2nd Quiz of MLL100

- Date: 12-02-2022 (Saturday)
- Time: 10:30 am – 10:45 am
- Duration: 15 minutes
- Via: Moodle
- Question type: Multiple-choice
- Negative marking: No
- Navigation: Sequential
- Syllabus: Phase diagram, equilibria and transformation

Minor exam of MLL100

- Date: 16-02-2022 (Wednesday)
- Time: 3:45 pm – 4:45 pm
- Duration: 1 h
- Via: Moodle
- Question type: Multiple-choice
- Negative marking: Yes
- Navigation: Off
- Syllabus: Content covered until 12-02-2022

MLL 100

Introduction to Materials Science and Engineering

Lecture-16 (February 11, 2022)

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

IIT Delhi
Department of Materials Science and Engineering

What have we learnt in Lecture-15?

- ❑ Steps involved in Phase transformation
- ❑ Gibb’s free energy
- ❑ Chemical potential
- ❑ Types of nucleation
- ❑ Critical radius and critical free energy of homogeneous nucleation

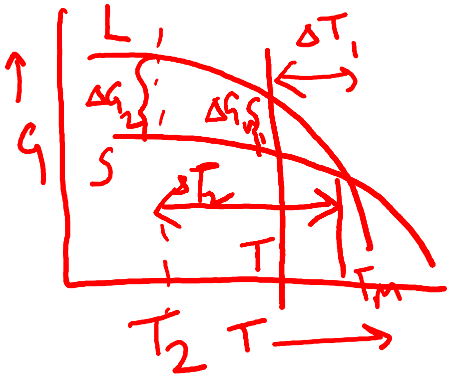
Variation of r* and ΔG* with undercooling

Critical nucleus size, $r^* = \dfrac{2.\gamma_{sl}}{\Delta G_v}$

$$r^* = \frac{2.\gamma_{sl} T_m}{L.\Delta T}$$

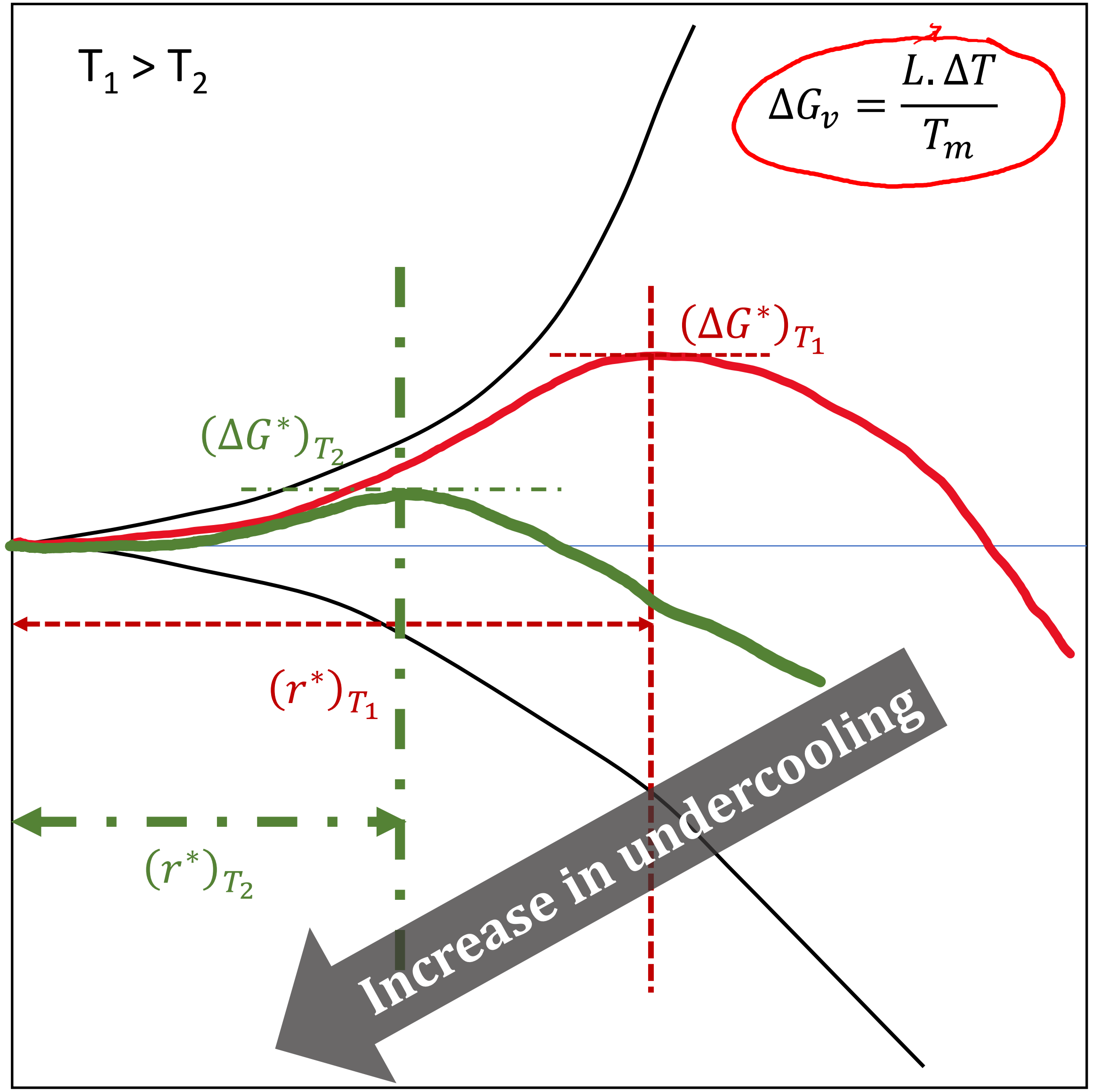
Free energy change for a nucleus with critical size,

