Thermodynamic properties.

① Condensation energy.

1st law thermodynamics: $dU = \underbrace{dQ}_{\text{heat}:\ TdS} + \overline{dW}^{\text{work}}$

how to calc. work?

if $H=0 \Rightarrow dW=0$ for finite H: field needs to be expelled (Meissner effect)

Let us take ∞ cylindrical sample

∞ long solenoid with current I:

$$\bar{H} = \frac{N}{L}\cdot I \, \bar{e}_z$$

E.M.F. of single turn: $\mathcal{E} = -\frac{d\phi}{dt}$ $\phi = \text{flux} = B\cdot A$.

to go from I to $I+dI$ work done in dt: $dW = -N\cdot\mathcal{E}\cdot I\cdot dt$

$$= +N\frac{d\phi}{dt} I\, dt$$

$$= N I\, d\phi$$

$$= N I A\, dB$$

$$= N\cdot\left(\frac{L}{N}\bar{H}\right) A\, d\bar{B}$$

$$= V\cdot\bar{H}\cdot d\left[\mu_0(\bar{M}+\bar{H})\right]$$

$$= \mu_0 V\left(\bar{H}\, d\bar{M} + \underbrace{\bar{H}\, d\bar{H}}_{\text{work done to build up field in vacuum}}\right)$$

neglect here ⇐

so $dW = \mu_0 V \bar{H} \cdot d\bar{M}$ and.

$dU = TdS + \mu_0 V \bar{H} \cdot d\bar{M}$ (compare in gas: $dU = TdS - pdV$)

$\equiv$ 1st law thermo for magnetic medium.

using analogy $pdV \Rightarrow -\mu_0 V \bar{H} \cdot d\bar{M}$

Helmholtz free energy $F = U - TS$

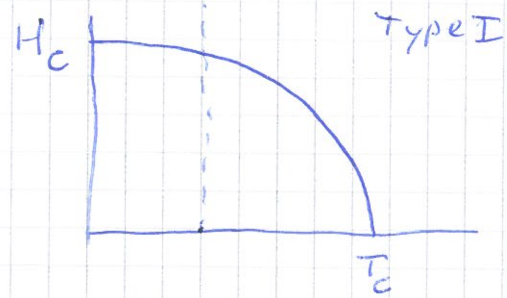
Gibbs free energy $G = U - TS - \mu_0 V \bar{H} \cdot \bar{M}$

so that for instance entropy: $S = -\frac{\partial G}{\partial T}$

and magnetization: $\bar{M} = -\frac{1}{\mu_0 V} \frac{\partial G}{\partial \bar{H}}$

$G = G(T, H)$ => useful since (T, H) exptl. parameters.

what is the energy difference between normal and S.C. state?



we'd like to know $G_s(T,0) - G_n(T,0)$

Let's first look at $G_s(T, H_c) - G_s(T, 0) =$

$$\int_0^{H_c} dG = \int_0^{H_c} -\mu_0 V H \cdot dM$$

in type I: $M = -H$ so $= \int_0^{H_c} \mu_0 V M \, dM = \mu_0 V \frac{H_c^2}{2}$

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so $G_s(T, H_c) - G_s(T, 0) = \mu_0 \frac{H_c^2}{2} V$ Ⓑ

at H_c: normal & superconducting state in equil.
i.e. same G.

$\Rightarrow$ $G_s(T, H_c) = G_N(T, H_c)$ Ⓐ

in normal state $M \approx 0$ (neglect pauli para., etc).

if not superconducting:

$$G_N(T, H_c) - G_N(T, 0) = \int_0^{H_c} dG = \int_0^{H_c} -\mu_0 V \vec{M} \cdot d\vec{H} \approx 0$$

so $G_N(T, 0) \simeq G_N(T, H_c)$.

and thus Ⓐ $G_N(T, 0) \simeq G_s(T, H_c)$.

or Ⓑ $G_N(T, 0) - G_s(T, 0) = \mu_0 \frac{H_c^2}{2} V$

indeed $G_s(T, 0) < G_N(T, 0)$ by amount

$\mu_0 H_c^2/2 \, V$

in terms of Helmholtz free energy:

$F = G - \mu_0 V H M$ using $H = M = 0$ (no field).

similarly.

$$F_s(T, 0) - F_N(T, 0) = -\mu_0 V \frac{H_c^2}{2}$$

$\Rightarrow$ from H_c one can determine
condensation energy !!

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example Nb:

$T_c = 9\ K$

$H_c = 160\ kA/m \quad (B_c = \mu_0 H_c = 0.2T)$

condensation energy: $\mu_0 \frac{H_c^2}{2} \approx 16.5\ kJ/m^3$

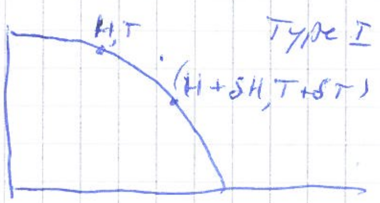
Nb: BCC xtal, unit cell 3.3 Å

$\Rightarrow$ condensation energy $\approx 2\ \mu eV$ / atom.

