결정화기술 연구회

결정화분리기술 사업단

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Introduction

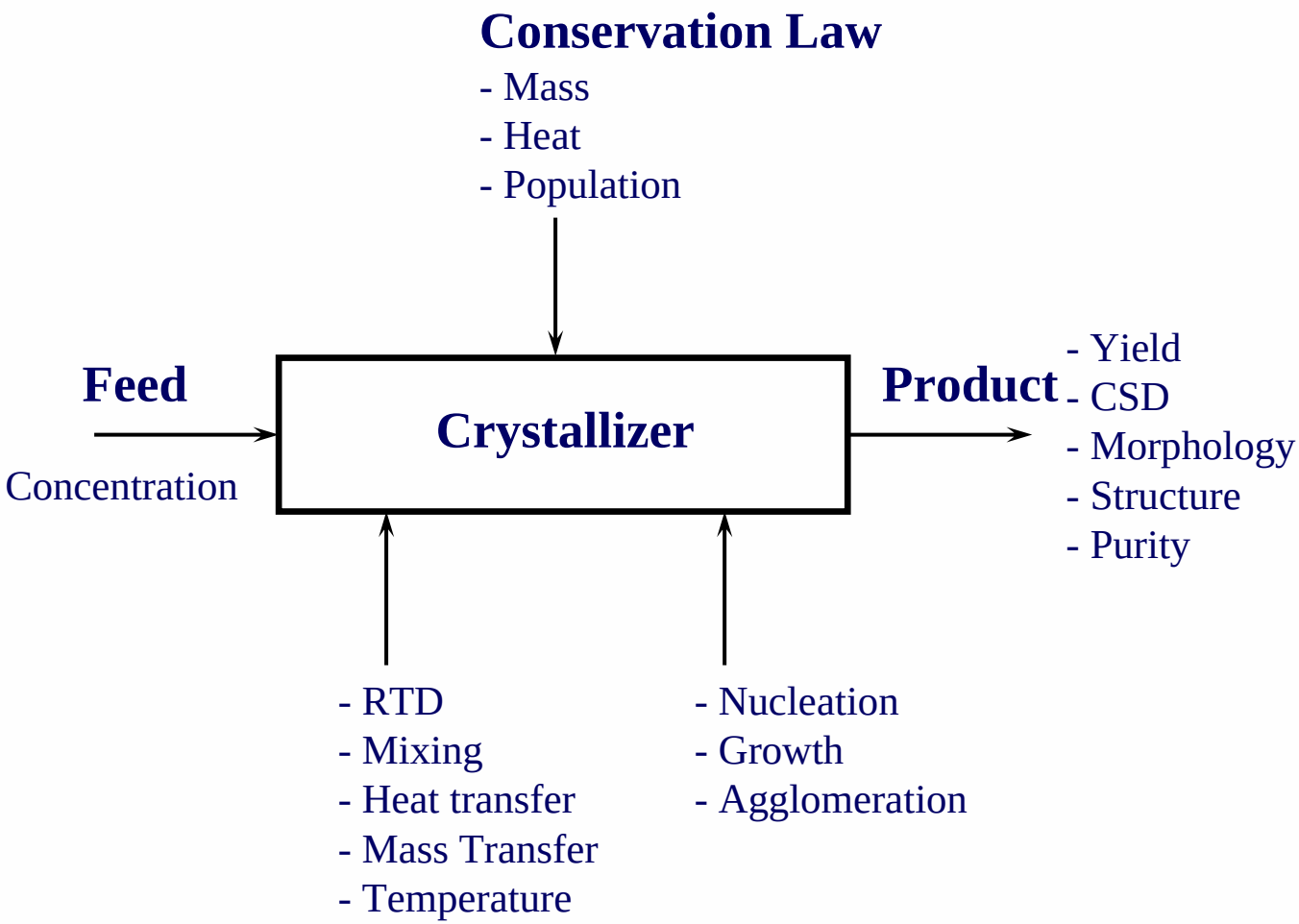
Why crystallization?

- The constituent atoms, ions or molecules of a crystal are arranged in a regular infinite manner.
  → **self-assembly**
- Crystals allow only similar molecular-scale growth units to attach themselves to the crystal lattice.
  → **molecular recognition**
- **Crystallization :**
  - purification technique
  - separation process
  - particle technology
- **Scale of crystals :**
  - nano-meter : catalyst, active metals
  - submicro-meter : pigment, silver halide, pharmaceuticals
  - millimeter : salt, sugar, diamond, quartz

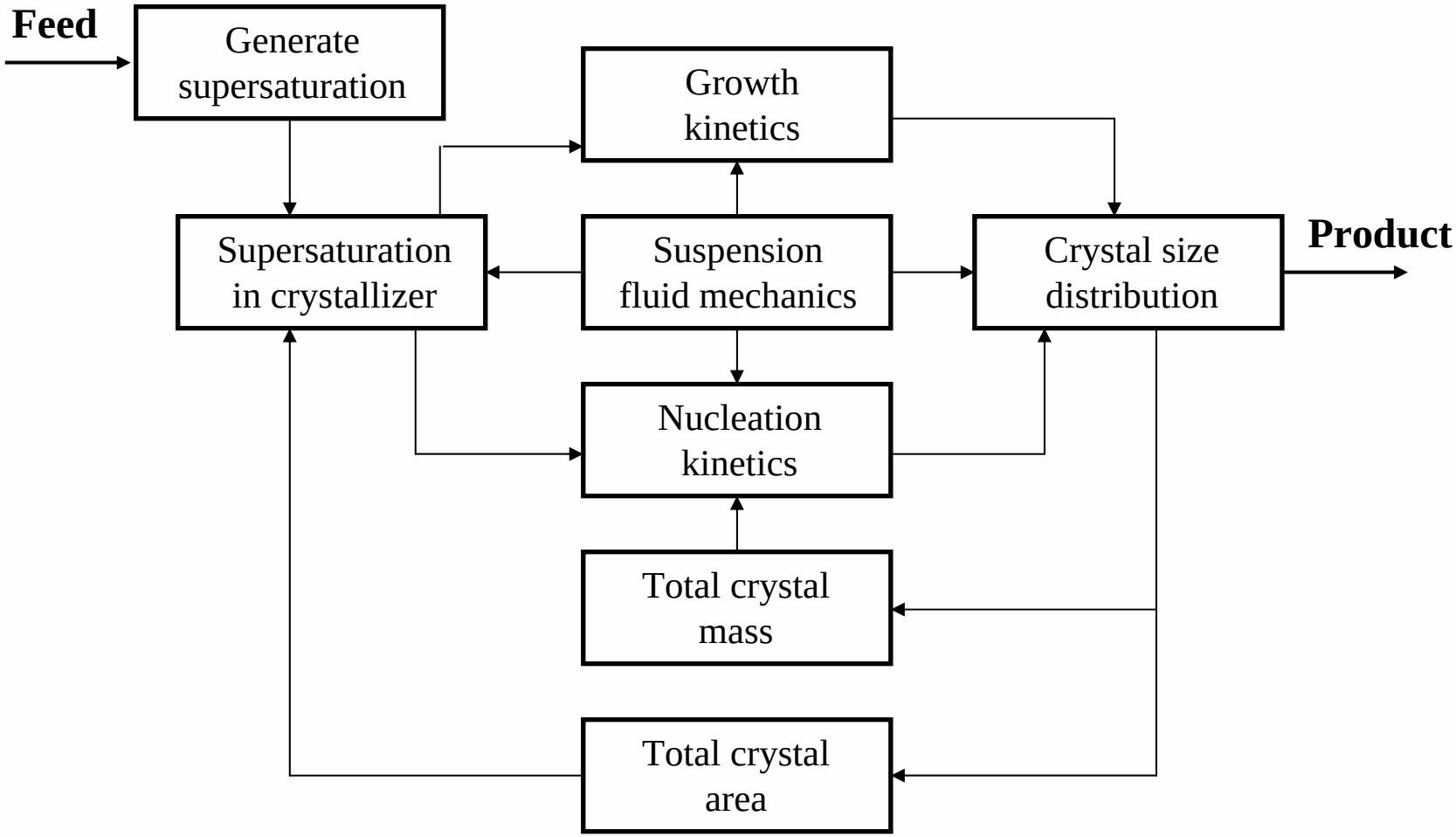
What do we need to know?

- ***Thermodynamics***
  - Phase equilibrium : solid-liquid, solid-solid, liquid
- ***Kinetics***
  - Crystal nucleation
  - Crystal growth
  - Crystal agglomeration/breakage
- ***Process***
  - Reaction
  - Mass transfer
  - Heat transfer
  - Mixing
  - Flow rate

➢ Framework for designing crystallizer behavior



➢ Interaction influencing crystallizer behavior



What are crystals and how do we recognize them.

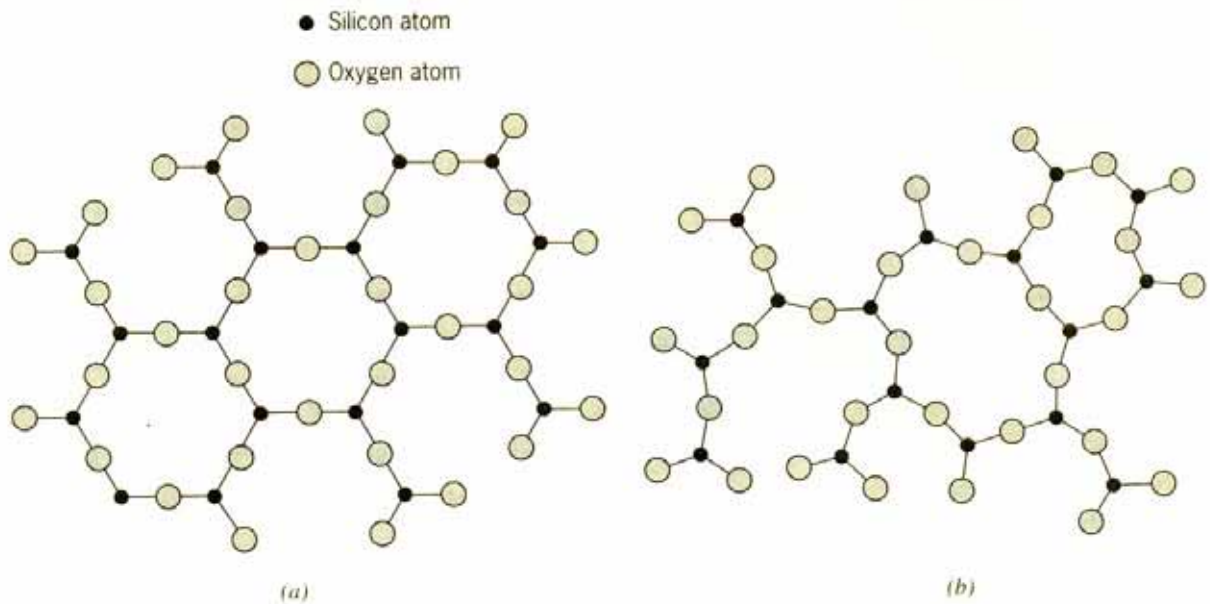
◆ **Solid defined by way of constituent packing**

- Crystalline : single crystal, poly-crystal

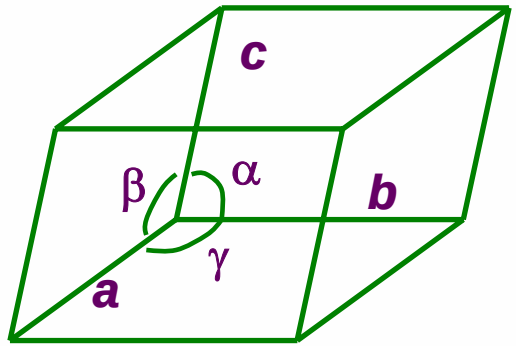
Long-range order + short-range order

- Amorphous :

Short-range order

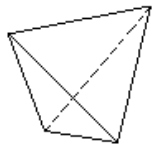


◆ **Space group : six parameter to define three dimensional space of unit cell**

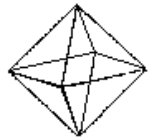


Crystal system (7 systems)

