Freezing by Nucleation [pln37]

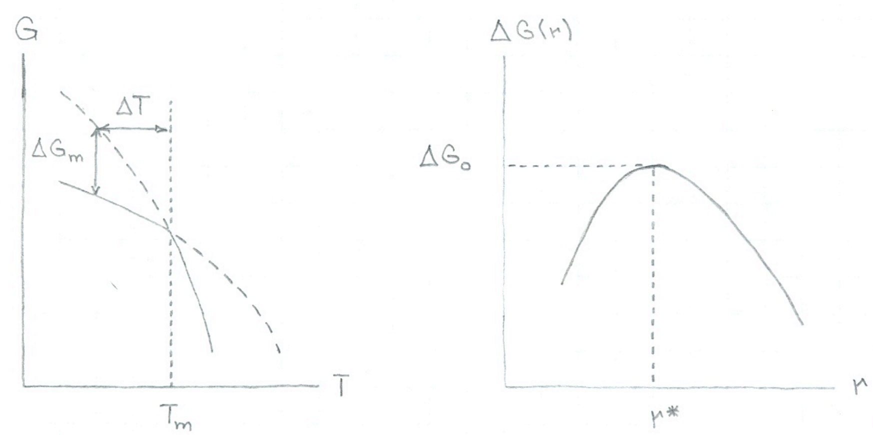
Homogeneous nucleation:

Spontaneous formation of crystal nuclei of radius r in undercooled melt:

Gibbs free energy relative to undercooled liquid state:

$$\Delta G(r) = \underbrace{-\frac{4\pi}{3} r^3 \frac{L_\mathrm{m}}{T_\mathrm{m}} \Delta T}_{\text{volume}} + \underbrace{4\pi r^2 \gamma_\mathrm{sl}}_{\text{interface}},$$

- T_m: melting temperature,
- L_m: latent heat of melting (per volume),
- $\Delta T \doteq T_\mathrm{m} - T > 0$: undercooling temperature,
- $S_\mathrm{m} = -\frac{L_\mathrm{m}}{T_\mathrm{m}}$: drop in entropy (per volume) during freezing,
- $\Delta G_\mathrm{m} = -S_\mathrm{m}(-\Delta T) = -\frac{L_\mathrm{m}}{T_\mathrm{m}}\Delta T$: change in free energy (per volume),
- γ_sl: liquid-solid interfacial tension.



Find location and height of free-energy barrier:

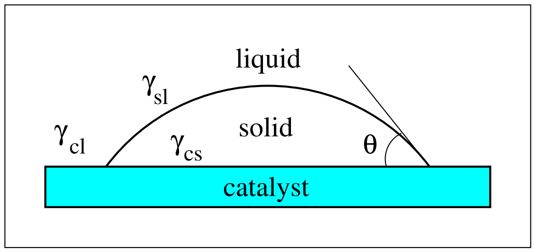
$$\left.\frac{d\Delta G(r)}{dr}\right|_{r^*} = 0 \quad \Rightarrow \; r^* = \frac{2\gamma_\mathrm{sl} T_\mathrm{m}}{L_\mathrm{m}\Delta T}, \quad \Delta G_0 = \frac{16\pi}{3}\gamma_\mathrm{sl}^3 \left(\frac{T_\mathrm{m}}{L_\mathrm{m}\Delta T}\right)^2.$$

- Spontaneously created crystal nuclei with $r < r*$ ($r > r^*$) tend to shrink (grow).
- Probability of nucleation is $\propto \exp\big(-\Delta G_0/k_\mathrm{B}T\big)$.
- Homogeneous nucleation typically requires $\Delta T \gtrsim 10^\circ$ C.

Heterogeneous nucleation:

Container walls or contaminant particles provide sites of nucleation with lower activation barriers. They become catalysts for crystallization.

Example worked out in [pex21]: spherical cap nucleated at planar catalyst surface.



The angle θ depends on the interfacial tensions between liquid (l), solid (s), and catalyst (c) via Young's equation, $\gamma_{sl}\cos\theta = \gamma_{cl} - \gamma_{cs}$.

The free-energy depends on the radius r of the cap and has a maximum at r_c:

$$r_c = \frac{2\gamma_{sl}T_m}{L_m\Delta T}, \quad \Delta G(r_c) = \underbrace{\frac{1}{4}(1-\cos\theta)^2(2+\cos\theta)}_{g(\theta)}\Delta G_0.$$

- $0 < g(\theta) < 1$: geometric factor,
- $g(\pi) = 1$: limit of homogeneous nucleation,
- ΔG_0: energy barrier for homogeneous nucleation.

[extracted in part from Jones 2002]