

3.1.1 Symmetry breaking

The properties of a solid are closely related to its *symmetry*. In many cases, symmetry properties can be described by a space group. A second order phase transition is combined with a change of the symmetry of the system. Hence, its properties change as well. This may lead to a spontaneous emergence of additional quantities, e. g., magnetization, dielectric polarization, or—in the case of superconductors—the appearance of a superconducting condensate.

In contrast to a first order transition, in a second order transition the state of the system changes continuously during the phase transition (compare Figure 3.1). Exactly at the transition point, i. e., at $T = T_c$, the states of the high- and low-temperature phase coincide. Consequently, the space group of one phase must be a subgroup of the other phase. In most cases (in particular in superconductors) the higher symmetry phase corresponds to the high-temperature phase and the lower symmetry phase corresponds to the low-temperature phase.

3.1.2 Order parameter

According to the postulates of thermodynamics, it is possible to characterize the high-symmetry phase by a small number of state variables (for example pressure and temperature). If the system undergoes the phase transition, then it enters a lower symmetry, and, hence, the description of the system only by pressure and temperature (as in the high-symmetry state) becomes insufficient. Thus, an additional variable is required: the *order parameter* ψ . The order parameter is an abstract quantity. It describes the origin of the phase transition, and it is possible to identify it with a specific microscopic process. The order parameter is defined in such a way as it is zero in the high-symmetric phase and it becomes non-zero

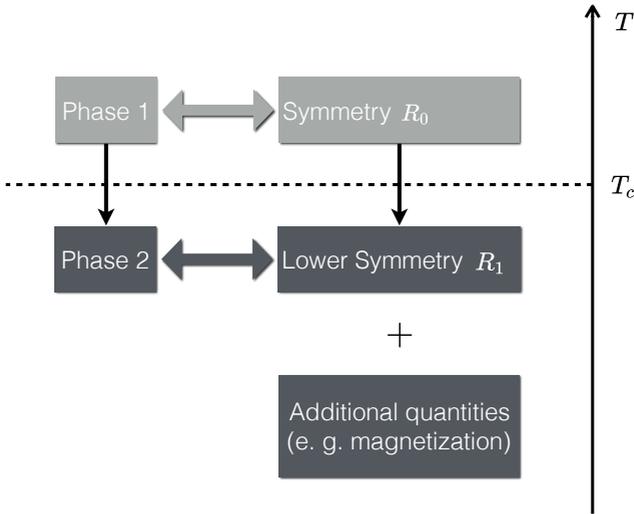


Figure 3.1: Schematic picture of a phase transition within the Landau theory.

in the low-symmetry phase,

$$\psi = \begin{cases} 0 & , T > T_c \text{ (high symmetry phase)} \\ \psi(T) \neq 0 & , T < T_c \text{ (low symmetry phase)} \end{cases}.$$

3.1.3 Landau potential

To describe the phase transition correctly, the order parameter ψ has to be taken into account as an *additional* variable in the free energy $F(p, T)$. Thereby, ψ is not an independent variable as p and T , because it emerges as an additional parameter to the subgroup R_1 . While p and T can be fixed arbitrary by external conditions, the equilibrium value of ψ is determined by the condition that the free energy takes its minimum value in the thermodynamic equilibrium.

Close to the phase transition the order parameter takes small values. Thus, if we formulate a theory designated to states close to the phase transition, then a Taylor expansion of the free energy with respect to ψ is allowed,

$$F(p, T, \psi) = F_0(p, T) + A(p, T)\psi^2 + \frac{B(p, T)}{2}\psi^4, \quad (3.1)$$

where the expansion coefficients F_0 , A , and B , in principle, depend on pressure and temperature. Terms of first and third order in ψ are not taken into account since they lead to unstable states at the transition point and at high temperatures. The value of the order parameter is determined by the minimization equation

$$\frac{\partial F(p, T, \psi)}{\partial \psi} = 0.$$

3.1.4 Superconducting transition

Now we apply the general concepts of the Landau theory to the phase transition from a metallic state to the superconducting state. Basic idea is the assumption that the superconducting particles form a *macroscopic wave function* $\psi(\vec{r})$ which describes a superconducting condensate. We set this wave function equal to the Landau order parameter of the superconducting phase. As any other wave function, $\psi(\vec{r})$ can be considered in quantum mechanics as a scalar product

$$\psi(\vec{r}) = \langle \vec{r} | \psi \rangle \quad (3.2)$$

between an eigenvector $|\vec{r}\rangle$ of the position operator \hat{r} and the superconducting state vector $|\psi\rangle$. According to this structure, we claim that the order parameter of the superconducting phase—in the following called superconducting order parameter—is a *complex* number,

$$\psi(\vec{r}) = |\psi(\vec{r})| e^{i\Theta(\vec{r})}, \quad (3.3)$$

where its absolute value $|\psi(\vec{r})|$ and also its phase $\Theta(\vec{r})$ generally depend on position vector \vec{r} . Thus, the superconducting order parameter is characterized by the two real fields $|\psi(\vec{r})|$ and $\Theta(\vec{r})$ or, alternatively, by the complex field $\psi(\vec{r})$.