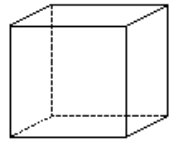
- Cubic	($a=b=c$)	($\alpha=\beta=\gamma=90^o$)
- Hexagonal	($a=b\neq c$)	($\alpha=\beta=\gamma=90^o$)
- Tetragonal	($a=b\neq c$)	($\alpha=\beta=90^o$, $\gamma=120^o$)
- Rhombohedral	($a=b=c$)	($\alpha=\beta=\gamma\neq90^o$)
- Orthorhombic	($a\neq b\neq c$)	($\alpha=\beta=\gamma=90^o$)
- Monoclinic	($a\neq b\neq c$)	($\alpha=\gamma=90^o\neq\beta$)
- Triclinic	($a\neq b\neq c$)	($\alpha=\beta=\gamma\neq90^o$)



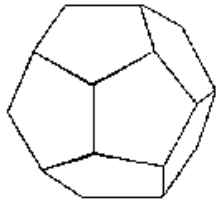
Tetrahedron (4)



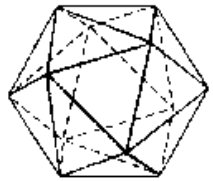
Octahedron (6)



Cube (8)

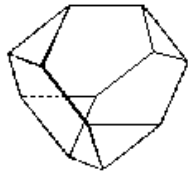


Pentagonal Dodecahedron (20)

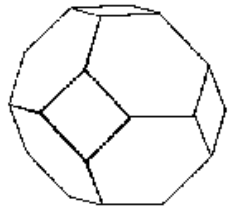


Icosahedron (20)

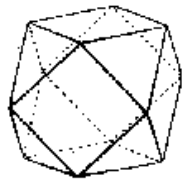
The regular solid polyhedra



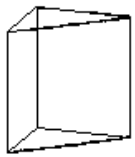
Truncated Tetrahedron (12)



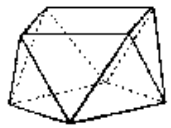
Truncated Octahedron (24)



Cuboctahedron (12)



Trigonal prism (5)

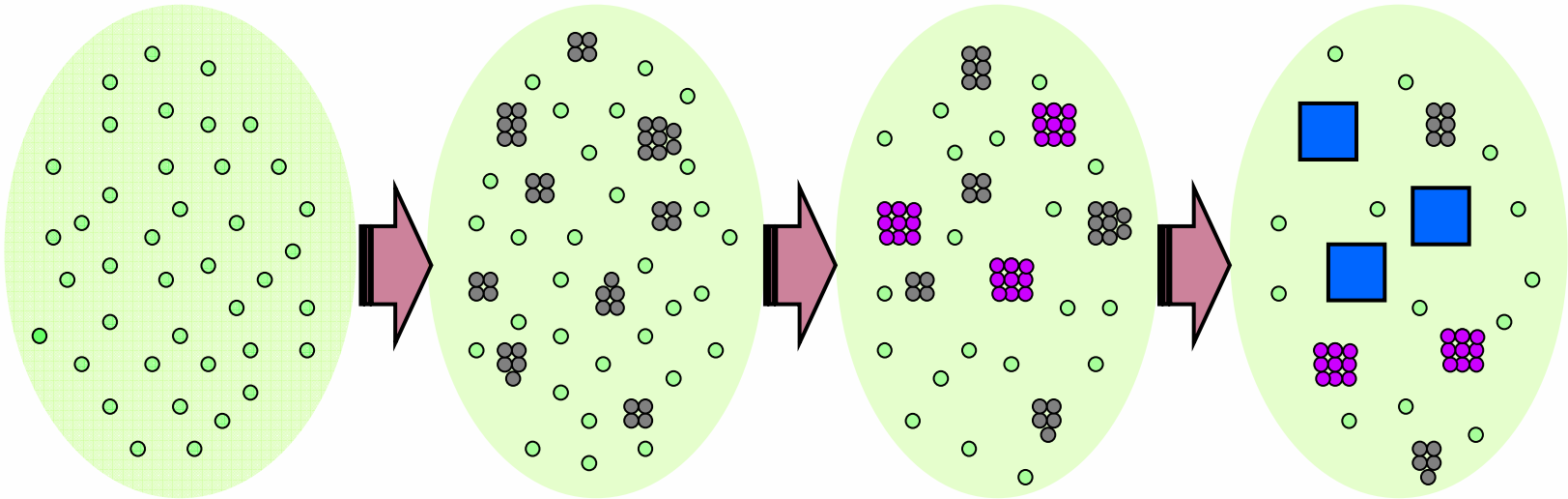


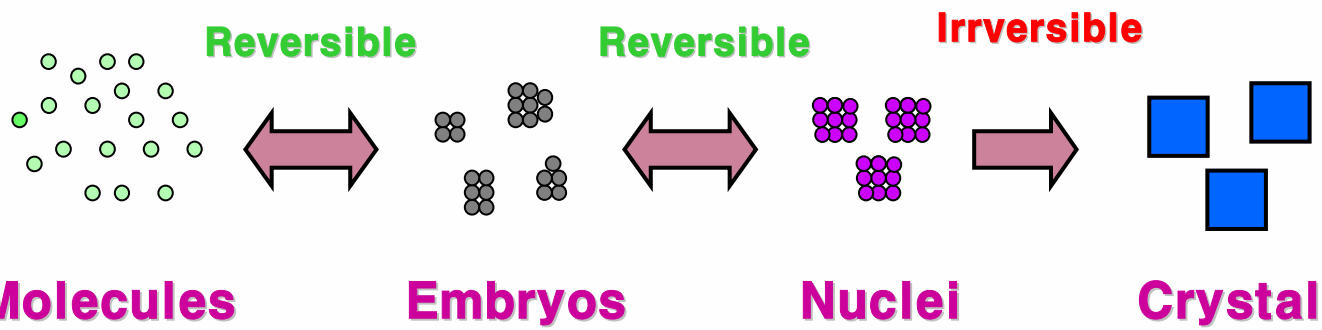
Squara Antiprism (8)

Archimedean semi-regular solid polyhedra

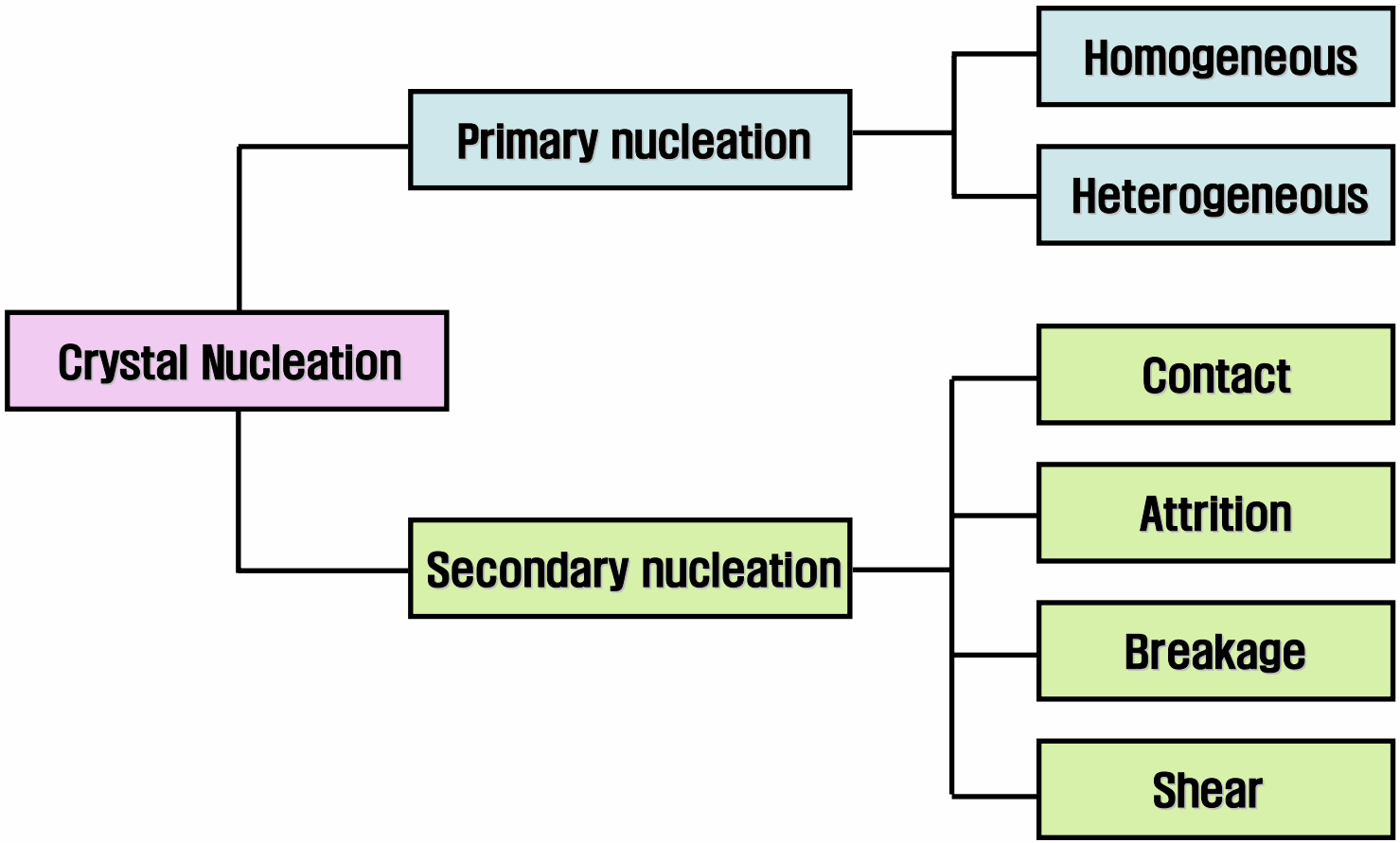
Crystal Nucleation

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





◆ Classification of Nucleation



◆ Homogeneous Nucleation

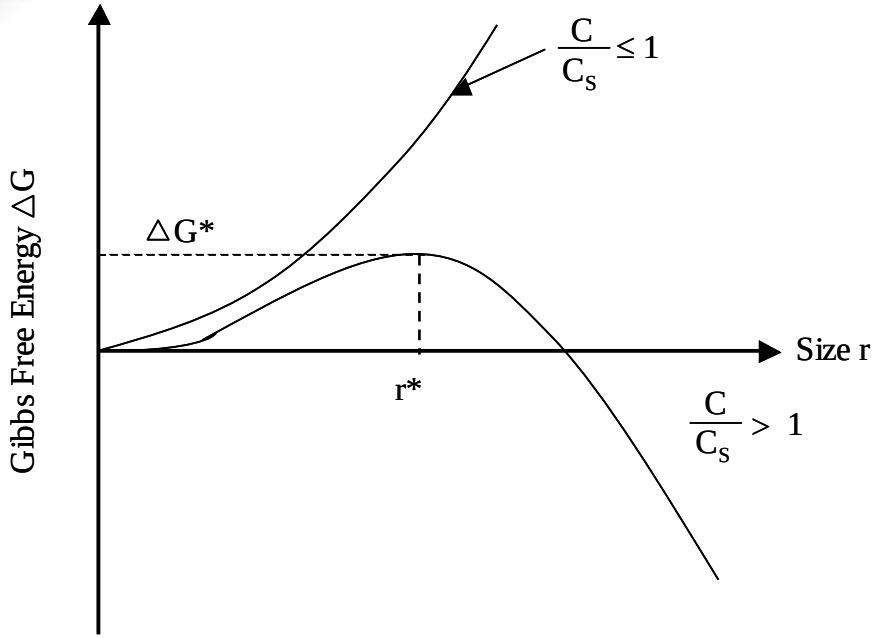
$$\Delta G = V \Delta G_V + A \Delta G_A$$

$$\Delta G_A = \sigma$$

$$\Delta G_V = - (kT / V_M) \ln(a / a_0)$$

If embryo were spherical,

$$\Delta G = - 4/3 \pi r^3 (kT / V_M) \ln(C / C_S) + 4 \pi r^2 \sigma$$



Maximum point is

$$\Delta G^* = 16 \pi \sigma^3 / 3 \left((k T / V_M) \ln(C/C_S) \right)^2$$

$$\text{at} \quad r_C = 2 \sigma / (k T / V_M) \ln(C/C_S)$$

◆ Nucleation Rate

$z_c A \rightarrow A_c$

Then, equilibrium constant, K_z, is

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

Since K_z is expressed as, $lnK_z = -\Delta G^* / RT$, then

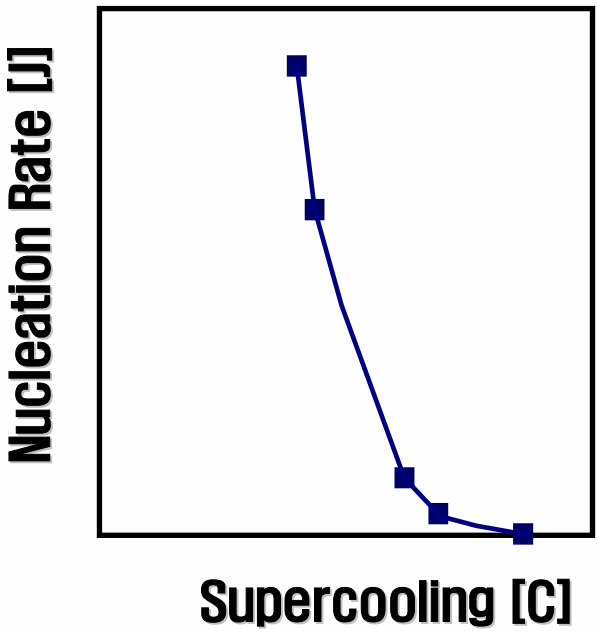
$$[A_c] = [A]^{zc} \exp(-\Delta G^* / RT)$$

