

SECOND DERIVATIVES OF CHARACTERISTIC POTENTIAL

— Related to "RESPONSE FUNCTION"

Response functions:

(eg) Control T, p experimentally

* fix p , change $T \rightarrow$ look at response of the system.

$$1. \delta Q \rightsquigarrow C_p = \left(\frac{\delta Q}{dT} \right)_p = T \left(\frac{\partial S}{\partial T} \right)_p \quad [\text{II Law}]$$

$$2. \Delta V \rightsquigarrow \beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p$$

* fix T , change $p \rightarrow$ look at response

$$1. \Delta V \rightsquigarrow \bar{K} = \frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T$$

In general: response function $\rightsquigarrow \frac{\partial(\text{freely varying state variable})}{\partial(\text{expt. controlled state variable})}$

$$\text{Usually } \rightsquigarrow \frac{\partial(\text{extensive})}{\partial(\text{intensive})}$$

* Coming back to char. potentials:

(example) constant $T, p \rightsquigarrow$ char. potential $G(T, p)$

$$G = U - TS + pV$$

$$dG = -SdT + Vdp$$

* EOS:

$$S = - \left(\frac{\partial G}{\partial T} \right)_p \quad V = \left(\frac{\partial G}{\partial p} \right)_T$$

S, V are allowed to freely vary in experiment

* second derivatives of G (Hessian):

$$\left(\frac{\partial^2 G}{\partial T^2} \right) = \frac{\partial}{\partial T} \left(\frac{\partial G}{\partial T} \right) = - \left(\frac{\partial S}{\partial T} \right)_p = - \frac{1}{T} T \left(\frac{\partial S}{\partial T} \right)_p = - \frac{C_p}{T}$$

$$\left(\frac{\partial^2 G}{\partial p^2} \right) = -V\bar{K}$$

$$\frac{\partial^2 G}{\partial T \partial p} = \frac{\partial^2 G}{\partial p \partial T} = \left(\frac{\partial V}{\partial T} \right)_p = - \left(\frac{\partial S}{\partial p} \right)_T = V\beta$$

↑
Maxwell's relation.

$$\text{Hessian: } \begin{bmatrix} \frac{\partial^2 G}{\partial T^2} & \frac{\partial^2 G}{\partial T \partial p} \\ \frac{\partial^2 G}{\partial T \partial p} & \frac{\partial^2 G}{\partial p^2} \end{bmatrix} = \begin{bmatrix} -\left(\frac{C_p}{T}\right) & V\beta \\ V\beta & -V\bar{\kappa} \end{bmatrix}$$

(eg) control $T, V \longrightarrow F = U - TS = F(T, V)$

$$dF = -SdT - pdV$$

* EOS: $\left(\frac{\partial F}{\partial T}\right)_V = -S \quad \left(\frac{\partial F}{\partial V}\right)_T = -p$

* second derivative: $\begin{bmatrix} \frac{\partial^2 F}{\partial T^2} & \frac{\partial^2 F}{\partial T \partial V} \\ \frac{\partial^2 F}{\partial T \partial V} & \frac{\partial^2 F}{\partial V^2} \end{bmatrix} = \begin{bmatrix} -C_p/T & -p/\bar{\kappa} \\ -p/\bar{\kappa} & \frac{1}{V\bar{\kappa}} \end{bmatrix}$

EQUILIBRIUM (CRITERIA:

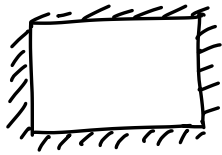
Second Law of Thermodynamics

$$dS \geq \frac{\delta Q}{T}$$

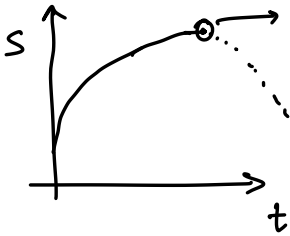
Consider an isolated system:

Consider an isolated system \rightarrow all extensive variables are constant

(eg) Volume can't change \Rightarrow no p-V work



II law: $dS \geq 0$



STOP equilibrium \rightarrow cannot evolve since entropy would decrease

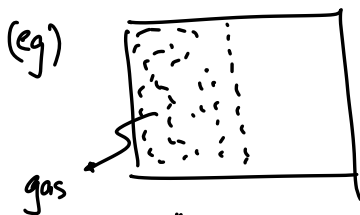
$$dS = \frac{du}{T} + \frac{p}{T} dV$$

$u \rightarrow$ constant

$V \rightarrow$ constant

what are we maximizing over?

