Homogenous Nucleation:

- In order to understand whether nucleation of solid particles from a liquid is fast or slow, we need to compute the Gibbs free energy change as a function of nucleus size, i.e., over what range of nucleus sizes will nucleation spontaneously occur:

$$\boxed{\Delta G(r) = \underbrace{N}_{\text{no. atoms}}\overbrace{\Delta\mu}^{\text{solid-liquid free energy difference}} + \overbrace{A}^{\text{area}}\underbrace{\gamma}_{\substack{\text{solid liquid}\\ \text{interface free energy}\\ \text{(surface tension)}}} = \overbrace{\tfrac{4}{3}\pi r^3 \Delta\mu \underbrace{n}_{\text{number density of atoms}}}^{\text{volume term}} + \overbrace{4\pi r^2 \gamma}^{\text{interfacial term}}}$$

- $\Delta\mu$, which is the difference in chemical potential between the solid and liquid phases, is the amount of energy released when the supercooled liquid transforms into a solid

$$\left.\frac{dG}{dr}\right|_{r=r_c} = 0 \longrightarrow 0 = \overbrace{-4\pi r_c^2 \Delta\mu n}^{\text{negative free energy contribution to volume when solid forms}} + 8\pi r_c\gamma \longrightarrow \cancel{4\pi r_c}^{\,1/2}\cancel{^{2}}\,\Delta\mu n = \cancel{8\pi r_c}\,\gamma$$

$$\downarrow$$

$$\frac{r_c \Delta\mu n}{2} = \gamma \longrightarrow \boxed{r_c = \frac{2\overbrace{\gamma}^{J/m^2}}{\underbrace{\Delta\mu}_{J/atom}\overbrace{n}^{\text{atoms}/m^3}}}$$

atoms/m³ i.e., $n_a = \frac{\rho N_A}{M}$

$$\overbrace{\Delta G_c}^{J} = 4\pi\left(\frac{2\gamma}{\Delta\mu n}\right)^2\gamma - \frac{4\pi}{3}\left(\frac{2\gamma}{\Delta\mu n}\right)^3\Delta\mu = \frac{16\pi\gamma^3}{\Delta\mu^2 n^2} - \frac{32\pi\gamma^3\cancel{\Delta\mu n}}{3\Delta\mu^{\cancel{3}\,2}n^{\cancel{3}\,2}} \longrightarrow \frac{48\pi\gamma^3 - 32\pi\gamma^3}{3\Delta\mu^2 n^2} = \frac{16\pi\gamma^3}{3\Delta\mu^2 n^2}$$

i.e., the energy barrier that must be overcome for nucleation to occur

- We would like to know r_c as a function of temperature and so must express $\Delta\mu$, the free energy associated with a change in volume, to the latent heat of transformation:

$$\Delta\mu = \underbrace{\mu}_{\substack{\text{energy absorbed/released due to}\\ \text{a change in particle number of that species}}}{}_{solid} - \mu_{liquid}\ , \quad \text{at } T = T_m \text{ (equilibrium)},\ \mu_{solid} = \mu_{liquid} \ \therefore\ \Delta\mu = 0$$

$\frac{d\mu}{dT} \approx -\frac{L}{T_m}$ based on the Clausius-Clapeyron equation, and assuming a small undercooling (ΔT) $\Delta\mu \approx \frac{d\mu}{dT}\Delta T = -\frac{L}{T_m}\Delta T$

in J/mol. divide by N_A to convert to per atom

Expressing in terms of mass-based quantities, we get:

$$\Delta\mu = \frac{\overbrace{L}^{\text{latent heat (J/mol)}}\overbrace{\Delta T}^{\text{undercooling }(T_m - T)}\overbrace{\rho}^{\text{density }(kg/m^3)}}{\underbrace{T_m}_{\text{melting temperature (K)}}\underbrace{M}_{\text{molar mass (kg/mol)}}\underbrace{n}_{\text{atoms}/m^3}} \longrightarrow r_c(T) = \frac{2\gamma T_m M\cancel{n}}{L\Delta T\rho\cancel{n}}$$

As $T \to T_m$, $\Delta T \to 0 \therefore r_c \to \infty$ which tells us that at equilibrium no nucleation occurs because the energy barrier is too high. As T decreases (more undercooling), r_c gets smaller making it easier for stable nuclei to form.

- Since we have an expression for $\Delta\mu$ as a function of temperature, we can now derive an expression for ΔG_c as a function of temperature:

$$\Delta G_c = \frac{16\pi\gamma^3}{3\Delta\mu^2 n^2} = \frac{16\pi\gamma^3}{3\cancel{n^2}}\cdot\left(\frac{T_m M\cancel{n}}{L\rho\Delta T}\right)^2 = \frac{16\pi\gamma^3}{3L^2}\left(\frac{T_m M}{\rho\Delta T}\right)^2$$