$\Delta T \uparrow \quad \Delta G_v \uparrow$



$$\Delta G^* = \frac{16\pi\gamma_{sl}^3}{3.(\Delta G_v)^2}$$

$$\Delta G^* = \frac{16\pi\gamma_{sl}^3 T_m^2}{3.L^2(\Delta T)^2}$$



G=H-TS

Both the 'critical nucleus size' and the 'free energy required to form that critical nucleus' ***decrease with undercooling****.*

$$\boxed{\Delta G = \Delta H - T\Delta S} \quad \text{(1)}$$

$G \Rightarrow$ Gibb's free energy

$H \Rightarrow$ Enthalpy

$T \Rightarrow$ Temperature

$S \Rightarrow$ Entropy

At $T = T_M$, $G = 0$

$(\because G_S = G_L)$

$$\therefore \Delta G = 0 = (\Delta H - T_M \Delta S)$$

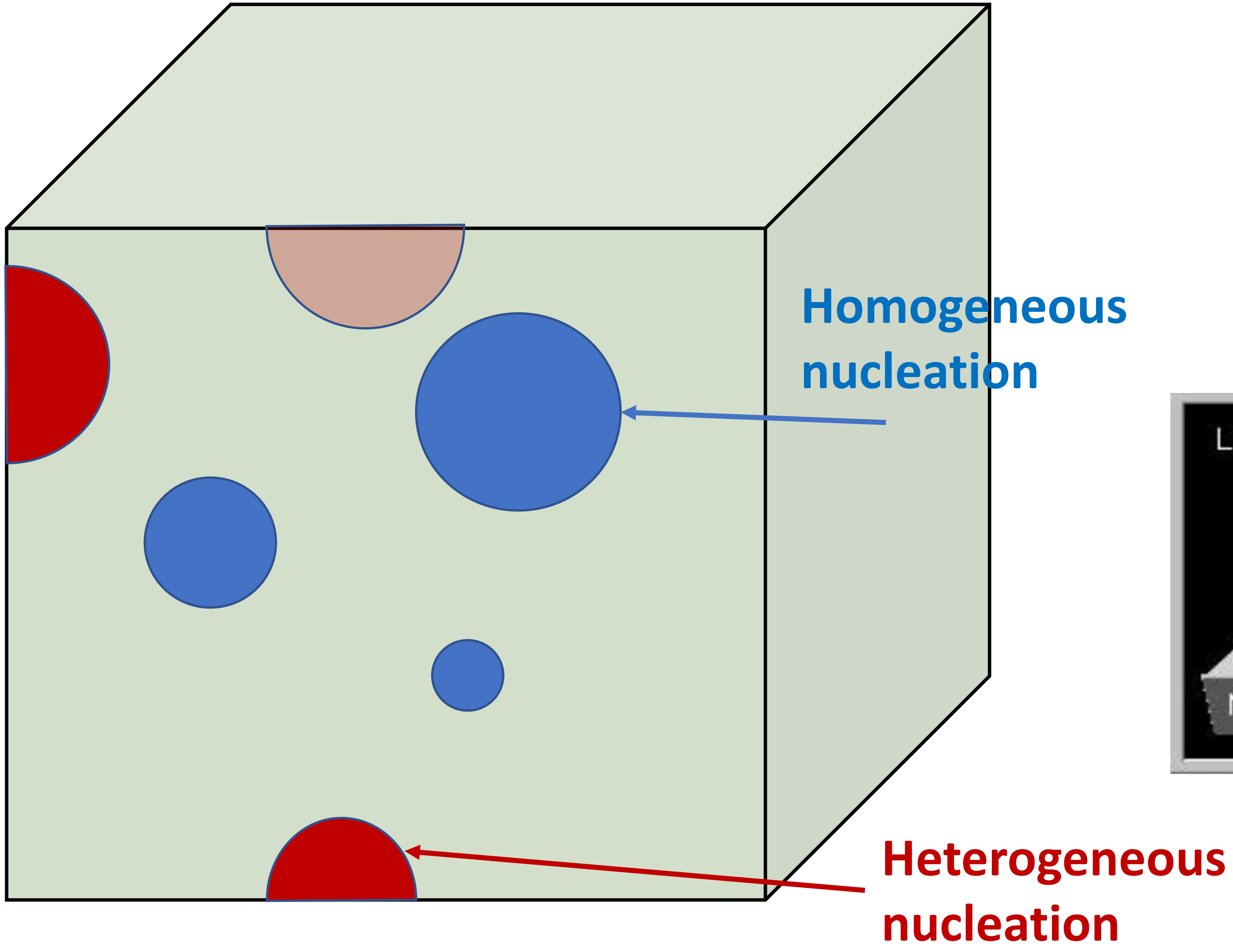
At $T = T_M$, $H =$ Latent heat (L)

