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Superconductivity and Low Temperature Physics I

Lecture Notes
Winter Semester 2023/2024

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Chapter 2

Thermodynamic Properties of Superconductors

2. Thermodynamic Properties of Superconductors

2. Thermodynamic Properties of Superconductors

- **already in 1924:**
  → W.H. Keesom tries to describe the superconducting state using basic laws of thermodynamics
  → Meißner effect not known that time ➔ unclear whether superconducting state is a ***thermodynamic phase***
- **after 1933:**
  → after discovery of Meißner effect it is evident that ***superconducting state is real thermodynamic phase***
  → this fact is used in development of GLAG theory
- **questions:**
  → what is the suitable thermodynamic potential to describe superconductors ?
  → what can we learn on superconductors from their basic thermodynamic properties (e.g. specific heat) ?

2.1 Thermodynamic Potentials

- **thermodynamics:**
  → describes systems with large particle number by small quantity of variables: ***T, V, N, …***
- ***extensive variables***: ***V, S, N, …***
  → depend on system size (amount of substance)
- ***intensive variables***: ***T, p, n, …***
  → do not depend on system size
- ***thermodynamic potentials***:
  → used for the description of equilibrium states
  → equilibrium state: determined by extremal value of the potential

  - ***example***:
    S, ***V*** and ***N*** are the natural variables of a systems, all other fixed by external constraints
    ➔ ***internal energy*** $U(S,V,N)$ yields full information on the system

$$dU = TdS - pdV + \mu dN$$

    ➔ ***adiabatic-isochore processes*** are characterized by minimum of ***U***

  - ***other potentials***:
    - ***Helmholtz free energy*** $F(T,V,N)$
    - ***enthalpy*** $H(S,p,N)$
    - ***free enthalpy or Gibb energy*** $G(T,p,N)$

2.1 Thermodynamic Potentials

- **question**:
  what is the suitable potential to represent the system under consideration ?
  → find the set of independent variables

- **discussion of magnetic and electronic systems**:
  → additional variables such as ***polarization P*** and ***magnetization M***

- **discussion of systems with $N = const.$**

A: Internal Energy

- differential of the internal energy

$$\mathbf{d}U = \delta Q + \delta W_{\mathrm{mech}} + \delta W_{\mathrm{em}} = T\mathbf{d}S - p\mathbf{d}V + \mathbf{B}\cdot\mathbf{dm}$$

infinitesimal heat flow into the system (δQ)

infinitesimal mechanical work done on the system (δW_{mech})

infinitesimal electromagnetic work done on the system (δW_{em})

$$\delta W_{\mathrm{em}} = \sum_i \mathbf{F}_{Z_i} \cdot \mathrm{d}\mathbf{Z}_i$$

$\mathbf{F}_{Z_i}$: generalized force; $\mathbf{Z}_i$: state variable

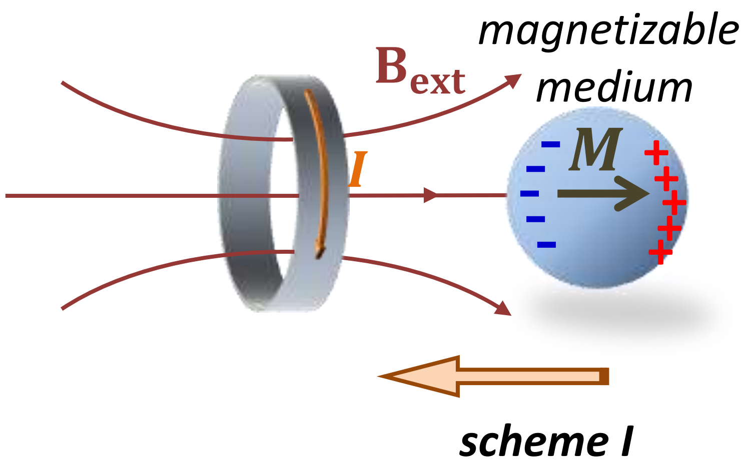
$\mathbf{m}$ = magnetic moment
$\mathbf{M} = \mathbf{m}/V$ = magnetization

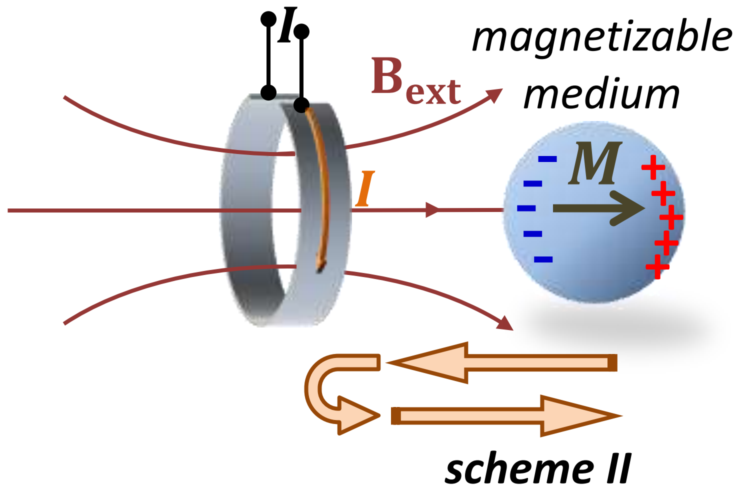
$\mathbf{m}\cdot\mathbf{B} = m\,B$ or $-m\,B$, since magnetization is mostly parallel or anti-parallel to B

2.1 Thermodynamic Potentials

- **important question**:
  → how to calculate the em work ?
  → do we have to use $m\mathrm{d}B$ or $B\mathrm{d}m$ in the expression of $\mathrm{d}U$?

