

Chapter 3

Thermodynamic Properties

In the previous chapter we concluded that the Meissner-Ochsenfeld effect of a superconductor guarantees that its states are path independent and, thus, are uniquely characterized by both the temperature T and the magnetic induction \mathbf{B} . This allows to apply the useful concepts of the thermodynamics to describe a superconductor.

3.1 Fundamental Idea

A macroscopic physical system consists of a large number of independent degrees of freedom of its individual particles. But despite of that thermodynamics yields a reduced description with just a few macroscopic system variables. With this thermodynamics describes system properties from a macroscopic point of view, for instance, it can provide conditions for the stability of a phase. In particular, it deals with the equilibrium properties of a system, which emerge under certain experimental conditions. Note that experimentally an equilibrium is reached only quite slowly as it involves adiabatic parameter changes. Furthermore, exchanges, for instance, of energy and particles between the system and the environment are involved. Consequently, thermodynamic statements about an equilibrium state are, in principle, completely independent from the practical question how to realize it experimentally.

Such problems in thermodynamics are discussed by analyzing a thermodynamic potential. To this end, one generically proceeds as follows:

1. Find the thermodynamic variables, which uniquely characterize a system state.
2. Find the thermodynamic potential, which has the independent variables from 1. as natural variables.
3. Equilibrium states are determined by extremizing the thermodynamic potential from 2.
4. Two phases are in equilibrium provided that the thermodynamics potentials of both phases are equal.

In the following we apply this procedure to describe a superconductor within the realm of thermodynamics.

3.2 Thermodynamic Potential

We start with the thermodynamic description by involving the basic relation for reversible processes, which combines the first and the second law of thermodynamics as follows:

$$dU = TdS - PdV + \mu_0 Hd(VM). \quad (3.1)$$

Here we determine the change of the inner energy dU by adding products of the intensive variables (T, P, H) with the total differentials of the respective extensive variables (S, V, VM). Note that M denotes here the magnetization, i.e. the magnetic moment per volume, so VM represents the magnetic moment of the material, which is extensive. Furthermore, we remark that we assume the systemegoistic convention, i.e. whatever is good for the system is counted positively. For instance, the inner energy U increases (decreases) for increasing (decreasing) the magnetization M of a paramagnet (diamagnet). Or in other words: for a paramagnet (diamagnet) magnetic field energy is built up (reduced) due to an increase (decrease) of the magnetization $dM > 0$ ($dM < 0$), involving the magnetization work $\mu_0 Hd(VM) > 0$ ($\mu_0 Hd(VM) < 0$) being put into (freed from) the system.

We read off from (3.1) that the inner energy U is a thermodynamic potential, which has the extensive variables (S, V, VM) as the natural variables:

$$U = U(S, V, VM). \quad (3.2)$$

This means that the respective intensive variables (T, P, H) follow from differentiations:

$$T = \left. \frac{\partial U}{\partial S} \right|_{V, M}, \quad P = - \left. \frac{\partial U}{\partial V} \right|_{S, M}, \quad H = \frac{1}{\mu_0} \left. \frac{\partial U}{\partial (VM)} \right|_{S, V}. \quad (3.3)$$

But both the entropy S and the magnetization M are physical quantities, which are not directly accessible in the laboratory. Therefore, it is advantageous to switch the description from the extensive variables S, VM to their respective canonically conjugated intensive variables T, H . This is accomplished by performing a double Legendre transformation from the inner energy U to the (magnetic) free enthalpy, which is also called (magnetic) Gibbs free energy

$$G = U - TS - \mu_0 HV M. \quad (3.4)$$

For the total differential of (3.4) we conclude by taking into account (3.1):

$$dG = -SdT - PdV - \mu_0 VMdH. \quad (3.5)$$

Thus, G is now a thermodynamic potential, which has (T, V, H) as the natural variables:

$$G = G(T, V, H). \quad (3.6)$$

The canonically conjugated variables follow again from differentiations:

$$S = - \left. \frac{\partial G}{\partial T} \right|_{V,H}, \quad P = - \left. \frac{\partial G}{\partial V} \right|_{T,H}, \quad M = - \left. \frac{1}{\mu_0 V} \frac{\partial G}{\partial H} \right|_{T,V}. \quad (3.7)$$