It is the basic idea of the Ginzburg-Landau theory that the superconductivity emerges from an electronic many-particle system which is described by one unique wave function (3.3). This wave function is set equal to the superconducting order parameter. Due to the wave function property, the quantity $|\psi(\vec{r})|^2$ corresponds to the *density* of superconducting particles. The complex nature of the order parameter is specific to the superconducting state and arises from the property that $\psi(\vec{r})$ is equal to a macroscopic wave function. The microscopic origin of the wave function remains unknown.

3.2 Homogeneous superconductor

At first, let us consider the simplest possible realization of a superconducting state: A homogeneous material where the order parameter $\psi(\vec{r}) = \psi$ is a constant value. In this case, $|\psi|^2 = n_S^*$ is the (spatially independent) density of superconducting particles. The physical meaning of this quantity corresponds to the density n_S of the superconducting 'liquid' introduced within the London theory. As will be shown later, in the Ginzburg-Landau theory n_S^* describes the density of *Cooper pairs*, whereas in the London theory n_S refers to the density of 'superconducting electrons'. Note that, in contrast to the London theory which is formulated to describe the low temperature limit $T \ll T_c$, the Ginzburg-Landau theory accesses temperatures close to T_c . According to (3.1), the free energy density (related to the volume of the material) reads

$$f_S(T, \psi) = f_N(T) + r(T)|\psi|^2 + \frac{u(T)}{2}|\psi|^4, \quad (3.4)$$

where f_N is the free energy density of the normal state. For simplicity, the pressure dependence is omitted. As already mentioned above, the phenomenological parameters $r(T)$ and $u(T)$ have to be determined experimentally or by a microscopic theory. Nevertheless, it is possible—even without this knowledge—to gain much insight about the temperature behavior of the order parameter close to the transition point. This will become clear in the following.

The free energy (3.4) is invariant under a continuous gauge transformation $\psi \rightarrow e^{i\alpha}\psi$ of the complex order parameter,

$$f_S(e^{i\alpha}\psi) = f_S(\psi).$$

It means that the free energy is symmetric with respect to the phase of the order parameter.

We now search the particular value of the superconducting order parameter corresponding to the thermodynamic equilibrium. This is the value for which the free energy $f_S(T, \psi)$ at a given temperature T (representing the thermodynamic equilibrium) becomes minimal. To find this value of ψ , it is sufficient to minimize the free energy with respect to $|\psi|^2$. We form the first and second derivative of (3.4) with respect to $|\psi|^2$,

$$\frac{\partial f_S}{\partial(|\psi|^2)} = r(T) + u(T)|\psi|^2, \quad (3.5)$$

$$\frac{\partial^2 f_S}{\partial(|\psi|^2)^2} = u(T). \quad (3.6)$$

As is seen from the second derivative (3.6), f_S has a minimum only in the case $u(T) > 0$. Thus, in a superconducting material the parameter $u(T)$ must be always positive. Otherwise the system would be thermodynamically unstable. Setting the first derivative to zero, we obtain from (3.5) the equilibrium value of $|\psi|^2$ for which $f_S(T, \psi)$ becomes minimal,

$$|\psi|^2 = -\frac{r(T)}{u(T)} \quad \text{with} \quad u(T) > 0. \quad (3.7)$$

Note that r is changed by a variation of temperature. Therefore, depending on the value of r , we have to distinguish between two important cases.

Case $r > 0$

There is no finite solution for $|\psi|^2$ since the right hand side of (3.7) is negative. According to (3.4), for $r > 0$ and $u > 0$ the free energy f_S becomes larger than the normal state value f_N for any finite value of $|\psi|^2$. Thus, in the case $r > 0$, the free energy f_S is minimal for $\psi = 0$,

$$|\psi| = 0 \quad \text{for} \quad r(T) > 0, \quad (3.8)$$

and the system stays in the normal state as long as r has a positive value.