- **answer**: depends on experimental situation





closed metallic ring with infinite conductivity:
→ flux density in ring stays constant

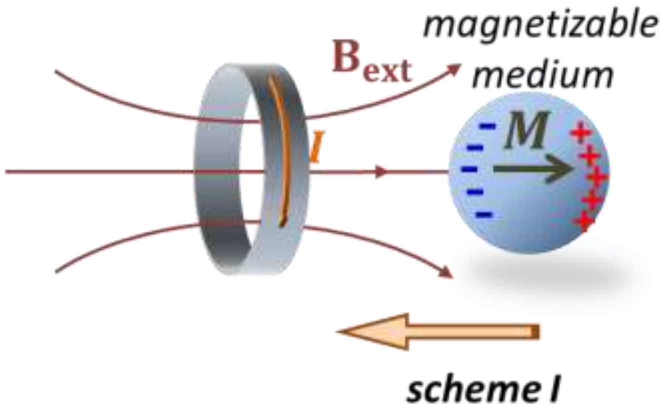
interaction energy of dipole with field has to be taken into account

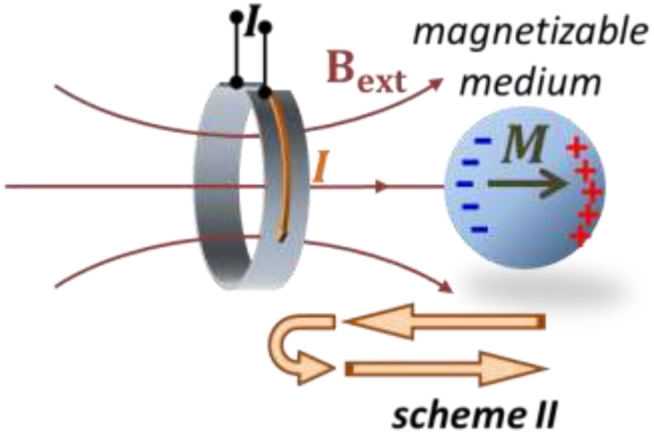
open metallic ring with current source attached:
→ current through ring (magnetic field) stays constant

no interaction energy of dipole and field as dipole is brought to infinite distance

2.1 Thermodynamic Potentials

(1) bring magnetic moment $\mathbf{m}$ from ∞ to position r_1 in field $\mathbf{B}_{\text{ext}}$





(1) bring unmagnetized sample from ∞ to r_1 in field $\mathbf{B}_{\text{ext}}$
(2) freeze-in magnetic moment $\mathbf{m}_1$
(3) bring magnetic moment $\mathbf{m}_1$ from r_1 to ∞

$$\mathbf{F}_{\text{mag}} = -\mu_0 \mathbf{m} \cdot \nabla \mathbf{H}_{\text{ext}}$$

$$W_{\text{I}} = \int_{\infty}^{r_1} \mathbf{F}_{\text{mag}} \cdot \mathrm{d}\mathbf{r} = -\int_0^{H_1} \mu_0 \mathbf{m} \cdot \mathrm{d}\mathbf{H}_{\text{ext}} = -\int_0^{B_1} \mathbf{m} \cdot \mathrm{d}\mathbf{B}_{\text{ext}}$$

$$\delta W_{\text{I}} = -\mathbf{m} \cdot \mathrm{d}\mathbf{B}_{\text{ext}}$$

$$\delta W_{\text{I}} = -\mathrm{d}(\mathbf{m} \cdot \mathbf{B}_{\text{ext}}) + \mathbf{B}_{\text{ext}} \cdot \mathrm{d}\mathbf{m}$$

change of the interaction energy

magnetization work

$$W_{\text{II}}^{(1)} = \int_{\infty}^{r_1} \mathbf{F}_{\text{mag}} \cdot \mathrm{d}\mathbf{r} = -\int_0^{H_1} \mu_0 \mathbf{m} \cdot \mathrm{d}\mathbf{H}_{\text{ext}} = -\int_0^{B_1} \mathbf{m} \cdot \mathrm{d}\mathbf{B}_{\text{ext}}$$

$$W_{\text{II}}^{(3)} = -\int_{H_1}^{0} \mu_0 \mathbf{m}_1 \cdot \mathrm{d}\mathbf{H}_{\text{ext}} = -\mu_0 \mathbf{m}_1 \cdot \int_{H_1}^{0} \mathrm{d}\mathbf{H}_{\text{ext}} = \mu_0 \mathbf{m}_1 \cdot \mathbf{H}_1 = \mathbf{m}_1 \cdot \mathbf{B}_1$$

$$\delta W_{\text{II}}^{(1)} = -\mathrm{d}(\mathbf{m}_1 \cdot \mathbf{B}_{\text{ext}}) + \mathbf{B}_{\text{ext}} \cdot \mathrm{d}\mathbf{m}$$

$$\delta W_{\text{II}}^{(3)} = +\mathrm{d}(\mathbf{m}_1 \cdot \mathbf{B}_{\text{ext}})$$

interaction energy drops out as dipole is brought to an infinite distance

$$\delta W_{\text{I}} = -\mathbf{m} \cdot \mathrm{d}\mathbf{B}_{\text{ext}} \quad \Longleftrightarrow \quad \delta W_{\text{II}} = \mathbf{B}_{\text{ext}} \cdot \mathrm{d}\mathbf{m}$$

2.1 Thermodynamic Potentials

A: Internal Energy U

$$\mathrm{d}U_\mathrm{I} = T\mathrm{d}S - p\mathrm{d}V - \mathbf{m} \cdot \mathrm{d}\mathbf{B}_\mathrm{ext}$$

$$\mathrm{d}U_\mathrm{II} = T\mathrm{d}S - p\mathrm{d}V + \mathbf{B}_\mathrm{ext} \cdot \mathrm{d}\mathbf{m}$$

two different expressions ➔ depend on definition of the considered systems

Scheme I: interaction energy $-\mathrm{d}(\mathbf{m_1} \cdot \mathbf{B}_1)$ is included into the considered systems

Scheme II: interaction energy $-\mathrm{d}(\mathbf{m_1} \cdot \mathbf{B}_1)$ is not included

→ it is assigned to external circuit which performs work on the system and is not part of the considered system

B: Helmholtz Free Energy F

- definition: $F = U - TS$
- differential: $\mathrm{d}F = \mathrm{d}U - T\mathrm{d}S - S\mathrm{d}T$

$$\mathrm{d}U_{\mathrm{I}} = T\mathrm{d}S - p\mathrm{d}V - \mathbf{m}\cdot\mathrm{d}\mathbf{B}_{\mathrm{ext}} \qquad \mathrm{d}U_{\mathrm{II}} = T\mathrm{d}S - p\mathrm{d}V + \mathbf{B}_{\mathrm{ext}}\cdot\mathrm{d}\mathbf{m}$$

$$\mathrm{d}F_{\mathrm{I}} = -S\mathrm{d}T - p\mathrm{d}V - \mathbf{m}\cdot\mathrm{d}\mathbf{B}_{\mathrm{ext}} \qquad \mathrm{d}F_{\mathrm{II}} = -S\mathrm{d}T - p\mathrm{d}V + \mathbf{B}_{\mathrm{ext}}\cdot\mathrm{d}\mathbf{m}$$

