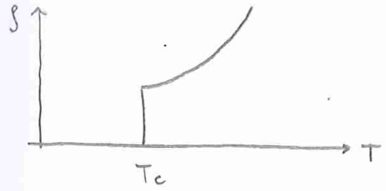
# Superprevodnost

K. Onnes ~1911 $\quad$ Hg, $T_c = 4K$



Superprevodne snovi:

a) ELEMENTARNE KOVINE

Al, Hg, Pb, Nb ($T_c = 9K$) → NISO FEROMAGNETI! (Fe, Ni, Co)

b) ZLITINE, SPOJINE (binarne, terciarne (št. atomov))

npr.: $Nb_3Ge$ (23K) (standardni SP, ~70. leta)

in $Nb_3Sb$

zanimivost: $MgB_2$ (2001) $T_c = 39K$

c) HTC (visokotemperaturni superprevodniki) → NESTANDARDNI SP?

- ponavadi bazirani na $CuO_2$

$LaCuO_4$ → $La_{2-x}Ba_xCuO_4$ / $La_{2-x}Sr_xCuO_4$ (1985) $T_c = 35K$

Standardni $YBaCuO_3$ ($T_c = 93K$)

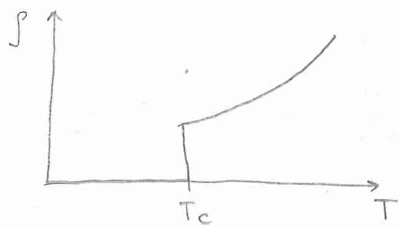
⋮ max 135 K, pod tlakom do 165 K

Glavne značilnosti SP stanja:

a) <u>idealna električna prevodnost</u>

$\rho(T < T_c) = 0$

↑ upornost

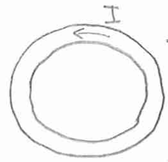


b) trajni (persistent) tokovi

(velja za $I < I_c$ ← kritični tok)

$\tau > 10^5$ let

↑ čas da tok pade



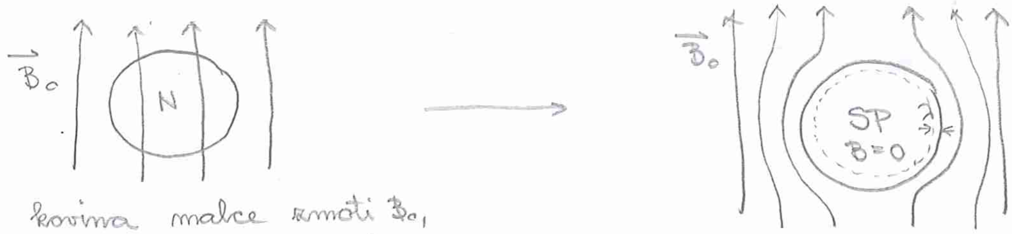
$T < T_c$

→ induciramo tok v prstanu

⇒ tok po tem vztraja nemerljivo dolgo

$I > I_c$ → prehod v normalno stanje

## b) Idealni diamagnetizem (Meissner, Ochsenfeld, 1933)




λ… vdorna globina (~100 nm)

kovina malce zmoti $B_0$, a $\chi_m$ je zelo majhna

($B_0$… zun. polje)

SP izrine magnetno polje $B_0$ ($T<T_c$)

(ne glede na to kako smo to dosegli)
↳ ohladimo kovino v $B_0$ ali pa
↳ damo SP v $B_0$

"Kaj ma to veze z diamagnetizmom?"

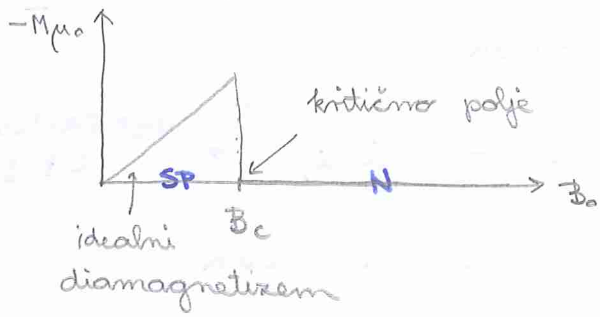
$$\vec{B} = \mu_0 (\vec{H} + \vec{M}) = 0 \quad \text{v SP pri } T<T_c$$

$$\Rightarrow \vec{M} = -\vec{H}$$

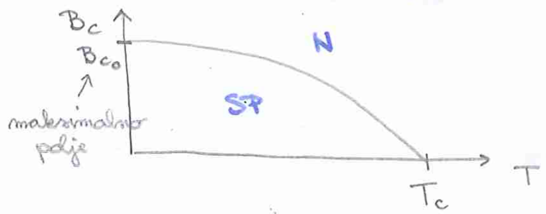
po definiciji je $\vec{M} = \chi_m \vec{H} \Rightarrow \boxed{\chi = -1}$

$\chi_m$ tipično $10^{-5}$

(za SP prve vrste)




SP I. vrste: fazni diagram




$$B_c = B_{c0}\left(1 - \frac{T^2}{T_c^2}\right)$$

## c) Energijska vrzel (SC gap)

$\boxed{\Delta_0 = \xi k_B T_c}$

⇒ kvanten pojav

$\Delta_0$ ⇒ loči osnovno stanje SP od vzbujenih stanj

(prozorno za fotone z $W_f < \Delta_0$)

optična absorpcija, ultrazvočna absorpcija

$\hbar\omega_0 < \Delta_0$

⇒ SP je kvanten pojav.

# THEORY OF SUPERCONDUCTIVITY

## A Primer

by

Helmut Eschrig

(2001, updated 09/2008)

# 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.

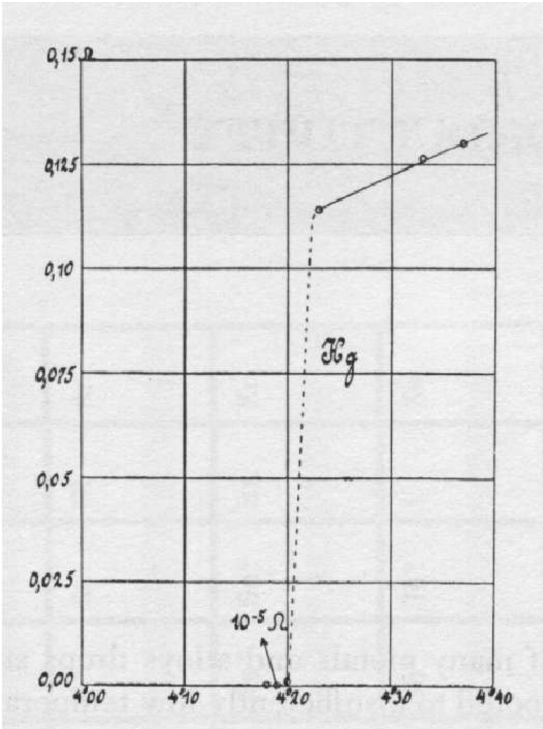



Figure 1: Resistance in ohms of a specimen of mercury versus absolute temperature. This plot by Kamerlingh Onnes marked the discovery of superconductivity. (Taken from: Ch. Kittel, *Introduction to Solid State Physics*, Wiley, New York, 1986, Chap. 12.)

