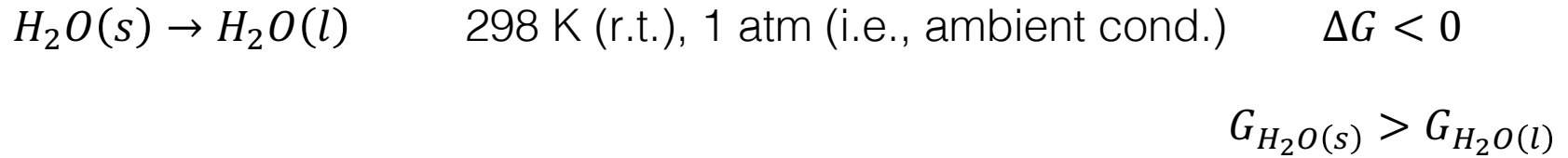


Phase transitions – an introduction (the Gibbs energy perspective)



Therefore, this (ice melts into liquid water) is a spontaneous process at ambient condition

- i.e., Gibbs energy decrease is a driving force for the phase transition of water
- With Legendre transformation, we know

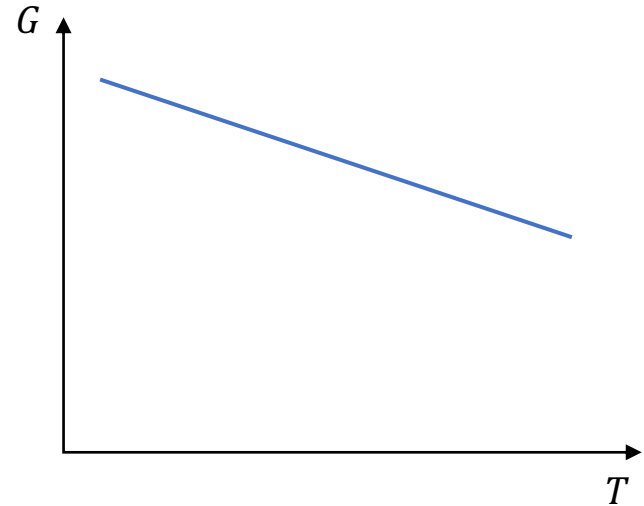
$$\left(\frac{\partial G}{\partial T}\right)_P = -S < 0 \quad \text{Meaning,} \quad (T \uparrow) \rightarrow (G \downarrow)$$

What's the indication of the above simple relation?

Phase transitions – an introduction (the Gibbs energy perspective)

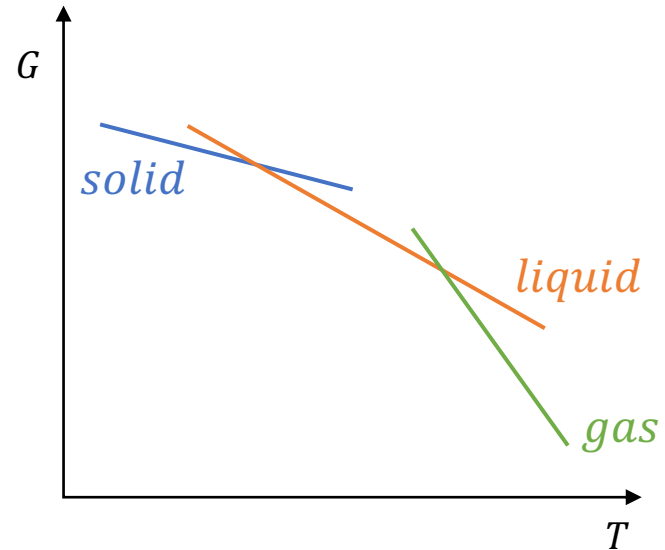
1) Because of $\left(\frac{\partial G}{\partial T}\right)_P = -S < 0$,
generally, we have

