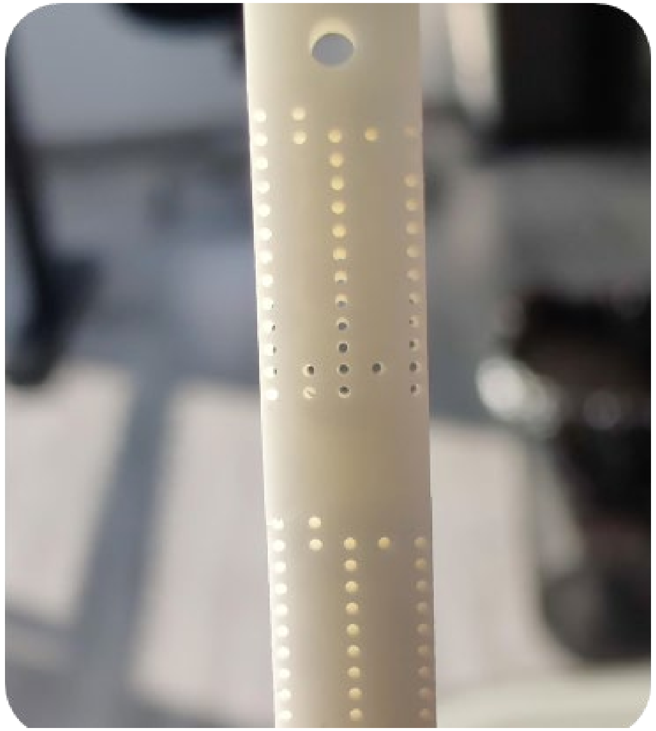
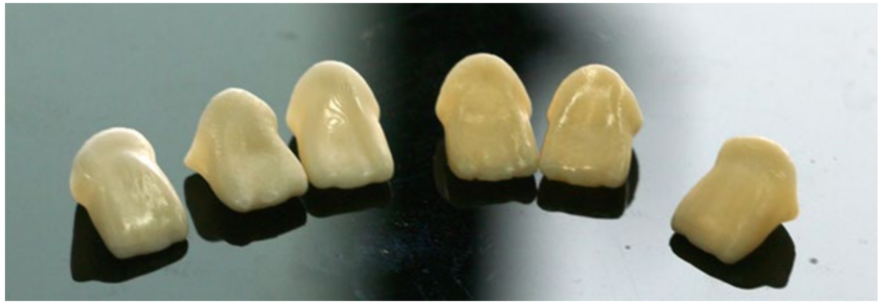
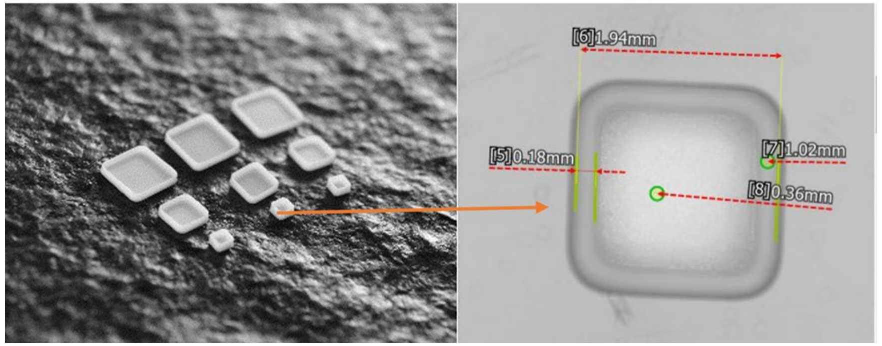
MSE 495 – Advanced Ceramics Technology

Michael Stuer (Empa) - Andrea Testino (PSI)

Week 3 – Synthesis







Synthesis

Top-down

bulk

Several µm to mm

Milling

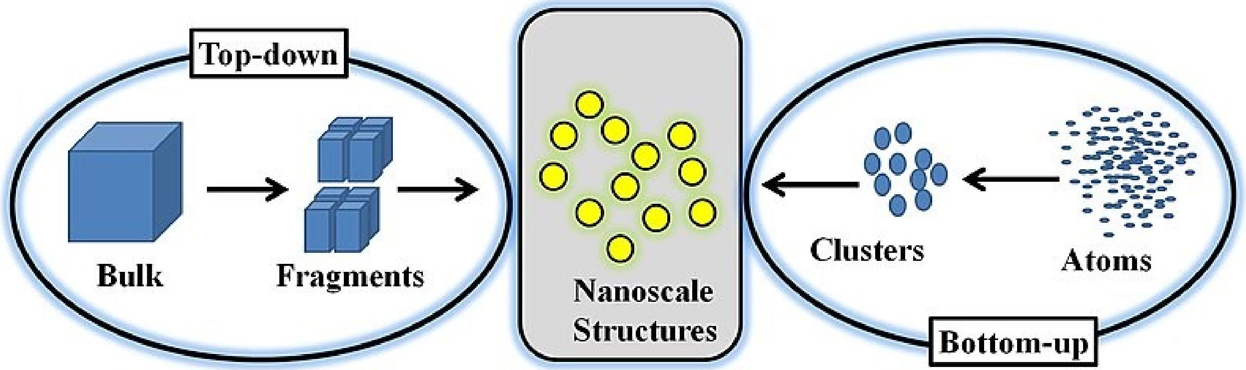
● From ≈ 100 nm to *few* µm (1-2)

Bottom-up

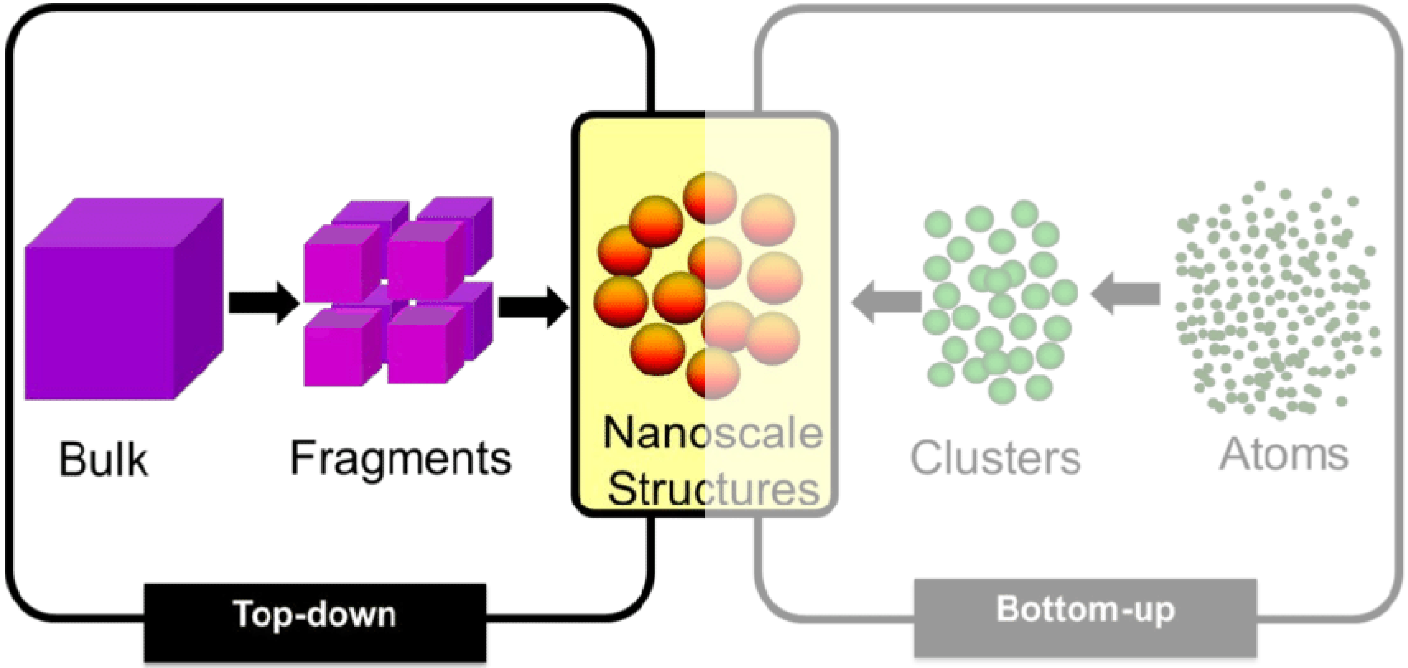
solutions

● From *few* nm to µm

If the target is really nm particles, bottom-up is the only way



Top down


Bulk
Fragments
Nanoscale Structures
Clusters
Atoms
Top-down
Bottom-up

Thermal Decomposition of Solids

- Temperature at which decomposition becomes thermodynamically favorable depends on
  - the strength of the chemical bond of the solid in question and if
  - a gas is produced, the partial pressure of this gas in the surrounding atmosphere.