F_{I} is potential for the natural variables T, V, B_{ext}, F_{II} for T, V, m

→ isothermal-isochore processes at $B_{\mathrm{ext}} = const.$ are characterized by minimum of F_{I}
→ isothermal–isochore processes at $m = const.$ are characterized by minimum of F_{II}
→ problem: ***in experiments it is difficult to keep V and m constant***

→ ***use free enthalpy or Gibbs energy***

2.1 Thermodynamic Potentials

C: Free Enthalpy G

- definition: $G = U - TS + pV - \mathbf{m} \cdot \mathbf{B}_{\text{ext}}$
- differential: $\mathrm{d}G = \mathrm{d}U - T\mathrm{d}S - S\mathrm{d}T + p\mathrm{d}V + V\mathrm{d}p - \mathrm{d}(\mathbf{m} \cdot \mathrm{d}\mathbf{B}_{\text{ext}})$

$\mathrm{d}U_{\text{I}} = T\mathrm{d}S - p\mathrm{d}V - \mathbf{m} \cdot \mathrm{d}\mathbf{B}_{\text{ext}}$

$\mathrm{d}U_{\text{I}} = T\mathrm{d}S - p\mathrm{d}V - \mathrm{d}(\mathbf{m} \cdot \mathrm{d}\mathbf{B}_{\text{ext}}) + \mathbf{B}_{\text{ext}} \cdot \mathrm{d}\mathbf{m}$

interaction energy already included in $\mathrm{d}U_{\text{I}}$ and thus has to be omitted in expression for G to avoid double counting

$$\mathrm{d}G_{\text{I}} = -S\mathrm{d}T + V\mathrm{d}p - \mathbf{m} \cdot \mathrm{d}\mathbf{B}_{\text{ext}}$$

$\mathrm{d}U_{\text{II}} = T\mathrm{d}S - p\mathrm{d}V + \mathbf{B}_{\text{ext}} \cdot \mathrm{d}\mathbf{m}$

interaction energy not included in $\mathrm{d}U_{\text{II}}$, as it is included into expression for G, we obtain $\mathrm{d}G_{\text{I}} = \mathrm{d}G_{\text{II}}$

$$\mathrm{d}G_{\text{II}} = -S\mathrm{d}T - p\mathrm{d}V - \mathbf{m} \cdot \mathrm{d}\mathbf{B}_{\text{ext}}$$

G is potential for the natural variables $T, p, B_{\text{ext}} = \mu_0 H_{\text{ext}}$

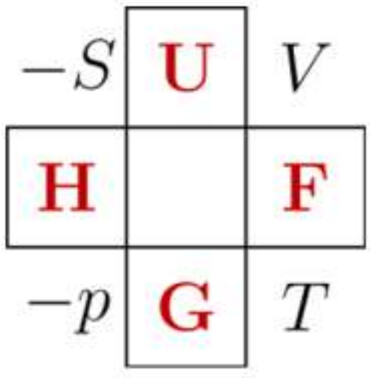
→ isothermal-isobaric processes at $B_{\text{ext}} = const.$ are characterized by minimum of G
→ this is appropriate for most experimental situations

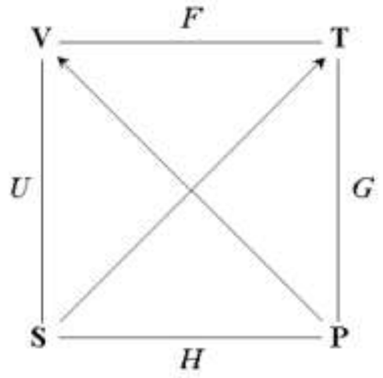
2.1 Thermodynamic Potentials

- if the suitable thermodynamic potential is known

  → ***derivation of various thermodynamic quantities is obtained by partial differentiation***

$$-\left(\frac{\partial G}{\partial T}\right)_{p,B_\mathrm{ext}} = S \qquad \left(\frac{\partial G}{\partial p}\right)_{T,B_\mathrm{ext}} = V \qquad -\left(\frac{\partial G}{\partial B_\mathrm{ext}}\right)_{p,T} = m$$





- **specific heat** $C \equiv \Delta Q / \Delta T$

  for $p, B_\mathrm{ext} = const.$

  → $\mathrm{d}U = \delta Q_\mathrm{rev} = T\mathrm{d}S$

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_{p,B_\mathrm{ext}} = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_{p,B_\mathrm{ext}}$$

2.1 Thermodynamic Potentials

superconductor in external magnetic field: free energy F

- normal state: $F_n = V_s f_n + \frac{1}{2}\mu_0 H_{\text{ext}}^2\, V$ ← total volume
- superconducting state: $F_s = V_s f_s + \frac{1}{2}\mu_0 H_{\text{ext}}^2\, V_a$ ← volume outside SC

⇒ $F_n - F_s = V_s(f_n - f_s) + \frac{1}{2}\mu_0 H_{\text{ext}}^2\, V_s$ ← volume of SC

with $f_n - f_s = \frac{1}{2}\mu_0 H_{\text{cth}}^2$ we obtain for $H_{\text{ext}} = H_{\text{cth}}$

$$F_n - F_s\Big|_{H_{\text{ext}}=H_{\text{cth}}} = \mu_0 H_{\text{cth}}^2\, V_s = \frac{B_{\text{cth}}^2}{\mu_0}\mathrm{V_s}$$

→ problem: free energies of normal and superconducting state do not coincide at phase boundary

→ origin of discrepancy: interaction energy of magnetic moment of SC with H_{ext}

with $\mathbf{M} = -\mathbf{H}_{\text{ext}}$ and $\mathbf{m} = V_s\mathbf{M}$ we obtain

$$F_n - F_s\Big|_{H_{\text{ext}}=H_{\text{cth}}} = -\mu_0 \mathbf{m}_{\text{cth}} \cdot \mathbf{H}_{\text{cth}} = -\mathbf{m}_{\text{cth}} \cdot \mathbf{B}_{\text{cth}}$$

2.1 Thermodynamic Potentials

- **where is the energy coming from ?**

  → it is provided by the current source maintaining $B_{\text{ext}} = \mu_0 H_{\text{ext}} = const.$ by doing work against the back electromotive force induced as the flux is entering the sample

- at $H_{\text{ext}} = H_{\text{cth}}$, superconductivity collapses
  → flux density $B_{\text{ext}} = \mu_0 H_{\text{ext}} = B_{\text{cth}}$ enters the volume V_s of the superconductor