Case $r < 0$

If r becomes negative, then the situation changes dramatically. Now the free energy is minimal if the order parameter takes the finite value

$$|\psi| = \sqrt{\frac{|r(T)|}{u(T)}} \quad \text{for} \quad r(T) < 0. \quad (3.9)$$

Consequently, the system now prefers the superconducting state rather than the normal state (characterized by $|\psi| = 0$). The new state is characterized by a finite order parameter ψ depending on temperature T via the phenomenological parameters $r(T)$ and $u(T)$, and has a lower free energy than the normal state. The non-zero solution leads to a spontaneous symmetry breaking in the superconducting phase. The critical temperature T_c can be fixed by the zero of the function $r(T)$, i. e.,

$$r(T_c) = 0.$$

3.2.1 Order parameter and critical field

We now study important consequences for the properties of measurable quantities close to the transition point. To determine the temperature dependence, we Taylor expand the parameters $r(T)$ and $u(T)$ with respect to T around T_c ,

$$r(T) = \tilde{r}_0(T - T_c) + \dots, \quad (3.10)$$

$$u(T) = \tilde{u}_0 + \tilde{u}_1(T - T_c) + \dots, \quad (3.11)$$

where \tilde{r}_0 , \tilde{u}_0 and \tilde{u}_1 are temperature-independent coefficients. This expansion allows us to calculate the temperature dependence of the superconducting order parameter $|\psi|$ from equations (3.8) and (3.9),

$$|\psi| = \begin{cases} 0 & T > T_c \\ \propto \sqrt{T_c - T} & T < T_c \end{cases}, \quad (3.12)$$

where only the lowest order in $(T - T_c)$ is considered. The result (3.12) describes the temperature behavior of the order parameter very close to the transition point (compare Figure 3.2). It follows a typical power law $\propto (T_c - T)^\beta$ with an exponent $\beta = 1/2$ being characteristic for a mean field theory.

According to the ideas presented in Section 1.3, the energy gain $F_S - F_N$ of the superconducting material in relation to the material in the normal conducting state is closely connected to the critical magnetic field. Thus, by calculating this energy gain from (3.4), we are able to calculate the approximate temperature behavior of the critical field close to T_c . Using (3.4) and (3.9), we obtain at first

$$\begin{aligned} \Delta f = f_S - f_N &= r|\psi|^2 + \frac{u}{2}|\psi|^4 = r\frac{|r|}{u} + \frac{u}{2}\frac{|r|^2}{u^2} \\ &= -\frac{|r|^2}{2u}. \end{aligned} \quad (3.13)$$

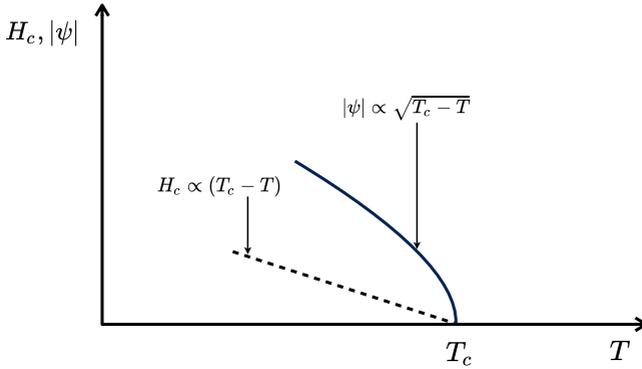


Figure 3.2: Temperature behavior of the superconducting order parameter $|\psi|$ and the critical magnetic field H_c close to the transition temperature T_c .

The energy difference is negative. Hence, the superconducting state is energetically favorable over the normal state. On the other hand, according to (1.6), this energy difference is related to the critical magnetic field. Here we consider the field free case $H = 0$ and all energy values are related to the volume V . Note that in the field free case the free energy F is equal to the Gibbs free energy G (compare Section 4.1). Thus, equation (1.6) gives

$$f_S - f_N = \frac{F_S(T, H = 0) - F_N(T)}{V} = -\frac{H_c^2(T)}{8\pi}. \quad (3.14)$$

Equalizing the results (3.13) and (3.14), we find for the critical magnetic field

$$\boxed{H_c(T) = 2|r|\sqrt{\frac{\pi}{u}}}. \quad (3.15)$$

Due to $r \propto (T - T_c)$, the temperature dependence of H_c close to

the phase transition reads

$$H_c(T) \propto (T_c - T) \quad \text{close to } T_c.$$

In contrast to the order parameter, the critical field depends linearly on T near the transition point (compare Figure 3.2).

Finally, one should mention that the parameters r and u are quantities which are relatively difficult to measure. However, one can easily express r and u in terms of the measurable quantities H_c and the density of superconducting particles $n_S^* = |\psi|^2 = |r|/u$.