In the following we simplify the thermodynamic discussion by assuming a normal conductor or a superconductor, where the volume does not change:

$$dV = 0. \quad (3.8)$$

Thus, we consider the volume V from now on as a fixed dummy thermodynamic variable, which can be ignored due to its redundancy. This reduces (3.5) to

$$dG = -SdT - \mu_0 V M dH, \quad (3.9)$$

so the free enthalpy G in (3.6) turns out to be only a function of the temperature T and the magnetic field H alone:

$$G = G(T, H). \quad (3.10)$$

The entropy S and the magnetization M then follow from

$$S = - \left. \frac{\partial G}{\partial T} \right|_H, \quad (3.11)$$

$$M = - \left. \frac{1}{\mu_0 V} \frac{\partial G}{\partial H} \right|_T. \quad (3.12)$$

Within this framework we characterize now the free enthalpy of a normal and a superconductor.

3.3 Free Enthalpy of Both Phases

In Chapter 2 we stated that a superconductor is characterized by the Meissner-Ochsenfeld effect. This implies for the magnetization

$$B = \mu_0(H + M) = 0 \quad \Longrightarrow \quad M(H) = -H. \quad (3.13)$$

Taking into account (3.13) we now integrate isothermally (3.12) from $(T, 0)$ to (T, H) , yielding for the free enthalpy of the superconductor:

$$G_s(T, H) = G_s(T, 0) + \frac{\mu_0}{2} V H^2. \quad (3.14)$$

The temperature independence of the magnetization (3.13) then implies due to (3.11) and (3.14) that the entropy of the superconductor does not depend on the magnetic field H :

$$S_s(T, H) = - \left. \frac{\partial G_s(T, H)}{\partial T} \right|_H = - \left. \frac{\partial G_s(T, 0)}{\partial T} \right|_H = S_s(T, 0). \quad (3.15)$$

A subsequent differentiation of the entropy S with respect to the temperature T yields the heat capacity C :

$$C = T \left. \frac{\partial S}{\partial T} \right|_H. \quad (3.16)$$

Indeed, differentiating the double Legendre transformation (3.4) with respect to the temperature T yields

$$\left. \frac{\partial G}{\partial T} \right|_H = \left. \frac{\partial U}{\partial T} \right|_H - S - T \left. \frac{\partial S}{\partial T} \right|_H - \mu_0 V H \left. \frac{\partial M}{\partial T} \right|_H, \quad (3.17)$$

so we conclude that the heat capacity

$$C = \left. \frac{\partial U}{\partial T} \right|_H \quad (3.18)$$

reduces to (3.16) due to the entropy (3.11) and the magnetization (3.13). Thus, we read off from (3.15) and (3.16) that also the heat capacity of a superconductor turns out to be independent of the magnetic field H :

$$C_s(T, H) = T \left. \frac{\partial S_s(T, H)}{\partial T} \right|_H = T \left. \frac{\partial S_s(T, 0)}{\partial T} \right|_H = C_s(T, 0). \quad (3.19)$$

Correspondingly, a normal conductor, which is paramagnetic, is characterized by an approximately vanishing magnetization:

$$M = 0. \quad (3.20)$$

An isothermal integration of (3.12) with (3.20) from $(T, 0)$ to (T, H) thus yields

$$G_n(T, H) = G_n(T, 0). \quad (3.21)$$

This means that the free enthalpy of a normal conductor does not depend on the magnetic field H . As a consequence we obtain also for the normal conductor due to (3.11), (3.21) that its entropy does not depend on the magnetic field H :

$$S_n(T, H) = - \left. \frac{\partial G_n(T, H)}{\partial T} \right|_H = - \left. \frac{\partial G_n(T, 0)}{\partial T} \right|_H = S_n(T, 0). \quad (3.22)$$

