# 3 Thermodynamic Properties:

Meissner-Ochsenfeld effect: state of SC path-independent

## 3.1 Fundamental Idea:

macroscopic system: few degrees of freedom in thermodynamics
but a lot of microscopic degrees of freedom
→ reduced description for equilibrium properties
- adiabatic changes of control parameters
- free exchange of energy (particles) with environment

due to path-independence it is irrelevant how a state is reached.

Analyze a thermodynamic potential:

1) First we have to identify the thermodynamic variables which uniquely characterise the system state
2) Find thermodynamic potential which has the variables in 1) as natural variables.
3) Equilibrium states are determined by extremising thermodynamic potential.

4) Two phases are in equilibrium provided that their thermodynamic potential coincide.

## 3.2 Thermodynamic potential:

basic relation of thermodynamics for reversible processes which uses 1- and 2- law of thermodynamics

$$dU = T\,dS - p\,dV + \underbrace{B}_{=\mu_0 H}\, d\underbrace{m}_{\substack{\text{magnetic moment} \\ = \underbrace{M}_{} V}} \Rightarrow \underbrace{U = U(S, V, \underbrace{MV}_{=m})}_{\text{natural variables}}$$

$$\text{magnetization} = \frac{\text{magnetic moment}}{\text{volume}}$$

convention: systemegoistic

$$T = \frac{\partial U}{\partial S}\bigg|_{V,M}, \quad P = -\frac{\partial U}{\partial V}\bigg|_{S,MV}, \quad H = \frac{1}{V\mu_0}\frac{\partial U}{\partial M}\bigg|_{S,V}$$

change of variables: $S \to T$, $MV \to H$

double Legendre transformation to (magnetic) free enthalpy

$$G = U - TS - \mu_0 H\, V M$$

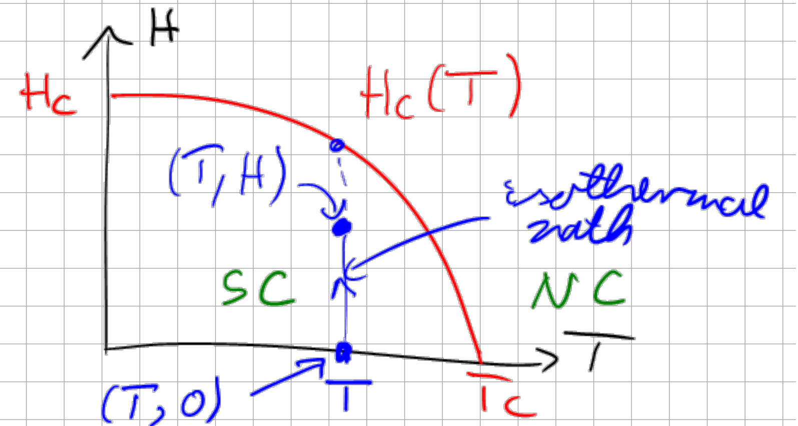
$$dG = -S\,dT - \cancel{P\,dV} - \mu_0 V M\, dH \Rightarrow G = G(T, V, H)$$

$$S = -\frac{\partial G}{\partial T}\Big|_{V,H}, \quad p = -\frac{\partial G}{\partial V}\Big|_{T,H}, \quad M = -\frac{1}{\mu_0 V}\frac{\partial G}{\partial H}\Big|_{T,V}$$

simplifying assumption: $dV = 0 \;\hat{=}\; V = \text{const.} \Rightarrow G = G(T,H)$

$$S = -\frac{\partial G}{\partial T}\Big|_{H}, \quad \boxed{M = -\frac{1}{\mu_0 V}\frac{\partial G}{\partial H}\Big|_{T}}$$

determine G for both a SC and a NC.




## 3.3 Free Enthalpy of Both Phases:

### A) SC:

Meissner-Ochsenfeld effect:

$$B = \mu_0(H + M) \stackrel{!}{=} 0 \Rightarrow \boxed{M(H) = -H}$$

independent of temperature

$$G_s(T,H) = -\mu_0 V \int_0^H d\tilde{H}\, M(\tilde{H}) + G_s(T,0) = G_s(T,0) + \boxed{\frac{\mu_0}{2} V H^2}$$

$$S_s(T,H) = -\frac{\partial G_s(T,H)}{\partial T}\Big|_H = -\frac{\partial G_s(T,H)}{\partial T}\Big|_{H=0} = S_s(T,0)$$

$$C = \frac{\partial U}{\partial T}\Big|_H \Rightarrow C_s^{(T,H)} = T\,\frac{\partial S_s(T,H)}{\partial T}\Big|_H \Rightarrow C_s(T,H) = C_s(T,0)$$

$$G = U - ST - \mu_0 V M H$$

$$\cancel{\frac{\partial G}{\partial T}\Big|_H} = \frac{\partial U}{\partial T}\Big|_H - \cancel{S} - \frac{\partial S}{\partial T}\Big|_H T - \mu_0 V H \overbrace{\frac{\partial M}{\partial T}}^{=0}\Big|_H$$

