9 Ginzburg–Landau Theory of Superconductivity

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1 Introduction

Historically, the first major step in the theoretical description of superconductivity was taken by the brothers F. and H. London [1]. They proposed a theory for the electromagnetic properties of superconductors—the ideal conductivity and the Meißner–Ochsenfeld effect—based on a two-fluid picture. Specifically, they proposed that part of the electrons in a superconductor behave like a dissipationless superfluid, whereas the rest behave like a normal fluid showing Ohmic dissipation. Conceptually, London theory augments the Maxwell equations of electromagnetism by constitutive equations describing superconducting materials. The density of the superfluid, n_s, is treated as given and there is no way to understand the dependence of n_s on, for example, temperature or magnetic field. Moreover, n_s is assumed to be constant in time and uniform in space—an assumption that is expected to fail close to the surface of a superconductor.

These deficiencies were cured by the Ginzburg–Landau theory [2] put forward in 1950. The starting point is the much more general Landau theory of phase transitions [3]. Both these theories are phenomenological in the sense that they do not rely on a particular microscopic mechanism but only on quite general symmetry principles.

The next large step was the microscopic mean-field theory of superconductivity developed by Bardeen, Cooper, and Schrieffer (BCS) [4] in 1957. Soon thereafter, Gor'kov [5] derived Ginzburg–Landau theory from BCS theory and thus clarified the microscopic interpretation of the quantities appearing in Ginzburg–Landau theory. The relation between Ginzburg–Landau theory and BCS theory is somewhat similar to the one between phenomenological thermodynamics and statistical physics. In particular, the development of the latter does not diminish the usefulness of the former. For example, predictions derived in the framework of Ginzburg–Landau theory do not suffer from lack of knowledge of the underlying microscopic mechanisms.

2 Landau theory of phase transitions

Landau [3] introduced the concept of the *order parameter* to describe phase transitions. In this context, an order parameter is a thermodynamic variable that is zero on one side of the transition and nonzero on the other. The theory neglects fluctuations, which means that the order parameter is assumed to be constant in space and time. The appropriate thermodynamic potential is written as a function of the order parameter Δ and certain other thermodynamic variables such as pressure or volume, magnetic field, etc. We will always call the potential the *free energy* F, but whether it really is a free energy, a free enthalpy, or something else depends on which quantities are given (pressure vs. volume etc.). Hence, we write $F = F(\Delta, T)$, where T is the temperature, and further variables have been suppressed. The equilibrium state at temperature T is the ensemble state that minimizes the free energy $F(\Delta, T)$.

Landau's idea was to expand F in terms of Δ, including only those terms that are allowed by the symmetry of the system and keeping the minimum number of the lowest-order terms required to get nontrivial results. The strength of Landau theory is that we do not need to know the underlying microscopic description, e.g., the Hamiltonian, but only the character of the order parameter and the symmetries of the system.

As an example, we consider the ferromagnetic Heisenberg model. The order parameter is the magnetization $\mathbf{M} \in \mathbb{R}^3$. The underlying Hamiltonian and thus also the free energy F are invariant under all rotations of $\mathbf{M}$. This is a $\mathrm{SO}(3)$ symmetry since $\mathrm{SO}(3)$ is the group of all proper rotation matrices in three-dimensional space. Furthermore, it is invariant under time reversal, which flips the magnetization, $\mathbf{M} \mapsto -\mathbf{M}$. This time-reversal symmetry is redundant in this case but not in general.

Following Landau, we assume F to be a smooth function at $\mathbf{M} = 0$ so that we can expand F in a Taylor series in $\mathbf{M}$ about $\mathbf{M} = 0$, with nonzero radius of convergence. The leading terms are

$$F = F_0 + \alpha\, \mathbf{M} \cdot \mathbf{M} + \frac{\beta}{2}\, (\mathbf{M} \cdot \mathbf{M})^2 + \mathcal{O}\big((\mathbf{M} \cdot \mathbf{M})^3\big), \tag{1}$$

where $\mathcal{O}\big((\mathbf{M} \cdot \mathbf{M})^3\big)$ represents terms of higher order, which we suppress from now on. It is by no means necessary to truncate the expansion at this order but this truncation is sufficient to describe second-order phase transitions. We must include enough terms to make F bounded from below. For example, the above truncation would be invalid for $\beta < 0$. Including an explicit factor of $1/2$ in the β term is a convention. F_0, α, and β are functions of temperature (and possibly pressure etc.).

The zero-order term F_0 is the free energy of the nonmagnetic state. While it may have a strong temperature dependence, it is irrelevant for the magnetic phase transition. One therefore commonly drops this term, which means that F is taken to be the *difference* of the free energies in the magnetic and the nonmagnetic states. We will follow this practice.

What is the corresponding expansion for a superfluid or superconductor? Lacking a microscopic theory but suspecting an analogy to the well-understood Bose–Einstein condensation, Ginzburg and Landau [2] assumed that a superfluid is described by a single one-particle wave function $\Psi_s(\mathbf{r})$. They imposed the plausible normalization

$$\int d^3r\, |\Psi_s(\mathbf{r})|^2 = N_s = n_s V, \tag{2}$$

where N_s is the total number of particles in the condensate and V is the volume of the system. They then chose the complex amplitude ψ of $\Psi_s(\mathbf{r})$ as the order parameter, with the normalization $|\psi|^2 \propto n_s$. They thereby neglected the spatial variation of $\Psi_s(\mathbf{r})$ on an atomic scale. The order parameter is a complex number.

The free energy must not depend on the global phase of ψ since the global phase of quantum states is not observable. The relevant symmetry is thus a global $\mathrm{U}(1)$ symmetry under phase change. ($\mathrm{U}(1)$ is the group of $1{\times}1$ unitary matrices, i.e., numbers on the unit circle in the complex plane.) Thus we obtain the expansion

$$F = \alpha\, \psi^*\psi + \frac{\beta}{2}\, (\psi^*\psi)^2 = \alpha\, |\psi|^2 + \frac{\beta}{2}\, |\psi|^4. \tag{3}$$

Odd powers are excluded since they are not differentiable at $\psi = 0$. If $\beta > 0$, which is not guaranteed by symmetry but is true for superconductors and superfluids, $F(\psi)$ is bounded from below. Now there are two cases, which are illustrated in Fig. 1:

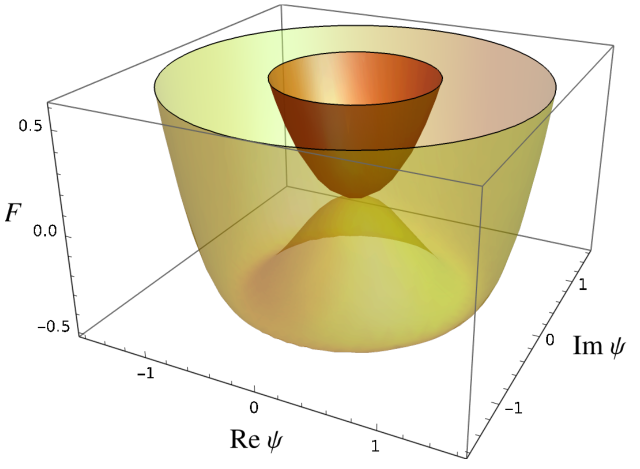

Fig. 1: *Landau free energy $F(\psi)$ for a superfluid or superconductor with $\alpha/\beta = 1$ (orange) and $\alpha/\beta = -1$ (yellow).*

- For $\alpha \geq 0$, $F(\psi)$ has a single minimum at $\psi = 0$. Thus the equilibrium state has $n_s = 0$. This is clearly a normal fluid or normal metal.
- For $\alpha < 0$, $F(\psi)$ has a ring of minima with equal modulus $|\psi|$ but arbitrary phase. This shape is often called the wine-bottle or Mexican-hat potential. We easily see that

$$\frac{\partial F}{\partial|\psi|} = 2\alpha\,|\psi| + 2\beta\,|\psi|^3 \stackrel{!}{=} 0 \tag{4}$$

has the solutions $|\psi| = 0$, which describes a maximum, and

$$|\psi| = \sqrt{-\frac{\alpha}{\beta}}, \tag{5}$$

which describes the ring of minima. Note that the radicand is positive.

In Landau theory, the phase transition clearly occurs when $\alpha = 0$. Since then $T = T_c$ by definition, it is useful to expand α and β to leading order in T around T_c. Hence,

$$\alpha \cong \alpha'\,(T - T_c), \qquad \alpha' > 0, \tag{6}$$

$$\beta \cong \text{const.} \tag{7}$$

Then the order parameter satisfies

$$|\psi| \cong \sqrt{-\frac{\alpha'\,(T - T_c)}{\beta}} = \sqrt{\frac{\alpha'}{\beta}}\,\sqrt{T_c - T} \quad \text{for} \quad T \leq T_c. \tag{8}$$

The scaling $|\psi| \propto (T_c - T)^{1/2}$ with exponent $1/2$ is characteristic for mean-field theories. Mean-field theories do not predict the true value of the critical exponent since they neglect fluctuations. However, this is not a dramatic problem for superconductors in three dimensions since deviations from mean-field behavior are limited to a very narrow temperature interval around T_c and are typically unobservable [6].

All solutions with this value of $|\psi|$ minimize the free energy. In a given experiment, only one of them is realized. This specific equilibrium state has an order parameter $\psi = |\psi|\, e^{i\phi}$ with some fixed phase ϕ and is thus not invariant under changes of the phase. We say that the global $\mathrm{U}(1)$ symmetry is *spontaneously broken* since the free energy F has it but the specific equilibrium state does not.

The expansion of F up to fourth order is only justified as long as ψ is small. Its quantitative validity is thus limited to temperatures not too far below T_c. However, one can often gain insight into the qualitative behavior of a system by applying Landau theory outside of this range.

Note that the true thermodynamic free energy as a function of given variables (here temperature) is F evaluated at the equilibrium solution for ψ. From this, we can calculate further thermodynamic variables. In particular, the entropy is $S_s = -\partial F/\partial T$. Since the expression for F above only includes the contributions of the superfluid the entropy calculated from it will also only contain these contributions, which is here indicated by the subscript "*s*". The missing contribution from the normal state is generally large but smooth at T_c. For $T \geq T_c$, the free energy is $F(\psi{=}0) = 0$ and thus we find $S_s = 0$. For $T < T_c$ we instead obtain

$$\begin{aligned} S_s &= -\frac{\partial}{\partial T}\, F\left(\sqrt{-\frac{\alpha}{\beta}}\right) = -\frac{\partial}{\partial T}\left(-\frac{\alpha^2}{\beta} + \frac{1}{2}\frac{\alpha^2}{\beta}\right) = \frac{\partial}{\partial T}\,\frac{\alpha^2}{2\beta} \\ &\cong \frac{\partial}{\partial T}\,\frac{(\alpha')^2}{2\beta}\,(T{-}T_c)^2 = \frac{(\alpha')^2}{\beta}\,(T{-}T_c) = -\frac{(\alpha')^2}{\beta}\,(T_c{-}T) < 0. \end{aligned} \tag{9}$$

The entropy is continuous at $T = T_c$. The corresponding heat-capacity contribution is

$$C_s = T\,\frac{\partial S_s}{\partial T} = \begin{cases} \dfrac{(\alpha')^2}{\beta}\,T & \text{for } T < T_c, \\ 0 & \text{for } T \geq T_c. \end{cases} \tag{10}$$

Thus, the heat capacity has a jump discontinuity of

$$\varDelta C_s = -\frac{(\alpha')^2}{\beta}\,T_c \tag{11}$$

at T_c. The phase transition is of *second* order since a second derivative of the thermodynamic potential F with respect to its natural variable T is the lowest discontinuous one.