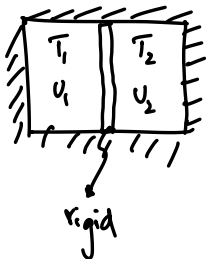
FIND EQUILIBRIUM STATE BY MAXIMIZING S OVER SOME INTERNAL EXTENSIVE VARIABLES



"internal" degree of freedom \rightarrow volume of the gas

$S \rightarrow$ maximized when gas fills the whole volume.

① THERMAL EQUILIBRIUM:



$U = U_1 + U_2 = \text{constant}$ since no work or heat exchange with the environment

$$dU_1 = dU_2 = 0$$

Let U_1 be the independent internal extensive variable

$$dU_1 = T dS_1 - p dV_1 \stackrel{0}{\rightarrow}$$

$$\boxed{dU_1 = T_1 dS_1}$$

$$dU = 0$$

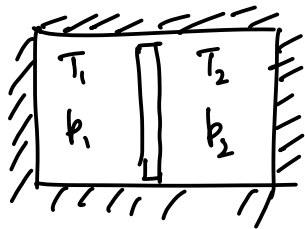
$$\Rightarrow dU_1 = -dU_2$$

$$S = S_1 + S_2 \Rightarrow dS = dS_1 + dS_2 = \frac{dU_1}{T_1} + \frac{dU_2}{T_2} = dU_1 \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$S(U_1) \rightarrow \boxed{\frac{dS}{dU_1} = \frac{1}{T_1} - \frac{1}{T_2}}$$

$$\text{only if } T_1 = T_2 \Rightarrow \boxed{dS = 0} \rightarrow \text{ENTROPY MAXIMIZED}$$

② THERMAL & MECHANICAL ^{AND THERMAL} EQUILIBRIUM:



$$\begin{aligned} U &= \text{constant} \\ &= U_1 + U_2 \\ dU = 0 &\Rightarrow dU_1 = -dU_2 \end{aligned}$$

$$V = \text{constant}$$

$$dV = 0 \Rightarrow dV_1 = -dV_2$$

fundamental equation:

$$dS_1 = \frac{dU_1}{T_1} + \frac{k_1}{T_1} dV_1 \quad \& \quad dS_2 = \frac{dU_2}{T_2} + \frac{k_2}{T_2} dV_2$$

2 independent internal extensive variables:

$$U_1 \quad \& \quad V_1$$

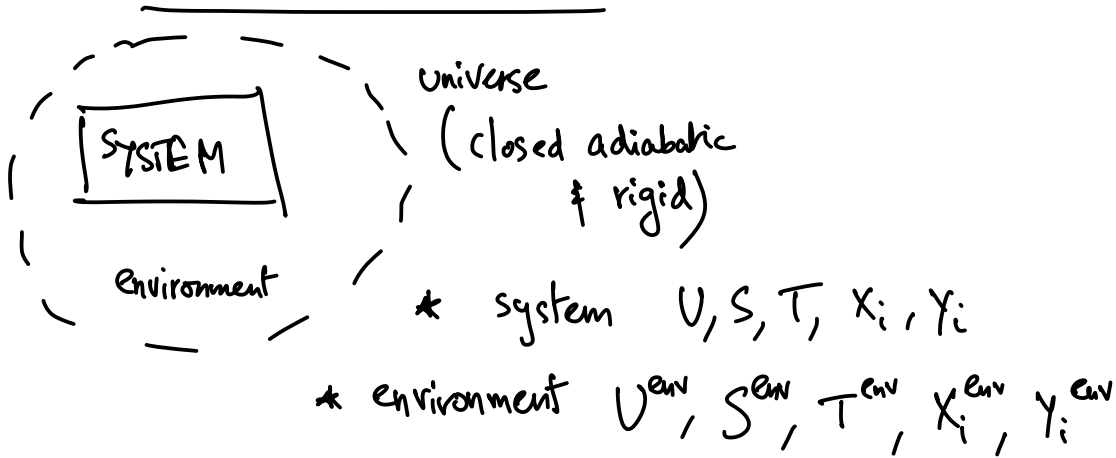
$$dS = \left(\frac{1}{T_1} - \frac{1}{T_2} \right) dU + \left(\frac{k_1}{T_1} - \frac{k_2}{T_2} \right) dV_1$$