B) NC: $M \approx 0$ independent of T

$\Rightarrow G_n(T,H) = G_n(T,0)$

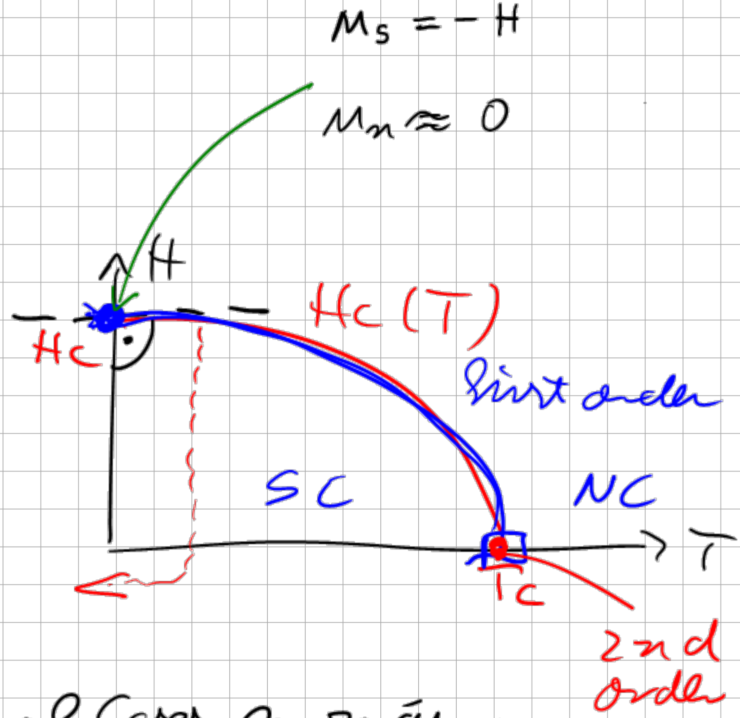
$\Rightarrow S_n(T,H) = S_n(T,0)$, $C_n(T,H) = C_n(T,0)$

## 3.4 Consequences for Critical Line:

4) in section 3.1: on critical line

$$G_s(T, H_c(T)) = G_n(T, H_c(T))$$

$$\boxed{G_s(T,0) + \frac{\mu_0}{2} V H_c(T)^2 = G_n(T,0)}\ ; \quad 0 \leq T \leq T_c$$




1) $G_n(T,0) \geq G_s(T,0)$ due to formation of Cooper pairs

2) $H_c(T) \longleftrightarrow$ thermodynamic properties

## 3.5 Entropy:

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

A) $T = 0$: 3. law of thermodynamics $S_s(0,0) = 0 = S_n(0,0)$

$$\lim_{T \downarrow 0} H_c(T) = H_c > 0 \Rightarrow \lim_{T \downarrow 0} \frac{\partial H_c(T)}{\partial T} = 0$$

B) $0 < T < T_c$: $\frac{\partial H_c(T)}{\partial T} < 0$, $0 < T < T_c$

latent heat: $\Delta Q = T\{S_n(T,0) - S_s(T,0)\}$

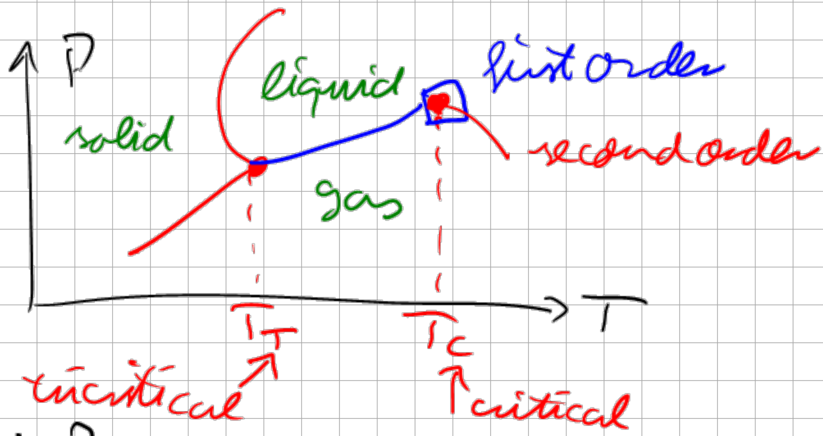
$$\Delta Q = -\mu_0 V H_c(T) \frac{\partial H_c(T)}{\partial T} > 0 \Rightarrow S_n(T,0) > S_s(T,0)$$

due to Cooper pairs

Remark: Clausius Clapeyron relation

$$\frac{\partial P}{\partial T} = \frac{S_g - S_e}{V_g - V_e} \Rightarrow \Delta Q = T\underbrace{(S_g - S_e)}_{>0}$$

$$= T\underbrace{(V_g - V_e)}_{>0}\underbrace{\frac{\partial P}{\partial T}}_{>0}$$