The same is also true for its heat capacity due to (3.16), (3.22):

$$C_n(T, H) = T \left. \frac{\partial S_n(T, H)}{\partial T} \right|_H = T \left. \frac{\partial S_n(T, 0)}{\partial T} \right|_H = C_n(T, 0). \quad (3.23)$$

3.4 Consequences From Critical Line

Along the critical curve $H_c(T)$ in the H - T plane of control parameters an equilibrium exists between the normal conducting phase and the superconductor phase, see Fig. 3.1. According

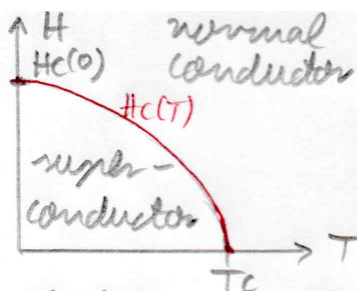


Figure 3.1: Critical curve $H_c(T)$ in the H - T plane between the normal conducting phase and the superconductor phase.

to the basic laws of thermodynamics this implies that the free enthalpy of both phases have to be equal along this critical curve:

$$G_s(T, H_c(T)) = G_n(T, H_c(T)) . \quad (3.24)$$

This implies due to (3.14) and (3.21):

$$G_s(T, 0) + \frac{\mu_0}{2} V H_c(T)^2 = G_n(T, 0) . \quad (3.25)$$

At first, we conclude from (3.25) for $T \leq T_c$

$$G_n(T, 0) \geq G_s(T, 0) . \quad (3.26)$$

This means that the free enthalpy of the superconducting phase is smaller than the corresponding one of the normal conducting phase. Thus, it is energetically more favorable to realize the superconducting phase. Secondly, (3.25) implies that the entropy (3.15) and the heat capacity (3.19) of the superconductor follow from the corresponding quantities of the normal conductor (3.22), (3.23) and the critical curve $H_c(T)$. This is investigated in more detail in the next two sections. There we will see that properties of $H_c(T)$ have thermodynamic consequences and, conversely, thermodynamics has implications for $H_c(T)$.

3.5 Entropy

Inserting (3.25) into (3.15) yields together with (3.22):

$$S_s(T, 0) = S_n(T, 0) + \mu_0 V H_c(T) \frac{\partial H_c(T)}{\partial T} . \quad (3.27)$$

At zero temperature the third law of thermodynamics holds, which implies

$$S_s(0, 0) = S_n(0, 0) . \quad (3.28)$$

Thus, as $H_c(0) \neq 0$, we read off from (3.27) at zero temperature

$$\lim_{T \downarrow 0} \frac{\partial H_c(T)}{\partial T} = 0 . \quad (3.29)$$

This means that the critical line $H_c(T)$ must have a horizontal tangent at $T = 0$.

In the temperature range from zero temperature to the critical temperature we know that the critical line $H_c(T)$ has a negative slope:

$$\frac{\partial H_c(T)}{\partial T} < 0, \quad 0 < T < T_c. \quad (3.30)$$

This implies for the latent heat

$$\Delta Q = T \left[S_n(T, 0) - S_s(T, 0) \right], \quad (3.31)$$

which it is always positive due to (3.27), (3.30), and (3.31):

$$\Delta Q = -\mu_0 V T H_c(T) \frac{\partial H_c(T)}{\partial T} > 0, \quad 0 < T < T_c. \quad (3.32)$$

Thus, at the transition from a normal to a superconductor heat is freed and a first-order phase transition occurs.

Note that (3.32) can be reformulated according to

$$\Delta Q = -\mu_0 V \left[0 + H_c(T) \right] T \frac{\partial H_c(T)}{\partial T} > 0, \quad (3.33)$$

so that it becomes transparent that it represents an analogue of the seminal Clausius-Clapeyron relation for the transition line between a gas and a liquid:

$$\frac{\partial P}{\partial T} = \frac{S_g - S_l}{V_g - V_l} \quad \implies \quad \Delta Q = T (S_g - S_l) = (V_g - V_l) T \frac{\partial P}{\partial T} > 0. \quad (3.34)$$

Thus, the positivity of the latent heat ΔQ for the gas-liquid transition (3.34) is guaranteed due to $V_g - V_l > 0$ and $\partial P/\partial T > 0$, see Fig. 3.2. In contrast to that we have for the normal conductor-superconductor transition (3.33) that the difference of magnetic moments $V(M_n - M_s) = V[0 - (-H_c)]$ is also positive, but the slope $\partial H_c(T)/\partial T$ is negative.