# 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).

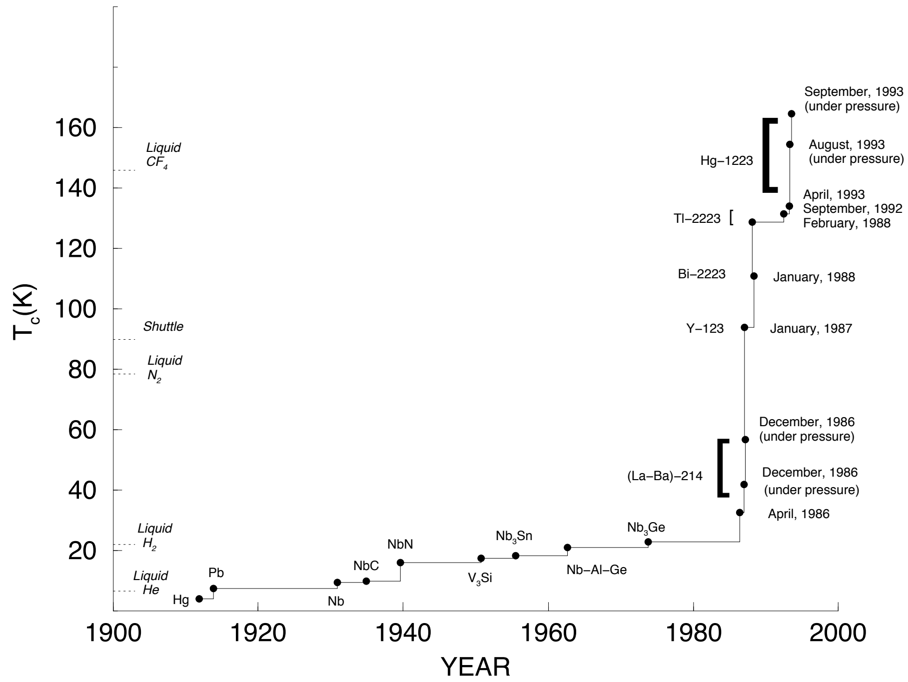



Figure 2: The evolution of $T_c$ with time (from C. W. Chu, *Superconductivity Above 90K and Beyond* in: B. Batlogg, C. W. Chu, W. K. Chu D. U. Gubser and K. A. Müller (eds.) Proc. HTS Workshop on Physics, Materials and Applications, World Scientific, Singapore, 1996.).

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 $\Psi$ 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 $\mu_B$ 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 $n_B = \text{const.}$ 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, $\phi_{\text{el}}$, and of the supercurrent, $\phi$, 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 $\frac{\partial}{\partial\boldsymbol{r}} \times \left(\frac{\partial}{\partial\boldsymbol{r}} \times \boldsymbol{B}\right) = \frac{\partial}{\partial\boldsymbol{r}}\left(\frac{\partial\boldsymbol{B}}{\partial\boldsymbol{r}}\right) - \frac{\partial^2}{\partial\boldsymbol{r}^2}\boldsymbol{B}$:

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

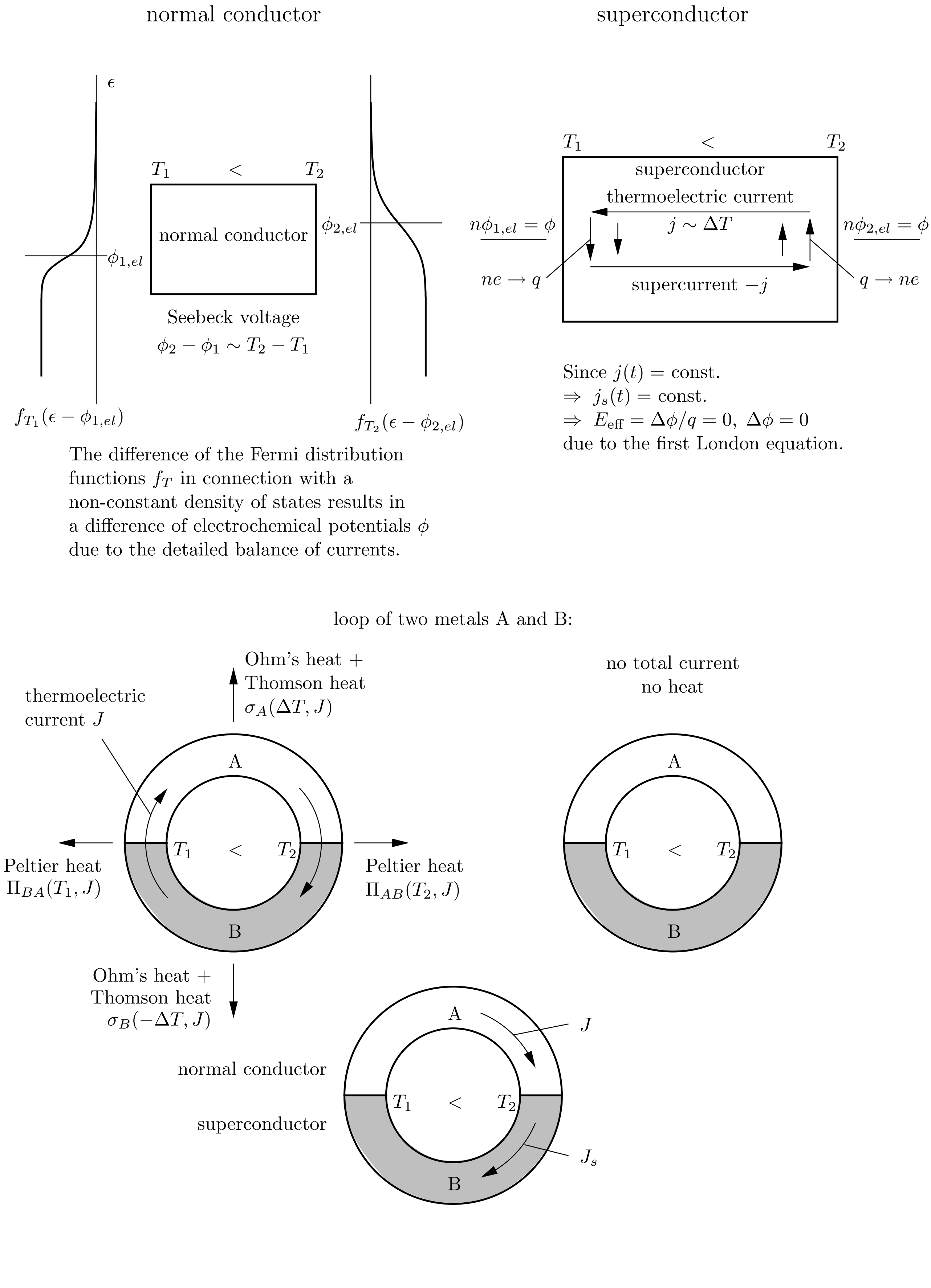


Figure 3: Thermoelectric phenomena in normal conductors and superconductors.

