
MLL 100

Introduction to Materials Science and Engineering

Lecture-15 (February 09, 2022)

Dr. Sangeeta Santra (ssantra@mse.iitd.ac.in)



IIT Delhi

Department of Materials Science and Engineering

What have we learnt in Lecture-14?

- ☐ Radius ratio rule (Pauling's rule) for ionic structure
- ☐ Pearlite

Phase transformation

Change in 'state'



Solid

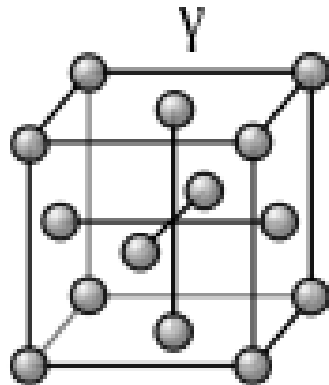
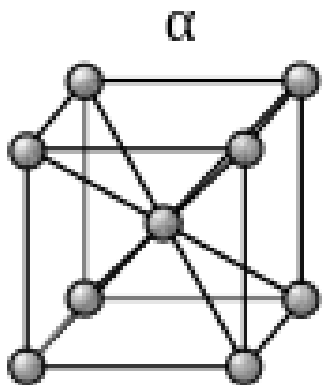


Liquid



Gas

Change in 'crystal structure'



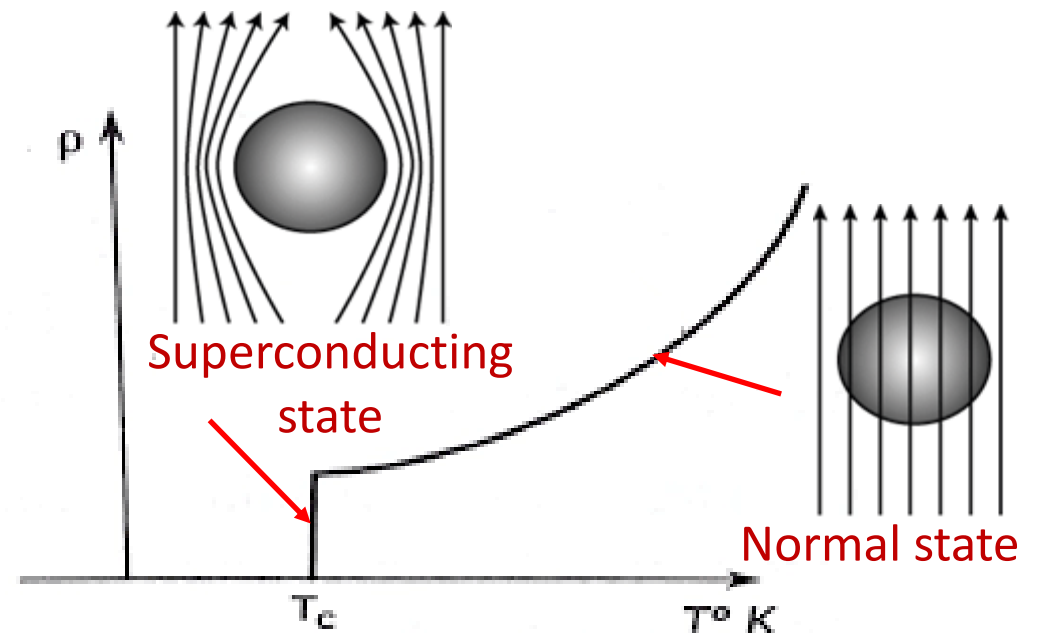
Change in 'Property'