3 Ginzburg–Landau theory for neutral superfluids

To be able to describe spatially nonuniform situations, Ginzburg and Landau had to go beyond the Landau description for a constant order parameter [2]. To do so, they included gradient terms in the free energy. We will first discuss the case of a superfluid of electrically neutral particles (think of ^{4}He). We define a macroscopic condensate wave function $\psi(\mathbf{r})$, which is essentially given by $\varPsi_s(\mathbf{r})$ averaged over length scales large compared to atomic distances. In the spirit of Landau theory, Ginzburg and Landau included the simplest term containing gradients of ψ and allowed by symmetry into the free energy:

$$F[\psi] = \int d^3r\, \left[\alpha\,|\psi(\mathbf{r})|^2 + \frac{\beta}{2}\,|\psi(\mathbf{r})|^4 + \gamma\,\big(\nabla\psi(\mathbf{r})\big)^*\!\cdot\nabla\psi(\mathbf{r})\right], \tag{12}$$

where α and β are now defined as densities. We expect spatial changes of $\psi(\mathbf{r})$ to cost energy—this is analogous to the energy of domain walls in magnetic systems—which implies that $\gamma>0$. The free energy is now a *functional* of ψ, also called the Ginzburg–Landau functional. Functionals are usually written with their argument (a function) in square brackets.

If we interpret $\psi(\mathbf{r})$ as a coarse-grained condensate wave function it is natural to identify the gradient term as a kinetic energy by writing

$$F[\psi] = \int d^3r \left[\alpha\, |\psi|^2 + \frac{\beta}{2}\, |\psi|^4 + \frac{1}{2m^*} \left| \frac{\hbar}{i}\, \nabla\psi \right|^2 \right], \tag{13}$$

where m^* is an effective mass and $\gamma = \hbar^2/2m^*$. We have suppressed the spatial argument for ease of writing.

The free energy is minimal in equilibrium for the canonical ensemble. So, in principle, we have to find the distribution of microstates that minimizes F. Following Ginzburg and Landau, we use a mean-field approximation, where this distribution is described only in terms of the spatially dependent order-parameter field $\psi(\mathbf{r})$. Again, $F[\psi]$ is the true free energy in the thermodynamic sense only for the equilibrium solution for ψ. From $F[\psi]$, we can derive a differential equation for the function $\psi(\mathbf{r})$ that minimizes F. The derivation is very similar to the derivation of the Lagrange equation of the second kind from Hamilton's principle known from classical mechanics. We write the condition in terms of a functional derivative,

$$\frac{\delta F}{\delta\psi^*(\mathbf{r})} = 0 \tag{14}$$

and recall that ψ and ψ^* have to be treated as independent since $\operatorname{Re}\psi$ and $\operatorname{Im}\psi$ are independent. We perform an integration by parts for the kinetic-energy term, ignore an irrelevant boundary term, and obtain

$$\begin{aligned}
\frac{\delta F}{\delta\psi^*(\mathbf{r})} &= \frac{\delta}{\delta\psi^*(\mathbf{r})} \int d^3r' \left[\alpha\, \psi^*(\mathbf{r}')\psi(\mathbf{r}') + \frac{\beta}{2}\, [\psi^*(\mathbf{r}')]^2\, \psi^2(\mathbf{r}') - \frac{\hbar^2}{2m^*}\, \psi^*(\mathbf{r}')[\nabla']^2\psi(\mathbf{r}') \right] \\
&= \int d^3r' \left[\alpha\, \delta(\mathbf{r}'-\mathbf{r})\psi(\mathbf{r}') + \beta\, \delta(\mathbf{r}'-\mathbf{r})\psi^*(\mathbf{r}')\, \psi^2(\mathbf{r}) - \frac{\hbar^2}{2m^*}\, \delta(\mathbf{r}'-\mathbf{r})[\nabla']^2\psi(\mathbf{r}') \right] \\
&= \alpha\, \psi(\mathbf{r}) + \beta\, \psi^*(\mathbf{r})\, \psi^2(\mathbf{r}) - \frac{\hbar^2}{2m^*}\, \nabla^2\psi(\mathbf{r}) = 0.
\end{aligned} \tag{15}$$

Rearranging terms and suppressing the spatial argument yields

$$-\frac{\hbar^2}{2m^*}\, \nabla^2\psi + \alpha\, \psi + \beta\, |\psi|^2\psi = 0. \tag{16}$$

This equation is very similar to the time-independent Schrödinger equation but, interestingly, contains a nonlinear term. It is also called the (time-independent) Gross–Pitaevskii equation, in particular when derived from a microscopic description of an interacting superfluid [7, 8]. The nonlinear term describes a self-interaction of the condensate.

As an example, we apply this equation to find the variation of $\psi(\mathbf{r})$ close to the surface of a superfluid filling the half space $x > 0$. We impose the boundary condition $\psi(x{=}0) = 0$ and

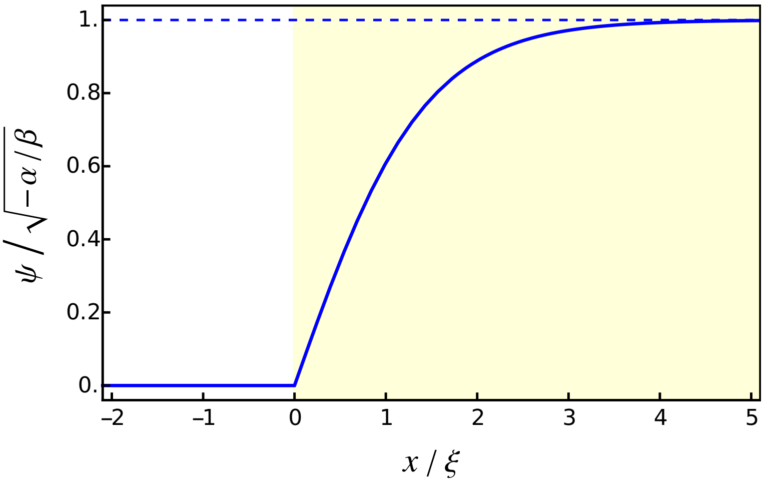

Fig. 2: *Superfluid order parameter ψ as a function of spatial coordinate x, from Ginzburg–Landau theory. The superfluid fills the half space $x > 0$.*

assume that the solution only depends on x. Then

$$-\frac{\hbar^2}{2m^*}\,\psi''(x) + \alpha\,\psi(x) + \beta\,|\psi(x)|^2\,\psi(x) = 0. \tag{17}$$

For $x \to \infty$, we should obtain the uniform Landau solution

$$\lim_{x\to\infty} \psi(x) = \sqrt{-\frac{\alpha}{\beta}}. \tag{18}$$

Writing

$$\psi(x) = \sqrt{-\frac{\alpha}{\beta}}\, f(x), \tag{19}$$

we obtain

$$\underbrace{-\frac{\hbar^2}{2m^*\alpha}}_{>0} f''(x) + f(x) - f(x)^3 = \xi^2\, f''(x) + f(x) - f(x)^3 = 0. \tag{20}$$

This equation contains a characteristic length scale, the *Ginzburg–Landau coherence length*

$$\xi \equiv \sqrt{-\frac{\hbar^2}{2m^*\alpha}} \cong \sqrt{\frac{\hbar^2}{2m^*\alpha'\,(T_c{-}T)}}. \tag{21}$$

It has a strong temperature dependence and actually diverges for $T \to T_c^-$. Although it is nonlinear, Eq. (20) can be solved analytically. It is easy to check that

$$f(x) = \tanh\frac{x}{\sqrt{2}\,\xi} \tag{22}$$

is a solution satisfying the boundary conditions at $x = 0$ and $x \to \infty$. The solution is sketched in Fig. 2.

3.1 Fluctuations for $T > T_c$

So far, we have only considered the state ψ_0 that minimizes the functional $F[\psi]$. At nonzero temperatures, the system will fluctuate about ψ_0. For a uniform system we have

$$\psi(\mathbf{r}) = \psi_0 + \delta\psi(\mathbf{r}), \tag{23}$$

with $\psi_0 = \text{const}$. We consider the cases $T > T_c$ and $T < T_c$ separately.

For $T > T_c$, the mean-field solution is $\psi_0 = 0$ so that $\psi(\mathbf{r}) = \delta\psi(\mathbf{r})$. We now write the partition function Z as a sum of Boltzmann factors containing the Ginzburg–Landau functional of all possible states,

$$Z = \int D^2\psi \; e^{-F[\psi]/k_B T}. \tag{24}$$

This equation requires some discussion. We are obviously using $F[\psi]$ as if it were the Hamiltonian of the field $\psi(\mathbf{r})$, although we have introduced it as a generalized free energy. Recall that $\psi(\mathbf{r})$ is the condensate wave function, averaged over atomic length scales. More precisely, fluctuations of the wave function on shorter length scales have been integrated out so that $F[\psi]$ can be understood as a thermodynamic free energy with respect to these small-scale fluctuations but it is the *energy* for the longer-scale fluctuations we are considering here. This has been explained nicely by Ma in Ref. [9].

Equation (24) contains a functional integral over infinitely many complex variables, namely the values of $\psi(\mathbf{r}) \in \mathbb{C}$ for all $\mathbf{r}$. The mathematical details go beyond the scope of this lecture but are not essential to understand the physics. A good introduction can be found in Ref. [10]. The integral is difficult to evaluate. In the common *Gaussian approximation*, we restrict $F[\psi]$ to second order in $\delta\psi = \psi$. This allows to evaluate Z by Fourier transformation: We start from

$$F[\psi] \cong \int d^3r \left[\alpha\, \psi^*(\mathbf{r})\psi(\mathbf{r}) + \frac{\hbar^2}{2m^*} \left(\frac{1}{i}\,\nabla\psi(\mathbf{r})\right)^* \cdot \frac{1}{i}\nabla\psi(\mathbf{r})\right] \tag{25}$$

and insert

$$\psi(\mathbf{r}) = \frac{1}{\sqrt{V}} \sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}}\, \psi_{\mathbf{k}}, \tag{26}$$

with the large volume V of the system, which gives

$$F[\psi] \cong \frac{1}{V} \sum_{\mathbf{k}\mathbf{k}'} \underbrace{\int d^3r\, e^{-i\mathbf{k}\cdot\mathbf{r}+i\mathbf{k}'\cdot\mathbf{r}}}_{V\delta_{\mathbf{k}\mathbf{k}'}} \left[\alpha\, \psi^*_{\mathbf{k}}\psi_{\mathbf{k}'} + \frac{\hbar^2}{2m^*}\,(\mathbf{k}\psi_{\mathbf{k}})^* \cdot \mathbf{k}'\psi_{\mathbf{k}'}\right] = \sum_{\mathbf{k}} \left(\alpha + \frac{\hbar^2k^2}{2m^*}\right) \psi^*_{\mathbf{k}}\psi_{\mathbf{k}}. \tag{27}$$

Thus we obtain a Gaussian integral, which is easily evaluated:

$$Z \cong \prod_{\mathbf{k}} \left\{ \int_{\mathbb{C}} d^2\psi\, \exp\left(-\frac{1}{k_BT}\left(\alpha + \frac{\hbar^2k^2}{2m^*}\right)\psi^*\psi\right)\right\} = \prod_{\mathbf{k}} \frac{\pi k_B T}{\alpha + \frac{\hbar^2k^2}{2m^*}}. \tag{28}$$

From this, we can obtain thermodynamic quantities. For example, the superfluid contribution to the heat capacity is

$$C_s = -T\,\frac{\partial^2 F}{\partial T^2} = T\frac{\partial^2}{\partial T^2}\,k_BT\ln Z \cong k_BT\,\frac{\partial^2}{\partial T^2}\,T\sum_{\mathbf{k}} \ln\frac{\pi k_BT}{\alpha + \frac{\hbar^2k^2}{2m^*}}. \tag{29}$$

We only consider the term that is singular at T_c. It stems from the temperature dependence of $\alpha \cong \alpha' \, (T - T_c)$. This term is

$$C_{\text{crit}} \cong -k_B T^2 \frac{\partial^2}{\partial T^2} \sum_{\mathbf{k}} \ln \left(\alpha + \frac{\hbar^2 k^2}{2m^*} \right) = k_B T^2 \sum_{\mathbf{k}} \frac{(\alpha')^2}{\left(\alpha + \frac{\hbar^2 k^2}{2m^*} \right)^2}. \tag{30}$$

Going over to an integral over $\mathbf{k}$, corresponding to the thermodynamic limit $V \to \infty$, we obtain

$$C_{\text{crit}} \cong k_B T^2 \left(\frac{2m^*}{\hbar^2} \right)^2 (\alpha')^2 \, V \int \frac{d^3k}{(2\pi)^3} \, \frac{1}{\left(k^2 + \frac{2m^* \alpha}{\hbar^2} \right)^2} = \frac{k_B T^2}{2\sqrt{2}\,\pi} \, \frac{(m^*)^{3/2}}{\hbar^3} \, (\alpha')^2 \, V \, \frac{1}{\sqrt{\alpha}}. \tag{31}$$

We obtain $C_{\text{crit}} \propto (T - T_c)^{-1/2}$. The exponent $-1/2$ of the specific heat is characteristic for Gaussian fluctuations. Recall that at the mean-field level, C_s just showed a step at T_c. We find that superfluid fluctuations in the normal state lead to a divergence for $T \to T_c^+$.

