Chapter 5

Thermodynamics

5.1 Free energy of a magnetic body

In real experiment, it is more practical to keep constant temperature and constant pressure rather than constant volume. Thus the Gibbs free energy is frequently used. The Gibbs free energy of a magnetic body is given by:

$$G = U - TS + pV - \mu_0 H_a M. \tag{5.1}$$

One can treat $\mu_0 H_a$ as the external intensity variable p, while M corresponds to the intrinsic variable as $-V$. The opposite sign comes up since energy must be given to a body to increase its magnetization, whereas work is done by a body as it increase its volume against an external pressure.

Small changes in the conditions will produce a change in G as:

$$dG = dU - TdS - SdT + pdV + Vdp - \mu_0 H_a dM - \mu_0 M dH_a. \tag{5.2}$$

When the temperature and the pressure are kept constant, the change in free energy by changing the applied field $H_a$is given by:

$$dG = dU - TdS + pdV - \mu_0 H_a dM - \mu_0 M dH_a. \tag{5.3}$$

For a magnetic body sitting at a constant temperature and a stable pressure, its internal energy change is:

$$dU = TdS \underbrace{- pdV + \mu_0 H_a dM}_{\text{work done on body}}. \tag{5.4}$$

Therefore, the free energy change is:

$$dG = -\mu_0 M dH_a. \tag{5.5}$$

And the total free energy change of a body when it is magnetized to a magnetic moment of M by the application of an external field strength H_a is then:

$$G(H_a) - G(0) = -\mu_0 \int_0^{H_a} M dH_a. \tag{5.6}$$

5.2 Free energy of a superconductor

For a superconductor, we know from the Meissner effect that:

$$M = -H. \tag{5.7}$$

Then the Gibbs free energy per unit volume $g_s(T, H)$ of the superconductor in the superconducting state would vary with the application of magnetic field H_a:

$$\begin{aligned} g_s(T, H_a) &= g_s(T, 0) - \mu_0 \int_0^{H_a} M dH_a \\ &= g_s(T, 0) + \mu_0 \int_0^{H_a} H dH_a \qquad (5.8) \\ &= g_s(T, 0) + \frac{1}{2}\mu_0 H_a^2. \qquad (5.9) \end{aligned}$$

As shown in Fig.5.1, when the applied field reaches some certain value, the free energy of the superconducting state would surpass that of the nomal state $g_n(T, 0)$. The superconductor would loose its superconductivity and enters the normal state. This field value is the critical field H_c and we have:

$$g_s(T, H_c) = g_n(T, 0), \tag{5.10}$$

$$\Rightarrow \frac{1}{2}\mu_0 H_c^2(T) = g_n(T, 0) - g_s(T, 0). \tag{5.11}$$

The Gibbs free energy of the normal state is almost independent of the applied field since the magnetization of a metal is typically negligible.

5.3 Entropy of the superconducting state

The change of the Gibbs free energy is given by Eq.(5.2) when the external conditions is altered. If the pressure and magnetic field are kept constant but the temperature is varied by dT, then the change of free energy is:

$$dG = dU - TdS - SdT + pdV - \mu_0 H_a dM. \tag{5.12}$$

As the internal energy change is given by Eq.(5.4), so:

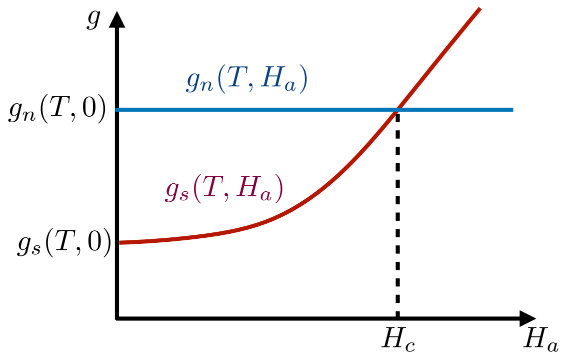

Figure 5.1: Variation of Gibbs energy of a superconductor in the application of magnetic field.

$$dG = -SdT, \tag{5.13}$$

$$S = -\left(\frac{\partial G}{\partial T}\right)_{p,H_a}. \tag{5.14}$$

Now lets us derive the entropy difference between the normal and superconducting states. As discussed in the above section, the Gibbs free energy difference between the normal and superconducting states is:

$$g_n(T, H_a) - g_s(T, H_a) = \frac{1}{2}\mu_0 H_c^2(T) - \frac{1}{2}\mu_0 H_a^2. \tag{5.15}$$

As H_a has no temperature dependence. Then one obtains:

$$s_n(T, H_a) - s_s(T, H_a) = -\mu_0 H_c(T)\frac{dH_c}{dT}. \tag{5.16}$$

$$\frac{dH_c}{dT} < 0 \Rightarrow s_n(T, H_a) > s_s(T, H_a). \tag{5.17}$$

The entropy of the superconducting state is smaller than that of the normal state. So the superconducting state is more ordered than the normal state.