- Thermal decomposition of $MgCO_3$ is a good illustration of this type of reaction

$$MgCO_3 \rightarrow \boxed{MgO} + CO_2$$

- The enthalpy of reaction, ΔH_r^0 from $MgCO_3$ to MgO and CO_2 at 298 K is 105 KJ/mol (endothermic).
- Therefore, thermal energy will promote the decomposition of the compound.

Variation of the standard enthalpy, ΔH^0: it is the change in enthalpy when a substance(s) passes from its (their) initial to final state, in standard conditions. “Standard conditions” means in its (their) pure form at a given temperature and under a pressure of 1 bar.

Thermal Decomposition of Solids

$$\Delta_r G^0(T) = -RT \ln K_{eq}$$

System in equilibrium

$$\Delta_r G(T) = \Delta_r G^0(T) + RT \ln Q_r$$

System out-of-equilibrium

$\Delta_r G$ is the free energy of reaction; $\Delta_r G^0$ standard free energy

R the gas constant, T the temperature (K) and

Q_r reaction quotient

- *a* (activity) for liquids
- *f* (fugacity) for gases
- *a* =1 for solids

$$Q_r = \frac{\prod_j (a_j)^{\nu_j}}{\prod_i (a_i)^{\nu_i}}$$

j : products
i : reagents

examples

$2A_{(aq)} + B_{(aq)} \rightarrow 3C_{(aq)}$

$$Q_r = \frac{(a_C)^3}{(a_A)^2 (a_B)}$$

$2A_{(s)} + B_{(aq)} \rightarrow C_{(g)}$

$$Q_r = \frac{f_C}{a_B}$$

Thermal Decomposition of Solids

$$MgCO_3 \rightarrow MgO + CO_2$$

influence of the atmosphere on the decomposition temperature of solids

$$Q_r = \frac{f_{CO_2} \cdot \overset{\nearrow 1}{a_{MgO}}}{\underset{\searrow 1}{a_{MgCO_3}}} \cong p_{CO_2}$$

$$p_i = x_i \cdot p_t \qquad p_t = \sum_i p_i \qquad n_t = \sum_i n_i$$

$$x_i = \frac{n_i}{n_t} \qquad \sum_i x_i = 1$$

n_i: mol of *i*
x_i : molar fraction of *i*
p_i : partial pressure of *i*
p_t : total pressure
n_t: total mol

As in solution concentration is an approx. of activity, partial pressure is an approx. of fugacity

$$\Delta_r G(T) = \Delta_r G^0(T) + \mathrm{RT} \ln p_{CO_2}$$

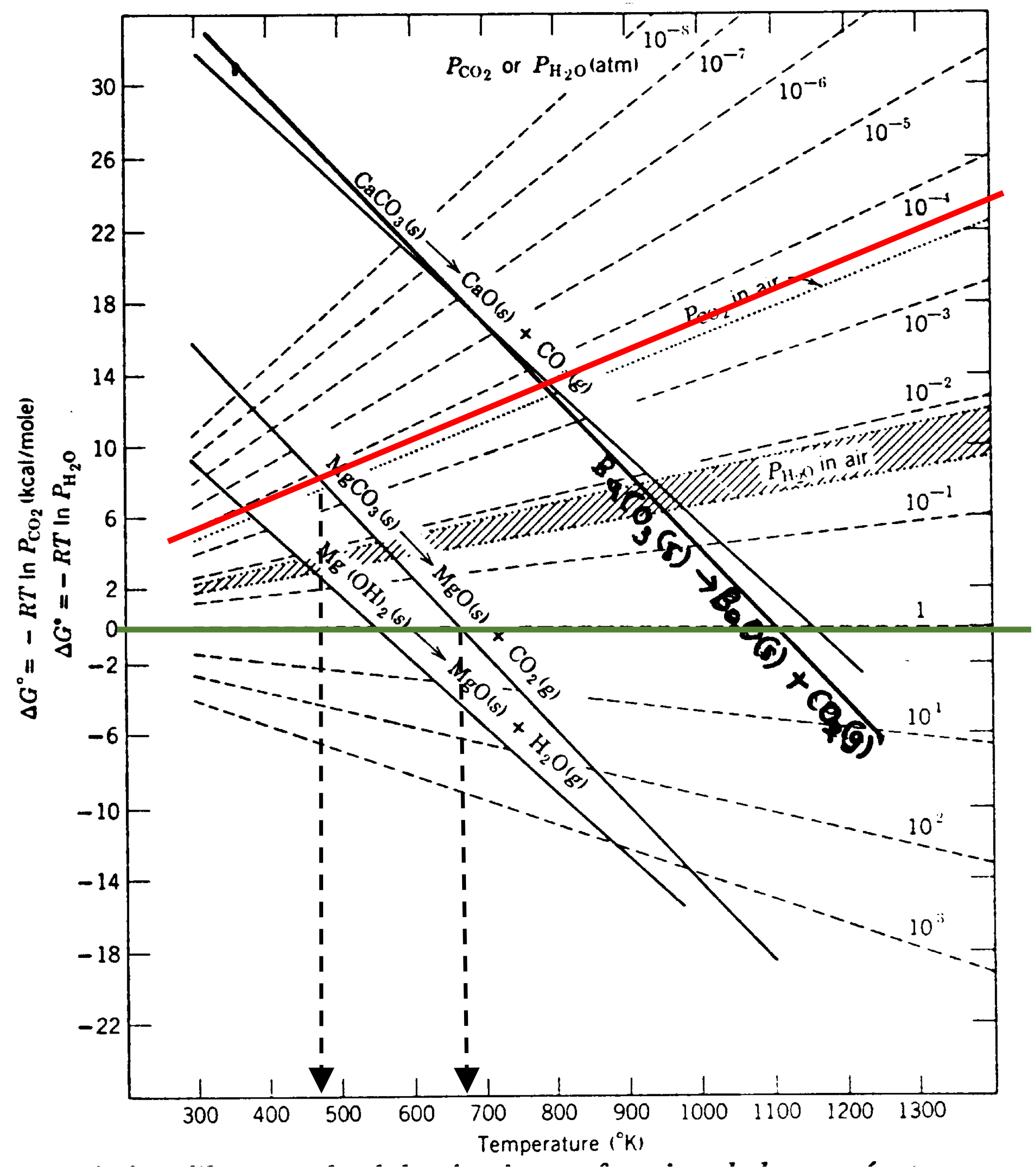
$p_{CO_2} = 1;\ \ln 1 = 0$
$\Delta_r G(T) = \Delta_r G^0(T)$

Reaction to take place spontaneously when $\Delta_r G < 0$

For a given system under a product gas atmosphere (standard conditions), there is only one equilibrium temperature. When decompositions are carried out in air: $P_{CO2} = 5 \times 10^{-4}$ bar.

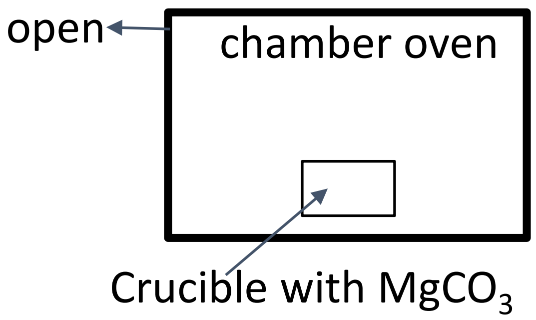
Large effect of atmosphere on decomposition temperature.

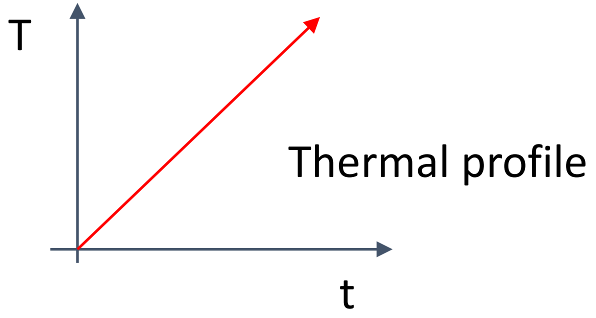
Thermal Decomposition of Solids



- $\Delta G_R = 0$ for $MgCO_3$ at 672 K,
- T> 672 K $MgCO_3$ will decompose spontaneously at atmospheric pressure ($p_{CO2} > 1$ bar)
- For air $p_{CO2} = 5 \times 10^{-4}$ bar, $MgCO_3$ starts to decompose at around 480 K

- Once the thermodynamic conditions are fulfilled, the transformation kinetics are governed by
  - Diffusion of the CO_2 produced from the interface through the formed product layer
  - Heat transport to the interface
  - Chemical reaction itself.