The derivation shows that for any $\mathbf{k}$ we have two fluctuation modes with dispersion $\epsilon_{\mathbf{k}} = \alpha + (\hbar^2/2m^*) \, k^2$, corresponding to the real and imaginary parts of $\psi_{\mathbf{k}}$. The dispersion has an *energy gap* $\alpha > 0$. In the language of field theory, one says that the superfluid fluctuations above T_c form two degenerate *massive* branches.

3.2 Fluctuations for $T < T_c$

Below T_c, the situation is more complex due to the wine-bottle potential from Fig. 1: All states with amplitude $|\psi_0| = \sqrt{-\alpha/\beta}$ are equally good mean-field solutions. It is plausible that fluctuations of the phase have low energies since global changes of the phase do not change F. To see this, we write $\psi(\mathbf{r}) = \left[\psi_0 + \delta\psi(\mathbf{r})\right] e^{i\phi(\mathbf{r})}$, where ψ_0 and $\delta\psi$ are now real and $\psi_0 = \sqrt{-\alpha/\beta} > 0$. The Ginzburg–Landau functional becomes

$$\begin{aligned} F[\psi] \cong \int d^3r \bigg[&\alpha \, (\psi_0 + \delta\psi)^2 + \frac{\beta}{2} \, (\psi_0 + \delta\psi)^4 + \frac{\hbar^2}{2m^*} \left(\frac{1}{i} \, (\nabla\delta\psi) e^{i\phi} + (\psi_0 + \delta\psi)(\nabla\phi) e^{i\phi} \right)^* \\ &\cdot \left(\frac{1}{i} \, (\nabla\delta\psi) e^{i\phi} + (\psi_0 + \delta\psi)(\nabla\phi) e^{i\phi} \right) \bigg]. \end{aligned} \tag{32}$$

Keeping only terms up to second order in the fluctuations (Gaussian approximation), we obtain

$$\begin{aligned} F[\delta\psi, \phi] &\cong \int d^3r \, \bigg[\alpha \, \delta\psi^2 + 3\beta\psi_0^3 \, \delta\psi^2 + \frac{\hbar^2}{2m^*} \left(\frac{1}{i} \, \nabla\delta\psi \right)^* \cdot \frac{1}{i} \, \nabla\delta\psi \\ &\quad + \frac{\hbar^2}{2m^*} \underbrace{\left(\left(\frac{1}{i} \, \nabla\delta\psi \right)^* \cdot \psi_0 \nabla\phi + (\psi_0 \nabla\phi)^* \cdot \frac{1}{i} \, \nabla\delta\psi \right)}_{=\,0} + \frac{\hbar^2}{2m^*} \, (\psi_0 \nabla\phi)^* \cdot \psi_0 \nabla\phi \bigg] \\ &= \int d^3r \, \left[-2\alpha \, \delta\psi^2 + \frac{\hbar^2}{2m^*} \left(\frac{1}{i} \, \nabla\delta\psi \right)^* \cdot \frac{1}{i} \, \nabla\delta\psi - \frac{\hbar^2}{2m^*} \frac{\alpha}{\beta} \, (\nabla\phi)^* \cdot \nabla\phi \right], \end{aligned} \tag{33}$$

up to an irrelevant constant. First-order terms have to cancel. The functional can be simplified by Fourier transformation, in analogy to the case $T > T_c$:

$$F[\delta\psi, \phi] \cong \sum_{\mathbf{k}} \left[\left(-2\alpha + \frac{\hbar^2 k^2}{2m^*} \right) \delta\psi_{\mathbf{k}}^* \, \delta\psi_{\mathbf{k}} - \frac{\alpha}{\beta} \, \frac{\hbar^2 k^2}{2m^*} \, \phi_{\mathbf{k}}^* \phi_{\mathbf{k}} \right]. \tag{34}$$

Up to second order, there are no terms mixing amplitude fluctuations $\delta\psi$ and phase fluctuations ϕ. The amplitude fluctuations are massive with an energy gap $-2\alpha = 2\alpha'\,(T_c{-}T)$. They are not degenerate. On the other hand, phase fluctuations are *massless* with energies

$$\epsilon^{\phi}_{\mathbf{k}} = -\frac{\alpha}{\beta}\,\frac{\hbar^2}{2m^*}\,k^2. \tag{35}$$

The appearance of these ungapped so-called *Goldstone modes* is characteristic for systems with spontaneously broken continuous symmetries. We note without derivation that the heat capacity diverges like $C \sim (T_c{-}T)^{-1/2}$ for $T \to T_c^-$, analogous to the case $T > T_c$.

3.3 Time-dependent Ginzburg–Landau theory

The Ginzburg–Landau approach can be extended to describe dynamics. The coarse-grained wave function $\psi(\mathbf{r},t)$ is then time dependent. The relevant quantity is the Lagrange-density functional $\mathcal{L}[\psi,\nabla\psi,\dot\psi]$, from which one obtains the action

$$\mathcal{S} = \int_{t_i}^{t_f} dt\, L = \int_{t_i}^{t_f} dt \int d^3r\, \mathcal{L}, \tag{36}$$

where t_i and t_f are the initial and final time, respectively, and L is the Lagrange functional. Equations of motion for $\psi(\mathbf{r},t)$ follow from the variational principle $\delta\mathcal{S} = 0$, in analogy to the Maxwell equations in electrodynamics [10].

We only give the main expressions for the case of a neutral superfluid, without derivations. The Lagrange density is

$$\mathcal{L} = i\hbar\,\psi^*\,\frac{\partial\psi}{\partial t} - \alpha\,|\psi|^2 - \frac{\beta}{2}\,|\psi|^4 - \frac{\hbar^2}{2m^*}\,|\nabla\psi|^2 \tag{37}$$

so that the Lagrange functional reads

$$L = \int d^3r\, i\hbar\,\psi^*\,\frac{\partial\psi}{\partial t} - F[\psi], \tag{38}$$

with the Ginzburg–Landau functional F. From $\delta\mathcal{S} = 0$, we then obtain, in analogy to the derivation of Eq. (16),

$$i\hbar\,\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m^*}\,\nabla^2\psi + \alpha\,\psi + \beta\,|\psi|^2\psi. \tag{39}$$

This time-dependent Ginzburg–Landau or Gross–Pitaevskii equation [7,8] is clearly a nonlinear generalization of the time-dependent Schrödinger equation. It allows us to calculate the time evolution of the macroscopic wave function.

For illustration, we revisit the superfluid fluctuations for $T < T_c$ starting from time-dependent Ginzburg–Landau theory. Making the time-derivative term more symmetric by means of integration by parts and writing $\psi(\mathbf{r},t) = \big[\psi_0{+}\delta\psi(\mathbf{r},t)\big]\, e^{i\phi(\mathbf{r},t)}$ in analogy to Sec. 3.2, we obtain

$$\frac{i\hbar}{2}\,\psi^*\,\frac{\partial\psi}{\partial t} - \frac{i\hbar}{2}\,\frac{\partial\psi^*}{\partial t}\,\psi = \frac{i\hbar}{2}\,(\psi_0{+}\delta\psi)\,\frac{\partial\delta\psi}{\partial t} + \frac{i\hbar}{2}\,(\psi_0{+}\delta\psi)^2\, i\,\frac{\partial\phi}{\partial t}$$

$$
\begin{aligned}
&- \frac{i\hbar}{2} \frac{\partial \delta\psi}{\partial t} (\psi_0 + \delta\psi) - \frac{i\hbar}{2} (\psi_0 + \delta\psi)^2 (-i) \frac{\partial \phi}{\partial t} \\
&= -\hbar (\psi_0 + \delta\psi)^2 \frac{\partial \phi}{\partial t}
\end{aligned} \tag{40}
$$

and thus, to second order,

$$
\mathcal{L} \cong -2\hbar \sqrt{-\frac{\alpha}{\beta}}\, \delta\psi \frac{\partial \phi}{\partial t} + 2\alpha\, \delta\psi^2 - \frac{\hbar^2}{2m^*} \left(\frac{1}{i} \nabla \delta\psi \right)^* \cdot \frac{1}{i} \nabla \delta\psi + \frac{\hbar^2}{2m^*} \frac{\alpha}{\beta} (\nabla\phi)^* \cdot \nabla\phi. \tag{41}
$$

First-order terms cancel due to Eq. (39). This form shows that the *canonically conjugate field* to the phase ϕ is

$$
\pi \equiv \frac{\partial \mathcal{L}}{\partial \dot{\phi}} = -2\hbar \sqrt{-\frac{\alpha}{\beta}}\, \delta\psi, \tag{42}
$$

i.e., the amplitude modes. Here, $\dot{\phi} \equiv \partial\phi/\partial t$. The phase and amplitude fluctuations thus stand in the same relationship as coordinates and momenta in classical mechanics.
Like in classical mechanics, one can go from the Lagrangian description to a Hamiltonian description by a Legendre transformation. The Hamiltonian density is

$$
\mathcal{H} = \pi\dot{\phi} - \mathcal{L} = -2\alpha\, \delta\psi^2 + \frac{\hbar^2}{2m^*} \left(\frac{1}{i} \nabla \delta\psi \right)^* \cdot \frac{1}{i} \nabla \delta\psi - \frac{\hbar^2}{2m^*} \frac{\alpha}{\beta} (\nabla\phi)^* \cdot \nabla\phi. \tag{43}
$$

We thus recover Eq. (33).

4 Ginzburg–Landau theory for superconductors

To describe superconductors, one has to take the charge q of the particles forming the condensate into account. We allow for the possibility that q is not the electron charge $-e$. There are two additional terms in the Ginzburg–Landau functional [2], where we use Gaussian units:

- The canonical momentum has to be replaced by the kinetic momentum or, equivalently, the gradient has to be replaced by the gauge-covariant derivative by way of minimal coupling

$$
\frac{\hbar}{i} \nabla \to \frac{\hbar}{i} \nabla - \frac{q}{c} \mathbf{A}(\mathbf{r}), \tag{44}
$$

  where $\mathbf{A}(\mathbf{r})$ is the vector potential.

- The energy density of the magnetic field, $B^2/8\pi$, has to be included.