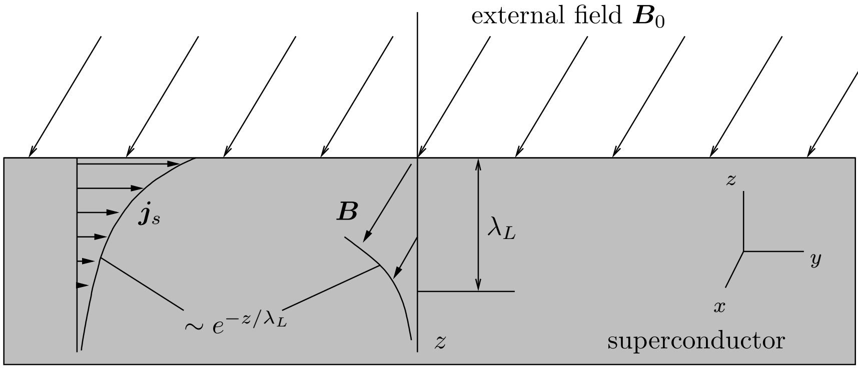


Figure 4: Penetration of an external magnetic field into a superconductor.

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

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. $\lambda_L$ 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 $\lambda_L$. 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 $\Phi$ 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 $\Phi$ is the magnetic flux through $A$.

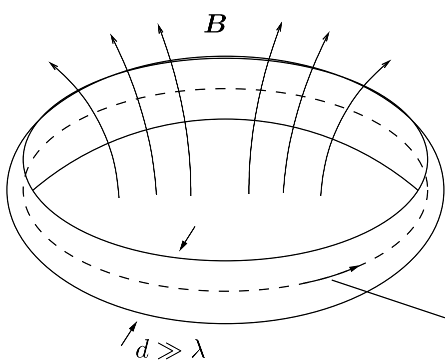


Figure 5: Flux through a superconducting ring.

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 $\Phi$ 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 $\theta$ of the wavefunction (7) around the contour, which must be an integer multiple of $2\pi$ 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* $\Phi_0$ 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 $\Phi$ 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 $\Psi$ 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 $\phi$ 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 $\chi$ 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 $\lambda_L$, 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

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

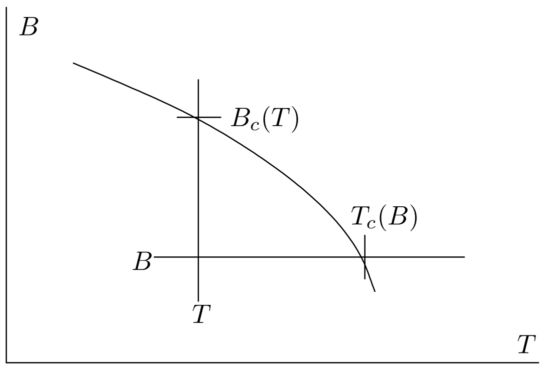


Figure 6: The critical temperature as a function of the applied magnetic field and the thermodynamic critical field as a function of temperature.

### 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 $\boldsymbol{B} = 0$.

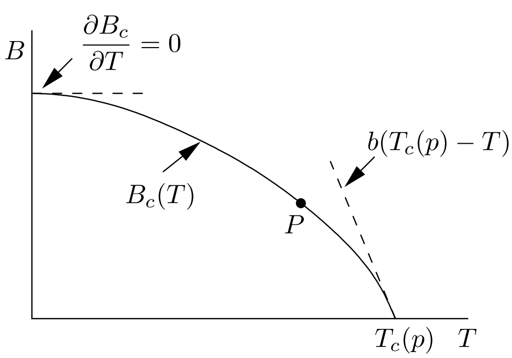


FIG. 7: The thermodynamic critical field.

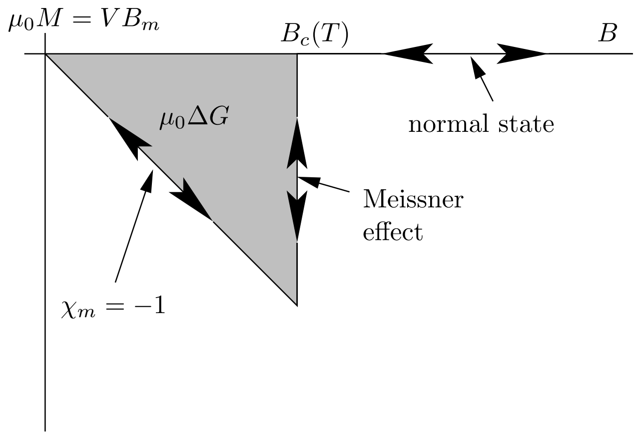


FIG. 8: The magnetization curve of a superconductor.

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

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

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

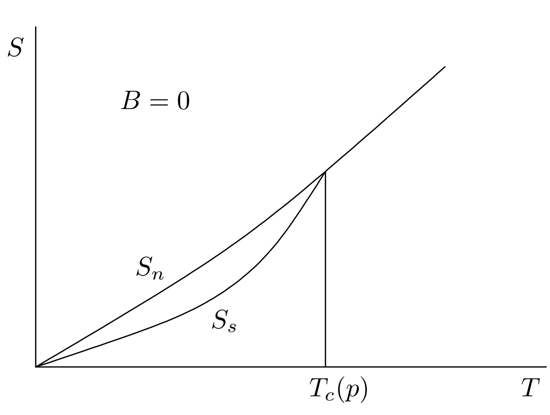


FIG. 9: The entropy of a superconductor.

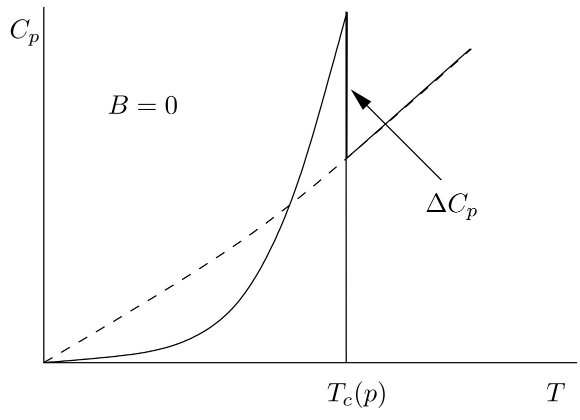


FIG. 10: The heat capacity of a superconductor.

# 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 $\phi$ has a certain value which breaks the global gauge symmetry by fixing the time-derivative of the phase $\theta$ of $\Psi$ (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:

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

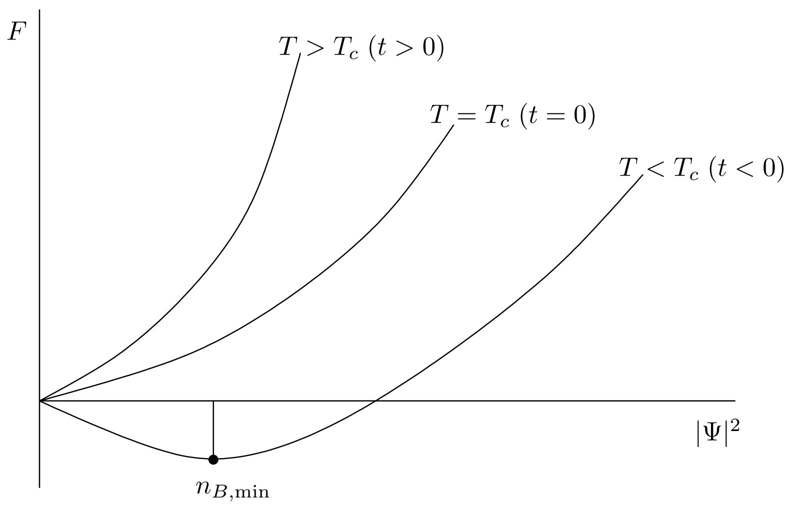


Figure 11: The Free Energy function.