If $J \sim [A_c]$, then

$$J = P[A_c] = P[A]^{zc} \exp(-\Delta G^* / RT)$$

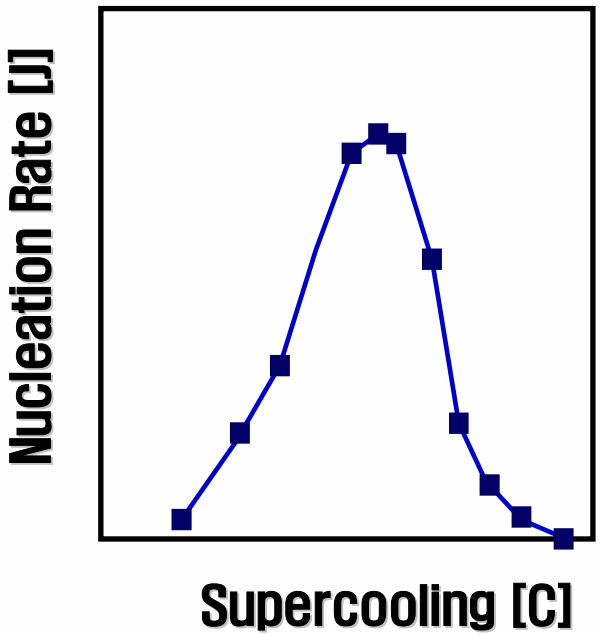
◆ Transport Resistance to Nucleation

Without transport resistance



$$J = P[A]^{zc} \exp(-\Delta G^{*}/RT)$$

With transport resistance



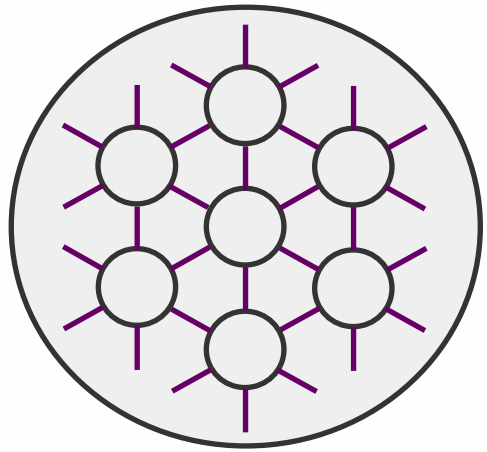
$$J = P[A]^{zc} \exp(-\Delta G^{*}/RT + \Delta G_{tr}/RT)$$

Solubility of small crystal

◆ Interfacial tension = Pressure different exposed to molecules between in crystal and fluid phase.

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

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



At equilibrium

$$\mu_b\,(T, p^b) = \mu_0 + RT\,ln\,C_{eq}(r)$$

$$\mu_b\,(T, p^f) = \mu_0 + RT\,ln\,C_{eq}(\infty)$$

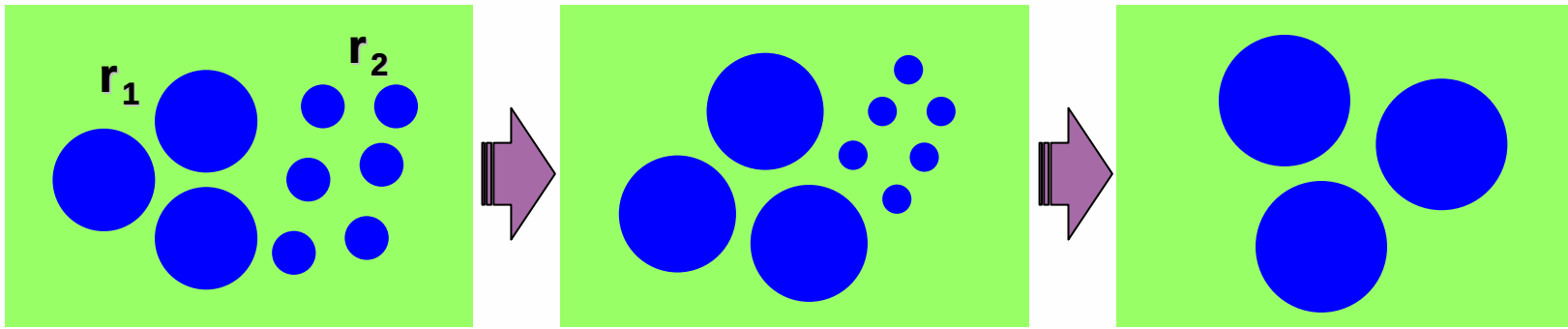
Then,

$$ln\,C_{eq}(r)\,/C_{eq}(\infty) = 2\gamma / RTr$$

Ostwald-Freundlich Equation

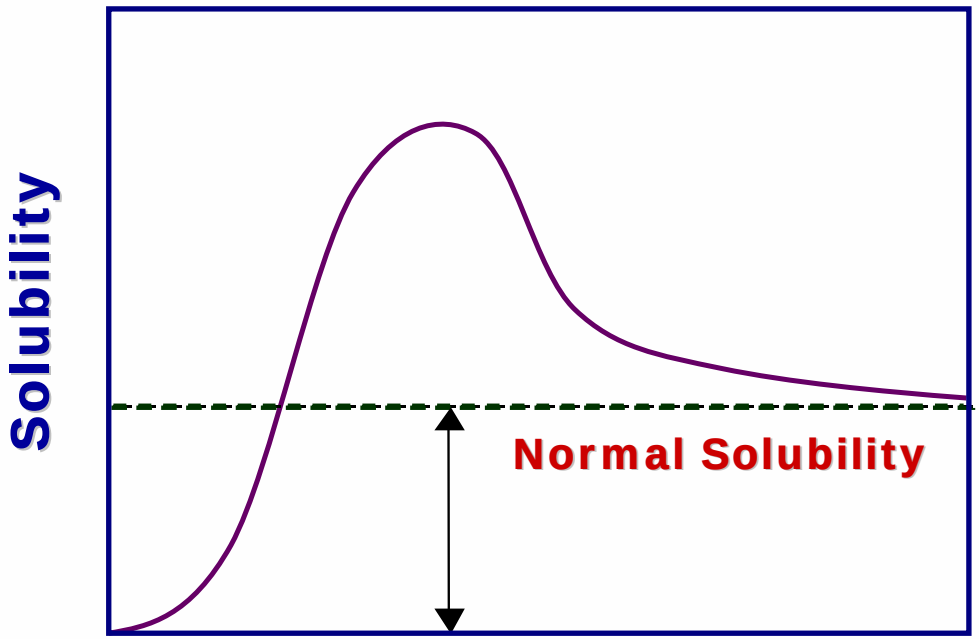
◆ **Solid-Liquid Equilibrium**

$$C_s(r_1) < C_s(r_2)$$



Ostwald Ripening !!!

◆ Solid-Liquid Equilibrium

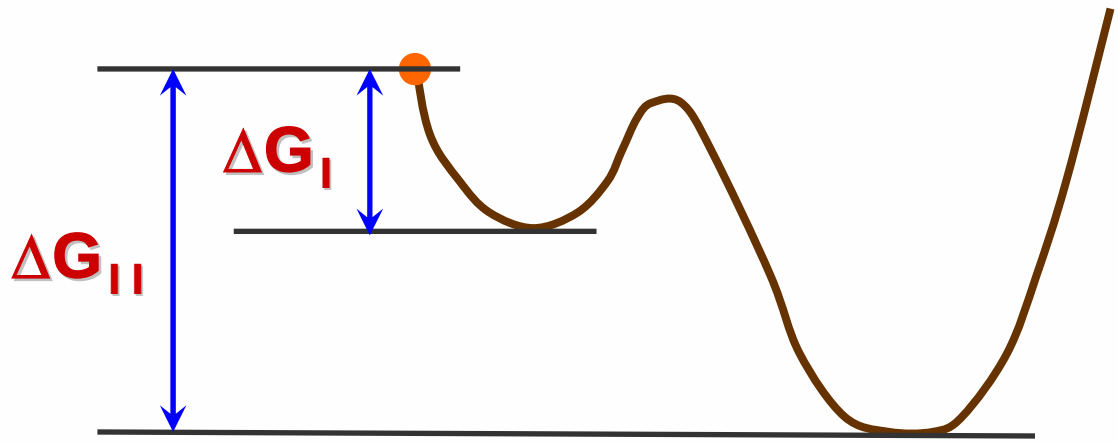


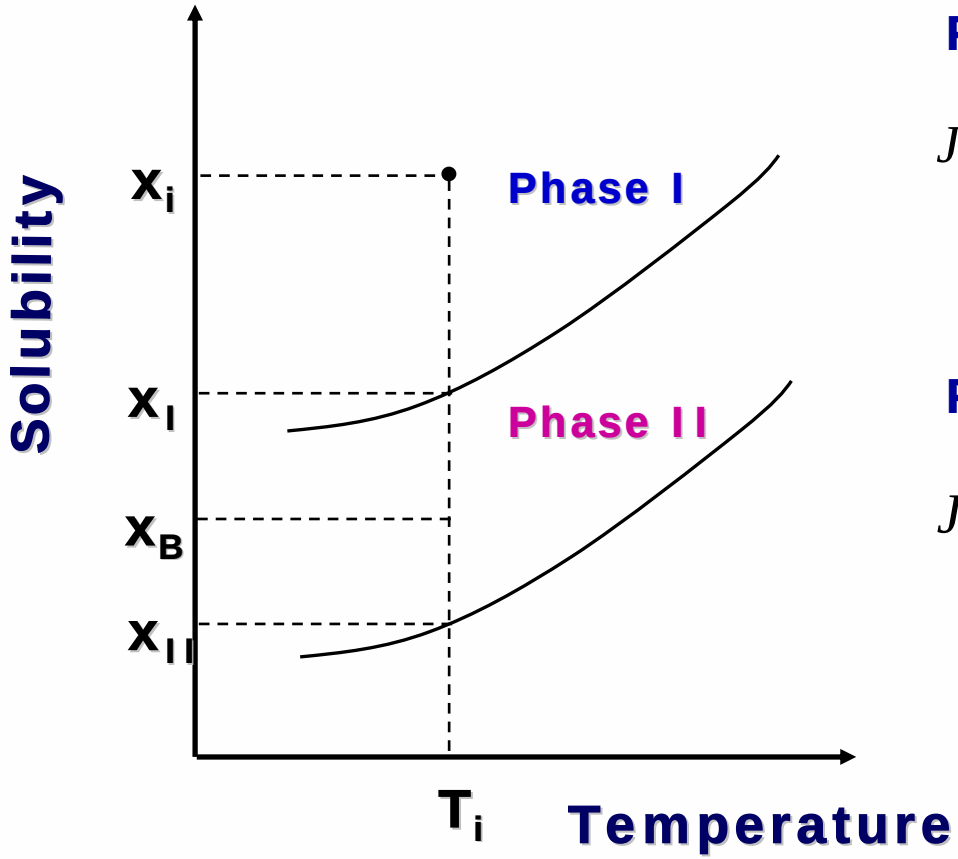
$$\frac{C_S(r)}{C_S(\infty)} = \exp\left(\frac{A}{r} - \frac{B}{r^4}\right)$$

Nucleation in Polymorphic System

Rule of Stages (Ostwald) :

- A crystallizing system progresses from supersaturated state to equilibrium in stages, each stage representing the smallest possible change in free energy.



