* (eg) Carbon

→ graphite
→ diamond

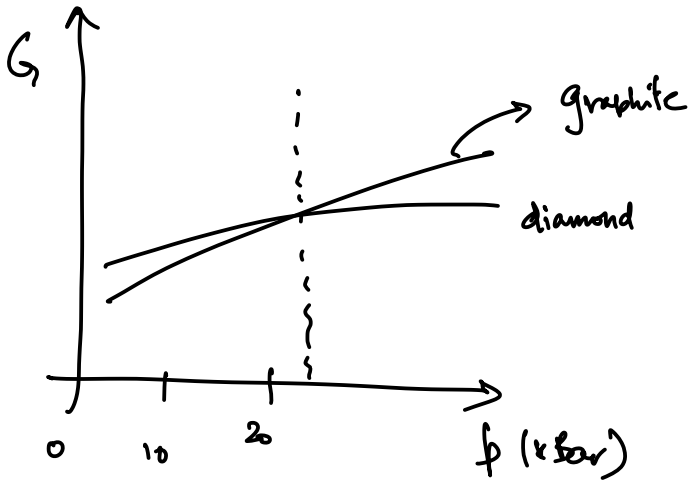
] distinguished by physical properties and crystal structure.

from experiment:

below $p \simeq 20$ kbar * graphite is most stable

* if diamond is present, it can potentially transform to graphite

above $p \sim 20$ kbar * diamond is more stable



$p_{atm} \sim 1$ bar

Recall: $dG = Vdp - SdT$

$$\Rightarrow \left(\frac{\partial G}{\partial p}\right)_T = V$$

$V \rightarrow$ +ve

define: $\Delta G = G^{graphite} - G^{diamond}$

crossing point of Gibbs free energy

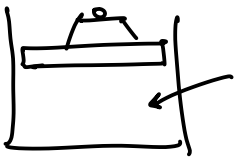
$\Rightarrow \Delta G = 0 \longrightarrow$ gives equilibrium transition pressure

$\Delta G < 0 \Rightarrow G^{graphite} < G^{diamond} \longrightarrow$ graphite stable

$\Delta G > 0 \Rightarrow G^{diamond} < G^{graphite} \longrightarrow$ diamond stable.

* Significance of ΔH: (at constant T & p)

- Consider a system at constant T & p transforming from a metastable state to a stable state



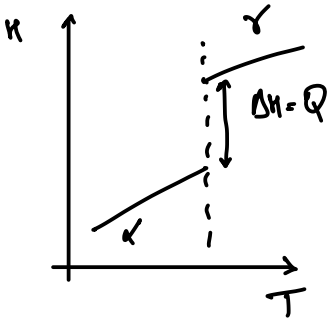
- change of state accompanied by a change in Volume (ΔV) [for example H_2O @ 0°C; $\bar{V}^{solid} > \bar{V}^{liquid}$]

$\Rightarrow$ environment performs $-p\Delta V$ work on the system

I Law: $\Delta U = Q - p\Delta V \Rightarrow \boxed{Q = \Delta U + p\Delta V = \Delta H}$

during the transformation latent heat is given off or absorbed due to a change in enthalpy

$$\Delta H = H^{\alpha} - H^{\gamma}$$



ASIDE: How do we determine $H^{\alpha}(T)$?

$$dH_p^{\alpha} = C_p^{\alpha}\, dT$$

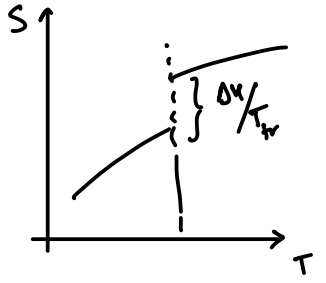
$$\Rightarrow \boxed{H^{\alpha}(T) - H^{\alpha}(T_0) = \int_{T_0}^{T} C_p^{\alpha}\, dT}$$