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 $\Delta C_p$ 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 $\Psi$ 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 $\Psi$, 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 $\Psi$:

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

The Free Energy is obtained by minimizing (56a) with respect to $\Psi(\boldsymbol{r})$ and $\Psi^*(\boldsymbol{r})$. To prepare for a variation of $\Psi^*$, 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

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

$\mathcal{F}$ 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 $\Psi$ 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 $\Psi^*$, $\Psi$ 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

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

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 $(\partial/\partial\boldsymbol{r})\times\boldsymbol{B}_m = (\partial/\partial\boldsymbol{r})\times\boldsymbol{B}_{\rm tot}$, 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 $\Psi$ 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 $\Psi^*$ 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.

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

## 4.3 The Ginsburg-Landau parameter

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

$$\frac{\partial^2 B_{\rm tot}}{\partial\boldsymbol{r}^2}=\frac{B_{\rm tot}}{\lambda^2},\quad \lambda^2=\frac{m}{2\mu_0e^2|\Psi|^2}=\frac{m\beta}{2\mu_0e^2\alpha|t|}, \tag{63}$$

where (51) was taken into account in the last expression. $\lambda$ 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 $\Psi$, $|\Psi|^2\ll\alpha|t|/\beta$, 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 $T_c$. $\xi$ is the *Ginsburg-Landau coherence length* of such order parameter fluctuations. It has the same temperature dependence as $\lambda$, and their ratio,

$$\kappa=\frac{\lambda}{\xi}=\sqrt{\frac{2m^2\beta}{\hbar^2\mu_0e^2}}, \tag{65}$$

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

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

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 $\kappa$.

## 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.

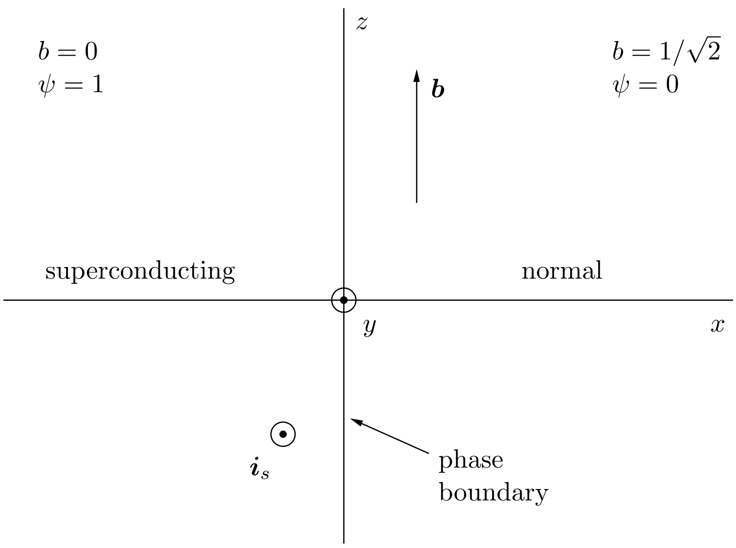


Figure 12: Geometry of a plane phase boundary.

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 $\psi$ depends on $y$. We consider $y = 0$ and may then choose $\psi$ 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 $\psi_0$ denotes the value of $\psi(x)$ where the field drops:

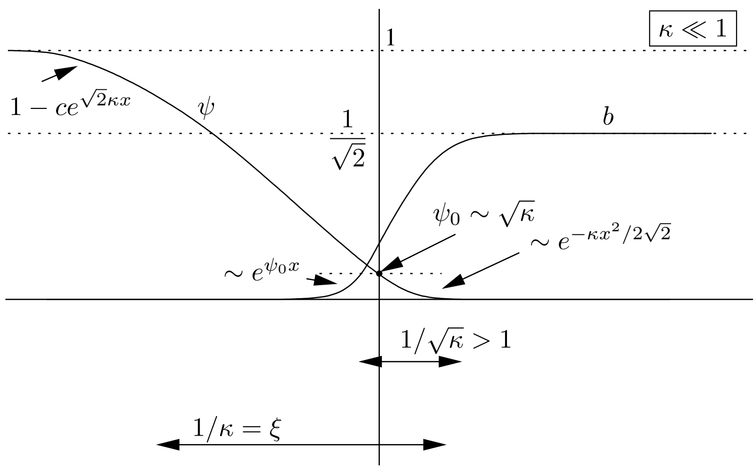


Figure 13: The phase boundary of a type I superconductor.

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

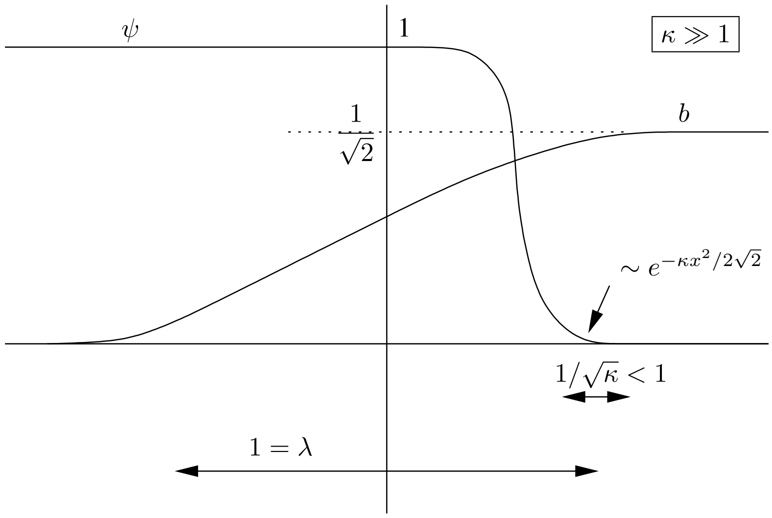


Figure 14: The phase boundary of a type II superconductor.

## 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 $\lambda$)

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

First an integration per parts of ${\psi'}^2$ 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 $\psi^2$ increases and $\psi = 0$ at $b = 1/\sqrt{2}$, $(b - 1/\sqrt{2}) = (a' - 1/\sqrt{2})$ and $\psi^2$ 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):

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

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

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

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).

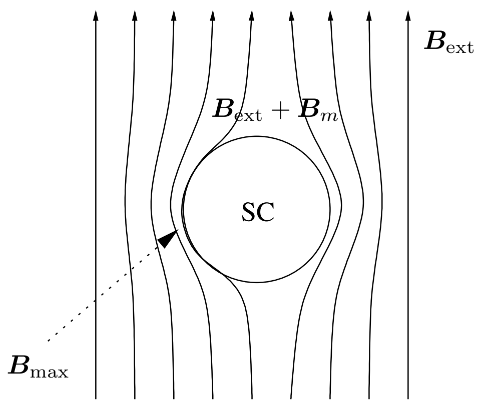


FIG. 15: Total (external plus induced) magnetic field around a type I superconductor.

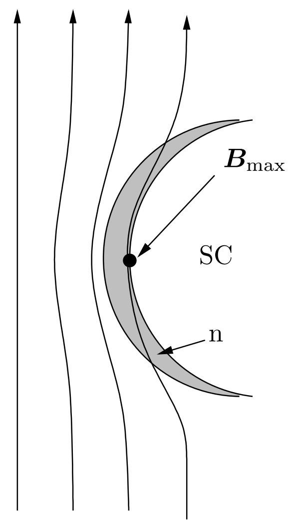


FIG. 16.