$$(T \uparrow) \rightarrow (G \downarrow)$$

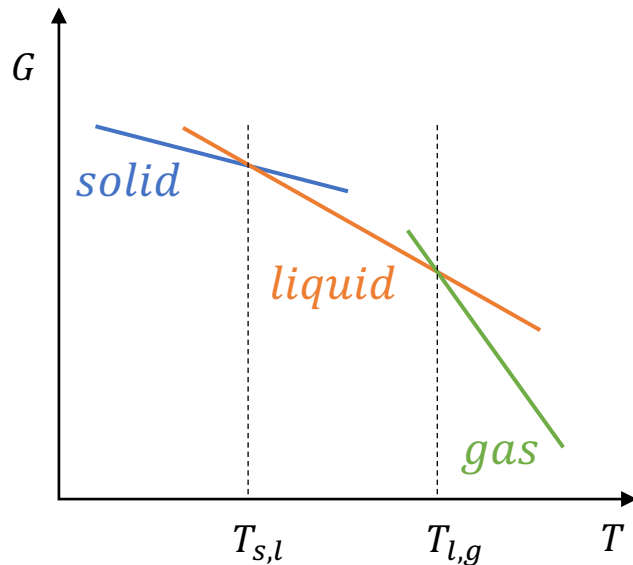


2) Generally, $S(s) < S(l) < S(g)$, we have

- i.e., the slope $\left(\frac{\partial G}{\partial T}\right)_P$ is becoming more and more negative (steeper) in going from *solid* \rightarrow *liqui* $<$ *gas*
- i.e., it is guaranteed to have crossings amongst *solid*, *liqui*, and *gas*

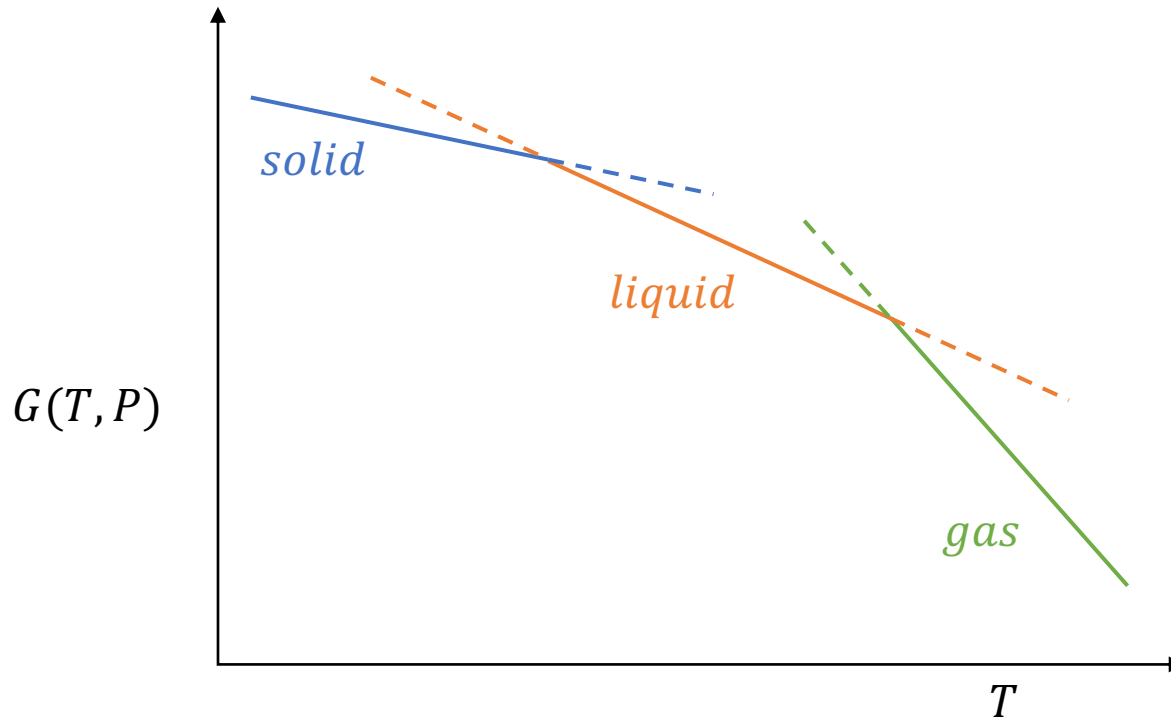


Phase transitions – an introduction (the Gibbs energy perspective)



