

3. Nucleation

The process of creating a new solid phase from a supersaturated homogeneous mother phase.

Kinds of nucleation

1. Primary nucleation
 - Homogeneous nucleation
 - Heterogeneous nucleation

2. Secondary nucleation
 - Contact
 - Attrition
 - Shear

3.1. The kinetics of nucleation

- Critical size

$z_c(S)$

$$\Delta G = - z k T \ln(x_{ss}/x_{eq}) + \beta \gamma z^{2/3}$$

- Solubility of small crystal

pressure different exposed to molecules between in crystal and fluid phase.

$$p^b - p^f = 2\gamma/r$$

$$\mu_b(T, p^b) = \mu_b(T, p^f) + (p^b - p^f)v_c$$

$$\mu_b(T, p^b) = \mu_b(T, p^f) + 2\gamma v_c / r$$

where v_c is the molar volume of crystal.

$$\mu_b(T, p^b) = \mu^0 + RT \ln x(r)$$

$$\mu_b(T, p^f) = \mu^0 + RT \ln x(\infty)$$

At equilibrium

$$\mu_b = \mu_{eq} = \mu^0 + RT \ln x_{eq}(r)$$

then,

$$\mu_b(T, p^b) = \mu^0 + RT \ln x_{eq}(r)$$

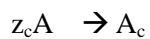
$$\mu_b(T, p^f) = \mu^0 + RT \ln x_{eq}(\infty)$$

Therefore,

$$\ln x_{eq}(r) / x_{eq}(\infty) = 2\gamma_c / rRT$$

where $x_{eq}(r)$ and $x_{eq}(\infty)$ are the equilibrium concentration of crystal size r and the infinite, respectively. This is called as Ostwald-Freundlich equation.

- Rate equation



Then, equilibrium constant, K_z , is

$$K_z = \frac{[A_c]}{[A]^{z_c}}$$

Since K_z is expressed as , $\ln K_z = -\Delta G_c / RT$,

then,

$$[A_c] = [A]^{z_c} \exp(-\Delta G_c / RT)$$

$$J = P[A_c] = P[A]^{z_c} \exp(-\Delta G_c / RT)$$

$$= P[A]^{z_c} \exp\left(-\frac{16\gamma^3 v_c^2}{3R^3 T^3 \sigma^2}\right)$$

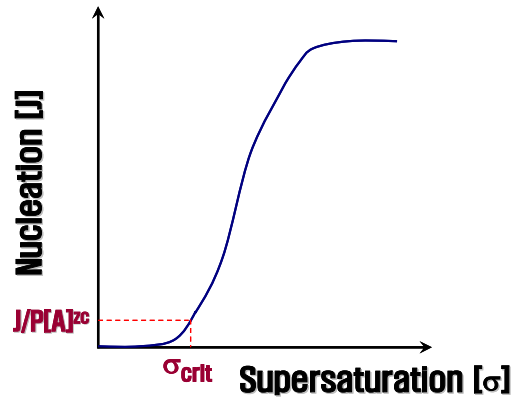
3.2 Some additional comments

- Critical supersaturation ;

The critical supersaturation, (σ_{crit}) corresponding to the boundary of metastable and labile zones is

$$J / P[A_c] = e = \exp\left(-\frac{16\gamma^3 v_c^2}{3R^3 T^3 \sigma_{crit}^2}\right)$$

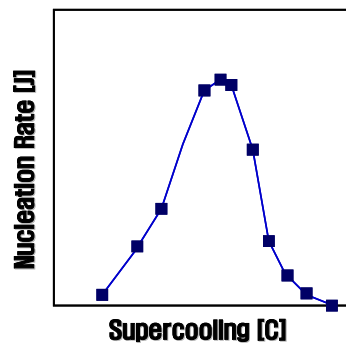
$$\sigma_{crit} = \left(\frac{16\gamma^3 v_c^2}{3R^3 T^3}\right)^{1/2}$$