The result is [2]

$$
F = \int d^3r \left[\alpha\, |\psi|^2 + \frac{\beta}{2} |\psi|^4 + \frac{1}{2m^*} \left| \left(\frac{\hbar}{i} \nabla - \frac{q}{c} \mathbf{A} \right) \psi \right|^2 + \frac{B^2}{8\pi} \right], \tag{45}
$$

where $\mathbf{B} = \nabla \times \mathbf{A}$. This is the *Helmholtz* free energy $F[\mathbf{B}]$ with natural variable $\mathbf{B}$, at least with respect to the fluctuations on microscopic scales, as noted above. If we understand F as the difference of the free energies in the superconducting and the normal state, we should

subtract the latter, which introduces an additional term $-B_n^2/8\pi$ under the integral, where $\mathbf{B}_n$ is the magnetic induction in the normal state, which we take to be uniform.
Minimizing the free-energy functional F with respect to the coarse-grained wave function ψ, we obtain, in analogy to Sec. 3,

$$\frac{1}{2m^*}\left(\frac{\hbar}{i}\nabla-\frac{q}{c}\mathbf{A}\right)^2\psi+\alpha\,\psi+\beta\,|\psi|^2\psi=0. \tag{46}$$

Other than for neutral superfluids, the mean-field state of the system is now characterized not only by $\psi(\mathbf{r})$ but also by the vector potential $\mathbf{A}(\mathbf{r})$. Hence, we also have to minimize F with respect to $\mathbf{A}$,

$$\begin{aligned}
\frac{\delta F}{\delta A_n(\mathbf{r})} &= \frac{\delta}{\delta A_n(\mathbf{r})}\int d^3r'\left[\frac{1}{2m^*}\left(\left[-\frac{\hbar}{i}\nabla'-\frac{q}{c}\mathbf{A}(\mathbf{r}')\right]\psi^*(\mathbf{r}')\right)\cdot\left(\frac{\hbar}{i}\nabla'-\frac{q}{c}\mathbf{A}(\mathbf{r}')\right)\psi(\mathbf{r}')\right.\\
&\qquad\left.+\frac{1}{8\pi}\left(\nabla'\times\mathbf{A}(\mathbf{r}')\right)^2\right]\\
&=\int d^3r'\left[-\frac{q}{2m^*c}\,\delta(\mathbf{r}'-\mathbf{r})\,\psi^*(\mathbf{r}')\left(\frac{\hbar}{i}\frac{\partial}{\partial r'_n}-\frac{q}{c}A_n(\mathbf{r}')\right)\psi(\mathbf{r}')\right.\\
&\qquad-\frac{q}{2m^*c}\left(\left[-\frac{\hbar}{i}\frac{\partial}{\partial r'_n}-\frac{q}{c}A_n(\mathbf{r}')\right]\psi^*(\mathbf{r}')\right)\delta(\mathbf{r}'-\mathbf{r})\,\psi(\mathbf{r}')\\
&\qquad\left.+\frac{1}{4\pi}\sum_{ij}B_i(\mathbf{r}')\,\epsilon_{ijn}\frac{\partial}{\partial r'_j}\delta(\mathbf{r}'-\mathbf{r})\right]\\
&= i\,\frac{q\hbar}{2m^*c}\,\psi^*(\mathbf{r})\,\frac{\partial\psi}{\partial r_n}-i\,\frac{q\hbar}{2m^*c}\frac{\partial\psi^*}{\partial r_n}\,\psi(\mathbf{r})+\frac{q^2}{m^*c^2}\,\psi^*(\mathbf{r})\psi(\mathbf{r})\,A_n(\mathbf{r})\\
&\quad-\frac{1}{4\pi}\sum_{ij}\epsilon_{ijn}\frac{\partial}{\partial r_j}B_i(\mathbf{r})=0.
\end{aligned} \tag{47}$$

Collecting the three equations for $n=x,y,z$, we obtain

$$-i\,\frac{q\hbar}{2m^*c}\left([\nabla\psi^*]\psi-\psi^*\nabla\psi\right)+\frac{q^2}{m^*c^2}\,|\psi|^2\mathbf{A}+\frac{1}{4\pi}\nabla\times\mathbf{B}=0. \tag{48}$$

With Ampère's law

$$\nabla\times\mathbf{B}=\frac{4\pi}{c}\,\mathbf{j}, \tag{49}$$

we find

$$\mathbf{j}=\frac{c}{4\pi}\nabla\times\mathbf{B}=i\,\frac{q\hbar}{2m^*}\left([\nabla\psi^*]\psi-\psi^*\nabla\psi\right)-\frac{q^2}{m^*c}\,|\psi|^2\mathbf{A}. \tag{50}$$

In the limit of uniform ψ, Eq. (50) simplifies to

$$\mathbf{j}=-\frac{q^2|\psi|^2}{m^*c}\,\mathbf{A}. \tag{51}$$

This should reproduce the London equation [1] for the current density, $\mathbf{j}=-(e^2n_s/mc)\,\mathbf{A}$, where n_s is the superfluid density. This obviously requires that

$$\frac{q^2|\psi|^2}{m^*}=\frac{e^2n_s}{m}. \tag{52}$$

Equation (51) is evidently not gauge invariant since a gauge transformation $\mathbf{A} \to \mathbf{A} + \nabla\chi$ changes the current. Charge conservation requires $\nabla\cdot\mathbf{j} = 0$ and thus the vector potential must satisfy $\nabla\cdot\mathbf{A} = 0$. This choice of gauge is called *London gauge* in this context and *Coulomb gauge* in general.

Based on flux-quantization experiments, it is natural to set $q = -2e$. For m^* one might then insert twice the effective electron (band) mass of the metal. However, it turns out to be difficult to measure m^* independently of the superfluid density n_s and it is therefore common to set m^* to twice the bare electron mass, $m^* = 2m \equiv 2m_e$. All system-specific properties are thus absorbed into

$$n_s = \frac{m}{e^2}\,\frac{q^2|\psi|^2}{m^*} = \frac{m}{e^2}\,\frac{4e^2|\psi|^2}{2m} = 2\,|\psi|^2. \tag{53}$$

With this normalization of $\psi(\mathbf{r})$, London theory follows as a special case from Ginzburg–Landau theory.

Taking the curl of Eq. (51), we obtain the *second London equation* [1]

$$\nabla\times\mathbf{j} = -\frac{q^2|\psi|^2}{m^*c}\,\nabla\times\mathbf{A} = -\frac{q^2|\psi|^2}{m^*c}\,\mathbf{B}. \tag{54}$$

The curl of Ampère's law Eq. (49) now gives

$$\nabla\times(\nabla\times\mathbf{B}) = \frac{4\pi}{c}\,\nabla\times\mathbf{j} = -\frac{4\pi q^2|\psi|^2}{m^*c^2}\,\mathbf{B}. \tag{55}$$

Using the so-called BAC-CAB rule from vector calculus, we find

$$\nabla^2\mathbf{B} - \nabla(\nabla\cdot\mathbf{B}) = \nabla^2\mathbf{B} = \frac{4\pi q^2|\psi|^2}{m^*c^2}\,\mathbf{B}. \tag{56}$$

After introducing the *magnetic penetration depth*

$$\lambda \equiv \sqrt{\frac{m^*c^2}{4\pi q^2|\psi|^2}}, \tag{57}$$

this equation assumes the simple form

$$\nabla^2\mathbf{B} = \frac{1}{\lambda^2}\,\mathbf{B}. \tag{58}$$

Let us consider a semi-infinite superconductor filling the half space $x > 0$. An induction field $\mathbf{B}_{\text{appl}} = B_{\text{appl}}\,\hat{\mathbf{y}}$ is applied parallel to the surface. One can immediately see that the equation is solved by

$$\mathbf{B}(x) = B_{\text{appl}}\,\hat{\mathbf{y}}\,e^{-x/\lambda} \quad \text{for } x \geq 0. \tag{59}$$

The magnetic field thus decreases exponentially with the distance from the surface of the superconductor, with the decay length given by the penetration depth λ. In the bulk we indeed find $\mathbf{B} \to 0$, and thus perfect diamagnetism, which is the Meißner–Ochsenfeld effect.

The penetration depth can be written as

$$\lambda = \sqrt{\frac{mc^2}{8\pi e^2|\psi|^2}} \cong \sqrt{\frac{mc^2}{8\pi e^2\left(-\frac{\alpha}{\beta}\right)}}. \tag{60}$$

We have found two characteristic length scales: λ describing the penetration of the magnetic field and ξ describing the variation of the coarse-grained superconducting wave function (order parameter). Within the mean-field theories we have so far employed, both quantities scale as

$$\lambda, \xi \propto \frac{1}{\sqrt{-\alpha}} \propto \frac{1}{\sqrt{T_c - T}} \tag{61}$$

close to T_c. Thus their dimensionless ratio $\kappa \equiv \lambda/\xi$ is roughly temperature independent. It is called the *Ginzburg–Landau parameter*.

4.1 Type-I and type-II superconductors

The Ginzburg–Landau parameter κ determines the behavior of superconductors in an applied magnetic field. Superconductors with small κ are said to be of *type I*. The exact condition is $\kappa < 1/\sqrt{2}$. This means that spatial changes of the magnetic induction $\mathbf{B}$ are less costly than changes of the wave function. In other words, the magnetic field is less stiff than the wave function. Conventional superconductors are usually of type I.

A system will only become superconducting if this reduces its free energy. The experimental situation we have in mind is that the sample is placed in a large solenoid, which maintains a constant magnetic field. When the sample becomes superconducting, the source that drives a current through the solenoid has to do work to keep the field constant. This work has to be taken into account in the energy balance between the superconducting and the normal-conducting states but the Helmholtz free energy F does not contain it [6]. The calculation of this additional energy is a standard problem in macroscopic electrodynamics. (The simplest setup for an explicit derivation involves an infinitely long cylindrical body concentric within an infinitely long solenoid. In this setup, the magnetic field $\mathbf{H}$ is continuous and given in terms of the sheet current density $\mathbf{K}$ carried by the solenoid.) The result for the additional energy is

$$-\int d^3r\, \frac{\mathbf{H} \cdot \mathbf{B}}{4\pi}\,, \tag{62}$$

where the magnetic field $\mathbf{H}$ is given by

$$\mathbf{H}(\mathbf{r}) = 4\pi\, \frac{\delta F}{\delta \mathbf{B}(\mathbf{r})}\,. \tag{63}$$

Adding this contribution to the Ginzburg–Landau functional yields

$$G[\mathbf{H}] = F[\mathbf{B}] - \int d^3r\, \frac{\mathbf{H} \cdot \mathbf{B}}{4\pi}\,. \tag{64}$$

Thermodynamically speaking, this equation is the Legendre transformation from the *Helmholtz* free energy F with natural variable $\mathbf{B}$ to the *Gibbs* free energy G with natural variable $\mathbf{H}$.

The Helmholtz free energy F is given in Eq. (45). For the evaluation of Eq. (63), we require the functional derivative of $\mathbf{A}$ with respect to $\mathbf{B}$. To find it, we note that the relation $\mathbf{B} = \nabla\times\mathbf{A}$ can be explicitly inverted:

$$\mathbf{A}(\mathbf{r}) = \frac{1}{4\pi} \int d^3r'\, \mathbf{B}(\mathbf{r}')\times \frac{\mathbf{r}-\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|^3}\,. \tag{65}$$

This expression respects the Coulomb gauge, i.e., $\nabla\cdot\mathbf{A} = 0$. The derivation is formally analogous to the one of the Biot–Savart law for $\mathbf{B}$ for given current density $\mathbf{j}$ [11]. From Eq. (65), we obtain

$$\frac{\delta A_i(\mathbf{r})}{\delta B_j(\mathbf{r}')} = \frac{1}{4\pi} \sum_k \epsilon_{ijk} \frac{r_k - r'_k}{|\mathbf{r}-\mathbf{r}'|^3} . \tag{66}$$

We can then evaluate Eq. (63). A lengthy calculation gives

$$\begin{aligned} \mathbf{H}(\mathbf{r}) = \frac{1}{c} \int d^3r' \left[i \frac{q\hbar}{2m^*} \big([\nabla'\psi^*(\mathbf{r}')]\psi(\mathbf{r}') - \psi^*(\mathbf{r}')\nabla'\psi(\mathbf{r}') \big) - \frac{q^2}{m^*c} |\psi(\mathbf{r}')|^2 \mathbf{A}(\mathbf{r}') \right] \\ \times \frac{\mathbf{r}'-\mathbf{r}}{|\mathbf{r}'-\mathbf{r}|^3} + \mathbf{B}(\mathbf{r}) \qquad = -\frac{1}{c} \int d^3r'\, \mathbf{j}(\mathbf{r}') \times \frac{\mathbf{r}-\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|^3} + \mathbf{B}(\mathbf{r}), \end{aligned} \tag{67}$$

where the current density $\mathbf{j}$ is the one appearing in the second Ginzburg–Landau equation (50). One can write the result as $\mathbf{H} = -4\pi\mathbf{M}+\mathbf{B}$ with the magnetization due to the screening currents,

$$\mathbf{M}(\mathbf{r}) = \frac{1}{4\pi c} \int d^3r'\, \mathbf{j}(\mathbf{r}') \times \frac{\mathbf{r}-\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|^3} . \tag{68}$$

