

The background of the slide is a photograph of an industrial facility, likely a refinery or chemical plant. It features a complex network of large, silver-colored metal pipes and structures. The pipes are arranged in various directions, some running horizontally and others vertically. The sky is a clear, bright blue with some light, wispy clouds. The overall scene is brightly lit, suggesting a sunny day.

ΔΙΕΡΓΑΣΙΕΣ ΔΙΑΧΩΡΙΣΜΟΥ

Μάθημα 9ο

Ακαδημαϊκό έτος 2017-2018

Separation Processes

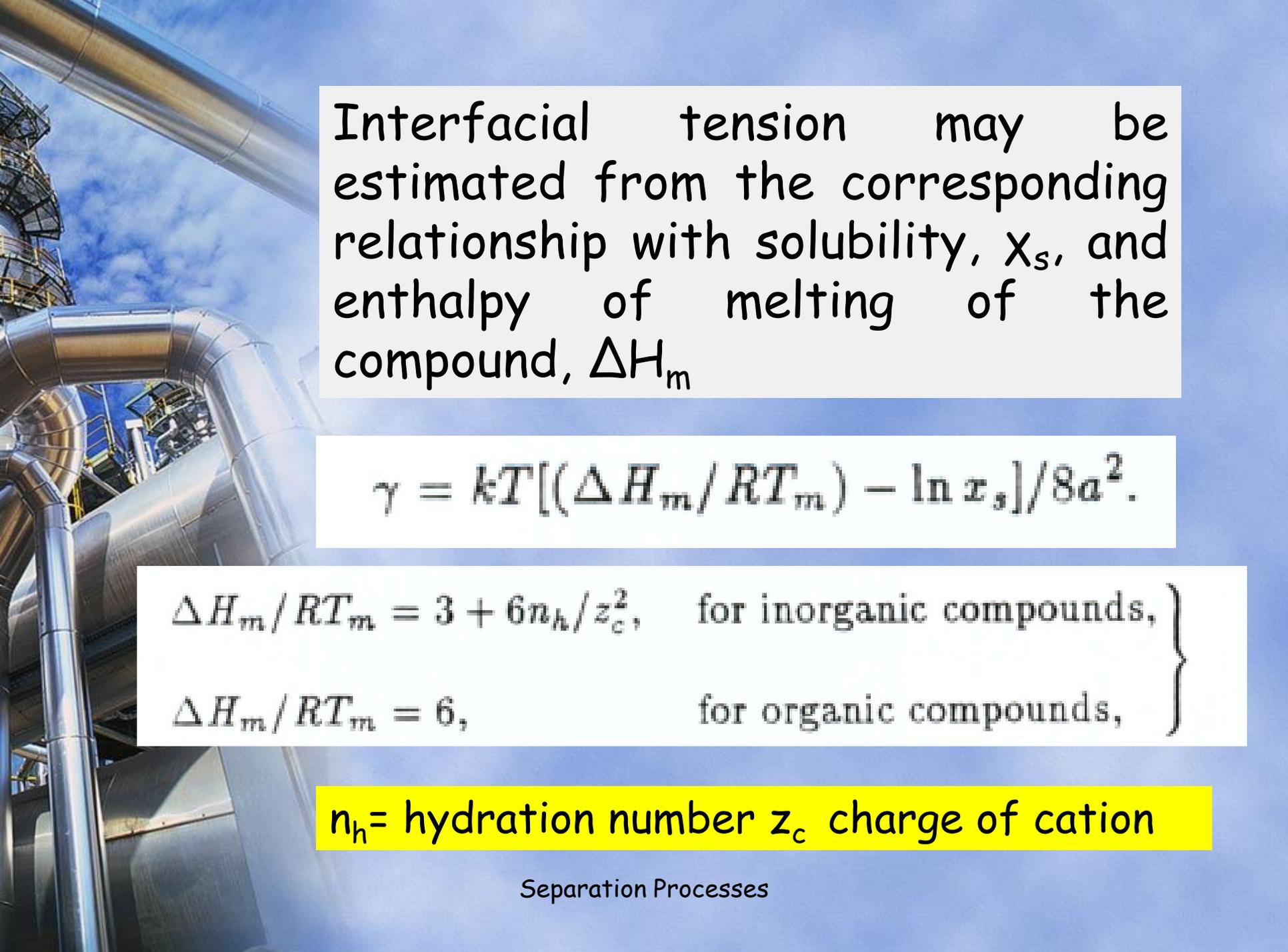
For mononuclear mechanism:

$$S_{\max} = \exp \left(\frac{16\pi\gamma^3\Omega^2}{3k^3T^3 \ln J_o} \right)^{1/2}$$

For polynuclear mechanism using typical values $\alpha_1 = \pi/3$, $\alpha = 10^{-4}$ $C = 0.1 \mu\text{S/s}$, and $t_{\text{ind}} = 1\text{s}$ for the polynuclear mechanism we have:

$$S_{\max} = \exp \left(\frac{16\pi\gamma^3\Omega^2}{3k^3T^3 \ln(10^{-10}J_o)} \right)^{1/2}$$

As may be seen S_{\max} for polynuclear mechanism is higher
Calculation possible if interfacial tension, γ , is known

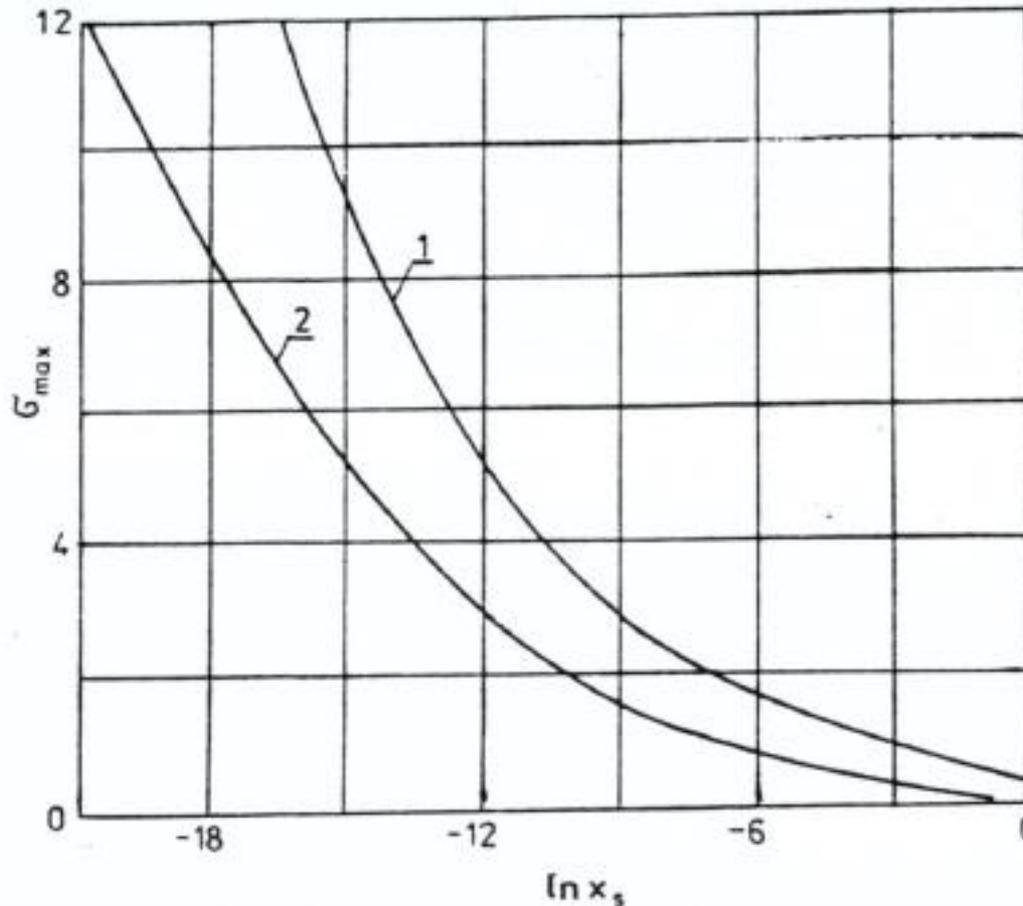


Interfacial tension may be estimated from the corresponding relationship with solubility, x_s , and enthalpy of melting of the compound, ΔH_m

$$\gamma = kT[(\Delta H_m / RT_m) - \ln x_s] / 8a^2.$$

$$\left. \begin{array}{l} \Delta H_m / RT_m = 3 + 6n_h / z_c^2, \quad \text{for inorganic compounds,} \\ \Delta H_m / RT_m = 6, \quad \text{for organic compounds,} \end{array} \right\}$$

n_h = hydration number z_c charge of cation



Dependence of metastable-zone width on solubility for different values of $\Delta H_m/RT_m$ [61]: (1) $\Delta H_m/RT_m = 3.7$ and (2) $\Delta H_m/RT_m = 6$.

$$\gamma = 0.414 kT \Omega^{-2/3} \ln(c_s/c_o),$$

Mersmann

where the solute concentration $c_o = \rho/M$, with ρ as the density of the crystal (kg/m^3) and M as its molar mass (kg/kmol). A similar equation has been

A photograph of an industrial facility with large, shiny metal pipes and structures against a blue sky with light clouds. The pipes are arranged in a complex network, with some curving upwards and others running horizontally.

Experimental methods for the measurement of MSZW

- Indirect methods

- Determination of parameters such as solubility, enthalpy of dissolution and interfacial tension

Direct Methods

based on programmed cooling of the solution to the detection of first crystal directly or indirectly- change of physicochemical property undergoing sudden change: density, electrical conductivity, RI of light, pH

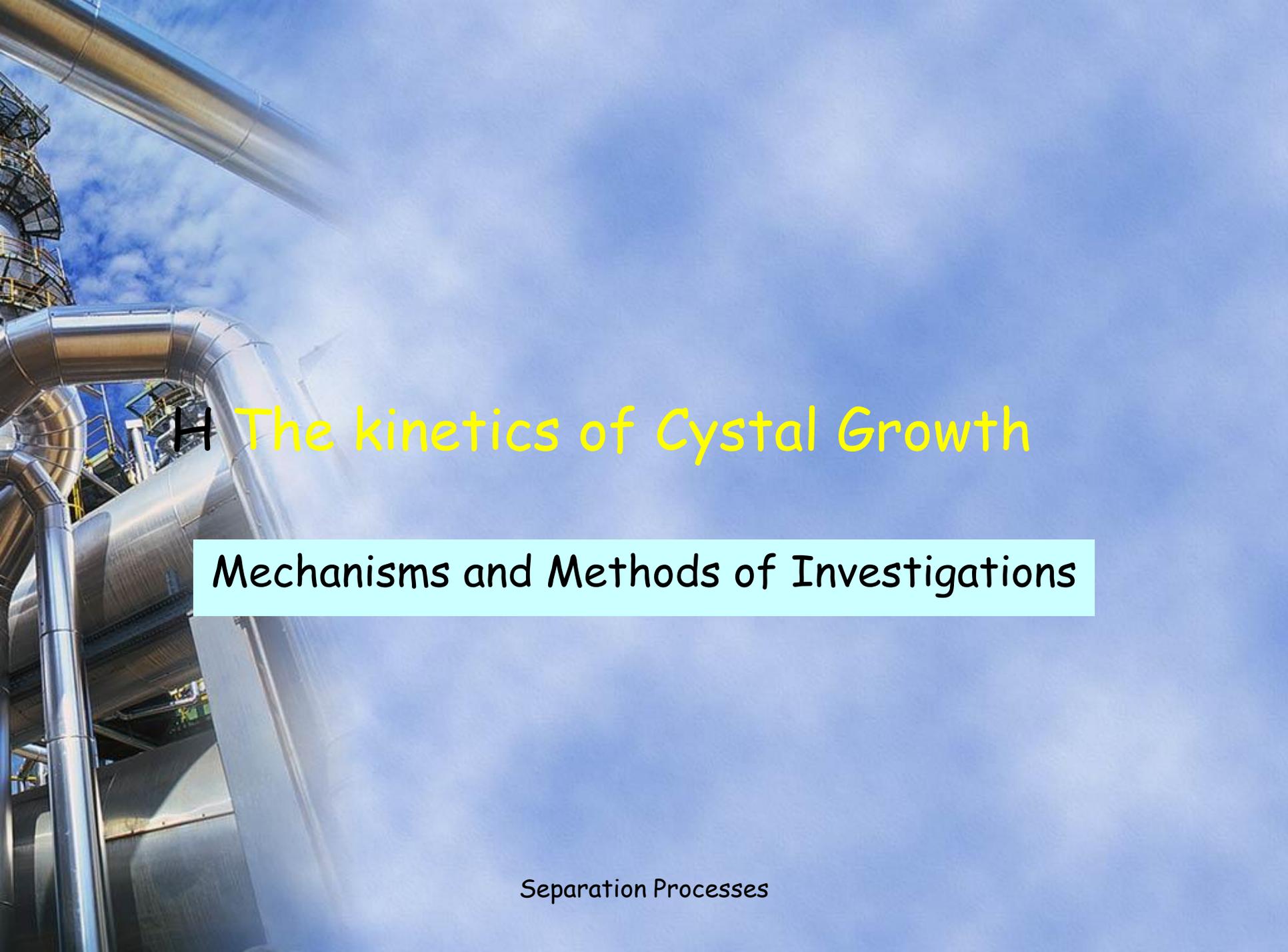
Values obtained by different methods may differ but depend mainly on the cooling rate and the method of solution preparation before the measurements