From the third law of thermodynamics, we know that the entropy must goes to zero at the absolute zero temperature $T = 0$. Therefore, both s_n and s_s must be equal to zero at $T = 0$:

$$s_n(T = 0) = s_s(T = 0). \tag{5.18}$$

Since the critical field at $T = 0$ is nonzero,

$$H_c(T = 0) > 0. \tag{5.19}$$

Then from Eq.(5.16) we have:

$$\frac{dH_c}{dT}\mid_{T=0}=0. \tag{5.20}$$

At zero field T_c, the critical field is zero. Therefore the entropy of the normal at superconducting states are also the same at T_c:

$$H_c(T=T_c)=0, \tag{5.21}$$

$$\Rightarrow s_n(T_c)=s_s(T_c) \tag{5.22}$$

Figure 5.2(a) displays the temperature variations of the entropy for normal and superconducting states of a superconductor.Therefore, at zero field, the first derivative of the free energy, i.e. entropy is continous at the superconducting transition. Such a transition is called a *second order phase transition.* And no latent heat is present $L=T(s_n-s_s)_{H_a=0,T_c}=0$.

However, things are different when magnetic field is applied. In the presence of magnetic field, the critical temperature shifts to lower temperature and the critical field is non-zero. There is a discontinuity in the entropy as shown in Eq.(5.16). And there exists latent heat:

$$L(H_a>0)=T(s_n-s_s)_{H_a}=-T\mu_0 H_c(T)\frac{dH_c}{dT}.$$

Thus, at non-zero field, the superconducting transition is of *first order.*

5.4 Specific Heat

The specific heat is the amount of heat ΔQ needed to raise the temperature of an object by ΔT. In real experiments, the specific heat is measured at constant pressure. The specific heat is then given by:

$$C_p=\lim_{\Delta T\to 0}\frac{\Delta Q}{\Delta T}=\frac{dQ}{dT}, \tag{5.23}$$

$$dQ=Tds, \tag{5.24}$$

$$C_p=T\left(\frac{\partial s}{\partial T}\right)_{p,H}=-T\left(\frac{\partial^2 g}{\partial T^2}\right)_{p,H}. \tag{5.25}$$

According to Eq.(5.16), one finds the difference in the specific heats of the superconducting and normal states:

$$C_s-C_n=T\mu_0 H_c\frac{d^2H_c}{dT^2}+T\mu_0\left(\frac{dH_c}{dT}\right)^2. \tag{5.26}$$

At zero field field T_c, $H_c=0$, and:

$$(C_s-C_n)_{T_c}=T_c\mu_0\left(\frac{dH_c}{dT}\right)^2. \tag{5.27}$$

This is the Rutgers' formula, which predicts a discontinuity in the specific heat at the superconducting transition.

The specific heat of a metal is contributed from the lattice and conduction electrons.

$$C_p = C_{latt} + C_{el}. \tag{5.28}$$

The properties of the lattice heat capacity do not change at the transition.

$$C_s - C_n = (C_{el})_s - (C_{el})_n. \tag{5.29}$$

For a normal metal:

$$C_n = C_{latt} + (C_{el})_n = A\left(\frac{T}{\theta}\right)^3 + \gamma T, \tag{5.30}$$

where A is a constant with the same value for all metals, θ is the Debye temperature and the Sommerfeld coefficient $\gamma = \frac{2}{3}\pi^2 k_B^2 N(0)$ is a measure of the density of electron states $N(0)$ at the Fermi surface.

When the applied field $H_a > H_c$, the system is in the normal staten and the specific heat is:

$$\frac{C_n}{T} = (\frac{A}{\theta^3})T^2 + \gamma. \tag{5.31}$$

From which the slope A/θ^3 and the intercept γ can be determined by a linear plot of $\frac{C_n}{T}$ vs T^2. And the lattice contribution $C_{latt} = A(T/\theta)^3$ can be determined.

Then the electronic contribution to the superconducting state can be evaluated by subtracting the $C_{latt} = A(T/\theta)^3$ from the total specific heat:

$$(C_{el})_s = C_s - C_{latt}. \tag{5.32}$$

$$(C_{el})_n = \gamma T \tag{5.33}$$

$$(C_{el})_s = aexp(-b/k_B T) \tag{5.34}$$

The electronic heat capacity of the superconducting state has the form of form of the thermal activation, which hints of an energy gap b. This gap rapidly decreases to zero when the temperature is raised close to T_c.

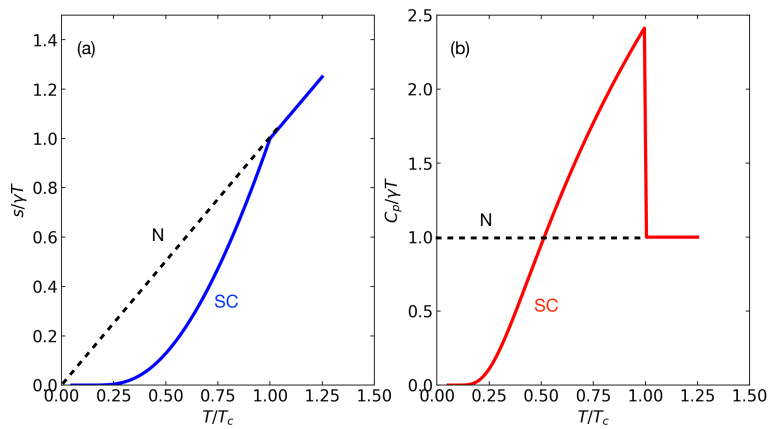

Figure 5.2: The entropy (a) and electronic heat capacity (b) of the superconducting and normal states.