- work done by current source $W = \int_a^b U\, I_{\text{coil}}\, \mathrm{d}t = \int_a^b -N\dot{\Phi}\; I_{\text{coil}}\, \mathrm{d}t = \int_{a'}^{b'} -N I_{\text{coil}}\, \mathrm{d}\Phi$

$$W = N I_{\text{coil}} \int_0^{B_{\text{cth}}} A\, \mathrm{d}B_{\text{ext}} = N\, I_{coil} A\, B_{\text{cth}}$$

with $B_{\text{ext}} = \mu_0 I_{\text{coil}} N/L$ and $V_s = A\, L$

$$W = N \frac{B_{\text{cth}} L}{\mu_0 N}\, A\, B_{\text{cth}} = V_s \frac{B_{\text{cth}}^2}{\mu_0}$$

superconductor in external field: free enthalpy G

with $G = U - TS + pV - \mathbf{m} \cdot \mathbf{B}_{\rm ext} = F + pV - \mathbf{m} \cdot \mathbf{B}_{\rm ext}$ and $\mathbf{m} = V_s \mathbf{M} = -V_s \mathbf{H}_{\rm ext}$ we obtain

- normal state: $(\mathbf{m} = 0)$ $$G_n = V_s f_n + \frac{1}{2}\mu_0 H_{\rm ext}^2 V_s + \frac{1}{2}\mu_0 H_{\rm ext}^2 V_a$$ (we neglect volume changes)

- superconducting state: $(\mathbf{m} = -V_s \mathbf{H}_{\rm ext})$ $$G_s = V_s f_s + \frac{1}{2}\mu_0 H_{\rm ext}^2 V_a + \mu_0 H_{\rm ext}^2 V_s$$

⇒

$$G_n - G_s \Big|_{H_{\rm ext} = H_{\rm cth}} = V_s (f_n - f_s) - \frac{1}{2}\mu_0 H_{\rm cth}^2 V_s$$

with $f_n - f_s = \frac{1}{2}\mu_0 H_{\rm cth}^2$ we obtain for $H_{\rm ext} = H_{\rm cth}$

$$G_n - G_s \Big|_{H_{\rm ext} = H_{\rm cth}} = 0$$

Summary of Lecture No. 2 (1)

- **discussion of basic properties of superconductors**

  perfect conductivity – perfect diamagnetism – type-I and type-II superconductivity – fluxoid quantization

- **superconducting materials and transition temperatures**

  discussion of different families of superconducting materials and their transition temperature

- **thermodynamic properties of superconductors**
  - revision of key apsects of thermodynamics
  - thermodynamic potentials: inner energy, free energy, free enthalpy
  - free energy is suitable potential for describing situations at constant volume
  - free enthalpy is suitable potential for describing situations at constant pressure

- **free energy and free enthalpy of a superconductor in an applied magnetic field**
  - discussion of pitfalls in deriving the free energy

Superconductivity and Low Temperature Physics I

Lecture No. 3

R. Gross

2. Thermodynamic Properties of Superconductors

2.2 Type-I Superconductor in B_{ext}

- perfect diamagnetism → $\mathbf{M} = \frac{\mathbf{m}}{V} = -\mathbf{H}_{ext} = -\frac{\mathbf{B}_{ext}}{\mu_0}$
- we assume $p, T = const.$

→ $dG = -SdT + Vdp - \mathbf{m}\cdot d\mathbf{B}_{ext} = -\mathbf{m}\cdot d\mathbf{B}_{ext}$

$dG_s = \frac{V}{\mu_0} B_{ext} dB_{ext} \qquad dg_s = dG_s/V$

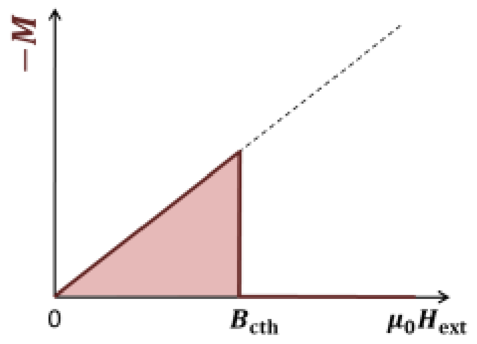
→ integration yields

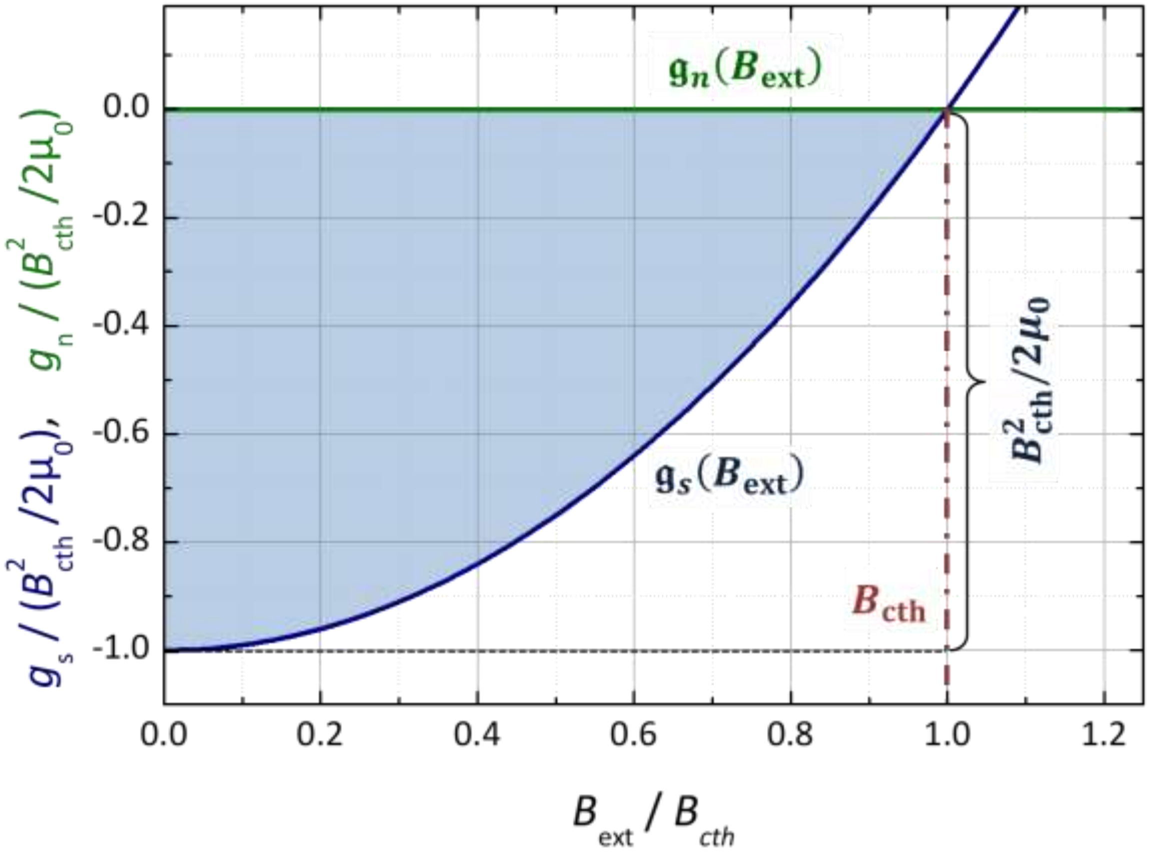
$$g_s(B_{ext},T) - g_s(0,T) = \frac{1}{\mu_0}\int_0^{B_{ext}} B'\,dB' = \frac{B_{ext}^2}{2\mu_0}$$