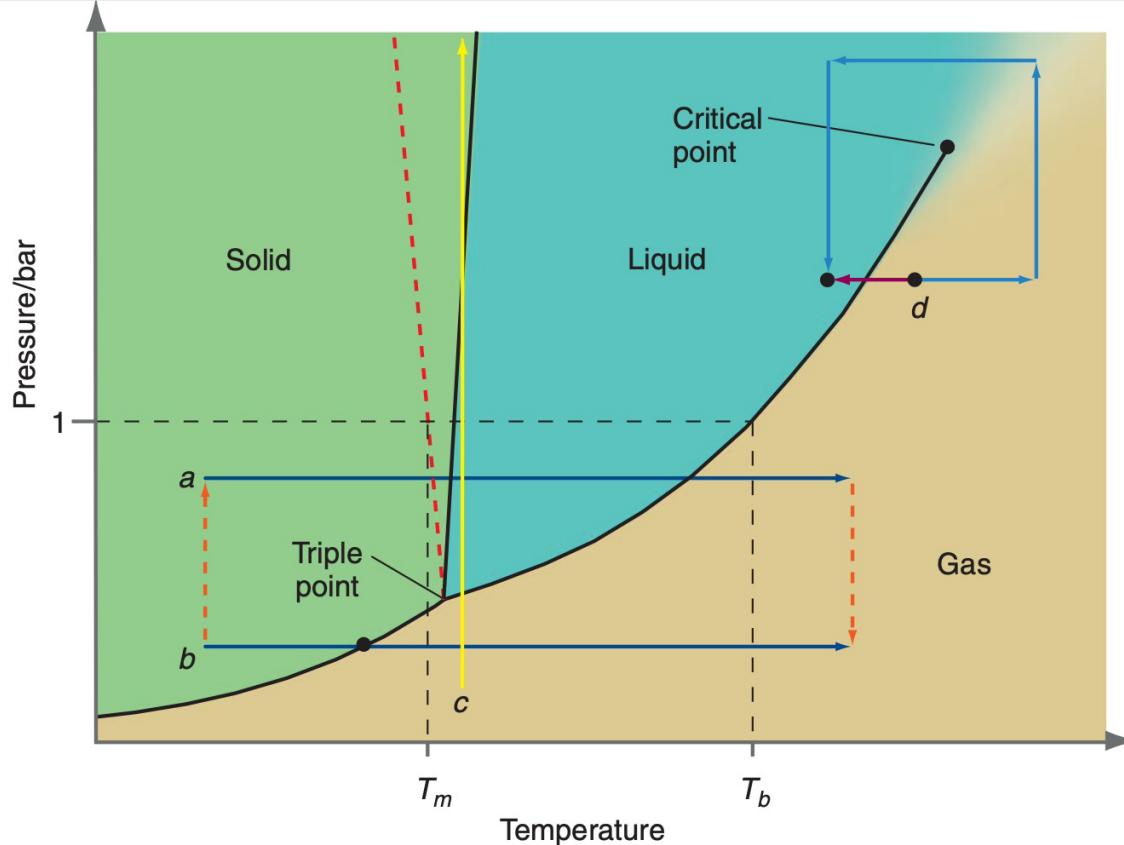
- 1) At $T_{s,l}$, $G_{solid} = G_{liquid}$, therefore $\Delta G = 0$,
 - 2) i.e., “equilibrium”, meaning solid-liquid coexist
 - 3) i.e., the so-called “melting point”, or more formally, “fusion temperature”
-
- 1) At $T_{l,g}$, $G_{liquid} = G_{gas}$, therefore $\Delta G = 0$,
 - 2) i.e., “equilibrium”, meaning liquid-gas coexist
 - 3) i.e., the so-called “boiling point”, or more formally, “vaporization temperature”

Phase transition – a close look



- Did we miss something?
- Gibbs energy is a Legendre transformed function of in terms of (T, P) , we only looked at T