Gypsum

"Cave of the Giant Crystals"

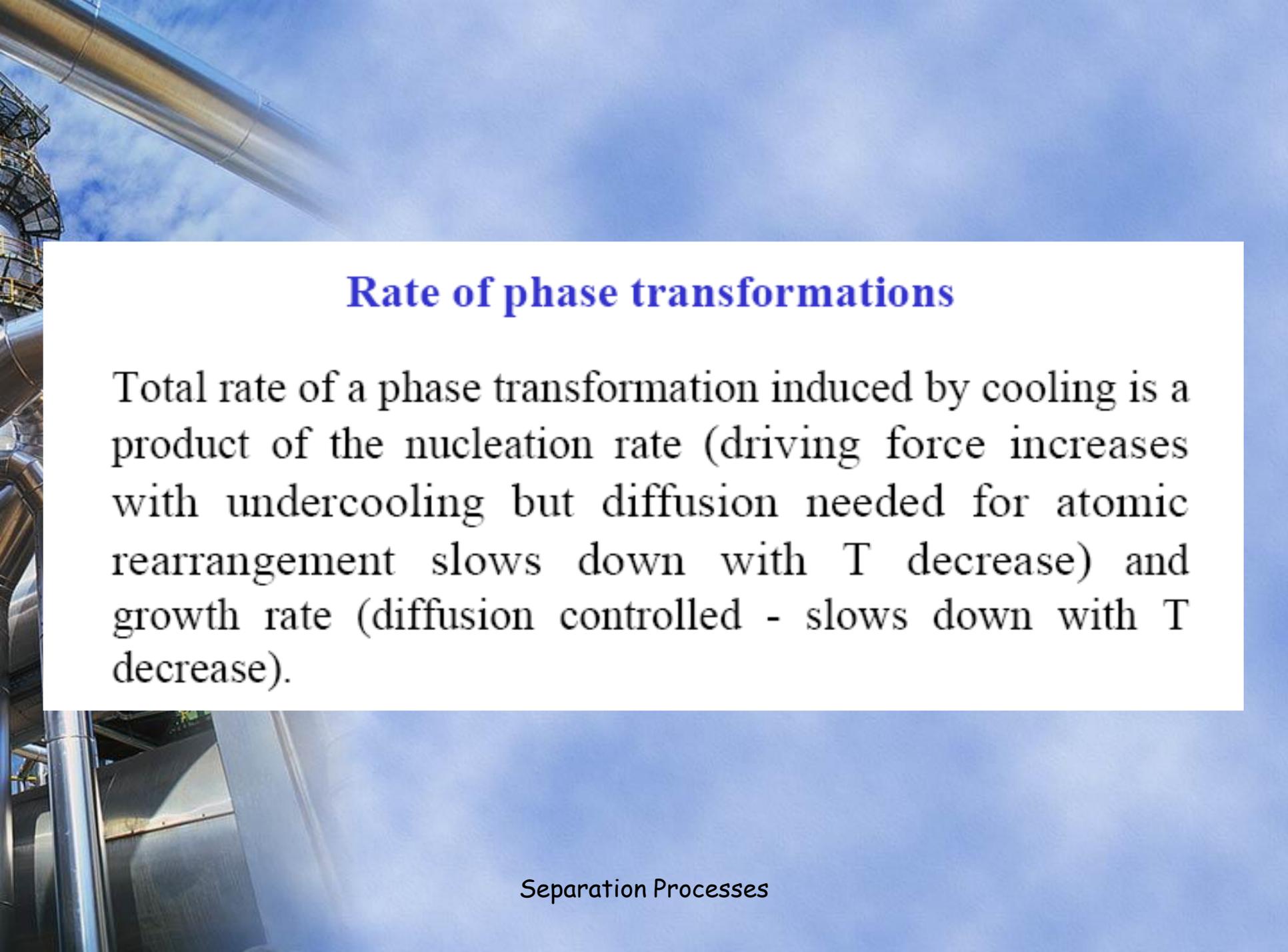
Chihuahua, Mexico



H The kinetics of Crystal Growth

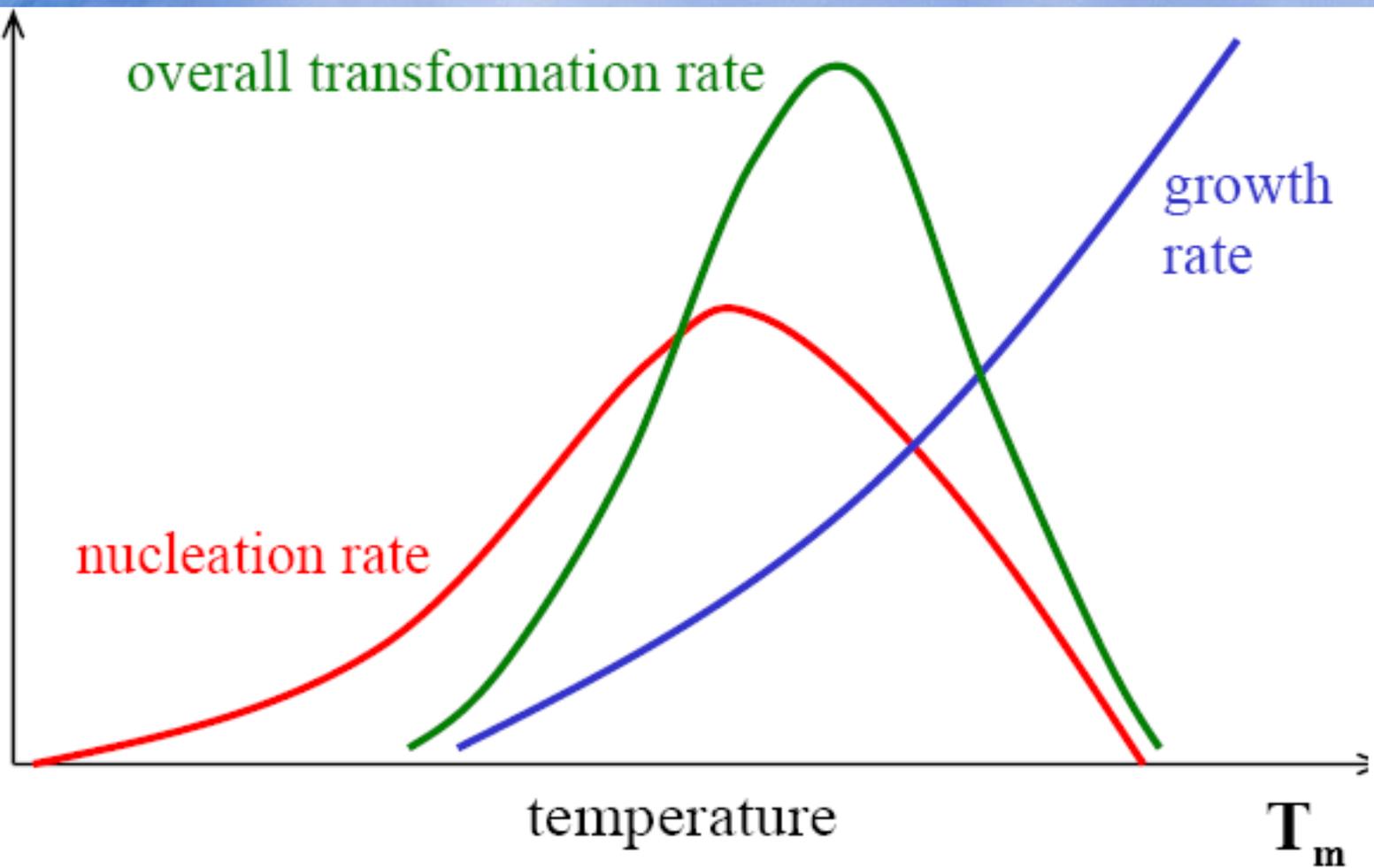
Mechanisms and Methods of Investigations

Separation Processes



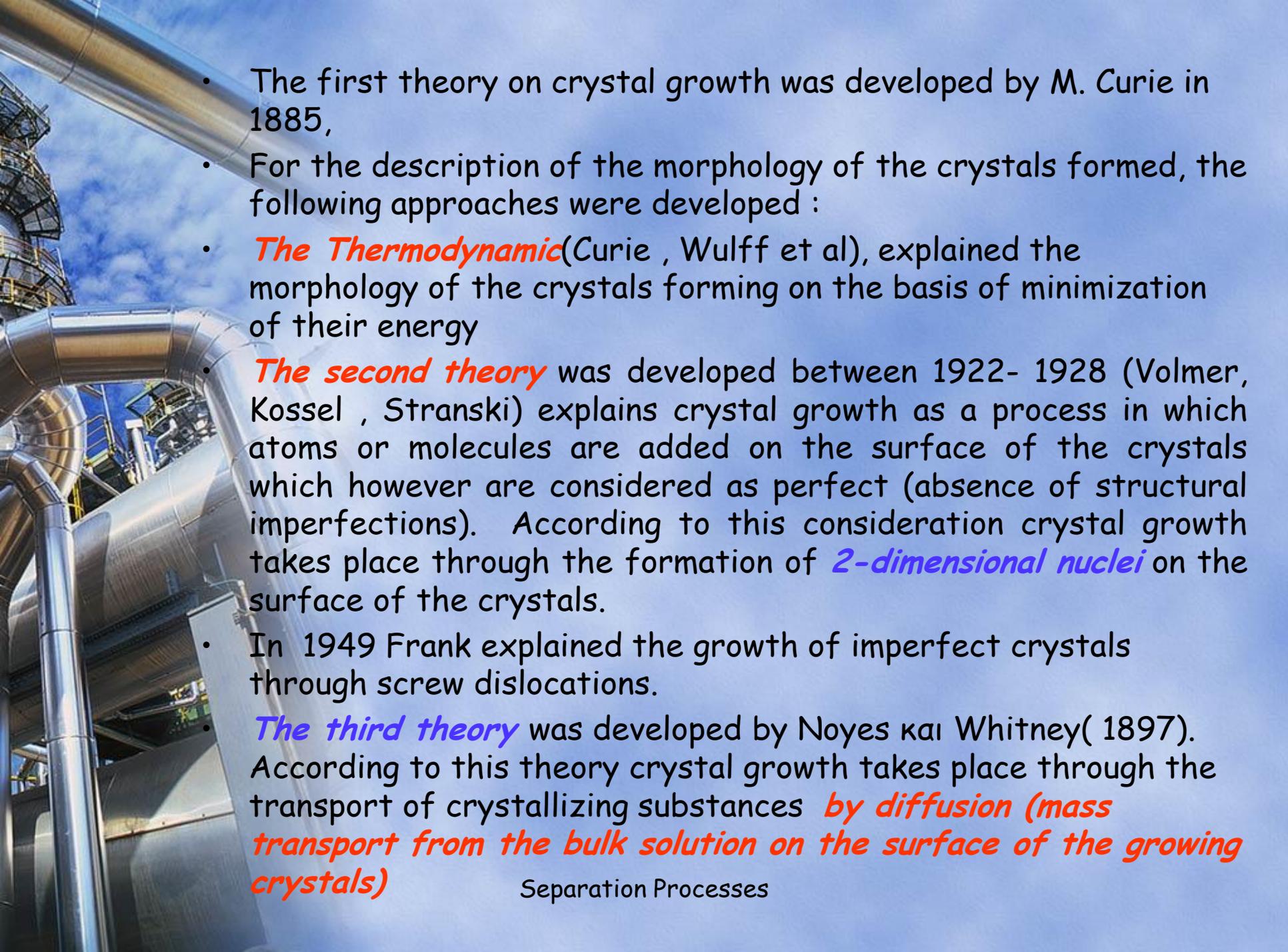
Rate of phase transformations

Total rate of a phase transformation induced by cooling is a product of the nucleation rate (driving force increases with undercooling but diffusion needed for atomic rearrangement slows down with T decrease) and growth rate (diffusion controlled - slows down with T decrease).



high T (close to T_m): low nucleation and high growth rates
→ coarse microstructure with large grains

low T (strong undercooling): high nucleation and low growth rates → fine structure with small grains

- 
- The background of the slide features a photograph of an industrial facility, likely a refinery or chemical plant. It shows a complex network of large, silver-colored metal pipes and structures, some with scaffolding, set against a clear blue sky with a few wispy clouds. The pipes are arranged in various directions, some running vertically and others horizontally or at angles.
- The first theory on crystal growth was developed by M. Curie in 1885,
 - For the description of the morphology of the crystals formed, the following approaches were developed :
 - **The Thermodynamic**(Curie , Wulff et al), explained the morphology of the crystals forming on the basis of minimization of their energy
 - **The second theory** was developed between 1922- 1928 (Volmer, Kossel , Stranski) explains crystal growth as a process in which atoms or molecules are added on the surface of the crystals which however are considered as perfect (absence of structural imperfections). According to this consideration crystal growth takes place through the formation of **2-dimensional nuclei** on the surface of the crystals.
 - In 1949 Frank explained the growth of imperfect crystals through screw dislocations.
 - **The third theory** was developed by Noyes kai Whitney(1897). According to this theory crystal growth takes place through the transport of crystallizing substances **by diffusion (mass transport from the bulk solution on the surface of the growing crystals)**