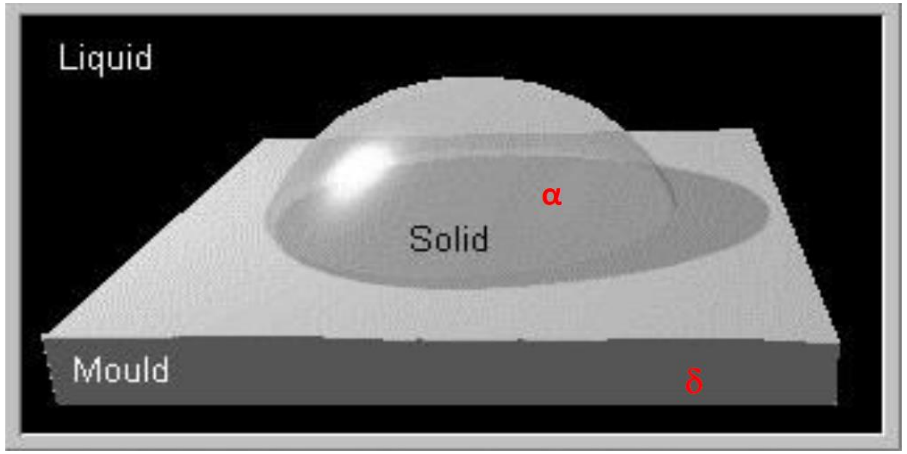
$$\therefore L = T_M S \quad \therefore S = \left(\frac{L}{T_M}\right) \quad \text{(2)}$$

Substitute (2) in (1):

$$\Delta G = L - T\left(\frac{L}{T_M}\right) = L\left[1 - \frac{T}{T_M}\right] = L\left[\frac{T_M - T}{T_M}\right] = \left(\frac{L \cdot \Delta T}{T_M}\right)$$

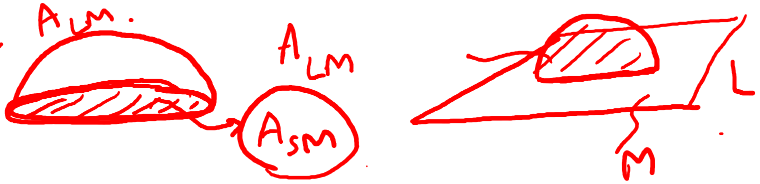
Heterogeneous nucleation





$\Delta G_{het} = -V_s(\Delta G_v) + A_{SL}(\gamma_{SL}) + A_{SM}\gamma_{SM} - A_{LM}\gamma_{LM}$

Earlier A_{LM}.

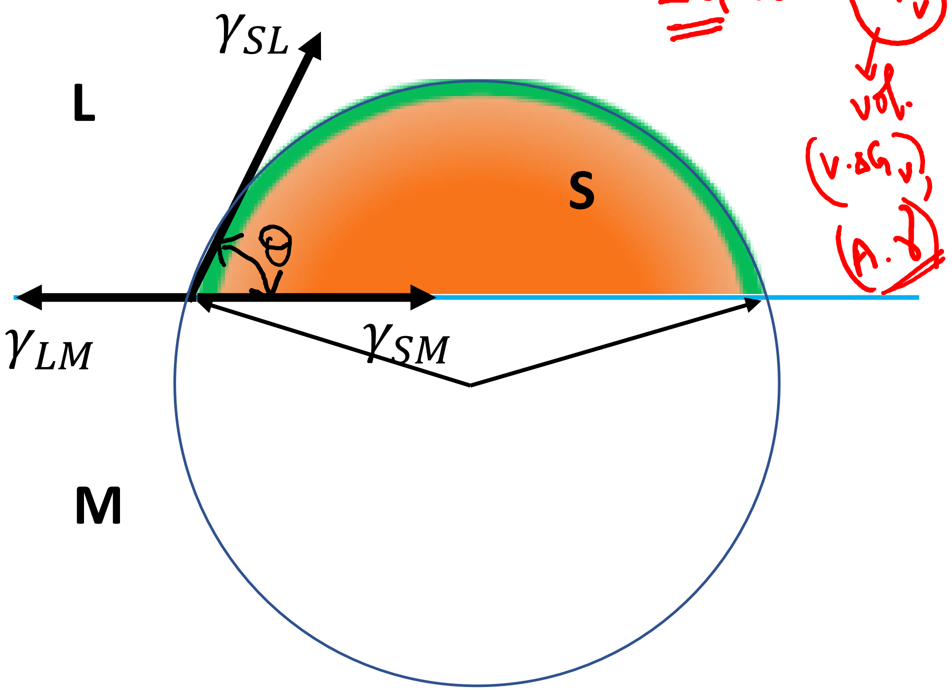


$\underline{\underline{\Delta G}} \propto \Delta G_v, \gamma$

vol.

