

# Thermodynamics of superconductor

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## PROBLEM

A metal has two phases,  $N$  (normal) and  $S$  (superconducting). Assume that in the normal phase the magnetization  $M$  (per unit volume) due to an applied external magnetic field  $H$  is negligible, so the magnetic induction or flux density  $B = \mu_0(H + M) = \mu_0 H$  in the normal meta phase.

The metal is cooled down to a temperature  $T$  in a large magnetic field  $H$  and then  $H$  is reduced to zero. At temperature  $T < T_c$ , it is observed that as  $H$  is reduced there is a critical field

$$H_c(T) = H_0 \left[ 1 - \left( \frac{T}{T_c} \right)^2 \right],$$

where a first-order phase transition from the normal state to the superconducting state occurs. The magnetic flux is completely expelled from the metal, and  $B = 0$  in its interior (Meissner effect) for  $H < H_c(T)$  in the superconducting state.

Recall that the magnetic variant of the Gibbs free energy (per unit volume) is  $G(T, H) = U - T - M'H$ , where  $M' = \mu_0 M$  in SI units. (Ignore any thermal expansion of the metal, and treat its volume as fixed).

- Find the difference of the entropy densities  $\Delta S(T) = S_N(T) - S_S(T)$  between the normal and the superconducting phases (with the assumption of negligible magnetization in the normal phase,  $S_N(T)$  is independent of  $H$ ).
- If the system is heated in the absence of a magnetic field (at  $H = 0$ ) it undergoes a continuous (second-order) phase transition from superconductor to normal metal at  $T = T_c$ . What is the discontinuity in its specific heat per unit volume at this phase transition? (Make a sketch showing how the specific heat varies with temperature near the transition). Which phase has the larger specific heat?
- By how much is the ground state ( $T = 0$ ) energy per unit volume of the superconductor lower than that of the normal metal, when  $H = 0$ ?

## SOLUTION TO PART A

The Gibbs free energy for normal state and the superconductor state is the same on the phase boundary:

$$G_N(T, H) = G_S(T, H)$$

Now we take the total differential of this equation, and we get

$$\frac{\partial G_N}{\partial T} dT = \frac{\partial G_S}{\partial T} dT + \frac{\partial G_S}{\partial H} dH$$

We also know that for Gibbs free energy, the entropy and the magnetization are given by  $S = -\partial_T G$ , and  $\mu_0 M = -\partial_H G$ . So it is easy to find the entropy difference on the phase boundary

$$\Delta S(T) = S_N(T) - S_S(T) = \mu_0 M_S \frac{dH}{dT}$$

We know that in the superconducting phase the magnetization is  $M_S = -H$ . Also on the phase boundary we have

$$\frac{dH_c}{dT} = -H_0 \frac{2T}{T_c^2}$$

Take all of these things into consideration, we get the entropy difference at phase transition point

$$\Delta S(T) = \frac{2\mu_0 H_0^2 T}{T_c^2} \left(1 - \frac{T^2}{T_c^2}\right).$$

### SOLUTION TO PART B

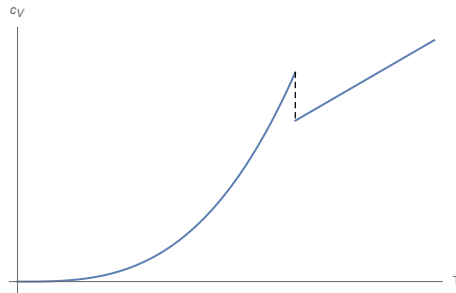
In the normal state, there is no magnetization at all, so the entropy doesn't have dependence on the external magnetic field  $H$ . For the superconducting state, by Maxwell relation, we have

$$\frac{\partial S_S}{\partial H} = -\frac{\partial^2 G_S}{\partial T \partial H} = \mu_0 \frac{\partial M}{\partial T}$$

But because of the Meissner effect, magnetization only depends on the external magnetic field  $M = -H$ , so  $\partial_T M = 0$ , which tells us that the entropy in superconducting state doesn't depend on external field either. So the entropy difference we get in part a is correct not only at the critical magnetic field. It is correct at any given magnetic field  $H$ . By the definition, we can find the heat capacity jump at the critical temperature without magnetic field:

$$\Delta c_V = c_V^N - c_V^S = T_c \left. \frac{\partial \Delta S(T)}{\partial T} \right|_{T=T_c} = -\frac{4\mu_0 H_0^2}{T_c} < 0$$

That means at the phase transition point the heat capacity of superconducting state is higher than that of normal state. A brief sketch of the heat capacity is shown in the following figure:



### SOLUTION TO PART C

When there is no external magnetic field, the Gibbs free energy is given by  $G = U - TS$ . Because the phase transition at zero field is first-order, the entropy of the two phases is the same, which tells us the internal energy  $U$  for the two

phases are the same. Then the zero temperature difference at zero temperature is

$$\begin{aligned}
 \Delta U &= \int_0^{T_c} [c_V^S(T) - c_V^N(T)] dT \\
 &= - \int_0^{T_c} T \frac{\partial \Delta S(T)}{\partial T} dT \\
 &= \int_0^{T_c} \Delta S(T) dT - T \Delta S(T) \Big|_{T=0}^{T=T_c} \\
 &= \int_0^{T_c} \Delta S(T) dT \\
 &= \frac{\mu_0 H_0^2}{2} .
 \end{aligned}$$