$$dS = 0 \rightarrow \text{max entropy.}$$

$$\Rightarrow \left(\frac{\partial S}{\partial U} \right)_{V_1} = 0 \Rightarrow T_1 = T_2 \quad ; \quad \left(\frac{\partial S}{\partial V_1} \right)_{U_1} = 0 \Rightarrow k_1 = k_2$$

INTENSIVE VARIABLES CONJUGATE TO FREELY VARYING INTERNAL EXTENSIVE VARIABLES ARE EQUAL BETWEEN ALL SUBSYSTEMS

* GENERAL EQUILIBRIUM CRITERIA:



$$U^{env} + U = \text{constant}$$

$$X_i^{env} + X_i = \text{constant} \leftarrow \text{Conserved extensive variables}$$

initial state:

$$T = T^{env}$$

$$Y_i = Y_i^{env}$$

find eq^m state

$$T = T^{env}$$

$$Y_i = Y_i^{env}$$

Environment is large enough such that transformation in the system does not affect intensive variables.

CHANGE OF STATE OF THE SYSTEM

$$\Delta U, \Delta X_i, \Delta S, \dots$$

for the environment: (EULER)

$$\Delta U^{env} = T^{env} \Delta S^{env} + \sum_i Y_i^{env} \Delta X_i^{env}$$

$$\Delta U^{env} = -\Delta U$$

$$\Delta X^{env} = -\Delta X$$

$$\Rightarrow -\Delta U = T^{\text{env}} \Delta S - \sum_i Y_i^{\text{env}} \Delta X_i$$

$$\underline{\underline{\text{II Law}}} \quad \Delta S^{\text{env}} + \Delta S \geq 0$$

$$\Rightarrow \Delta S^{\text{env}} \geq -\Delta S$$

$$T^{\text{env}} \Delta S^{\text{env}} \geq -T^{\text{env}} \Delta S$$

$$-\Delta U + \sum_i Y_i^{\text{env}} \Delta X_i \geq -T^{\text{env}} \Delta S$$

$$\Rightarrow \boxed{0 \geq \Delta U - T^{\text{env}} \Delta S - \sum_i Y_i^{\text{env}} \Delta X_i}$$

- all freely varying extensive variables are system variables

- intensive variables are set by the environment

$$\Rightarrow \boxed{0 \geq \Delta U - T \Delta S - \sum_i Y_i \Delta X_i}$$

change of state can be irreversible
only end points need to be in eq^m

EQ^m UNDER DIFFERENT BOUNDARY CONDITIONS:

① fix all extensive variables

$$S_i, X_i = \text{constant}$$

$$\Rightarrow \Delta U \leq 0 \longrightarrow U \text{ has to be minimal}$$

U is the characteristic potential.

② fix T and all extensive mechanical variables

$$\Delta X_i = 0, \text{ since } X_i \text{ is fixed.}$$

$$\Delta U - T \Delta S \leq 0$$

$$\Delta F \leq 0 \longrightarrow \text{minimize the characteristic potential } F(T, v)$$

③ fix T & p:

$$\Delta U - T \Delta S + p \Delta V \leq 0$$

$$\boxed{\Delta G \leq 0} \longrightarrow \text{minimize the characteristic potential } G(T, p)$$

INGENERAL: Given boundary conditions $(Y_i, X_i) \rightarrow \text{minimize } \boxed{\Delta \Lambda = 0 - \sum_i Y_i X_i}$

PHASE TRANSITIONS & ONE COMPONENT SYSTEMS:

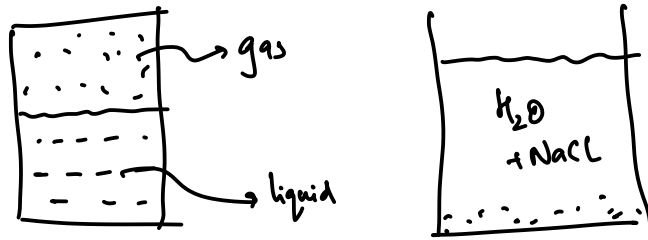
We will control $T, p \rightarrow$ look for states (phases) with lowest G

To find the lowest energy state we need to know how G changes with T, p .

$$\Rightarrow \boxed{dG = -SdT + Vdp}$$

* Reminder:

What is a phase?