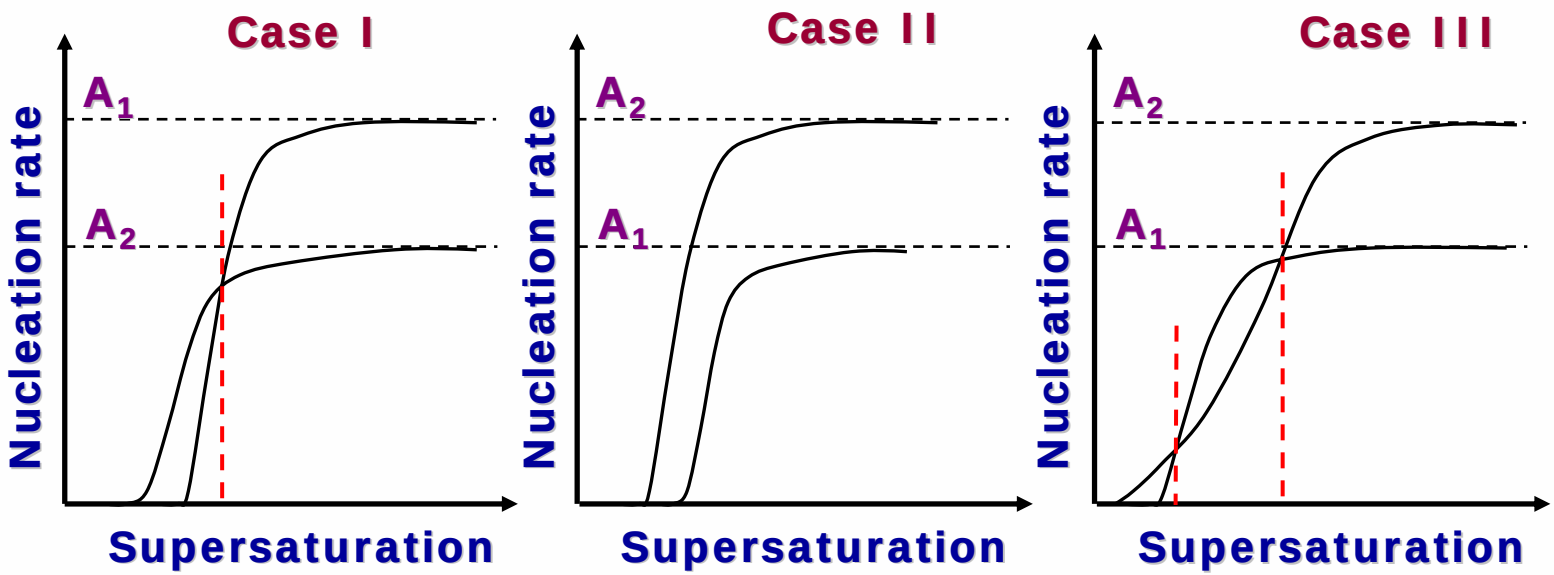


For Phase-I

$$J_I = K_I \exp(-\frac{B_I}{(\sigma_i - \sigma_x)^2})$$

For Phase-I

$$J_{II} = K_{II} \exp(-\frac{B_{II}}{\sigma_i^{\,2}})$$


Case I
Nucleation rate
A1
A2
Supersaturation
Case II
Nucleation rate
A2
A1
Supersaturation
Case III
Nucleation rate
A2
A1
Supersaturation

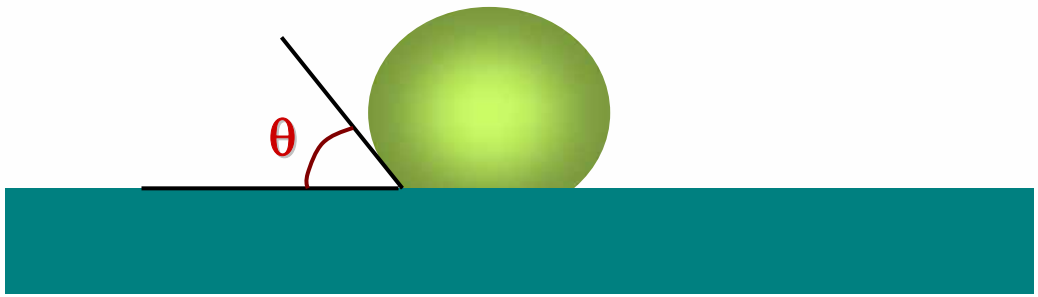
Heterogeneous Nucleation

- Heterogeneous surface will reduce the interface energy required for producing stable solid.

$$J_{homo} = P[A]^{zc} \exp(-\Delta G^* / RT)$$

$$J_{hetero} = P'[A]^{zc'} \exp(-\Delta G^{**} / RT)$$

$$\Delta G^{**} = \phi \Delta G^*, \text{ where } \phi = \{(2+\cos\theta)(1-\cos\theta)^2\}/4$$



➢ Heterogeneous surface conditions

- ✓ Non-oriented adsorption
- ✓ Oriented adsorption (Epitaxial Effect)

Secondary Nucleation

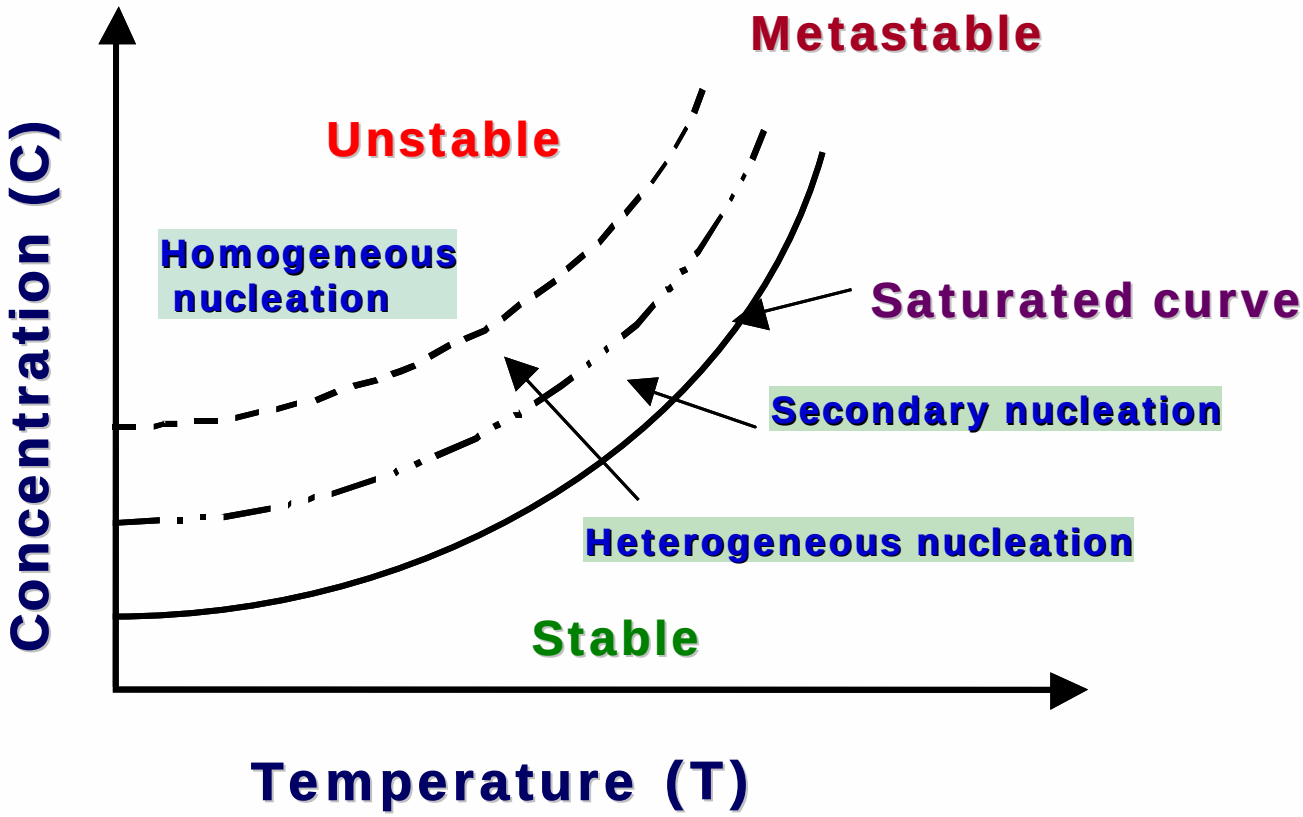
- Nucleation on crystal surface providing the best condition for the crystal nucleation by virtue of identical epitaxial structure.

$$J_{sec} = k_b M_T^j N^k \Delta C^b$$

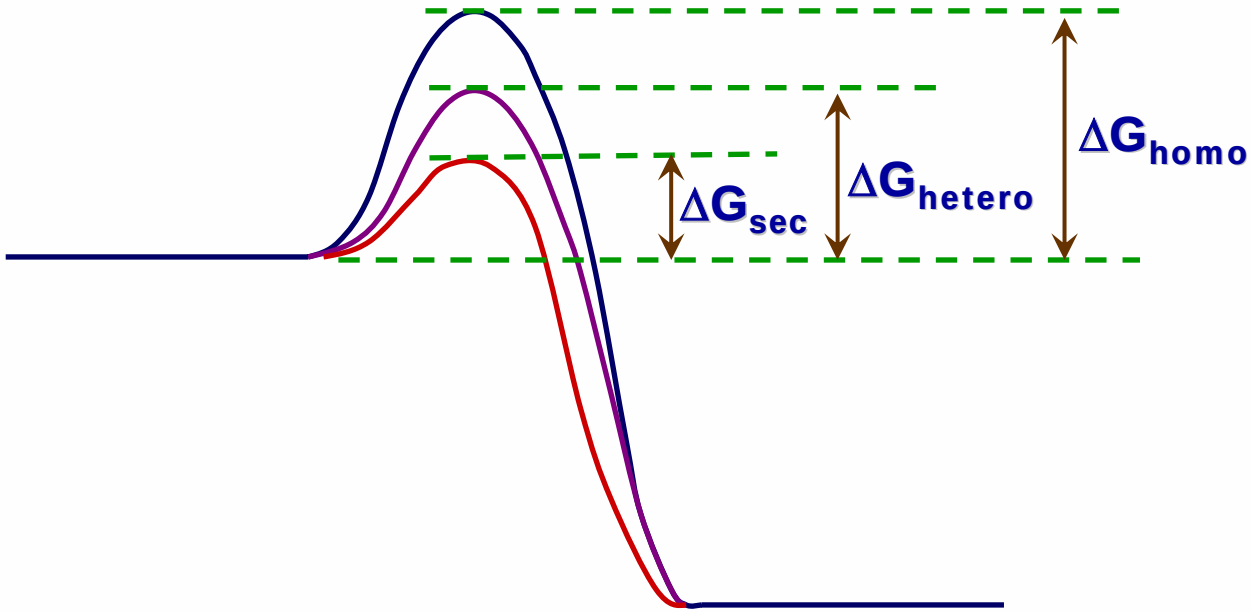
k_b : Nucleation coeffecient

M_T : Magma density
(Solid mass per unit volume of suspension)

N : Agitation speed [rpm]


Metastable
Unstable
Homogeneous nucleation
Saturated curve
Secondary nucleation
Heterogeneous nucleation
Stable
Concentration (C)
Temperature (T)