$(V \cdot \Delta G_v)$

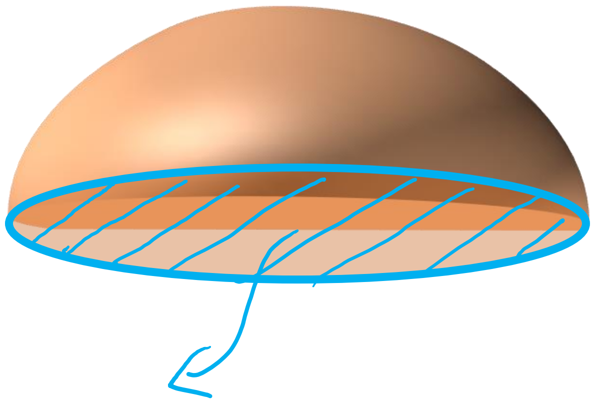
$(A \cdot \gamma)$



- Consider a solid nucleus (S) (of cap-shaped) on a mould (M) surface forming from liquid (L).

- Free energy associated with the heterogeneously nucleated solid particle,

$$\Delta G_{het} = -V_S \Delta G_v + A_{SL}\gamma_{SL} + A_{SM}\gamma_{SM} - A_{SM}\gamma_{LM}$$



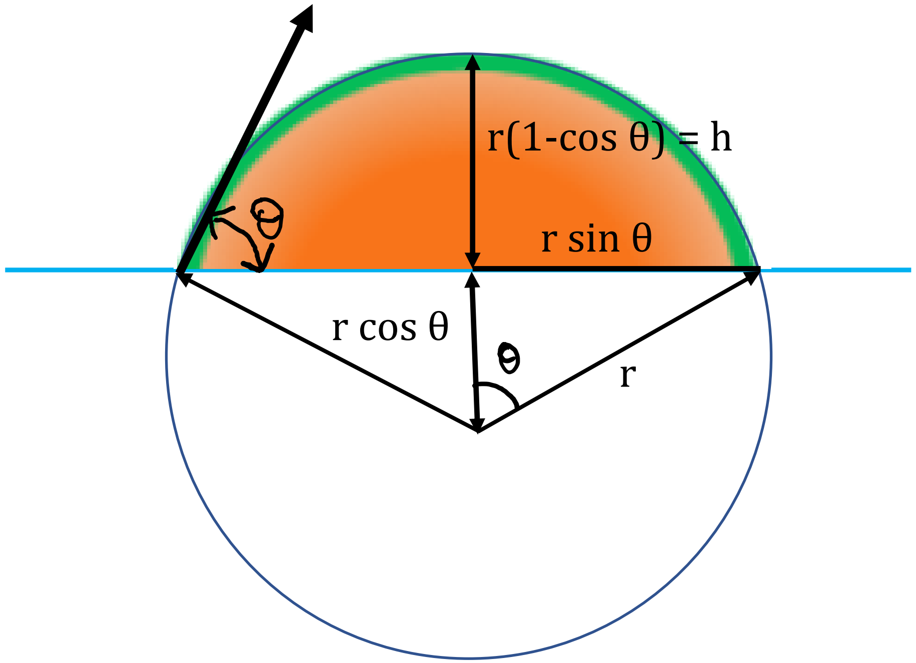
Creation of A_{SM} *Destruction of A_{LM}*

$$\Delta G_{het} = -V_S \Delta G_v + A_{SL}\gamma_{SL} + A_{SM}(\gamma_{SM} - \gamma_{LM})$$

Surface tension force balance parallel to the mould surface

$$\gamma_{LM} = \gamma_{SM} + \gamma_{SL} . \cos\theta$$

$$\cos\theta = \frac{(\gamma_{LM} - \gamma_{SM})}{\gamma_{SL}}$$



- Area of solid-liquid interface:

$$\begin{aligned} A_{SL} &= 2.\pi.r.h \\ &= 2.\pi.r.(r - r\cos\theta) \\ &= 2.\pi.r^2.(1-\cos\theta) \end{aligned}$$

- Area of solid-mould interface:

$$A_{SM} = \pi(r\sin\theta)^2$$

- Volume of the solid nucleus cap:

$$V = \frac{\pi}{6}h\left(3r^2 + h^2\right)$$

$$= \frac{\pi}{3}r^3\left(2 - 3\cos\theta + cos^3\theta\right)$$

- Substitution of these values in:

$$\Delta G_{het} = -V_S\Delta G_v + A_{SL}\gamma_{SL} + A_{SM}(\gamma_{SM} - \gamma_{LM})$$