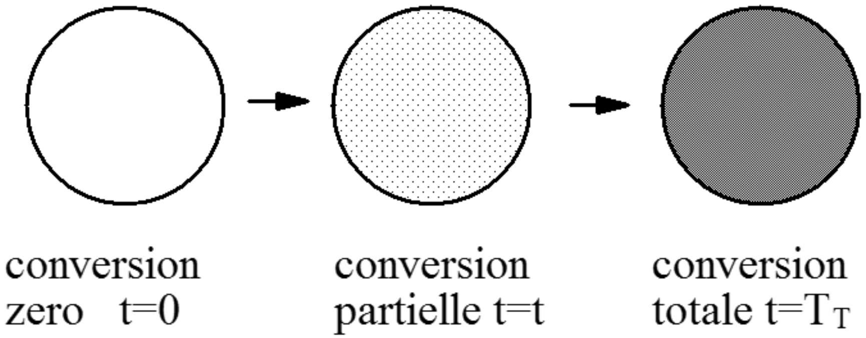

open
chamber oven
Crucible with $MgCO_3$



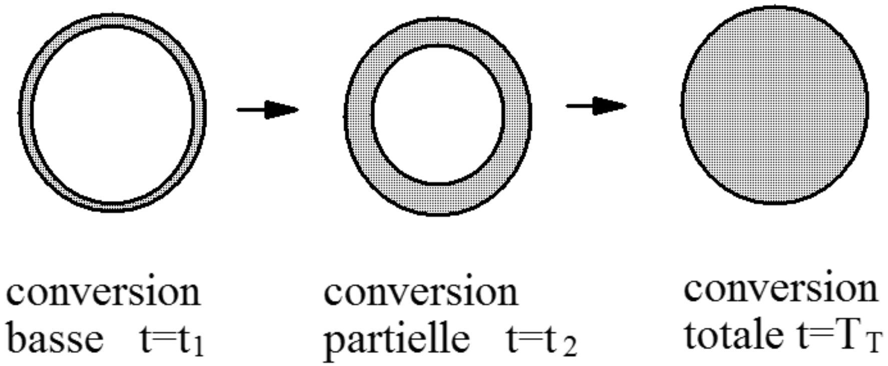
Thermal profile

Thermal Decomposition of solids - Kinetics - models

(a) Conversion progressive



(b) Coeur rétrécissant

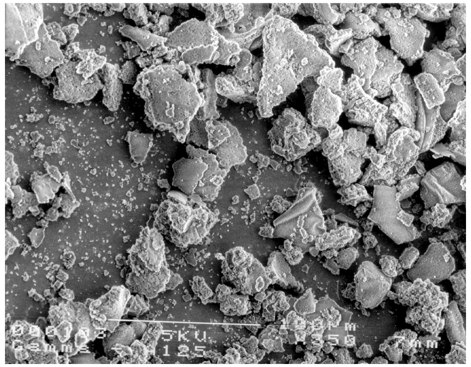


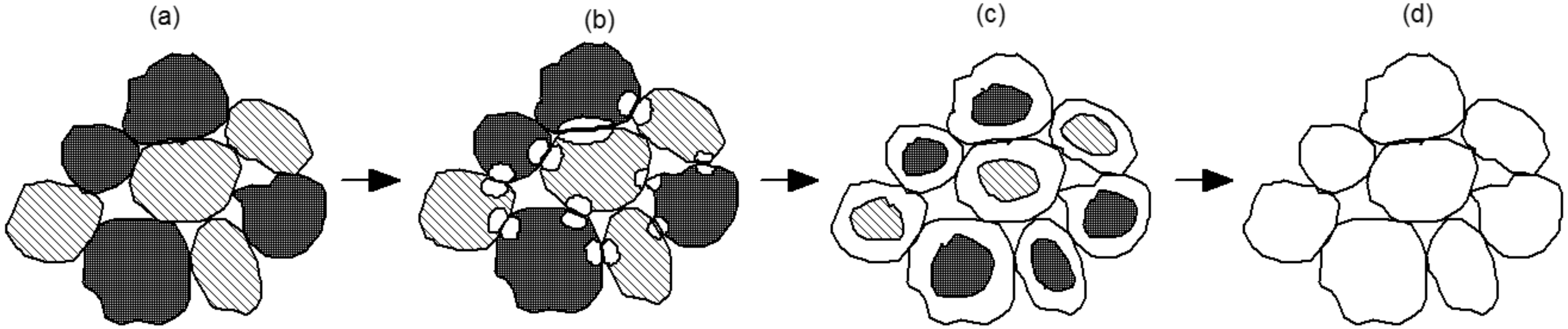
- **Gradual conversion**
- Porous Particles
- Product gas evacuated quickly
- Good heat conductor
- Gradients of T or Conc (gas) avoided

- **Shrinking core** – different possible rate limiting stages
- (i) Mass transfer of a reagent through a film (boundary layer)
- (ii) Diffusion through a product layer
- (iii) Surface chemical reaction (first order reaction)

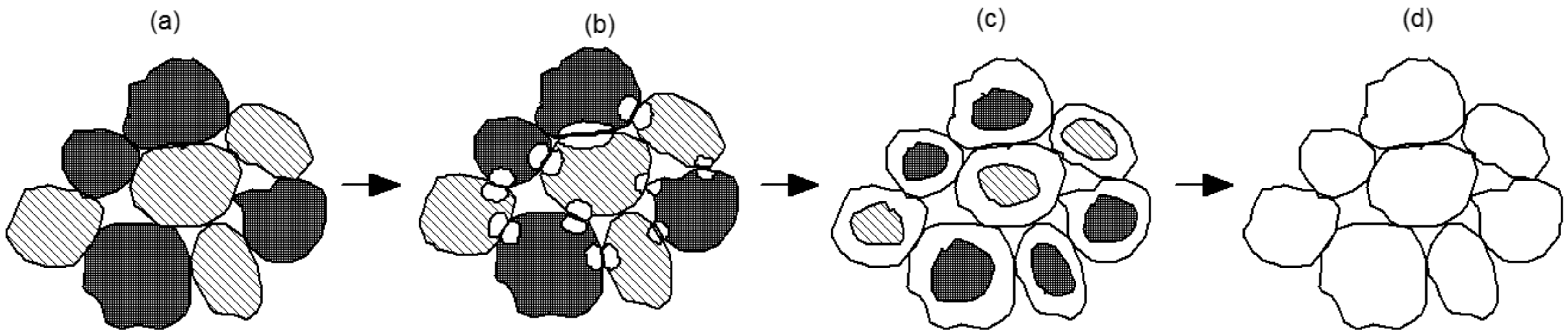
Solid-Solid Reaction

- Many ceramic powders are made by this method when a complex oxide formed from several cations is the end product.
- The traditional method
  - mix the powders containing the necessary cations,
  - often in the form of carbonates or oxides, then
  - heat for interdiffusion of the various ionic species.



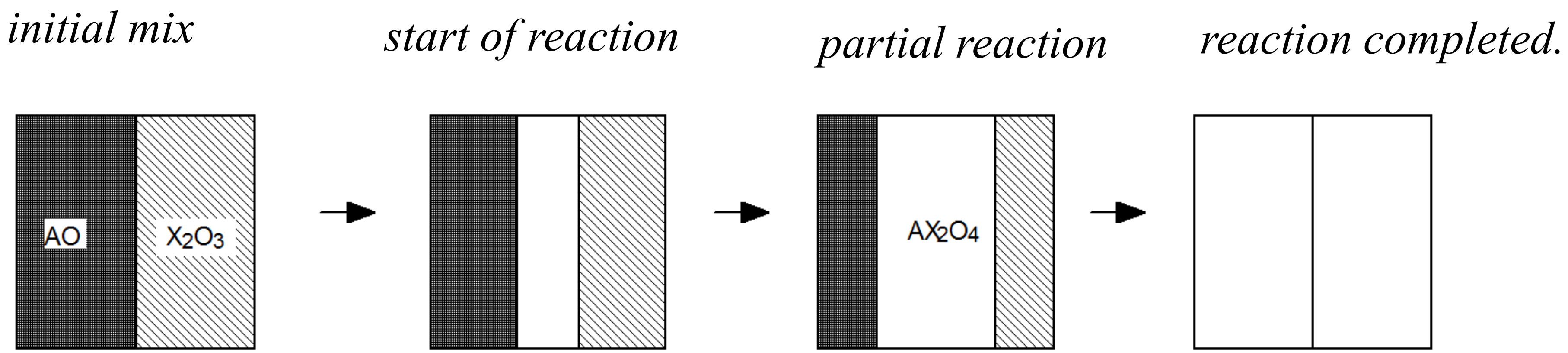


Solid-Solid Reaction – effects of size degree of mixing



- Two important parameters are
  - the degree of initial mixing and the particle sizes.
  - Influence diffusion lengths of various ions.
- Small size - mix is intimate – e.g by co-milling
- If particles too large - incomplete conversion – need a 2nd milling

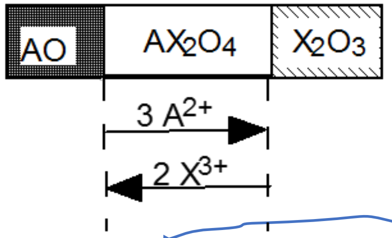
Solid-Solid Reaction - Interfaces - mechanisms