* Significance of ΔS:

at the transition temperature $\Delta G = 0$

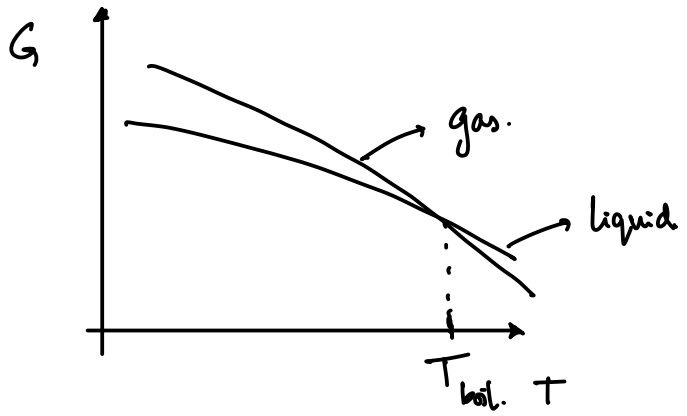
$$\Rightarrow \Delta H = T\Delta S$$

$$\textcircled{@} \quad \Delta S = S^{\alpha}(T = 912) - S^{\gamma}(T = 912) = \frac{H^{\alpha}(T_{tr} = 912) - H^{\gamma}(T_{tr} = 912)}{T_{transition}}$$



ONLY VALID AT THE TRANSITION TEMPERATURE

★ Estimating the Boiling Point of Water:



$G(T)$ is NOT a linear function of T

however, the free energy difference b/w two phases:

$$\Delta G(T) = G^{\alpha}(T) - G^{\beta}(T) \approx \text{linear.}$$

(eg) estimating T_{Boil} of water from data @ room temperature.

@ 293 K: $\Delta H_{l \to g} = 44.17\ kJ/mol.$

$\Delta S_{l \to g} = 119.5\ J/mol$

$$\Delta G(T) = G^{gas}(T) - G^{liq}(T) = \underbrace{\left[H^{gas} - H^{liq}\right]}_{\Delta H} - T\underbrace{\left[S^{gas} - S^{liq}\right]}_{\Delta S} = \Delta H(T) - T\Delta S(T)$$

@ the boiling point

$\Delta G(T) = 0$

Assume $\Delta H(T) \longrightarrow$ constant; $\Delta S(T) \longrightarrow$ constant.

$$T_{boil} = \frac{\Delta H(T_{boil})}{\Delta S(T_{boil})} \approx \frac{\Delta H^{l \to g}}{\Delta S^{l \to g}} = 370\ K$$

↑ off by ≈ 3c

★ Approximating ΔG:

$$\Delta H_{PT} = T_{PT}\,\Delta S_{PT}$$

↳ phase transition

$\Delta G = \Delta H - T\Delta S$

linearize ΔG

$$\boxed{\Delta G \approx \Delta H_{PT}\left(1 - \frac{T}{T_{PT}}\right)}$$ ← VERY USEFUL!!

* Physical meaning of the approximation:

$$\left(\frac{\partial(\Delta H)}{\partial T}\right)_p = 0 \quad \text{and} \quad \left(\frac{\partial(\Delta S)}{\partial T}\right)_p = 0$$

$$\Delta G_p = G_p^{\alpha} - G_p^{\beta} \cong 0$$

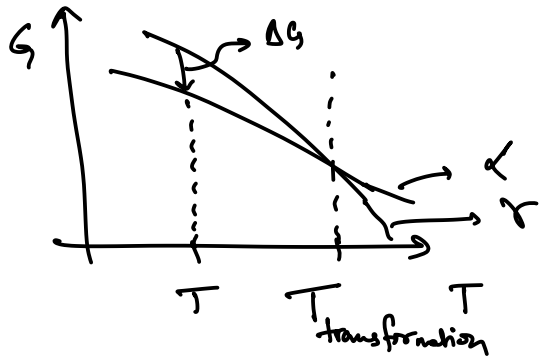
* NOTE: Real transformations rarely happen exactly at $T = T_{transformation}$

