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Thermal Fluctuations of the superconducting order parameter in the Ginzburg-Landau theory

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Introduction

Superconductivity is maybe amongst the most important physical phenomena of the last century. Not only it has been studied in every aspect (theoretical and experimental), but since its discovery in 1911 we are still finding new aspects and new effects, leading to new results and practical applications.
In this thesis I will briefly explain the first attempt to describe theoretically superconductivity and its main consequences, the *Ginzburg-Landau theory*, proposed as a phenomenological theory by Vitalij Ginzburg and Lev Landau in 1950 as a generalization of *London theory*. The interesting thing of this theory is that it ignores the microscopical point of view, trying to describe superconductivity and its effects by using tools and considerations coming from thermodynamics, avoiding (where possible) the language of quantum mechanics.
The strength of this theory has been confirmed in 1959 by Lev Gor'kov, who showed that it was possible to derive the *Ginzburg-Landau theory* from the *BCS theory*, a microscopic theory of superconductivity proposed in 1957 by Bardeen, Cooper and Schrieffer, also giving microscopic interpretation of all its parameters.

In this thesis I will firstly describe the phenomenological aspects of superconductivity: from the first experiment performed by H. Kamerlingh Onnes in 1911 to the first attempt to give a phenomenological theory of the various phenomena made by Fritz and Heinz London. Secondly I will introduce the formalism of *Ginzburg-Landau theory*, showing the physical starting point and the basic calculations, including nonuniform systems. Finally I will consider the thermal fluctuations near the critical temperature of a superconductor, leading to some theoretical results concerning some thermodynamic quantities and the appropriate definition of the critical temperature.

Chapter 1

Phenomenological aspects of superconductivity

1.1 Drude theory of conduction in metal

DURING our studies we first find a microscopic point of view when we try to describe the conduction in metals. As a matter of fact we consider the flow of electrons in a metal, and this leads to Drude theory of conducting metals. We remember that in this theory we can relate the conductivity of a metal with other microscopical quantities using the relation

$$\sigma = \frac{ne^2\tau}{m} \tag{1.1.0.1}$$

where σ is the conductivity, e is the electron charge and τ is the average lifetime for free motion of the electrons between collisions. The Eq. (1.1.0.1) relates the conductivity with the temperature of the metal, via the different scattering processes that occur during the lifetime τ. After having defined the resistivity ρ of a metal such that

$$\rho = \frac{1}{\sigma} = \frac{m}{ne^2}\tau^{-1} \tag{1.1.0.2}$$

we can consider that the average scattering rate τ^{-1} is related to the different process that relates the electron with the rest of the metal: scattering by impurities, by electron-electron interaction and by electron-phonon collision, all processes which are independent so that we can easily write

$$\tau^{-1} = \tau_{imp}^{-1} + \tau_{el-el}^{-1} + \tau_{el-ph}^{-1} \tag{1.1.0.3}$$

In this way the total resistivity could be define as the sum of all this processes

$$\rho = \frac{m}{ne^2}\left(\tau_{imp}^{-1} + \tau_{el-el}^{-1} + \tau_{el-ph}^{-1}\right) \tag{1.1.0.4}$$

Each of this rate is a charateristic function of temperature:

- $\tau^{-1}_{\mathbf{imp}}$: independent of temperature, it is just considering the impurities in the metal;
- $\tau^{-1}_{\mathbf{el-el}}$: proportional to T^2;
- $\tau^{-1}_{\mathbf{el-ph}}$: proportional to T^5 if the temperature is under the *Debye temperature*.

Therefore at low temperatures we expect a relation between resistivity and temperature of this form

$$\rho = \rho_0 + aT^2 + \dots \tag{1.1.0.5}$$

where ρ_0 is the resistivity depending only on the concentration of impurities.

1.2 The discovery of superconductivity

After having liquified Helium, H. Kamerlingh Onnes wanted to test the validity of Drude theory al low temperatures, turning his attention to mercury because of its low concentration of impurities; it was 1911 [1][2]. What he discovered was unbelievable: instead of measuring low levels of resistivity (something that we could expect considering the low concentration of impurities) he observed that all signs of resistivity vanished rapidly at a *critical temperature* T_c of about 4.1 K, as shown in Fig. (1.1). This set forth the discovery of a new state of matter, which was not predicted by Drude theory: superconductivity.

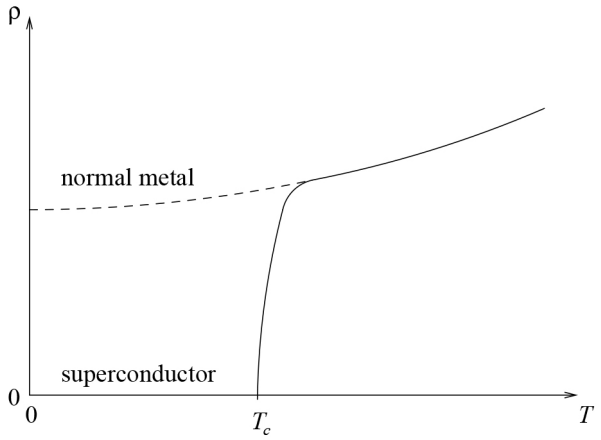


Figure 1.1: Rapid decreasing of resistivity at T_c (adapted from [2]).

If we are interested in measuring the resistivity of a superconducting material we can measure the (no)decay of persistant currents: first we set up a current (for example by induction) in a superconducting ring and assuming an exponential decay such that $i(t) = i_0 e^{-\frac{t}{\tau}}$ we can find a lower bound on the decay time τ and therefore an upper bound for ρ, which is

$$\rho \leq 10^{-25}\ \Omega \tag{1.2.0.1}$$

which compared to the resistivity of copper $\rho_{Cu} \approx 1.7 \cdot 10^{-8}\ \Omega$ gives the idea of the main effect of superconductivity.

We have come to the conclusion that if $T < T_c$ we reach a new state of matter, a superconductive state, whose main characteristic is that $\rho = 0$. If we consider the main relation which relates the current density j and the electric field E

$$j = \sigma \mathbf{E} \tag{1.2.0.2}$$

we thus find that in order to have finite values of j we must have

$$\mathbf{E} = 0 \tag{1.2.0.3}$$

at all points inside the superconductor, and so we have a current flow without electric field.

1.3 The Meissner-Ochsenfeld effect

The real definition of superconductivity is actually based on the demonstration of the so called Meissner-Ochsenfeld effect, a phenomenon that consists on the expulsion of a weak external magnetic field from the inside of a superconductor.
Let begin from a representation of the situation: in Fig. (1.2) we can see a sample of a superconductor, whose temperature T is greater than the critical temperature T_c and the external magnetic field $\mathbf{B}_{ext} = 0$; we then decrease the temperature to reach the condition $T < T_c$ and after that we switch on the field $\mathbf{B}_{ext}$.
If we consider the Maxwell equation

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \tag{1.3.0.1}$$

and we combine this with Eq. (1.2.0.3) we find that at all points inside the superconductor it must be

$$\frac{\partial \mathbf{B}}{\partial t} = 0 \tag{1.3.0.2}$$

which means that if we apply an external magnetic field to a superconductor, inside it there is no magnetic field, i.e. $\mathbf{B}_{int} = 0$.

But the real Meissner-Ochsenfeld effect is another one: always considering Fig. (1.2) if we now begin by switching on the magnetic field $\mathbf{B}_{ext} = 0$ and then we cool the sample to reach the superconductive state, we find out that the sample expels the magnetic field thus reaching the condition $\mathbf{B}_{int} = 0$. The main difference from the other situation is the fact that this phenomenon could not be explained considering the condition $\rho = 0$, and that leads to a new definition of the superconductive state.
We now give a brief demonstration of the Meissner-Ochsenfeld effect. First of all we can easily understand that the expulsion of the external magnetic field $\mathbf{B}_{ext}$ is related to the presence of screening currents flowing around the edges of the sample; the magnetic field $\mathbf{B}_{int}$ produced by these currents is equal and opposite to the external field, thus leaving

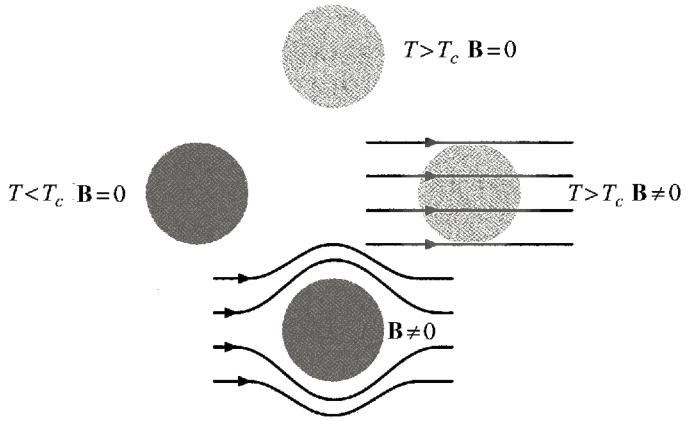


Figure 1.2: Comparison between the two situations: the one on the right is the Meissner-Ochsenfeld effect (adapted from [1]).

zero field inside the superconductor.