3.2.2 Thermodynamics of the homogeneous system

Following the ideas introduced in the previous subsection, we now investigate the temperature dependence of thermodynamic quantities close to the transition point. In particular, the specific heat capacity is experimentally very well accessible and shows a characteristic jump when the material undergoes the transition from the superconducting to the normal state (compare Figure 1.7).

Let us start with the *entropy* difference between the superconducting and the normal state and then calculate the specific heat close to the transition point. According to (1.3), the entropy of a thermodynamic system is given by the negative partial derivative of the free energy (in the field-free case) with respect to temperature. Thus, the difference $\Delta s = s_S - s_N$ between the entropy values per volume in the superconducting state s_S and the normal state s_N is given by

$$\Delta s = s_S - s_N = -\frac{\partial \Delta f}{\partial T},$$

where the temperature dependence of the free energy difference per volume, $\Delta f = f_S - f_N$, is determined by $r(T)$ and $u(T)$ via equation (3.13).

We are interested again in the narrow temperature range close to the transition temperature and use the expansions (3.10) and (3.11) to find $\Delta f(T)$. Using (3.13), considering the lowest order in $(T - T_c)$, and forming the temperature derivative, we obtain

$$\Delta s = \frac{\partial}{\partial T} \frac{|r|^2}{2u} \approx \frac{\tilde{r}_0^2}{2\tilde{u}_0} \frac{\partial}{\partial T} (T - T_c)^2 = -\frac{\tilde{r}_0^2}{2\tilde{u}_0} (T_c - T). \quad (3.16)$$

From this equation we may draw an important conclusion. In the superconducting state, $T < T_c$, the entropy difference is negative, i. e., the entropy s_S in the superconducting state is lower than in the normal state. From the concepts of thermodynamics we know that the entropy represents the 'degree of disorder' of a thermodynamic system. Such a relation allows the conclusion that the superconducting state has a higher order than the normal state. This property is represented by the emergence of the superconducting order parameter ψ .

The specific heat per volume is obtained from the temperature derivative of the entropy per volume. We consider again the difference $\Delta c = c_S - c_N$ between the specific heat densities c_S and c_N in the superconducting and normal state. The corresponding thermodynamic law reads

$$\Delta c = c_S - c_N = T \frac{\partial \Delta s}{\partial T}.$$

For temperatures close to the transition, Δs is given by (3.16), and the derivative can be calculated explicitly. The result is a linear T -dependence,

$$\Delta c \approx \frac{\tilde{r}_0^2}{2\tilde{u}_0} T, \quad (3.17)$$

in the vicinity of the transition point. This result explains the discontinuity in the electronic part of the specific heat, which has

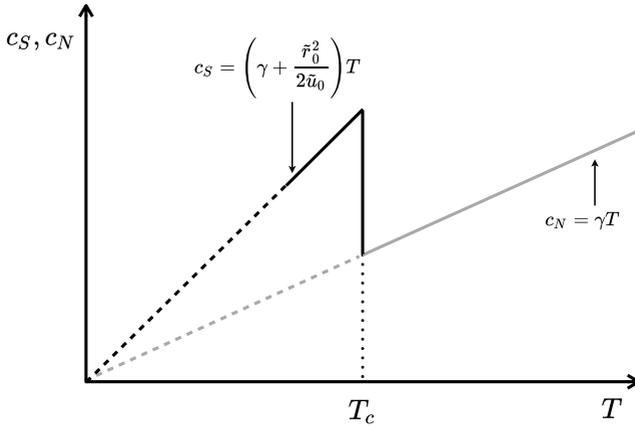


Figure 3.3: Linear temperature behavior of the specific heat in the superconducting state (black solid line) close to the transition temperature T_c . The normal state specific heat (grey solid line) is also linear but has a smaller slope. Since both c_S and c_N approach to zero for $T \rightarrow 0$ (dashed lines), a discontinuity must appear at T_c .

been found by many experiments (compare Subsection 1.4). If we assume that the superconducting state is a phenomenon caused by the conduction electrons, then the value Δc has to be attributed to the electronic part of the specific heat. Then the normal state heat capacity c_N follows a linear T behavior, $c_N = \gamma T$. Consequently, according to (3.17), the specific heat c_S in the *superconducting state* follows a linear behavior as well,

$$c_S \approx c_N + \frac{\tilde{r}_0^2}{2\tilde{u}_0} T = \left(\gamma + \frac{\tilde{r}_0^2}{2\tilde{u}_0} \right) T.$$

The T -dependence of c_S and c_N is illustrated in Figure 3.3. Both $c_S(T)$ and $c_N(T)$ describe straight lines, but the lines have different

slopes. The slope of c_S is by the value $\tilde{r}_0^2/(2\tilde{u}_0)$ larger than the slope of c_N . Both lines end in the origin, i. e., $c_S(T \rightarrow 0) = c_N(T \rightarrow 0) = 0$. Such a behavior implies that the specific heat has a *discontinuity* at the critical temperature T_c , in agreement with the experimental finding schematically shown by Figure 1.7. The height of the jump is approximately $\Delta c(T = T_c) \approx (\tilde{r}_0^2 T_c)/(2\tilde{u}_0)$.

