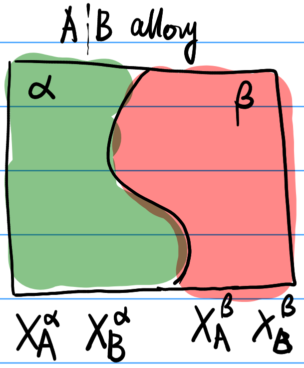
MATE 664 L13

Introduction to phase transformation



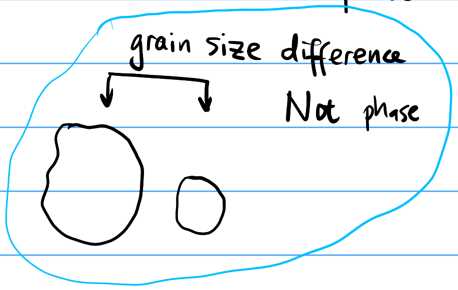
Phase transformation

1) How can $\alpha \rightleftarrows \beta$ transform?

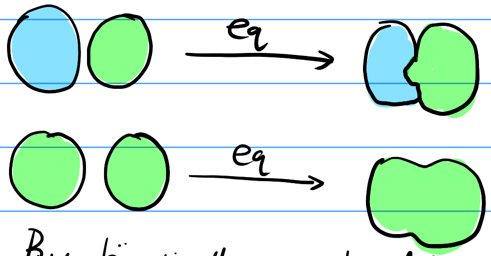
2) How fast ?

phase - diagram: many ways

what counts as a "phase" ?



1. Scalar descriptor of material
2. distinct values across region
3. phase interface clear distinction
4. Same phase of material at eq. → 1 phase



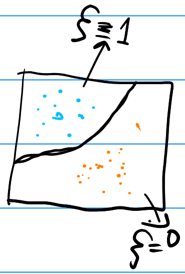
But kinetically may be difficult !

Landau's treatment of "order parameter"

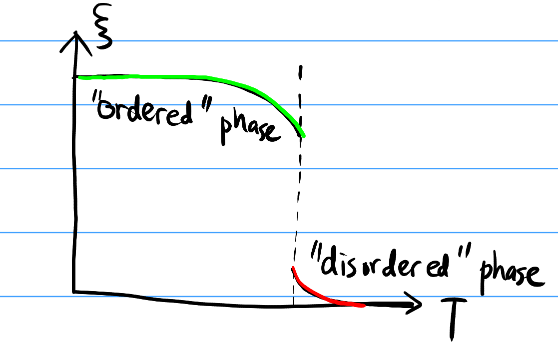
Free energy $F(T, \xi)$ ξ also dependent on T

Usually $\begin{cases} \xi \to 0 \text{ for high } T \text{ / disordered phase} \\ \xi \to 1 \text{ for low } T \text{ / ordered phase} \end{cases}$

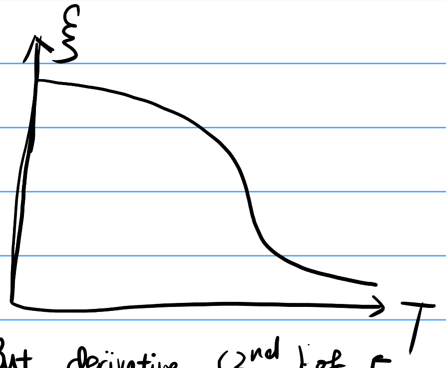
ξ can be arbitrary factor $\rightleftharpoons$ "classifier in machine learning"
(or inverse to entropy)