- In practice, the nucleation of a new phase at the interface is often faster than the transport of material to the interface.
- Transport speeds of various
    - cations,
    - anions (oxygen) (or even $O_{2\,(gas)}$) and
    - electrons
- Control the kinetics accordingly

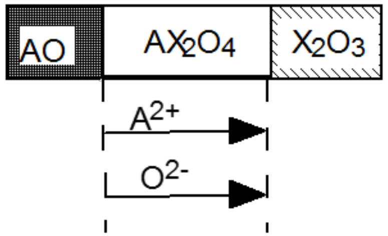
Solid-Solid Reaction - Interfaces - mechanisms

$$AO + X_2O_3 = AX_2O_4$$

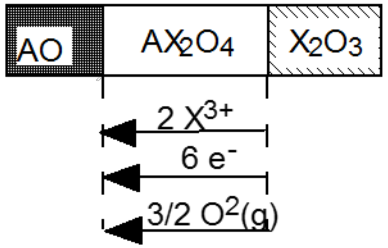


$$4AO + 2X^{3+} = AX_2O_4 + 3A^{2+}$$

$$4X_2O_3 + 3A^{2+} = 3AX_2O_4 + 2X^{3+}$$



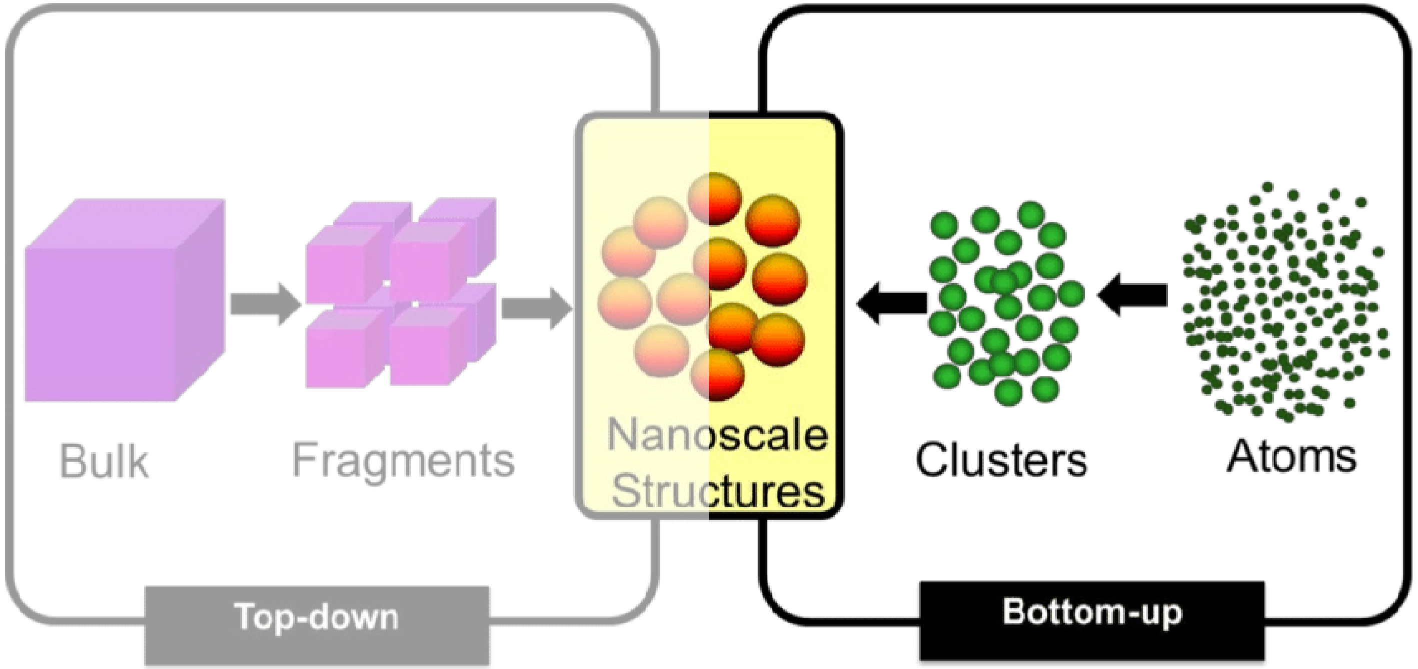
$$A^{2+} + O^{2-} + X_2O_3 = AX_2O_4$$



$$AO + 2X^{3+} + 6e^- + \tfrac{3}{2}O_2(g) = AX_2O_4$$

- For the development of the kinetic expressions the following assumptions are made
  - the cations show similar diffusion rates
  - the product layer is uniform,
  - that the reactants and the products have the same molar volume

Bottom-up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Why (spontaneous) precipitation take place?

When a substance is transformed from one phase into another, such as **solid formation from solution**, the Gibbs free energy[1] change associated to the process at constant temperature and pressure may be written as

$$\Delta G_V = (\mu_2 - \mu_1)\Delta n$$

where Δn, is the amount of substance and $\boldsymbol{\mu_1}$ and $\boldsymbol{\mu_2}$ the chemical potentials of the two phases involved in transformation, respectively. In term of intensive[2] quantities:

$$\varphi = -\frac{\Delta G_V}{\Delta n} = -\Delta\mu = \mu_1 - \mu_2 = k_B T \ln\left(\frac{a_1}{a_2}\right)$$

The molar affinity, φ, is the driving force of the transformation. Of course, when $\varphi>0$ transformation from 1 to 2 is a spontaneous process whereas when $\varphi<0$ the process is thermodynamically unfavourable, and it does not occur (at the macroscopic scale[3]).

[1] It refers to the overall volume (mass) of the substance, the so-called bulk contribution.

[2] Mass independent.

[3] Remember the relationship between thermodynamic equilibrium constant K and the kinetic constants k_1 and k_{-1}

If we identify the phase$_1$ as a dissolved matter and phase$_2$ as the pure solute in equilibrium with a macroscopic crystal, we obtain

$$\varphi = k_B T \ln\left(\frac{a_{(aq)}}{a_{(s)}}\right) = k_B T \ln S$$

where *S* is the (super)saturation.

$$S = \frac{a_{(aq)}}{a_{(s)}}$$

Thus, the driving force (φ) towards the solid formation from a supersaturated solution (precipitation) is proportional to ln*S*.

$$S(t) = \frac{Chemical\ speciation\ in\ solut.(t)}{Equlibiurm\ with\ solid}$$

Supersaturation can be induced in systems in several ways:

1. Temperature change (with thermodynamic and kinetic effects);
2. Mixing of solutions (same solvent, e.g. water);
3. Add another solvent (variation of dielectric constant of the solvent);
4. Induce a pH change (adding acid or alkaline solution, or consequence of another induced reaction);
5. Evaporation;
6. Gas dissolution (e.g. CO_2 partial pressure);
7. And so on…

The way and speed we apply to induce supersaturation in a system will define the precipitation pathway and thus the powder properties.

It is a combination of ThermoDynamics and Kinetics (TD-K)

This concept will be recalled in the exercise

Another term contributes to the overall Gibbs free energy: the surface energy

$$\Delta G_S$$

The free energy of the substance forming the surface layer is greater than the free energy of the bulk material: molecules (or ions, atoms) on the surface layer are in a state of higher potential energy (less, and weaker bonds) than internal molecules (or ions, atoms). This excess of free energy can be expressed by the surface tension γ (energy per unit area).

The expression of the Gibbs free energy, including the surface contribution, becomes:

$$\Delta G = \Delta G_V + \Delta G_S = -\left(\frac{V_n}{\nu}\right) k_B T \ln(S) + \oint_A \gamma dA$$

V_n : Particle volume
ν : Molecular volume

γ :Surface energy

When is the surface relevant? How does it affect material properties?
A 1 nm cubic particle shows about 60% of the atoms on the surface. For a cubic particle of 1000 nm (1μm) the fraction of surface atoms is about 0.06%.
Size has a huge impact on all material properties such as solubility and melting point. For instance, bulk CdSe melts at 1678 K but 3 nm particles melt at 700K! Ag melts at 961 °C but Ag nanoparticles sintering occurs at T < 200 °C, that means they sinter as soon as you try to dry them after synthesis!

Decreasing the size of the solid the definition of “surface” and its properties are rather ambiguous. The surface tension is size dependent.

Nevertheless, considering the *classical nucleation theory*, the surface tension[1] is assumed to be size-independent and it refers to that of the macroscopic crystal (the so-called *capillary assumption*).

This assumption simplifies the mathematics, but it is the major criticism of this theoretical framework. Despite this critical approximation the classical nucleation theory is able to describe the solid formation in solution, in many cases.

[1] or interfacial energy or surface energy. It is worth noting that surface tensions of solids are rather ill-defined, even in vacuum.