Kinetics of crystal growth

- The rate is expressed as the displacement along a vector perpendicular to the individual face
- Rates are linear

The linear rate of growth of a crystal face of surface area A is:

$$v_g = JV_m = j(V_m A)$$

J : molecular flux (molecules per unit time and surface area) and $j(=dn_i/dt)$ rate of moles deposition; V_m : molar volume

In polycrystalline systems, a mean linear rate is calculated (derivative with respect to time of a sphere the volume of which is equal to the mean volume of a crystal)

For a closed system without nucleation

$$\bar{V} = \frac{n_i V_m}{N}$$

N_i : no of. moles of substance i deposited from a unit volume and N the number of crystallites formed per unit volume

$$\dot{r} = n_i \frac{\dot{V}_m}{4\pi r^2 N}$$

In case new nuclei are formed in the closed system, the instantaneous overall rate shall be :

$$\dot{r} = - \frac{\dot{V}_m}{A_s} c$$

$$\dot{c} = \frac{dc}{dt}$$

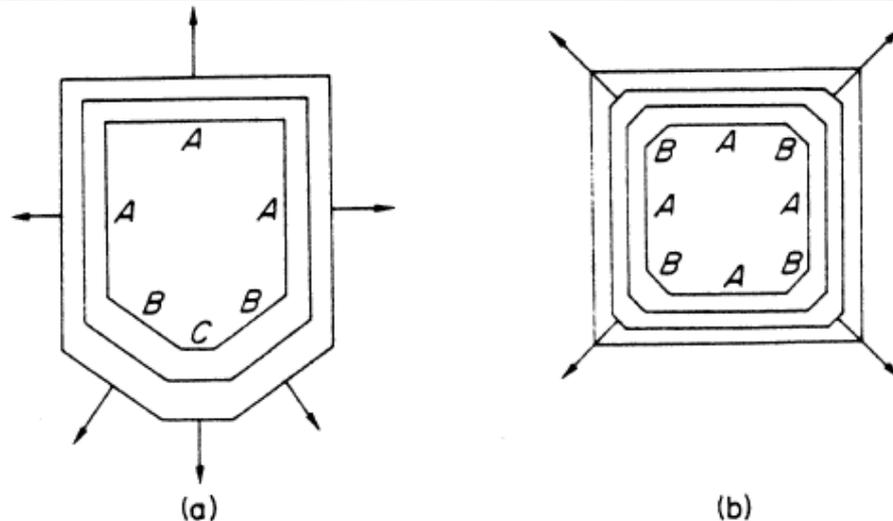
A_s : total surface area present per unit volume of the suspension

Θεωρίες κρυστάλλωσης

- Επιφανειακής ενέργειας (ελαχιστοποίηση της ενέργειας) Gibbs-Curie-Wulff: Οι κρύσταλλοι (οι κρυσταλλικές έδρες) αναπτύσσονται αναλόγως της επιφανειακής των ενέργειας
- Έδρες μικρής πυκνότητας (μεγάλες τιμές δεικτών Miller) αναπτύσσονται ταχύτερα και άρα εξαφανίζονται

$$\sum_1^n a_i g_i = \text{minimum}$$

Οι θεωρίες αυτές δεν μπορούν να ερμηνεύσουν την επίδραση του υπερκορεσμού στην κρυσταλλική ανάπτυξη



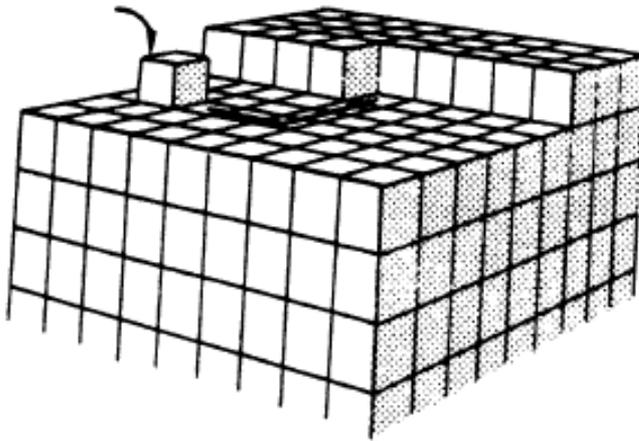
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Figure 6.1. Velocities of crystal growth faces: (a) invariant crystal; (b) overlapping

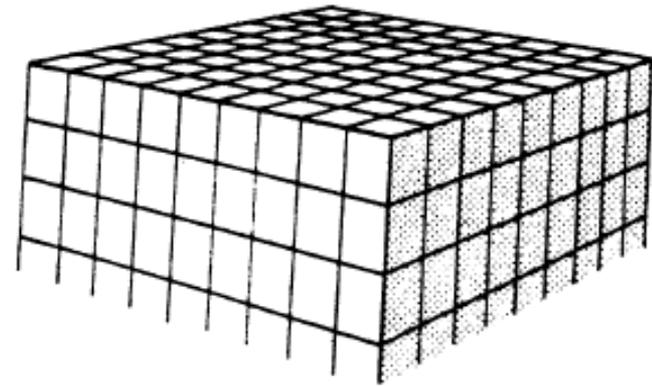
Θεωρίες προσρόφησης στρώματος (Volmer)

Προσρόφηση ατόμων ή μορίων της διαλυμένης ουσίας στην επιφάνεια του κρυστάλλου

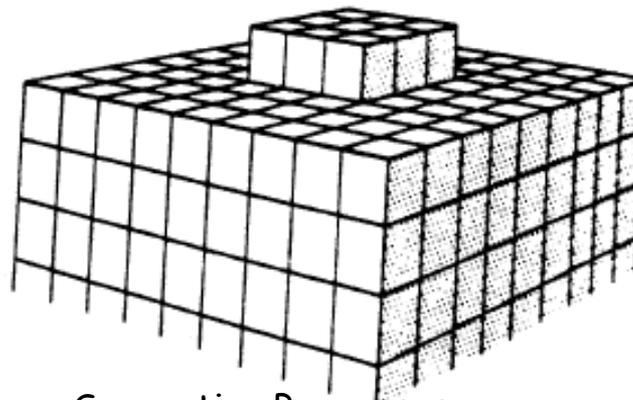
1-10 nm πάχος στρώματος



(a)



(b)



Separation Processes

(c)

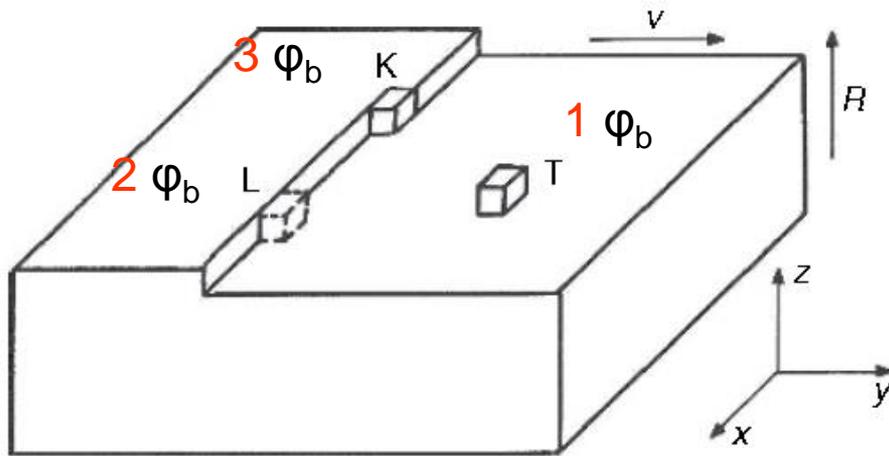


Figure 3.1 Different positions for the attachment of growth units at a flat crystal-medium interface of a simple cubic lattice

Η πιθανότητα 'σύλληψης' μιας δομικής μονάδας στην επιφάνεια του αναπτυσσόμενου κρυστάλλου περιλαμβάνει όρους του τύπου

$$\exp\left(\frac{n\phi_b}{kT}\right)$$

Όπου n ο αριθμός των σχηματιζόμενων δεσμών και ϕ_b η ενέργεια σύνδεσης ανά ζεύγος

Μεγαλύτερη πιθανότητα σύνδεσης της δομικής μονάδας σε θέση kink (κόγχη)

Separation Processes

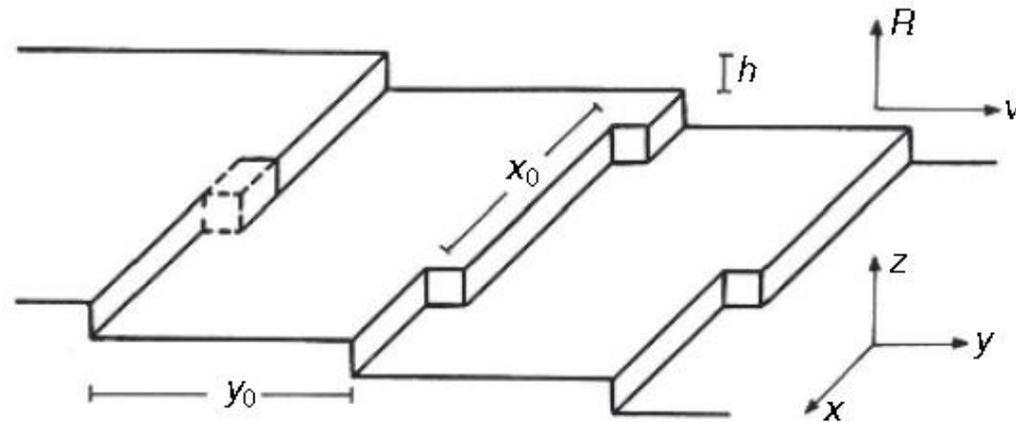


Figure 3.2 Incorporation of growth units of dimensions a , b and c in the x , y and z directions, respectively, in kinks of steps parallel to the x direction in the (001) face

The different steps of the crystallization process

Crystal growth

In crystallization, growth plays an essential influence on the crystal **size and shape**

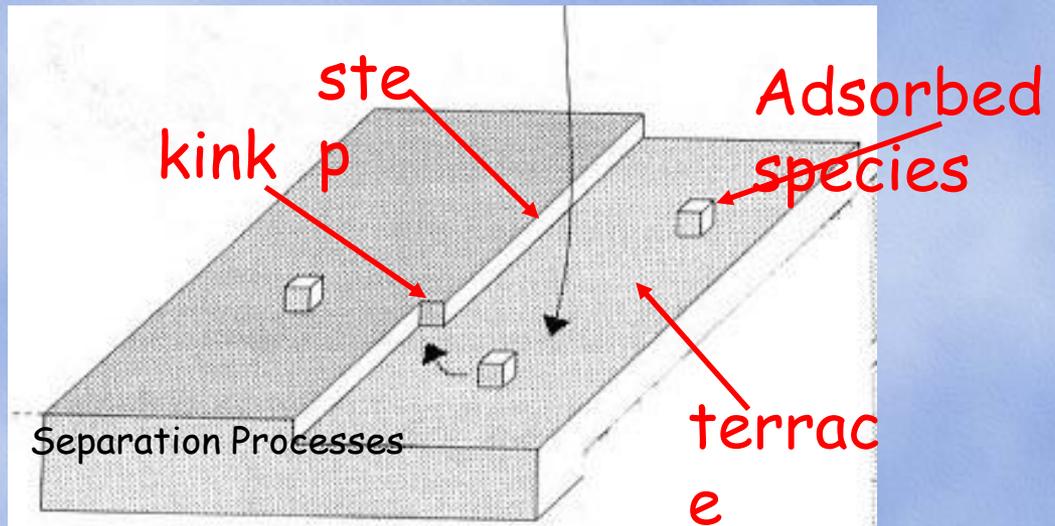
The growth of a crystal face results from the progressive **integration of atoms or ions into the crystal lattice**

The growth kinetic process is divided in several consecutive **steps**

The growth rate is determined by the slowest step (**rate-determining step**)

Representation of the crystal surface :

Different adsorption sites : terrace (1 bond), step (2 bonds), kink (3 bonds)

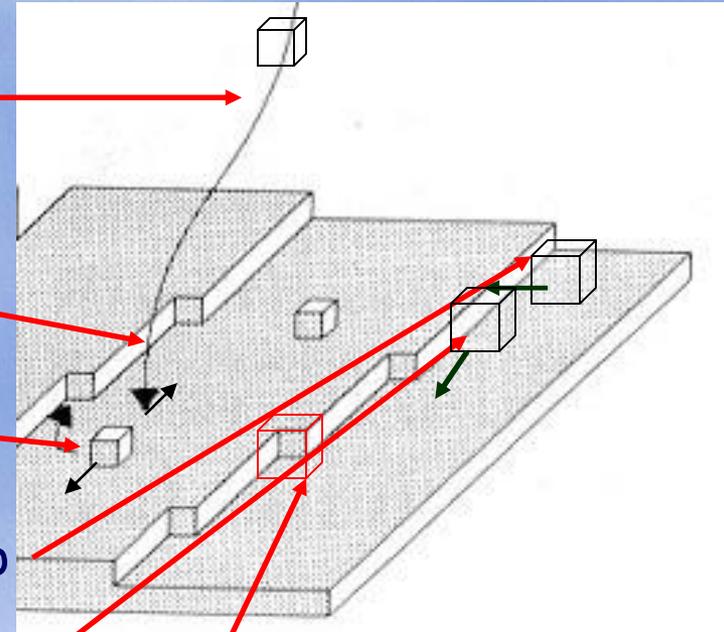


The different steps of the crystallization process

Crystal growth (continued)

The different steps of the growth mechanism

- 1- **Transport** (bulk diffusion of the solute ions or molecules towards the crystal face)
- 2- **Adsorption** onto the crystal surface \Rightarrow potential **growth units**
- 3- Bi-dimensional **diffusion** of the growth units on a terrace
- 4- **Adsorption** of the growth unit onto a step
- 5- Unidimensional **diffusion** along a step
- 6- **Adsorption** of the growth unit onto a kink \equiv **integration** to the crystal lattice



Consequence : progressive filling of the step by growth units, progression of the step on the surface, formation of the crystal lattice layer by layer

The different steps of the crystallization process

Crystal growth (continued)

Crystal growth mechanisms :

a **kinetic** assumption (what **rate-determining step**?)

and a **morphological** assumption (**rough** or **smooth** interface ?)