We will now consider Maxwell's equations in a magnetic medium: we can define the total current as the sum of the externally applied currents j_{ext} and the internal screening currents j_{int}

$$j = j_{ext} + j_{int} \tag{1.3.0.3}$$

In this way the internal currents generate a magnetization per unit volume $\mathbf{M}$ of the sample, defined by

$$\nabla \times \mathbf{M} = j_{int} \tag{1.3.0.4}$$

In a similar way we can define the magnetic field H generated by the external currents

$$\nabla \times \mathbf{H} = j_{ext} \tag{1.3.0.5}$$

which is linked with B and M by the relation

$$\mathbf{B} = \mu_0 \left(\mathbf{H} + \mathbf{M}\right) \tag{1.3.0.6}$$

where μ_0 is the permeability constant.
We then recall the other Maxwell's equation

$$\nabla \cdot \mathbf{B} = 0 \tag{1.3.0.7}$$

so that considering this equation we have that the component of $\mathbf{B}$ perpendicular to the surface of the sample must remain constant, while from equation (1.3.0.5) we have that the component of $\mathbf{H}$ parallel to the surface must remain constant, thus leading to the boundary conditions

$$\begin{aligned} \Delta \mathbf{B}_{\perp} &= 0 \\ \Delta \mathbf{H}_{\parallel} &= 0 \end{aligned} \tag{1.3.0.8}$$

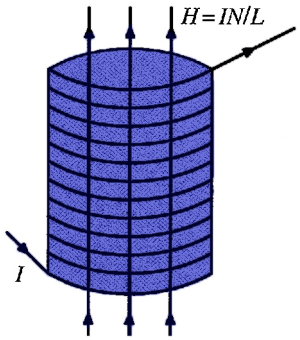


Figure 1.3: Cylindrical sample (adapted from [1]).

We can now consider a cylindrical sample, so that we can easily think about it as an infinitely long solenoid of length L with N coils, as shown in Fig. (1.3). In this case we have that the field $\mathbf{H}$ is uniform inside the sample,

$$\mathbf{H} = j\frac{N}{L}\hat{\mathbf{k}} \tag{1.3.0.9}$$

where j is the current flowing through the solenoid coil and $\hat{\mathbf{k}}$ is a unit vector along the solenoid axis.

In this way we can impose the Meissner condition $\mathbf{B} = 0$ in equation (1.3.0.6) which immediately gives

$$\mathbf{M} = -\mathbf{H} \tag{1.3.0.10}$$

and considering the fact that the magnetic susceptibility χ is defined by

$$\chi = \left.\frac{d\mathbf{M}}{d\mathbf{H}}\right|_{\mathbf{H}=0} \tag{1.3.0.11}$$

we find that for a superconductor

$$\chi = -1 \tag{1.3.0.12}$$

and so a superconductor is a perfect diamagnet.
In this way it is possible to measure χ and to establish if a sample (once we have reached the critical temperature T_c) is a superconductor.

1.4 Type I and type II superconductivity

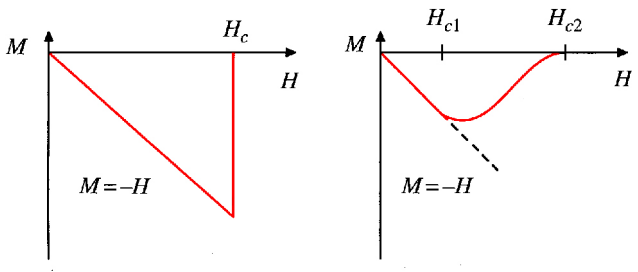


Figure 1.4: Magnetization $\mathbf{M}$ as a function of $\mathbf{H}$ in type I (left) and type II (right) superconductor (adapted from [2]).

What we have learned in the previous section works only in the limit of very weak external field. If the field becomes stronger there are two possible behaviours for the superconductor.
The first case is the type I superconductor: in this case the internal magnetic field $\mathbf{B}_{int}$ remains zero until the superconductive state is suddenly destroyed. This does not happen when we exceed the critical temperature T_c, but when we reach a precise value for the field, named critical field $\mathbf{H}_c$. The magnetization $\mathbf{M}$ obeys the Eq. (1.3.0.10) for all fields less than $\mathbf{H}_c$, when it becomes almost zero.
The other possibility is what we call a type II superconductor: now we have two different critical fields, namely the lower critical field $\mathbf{H}_{c1}$ and the upper critical field $\mathbf{H}_{c2}$. In this case the magnetization follows the Eq. (1.3.0.10) only for small values of $\mathbf{H}$, while when we reach $\mathbf{H}_{c1}$ the magnetic flux begins to enter the superconductor so that $\mathbf{B}_{int} \neq 0$ and the magnetization $\mathbf{M}$ starts to decrease. In this way the magnetic flux gradually increase until we reach $\mathbf{H}_{c2}$, when the superconductive state is completely destroyed and so $\mathbf{M} = 0$. The two possibilities are sketched in Fig. (1.4).

We can now describe the variation of the critical fields as a function of temperature T, i.e. draw a thermodynamic phase diagram for the critical fields: first of all we find out that they all approach zero at critical temperature T_c, as shown in Fig. (1.5).

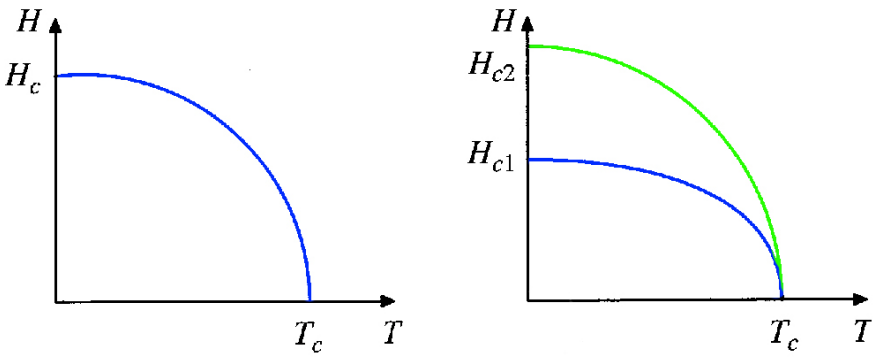


Figure 1.5: Critical fields $\mathbf{H}$ as a function of temperature T in type I (left) and type II (right) superconductor (adapted from [1]).

Something very interesting happens when we consider type II superconductor: infact there is a great difference between the trend of the lower critical field $\mathbf{H}_{c1}$ and the upper on $\mathbf{H}_{c2}$; the explanation of this difference was given by Abrikosov, who was capable to show that the magnetic field can enter inside the superconductor in the form of vortices. A vortex is just a region of circulating supercurrent around a center core which actually has become normal metal. With this composition, the magnetic field can enter passing through the metal core, and the surrounding supercurrent screen the magnetic field from the rest of the superconductor outside the vortex.

1.5 London theory

In 1935 Frizt and Heinz London proposed a phenomenological theory to describe the electrodynamic properties of a superconductor. Their main assumption is that the electrons form a "normal" fluid concentration n_n and a superfluid concentration n_s, such that $n_n + n_s = n = \frac{N}{V}$: this is called a *two-fluid picture.*
While the "normal" fluid behaves normally (following Drude's theory of conduction), the superfluid is assumed to be insensitive to scattering, and in this frame we could write for the current

$$\mathbf{j}_s = -en_s\mathbf{v}_s \tag{1.5.0.1}$$

Combining Eq. (1.5.0.1) with the Newton's equation of motion

$$\frac{d}{dt}\mathbf{v}_s = \frac{\mathbf{F}}{m} = -\frac{e\mathbf{E}}{m} \tag{1.5.0.2}$$

we obtain the *first London equation*

$$\frac{\partial \mathbf{j}_s}{\partial t} = \frac{e^2 n_s}{m}\mathbf{E} \tag{1.5.0.3}$$

Considering the superconductor to be in a *stationary state* (so that the two densities n_n and n_s are assumed to be *uniform* in space) we can take the curl of both sides of Eq. (1.5.0.3)

$$\frac{\partial}{\partial t}\nabla \times \mathbf{j}_s = \frac{e^2 n_s}{m}\nabla \times \mathbf{E} = -\frac{e^2 n_s}{m}\frac{\partial \mathbf{B}}{\partial t} \tag{1.5.0.4}$$

which integrated in time gives

$$\nabla \times \mathbf{j}_s = -\frac{e^2 n_s}{m}\mathbf{B} \tag{1.5.0.5}$$

which is the *second London equation.*
Considering the static Maxwell equation

$$\nabla \times \mathbf{B} = \mu_0 \mathbf{j} \tag{1.5.0.6}$$

and combining these two equations we obtain

$$\nabla \times \nabla \times \mathbf{B} = \nabla(\nabla \cdot \mathbf{B}) - \nabla^2\mathbf{B} = -\nabla^2\mathbf{B} = -\frac{\mu_0 e^2 n_s}{m}\mathbf{B} \tag{1.5.0.7}$$

which gives

$$\nabla^2\mathbf{B} = \frac{\mu_0 e^2 n_s}{m}\mathbf{B} \tag{1.5.0.8}$$

We can now define the *London penetration depth* λ_L

$$\lambda_L := \sqrt{\frac{m}{\mu_0 e^2 n_s}} \tag{1.5.0.9}$$

which is the distance inside the surface over which an external magnetic field is screened out to zero, given that $\mathbf{B} = 0$ inside the superconductor.

