Lecture 2: Superconductors - phenomenology (part 2)

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I. THERMODYNAMICS OF SUPERCONDUCTORS - CONTINUED

Last lecture: we found the relation between the free density energy for the N/S states and the critical field. We discuss how this can be used to extract useful information on the nature of the phase transition based only on thermodynamic arguments.

A. Phase transition in a magnetic field: latent heat and specific heat

The dependence of the critical field on the temperature can be used to extract useful parameters related to the phase transition. $H_c(T)$ varies between a maximum value H_{c0} at $T = 0$ and zero at the critical temperature T_c. Empirically it is found that the law

$$H_c(T) = H_c0 \left(1 - \left(\frac{T}{T_c}\right)^2\right) \tag{1}$$

(see Fig. 1) is well satisfied for many superconductors [1].

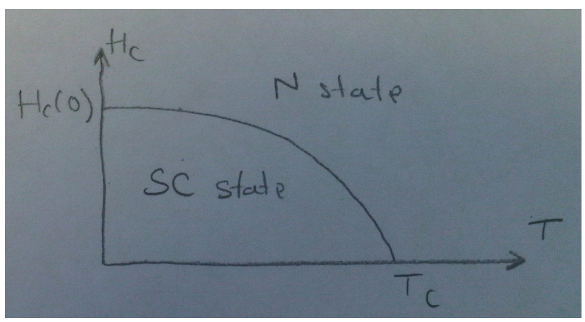

FIG. 1. Phase diagram of a superconductor, showing the critical field versus temperature.

The entropy is defined with respect to the free energy F as

$$S = -V\left(\frac{\partial F}{\partial T}\right). \tag{2}$$

We have

$$S_S(T) - S_N(T) = V \times \mu_0 H_c \frac{\partial H_c(T)}{\partial T} \tag{3}$$

which based on 1 (in fact the monotonous decrease of the critical field is sufficient) leads to

$$S_S(T) - S_N(T) < 0. \tag{4}$$

The difference $S_S(T) - S_N(T)$ vanishes at $T = T_c$ because $H_c(T_c) = 0$ (we assume that $\frac{\partial H_c}{\partial T}(T_c)$ is finite, consistent with 1). The transition in zero field is therefore a 2nd order phase transition (no latent heat).

We can also calculate the difference between the specific heat for the superconducting and the normal state

$$C_S - C_N = T\frac{\partial}{\partial T}(S_S - S_N) = TV\mu_0\left(\left(\frac{\partial H_c}{\partial T}\right)^2 + H_c\frac{\partial^2 H_c}{\partial T^2}\right). \tag{5}$$

At T_c one has

$$(C_S - C_N)|_{T_c} = T\mu_0\left(\frac{\partial H_c}{\partial T}\right)^2 > 0. \tag{6}$$

The general behaviour of the specific heat is shown in Fig/ 2.

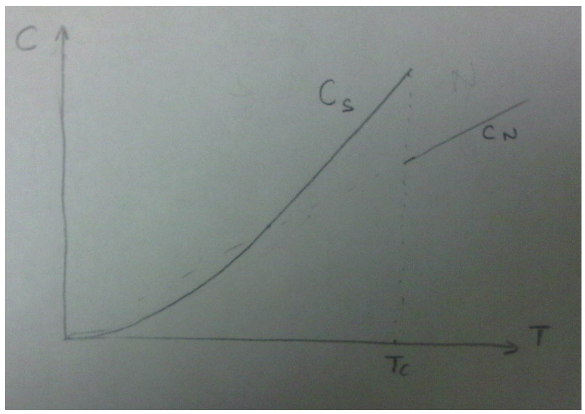

FIG. 2. Dependence of the specific heat, in the superconducting (C_S) and normal (C_N) states, on temperature.