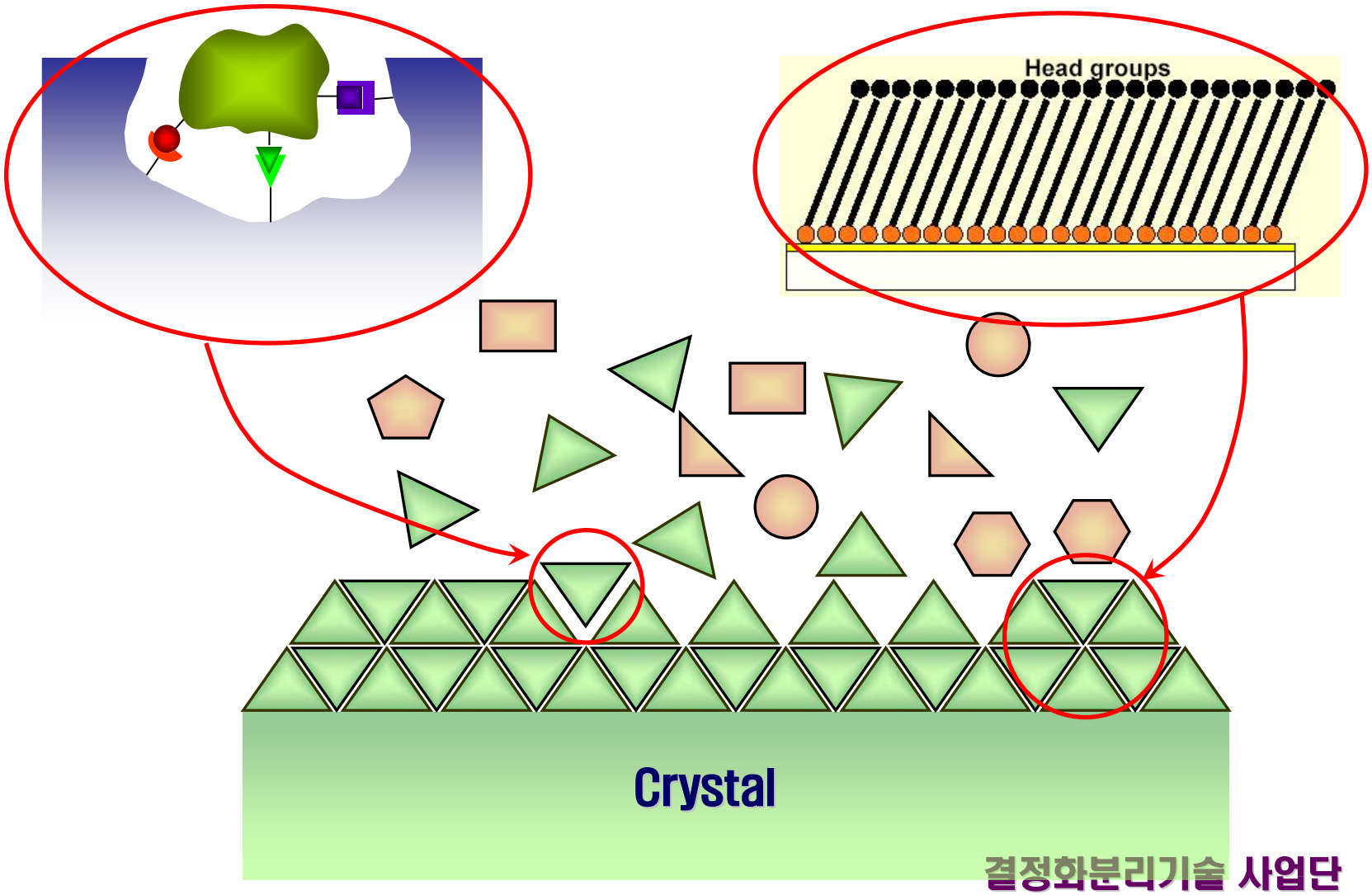
Energy Barrier for Nucleation



Crystal Growth

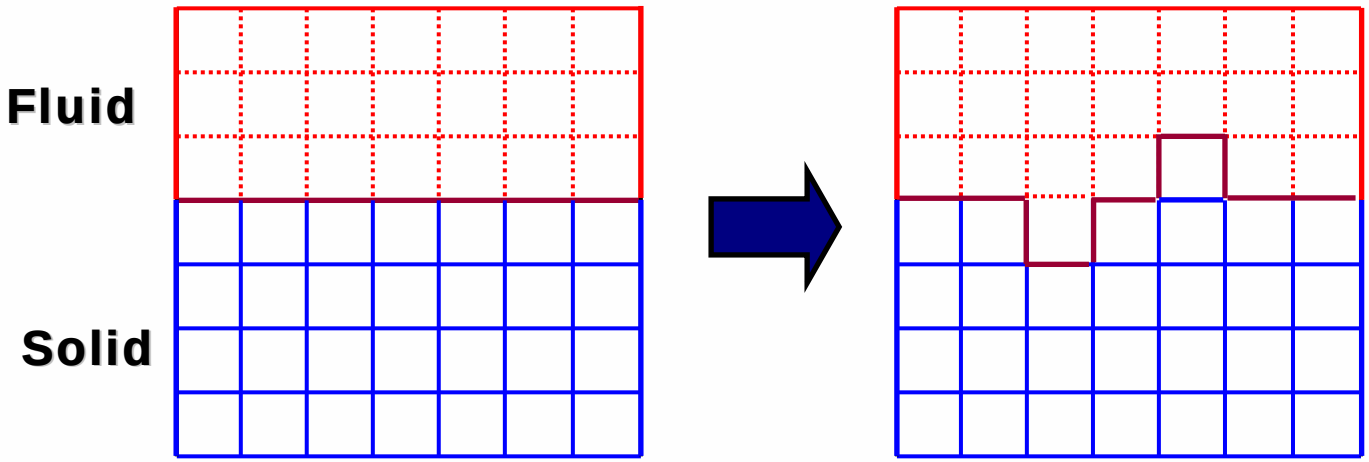
➢ Molecular Recognition

➢Self Assembly



Multilayer Model (Tempkin, 1966)

➢ **Energy change by molecular growth**



$$\Delta E = 2\phi_{ss} + 2\phi_{ff} - 4\phi_{sf}$$

ϕ_{ss} = Binding energy between solid-solid

ϕ_{ff} = Binding energy between fluid-fluid

ϕ_{sf} = Binding energy between solid-fluid

Dimensionless parameter, α

$\alpha = \Delta E / kT$

Low α : low energy to form growth sites

High α : high energy to form growth sites

✓ For vapor and melt growth

$\alpha = \xi \Delta H / RT$

✓ For solution growth

$\alpha = \xi [\Delta H_f / RT - \ln C_{eq}]$

ΔH : Heat of fusion

Growth Mechanisms

- **Continuous growth, $\alpha < 3$**

$$v = k_{CG}\sigma$$

- **Surface nucleation, $3 < \alpha < 5$**

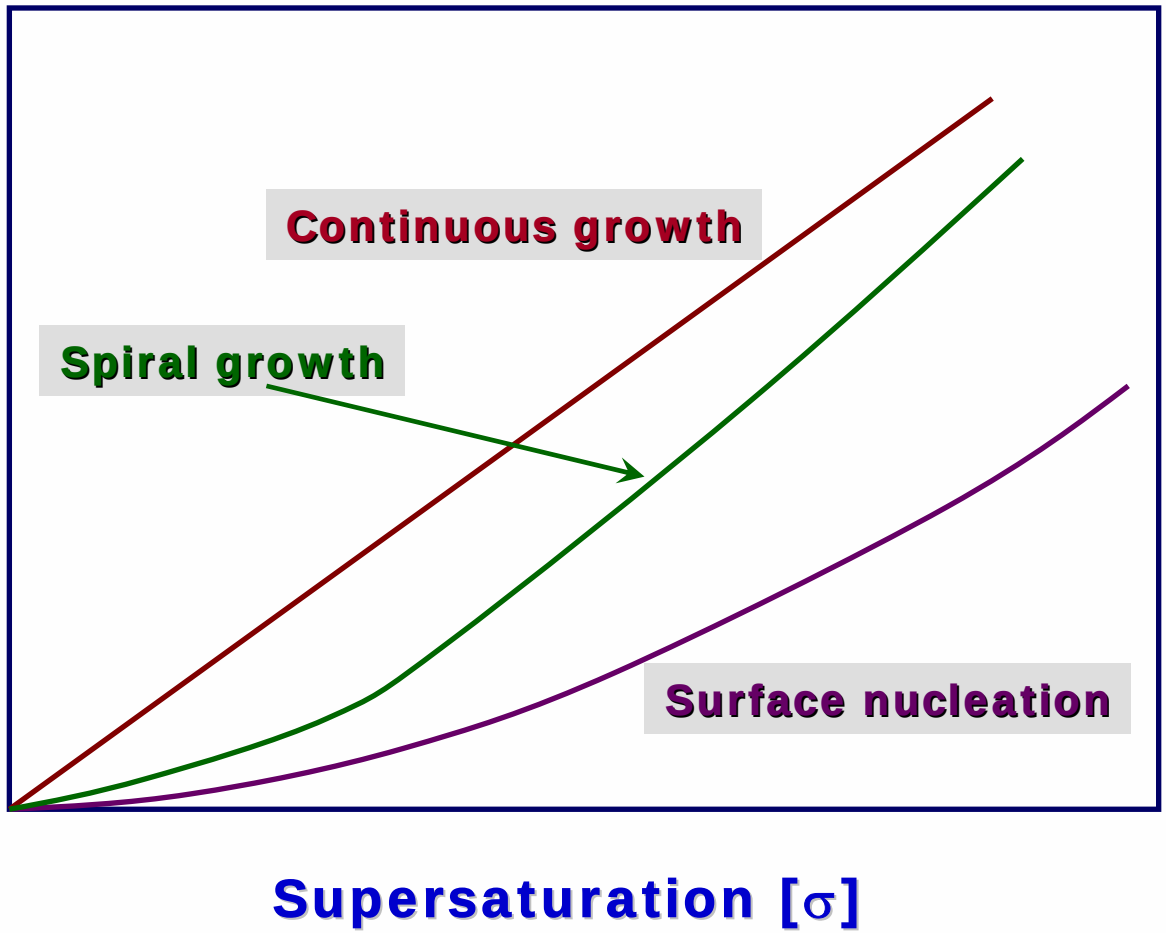
$$v = k_{SN}\sigma^{5/6}\exp[-\frac{\pi}{3\sigma}(\frac{\gamma_e}{kT})^2]$$

- **Spiral growth, $5 < \alpha$ (BCF model)**

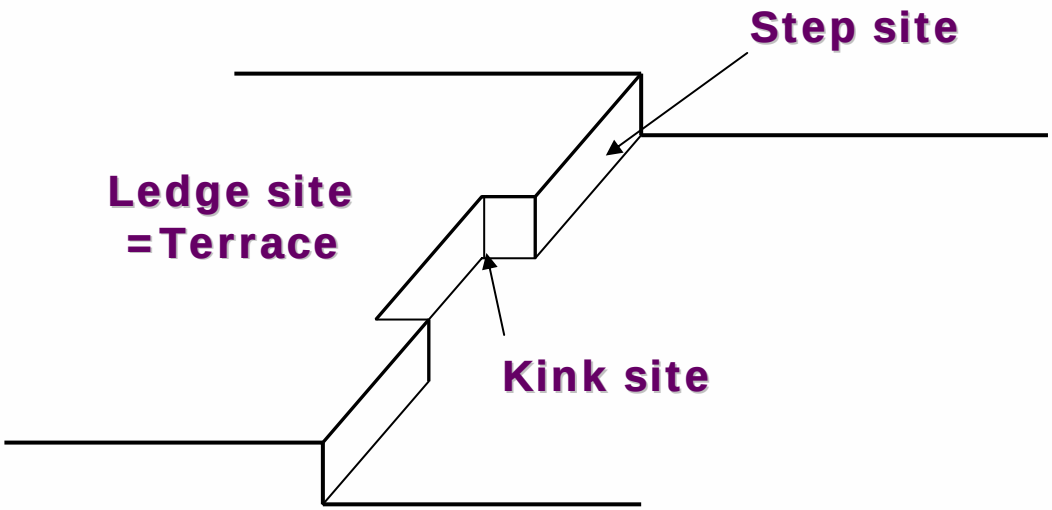
$$v = k_{SG}\frac{\sigma^2}{\sigma_1^2}\tanh(\frac{\sigma_1}{\sigma}) \quad \text{where} \quad \sigma_1 \propto \frac{\gamma_e}{s}$$

