Superconductivity and Low Temperature Physics I

Lecture Notes
Winter Semester 2021/2022

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Chapter 2

Thermodynamic Properties of Superconductors

2.   Thermodynamic Properties of Superconductors

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- **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) ?

- **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* $G(T, p, N)$

- **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

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

generalized force   state variable

- differential of the internal energy

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

infinitesimal heat flow into the system

**infinitesimal mechanical work done on the system**

infinitesimal electromagnetic work done on the system

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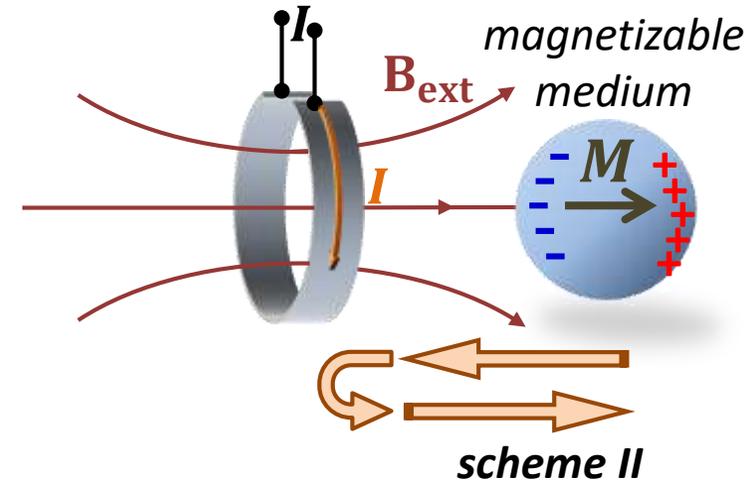
- **important question**:
  - → how to calculate the em work ?
  - → do we have to use $m\mathrm{d}B$ or $B\mathrm{d}m$ in the expression of $\mathrm{d}U$?

- **answer**: depends on experimental situation

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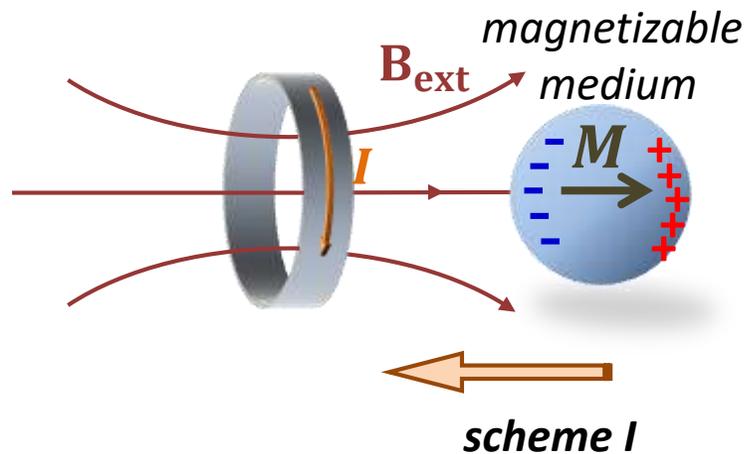
closed metallic ring with infinite conductivity:
→ flux density in ring stays constant

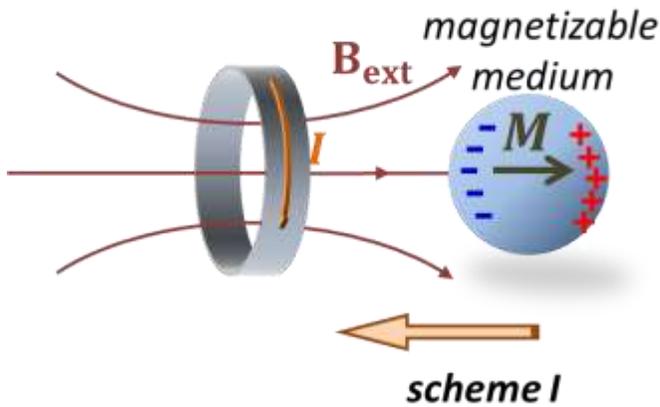*interaction energy of dipole with field has to be taken into account*