Could be surprising, $\left\{ \begin{array}{l} kT_c = 0.78\ meV \text{ for Nb} \\ E_F = 5.3\ eV \text{ for Nb} \end{array} \right.$

from BCS: $E_{cond.} \sim (k_B T_c)^2 \cdot g(E_F)$ $\quad 1K \triangleq 86.2\ \mu eV$

Entropy change:



everywhere on $H_c(T)$: $G_N = G_S$

or $\delta G_N = \delta G_S$

$-S_S\, dT - \mu_0 V M_S\, dH = -S_N\, dT - \mu_0 V M_N\, dH$

normal state: $M_N = 0$.

supercond. state: $M_S = -H$.

$-S_S dT - \mu_0 V H\, dH = -S_N\, dT$

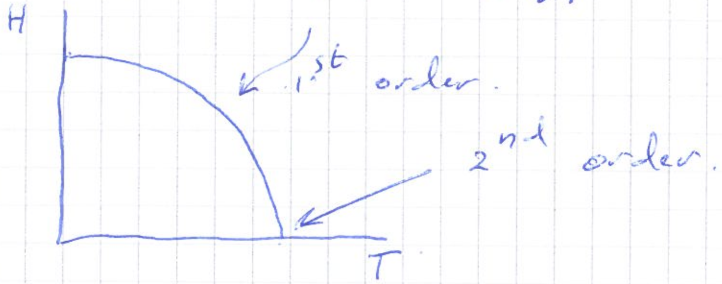
$(S_S - S_N)\, dT = -\mu_0 V H\, dH$.

$$(S_S - S_N) = \mu_0 V H_c \frac{dH_c}{dT}$$

So phase transition has latent heat.

$$L = T\Delta S = T(S_N - S_S)$$

$$= -\mu_0 T H_c \frac{dH_c}{dT}.$$



((Clausius - Clapeyron ~~...~~ gas: $L = VT\frac{dP}{dT}$.

vapor-liquid line

$V \to -\mu_0 M = -\mu_0 H_c$.

$P \to H_c$.)

$\Rightarrow$ entropy from $H_c(T)$!!

Ginzberg - Landau theory

central idea (landau): Order parameter (i.e. M below T_c in magnet)

$\to$ macroscopic wavefunction

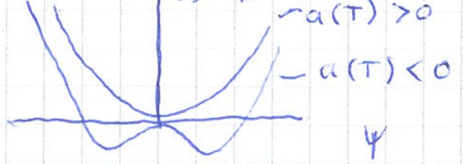
GL theory: complex parameter ψ

such that $\begin{cases} \psi = 0 & T > T_c \\ \psi(T) \neq 0 & T < T_c \end{cases}$

free energy $F_S(T) = F_N(T) + a(T)|\psi|^2 + b(T)|\psi|^4 + \ldots$

- $b > 0$ otherwise no minimum.

$F_S(T)$: - real (is energy).
- differentiable near $\psi = 0$ for ψ and ψ^*



$\to$ minima $|\psi|^2 = -\frac{a(T)}{b(T)}$

near T_c Taylor expansion.

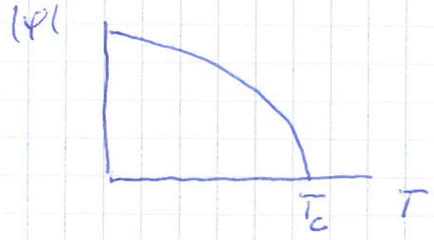
$$a(T) \overset{\swarrow\,=0}{=} a + \alpha \cdot (T - T_c) + \ldots$$

$=0$ since phase transition, where a should change sign.

$$b(T) \simeq \beta + \ldots$$

minimal. $F \Rightarrow \quad |\psi| = \left(\frac{\alpha}{\beta}\right)^{1/2} (T_c - T)^{1/2} \quad T < T_c$

$$= 0 \quad T > T_c$$



ψ complex : $\psi = |\psi| e^{i\varphi}$ at T_c : φ assumes value.
(like M takes $\pm$ in ferromagnet)

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↑

we also know: $F_S(T) - F_N(T) = -\frac{\alpha^2 (T - T_c)^2}{2\beta} = -\mu_0 \frac{H_c^2}{2}$

or $H_c = \frac{\alpha}{\sqrt{\mu_0 \beta}} (T_c - T)$

<u>entropy</u>

From free energy : $S = -\frac{\partial F}{\partial T}$

$\Rightarrow S_S(T) - S_N(T) = -\frac{\alpha^2}{\beta} (T_c - T)$: linear in T

No discontinuity in $S \Rightarrow$ <u>2^{nd} order p.T.</u>

<u>heat cap.</u>

$$C_V = T \frac{dS}{dT}$$

$$C_{V_S} - C_{V_N} = \begin{cases} T \frac{\alpha}{\beta} & T < T_c \\ 0 & T > T_c \end{cases}$$

discontinuity in C_V $\Delta C_V = T_c \frac{\alpha^2}{\beta}$

↳ <u>2^{nd} order PT</u>