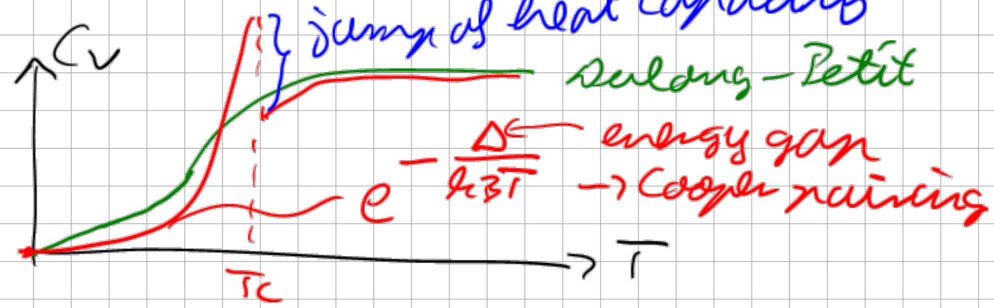



$$T\{S_n(T,0) - S_s(T,0)\} = \mu_0 V \underbrace{\{0 - (-H_c(T))\}}_{>0}\underbrace{\frac{\partial H_c(T)}{\partial T}}_{<0} > 0$$

c) $T = T_c$:

expectation: 2nd order phase transition implies $\Delta Q = 0$

$\hat{=}$ $\left.\frac{\partial H_c(T)}{\partial T}\right|_{T=T_c}$ finite and $H_c(T_c) \equiv 0$




## 3.6 Heat Capacity:

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

$$H_c(T_c) = 0, \quad \frac{\partial^2 H_c(T)}{\partial T^2} \text{ finite}$$

$$\underbrace{C_s(T_c,0) - C_n(T_c,0)}_{\text{jump}} = \mu_0 V T_c \underbrace{\left[\frac{\partial H_c(T)}{\partial T}\Big|_{T_c}\right]^2}_{>0} > 0$$