1st order phase transformation



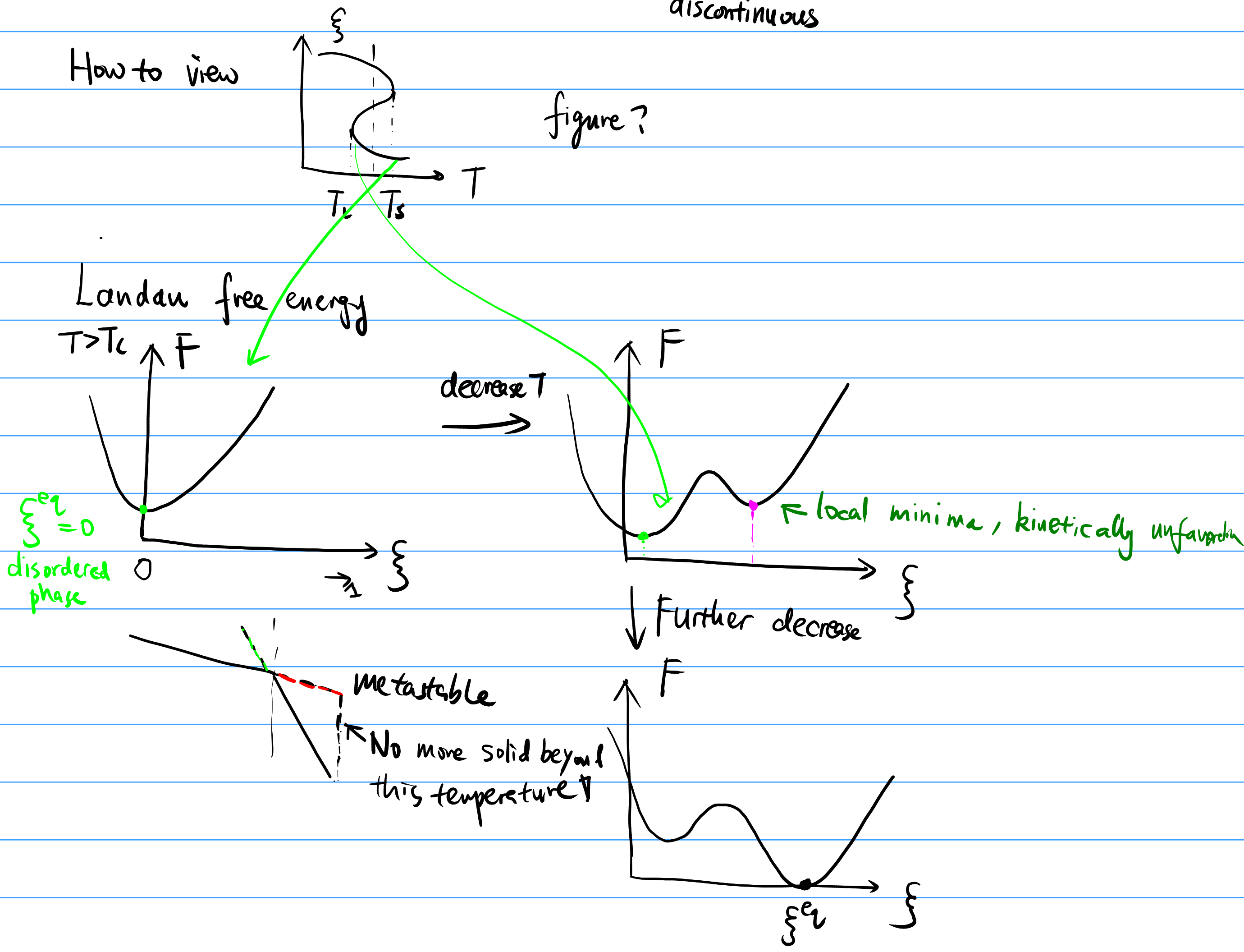
2nd order



But derivative (2nd) of F will be discontinuous

How to view figure?

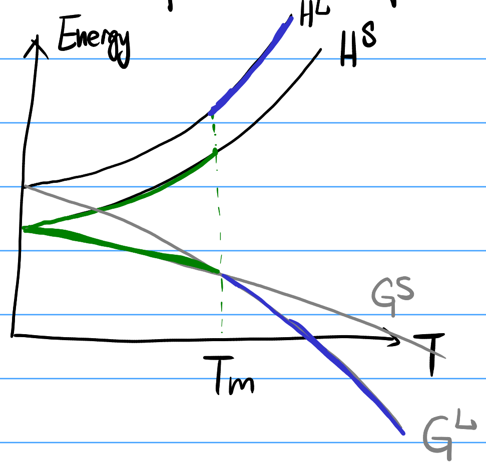
Landau free energy



Thermodynamic considerations

Specific heat $C_p \leftarrow$ constant p | $C_v \leftarrow$ constant V

We could compare Gibbs free energy for 2 phases (arbitrary)



Most stable phase $\Rightarrow$ G min

H_L always higher than H^S

Relation $\quad H = \int_{T^0}^{T} C_p \, dT' \quad$ or $\quad C_p = \left(\frac{\partial H}{\partial T}\right)_p$

$$\frac{S}{T} = \int_0^T \frac{C_p}{T} dT' \quad \text{or} \quad \frac{C_p}{T} = \left(\frac{\partial S}{\partial T}\right)_p$$

Thermodynamic Matrix

$$\begin{array}{r|c|c|} \multicolumn{3}{r}{\xrightarrow{+pV}} \\ \cline{2-3} -Ts\downarrow & U & H \\ \cline{2-3} & F & G \\ \cline{2-3} \end{array}$$