The *second London equation* Eq. (1.5.0.5) could be rewritten in terms of the magnetic vector potential $\mathbf{A}$ which is defined by

$$\mathbf{B} = \nabla \times \mathbf{A} \tag{1.5.0.10}$$

and it gives

$$\begin{aligned} \mathbf{j}_s &= -\frac{n_s e^2}{m}\mathbf{A} \\ &= -\frac{1}{\mu_0 \lambda^2}\mathbf{A} \end{aligned} \tag{1.5.0.11}$$

In this way we can think of $\mathbf{j}_s$ as the *screening current* which is required to keep the magnetic field outside the superconductor, so that London theory could explain the expulsion of the magnetic field from a superconductor.
The main weakness of this theory is the restriction of a *stationary state*: therefore we cannot explain the *Meissner-Ochsenfeld* effect, because in that case n_s would not be constant (as required by London's theory). The *Ginzburg-Landau* will overcome this complication.

Chapter 2

Ginzburg-Landau theory

2.1 Landau's approach to phase transition

In the 1930s Landau developed a general approach to the theory of second-order phase transitions. Generally a phase transition is a phenomenon which consists in a system passing from an initial state to a final one, followed by a drastic change of one or more physical quantities. In particular we have a second-order phase transition if the second derivatives are singular (or *discontinuous*), thus resulting in a particular curve called *lambda point* [3].
This is a typical thermodynamic approach (we find phase transition for the first time when we talk about aggregation state of matter), but the interesting ingredient used by Landau in his theory is the order parameter, a concept used to describe the way the phase transition works. To better understand this new concept we can think of an isotropic ferromagnet: above the Curie temperature T_{Curie} it has no magnetic moment, while below T_{Curie} it develops a spontaneous magnetic moment; in this way the magnetization $\mathbf{M}(\mathbf{r})$ is a suitable order parameter.

2.2 Landau theory and superconductivity

We may ask now how we could apply this approach to superconductivity. The answer relies on the fact that Ginzburg and Landau postulated the existence of an order parameter ψ which characterizes the state of the system, in a way such that

$$\psi = \begin{cases} 0 & T > T_c \\ \psi(T) \neq 0 & T < T_c \end{cases} \tag{2.2.0.1}$$

This is the starting point of *Ginzburg-Landau* (GL) theory.
In this way the superconductive state is characterized by a non-zero order parameter. Moreover Ginzburg and Landau assumed that this parameter should be a complex number, thinking of it as a macroscopic wave function for the superconductor, in perfect analogy with the wave function proposed to describe Bose-Einstein condensate and superfluid

helium [2]. It is relevant to say that the real meaning of ψ was deeply understood only after the work made by Gor'kov to show the connection between the *GL* theory and the *BCS* theory.
After having chosen the order parameter, we thus have to find the relation between the order parameter ψ and the free energy $\mathcal{F}$; in this way Ginzburg and Landau assumed that the free energy must depend smoothly on $|\psi|$, and this is because the free energy is a real number and the global phase of a quantum state (the superconductive state) is not observable. Furthermore ψ goes to zero at the critical temperature T_c and so we can Taylor expand the free energy $\mathcal{F}$ in powers of $|\psi|$.
Given all this assumptions we thus find out that the free energy $\mathcal{F}$ must be of the form

$$\mathcal{F}(T) = \mathcal{F}_n(T) + \mathcal{F}_s(T) = \mathcal{F}_n(T) + a(T)|\psi|^2 + \frac{b}{2}|\psi|^4 + \dots \tag{2.2.0.2}$$

where $\mathcal{F}_n(T)$ represents the "normal" free energy (the non superconductive state) and $\mathcal{F}_s$ the superconductive-free energy; here $a(T)$ and $b(T)$ are temperature dependent phenomenological parameters. Notice that odd powers of $|\psi|$ are excluded since they are not differentiable at $\psi = 0$.
The general way to approach the free energy is to minimize it; to do this we have to assume that $b(T)$ is positive, otherwise we would not have a minimum for free energy, which is a non physical solution. Minimizing the free energy $\mathcal{F}_s$ leads us to two possibilities:

- $\mathbf{a(T) \geq 0}$, and so $\mathcal{F}_s$ has a single minimum for $\psi = 0$;

- $\mathbf{a(T) < 0}$, and $\mathcal{F}_s$ has a ring of minima with equal amplitude but different phase, in fact we have that

$$\frac{\partial \mathcal{F}_s}{\partial \psi} = 2a|\psi| + 2b|\psi|^3 = 0 \quad \Longrightarrow \quad |\psi| = 0 \ (maximum), \quad |\psi| = \sqrt{-\frac{a(T)}{b(T)}}$$

which is consistent with the fact that $b(T)$ must be positive. The fact that we have an infinite number of minima for $a(T) < 0$ is related to the fact that ψ is a complex number that can be written as

$$\psi = |\psi| e^{i\theta} \tag{2.2.0.3}$$

where θ is the phase and its an arbitrary value which gives us the infinite number of solutions. The situation is plotted in Fig. (2.1).

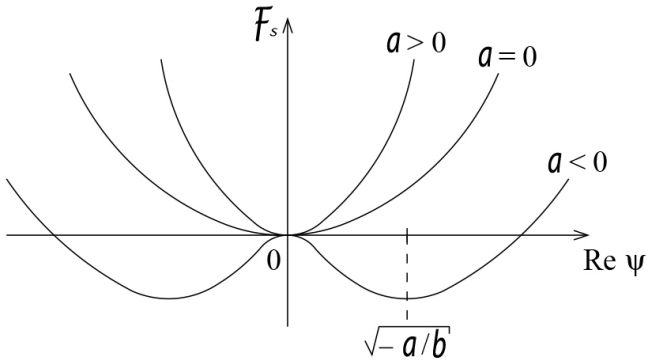


Figure 2.1: Minima of the free energy $\mathcal{F}_s$ at different values of a (adapted from [2]).

We understand that the phase transition from a normal state to a superconductive state is related to the sign of $a(T)$: Ginzburg and Landau assumed that for high temperatures (above T_c) $a > 0$ and we have a normal state; while the temperature decreases, $a(T)$ decreases too, and when $a(T) = 0$ we have the phase transition, thus changing the minimum free energy solution. In this way, assuming that $a(T)$ and $b(T)$ change smoothly with temperature, it is useful to make a Taylor expansion to leading order in T around the critical temperature T_c, so that we have

$$\begin{aligned} a(T) &\approx a' (T - T_c) + \dots \\ b(T) &\approx b + \dots \end{aligned} \tag{2.2.0.4}$$

with a' and b two phenomenological constants both positive.
In terms of these new parameters it is easy to see that the order parameter $|\psi|$ has this form

$$|\psi| = \begin{cases} \sqrt{\frac{a'}{b}}\sqrt{T_c - T} & T < T_c \\ 0 & T > T_c \end{cases} \tag{2.2.0.5}$$

In Fig. (2.2) it is shown the order parameter $|\psi|$ as a function of the temperature T: we can easily see that passing the critical temperature T_c we have an incredible change in the values of $|\psi|$. Moreover Fig. (2.3) represents the behaviour of magnetization $\mathbf{M}$ in a ferromagnet near its Curie point: the similarity between these situations is a consequence of the fact that both represent a second-order phase transition within Landau's general theory.

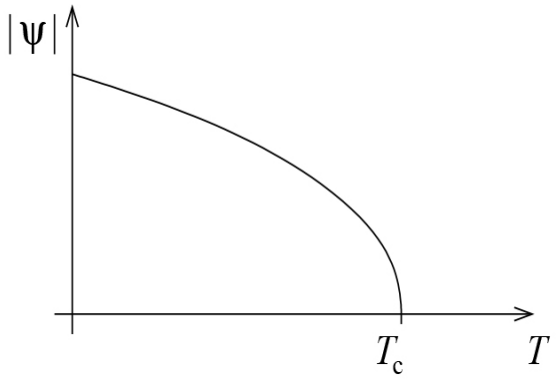


Figure 2.2: Order parameter $|\psi|$ as a function of temperature (adapted from [1]).

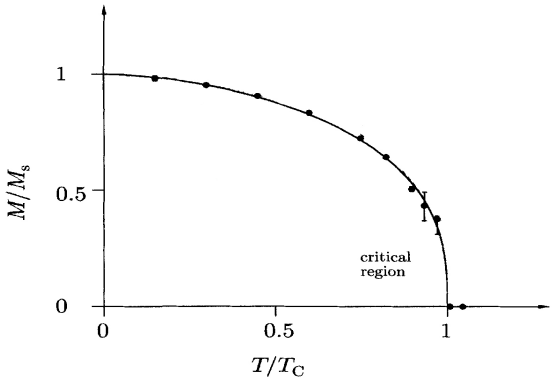


Figure 2.3: Magnetization **M** as a function of temperature (adapted from [4]).

Entropy and specific heat

As an example of application of the GL theory we can calculate some thermodynamic variables such as the entropy $\mathcal{S}$ and the specific heat $\mathcal{C}$. We remember that

$$\mathcal{S} = -\frac{\partial \mathcal{F}}{\partial T} \tag{2.2.0.6}$$

Since $\mathcal{F}$ contains both the contributions of the "normal" state and the "superconductive" one, also $\mathcal{S}$ will contain these contributions. In this way we find out that for $T \geq T_c$ the free energy is $\mathcal{F} = \mathcal{F}_n$ so that there is no contribution to entropy from the superconductive state; but when $T < T_c$ we have that

$$\mathcal{S} = \mathcal{S}_n + \mathcal{S}_s = \mathcal{S}_n - \frac{\partial}{\partial T}\mathcal{F}_s\left(\sqrt{-\frac{a(T)}{b(T)}}\right) \tag{2.2.0.7}$$

and thus we obtain that the contribution to entropy from the superconductive state is

$$\begin{aligned} \Delta\mathcal{S} = \mathcal{S} - \mathcal{S}_n &= -\frac{\partial}{\partial T}\mathcal{F}_s\left(\sqrt{-\frac{a(T)}{b(T)}}\right) = \frac{\partial}{\partial T}\left(\frac{a^2(T)}{2b(T)}\right) \\ &\approx \frac{\partial}{\partial T}\left(\frac{(a')^2}{2b}(T_c - T)^2\right) = -\frac{(a')^2}{b}(T_c - T) \end{aligned} \tag{2.2.0.8}$$

We find that the entropy is continuous at $T = T_c$, in agreement with the fact that the phase transition is *continuous*, i.e. not of first order.

