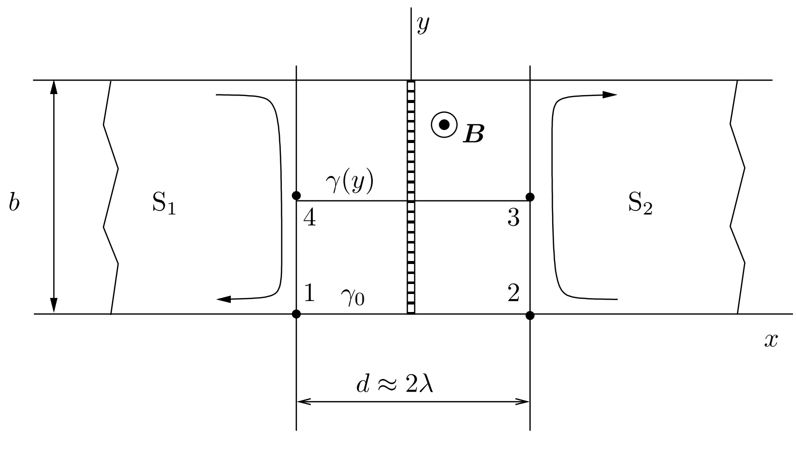


Figure 28: A Josephson junction in an external magnetic field $\boldsymbol{B}$.

Let us consider $\gamma(y)$, and let $\gamma(0) = \gamma_0$ at the edge $y = 0$. We have

$$Byd = \int_{1234} d\boldsymbol{s} \cdot \boldsymbol{A} = \int_1^2 dx A_x + \int_2^3 dy A_y + \int_3^4 dx A_x + \int_4^1 dy A_y.$$

In the junction we choose the gauge $A_x = -By$, $A_y = 0$. Then, the y-integrals vanish, and from (92),

$$\gamma(0) = \theta_2 - \theta_1 = \gamma_0, \quad \gamma(y) = \gamma_0 + \frac{2\pi}{\Phi_0} \int_4^3 dx By = \gamma_0 + \frac{2\pi Bd}{\Phi_0} y.$$

The d.c. Josephson current density through the junction oscillates with y according to

$$j_s(y) = j_m \sin\left(\gamma_0 + \frac{2\pi Bd}{\Phi_0} y\right).$$

In experiment, at $B = 0$ one always starts from a biased situation with $j_s = j_m$, hence $\gamma_0 = \pi/2$, and

$$j_s(y) = j_m \cos \frac{2\pi Bd}{\Phi_0} y. \tag{95}$$

The total current through the junction is

$$I_s = c j_m \int_0^b dy \cos \frac{2\pi Bd}{\Phi_0} y,$$

where c is the thickness in z-direction. $F = bc$ is the area of the junction. With

$$\int_0^b dy \cos(\beta y) = \Re \int_0^b dy e^{i\beta y} = \Re \frac{e^{i\beta b} - 1}{i\beta} = \frac{\sin(\beta b)}{\beta}$$

we find that, depending on the phase γ_0, the maximal current at a given field B is

$$I_{s,\max} = F j_m \frac{|\sin(2\pi Bbd/\Phi_0)|}{2\pi Bbd/\Phi_0}. \tag{96}$$

An even simpler situation appears, if one splits the junction into a double junction: Now, $\oint d\boldsymbol{s} \cdot \boldsymbol{A} = \Phi$ is the magnetic flux through the cut-out, and

$$\gamma_a - \gamma_b = \frac{2\pi}{\Phi_0} \oint d\boldsymbol{s} \cdot \boldsymbol{A} = 2\pi \frac{\Phi}{\Phi_0}.$$

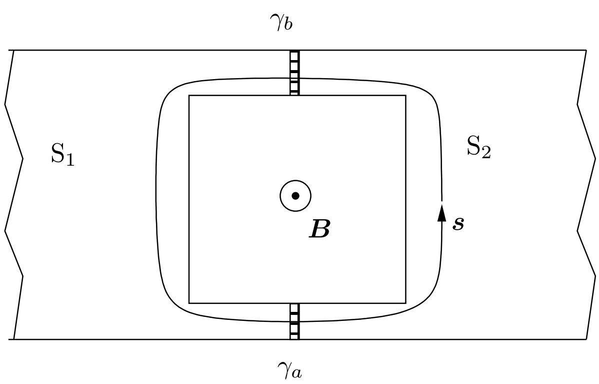


Figure 29: A simple SQUID geometry.

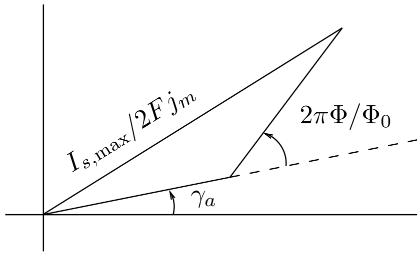


Figure 30: Phase relations in Eq.(97).

Hence, the maximal d.c. Josephson current is

$$I_{s,\max} = Fj_m \max_{\gamma_a}\left[\sin\gamma_a + \sin\left(\gamma_a + \frac{2\pi\Phi}{\Phi_0}\right)\right].$$

$$I_{s,\max} = 2Fj_m\left|\cos\left(\pi\frac{\Phi}{\Phi_0}\right)\right|. \tag{97}$$

This is the basis to experimentally count flux quanta with a device called superconducting quantum interferometer (SQUID).

6.2 The a.c. Josephson effect

We return to (93) and (94), and apply a voltage $\phi_2 - \phi_1 = V$ to the junction, that is, $\gamma = (2e/\hbar)Vt$. An *a.c. Josephson current*

$$j_s(t) = j_m \sin\omega_J t, \quad \omega_J = 2eV/\hbar \tag{98}$$

results, although a *constant* voltage is applied. For a voltage of 10 μV a frequency $\omega_J/2\pi = 4.8$ GHz is obtained: the a.c. Josephson effect is in the microwave region.

If one overlays a radio frequency voltage over the constant voltage,

$$\phi_2 - \phi_1 = V + V_r\cos(\omega_r t), \tag{99}$$

one obtains a frequency modulation of the a.c. Josephson current:

$$\begin{aligned} j_s &= j_m \sin\left(\omega_J t + \frac{2eV_r}{\hbar\omega_r}\sin(\omega_r t)\right) = \\ &= j_m \sum_{n=-\infty}^{\infty} J_{|n|}\left(\frac{2eV_r}{\hbar\omega_r}\right)\sin(\omega_J + n\omega_r)t. \end{aligned} \tag{100}$$

$J_{|n|}$ is the Bessel function of integer index.

To interpret the experiments one must take into account that a non-zero voltage across the junction causes also a dissipative normal current $I_n = V/R$, where R is the resistance of the junction for normal electrons.

The experimental issue depends on the coupling in of the radio frequency.[1] If the impedance of the radio source is small compared to that of the junction, we have a voltage-source situation, and the total current through the junction averaged over radio frequencies is

$$I = I_s + V/R, \quad I_s = \overline{j_s}F. \tag{101}$$

[1] S. Shapiro, Phys. Rev. Lett. **11**, 80 (1963).

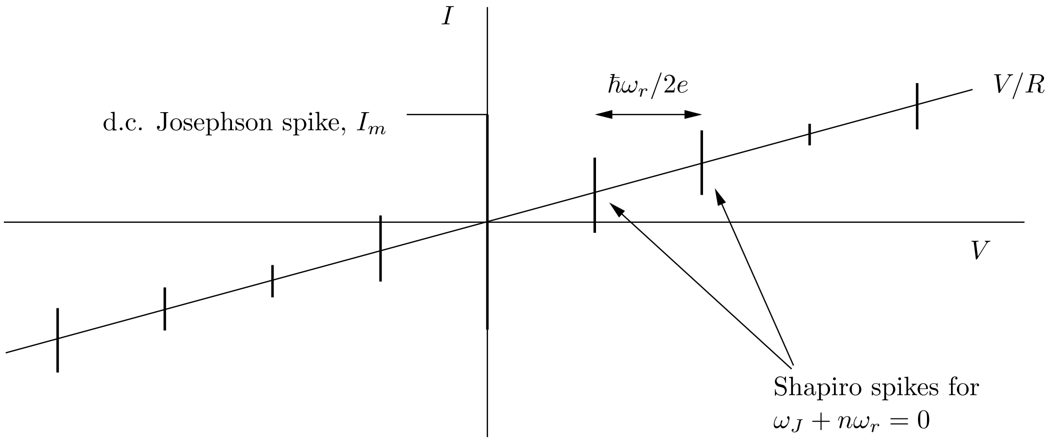


Figure 31: Josephson current vs. voltage in the voltage-source situation.

If the impedance of the radio source is large compared to the impedance of the Josephson junction, as is usually the case, we have a current-source situation, where the fed-in total current determines the voltage across the junction:

$$V = \frac{\hbar}{2e}\frac{d\gamma}{dt} = R(I - I_s) = R(I - I_m \sin\gamma). \tag{102}$$

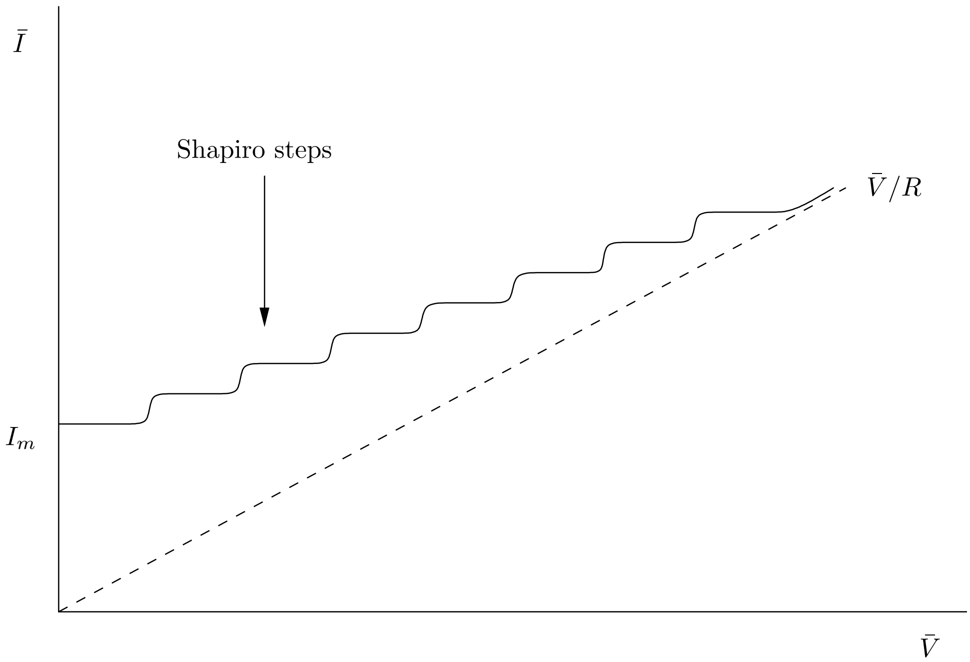


Figure 32: Josephson current vs. voltage in the current-source situation.

The a.c. Josephson effect yields a possibility of precise measurements of h/e.

7 MICROSCOPIC THEORY: THE FOCK SPACE

The Schrödinger wavefunction of an (isolated) electron is a function of its position, $\boldsymbol{r}$, and of the discrete spin variable, $s : \phi = \phi(\boldsymbol{r}, s)$. Since there are only two independent spin states for an electron — the spin component with respect to any (single) chosen axis may be either up (↑) or down (↓) —, s takes on only two values, + and −, hence ϕ may be thought as consisting of two functions

$$\phi(\boldsymbol{r}, s) = \begin{pmatrix} \phi(\boldsymbol{r}, +) \\ \phi(\boldsymbol{r}, -) \end{pmatrix} \tag{103}$$

forming a spinor function of $\boldsymbol{r}$. The expectation value of any (usually local) one-particle operator $A(\boldsymbol{r}, s, \boldsymbol{r}', s') = \delta(\boldsymbol{r} - \boldsymbol{r}')\hat{A}(\boldsymbol{r}, s, s')$ is

$$\langle A \rangle = \sum_{s,s'} \int d^3r \phi^*(\boldsymbol{r}, s)\hat{A}(\boldsymbol{r}, s, s')\phi(\boldsymbol{r}, s'). \tag{104}$$

We will often use a short-hand notation $x \equiv (\boldsymbol{r}, s)$.

The Schrödinger wavefunction $\Psi(x_1 \dots x_N)$ of a (fermionic) many-particle quantum state must be totally antisymmetric with respect to particle exchange (Pauli principle):

$$\Psi(\dots x_i \dots x_k \dots) = -\Psi(\dots x_k \dots x_i \dots). \tag{105}$$

For a piece of a solid, $N \sim 10^{23}$, this function is totally incomprehensible and practically inaccessible: For any set of N values, + or − for each s_i, it is a function of $3N$ positional coordinates. Although by far not all of those 2^N functions are independent — with the symmetry property (105) the +- and −-values can always be brought to an order that all −-values precede all +-values, hence we have only to distinguish 0, 1, 2, ..., N −-values, that is $(N + 1)$ cases — and although each of those $(N + 1)$ functions need only be given on a certain sector of the $3N$-dimensional position space — again with the symmetry property (105) each function need only be given for a certain order of the particle coordinates for all $s_i = -$ and for all $s_i = +$ particles —, it is clear that even if we would be content with 10 grid points along each coordinate axis we would need $\sim 10^{10^{23}}$ grid points for a very crude numerical representation of that Ψ-function. Nevertheless, for formal manipulations, we can introduce in a systematic manner a functional basis in the functional space of those horrible Ψ-functions.

7.1 Slater determinants

Consider some (for the moment arbitrarily chosen) complete orthonormal set of one-particle spinor functions ,

$$\phi_l(x), \qquad (\phi_l|\phi_{l'}) = \sum_s \int d^3r \phi_l^*(\boldsymbol{r}, s)\phi_{l'}(\boldsymbol{r}, s) = \delta_{ll'},$$

$$\sum_l \phi_l(x)\phi_l^*(x') = \delta(x - x') = \delta_{ss'}\delta(\boldsymbol{r} - \boldsymbol{r}'). \tag{106}$$

They are commonly called *(spinor-)orbitals.* The quantum number l refers to both the spatial and the spin state and is usually already a multi-index (for instance $(nlm\sigma)$ for an atomic orbital or $(\boldsymbol{k}\sigma)$ for a plane wave), and we agree upon a certain once and forever given linear order of those l-indices. Choose N of those orbitals, $\phi_{l_1}, \phi_{l_2}, \dots, \phi_{l_N}$, in ascending order of the l_i and form the determinant

$$\Phi_L(x_1 \dots x_N) = \frac{1}{\sqrt{N!}} \det \|\phi_{l_i}(x_k)\|. \tag{107}$$

$L = (l_1 \dots l_N)$ is a new (hyper-)multi-index which labels an *orbital configuration.* This determinant of a matrix $a_{ik} = \phi_{l_i}(x_k)$ for every point $(x_1 \dots x_N)$ in the spin-position space has the proper symmetry property (105). In view of (106) it is normalized, if all l_i are different, and it would be identically zero, if at least two of the l_i would be equal (determinant with two equal raws): Two fermions cannot be in the same spinor-orbital. This is the compared to (105) very special case of the Pauli principle (which is the commonly known case).