3.3 Superconductor without magnetic field

We now generalize our theoretical description of a superconducting material to a system in which the superconducting order parameter may change in space. The perhaps simplest realization of such a system might be a superconducting material that is bounded to a normal conducting material. We are interested in the spatial dependence of the superconducting order parameter nearby the boundary to the normal conducting region. We will show that the order parameter varies within a typical length scale which is determined by the coherence length ξ .

At first, we have to generalize the expression (3.4) for the free energy to a situation where the order parameter ψ may change in space, $\psi \rightarrow \psi(\vec{r})$, i. e., it becomes a function of the position vector \vec{r} . The postulate of the Ginzburg-Landau theory is that the superconducting order parameter corresponds to the quantum mechanical wave function (3.2) describing the state of the superconducting condensate. As for any other spatially dependent wave function, the free energy must contain a term proportional to

$$\int_{\mathcal{V}} d^3r \frac{\hbar^2}{2m^*} |\vec{\nabla} \psi(\vec{r})|^2 := \int_{\mathcal{V}} d^3r \frac{\hbar^2}{2m^*} \vec{\nabla}[\psi(\vec{r})] \cdot \vec{\nabla}[\psi^*(\vec{r})] \quad (3.18)$$

describing the kinetic energy of the many-particle wave function. The integral runs over the volume \mathcal{V} of the superconductor. The brackets \square mean that the Nabla operator acts solely on the par-

ticular function inside the brackets. The effective mass of the superconducting particles is denoted by m^* . Note that in quantum mechanics the operator $\hbar\vec{\nabla}$ has the meaning of the one-particle momentum operator.

The extension of (3.4) to a spatially dependent order parameter is simply the replacement of the volume with a spatial integration over the second and third term of (3.4). In addition, the integration over the kinetic energy (3.18) is introduced. Thus, assigning the superconducting particle a mass m^* , the quantum mechanical formulation of the total free energy for the superconducting condensate reads

$$F_S[\psi] = F_N + \int_{\mathcal{V}} d^3r \left[\frac{\hbar^2}{2m^*} |\vec{\nabla}\psi(\vec{r})|^2 + r|\psi(\vec{r})|^2 + \frac{u}{2} |\psi(\vec{r})|^4 \right], \quad (3.19)$$

where F_N is the free energy of the normal state. The phenomenological parameters u and r depend on temperature and may, in principle, also depend on \vec{r} . For simplicity, however, let us here consider spatially constant parameters $u(T)$ and $r(T)$. The notation $F_S[\psi]$ means that the free energy F_S is a *functional* with respect to the complex field $\psi(\vec{r})$. The mathematical meaning is that any complex function $\psi(\vec{r})$ a number $F_S[\psi]$ is assigned.

As can be seen in (3.19), the functional $F_S[\psi]$ is invariant under a *global* gauge transformation,

$$\psi(\vec{r}) \rightarrow e^{i\alpha}\psi(\vec{r}),$$

where α is constant. In general, one has to take into account two degrees of freedom, the order parameter ψ and its conjugate ψ^* .

3.3.1 Minimization of the free energy

Now we have to search again for the particular order parameter function $\psi(\vec{r})$ for which the free energy (3.19) becomes minimal.

According to the postulates of thermodynamics, this mathematical solution is taken by the system in the thermodynamic equilibrium. The central task of the Ginzburg-Landau theory is to find this solution with respect to the given boundary conditions (surface of the superconductor).

To perform the minimization of the functional $F_S[\psi]$, we introduce at first an infinitesimal variation of the wave function $\psi(\vec{r})$. We consider the function

$$\psi(\vec{r}) + \delta\psi(\vec{r}), \quad (3.20)$$

where $\delta\psi(\vec{r})$ is an arbitrary function taking infinitesimally small values at any \vec{r} , except on the surface of the superconductor where $\delta\psi(\vec{r})$ is set to zero. The function (3.20) is thought of as an infinitesimally small variation of $\psi(\vec{r})$, thereby fulfilling the boundary conditions.