We recall now how to calculate the heat capacity

$$\mathcal{C} = T\frac{\partial \mathcal{S}}{\partial T} \tag{2.2.0.9}$$

As seen before the heat capacity $\mathcal{C}$ will be the sum of the two contributions related to the "normal" and the superconductive state. In this way we can calculate the variation of the heat capacity

$$\Delta\mathcal{C} = \mathcal{C} - \mathcal{C}_n = \mathcal{C}_s \tag{2.2.0.10}$$

In this way when $T \geq T_c$, $\Delta\mathcal{C} = 0$ because there is no contribution from the superconductive state; but when $T < T_c$ we find that

$$\Delta\mathcal{C} = \frac{(a')^2}{b}T \tag{2.2.0.11}$$

Thus the heat capacity has a *jump discontinuity* of

$$\Delta\mathcal{C} = \frac{(a')^2}{b}T_c \tag{2.2.0.12}$$

at T_c, as shown in Fig. (2.4) where it is plotted the heat capacity $\mathcal{C}_V$ per unit volume as a function of T.

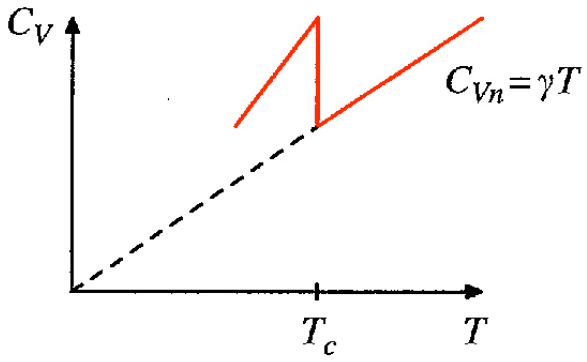


Figure 2.4: Heat capacity per unit volume $\mathcal{C}_V$ near the critical temperature T_c (adapted from [1]).

As we can see in the figure there is a discontinuity and then a change of slope. The linear trend of the function for $T \geq T_c$ is described by the Sommerfeld constant γ.

2.3 Ginzburg-Landau theory for inhomogeneous systems

The next step in *GL* theory is to consider spatially non-uniform situations, i.e. the order parameter could depend on position, $\psi(\mathbf{r})$. To do so, Ginzburg and Landau postulated that the free energy is essentially the one described before, with a new term (the simplest one) depending on the gradient of $\psi(\mathbf{r})$. In this way they could write a new definition of the free energy $\mathcal{F}$

$$\mathcal{F} = \mathcal{F}_n(T) + \int \left(a(T)|\psi(\mathbf{r})|^2 + \frac{b}{2}|\psi(\mathbf{r})|^4 + \gamma|\nabla\psi(\mathbf{r})|^2 \right) d^3r \tag{2.3.0.1}$$

We notice that the superconductive-state-free energy $\mathcal{F}_s$ is therefore a *functional* of $\psi(\mathbf{r})$, so that we can denote it as $\mathcal{F}_s[\psi]$, meaning that the scalar number $\mathcal{F}_s$ depends on the *whole* function $\psi(\mathbf{r})$ at all points in the system.
We then have to give a definition of the parameter γ. We recall that at the very beginning of section 2.2 we noticed the fact the Ginzburg and Landau assumed the order parameter ψ to be a macroscopic wave function for the superconductor; in this way the term with the gradient of $\psi(\mathbf{r})$ could be considered as a kinetic term, and by analogy with the Schrödinger equation we can write

$$\gamma = \frac{\hbar^2}{2\tilde{m}} \tag{2.3.0.2}$$

where $\tilde{m}$ is an effective mass for the quantum system.

In order to find the *new* order parameter $\psi(\mathbf{r})$ we have two possibilities:

1. To consider an infinitesimal variation in the function $\psi(\mathbf{r})$

$$\psi(\mathbf{r}) \to \psi(\mathbf{r}) + \delta\psi(\mathbf{r}) \tag{2.3.0.3}$$

   and minimize the total free energy with the condition $\delta\mathcal{F}_s = 0$;

2. To consider that $\mathcal{F}_s[\psi(\mathbf{r})]$ actually is a functional of $\psi(\mathbf{r})$, which is minimized by a function which satisfies

$$\frac{\partial\mathcal{F}_s[\psi]}{\partial\psi(\mathbf{r})} = 0 \qquad \frac{\partial\mathcal{F}_s[\psi]}{\partial\psi^*(\mathbf{r})} = 0 \tag{2.3.0.4}$$

   where $\psi^*(\mathbf{r})$ is the complex conjugate of $\psi(\mathbf{r})$.

We will pursue this second possibility. First of all we notice that Eq. (2.3.0.4) are mathematically *functional derivatives*, and in this way there is a tremendous analogy with partial derivatives.
In fact if we have a function on many variables $f(x_1, x_2, x_3, \ldots)$ we can easily express how this function changes due to infinitesimal variation of its variables

$$df = \frac{\partial f}{\partial x_1}dx_1 + \frac{\partial f}{\partial x_2}dx_2 + \frac{\partial f}{\partial x_3}dx_3 + \ldots \tag{2.3.0.5}$$

In a similar way we can write a formula for the superconductive-state-free energy, which indeed is a function of infinitely many variables $\psi(\mathbf{r})$ and $\psi^*(\mathbf{r})$

$$d\mathcal{F}_s = \int \left(\frac{\partial\mathcal{F}_s[\psi]}{\partial\psi(\mathbf{r})}d\psi(\mathbf{r}) + \frac{\partial\mathcal{F}_s[\psi]}{\partial\psi^*(\mathbf{r})}d\psi^*(\mathbf{r}) \right) d^3r \tag{2.3.0.6}$$

Now we can calculate the two expressions in Eq. (2.3.0.4), and we easily obtain

$$\begin{aligned} \frac{\partial\mathcal{F}_s[\psi]}{\partial\psi^*(\mathbf{r})} &= -\frac{\hbar^2}{2\tilde{m}}\nabla^2\psi + a(T)\psi + b(T)\psi|\psi|^2 \\ \frac{\partial\mathcal{F}_s[\psi]}{\partial\psi(\mathbf{r})} &= \left(-\frac{\hbar^2}{2\tilde{m}}\nabla^2\psi + a(T)\psi + b(T)\psi|\psi|^2 \right)^* \end{aligned} \tag{2.3.0.7}$$

where the second equation is just the complex conjugate of the first one.
Thus we have found that the process of minimization of the total free energy leads to what seems to be a Schrödinger equation for $\psi(\mathbf{r})$

$$-\frac{\hbar^2}{2\tilde{m}}\nabla^2\psi(\mathbf{r}) + \left(a + b|\psi(\mathbf{r})|^2\right)\psi(\mathbf{r}) = 0 \tag{2.3.0.8}$$

However, unlike the usual Schrödinger equation, this is a *nonlinear* equation because of the second term in the brackets.

Coherence length

Eq. (3.3.0.2) has several useful applications; one of these is to study the properties of surfaces and interfaces of a superconductor.
For example we can consider this simple model for the interface between a normal metal and a superconductor: suppose that the interface lies in the yz plane, separating the normal metal ($x < 0$) where $\psi(\mathbf{r})$ must be zero, from the superconductor ($x > 0$) where $\psi(\mathbf{r})$ must be continuous. In this way we have to solve the nonlinear Schrödinger equation

$$-\frac{\hbar^2}{2\tilde{m}}\frac{d^2\psi(x)}{dx^2} + a(T)\psi(x) + b(T)\psi^3(x) = 0 \tag{2.3.0.9}$$

in the region $x > 0$ with the boundary condition $\psi(0) = 0$.
The solution of Eq. (2.3.0.9) is

$$\psi(x) = \psi_0 \tanh\left(\frac{x}{\sqrt{2}\xi(T)}\right) \tag{2.3.0.10}$$

where ψ_0 is the order uniform-order parameter defined in Sec. (2.2) and $\xi(T)$ is defined as

$$\xi(T) = \sqrt{\frac{\hbar^2}{2\tilde{m}a(T)}} \tag{2.3.0.11}$$

and it is called *Ginzburg-Landau coherence length.*

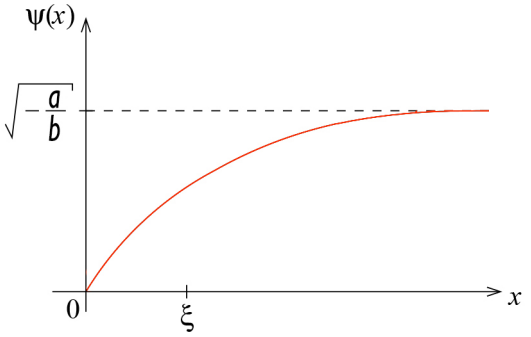


Figure 2.5: Order parameter $\psi(x)$ near the surface of a superconductor (adapted from [2]).