Paramagnetic



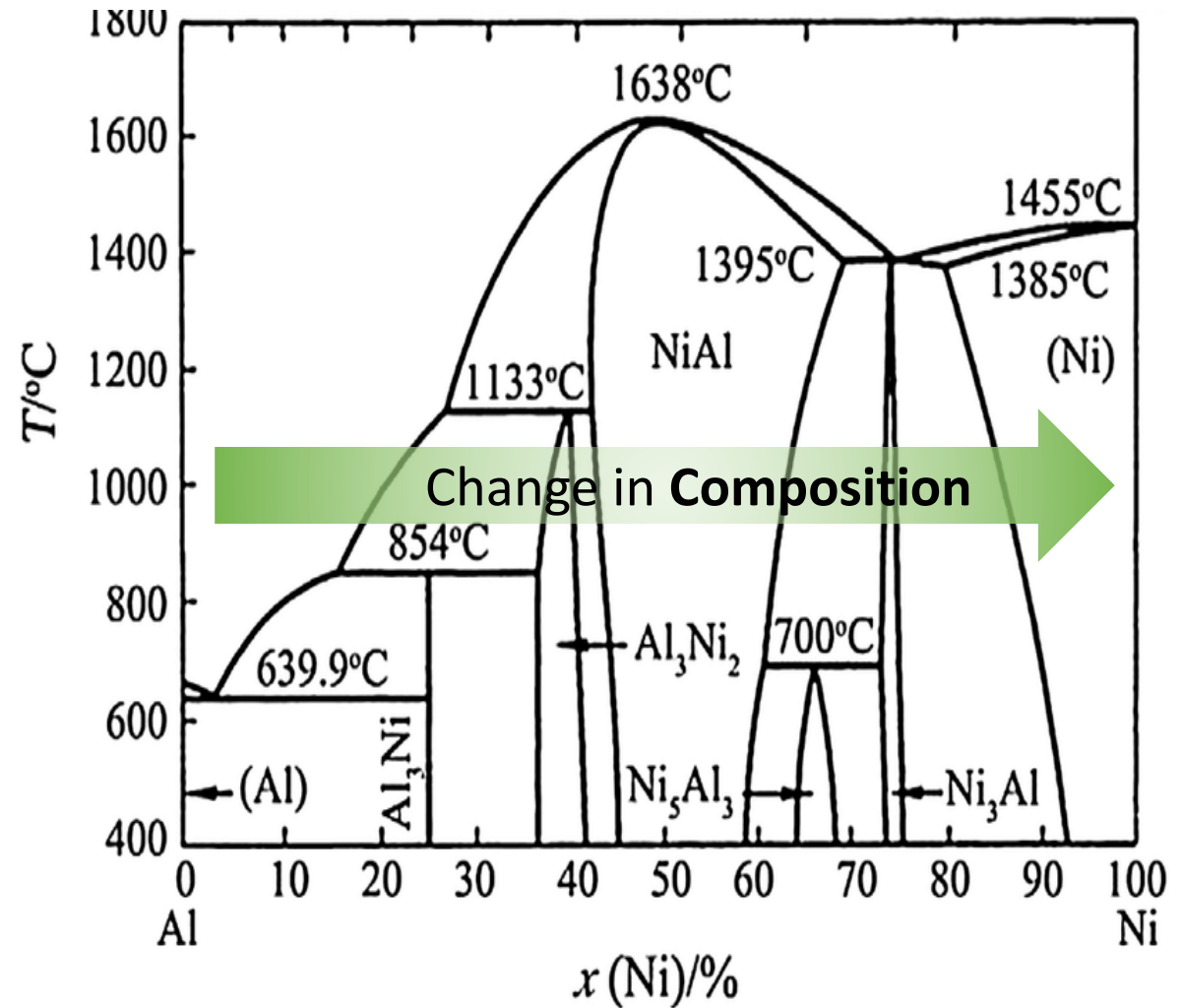
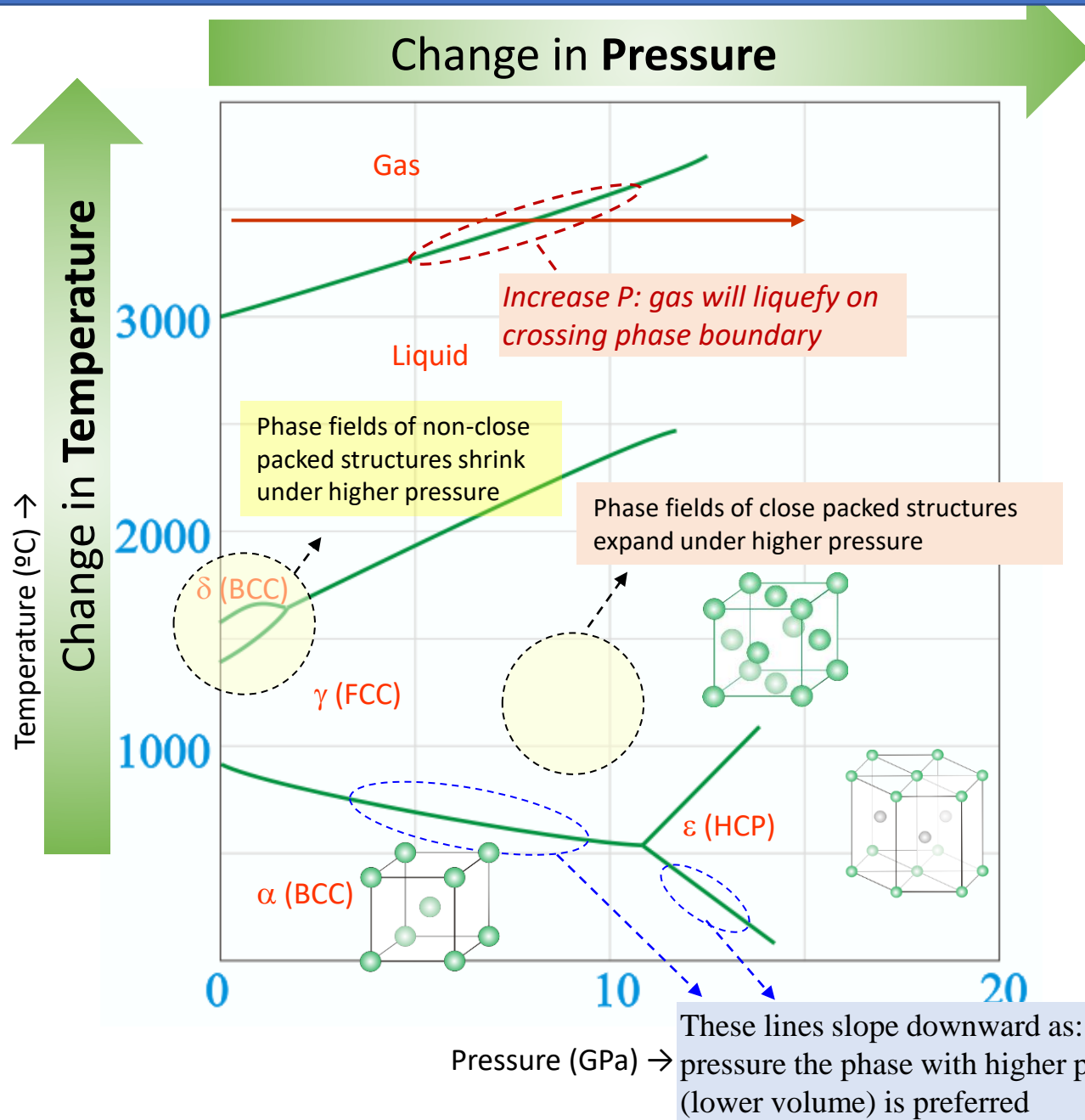
Ferromagnetic