Finally, let us evaluate (3.32) at the critical temperature $T = T_c$. From experimental observations we know on the one hand that there occurs a second-order phase transitions, i.e. the latent heat must vanish

$$\Delta Q = 0, \quad T = T_c. \quad (3.35)$$

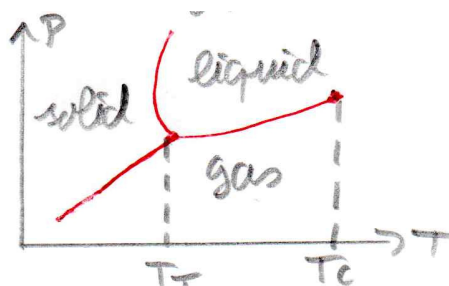
On the other hand, the critical curve $H_c(T)$ for $T \leq T_c$ is found to be a smoothly differentiable function with the properties that at $T = T_c$ the critical magnetic field vanishes, i.e.

$$H_c(T_c) = 0 \quad (3.36)$$

with a finite slope, i.e.

$$\left. \frac{\partial H_c(T)}{\partial T} \right|_{T=T_c} \text{ finite}. \quad (3.37)$$

Thus, we conclude that (3.36) and (3.37) immediately imply (3.35) due to (3.32).

Figure 3.2: Physical states solid, liquid, gas within the P - T -diagram.

3.6 Heat Capacity

Inserting (3.27) into (3.19) yields together with (3.23) for the specific heat

$$C_s(T, 0) = C_n(T, 0) + \mu_0 VT \left\{ H_c(T) \frac{\partial^2 H_c(T)}{\partial T^2} + \left[\frac{\partial H_c(T)}{\partial T} \right]^2 \right\}. \quad (3.38)$$

Thus, evaluating (3.38) at the critical temperature, we obtain from (3.36) and a finite curvature of the critical $H_c(T)$ at $T = T_c$, i.e.

$$\left. \frac{\partial^2 H_c(T)}{\partial T^2} \right|_{T=T_c} \text{ finite}, \quad (3.39)$$

that the difference of the heat capacities of a normal and a superconductor follows the Rutgers formula

$$C_s(T_c, 0) - C_n(T_c, 0) = \mu_0 VT_c \left[\left. \frac{\partial H_c(T)}{\partial T} \right|_{T=T_c} \right]^2 > 0. \quad (3.40)$$

Thus, at the critical temperature $T = T_c$ the heat capacity makes a jump, which is characteristic for a second-order phase transition. And from the magnitude of that jump one can deduce the slope of the critical curve $H_c(T)$ at $T = T_c$ according to (3.40).

3.7 Kok Formula

A good empirical approximation for the critical line $H_c(T)$ is provided by the Kok formula

$$H_c(T) = H_c(0) \left[1 - \left(\frac{T}{T_c} \right)^2 \right]. \quad (3.41)$$

With this we can now concretely calculate the differences for the enthalpy, the entropy, and the heat capacity in the normal and the superconducting phase.

The difference of the respective free enthalpies follows from (3.25) and (3.41) to be

$$\Delta G_{s,n} = G_s(T, 0) - G_n(T, 0) = -\frac{\mu_0}{2} V H_c(0)^2 \left[1 - \left(\frac{T}{T_c} \right)^2 \right]. \quad (3.42)$$