@ $T = T_{transformation}$

$\Delta G = 0$ (no driving force)

↳ equivalent to $\Delta S^{universe} = 0$

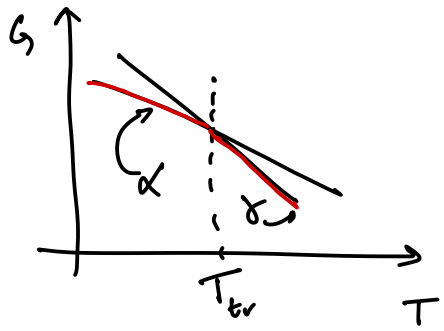
always need to undercool or overheat for a transformation.

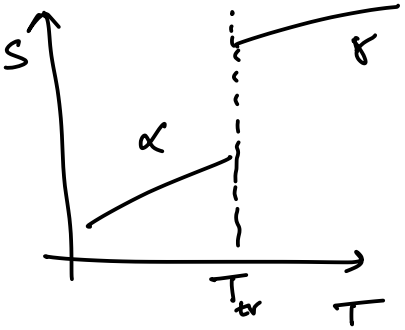


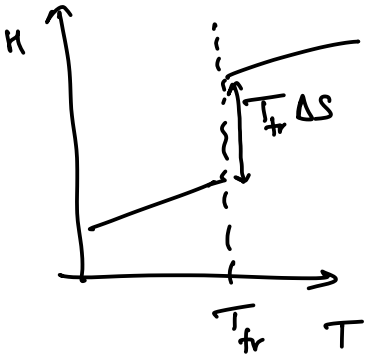
at $T < T_{transformation}$; $\Delta G < 0$

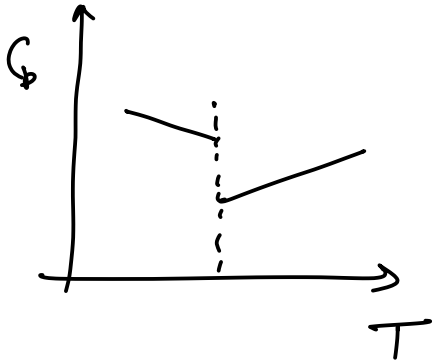
EHRENFEST CLASSIFICATION OF PHASE TRANSITIONS:

① 1st order phase transitions:

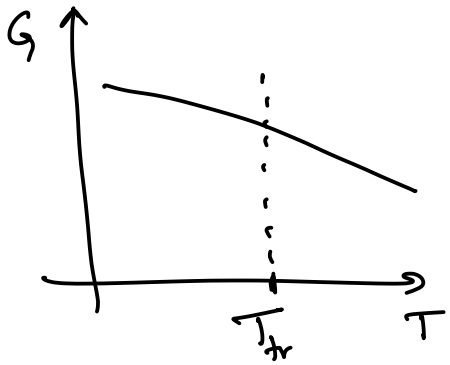


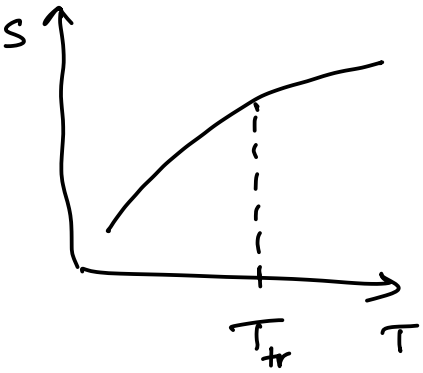


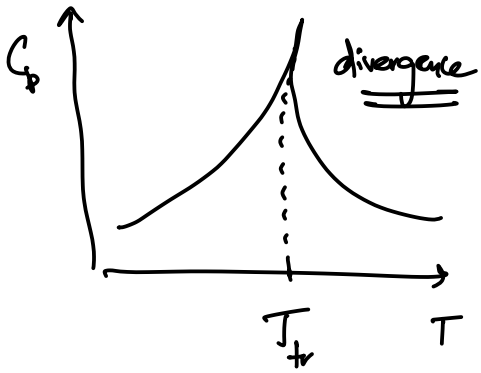




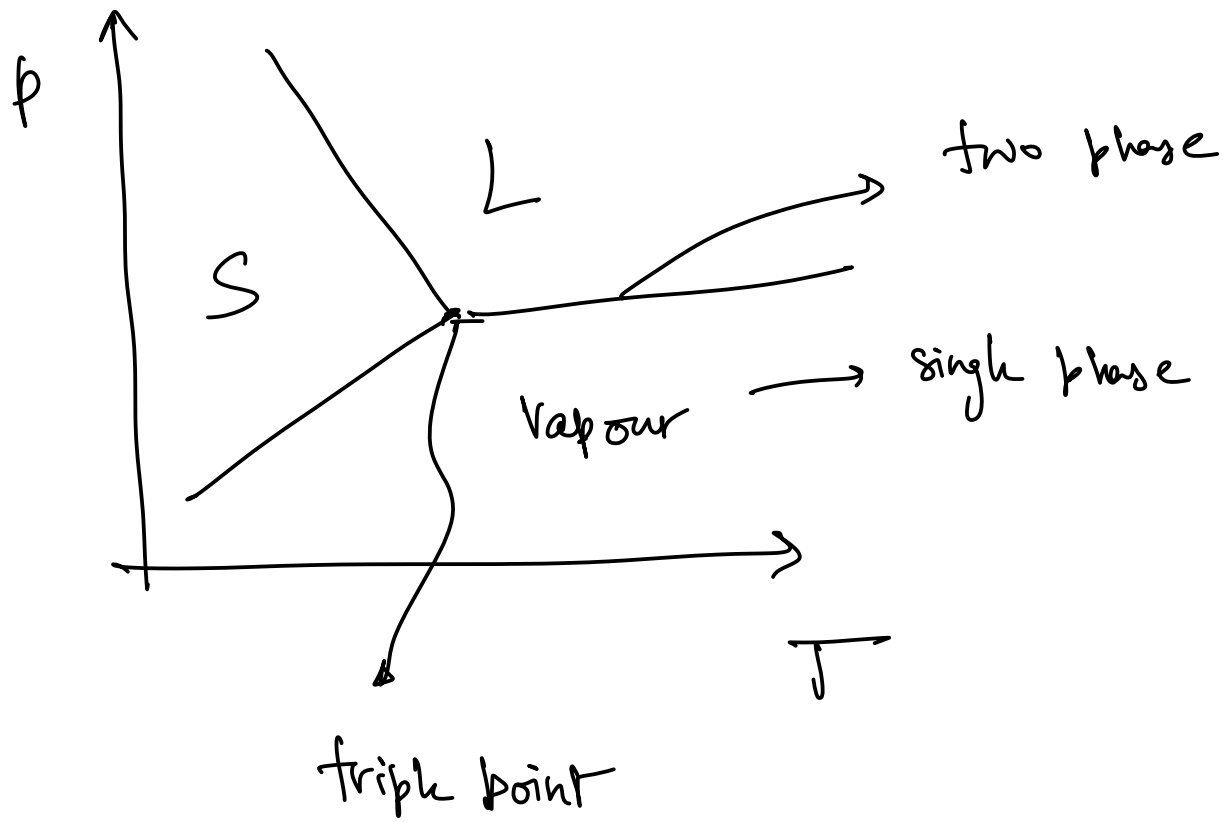
② 2nd order phase transition: 2nd derivative of G is discontinuous:

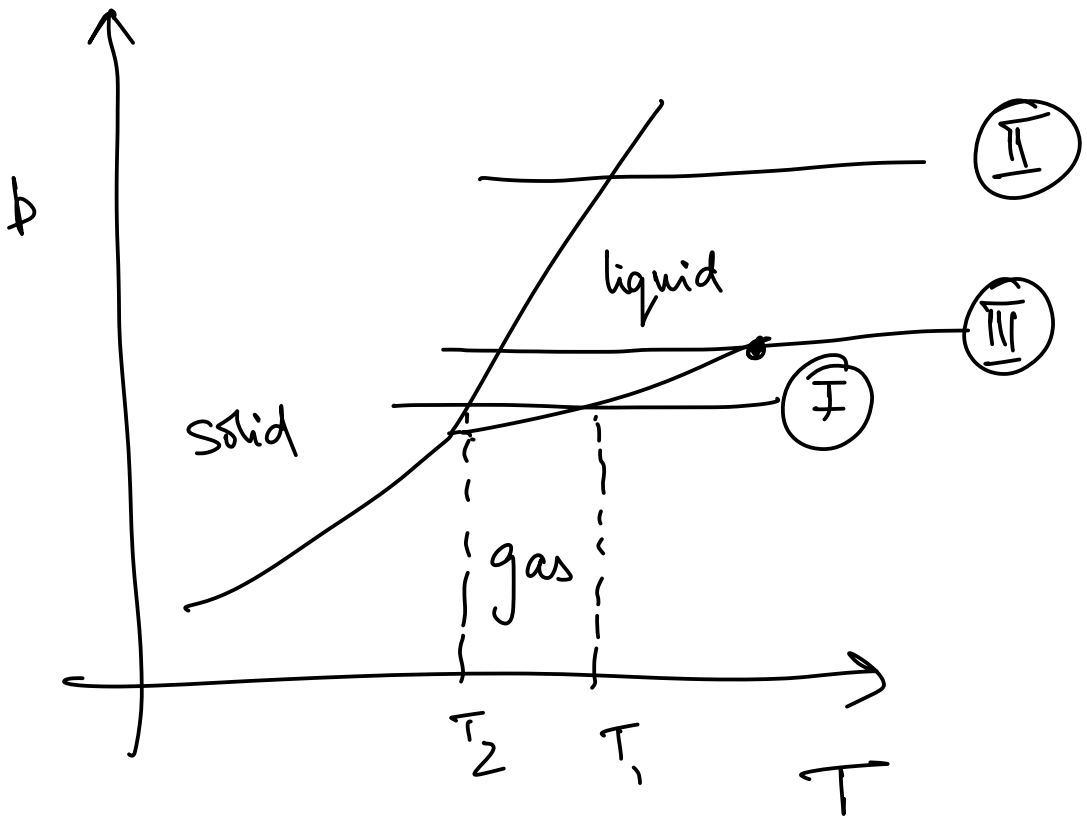




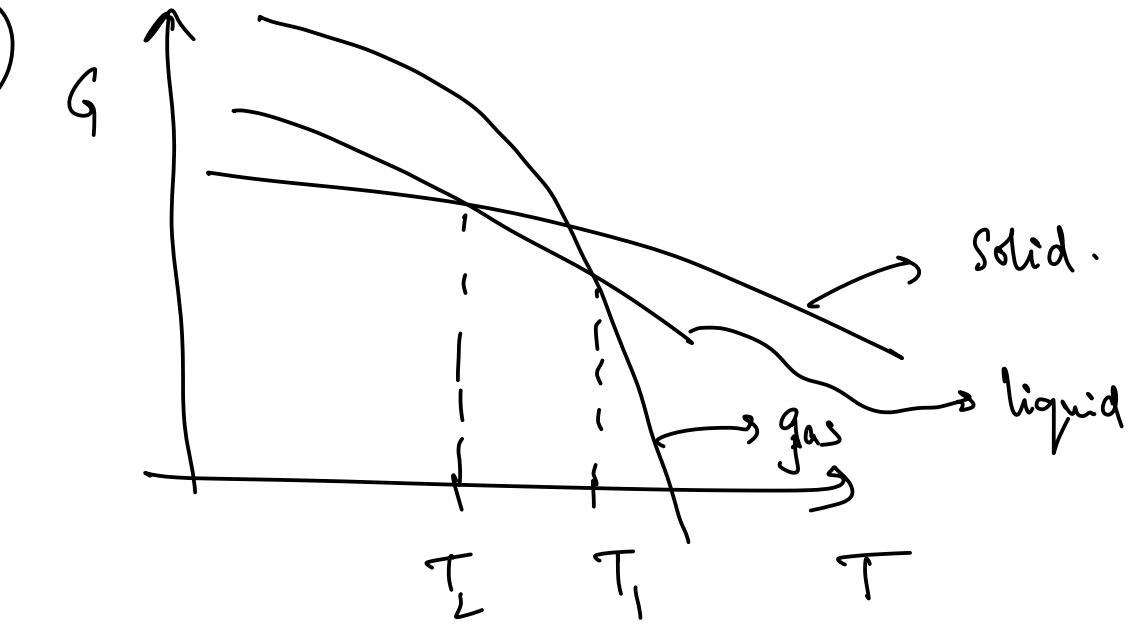


