Thermodynamics of the Superconducting Transition

We know that thermodynamics can be well applied to all reversible processes. Meissner effect suggests that the transition between the normal and superconducting states is thermodynamically reversible just in the same sense that the transition between liquid and vapour phases of a substance is reversible under the condition of slow evaporation.

This is because the superconducting currents do not die away with the production of Joule heat when superconductivity is destroyed by the application of a magnetic field .We may therefore apply thermodynamics to the transition.

We may treat only a type 1 superconductor with complete Meissner effect so that $B=0$ inside the super conductor.

Gibbs free energy is given by

$$G=U-TS+PV \qquad 1$$

The Gibbs free energy per unit volume in a magnetic field.

$$G=U-TS-\mu_0 HM \quad (2)$$

By comparing (1) and (2)

$\mu_0 H$ plays the role of P and M plays the role of –V

Where M is the magnetization induced in the specimen by the magnetic field H and S is the entropy.

$$dG=dU-TdS-SdT-\mu_0 HdM-\mu_0 MdH$$

Since $$dU=TdS+\mu_0 HdM$$

$$dG=-SdT-\mu_0 MdH$$

For a process at constant temperature we have ,

$$dG=-\mu_0 MdH \quad (3)$$

The normal state of the most superconductor is paramagnetic and magnetization is small compared with that of superconducting state. Therefore we can neglect the normal state magnetization. Consequently from equation (3)

We get $dG=0$ or we can state that Gibbs function G_N in normal state is not changed by the application of magnetic field.

Hence $G_N(T,H)=G_N(T,0)$ 4

But superconducting state of the specimen under constant pressure, temperature and magnetic field ,we know that

$$B=0$$

$$B=\mu_0(H+M)$$

$$M=-H$$

So that from equn (3) with $dT=0$ we get

$$dG=\mu_0 HdH$$

or on integrating

$$G_S(T,H_C)-G_S(T,0)=\mu_0\int_0^{H_C} HdH$$

$$G_S(T,H_C)=G_S(T,0)+1/2\ \mu_0 H_c^2 \qquad 5$$

In this case the Gibbs free energy of the specimen is increased on placing it in a magnetic field.

At the critical field H_C, however the energies of the normal and superconducting states must be equal if the two states are to be in equilibrium at H_C that

$G_N(T,H_C)=G_S(T.H_C)$ 6

Combining (5) and (6) we get

$G_N(T,H_c)=G_S(T,0)+1/2\ \mu_0 H_c^2$

Using equation (4)

$G_N(T,0)=G_S(T,0)+1/2\ \mu_0 H_c^2$ 7

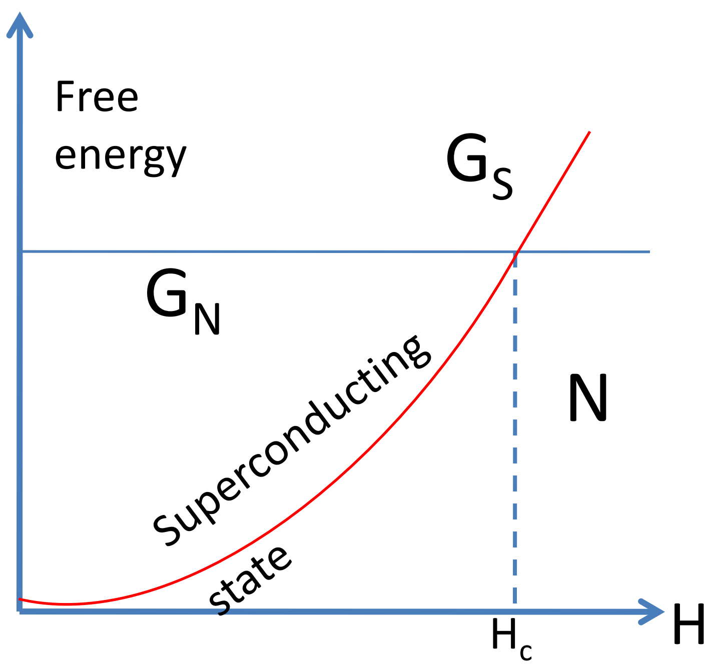
When $H>H_C$ we have $G_S>G_N$ So we find magnetic fields

$H>H_C$,the normal state is more stable. That is the material cannot be in the superconducting state when $H>H_C$

Below critical field H_C

$G_S<G_N$

Hence superconducting phase is more stable.



Entropy

Let us now calculate the difference in entropy of two phases. For entropy S is given by $S = -\left(\frac{dG}{dT}\right)_H$

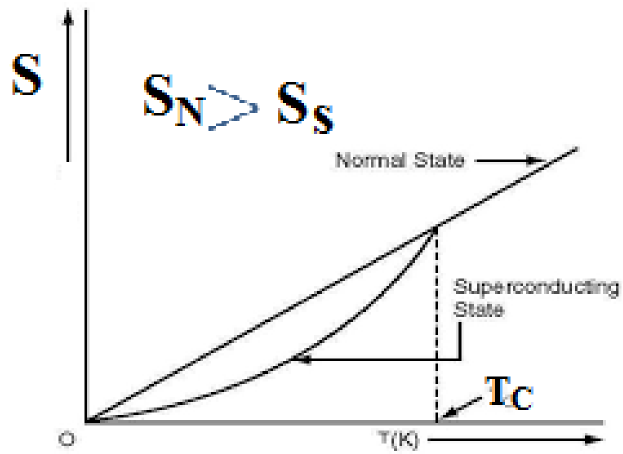
From Equation (7) we get

$$\left(-\frac{dG_N}{dT}\right) = \left(-\frac{dG_S}{dT}\right) - \frac{1}{2}\mu_0 \frac{d}{dT} H_c^2$$

$$S_N = S_S - \frac{1}{2}\mu_0 \frac{d}{dH_c} H_c^2 \frac{dH_c}{dT}$$

$$= S_s - \frac{1}{2}\mu_0 2H_c \frac{dH_c}{dT}$$

$$= S_s - \mu_0 H_c \frac{dH_c}{dT}$$



At $T = T_C$, $H_C = 0$,so the above equation yields $S_N = S_S$

The entropies of the phases are equal at the critical temperature and any lower temperature $H_C > 0$, and dH_C/dT is negative so that $S_N > S_S$