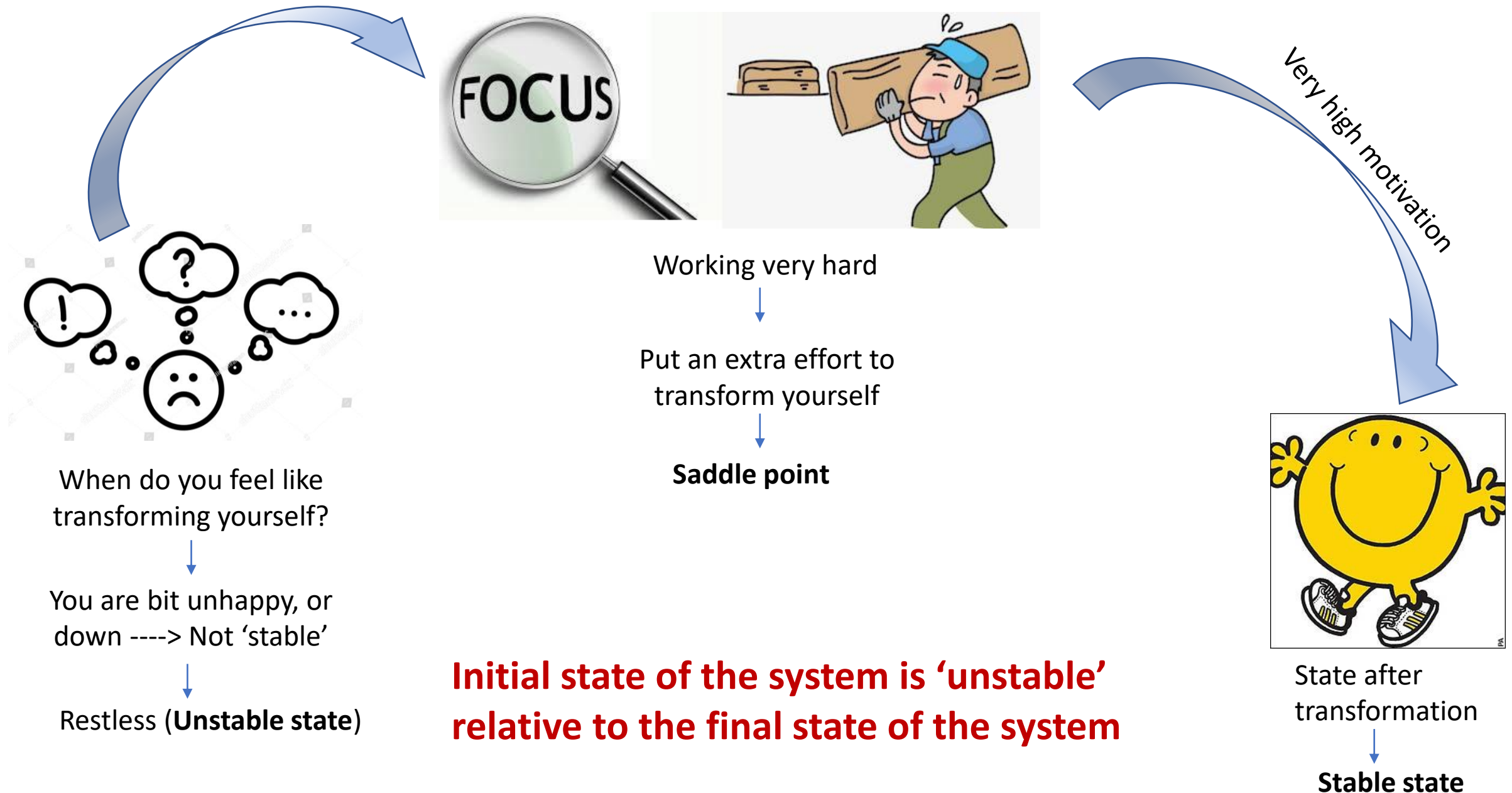
Transformation of one phase to another involving a change in chemical, structural, or physical properties caused by any external stimulus.

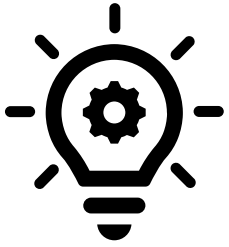
What could be those external stimuli?

Factors aiding phase transformation



Why does 'Phase transformation' occur?

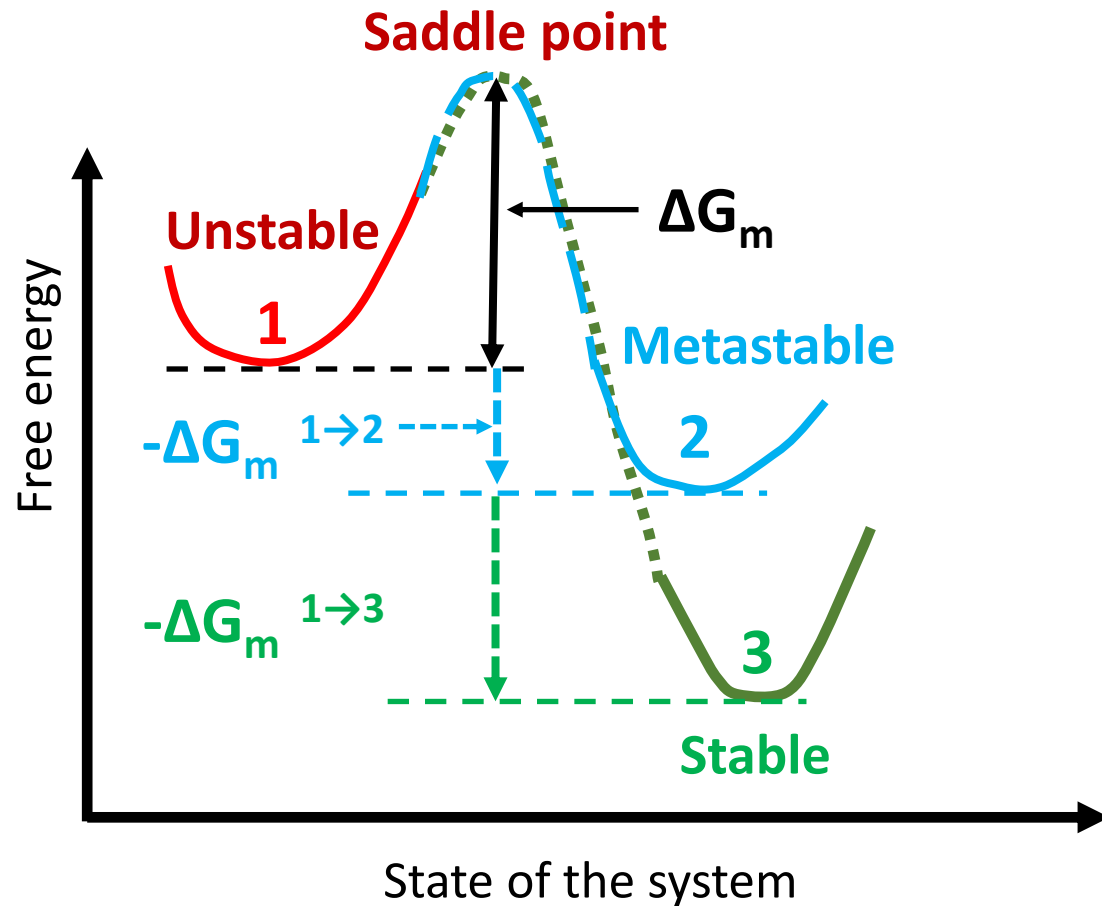




When will the phase be called in an 'unstable' state?