Growth rate = mole or mass flux or **rate of linear growth**

$$G = \frac{dL}{dt}$$

A few typical cases of growth rate laws

Growth rate with rate-determining bulk diffusion : (no influence of morphology...)

Growth rate \approx diffusion flux \approx concentration gradient in the interfacial layer $\approx k_d (C - C_s) \approx k_d s$, k_d mass-transfer coefficient

k_d expressed from correlations : *example*

$$Sh = \frac{k_d L}{D} = 2 + 0.81 Re_p^{1/2} Sc^{1/3} \quad (Sh : \text{Sherwood number} ; Sc : \text{Schmidt number})$$

The different steps of the crystallization process

Crystal growth

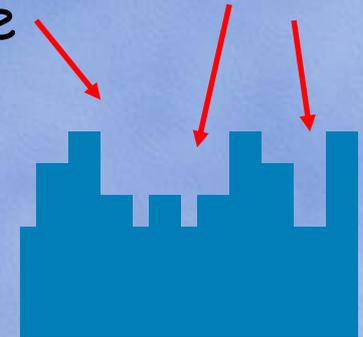
A few typical cases of growth rate laws (continued...)

Rate-determining interfacial steps

Two different cases according to the surface roughness

❖ rough interface :

- an adsorption site \equiv a kink \Rightarrow only step 6 of the mechanism
- **growth rate $\approx s$**



❖ smooth interface : Growth is possible in spite of the absence of steps and kinks

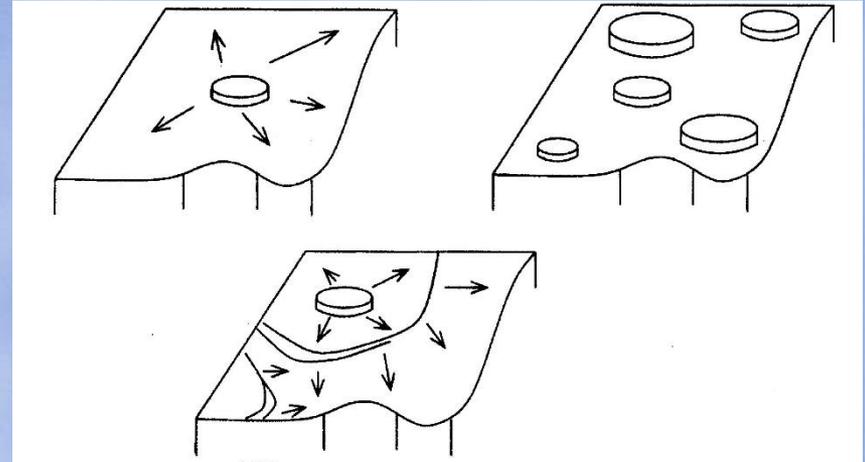
Two explanations...

- in the case of **high supersaturation levels** : many atoms are adsorbed on the terraces \Rightarrow temporary aggregates \equiv **bi-dimensional nuclei**

The different steps of the crystallization process

Crystal growth

A few typical cases of growth rate laws (continued...)

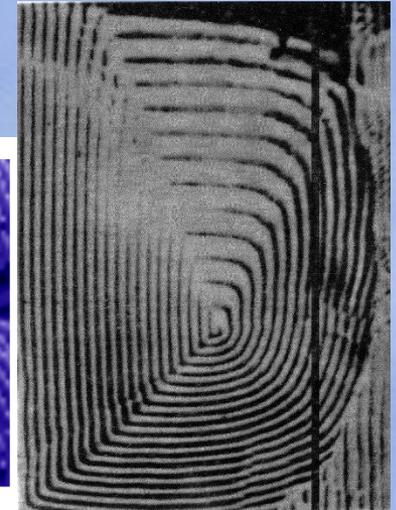
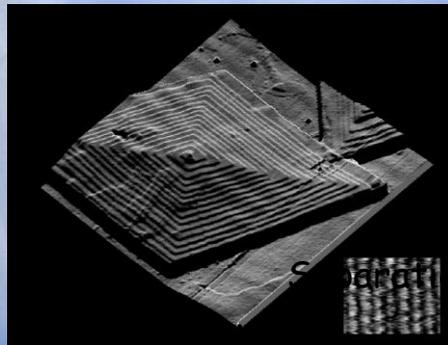


❖ smooth interface and high supersaturation level (continued)

Different situations of growth of the bidimensional nucleus

❖ smooth interface and low supersaturation level

microphotographs show steps in form of spirals



Crystallization Processes

8 by 8 micrometers

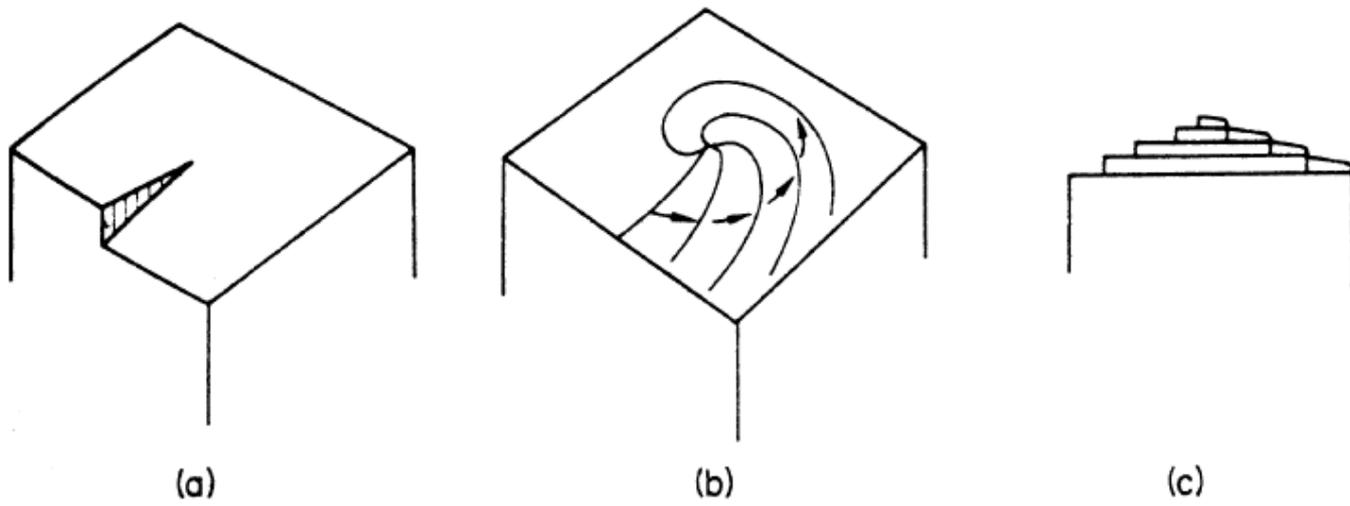


Figure 6.4. *Development of a growth spiral starting from a screw dislocation*

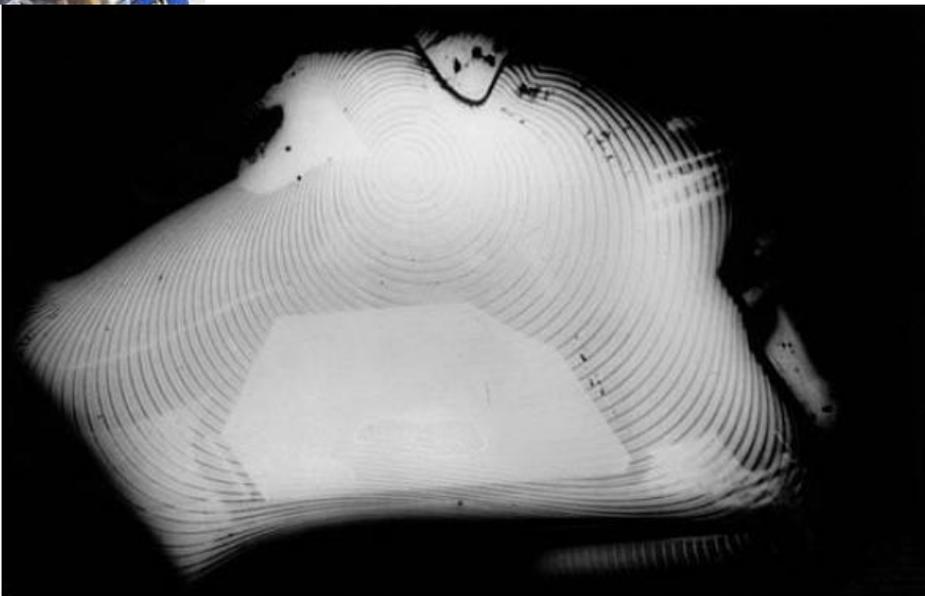


Figure 6.5. *A circular spiral on a silicon carbide crystal. (Courtesy*

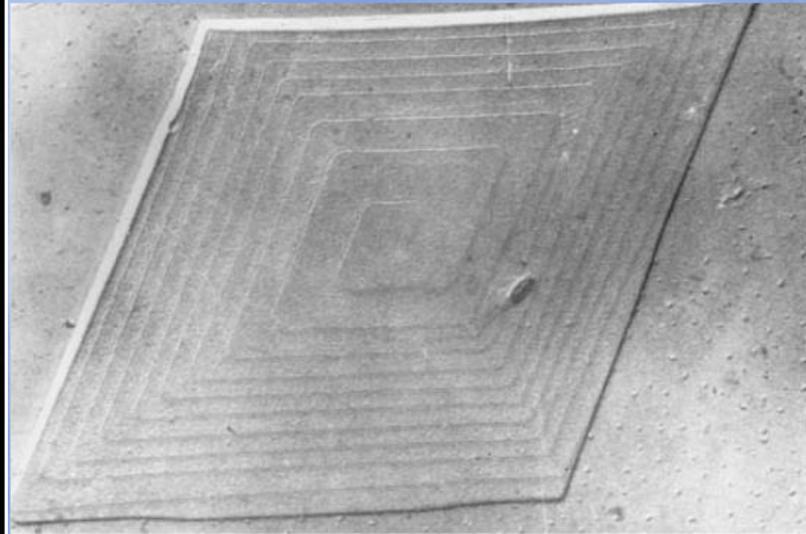


Figure 6.7. *A polygonized spiral on the face of a C₃₆ normal alkane crystal.*

The different steps of the crystallization process

Crystal growth

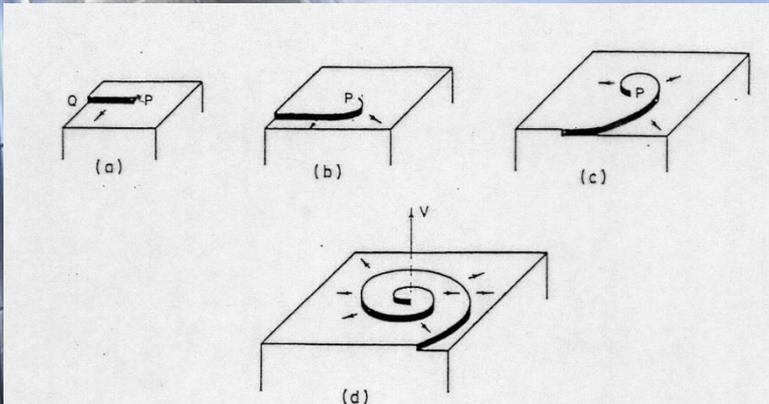
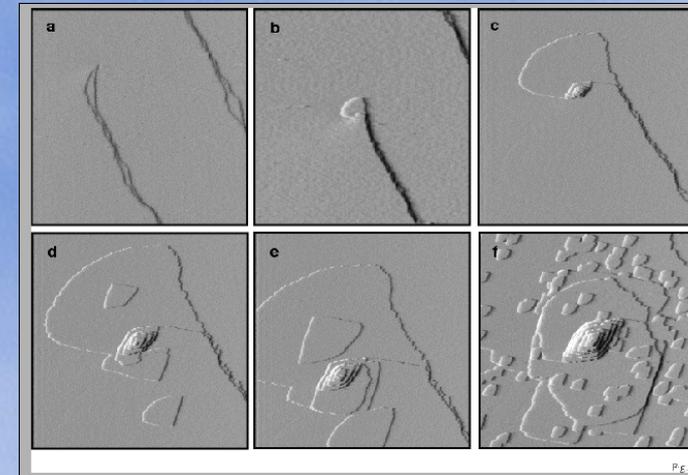
A few typical cases of growth rate laws

(continued...)