Both containers have "distinct portions" with properties that are markedly different

(eg) ρ_{liquid} v/s $\rho_{\text{solid}} \rightarrow$ densities

each "distinct portion" \rightarrow PHASE

* The shape of the Gibbs free energies:

$$dG = Vdp - SdT$$

Curvature

$$\left(\frac{\partial G}{\partial p}\right)_T = V > 0$$

$$\left(\frac{\partial G}{\partial T}\right)_p = -S < 0$$

$$\left(\frac{\partial^2 G}{\partial T^2}\right)_p = -\left(\frac{\partial S}{\partial T}\right)_p$$

$$= -C_p/T < 0$$

$$\left(\frac{\partial^2 G}{\partial p^2}\right)_T = \left(\frac{\partial V}{\partial p}\right)_T = -V\bar{\kappa}$$

< 0

* The phases and phase diagram of water:

Water is commonly known to have 3 PHASES

- Solid
- Liquid
- Gas

Let $\alpha \rightarrow$ denote one of these phases of water

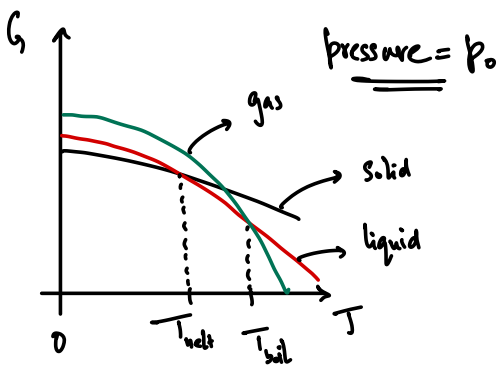
$$G^\alpha = U^\alpha - TS^\alpha + pV^\alpha \rightarrow \text{we control } T \text{ \& } p$$

$$\boxed{G^\alpha = H^\alpha - TS^\alpha}$$

Notice @ $T=0$

$$G^\alpha = H^\alpha$$

$$\text{Usually } \left[\begin{array}{l} S^{\text{gas}} > S^{\text{liquid}} > S^{\text{solid}} \\ H^{\text{gas}}(T=0) > H^{\text{liquid}}(T=0) > H^{\text{solid}}(T=0) \end{array} \right]$$



Recall for eq^m: $dG \leq 0$ @ G (the characteristic potential) is minimized

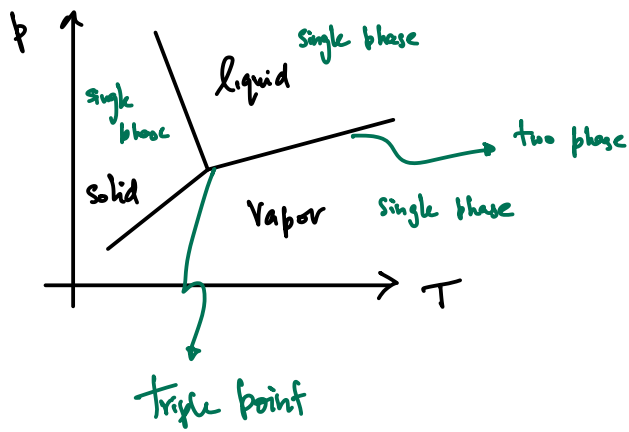
\Rightarrow At any given temperature the phase with the lowest Gibbs free energy is the eq^m phase

$$\left. \begin{array}{l} T < T_{\text{melt}} \rightarrow \text{solid} \\ T_{\text{melt}} < T < T_{\text{boil}} \rightarrow \text{liquid} \\ T_{\text{boil}} < T \rightarrow \text{gas} \end{array} \right\}$$

$$\text{At } T = T_{\text{melt}} \quad (G^{\text{solid}} = G^{\text{liquid}}) < G^{\text{gas}}$$