Evidently, the thermodynamic relation (63) forces us to treat $\mathbf{j}$ as an *induced*, not free, current density. This is also reasonable from the point of view of electrodynamics: In macroscopic magnetostatics as presented in textbooks [11], we are used to divide the current into bound and free currents, where notionally the former are restricted to the atomic scale. However, the correct distinction is between currents that are induced by the applied field and currents imposed by the experimenter. The screening currents in superconductors are free currents in the sense that charge carriers are flowing over macroscopic distances—famously so—but they are nevertheless induced by the applied magnetic field, expressed by the perfect diamagnetism. With Eqs. (45), (64), and (67), the Gibbs free energy becomes

$$G = \int d^3r \left[\alpha\, |\psi|^2 + \frac{\beta}{2}\, |\psi|^4 + \frac{1}{2m^*} \left| \left(\frac{\hbar}{i} \nabla - \frac{q}{c}\, \mathbf{A} \right) \psi \right|^2 - \frac{H^2}{8\pi} + 2\pi M^2 \right] . \tag{69}$$

The awkward factor of 2π instead of $1/8\pi$ in front of M^2 is due to using Gaussian units.
In the normal state, we have $\psi = 0$ and $\mathbf{H} = \mathbf{H}_{\text{appl}}$, the applied field. Now taking G to be the difference of the Gibbs free energies of the superconducting and normal states, we obtain

$$G = G_s - G_n = \int d^3r \left[\alpha\, |\psi|^2 + \frac{\beta}{2}\, |\psi|^4 + \frac{1}{2m^*} \left| \left(\frac{\hbar}{i} \nabla - \frac{q}{c}\, \mathbf{A} \right) \psi \right|^2 - \frac{H^2}{8\pi} + 2\pi M^2 + \frac{H_{\text{appl}}^2}{8\pi} \right] . \tag{70}$$

The evaluation becomes simple in the case of a uniform system: In the superconducting state, the uniform solution of the Ginzburg–Landau equation (46) is $|\psi|^2 = -\alpha/\beta > 0$ and the $\mathbf{B}$ field in the bulk vanishes due to the Meißner–Ochsenfeld effect. Hence, we can, on the one hand, choose a gauge with $\mathbf{A} = 0$ and, on the other, we get

$$-\frac{H^2}{8\pi} + 2\pi M^2 = -2\pi M^2 + 2\pi M^2 = 0. \tag{71}$$

This leads to the simple result

$$G = \int d^3r \left(-\frac{\alpha^2}{2\beta} + \frac{H_{\text{appl}}^2}{8\pi} \right). \tag{72}$$

Superconductivity occurs for $G < 0$. Not surprisingly, the applied magnetic field hinders superconductivity. The *critical field* H_c at which superconductivity is destroyed is obtained from the condition $G = 0$, which yields

$$H_c = \sqrt{4\pi \frac{\alpha^2}{\beta}} \cong \sqrt{\frac{4\pi}{\beta}}\, \alpha' \,(T_c - T). \tag{73}$$

We can now express the phenomenological parameters α and β in terms of the measurable quantities λ and H_c as

$$\alpha = -\frac{2e^2}{mc^2}\, \lambda^2 H_c^2, \tag{74}$$

$$\beta = 4\pi \left(\frac{2e^2}{mc^2} \right)^2 \lambda^4 H_c^2. \tag{75}$$

One can also show that the free energy of domain walls between normal-conducting and superconducting regions is positive, which explains why type-I superconductors favor uniform states [6].

Conversely, type-II superconductors are defined by a large Ginzburg–Landau parameter $\kappa > 1/\sqrt{2}$. The free energy of domain walls is then negative [6]. Hence, the system tends to maximize the total area of domain walls. This tendency is counterbalanced by flux quantization—the magnetic flux in a normal region cannot be split into portions smaller than the flux quantum $\Phi_0 \equiv hc/2e$, as we show in the following.

Consider an arbitrary closed path ∂S forming the edge of a surface S. The magnetic flux Φ through the surface S is

$$\Phi = \int_S d\mathbf{a} \cdot \mathbf{B} = \int_S d\mathbf{a} \cdot (\nabla \times \mathbf{A}) = \oint_{\partial S} d\mathbf{s} \cdot \mathbf{A}, \tag{76}$$

by Stokes' theorem. We solve the second Ginzburg–Landau equation (50) for $\mathbf{A}$ and insert the result,

$$\begin{aligned} \Phi &= \oint_{\partial S} d\mathbf{s} \cdot \left[-\frac{m^* c}{q^2 |\psi|^2}\, \mathbf{j} + i\, \frac{\hbar c}{2q|\psi|^2} \big([\nabla \psi^*]\psi - \psi^* \nabla \psi \big) \right] \\ &= \oint_{\partial S} d\mathbf{s} \cdot \left[-\frac{mc}{e^2 n_s}\, \mathbf{j} + i\, \frac{\hbar c}{2q}\, (-2i) \nabla \phi \right] = \frac{mc}{e} \oint_{\partial S} d\mathbf{s} \cdot \mathbf{v}_s - \frac{\hbar c}{2e} \oint_{\partial S} d\mathbf{s} \cdot \nabla \phi, \end{aligned} \tag{77}$$

where $\mathbf{v}_s \equiv -\mathbf{j}/en_s$ is the superfluid velocity. The last term contains the change of the phase of the macroscopic wave function along the whole path, which must be an integer multiple of 2π for $\psi(\mathbf{r})$ to be continuous:

$$\oint_{\partial S} d\mathbf{s} \cdot \nabla \phi = -2\pi n, \quad n \in \mathbb{Z}. \tag{78}$$

The minus sign is a convention, which is useful for negatively charged condensates. Thus we find for the so-called *fluxoid*

$$\Phi' \equiv \Phi - \frac{mc}{e} \oint_{\partial S} d\mathbf{s} \cdot \mathbf{v}_s = \frac{\hbar c}{2e}\, 2\pi n = \frac{hc}{2e}\, n = n\Phi_0, \quad n \in \mathbb{Z}. \tag{79}$$

Here n is the *winding number* enclosed by the path ∂S. We see that the fluxoid is quantized. Moreover, if the path ∂S everywhere lies deep inside a superconductor the current vanishes, Φ' equals Φ, and the flux Φ itself is quantized.

The smallest amount of fluxoid that can penetrate a superconductor is one flux quantum Φ_0. It does so as a *vortex line*. Following the above arguments, the phase ϕ of ψ changes by -2π as one circles a vortex in the positive direction, where, by convention, the direction of a vortex is the direction of the magnetic induction $\mathbf{B}$. Thus at the center of the vortex line (the *vortex core*), the phase is undefined. This is only consistent with a continuous ψ if $\psi = 0$ holds there. Because of the phase winding, a vortex cannot end anywhere in the interior of a superconductor. Vortices can thus only terminate at a surface or form closed loops. One can understand the winding of the phase as a *topological* property of the vortex since it cannot be changed by any continuous deformation of $\psi(\mathbf{r})$ unless ψ is tuned to zero. In this sense, vortices are *topological defects* of the condensate.

To obtain the coarse-grained wave function $\psi(\mathbf{r})$ and the magnetic induction $\mathbf{B}(\mathbf{r})$ for a vortex line, one has to solve the Ginzburg–Landau equations (46) and (50) together with Ampère's law Eq. (49) [6]. This can only be done numerically. One finds that $|\psi|$ starts to grow linearly with the distance from the vortex core. The characteristic length scale of this rise is, not surprisingly, the coherence length ξ. On the other hand, $\mathbf{B}$ falls off with distance on the scale of the magnetic penetration depth λ.

One also finds a more complicated phase diagram than for type-I superconductors. At weak applied fields $H < H_{c1}$, the flux is expelled completely. In an intermediate field range $H_{c1} < H < H_{c2}$, the equilibrium state is a regular lattice of vortex lines [12], specifically a triangular lattice of parallel straight lines. The properties of the vortex lattice and the critical fields H_{c1} and H_{c2} can be evaluated within Ginzburg–Landau theory. Details can be found in Refs. [6,13].

4.2 The Anderson–Higgs mechanism

When discussing fluctuations about the mean-field state of a superconductor, we have to take the coupling to the electromagnetic field into account. The suitable thermodynamic potential in this case is the Helmholtz free energy

$$F = \int d^3r \left[\alpha\, |\psi|^2 + \frac{\beta}{2}\, |\psi|^4 + \frac{1}{2m^*} \left| \left(\frac{\hbar}{i}\, \nabla - \frac{q}{c}\, \mathbf{A} \right) \psi \right|^2 + \frac{B^2}{8\pi} - \frac{B_{\text{appl}}^2}{8\pi} \right], \tag{80}$$

which expresses that fluctuations of the magnetic field *increase* the energy. We proceed analogously to the case of a neutral superfluid and employ the Gaussian approximation throughout, i.e., we expand F up to second order in fluctuations.

For $T > T_c$, we note that the kinetic term

$$\frac{1}{2m^*} \left| \left(\frac{\hbar}{i} \nabla - \frac{q}{c} \mathbf{A} \right) \psi \right|^2 \tag{81}$$

is explicitly of second order in the fluctuations $\delta\psi = \psi$ so that electromagnetic-field fluctuations only appear in even higher orders. Thus to second order, the order-parameter fluctuations decouple from the electromagnetic fluctuations,

$$F \cong \int d^3r \left[\alpha\, \psi^*\psi + \frac{1}{2m^*} \left| \frac{\hbar}{i} \nabla\psi \right|^2 + \frac{B^2}{8\pi} \right] = \sum_{\mathbf{k}} \left(\alpha + \frac{\hbar^2 k^2}{2m^*} \right) \psi^*_{\mathbf{k}} \psi_{\mathbf{k}} + \sum_{\mathbf{k}\neq 0} \frac{\mathbf{B}^*_{\mathbf{k}} \cdot \mathbf{B}_{\mathbf{k}}}{8\pi}. \tag{82}$$

The superconducting fluctuations consist of two degenerate massive branches with dispersion $\epsilon_{\mathbf{k}} = \alpha + \hbar^2 k^2 / 2m^*$, like for the neutral superfluid. The magnetic-field fluctuations decouple and are those of a free field. The final sum excludes the uniform magnetic-field mode, which is the applied field subtracted in Eq. (80).

The case of $T < T_c$ is more interesting. Writing $\psi = (\psi_0 + \delta\psi)\, e^{i\phi}$ as above, we obtain, to second order,

$$\begin{aligned}
F \cong \int d^3r \Bigg[& \alpha\, \delta\psi^2 + 3\beta\psi_0^2\, \delta\psi^2 + \frac{1}{2m^*} \left(\frac{\hbar}{i} \nabla\delta\psi \right)^* \cdot \frac{\hbar}{i} \nabla\delta\psi \\
& + \frac{1}{2m^*} \Bigg(\underbrace{\left(\frac{\hbar}{i} \nabla\delta\psi \right)^* \cdot \hbar\psi_0\nabla\phi + (\hbar\psi_0\nabla\phi)^* \cdot \frac{\hbar}{i} \nabla\delta\psi}_{=0} \Bigg) + \frac{1}{2m^*} (\hbar\psi_0\nabla\phi)^* \cdot \hbar\psi_0\nabla\phi \\
& + \frac{1}{2m^*} \Bigg(\underbrace{\left(\frac{\hbar}{i} \nabla\delta\psi \right)^* \cdot \left(-\frac{q}{c} \right) \mathbf{A}\psi_0 + \left(-\frac{q}{c} \mathbf{A}\psi_0 \right)^* \cdot \frac{\hbar}{i} \nabla\delta\psi}_{=0} \Bigg) \\
& + \frac{1}{2m^*} \left((\hbar\psi_0\nabla\phi)^* \cdot \left(-\frac{q}{c} \right) \mathbf{A}\psi_0 + \left(-\frac{q}{c} \mathbf{A}\psi_0 \right)^* \cdot \hbar\psi_0\nabla\phi \right) \\
& + \frac{1}{2m^*} \left(-\frac{q}{c} \mathbf{A}\psi_0 \right)^* \cdot \left(-\frac{q}{c} \right) \mathbf{A}\psi_0 + \frac{1}{8\pi} (\nabla\times\mathbf{A})^* \cdot (\nabla\times\mathbf{A}) \Bigg] \\
= \int d^3r \Bigg[& -2\alpha\, \delta\psi^2 + \frac{1}{2m^*} \left(\frac{\hbar}{i} \nabla\delta\psi \right)^* \cdot \frac{\hbar}{i} \nabla\delta\psi \\
& - \frac{\hbar^2}{2m^*} \frac{\alpha}{\beta} \left(\nabla\phi - \frac{q}{\hbar c} \mathbf{A} \right)^* \cdot \left(\nabla\phi - \frac{q}{\hbar c} \mathbf{A} \right) + \frac{1}{8\pi} (\nabla\times\mathbf{A})^* \cdot (\nabla\times\mathbf{A}) \Bigg],
\end{aligned} \tag{83}$$