❖ smooth interface and low supersaturation level (spiral growth-continued)

➤ Screw-dislocations \equiv source of new steps (Burton-Cabrera-Frank "BCF" model)

➤ Spatial structures and stationary processes



Simplification :

$G \approx s$ (high supersaturation)

$G \approx s^2$ (low supersaturation)

➤ growth rate law :

$$G = \frac{K' \sigma^2 \tanh\left(\frac{K''}{\sigma}\right)}{\text{Separation Processes } \sigma}$$

The Burton–Cabrerera–Frank (BCF) relationship may be written

$$R = A\sigma^2 \tanh(B/\sigma)$$

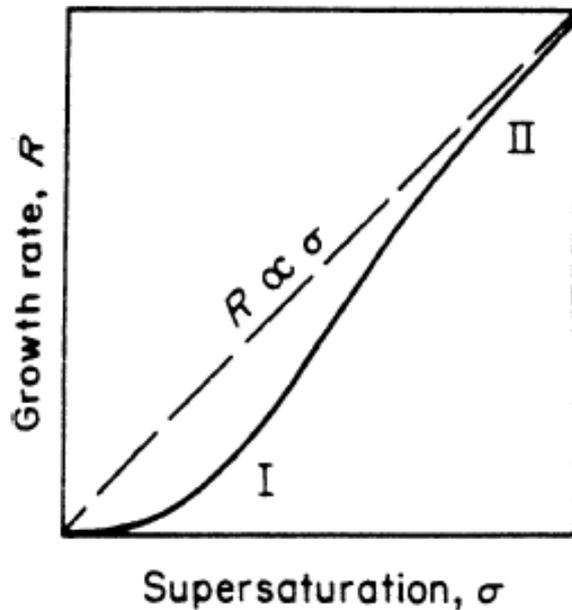
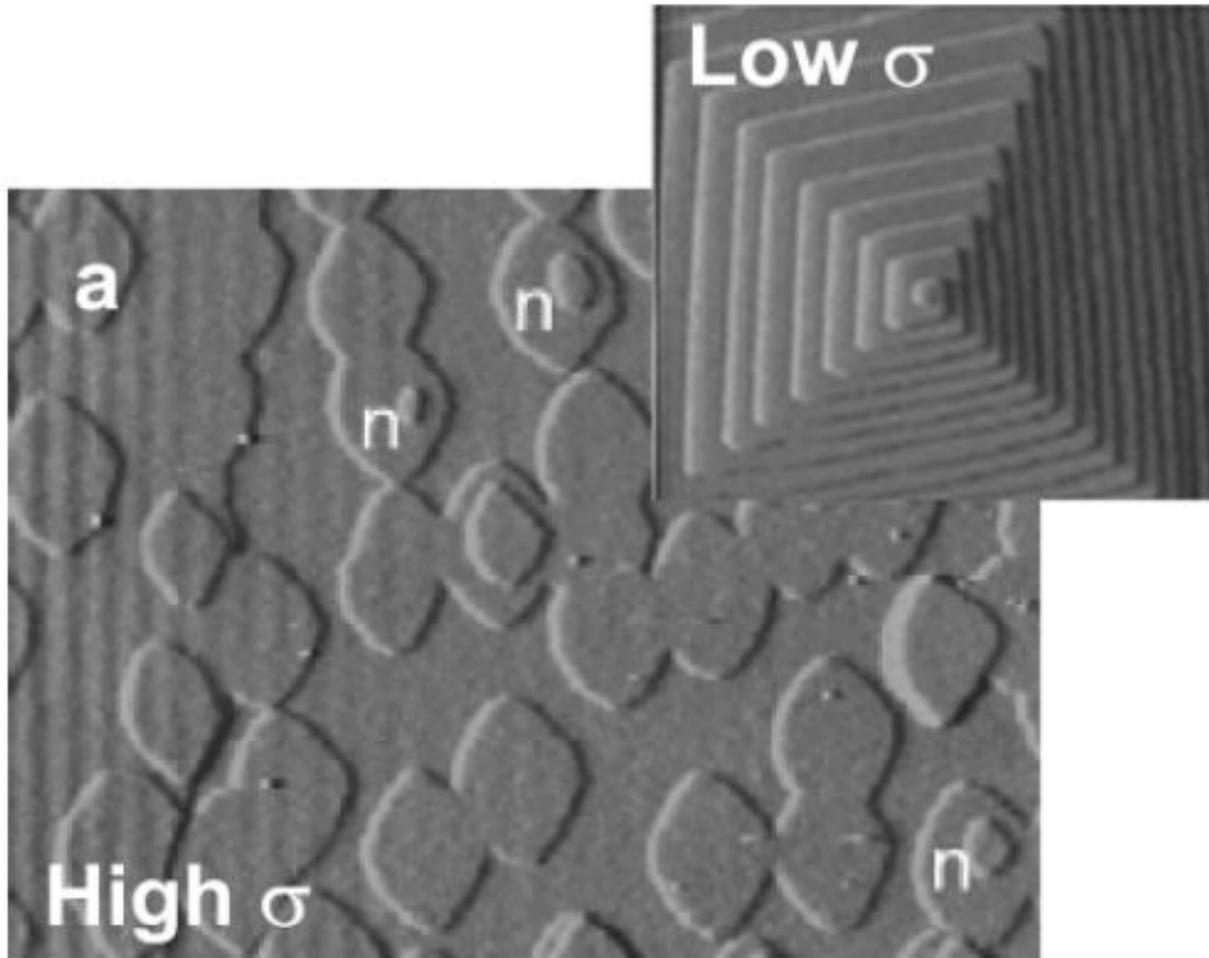
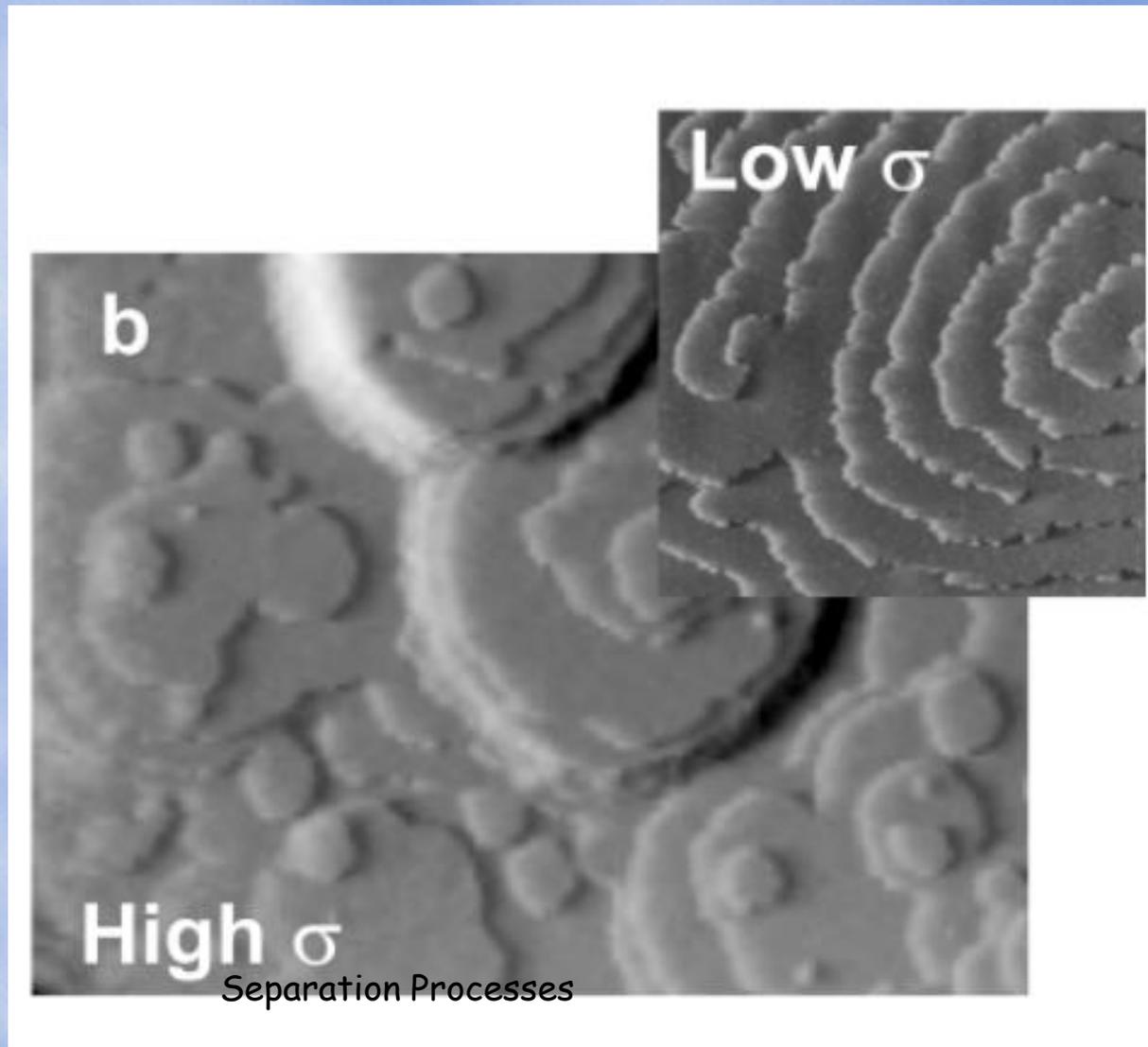


Figure 6.8. The Burton–Cabrerera–Frank (BCF) supersaturation–growth relationship (I, $R \propto \sigma^2$; II, an approach to $R \propto \sigma$)



Separation Processes



High σ

Low σ

b

Separation Processes

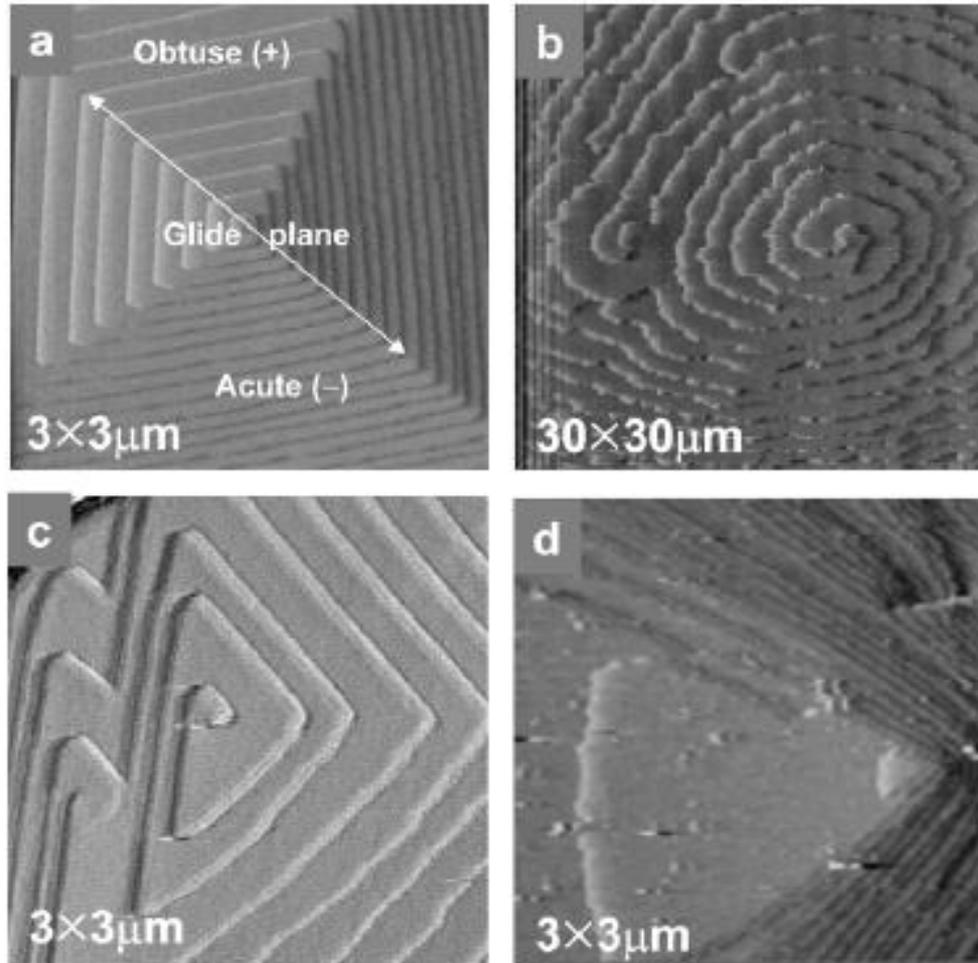
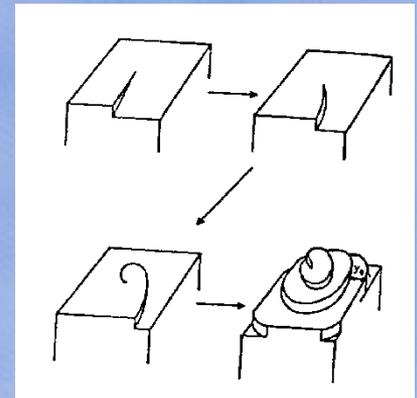
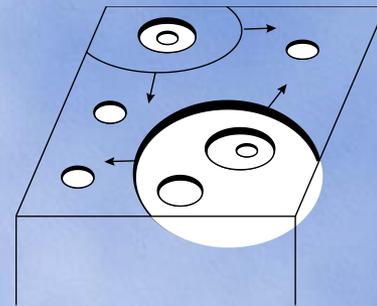
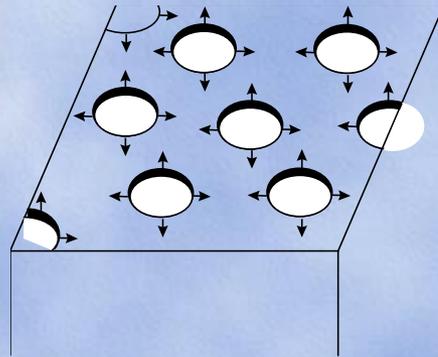
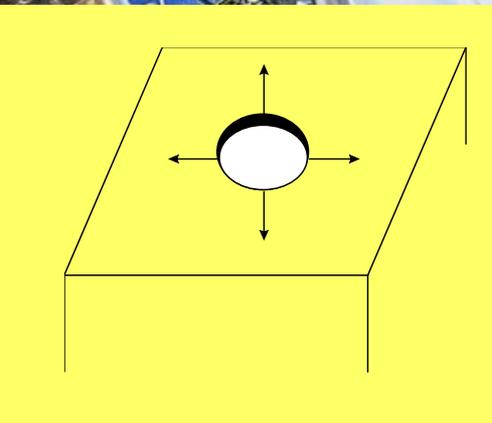


Figure 19. AFM images of dislocation separation processes in (a) canavalin (c) brushite and (d) calcium oxalate monohydrate.