Now, given a complete set of orbitals (106), we mention without proof that all possible orbital configurations of N orbitals (107) form a complete set of N-fermion wavefunctions (105), that is, any wavefunction (105) may be represented as

$$\Psi(x_1 \dots x_N) = \sum_L C_L \Phi_L(x_1 \dots x_N) \tag{108}$$

with certain coefficients C_L, $\sum_L |C_L|^2 = 1$ ('configuration interaction').

For any operator which can be expanded into its one-particle, two-particle- and so on parts as for instance a Hamiltonian with (possibly spin-dependent) pair interactions,

$$\hat{H} = \sum_i \hat{h}_{s_i s'_i}(\boldsymbol{r}_i) + \frac{1}{2} \sum_{i \neq j} w_{s_i s'_i, s_j s'_j}(\boldsymbol{r}_i, \boldsymbol{r}_j), \tag{109}$$

the matrix with Slater determinants is

$$\begin{aligned} H_{LL'} = \langle \Phi_L | \hat{H} | \Phi_{L'} \rangle \quad &= \quad \sum_i \sum_{\mathcal{P}} (l_{\mathcal{P}i} | h | l'_i) \, (-1)^{|\mathcal{P}|} \prod_{j(\neq i)} \delta_{l_{\mathcal{P}j} l'_j} + \\ &+ \frac{1}{2} \sum_{i \neq j} \sum_{\mathcal{P}} (l_{\mathcal{P}i} l_{\mathcal{P}j} | w | l'_j l'_i) \, (-1)^{|\mathcal{P}|} \prod_{k(\neq i,j)} \delta_{l_{\mathcal{P}k} l'_k}, \end{aligned} \tag{110}$$

where $\mathcal{P}$ is any permutation of the subscripts i, j, k, and $|\mathcal{P}|$ is its order. The matrix elements are defined as

$$(l_i | h | l'_i) = \sum_{ss'} \int d^3 r \phi^*_{l_i}(\boldsymbol{r}, s) \hat{h}_{ss'}(\boldsymbol{r}) \phi_{l'_i}(\boldsymbol{r}, s'), \tag{111}$$

and

$$(l_i l_j | w | l'_j l'_i) = \sum_{s_i s'_i, s_j s'_j} \int d^3 r_i d^3 r_j \; \phi^*_{l_i}(\boldsymbol{r}_i, s_i) \phi^*_{l_j}(\boldsymbol{r}_j, s_j) \; w_{s_i s'_i, s_j s'_j}(\boldsymbol{r}_i, \boldsymbol{r}_j) \; \phi_{l'_j}(\boldsymbol{r}_j, s'_j) \phi_{l'_i}(\boldsymbol{r}_i, s'_i). \tag{112}$$

(Note our convention on the order of indices which may differ from that in other textbooks but leads to a certain canonical way of writing of formulas later on.) The first line on the r.h.s. of (110) is non-zero only if the two configurations L and L' differ at most in one orbital, and the sum over all permutations $\mathcal{P}$ has only one non-zero term in this case, determining the sign factor for that matrix element. The second line is non-zero only if the two configurations differ at most in two orbitals, and the sum over all permutations has two non-zero terms in that case: if $\mathcal{P}$ is a perturbation with $l_{\mathcal{P}k} = l'_k$ for all $k \neq i, j$, then the corresponding contribution is $(1/2)[(l_{\mathcal{P}i} l_{\mathcal{P}j} | w | l'_j l'_i) - ((l_{\mathcal{P}j} l_{\mathcal{P}i} | w | l'_j l'_i)](-1)^{|\mathcal{P}|}$. For $L = L'$ and $\mathcal{P}$ = identity (and sometimes also in the general case) the first matrix element is called *direct interaction* and the second one *exchange interaction.*

7.2 The Fock space

Up to here we considered representations of quantum mechanics by wavefunctions with the particle number N of the system fixed. If this number is macroscopically large, it cannot be fixed at a single definite value in experiment. Zero mass bosons as e.g. photons may be emitted or absorbed in systems of any scale. (In a relativistic description any particle may be created or annihilated, possibly together with its antiparticle, in a vacuum region just by applying energy.) From a mere technical point of view, quantum statistics of identical particles is much simpler to formulate with the grand canonical ensemble with varying particle number, than with the canonical one. Hence there are many good reasons to consider quantum dynamics with changes in particle number.

In order to do so, we start with building the Hilbert space of quantum states of this wider frame: the Fock space. The considered up to now Hilbert space of all N-particle states having the appropriate symmetry with respect to particle exchange will be denoted by $\mathcal{H}_N$. In the last subsection we introduced a basis $\{\Phi_L\}$ in $\mathcal{H}_N$. Instead of specifying the multi-index L as a raw of N indices l_i we may denote a basis state by specifying the occupation numbers n_i (being either 0 or 1) of *all* orbitals i:

$$|n_1 \dots n_i \dots\rangle, \quad \sum_i n_i = N. \tag{113}$$

Our previous determinantal state (107) is now represented as

$$|\Phi_L\rangle = |0 \dots 01_{l_1} 0 \dots 01_{l_2} 0 \dots 01_{l_N} 0 \dots\rangle.$$

Two states (113) not coinciding in all occupation numbers n_i are orthogonal. $\mathcal{H}_N$ is the complete linear space spanned by the basis vectors (113), i.e. the states of $\mathcal{H}_N$ are either linear combinations $\sum |\Phi_L\rangle C_L$ of states (113) (with the sum of the squared absolute values of the coefficients C_L equal to unity) or limits of Cauchy sequences of such linear combinations. (A Cauchy sequence is a sequence $\{|\Psi_n\rangle\}$ with $\lim_{m,n\to\infty} \langle \Psi_m - \Psi_n | \Psi_m - \Psi_n \rangle = 0$. The inclusion of all limits of such sequences into $\mathcal{H}_N$ means realizing the *topological* completeness property of the Hilbert space, being extremely important in all considerations of limits. This completeness of the space is not to be confused with the completeness of a basis set $\{\phi_i\}$.

The extended Hilbert space $\mathcal{F}$ (Fock space) of all states with the particle number N not fixed is now defined as the completed direct sum of all $\mathcal{H}_N$. It is spanned by all state vectors (113) for *all* N with the above given definition of orthogonality retained, and is completed by corresponding Cauchy sequences, just as the real line is obtained from the rational line by completing it with the help of Cauchy sequences of rational numbers.

Note that $\mathcal{F}$ now contains not only quantum states which are linear combinations with varying n_i so that n_i does not have a definite value in the quantum state (occupation number fluctuations), but also linear combinations with varying N so that now quantum fluctuations of the total particle number are allowed too. (For bosonic fields as e.g. laser light those quantum fluctuations can become important experimentally even for macroscopic N.)

7.3 Occupation number representation

We now completely abandon the awful wavefunctions (105) and will exclusively work with the occupation number eigenstates (113) and matrix elements between them. The simplest operators are those which provide just a transition between basis states (113) which are as close to each other as possible: those which differ in one occupation number only.

The definition of these *creation and annihilation operators* for fermions must have regard to the antisymmetry of the quantum states and to Pauli's exclusion principle following from this antisymmetry. They are defined as

$$\hat{c}_i|\dots n_i \dots\rangle = |\dots n_i - 1 \dots\rangle \, n_i \, (-1)^{\sum_{j<i} n_j}, \tag{114}$$

$$\hat{c}_i^\dagger|\dots n_i \dots\rangle = |\dots n_i + 1 \dots\rangle \, (1 - n_i) \, (-1)^{\sum_{j<i} n_j}. \tag{115}$$

The usefulness of the sign factors will become clear below. By considering the matrix elements with all possible occupation number eigenstates (113), it is easily seen that these operators have all the needed properties, do particularly not create non-fermionic states (that is, states with occupation numbers n_i different from 0 or 1 do not appear: application of $\hat{c}_i$ to a state with $n_i = 0$ gives zero, and application of $\hat{c}_i^\dagger$ to a state with $n_i = 1$ gives zero as well). The $\hat{c}_i$ and $\hat{c}_i^\dagger$ are mutually Hermitian conjugate, obey the key relations

$$\hat{n}_i|\dots n_i \dots\rangle \equiv \hat{c}_i^\dagger \hat{c}_i|\dots n_i \dots\rangle = |\dots n_i \dots\rangle \, n_i \tag{116}$$

and

$$[\hat{c}_i, \hat{c}_j^\dagger]_+ = \delta_{ij}, \quad [\hat{c}_i, \hat{c}_j]_+ = 0 = [\hat{c}_i^\dagger, \hat{c}_j^\dagger]_+ \tag{117}$$

with the *anticommutator* $[\hat{c}_i, \hat{c}_j^\dagger]_+ = \hat{c}_i\hat{c}_j^\dagger + \hat{c}_j^\dagger\hat{c}_i$ defined in standard way. Reversely, the *canonical anticommutation relations* (117) define all the algebraic properties of the $\hat{c}$-operators and moreover define up to unitary equivalence the Fock-space representation (114, 115). (There are, however, vast classes of further representations of those algebraic relations with a different structure and not unitary equivalent to the Fock-space representation.)

The basis (113) of the Fock space is systematically generated out of a single basis vector, the *vacuum state* $|\rangle \equiv |0\ldots 0\rangle$ (with N=0) by applying $\hat{c}^\dagger$-operators:

$$|n_1 \ldots n_i \ldots\rangle = \ldots \hat{c}_i^\dagger \ldots \hat{c}_1^\dagger|\rangle. \tag{118}$$

Observe again the order of operators defining a sign factor in view of (117) in agreement with the sign factors of (114, 115). Since products of a given set of N $\hat{c}^\dagger$-operators written in any order agree with each other up to possibly a sign, all possible expressions (118) do not generate more *different* basis vectors than those of (107) with the convention on the order of the l_i as agreed upon there. Henceforth, by using (118) we need not bother any more about the given linear order of the orbital indices.

With the help of the $\hat{c}$-operators, any linear operator in the Fock space may be expressed. It is not difficult to demonstrate that the Hamiltonian

$$\hat{H} = \sum_{ij} \hat{c}_i^\dagger (i|h|j)\hat{c}_j + \frac{1}{2}\sum_{ijkl} \hat{c}_i^\dagger\hat{c}_j^\dagger (ij|w|kl)\hat{c}_k\hat{c}_l \tag{119}$$

has the same matrix elements with occupation number eigenstates (113) as the Hamiltonian (109)) has with determinantal states in (110). Because of the one-to-one correspondence between the determinantal states (107) and the occupation number eigenstates and because both span the Fock space, by linearity the Hamiltonians (109) and (119) are equivalent. The building principle of the equivalent of any linear operator given in the Schrödinger representation is evident from (119).

The Schrödinger wavefunction of a bosonic many-particle quantum state must be totally symmetric with respect to particle exchange (omission of the minus sign in (105)). The determinants are then to be replaced by symmetrized products (permanents), with a slightly more involved normalization factor. The orbitals may now be occupied with arbitrary many particles: $n_i = 0, 1, 2, \ldots$. This case may be realized with *bosonic creation and annihilation operators*

$$\hat{b}_i|\ldots n_i \ldots\rangle = |\ldots n_i - 1 \ldots\rangle\sqrt{n_i}, \tag{120}$$

$$\hat{b}_i^\dagger|\ldots n_i \ldots\rangle = |\ldots n_i + 1 \ldots\rangle\sqrt{n_i + 1}, \tag{121}$$

$$\hat{n}_i|\ldots n_i \ldots\rangle \equiv \hat{b}_i^\dagger\hat{b}_i|\ldots n_i \ldots\rangle = |\ldots n_i \ldots\rangle n_i. \tag{122}$$

with the *canonical commutation relations*

$$[\hat{b}_i, \hat{b}_j^\dagger]_- = \delta_{ij}, \quad [\hat{b}_i, \hat{b}_j]_- = 0 = [\hat{b}_i^\dagger, \hat{b}_j^\dagger]_-. \tag{123}$$

The basis states of the Fock space are created out of the vacuum according to

$$|n_1 \ldots n_i \ldots\rangle = \frac{\big(\hat{b}_1^\dagger\big)^{n_1}}{\sqrt{n_1!}} \cdots \frac{\big(\hat{b}_i^\dagger\big)^{n_i}}{\sqrt{n_i!}} \cdots |\rangle. \tag{124}$$

The order of these operators in the product does not make any difference. The choice of factors on the r.h.s. of (120, 121) not only ensures that (122) holds but also ensure the mutual Hermitian conjugation of $\hat{b}_i$ and $\hat{b}_i^\dagger$.

7.4 Field operators

A spatial representation may be introduced in the Fock space by defining field operators

$$\hat{\psi}(x) = \sum_i \phi_i(x)\hat{a}_i, \quad \hat{\psi}^\dagger(x) = \sum_i \phi_i^*(x)\hat{a}_i^\dagger, \tag{125}$$

where the $\hat{a}_i$ mean either fermionic operators $\hat{c}_i$ or bosonic operators $\hat{b}_i$. The field operators $\hat{\psi}(x)$ and $\hat{\psi}^\dagger(x)$ obey the canonical (anti-)commutation relations

$$[\hat{\psi}(x), \hat{\psi}^\dagger(x')]_\pm = \delta(x - x'), \quad [\hat{\psi}(x), \hat{\psi}(x')]_\pm = 0 = [\hat{\psi}^\dagger(x), \hat{\psi}^\dagger(x')]_\pm. \tag{126}$$

They provide a spatial particle density operator

$$\hat{n}(\boldsymbol{r}) = \sum_s \hat{\psi}^\dagger(\boldsymbol{r}, s)\hat{\psi}(\boldsymbol{r}, s) \tag{127}$$

having the properties

$$\langle n(\boldsymbol{r})\rangle = \sum_{ij} \sum_s \phi_i^*(\boldsymbol{r}, s)\langle \hat{a}_i^\dagger \hat{a}_j\rangle \phi_j(\boldsymbol{r}, s), \quad \int d^3r\ \hat{n}(\boldsymbol{r}) = \sum_i \hat{a}_i^\dagger \hat{a}_i. \tag{128}$$

These relations are readily obtained from those of the creation and annihilation operators, and by taking into account the completeness and orthonormality (106) of the orbitals ϕ_i.

In terms of field operators, the Hamiltonian (109) or (119) reads

$$\begin{aligned}\hat{H} &= \sum_{ss'} \int d^3r\ \hat{\psi}^\dagger(\boldsymbol{r}, s)\ \hat{h}_{ss'}(\boldsymbol{r})\ \hat{\psi}(\boldsymbol{r}, s') + \\ &+ \frac{1}{2} \sum_{s_1 s_1' s_2 s_2'} \int d^3r_1 d^3r_2\ \hat{\psi}^\dagger(\boldsymbol{r}_1, s_1)\hat{\psi}^\dagger(\boldsymbol{r}_2, s_2)\ w_{s_1 s_1', s_2 s_2'}(\boldsymbol{r}_1, \boldsymbol{r}_2)\ \hat{\psi}(\boldsymbol{r}_2, s_2')\hat{\psi}(\boldsymbol{r}_1, s_1').\end{aligned} \tag{129}$$

It is obtained by combining (119) with (125) and (111, 112).