Thermodynamics: Surface energy

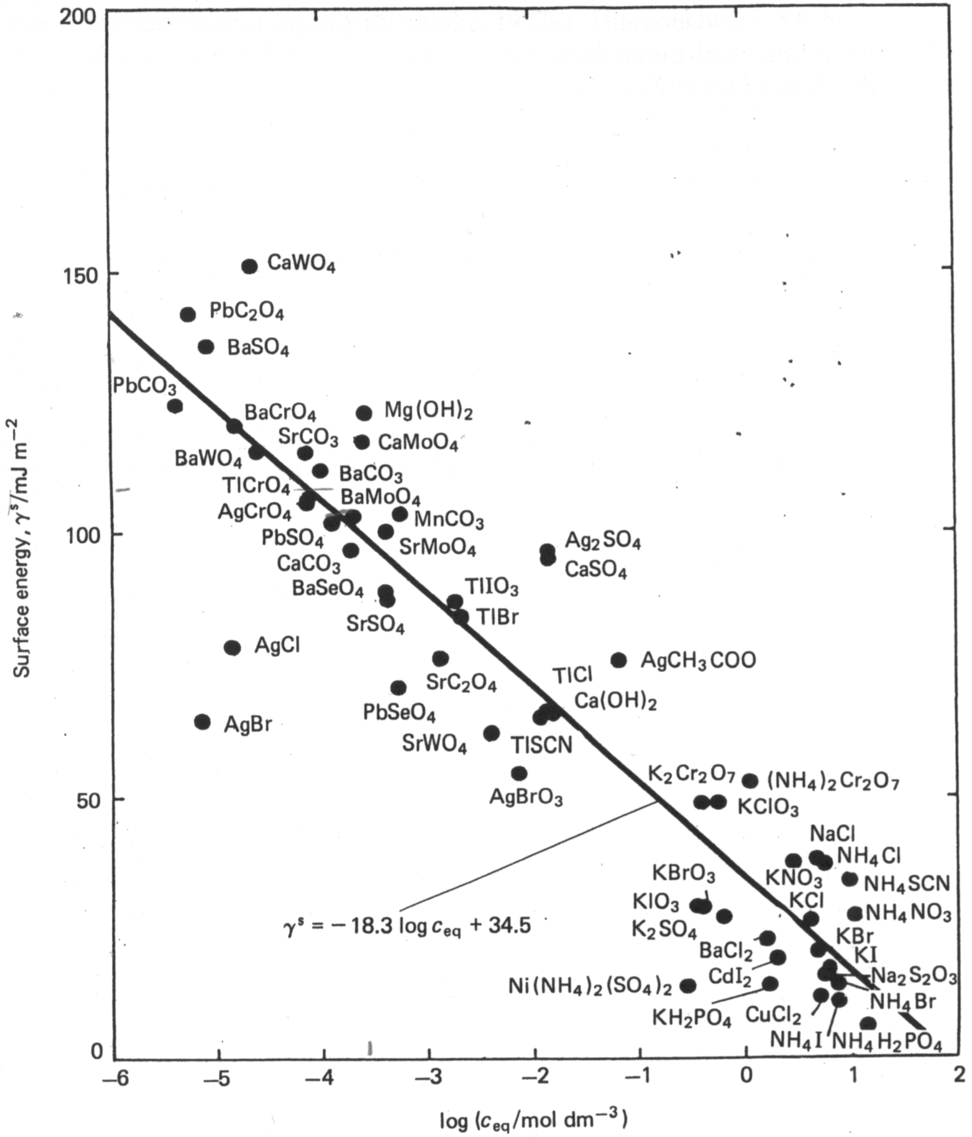
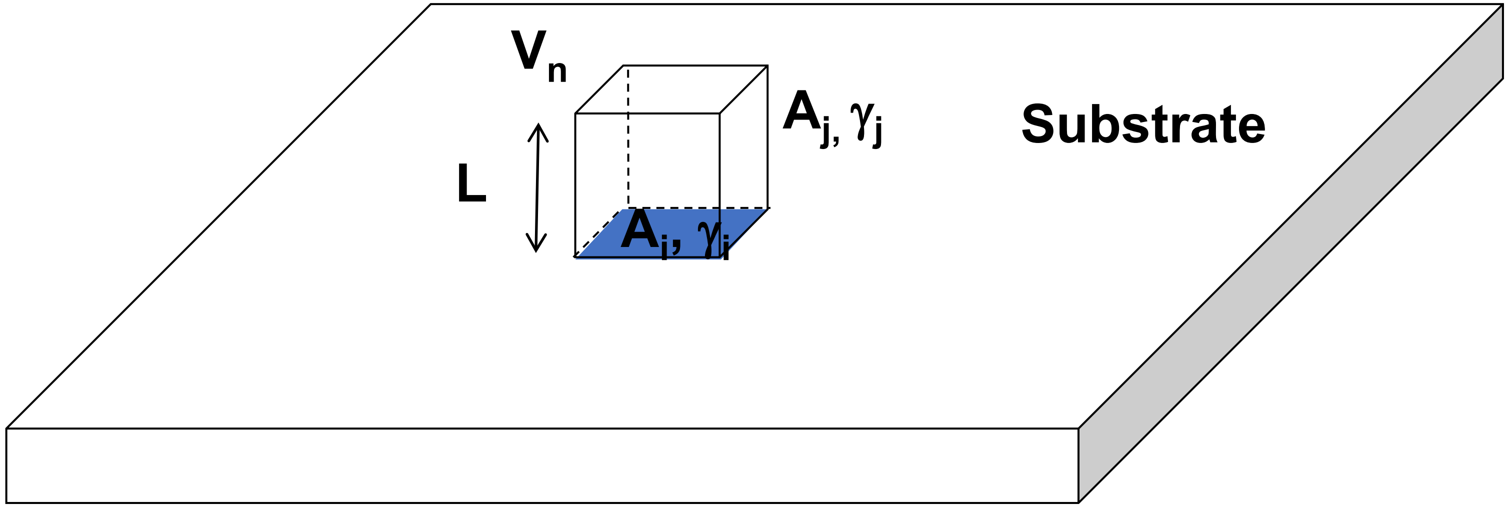


Figure 2.3 Experimentally determined surface energy, γ^s, as a function of equilibrium solubility, c_{eq}

Thermodynamics: Gibbs free energy

$$\Delta G = \Delta G_V + \Delta G_S$$

A further contribution to the Gibbs free energy is due to the interaction with a surface, ΔG_I



$$\Delta G = \Delta G_V + \Delta G_S + \Delta G_I = -\left(\frac{V_n}{\nu}\right) k_B T \ln(S) + \oint_{A_j} \gamma_j dA + \oint_{A_i} (\gamma_i + \beta_{adh}) dA$$

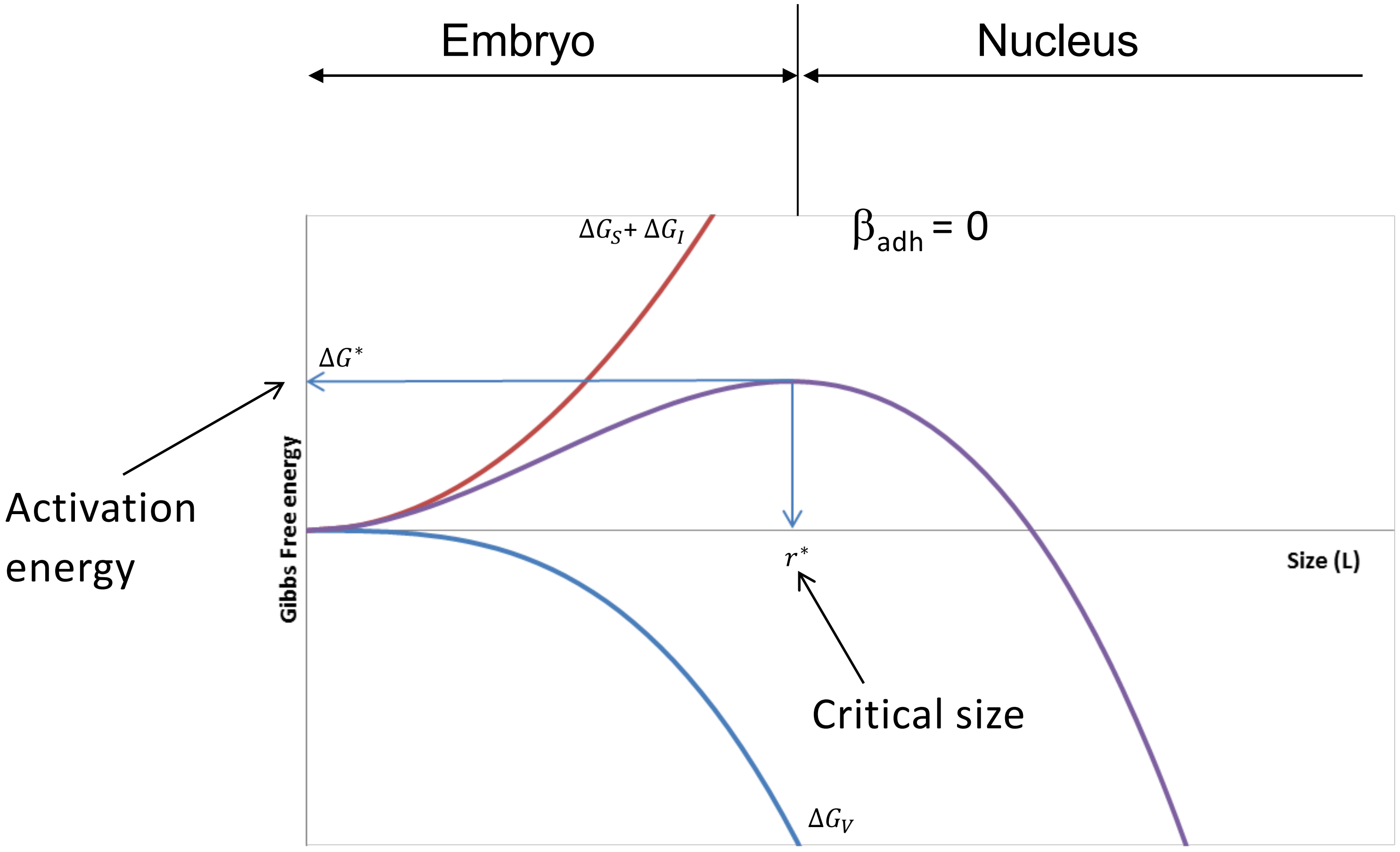
Also ΔG_I is a surface contribution!