Is it necessary for a transformation to reach the stable state directly from an unstable state?

How is stability of a system measured?



- Thermodynamic control involves lowering of Gibbs free energy, $G = G_m(T, P, n)$

$$dG = -SdT + VdP + \sum_{i=1}^N \mu_i dN_i$$

$$\left(\frac{dG}{dN_i} \right)_{T,P} = \mu_i$$

Chemical potential

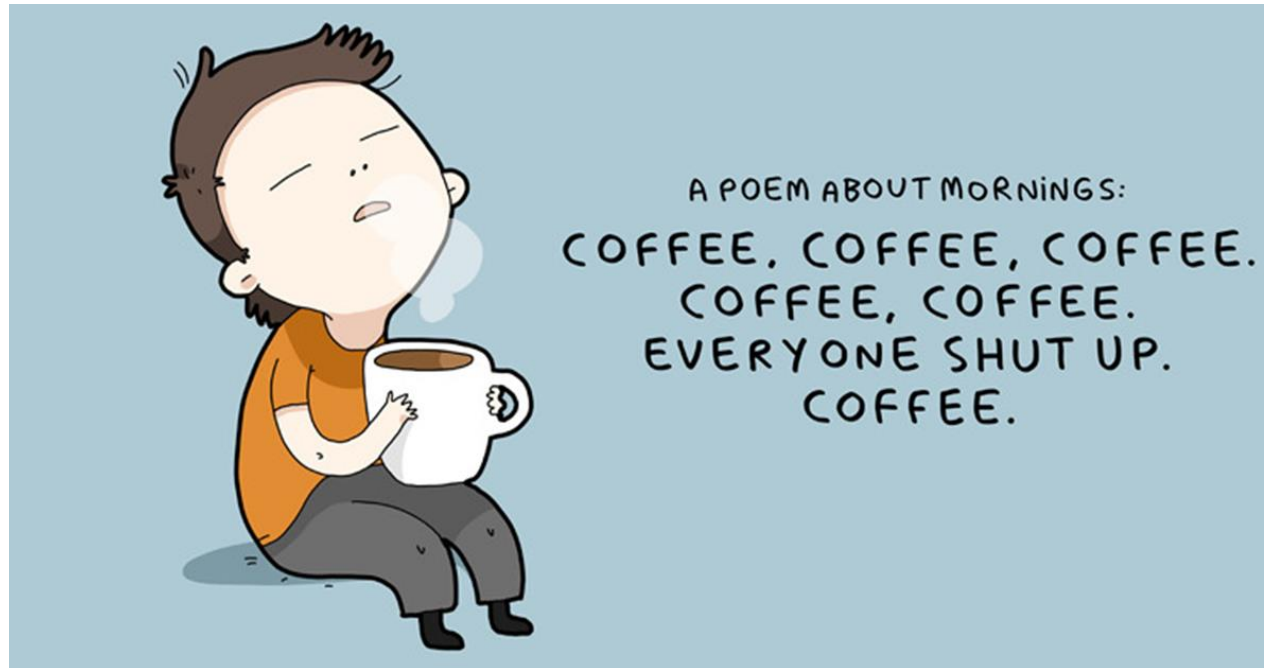
Does only 'Gibbs free energy' dictate the phase stability?



The dictating thermodynamic potential depends on the state variables which are held constant during the process.

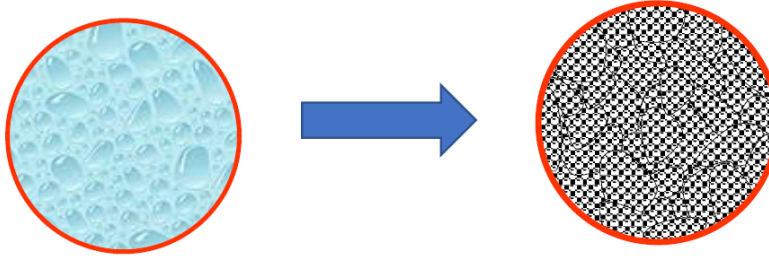
On cooling just below T_m solid becomes stable, i.e. $G_{\text{Liquid}} > G_{\text{solid}}$

However, when we are just below T_m solidification does not 'start'.
E.g. liquid Ni can be undercooled 250 K below T_m .



Driving force for phase transformation

Liquid \rightarrow Solid (α)



Thermodynamic driving force for a phase transformation?

