Rate of Heterogeneous Nucleation of β-phase at grain boundaries of α-phase:

$$I_{gb} = \left(\frac{KT}{h}\right)\cdot N_{s^*}\cdot N_{gb}\cdot \exp\left(-\frac{\Delta G^*_{gb}+\Delta G_D}{KT}\right)$$

N_{s^*} → Number of atoms at the ~~interface~~ surface of critical embryo in the parent phase, α.

N_{gb} → Number of atoms per unit volume of α at grain boundaries of α.

⊙ ΔG^*_{gb} in terms of ΔG^*_h :

$$\Delta G^*_{gb} = \frac{1}{2}\Delta G^*_h (2 - 3\cos\theta + \cos^3\theta)$$

$$+ \quad \Delta G^*_{gb} = \frac{8\pi}{3} \cdot \frac{(\sigma_{\alpha\beta})^3}{(\Delta G_v)^2} \cdot (2 - 3\cos\theta + \cos^3\theta) = -\frac{\Delta G_v \cdot V^*_{gb}}{2}$$

$\Delta G^*_{gb} \rightarrow$ Gibbs energy of formation of critical embryo formed at a planer grain boundary of α.

$\Delta G^*_h \rightarrow$ Gibbs energy of formation of critical embrya during homogeneous nucleation.

$V^*_{gb} \rightarrow$ Volume of critical embryo formed heterogeneously at planer grain boundary.

- Gibbs energy of formation of critical embryo formed at a planer grain boundary of α (ΔG^*_{gb}) can obtainded by substituting R^* in place of R in the expression of $(\Delta G')$.

then,

$$\boxed{\Delta G^*_{gb} = \frac{8\pi}{3} \cdot \frac{(\sigma_{\alpha\beta})^3}{(\Delta G_v)^2} \cdot (2 - 3\cos\theta + \cos^3\theta)}$$

$$\Rightarrow \frac{dG'}{dR} = \frac{2}{\cancel{3}}\pi \times \cancel{3} R^2 \Delta G_v f(\theta) + 2\pi \times 2R\sigma_{\alpha\beta} f(\theta)$$

$$\Rightarrow \frac{dG'}{dR} = 2\pi f(\theta)\left[R^2 \Delta G_v + 2R \cdot \sigma_{\alpha\beta}\right] \quad \Rightarrow \frac{dG'}{dR} = 0$$

$$\Rightarrow 0 = R^2 \Delta G_v + 2R\sigma_{\alpha\beta} \quad \Rightarrow R^{\cancel{2}} \Delta G_v = -2\cancel{R}\sigma_{\alpha\beta}$$

$$\Rightarrow \boxed{R^* = -2\sigma_{\alpha\beta}/\Delta G_v}$$ Proved//. $\Delta G'$ is maximum at critical Radius (R^*).

- Radius of curvature of spherical sections of the critical embryo is same as radius of critical embryo during homogeneous Nucleation.

A :

$$\Delta G' = V\,\Delta G_v + A\,\sigma_{\alpha\beta} - \pi r^2\,\sigma_{\alpha\delta}$$

$$\Rightarrow \Delta G' = \frac{2}{3}\pi R^3\left(2 - 3\cos\theta + \cos^3\theta\right)\Delta G_v + 4\pi R^2(1-\cos\theta)\,\sigma_{\alpha\beta} - \pi (R\sin\theta)^2\, 2\sigma_{\alpha\beta}\cos\theta$$

$$\Rightarrow \Delta G' = \frac{2}{3}\pi R^3\left(2 - 3\cos\theta + \cos^3\theta\right)\Delta G_v + 4\pi R^2(1-\cos\theta)\,\sigma_{\alpha\beta} - \pi\left(R^2(1-\cos^2\theta)\right) 2\sigma_{\alpha\beta}\cos\theta$$

$$\Delta G' = \underline{\qquad\qquad\qquad} + 2\pi R^2\left[2(1-\cos\theta) - \overset{\cos\theta}{1}(1-\cos^2\theta)\right]\sigma_{\alpha\beta}$$

$$\Delta G' = \underline{\qquad\qquad\qquad} + 2\pi R^2\sigma_{\alpha\beta}\left[2 - 2\cos\theta - \overset{\cos\theta}{1} + \cos^3\theta\right]$$

$$\Delta G' = \underline{\qquad\qquad\qquad} + 2\pi R^2\sigma_{\alpha\beta}\left[2 - 3\cos\theta + \cos^3\theta\right]$$

$$\boxed{\Delta G' = \left(2 - 3\cos\theta + \cos^3\theta\right)\left[\frac{2}{3}\pi R^3\,\Delta G_v + 2\pi R^2\sigma_{\alpha\beta}\right]}$$

- Volume of the embryo is given by :

$$\boxed{V = \frac{2}{3}\pi R^3 (2 - 3\cos\theta + \cos^3\theta)}$$

- Surface area is given by :

$$\boxed{A = 4\pi R^2 (1 - \cos\theta)}$$

- Gibbs energy of the formation of the embryo ($\Delta G'$) :

$$\boxed{\Delta G' = V\Delta G_v + A\sigma_{\alpha\beta} - \pi r^2 \sigma_{\alpha\alpha}}$$

- Term $(-\pi r^2 \sigma_{\alpha\alpha})$ is due to decrease in grain boundary area of α by πr^2.

- $\sigma_{\alpha\alpha} \rightarrow$ Interface energies of α/α grain boundaries.

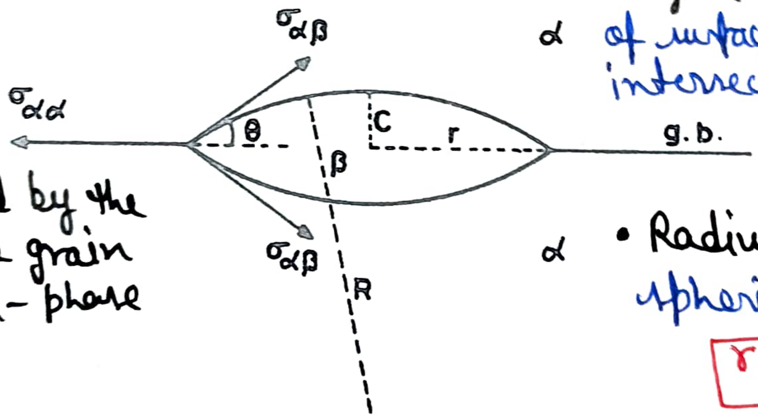
$\sigma_{\alpha\beta} \rightarrow$ Interface energies of α/β interface.

r & $c \rightarrow$ These parameters are related to radius of curvature of the spherical caps (R).

$$\boxed{r = R \sin\theta}$$

&

$$\boxed{c = R(1 - \cos\theta)}$$



- Angle (θ) is defined by the balance of surface tension forces at the intersection of embryo + grain boundary: $\boxed{\sigma_{\alpha\alpha} = 2\sigma_{\alpha\beta}\cos\theta}$

- Area enclosed by the embryo on the grain boundary of α-phase is (πr^2).

- Radius of curvature (R) of spherical caps: $\boxed{r = R\sin\theta}$

Nucleation at Grain boundaries

- Consider, Heterogeneous Nucleation of β-phase at grain boundari of α-phase during $(\alpha \rightarrow \beta)$ Solid State transformation.
- Assumption: α/β interfacial energy is isotropic, then shape of β embryo formed at a planar grain boundary of α-phase would be as follows:
- It is enclosed by two identical spherical sections of radius (R), forming a lens shape on the grain boundary of α.