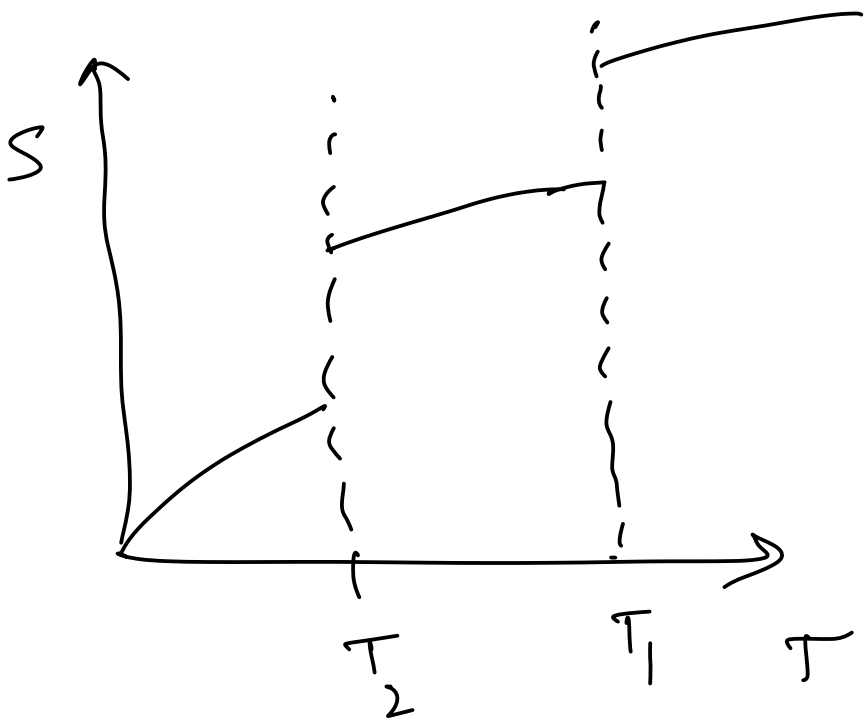
SINGLE COMPONENT PHASE DIAGRAM:

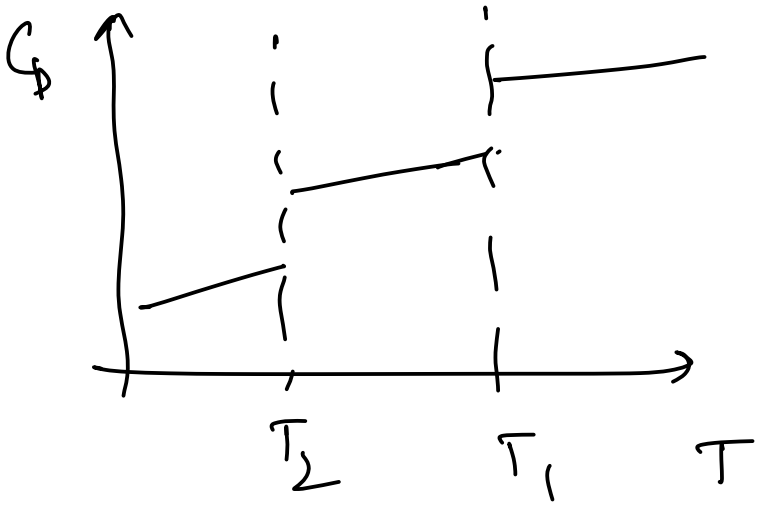




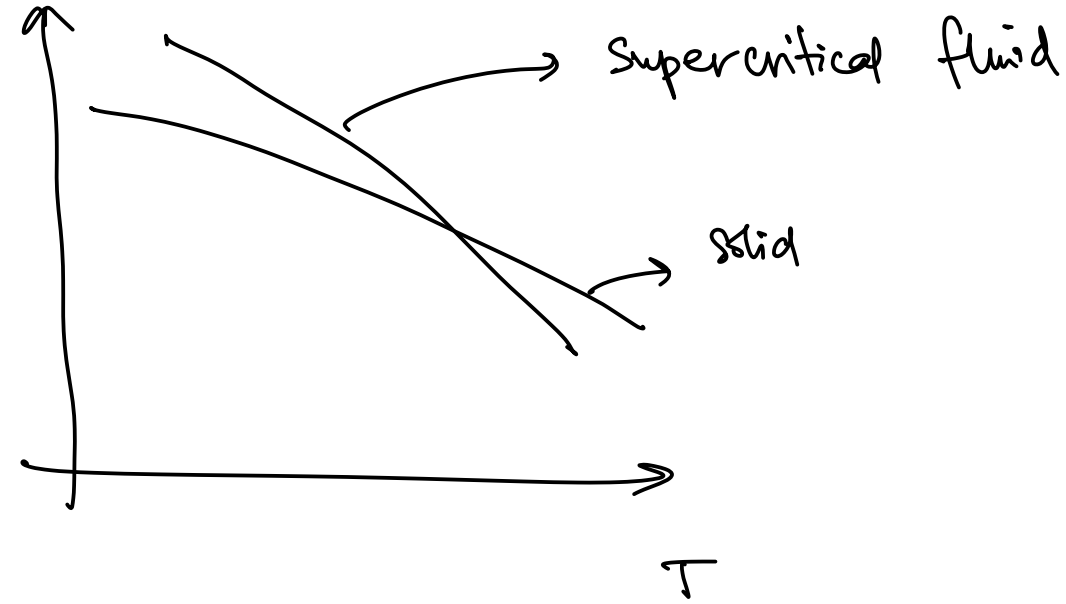
(I)