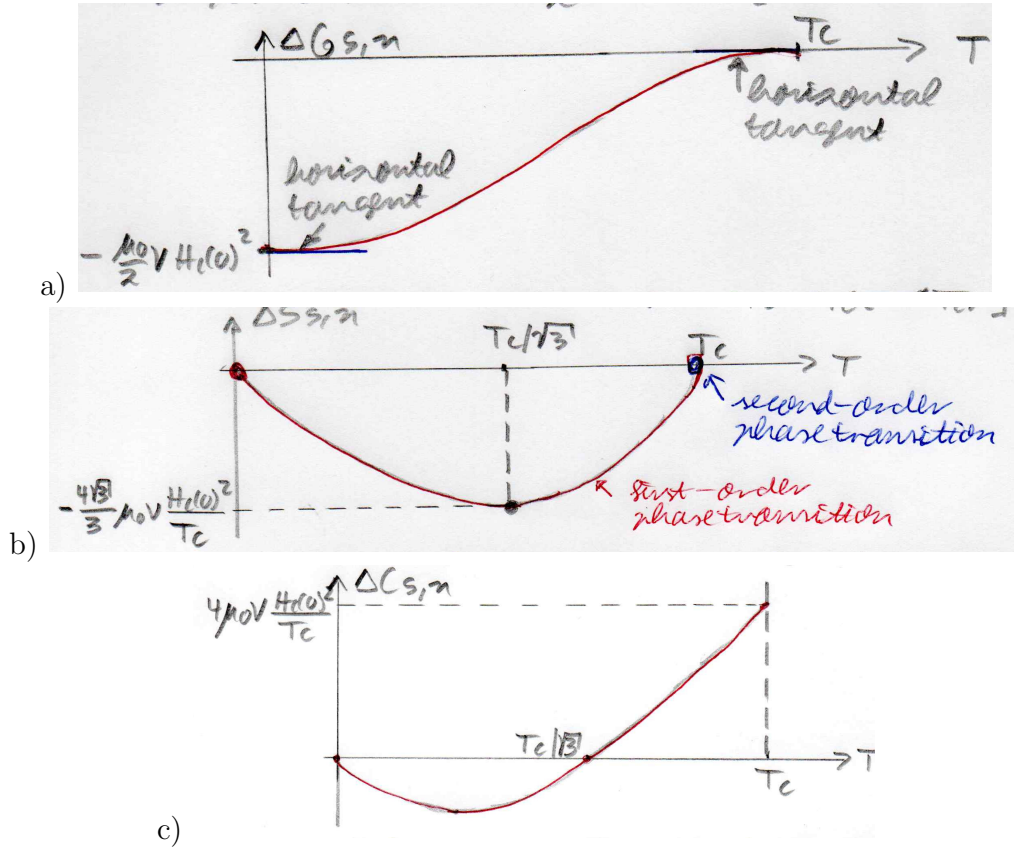


Figure 3.3: Temperature dependences of free enthalpies (3.42), entropies (3.43), and heat capacities (3.44) in superconducting and normal conducting phase.

The superconducting state has for $0 \leq T < T_c$ a lower free enthalpy than the normal conducting state, see Fig. 3.3a).

For the difference of the entropies we obtain from (3.27) and (3.41), see Fig. 3.3b):

$$\Delta S_{s,n} = S_s(T, 0) - S_n(T, 0) = -2\mu_0 V \frac{H_c(0)^2}{T_c} \frac{T}{T_c} \left[1 - \left(\frac{T}{T_c} \right)^2 \right]. \quad (3.43)$$

Note that at $T = 0$ we have a first-order phase transition, although no latent heat occurs. According to the Ehrenfest classification just one first derivative of the thermodynamic potential must have a jump. And this jump occurs even at $T = 0$, namely the magnetization jumps from $M_n = 0$ in the normal conducting phase to $M_s = -H$ in the superconducting phase.

The difference of the heat capacities is provided by the Rutgers formula (3.38) and (3.41):

$$\Delta C_{s,n} = C_s(T, 0) - C_n(T, 0) = 2\mu_0 V \frac{H_c(0)^2}{T_c} \frac{T}{T_c} \left[3 \left(\frac{T}{T_c} \right)^2 - 1 \right]. \quad (3.44)$$

Note that the negativity of the heat capacity difference (3.44) for $0 < T < T_c/\sqrt{3}$, see Fig. 3.3c), indicates that for low temperatures the superconducting heat capacity decreases faster than the normal conducting one. This is an indication of the presence of an energy gap in the superconductor.