- Transport resistance

$$J = P[A_c] = P[A]^{z_c} \exp(-\Delta G_c / RT + \Delta G_{tr} / RT)$$

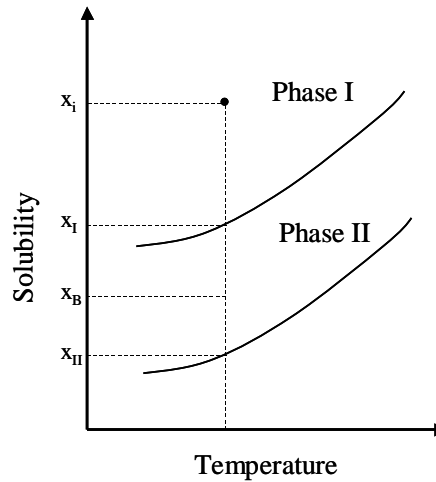
$$= P[A]^{z_c} \exp\left(-\frac{16\gamma^3 v_c^2}{3R^3 T^3 \sigma^2} + \Delta G_{tr} / RT\right)$$



3.3 Nucleation in polymorphic systems

$$J_I = K_I \exp\left(-\frac{B_I}{(\sigma_i - \sigma_x)^2}\right) \text{ for Phase-I}$$

$$J_{II} = K_{II} \exp\left(-\frac{B_{II}}{\sigma_i^2}\right) \text{ for Phase-II}$$



Here, define some lump parameters (Cardew and Davey, 1993)

$$a = \frac{\sigma_x}{B_{II}^{1/2}}$$

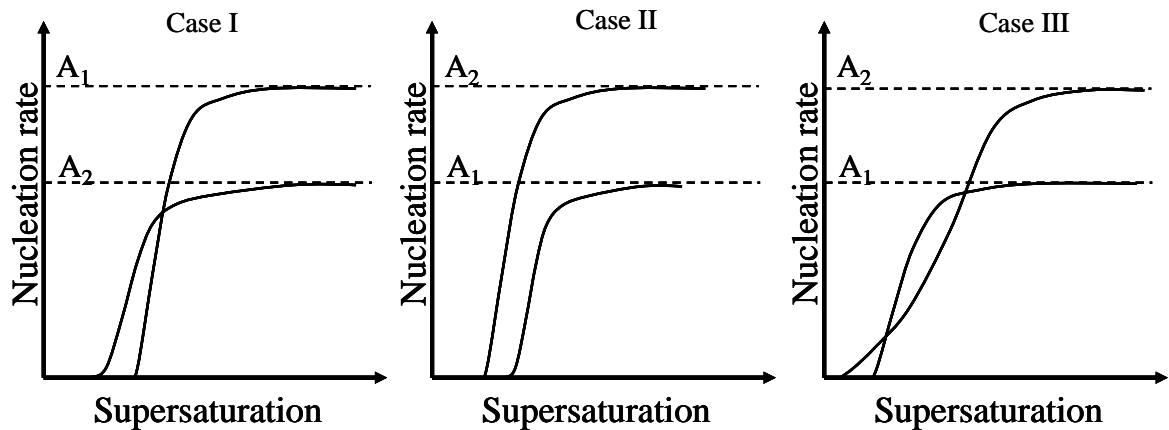
$$b = \frac{B_I}{B_{II}}$$

$$c = \left[\frac{a}{\ln\left(\frac{K_{II}}{K_I}\right)}\right]^{1/3}$$

Case I: $K_I > K_{II}$, above some value of supersaturation, the metastable phase 1 has the higher nucleation rate whereas below this value the stable phase 2 appears more rapidly.

Case II: $K_{II} > K_I$ and $(1-a/c)^3 < b$, the stable phase 2 has the higher nucleation rate at all supersaturations.

Case III: $K_{II} > K_I$ and $(1-a/c)^3 > b$, the metastable phase 1 has the higher nucleation rate only over the intermediate range of supersaturations.



3.4 Heterogeneous nucleation

- Heterogeneous surface will reduce the interfacial energy required for producing stable solids.
Non-oriented adsorption of solutes on the heterogeneous surface
Oriented adsorption of solutes on the heterogeneous surface having similar structure with solute crystals (epitaxial effect)

3.5 Secondary nucleation

- Crystal surfaces will provide the best condition for the crystal nucleation on the surface having identical epitaxial structure.
- Nucleation rate is

$$B = k_b M_T^j N^k \Delta C^b$$

where M_T is magma density, N agitation speed, ΔC is concentration driving force.