β_{adh}: energy of *adhesion (or cohesion)*

Adhesion or cohesion? Adhesion generally refers to interaction between two different solids with poor crystallographic matching; cohesion generally refers to perfect epitaxial match between the two solids, which can be of the same nature: both definitions are only partially correct in this context, since the two solids can have the same nature, and the perfect epitaxial matching is not required. As for many other terms in these slides, it is important to have a clear understanding on the term into the specific context.

Definitions

$$\Delta G = \Delta G_V + \Delta G_S$$

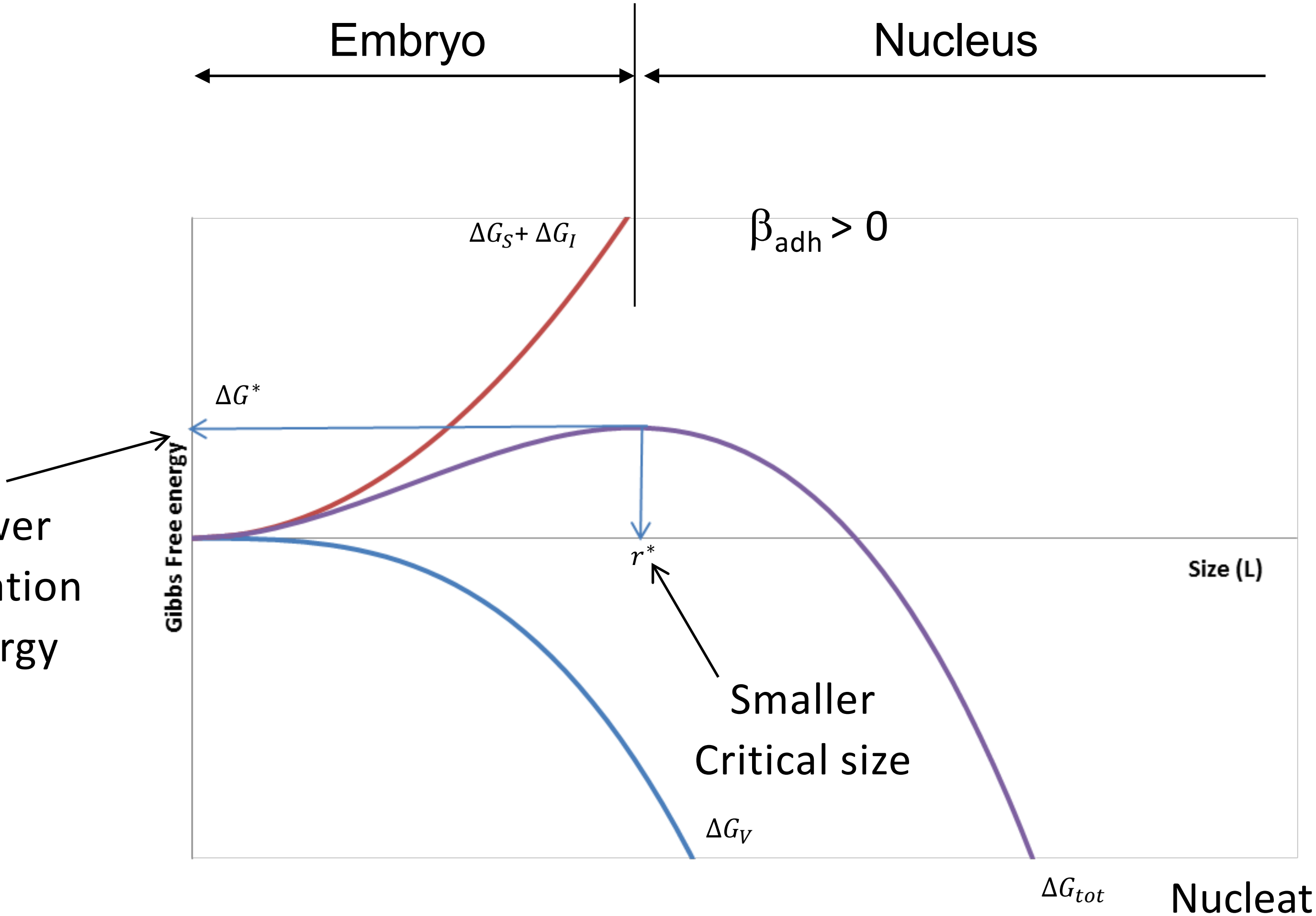


Activation energy

Critical size

If adhesion is considered …

$$\Delta G = \Delta G_V + \Delta G_S + \Delta G_I$$



Lower activation energy

Smaller Critical size

When does particle grow start?
Where is the border between nucleation and growth?
Can we really separate nucleation and growth?

Kinetics:

Nucleation rate: # of nuclei per unit of time and volume

Growth rate: size enlargement just after nucleation

Critical coordinates for nucleation

For a cubic nucleus:

$$L^* = \frac{2}{3}\frac{\nu(6\gamma - \beta)}{k_B T \ln(S)}$$

$$\Delta G^*_{3D} = \frac{4}{27}\frac{\nu^2\gamma^3}{k_B^2 T^2 \ln^2(S)}\left(6 - \frac{\beta}{\gamma}\right)^3$$

$$\Delta G^*_{3D} = 32\frac{\nu^2\gamma^3}{k_B^2 T^2 \ln^2(S)} \quad (\beta = 0)$$

$$\Delta G^*_{3D} = \frac{4}{27}\frac{\nu^2\gamma^3_{eq}}{k_B^2 T^2 \ln^2(S)} \quad (\beta > 0) \qquad \gamma_{eq} = \frac{\gamma}{6}\left(6 - \frac{\beta}{\gamma}\right)$$

How can these values be calculated?

Equilibrium constant

Chemical equilibrium of electrolytes in solution: $(A_aB_b)^n(aq) \rightleftarrows aA^m(aq) + bB^m(aq)$ → $K_{eq} = \frac{[A^m]^a[B^m]^b}{[(A_aB_b)^n]}$

Example: $(Ca_3(PO_4)_2)^0(aq) \rightleftarrows 3Ca^{2+}(aq) + 2PO_4{}^{3-}(aq)$ → $K_{eq} = \frac{[Ca^{2+}]^3[PO_4{}^{3-}]^2}{[(Ca_3(PO_4)_2)^0]}$

Chemical equilibrium (solubility): $(A_aB_b)^n(s) \rightleftarrows aA^m(aq) + bB^m(aq)$ → $K_{sp} = [A^m]^a[B^m]^b$

Example: $BaSO_4(s) \rightleftarrows Ba^{2+}(aq) + SO_4{}^{2-}(aq)$ → $K_{sp} = [Ca^{2+}][SO_4{}^{2-}]$

- Squared brackets, [ ],indicate molar concentration; $[C] = mol/L$
- Equilibrium constant depends on temperature only; $K_{sp} = K_{sp}(T)$
- Molar concentrations are approximation of activities. $a_i = \gamma_i \cdot [C]_i$

Estimation of activity coefficients

There are different equation that can be used, each more appropriate in a defined ionic strength (IS or I) range.

$$I = \frac{1}{2}\sum_i z_i^2\, c_i$$

c_i: conc of i

z_i: charge of i

For low IS (e.g. < 0.2 M), the Debye-Hückel equation offer a good estimation

$$-\log \gamma_i = \frac{A \cdot z_i^2 \sqrt{I}}{1 + B \cdot d_i \sqrt{I}}$$

$$A = 1.8246\ 10^6 \times (\varepsilon_r T)^{-3/2}\ \left[\mathrm{mol^{-1/2}L^{1/2}}\right]$$

$$B = 502.9 \times (\varepsilon_r T)^{-1/2}\ \left[\mathrm{nm^{-1}mol^{-1/2}L^{1/2}}\right]$$

$$\varepsilon_r = 251.629 - 0.803 \times T + 0.000744 \times T^2$$

ε_r: relative permittivity of the solvent (pure water in this case)