8 MICROSCOPIC THEORY: THE BCS MODEL

The great advantage of the use of creation and annihilation or field operators lies in the fact that we can use them to manipulate quantum states in a physically comprehensible way without explicitly knowing the wavefunction. We even can think of modified operators of which we know little more than their algebraic properties. The point is that the occupation number formalism applies for *every* orbital set (106). The transition from one set of operators obeying canonical (anti-)commutation relations to another such set is called a *canonical transformation* in quantum theory.

8.1 The normal Fermi liquid as a quasi-particle gas

A normal conducting Fermi liquid has a fermionic quasi-particle excitation spectrum which behaves very much like a gas of independent particles with energies ϵ_k (for the sake of simplicity we assume it isotropic in $\boldsymbol{k}$-space although this assumption is not essential here). Non-interacting fermions would have a ground state with all orbitals with $\epsilon < \mu$ occupied and all orbitals with $\epsilon > \mu$ empty; μ is the chemical potential. By adding or removing a fermion with $\epsilon = \mu$ new ground states with $N \pm 1$ fermions are obtained. By adding a fermion with $\epsilon > \mu$ an excited state is obtained with excitation energy $\epsilon - \mu$. By removing a fermion with $\epsilon < \mu$ — that is, creating a hole in the original ground state — an excited state is obtained with excitation energy $|\epsilon - \mu|$: first lift the fermion to the level μ and then remove it without changing the character of the state any more (Figs. 33 and 34).

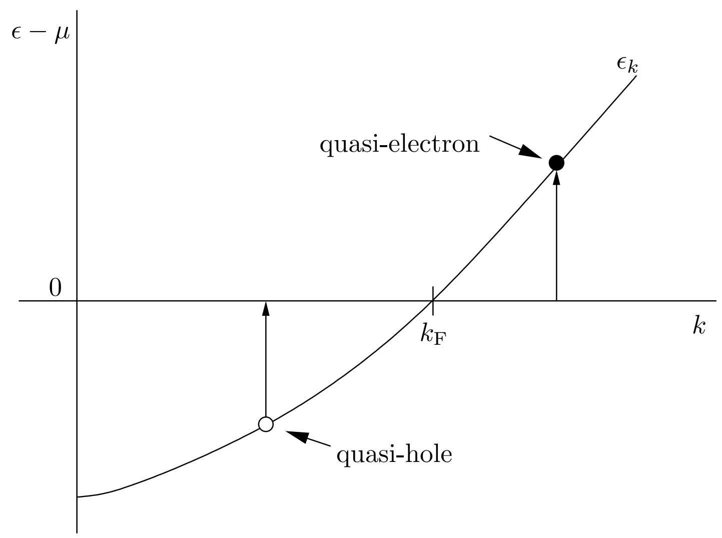


FIG. 33: Creation of an excited electron and of a hole, resp.

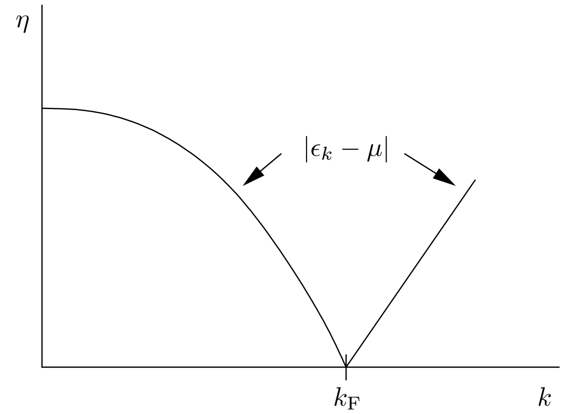


FIG. 34: Excitation spectrum of a Fermi gas.

The ground state $|0\rangle$ of a normal metal has much the same properties: conduction electrons with $\epsilon > \mu$ and holes with $\epsilon < \mu$ may be excited with excitation energies as above. These are not the original electrons making up the metal together with the atomic nuclei. Rather they are electrons or missing electrons surrounded by polarization clouds of other electrons and nuclei in which nearly all the Coulomb interaction is absorbed. We do not precisely know these excitations nor do we know the ground state $|0\rangle$ (although a quite elaborate theory exists for them which we ignore here). We just assume that they may be represented by fermionic operators with properties like those in the gas:

$$\epsilon_k < \mu : \qquad \hat{c}^\dagger_{\boldsymbol{k}\sigma}|0\rangle = 0, \quad \hat{c}^\dagger_{\boldsymbol{k}\sigma}\hat{c}_{\boldsymbol{k}\sigma}|0\rangle = |0\rangle, \tag{130}$$

$$\epsilon_k > \mu : \qquad \hat{c}_{\boldsymbol{k}\sigma}|0\rangle = 0, \quad \hat{c}_{\boldsymbol{k}\sigma}\hat{c}^\dagger_{\boldsymbol{k}\sigma}|0\rangle = |0\rangle, \tag{131}$$

$\boldsymbol{k}$ is the wavevector and σ the spin state of the quasi-particle.

Since all interactions present in the ground state $|0\rangle$ are already absorbed in the quasi-particle energies ϵ_k, only excited conduction electrons or holes exert a remainder interaction. Hence, we may write down an effective Hamiltonian

$$\begin{aligned}\hat{\tilde{H}} \;=\; \sum_{\boldsymbol{k}\sigma} \hat{c}^\dagger_{\boldsymbol{k}\sigma}(\epsilon_k-\mu)\hat{c}_{\boldsymbol{k}\sigma} \;&+\; \frac{1}{2}\sum_{\boldsymbol{k}\sigma,\,\boldsymbol{k}'\sigma',\,\boldsymbol{q}}^{\epsilon_k>\mu,\,\epsilon_{k'}>\mu} \hat{c}^\dagger_{\boldsymbol{k}+\boldsymbol{q}\sigma}\hat{c}^\dagger_{\boldsymbol{k}'-\boldsymbol{q}\sigma'}\, w_{\boldsymbol{k}\boldsymbol{k}'\boldsymbol{q}}\, \hat{c}_{\boldsymbol{k}'\sigma'}\hat{c}_{\boldsymbol{k}\sigma} \;+\\ &+\; \sum_{\boldsymbol{k}\sigma,\,\boldsymbol{k}'\sigma',\,\boldsymbol{q}}^{\epsilon_k>\mu,\,\epsilon_{k'}<\mu} \hat{c}^\dagger_{\boldsymbol{k}+\boldsymbol{q}\sigma}\hat{c}_{\boldsymbol{k}'-\boldsymbol{q}\sigma'}\, w_{\boldsymbol{k}\boldsymbol{k}'\boldsymbol{q}}\, \hat{c}^\dagger_{\boldsymbol{k}'\sigma'}\hat{c}_{\boldsymbol{k}\sigma} \;+\\ &+\; \frac{1}{2}\sum_{\boldsymbol{k}\sigma,\,\boldsymbol{k}'\sigma',\,\boldsymbol{q}}^{\epsilon_k<\mu,\,\epsilon_{k'}<\mu} \hat{c}_{\boldsymbol{k}+\boldsymbol{q}\sigma}\hat{c}_{\boldsymbol{k}'-\boldsymbol{q}\sigma'}\, w_{\boldsymbol{k}\boldsymbol{k}'\boldsymbol{q}}\, \hat{c}^\dagger_{\boldsymbol{k}'\sigma'}\hat{c}^\dagger_{\boldsymbol{k}\sigma}. \end{aligned} \tag{132}$$

The matrix elements in the three lines are qualitatively different: they are predominantly repulsive in the first and last line and attractive in the second line; electrons and holes have opposite charges. With the relations (130, 131) one finds easily

$$\hat{\tilde{H}}|0\rangle = |0\rangle\tilde{E}_0, \qquad \tilde{E}_0 = \langle 0|\hat{\tilde{H}}|0\rangle = \sum_{\boldsymbol{k}\sigma}^{\epsilon_k<\mu} (\epsilon_k-\mu). \tag{133}$$

We subtract this constant energy from the Hamiltonian and have

$$\hat{H} \equiv \hat{\tilde{H}} - \tilde{E}_0, \qquad \hat{H}|0\rangle = 0. \tag{134}$$

We may create a quasi-particle above μ in this ground state:

$$\epsilon_{k_1} > \mu: \qquad |\boldsymbol{k}_1\sigma_1\rangle = \hat{c}^\dagger_{\boldsymbol{k}_1\sigma_1}|0\rangle, \quad \hat{H}|\boldsymbol{k}_1\sigma_1\rangle = |\boldsymbol{k}_1\sigma_1\rangle\,(\epsilon_{k_1}-\mu). \tag{135}$$

The last relation is easily verified with our previous formulas. For $k\sigma \neq k_1\sigma_1$, we have $\hat{c}^\dagger_{\boldsymbol{k}\sigma}\hat{c}_{\boldsymbol{k}\sigma}\hat{c}^\dagger_{\boldsymbol{k}_1\sigma_1} = \hat{c}^\dagger_{\boldsymbol{k}_1\sigma_1}\hat{c}^\dagger_{\boldsymbol{k}\sigma}\hat{c}_{\boldsymbol{k}\sigma}$, and together with $\hat{c}_{\boldsymbol{k}_1\sigma_1}\hat{c}^\dagger_{\boldsymbol{k}_1\sigma_1}|0\rangle = |0\rangle$ one finds the above result. Likewise

$$\epsilon_{k_1} < \mu: \qquad |\boldsymbol{k}_1\sigma_1\rangle = \hat{c}_{\boldsymbol{k}_1\sigma_1}|0\rangle, \quad \hat{H}|\boldsymbol{k}_1\sigma_1\rangle = |\boldsymbol{k}_1\sigma_1\rangle\,|\epsilon_{k_1}-\mu| \tag{136}$$

is obtained. Here, $\hat{c}^\dagger_{\boldsymbol{k}_1\sigma_1}\hat{c}_{\boldsymbol{k}_1\sigma_1}\hat{c}_{\boldsymbol{k}_1\sigma_1} = 0$, so that one term has to be removed from the sum of (133). Hence, the single-particle excitation spectrum of our effective Hamiltonian above the state $|0\rangle$ is just

$$\eta_k = |\epsilon_k - \mu|, \tag{137}$$

and the excited states are $|\boldsymbol{k}_1\sigma_1\rangle$ of (135, 136), whatever the wavefunction of $|0\rangle$ might be.

To say the truth, this all is only approximately right. There are no fermionic operators for which the relations (130, 131) hold true exactly for the true ground state $|0\rangle$. Therefore, the first relation (133) and the last relations (135, 136) are also not rigorous. The quasi-particles have a finite lifetime which may be expressed by complex energies η_k. However, for $|\eta_k| \ll \mu$ the approximation is quite good in normal, weakly correlated metals.

Consider now a state with two excited particles:

$$|\boldsymbol{k}_1\sigma_1\,\boldsymbol{k}_2\sigma_2\rangle = \hat{c}^\dagger_{\boldsymbol{k}_1\sigma_1}\hat{c}^\dagger_{\boldsymbol{k}_2\sigma_2}|0\rangle. \tag{138}$$

To be specific we consider two excited electrons, the cases with holes or with an electron and a hole are completely analogous. The application of the effective Hamiltonian yields

$$\hat{H}\,\hat{c}^\dagger_{\boldsymbol{k}_1\sigma_1}\hat{c}^\dagger_{\boldsymbol{k}_2\sigma_2}|0\rangle = \hat{c}^\dagger_{\boldsymbol{k}_1\sigma_1}\hat{c}^\dagger_{\boldsymbol{k}_2\sigma_2}|0\rangle\,(\eta_{k_1}+\eta_{k_2}) + \sum_{\boldsymbol{q}} \hat{c}^\dagger_{\boldsymbol{k}_1+\boldsymbol{q}\sigma_1}\hat{c}^\dagger_{\boldsymbol{k}_2-\boldsymbol{q}\sigma_2}|0\rangle\, w_{\boldsymbol{k}_1\boldsymbol{k}_2\boldsymbol{q}}. \tag{139}$$

The interaction term is obtained with the rule $c_{\boldsymbol{k}_i\sigma_i}c^\dagger_{\boldsymbol{k}_i\sigma_i}|0\rangle = |0\rangle$. One contribution appears from $\boldsymbol{k}\sigma = \boldsymbol{k}_1\sigma_1$, $\boldsymbol{k}'\sigma' = \boldsymbol{k}_2\sigma_2$, and another contribution $-\hat{c}^\dagger_{\boldsymbol{k}_2+\boldsymbol{q}\sigma_2}\hat{c}^\dagger_{\boldsymbol{k}_1-\boldsymbol{q}\sigma_1}|0\rangle\, w_{\boldsymbol{k}_2\boldsymbol{k}_1\boldsymbol{q}}$ from $\boldsymbol{k}'\sigma' = \boldsymbol{k}_1\sigma_1$,

$\boldsymbol{k}\sigma = \boldsymbol{k}_2\sigma_2$. The minus sign in this contribution is removed by anticommuting the two $\hat{c}^\dagger$-operators, and then, by replacing $\boldsymbol{q}$ with $-\boldsymbol{q}$ under the $\boldsymbol{q}$-sum and observing $w_{\boldsymbol{k}_2\boldsymbol{k}_1-\boldsymbol{q}} = w_{\boldsymbol{k}_1\boldsymbol{k}_2\boldsymbol{q}}$ which derives from $w(\boldsymbol{r}_1, \boldsymbol{r}_2) = w(\boldsymbol{r}_2, \boldsymbol{r}_1)$, this second contribution is equal to the first one, whence omitting the factor (1/2) in front. (This is how exchange terms appear automatically with $\hat{c}$-operators since their anticommutation rules automatically retain the antisymmetry of states.) For the simplicity of writing we omitted here and in (132) the spin dependence of the interaction matrix element. It is always present in the effective quasi-particle interaction, and it may always be added afterwards without confusion. (We might introduce a short-hand notation k for $\boldsymbol{k}\sigma$.) The effective interaction of two quasi-particles with equal spin differs from that of two quasi-particles with opposite spin. The *spin-flip scattering* of quasi-particles — an interaction with changing σ_1 and σ_2 into σ_1' and σ_2' — may often be neglected. Then, the $\boldsymbol{q}$-sum of (139) need not be completed by additional spin sums.