Phase transition – typical phase diagram



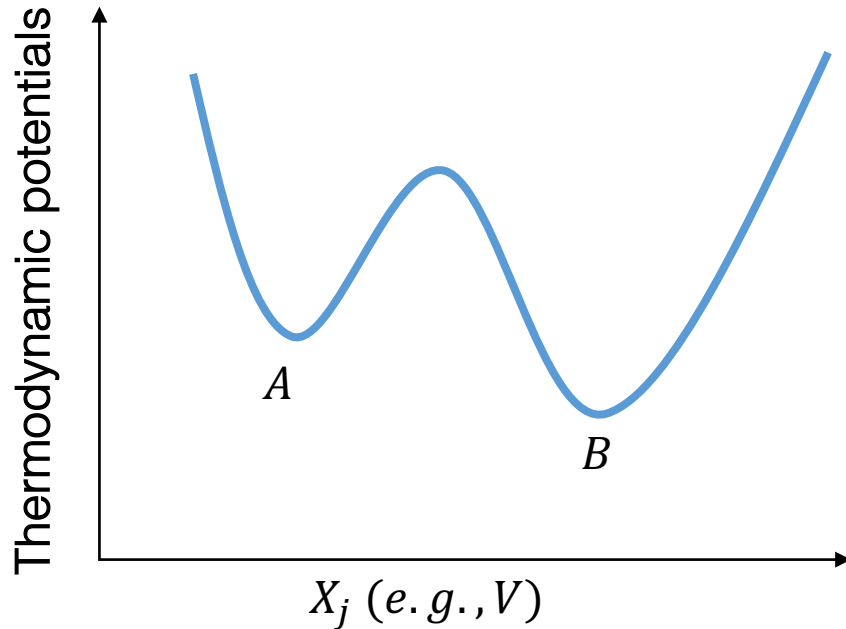
NOTE that, P in the diagram refers to external pressure

- **Coexistence curve:** where two phases coexist at equilibrium
- Typically, solid is more dense than liquid; thus, the slope of the coexistence curve of *solid – liquid* is positive
- *However, water is one of the a few substances that expands when solidified (interesting consequences, ocean ecosystem)*

Phase transition – a more detailed look

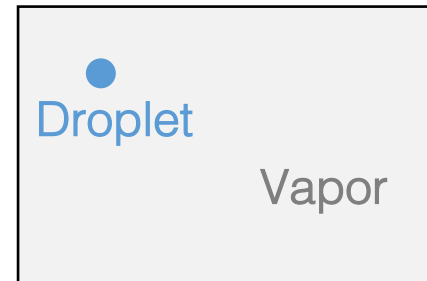
- We learned thermodynamic stability in the form of Legendre transforms

(i.e., thermodynamic potentials): $\frac{\partial^2 \Upsilon_\psi}{\partial X_j^2} \geq 0$