The coherence length $\xi(T)$ is therefore an important physical parameter for a superconductor, which is a measure of the distance from the surface over which the order parameter $\psi(x)$ has become nearly to the uniform value $|\psi| = \sqrt{-\frac{a}{b}}$. It is interesting to notice that from Eq. (2.3.0.11) the coherence length $\xi(T)$ diverges at the critical temperature T_c.

2.4 Ginzburg-Landau theory in a magnetic field

Until now we have considered the *GL* theory without considering the presence of a magnetic field, and in this way we have neglected the effect of the charge of the superconductive state.
In order to do so we assume that the magnetic field affects the order parameter $\psi(\mathbf{r})$ as if it is the wave function for charged particles, applying the usual replacement in quantum mechanics

$$\frac{\hbar}{i}\nabla \to \frac{\hbar}{i}\nabla - q\mathbf{A} \tag{2.4.0.1}$$

where $\mathbf{A}$ is the magnetic vector potential. Moreover the total free energy of the system should include also an additional term corresponding to the electromagnetic energy of the field $\mathbf{B}$, and therefore Eq. (2.3.0.1) becomes

$$\begin{aligned}\mathcal{F} = \mathcal{F}_n(T) + \int \left(a|\psi(\mathbf{r})|^2 + \frac{b}{2}|\psi(\mathbf{r})|^4 + \frac{1}{2\tilde{m}}\left|\left(\frac{\hbar}{i}\nabla - q\mathbf{A}\right)\psi(\mathbf{r})\right|^2 \right) d^3r \\ + \frac{1}{2\mu_0}\int \mathbf{B}^2(\mathbf{r})\, d^3r\end{aligned} \tag{2.4.0.2}$$

In order to find the minimum free energy we have to do a functional differentiation of Eq. (2.4.0.2) with respect to $\psi(\mathbf{r})$ and $\psi^*(\mathbf{r})$, which results again in a nonlinear Schrödinger equation, with an additional term containg $\mathbf{A}$

$$-\frac{\hbar^2}{2\tilde{m}}\left(\nabla - \frac{qi}{\hbar}\mathbf{A}\right)^2 \psi(\mathbf{r}) + \left(a + b|\psi(\mathbf{r})|^2\right)\psi(\mathbf{r}) = 0 \tag{2.4.0.3}$$

If we then differentiate functionally the free energy $\mathcal{F}_s$ with respect to $\mathbf{A}$ we obtain a formula for the supercurrent

$$\mathbf{j}_s = -\frac{q\hbar i}{2\tilde{m}}\left(\psi^*\nabla\psi - \psi\nabla\psi^*\right) - \frac{q^2}{\tilde{m}}|\psi|^2\mathbf{A} \tag{2.4.0.4}$$

which is a more general equation if compared with what we have obtained with *London theory* in Sec. (1.5); in fact considering the approximation of uniform $\psi(\mathbf{r})$ Eq. (2.4.0.4) simplifies to

$$\mathbf{j}_s = -\frac{q^2|\psi|^2}{\tilde{m}}\mathbf{A} \tag{2.4.0.5}$$

which should reproduce the London equation obtained in the end of Sec. (1.5).

Chapter 3

Thermal fluctuations in Ginzburg-Landau theory

The *GL* theory described so far is actually a *mean-field theory*: all kinds of fluctuation are neglected, so that the order parameter is assumed to be constant in time and space. Using this approximation we have defined the free energy $\mathcal{F}_s[\psi]$ as a functional of the order parameter $\psi(\mathbf{r})$, and in order to find this order parameter we have minimized the free energy.
Actually the *GL* theory could be easily extended to consider *thermal fluctuations*; in this way we can analize the situation close to the minimum of the free energy, in particular we can consider the real order parameter $\psi_0 = |\psi|$ as the one obtained in Sec. (2.2) by expanding the free energy $\mathcal{F}_s$ in powers of $|\psi|$

$$\psi(\mathbf{r}) = \psi_0 + \eta(\mathbf{r}) \tag{3.0.0.1}$$

where $\eta(\mathbf{r})$ represents a fluctuation with respect to the uniform configuration ψ_0.
The aim of this chapter is to give a formulation of the contribution of fluctuations to ψ_0, reviewing the definition of critical temperature T_c with the introduction of thermal fluctuations.

3.1 Thermal fluctuations and heat capacity

We firstly consider thermal fluctuations in order to find the expression of the heat capacity, and compare it with the formula found in Sec. (2.2). We consider a system above the critical temperature, $T > T_c$.
Considering Eq. (3.0.0.1) we recall that $\psi_0 = 0$ for $T > T_c$, therefore the free energy actually is the energy of excitations

$$\mathcal{F}_s[\psi] = \mathcal{F}_s[\eta] \tag{3.1.0.1}$$

In this way in thermal equilibrium the system would have some probability to be in a state different from ψ_0; each possibile state must follow the Boltzmann probability distribution,

which gives

$$\mathcal{P}[\psi] = \frac{1}{\mathcal{Z}_s} e^{-\beta \mathcal{F}_s[\psi]} \tag{3.1.0.2}$$

where $\beta = k_B T$ with k_B Boltzmann constant, T temperature and $\mathcal{Z}$ is the *partition function* defined as

$$\mathcal{Z}_s = \int \mathcal{D}[\psi]\mathcal{D}[\psi^*] e^{-\beta \mathcal{F}_s[\psi]} \tag{3.1.0.3}$$

It is easy to see that $\mathcal{Z}_s$ is a functional integral, which is actually quite difficult to evaluate. In order to do so we can use what it is called *Gaussian approximation*: in the definition of the free energy $\mathcal{F}_s[\psi]$ we neglect the fourth-order term $\frac{b}{2}|\psi|^4$, and thus it gives (not writing the temperature-dependance)

$$\mathcal{F}_s[\psi] \approx \int \left(a|\psi(\mathbf{r})|^2 + \frac{\hbar^2}{2\tilde{m}} |\nabla \psi(\mathbf{r})|^2 \right) d^3 \tag{3.1.0.4}$$

Considering Eq. (3.1.0.3) we see that there is infinite number of integral to solve, corresponding to an infinite set of points in the domain. To solve this integral we use the Fourier transformation of $\psi(\mathbf{r})$ and $\psi^*(\mathbf{r})$

$$\psi(\mathbf{r}) = \frac{1}{\sqrt{V}} \sum_{\mathbf{k}} \psi_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}} \tag{3.1.0.5}$$

where V is the volume and $\mathbf{k}$ is the wave vector. We therefore insert Eq. (3.1.0.5) in Eq. (3.1.0.4) and we find

$$\begin{aligned}
\mathcal{F}_s[\psi] &\approx \int \left(a\psi^*(\mathbf{r})\psi(\mathbf{r}) + \frac{1}{2\tilde{m}} \left(\frac{\hbar}{i} \nabla \psi(\mathbf{r}) \right)^* \frac{\hbar}{i} \nabla \psi(\mathbf{r}) \right) d^3 r \\
&= \frac{1}{V} \sum_{\mathbf{k}\mathbf{k}'} \int \left(a\psi^*_{\mathbf{k}} \psi_{\mathbf{k}'} + \frac{1}{2\tilde{m}} (\hbar \mathbf{k} \psi_{\mathbf{k}})^* \hbar \mathbf{k}' \psi_{\mathbf{k}'} \right) e^{-i\mathbf{k}\cdot\mathbf{r} + i\mathbf{k}'\cdot\mathbf{r}} \, d^3 r \\
&= \sum_{\mathbf{k}} \left(a\psi^*_{\mathbf{k}} \psi_{\mathbf{k}} + \frac{\hbar^2 k^2}{2\tilde{m}} \psi^*_{\mathbf{k}} \psi_{\mathbf{k}} \right) \\
&= \sum_{\mathbf{k}} \left(a + \frac{\hbar^2 k^2}{2\tilde{m}} \right) \psi^*_{\mathbf{k}} \psi_{\mathbf{k}}
\end{aligned} \tag{3.1.0.6}$$

After having calculated $\mathcal{F}_s[\psi]$ we have to write the partition function $\mathcal{Z}_s$; inserting Eq. (3.1.0.5) in Eq. (3.1.0.3) we can write for the partition function

$$\mathcal{Z}_s = \prod_{\mathbf{k}} \left(\int d\psi_{\mathbf{k}} d\psi^*_{\mathbf{k}} \right) e^{-\beta \mathcal{F}_s[\psi]} \tag{3.1.0.7}$$

and therefore we can insert Eq. (3.1.0.6) which gives

$$\mathcal{Z}_s = \prod_{\mathbf{k}} \int \exp \left[-\beta \left(a + \frac{\hbar^2 k^2}{2\tilde{m}} \right) \psi^*_{\mathbf{k}} \psi_{\mathbf{k}} \right] d\psi_{\mathbf{k}} d\psi^*_{\mathbf{k}} \tag{3.1.0.8}$$

At this point we can change variable in order to have a solvable integral [2]

$$\psi^*_{\mathbf{k}},\ \psi_{\mathbf{k}} \to \Re[\psi_{\mathbf{k}}],\ \Im[\psi_{\mathbf{k}}] \tag{3.1.0.9}$$

and Eq. (3.1.0.8) becomes

$$\mathcal{Z}_s = \prod_{\mathbf{k}} \int \exp\left[-\beta\left(a + \frac{\hbar^2 k^2}{2\tilde{m}}\right)\Re^2[\psi^*_{\mathbf{k}}] + \Im^2[\psi_{\mathbf{k}}]\right] d\Re[\psi_{\mathbf{k}}] d\Im[\psi_{\mathbf{k}}] \tag{3.1.0.10}$$