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).

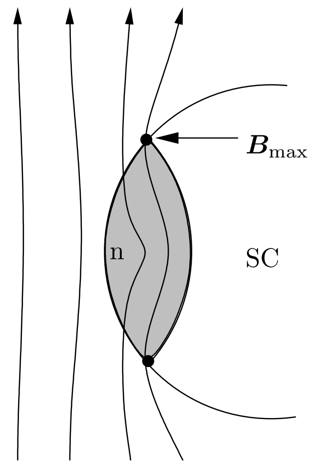


FIG. 17.

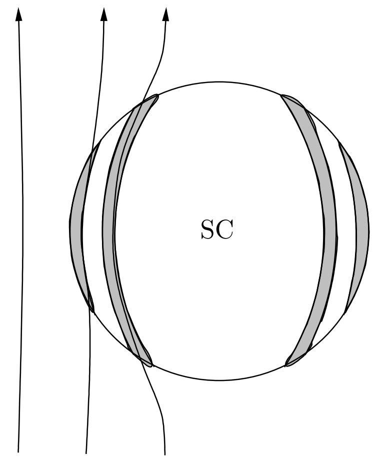


FIG. 18.

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 $B_c$.

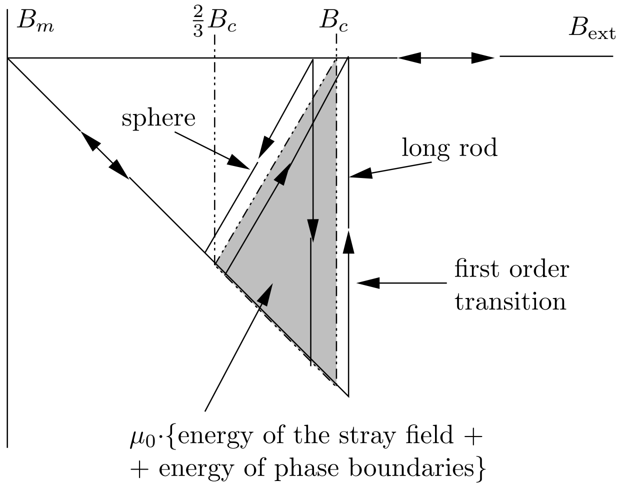


Figure 19:

# Superconductivity: Microscopics

For repulsive interactions the properties of an interacting Fermi system are not qualitatively different from the noninteracting system: the quantitative values of parameters are modified as described by Fermi liquid theory. Attractive interactions however, no matter how weak, lead to an entirely new state of superconductivity. It took almost 50 years from the discovery by Kammerlingh-Onnes in 1911 to the BCS theory by Bardeen, Cooper and Schrieffer in 1956 for this remarkable new state of matter to be understood.

## The Cooper Problem

A simple indication of the strange consequences of attractive interactions added to the Fermi gas was demonstrated by Cooper [Phys. Rev. **104**, 1189 (1956) ].

First consider the familiar problem of pair binding by free particles with an attractive pair interaction $u(r)$, but in a momentum representation. Schrodinger's equation for the problem is

$$\left[\frac{-\hbar^2}{2\mu}\nabla^2 + u(r)\right]\phi(\mathbf{r}) = E\phi(\mathbf{r}) \tag{1}$$

with $\mu = m/2$ the reduced mass and $\phi(\mathbf{r})$ the wave function of the relative coordinate $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$. Introduce the Fourier representation

$$\phi(\mathbf{r}) = \sum_{\mathbf{k}'} \phi_{\mathbf{k}'} e^{i\mathbf{k}'\cdot\mathbf{r}} = \sum_{\mathbf{k}'} \phi_{\mathbf{k}'} e^{i\mathbf{k}'\cdot(\mathbf{r}_1-\mathbf{r}_2)}, \tag{2}$$

substitute, multiply through by $e^{-i\mathbf{k}\cdot\mathbf{r}}$ and integrate over the volume $V$ gives

$$(2\varepsilon_k - E)\phi_{\mathbf{k}} + \frac{1}{V}\sum_{\mathbf{k}'} \tilde{u}(\mathbf{k},\mathbf{k}')\phi_{\mathbf{k}'} = 0, \tag{3}$$

with $\varepsilon_k = \hbar^2 k^2/2m$ and

$$\tilde{u}(\mathbf{k},\mathbf{k}') = \tilde{u}(\mathbf{k}-\mathbf{k}') = \int u(\mathbf{r}) e^{-i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}}. \tag{4}$$

Cooper considered the following problem. Imagine two particles interacting with each other above a sea of states $k < k_F$ that are excluded from participation. The sea of states is meant to represent the Fermi sea, and the two particles cannot scatter into these states by the exclusion principle. In this case the wave function must be constructed of states with $k > k_F$

$$\phi(\mathbf{r}) = \sum_{\substack{\mathbf{k}' \\ k'>k_F}} \phi_{\mathbf{k}'} e^{i\mathbf{k}'\cdot\mathbf{r}}, \tag{5}$$

and the sum in Eq. (3) is also restricted to $k' > k_F$. To make the calculation tractable, Cooper assumed a simple attractive *separable, band limited* potential

$$\tilde{u}(\mathbf{k},\mathbf{k}') = \begin{cases} -g & k_F < k, k' < k_F + k_c \\ 0 & \text{otherwise} \end{cases}, \tag{6}$$

with $g$ the coupling constant. Equation (3) now becomes

$$(2\varepsilon_k - E)\phi_{\mathbf{k}} - g\frac{1}{V}\sum_{\text{band}} \phi_{\mathbf{k}'} = 0. \tag{7}$$

We are interested in the question of whether a bound state forms with total energy $E < 2\varepsilon_F$, and so it is convenient to measure energies with respect to the Fermi energy

$$\xi_k = \varepsilon_k - \varepsilon_F \tag{8}$$

and define the binding energy $E_B$ by $E = 2\varepsilon_F - E_B$ (then $E_B$ is positive for a bound state). This gives

$$(2\xi_k + E_B)\phi_{\mathbf{k}} - g\frac{1}{V}\sum_{\text{band}}\phi_{\mathbf{k}'} = 0. \tag{9}$$

Clearly the solution is

$$\phi_{\mathbf{k}} = \frac{A}{(2\xi_k + E_B)} \tag{10}$$

and substituting back gives the eigenvalue equation

$$1 = g\frac{1}{V}\sum_{\text{band}}\frac{1}{(2\xi_k + E_B)}. \tag{11}$$

Replacing the sum over wave vectors by an integral over energy states gives

$$1 = gN(0)\int_0^{\hbar\omega_c}\frac{1}{(2\xi + E_B)}d\xi \tag{12}$$

with $\omega_c = v_F k_c$ the cutoff frequency and $N(0)$ the density of states of one spin system at the Fermi surface [1]. The integral is a log, giving

$$E_B = \frac{2\omega_c}{e^{2/N(0)g} - 1} \simeq 2\omega_c e^{-2/N(0)g} \tag{13}$$

where I have assumed the *weak coupling limit* $N(0)g \ll 1$ (roughly, interaction potential much less than the Fermi energy).