8.2 The Cooper problem[1]

From (139) it can be seen that the state (138) is not any more an eigenstate of the effective Hamiltonian, not even within the approximations made in the previous subsection. The two excited quasi-particles interact and thus form a correlated pair state. We try to find this pair state of lowest energy for two electrons ($\eta > 0$) within our approximate approach. Since we expect that this state is formed out of quasi-particle excitations with energies $\eta \approx 0$ our approximations cannot be critical. (The quasi-particle lifetime becomes infinite for $|\eta| \to 0$.) We expect that the state lowest in energy has zero total momentum, hence we build it out of quasi-particle pairs with $\boldsymbol{k}_2 = -\boldsymbol{k}_1$:

$$|\psi\rangle = \sum_{\boldsymbol{k}} a_{\boldsymbol{k}} \, |\boldsymbol{k}\sigma \; -\boldsymbol{k}\sigma'\rangle. \tag{140}$$

where we assume a fixed combination of σ and σ' and the yet unknown expansion coefficients to depend on $\boldsymbol{k}$ only, because the sought state is to be expected to have a definite total spin. (Recall that we are considering an isotropic metal in this chapter.) We want that this pair state $|\psi\rangle$ is an eigenstate of $\hat{H}$:

$$\hat{H}\,|\psi\rangle = |\psi\rangle E, \quad \hat{H}\,|\psi\rangle = \sum_{\boldsymbol{k}} \hat{c}^\dagger_{\boldsymbol{k}\sigma}\hat{c}^\dagger_{-\boldsymbol{k}\sigma'}|0\rangle\, 2\eta_k a_{\boldsymbol{k}} + \sum_{\boldsymbol{kq}} \hat{c}^\dagger_{\boldsymbol{k}+\boldsymbol{q}\sigma}\hat{c}^\dagger_{-\boldsymbol{k}-\boldsymbol{q}\sigma'}|0\rangle\, w_{\boldsymbol{k}-\boldsymbol{k}\boldsymbol{q}}\, a_{\boldsymbol{k}}. \tag{141}$$

Multiply the last relation with $\langle 0|\hat{c}_{-\boldsymbol{k}'\sigma'}\hat{c}_{\boldsymbol{k}'\sigma}$ and observe $\langle 0|\hat{c}_{-\boldsymbol{k}'\sigma'}\hat{c}_{\boldsymbol{k}'\sigma}\hat{c}^\dagger_{\boldsymbol{k}\sigma}\hat{c}^\dagger_{-\boldsymbol{k}\sigma'}|0\rangle = \langle 0|\hat{c}_{-\boldsymbol{k}'\sigma'}(\delta_{\boldsymbol{kk}'} - \hat{c}^\dagger_{\boldsymbol{k}\sigma}\hat{c}_{\boldsymbol{k}'\sigma})\hat{c}^\dagger_{-\boldsymbol{k}\sigma'}|0\rangle = \delta_{\boldsymbol{kk}'}\langle 0|(\delta_{\boldsymbol{kk}'} - \hat{c}^\dagger_{-\boldsymbol{k}\sigma'}\hat{c}_{-\boldsymbol{k}'\sigma'})|0\rangle - \langle 0|\hat{c}_{-\boldsymbol{k}'\sigma'}\hat{c}^\dagger_{\boldsymbol{k}\sigma}(\delta_{-\boldsymbol{kk}'}\delta_{\sigma\sigma'} - \hat{c}^\dagger_{-\boldsymbol{k}\sigma'}\hat{c}_{\boldsymbol{k}'\sigma})|0\rangle = \delta_{\boldsymbol{kk}'} - \langle 0|(\delta_{-\boldsymbol{kk}'}\delta_{\sigma\sigma'} - \hat{c}^\dagger_{\boldsymbol{k}\sigma}\hat{c}_{-\boldsymbol{k}'\sigma'})\delta_{-\boldsymbol{kk}'}\delta_{\sigma\sigma'}|0\rangle = \delta_{\boldsymbol{kk}'} - \delta_{-\boldsymbol{kk}'}\delta_{\sigma\sigma'}$ to obtain

$$E\big(a_{\boldsymbol{k}'} - a_{-\boldsymbol{k}'}\delta_{\sigma\sigma'}\big) = 2\eta_{k'}\big(a_{\boldsymbol{k}'} - a_{-\boldsymbol{k}'}\delta_{\sigma\sigma'}\big) + \sum_{\boldsymbol{q}} w_{\boldsymbol{k}'-\boldsymbol{q},-\boldsymbol{k}'+\boldsymbol{q},\boldsymbol{q}}\big(a_{\boldsymbol{k}'-\boldsymbol{q}} - a_{-\boldsymbol{k}'+\boldsymbol{q}}\delta_{\sigma\sigma'}\big). \tag{142}$$

In the last term, we also used again $w_{-\boldsymbol{k}'-\boldsymbol{q},\boldsymbol{k}'+\boldsymbol{q},\boldsymbol{q}} = w_{\boldsymbol{k}'+\boldsymbol{q},-\boldsymbol{k}'-\boldsymbol{q},-\boldsymbol{q}}$ and then replaced the sum over $\boldsymbol{q}$ by a sum over $-\boldsymbol{q}$.

Due to the isotropy of our problem we expect the solution to be an angular momentum eigenstate, hence $a_{\boldsymbol{k}}$ should have a definite parity. It is immediately seen that a non-trivial solution with even parity $a_{-\boldsymbol{k}} = a_{\boldsymbol{k}}$ (even angular momentum) is only possible, if $\delta_{\sigma\sigma'} = 0$, that is for a singlet $\sigma' = -\sigma$. For a spin triplet $\sigma' = \sigma$ only a non-trivial solution with odd parity (odd angular momentum) is possible. To be specific, consider the singlet case. (The triplet case is analogous.) Assume

$$a_{\boldsymbol{k}} = a_k Y_{lm}(\boldsymbol{k}/k) \tag{143}$$

with even l. In (142), rename $\boldsymbol{k}' \to \boldsymbol{k}$, $\boldsymbol{k}' - \boldsymbol{q} \to \boldsymbol{k}'$. The matrix element $w_{\boldsymbol{k}',-\boldsymbol{k}',\boldsymbol{k}-\boldsymbol{k}'}$ determines the scattering amplitude from states $\boldsymbol{k}, -\boldsymbol{k}$ into states $\boldsymbol{k}', -\boldsymbol{k}'$. we use an expansion

$$w_{\boldsymbol{k}',-\boldsymbol{k}',\boldsymbol{k}-\boldsymbol{k}'} = \sum_{lm} \lambda_l w^l_k w^{l*}_{k'} Y_{lm}(\boldsymbol{k}) Y^*_{lm}(\boldsymbol{k}'). \tag{144}$$

[1] L. N. Cooper, Phys. Rev. **104**, 1189 (1956).

This reduces (142) to

$$a_k = \frac{\lambda_l w_k^l C}{E_{lm} - 2\eta_k}, \quad C = \sum_{k'} w_{k'}^{l*} a_{k'}. \tag{145}$$

Inserting the left relation into the right one yields

$$1 = \lambda_l \sum_k |w_k^l|^2 \frac{1}{E_{lm} - 2\eta_k} = \lambda_l F(E_{lm}). \tag{146}$$

The sought lowest pair energy corresponds to the lowest solution of $F(E_{lm}) = 1/\lambda_l$.

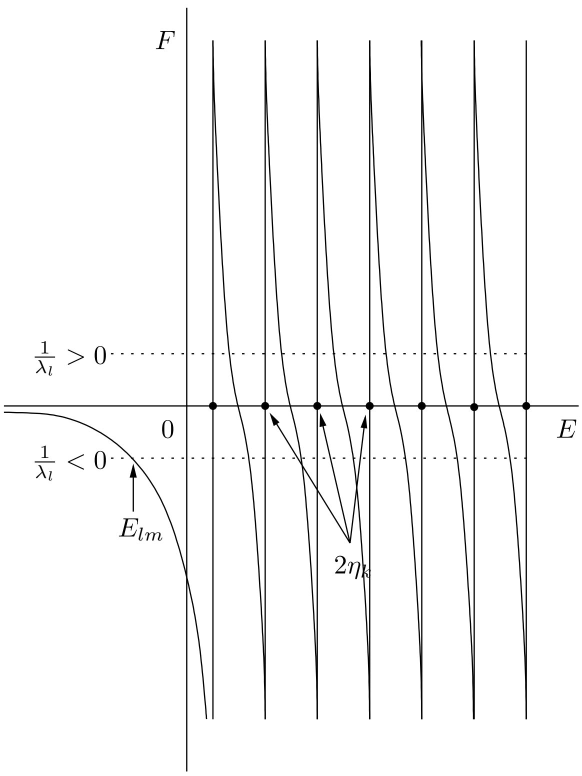


Figure 35: The function $F(E)$ from Eq. (146).

The function $F(E_{lm})$ has poles for $E_{lm} = 2\eta_k$ where it jumps from $-\infty$ to $+\infty$. Recall that the η_k-values are all positive and start from zero. For $E_{lm} \to -\infty$, $F(E_{lm})$ approaches zero from negative values. Hence, if $\lambda_l > 0$, then the lowest solution E_{lm} of (146) is positive and the ground state $|0\rangle$ of the normal metal is stable. If at least one λ_l-value is negative (attractive interaction), then there is unavoidably a negative solution E_{lm} of (146): the 'excited pair' has negative energy and the normal ground state $|0\rangle$ is unstable against forming of pairs of bound quasi-particles, no matter how small $|\lambda_l|$ is (how weak the attractive interaction is). Pairs are spontaneously formed and the ground state reconstructs. This is the content of *Cooper's theorem.*

If the interaction is cut of at some energy ω_c,

$$w_k^l = \begin{cases} 1 & \text{for } 0 < \eta_k < \omega_c \\ 0 & \text{elsewhere} \end{cases}, \tag{147}$$

and the density of states for η_k is nearly constant in this interval, $N(\eta) = N(0)$, then, with negative E_{lm},

$$\sum_{\boldsymbol{k}} |w_k^l|^2 \frac{1}{E_{lm} - 2\eta_k} = -N(0) \int_0^{\omega_c} d\eta \, \frac{1}{|E_{lm}| + 2\eta} = -\frac{N(0)}{2} \ln\left[\frac{|E_{lm} + 2\omega_c}{|E_{lm}|}\right],$$

hence,

$$|E_{lm}| = \frac{2\omega_c}{\exp\left[\frac{2}{N(0)|\lambda_l|}\right] - 1}. \tag{148}$$

This yields

$$|E_{lm}| \approx \begin{cases} 2\omega_c \exp\left[-\dfrac{2}{N(0)|\lambda_l|}\right] \\ N(0)|\lambda_l|\omega_c \end{cases} \text{for } N(0)|\lambda_l| \begin{matrix} \ll \\ \gg \end{matrix} 1 \tag{149}$$

in the weak and strong coupling limits. In this chapter we only consider the weak coupling limit where $|E_{lm}|$ is exponentially small.

The whole analysis may be repeated for the case where the pair has a non-zero total momentum $\boldsymbol{q}$. In that case the denominator of (146) is to be replaced with $E_{lm}(q) - \eta_{\boldsymbol{k}+\boldsymbol{q}/2} - \eta_{-\boldsymbol{k}+\boldsymbol{q}/2}$ where now $|\boldsymbol{k} \pm \boldsymbol{q}/2|$ must be larger than k_F. For small q, this condition reduces the density of states in effect in an interval of thickness $|\partial\eta/\partial\boldsymbol{k}|q/2 = v_F q/2$ at the lower η-integration limit; v_F is the Fermi velocity. The result is

$$E_{lm}(q) \approx E_{lm} + v_F q/2. \tag{150}$$

In the weak coupling limit, $E_{lm}(q)$ can only be negative for exponentially small q.

We performed the analysis with a pair of particles. It can likewise be done with a pair of holes with an analogous result.

8.3 The BCS Hamiltonian

Fröhlich[1] was the first to point out that the electron-phonon interaction is capable of providing an effective attraction between conduction electrons in the energy range of phonon energies.

From Cooper's analysis it follows that, if there is a weak attraction, it can only be effective for pairs with zero total momentum, that is, between $\boldsymbol{k}$ and $-\boldsymbol{k}$. With the assumption that the attraction is in the $l = 0$ spin singlet channel, this led Bardeen, Cooper and Schrieffer[2] to the simple model Hamiltonian

$$\hat{H}_{\mathrm{BCS}} = \sum_{\boldsymbol{k}\sigma} \hat{c}^\dagger_{\boldsymbol{k}\sigma}(\epsilon_k - \mu)\hat{c}_{\boldsymbol{k}\sigma} - \frac{g}{V} \sum_{\boldsymbol{k}\boldsymbol{k}'}^{\mu-\omega_c<\epsilon_k,\epsilon_{k'}<\mu+\omega_c} \hat{c}^\dagger_{\boldsymbol{k}'\uparrow}\hat{c}^\dagger_{-\boldsymbol{k}'\downarrow}\hat{c}_{-\boldsymbol{k}\downarrow}\hat{c}_{\boldsymbol{k}\uparrow}. \tag{151}$$

Here, $g > 0$ is the BCS coupling constant, and V is the normalization volume. Since the density of plane-wave states in $\boldsymbol{k}$-space is $V/(2\pi)^3$: $\sum_{\boldsymbol{k}} = V/(2\pi)^3 \int d^3k$, the matrix element of an n-particle interaction (appearing in an n-fold $\boldsymbol{k}$-sum) must be proportional to $V^{-(n-1)}$ in order that the Hamiltonian is extensive ($\sim V$). The modeled attractive interaction is assumed in an energy range of width $2\omega_c$ around the chemical potential (Fermi level in the case $T = 0$), where ω_c is a characteristic phonon energy for which the Debye energy of the lattice can be taken.

The state $|0\rangle$ of (130, 131) cannot any more be the ground state of this Hamiltonian since Cooper's theorem tells us that this state is unstable against spontaneous formation of bound pairs with the gain of their binding energy. The problem to solve is now to find the ground state and the quasi-particle spectrum of the BCS-Hamiltonian. This problem was solved by Bardeen, Cooper and Schrieffer, and, shortly thereafter and independently by means of a canonical transformation, by Bogoliubov and Valatin. Bardeen, Cooper and Schrieffer thus provided the first microscopic theory of superconductivity, 46 years after the discovery of the phenomenon.

8.4 The Bogoliubov-Valatin transformation[3]

Suppose the ground state contains a bound pair. Exciting one particle of that pair leaves its partner behind, and hence also in an excited state. If one wants to excite only one particle, one must annihilate simultaneously its partner. Led by this consideration, for the quasi-particle operators in the ground state of (151) an ansatz

$$\hat{b}_{\boldsymbol{k}\uparrow} = u_k\hat{c}_{\boldsymbol{k}\uparrow} - v_k\hat{c}^\dagger_{-\boldsymbol{k}\downarrow}, \quad \hat{b}_{\boldsymbol{k}\downarrow} = u_k\hat{c}_{\boldsymbol{k}\downarrow} + v_k\hat{c}^\dagger_{-\boldsymbol{k}\uparrow}$$

[1] H. Fröhlich, Phys. Rev. **79**, 845 (1950).

[2] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).