In this way it is easy to see that for each $\mathbf{k}$ we have a two-dimensional gaussian integral (hence the name *Gaussian approximation* [2]), and so we have for the partition function

$$\mathcal{Z}_{\int} = \prod_{\mathbf{k}} \frac{\pi}{\beta\left(a + \frac{\hbar^2 k^2}{2\tilde{m}}\right)} \tag{3.1.0.11}$$

Once we have calculated the partition function $\mathcal{Z}_s$ it is possible to evaluate all thermodynamic quantities of interest, for example the heat capacity $\mathcal{C}$; we recall that for the entropy we have [2]

$$\mathcal{S} = \frac{\partial}{\partial T} k_B T \ln \mathcal{Z}_s \tag{3.1.0.12}$$

and so

$$\begin{aligned} \mathcal{C} = T\frac{\partial \mathcal{S}}{\partial T} &= T\frac{\partial^2}{\partial T^2} k_B T \ln \mathcal{Z}_s \\ &= k_B T \frac{\partial^2}{\partial T^2} T \sum_{\mathbf{k}} \ln \frac{\pi}{\beta\left(a + \frac{\hbar^2 k^2}{2\tilde{m}}\right)} \end{aligned} \tag{3.1.0.13}$$

In order to do the differentiation we consider only the term which is singular at T_c, and this is a, therefore we do not differentiate the other factors of T

$$\begin{aligned} \mathcal{C}_{crit} &\approx -k_B T \frac{\partial}{\partial T}\left(\sum_{\mathbf{k}} \frac{T\frac{da}{dT}}{a + \frac{\hbar^2 k^2}{2\tilde{m}}}\right) \\ &= k_B T^2 \left(\frac{da}{dT}\right)^2 \sum_{\mathbf{k}} \frac{1}{\left(a + \frac{\hbar^2 k^2}{2\tilde{m}}\right)^2} \end{aligned} \tag{3.1.0.14}$$

Considering now the *thermodynamic limit* $V \to \infty$ we can go over to an integral over $\mathbf{k}$, and therefore

$$\begin{aligned} \mathcal{C}_{crit} &\approx k_B T^2 \left(\frac{da}{dT}\right)^2 V \int \frac{d^3k}{(2\pi)^3} \frac{1}{\left(a + \frac{\hbar^2 k^2}{2\tilde{m}}\right)^2} \\ &= \frac{k_B T^2}{2\sqrt{2}\pi} \frac{(\tilde{m})^{\frac{3}{2}}}{\hbar^3} \frac{V}{\sqrt{a}} \left(\frac{da}{dT}\right)^2 \end{aligned} \tag{3.1.0.15}$$

and considering that $a = a'(T - T_c)$ we find out that

$$\mathcal{C}_{crit} \approx \frac{k_B T^2}{2\sqrt{2}\pi} \frac{(\tilde{m})^{\frac{3}{2}}}{\hbar^3} \frac{(a')^2 V}{\sqrt{a'(T - T_c)}} \tag{3.1.0.16}$$

This calculation shows that the thermal fluctuations could make a large contribution to the heat capacity, particularly when approaching to critical temperature T_c, where there is a divergence (typical of mean-field theory). In Fig. (3.1) we can see a comparison between the heat capacity calculated in Sec. (2.2) (dotted black line) and the heat capacity with the contribution of thermal fluctuation (red line).

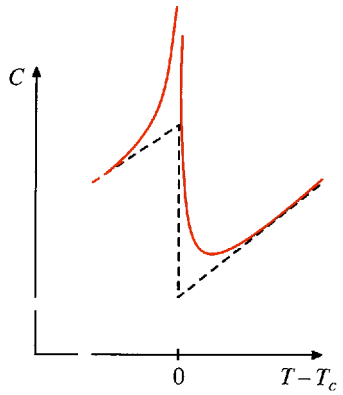


Figure 3.1: Contribution of thermal fluctuations to heat capacity (adapted from [1]).

3.2 Bogoliubov, HFB and Popov approximations

In order to understand the following calculations for the thermal fluctuations, it is important to consider the approximations that will be used.
In the very beginning of Sec. (2.2) it has pointed out the analogy between Bose-Einstein condensate and superconductors, which can be considered as the starting point of the *GL* theory. This analogy will continue because the approximations that we are going to use come from the equation that defines a condensate, namely the *Gross-Pitaevskii equation*, equation that we will obtain rapidly.

We are considering the *second quantization of matter* and our starting point is the exact Heisenberg equation of motion for the Bose field operator $\hat{\psi}(\mathbf{r})$ [5]

$$i\hbar \frac{\partial \hat{\psi}(\mathbf{r}, t)}{\partial t} = \left(-\frac{\hbar^2 \nabla^2}{2m} + U_{ext}(\mathbf{r}) - \mu \right) \hat{\psi}(\mathbf{r}, t) + g\hat{\psi}^\dagger(\mathbf{r}, t)\hat{\psi}(\mathbf{r}, t)\hat{\psi}(\mathbf{r}, t) \tag{3.2.0.1}$$

where $U_{ext}(\mathbf{r})$ is a static external potential that traps the atoms, μ is the chemical potential and we have assumed [5] a short-range interaction $V(\mathbf{r} - \mathbf{r}') = g\delta(\mathbf{r} - \mathbf{r}')$.
In this way the equation for the condensate wavefunction is obtained by taking an average appropriate to a Bose broken symmetry; separating the condensate part from the noncondensate one we can write

$$\hat{\psi}(\mathbf{r}, t) = \Phi(\mathbf{r}) + \tilde{\psi}(\mathbf{r}, t) \tag{3.2.0.2}$$

where $\Phi(\mathbf{r}) = \left\langle \hat{\psi}(\mathbf{r},t) \right\rangle$ is a spatially varying macroscopic Bose field, and $\tilde{\psi}(\mathbf{r},t)$ is the noncondensate field operator with $\left\langle \tilde{\psi}(\mathbf{r},t) \right\rangle = 0$ [5]. Therefore Eq. (3.2.0.2) becomes

$$i\hbar\frac{\partial\Phi(\mathbf{r},t)}{\partial t} = \left(-\frac{\hbar^2\nabla^2}{2m} + U_{ext}(\mathbf{r}) - \mu\right)\Phi(\mathbf{r},t) + g\left\langle \hat{\psi}^\dagger(\mathbf{r},t)\hat{\psi}(\mathbf{r},t)\hat{\psi}(\mathbf{r},t)\right\rangle \tag{3.2.0.3}$$

Using Eq. (3.2.0.2) we can rewrite the last term of Eq. (3.2.0.1)

$$\hat{\psi}^\dagger\hat{\psi}\hat{\psi} = |\Phi|^2\Phi + 2|\Phi|^2\tilde{\psi} + \Phi^2\tilde{\psi}^\dagger + \Phi^*\tilde{\psi}\tilde{\psi} + 2\Phi\tilde{\psi}^\dagger\tilde{\psi} + \tilde{\psi}^\dagger\tilde{\psi}\tilde{\psi} \tag{3.2.0.4}$$

and by taking the average we have

$$\left\langle \hat{\psi}^\dagger\hat{\psi}\hat{\psi}\right\rangle = n_c\Phi + \tilde{m}\Phi^* + 2\tilde{n}\Phi + \left\langle \tilde{\psi}^\dagger\tilde{\psi}\tilde{\psi}\right\rangle \tag{3.2.0.5}$$

which is actually the last term of Eq. (3.2.0.3); here we have introduced the following local quantities [5]

$$\begin{aligned} n_c(\mathbf{r},t) &\equiv |\Phi(\mathbf{r},t)|^2 \qquad \text{the local condensate density} \\ \tilde{n}(\mathbf{r},t) &\equiv \left\langle \tilde{\psi}^\dagger(\mathbf{r},t)\tilde{\psi}(\mathbf{r},t)\right\rangle \qquad \text{the noncondensate density} \\ \tilde{m}(\mathbf{r},t) &\equiv \left\langle \tilde{\psi}(\mathbf{r},t)\tilde{\psi}(\mathbf{r},t)\right\rangle \qquad \text{the "anomalous" density} \end{aligned} \tag{3.2.0.6}$$

Using these definitions the *generalized Gross-Pitaevskii* (*GP*) *equation* is obtained

$$\begin{aligned} i\hbar\frac{\partial\Phi(\mathbf{r},t)}{\partial t} = \left(-\frac{\hbar^2\nabla^2}{2m} + U_{ext}(\mathbf{r}) - \mu\right)\Phi(\mathbf{r},t) &+ g\left[n_c(\mathbf{r},t) + 2\tilde{n}(\mathbf{r},t)\right]\Phi(\mathbf{r},t) \\ &+ g\tilde{m}(\mathbf{r},t)\Phi^* + g\left\langle \tilde{\psi}^\dagger(\mathbf{r},t)\tilde{\psi}(\mathbf{r},t)\tilde{\psi}(\mathbf{r},t)\right\rangle \end{aligned} \tag{3.2.0.7}$$

Having now written the general form for the *GP* equation, it is time to introduce the possible approximations that could be used to simplify Eq. (3.2.0.7):

- **Bogoliubov** approximation: this approximation for Φ corresponds to neglecting $\tilde{n}(\mathbf{r},t)$, $\tilde{m}(\mathbf{r},t)$ and the three-field correlation function $\left\langle \tilde{\psi}^\dagger\tilde{\psi}\tilde{\psi}\right\rangle$. In this way Eq. (3.2.0.7) becomes

  $$i\hbar\frac{\partial\Phi(\mathbf{r},t)}{\partial t} = \left(-\frac{\hbar^2\nabla^2}{2m} + U_{ext}(\mathbf{r}) - \mu + gn_c(\mathbf{r},t)\right)\Phi(\mathbf{r},t) \tag{3.2.0.8}$$

  which is the *GP* equation that describes a Bose-Einstein condensate at $T = 0$ [5];

- **Hartree-Fock-Bogoliubov** (**HFB**) approximation: in this approximation we neglect only the term $\left\langle \tilde{\psi}^\dagger\tilde{\psi}\tilde{\psi}\right\rangle$;

- **Popov** approximation: this approximation (also called *dynamic Popov approximation*) corresponds to neglecting both $\left\langle \tilde{\psi}^\dagger\tilde{\psi}\tilde{\psi}\right\rangle$ and $\tilde{m}(\mathbf{r},t)$.