Κινητικές εξισώσεις

$$R_g = k_g f(S) \sigma^n$$



a: Mononuclear model. b: polynuclear in one crystal step. c: polynuclear in multiple steps: Birth and Spread. d Spiral model

Κινητικές εξισώσεις

Πολυπυρηνικό πρότυπο

$$R = A \left(\frac{\gamma v}{kT} \right)^2 (\ln S)^{-3/2} \exp \left(\frac{-B}{T^2} \ln S \right)$$

$$R = C \frac{\sigma^2}{\sigma_1} \tanh \frac{\sigma_1}{\sigma}$$

Χαμηλός

$$R = C \frac{\sigma^2}{\sigma_1}$$

υψηλός

$$R = C \sigma$$

Ohara and Reid introduced three models, all denoting the relationship between the growth rate v and the supersaturation as follows

$$v = A' \sigma^p \exp\left(-\frac{B'}{\sigma}\right)$$

A borderline case is the so-called mononuclear model, whereas the spreading rate of this layer is very rapid compared to the surface nucleation rate and $p = 1/2$

The other extreme configuration is the polynuclear mechanism, where the spreading rate of this layer is slow compared to always new nuclei formed; in this case, $p = 3/2$.

In between these two borderline cases is the **birth and spread (B&S) model** with $p = 5/6$, considered for the first time by Hilling and also known as the **nuclei-above-nuclei (NAN) model**

$$v_{B+S} = A\sigma^{2/3}(\nu \ln S)^{1/6} \exp\left(-\frac{B}{\nu \ln S}\right)$$

with

$$A = \left(\frac{16}{\pi}\right)^{1/3} a^{1/6} D_{\text{surf}} (V_m \Gamma N_A)^{5/6} \left(\frac{\beta' \Gamma^*}{x_s}\right)^{2/3}$$

$$B = \frac{\pi}{3} V_m a \left(\frac{\gamma_{CL}}{kT}\right)^2 \approx \frac{\pi}{3} \left[K \ln\left(\frac{C_C}{C^*}\right) \right]^2$$

With $\ln S \sim \sigma$, and in terms of dimensionless numbers :

$$\frac{v_{B+S}}{AB^{5/6}} = \left(\frac{\sigma}{B}\right)^{5/6} \exp\left(-\frac{B}{\sigma}\right)$$

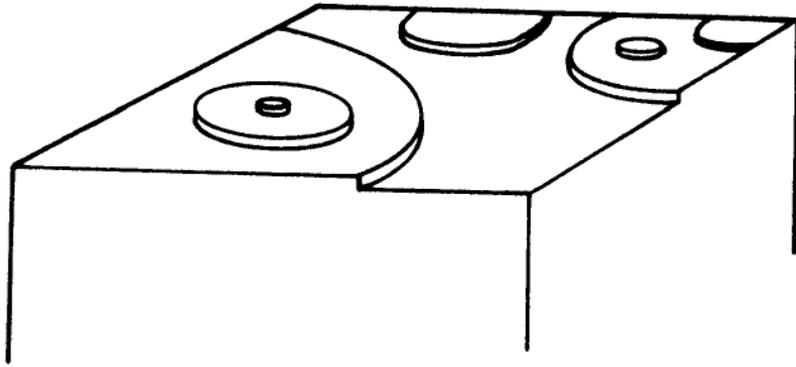


Figure 6.13. *Development of polynuclear growth by the birth and spread ($B + S$) mechanism*



Miers 1904, KClO_3 . RI measurements have shown the solution on the crystal surface was supersaturated!

Berthoud (1912) and Valeton (1924)

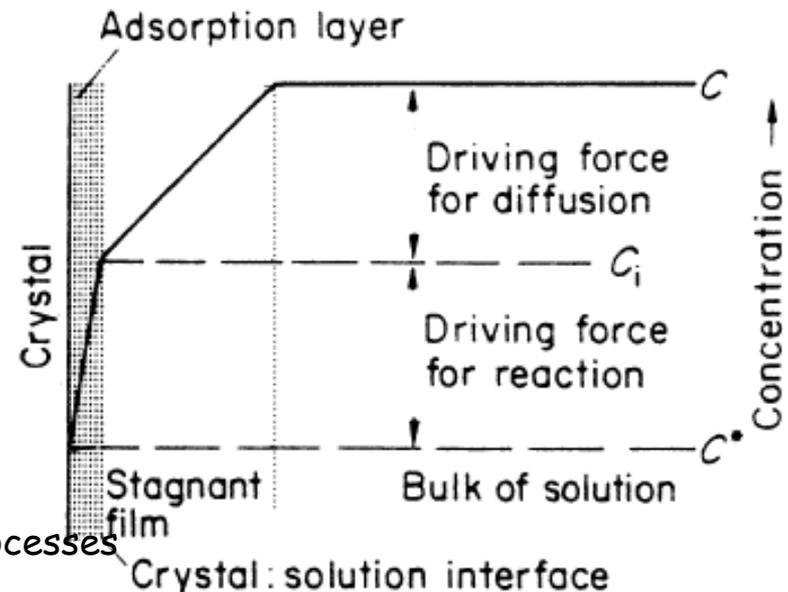
$$\frac{dm}{dt} = k_d A (c - c_i) \quad (\text{diffusion})$$

and

$$\frac{dm}{dt} = k_r A (c_i - c^*) \quad (\text{reaction})$$

And since it is not possible to measure concentrations at the crystal-fluid interface:

$$\frac{dm}{dt} = K_G A (c - c^*)^g$$



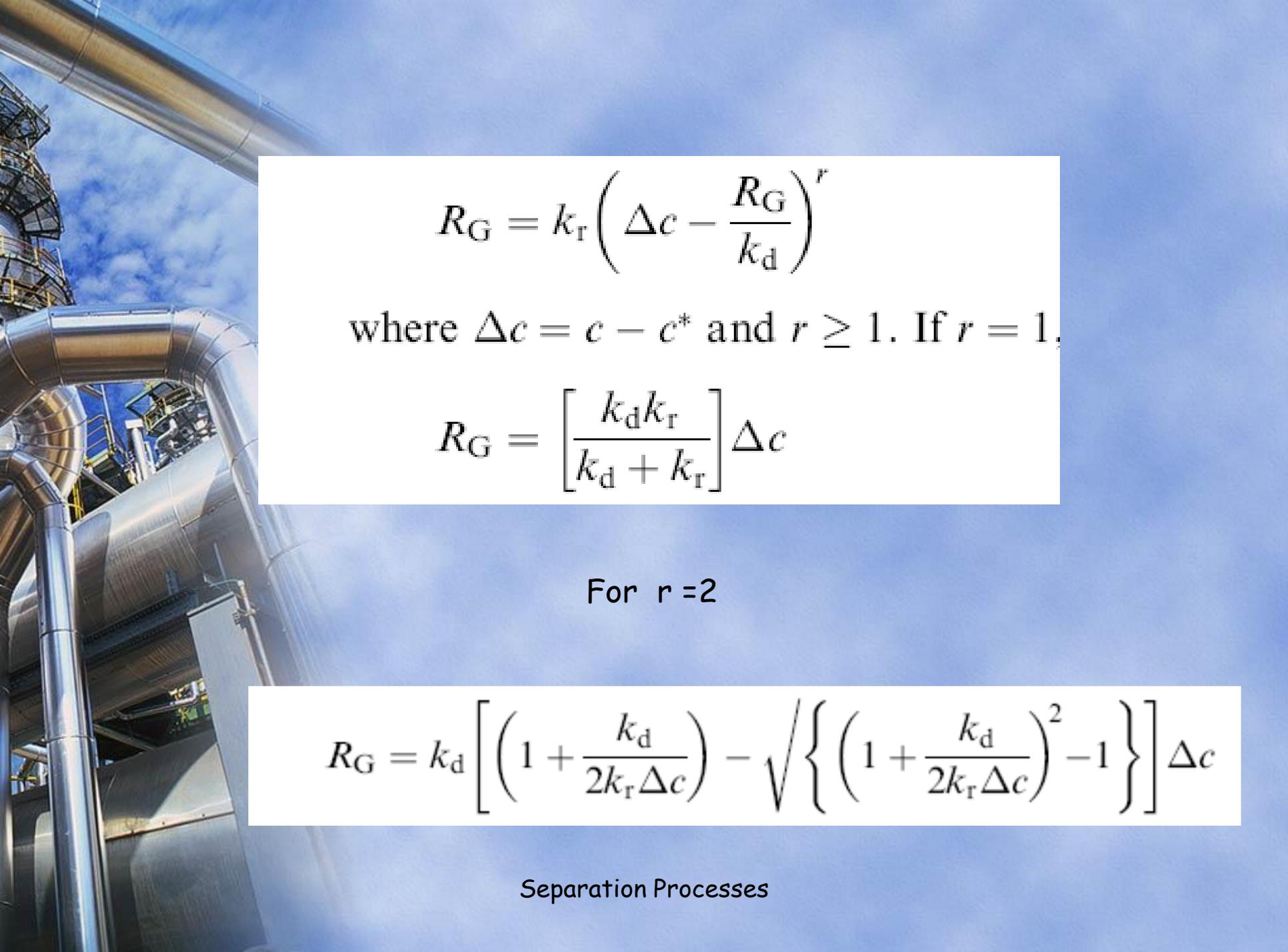
Για $g=1$

$$\frac{dm}{dt} = \frac{A(c - c^*)}{1/k_d + 1/k_r}$$

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

$$K_G = \frac{k_d k_r}{k_d + k_r}$$

$$\begin{aligned} R_G &= \frac{1}{A} \cdot \frac{dm}{dt} = k_d(c - c_i) && \text{(diffusion)} \\ &= k_r(c_i - c^*)^r && \text{(reaction)} \\ &= K_G(c - c^*)^g && \text{(overall)} \end{aligned}$$


$$R_G = k_r \left(\Delta c - \frac{R_G}{k_d} \right)^r$$

where $\Delta c = c - c^*$ and $r \geq 1$. If $r = 1$,

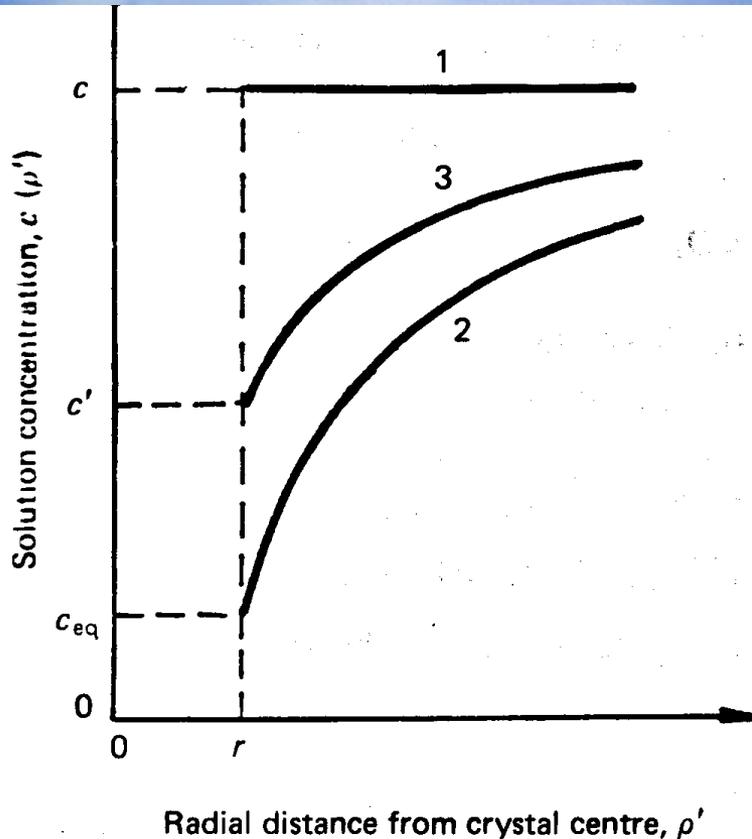
$$R_G = \left[\frac{k_d k_r}{k_d + k_r} \right] \Delta c$$