[3] N. N. Bogoliubov, Nuovo Cimento **7**, 794 (1958); J. G. Valatin, Nuovo Cimento **7**, 843 (1958).

is made. u_k and v_k are variational parameters. Again we consider the isotropic problem and hence their dependence on $k = |\boldsymbol{k}|$ only. The reason of the different signs in the two relations becomes clear in a minute. Since for each orbital annihilated by $\hat{c}_{\boldsymbol{k}\uparrow},\ \hat{c}_{-\boldsymbol{k}\downarrow},\ \hat{b}_{\boldsymbol{k}\uparrow},\ \hat{b}_{-\boldsymbol{k}\downarrow}$ an $\boldsymbol{r}$-independent phase factor may be arbitrarily chosen, u_k and v_k may be assumed real without loss of generality.[1] These Bogoliubov-Valatin transformations together with their Hermitian conjugate may be summarized as

$$\hat{b}_{\boldsymbol{k}\sigma} = u_k\hat{c}_{\boldsymbol{k}\sigma} - \sigma v_k\hat{c}^\dagger_{-\boldsymbol{k}-\sigma}, \quad \hat{b}^\dagger_{\boldsymbol{k}\sigma} = u_k\hat{c}^\dagger_{\boldsymbol{k}\sigma} - \sigma v_k\hat{c}_{-\boldsymbol{k}-\sigma}. \tag{152}$$

We want these transformations to be canonical, that is, we want the new operators $\hat{b}_{\boldsymbol{k}\sigma},\ \hat{b}^\dagger_{\boldsymbol{k}\sigma}$ again to be fermionic operators. One easily calculates

$$[\hat{b}_{\boldsymbol{k}\sigma},\ \hat{b}_{\boldsymbol{k}'\sigma'}]_+ = -u_k v_{k'}\Big(\sigma'[\hat{c}_{\boldsymbol{k}\sigma},\ \hat{c}^\dagger_{-\boldsymbol{k}'-\sigma'}]_+ + \sigma[\hat{c}^\dagger_{-\boldsymbol{k}-\sigma},\ \hat{c}_{\boldsymbol{k}'\sigma'}]_+\Big) =$$

$$= -u_k v_{k'}\left(\sigma'\delta_{\boldsymbol{k}-\boldsymbol{k}'}\delta_{\sigma-\sigma'} + \sigma\delta_{-\boldsymbol{k}\boldsymbol{k}'}\delta_{-\sigma\sigma'}\right) = -u_k v_k\delta_{-\boldsymbol{k}\boldsymbol{k}'}(-\sigma+\sigma) = 0.$$

In the first equality it was already considered that annihilation and creation operators $\hat{c}$ and $\hat{c}^\dagger$, respectively, anticommute among themselves. The analogous result for the $\hat{b}^\dagger$-operators is obtained in the same way. The sign factor σ in the transformation ensures that the anticommutation is retained for the $\hat{b}$- and $\hat{b}^\dagger$-operators, respectively. Analogously,

$$[\hat{b}_{\boldsymbol{k}\sigma},\ \hat{b}^\dagger_{\boldsymbol{k}'\sigma'}]_+ = u_k^2[\hat{c}_{\boldsymbol{k}\sigma},\ \hat{c}^\dagger_{\boldsymbol{k}'\sigma'}]_+ + \sigma\sigma' v_k^2[\hat{c}^\dagger_{-\boldsymbol{k}-\sigma},\ \hat{c}_{-\boldsymbol{k}'-\sigma'}]_+ = \left(u_k^2+v_k^2\right)\delta_{\boldsymbol{k}\boldsymbol{k}'}\delta_{\sigma\sigma'},$$

hence the condition

$$u_k^2 + v_k^2 = 1 \tag{153}$$

ensures that the transformation is canonical and the new operators are again fermionic operators.

Multiplying the first relation (152) by u_k, replacing in the second one $\boldsymbol{k}\sigma$ with $-\boldsymbol{k}-\sigma$, multiplying it with σv_k, and then adding both results yields with (153) the inverse transformation

$$\hat{c}_{\boldsymbol{k}\sigma} = u_k\hat{b}_{\boldsymbol{k}\sigma} + \sigma v_k\hat{b}^\dagger_{-\boldsymbol{k}-\sigma}, \quad \hat{c}^\dagger_{\boldsymbol{k}\sigma} = u_k\hat{b}^\dagger_{\boldsymbol{k}\sigma} + \sigma v_k\hat{b}_{-\boldsymbol{k}-\sigma}. \tag{154}$$

Observe the reversed sign factor.

The next step is to transform the Hamiltonian (151). With

$$\hat{c}^\dagger_{\boldsymbol{k}\sigma}\hat{c}_{\boldsymbol{k}\sigma} = \Big(u_k\hat{b}^\dagger_{\boldsymbol{k}\sigma} + \sigma v_k\hat{b}_{-\boldsymbol{k}-\sigma}\Big)\Big(u_k\hat{b}_{\boldsymbol{k}\sigma} + \sigma v_k\hat{b}^\dagger_{-\boldsymbol{k}-\sigma}\Big) =$$

$$= u_k^2\hat{b}^\dagger_{\boldsymbol{k}\sigma}\hat{b}_{\boldsymbol{k}\sigma} + v_k^2\hat{b}_{-\boldsymbol{k}-\sigma}\hat{b}^\dagger_{-\boldsymbol{k}-\sigma} + \sigma u_k v_k\Big(\hat{b}^\dagger_{\boldsymbol{k}\sigma}\hat{b}^\dagger_{-\boldsymbol{k}-\sigma} + \hat{b}_{-\boldsymbol{k}-\sigma}\hat{b}_{\boldsymbol{k}\sigma}\Big)$$

and the anticommutation rules it is easily seen that the single-particle part of the BCS-Hamiltonian transforms into

$$2\sum_{\boldsymbol{k}}(\epsilon_k-\mu)v_k^2 + \sum_{\boldsymbol{k}}(\epsilon_k-\mu)(u_k^2-v_k^2)\sum_\sigma\hat{b}^\dagger_{\boldsymbol{k}\sigma}\hat{b}_{\boldsymbol{k}\sigma} + 2\sum_{\boldsymbol{k}}(\epsilon_k-\mu)u_k v_k\Big(\hat{b}^\dagger_{\boldsymbol{k}\uparrow}\hat{b}^\dagger_{-\boldsymbol{k}\downarrow} + \hat{b}_{-\boldsymbol{k}\downarrow}\hat{b}_{\boldsymbol{k}\uparrow}\Big).$$

It has also been used that under the $\boldsymbol{k}$-sum $\boldsymbol{k}$ may be replaced by $-\boldsymbol{k}$. Further, with

$$\begin{aligned}\hat{B}_{\boldsymbol{k}} &= \hat{c}_{-\boldsymbol{k}\downarrow}\hat{c}_{\boldsymbol{k}\uparrow} = \Big(u_k\hat{b}_{-\boldsymbol{k}\downarrow} - v_k\hat{b}^\dagger_{\boldsymbol{k}\uparrow}\Big)\Big(u_k\hat{b}_{\boldsymbol{k}\uparrow} + v_k\hat{b}^\dagger_{-\boldsymbol{k}\downarrow}\Big) = \\ &= u_k^2\hat{b}_{-\boldsymbol{k}\downarrow}\hat{b}_{\boldsymbol{k}\uparrow} - v_k^2\hat{b}^\dagger_{\boldsymbol{k}\uparrow}\hat{b}^\dagger_{-\boldsymbol{k}\downarrow} + u_k v_k\Big(\hat{b}_{-\boldsymbol{k}\downarrow}\hat{b}^\dagger_{-\boldsymbol{k}\downarrow} - \hat{b}^\dagger_{\boldsymbol{k}\uparrow}\hat{b}_{\boldsymbol{k}\uparrow}\Big),\end{aligned} \tag{155}$$

the full transformed BCS-Hamiltonian reads

$$\begin{aligned}\hat{H}_{\mathrm{BCS}} &= 2\sum_{\boldsymbol{k}}(\epsilon_k-\mu)v_k^2 + \sum_{\boldsymbol{k}}(\epsilon_k-\mu)(u_k^2-v_k^2)\sum_\sigma\hat{b}^\dagger_{\boldsymbol{k}\sigma}\hat{b}_{\boldsymbol{k}\sigma} + \\ &\quad +2\sum_{\boldsymbol{k}}(\epsilon_k-\mu)u_k v_k\Big(\hat{b}^\dagger_{\boldsymbol{k}\uparrow}\hat{b}^\dagger_{-\boldsymbol{k}\downarrow} + \hat{b}_{-\boldsymbol{k}\downarrow}\hat{b}_{\boldsymbol{k}\uparrow}\Big) - \frac{g}{V}\sum_{\boldsymbol{k}\boldsymbol{k}'}\hat{B}^\dagger_{\boldsymbol{k}'}\hat{B}_{\boldsymbol{k}},\end{aligned} \tag{156}$$

[1] In fact a phase $u_k \to e^{i\alpha_k}u_k,\ v_k \to e^{-i\alpha_k}v_k$ will nearly not change the following analysis, except that u_k^2 and v_k^2 are to be replaced by $|u_k|^2$ and $|v_k|^2$. The deep influence of this $U(1)$ symmetry which is spontaneously broken in the BCS ground state $|\Psi_0\rangle$ will not be considered here. See P. W. Anderson, Phys. Rev. **112**, 1900 (1958).

where for brevity we omitted the bounds of the last sum.

Now, we introduce the occupation number operators

$$\hat{n}_{\boldsymbol{k}\sigma} = \hat{b}^\dagger_{\boldsymbol{k}\sigma}\hat{b}_{\boldsymbol{k}\sigma} \tag{157}$$

of the $\hat{b}$-operators and assume analogous to (130, 131) that for properly chosen $\hat{b}$-operators the ground state $|\Psi_0\rangle$ of the BCS-Hamiltonian is an occupation number eigenstate with eigenvalues $n_{\boldsymbol{k}\sigma} = 0$. Then, the energy of a general occupation number eigenstate is found to be

$$E = 2\sum_{\boldsymbol{k}}(\epsilon_k - \mu)v_k^2 + \sum_{\boldsymbol{k}}(\epsilon_k - \mu)(u_k^2 - v_k^2)(n_{\boldsymbol{k}\uparrow} + n_{\boldsymbol{k}\downarrow}) - \frac{g}{V}\left[\sum_{\boldsymbol{k}} u_k v_k (1 - n_{\boldsymbol{k}\uparrow} - n_{\boldsymbol{k}\downarrow})\right]^2. \tag{158}$$

The $n_{\boldsymbol{k}\sigma}$ are the eigenvalues (0 or 1) of the occupation number operators (157).

This energy expression still contains the variational parameters u_k and v_k which are connected by (153), whence $\partial v_k/\partial u_k = -u_k/v_k$. For given occupation numbers, (158) has its minimum for

$$\frac{\partial E}{\partial u_k} = \left[-4(\epsilon_k - \mu)u_k + 2\Delta\frac{u_k^2 - v_k^2}{v_k}\right]\big(1 - n_{\boldsymbol{k}\uparrow} - n_{\boldsymbol{k}\downarrow}\big) = 0,$$

$$\Delta = \frac{g}{V}\sum_{\boldsymbol{k}} u_k v_k \big(1 - n_{\boldsymbol{k}\uparrow} - n_{\boldsymbol{k}\downarrow}\big). \tag{159}$$

Hence, u_k and v_k are determined by (153) and

$$2(\epsilon_k - \mu)u_k v_k = \Delta\big(u_k^2 - v_k^2\big). \tag{160}$$

Their combination yields a biquadratic equation with the solution

$$\left.\begin{matrix} u_k^2 \\ v_k^2 \end{matrix}\right\} = \frac{1}{2}\left[1 \pm \frac{(\epsilon_k - \mu)}{\sqrt{(\epsilon_k - \mu)^2 + \Delta^2}}\right], \quad 2u_k v_k = \frac{\Delta}{\sqrt{(\epsilon_k - \mu)^2 + \Delta^2}}. \tag{161}$$

Insertion into (159) results in the self-consistency condition

$$1 = \frac{g}{2V}\sum_{\boldsymbol{k}} \frac{1 - n_{\boldsymbol{k}\uparrow} - n_{\boldsymbol{k}\downarrow}}{\sqrt{(\epsilon_k - \mu)^2 + \Delta^2}}, \tag{162}$$

which determines Δ as a function of the BCS coupling constant g, the dispersion relation ϵ_k of the normal state $\hat{c}$-quasi-particles (in essence the Fermi velocity), and the occupation numbers $n_{\boldsymbol{k}\sigma}$ of the $\hat{b}$-quasi-particles of the superconducting state (in essence the temperature as seen later).

The parameters u_k and v_k are depicted in the figure on the right. Formally, interchanging u_k with v_k would also be a solution of the biquadratic equation. It is, however, easily seen that this would not lead to a minimum of (158). With (161) it is readily seen that the second sum of (158) is positive definite. Hence, the absolute minimum of energy (ground state) is attained, if all occupation numbers of the $\hat{b}$-orbitals are zero.

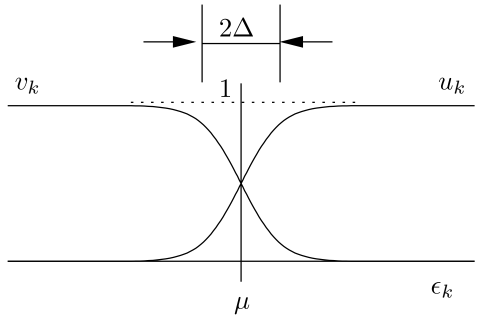


Figure 36: The functions u and v.

For the ground state, the self-consistency condition (162) reduces to

$$1 = \frac{g}{2V}\sum_{\boldsymbol{k}} \frac{1}{\sqrt{(\epsilon_k-\mu)^2+\Delta_0^2}} = \frac{gN(0)}{2}\int_{-\omega_c}^{\omega_c} d\omega \frac{1}{\sqrt{\omega^2+\Delta_0^2}} = \frac{gN(0)}{2}\ln\frac{\sqrt{\omega_c^2+\Delta_0^2}+\omega_c}{\sqrt{\omega_c^2+\Delta_0^2}-\omega_c} \approx$$

$$\approx \frac{gN(0)}{2}\ln\frac{4\omega_c^2}{\Delta_0^2}$$

resulting in

$$\Delta_0 = 2\omega_c \exp\left\{-\frac{1}{gN(0)}\right\} \tag{163}$$

for the value of Δ in the ground state (at zero temperature).

If one replaces the last term $-(g/V)\sum \hat{B}^\dagger_{\boldsymbol{k}'}\hat{B}_{\boldsymbol{k}}$ of the transformed BCS-Hamiltonian (156) by the mean-field approximation $-\Delta\sum_{\boldsymbol{k}}\big[\hat{B}_{\boldsymbol{k}}+\hat{B}^\dagger_{\boldsymbol{k}}\big]$ (recall that Δ was introduced as $\Delta = (g/V)\langle\Psi_0|\sum_{\boldsymbol{k}}\hat{B}_{\boldsymbol{k}}|\Psi_0\rangle$, cf. (155, 159)), than it is readily seen that the relation (160) makes the anomalous terms (terms $\hat{b}^\dagger\hat{b}^\dagger$ or $\hat{b}\hat{b}$) of this Hamiltonian vanish: In mean-field approximation the BCS-Hamiltonian is diagonalized by the Bogoliubov-Valatin transformation, resulting in

$$\begin{aligned}
\hat{H}_{\text{m-f}} &= 2\sum_{\boldsymbol{k}}(\epsilon_k-\mu)v_k^2 + \sum_{\boldsymbol{k}\sigma}(\epsilon_k-\mu)(u_k^2-v_k^2)\hat{b}^\dagger_{\boldsymbol{k}\sigma}\hat{b}_{\boldsymbol{k}\sigma} - 2\Delta\sum_{\boldsymbol{k}}u_kv_k\left(1-\sum_\sigma \hat{b}^\dagger_{\boldsymbol{k}\sigma}\hat{b}_{\boldsymbol{k}\sigma}\right) = \\
&= \text{const.} + \sum_{\boldsymbol{k}\sigma}\Big[(\epsilon_k-\mu)(u_k^2-v_k^2)+2\Delta u_kv_k\Big]\hat{b}^\dagger_{\boldsymbol{k}\sigma}\hat{b}_{\boldsymbol{k}\sigma} = \\
&= \text{const.} + \sum_{\boldsymbol{k}\sigma}\eta_{\boldsymbol{k}\sigma}\hat{b}^\dagger_{\boldsymbol{k}\sigma}\hat{b}_{\boldsymbol{k}\sigma}
\end{aligned} \tag{164}$$

with the $\hat{b}$-quasi-particle energy dispersion relation

$$\eta_k = \sqrt{(\epsilon_k-\mu)^2+\Delta^2} \tag{165}$$

obtained by inserting (161) into the second line of (164).