scheme II

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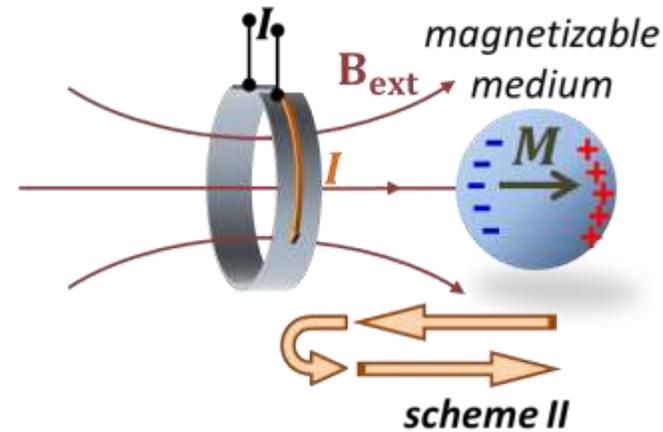→ current through ring (magnetic field) stays constant

no interaction energy of dipole and field

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

scheme I

(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 ∞

scheme II

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

$$W_{\text{I}} = \int_{\infty}^{r_1} \mathbf{F}_{\text{mag}} \cdot \mathrm{d}\mathbf{r} = -\int_{0}^{H_1} \mu_0 \mathbf{m} \cdot \mathrm{d}\mathbf{H}_{\text{ext}} = -\int_{0}^{B_1} \mathbf{m} \cdot \mathrm{d}\mathbf{B}_{\text{ext}}$$

$$W_{\text{II}}^{(1)} = \int_{\infty}^{r_1} \mathbf{F}_{\text{mag}} \cdot \mathrm{d}\mathbf{r} = -\int_{0}^{H_1} \mu_0 \mathbf{m} \cdot \mathrm{d}\mathbf{H}_{\text{ext}} = -\int_{0}^{B_1} \mu_0 \mathbf{m} \cdot \mathrm{d}\mathbf{B}_{\text{ext}}$$

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

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

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

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

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

change of the interaction energy   magnetization work

$$\delta W_{\text{I}} = -\mathbf{m} \cdot \mathrm{d}\mathbf{B}_{\text{ext}} \qquad\Longleftrightarrow\qquad \delta W_{\text{II}} = \mathbf{B}_{\text{ext}} \cdot \mathrm{d}\mathbf{m}$$
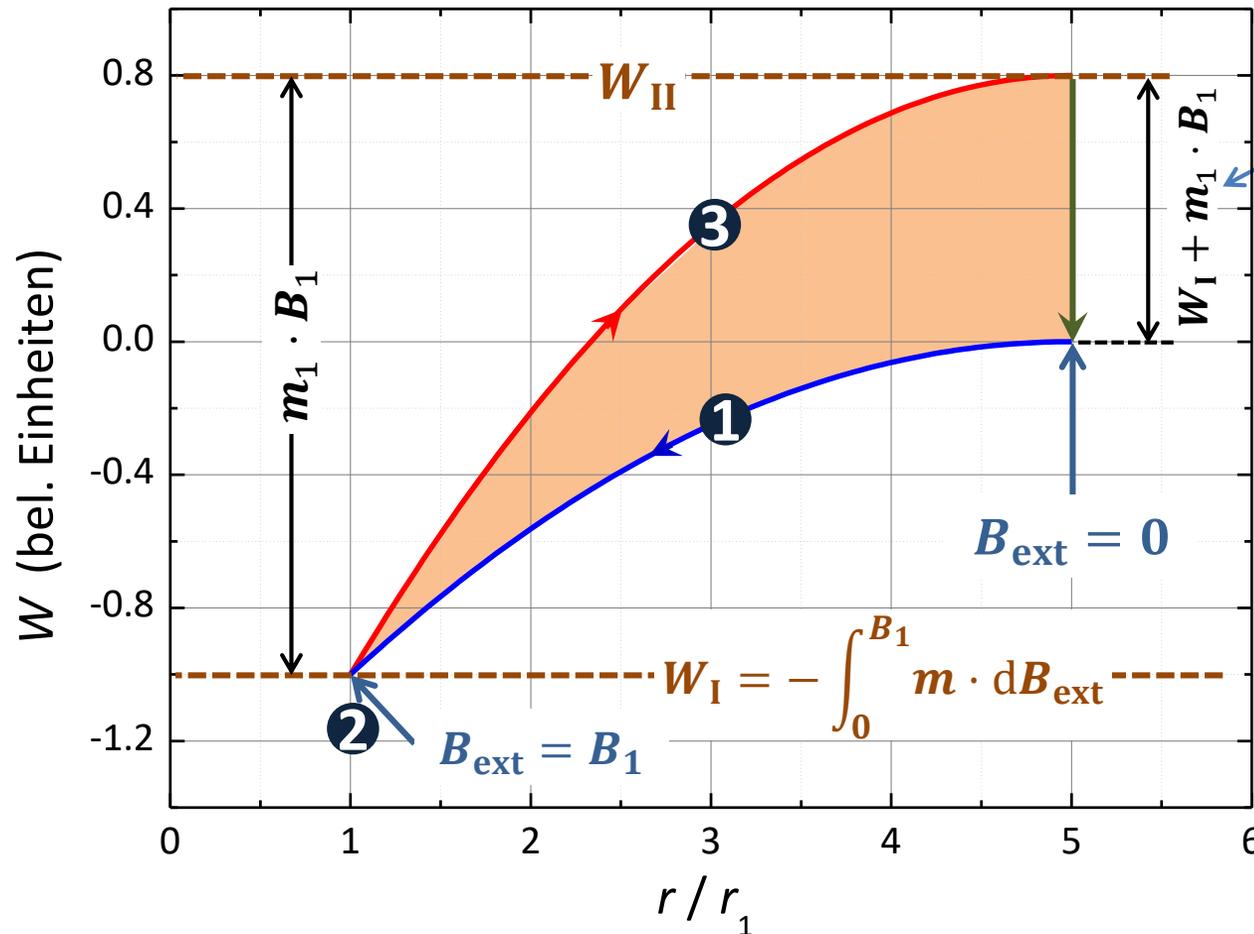
work required to magnetize the sample in a coil