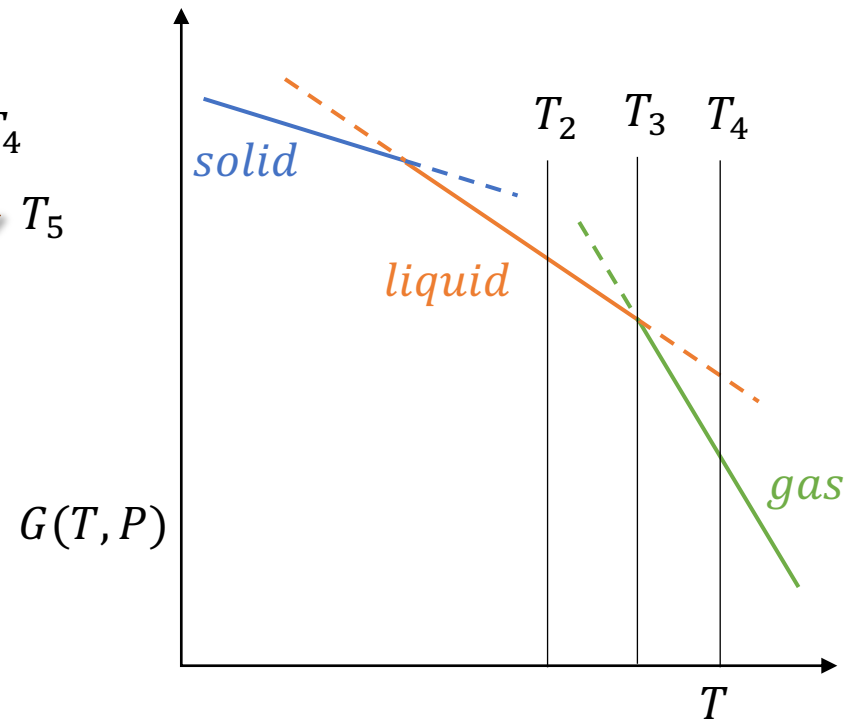
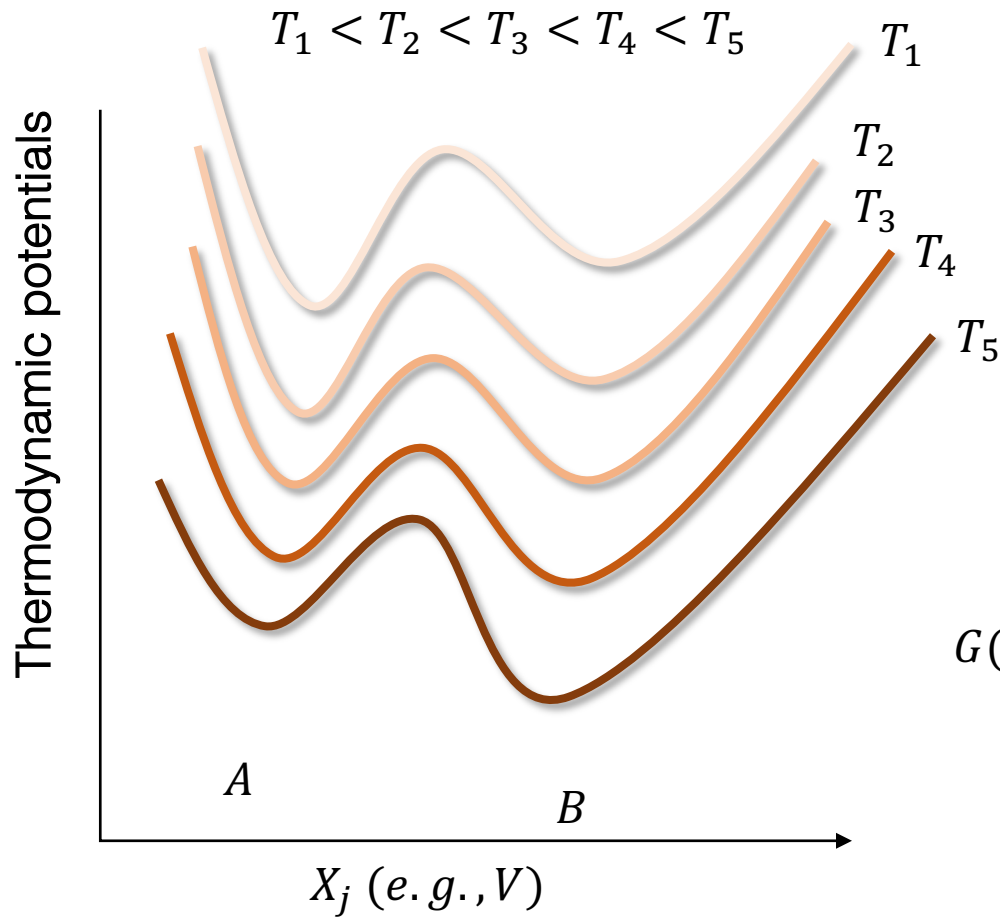
A: the liquid phase
B: the gas phase

- Imagine a space filled with water vapor (e.g., $P=1$ atm, $T > 373.15$ K)
- Transient overcome of the shallow barrier from B to A will allow the formation of droplets occasionally, live briefly, then evanesce.



- How could you reconcile this schematic with the $G(T, P) - T$ diagram?