If $\sigma << \sigma_1$ $\quad v \propto \sigma^2$ (parabolic growth rate)

If $\sigma_1 << \sigma$ $\quad v \propto \sigma$ (linear rate)

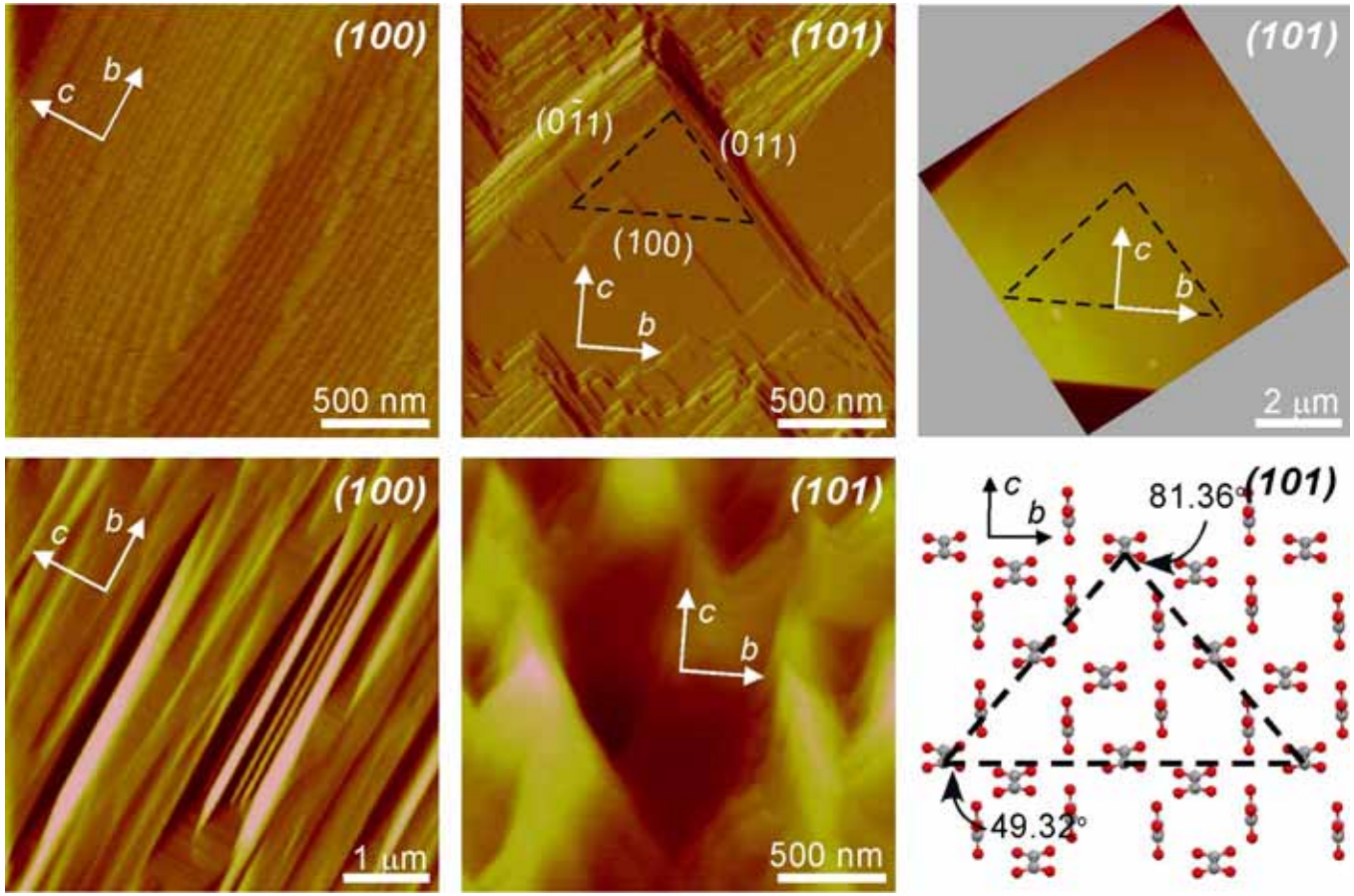

Growth Rate [ν]
Continuous growth
Spiral growth
Surface nucleation
Supersaturation [σ]

◆ BCF model



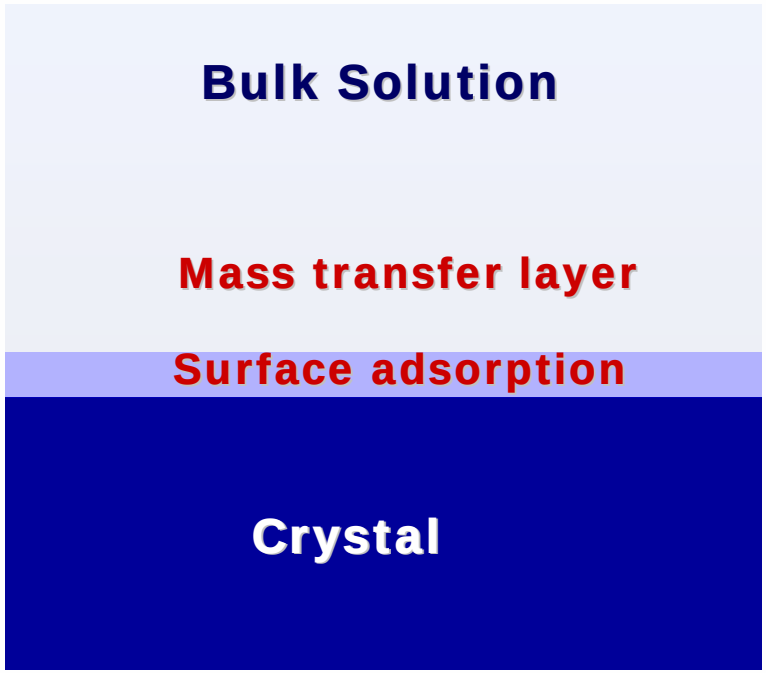
$$v_K \geq v_S \geq v_F$$

◆ Hillocks in growth and Pits in dissolution



Two Step Growth model

- Two consecutive steps for crystal growth
  - mass transfer step
  - surface integration step



$$R_G = k_d \Delta (C_\infty - C_i)$$

$$R_G = k_r \Delta (C_i - C_{eq})^r$$

Then,

$$R_G = k_r[(C_\infty - C_{eq}) - R_G / k_d]^r$$

If r = 1,

$$R_G = k_G(C_\infty - C_{eq}) \quad \text{where } 1/k_G = 1/k_d + 1/k_r$$

➢ Effectiveness factor

$$\eta_r = \frac{\text{Growth rate at interface condition}}{\text{Growth rate if interface were exposed to bulk condition}}$$

Then,

$$\eta_r = [1 - \eta_r Da]^r$$

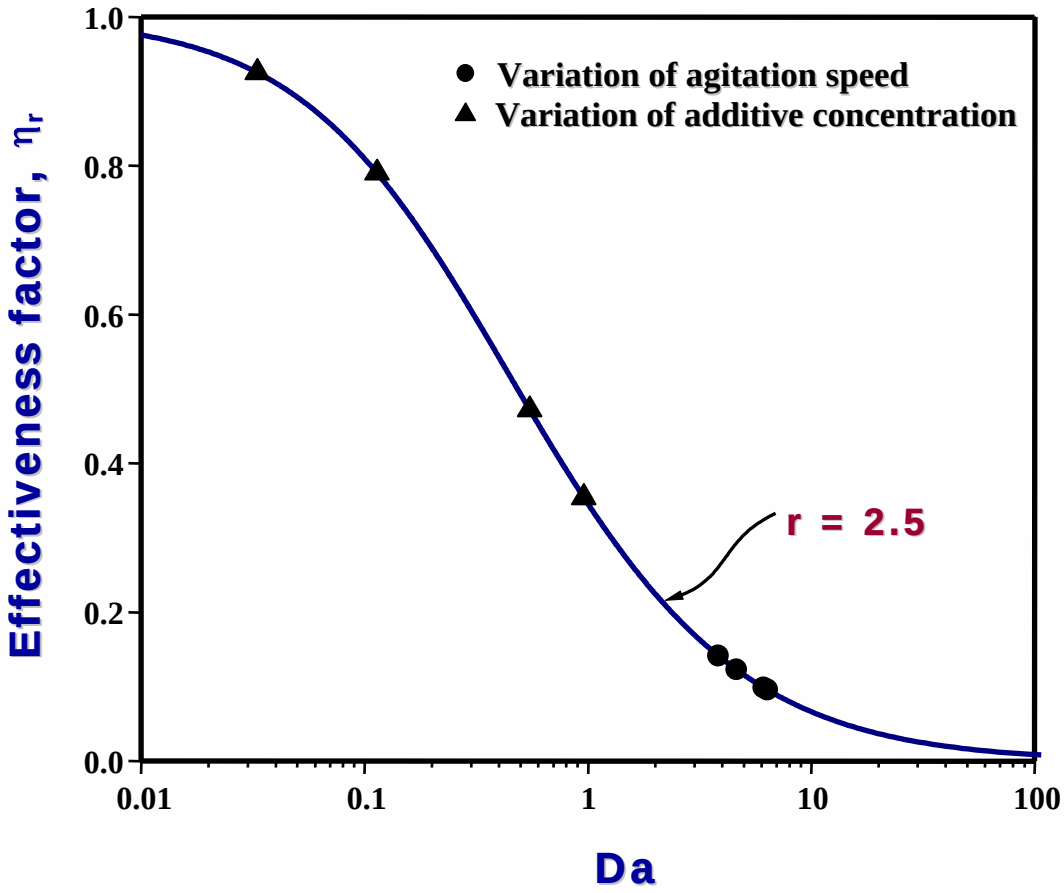
where,

$$Da = k_r[C_\infty - C_{eq}]^{r-1} / k_d$$

✓ If $Da >> 1$, $\eta_r = 0$; mass transfer controlling growth

✓ If $Da << 1$, $\eta_r = 1$; surface integration controlling growth

(Journal of Crystal Growth, 235, 529-540 (2002))



- ✓ If Da>>1, η_r=0; mass transfer controlling growth
- ✓ If Da<<1, η_r=1; surface integration controlling growth

Crystal Morphology

Morphology = Shape = Habit = Form

- **Equilibrium morphology**

  Crystal shape equilibrated with surroundings to minimize the surface free energy of crystal