II. GINZBURG LANDAU THEORY

A. Ginzburg Landau free energy

Ginzburg Landau theory is a phenomenological theory of superconductivity, formulated in 1950, before the discovery of the microscopic theory. Despite it being a phenomenological theory, it represented a major step towards a complete understanding of superconductivity. Theoretical work subsequent to the microscopic theory of superconductivity has shown that GL can be deduced from the microscopic theory and that it is valid near the transition temperature. GL is preferred to the microscopic theory in problems in which the system is inhomogeneous, as the direct incorporation of spatial variations in the microscopic theory is extremely cumbersome. Even when the condition $T \lesssim T_c$ is not satisfied, the GL theory can still provide valuable insight.

GL theory builds on Landau's theory of second order phase transitions. In this theory, an order parameter is the physical quantity which is representative of the two phases under consideration. For example, the order parameter in ferromagnetism is the magnetization; above the transition temperature, magnetization vanishes; below the transition temperature it is finite and increases gradually as the temperature is lowered. For the N/S transition, a *complex* order parameter ψ is introduced. This was chosen by GL with the intuition that superconductivity is a quantum phenomenon, and therefore the order has to be complex, as a wavefunction in quantum mechanics is.

The first contribution to the free energy density is an even order expansion in terms of the amplitude of order parameter:

$$F_0(T) = \alpha(T)|\psi|^2 + \frac{\beta(T)}{2}|\psi|^4. \tag{7}$$

This is the generic expansion used in Landau's theory of second order phase transitions. The parameter β is taken to be (approximately) constant and positive around T_c, whereas α is proportional with $T - T_c$. For $T > T_c$ the minimum free energy parameter corresponds to $|\psi| = 0$ whereas at $T < T_c$ the minimum value of the free energy corresponds to a finite order parameter

$$|\psi|^2 = |\psi_\infty|^2 = -\frac{\alpha}{\beta}. \tag{8}$$

This is illustrated in Fig. 3. In 8 we introduced the parameter $|\psi_\infty|$ - this is the order parameter at a given temperature deep inside a superconductor where it approaches a constant value, as we will see below. Based on 8 and the variation $\alpha(t) \approx \alpha'(1)(1-t)$ with temperature (we introduced the reduced temperature $t = T/T_c$) we find $|\psi|^2 \propto 1 - t$. This is consistent with identifying the absolute values squared of the order parameter with the superfluid density n_s (experimentally it is found that the penetration depth λ, which based on London equation is proportional with $n_s^{-1/2}$, varies $\propto (1-t)^{-1/2}$; see [1]).

A second contribution to the energy is related to gradients and the interaction with a magnetic field:

$$F_{kin} = \frac{1}{2 \times 2m}|\left(\frac{\hbar}{i}\nabla - 2e\boldsymbol{A}\right)\psi|^2. \tag{9}$$

The expression above is connected with the expression $\frac{1}{2m^*}\left(\frac{\hbar}{i}\nabla - q^*\boldsymbol{A}\right)^2$ for the kinetic energy operator of a particle of mass m^* and charge q^* in a magnetic field of vector potential $\boldsymbol{A}$ (this point will become more clear below where the GL equations will be derived). In 9

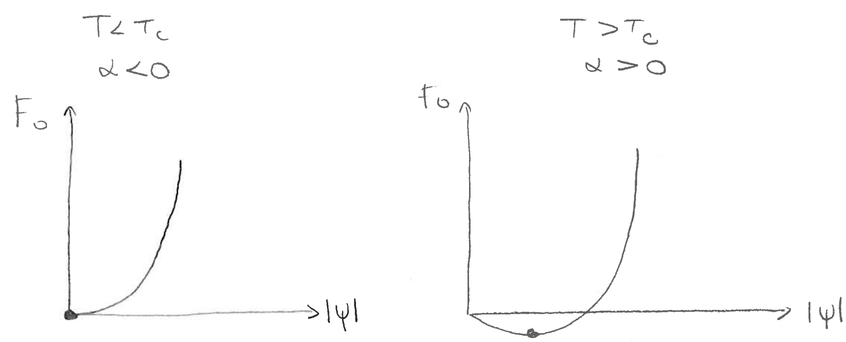

FIG. 3. Plot of the free energy (neglecting gradients and magnetic field) versus order parameter above (left) and below (right) the transition temperature.

we anticipated a result of microscopic theory: the electrons are paired, therefore the charge is taken to be $2e$ and the mass is taken $2m$[1].

