5. Crystal morphology

5.1 Introduction

shape, form, habit, morphology

- "Equilibrium morphology"

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

- "Growth morphology"

Crystal shape developed in the course of crystal growth.

5.2 Predicting crystal morphology

- Attachment energy E_{atb}, energy released per mole of layer added to a crystal surface, is directly proportional to the growth rare of a given face.

- Bravais-Friedel-Donnay-Harker **(prediction for growth morphology)**

The binding energy between crystal planes is inversely proportional to the interplanar spacing. As such, the growth rate v_{hkl} of (hkl) face is proportional to $1/d_{hkl}$.

- Specific force field (molecular mechanics) **(prediction for growth morphology)**

The interaction energy Eij between the individual *i*-th and *j*-th non-bonded atoms of the molecules that constitute the crystal calculated in terms of van der Waals and electrostatic contributions.

$$E_{ij} = -\frac{A}{r_{ij}^{6}} + \frac{B}{r_{ij}^{12}} + \frac{q_i q_j}{\varepsilon r_{ij}}$$

- Atomistic lattice simulation **(prediction for equilibrium morphology)**

$$\gamma_{hkl} = 0.5(E_{hkl}^{B} - 2E_{hkl}^{S})$$

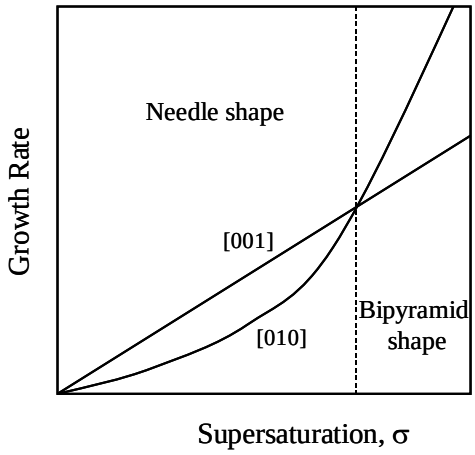
where E_{hkl}^{B} *and* E_{hkl}^{S} are energy of crystal plane (hkl) in bulk and surface, respectively.

5.3 Influence of supersaturation, temperature, solvents, additives, impurities.

- Supersaturation

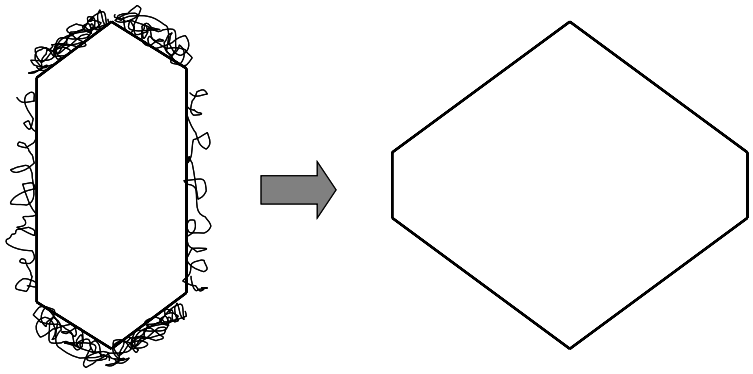
Growth rate of each crystal face depending on the supersaturation brings about the morphological change with supersaturation level.

Ex) paracetamol crystal



- Additives & Impurities

Selective adsorption of impurities on the crystal surface will modify the crystal morphology.



Langmuir isotherm (*Chem. Eng. Comm., Vol. 120, 119 (1993), Chem. Eng. Sci., 55, 733-747 (2000,* Crystal Research & Technology, Vol. 40(6), 586-592 (2005)))

$$\frac{L - L_0}{L_{eq} - L_0} = \frac{K_{ad} C_{add}}{1 + K_{ad} C_{Add}}$$

$$v_i = v_\infty (1 - 2r_c / l)^{1/2}$$

where r_c is the critical radius of two-dimensional nucleus and l is the distance separated between impurities adsorbed on crystal surface.

- ***Some additive*** is integrated into growth site of crystal, disrupting further growth.

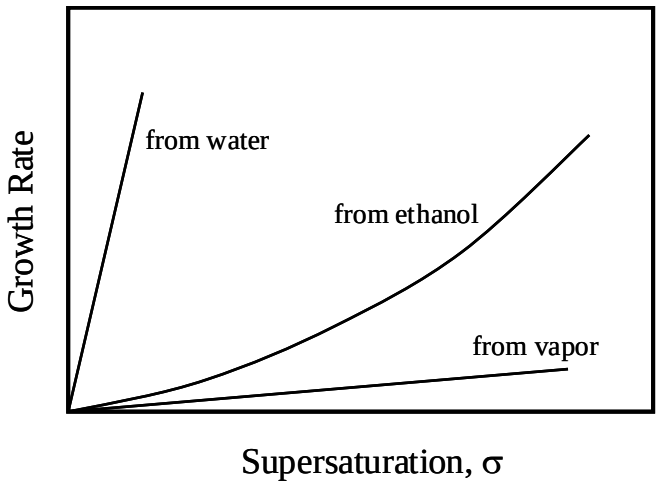
To perform this fuction effectively, the additive molecule must resemble the crystallizing molecules while containing small difference in stereochemistry or functionality.

→ "tailor-made additives".

- ***Solvent***

The solvent will modify α in the solution crystallization.

$$\alpha = \xi[\frac{\Delta H_f}{RT} - \ln x_{eq}]$$



5.5 Crystal purity

agrochemicals, pharmaceuticals, polymer intermediates, electronic materials.

- ***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, the extent of incorporation of an impurity or additive will depended on
  - the relative size
  - the stereochemistry
  - the functionality

  of additive molecules when compared with crystallizing solute.

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