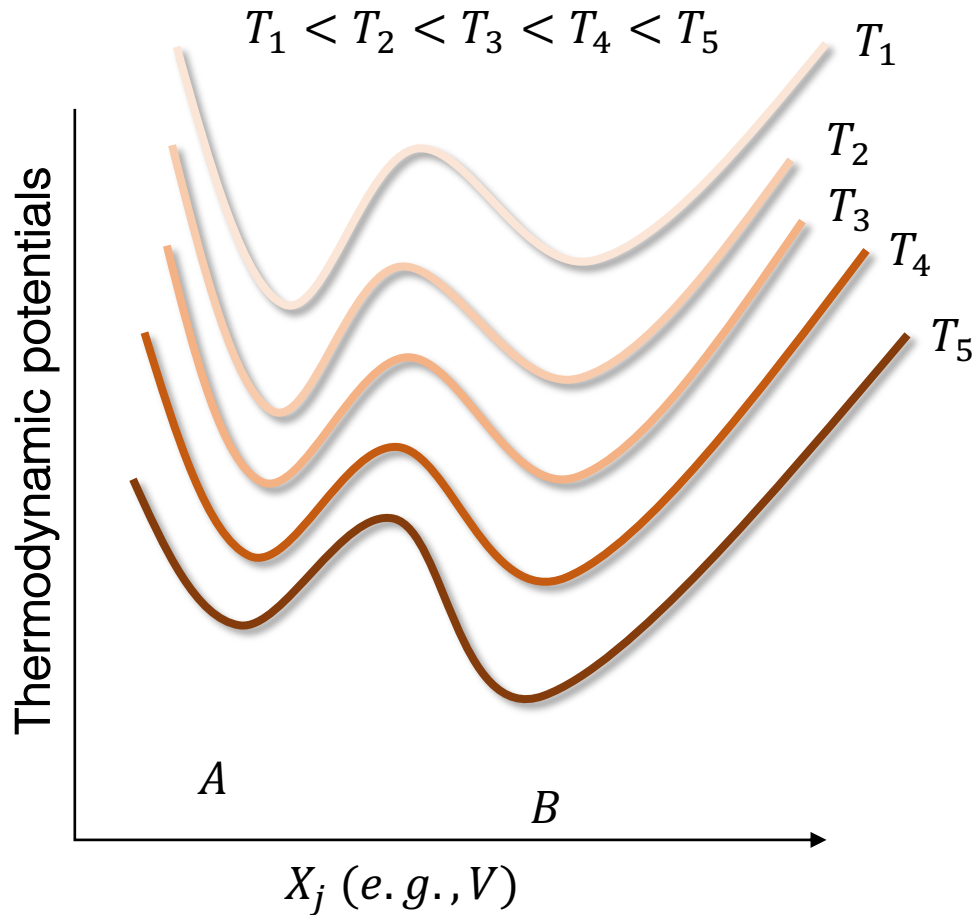
Phase transition – a more detailed look



A: the liquid phase

B: the gas phase

Phase transition – a more detailed look



- What is the change from T_1 (or T_5) to T_5 (or T_1) is very fast (faster than system relaxation time)?
- Superheated water, or supercooled liquid:
 - 1) Superheated/supercooled phase is globally unstable based on the stability requirement $\frac{\partial^2 Y_\psi}{\partial X_j^2} \geq 0$
 - 2) Barriers can be overcome (easily, sometimes) via fluctuations