The expression (13) for the binding energy provides interesting insights. There is *always* a bound state, no matter how weak the attractive interaction. The binding energy dependence on the coupling constant $g$ is nonanalytic—an essential singularity as $g \to 0$. These results are analogous to pair binding of free particles in two spatial dimension, and indeed the particles effectively "skate" on the two dimensional Fermi surface. Finally the wave function

$$\phi(\mathbf{r}) \propto \sum_{\text{band}}\frac{1}{(2\xi_k + E_B)}e^{i\mathbf{k}\cdot\mathbf{r}} \tag{14}$$

is the superposition of plane waves with $\mathbf{k}$ in a band of wave numbers of width $E_B/\hbar v_F$ near $k_F$. So the wave function will oscillate with a wavelength of order $k_F^{-1}$ and will decay on a much longer length of order $\hbar v_F/E_B$. If we suppose $E_B$ sets the energy scale of the superconducting state, and so can be estimated as $k_B T_c$ with $T_c$ the transition temperature to the superconducting state, the pair radius is of order $(\varepsilon_F/k_B T_c)k_F^{-1}$, much larger than the interparticle spacing $k_F^{-1}$ since $k_B T_C \ll \varepsilon_F$.

The wave function $\phi(\mathbf{r}_1 - \mathbf{r}_2)$ is symmetric under the exchange of particles, and so the spin state of the pair has to be the antisymmetric singlet $1/\sqrt{2}(\uparrow\downarrow - \downarrow\uparrow)$.

Many of the features of the solution to the Cooper problem survive in the full treatment. However the calculation is inconsistent, since the two particles are excluded from the Fermi sea because they are indistinguishable from the particles there, but we have supposed a different interaction term (none) with these. Adding this interaction means that the pair under focus will excite other particle-hole pairs, so we must consider the many body problem of many interacting particles and holes with $k$ near $k_F$. This is the problem BCS solved. But first it is interesting to ask: Where does the attractive interaction come from?

[1] A notation confusion: in the original solution set to homework 2 the TA used $N(0)$ as the *total* density of states at the Fermi surface—two times my $N(0)$. I have changed this in a revised version, but if you have the original version you should be aware of this when you make a comparison.

## Attractive Interaction

See Ashcroft and Mermin §26.

## BCS Theory

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The BCS approach can be motivated in terms of a Bose condensed pair wave function variational ansatz

$$\Psi \propto \mathcal{A}\left[\phi(\mathbf{r}_1 - \mathbf{r}_2; \sigma_1\sigma_2)\phi(\mathbf{r}_3 - \mathbf{r}_4; \sigma_3\sigma_4)\ldots\phi(\mathbf{r}_{N-1} - \mathbf{r}_N; \sigma_{N-1}\sigma_N)\right] \tag{15}$$

with $\mathcal{A}$ the antisymmetrization operator. For conventional superconductors the *pair wave function* $\phi$ is an s-wave, spin singlet state, and I will focus on this case. In superfluid $He^3$ $\phi$ is a p-wave, spin triplet state, and in high-T$_c$ superconductors a d-wave, spin singlet state.

The Fourier representation for the s-wave singlet state is

$$\phi(\mathbf{r}_1 - \mathbf{r}_2; \sigma_1\sigma_2) = \sum_{\mathbf{k}} e^{i\mathbf{k}\cdot(\mathbf{r}_1-\mathbf{r}_2)}\chi(k)\frac{1}{\sqrt{2}}(\uparrow_1\downarrow_2 - \downarrow_1\uparrow_2) \tag{16}$$

which we can write as the state

$$|\phi\rangle = \sum_{\mathbf{k}} \frac{1}{\sqrt{2}}\chi(k)\left[(\mathbf{k}\uparrow)_1(-\mathbf{k}\downarrow)_2 - (-\mathbf{k}\downarrow)_1(\mathbf{k}\uparrow)_2)\right] \tag{17}$$

(using $\mathbf{k} \to -\mathbf{k}$ in the second term). This shows that in the wave function $\Psi$ the states $(\mathbf{k}\uparrow, -\mathbf{k}\downarrow)$ are always occupied together or are empty together.

Keeping track of the amplitudes of the different combinations of the $(\mathbf{k}\uparrow, -\mathbf{k}\downarrow)$ states in $\Psi$ is very complicated. BCS theory is equivalent to the assumption of a product state in Fourier representation

$$\Psi_{BCS} = \prod_{\mathbf{k}} \phi_{\mathbf{k}}, \tag{18}$$

with

$$\phi_{\mathbf{k}} = u_k\,|0,0\rangle + v_k\,|1,1\rangle\,, \tag{19}$$

for occupation of the $\mathbf{k}\uparrow$ and $-\mathbf{k}\downarrow$ states. Here $u_k, v_k$ are functions to be found (with $|u_k|^2 + |v_k|^2 = 1$ by normalization). The assumption of s-wave pairing means they are functions of $|\mathbf{k}|$ only. To actually do the manipulations it is often useful to go to second quantized representation. In this notation $\Psi_{BCS}$ is

$$\Psi_{BCS} = \prod_{\mathbf{k}}(u_k + v_k a^+_{\mathbf{k}\uparrow}a^+_{-\mathbf{k}\downarrow})\,|0\rangle\,, \tag{20}$$

with $|0\rangle$ the no-particle or vacuum state.

To find $u_k, v_k$ minimize $E - \mu N$ for this trial wave function. The kinetic energy relative to $N\mu$ is

$$\langle E_{\text{kin}} - \mu N\rangle = \sum_{\mathbf{k}} 2\xi_k\,|v_k|^2\,, \tag{21}$$

since there is probability $|v_k|^2$ of both $\mathbf{k}\uparrow$ and $-\mathbf{k}\downarrow$ to be occupied. The potential energy comes from sums of terms with matrix elements for the potential component $\tilde{u}(\mathbf{k},\mathbf{k}')$ scattering a pair from occupied states $(\mathbf{k}\uparrow, -\mathbf{k}\downarrow)$ to empty states $(\mathbf{k}'\uparrow, -\mathbf{k}'\downarrow)$. The initial state has amplitude $v_k u_{k'}$ and the final state has amplitude $u_k v_{k'}$ so that the potential given by the sum of such terms is

$$\left\langle E_{\text{pot}}\right\rangle = \frac{1}{V}\sum_{\mathbf{k},\mathbf{k}'}\tilde{u}(\mathbf{k},\mathbf{k}')u^*_k v^*_{k'} u_{k'} v_k. \tag{22}$$

This is the right answer, but to make sure the numerical factors are right it is more reliable to take the expectation value of the second quantized version

$$U = \frac{1}{2V}\sum_{\mathbf{k},\mathbf{k}'} \tilde{u}(\mathbf{q}) a^{+}_{\mathbf{k}+\mathbf{q},\sigma} a_{\mathbf{k}'-\mathbf{q},\sigma'} a_{\mathbf{k}',\sigma'} a_{\mathbf{k},\sigma} \tag{23}$$

in the state (20).