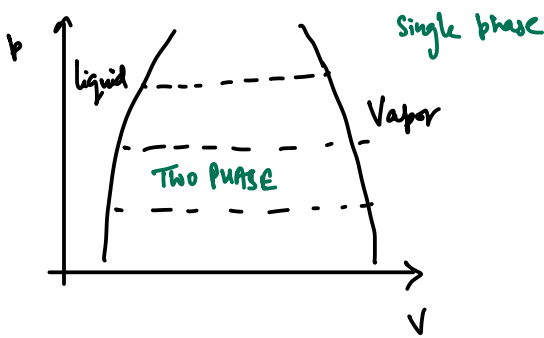
$$\text{At } T = T_{\text{boil}} \quad (G^{\text{liquid}} = G^{\text{gas}}) < G^{\text{solid}}$$

Repeat the exercise at many different pressures: \rightarrow collect T_{melt} , T_{boil} at each pressure



\rightarrow phase diagram of 2 intensive variables

p-V phase diagram of water:



\rightarrow phase diagram of an intensive v/s an extensive variable.

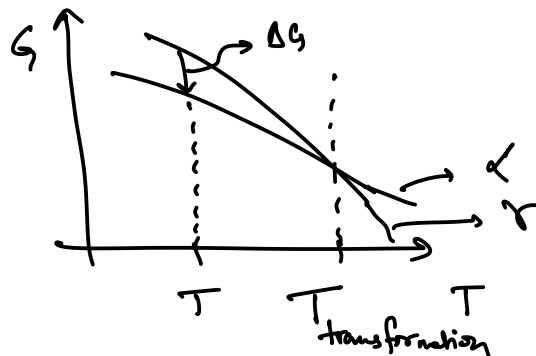
* NOTE: Real transformations rarely happen exactly at $T = T_{\text{transformation}}$

@ $T = T_{\text{transformation}}$

$$\Delta G = 0 \quad (\text{no driving force})$$

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

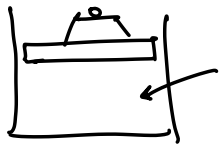
always need to undercool or overheat for a transformation.



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

* Significance of ΔH : (at constant $T \neq p$)

- Consider a system at constant $T \neq p$ transforming from a metastable state to a stable state



- change of state accompanied by a change in Volume (ΔV) [for example $H_2O @ 0^\circ C; \bar{V}^{solid} > \bar{V}^{liquid}$]
 \Rightarrow environment performs $-p\Delta V$ work on the system

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

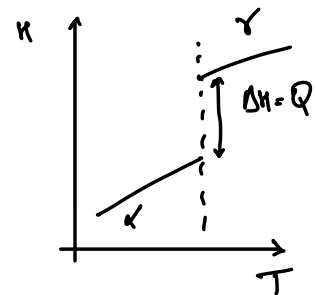
during the transformation latent heat is given off or absorbed due to a change in enthalpy

$$\Delta H = H^\alpha - H^\beta$$

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

$$dH_p^\alpha = C_p^\alpha dT$$

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

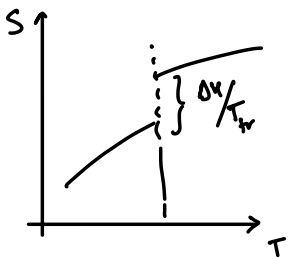


* Significance of ΔS :