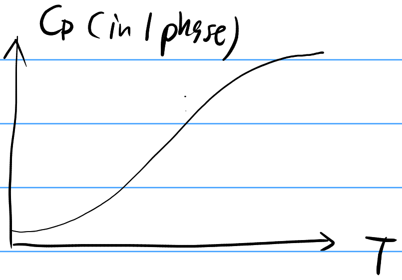
$$G = U + PV - TS$$

$$\frac{\partial G}{\partial T} = -S \qquad \frac{\partial G}{\partial p} = V$$

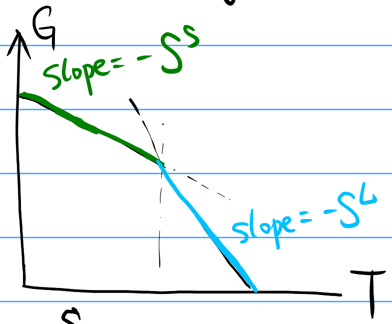
Slope in H-T diagram $\left(\frac{\partial H}{\partial T}\right)_p = C_p$, at T_m C_p undefined,

$$C_p^L\Big|_{T_m} \not\approx C_p^S\Big|_{T_m}$$

Why the jump in H?



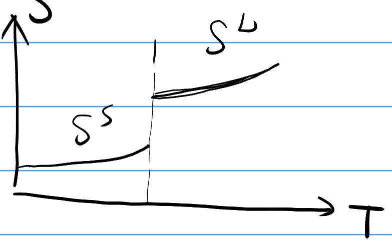
Slope in G-T diagram



$$\frac{\partial G}{\partial T}\Big|_p = \frac{\partial (H-TS)}{\partial T}\Big|_p = \overset{\overset{C_p}{\Uparrow}}{\frac{\partial H}{\partial T}\Big|_p} - \frac{\partial (TS)}{\partial T}\Big|_p$$

$$= \cancel{C_p} - S - \underbrace{\cancel{T\left(\frac{\partial S}{\partial T}\right)_p}}_{\Downarrow\ \cancel{\frac{C_p}{T}}}$$

$$= -S$$



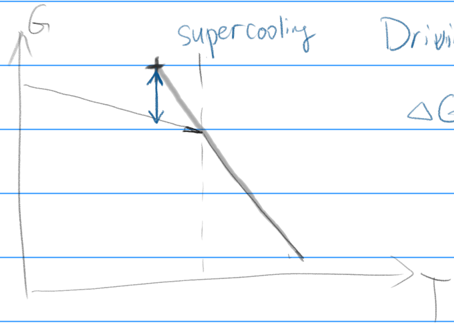
makes sense?

$S = k_B \ln \Omega$

C_p may be different, but S has discontinuity

$S^L - S^S = \Delta S = \frac{L}{T_m}$ (molar ~~latent~~ entropy)

⑦



Driving force

$$\Delta G = (G^L - G^S)\Big|_{T<T_m}$$
$$= H^L - TS^L - (H^S - TS^S)$$
$$= \underbrace{(H^L - H^S)}_{\simeq L} - T\underbrace{(S^L - S^S)}_{\frac{L}{T_m}}$$
$$= L\left(1 - \frac{T}{T_m}\right)$$
$$= L\frac{(T_m - T)}{T_m}$$

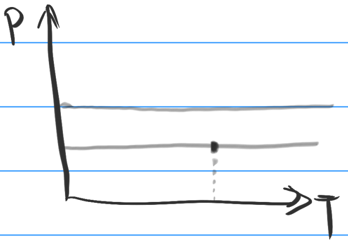
Can we use the non equilibrium ?

$$\Delta G = \boxed{\frac{L}{T_m}}\underbrace{(T_m - T)}_{\text{Thermal driving force ?}}$$

⇓

ΔS^m but ?

⑧ Quick review: Inclusion of additional factors ?

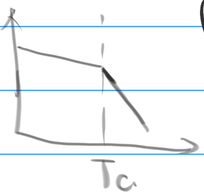


Common single component phase diagram

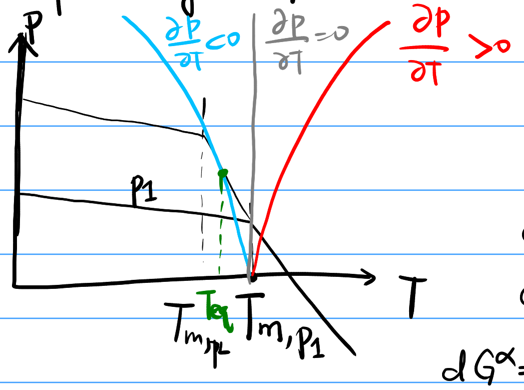
$$\left(\frac{\partial G}{\partial T}\right) = -S$$

$$\left(\frac{\partial G}{\partial p}\right) = V \Leftarrow \text{molar volume}$$

Each p:



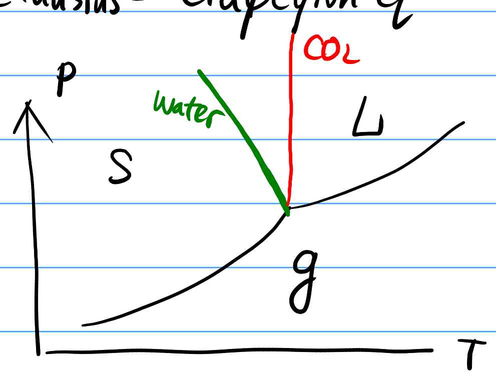
Dependency on P



How do we know $\frac{\partial P}{\partial T}$?

$$dG^\alpha = V_m^\alpha dp - S^\alpha dT$$
$$dG^\beta = V_m^\beta dp - S^\beta dT$$
$$dG^\alpha = dG^\beta$$
$$\Rightarrow \left(\frac{\partial P}{\partial T}\right) = \frac{S^\beta - S^\alpha}{V_m^\beta - V_m^\alpha} = \frac{\Delta S_m}{\Delta V_m} = \frac{\Delta H}{T_{eq} \Delta V_m}$$

Clausius - Clapeyron eq



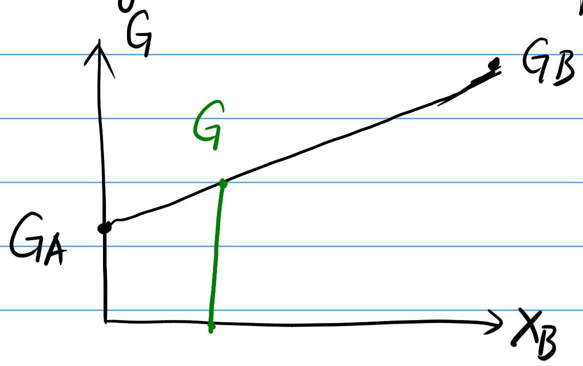
ΔH_r right > left

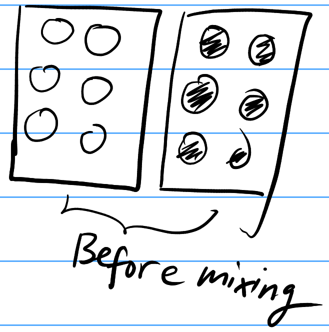
ΔV_m = molar volume change

1) $\Delta V_m < 0$ (liquid V_m < solid, water)

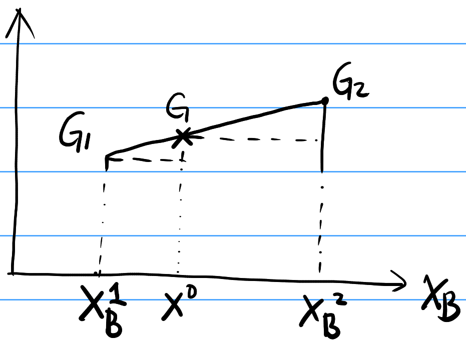
2) Increase p → lower T_m

Binary mixture solution phase diagram





Lever rule

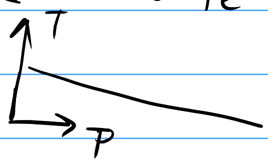


$$G^0 = f_1 G_1 + f_2 G_2 \ ; \ f_1 + f_2 = 1$$

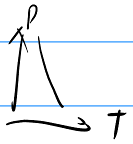
$$f_1 = \frac{X_B^2 - X_B^0}{X_B^2 - X_B^1} \qquad f_2 = \frac{X_B^0 - X_B^1}{X_B^2 - X_B^1}$$

$$(G^0 - G_1) \cdot (X^0 - X_B^1) = (G^2 - G^1)(X_B^2 - X_B^1)$$

Iron allotrope : α-Fe $\longrightarrow$ γ Iron



$\Longleftrightarrow$

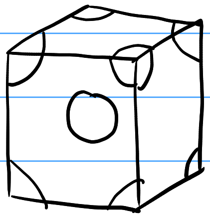


$\frac{\partial p}{\partial T} < 0$

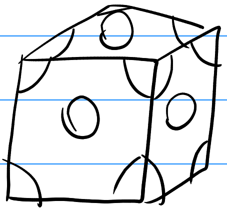
$V_m(\gamma\text{-Iron}) < V_m(\alpha\text{-Iron})$

α-Iron

BCC



γ-Iron



Volume filling BCC < FCC $\longrightarrow$ $V_m(\text{BCC}) > V_m(\text{FCC})$

Increasing p $\longrightarrow$ lower α/γ T_m

much $\longrightarrow$