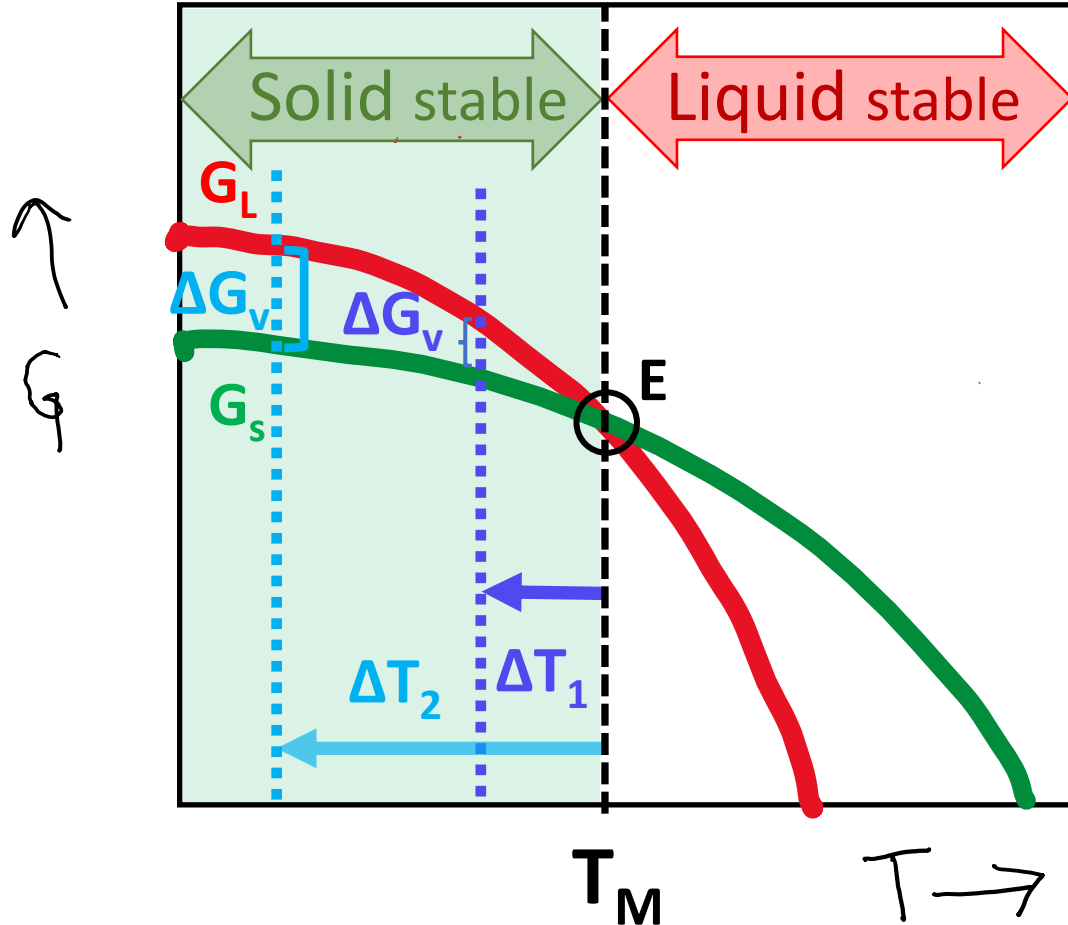
Decrease in Gibbs free energy

Liquid \rightarrow solid

$$G_s - G_l = \Delta G = -ve$$

Lower the free energy, stable is the phase.

$$\Delta G = (G_S - G_L) < 0$$



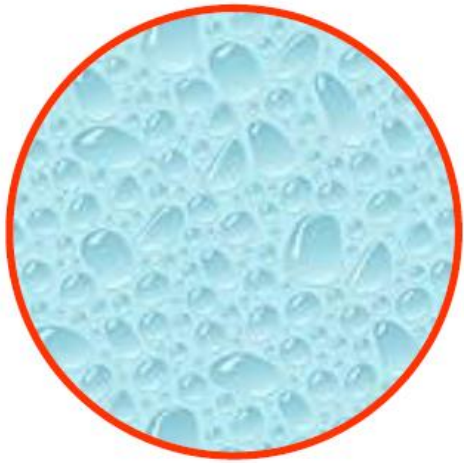
- G_S : Free energy of solid
- G_L : Free energy of liquid
- At 'E', $G_S = G_L$
- ΔT : Undercooling or supercooling



□ When will the solid transform to the liquid?

Mechanism (Steps) of a phase transformation

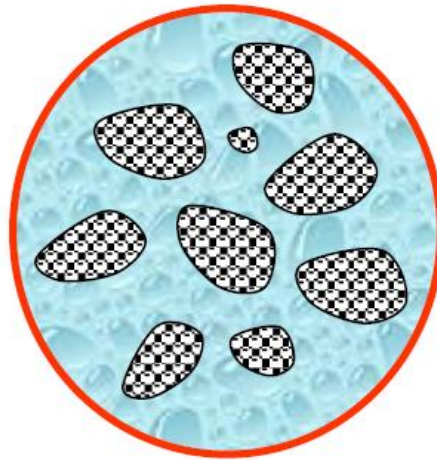
Solidification



=

Nucleation

of solid crystals from melt

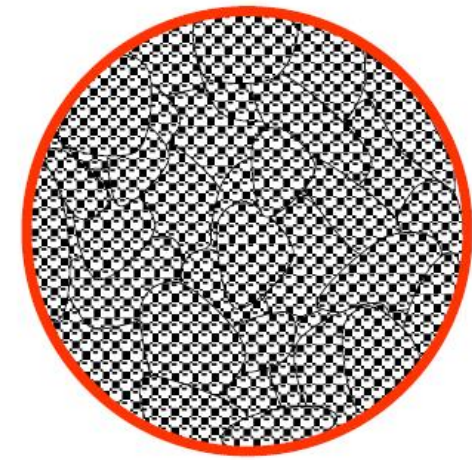


*Formation of stable
particles of solid*

+

Growth

of nucleated crystals till liquid is exhausted



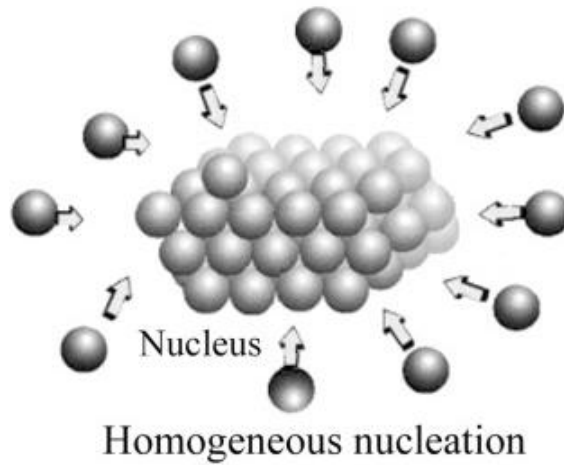
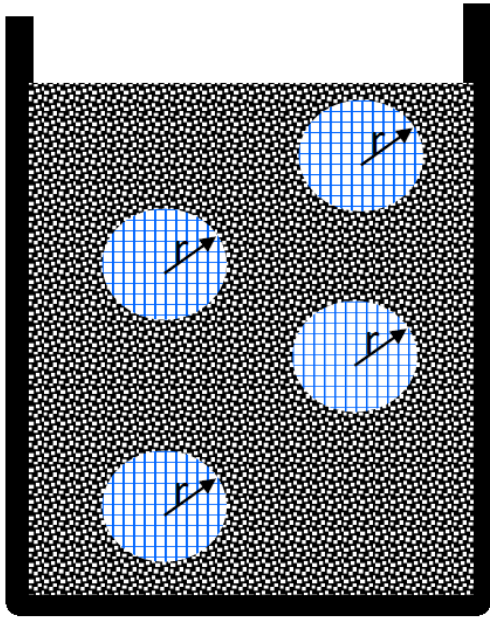
*Increase in size of the formed
stable particles of solid*

Nucleation

- ❑ Formation of a nucleus of a phase from a second phase (in general, for any kind of phase transformation).
- ❑ Formation of a solid nucleus from liquid phase (in particular, for solidification).