This means entropy in superconducting state is lower which implies that superconducting state is more ordered state

Specific heat

$$C_v = \left(\frac{dQ}{dT}\right)_V$$

$$= \left(\frac{TdS}{dT}\right)_V$$

$$= T\left(\frac{dS}{dT}\right)_V$$

We have

$$S_N - S_S = -\mu_0 H_C \frac{dH_C}{dT}$$

$$T\frac{dS_N}{dT} - T\frac{dS_S}{dT} = -T\frac{d}{dT}\left(\mu_0 H_C \frac{dH_C}{dT}\right)$$

$$C_N - C_S = -\mu_0 H_C T\frac{d^2 H_C}{dT^2} - \mu_0 T \frac{dH_C}{dH_C}\frac{dH_C}{dT}\frac{dH_C}{dT}$$

$$= -\mu_0 H_C T\frac{d^2 H_C}{dT^2} - \mu_0 T\left(\frac{dH_C}{dH_C}\right)^2$$

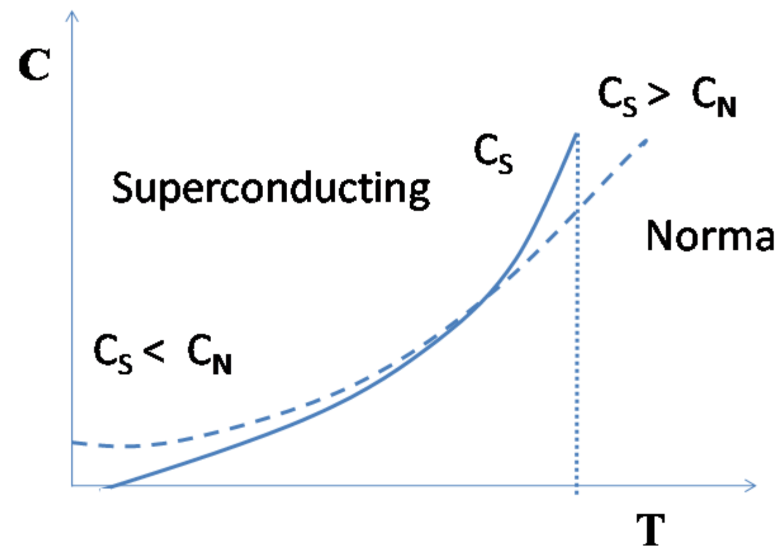
At $T = T_C$ $H_C = 0$

$$\Delta C = C_N - C_S = -\mu_0 T_C \left(\frac{dH_C}{dT} \right)^2$$

Which shows that if the metal is cooled or warmed in absence of magnetic field there will be a discontinuity in specific heat in passing through the transition temperature.

For $H_C = 0$

$$C_S > C_N$$



For the same decreasing temperature superconducting state rejects more heat than the normal state.

The fact indicates there occur some sort of extra ordering which causes the extra heat to be rejected at $T < T_C$

At $T<T_C$

$$C_N - C_S = -\mu_0 T\left[\frac{dH_C}{dT}\right]^2 - \mu_0 H_C T\frac{d^2H_C}{dT^2}$$

As T tends to zero $dH_C/dT=0$

$$C_N - C_S = -\mu_0 H_C T\frac{d^2H_C}{dT^2}$$

$$= -\mu_0 H_C T(-ve)$$

$$= +ve$$

1 st Order Transition (In presence of field)

Except at the critical temperature where the phase transition occur at zero magnetic field, for all other temperatures the phase transition occur at a definite applied magnetic field . There

$G_N = G_S$, but $S_N - S_S \neq 0$ since $S = -\left(\frac{dG}{dT}\right)_H$

$$S_N - S_S = -\mu_0 H_C \frac{dH_C}{dT}$$

It implies that 1 st order diff of G w.r.t. T is not continuous i.e. in presence of any magnetic field the phase transition is 1 st order and there is a latent heat L for transition between two states.

From 2 nd law of thermodynamics

$$dQ=TdS=T(S_N-S_S)$$

Again $$L=dQ$$

$$L=T(S_N-S_S)$$

$$L=-T\mu_0 H_C \frac{dH_C}{dT}$$

Therefore in presence of applied magnetic field the super conductivity to normal region is of the 1st order. Although *G* is continuous but *dG/dT* is not

2^{nd} order transition

The phase transition at $T=T_C$ is 2nd order in nature in absence of applied magnetic field .Both G and its first derivative w.r.t .T $S=-dG/dT$ is continuous during phase transitions.
The discontinuity occurs only in the specific heat i.e. 2 nd order derivative of G

$$C_v = T\frac{dS}{dT} = -T\frac{d^2G}{dT^2}$$

Hence it is a 2 nd order phase transition
At this phase transition $S_N - S_S=0$

$$dS=0$$

$$dG/T=0$$

$$\text{or} \quad L/T=0$$

$$\text{or} \quad L=0$$

Hence 2 nd order phase transition does not involve any latent heat.