The dispersion relation η_k together with the normal state dispersion relation $\epsilon_k - \mu$ and the normal state excitation energy dispersion $|\epsilon_k - \mu|$ is depicted on the right. It is seen that the physical meaning of Δ is the gap in the $\hat{b}$-quasiparticle excitation spectrum of the superconducting state. The name *bogolons* is often used for these quasi-particles.

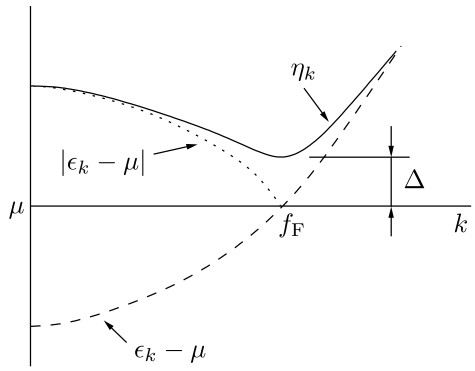


Figure 37: Quasi-particle dispersion relation in the superconducting state.

The fact that the Bogoliubov-Valatin transformation diagonalizes the BCS-Hamiltonian at least in mean-field approximation justifies *a posteriori* our assumption that the ground state may be found as an eigenstate of the $\hat{b}$-occupation number operators. In the literature, the key relations (160) are often derived as diagonalizing the mean-field BCS-Hamiltonian instead of minimizing the energy expression (158). In fact both connections are equally important and provide only together the solution of that Hamiltonian. Clearly, the BCS-theory based on that solution is a mean-field theory.

From (152) one could arrive at the conclusion that a bogolon consists partially of a normal-state electron and partially of a hole, and hence would not carry an integer charge quantum. However, as first was pointed out by Josephson, the true $\hat{b}$-quasi-particle annihilation and creation operators are

$$\hat{\beta}_{\boldsymbol{k}\sigma} = u_k \hat{c}_{\boldsymbol{k}\sigma} - \sigma v_k \hat{P} \hat{c}^\dagger_{-\boldsymbol{k}-\sigma}, \quad \hat{\beta}^\dagger_{\boldsymbol{k}\sigma} = u_k \hat{c}^\dagger_{\boldsymbol{k}\sigma} - \sigma v_k \hat{c}_{-\boldsymbol{k}-\sigma} \hat{P}^\dagger, \tag{166}$$

where $\hat{P}$ annihilates and $\hat{P}^\dagger$ creates a bound pair with zero momentum and zero spin as considered in the Cooper problem. Its wavefunction will be considered in the next chapter. Now, a bogolon is annihilated, that is, a hole-bogolon is created, by partially creating a normal-state hole and partially annihilating an electron pair and replacing it with a normal-state electron. The second part of the process also creates a *positive* charge, whence the hole-bogolon (with $|\boldsymbol{k}| < k_F$) carries an integer positive charge quantum. Likewise, an electron-bogolon (with $|\boldsymbol{k}| > k_F$) is created partially by creating a normal-state electron and partially by creating an electron pair and simultaneously annihilating a normal-state electron. Again, the bogolon carries an integer (negative) charge quantum. The $\hat{P}$-operators make the $\hat{b}$-bogolon be surrounded by a superconducting *back flow* of charge which ensures that an integer charge quantum travels with the bogolon. It is positive for $|\boldsymbol{k}| < k_F$ and negative for $|\boldsymbol{k}| > k_F$.

Of course, it remains to show that the new ground state $|\Psi_0\rangle$ is indeed superconducting.

9 MICROSCOPIC THEORY: PAIR STATES

In mean-field BCS theory, the ground state is determined by the complete absence of quasi-particles. With the properties of the Bogoliubov-Valatin transformation, this ground state is found to be the condensate of Cooper pairs in plane-wave $\boldsymbol{K} = 0$ states of their centers of gravity. By occupying quasi-particle states according to Fermi statistics, thermodynamic states of the BCS superconductor are obtained.

9.1 The BCS ground state

In Section 8.D the BCS ground state $|\Psi_0\rangle$ was assumed to be an occupation number eigenstate of $\hat{n}_{\boldsymbol{k}\sigma} = \hat{b}^\dagger_{\boldsymbol{k}\sigma}\hat{b}_{\boldsymbol{k}\sigma}$, and the $\hat{b}_{\boldsymbol{k}\sigma}$ were determined accordingly. Then, it was found after (162) that all occupation numbers $\hat{n}_{\boldsymbol{k}\sigma}$ are zero in the ground state. This implies that $\langle\Psi_0|\hat{b}^\dagger_{\boldsymbol{k}\sigma}\hat{b}_{\boldsymbol{k}\sigma}|\Psi_0\rangle = 0$, and hence

$$\hat{b}_{\boldsymbol{k}\sigma}|\Psi_0\rangle = 0 \tag{167}$$

for all $\boldsymbol{k}\sigma$: The (mean-field) BCS ground state is the (uniquely defined) $\hat{b}$-vacuum. We show that

$$|\Psi_0\rangle = \prod_{\boldsymbol{k}}\big(u_k + v_k\hat{c}^\dagger_{\boldsymbol{k}\uparrow}\hat{c}^\dagger_{-\boldsymbol{k}\downarrow}\big)|\rangle \tag{168}$$

is the properly normalized state with properties (167). The normal metal ground state $|0\rangle$ of (130, 131) is

$$|0\rangle = \prod_{\boldsymbol{k}\sigma}^{\epsilon_k<\mu}\hat{c}^\dagger_{\boldsymbol{k}\sigma}|\rangle = \prod_{\boldsymbol{k}}^{\epsilon_k<\mu}\hat{c}^\dagger_{\boldsymbol{k}\uparrow}\hat{c}^\dagger_{-\boldsymbol{k}\downarrow}|\rangle \tag{169}$$

and hence has the form (168) too, with $u_k = 0$ for $\epsilon_k < \mu$ and $u_k = 1$ for $\epsilon_k > \mu$ and the opposite behavior for v_k.

We now demonstrate the properties of (168). Since

$$\langle|\big(u_k + v_k\hat{c}_{-\boldsymbol{k}\downarrow}\hat{c}_{\boldsymbol{k}\uparrow}\big)\big(u_k + v_k\hat{c}^\dagger_{\boldsymbol{k}\uparrow}\hat{c}^\dagger_{-\boldsymbol{k}\downarrow}\big)|\rangle = u_k^2 + v_k^2 = 1,$$

$|\Psi_0\rangle$ of (168) is properly normalized. Moreover,

$$\begin{aligned}
\hat{b}_{\boldsymbol{k}'\uparrow}|\Psi_0\rangle &= \left[\prod_{\boldsymbol{k}(\neq\boldsymbol{k}')}\big(u_k + v_k\hat{c}^\dagger_{\boldsymbol{k}\uparrow}\hat{c}^\dagger_{-\boldsymbol{k}\downarrow}\big)\right]\big(u_{k'}\hat{c}_{\boldsymbol{k}'\uparrow} - v_{k'}\hat{c}^\dagger_{-\boldsymbol{k}'\downarrow}\big)\big(u_{k'} + v_{k'}\hat{c}^\dagger_{\boldsymbol{k}'\uparrow}\hat{c}^\dagger_{-\boldsymbol{k}'\downarrow}\big)|\rangle = \\
&= \left[\prod_{\boldsymbol{k}(\neq\boldsymbol{k}')}\big(u_k + v_k\hat{c}^\dagger_{\boldsymbol{k}\uparrow}\hat{c}^\dagger_{-\boldsymbol{k}\downarrow}\big)\right]u_{k'}v_{k'}\big(\hat{c}_{\boldsymbol{k}'\uparrow}\hat{c}^\dagger_{\boldsymbol{k}'\uparrow}\hat{c}^\dagger_{-\boldsymbol{k}'\downarrow} - \hat{c}^\dagger_{-\boldsymbol{k}'\downarrow}\big)|\rangle = \\
&= \left[\prod_{\boldsymbol{k}(\neq\boldsymbol{k}')}\big(u_k + v_k\hat{c}^\dagger_{\boldsymbol{k}\uparrow}\hat{c}^\dagger_{-\boldsymbol{k}\downarrow}\big)\right]u_{k'}v_{k'}\Big(\big(1 - \hat{c}^\dagger_{\boldsymbol{k}'\uparrow}\hat{c}_{\boldsymbol{k}'\uparrow}\big)\,\hat{c}^\dagger_{-\boldsymbol{k}'\downarrow} - \hat{c}^\dagger_{-\boldsymbol{k}'\downarrow}\Big)|\rangle = 0
\end{aligned} \tag{170}$$

and analogously $\hat{b}_{\boldsymbol{k}'\downarrow}|\Psi_0\rangle = 0$. This completes our proof. Historically, Bardeen, Cooper and Schrieffer solved the BCS model with the ansatz (168), before the work of Bogoliubov and Valatin.

9.2 The pair function

Next we find the wavefunctions contained in $|\Psi_0\rangle$. Recall, that $\hat{c}^\dagger_{\boldsymbol{k}\sigma}$ creates a conduction electron in the plane-wave state $\sim \exp(i\boldsymbol{k}\cdot\boldsymbol{r})\chi_\sigma(s)$ so that the field operator $\hat{\psi}^\dagger(\boldsymbol{r}s)$ is

$$\hat{\psi}^\dagger(\boldsymbol{r}s) = \sum_{\boldsymbol{k}\sigma} \hat{c}^\dagger_{\boldsymbol{k}\sigma} \exp(i\boldsymbol{k}\cdot\boldsymbol{r})\chi_\sigma(s). \tag{171}$$

(That is, $\boldsymbol{r}s$ denotes the center of gravity and the spin of the electron with its polarization cloud which together make up the 'conduction electron'.)

The N-particle wavefunction contained in $|\Psi_0\rangle$ and depending on these variables is

$$\Psi_0(x_1,\dots,x_N) = \langle x_1\dots x_N|\Psi_0\rangle = \langle|\hat{\psi}(x_N)\cdots\hat{\psi}(x_1)\prod_{\boldsymbol{k}}(u_k + v_k\hat{c}^\dagger_{\boldsymbol{k}\uparrow}\hat{c}^\dagger_{-\boldsymbol{k}\downarrow})|\rangle. \tag{172}$$

For the sake of brevity we suppress the spinors χ, and find

$$\begin{aligned}
&\Psi_0(x_1,\dots,x_N) = \\
&= \sum_{\boldsymbol{k}_1\dots\boldsymbol{k}_N} \langle| \underbrace{e^{i\boldsymbol{k}_N\cdot\boldsymbol{r}_N}\hat{c}_{\boldsymbol{k}_N\sigma_N}e^{i\boldsymbol{k}_{N-1}\cdot\boldsymbol{r}_{N-1}}\hat{c}_{\boldsymbol{k}_{N-1}\sigma_{N-1}}\cdots e^{i\boldsymbol{k}_1\cdot\boldsymbol{r}_1}\hat{c}_{\boldsymbol{k}_1\sigma_1}}_{=0,\text{ if not } \boldsymbol{k}_i\sigma_i\neq\boldsymbol{k}_j\sigma_j \text{ for } i\neq j} \prod_{\boldsymbol{k}}\Big(1+g_k\hat{c}^\dagger_{\boldsymbol{k}\uparrow}\hat{c}^\dagger_{-\boldsymbol{k}\downarrow}\Big)\prod_{\boldsymbol{k}}u_k\;|\rangle = \\
&= \sum_{\boldsymbol{k}_1\dots\boldsymbol{k}_N}{}' e^{i(\boldsymbol{k}_1\cdot\boldsymbol{r}_1+\dots+\boldsymbol{k}_N\cdot\boldsymbol{r}_N)} \underbrace{\langle|\,\hat{c}_{\boldsymbol{k}_N\sigma_N}\cdots\hat{c}_{\boldsymbol{k}_1\sigma_1}\overbrace{\prod_{\boldsymbol{k}}g_k\,\hat{c}^\dagger_{\boldsymbol{k}\uparrow}\,\hat{c}^\dagger_{-\boldsymbol{k}\downarrow}}^{N/2}\,|\rangle}_{\text{sum over all possible contractions}} \left(\prod_{\boldsymbol{k}}u_k\right) \sim \\
&\sim \sum_{\{\boldsymbol{k}_{2i}\}}{}' \left(e^{i\boldsymbol{k}_2\cdot(\boldsymbol{r}_1-\boldsymbol{r}_2)}g_{\boldsymbol{k}_2}\delta_{\sigma_1-\sigma_2}\cdots e^{i\boldsymbol{k}_N\cdot(\boldsymbol{r}_{N-1}-\boldsymbol{r}_N)}g_{\boldsymbol{k}_N}\delta_{\sigma_{N-1}-\sigma_N}\pm\cdots\right) = \\
&\sim \mathcal{A}\phi(\boldsymbol{r}_1-\boldsymbol{r}_2)\chi_{\text{singlet}}\phi(\boldsymbol{r}_3-\boldsymbol{r}_4)\chi_{\text{singlet}}\cdots\phi(\boldsymbol{r}_{N-1}-\boldsymbol{r}_N)\chi_{\text{singlet}}
\end{aligned} \tag{173}$$

with

$$\phi(\boldsymbol{\rho}) \sim \sum_{\boldsymbol{k}} g_k e^{i\boldsymbol{k}\cdot\boldsymbol{\rho}}, \qquad g_k = \frac{v_k}{u_k}. \tag{174}$$

In the second line of (173), (171) was inserted for the $\hat{\psi}(x_i)$ of (172), and the u_ks were factored out of the product of (172) (leaving $g_k = v_k/u_k$ behind in the second item of the factors). The $\boldsymbol{k}$-products run over all grid points of the (infinite) $\boldsymbol{k}$-mesh, e.g. determined by periodic boundary conditions for the sample volume V, while the sum runs over all possible products for sets of N disjunct $\boldsymbol{k}$-values out of that mesh. This disjunct nature of the $\boldsymbol{k}$-sums is indicated by a dash at the sum in the following lines. Expansion of the first $\boldsymbol{k}$-product yields terms with 0, 2, 4, $\dots\hat{c}^\dagger$-operators of which only the terms with exactly those N $\hat{c}^\dagger$-operators that correspond to the N $\hat{c}$-operators of an item of the $\boldsymbol{k}$-sum left to the product produce a non-zero result between the $\hat{c}$-vacuum states $\langle|\cdots|\rangle$. These results are most easily obtained by anticommuting all annihilation operators to the right of all creation operators and are usually called contractions; depending on the original order of the operators, each result is ±1. The product over the u_k, which multiplies each contribution and which as previously runs over all infinitely many $\boldsymbol{k}$-values of the full mesh, yields a normalizing factor which is independent of the values of $\boldsymbol{k}_1,\dots,\boldsymbol{k}_N$ of the sums. Like each individual factor u_k, it depends on the chemical potential μ and on the gap Δ_0. At this point one must realize that the g_k are essentially non-zero inside of the Fermi surface (cf. (161)). Hence, the contribution to $\Psi_0(x_1,\dots,x_N)$ has a non-negligible value only for all $\boldsymbol{k}_i$-vectors inside the Fermi surface, and this value increases with an increasing number of such $\boldsymbol{k}_i$-vectors and decreases again, if an appreciable number of $\boldsymbol{k}_i$-vectors falls outside of the Fermi surface: the norm of (172) is maximal for N-values such that the $\boldsymbol{k}_{2i}$ occupy essentially all mesh points inside the Fermi surface. That is, this norm is non-negligible only for those N-values corresponding to the electron number in the original normal Fermi liquid: $|\Psi_0\rangle$ is a grand-canonical state with a sharp particle-number maximum at the canonical N-value. We did not trace normalizing factors in (173) and use a sign of approximation in (174) again, assumig $\phi(\rho)$ to be normalized.