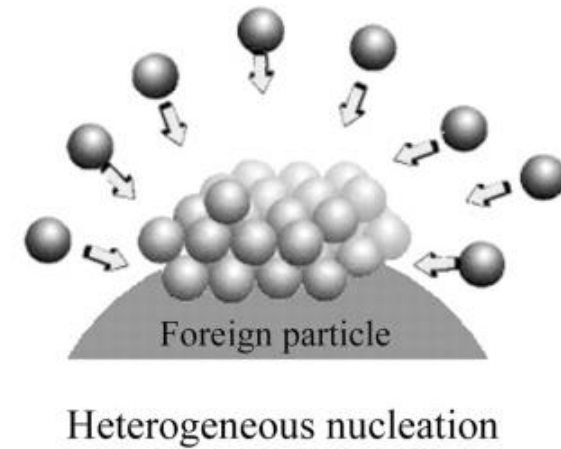
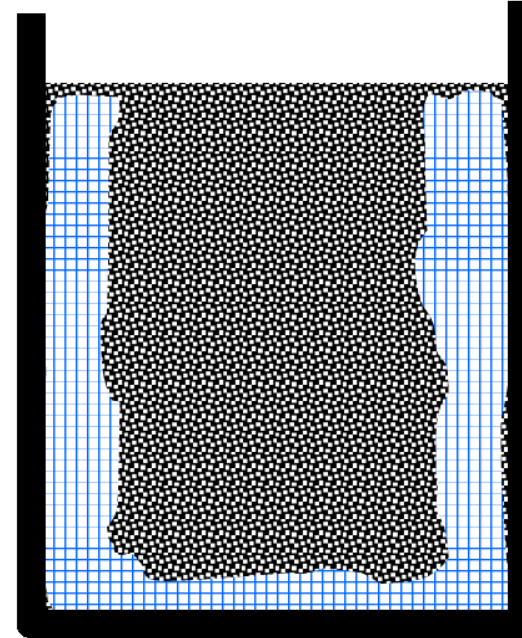
Types of Nucleation

Homogeneous Nucleation



Probability of nucleation occurring at any given site in volume of parent phase is identical to that at any other site

Heterogeneous Nucleation

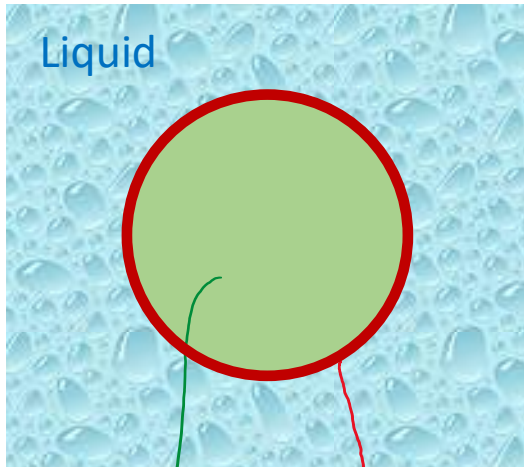


Probability of nucleation occurring at preferred site (e.g. grain boundaries, dislocations, inclusions, mould wall) is much more than that at any other site

Homogeneous nucleation

- Consider L→S transformation taking place by homogenous nucleation.
- Let the system be undercooled to a fixed temperature.
- Let us consider the formation of a spherical crystal of radius 'r' from the melt.
- The change in 'G' during the process, if be, ΔG .

$$T < T_M$$



Total change in energy,

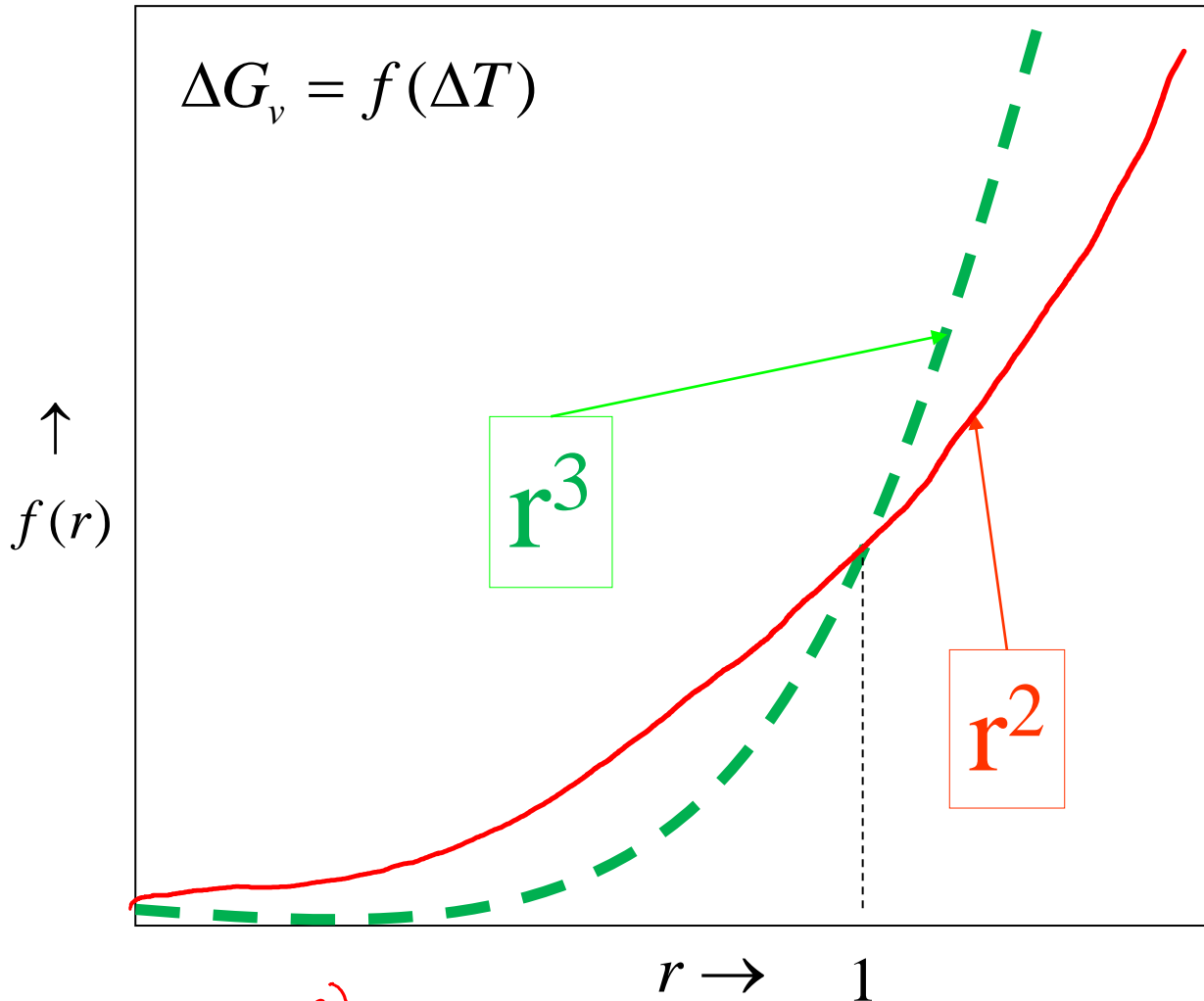
$$\Delta G = - (V \cdot \Delta G_v) + (A \cdot \sigma_{sl})$$