Finally, one has to consider the free energy of the magnetic field

$$F_{magn} = \frac{1}{2\mu_0}\boldsymbol{B}^2. \tag{10}$$

Summing 7, 9, and 10 we obtain the complete expression for the GL free energy

$$F_{GL}(\boldsymbol{r}) = \alpha(T)|\psi(\boldsymbol{r})|^2 + \frac{\beta(T)}{2}|\psi(\boldsymbol{r})|^4 + \frac{1}{2\times 2m}|\left(\frac{\hbar}{i}\nabla - 2e\boldsymbol{A}(\boldsymbol{r})\right)\psi(\boldsymbol{r})|^2 + \frac{1}{2\mu_0}\boldsymbol{B}(\boldsymbol{r})^2. \tag{11}$$

B. Ginzburg Landau equations

The GL equations are obtained by minimization of the total free energy

$$\mathcal{F} = \int d\boldsymbol{r} F_{GL}(\boldsymbol{r}) \tag{12}$$

with respect to variations of $\psi(\boldsymbol{r})$ (12 is to be seen as a functional of ψ and $\boldsymbol{A}$). We use standard variational techniques to obtain the optimal position-dependent order parameter and vector potential.

Considering first variations $\partial\mathcal{F}$ arising from small variations $\delta\phi(\boldsymbol{r})$. We require $\delta\mathcal{F} = 0$ in first order in $\partial\phi(\boldsymbol{r})$. We obtain

$$\alpha\psi + \beta|\psi(\boldsymbol{r})|^2\psi + \frac{1}{2\times 2m}\left(\frac{\hbar}{i}\nabla - 2e\boldsymbol{A}\right)^2\psi = 0. \tag{13}$$

[1] In Section 4.1 of [1] a discussion can be found on the possible choices for parameters in 9 and in general for the GL equation.

Carrying next the procedure of optimization with respect to variations in $\boldsymbol{A}$ we obtain

$$\nabla \times \left(\frac{1}{\mu_0}\nabla \times \boldsymbol{A}\right) = \frac{2e\hbar}{2 \times 2mi}\left(\psi^*\nabla\psi - \psi\nabla\psi^*\right) - \frac{(2e)^2}{2m}|\psi|^2\boldsymbol{A} \tag{14}$$

which becomes

$$\boldsymbol{j} = \frac{2e\hbar}{2 \times 2mi}\left(\psi^*\nabla\psi - \psi\nabla\psi^*\right) - \frac{2e^2}{m}|\psi|^2\boldsymbol{A} \tag{15}$$

if we use

$$\boldsymbol{j} = \nabla \times \boldsymbol{H}. \tag{16}$$

We focused on the minimization of the free energy. When the superconductor is placed in a magnetic field generated by external sources, we have to consider instead the minimization of the Gibbs potential

$$\mathcal{G} = \int d\boldsymbol{r}\left(F_{GL}(\boldsymbol{r}) - \boldsymbol{B}(\boldsymbol{r})\boldsymbol{H}_{ext}(\boldsymbol{r})\right) \tag{17}$$

where the field $\boldsymbol{H}_{ext}(\boldsymbol{r})$ is the field produced by the external sources, related to external currents $\boldsymbol{j}_{ext}$ through $\nabla\boldsymbol{H}_{ext} = \boldsymbol{j}_{ext}$. As it turns out the minimization of the Gibbs potential with respect to ψ and $\boldsymbol{A}$ leads to the same equations, 13 and 15. However, the Gibbs potential is the proper quantity to consider when calculating the structure of a mixed state (this will be discussed below for the wall energy).