@ $B_{ext} = B_{cth}$: $g_s(B_{cth},T) = g_n(B_{cth},T) \simeq g_n(0,T)$

$$\Delta g(T) = g_n(0,T) - g_s(0,T)$$
$$= g_s(B_{cth},T) - g_s(0,T) = \frac{B_{cth}^2(T)}{2\mu_0}$$

⇒ $\Delta g(T) = \frac{B_{cth}^2(T)}{2\mu_0}$ ***condensation energy***





temperature dependence of the free enthalpy densities g_n and g_s

$$g_s(T) = g_n(T) - \Delta g(T), \qquad \text{with } \Delta g(T) = \frac{B_{cth}^2(T)}{2\mu_0}$$

$$\Rightarrow \quad g_s(T) = g_n(T) - \frac{B_{cth}^2(T)}{2\mu_0}$$

– temperature dependence of B_{cth}:

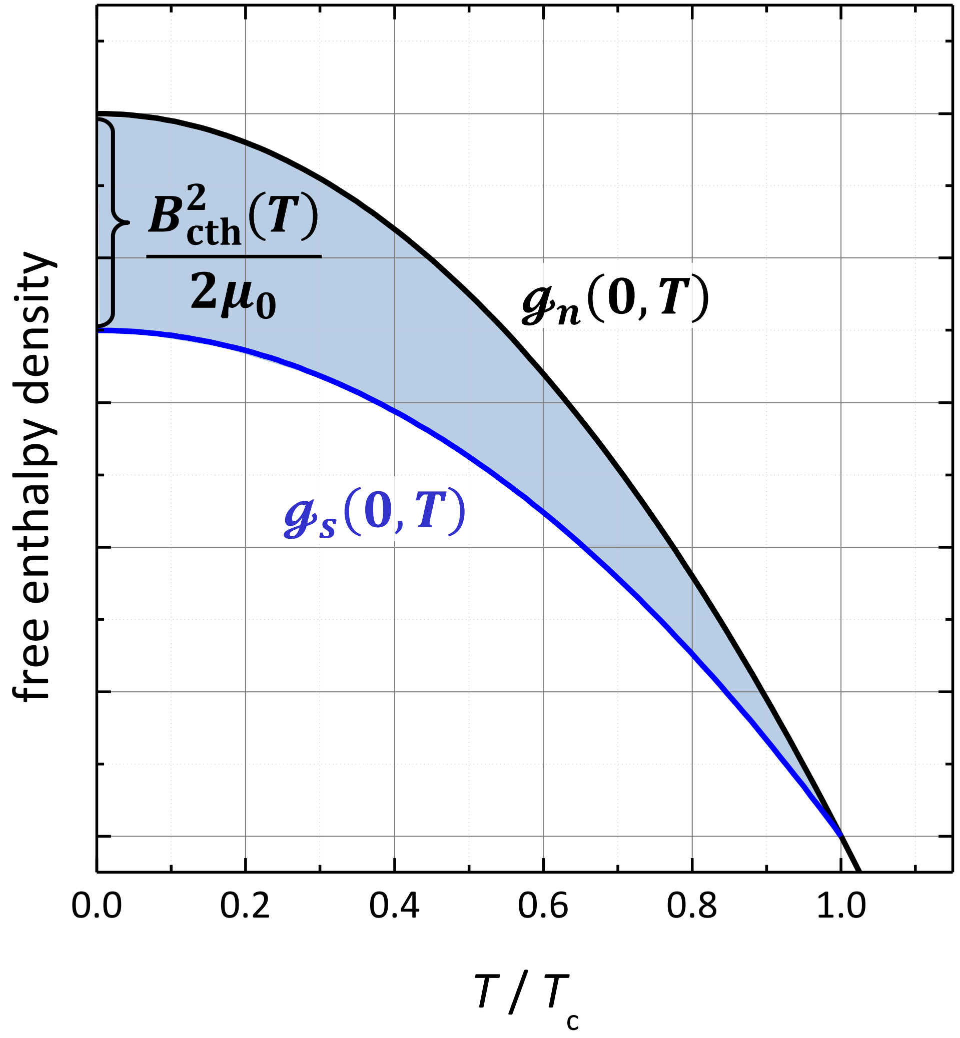
$$B_{cth}(T) = B_{cth}(0)\left[1 - \left(\frac{T}{T_c}\right)^2\right]$$

(empirical relation, calculation within BCS theory)

– entropy density of normal metal (free electron gas):

$$s_n(T) \propto T, \quad dg_n = -s_n dT \quad (@\ B_{ext} = 0)$$

$$g_n(T) = -\int_0^T s_n(T')dT' \propto -T^2$$



➔ *determination of entropy density $s_s(T)$ and specific heat $c_p(T)$ by calculating the temperature derivative of $g_s(T)$*

2.2 Type-I Superconductor in B_{ext}

temperature dependence of the entropy density $s_s = S_s/V$

- with $-\left(\frac{\partial G}{\partial T}\right)_{p,B_{ext}} = S$ and $s_s = S_s/V,\ \ s_n = S_n/V$

$$s_{s,n}(T) = -\left(\frac{\partial g_{s,n}}{\partial T}\right)_{p,B_{ext}}$$

$$\Rightarrow \Delta s(T) = s_n(T) - s_s(T) = -\left(\frac{\partial \Delta g(T)}{\partial T}\right)_{p,B_{ext}}$$