Transformation of a liquid portion to a solid portion with lower energy

Creation of an interface

Considering the nucleus to have a spherical shape with radius 'r':

$$\Delta G = - \left(\frac{4}{3} \pi r^3 \cdot \Delta G_v \right) + (4 \pi r^2 \cdot \sigma_{sl})$$



ΔG

$$= - \left(\frac{4}{3} \pi r^3 \cdot \Delta G_v \right) + (4 \pi r^2 \cdot \sigma_{sl})$$

- Smaller radius (r) : ' r^2 ' term will be greater than ' r^3 ', therefore, the interfacial energy term will dominate the nucleation.
- Larger radius (r) : ' r^3 ' term will be greater than ' r^2 ', therefore, the volume free energy term will dominate the nucleation.

$(r^2 > r^3) \quad r = 0.1 \quad r^2 = 0.01, \quad r^3 = 0.001$
 $(r^2 < r^3) \quad r = 10 \quad r^2 = 100, \quad r^3 = 1000$

$$\Delta G = - \left(\frac{4}{3} \pi r^3 \cdot \Delta G_v \right)$$

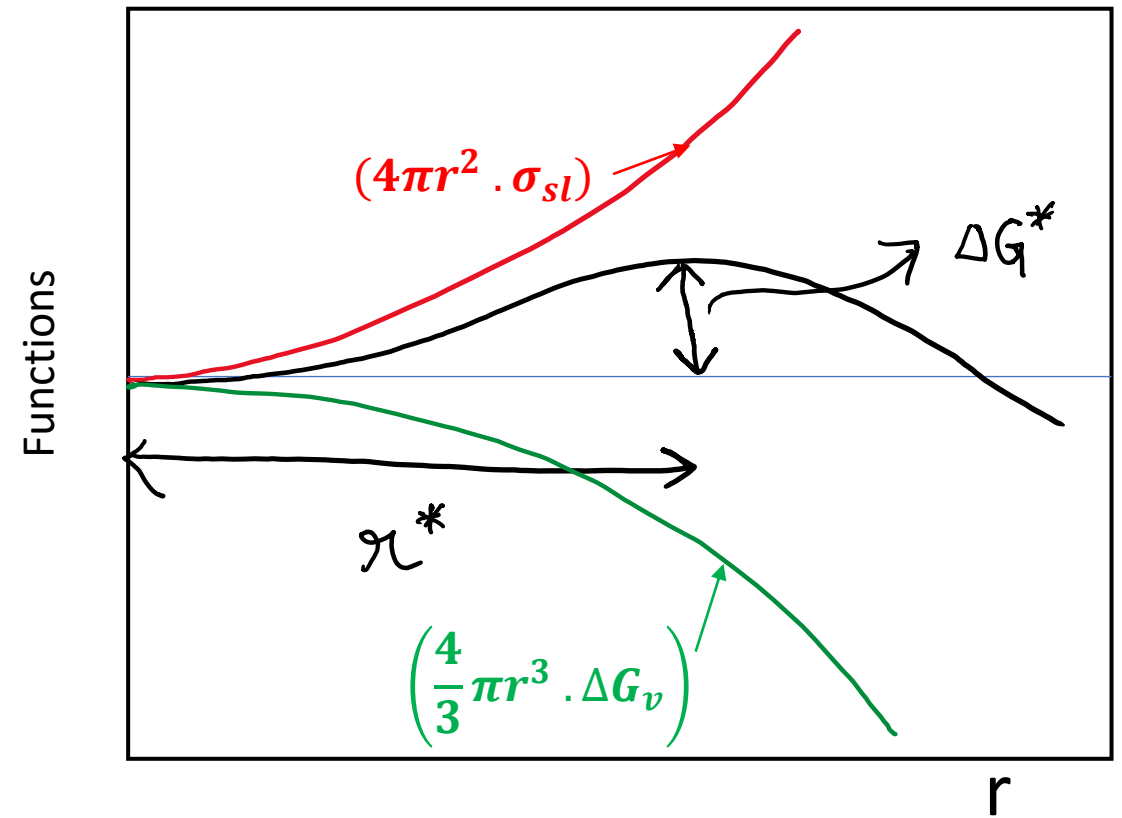
supports $L \rightarrow S$

The energy which a system already has

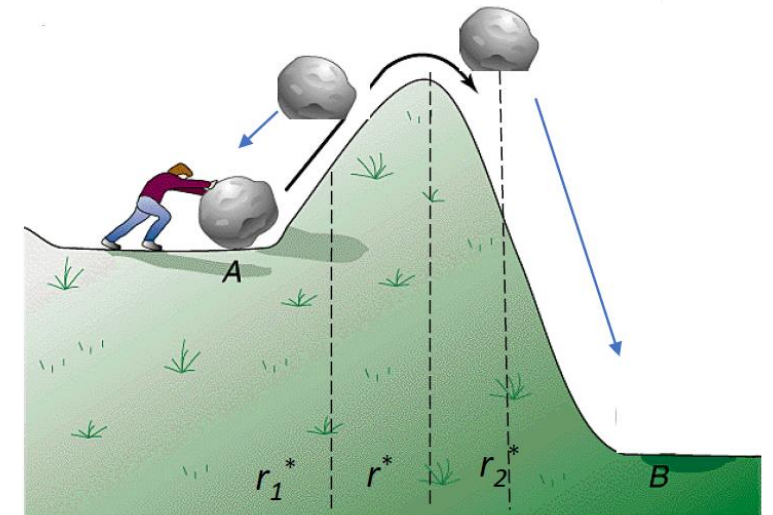
$$+ (4\pi r^2 \cdot \sigma_{sl})$$

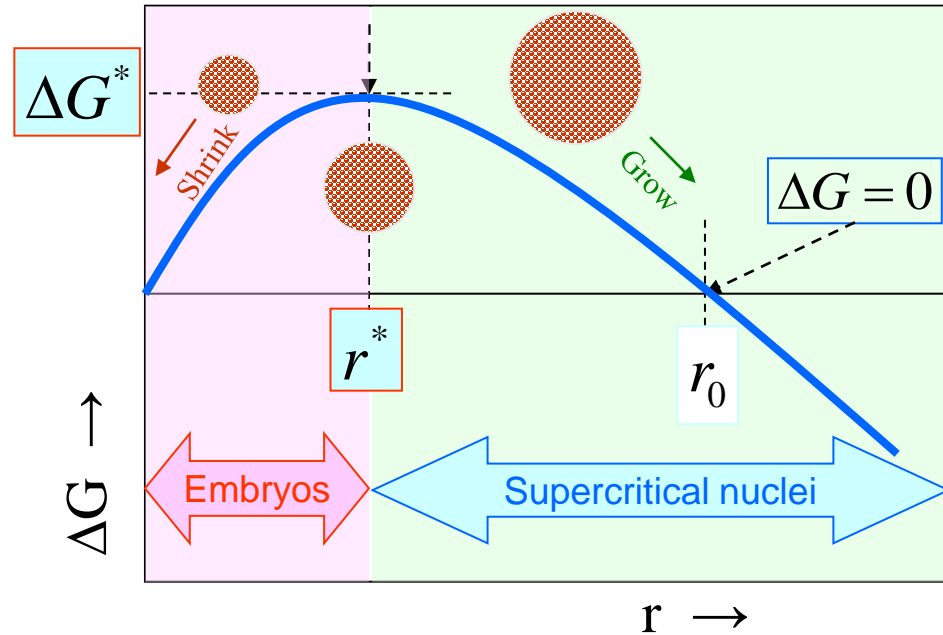
Opposes $L \rightarrow S$

Additional energy which a system needs to be supplied with



- There should be a minimum or maximum in the function of the free energy change for $L \rightarrow S$.
- What governs that minimum/maximum? σ_{sl} and ΔG_v
- $f(\sigma_{sl}) \propto r^2$ and $f(\Delta G_v) \propto r^3$
- For lower limit of 'r', σ_{sl} dominates, and higher limit of 'r', ΔG_v dominates





- ΔG vs r plot goes through a maximum: 'G' increases when a small crystal forms and would tend to dissolve.
- Maximum of ΔG vs r plot is obtained by setting $d\Delta G/dr = 0$. The maximum value of ΔG corresponds to a value of ' r ' called the critical radius (r^*).