  ✓ ***Atomistic lattice simulation***

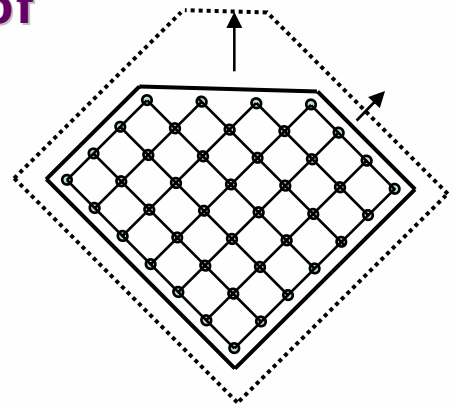
- **Growth morphology**

  Crystal shape developed in the course of crystal growth

  ✓ ***Bravais-Friedel-Dinnay-Harker***

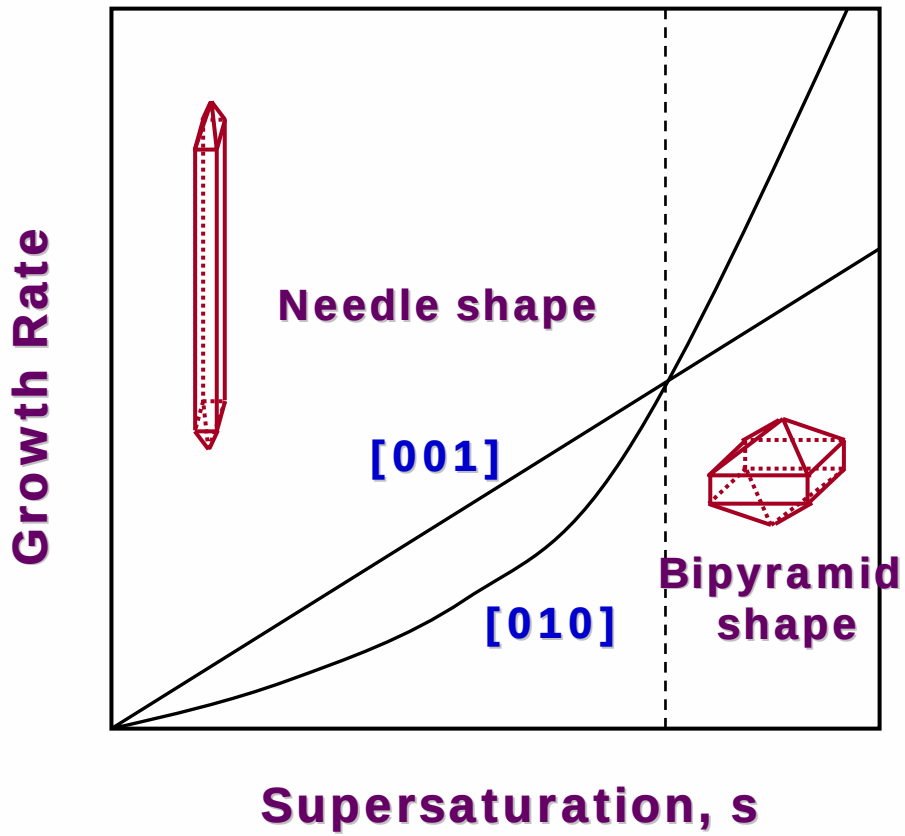
  ✓ ***Molecular mechanics***

  ✓ ***Attachment energy***

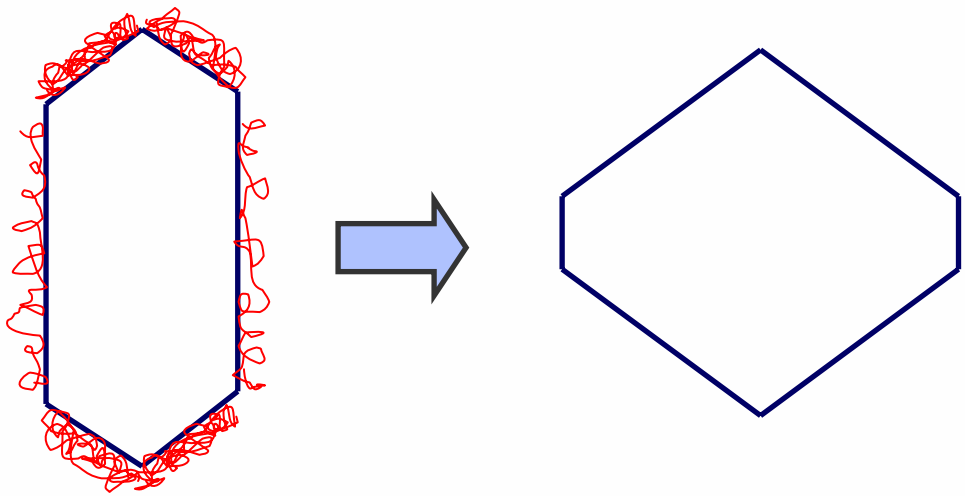


Influencing factors

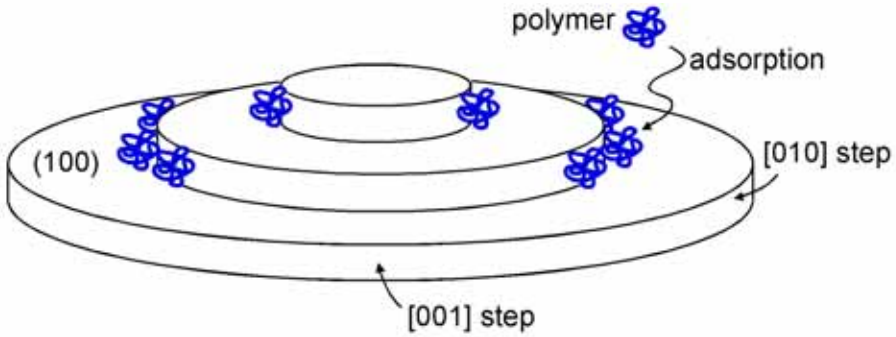
- **Supersaturation**

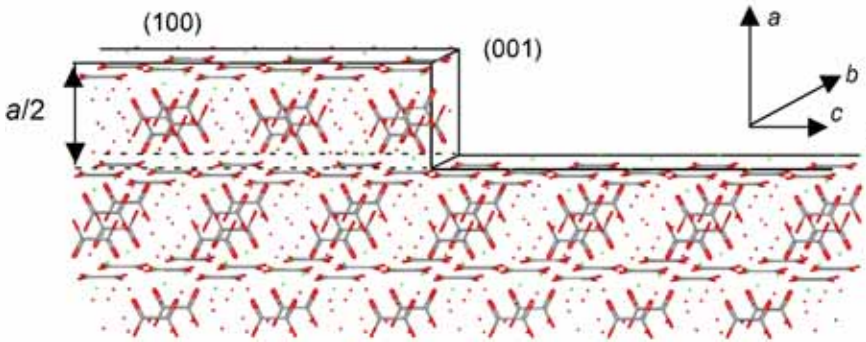


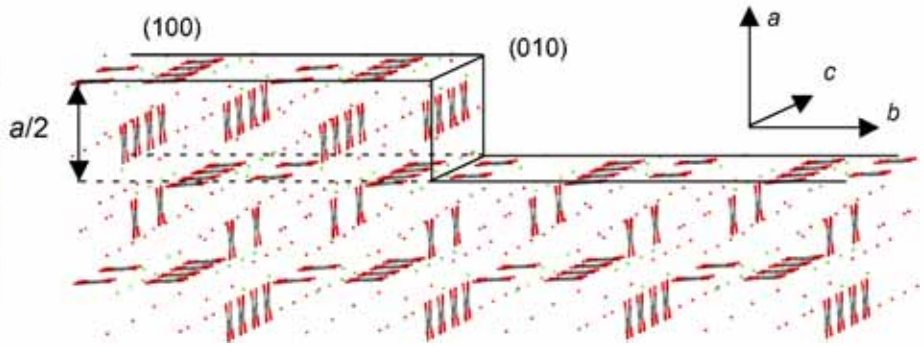
➢ Impurity & Additives



- ✓ *Molecular orientation / arrangement*
- ✓ *Selective adsorption on crystal faces*
- ✓ *Different affinity to crystal faces*







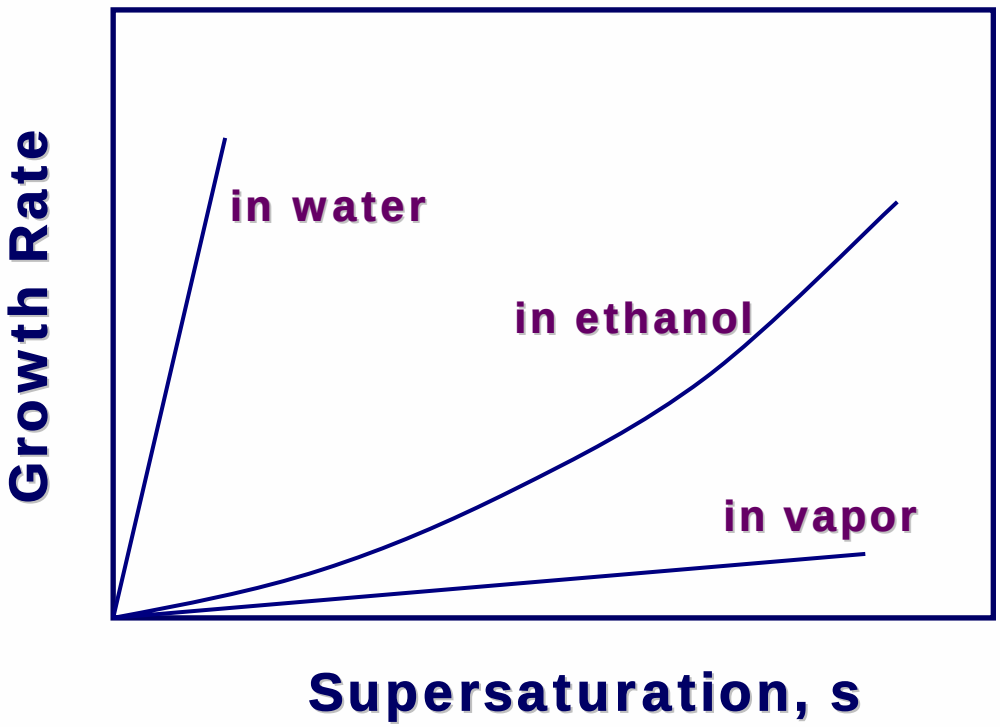
*"**Local binding** between the carboxylate side chains and calcium ions on the crystal surface is responsible for growth inhibition."*

*"**Self-replicating process of crystal growth** and **electrostatic matching** between the crystal and additives can give a clue for explaining the **step-specific binding**." **(tailor-made additive)***

➢ Solvent

The solvent will modify α in the solution crystallization.

$$\alpha = \xi\,[\Delta H_f / RT - \ln C_{eq}]$$



Crystal Purity

- Degree of purification, D_i

$$D_i = \frac{\text{Mass of impurity per mass of solute in crystal}}{\text{Mass of impurity per mass of solute in solution}}$$

  - ✓ If $D_i > 1$; no purification by crystallization
  - ✓ If $D_i < 1$; purification by crystallization

- In general, purity of crystal depends on
  - the relative size
  - the stereochemistry
  - fuctionality

  of impurity when compared with crystallizing solute.

- The more dissimilar component, the purer the crystals are likely to be

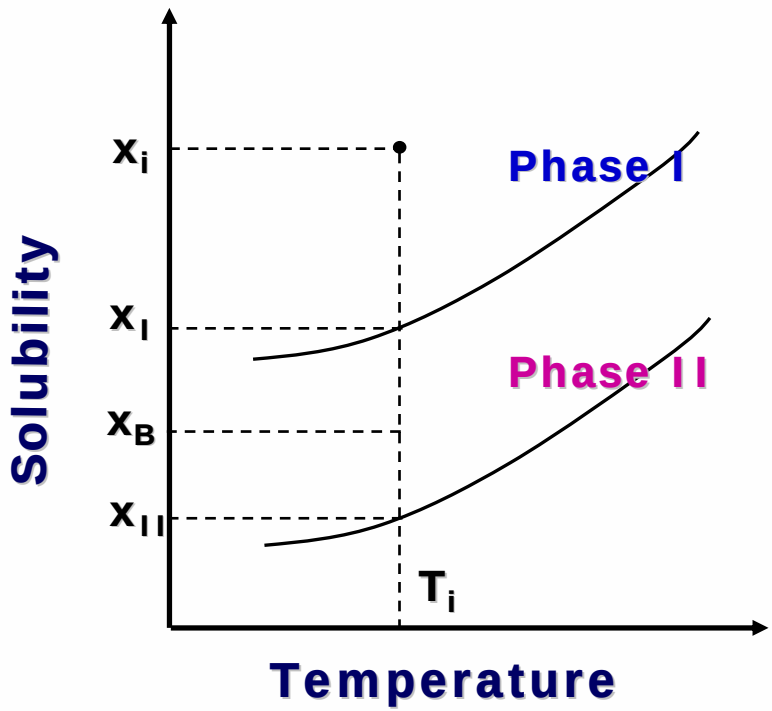
Polymorphism

- The higher driving force for the crystallization, the more polymorphic crystals in the product

