## 8.231 Physics of Solids I — Fall 2017 Recitation 8

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In this recitation, we will introduce Ginzburg-Landau theory of superconductivity.

## 1 Ginzburg-Landau Free Energy

Ginzburg-Landau (GL) theory is a phenomenological theory for superconductivity. It was first proposed by Ginzburg and Landau in 1950, way before the BCS microscopic theory (1957). It was later shown by Gor'kov that one can deduce GL theory from BCS theory rigorously (1959).

The central ingredient of the theory is a pseudowavefunction  $\psi(\mathbf{r})$ , whose magnitude  $|\psi(\mathbf{r})|^2$  is interpreted as the local density of superconducting electrons  $n_s(\mathbf{r})$ .

Assume  $\psi$  is small and varies slowly in space. The free energy density of the whole system can be expanded to the leading order of  $|\psi|^2$  and  $|\nabla \psi|^2$ :

$$f = f_n + \alpha |\psi|^2 + \frac{\beta}{2} |\psi|^4 + \frac{1}{2m^*} \left| \left( -i\hbar\nabla - \frac{e^*}{c} \mathbf{A} \right) \psi \right|^2 + \frac{(\nabla \times \mathbf{A})^2}{8\pi},$$
(1)

where  $f_n$  is the free energy of electrons in the normal state in the absence of the field,  $(\nabla \times \mathbf{A})^2/(8\pi)$  is the energy for the magnetic field,  $\alpha$  and  $\beta$  are phenomenological parameters,  $m^*$  is the effective mass and  $e^* = 2e$  is the effective charge. The configuration of  $\psi$  is such that the free energy is minimized. Note that  $\beta > 0$  otherwise the energy is unbounded from below.

**Homogeneous Case** Let us first consider the simple case when there is no magnetic field and spatial gradients  $\mathbf{A} = \nabla \psi = 0$ . Then

$$f - f_n = \alpha |\psi|^2 + \frac{\beta}{2} |\psi|^4.$$
 (2)

There are two scenarios:

- $\alpha > 0$ . The free energy minimum is located at  $\psi = 0$ , hence  $n_s = 0$ . There is no superconducting electron and thus  $T > T_c$ , where  $T_c$  is the superconducting phase transition temperature.
- $\alpha < 0$ . The free energy minimum is located at  $|\psi|^2 = -\alpha/\beta$ , which is  $f f_n|_{|\psi|^2 = -\alpha/\beta} = -\alpha^2/(2\beta)$ . This belongs to the case when  $T < T_c$ . Note that in this way we can conclude the GL theory is a good approximation near  $T_c$  because  $|\psi|^2$  is small.

Note that  $-\alpha^2/(2\beta)$  is the energy gain of having superconducting electrons. There is another energy cost of repelling all the magnetic field out of the superconductor<sup>1</sup>. Whether the material is superconducting or not depends on which of the two energies are larger. Thus  $\alpha^2/(2\beta) \equiv H_c^2/(8\pi)$  defines a critical field. Large magnetic field  $H > H_c$  kills the superconductivity through a first order phase transition.

<sup>&</sup>lt;sup>1</sup>In fact, this argument is rather subtle. The proper thermodynamic potential to use in this context is the Gibbs free energy G(T, H) instead of the Helmholtz free energy F(T, M). The state variables for Helmholtz free energy are temperature and magnetism: dF = -SdT + HdM. However, in the experiments it is easier to control external field H (suppose magnetic field is

In principle, both  $\alpha$  and  $\beta$  are complicated functions of temperature T. Neat  $T = T_c$ , both  $\alpha$  and  $\beta$  can be expanded to the leading order of  $T - T_c$ :

$$\alpha(t) = \alpha_1(t-1), \quad \alpha_1 > 0, \tag{5}$$

$$\beta(t) = \beta_0, \quad \beta_0 > 0, \tag{6}$$

where  $t \equiv T/T_c$ . Then near  $T_c$  the density of superconducting electrons increases linearly:  $n_s \propto (1-t)$ .

So far, this is exactly the Landau second order phase transition theory. The functional form of the free energy is similar to that in the ferromagnetic-paramagnetic phase transition in the Ising model.