C. Coherence length and penetration depth

We consider the case in which no magnetic field is applied ($\boldsymbol{A} = 0$). We also express the order parameter as

$$\psi(\boldsymbol{r}) = f(\boldsymbol{r})\psi_\infty. \tag{18}$$

Then in one dimension 13 becomes

$$\frac{\hbar^2}{4m|\alpha|}\frac{d^2 f}{dx^2} + f - f^3 = 0 \tag{19}$$

We can take f to be real as the equation has only real coefficients. This makes it natural to introduce a length scale called the *Ginzburg Landau coherence length* and given by

$$\xi^2 = \frac{\hbar^2}{4m|\alpha(T)|} \propto \frac{1}{1-t} \tag{20}$$

Note that this is different of the BCS coherence length to be introduced in the next lecture.

We next show how a finite magnetic field penetration length can be deduced as a result of the GL equations. We consider $\psi = |\psi| e^{i\phi}$, with both the amplitude and the phase position dependent in general We can rewrite 15 as

$$\boldsymbol{j} = \frac{e}{m} |\psi|^2 \left(\hbar \nabla \phi + 2e\boldsymbol{A} \right). \tag{21}$$

We insert $\boldsymbol{j} = \frac{1}{\mu_0} \nabla \times \boldsymbol{B}$ in 21 and then take the curl:

$$\nabla \times \left(\frac{1}{\mu_0} \nabla \times \boldsymbol{B} \right) = -\frac{2e^2}{m} \nabla \times \boldsymbol{A}. \tag{22}$$

We find

$$\triangle \boldsymbol{B} - \lambda_{eff}^{-2} \boldsymbol{B} = 0 \tag{23}$$

with

$$\lambda_{eff} = \sqrt{\frac{m}{2e^2 \mu_0 |\psi|^2}} \tag{24}$$

We thus recover the result derived based on London theory. The same result is obtained as based on London's equation if we identify $|\psi|^2 = n_s/2$.

III. FLUXOID QUANTIZATION

Take a countour Γ contained in the superconductor. We integrate 21 over this countour. We define the fluxoid number n as the integral

$$n = \oint_\Gamma \frac{1}{2\pi} \nabla \phi d\boldsymbol{r}. \tag{25}$$

n has to be an integer if the order parameter is to have a uniquely defined phase. We have

$$\Phi_\Gamma = n\Phi_0 + \mu_0 \lambda_{eff}^2 \oint_\Gamma \boldsymbol{j} d\boldsymbol{r}, \tag{26}$$

with $\Phi_0 = \frac{h}{2|e|}$ the flux quantum, and Φ_Γ the magnetic flux threading the countour Γ. This is a very important result. Note that for a simply connected conductor n can only be equal to zero; otherwise the current would be divergetn. For a multiply connected conductor, we also have $n = 0$ as long as the contour does not encircle any hole in the superconductor. However, if a hole is encircled, then n can be any integer.

When the contour Γ goes deep inside the superconductor, where the magnetic field is screened and the current vanishes, the second term of the RHS of 26 is negligible. The magnetic flux is thus quantized. The experimental observation of quantization of flux, with a basic quantum equal to $h/2|e|$ also represents important validation of the microcopic theory: this result is indeed consistent with units of charge of $2e$, as predicted by the microscopic theory.

IV. SUPERCONDUCTORS OF TYPE I AND TYPE II

GL theory provides the basis of a discussion of the energy of the surface between a normal and a superconducting region in a superconductor. This quantity is important when discussing the intermediate state of superconductors.

A representation of the magnetic field and order parameter at a N/S boundary is given in Fig. 4. The externally applied field is H_c - this is the field at which the (bulk) normal and superconducting Gibbs energies are equal. At the boundary, the magnetic field decreases over a length λ (the penetration depth) and the order parameter increases over a a length ξ (the coherence length). The Gibbs potential can be calculated using the expression 17. We denote its surface density by

$$\frac{G_{\text{wall}}}{\text{surface}} = \frac{1}{2}\mu_0 H_c^2 \delta, \tag{27}$$