Speciation for $CaCO_3$ system

$$Ca(NO_3)_2 + K_2CO_3 \xrightarrow{H_2O} CaCO_{3\,(s)} + 2K^+ + 2NO_3^-$$

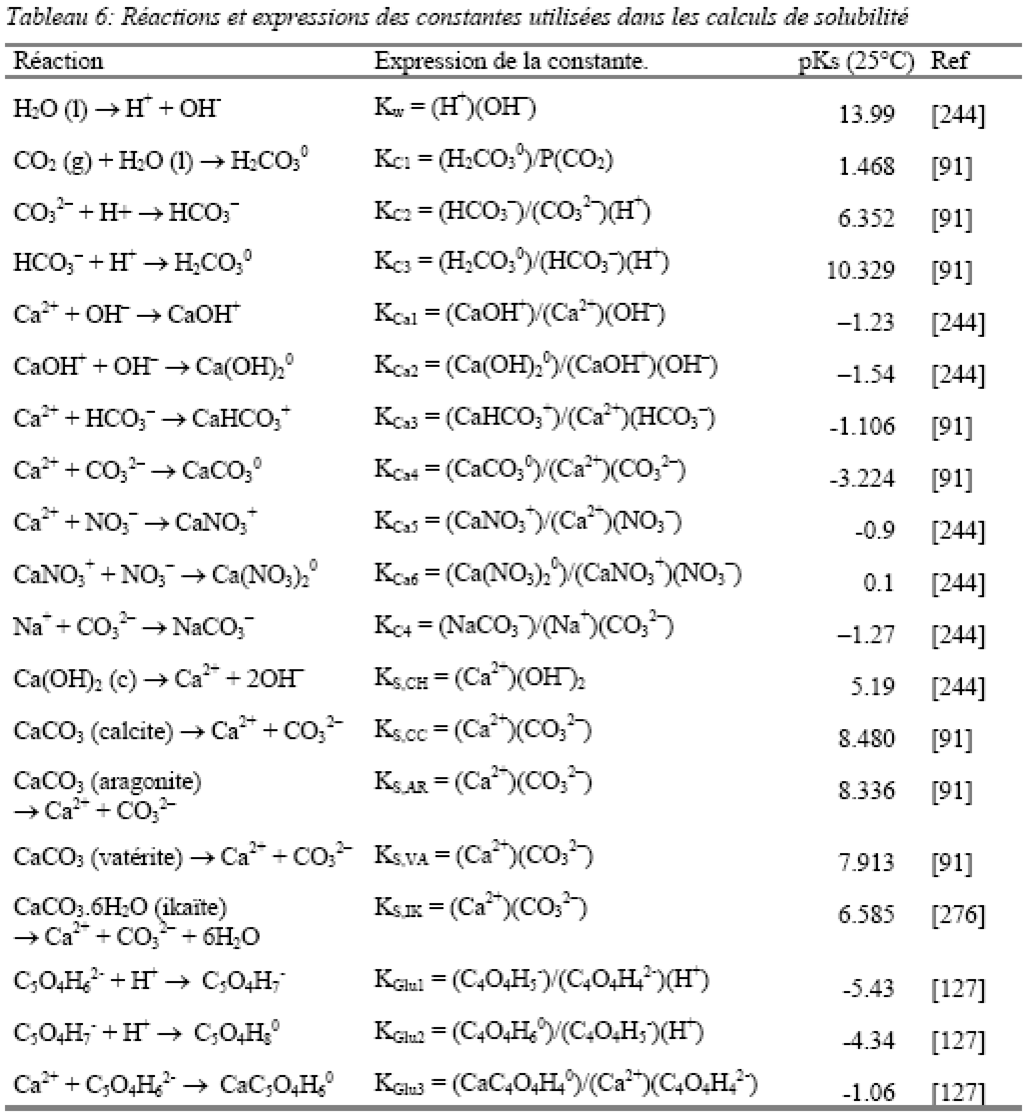


Tableau 6: Réactions et expressions des constantes utilisées dans les calculs de solubilité

Réaction	Expression de la constante.	pKs (25°C)	Ref
$H_2O\ (l) \rightarrow H^+ + OH^-$	$K_w = (H^+)(OH^-)$	13.99	[244]
$CO_2\ (g) + H_2O\ (l) \rightarrow H_2CO_3^0$	$K_{C1} = (H_2CO_3^0)/P(CO_2)$	1.468	[91]
$CO_3^{2-} + H+ \rightarrow HCO_3^-$	$K_{C2} = (HCO_3^-)/(CO_3^{2-})(H^+)$	6.352	[91]
$HCO_3^- + H^+ \rightarrow H_2CO_3^0$	$K_{C3} = (H_2CO_3^0)/(HCO_3^-)(H^+)$	10.329	[91]
$Ca^{2+} + OH^- \rightarrow CaOH^+$	$K_{Ca1} = (CaOH^+)/(Ca^{2+})(OH^-)$	–1.23	[244]
$CaOH^+ + OH^- \rightarrow Ca(OH)_2^0$	$K_{Ca2} = (Ca(OH)_2^0)/(CaOH^+)(OH^-)$	–1.54	[244]
$Ca^{2+} + HCO_3^- \rightarrow CaHCO_3^+$	$K_{Ca3} = (CaHCO_3^+)/(Ca^{2+})(HCO_3^-)$	-1.106	[91]
$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3^0$	$K_{Ca4} = (CaCO_3^0)/(Ca^{2+})(CO_3^{2-})$	-3.224	[91]
$Ca^{2+} + NO_3^- \rightarrow CaNO_3^+$	$K_{Ca5} = (CaNO_3^+)/(Ca^{2+})(NO_3^-)$	-0.9	[244]
$CaNO_3^+ + NO_3^- \rightarrow Ca(NO_3)_2^0$	$K_{Ca6} = (Ca(NO_3)_2^0)/(CaNO_3^+)(NO_3^-)$	0.1	[244]
$Na^+ + CO_3^{2-} \rightarrow NaCO_3^-$	$K_{C4} = (NaCO_3^-)/(Na^+)(CO_3^{2-})$	–1.27	[244]
$Ca(OH)_2\ (c) \rightarrow Ca^{2+} + 2OH^-$	$K_{S,CH} = (Ca^{2+})(OH^-)_2$	5.19	[244]
$CaCO_3$ (calcite) $\rightarrow Ca^{2+} + CO_3^{2-}$	$K_{S,CC} = (Ca^{2+})(CO_3^{2-})$	8.480	[91]
$CaCO_3$ (aragonite) $\rightarrow Ca^{2+} + CO_3^{2-}$	$K_{S,AR} = (Ca^{2+})(CO_3^{2-})$	8.336	[91]
$CaCO_3$ (vatérite) $\rightarrow Ca^{2+} + CO_3^{2-}$	$K_{S,VA} = (Ca^{2+})(CO_3^{2-})$	7.913	[91]
$CaCO_3.6H_2O$ (ikaïte) $\rightarrow Ca^{2+} + CO_3^{2-} + 6H_2O$	$K_{S,IK} = (Ca^{2+})(CO_3^{2-})$	6.585	[276]
$C_5O_4H_6^{2-} + H^+ \rightarrow C_5O_4H_7^-$	$K_{Glu1} = (C_4O_4H_5^-)/(C_4O_4H_4^{2-})(H^+)$	-5.43	[127]
$C_5O_4H_7^- + H^+ \rightarrow C_5O_4H_8^0$	$K_{Glu2} = (C_4O_4H_6^0)/(C_4O_4H_5^-)(H^+)$	-4.34	[127]
$Ca^{2+} + C_5O_4H_6^{2-} \rightarrow CaC_5O_4H_6^0$	$K_{Glu3} = (CaC_4O_4H_4^0)/(Ca^{2+})(C_4O_4H_4^{2-})$	-1.06	[127]