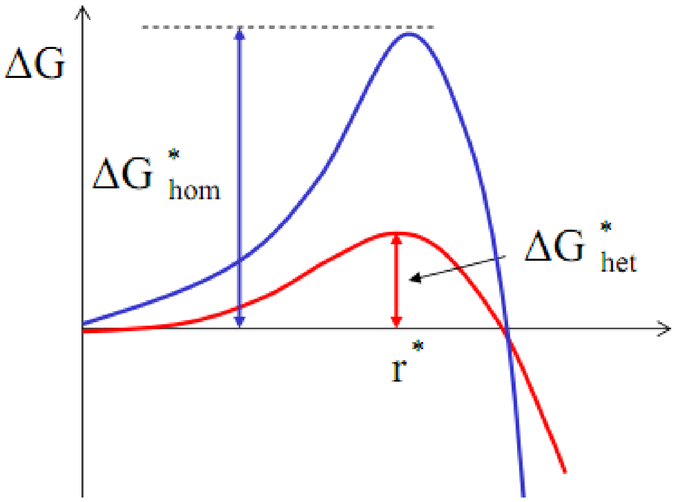
$$\cos\theta = \frac{(\gamma_{LM} - \gamma_{SM})}{\gamma_{SL}}$$

- Re-arranging the terms in: $$\Delta G_{het}= -\frac{4}{3}\pi r^3 \Delta G_v \left(\frac{2-3\cos\theta+cos^3\theta}{4}\right) + 4\pi r^2 \gamma_{SL}\left(\frac{2-3\cos\theta+cos^3\theta}{4}\right)$$

- Simplifying by taking the shape factor in common: $$\Delta G_{het}= [-\frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma_{SL}]\left(\frac{2-3\cos\theta+cos^3\theta}{4}\right)$$

- The relation between free energy change for heterogeneous and homogeneous nucleation: $$\Delta G_{het}= [\Delta G_{hom}]\left(\frac{2-3\cos\theta+cos^3\theta}{4}\right)$$

$$\frac{\Delta G_{het}}{\Delta G_{hom}} = \left(\frac{2-3\cos\theta+cos^3\theta}{4}\right)$$



- Free energy change at critical nucleus size for heterogeneous nucleation: $$\Delta G^*_{het}= \frac{4\pi\gamma_{SL}^3}{3(\Delta G_v)^2}(2-3\cos\theta+cos^3\theta)$$

- Free energy change at critical nucleus size for heterogeneous nucleation:

$$\Delta G^*_{het} = \frac{4\pi\gamma_{SL}^3}{3(\Delta G_v)^2}(2 - 3\cos\theta + cos^3\theta)$$

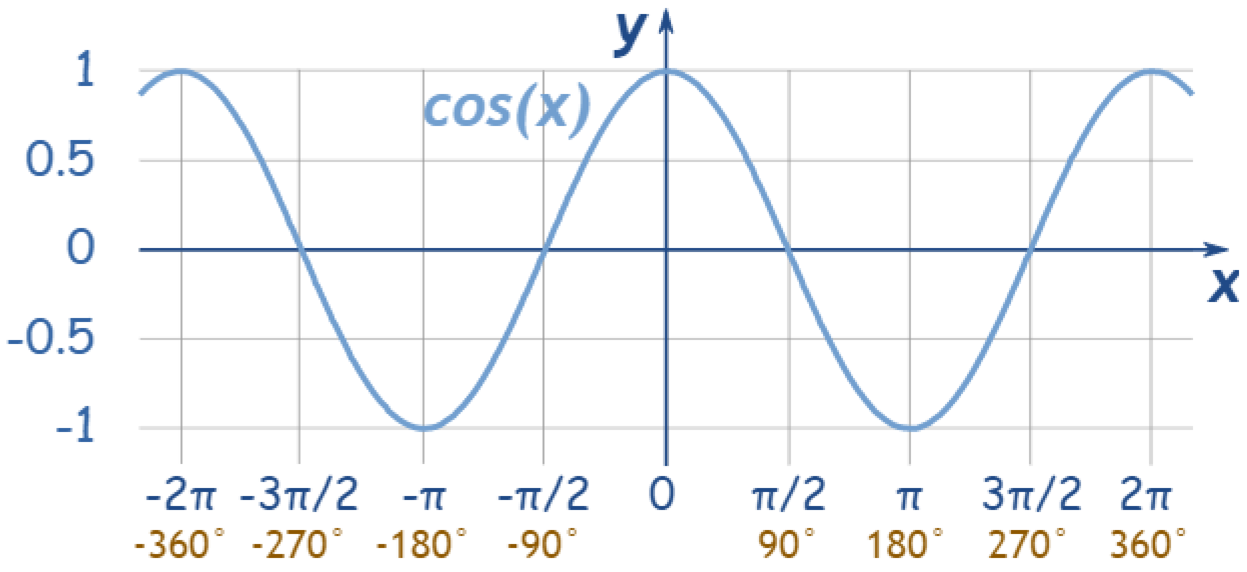
- Free energy change at critical nucleus size for homogeneous nucleation:

$$\Delta G^*_{hom} = \frac{16\pi\gamma_{SL}^3}{3(\Delta G_v)^2}$$

How can you relate the free energy changes for homogeneous and heterogeneous nucleation?