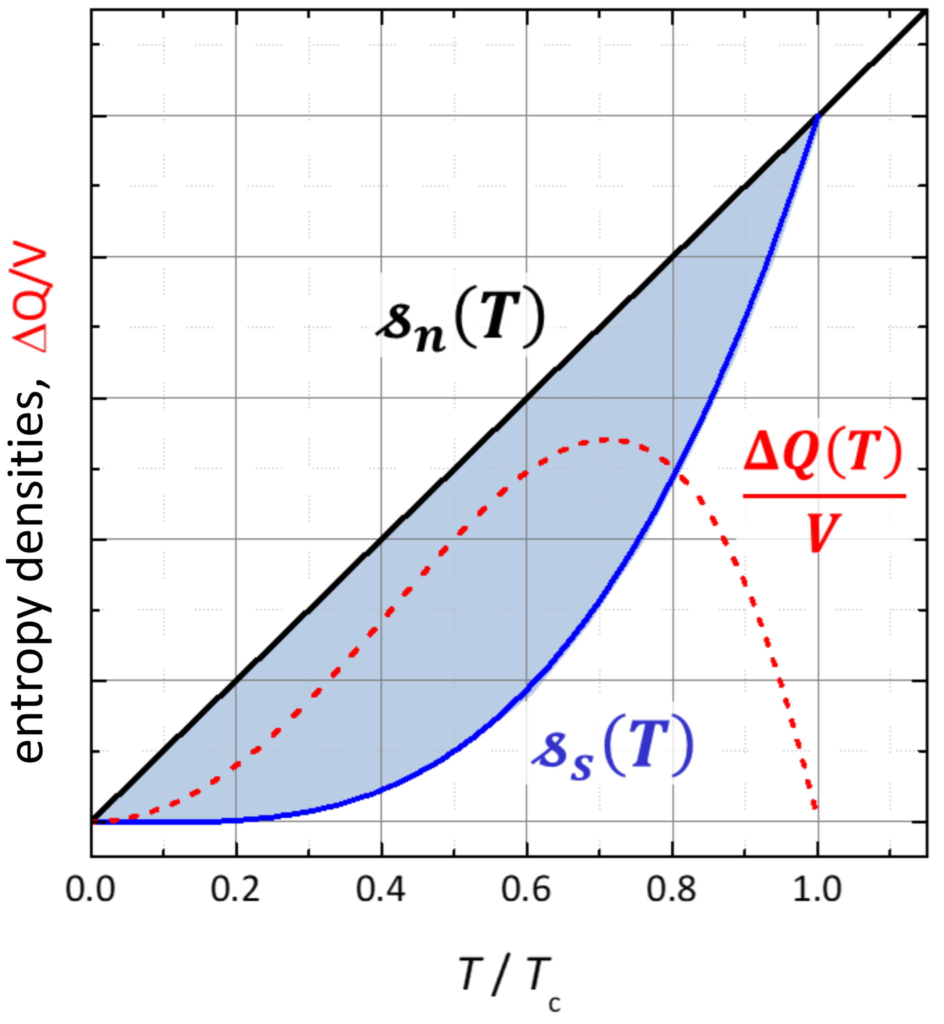
- with $\Delta g(T) = \frac{B_{cth}^2(T)}{2\mu_0}$ we obtain

$$\Delta s(T) = -\frac{B_{cth}}{\mu_0}\frac{\partial B_{cth}}{\partial T}$$ with $B_{cth}(T) = B_{cth}(0)\left[1-\left(\frac{T}{T_c}\right)^2\right]$

- how does $s_n(T)$ look like?

  we use $c_p = T\ (\partial s_n/\partial T)_{B_{ext},p}$ and $c_p = \gamma T$ (free electron gas)

  $\Rightarrow$ s_n proportional T



2.2 Type-I Superconductor in B_{ext}

discussion of the temperature dependence of the entropy difference Δs

$$\Delta s(T) = -\frac{B_{cth}}{\mu_0}\frac{\partial B_{cth}}{\partial T}$$

mit $B_{cth}(T) = B_{cth}(0)\left[1-\left(\frac{T}{T_c}\right)^2\right]$

i. $T \to T_c$:

$B_{cth} \to 0$ and therefore $\Delta s \to 0$ and $\frac{\Delta Q}{V} = T_c\Delta s \to 0$

(no latent heat, 2nd order phase transition)

ii. $T \to 0$:

$\frac{\partial B_{cth}}{\partial T} \to 0$ and therefore $\Delta s \to 0$

(3. law of thermodynamics, Nernst theorem)

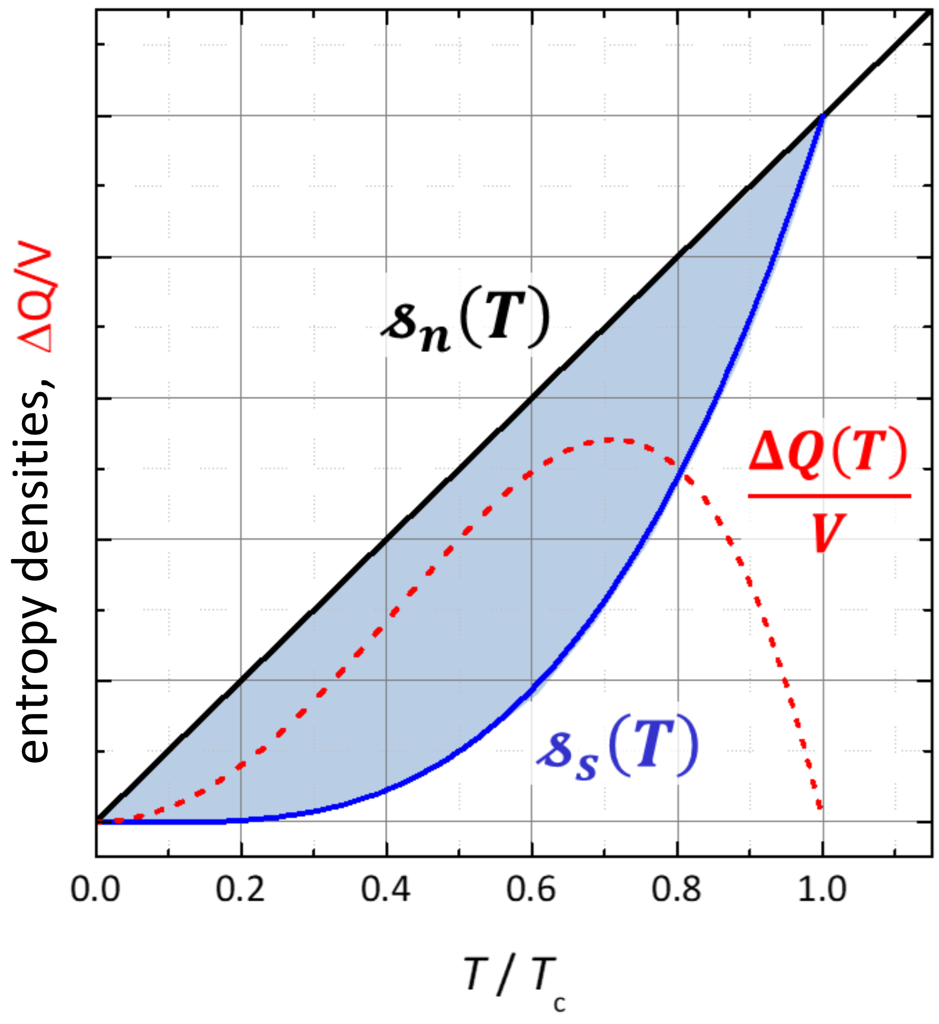
iii. $0 < T < T_c$:

$\frac{\partial B_{cth}}{\partial T} < 0, \quad B_{cth} > 0$ and therefore $\Delta s > 0$

➔ entropy density larger in N-phase than in S-phase

➔ S-phase is phase with larger order (correlation of electrons to Cooper pairs)

➔ since $\Delta s > 0$ also $\frac{\Delta Q}{V} = T_c(\mathrm{B_{ext}})\Delta s > 0$ (finite latent heat, 1st order phase transition)



temperature dependence of specific heat

Rutgers formula

$$\Delta c(T) = c_n(T) - c_s(T) = -\frac{T}{\mu_0}\left[\underbrace{B_{cth}\frac{\partial^2 B_{cth}}{\partial T^2}}_{<0 \text{ for all } T} + \underbrace{\left(\frac{\partial B_{cth}}{\partial T}\right)^2}_{\text{decreases with } T}\right]$$

➔ Δc changes sign

- we use the general relations

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_{p,B_{ext}} = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_{p,B_{ext}}$$

and $\Delta g = g_n(T) - g_s(T) = \frac{B_{cth}^2(T)}{2\mu_0}$

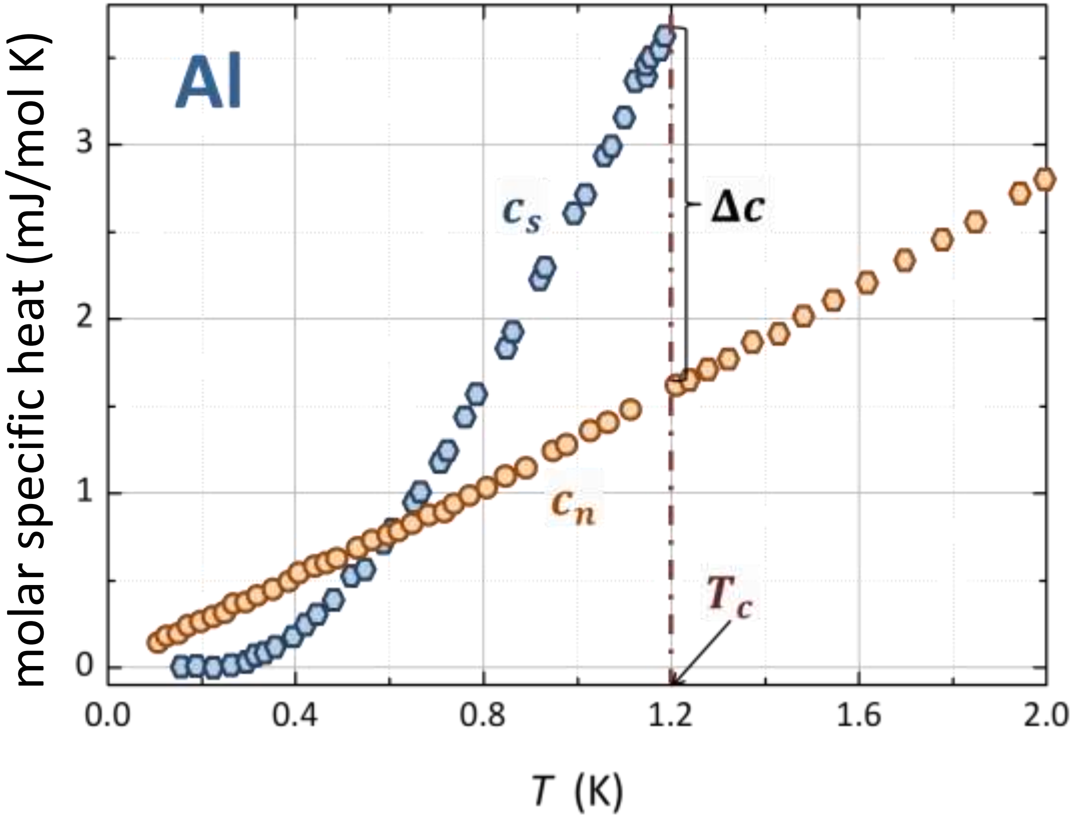
- jump of specific heat at $T = T_c$

$$\Delta c_{T=T_c} = -\frac{T_c}{\mu_0}\left(\frac{\partial B_{cth}}{\partial T}\right)^2_{T=T_c}$$

- agrees well with experiment
- $c_s = c_n$ at temperature, where $\Delta s = s_n - s_s = \max$

for $B_{cth}(T) = B_{cth}(0)\left[1-\left(\frac{T}{T_c}\right)^2\right]$:

$$\Delta c_{T=T_c} = -\frac{8}{T_c}\frac{B_{cth}^2(0)}{2\mu_0}$$



determination of the Sommerfeld coefficient γ:

- for $T \ll T_c$, we can neglect c_s compared to c_n
- we use $c_n(T) = \gamma \cdot T$ (γ = Sommerfeld coefficient)

$$\Rightarrow \gamma = \frac{\Delta c}{T} = -\frac{1}{\mu_0}\left[B_{\rm cth}\frac{\partial^2 B_{\rm cth}}{\partial T^2} + \left(\frac{\partial B_{\rm cth}}{\partial T}\right)^2\right] \simeq -\frac{1}{\mu_0} B_{\rm cth}\frac{\partial^2 B_{\rm cth}}{\partial T^2}$$

$$B_{\rm cth}\frac{\partial^2 B_{\rm cth}}{\partial T^2} \gg \left(\frac{\partial B_{\rm cth}}{\partial T}\right)^2$$