where constant terms have been dropped and first-order terms again cancel. We see that the phase ϕ of the macroscopic wave function and the vector potential appear in the combination $\nabla\phi - (q/\hbar c)\mathbf{A}$. This property is a consequence of gauge invariance: Observable physical properties are invariant under the simultaneous gauge transformation

$$\mathbf{A}' = \mathbf{A} + \nabla\chi, \tag{84}$$

$$U' = U - \frac{1}{c} \frac{\partial\chi}{\partial t}, \tag{85}$$

$$\psi' = e^{iq\chi/\hbar c}\,\psi, \tag{86}$$

where we here use U for the scalar electric potential and $\chi(\mathbf{r},t)$ is an arbitrary scalar field. Equation (86) means that the phase of ψ transforms as

$$\phi' = \phi + \frac{q}{\hbar c}\,\chi. \tag{87}$$

Besides $\nabla\phi - (q/\hbar c)\mathbf{A},\ \mathbf{B} = \nabla\times\mathbf{A}$ is also gauge invariant since $\nabla\times\nabla\chi = 0$.
Gauge invariance is not a symmetry of the physical system but a redundancy in its description. Hence, variations of ϕ and $\mathbf{A}$ that take the form of Eqs. (84) and (87) are not physical fluctuations. One way to deal with this is to choose a particular gauge from the manifold of equivalent descriptions. A useful choice in this case is to make the new collective wave function real, i.e., to require $\phi' = 0$. Equations (84) and (87) then imply that the new vector potential is

$$\mathbf{A}' = \mathbf{A} - \frac{\hbar c}{q}\,\nabla\phi. \tag{88}$$

The Ginzburg–Landau functional can be expressed in terms of the new vector potential and the amplitude fluctuations $\delta\psi$ as

$$\begin{aligned} F[\delta\psi,\mathbf{A}'] \cong \int d^3r \,\bigg[&-2\alpha\,\delta\psi^2 + \frac{1}{2m^*}\left(\frac{\hbar}{i}\,\nabla\delta\psi\right)^{*}\cdot\frac{\hbar}{i}\,\nabla\delta\psi \\ &- \frac{\alpha}{\beta}\,\frac{q^2}{2m^*c^2}\,\mathbf{A}'^{*}\cdot\mathbf{A}' + \frac{1}{8\pi}\,(\nabla\times\mathbf{A}')^{*}\cdot(\nabla\times\mathbf{A}')\bigg]. \end{aligned} \tag{89}$$

The procedure is often described by saying that the phase is absorbed into the vector potential by a gauge transformation.
Finally, we drop the prime and insert Fourier-transformed fields,

$$F[\delta\psi,\mathbf{A}] \cong \sum_{\mathbf{k}}\left[\left(-2\alpha + \frac{\hbar^2k^2}{2m^*}\right)\delta\psi_{\mathbf{k}}^{*}\,\delta\psi_{\mathbf{k}} - \frac{\alpha}{\beta}\,\frac{q^2}{2m^*c^2}\,\mathbf{A}_{\mathbf{k}}^{*}\cdot\mathbf{A}_{\mathbf{k}} + \frac{1}{8\pi}\,(\mathbf{k}\times\mathbf{A}_{\mathbf{k}})^{*}\cdot(\mathbf{k}\times\mathbf{A}_{\mathbf{k}})\right]. \tag{90}$$

Obviously, the massive amplitude fluctuations decouple from electromagnetic fluctuations to second order and behave like for a neutral superfluid. The amplitude modes $\delta\psi_{\mathbf{k}}$ are called *Higgs modes* [14] in this context.
For the interpretation of the last expression, it is useful to decompose the vector potential $\mathbf{A}$ into longitudinal components $\mathbf{A}_{\mathbf{k}}^{\parallel}$ parallel to the wave vector $\mathbf{k}$ and transverse components $\mathbf{A}_{\mathbf{k}}^{\perp}$ perpendicular to it:

$$\mathbf{A}_{\mathbf{k}} = \underbrace{\hat{\mathbf{k}}\,(\hat{\mathbf{k}}\cdot\mathbf{A}_{\mathbf{k}})}_{\equiv\,\mathbf{A}_{\mathbf{k}}^{\parallel}} + \underbrace{\mathbf{A}_{\mathbf{k}} - \hat{\mathbf{k}}\,(\hat{\mathbf{k}}\cdot\mathbf{A}_{\mathbf{k}})}_{\equiv\,\mathbf{A}_{\mathbf{k}}^{\perp}}, \tag{91}$$

with the unit vector $\hat{\mathbf{k}} = \mathbf{k}/k$. The magnetic-field energy density can now be written as

$$\begin{aligned} \frac{1}{8\pi}\,(\mathbf{k}\times\mathbf{A}_{\mathbf{k}})^{*}\cdot(\mathbf{k}\times\mathbf{A}_{\mathbf{k}}) &= \frac{1}{8\pi}\,(\mathbf{k}\times\mathbf{A}_{\mathbf{k}}^{\perp})^{*}\cdot(\mathbf{k}\times\mathbf{A}_{\mathbf{k}}^{\perp}) \\ &= \frac{1}{8\pi}\left[k^2\,\mathbf{A}_{\mathbf{k}}^{\perp *}\cdot\mathbf{A}_{\mathbf{k}}^{\perp} - (\mathbf{k}\cdot\mathbf{A}_{\mathbf{k}}^{\perp *})(\mathbf{k}\cdot\mathbf{A}_{\mathbf{k}}^{\perp})\right] = \frac{1}{8\pi}\,k^2\,\mathbf{A}_{\mathbf{k}}^{\perp *}\cdot\mathbf{A}_{\mathbf{k}}^{\perp} \end{aligned} \tag{92}$$

and the Ginzburg–Landau functional becomes

$$F[\delta\psi,\mathbf{A}] \cong \sum_{\mathbf{k}} \left[\left(-2\alpha + \frac{\hbar^2 k^2}{2m^*}\right) \delta\psi_{\mathbf{k}}^* \, \delta\psi_{\mathbf{k}} - \frac{\alpha}{\beta}\, \frac{q^2}{2m^* c^2}\, \mathbf{A}_{\mathbf{k}}^{\parallel *} \cdot \mathbf{A}_{\mathbf{k}}^{\parallel} - \frac{\alpha}{\beta}\, \frac{q^2}{2m^* c^2}\, \mathbf{A}_{\mathbf{k}}^{\perp *} \cdot \mathbf{A}_{\mathbf{k}}^{\perp} + \frac{1}{8\pi}\, k^2\, \mathbf{A}_{\mathbf{k}}^{\perp *} \cdot \mathbf{A}_{\mathbf{k}}^{\perp} \right]. \tag{93}$$

The terms proportional to $-\alpha/\beta = |\psi_0|^2$ are due to superconductivity. Without it, we would have the free-field functional

$$F_{\text{free}}[\mathbf{A}] = \sum_{\mathbf{k}} \frac{1}{8\pi}\, k^2 \mathbf{A}_{\mathbf{k}}^{\perp *} \cdot \mathbf{A}_{\mathbf{k}}^{\perp}, \tag{94}$$

which only contains the two transverse components. This result persists in quantum electrodynamics. The transverse modes do not have an energy gap—photons are massless.

In the presence of superconductivity, all three components of $\mathbf{A}$ appear. Moreover, all components obtain a *mass term*. This is the famous *Anderson–Higgs mechanism* first proposed for superconductors by P.W. Anderson [15, 16]. The same general idea also explains (most of) the masses of elementary particles, although in a more complicated case since the broken symmetry is more complicated than the $\mathrm{U}(1)$ symmetry of superconductivity [17–19]. The "Higgs bosons" in our case are the quanta of the amplitude fluctuations [14].

To extract the dispersion from Eq. (93), one has to go beyond our static picture and include the time or frequency dependence of the fields. The frequency-dependent term for the vector potential is of the form

$$-\frac{1}{8\pi}\, \frac{\omega^2}{c^2}\, \mathbf{A}_{\mathbf{k}}^* \cdot \mathbf{A}_{\mathbf{k}}. \tag{95}$$

This is plausible based on Eq. (94) and Lorentz invariance. Equation (93) then predicts that the longitudinal field components $\mathbf{A}_{\parallel}$ are dispersionless,

$$\omega^2 = -\frac{\alpha}{\beta}\, \frac{4\pi q^2}{m^*} = \frac{4\pi n_s e^2}{m} \equiv \omega_p^2. \tag{96}$$

Here, ω_p is the *plasma frequency*. This is the frequency with which charge inhomogeneities oscillate under the influence of the Coulomb interaction. These plasma oscillations are not restricted to superconductors and, in particular, also occur in normal metals, where n_s is replaced by the density $n = N/V$ of all conduction electrons. The dispersion of plasmons is encoded in the dielectric function $\epsilon(\mathbf{k},\omega)$ in the limit of small wave vectors $\mathbf{k}$, which can be calculated in the random-phase approximation (RPA) [10]. Such a calculation reveals that there are momentum-dependent corrections, i.e., the dispersion is not perfectly flat.

On the other hand, the transverse components are dispersive,

$$\omega^2 = \omega_p^2 + k^2 c^2. \tag{97}$$

This is because transverse plasma oscillations mix with the transverse electromagnetic field modes. They become indistinguishable from longitudinal plasma oscillations in the long-wavelength ($\mathbf{k} \to 0$) limit, giving the same frequency ω_p but quickly transform into electromagnetic-field-dominated modes with optical dispersion $\omega = kc$ for larger $\mathbf{k}$. The approximate

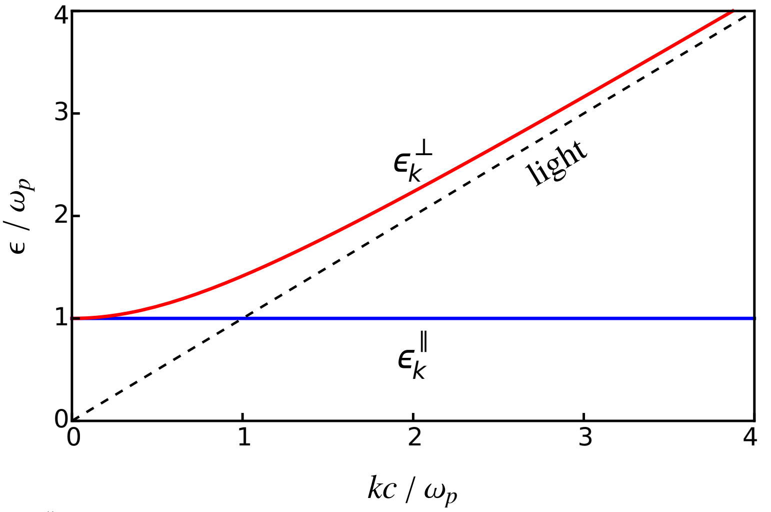

Fig. 3: *Dispersion $\epsilon_k^\parallel$ of longitudinal plasma modes and $\epsilon_k^\perp$ of transverse plasma modes. For comparison, the dispersion of light is shown as the dashed straight line.*

dispersions are sketched in Fig. 3. For completeness, we note that the RPA corrections to the dispersion of longitudinal plasma modes are on the order of $k^2 v_F^2$, where $v_F \ll c$ is the electronic Fermi velocity.