The basic idea of the minimization is constructed as follows. We calculate the free energy via equation (3.19) for the slightly varied wave function $\psi(\vec{r}) + \delta\psi(\vec{r})$ and compare the obtained value with the corresponding value of the free energy $F_S[\psi]$ without variation. Technically, this means we calculate the difference

$$\delta F_S = F_S[\psi + \delta\psi] - F_S[\psi], \quad (3.21)$$

where $\psi + \delta\psi$ denotes the function (3.20), and search for the particular function $\psi(\vec{r})$ for which $\delta F_S = 0$ for an arbitrary chosen variation $\delta\psi(\vec{r})$.

Let us at first evaluate $F_S[\psi + \delta\psi]$. Inserting (3.20) in (3.19) gives at first

$$\begin{aligned} F_S[\psi + \delta\psi] &= F_N + \int_{\mathcal{V}} d^3r \left[\frac{\hbar^2}{2m^*} \vec{\nabla}(\psi + \delta\psi) \cdot \vec{\nabla}(\psi^* + \delta\psi^*) \right. \\ &\quad \left. + r(\psi + \delta\psi)(\psi^* + \delta\psi^*) + \frac{u}{2}(\psi + \delta\psi)^2(\psi^* + \delta\psi^*)^2 \right]. \end{aligned}$$

Since the variation $\delta\psi$ is infinitesimally small, we are allowed to neglect all terms of second and higher order in the variation. The remaining terms are the 'zero' order, i. e., $F_S[\psi]$ and terms proportional to $\delta\psi$ and $\delta\psi^*$,

$$\begin{aligned}
 F_S[\psi + \delta\psi] &= F_S[\psi] \\
 &+ \int_{\mathcal{V}} d^3r \left[\frac{\hbar^2}{2m^*} \vec{\nabla}(\psi) \cdot \vec{\nabla}(\delta\psi^*) + \frac{\hbar^2}{2m^*} \vec{\nabla}(\delta\psi) \cdot \vec{\nabla}(\psi^*) \right. \\
 &\left. + r(\psi\delta\psi^* + \psi^*\delta\psi) + u|\psi|^2(\psi\delta\psi^* + \psi^*\delta\psi) \right]. \quad (3.22)
 \end{aligned}$$

To evaluate the minimization by setting (3.21) to zero, we now reformulate the first and second volume integral in (3.22) in such a way that the Nabla operator only applies to the fields ψ and ψ^* and not to the variations. By use of the general rule for an arbitrary scalar field $\alpha(\vec{r})$ and an arbitrary vector field $\vec{A}(\vec{r})$,

$$\vec{\nabla} \cdot (\alpha \vec{A}) = \vec{A} \cdot \vec{\nabla} \alpha + \alpha \vec{\nabla} \cdot \vec{A}, \quad (3.23)$$

the first volume integral in (3.22) can be written in the form

$$\begin{aligned}
 \int_{\mathcal{V}} d^3r \vec{\nabla}(\psi) \cdot \vec{\nabla}(\delta\psi^*) &= \int_{\mathcal{V}} d^3r \vec{\nabla} \cdot (\delta\psi^* \vec{\nabla} \psi) \\
 &- \int_{\mathcal{V}} d^3r \delta\psi^* \vec{\nabla} \cdot \vec{\nabla}(\psi). \quad (3.24)
 \end{aligned}$$

The first term is an integral over the divergence of a vector field. According to the Gauss theorem, it can be replaced with an integral over the surface \mathcal{S} of the superconducting material,

$$\int_{\mathcal{V}} d^3r \vec{\nabla} \cdot (\delta\psi^* \vec{\nabla} \psi) = \int_{\mathcal{S}} d\vec{A} \cdot (\delta\psi^* \vec{\nabla} \psi) = 0,$$

where $d\vec{A}$ is the surface element at a position \vec{r} on the surface \mathcal{S} . This surface integral vanishes since—throughout the surface—we

have set the variation $\delta\psi^*$ to zero. Thus, the volume integral (3.24) can be reformulated as follows,

$$\int_{\mathcal{V}} d^3r \vec{\nabla}(\psi) \cdot \vec{\nabla}(\delta\psi^*) = - \int_{\mathcal{V}} d^3r \delta\psi^* \vec{\nabla}^2\psi, \quad (3.25)$$

where on the right hand side the operator

$$\vec{\nabla}^2 = \vec{\nabla} \cdot \vec{\nabla} = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

(Laplace operator) now applies to ψ . The variation $\delta\psi^*$, however, appears as pre-factor.