Phase transition – a more detailed look

- Superheated water

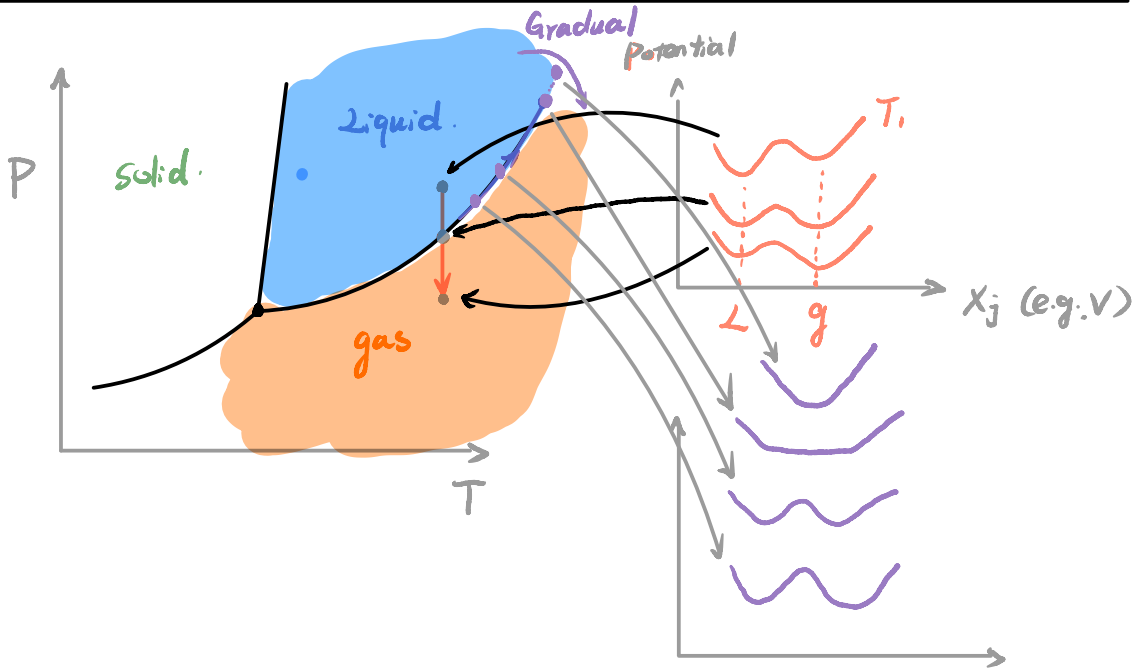


Phase transition – a more detailed look

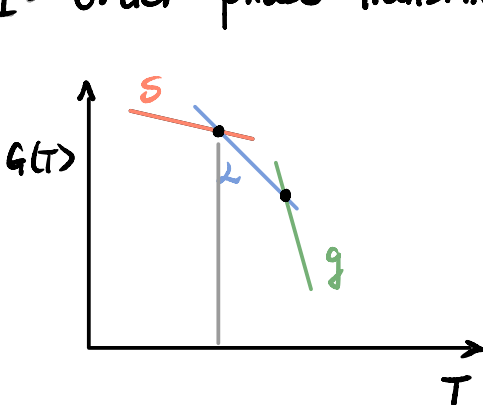
- Supercooled water



Obj. 11-12. 1st order phase transition and critical phenomena.



1st order phase transition



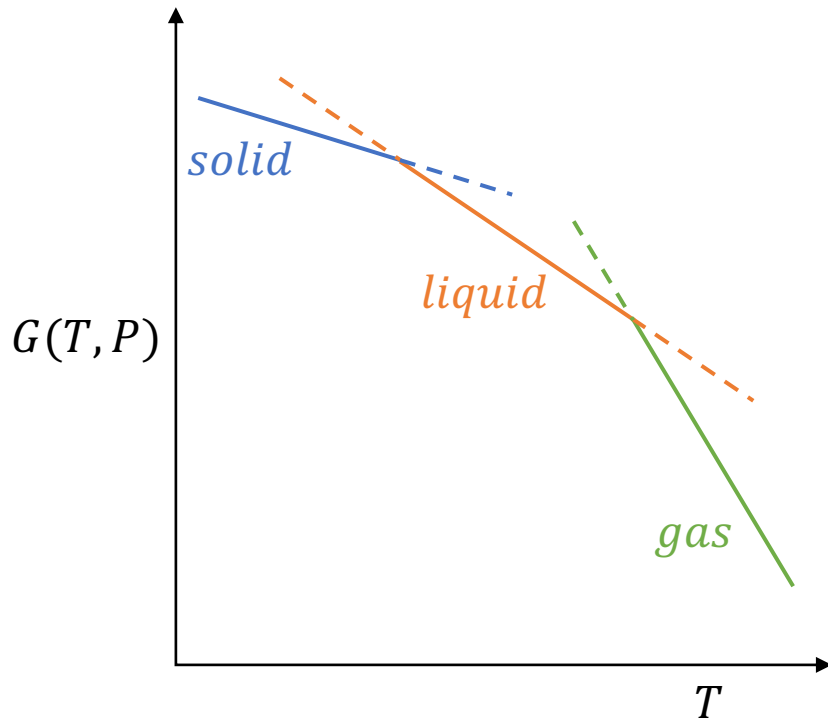
$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

↑
Entropy

Paul Ehrenfest:

The lowest order of derivative of G that shows a discontinuity upon crossing the coexistence

1st order phase transition – the Ehrenfest classification



- 1) These transitions are continuous in terms of the Gibbs energy change
- 2) HOWEVER, the sudden turning point at the equilibrium (coexistence) of two phases guarantees the slope is discontinuous

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

Paul Ehrenfest summarized that, *The order of the lowest derivative of the Gibbs energy showing a discontinuity upon crossing the coexistence curve is the order of a phase transition*

- *Could you imagine how a 2nd order phase transition may look like?*

curve defines the order of a phase transition.

*. Latent heat.

$$\rightarrow \Delta S$$

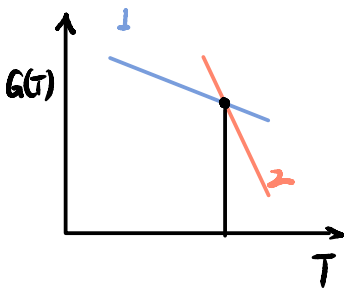
e.g. phase 1 \rightarrow phase 2
 S_1 S_2

$$\Delta S = [S_2 - S_1]$$

$$Q_L = T \Delta S$$

• Enthalpy. $Y_P = Y - \sum_i P_i X_i$

$$\left. \begin{aligned} H &\equiv U - (-P)V = U + PV \\ G &\equiv U - TS + PV \\ H &\equiv G + TS \end{aligned} \right\}$$