Thus

$$\langle E - \mu N\rangle = \sum_{\mathbf{k}} 2\xi_k |v_k|^2 + \frac{1}{V}\sum_{\mathbf{k},\mathbf{k}'} \tilde{u}(\mathbf{k},\mathbf{k}') u_k^* v_{k'}^* u_{k'} v_k. \tag{24}$$

This equation couples the phases of the $u_k, v_k$ at different $\mathbf{k}$. For s-wave paring there is an overall phase factor (which wold be the phase of the order parameter) which can be set to zero in calculating the energetics. Thus we may assume $u_k, v_k$ are real. For p- and d- wave pairing we would be dealing with functions $u_{\mathbf{k}}$ and $v_{\mathbf{k}}$ also depending on the direction of $\mathbf{k}$, and there would be nontrivial phases depending on this direction corresponding to the phase of the $l = 1, 2$ pair wave functions. From the normalization condition we can write for the s-wave case

$$u_k = \sin\theta_k, \qquad v_k = \cos\theta_k \tag{25}$$

giving

$$\langle E - \mu N\rangle = \sum_{\mathbf{k}} 2\xi_k (1 + \cos 2\theta_k) + \frac{1}{V}\sum_{\mathbf{k},\mathbf{k}'} \tilde{u}(\mathbf{k},\mathbf{k}')\frac{1}{4}\sin 2\theta_k \sin 2\theta_{k'} \tag{26}$$

with $\theta_k$ given by minimizing this energy. Minimizing gives

$$\tan 2\theta_k = \frac{1}{2\xi_k}\frac{1}{V}\sum_{\mathbf{k}'} \tilde{u}(\mathbf{k},\mathbf{k}') \sin 2\theta_{k'}. \tag{27}$$

Define the *gap function*

$$\Delta_k = -\frac{1}{2V}\sum_{\mathbf{k}'} \tilde{u}(\mathbf{k},\mathbf{k}') \sin 2\theta_{k'}, \tag{28}$$

and the function that will turn out to be the excitation energy

$$E_k = \sqrt{\xi_k^2 + \Delta_k^2}. \tag{29}$$

Then

$$\tan 2\theta_k = -\frac{\Delta_k}{\xi_k}, \qquad \sin 2\theta_k = \frac{\Delta_k}{E_k}, \tag{30}$$

and

$$u_k v_k = \frac{\Delta_k}{2E_k},\ v_k^2 = \frac{1}{2}(1 - \frac{\xi_k}{E_k}),\ u_k^2 = \frac{1}{2}(1 + \frac{\xi_k}{E_k}) \tag{31}$$

(Note that $v_k^2 \to 1$ for $k \ll k_F, \xi_k/E_k \to -1$, and $v_k^2 \to 0$ for $k \gg k_F, \xi_k/E_k \to 1$ as required: thus the sign chosen for $E_k$ is correct.)

Equation (28) becomes

$$\Delta_k = -\frac{1}{V}\sum_{\mathbf{k}'} \tilde{u}(\mathbf{k},\mathbf{k}')\frac{\Delta_{k'}}{2E_{k'}}, \tag{32}$$

which is a self consistency condition for the gap parameter $\Delta_k$.

Equation (32) defines the gap parameter $\Delta_k$ for given interaction potential. Again to make analytic progress it is useful to consider the simple model of the separable potential, now changed to be symmetric about $k_F$

$$\tilde{u}(\mathbf{k}, \mathbf{k}') = \begin{cases} -g & k_F - k_c < k, k' < k_F + k_c \\ 0 & \text{otherwise} \end{cases} . \tag{33}$$

This gives

$$\Delta_k = \begin{cases} \Delta_0 & k_F - k_c < k, k' < k_F + k_c \\ 0 & \text{otherwise} \end{cases} . \tag{34}$$

Transforming to an integration over energy for the spherically symmetric s-wave case the single parameter $\Delta_0$ is given by

$$1 = N(0)g \int_0^{\omega_c} \frac{1}{\sqrt{\xi^2 + \Delta_0^2}} \tag{35}$$

$$= N(0)g \sinh^{-1}(\hbar\omega_c/\Delta), \tag{36}$$

or

$$\Delta = \frac{\hbar\omega_c}{\sinh^{-1}(\hbar\omega_c/\Delta)} \simeq 2\hbar\omega_c e^{-1/N(0)g}, \tag{37}$$

using weak coupling in the last approximation. It is straightforward to check that $E - \mu N$ is lowered for this value of $\Delta$ relative to the normal state $\Delta = 0$.

To compare the results of this calculation with the Cooper problem it is useful to look at the average occupation number $\langle n_k \rangle = v_k^2$. The step function at $k = k_F$ in $v_k$ for the noninteracting problem is spread into a smooth variation over a width in $k \sim \Delta/\hbar v_F$ (a width in energy of about $\Delta$). This corresponds to the self consistent excitation of pairs out of the Fermi sea to gain the Cooper-type pairing energy.

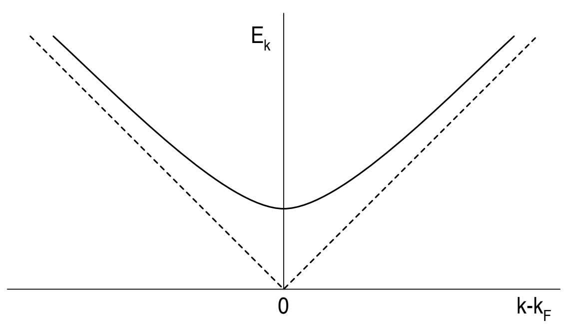


Figure 1: Excitation energy $E_k$ for a BCS superconductor (solid line) and normal state (dashed line). The energy is defined as the cost to add a particle to a state $\mathbf{k}$ with $k > k_F$ relative to the chemcial potential or to remove a particle from $\mathbf{k}$ with $k < k_F$ relative to $-\mu$. Thus the normal state spectrum is $v_F\,|k - k_F|$.

To see the significance of $\Delta$ and $E_k$ we look at the excited states of the system. For the states $\mathbf{k}\uparrow, -\mathbf{k}\downarrow$ in the product wave function the four eigenstates and energies measured with resect to the pair state are

| | State | Energy |
|---|---|---|
| pair | $u_k\,\lvert 0,0\rangle + v_k\,\lvert 1,1\rangle$ | 0 |
| broken pair | $\lvert 1,0\rangle$ | $E_k$ |
| broken pair | $\lvert 0,1\rangle$ | $E_k$ |
| excited state | $v_k\,\lvert 0,0\rangle - u_k\,\lvert 1,1\rangle$ | $2E_k$ |

(38)

Consider the broken pair state $|1,0\rangle$ which is the state with $\mathbf{k}\uparrow$ occupied and $-\mathbf{k}\downarrow$ empty. The contribution to kinetic energy $E_{\text{kin}} - N\mu$ is $\xi_k$ whereas in the pair state it is, from Eq. (21), $\xi_k(1-\xi_k/E_k)$. In the pairing energy Eq. (22) the state $\mathbf{k}$ is removed from the both wave vector sums, and so the pairing energy is reduced by

$$\frac{2}{V}\sum_{\mathbf{k}'}\tilde{u}(\mathbf{k},\mathbf{k}')u_k v_{k'} u_{k'} v_k = \frac{\Delta_k}{E_k}\sum_{\mathbf{k}'}\tilde{u}(\mathbf{k},\mathbf{k}')\frac{\Delta_{k'}}{2E_{k'}} = -\frac{\Delta_k^2}{E_k}, \tag{39}$$

and so the excitation energy is

$$\xi_k - \xi_k\left(1-\frac{\xi_k}{E_k}\right) + \frac{\Delta_k^2}{E_k} = E_k. \tag{40}$$