**Inhomogeneous Case** In order to minimize free energy in the general case, we take the variation of  $F[\psi, \psi^*, \mathbf{A}] = \int f d\mathbf{r}$  over  $\psi^*$  and  $\mathbf{A}$ .

$$\frac{\delta F}{\delta \psi^*} = 0, \quad \frac{\delta F}{\delta \mathbf{A}} = 0. \tag{7}$$

Let us first compute the first variation. It is helpful to integral by part and rewrite the kinetic energy as

$$\frac{1}{2m^*} \int d\mathbf{r} \left( i\hbar \nabla \psi^* - \frac{e^*}{c} \mathbf{A} \psi^* \right) \left( -i\hbar \nabla \psi - \frac{e^*}{c} \mathbf{A} \psi \right)$$
(8)

$$=\frac{1}{2m^*}\int d\mathbf{r} \left(-i\hbar\psi^*\nabla - \frac{e^*}{c}\mathbf{A}\psi^*\right) \left(-i\hbar\nabla\psi - \frac{e^*}{c}\mathbf{A}\psi\right)$$
(9)

$$=\frac{1}{2m^*}\int d\mathbf{r}\psi^* \left(-i\hbar\nabla - \frac{e^*}{c}\mathbf{A}\right)^2\psi.$$
(10)

In this way,  $\delta F / \delta \psi^* = 0$  becomes

$$\alpha\psi + \beta|\psi|^2\psi + \frac{1}{2m^*} \left(-i\hbar\nabla - \frac{e^*}{c}\mathbf{A}\right)^2\psi = 0.$$
(11)

Note that it is nonlinear with respect to  $\psi$  due to the presence of  $\beta$ .

For the second variation,  $\delta F/\delta \mathbf{A} = 0$  becomes

$$\frac{ie^*\hbar}{2m^*c}(\psi^*\nabla\psi - \psi\nabla\psi^*) + \frac{e^{*2}}{m^*c^2}\psi^*\psi\mathbf{A} + \frac{\nabla\times\mathbf{A}}{4\pi} = 0,$$
(12)

which is often rewritten into

$$\mathbf{J} = \frac{c}{4\pi} \nabla \times \mathbf{B} = \frac{e^* \hbar}{2m^* i} (\psi^* \nabla \psi - \psi \nabla \psi^*) - \frac{e^{*2}}{m^* c} \psi^* \psi \mathbf{A} = e^* |\psi|^2 \mathbf{v}_s.$$
(13)

Here the first equality is just the Ampère's circuital law.  $\mathbf{v}_s$  is the supercurrent velocity. If we rewrite  $\psi = |\psi|e^{i\varphi}$ , the supercurrent can be identified as

$$\mathbf{v}_s = \frac{1}{m^*} \left( \hbar \nabla \varphi - \frac{e^* \mathbf{A}}{c} \right). \tag{14}$$

Equations (11) and (12) are nonlinear coupled differential equations, which is often called GL equations.

parallel to the surface of the superconductor, thus H is the same in and out of the superconductor) instead of the magnetism M. It is thus convenient to use Gibbs free energy  $G = F - VBH/(4\pi)$ , and dG = -SdT - MdH. Note that  $\mathbf{B} = \mathbf{H} + 4\pi\mathbf{M}$  and  $\mathbf{H}$  is fixed constant.

In this way, the Gibbs free energy in the normal state is

$$G_n = V f_n - V \frac{H^2}{8\pi} - V_{\text{ext}} \frac{H^2}{8\pi},$$
(3)

where V is the volume of the system and  $V_{\text{ext}}$  is the volume of the remaining space with magnetic field. In the superconducting state,

$$G_s = V f_n - V \frac{H_c^2}{8\pi} - V_{\text{ext}} \frac{H^2}{8\pi},$$
(4)

where we have used Eq. (2) for the second term. Then  $G_n - G_s = -\frac{V}{8\pi} (H^2 - H_c^2)$ , which is positive for  $H < H_c$ .

## 2 Linearized Ginzburg-Landau Equation

Obviously,  $\beta |\psi|^4/2$  in the GL free energy is the origin of all the troubles. The linearized GL equation is obtained by just dropping the  $\beta |\psi|^2 \psi$  term in Eq. (11). This approximation is only justified when  $\alpha \psi \gg \beta |\psi|^2 \psi$ , which means  $|\psi|^2 \ll -\alpha/\beta$ , i.e. the superconducting electron density is rather small.