3.3 Shift of the critical temperature

In this section we want to consider the contribution of thermal fluctuation to critical temperature, in particular we want to find how the value of the critical temperature changes when introducing thermal fluctuations.
Firstly we call ψ_0 the uniform order parameter as calculated in Sec. (2.2) and T_{c_0} the related critical temperature; we do this in order to distinguish them from the following results. Then we could write the space-dependent order paramenter $\psi(\mathbf{r})$ in this way

$$\psi(\mathbf{r}) = \varphi_0 + \eta(\mathbf{r}) \tag{3.3.0.1}$$

where φ_0 represents a "new" uniform order parameter which include the contribution of thermal fluctuations, while $\eta(\mathbf{r})$ represents a fluctuation with respect to φ_0 [7].
The starting point of our calculation is the nonlinear Schrödinger equation obtained in Sec. (2.5)

$$\left(a(T) + b(T)|\psi(\mathbf{r})|^2\right)\psi(\mathbf{r}) - \gamma\nabla^2\psi(\mathbf{r}) = 0 \tag{3.3.0.2}$$

Now we insert Eq. (3.3.0.1) in Eq. (3.3.0.2) with the condition

$$\langle\eta\rangle = \langle\eta^*\rangle = 0 \tag{3.3.0.3}$$

where $\langle\cdot\rangle$ defines the thermal average. Physically speaking this condition is easily understandable: since η represents a fluctuation, when we take the average this must be zero. Therefore we obtain (not writing the dependencies)

$$a\varphi_0 + b\varphi_0^3 + a\eta + 2b\varphi_0^2\eta + b\varphi_0^2\eta^* + 2b\varphi_0\eta^*\eta + b\varphi_0\eta^2 + b\eta^*\eta\eta - \gamma\nabla^2\eta = 0 \tag{3.3.0.4}$$

We take the thermal average of Eq. (3.3.0.4), considering Eq. (3.3.0.3), and we find

$$\left(a + 2n\langle\eta^*\eta\rangle + b\left\langle\eta^2\right\rangle\right)\varphi_0 + b\varphi_0^3 + b\langle\eta^*\eta\eta\rangle = 0 \tag{3.3.0.5}$$

At this point it is fundamental to consider approximations, and here we have two possibilites:

- To consider a *Bogoliubov approximation*, so that we neglect all the thermal averages. In this way we simply obtain the definition of the uniform order parameter ψ_0;
- To consider a *Popov approximation*, neglecting the averages $\langle\eta^2\rangle$ and $\langle\eta^*\eta\eta\rangle$.

Considering the Popov approximation [7] we therefore obtain

$$\left(a + 2b\langle\eta^*\eta\rangle\right)\varphi_0 + b\varphi_0^3 = 0 \tag{3.3.0.6}$$

and consequently we find for the "new" uniform order parameter

$$\varphi_0 = \begin{cases} 0 & \text{for} \quad T \geq T_c \\ \sqrt{-\frac{a+2b\langle\eta^*\eta\rangle}{b}} & \text{for} \quad T < T_c \end{cases} \tag{3.3.0.7}$$

Notice that the order parameter φ_0 is definitely a new order parameter, different from ψ_0 as defined in Sec. (2.2); also the critical temperature T_c at which the order parameter φ_0 becomes different from zero is different from the one defined in Sec. (2.2). In this case the condition which determines the "new" critical temperature T_c is

$$a(T_c) + 2b \left\langle |\eta|^2 \right\rangle_c = 0 \tag{3.3.0.8}$$

where $\eta^* \eta = |\eta|^2$ and the subscript $\langle \cdot \rangle_c$ means that we are at T_c [7].
At this point we want to find a formula that could allow us to calculate $\langle |\eta|^2 \rangle$ at T_c, namely $\langle |\eta|^2 \rangle_c$; in order to do so we consider Eq. (3.3.0.4) and we insert Eq. (3.3.0.6). Then we have to treat self-consistently the fluctuation $\eta(\mathbf{r})$, and in order to do so we consider these conditions

$$\begin{aligned} |\eta|^2 \eta &\approx 2 \left\langle |\eta|^2 \right\rangle \eta \\ \eta^2 &\approx 0 \end{aligned} \tag{3.3.0.9}$$

as done by Griffin [6]. In this way Eq.(3.3.0.4) becomes

$$a\eta + 2b\varphi_0^2 \eta + 2b \left\langle |\eta|^2 \right\rangle \eta + b\varphi_0 \eta^* + 2b\varphi_0 |\eta|^2 - \gamma \nabla^2 \eta = 0 \tag{3.3.0.10}$$

As done in Sec. (3.1) we could work with $T \geq T_c$, so that the new uniform order parameter $\varphi_0 = 0$; then Eq. (3.3.0.10) reduces to

$$\left(a + 2b \left\langle |\eta|^2 \right\rangle \right) \eta - \gamma \nabla^2 \eta = 0 \tag{3.3.0.11}$$

This is a new nonlinear Schrödinger equation, from which we could easily find the formula for the new free energy $\mathcal{F}_{s,\eta}[\psi]$

$$\mathcal{F}_{s,\eta}[\eta(\mathbf{r})] = \int_{L^D} \left[\left(a(T) + 2b \left\langle |\eta|^2 \right\rangle \right) |\eta(\mathbf{r})|^2 + \gamma |\nabla \eta(\mathbf{r})|^2 \right] d^D r \tag{3.3.0.12}$$

where we are actually considering a general *ipervolume* of dimension D [7]. It is interesting to notice that the fourth-order term is completely disappeared, and Eq. (3.3.0.12) resembles Eq. (3.1.0.4); in this way we could talk of *gaussian approximation.*
Given this similarity between these expressions, we could follow the same steps of Sec. (3.1): in this way we could expand $\eta(\mathbf{r})$ using Fourier transformation

$$\eta(\mathbf{r}) = \frac{1}{\sqrt{L^D}} \sum_{\mathbf{k}} \eta_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}} \tag{3.3.0.13}$$

where $\mathbf{k}$ is the wave vector and $\eta_{\mathbf{k}}$ are the Fourier coefficients. Therefore, using Eq. (3.3.0.13) in Eq. (3.3.0.12), we could easily find that

$$\mathcal{F}_{s,\eta} = \sum_{\mathbf{k}} \left(a(T) + 2b \left\langle |\eta|^2 \right\rangle + \gamma k^2 \right) |\eta_{\mathbf{k}}|^2 \tag{3.3.0.14}$$

The procedure is absolutely identical with the one used in Sec. (3.1); we can calculate the thermal average of $|\eta|^2$ using

$$\left\langle |\eta|^2 \right\rangle = \frac{1}{\mathcal{Z}_s} \int \mathcal{D}[\eta(\mathbf{r})]\mathcal{D}[\eta^*(\mathbf{r})]|\eta(\mathbf{r})|^2 e^{-\beta \mathcal{F}_{s,\eta}[\eta(\mathbf{r})]} \tag{3.3.0.15}$$

where $\mathcal{Z}_s$ is the partition function as defined by Eq. (3.1.0.3); this gives as result [7]

$$\left\langle |\eta|^2 \right\rangle = \frac{1}{L^D} \sum_{\mathbf{k}} \frac{1}{\beta \left(a(T) + 2b \left\langle |\eta|^2 \right\rangle + \gamma k^2 \right)} \tag{3.3.0.16}$$

and if we are at $T = T_c$ then Eq. (3.3.0.16) reads

$$\left\langle |\eta|^2 \right\rangle_c = \frac{1}{L^D} \sum_{\mathbf{k}} \frac{1}{\beta \gamma k^2} = \frac{1}{L^D} \sum_{\mathbf{k}} \frac{k_B T_c}{\gamma k^2} \tag{3.3.0.17}$$

because Eq. (3.3.0.8) holds when $T = T_c$.
At this point we can easily use the thermodynamic limit in order to convert the sum to an integral

$$\sum_{\mathbf{k}} \to L^D \int \frac{1}{(2\pi)^D} \, d^D k \tag{3.3.0.18}$$

and moreover we consider the two dimensional case ($D = 2$) [7], finding

$$\left\langle |\eta|^2 \right\rangle_c = \int \frac{1}{(2\pi)^2} \frac{k_B T_c}{\gamma k^2} \, d^2 k \tag{3.3.0.19}$$

In order to do this integration, Larkin and Varlamov [8] suggest that there must be some physical constraints to the value of k; this could be physically understood if we consider that the superconductor has a limited volume. Calling Λ and k_0 the upper and the lower limit respectively [7][8], Eq. (3.3.0.19) gives

$$\left\langle |\eta|^2 \right\rangle_c = \frac{k_B T_c}{2\pi\gamma} \ln\left(\frac{\Lambda}{k_0}\right) \tag{3.3.0.20}$$

We can now define the *Ginzburg-Levanyuk number* Gi, which is a number that is associated to the possibility to use the *GL* theory according to thermal fluctuations: this is called the *Ginzburg-Levanyuk criterion*, which establishes that, near the transition point, the theory can be applied up to the temperature when the fluctuation corrections become comparable to the value of the corresponding physical quantities [8].