- *Example*:
  current I through coil of length L, cross-section A, and winding number $n = N/L$
  $$\rightarrow B_{\text{ext}} = \mu_0\, n \cdot I$$

  we fill the coil with magnetic medium:

  - change ΔM of magnetization $M = m/V = m/AL$ results in flux change $\delta\Phi = \mu_0\, A \cdot \Delta M$
  - temporal change of flux through coil induces voltage $V = -nL \cdot \mu_0 A\, \mathrm{d}M/\mathrm{d}t$
  - current source has to perform work
    $$W_{\text{em}} = -I\!\int V dt = \mu_0 n I \cdot AL \cdot \Delta M$$
    $$W_{\text{em}} = B_{\text{ext}}\, \Delta m$$

In the figure:

W_{II}

$m_1 \cdot B_1$

$W_{\text{I}} + m_1 \cdot B_1$

$B_{\text{ext}} = 0$

$B_{\text{ext}} = B_1$

$$W_{\text{I}} = -\int_0^{B_1} m \cdot \mathrm{d}B_{\text{ext}}$$

W (bel. Einheiten)

r / r_1

A: Internal Energy U

$$dU_{\mathrm{I}} = T dS - p dV - \mathbf{m} \cdot d\mathbf{B}_{\mathrm{ext}}$$

$$dU_{\mathrm{II}} = T dS - p dV + \mathbf{B}_{\mathrm{ext}} \cdot d\mathbf{m}$$

two different expressions ➜ depend on definition of the considered systems

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

Scheme II: interaction energy $-d(\mathbf{m_1} \cdot \mathbf{B}_1)$ 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: $\qquad F = U - TS$

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

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

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

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

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

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

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

$\rightarrow$ ***use free enthalpy or Gibbs energy***

C: Free Enthalpy G

- definition: $\qquad G = U - TS + pV - \mathbf{m} \cdot \mathbf{B}_{\text{ext}}$

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

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

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

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

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

$$\mathrm{d}G_{\mathrm{I}} = -S\mathrm{d}T + V\mathrm{d}p - \mathbf{m} \cdot \mathrm{d}\mathbf{B}_{\text{ext}} \qquad\qquad \mathrm{d}G_{\mathrm{II}} = -S\mathrm{d}T - p\mathrm{d}V - \mathbf{m} \cdot \mathrm{d}\mathbf{B}_{\text{ext}}$$
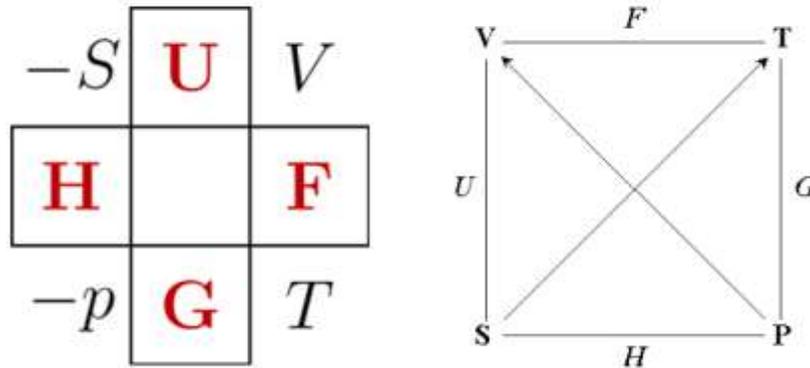
G is potential for the natural variables $T, p, B_{\text{ext}} = \mu_0 H_{\text{ext}}$