The second volume integral in (3.22) is the conjugate of the one just discussed and can be treated in the same way. Thus, inserting (3.25) in (3.22), we obtain the following expression for the variation δF_S of the free energy,

$$\begin{aligned} \delta F_S &= \int_{\mathcal{V}} d^3r \delta\psi^* \left(-\frac{\hbar^2}{2m^*} \vec{\nabla}^2\psi + r\psi + u|\psi|^2\psi \right) \\ &+ \int_{\mathcal{V}} d^3r \delta\psi \left(-\frac{\hbar^2}{2m^*} \vec{\nabla}^2\psi^* + r\psi^* + u|\psi|^2\psi^* \right). \end{aligned} \quad (3.26)$$

The free energy F_S is minimal if its variation δF_S with respect to an *arbitrary* variation $\delta\psi$ (and $\delta\psi^*$) is zero, $\delta F_S = 0$. Consequently, the particular solutions for $\psi(\vec{r})$ and $\psi^*(\vec{r})$ for which $F_S[\psi]$ becomes minimal are characterized by the property that both brackets in the volume integrals in (3.26) are zero. Thus, the order parameter functions in thermodynamic equilibrium fulfill the differential equations

$$-\frac{\hbar^2}{2m^*} \vec{\nabla}^2\psi + r\psi + u|\psi|^2\psi = 0, \quad (3.27)$$

$$-\frac{\hbar^2}{2m^*} \vec{\nabla}^2\psi^* + r\psi^* + u|\psi|^2\psi^* = 0. \quad (3.28)$$

These two equations are the time-independent Schrödinger equations for the superconducting order parameter $\psi(\vec{r})$ and its complex

conjugate $\psi^*(\vec{r})$. The second equation is the complex conjugate of the first equation. The two equations are equivalent since the parameters u and r are real numbers. Differences between ψ and ψ^* may enter only through the boundary conditions. If we consider the order parameter to be real throughout the boundary, then we are allowed to treat the order parameter as a real scalar field, $\psi(\vec{r}) = \psi^*(\vec{r})$.

3.3.2 Functional derivation

Before presenting a solution of the Ginzburg-Landau equation (3.27) for a simple case of an inhomogeneous superconductor, let us quickly discuss an alternative derivation of (3.27), based on the functional derivative of the free energy. For this purpose, we consider a specific function $F(\psi_0, \dots, \psi_N)$ depending on N real variables $\psi_0 \dots \psi_N$ in the following additive form,

$$F(\psi_0, \dots, \psi_N) = \sum_{m=0}^N f(\psi_m),$$

where $f(x)$ is an arbitrary function. Such a function F resembles in its shape the Ginzburg-Landau free energy in a discretized form. Now we search for the variation of the function F . If the function is given by a summation over equal functions f , then a simple way of variation is to consider the series of the partial derivatives,

$$\frac{\partial F}{\partial \psi_n} = f'(\psi_n) \quad \text{with} \quad n = 0, \dots, N. \quad (3.29)$$

This series of derivatives describes the 'sensitivity' of F with respect to 'local' variations represented by the index number n . In the continuum limit where

$$F[\psi(\vec{r})] = \int_{\mathcal{V}} d^3r' f(\psi(\vec{r}'))$$

describes a functional with respect to the function $\psi(\vec{r})$ we now define a local variation analog to the discrete case (3.29). The functional derivative defined by

$$\frac{\delta F}{\delta \psi(\vec{r})} := f'(\psi(\vec{r})) \quad (3.30)$$

represents the series of partial derivatives (3.29) in the continuum limit, where the index n is now replaced with the position vector \vec{r} . Note that the functional derivative is by its definition (3.30) a scalar field describing the 'local' variations with respect to $\psi(\vec{r})$ at position \vec{r} .

The advantage of introducing the functional derivative is that the minimization of the free energy can be done relatively quickly by calculating the first derivatives of the free energy density with respect to ψ and ψ^* . Namely, by partial integration the free energy (3.19) can be rewritten in the form

$$F_S = F_N + \int_{\mathcal{V}} d^3r f(\psi(\vec{r}), \psi^*(\vec{r})), \quad (3.31)$$

where the energy density f is formally a function of ψ and its conjugate ψ^* . The minimization of F_S is done by forming the functional derivatives of F_S with respect to ψ and ψ^* and setting them to zero.