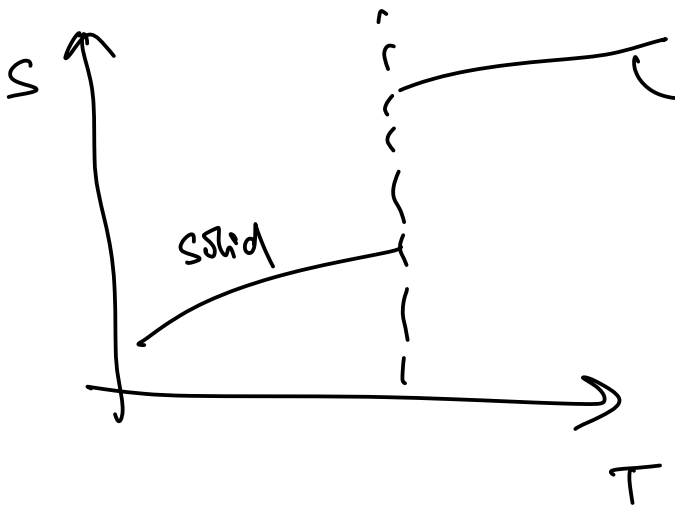


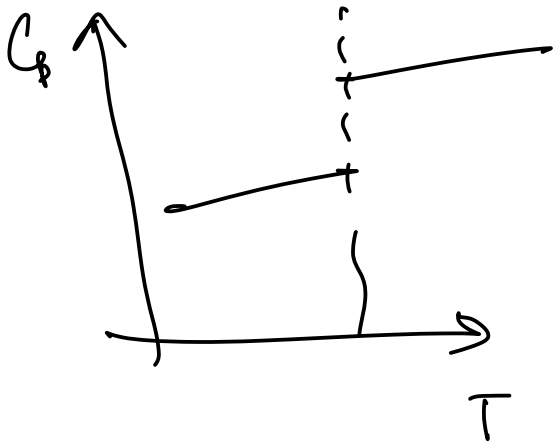




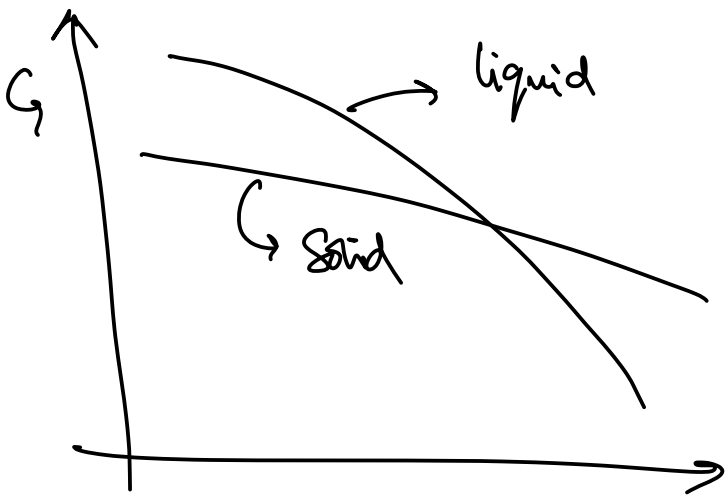
II

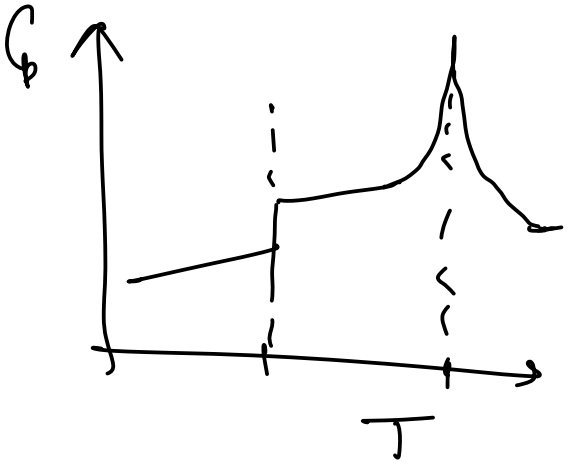


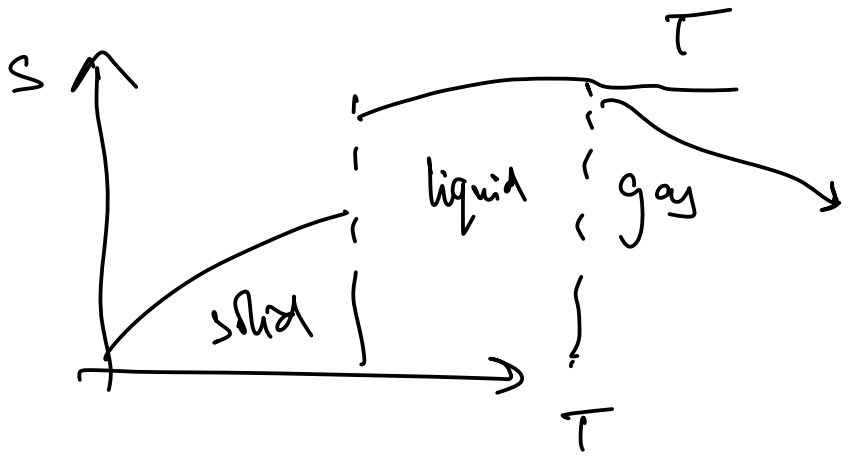




III







some kind of kink