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

- if the suitable thermodynamic potential is known

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

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

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

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

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

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

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

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

superconductor in external magnetic field: free energy F

- normal state: $\qquad F_n = V_s f_n + \frac{1}{2}\mu_0 H_{\text{ext}}^2\, V \quad \longleftarrow$ total volume

- superconducting state: $\quad F_s = V_s f_s + \frac{1}{2}\mu_0 H_{\text{ext}}^2\, V_a \quad \longleftarrow$ volume outside SC

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

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

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

→ 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

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

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

  $\rightarrow$ 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
     $\rightarrow$ 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
$$W = \int_a^b U \, I_{\text{coil}} \, \mathrm{d}t = \int_a^b -N\dot{\Phi} \; I_{\text{coil}} \, \mathrm{d}t = \int_{a'}^{b'} -NI_{\text{coil}} \, \mathrm{d}\Phi$$

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

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

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

   $(\mathbf{m} = 0)$

- superconducting state: $\quad\quad G_s = V_s f_s + \frac{1}{2} \mu_0 H_{\text{ext}}^2 V_a + \mu_0 H_{\text{ext}}^2 V_s$

   $(\mathbf{m} = -V_s \mathbf{H}_{\text{ext}})$

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

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

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

Superconductivity
and
Low Temperature
Physics I

Lecture No. 3
04 November 2021

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- **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

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2. Thermodynamic Properties of Superconductors

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- perfect diamagnetism $\rightarrow \mathbf{M} = \dfrac{\mathbf{m}}{V} = -\mathbf{H}_{ext} = -\dfrac{\mathbf{B}_{ext}}{\mu_0}$

- we assume $p, T = const.$

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

$$dG_s = \frac{V}{\mu_0} B_{ext} dB_{ext} \quad d\mathscr{g}_s = dG_s/V$$

$\rightarrow$ integration yields

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

@ $B_{ext} = B_{cth}$: $\mathscr{g}_s(B_{cth}, T) = \mathscr{g}_n(B_{cth}, T) \simeq \mathscr{g}_n(0, T)$

$$\Delta\mathscr{g}(T) = \mathscr{g}_n(0, T) - \mathscr{g}_s(0, T)$$

$$= \mathscr{g}_s(B_{cth}, T) - \mathscr{g}_s(0, T) = \frac{B_{cth}^2(T)}{2\mu_0}$$