The result is a state $|\Psi_0\rangle$ consisting of pairs of electrons in the geminal (pair-orbital) $\phi(\rho)\chi_{\text{singlet}}$. In order to analyze what this pair-orbital $\phi(\rho)$ looks like, recall that u_k and v_k may be written as functions of Δ_0 and $(\epsilon_k - \mu)/\Delta_0 \approx \hbar v_{\mathrm{F}} k/\Delta_0$ (cf. (161)). Hence, $g_k \approx \tilde{g}(\hbar v_{\mathrm{F}} k/\Delta_0)$, and

$$\begin{aligned}
\phi(\boldsymbol{\rho}) &\sim \int d^3k g_k e^{i\boldsymbol{k}\cdot\boldsymbol{\rho}} \sim \int_0^\infty dk k^2 g_k \int_{-1}^1 d\zeta e^{ik\rho\zeta} = \int_0^\infty dk k^2 g_k \frac{e^{ik\rho} - e^{-ik\rho}}{ik\rho} \sim \\
&\sim \frac{1}{\rho}\int_0^\infty dk k \tilde{g}\left(\frac{\hbar v_{\mathrm{F}} k}{\Delta_0}\right) \sin k\rho \sim \frac{1}{\rho}\int_0^\infty dx x \tilde{g}(x) \sin\left(\frac{\Delta_0 x \rho}{\hbar v_{\mathrm{F}}}\right) \sim f(\rho/\xi_0), \\
& \xi_0 \approx \frac{1}{\pi \delta k} = \frac{\hbar v_{\mathrm{F}}}{\pi \Delta_0}.
\end{aligned} \tag{175}$$

By comparison with (173), $\boldsymbol{\rho}$ is the distance vector of the two electrons in the pair, their distance on average being of the order of ξ_0, while the pair-orbital ϕ does not depend on the position $\boldsymbol{R}$ of the center of gravity of the pair: with respect to the center of gravity the pair is delocalized, it is a plane wave with wave vector $\boldsymbol{K} = 0$. Moreover, again due to (173), all $N/2 \sim 10^{23}$ electron pairs occupy the *same* delocalized pair-orbital ϕ in the BCS ground state $|\Psi_0\rangle$: this macroscopically occupied delocalized (that is, constant in $\boldsymbol{R}$-space) pair-orbital is the condensate wavefunction of the superconducting state, and hence *the structure (173) of* $|\Psi_0\rangle$ *ensures that the solution of the BCS model is a superconductor.*

For a real superconductor, the gap Δ_0 can be measured (for instance by measuring thermodynamic quantities which depend on the excitation spectrum or directly by tunneling spectroscopy. With the independently determined Fermi velocity v_{F} of electrons in the normal state, this measurement yields directly the average distance ξ_0 of the electrons in a pair which can be compared to the average distance r_s of to arbitrary conduction electrons in the solid given by the electron density. For a weakly coupled type I superconductor this ratio is typically

$$\frac{\xi_0}{r_s} \approx 10^3 \dots 10^4. \tag{176}$$

In this case, there are $10^9 \dots 10^{12}$ electrons of other pairs in the volume between a given pair: There is a pair correlation resulting in a condensation of all electrons into one and the same delocalized pair orbital in the superconducting state, however, the picture of electrons grouped into individual pairs would be by far misleading.

In order to create a supercurrent, the condensate wavefunction, that is, the pair orbital must be provided with a phase factor

$$\phi(\boldsymbol{\rho}, \boldsymbol{R}) \sim e^{i\boldsymbol{K}\cdot\boldsymbol{R}} \tag{177}$$

by replacing the creation operators in (168) with $\hat{c}^\dagger_{\boldsymbol{k}+\boldsymbol{K}/2\uparrow}\hat{c}^\dagger_{-\boldsymbol{k}+\boldsymbol{K}/2\downarrow}$. Obviously, it must be $K\xi_0 \ll 1$ in order not to deform (and thus destroy) the pair orbital itself. Hence, ξ_0 *has the meaning of the coherence length of the superconductor at zero temperature.*

9.3 Non-zero temperature

The transformed Hamiltonian (164) shows that the bogolons created by operators $\hat{\beta}^\dagger_{\boldsymbol{k}\sigma}$ of (166) and having an energy dispersion law η_k of (165) are fermionic excitations with charge e and spin σ above the BCS ground state $|\Psi_0\rangle$. Since they may recombine into Cooper pairs ϕ, the chemical potential of the Cooper pairs must be 2μ where μ is the chemical potential of bogolons. Hence, at temperature T the distribution of bogolons is

$$n_{\boldsymbol{k}\uparrow} = n_{\boldsymbol{k}\downarrow} = \frac{1}{e^{\eta_k/kT} + 1}. \tag{178}$$

The gap equation (162) then yields (cf. the analysis leading to (163))

$$\begin{aligned} 1 &= \frac{g}{2V}\sum_{\boldsymbol{k}} \frac{1-2\left(e^{\eta_k/kT}+1\right)^{-1}}{\eta_k} = \frac{gN(0)}{2}\int_{-\omega_c}^{\omega_c} \frac{d\omega}{\sqrt{\omega^2+\Delta^2}} \frac{e^{\sqrt{\omega^2+\Delta^2}/kT}-1}{e^{\sqrt{\omega^2+\Delta^2}/kT}+1} = \\ &= gN(0)\int_0^{\omega_c} \frac{d\omega}{\sqrt{\omega^2+\Delta^2}} \tanh\left(\frac{\sqrt{\omega^2+\Delta^2}}{2kT}\right) \end{aligned} \tag{179}$$

where in the last equation the symmetry of the integrand with respect to a sign change of ω was used. For $T \to 0$, with the limes $\tanh x \to 1$ for $x \to \infty$, (163) is reproduced.

For increasing temperature, the numerator of (162) decreases, and hence Δ must also decrease. It vanishes at the transition temperature T_c, whence

$$1 = gN(0)\int_0^{\omega_c} \frac{d\omega}{\omega} \tanh\frac{\omega}{2kT_c} = gN(0)\int_0^{\omega_c/2kT_c} \frac{dx}{x}\tanh x. \tag{180}$$

Integration of the last integral by parts yields

$$\begin{aligned} \int_0^{\omega_c/2kT_c} \frac{dx}{x}\tanh x &= -\int_0^{\omega_c/2kT_c} dx \frac{\ln x}{\cosh^2 x} + \ln\frac{\omega_c}{2kT_c}\tanh\frac{\omega_c}{2kT_c} \approx \\ \approx -\int_0^{\infty} dx\frac{\ln x}{\cosh^2 x} + \ln\frac{\omega_c}{2kT_c} &= \ln\frac{4\gamma}{\pi} + \ln\frac{\omega_c}{2kT_c} = \ln\frac{2\gamma\omega_c}{\pi kT_c}, \end{aligned}$$

where $\ln\gamma = C \approx 0.577$ is Euler's constant. The second line is valid in the weak coupling case $kT_c \ll \omega_c$ and the final result for that case is

$$kT_c = \frac{2\gamma}{\pi}\omega_c \exp\left\{-\frac{1}{gN(0)}\right\} = \frac{\gamma}{\pi}\Delta_0 \tag{181}$$

with $2\gamma/\pi \approx 1.13$, and $2\Delta_0/kT_c = 2\pi/\gamma \approx 3.52$.

The gap Δ as a function of temperature between zero and T_c must be calculated numerically from (178). However, the simple expression

$$\Delta(T) \approx \Delta_0\sqrt{1-\left(\frac{T}{T_c}\right)^3} \tag{182}$$

is a very good approximation.

From the energy expression (158), the thermodynamic quantities can be calculated, once $\Delta(T)$ and hence $\eta_k(T)$ is given. The main results are the condensation energy at $T = 0$,

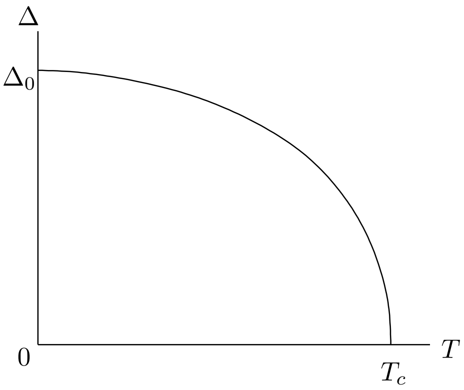


Figure 38: The gap as a function of T.

$$\frac{B_c(0)^2}{2\mu_0} = \frac{1}{2}N(0)\Delta_0^2, \tag{183}$$

yielding the thermodynamic critical field at zero temperature, the specific heat jump at T_c,

$$\frac{C_s - C_n}{C_n} \approx 1.43, \tag{184}$$

and the exponential behavior of the specific heat at low temperatures,

$$C_s(T) \sim T^{-3/2}e^{-\Delta_0/kT} \quad \text{for} \quad T \ll T_c. \tag{185}$$

10 MICROSCOPIC THEORY: COHERENCE FACTORS

As already done in the last section, thermodynamic states of a superconductor are obtained by occupying quasi-particle states with Fermi occupation numbers. External fields, however, in most cases couple to the $\hat{c}$-operator fields. Due to the coupling of $\hat{c}$-excitations in a superconductor interference terms appear in the response to such fields.

10.1 The thermodynamic state

Let $\{\boldsymbol{k}\sigma\}$ be any given disjunct set of quasi-particle quantum numbers. Then,

$$|\Psi_{\{\boldsymbol{k}\sigma\}}\rangle = \prod_{\boldsymbol{k}\sigma\in\{\boldsymbol{k}\sigma\}} \beta^\dagger_{\boldsymbol{k}\sigma}|\Psi_0\rangle \tag{186}$$

is a state with those quasi-particles excited above the superconducting ground state $|\Psi_0\rangle$. If there are many quasi-particle excitations present, they interact with each other and with the condensate in the ground state (the latter interaction is in terms of the operators $\hat{P}\hat{c}^\dagger_{\boldsymbol{k}\sigma}$ and $\hat{c}_{\boldsymbol{k}\sigma}\hat{P}^\dagger$), and this interaction leads to the temperature dependence of their energy dispersion law $\eta_k = \sqrt{(\epsilon_k-\mu)^2+\Delta^2}$ via the temperature dependence $\Delta = \Delta(T)$. The thermodynamic state is

$$\check{P} = \sum_{\{\boldsymbol{k}\sigma\}} |\Psi_{\{\boldsymbol{k}\sigma\}}\rangle \frac{\prod_{\boldsymbol{k}\sigma\in\{\boldsymbol{k}\sigma\}} f_k}{Z} \langle\Psi_{\{\boldsymbol{k}\sigma\}}|, \tag{187}$$

where the summation is over all possible sets of quasi-particle quantum numbers,

$$f_k = \frac{1}{\exp(\eta_k/kT)+1} \tag{188}$$

is the Fermi occupation number, and $Z = Z(T,\mu)$ is the partition function determined by

$$\mathrm{tr}\check{P} = \sum_{\{\boldsymbol{k}\sigma\}} \frac{\prod_{\boldsymbol{k}\sigma\in\{\boldsymbol{k}\sigma\}} f_k}{Z} = 1. \tag{189}$$

As usual, the thermodynamic expectation value of any operator $\hat{A}$ is obtained as $\mathrm{tr}\hat{A}\check{P}$. For instance the average occupation number itself of a quasi-particle in the state $\boldsymbol{k}'\sigma'$ is

$$\begin{aligned} n_{\boldsymbol{k}'\sigma'} &= \mathrm{tr}\Big(\hat{\beta}^\dagger_{\boldsymbol{k}'\sigma'}\hat{\beta}_{\boldsymbol{k}'\sigma'} \sum_{\{\boldsymbol{k}\sigma\}} |\Psi_{\{\boldsymbol{k}\sigma\}}\rangle \frac{\prod f_k}{Z} \langle\Psi_{\{\boldsymbol{k}\sigma\}}|\Big) = \\ &= \sum_{\{\boldsymbol{k}\sigma\}} \langle\Psi_{\{\boldsymbol{k}\sigma\}}|\hat{\beta}^\dagger_{\boldsymbol{k}'\sigma'}\hat{\beta}_{\boldsymbol{k}'\sigma'}|\Psi_{\{\boldsymbol{k}\sigma\}}\rangle \frac{\prod f_k}{Z} = f_{k'}\mathrm{tr}\check{P} = f_{k'}. \end{aligned} \tag{190}$$

The state $\hat{\beta}_{\boldsymbol{k}'\sigma'}|\Psi_{\{\boldsymbol{k}\sigma\}}\rangle$ is obtained from the state $|\Psi_{\{\boldsymbol{k}\sigma\}}\rangle$ by removing the quasi-particle $\boldsymbol{k}'\sigma'$. Hence, if one factors out $f_{k'}$, the remaining sum is again $\check{P}$.