with δ a characteristic length scale. We introduce the parameter

$$\kappa = \frac{\lambda_{\text{eff}}}{\xi}. \tag{28}$$

For $\kappa \ll 1$, the order parameter is significantly below the equilibrium superconducting value over a region where the magnetic field is nearly zero; so condensation energy is lost, which means that the wall energy density is positive ($\delta > 0$). For $\kappa \gg 1$, the magnetic field penetrates into the superconducting region over a significant length; this leads to a negative contribution to the Gibbs energy ($B^2/2\mu_0 - H_c B$), so the wall energy density is negative ($\delta < 0$). This is the distinction between type I and type II superconductors. The exact crossover occurs at

$$\kappa_{I/II} = \frac{1}{\sqrt{2}} \tag{29}$$

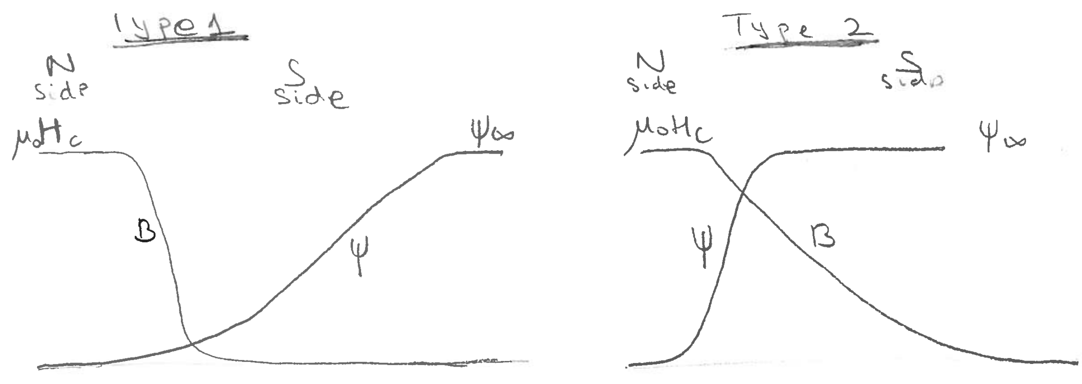

FIG. 4. Variation of the magnetic field and of the superconducting order parameter at the wall between the normal (N) and superconducting (S) phases, for type I (left) and type II (right) superconductors.

V. VORTICES

Abrikosov showed that the negative surface energy for type II SCs leads to a very important effect. In a type II SC the magnetic field penetrates as soon as the applied field exceeds H_{c1}, the *first critical field*. Field enters through fine filaments called *vortices*. Each vortex carries a magnetic flux of one flux quantum. As the field is increased, the density increases until reaching the *second critical field* H_{c2}, when the transition to the normal state occurs.

The behaviour of type II SCs has important consequences. Vortices are mobile, and their motion results both in dissipation and magnetic field noise. Both these effects are negative for the behaviour of superconducting devices. To prevent such effects, vortex pinning centers have to be introduced. Type I materials are preferable, as this problem does not occur.

VI. FURTHER READING ON PHENOMENOLOGICAL THEORY OF SUPERCONDUCTORS

The following books provide further a very detailed account of the phenomenological theory of superconductors:

- de Gennes [2]: very careful discussion of the thermodynamic potentials and treatment of the mixed state

- Tinkham [1]: concise and complete discussion of GL equations, and many applications. The treatment of the mixed state is also extremely good

- Schmidt[3] interesting discussion on thermodynamic properties

A good discussion of thermodynamic potentials, in particular related to work done by sources, can be found in [4] and [5].

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[1] M. Tinkham, *Introduction to superconductivity*, 2nd ed., edited by J. Shira and E. Castellano, Physics and Astronomy (McGraw-Hill, 1996).

[2] P. de Gennes, *Superconductivity of metals and alloys* (WA Benjamin, 1966).

[3] V. Schmidt, *The physics of superconductors* (Springer-Verlag, 1997).

[4] D. Goodstein, *States of matter* (Dover Pubns, 2002).

[5] L. D. Landau and E. M. Lifshitz, *Course of Theoretical Physics, vol 8 Electrodynamics of Continuous Media*, 2nd ed. (Pergamon Press, 1984).