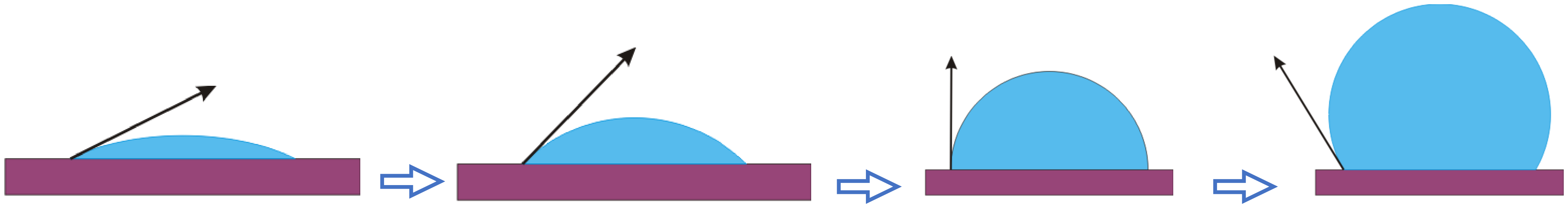
$$\Delta G^*_{het} = \frac{(\Delta G^*_{hom})}{4}(2 - 3\cos\theta + cos^3\theta)$$

$$\frac{\Delta G_{het}}{\Delta G_{hom}} = \left(\frac{2 - 3\cos\theta + cos^3\theta}{4}\right)$$



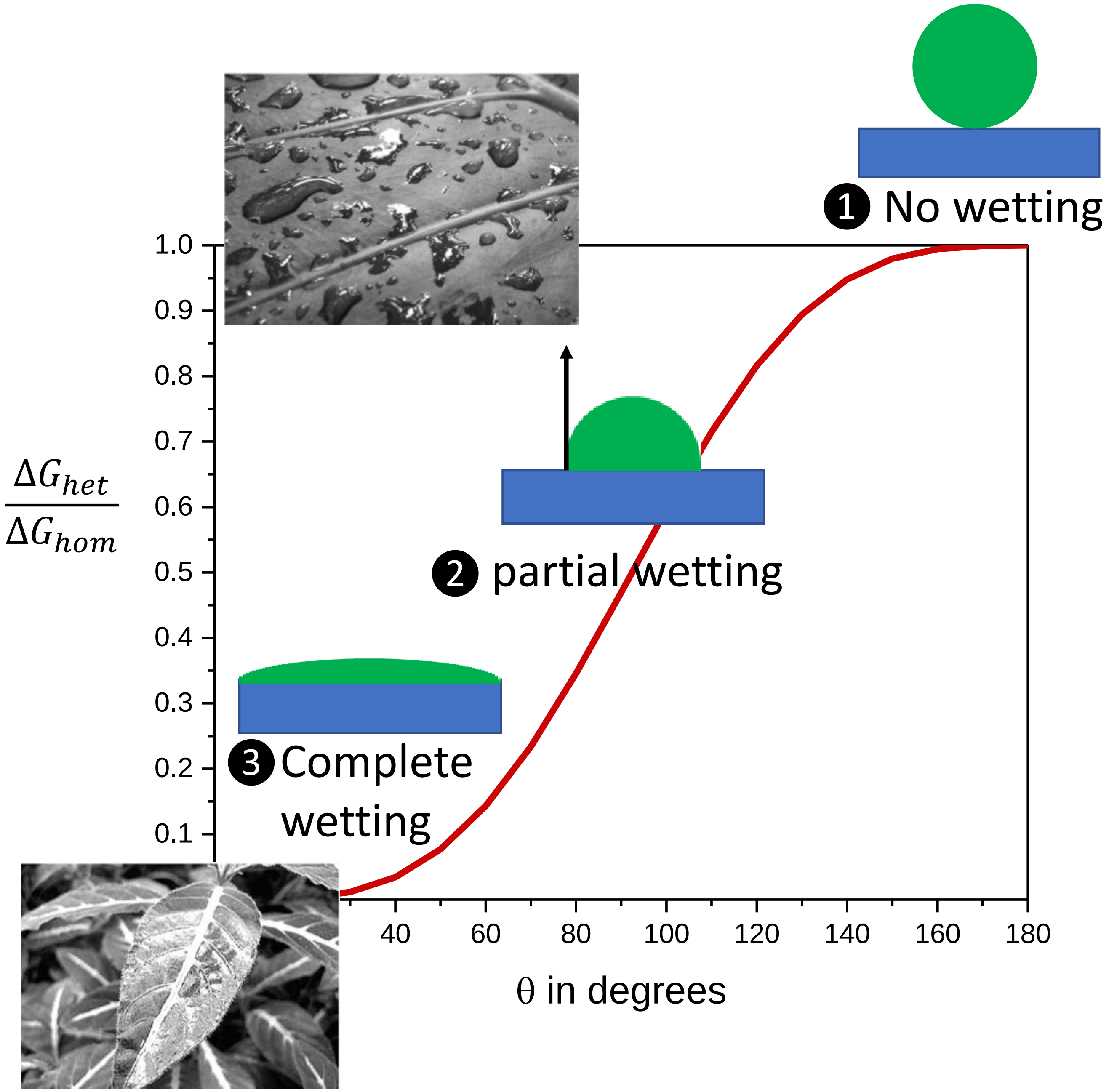
$$\Delta G_{het}^{*} = \frac{4\pi\gamma_{SL}^{3}}{3(\Delta G_v)^2}(2 - 3\cos\theta + cos^3\theta)$$