$$\Rightarrow \quad \Delta\mathscr{g}(T) = \frac{B_{cth}^2(T)}{2\mu_0} \quad \textit{condensation energy}$$
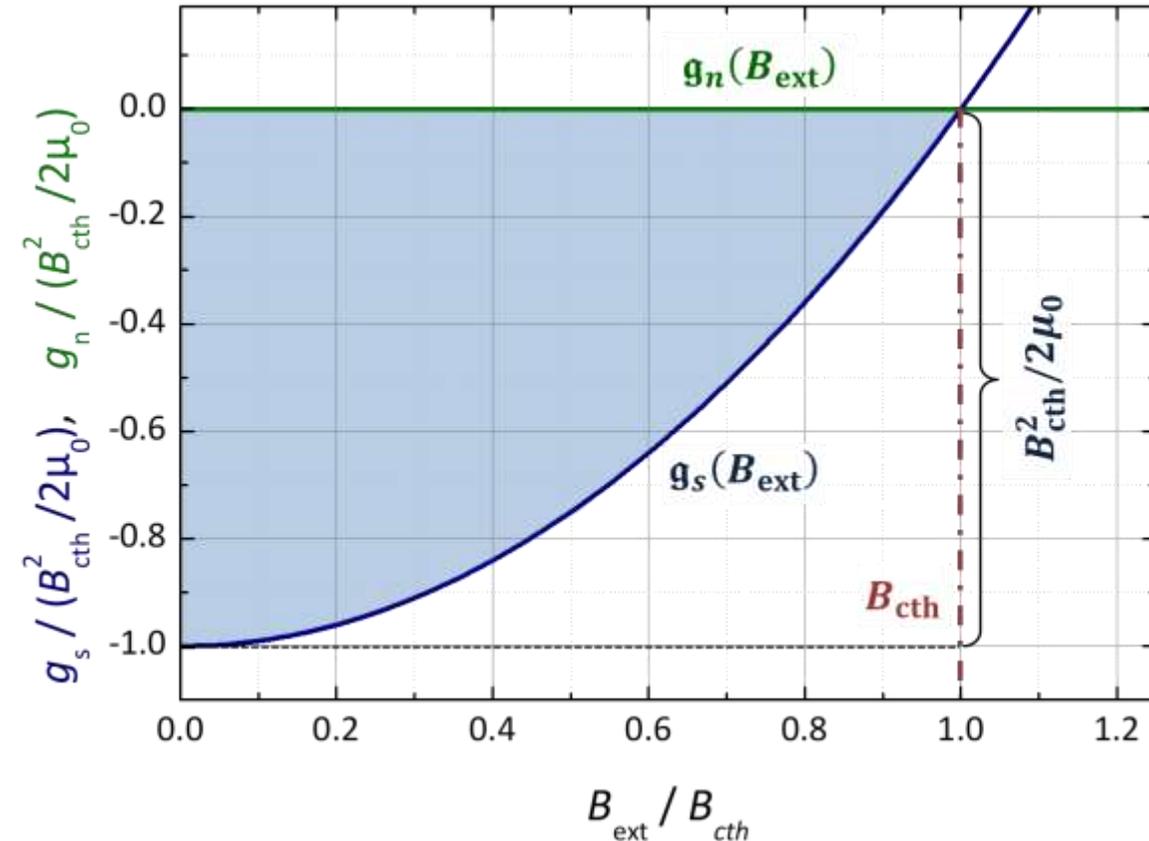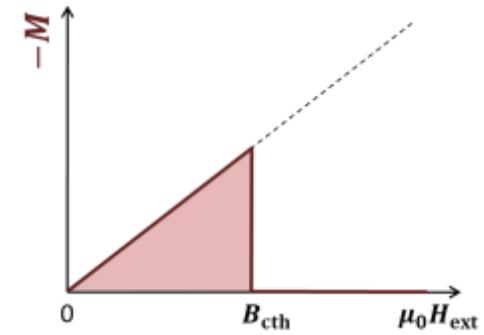
temperature dependence of the free enthalpy densities g_n and g_s

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

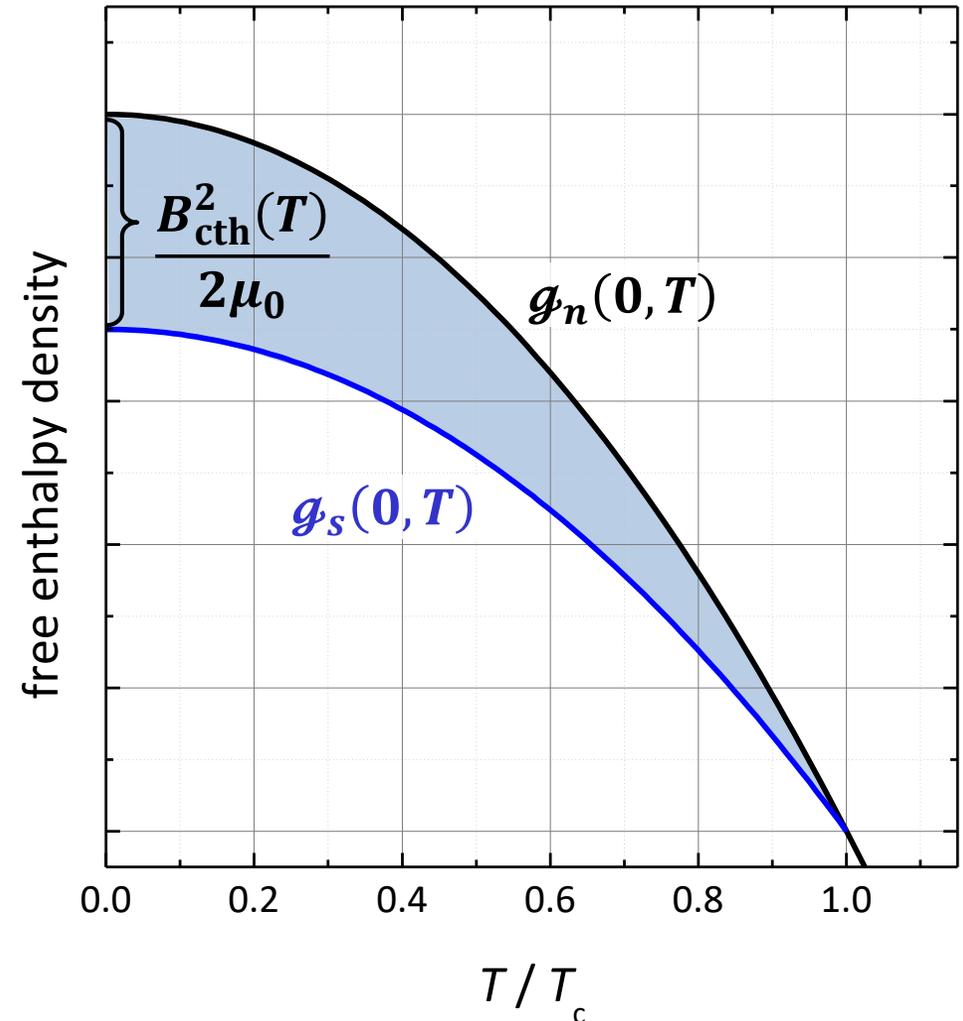➡ $$g_s(T) = g_n(T) - \frac{B_{cth}^2(T)}{2\mu_0}$$