The dispersion of the transverse modes also generates the Meißner–Ochsenfeld effect. To see this, we write the functional as

$$F \cong \sum_{\mathbf{k}} \left(-2\alpha + \frac{\hbar^2 k^2}{2m^*}\right) \delta\psi_{\mathbf{k}}^*\, \delta\psi_{\mathbf{k}} + \sum_{\mathbf{k}} \frac{1}{8\pi}\, \frac{1}{\lambda^2}\, \mathbf{A}_{\mathbf{k}}^{\parallel *} \cdot \mathbf{A}_{\mathbf{k}}^{\parallel} + \sum_{\mathbf{k}} \frac{1}{8\pi} \left(\frac{1}{\lambda^2} + k^2\right) \mathbf{A}_{\mathbf{k}}^{\perp *} \cdot \mathbf{A}_{\mathbf{k}}^{\perp}, \quad (98)$$

where λ is the magnetic penetration depth defined in Eq. (57). The photon mass is thus proportional to $1/\lambda$. We minimize the free energy with respect to the transverse components of the vector potential,

$$\frac{\partial F}{\partial \mathbf{A}_{\mathbf{k}}^{\perp *}} = \frac{1}{8\pi} \left(\frac{1}{\lambda^2} + k^2\right) \mathbf{A}_{\mathbf{k}}^{\perp} \stackrel{!}{=} 0. \quad (99)$$

Fourier transformation back to real space gives

$$\frac{1}{\lambda^2}\, \mathbf{A}^\perp - \nabla^2 \mathbf{A}^\perp = 0. \quad (100)$$

Taking the curl, we reobtain Eq. (58),

$$\frac{1}{\lambda^2}\, \mathbf{B} - \nabla^2 \mathbf{B} = 0. \quad (101)$$

4.3 Ginzburg–Landau theory as an effective field theory

So far, Ginzburg–Landau theory has been introduced as a phenomenological theory based on Landau theory and the idea that superconductivity involves the condensation of charged particles, which happen to have charge $-2e$. Two years after the publication of the microscopic BCS theory [4], Lev Gor'kov [5] managed to derive Ginzburg–Landau theory from BCS theory. The correspondence is perfect in the limit that the gap is sufficiently small, i.e., T is close to T_c, and the electromagnetic field varies sufficiently slowly. These are indeed the conditions under which Ginzburg and Landau expected their theory to be valid. Gor'kov's derivation links the parameters appearing in the Ginzburg–Landau functional to microscopic quantities. In particular, he found that $q = -2e$ and $m^* = 2m$.

Gor'kov [5] used equations of motion for electronic Green functions, which he decoupled using a mean-field-like approximation that allowed for spatial variations of the mean-field decoupling term. A more modern exposition using functional integrals is given by Altland and Simons [10]. While we cannot discuss this derivation here, the main ideas are recounted for students who have studied functional integrals: The partition function of the interacting electrons is written as a functional integral

$$Z = \int D\bar{\psi}\, D\psi\, e^{-S[\bar{\psi},\psi]}, \tag{102}$$

where ψ is a Grassmann field, i.e., a field of anticommuting variables, required for a functional integral describing fermions, and S is the action. The evaluation of the functional integral would be simple even for Grassmann fields if the action S were quadratic. However, it is not, due to the presence of a quartic interaction term. This interaction is decoupled with a Hubbard-Stratonovich transformation, which means that unity is introduced in the form of a Gaussian functional integral over a bosonic auxiliary field. This Gaussian integral is constructed in such a way that the interaction term is canceled. Physically speaking, the four-fermion interaction is replaced by the exchange of an auxiliary boson.

Replacing the auxiliary bosonic field by a constant that makes the action stationary corresponds to the mean-field approximation of BCS theory. Next, the action is expanded in the auxiliary field about this saddle-point solution and the, now Gaussian, functional integral over the *fermionic* field is performed. The result is the partition function expressed as a functional integral over the deviation of the bosonic field from the saddle-point value. The action in the integral, truncated at a suitable order, is essentially the time-dependent Ginzburg–Landau functional.

4.4 Ginzburg–Landau theory for nontrivial symmetries

Recall that the idea behind Landau and also Ginzburg–Landau theory is to expand the functional of interest in order parameters and external fields. This expansion should include all symmetry-allowed terms up to the order we find to be necessary. The general procedure is discussed in Ref. [20]. The relevant symmetries are crystal symmetries, in particular those described by the crystallographic point group, and time-reversal symmetry. In addition, all terms must be gauge invariant. Group theory and in particular representation theory of groups provides powerful methods for the analysis of symmetry and the construction of allowed terms, which cannot be derived here. The book Ref. [21] contains a good introduction from a condensed-matter-physics point of view. Many useful tables can be found on the Bilbao Crystallographic Server [22] and in Ref. [23]. Recent application of the ideas outlined here to specific superconductors can be found in Refs. [24, 25].

Above, we have assumed that only a single complex superconducting order parameter ψ is required to describe the physics. However, multiple complex order parameters can be relevant for two reasons:

- There is a single relevant order parameter but it is intrinsically of higher dimension—technically, this is the case for order parameters that transform according to higher-dimensional irreducible representations of the point group—or

- multiple order parameters of different symmetries are accidentally close in energy.

The Ginzburg–Landau functional can thus depend on several complex order-parameter fields $\psi_n(\mathbf{r})$ (belonging to different components of the same irreducible representation or to different irreducible representations) and on the local magnetic induction $\mathbf{B}(\mathbf{r})$. We here consider the Helmholtz free energy, see Eq. (45). The functional might also depend on other fields, such as magnetic order parameters or distortions, which can be treated analogously. To construct symmetry-allowed terms, we first have to determine how these fields transform under point-group operations and under time reversal.
The magnetic field transforms like a *pseudovector* (or axial vector) under point-group operations, i.e., $\mathbf{B}$ behaves like the spatial vector $\mathbf{r}$ under proper rotations but is even under inversion. Furthermore, $\mathbf{B}$ is odd under time reversal. The vector potential $\mathbf{A}$ transforms like a vector but is also odd under time reversal.
Moreover, ψ_n is mapped to ψ_n^* under time reversal. This is plausible in view of Eq. (50): Under time reversal, $\psi \mapsto \psi^*$ and $\mathbf{A} \mapsto -\mathbf{A}$ so that the current density $\mathbf{j}$ changes sign. In addition, the functional contains gauge-covariant derivatives

$$\mathbf{D} \equiv \nabla - i\,\frac{q}{\hbar c}\,\mathbf{A}(\mathbf{r}), \tag{103}$$

see Eq. (44). $\mathbf{D}$ transforms like a vector under point-group operations since $\nabla = \partial/\partial\mathbf{r}$ and $\mathbf{A}$ do. Moreover, under time reversal, $\mathbf{D}$ maps to $\mathbf{D}^*$ since $\mathbf{A}$ is odd. For later, we note that under the spatial integral, we have the equality

$$\begin{aligned}\int d^3r\, f^*\mathbf{D}g &= \int d^3r\,\Big(f^*\nabla g - f^* i\,\frac{q}{\hbar c}\,\mathbf{A}g\Big) = \int d^3r\,\Big[-(\nabla f)^* g + \Big(i\,\frac{q}{\hbar c}\,f\Big)^* g\Big] \\ &= -\int d^3r\,(\mathbf{D}f)^* g \end{aligned} \tag{104}$$

for any two differentiable functions $f(\mathbf{r})$ and $g(\mathbf{r})$ so that the integral converges. We have used integration by parts and dropped an irrelevant boundary term in the infinite.
So far, we have implicitly assumed *conventional* superconductivity in the sense that the superconducting order parameter ψ does not break lattice symmetries. In other words, ψ was taken to be invariant under all point-group operations, i.e., technically speaking, to transform according to the trivial irreducible representation. In the general case, superconducting order parameters ψ_n may transform nontrivially under point-group operations. How they transform is completely encoded in the irreducible representation to which they belong. A well-known example is the

cuprate high-temperature superconductors showing the famous $d_{x^2-y^2}$-wave pairing. The z-axis is a fourfold rotation axis of the crystal but the superconducting order parameter changes sign under rotation by $\pi/2$ about this axis, like the basis function $\mathbf{r} \mapsto x^2-y^2$.

The next step is to construct all combinations of the fields and the gauge-covariant derivative that are invariant under all point-group operations and under time reversal, are gauge invariant, and are real. Gauge invariance requires all terms to contain the same number of factors ψ_n as of factors ψ_n^*. This can already be seen by considering global phase rotations $\psi_n(\mathbf{r}) \mapsto e^{i\alpha}\psi_n(\mathbf{r})$, which is a special gauge transformation. (Time-reversal symmetry is not sufficient for this since a term proportional to $\psi_n + \psi_n^*$ is invariant under time reversal but forbidden by gauge invariance.)

As an example, we consider a cubic superconductor with point group O_h and a three-component order parameter $\boldsymbol{\psi} = (\psi_x, \psi_y, \psi_z)$ that transforms like a vector. This means that it transforms according to the irreducible representation (irrep) T_{1u} of O_h. All terms in the Ginzburg–Landau functional must transform according to the trivial irrep A_{1g}.

The second-order term must involve products of one component of $\boldsymbol{\psi}^*$ and one component of $\boldsymbol{\psi}$. It is very useful to consider the reduction of products of irreps, in this case [21–23]

$$T_{1u} \otimes T_{1u} = A_{1g} \oplus E_g \oplus T_{1g} \oplus T_{2g}. \tag{105}$$

Since A_{1g} appears exactly once in the above reduction there is one way to construct a fully symmetric term out of the two vectors $\boldsymbol{\psi}^*$ and $\boldsymbol{\psi}$. This term is $\boldsymbol{\psi}^* \cdot \boldsymbol{\psi} = \psi_x^*\psi_x + \psi_y^*\psi_y + \psi_z^*\psi_z$. To fourth order, we have to consider [21–23]

$$T_{1u} \otimes T_{1u} \otimes T_{1u} \otimes T_{1u} = 4\, A_{1g} \oplus 3\, A_{2g} \oplus 7\, E_g \oplus 10\, T_{1g} \oplus 10\, T_{2g}. \tag{106}$$

As A_{1g} occurs four times we could expect that there are four distinct terms of fourth order. This would indeed be correct for a product of four distinct vectors. However, here we have two factors of $\boldsymbol{\psi}^*$ and two of $\boldsymbol{\psi}$ and we will see shortly that one contribution drops out by being trivial. All these terms can be constructed from second-order products $\psi_m\psi_n$ and their complex conjugates. Equation (105) implies that these products can, in principle, be organized into terms transforming according to the four irreps A_{1g}, E_g, T_{1g}, and T_{2g}. The product of any of these irreps with itself contains the trivial A_{1g} exactly once. We can thus obtain the maximum number of four independent fourth-order terms in this way. The four possibilities are:

- The A_{1g} product of second order is $\boldsymbol{\psi} \cdot \boldsymbol{\psi} = \psi_x^2 + \psi_y^2 + \psi_z^2$, which gives the fourth-order term
$$(\boldsymbol{\psi}^* \cdot \boldsymbol{\psi}^*)(\boldsymbol{\psi} \cdot \boldsymbol{\psi}). \tag{107}$$

- The E_g combination of second order is [21–23] $(\psi_x^2-\psi_y^2, (1/\sqrt{3})(2\psi_z^2-\psi_x^2-\psi_y^2))$, which gives the fully symmetric fourth-order term
$$\left(\psi_x^2 - \psi_y^2, \frac{2\psi_z^2 - \psi_x^2 - \psi_y^2}{\sqrt{3}}\right)^{\!*} \cdot \left(\psi_x^2 - \psi_y^2, \frac{2\psi_z^2 - \psi_x^2 - \psi_y^2}{\sqrt{3}}\right)$$

$$= \frac{4}{3}\left[(\psi_x^*)^2\psi_x^2 + (\psi_y^*)^2\psi_y^2 + (\psi_z^*)^2\psi_z^2\right] - \frac{2}{3}\left[(\psi_y^*)^2\psi_z^2 + (\psi_z^*)^2\psi_x^2 + (\psi_x^*)^2\psi_y^2 + \text{c.c.}\right], \tag{108}$$

where "c.c." denotes the complex conjugate.

- The T_{1g} combination of second order would be [21–23]

$$\big(\psi_y\psi_z - \psi_z\psi_y, \psi_z\psi_x - \psi_x\psi_z, \psi_x\psi_y - \psi_y\psi_x\big) = (0,0,0). \tag{109}$$

  It vanishes because T_{1g} is the antisymmetric part of $T_{1u}\otimes T_{1u}$. Hence, we cannot construct an independent fourth-order term in this way.