10.2 The charge and spin moment densities

The operator of the $\boldsymbol{q}$ Fourier component of the charge density of electrons in a solid is

$$\hat{n}(\boldsymbol{q}) = -e\sum_{\boldsymbol{k}\sigma} \hat{c}^\dagger_{\boldsymbol{k}+\boldsymbol{q}\sigma}\hat{c}_{\boldsymbol{k}\sigma} = -e\sum_{\boldsymbol{k}}\Big(\hat{c}^\dagger_{\boldsymbol{k}+\boldsymbol{q}\uparrow}\hat{c}_{\boldsymbol{k}\uparrow} + \hat{c}^\dagger_{-\boldsymbol{k}\downarrow}\hat{c}_{-\boldsymbol{k}-\boldsymbol{q}\downarrow}\Big). \tag{191}$$

That of the spin moment density (in z-direction) is

$$\hat{m}(\boldsymbol{q}) = \mu_{\mathrm{B}}\sum_{\boldsymbol{k}\sigma} \hat{c}^\dagger_{\boldsymbol{k}+\boldsymbol{q}\sigma}\sigma\hat{c}_{\boldsymbol{k}\sigma} = \mu_{\mathrm{B}}\sum_{\boldsymbol{k}}\Big(\hat{c}^\dagger_{\boldsymbol{k}+\boldsymbol{q}\uparrow}\hat{c}_{\boldsymbol{k}\uparrow} - \hat{c}^\dagger_{-\boldsymbol{k}\downarrow}\hat{c}_{-\boldsymbol{k}-\boldsymbol{q}\downarrow}\Big). \tag{192}$$

The statistical operator $\check{P}$ of a normal metallic state is composed in analogy to (187) from eigenstates $|\Psi_{\{\boldsymbol{k}\sigma\}}\rangle$ of $\hat{c}$-operators. Then, in calculating thermodynamic averages, each item of the $\boldsymbol{k}\sigma$-sum of (191) and (192) is averaged independently. In the superconducting state, the items in parentheses of the last of those expressions are coupled and hence they are not any more averaged independently: there appear contributions due to their coherent interference in the superconducting states $|\Psi_{\{\boldsymbol{k}\sigma\}}\rangle$. Those contributions appear in the response of the superconducting state to external fields which couple to charge and spin densities.

Performing the Bogoliubov-Valatin transformation for the charge density operator yields

$$\begin{aligned}
\sum_{\boldsymbol{k}}\Big(\hat{c}^{\dagger}_{\boldsymbol{k}+\boldsymbol{q}\uparrow}\hat{c}_{\boldsymbol{k}\uparrow}+\hat{c}^{\dagger}_{-\boldsymbol{k}\downarrow}\hat{c}_{-\boldsymbol{k}-\boldsymbol{q}\downarrow}\Big) &= \\
= \sum_{\boldsymbol{k}}\Big[&\Big(u_{|\boldsymbol{k}+\boldsymbol{q}|}\hat{b}^{\dagger}_{\boldsymbol{k}+\boldsymbol{q}\uparrow}+v_{|\boldsymbol{k}+\boldsymbol{q}|}\hat{b}_{-\boldsymbol{k}-\boldsymbol{q}\downarrow}\Big)\Big(u_k\hat{b}_{\boldsymbol{k}\uparrow}+v_k\hat{b}^{\dagger}_{-\boldsymbol{k}\downarrow}\Big)+ \\
&+\Big(u_k\hat{b}^{\dagger}_{-\boldsymbol{k}\downarrow}-v_k\hat{b}_{\boldsymbol{k}\uparrow}\Big)\Big(u_{|\boldsymbol{k}+\boldsymbol{q}|}\hat{b}_{-\boldsymbol{k}-\boldsymbol{q}\downarrow}-v_{|\boldsymbol{k}+\boldsymbol{q}|}\hat{b}_{\boldsymbol{k}+\boldsymbol{q}\uparrow}\Big)\Big] = \\
= \sum_{\boldsymbol{k}}\Big[&u_{|\boldsymbol{k}+\boldsymbol{q}|}u_k\hat{b}^{\dagger}_{\boldsymbol{k}+\boldsymbol{q}\uparrow}\hat{b}_{\boldsymbol{k}\uparrow}+v_{|\boldsymbol{k}+\boldsymbol{q}|}v_k\hat{b}_{-\boldsymbol{k}-\boldsymbol{q}\downarrow}\hat{b}^{\dagger}_{-\boldsymbol{k}\downarrow}+u_{|\boldsymbol{k}+\boldsymbol{q}|}v_k\hat{b}^{\dagger}_{\boldsymbol{k}+\boldsymbol{q}\uparrow}\hat{b}^{\dagger}_{-\boldsymbol{k}\downarrow}+v_{|\boldsymbol{k}+\boldsymbol{q}|}u_k\hat{b}_{-\boldsymbol{k}-\boldsymbol{q}\downarrow}\hat{b}_{\boldsymbol{k}\uparrow}+ \\
&+u_k u_{|\boldsymbol{k}+\boldsymbol{q}|}\hat{b}^{\dagger}_{-\boldsymbol{k}\downarrow}\hat{b}_{-\boldsymbol{k}-\boldsymbol{q}\downarrow}+v_k v_{|\boldsymbol{k}+\boldsymbol{q}|}\hat{b}_{\boldsymbol{k}\uparrow}\hat{b}^{\dagger}_{\boldsymbol{k}+\boldsymbol{q}\uparrow}-u_k v_{|\boldsymbol{k}+\boldsymbol{q}|}\hat{b}^{\dagger}_{-\boldsymbol{k}\downarrow}\hat{b}^{\dagger}_{\boldsymbol{k}+\boldsymbol{q}\uparrow}-v_k u_{|\boldsymbol{k}+\boldsymbol{q}|}\hat{b}_{\boldsymbol{k}\uparrow}\hat{b}_{-\boldsymbol{k}-\boldsymbol{q}\downarrow}\Big] = \\
= \sum_{\boldsymbol{k}}\Big[&\Big(u_{|\boldsymbol{k}+\boldsymbol{q}|}u_k-v_{|\boldsymbol{k}+\boldsymbol{q}|}v_k\Big)\Big(\hat{b}^{\dagger}_{\boldsymbol{k}+\boldsymbol{q}\uparrow}\hat{b}_{\boldsymbol{k}\uparrow}+\hat{b}^{\dagger}_{-\boldsymbol{k}\downarrow}\hat{b}_{-\boldsymbol{k}-\boldsymbol{q}\downarrow}\Big)+ \\
&+\Big(u_{|\boldsymbol{k}+\boldsymbol{q}|}v_k+u_k v_{|\boldsymbol{k}+\boldsymbol{q}|}\Big)\Big(\hat{b}^{\dagger}_{\boldsymbol{k}+\boldsymbol{q}\uparrow}\hat{b}^{\dagger}_{-\boldsymbol{k}\downarrow}-\hat{b}_{\boldsymbol{k}\uparrow}\hat{b}_{-\boldsymbol{k}-\boldsymbol{q}\downarrow}\Big)\Big]
\end{aligned}$$

In obtaining the last equality some operator pairs were anticommuted which leads to the final result

$$\begin{aligned}
\hat{n}(\boldsymbol{q}) = -e\sum_{\boldsymbol{k}}\Big[&\Big(u_{|\boldsymbol{k}+\boldsymbol{q}|}u_k-v_{|\boldsymbol{k}+\boldsymbol{q}|}v_k\Big)\Big(\hat{b}^{\dagger}_{\boldsymbol{k}+\boldsymbol{q}\uparrow}\hat{b}_{\boldsymbol{k}\uparrow}+\hat{b}^{\dagger}_{-\boldsymbol{k}\downarrow}\hat{b}_{-\boldsymbol{k}-\boldsymbol{q}\downarrow}\Big)+ \\
&+\Big(u_{|\boldsymbol{k}+\boldsymbol{q}|}v_k+u_k v_{|\boldsymbol{k}+\boldsymbol{q}|}\Big)\Big(\hat{b}^{\dagger}_{\boldsymbol{k}+\boldsymbol{q}\uparrow}\hat{b}^{\dagger}_{-\boldsymbol{k}\downarrow}-\hat{b}_{\boldsymbol{k}\uparrow}\hat{b}_{-\boldsymbol{k}-\boldsymbol{q}\downarrow}\Big)\Big].
\end{aligned} \tag{193}$$

An analogous calculation yields

$$\begin{aligned}
\hat{m}(\boldsymbol{q}) = \mu_{\mathrm{B}}\sum_{\boldsymbol{k}}\Big[&\Big(u_{|\boldsymbol{k}+\boldsymbol{q}|}u_k+v_{|\boldsymbol{k}+\boldsymbol{q}|}v_k\Big)\Big(\hat{b}^{\dagger}_{\boldsymbol{k}+\boldsymbol{q}\uparrow}\hat{b}_{\boldsymbol{k}\uparrow}-\hat{b}^{\dagger}_{-\boldsymbol{k}\downarrow}\hat{b}_{-\boldsymbol{k}-\boldsymbol{q}\downarrow}\Big)+ \\
&+\Big(u_{|\boldsymbol{k}+\boldsymbol{q}|}v_k-u_k v_{|\boldsymbol{k}+\boldsymbol{q}|}\Big)\Big(\hat{b}^{\dagger}_{\boldsymbol{k}+\boldsymbol{q}\uparrow}\hat{b}^{\dagger}_{-\boldsymbol{k}\downarrow}+\hat{b}_{\boldsymbol{k}\uparrow}\hat{b}_{-\boldsymbol{k}-\boldsymbol{q}\downarrow}\Big)\Big].
\end{aligned} \tag{194}$$

The first line of these relations reflects the above mentioned coupling between $\hat{c}$-states, and the second reflects the coupling to the condensate. Both lines contain coherence factors composed of u and v.

10.3 Ultrasonic attenuation

As an example of a field (external to the electron system) coupling to the charge density we consider the electric field caused by a lattice phonon. The corresponding interaction term of the Hamiltonian is

$$\hat{H}_I = \frac{g}{\sqrt{V}}\sum_{\boldsymbol{q}}\sqrt{\omega_{\boldsymbol{q}}}(\hat{a}^{\dagger}_{-\boldsymbol{q}}+\hat{a}_{\boldsymbol{q}})\hat{n}(\boldsymbol{q}), \tag{195}$$

where g is a coupling constant relating the electric field of the phonon to its amplitude, V is the volume, ω is the phonon frequency and $\hat{a}^{\dagger}$ its creation operator.

We consider the attenuation of ultrasound with $\hbar\omega_{\boldsymbol{q}} < \Delta$, then, in lowest order pair processes do not contribute. According to Fermi's golden rule the phonon absorption rate may be written as

$$\begin{aligned} R_a(\boldsymbol{q}) &= \frac{2\pi}{\hbar}\mathrm{tr}\big(\hat{H}_I\delta(E_f - E_i)\hat{H}_I\check{P}\big) = \\ &= \frac{4\pi g^2}{\hbar V}\omega_{\boldsymbol{q}} n_{\boldsymbol{q}} \sum_{\boldsymbol{k}}\Big(u_{|\boldsymbol{k}+\boldsymbol{q}|}u_k - v_{|\boldsymbol{k}+\boldsymbol{q}|}v_k\Big)^2 f_k(1 - f_{|\boldsymbol{k}+\boldsymbol{q}|})\delta(\eta_{|\boldsymbol{k}+\boldsymbol{q}|} - \eta_k - \hbar\omega_{\boldsymbol{q}}). \qquad (196) \end{aligned}$$

Here, E_f and E_i are the total energies of the states forming the $\hat{H}_I$-matrix elements and $n_{\boldsymbol{q}}$ is the phonon occupation number of the thermodynamic state which in this case in extension of (187) also contains phononic excitations in thermic equilibrium. Half of the result of the last line is obtained from the first term in the first line of (193). After renaming $-\boldsymbol{k} - \boldsymbol{q} \to \boldsymbol{k}'$, the second term yields the same result. The phonon emission rate is analogously

$$\begin{aligned} R_e(\boldsymbol{q}) &= \frac{2\pi}{\hbar}\mathrm{tr}\big(\hat{H}_I\delta(E_f - E_i)\hat{H}_I\check{P}\big) = \\ &= \frac{4\pi g^2}{\hbar V}\omega_{\boldsymbol{q}} n_{\boldsymbol{q}} \sum_{\boldsymbol{k}}\Big(u_{|\boldsymbol{k}+\boldsymbol{q}|}u_k - v_{|\boldsymbol{k}+\boldsymbol{q}|}v_k\Big)^2 f_{|\boldsymbol{k}+\boldsymbol{q}|}(1 - f_k)\delta(\eta_{|\boldsymbol{k}+\boldsymbol{q}|} - \eta_k - \hbar\omega_{\boldsymbol{q}}). \qquad (197) \end{aligned}$$

With $f_k(1 - f_{|\boldsymbol{k}+\boldsymbol{q}|}) - f_{|\boldsymbol{k}+\boldsymbol{q}|}(1 - f_k) = f_k - f_{|\boldsymbol{k}+\boldsymbol{q}|}$, the attenuation rate is

$$\frac{dn_{\boldsymbol{q}}}{dt} = -\frac{4\pi g^2}{\hbar V}\omega_{\boldsymbol{q}} n_{\boldsymbol{q}} \sum_{\boldsymbol{k}}\Big(u_{|\boldsymbol{k}+\boldsymbol{q}|}u_k - v_{|\boldsymbol{k}+\boldsymbol{q}|}v_k\Big)^2 (f_k - f_{|\boldsymbol{k}+\boldsymbol{q}|})\delta(\eta_{|\boldsymbol{k}+\boldsymbol{q}|} - \eta_k - \hbar\omega_{\boldsymbol{q}}). \qquad (198)$$

The attenuation in the normal state is

$$\frac{dn_{\boldsymbol{q}}}{dt} = -\frac{4\pi g^2}{\hbar V}\omega_{\boldsymbol{q}} n_{\boldsymbol{q}} \sum_{\boldsymbol{k}}(f_k - f_{|\boldsymbol{k}+\boldsymbol{q}|})\delta(\epsilon_{|\boldsymbol{k}+\boldsymbol{q}|} - \epsilon_k - \hbar\omega_{\boldsymbol{q}}). \qquad (199)$$

From a measurement of the difference, $\Delta(T)$ can be inferred.

10.4 The spin susceptibility

With the interaction Hamiltonian

$$\hat{H}_I = -H(-\boldsymbol{q})\hat{m}(\boldsymbol{q}) + c.c., \qquad (200)$$

where H is an external magnetic field, the expectation value of the energy perturbation is obtained as

$$\Delta E(\boldsymbol{q}) = \mathrm{tr}\Big(\hat{H}_I(E_f - E_i)^{-1}\hat{H}_I\check{P}\Big). \qquad (201)$$

The susceptibility is

$$\begin{aligned} \chi(\boldsymbol{q}) &= -\frac{d^2\Delta E(\boldsymbol{q})}{dH(-\boldsymbol{q})} = -2\mu_{\mathrm{B}}^2\sum_{\boldsymbol{k}}\Bigg[\Big(u_{|\boldsymbol{k}+\boldsymbol{q}|}u_k + v_{|\boldsymbol{k}+\boldsymbol{q}|}v_k\Big)^2\frac{f_{|\boldsymbol{k}+\boldsymbol{q}|} - f_k}{\eta_{|\boldsymbol{k}+\boldsymbol{q}|} - \eta_k} + \\ &\qquad + \Big(u_{|\boldsymbol{k}+\boldsymbol{q}|}v_k - u_k v_{|\boldsymbol{k}+\boldsymbol{q}|}\Big)^2\frac{1 - f_k - f_{|\boldsymbol{k}+\boldsymbol{q}|}}{\eta_k + \eta_{|\boldsymbol{k}+\boldsymbol{q}|}}\Bigg]. \qquad (202) \end{aligned}$$

The susceptibility drops down below T_c and vanishes exponentially for $T \to 0$.

Coherence factors appear in similar manners in many more response functions as in the nuclear relaxation time, in the diamagnetic response, in the microwave absorption, and so on.

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