– 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):

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

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

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

temperature dependence of the entropy density $\mathscr{s}_s = S_s/V$

- with $-\left(\frac{\partial G}{\partial T}\right)_{p,B_{\text{ext}}} = S$ and $\mathscr{s}_s = S_s/V, \quad \mathscr{s}_n = S_n/V$

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

⟹ $\Delta\mathscr{s}(T) = \mathscr{s}_n(T) - \mathscr{s}_s(T) = -\left(\frac{\partial \Delta\mathscr{G}(T)}{\partial T}\right)_{p,B_{\text{ext}}}$
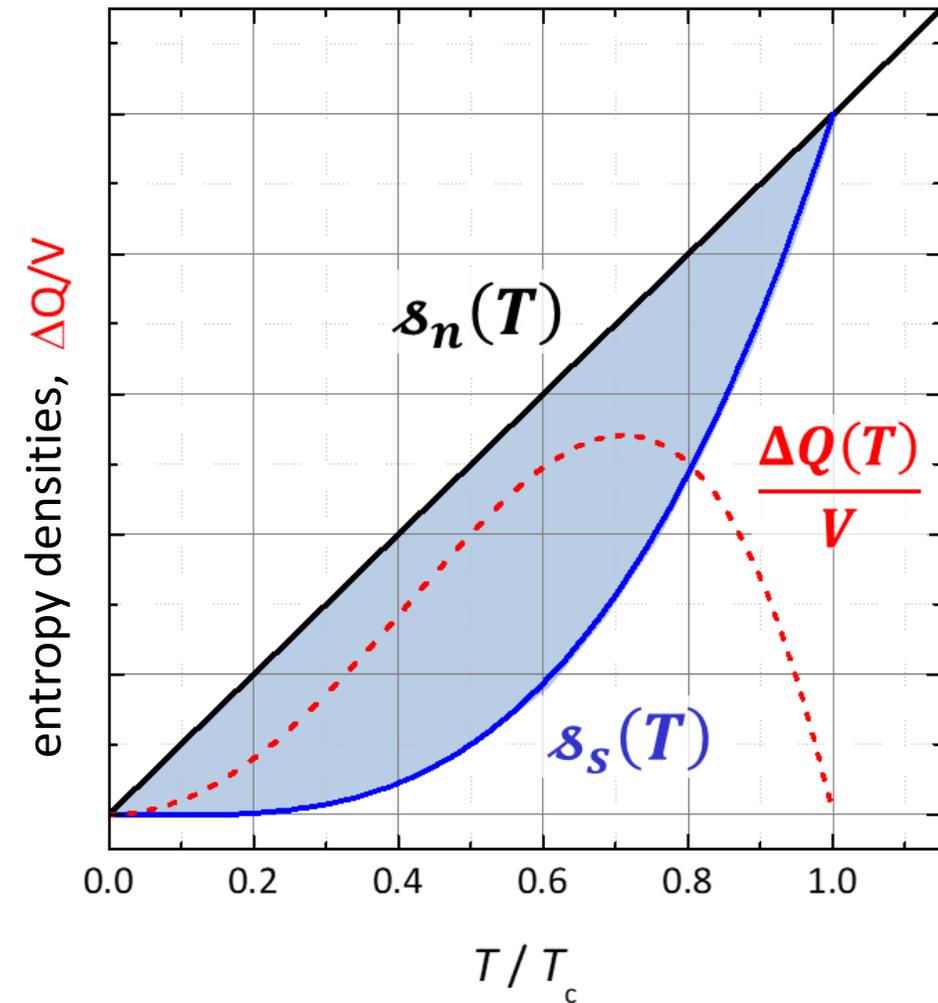
- with $\Delta\mathscr{G}(T) = \frac{B_{\text{cth}}^2(T)}{2\mu_0}$ we obtain