For $r = 2$

$$R_G = k_d \left[\left(1 + \frac{k_d}{2k_r \Delta c} \right) - \sqrt{\left\{ \left(1 + \frac{k_d}{2k_r \Delta c} \right)^2 - 1 \right\}} \right] \Delta c$$

Diffusion controlled crystal growth

Around every crystal growing in a solution, a steady-state diffusion field is established. For distances between the crystals > 20 particle diameters diffusion fields around crystals do not influence each other and may be taken to extend to infinity.



$$\frac{dm}{dt} = k_m A (c - c^*)$$

Noyes 1897

$$\frac{dm}{dt} = \frac{D}{\delta} A (c - c^*)$$

Nernst 1904

Solution concentration distribution around a crystal when growth is controlled by surface reaction (1), by transport of the material in the solution (2) and by both mechanisms (3)

C = bulk concentration

C' = concentration at crystal surfaces

C_{eq} = equilibrium concentration

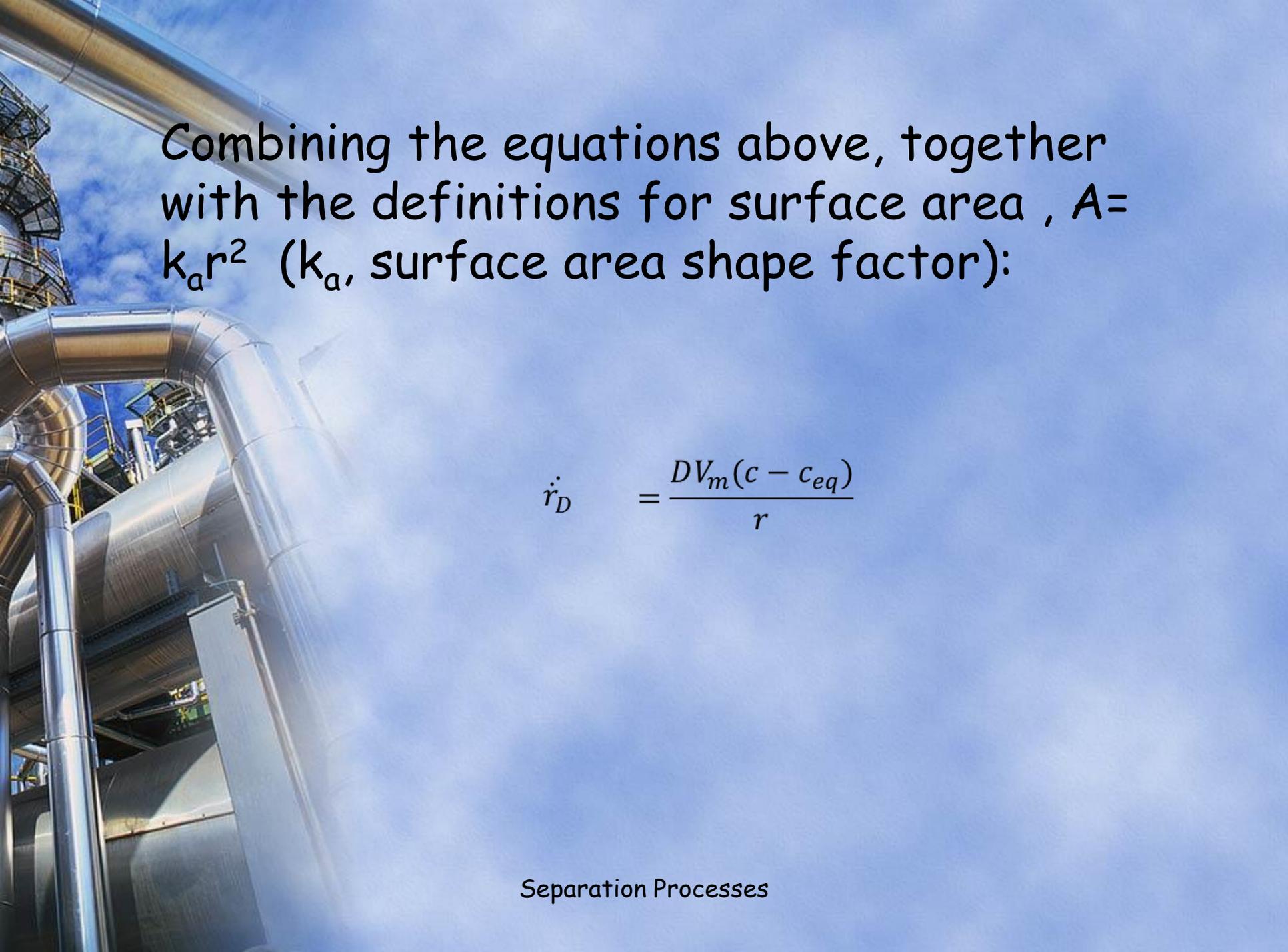
The diffusive steady state mass flow towards a crystal is given by Fick's law provided that $c\varphi_v \ll 1$ (φ_v being the partial molar volume of the solute):

$$j = \frac{dn_i}{dt} = [DA \text{grad}(c(\rho'))] \rho' = r$$

For small and spherical particles (e.g. $r < 5 \mu\text{m}$) in a stationary liquid, the concentration gradient in the neighborhood of the surface is:

$$\text{grad}c(\rho') = \frac{(c - c_{eq})}{r}$$

Provided that the solute concentration at the crystal surface is equal to the equilibrium value. If dn_i moles of the substance is incorporated into the lattice the crystal volume increases by:

A photograph of an industrial distillation column with a complex network of stainless steel pipes and ladders, set against a clear blue sky. The pipes are highly reflective and curve in various directions, creating a sense of depth and complexity. The background is a bright, clear blue sky with a few wispy clouds near the horizon.

Combining the equations above, together with the definitions for surface area, $A = k_a r^2$ (k_a , surface area shape factor):

$$\dot{r}_D = \frac{DV_m(c - c_{eq})}{r}$$

The diffusion controlled crystal growth rate, assuming spherical shape of the crystallites is

$$\dot{r}_D = \frac{DV_m(c - c_{eq})}{r}$$

And for dissociating electrolyte salts (AB) into A and B ions

$$\dot{r}_D = \frac{V_m}{2r} \left[c_A D_A + c_B D_B - \left((c_A D_A - c_B D_B)^2 + 4D_A D_B c_{A,eq} c_{B,eq} \right)^{1/2} \right]$$

For ions with molar mass < 1000 the diffusion coefficients of the ions are equal (other than H⁺, OH⁻). In this case and provided that $(c_A - c_B)^2 \gg c_{A,eq} c_{B,eq}$ the kinetic equation becomes:

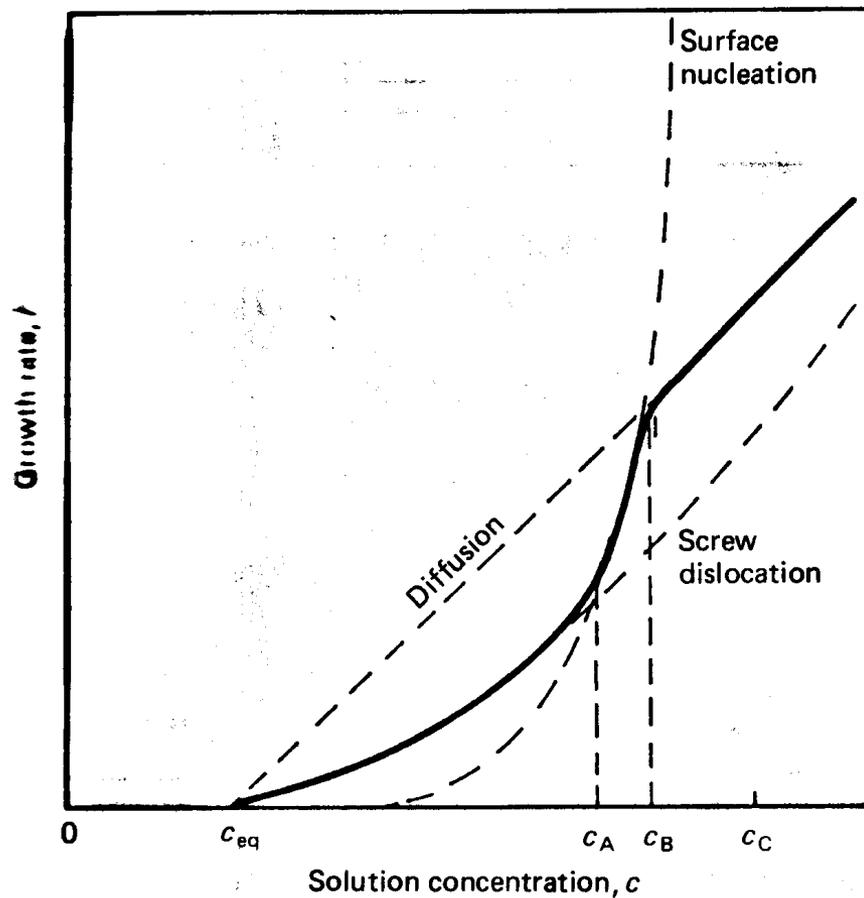
$$\dot{r}_D = \frac{DV_m c_x}{r}$$

Where $c_x = c_A$ if $c_A < c_B$ and $c_x = c_B$ if $c_A > c_B$

The equations indicate that the rate of diffusion controlled growth of an electrolyte from a solution with a non-stoichiometric ratio of ionic concentrations is a function of the deficit ion concentration and independent of the ionic concentration of the excess ion

Growth controlled by combined mechanisms

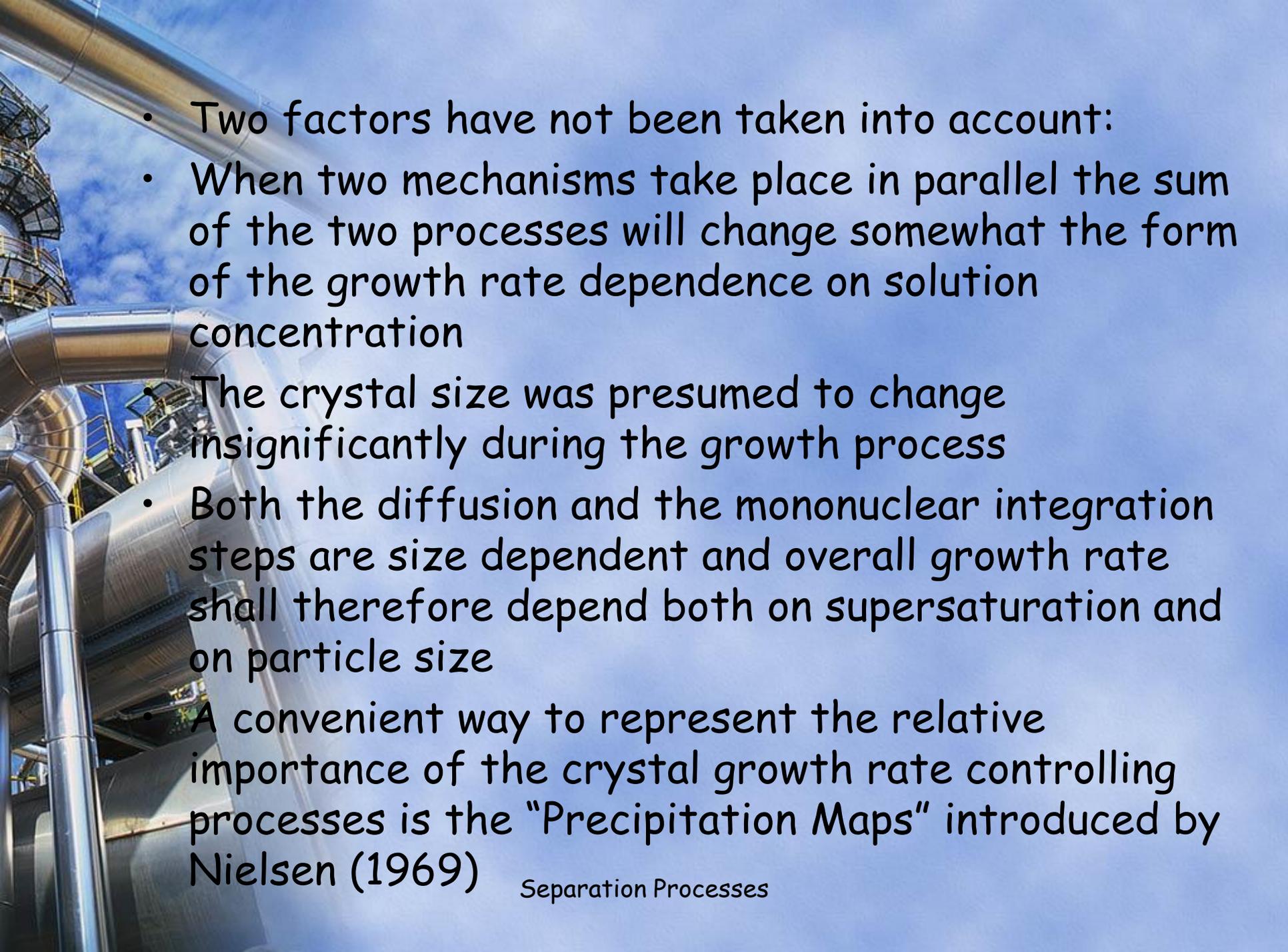
- It is rather unusual that the rate of crystal growth is controlled by a single mechanism: In several cases several mechanisms influence growth rate
- If the several mechanisms are thought to take place in parallel (e.g. polynuclear and screw dislocation surface processes) then the mechanism resulting in faster growth, controls the overall rate
- If the processes take place in series, as in the case of bulk diffusion followed by surface reaction then the slower of the participating mechanisms controls the overall rate



Growth rate of a crystal in a closed system with decreasing supersaturation as a function of the solution concentration

The dashed lines represent the dependence of growth rate, governed by various mechanisms, on solution concentration. If crystals start to grow in solution of concentration c_c the mechanism of the faster of the two surface reaction processes (here surface nucleation) is faster than the diffusion step, so growth shall be controlled by diffusion. At c_B , the surface reaction is the controlling mechanism because both reaction processes are slower than diffusion.