Generalizing the definition (3.30) to a function depending on two variables, we obtain the following equation for the minimization,

$$\frac{\delta F_S}{\delta \psi(\vec{r})} := \frac{\partial f(\psi, \psi^*)}{\partial \psi} = 0. \quad (3.32)$$

Note that before evaluating the partial derivative of f with respect to ψ , the integral is conveniently written in such a way that ψ appears *explicitly* and that no differential operator acts on ψ . This

becomes clear by considering the Ginzburg-Landau potential (3.19),

$$F_S[\psi] = F_N + \int_{\mathcal{V}} d^3r \left[\frac{\hbar^2}{2m^*} \vec{\nabla}[\psi(\vec{r})] \cdot \vec{\nabla}[\psi^*(\vec{r})] + r|\psi(\vec{r})|^2 + \frac{u}{2}|\psi(\vec{r})|^4 \right],$$

where (3.18) is used. Now we reformulate again the first volume integral such that the first Nabla operator acting on ψ is 'shifted' to apply on ψ^* . This can be done using the same arguments as for the derivation of expression (3.25) by applying the rules of vector analysis and choosing a surface outside the superconductor where $\psi = 0$. We obtain

$$F_S[\psi] = F_N + \int_{\mathcal{V}} d^3r \left[-\frac{\hbar^2}{2m^*} \psi(\vec{r}) \vec{\nabla}^2 \psi^*(\vec{r}) + r|\psi(\vec{r})|^2 + \frac{u}{2}|\psi(\vec{r})|^4 \right], \quad (3.33)$$

i. e., an expression of the form (3.31), where in the corresponding density function

$$\begin{aligned} f(\psi(\vec{r}), \psi^*(\vec{r})) &= -\frac{\hbar^2}{2m^*} \psi(\vec{r}) \vec{\nabla}^2 \psi^*(\vec{r}) + r|\psi(\vec{r})|^2 + \frac{u}{2}|\psi(\vec{r})|^4 \\ &= -\frac{\hbar^2}{2m^*} \psi \vec{\nabla}^2 \psi^* + r\psi\psi^* + \frac{u}{2}\psi^2(\psi^*)^2 \end{aligned} \quad (3.34)$$

the function ψ appears in the function $f(\psi, \psi^*)$ in a form such that no differential operator acts on ψ . Now we may calculate the functional derivative (3.32) by simply evaluating the partial derivative of (3.34) with respect to ψ . Setting the functional derivative to zero (minimization of the free energy), we immediately obtain the non-linear Schrödinger equation (3.28) for ψ^* ,

$$\frac{\partial f(\psi, \psi^*)}{\partial \psi} = -\frac{\hbar^2}{2m^*} \vec{\nabla}^2 \psi^* + r\psi^* + u\psi(\psi^*)^2 = 0. \quad (3.35)$$

The equation for ψ is obtained by evaluating the functional derivative with respect to ψ^* . It leads to the complex conjugate of equation (3.35).

3.3.3 Ginzburg-Landau coherence length

Now we study a solution of the Ginzburg-Landau equation (3.27) for a simple case of an inhomogeneous system, namely a superconducting material which is bounded to a normal conducting material. As will be shown in the following, the solution for ψ shows a characteristic behavior nearby the boundary and changes in space within a certain length scale, the Ginzburg-Landau coherence length.

We consider an infinite flat interface lying in the y - z plane and separating a normal metal in the region $x < 0$ from a superconductor in the region $x > 0$. The symmetry with respect to y and z reduces equation (3.27) to a one-dimensional problem, i. e., the order parameter ψ depends only on x and the Laplace operator $\vec{\nabla}^2$ can be replaced with the second derivative with respect to x ,

$$-\frac{\hbar^2}{2m^*} \frac{d^2\psi}{dx^2} + r\psi + u|\psi|^2\psi = 0. \quad (3.36)$$

We chose a gauge in which ψ is real. Furthermore, it is convenient to refer ψ to its bulk value, $\psi_0 = \sqrt{-r/u}$, as calculated in Section 3.2, i. e., we write $\psi(x)$ in the form $\psi(x) = \psi_0 f(x)$, where $f(x)$ is a dimensionless function with the property $f(x \rightarrow \infty) = 1$. On the boundary $x = 0$ to the normal state material the order parameter is zero, $\psi(x = 0) = f(x = 0) = 0$. Inserting in (3.36) $\psi(x) = \sqrt{-r/u} f(x)$, we obtain at first

$$-\frac{\hbar^2}{2m^*} \sqrt{-\frac{r}{u}} \frac{d^2 f(x)}{dx^2} + r \sqrt{-\frac{r}{u}} f(x) + u \left(-\frac{r}{u}\right)^{\frac{3}{2}} f^3(x) = 0.$$

Division by $(r\sqrt{-r/u})$ leads to

$$-\frac{\hbar^2}{2m^*r} \frac{d^2 f(x)}{dx^2} + f(x) + \frac{u}{r} \left(-\frac{r}{u}\right) f^3(x) = 0,$$