**Coherence Length** With this approximation, Equation (11) becomes

$$\left(-i\nabla - \frac{2\pi\mathbf{A}}{\Phi_0}\right)^2 \psi = -\frac{2m^*\alpha}{\hbar^2}\psi,\tag{15}$$

where  $\Phi_0 \equiv hc/e^*$  is the flux quantum. It is instructive to define the so-called "GL coherence length" or "healing length":

$$\xi \equiv \frac{\hbar}{\sqrt{-2m^*\alpha}} \propto \frac{1}{\sqrt{1-t}}.$$
(16)

It is a characteristic length scale for variation of  $\psi$ . To see this, simply set  $\mathbf{A} = 0$ . The solution of the wavefunction is simply

$$\psi \sim e^{\pm x/\xi}.\tag{17}$$

This means a small disturbance of  $\psi$  from its equilibrium will decay in a characteristic length of  $\xi$ . Coherence length can be roughly understood as the size of the Cooper pair. It is quite large  $\xi \approx 3000$ Å for typical classical superconductors. Therefore, Cooper pair in metals is really loosely bonded in real space.

**Bulk Nucleation** Suppose a magnetic field  $\mathbf{H} = H\hat{\mathbf{z}}$  is applied to the superconductor. Its vector potential can be chosen as  $A_y = Hx$ . The linearized GL equation becomes

$$\left[-\nabla^2 + \frac{4\pi i}{\Phi_0} H x \frac{\partial}{\partial y} + \left(\frac{2\pi H}{\Phi_0}\right)^2 x^2\right] \psi = \frac{1}{\xi^2} \psi.$$
(18)

Since the vector potential does not depend on y or z, we can separate variables:  $\psi = e^{ik_y y} e^{ik_z z} f(x)$ . The equation then becomes

$$-\frac{d^2f}{dx^2} + \left(\frac{2\pi H}{\Phi_0}\right)^2 (x - x_0)^2 f = \left(\frac{1}{\xi^2} - k_z^2\right) f,$$
(19)

where  $x_0 = k_y \Phi_0/(2\pi H)$ . This is exactly the Schrödinger equation for harmonic potentials (or Landau levels), whose energy eigenvalues are

$$\varepsilon_n = \left(n + \frac{1}{2}\right) \hbar \omega_c = \left(n + \frac{1}{2}\right) \hbar \left(\frac{2eH}{m^*c}\right),\tag{20}$$

which should be equated to  $\hbar^2/(2m^*)(\xi^{-2}-k_z^2)$ :

$$H = \frac{\Phi_0}{2\pi(2n+1)} \left(\frac{1}{\xi^2} - k_z^2\right).$$
 (21)

Evidently, H is highest for n = 0 and  $k_z = 0$ , beyond which the solution does not exist. This defines another characteristic magnetic field

$$H_{c2} = \frac{\Phi_0}{2\pi\xi^2}.$$
 (22)

The corresponding wavefunction is

$$f(x) = \exp\left[-\frac{(x-x_0)^2}{2\xi^2}\right],$$
(23)

which is a Gaussian wavepacket at  $x_0$ . This is called a superconducting vortex. The electrons are only superconducting near the vortices.

**Two Types of Superconductors** Depending on the relative ratio of  $H_c$  and  $H_{c2}$ , there are two types of superconductors.

- Type I superconductors  $H_{c2} < H_c$ . Starting from zero magnetic field and increase magnetic field, the superconductivity is killed completely when  $H > H_c$ .
- Type II superconductors  $H_{c2} > H_c$ . Starting from zero magnetic field and increase magnetic field, the vortices appear when  $H_{c2} > H > H_c$ . The superconductivity is completely killed only when  $H > H_c$ .

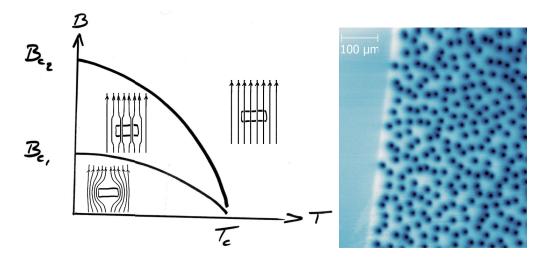


Figure 1: Left: Phase diagram of type II superconductors; Right: Vortices in high- $T_c$  superconductors filmed by scanning SQUID microscopy.