For the excited pair state the change in the kinetic energy is

$$\xi_k\left(1+\frac{\xi_k}{E_k}\right) - \xi_k\left(1-\frac{\xi_k}{E_k}\right). \tag{41}$$

In the pairing energy calculation of the amplitude for scattering involving the pair state $\mathbf{k}\uparrow, -\mathbf{k}\downarrow$, the product of amplitudes that the state is occupied before scattering and empty after scattering is $-v_k u_k$ instead of $u_k v_k$. Thus the contribution to the pairing energy is the negative of what it was for the ground state pair. This gives the excitation energy

$$\xi_k\left(1+\frac{\xi_k}{E_k}\right) - \xi_k\left(1-\frac{\xi_k}{E_k}\right) + \frac{2\Delta_k^2}{E_k} = 2E_k. \tag{42}$$

Thus $E_k$ plays the role of the excitation energy: to add a particle in the excited state costs an energy $E_k = \sqrt{\xi_k^2 + \Delta_k^2}$. with $\Delta_k = \Delta$ for $|k - k_F| < k_c$. The minimum energy is for $k = k_F$, $\xi_k = 0$, showing that $\Delta$ is the *energy gap* for excitations. The minimum energy cost to break a pair to form two broken pair states, or to form the excited pair state is $2\Delta$, and thermodynamic quantities at low temperatures will vary as $\exp(-2\Delta/k_B T_c)$.

In Homework 2 you transformed the Hamiltonian using a canonical transformation to new independent Fermi operators $\alpha_k$, $\beta_k$

$$a_{\mathbf{k}\uparrow} = u_k\alpha_{\mathbf{k}} + v_k\beta_{-\mathbf{k}}^+, \tag{43}$$

$$a_{-\mathbf{k}\downarrow} = u_k\beta_{-\mathbf{k}} - v_k\alpha_{\mathbf{k}}^+. \tag{44}$$

to the form

$$H = \text{const.} + \sum_{\mathbf{k}} E_k(\alpha_{\mathbf{k}}^+\alpha_{\mathbf{k}} + \beta_{-\mathbf{k}}^+\beta_{-\mathbf{k}}). \tag{45}$$

For the pair ground state $|\phi_{\mathbf{k}}\rangle = (u_k + v_k a_{\mathbf{k}\uparrow}^+ a_{-\mathbf{k}\downarrow}^+)\,|0\rangle$ you can show that the broken pair states corresponds to $\alpha_{\mathbf{k}}^+\,|\phi_{\mathbf{k}}\rangle$ and $\beta_{-\mathbf{k}}^+\,|\phi_{\mathbf{k}}\rangle$ with energy $E_k$ and the excited pair state to $\alpha_{\mathbf{k}}^+\beta_{-\mathbf{k}}^+\,|\phi_{\mathbf{k}}\rangle$ with energy $2E_k$, showing that the results of the two calculations agree. As you will probably agree, the canonical transformation arguments are less complicated.

## Thermodynamics

To calculate the finite temperature properties we could continue to enumerate the states by hand, but it is simpler to switch to the approach of Homework 2. There you found the gap equation

$$\Delta_k = \frac{1}{V}\sum_{\vec{k}'}\tilde{u}(\mathbf{k},\mathbf{k}')\left\langle a_{\mathbf{k}'\uparrow}a_{-\mathbf{k}'\downarrow}\right\rangle \tag{46}$$

and the quantum and thermal average $\langle a_{\mathbf{k}'\uparrow} a_{-\mathbf{k}'\downarrow} \rangle$ is easy to calculate from the inverse of the canonical transformation

$$a_{\vec{k}\uparrow} = u_k \alpha_{\vec{k}} + v_k \beta^+_{-\vec{k}} \tag{47}$$

$$a_{-\vec{k}\downarrow} = u_k \beta_{-\vec{k}} - v_k \alpha^+_{\vec{k}} \tag{48}$$

and the thermal averages of the noninteracting Fermions $\alpha_k$, $\beta_k$

$$\left\langle \alpha^+_{\vec{k}} \alpha_{\vec{k}'} \right\rangle = \left\langle \beta^+_{\vec{k}} \beta_{\vec{k}'} \right\rangle = f(E_k) \delta_{\vec{k}\vec{k}'} \tag{49}$$

whereas

$$0 = \left\langle \alpha^+_{\vec{k}} \beta_{\vec{k}'} \right\rangle = \left\langle \alpha^+_{\vec{k}} \beta^+_{\vec{k}'} \right\rangle = \ldots \text{etc} \tag{50}$$

with $f(E_k)$ the usual Fermi function

$$f(E_k) = \frac{1}{e^{E_k/k_B T} + 1}. \tag{51}$$

The equation for the gap parameter $\Delta_k(T)$ becomes

$$\Delta_k(T) = -\frac{1}{V} \sum_{\vec{k}'} \tilde{u}(\mathbf{k}, \mathbf{k}) \frac{\Delta_{k'}(T)}{2E_{k'}} \tanh\left(\frac{E_{k'}}{2k_B T}\right), \tag{52}$$

with now $E_k = \sqrt{\xi_k^2 + \Delta_k^2(T)}$. For the same separable potential the equation for the gap $\Delta(T)$ at nonzero temperature is

$$1 = N(0) g \int_0^{\hbar\omega_c} \frac{1}{E} \tanh\left(\frac{E}{2k_B T}\right) d\xi, \tag{53}$$

with $E = \sqrt{\xi^2 + \Delta^2(T)}$. At the transition temperature $T_c$ the superconducting gap goes to zero $\Delta \to 0$, and so $T_c$ is given by

$$1 = N(0) g \int_0^{\hbar\omega_c} \frac{1}{\xi} \tanh\left(\frac{\xi}{2k_B T_c}\right) d\xi. \tag{54}$$

In the weak coupling limit this gives

$$k_B T_c \simeq 1.14 \hbar\omega_c e^{-1/N(0)g}. \tag{55}$$

Note that the zero temperature gap is related to $T_c$ by

$$\frac{2\Delta_0}{k_B T_c} \simeq 3.52, \tag{56}$$

a universal result, independent of any other parameters.

The integrals in Eqs. (53) and (54) depend logarithmically on $\omega_c$ the cutoff frequency introduced in the interaction. However for the range $\xi \gg \Delta$ of the integrals contributing to this logarithmic dependence (assuming weak coupling) the integrands in Eqs. (53) and (54) are almost equal. Thus if we subtract, the contribution from large $\xi$ vanishes, and we can replace the upper limit by $\infty$, to give

$$\int_0^\infty \left[ \frac{1}{\sqrt{\xi^2 + \Delta^2(T)}} \tanh\left(\frac{\sqrt{\xi^2 + \Delta^2(T)}}{2k_B T}\right) - \frac{1}{\xi} \tanh\left(\frac{\xi}{2k_B T_c}\right) \right] d\xi = 0. \tag{57}$$

This gives a *universal* equation for $\Delta(T)/k_B T_c$ as a function of $T/T_c$. With some more effort it can be argued that this result does not in fact depend on the simple form assumed for the potential, but just on the weak coupling limit $k_B T_c \ll \hbar\omega_c$, true for any small enough attractive interaction. In this limit a universal prediction is obtained for the thermodynamics as a function of $T/T_c$ independent of details of the potential etc.