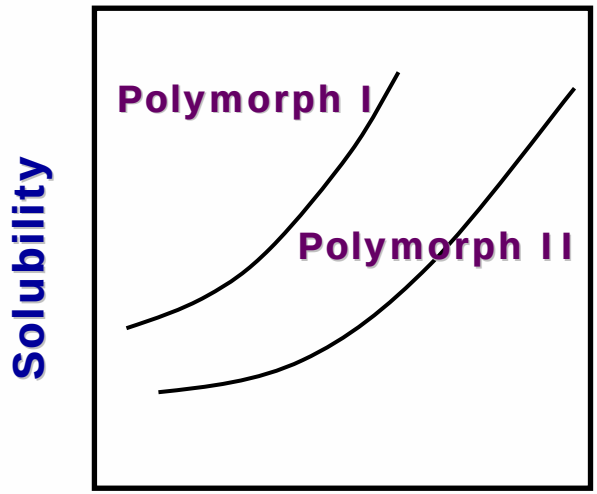
Chemical product	Number of polymorphs	Applications
Ammonium nitrate	5	Explosive, fertilizer
Aspirin	4	Pharmaceuticals
Calcium carbonate	3	Filler for plastics
Copper phthalocyanin	4	Pigment
Indigo	2	Disperse dye
Lead azide	2	Explosive
Lead chromate	2	Pigment
Pentaerythritol tetranitrate	2	Explosive
Phenobarbitone	13	Pharmaceuticals
Sorbitol	2	Sweetener
Sulphathiazole	4	Pharmaceuticals
Tetraethyl lea	6	Fuel additive
Titanium oxide	3	Pigment
Titanium trichloride	4	Catalyst
Tirglycerides	4	Fats and oils

➢ Chemical potentials between two polymorphs

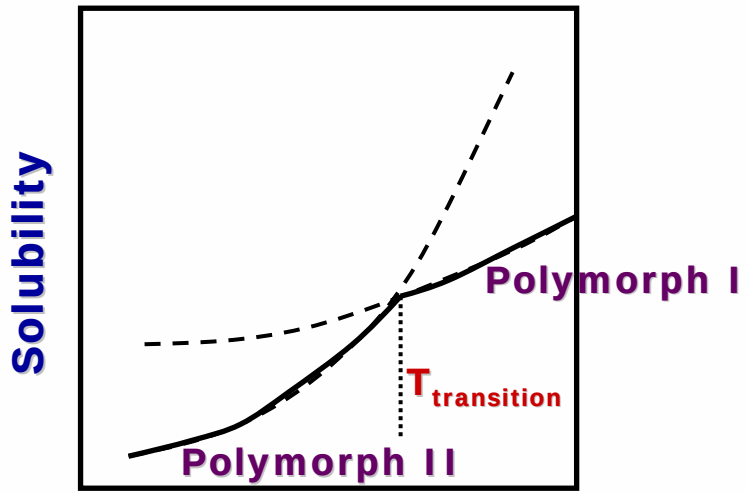
If $\mu_{solid}(II) < \mu_{solid}(I)$,
phase II is more stable than phase I and
$C_{eq}(II) < C_{eq}(I)$.



- **Monotropic Transformation (irreversible)**
  - ✓ relative solubility of polymorphs independent of temperature
- **Enantiotropic Transformation (reversible)**
  - ✓ relative solubility of polymorphs dependent on temperature



Monotropic



Enantiotropic

➢ Phase Transformation

✓ **Reconstructive transformation**

(= Solvent-mediated transformation)

recrystallization in solution

✓ **Displacive transformation**

(= Solid-state transformation)

transformation solid state

✓ **Order-disorder transformation**

$\Delta G = \Delta H - T\Delta S$

If endothermic ($\Delta H < 0$), $\Delta S > 0$ (disordered)

➢ Reconstructive transformation

✓ **Supersaturation for growth of phase-II**

$$\sigma = \frac{(x - x_{II})}{x_{II}}$$

✓ **Potential for phase transformation**

$$\sigma_{I,II} = \frac{(x_I - x_{II})}{x_{II}}$$

✓ **Dissolution rate of phase-I**

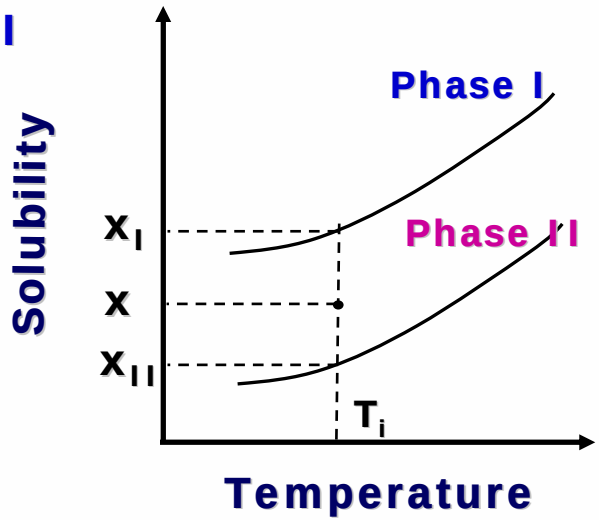
$$\frac{dr_I}{dt} = -k_D(\sigma_{I,II} - \sigma)$$

✓ **Growth rate of phase-II**

$$\frac{dr_{II}}{dt} = -k_G\sigma$$

✓ **Mass balance of phase transformation**

$$\sigma = \sigma_i - (\sigma_i - \sigma_{I,II})(\frac{r_I}{r_{I,i}})^3 - \sigma_i(\frac{r_{II}}{r_{II,f}})^3$$

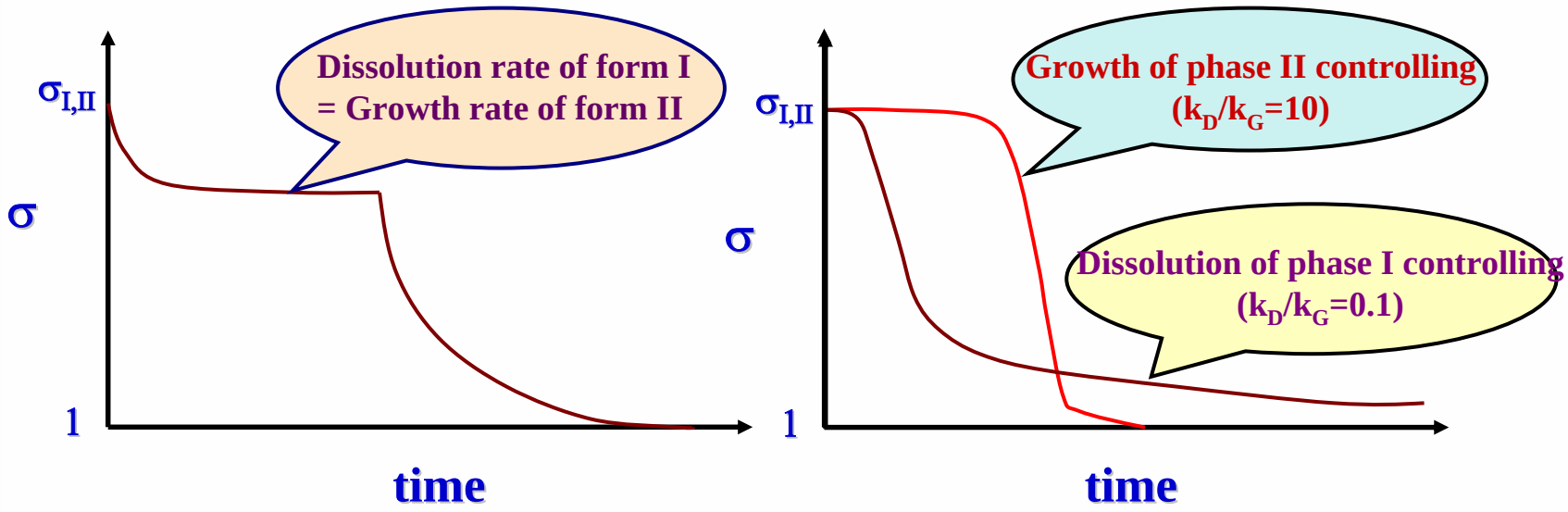


r_I : crystal size of phase-i

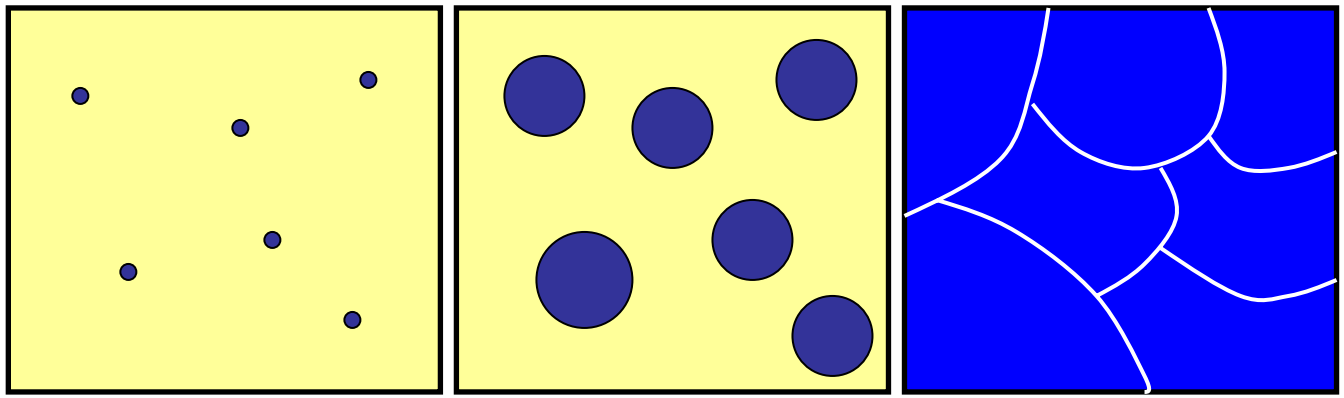
r_{II} : crystal size of phase-II

i : initial state

f : final state


σI,II
σ
1
time
Dissolution rate of form I
= Growth rate of form II
σI,II
σ
1
time
Growth of phase II controlling
(kD/kG=10)
Dissolution of phase I controlling
(kD/kG=0.1)

➢ Displacive transformation

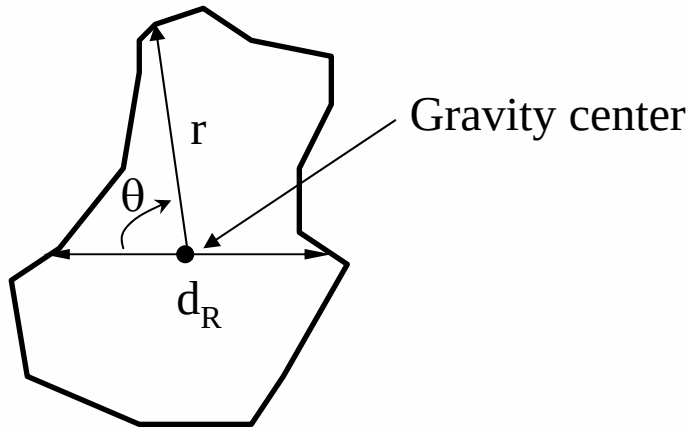


Crystal sizing

➢ Crystal size definition

✓ Statistical size ($\overline{d_R}$)

$$\overline{d_R} = \frac{1}{\pi}\int_0^{2\pi} r d\theta$$



➢ Mean crystal size

✓ Number-length mean diameter

$$d_{NL} = \frac{\sum N_i d_i}{\sum N_i}$$

✓ Geometrical mean diameter by number

$$d_{GN} = \log_{10} \frac{\sum N_i \log_{10} d_i}{\sum N_i}$$

✓ Number-surface mean diameter

$$d_{NS} = \left(\frac{\sum N_i d_i^{\,2}}{\sum N_i}\right)^{1/2}$$

✓ Number-volume mean diameter

$$d_{NV} = \left(\frac{\sum N_i d_i^{\,3}}{\sum N_i}\right)^{1/3}$$

✓ **Length-surface mean diameter**

$$d_{SL} = \frac{\sum N_i d_i^{\,2}}{\sum N_i d_i}$$

✓ **Length-volume mean diameter**

$$d_{VL} = \left(\frac{\sum N_i d_i^{\,3}}{\sum N_i d_i}\right)^{1/2}$$

✓ **Surface-volume mean diameter**

$$d_{VS} = \frac{\sum N_i d_i^{\,3}}{\sum N_i d_i^{\,2}}$$

✓ **Volume-moment mean diameter**

$$d_{VM} = \frac{\sum N_i d_i^{\,4}}{\sum N_i d_i^{\,3}}$$

Thanks you !!!