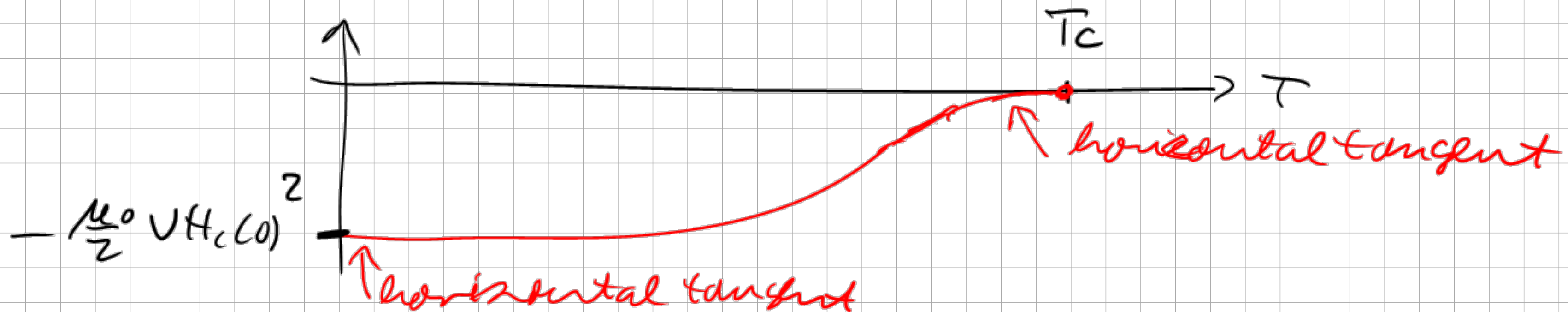
2nd order phase transition

## 3.7 Stark formula:

$$H_c(T) = H_c(0) \cdot \left\{1 - \left(\frac{T}{T_c}\right)^2\right\}$$

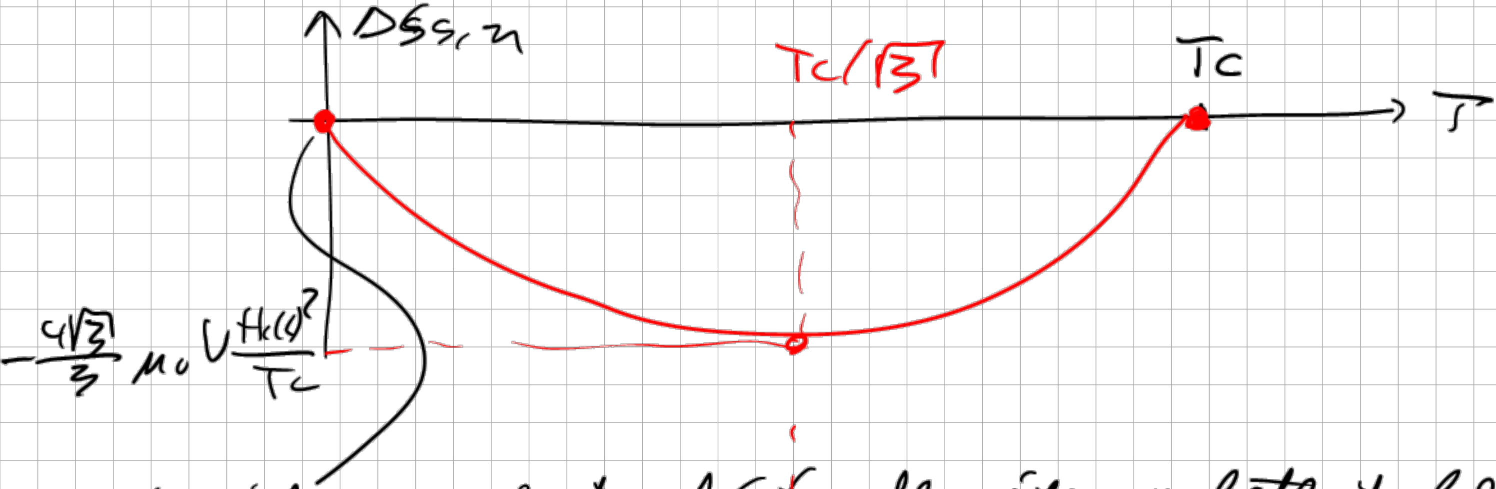
### 3.7.1 Free Enthalpy:

$$\underbrace{G_s(T,0) - G_n(T,0)}_{=\Delta G_{s,n}} = -\frac{\mu_0}{2} V H_c(0)^2 \left\{1 - \left(\frac{T}{T_c}\right)^2\right\}^2 \leq 0$$



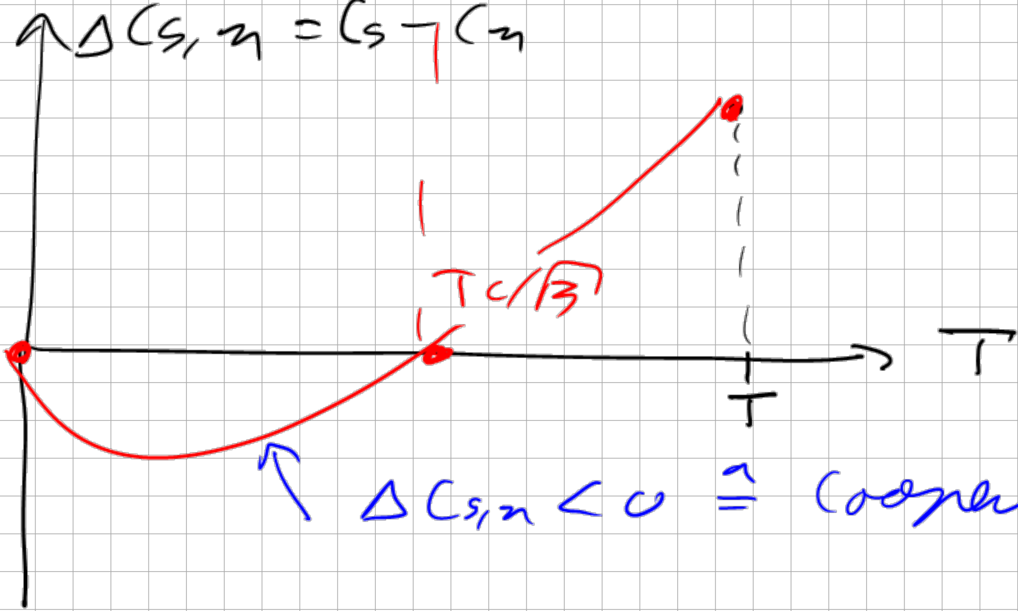

### 3.7.2 Entropy:

$$\underbrace{S_s(T,0) - S_n(T,0)}_{=\Delta S_{s,n}} = -2\mu_0 V \frac{H_c(0)^2}{T_c} \frac{T}{T_c} \left\{1 - \left(\frac{T}{T_c}\right)^2\right\}$$




special comment: $\Delta S \neq$ despite no latent heat!

## 3.7.3 Heat Capacity:




$\Delta C_{s,n} < 0 \;\hat{=}\;$ Cooper pairing