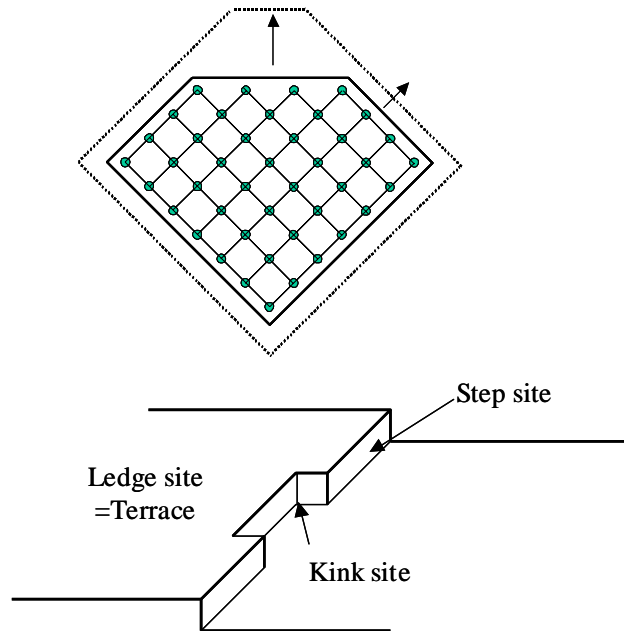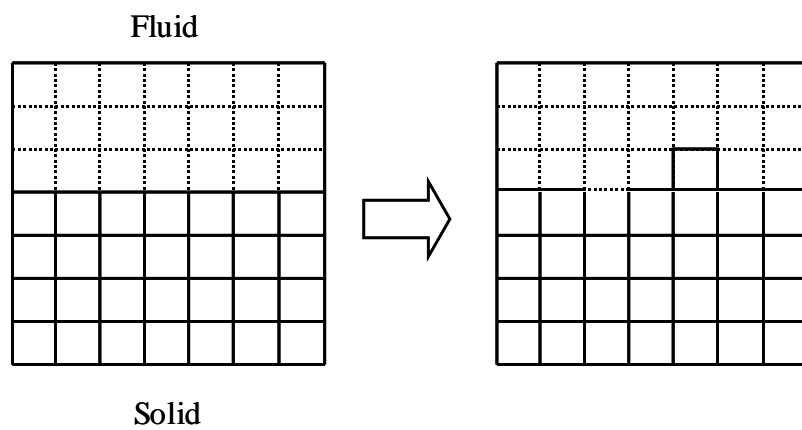# 4. Crystal growth

4.1 Crystal surface

$$v_K \geq v_S \geq v_F$$

where v_K, v_S and v_F are linear growth rates at kink, step and flat, respectively.

4.2 Crystal-fluid interface

- Multilayer model (Tempkin, 1966)

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

where

ΔE : the energy change occurring when a perfectly flat surface is roughened by removing one block from surface and using it to start a new layer.

ϕ_{ss} : the interaction energy between the sides of each solid block

ϕ_{ff} : the interaction energy between the sides of each fluid block

ϕ_{sf} : the interaction energy between the sides of fluid and solid block

Dimensionless term; α

$$\alpha = \frac{\Delta E}{kT}$$

If α is low, the growth can proceed easily with many sites always presents. ($2<\alpha<20$)

For vapor and melt growth,

$$\alpha = \xi \frac{\Delta H}{RT}$$

where ΔH is heat of sublimation and fusion

For solution growth,

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

where ΔH_f is heat of fusion and x_{eq} is the solubility.

– ξ is crystallographic factor describing intermolecular interactions in the crystal surface of interest.

$$\xi = \frac{E_{sl}}{E_{ss}} \approx \frac{z_s}{z_t}$$

where

E_{sl} : total interaction energy per molecule in the layer of the growth face

E_{ss} : total crystallization (lattice) energy

z_s, z_t : numbers of nearest neighbours.

- *Growth process*

   1) Desolvation

   2) Surface diffusion

   3) Integration into kink.

4.3 Growth mechanism

- *Continuous growth (α<3)*

   Every growth unit arriving at the surface will find a growth site.

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

- *Surface nucleation (3< α< 5)*

   Adsorbed growth units form surface nuclei or island.

   v=f_1(number of critical size nuclei formed per unit time)*f_2(step height)*f_3(step velocity)

Then,

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

- *Spiral growth (α>5)*

$v=f_1$(step velocity)$*f_2$(step height)$*f_3$(step density)

BCF equation

$$v = k_{SG} \frac{\sigma^2}{\sigma_1^2} \tanh(\frac{\sigma_1}{\sigma})$$

where $\sigma_1 \propto \frac{\gamma_e}{s}$.

If $\sigma \ll \sigma_1$, $v \propto \sigma^2$ (parabolic growth rate)

If $\sigma_1 \ll \sigma$, $v \propto \sigma$ (linear growth rate)

4.4 The importance of mass transfer

Two consecutive steps for crystal growth are

1) for surface integration step

$$R_G = k_r (c_i - c_{eq})^r$$

2) for mass transfer step

$$R_G = k_d (c_\infty - c_i)$$

Then,

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

If r=1, $R_G = k_G [(c_\infty - c_{eq})]$,

where,

$$\frac{1}{k_G} = \frac{1}{k_d} + \frac{1}{k_r}$$

- Effectiveness factor (η)

Definition,

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

Then,

$$\eta_r = (1 - \eta_r Da)^r$$

where *Da* is Damkohler number

$$Da = \frac{k_r(C_\infty - C_{eq})^{r-1}}{k_d}$$

If *Da*>>1, the crystal growth rate is controlled by mass transfer step.

If *Da*<<1, the crystal growth rate is controlled by surface integration step.

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