- If because of some '*statistical random fluctuation*' a crystal of 'preferred' crystal structure with **size** $> r^*$ (called **supercritical nuclei**) forms, then it can grow because of a favourable 'G' trend. Crystals smaller than r^* (called **embryos**) will tend to shrink to reduce 'G'. The critical value of ΔG at r^* is called ΔG^* .
- Reduction in G (below the liquid state) is obtained only after r_0 is obtained (which can be obtained by setting $\Delta G = 0$).

What is that minimum/maximum?:

$$\frac{d\Delta G}{dr} = - (4\pi r^2 \cdot \Delta G_v) + (8\pi r \cdot \sigma_{sl})$$

$$\frac{d}{dr} \left(\frac{4}{3} \pi r^3 \right) = 4 \pi r^2$$

At either minimum/maximum:

$$\frac{d\Delta G}{dr} = 0 \quad 0 = - (4\pi r^2 \cdot \Delta G_v) + (8\pi r \cdot \sigma_{sl})$$

$$r^* = \frac{2\sigma_{sl}}{\Delta G_v}$$

Critical nucleus size

$$(4\pi r^2 \cdot \Delta G_v) = (8\pi r \cdot \sigma_{sl})$$

The change in free energy for the critical nucleus size:

$$\begin{aligned} \Delta G &= - \left(\frac{4}{3} \pi r^3 \cdot \Delta G_v \right) + (4\pi r^2 \cdot \sigma_{sl}) \\ &= - \left[\frac{4}{3} \pi \left(\frac{2\sigma}{\Delta G_v} \right)^3 \cdot \Delta G_v \right] + \left[4\pi \left(\frac{2\sigma}{\Delta G_v} \right)^2 \cdot \sigma_{sl} \right] \\ &= - \left(\frac{4}{3} \pi \cdot \frac{8\sigma^3}{\Delta G_v^3} \cdot \Delta G_v \right) + \left(4\pi \cdot \frac{4\sigma^2}{\Delta G_v^2} \cdot \sigma_{sl} \right) \\ &= - \frac{8\pi \sigma^3}{\Delta G_v^2} \left(\frac{4}{3} - 2 \right) = \frac{16\pi \sigma^3}{3 \Delta G_v^2} = \Delta G^* \end{aligned}$$