$$G_1 = G_2$$

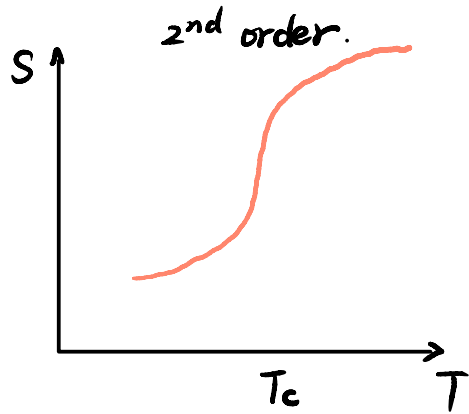
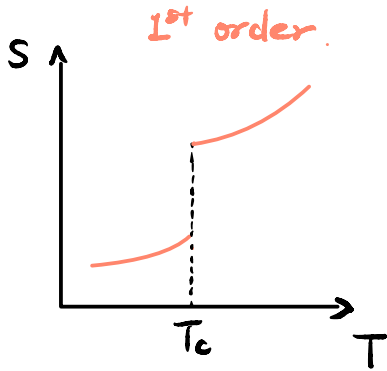
$$H_1 - H_2 = \Delta H$$

$$= \cancel{G_1} + TS_1 - (\cancel{G_2} + TS_2)$$

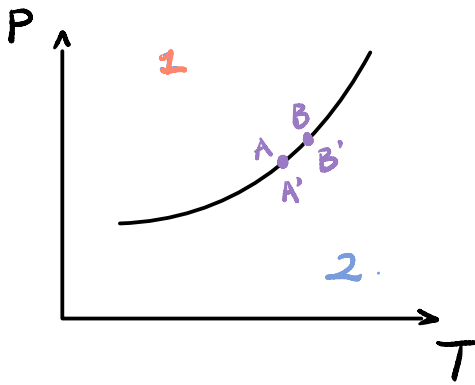
$$= T[S_1 - S_2]$$

$$= T \Delta S \equiv Q_L$$

*. Distinction of 1st vs 2nd order phase transitions



*. Clausius clapeyron Eq.



$$G_A = G_{A'}$$

$$G_B = G_{B'} \quad dG' = -S'dT + V'dP$$

$$\rightarrow G_A - G_B = G_{A'} - G_{B'}$$

$$dG = -SdT + VdP$$

$$\rightarrow -SdT + VdP = -S'dT + V'dP$$

$$\rightarrow \frac{dP}{dT} = \frac{S' - S}{V' - V} = \frac{dS}{dV} \rightarrow \frac{Q_L}{T}$$

since. $Q_L = T\Delta S \rightarrow$

$$\boxed{\frac{\Delta P}{\Delta T} = \frac{Q_L}{T\Delta V}} \quad *$$

Scenario:

Determine how much pressure is needed to melt ice at $T < 0^\circ\text{C}$ (e.g., $\Delta T = -6^\circ\text{C}$).

Knowing: $Q_L(\text{H}_2\text{O}) = 3.34 \times 10^5 \text{ J/kg}$, $\Delta V(\text{H}_2\text{O}^s - \text{H}_2\text{O}^l)$

$= -9.05 \times 10^{-5} \text{ m}^3/\text{kg}$, $T = 273 \text{ K}$

$$\Rightarrow \Delta P = \frac{Q_L}{T \Delta V} \Delta T = \frac{3.34 \times 10^5 \text{ J/kg} \times (-6 \text{ K})}{273 \text{ K} \times (-9.05 \times 10^{-5} \text{ m}^3/\text{kg})}$$

$$\Delta P = 8.1 \times 10^7 \text{ Pa} = 8.1 \times 10^3 \text{ kg} \cdot \text{m}^{-1} \cdot \text{s}^{-2}$$

Assuming Area $A = 1 \text{ cm}^2$, knowing

$$g = 9.8 \text{ m} \cdot \text{s}^{-2}$$

$$m = \frac{\Delta P \times A}{g} = \frac{8.1 \times 10^7 \text{ kg} \cdot \text{m}^{-1} \cdot \text{s}^{-2} \times 10^{-4} \text{ m}^2}{9.8 \text{ m} \cdot \text{s}^{-2}}$$

$$\approx 830 \text{ kg}$$

• Rhy. Rev. X 11.011025 (2021) of ice.

How T , P , and speed control the slipperiness