at the transition temperature $\Delta G = 0$

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

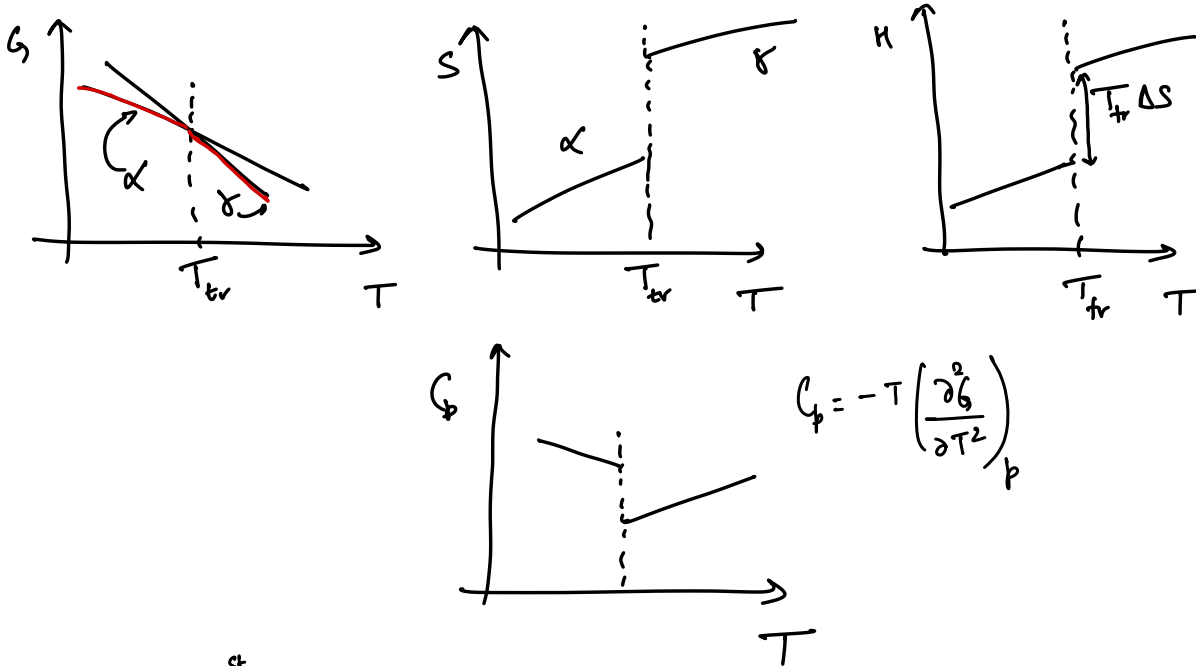
$$\textcircled{a} \Delta S = S^\alpha(T_{\text{transition}}) - S^\beta(T_{\text{transition}}) = \frac{H^\alpha(T_{\text{transition}}) - H^\beta(T_{\text{transition}})}{T_{\text{transition}}}$$



ONLY VALID AT
THE TRANSITION TEMPERATURE

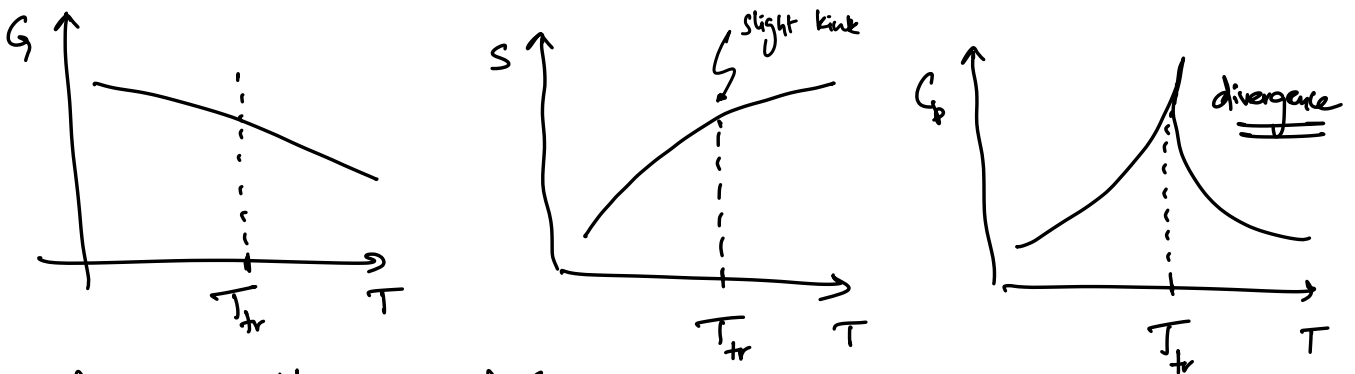
EHRENFEIST CLASSIFICATION OF PHASE TRANSITIONS:

① 1st order phase transitions:



KINETICALLY; 1st order phase transitions involve a **NUCLEATION AND GROWTH** mechanism
 - supercool, small nuclei form which then grow

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



original definition \rightarrow 2nd derivative of G is discontinuous.
 in reality \rightarrow response functions diverge

KINETICALLY: 2nd order phase transitions occur uniformly and continuously
 (NO NUCLEATION AND GROWTH)

Classical thermodynamics breaks down in the vicinity of a 2nd order phase transition. \rightarrow presence of large fluctuations.