In our two-dimensional case the Ginzburg-Levanyuk number is

$$Gi_{(2)} = \frac{b}{4\pi a' \gamma} \tag{3.3.0.21}$$

It is easy to see that Gi is a positive number and it depends only on the phenomenological parameters of the superconductor. Actually the proper definition of Gi lies on the

microscopic view of superconductivity typical of *BCS* theory [8]. We can take $k_B = 1$, and inserting Eq. (3.3.0.8) in Eq. (3.3.0.20) and remembering the definition of $a(T)$ we thus find

$$\frac{T_{c_0} - T_c}{T_c} = 4\ Gi_{(2)} \ln\left(\frac{\Lambda}{k_0}\right) \tag{3.3.0.22}$$

and always according to Larkin and Varlamov [7][8] we find these definitions for the two cutoffs of k

$$\begin{aligned} \Lambda &= \sqrt{\frac{a' T_c}{4\gamma}} \\ k_0 &= \sqrt{\frac{a' T_c\ Gi_{(2)}}{\gamma}} \end{aligned} \tag{3.3.0.23}$$

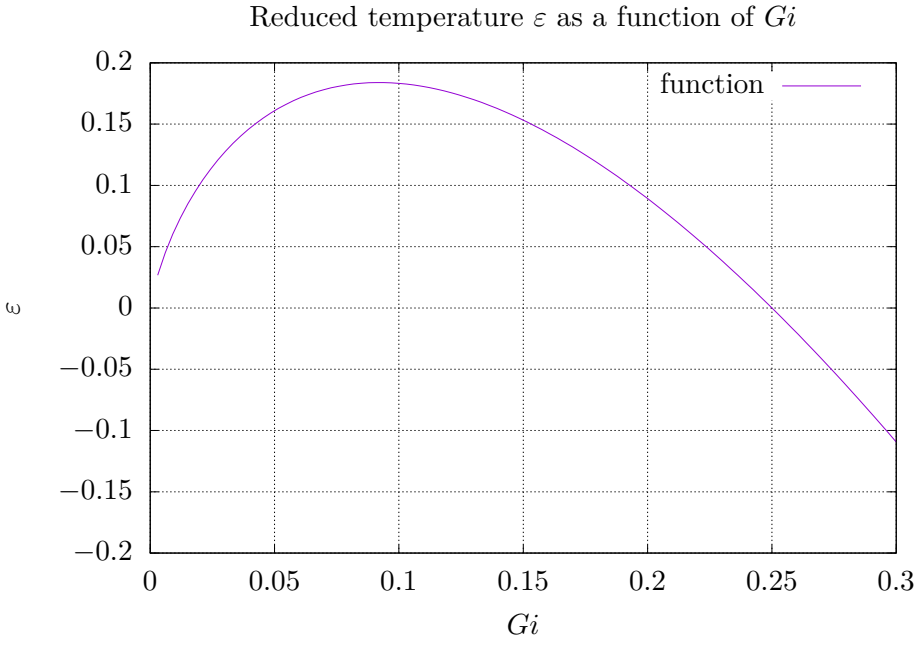
Moreover it is easy to see that $\Lambda = \frac{1}{2\xi}$, where ξ is the coherence length; inserting Eq. (3.3.0.23) in Eq. (3.3.0.22) we find

$$\frac{T_{c_0} - T_c}{T_c} = 2\ Gi_{(2)} \ln\left(\frac{1}{4\ Gi_{(2)}}\right) \tag{3.3.0.24}$$

Finally we have found a formula that gives us the shift of the critical temperature, depending only on the characteristics of the superconductor. It is interesting to understand if the shift of the critical temperature is downward or upward. If we define the *reduced temperature* ε as

$$\varepsilon = \frac{T_{c_0} - T_c}{T_c} \tag{3.3.0.25}$$

we can plot ε as a function of Ginzburg-Levanyuk number Gi



Looking at the plot it is easy to see that the reduced temperature ε is firstly positive, and then it becomes negative. Actually Ginzburg was the first one to estimate Gi in a clean, conventional superconductor, obtaining [8]

$$Gi \sim 10^{-12} \div 10^{-14} \tag{3.3.0.26}$$

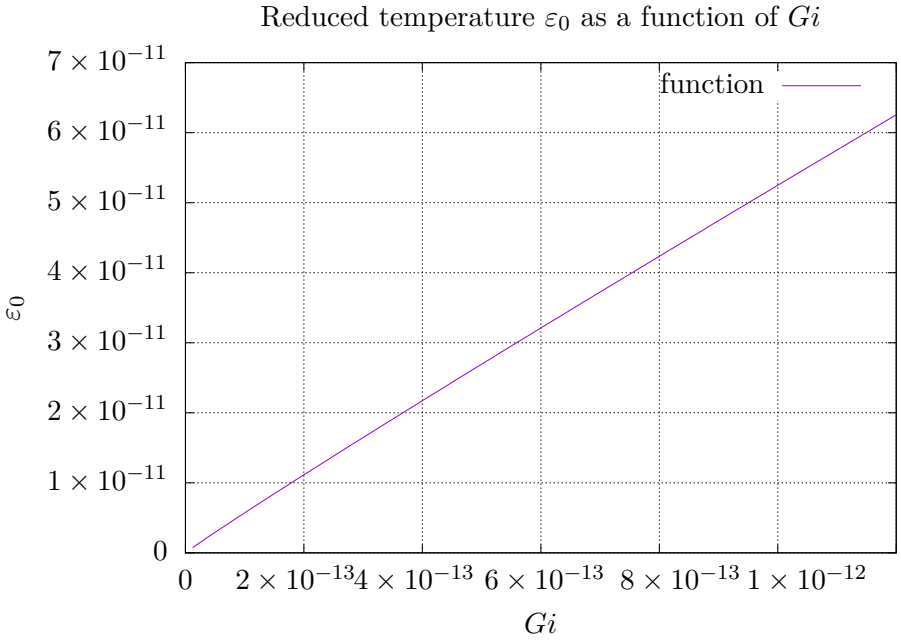
Given these values of Gi we therefore conclude that the reduced temperature ε (and thus the shift of the critical temperature) is positive, in perfect corrispondence with the results obtained by Larkin and Varlamov [8]. Moreover if we consider Eq. (3.3.0.24) and Eq. (3.3.0.26) we easily find out that the relative shift of the critical temperature ε is $\sim 10^{-11}$. We can also be interested in finding the shift of the critical temperature relative to the "old" critical temperature T_{c_0}; in this way we can rewrite Eq. (3.3.0.24) in order to express a new reduced temperature ε_0 defined as

$$\varepsilon_0 = \frac{T_{c_0} - T_c}{T_{c_0}} \tag{3.3.0.27}$$

With a rapid algebraic manipulation we find out that

$$\varepsilon_0 = \frac{2\ Gi_{(2)} \ln\left(\frac{1}{4\ Gi_{(2)}}\right)}{1 + 2\ Gi_{(2)} \ln\left(\frac{1}{4\ Gi_{(2)}}\right)} \tag{3.3.0.28}$$

As done before we can plot ε_0 as a function of Gi. We then zoom the graph in order to consider appropriate values of Gi,



It is easy to see that also in this case, using Eq.(3.3.0.26), the relative shift of the critical temperature ε_0 is $\sim 10^{-11}$, thus confirming the fact that the introduction of thermal fluctuations introduce a very small shift of the critical temperature.

Conclusions

In this thesis we have seen the importance of the *GL* theory as the first approach to superconductivity, based on the improvement of the previous *London* theory. As said at the beginning of Sec. (2.2) the strength of this theory lies on its correspondence with the microscopic approach of the *BCS* theory.
Another interesting point of the *GL* theory explained in this thesis is the possibility of considering the thermal fluctuations, in order to give new definitions of physical quantities, which can also be proved experimentally; in this way we reach a result for the new definition of the heat capacity $\mathcal{C}$ and for the shift of the critical temperature T_c confirmed by Larkin and Varlamov, who however considered a more sophisticated formalism, including normalition group and diagrams; furthermore we have only considered the two-dimensional case, while actually we can consider a general-dimensional case in order to find other solutions.
It is easy to understand that we could not have the possibility to explain every aspect of the *GL* theory (such as vortices, high temperature superconductivity, ...), and a rapid glance to the literature gives us the idea of how prolific this theory is.

Of course the main aim of this thesis was to get in touch with a subject that is not treated during the *laurea triennale* in Physics; the reason why I chose the *GL* theory as a subject for this thesis is the mixture of a lot of different topics, in order to describe correctly the behaviour of a superconductor: thermodynamic approach to phase transistion, the concept of quantum wave function, tools of statistical mechanics; moreover superconductivity (and thus *GL* and other theories) has led to huge practical applications, both in the research field (astronomical interferometers, atomic clocks, ...) and in daily living (for example the *Maglev* train). The possibility to test *GL* theory via experiments gives us the chance to improve this theory together with a more advanced mathematical formalism, and more it is to do in order to discover new superconductive materials and new applications.

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