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

- how does $\mathscr{s}_n(T)$ look like?

we use $c_p = T\left(\partial\mathscr{s}_n/\partial T\right)_{B_{\text{ext}},p}$ and $c_p = \gamma T$ (free electron gas)

⟹ $\mathscr{s}_n$ proportional T

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discussion of the temperature dependence of the entropy difference Δs

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

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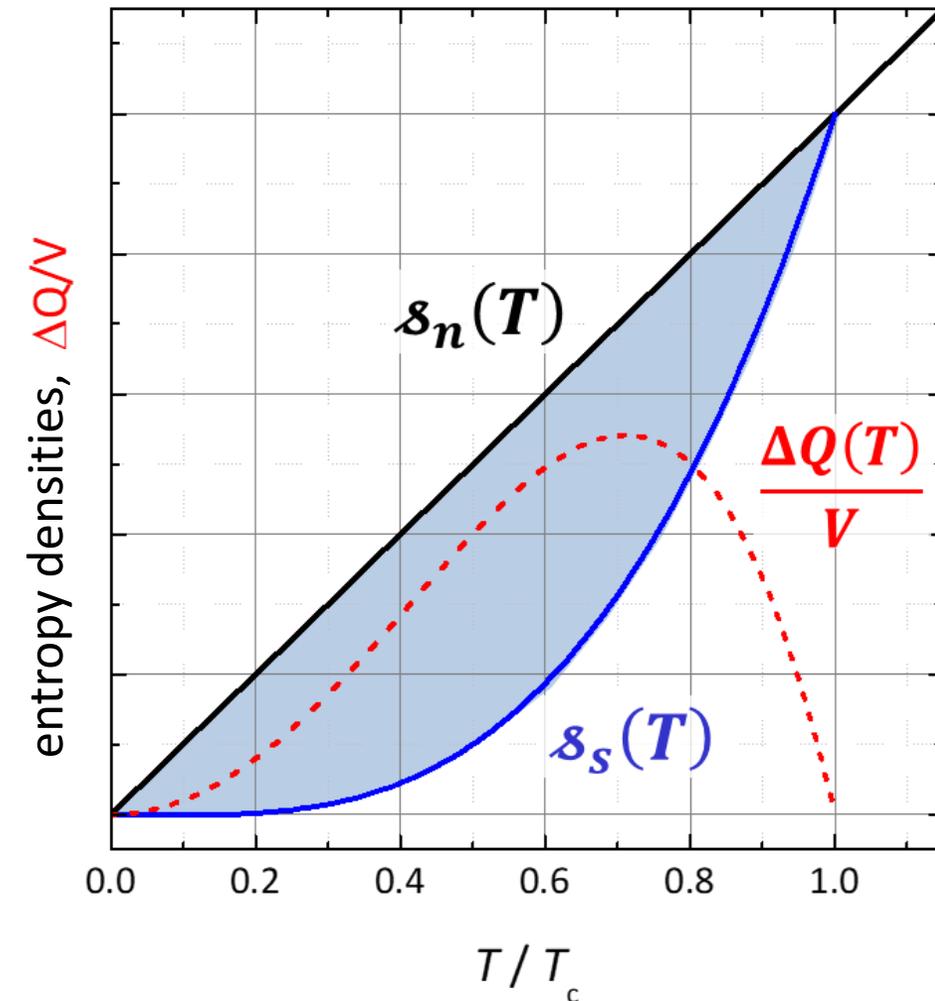
$\frac{\partial B_{cth}}{\partial T} < 0, \quad B_{cth} > 0$ and therefore $\Delta s > 0$

➔ 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 $\frac{\Delta Q}{V} = T_c(B_{ext})\Delta s > 0$

(finite latent heat, 1st order phase transition)

temperature dependence of specific heat

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- we use the general relations