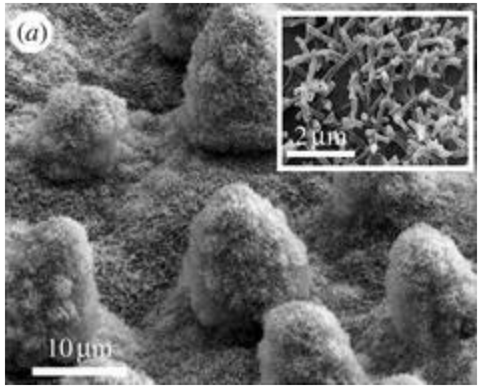
What happens when contact angle (θ) increases?



Tendency to wet the surface decreases

Wetting behaviour





$$\frac{\Delta G_{het}}{\Delta G_{hom}} = \left(\frac{2 - 3\cos\theta + \cos^3\theta}{4}\right)$$

1. θ = 180° : $\Delta G_{het} = \Delta G_{hom}$, such a surface does not favour heterogeneous nucleation.

2. θ = 90° : $\Delta G_{het} = 0.5\ \Delta G_{hom}$, energy barrier for heterogeneous nucleation is half of the homogeneous one.

3. θ = 0° : $\Delta G_{het} = 0$, no energy barrier for heterogeneous nucleation.

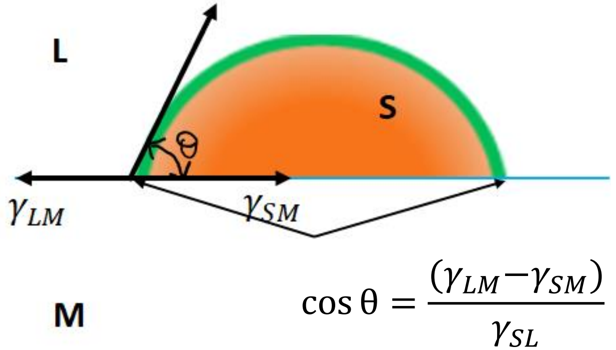
Selection of ‘heterogeneous nucleation site’

❑ How to make the contact angle (θ) small?

- By obtaining $(\gamma_{LM} - \gamma_{SM})$ closer to 1 -----> larger γ_{LM} and smaller γ_{SM}
- Choose an inoculant which can form a S-M interface with low γ_{SM}

Wetting ↑	cos 0°	1
	cos 90°	0
	cos 180°	-1

$$\Delta G^*_{het} = \frac{4\pi\gamma_{SL}^3}{3(\Delta G_v)^2}(2 - 3\cos\theta + \cos^3\theta)$$



$$\cos\theta = \frac{(\gamma_{LM} - \gamma_{SM})}{\gamma_{SL}}$$

❑ How to achieve a lower γ_{SM}?

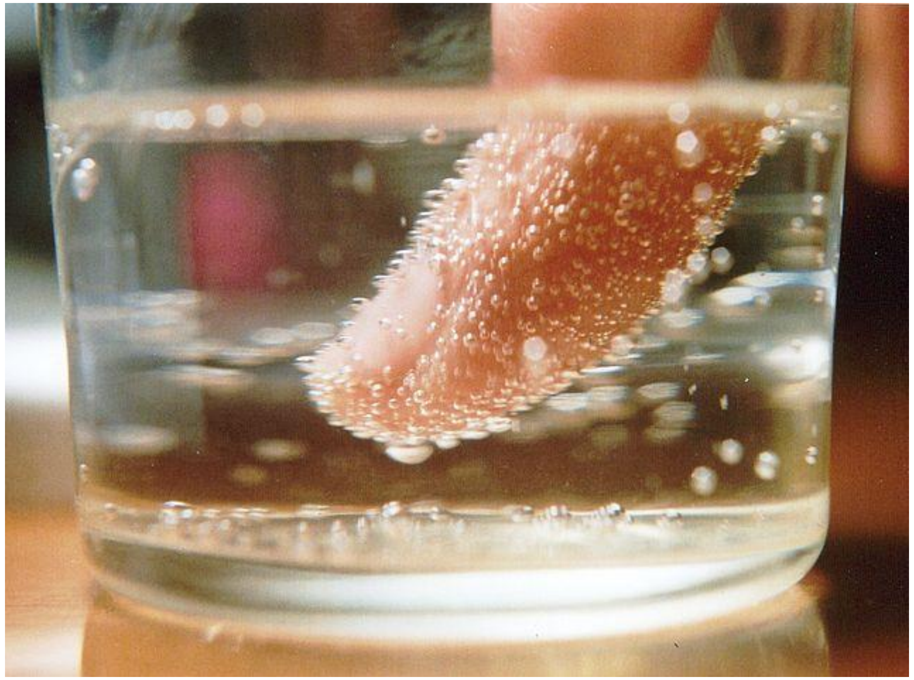
- Solid and inoculant have the same or a similar crystal structure
- Solid and inoculant have a similar lattice parameter, so as to have a fairly good matching at the interface.
- Nickel (FCC, 3.52 Å) as an inoculant in graphite (DC, 3.57 Å): helps producing artificial diamonds; TiB_2 to Al alloys