In the region between c_B, c_A , the nucleation mechanism is the faster of the two surface processes and is thus the controlling mechanism. At concentrations lower than c_A , the screw dislocation mechanism becomes controlling mechanism and under these conditions results in faster growth

- 
- A photograph of an industrial facility, likely a refinery or chemical plant, featuring large, shiny metal pipes and structures against a clear blue sky. The pipes are arranged in a complex network, with some curving upwards and others running horizontally. The background shows more industrial equipment, including what appears to be a distillation column or similar structure.
- Two factors have not been taken into account:
 - When two mechanisms take place in parallel the sum of the two processes will change somewhat the form of the growth rate dependence on solution concentration
 - The crystal size was presumed to change insignificantly during the growth process
 - Both the diffusion and the mononuclear integration steps are size dependent and overall growth rate shall therefore depend both on supersaturation and on particle size
 - A convenient way to represent the relative importance of the crystal growth rate controlling processes is the "Precipitation Maps" introduced by Nielsen (1969)

Precipitation maps

- The growth rate is in general a function for the supersaturation, crystal size and of the physical parameters of the system:

$$\dot{r} = f(S, r, v, \gamma^s, \dots)$$

- The physical parameters for a given system are constant, the controlling mechanism is determined by S and r
- The boundaries between the regions in which growth is controlled by any one of the mechanisms can be specified by determining the set of values of S and r for which the mechanisms on either side of the boundary are equally important

The boundaries are given by the loci of points where the rates of two mechanisms are the same

Table 3.3 *Boundaries between different growth mechanisms*

<i>Mechanisms</i>	<i>Expression</i>
Polynuclear/ mononuclear	$r_{PM} = \left[\frac{K_p F(S) d^3}{6D_s} \right]^{1/2} \exp \left[\frac{\beta' \gamma s^2 v^{4/3}}{3(kT)^2 v \ln S} \right]$
Polynuclear/ diffusion	$r_{PD} = \frac{DV_m \Delta c}{K_p F(S)} \exp \left[\frac{\beta' \gamma s^2 v^{4/3}}{3(kT)^2 v \ln S} \right]$
Diffusion/ screw dislocation	$r_{DS} = \frac{BDV_m c_{eq}^2}{C \Delta c \tanh(B/\sigma)}$
Mononuclear/ screw dislocation	$r_{MS} = \left[\frac{C_s \sigma^2 d^3 \tanh(B/\sigma)}{6B_s D_s} \right]^{1/2} \exp \left[\frac{\beta' \gamma s^2 v^{4/3}}{2(kT)^2 v \ln S} \right]$

The boundary between polynuclear and screw dislocation growth, both of which are size-independent is given by a certain value of the supersaturation calculated from:

$$F(S_{SP}) = \frac{C_S (S_{SP} - 1)^2 \tanh[B_s / (S_{SP} - 1)]}{B_S K_P} \exp \left[- \frac{\beta' \gamma^{s^2} \nu^{4/3}}{3(kT)^2 \nu \ln S_{SP}} \right]$$

Substituting values of constants for BaSO₄ the precipitation map for this salt may be constructed

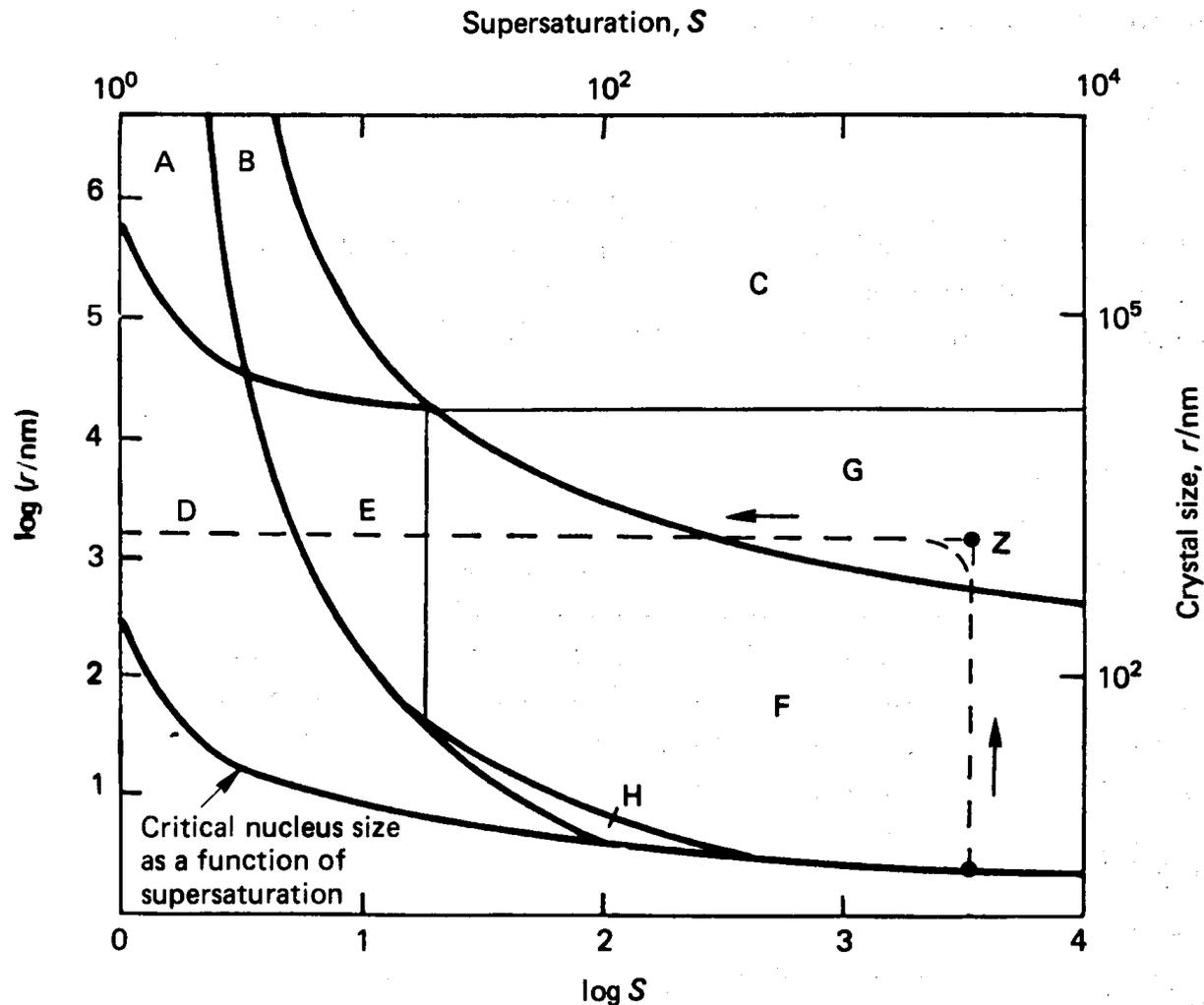
The lower limit of the map represents the dependence of the critical nucleus size on supersaturation

In order to determine the controlling growth mechanism in a particular case, the point representing the initial supersaturation of the system and the final average crystal size calculated from

Separation Processes

$$\left[\frac{V_p (c_0 - c_{eq})}{k_v N} \right]^{1/3}$$

is plotted



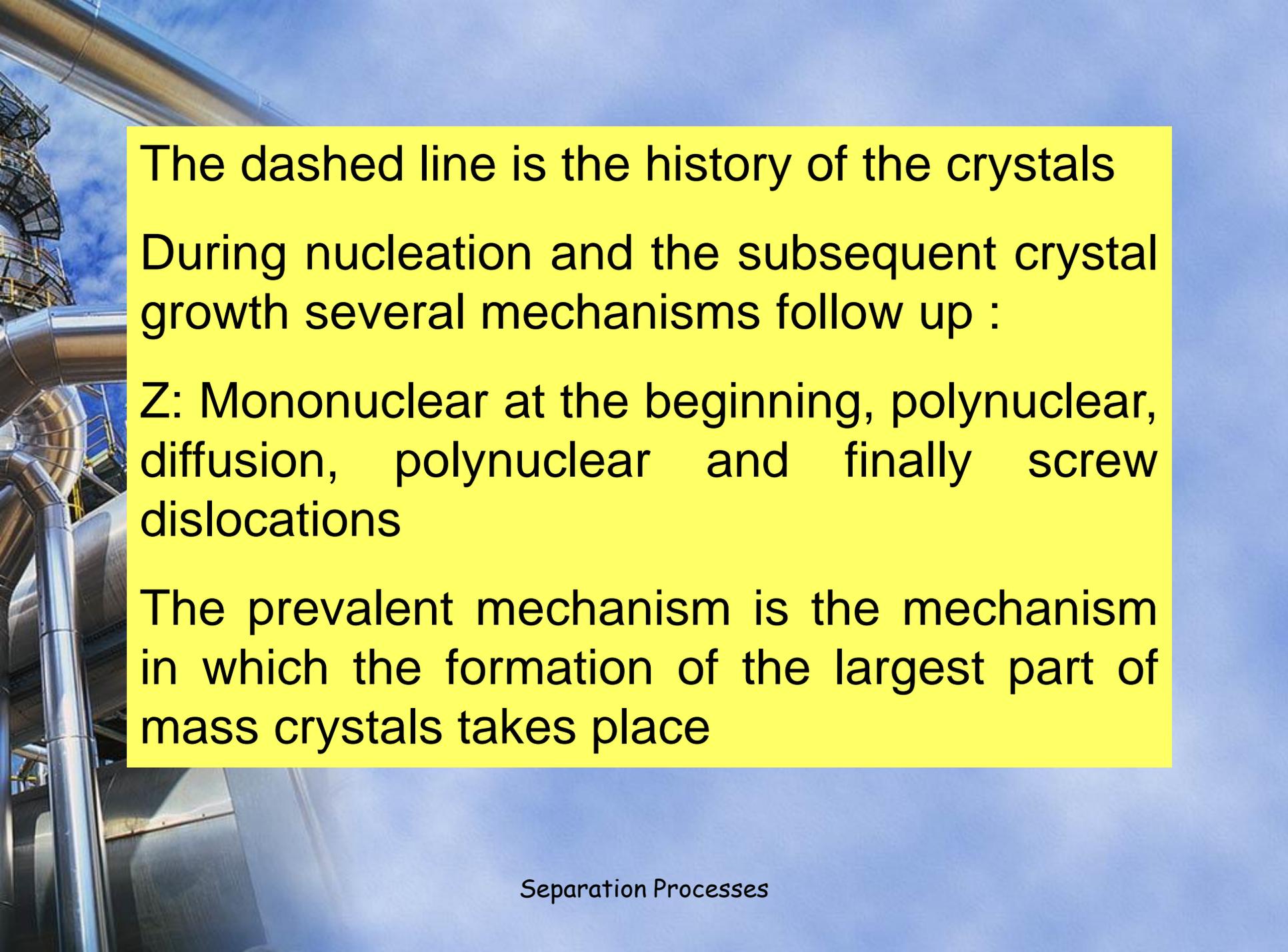
For a specific case, for the estimate of the rate determining mechanism the supersaturation is selected first and the corresponding crystal size is :

$$r = \left[\frac{V_m (c_0 - c_{eq})}{k_v N} \right]^{1/3}$$

Figure 3.29 Precipitation map for BaSO₄. Controlling growth mechanisms in the individual regions are: (A) – mononuclear or convection, (B) – polynuclear or convection, (C) – convection, (D) – mononuclear or screw dislocation, (E) – polynuclear or screw dislocation, (F) – polynuclear, (G) – diffusion, (H) – mononuclear

Separation Processes

Dashed line: The life history of the crystals during their growth 46



The dashed line is the history of the crystals

During nucleation and the subsequent crystal growth several mechanisms follow up :

Z: Mononuclear at the beginning, polynuclear, diffusion, polynuclear and finally screw dislocations

The prevalent mechanism is the mechanism in which the formation of the largest part of mass crystals takes place