- with $B_{\rm cth}(T) = B_{\rm cth}(0)\left[1 - \left(\frac{T}{T_c}\right)^2\right]$, we obtain $\frac{\partial^2 B_{\rm cth}}{\partial T^2} = -2B_{\rm cth}(0)/T_{\rm c}^2$ and hence:

$$\gamma = \frac{4}{T_c^2}\frac{B_{\rm cth}^2(0)}{2\mu_0}$$

➔ ***by measuring T_c und $B_{\rm cth}(0)$, we can determine γ and, in turn, the density of states at the Fermi level, $D(E_{\rm F})$***

$$\gamma = \frac{\pi^2}{3} k_{\rm B}^2 \frac{D(E_{\rm F})}{V}$$ (free electron gas model)

2.2 Type-I Superconductor in B_{ext}

- with $c_n(T_c) = \gamma\, T_c$ we obtain

$$\frac{\Delta c_{T=T_c}}{c_n} = -\frac{8}{\gamma T_c^2}\frac{B_{\mathrm{cth}}^2(0)}{2\mu_0}$$

- BCS theory predicts $g_n - g_s(0) = \frac{B_{\mathrm{cth}}^2(0)}{2\mu_0} = \frac{1}{4} D(E_F)\Delta^2(0)/V$, then with $\gamma = \frac{\pi^2}{3}\, k_{\mathrm{B}}^2 \frac{D(E_{\mathrm{F}})}{V}$ we obtain

$$\frac{\Delta c_{T=T_c}}{c_n} = -\frac{8}{\frac{\pi^2}{3}\, k_{\mathrm{B}}^2 \frac{D(E_{\mathrm{F}})}{V} T_c^2}\, \frac{\frac{1}{4} D(E_F)\Delta^2(0)}{V}$$

$$\frac{\Delta c_{T=T_c}}{c_n} = -\frac{6}{\pi^2}\left(\frac{\Delta(0)}{k_{\mathrm{B}} T_c}\right)^2$$

note that the factor $\frac{6}{\pi^2} \simeq 0.6079 \ldots$ comes from $B_{\mathrm{cth}}(T) = B_{\mathrm{cth}}(0)\left[1 - \left(\frac{T}{T_c}\right)^2\right]$ (phenomenological approximation), BCS theory yields instead $0.4583 \ldots$

$\Delta c_{T=T_c}/c_n$	Al	Nb	Pb
direct measurement	1.4	1.9	2.7
derived from measured $B_{\mathrm{cth}}(0), T_c, \gamma$	1.6	1.9	2.4
derived from measured $\Delta(0), T_c$ with factor $6/\pi^2$	1.7	2.2	2.9
derived from measured $\Delta(0), T_c$ with factor 0.4583	1.3	1.7	2.2

larger numbers for Pb caused by stronger electron-phonon coupling (discussed later)

calculation of $c_s(T)$ at low temperatures

$$c_n(T) - c_s(T) = -\frac{T}{\mu_0}\left[B_{cth}\frac{\partial^2 B_{cth}}{\partial T^2} + \left(\frac{\partial B_{cth}}{\partial T}\right)^2\right]$$

$$B_{cth}(T) = B_{cth}(0)\left[1 - \left(\frac{T}{T_c}\right)^2\right]$$

$$\frac{\partial B_{cth}(T)}{\partial T} = -B_{cth}(0)\frac{2T}{T_c^2}, \qquad \frac{\partial^2 B_{cth}(T)}{\partial T^2} = -B_{cth}(0)\frac{2}{T_c^2}$$

$$c_n(T) - c_s(T) = -\frac{T}{\mu_0}\left[B_{cth}(0)\left[1 - \left(\frac{T}{T_c}\right)^2\right]\left(-B_{cth}(0)\frac{2}{T_c^2}\right) + \left(-B_{cth}(0)\frac{2T}{T_c^2}\right)^2\right]$$

$$c_n(T) - c_s(T) = -\frac{4}{T_c}\frac{B_{cth}^2(0)}{2\mu_0}\left[-\left[1 - \left(\frac{T}{T_c}\right)^2\right]\left(\frac{T}{T_c}\right) + 2\left(\frac{T}{T_c}\right)^3\right] = -\frac{4}{T_c}\frac{B_{cth}^2(0)}{2\mu_0}\left[3\left(\frac{T}{T_c}\right)^3 - \left(\frac{T}{T_c}\right)\right]$$

- with $\gamma = \frac{4}{T_c^2}\frac{B_{cth}^2(0)}{2\mu_0}$ we obtain $c_n(T) = \gamma T = \frac{4T}{T_c^2}\frac{B_{cth}^2(0)}{2\mu_0}$

$$c_s(T) = \frac{4}{T_c}\frac{B_{cth}^2(0)}{2\mu_0}\left[3\left(\frac{T}{T_c}\right)^3 - \left(\frac{T}{T_c}\right)\right] + \frac{4T}{T_c^2}\frac{B_{cth}^2(0)}{2\mu_0}$$

$\Rightarrow$

$$c_s(T) = \frac{12}{T_c}\frac{B_{cth}^2(0)}{2\mu_0}\left(\frac{T}{T_c}\right)^3$$

- obviously, the phenomenological description predicts $c_s(T) \propto T^3$, therefore experimentalists initially tried to fit their data to a power law dependence
- later BCS predicts the correct exponential temperature dependence

2.2 Type-I Superconductor in B_{ext}

volume change at S/N phase transition:

- we use the general relation

$$V = \left(\frac{\partial G}{\partial p}\right)_{T,B_{\text{ext}}}$$

and $\Delta g = g_n(T) - g_s(T) = \frac{B_{\text{cth}}^2(T)}{2\mu_0}$

$$\Rightarrow \left(\frac{V_n - V_s}{V_n}\right)_{T,B_{\text{cth}}(T)} = \frac{B_{\text{cth}}(T)}{\mu_0}\left(\frac{\partial B_{\text{cth}}(T)}{\partial p}\right)_{T,B_{\text{cth}}(T)}$$

→ volume change approaches zero for $T \to T_c$ since $B_{\text{cth}}(T) \to 0$

→ $T < T_c$: usually $V_s > V_n$ as $\frac{\partial B_{\text{cth}}(T)}{\partial p} < 0 \;\Rightarrow$ ***superconductor has a larger volume***

typical relative volume change is very small: $\frac{V_n - V_s}{V_n} \approx 10^{-7} - 10^{-8}$

thermodynamic properties of type-II superconductors

- $B_{ext} < B_{c1}$ (***Meißner-phase***): same behavior of type-I and type-II superconductors
- $B_{c1} < B_{ext} < B_{c2}$ (***Shubnikov-phase***): different (more complicated) behavior of type-II superconductors

➔ functional form of $g_s(T, B_{ext})$ depends on details