❑ Orientation relationship

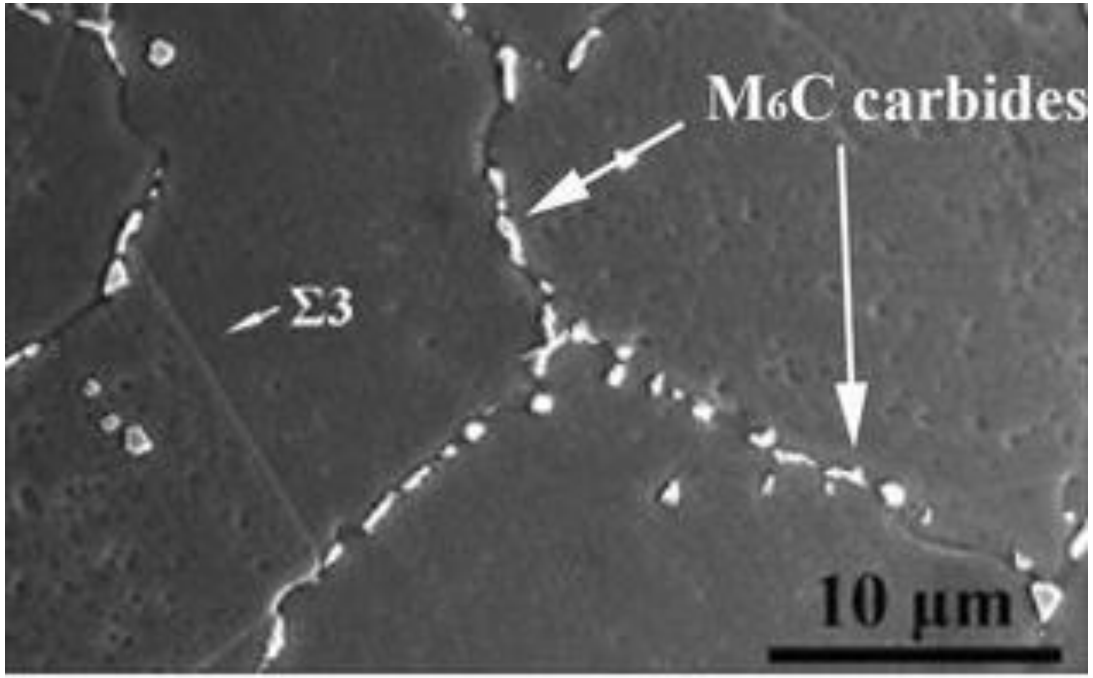
- Orientation relationship (OR) between certain crystallographic planes and directions at the interface: OR between parent and product phases helps achieving a coherent interface, and promotes heterogeneous nucleation.

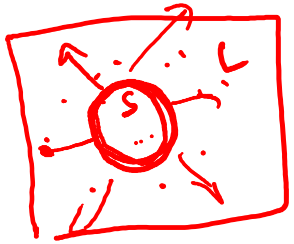
Heterogeneous nucleation

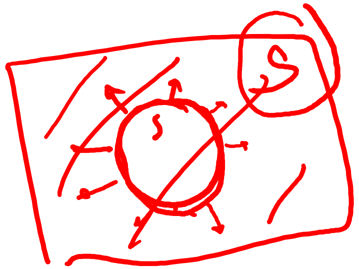
Nucleation in the liquid



Nucleation in the solid







stress (oppose transf.)

(change ΔG) $\propto$ ΔG_v, γ

(solid surf.) $+ A \gamma_s$

Why does we often encounter heterogeneous nucleation?

- The pre-exponential term is a function of the number of nucleation sites.

- The term that dominates is the exponential term and due to a lower ΔG^* the heterogeneous nucleation rate is typically higher.

$$I_{homo} \propto I^0_{homo}\, e^{-\left(\frac{\Delta G^*_{homo}}{kT}\right)}$$

= f(number of nucleation sites)
~ 10^{42}

$$I_{hetero} \propto I^0_{hetero}\, e^{-\left(\frac{\Delta G^*_{hetero}}{kT}\right)}$$

= f(number of nucleation sites)
~ 10^{26}

BUT
the exponential term dominates

$$I_{hetero} > I_{homo}$$