- The T_{2g} combination of second order is [21–23]

$$\big(\psi_y\psi_z + \psi_z\psi_y, \psi_z\psi_x + \psi_x\psi_z, \psi_x\psi_y + \psi_y\psi_x\big) \propto \big(\psi_y\psi_z, \psi_z\psi_x, \psi_x\psi_y\big), \tag{110}$$

  which gives the fourth-order term

$$\big(\psi_y\psi_z, \psi_z\psi_x, \psi_x\psi_y\big)^*\cdot \big(\psi_y\psi_z, \psi_z\psi_x, \psi_x\psi_y\big) = |\psi_y|^2|\psi_z|^2 + |\psi_z|^2|\psi_x|^2 + |\psi_x|^2|\psi_y|^2. \tag{111}$$

One can find three linear combinations of the three obtained terms that are more compact and more useful for discussing physics:

$$(\boldsymbol{\psi}^*\cdot\boldsymbol{\psi})^2, \tag{112}$$

$$(\boldsymbol{\psi}^*\cdot\boldsymbol{\psi}^*)(\boldsymbol{\psi}\cdot\boldsymbol{\psi}), \tag{113}$$

$$\boldsymbol{\mu}\cdot\boldsymbol{\mu}, \tag{114}$$

where

$$\boldsymbol{\mu} \equiv i\,(\boldsymbol{\psi}^*\times\boldsymbol{\psi}) = i\begin{pmatrix} \psi_y^*\psi_z - \psi_z^*\psi_y \\ \psi_z^*\psi_x - \psi_x^*\psi_z \\ \psi_x^*\psi_y - \psi_y^*\psi_x \end{pmatrix}. \tag{115}$$

This quantity is odd under time reversal (since $\psi_n \mapsto \psi_n^*$) and transforms like a pseudovector (T_{1g}). The factor i has been inserted to make $\boldsymbol{\mu}$ real. We return to the meaning of $\boldsymbol{\mu}$ below.

Similarly, we can find the terms of second order in the order parameter and containing two derivatives. In this case, we require products containing one component each of $\mathbf{D}^*$, $\mathbf{D}$, $\boldsymbol{\psi}^*$, and $\boldsymbol{\psi}$. Now we have four distinct vectors and Eq. (106) suggests that there are four terms of this type. But $\mathbf{D}^*$ and $\mathbf{D}$ are operators so that the order of factors matters. Due to gauge invariance, we must be able to express the functional in terms of the derivatives $D_m\psi_n$ and their complex conjugates only. Equation (105) implies that these derivatives can be organized into terms transforming according to the four irreps A_{1g}, E_g, T_{1g}, and T_{2g}:

- The A_{1g} combination is $\mathbf{D}\cdot\boldsymbol{\psi}$, which gives the fourth-order term $(\mathbf{D}\cdot\boldsymbol{\psi})^*\,(\mathbf{D}\cdot\boldsymbol{\psi})$.

- The E_g combination is $\big(D_x\psi_x - D_y\psi_y, (1/\sqrt{3})(2D_z\psi_z - D_x\psi_x - D_y\psi_y)\big)$, which gives the fully symmetric term

$$\begin{aligned}
&\left(D_x\psi_x - D_y\psi_y, \frac{2D_z\psi_z - D_x\psi_x - D_y\psi_y}{\sqrt{3}}\right)^* \cdot \left(D_x\psi_x - D_y\psi_y, \frac{2D_z\psi_z - D_x\psi_x - D_y\psi_y}{\sqrt{3}}\right) \\
&= \frac{4}{3}\left[(D_x\psi_x)^*(D_x\psi_x) + (D_y\psi_y)^*(D_y\psi_y) + (D_z\psi_z)^*(D_z\psi_z)\right] \\
&\quad - \frac{2}{3}\left[(D_y\psi_y)^*(D_z\psi_z) + (D_z\psi_z)^*(D_x\psi_x) + (D_x\psi_x)^*(D_y\psi_y) + \text{c.c.}\right]. \qquad (116)
\end{aligned}$$

- The T_{1g} combination is $\big(D_y\psi_z - D_z\psi_y, D_z\psi_x - D_x\psi_z, D_x\psi_y - D_y\psi_x\big)$, which does not vanish since $\mathbf{D}$ and $\boldsymbol{\psi}$ are distinct. This combination results in the fully symmetric term

$$\begin{aligned}
&(D_y\psi_z)^*(D_y\psi_z) + (D_z\psi_y)^*(D_z\psi_y) + (D_z\psi_x)^*(D_z\psi_x) + (D_x\psi_z)^*(D_x\psi_z) \\
&+ (D_x\psi_y)^*(D_x\psi_y) + (D_y\psi_x)^*(D_y\psi_x) - (D_y\psi_z)^*(D_z\psi_y) - (D_z\psi_y)^*(D_y\psi_z) \\
&- (D_z\psi_x)^*(D_x\psi_z) - (D_x\psi_z)^*(D_z\psi_x) - (D_x\psi_y)^*(D_y\psi_x) - (D_y\psi_x)^*(D_x\psi_y). \qquad (117)
\end{aligned}$$

- The T_{2g} combination is $\big(D_y\psi_z + D_z\psi_y, D_z\psi_x + D_x\psi_z, D_x\psi_y + D_y\psi_x\big)$, which gives the term

$$\begin{aligned}
&(D_y\psi_z)^*(D_y\psi_z) + (D_z\psi_y)^*(D_z\psi_y) + (D_z\psi_x)^*(D_z\psi_x) + (D_x\psi_z)^*(D_x\psi_z) \\
&+ (D_x\psi_y)^*(D_x\psi_y) + (D_y\psi_x)^*(D_y\psi_x) + (D_y\psi_z)^*(D_z\psi_y) + (D_z\psi_y)^*(D_y\psi_z) \\
&+ (D_z\psi_x)^*(D_x\psi_z) + (D_x\psi_z)^*(D_z\psi_x) + (D_x\psi_y)^*(D_y\psi_x) + (D_y\psi_x)^*(D_x\psi_y). \qquad (118)
\end{aligned}$$

However, the four terms we have constructed are not independent because of Eq. (104), which implies that $(D_i\psi_j)^*(D_j\psi_i) = (D_j\psi_j)^*(D_i\psi_i)$ up to an irrelevant boundary term. With that, we only obtain three independent terms, which can be written as

$$(\mathbf{D}\cdot\boldsymbol{\psi})^*\,(\mathbf{D}\cdot\boldsymbol{\psi}) = (D_x\psi_x + D_y\psi_y + D_z\psi_z)^*(D_x\psi_x + D_y\psi_y + D_z\psi_z), \qquad (119)$$

$$(D_x\psi_x)^*(D_x\psi_x) + (D_y\psi_y)^*(D_y\psi_y) + (D_z\psi_z)^*(D_z\psi_z), \qquad (120)$$

$$\begin{aligned}
&(D_y\psi_z)^*(D_y\psi_z) + (D_z\psi_y)^*(D_z\psi_y) + (D_z\psi_x)^*(D_z\psi_x) \\
&+ (D_x\psi_z)^*(D_x\psi_z) + (D_x\psi_y)^*(D_x\psi_y) + (D_y\psi_x)^*(D_y\psi_x). \qquad (121)
\end{aligned}$$

More interestingly, a term linear in the magnetic induction appears. Recall that $\boldsymbol{\mu}$ defined in Eq. (115) is a time-reversal-odd pseudovector (T_{1g}). Since $\mathbf{B}$ is also a time-reversal-odd pseudovector a term proportional to

$$\mathbf{B}\cdot\boldsymbol{\mu} = \mathbf{B}\cdot i\,(\boldsymbol{\psi}^*\times\boldsymbol{\psi}) = i\big(B_x\psi_y^*\psi_z + B_y\psi_z^*\psi_x + B_z\psi_x^*\psi_y\big) + \text{c.c.} \qquad (122)$$

is allowed. This means that the superconducting state carries a magnetization proportional to $\boldsymbol{\mu}$. It is nonzero if at least two of the components of $\boldsymbol{\psi}$ are nonzero and have a nontrivial phase difference. This is *exactly* the condition for the superconducting order parameter to break time-reversal symmetry. Microscopically, the presence of a magnetization is easy to understand since the most natural way to realize a multi-component order parameter is by means of spin-triplet (spin-1) Cooper pairs, which couple to $\mathbf{B}$ through the Zeeman interaction.

Finally, does the same mechanism also produce a term of linear order in derivatives? We try to construct terms that contain one factor each of $\mathbf{D}$, $\boldsymbol{\psi}$, and $\boldsymbol{\psi}^*$. $\mathbf{D}\cdot\boldsymbol{\mu}$ is not a good idea since

$$\mathbf{D}\cdot\boldsymbol{\mu} + \text{c.c.} = \nabla\cdot\boldsymbol{\mu} - i\,\frac{q}{\hbar c}\,\mathbf{A}\cdot\boldsymbol{\mu} + \nabla\cdot\boldsymbol{\mu} + i\,\frac{q}{\hbar c}\,\mathbf{A}\cdot\boldsymbol{\mu} = 2\,\nabla\cdot\boldsymbol{\mu} \tag{123}$$

is a total derivative and thus reduces to an irrelevant boundary term under the spatial integral. Hence, we instead consider

$$J \equiv \boldsymbol{\psi}^* \cdot (\mathbf{D}\times\boldsymbol{\psi}). \tag{124}$$

Using integration by parts, we find

$$\begin{aligned} J &= \psi_x^* D_y \psi_z + \psi_y^* D_z \psi_x + \psi_z^* D_x \psi_y + \text{c.c.} \\ &= \psi_x^* D_y \psi_z + \psi_y^* D_z \psi_x + \psi_z^* D_x \psi_y + \psi_x D_y^* \psi_z^* + \psi_y D_z^* \psi_x^* + \psi_z D_x^* \psi_y^*, \end{aligned} \tag{125}$$

up to an irrelevant boundary term. J is even under time reversal. Under proper rotations, J transforms like a scalar. However, it is the product of three vectors and is thus *odd* under inversion, i.e., it is a pseudoscalar transforming according to A_{1u}. Thus such a term is forbidden by inversion symmetry.

On the other hand, if the crystal does not possess inversion symmetry, i.e., if we are dealing with a noncentrosymmetric superconductor, the behavior under inversion is immaterial and the above term is allowed [26, 27]. Such terms of first order in derivatives are called *Lifshitz invariants*. In our example, the point group becomes O. The irreps A_{1g} and A_{1u} restricted to the subgroup O of O_h are identical and are called A_1 as an irrep of O.

Lifshitz invariants have interesting consequences: Let us consider the situation deep inside a noncentrosymmetric superconductor, where the $\mathbf{B}$ field vanishes and $\mathbf{A}$ can be gauged to zero. An ansatz $\boldsymbol{\psi}(\mathbf{r}) = \boldsymbol{\psi}_0\, e^{i\mathbf{q}\cdot\mathbf{r}}$ generates a term proportional to

$$J = \left(\mathbf{q} - \frac{q}{\hbar c}\,\mathbf{A}\right)\cdot i\,(\boldsymbol{\psi}_0^* \times \boldsymbol{\psi}_0) = \mathbf{q}\cdot\boldsymbol{\mu}_0, \tag{126}$$

with $\boldsymbol{\mu}_0 \equiv i\,(\boldsymbol{\psi}_0^*\times\boldsymbol{\psi}_0)$, in the free energy, which is linear in the wave vector $\mathbf{q}$. It is only present if $\boldsymbol{\mu}_0 \neq 0$, i.e., if time-reversal symmetry is broken. In addition, there are three positive terms of second order in derivatives, Eqs. (119)–(121), which generate terms of second order in $\mathbf{q}$. This means that the free energy is minimized by a solution with $\mathbf{q} \neq 0$ and spatially rotating phase factor $e^{i\mathbf{q}\cdot\mathbf{r}}$. The conclusion is that time-reversal-symmetry-breaking states in noncentrosymmetric superconductors are *helical states* [27].

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