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

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

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

< 0 for all T decreases with T

➔ Δc changes sign

- jump of specific heat at $T = T_c$

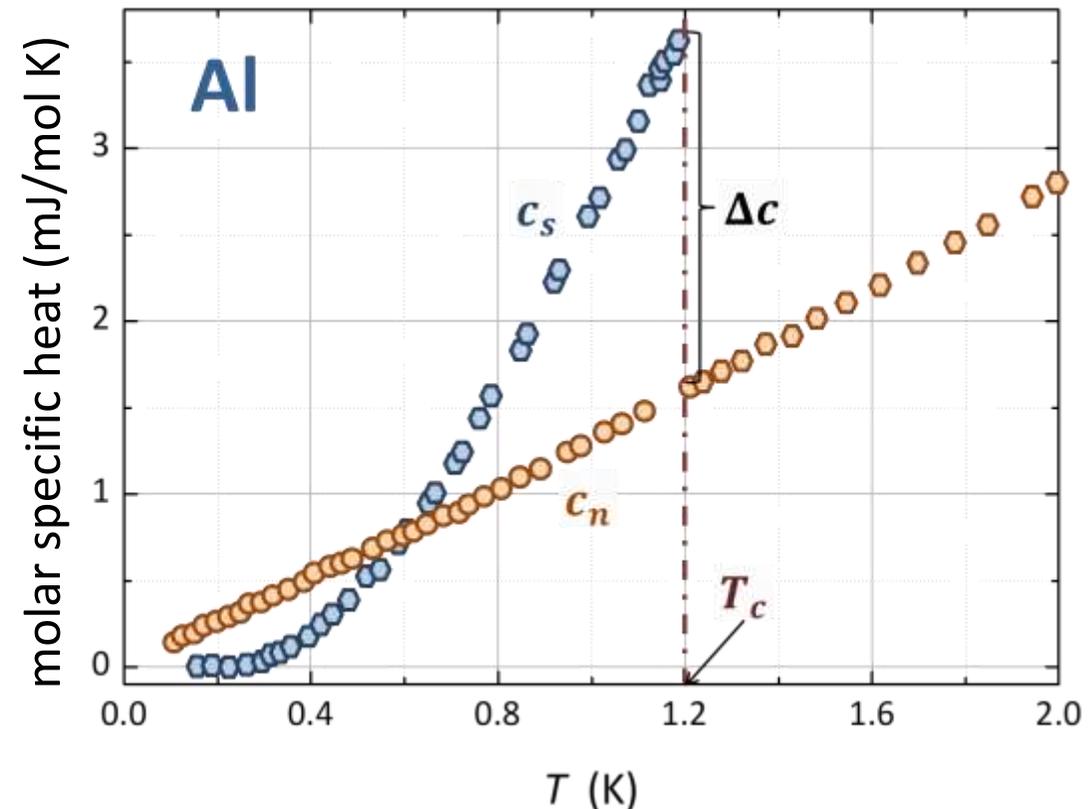$$\Delta c_{T=T_c} = -\frac{T_c}{\mu_0}\left(\frac{\partial B_{\text{cth}}}{\partial T}\right)^2_{T=T_c}$$

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

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

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

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)

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

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

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

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

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

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

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

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

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

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

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

note that the factor $\frac{6}{\pi^2} \simeq 0.6079\ldots$ comes from $B_{cth}(T) = B_{cth}(0)\left[1 - \left(\frac{T}{T_c}\right)^2\right]$

(phenomenological approximation), BCS theory yields instead 0.4583 …

$\Delta c_{T=T_c}/c_n$	Al	Nb	Pb
direct measurement	1.4	1.9	2.7
derived from measured $B_{cth}(0), T_c, \gamma$	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)

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calculation of $c_s(T)$ at low temperatures

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

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

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

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

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

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

$$c_s(T) = \frac{4}{T_c}\frac{B_{\text{cth}}^2(0)}{2\mu_0}\left[3\left(\frac{T}{T_c}\right)^3 - \left(\frac{T}{T_c}\right)\right] + \frac{4T}{T_c^2}\frac{B_{\text{cth}}^2(0)}{2\mu_0} \implies c_s(T) = \frac{12}{T_c}\frac{B_{\text{cth}}^2(0)}{2\mu_0}\left(\frac{T}{T_c}\right)^3$$

- 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

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 $\Delta\mathscr{G} = \mathscr{G}_n(T) - \mathscr{G}_s(T) = \dfrac{B_{\text{cth}}^2(T)}{2\mu_0}$

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

→ 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 $\dfrac{\partial B_{\text{cth}}(T)}{\partial p} < 0 \implies$ *superconductor has a larger volume*

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

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

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