Evolution of a precipitation reaction

$$A + B \leftrightarrows AB$$

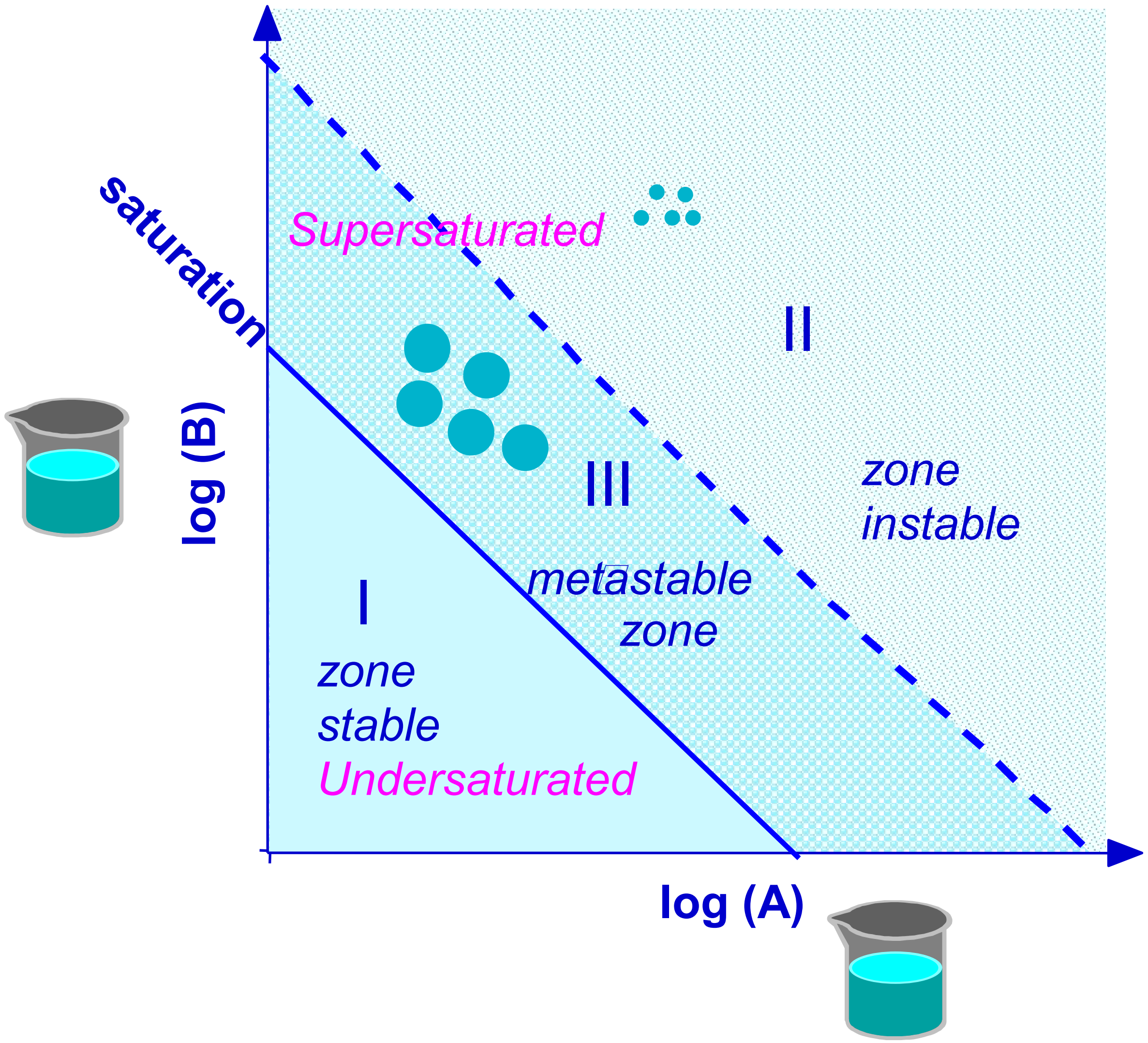
$$K_s = (A)_s \times (B)_s$$

$$\frac{(A)\times(B)}{K_s}$$

< 1 ⇨ under-saturation

$= 1$ ⇨ saturation

> 1 ⇨ super-saturation



I The material is dissolved in solution (one phase)

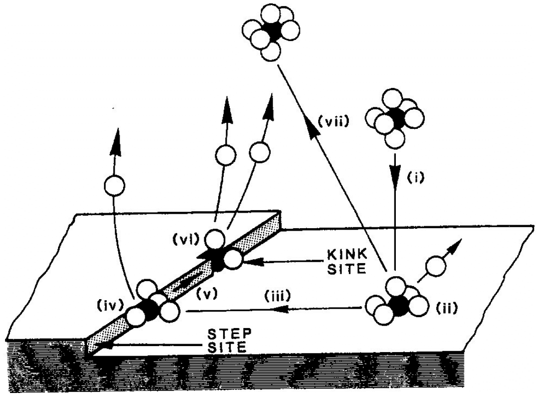
II Nucleation = formation of “solid entities” (embryo→ nucleus)

III Crystal growth and eventually agglomeration

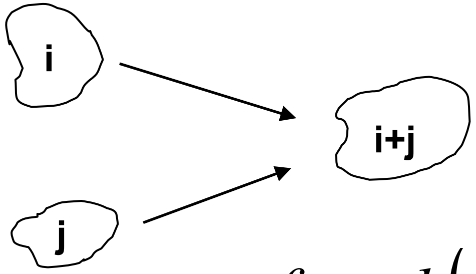
Elementary processes: definitions

- **Nucleation**
  - **Primary**
    - **Homogeneous (no influence of any surfaces)**
    - **Heterogeneous (catalysed by a foreign surface)**
  - **Secondary**
    - **True (initiated by the same phase)**
    - **Apparent (fragments)**
    - **Contact (reactor wall, stirrer, pump,…)**

Growth: molecular growth. Incorporation of new building units of molecular size into the crystal surface.



Aggregation: interaction between 2 particles to form a bigger one



$$f_{i,j} = k(r_i, r_j)n_i n_j$$

*Modelling Nucleation of organic crystal…R. SEARS**

J. P. Mithen, A. J. Callison, and R. P. Sear, J. Chem. Phys. 142,224505 (2015).

Nucleation from calculation model

*Department of Physics, University of Surrey, Guildford, Surrey GU2 7XH, United Kingdom – r.sear@surrey.ac.uk

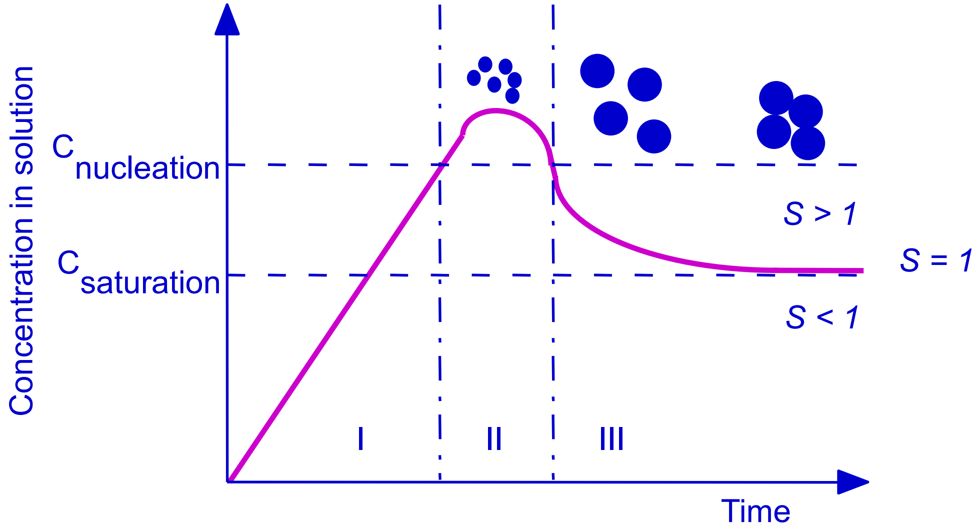
2D Nucleation + Growth

Evolution of a precipitation process

$$S_R = \frac{C_l}{C_s}$$ = saturation ratio (other possible definition, pay attention on how it is defined!)

C_l – conc. (activity) of the solute

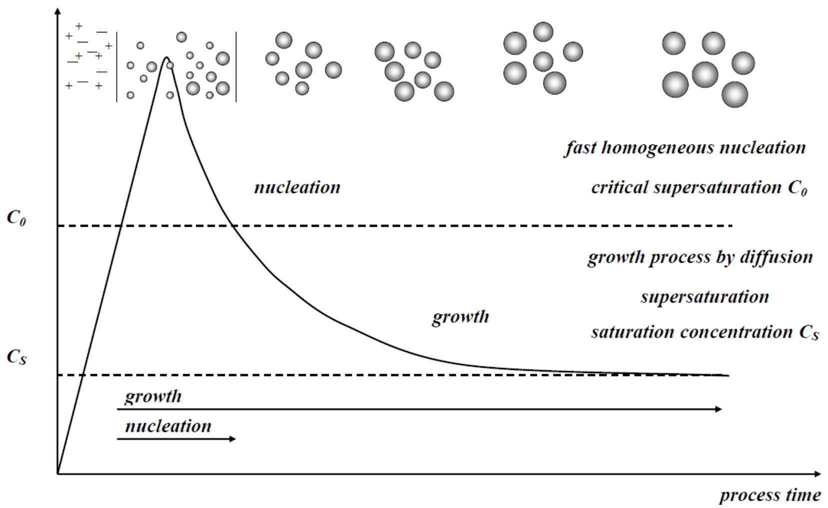
C_s – conc. (activity) at the equilibrium (solubility product)



Zone I: The activity is to low to induce nucleation

Zone II: Nucleation = Formation of nuclei

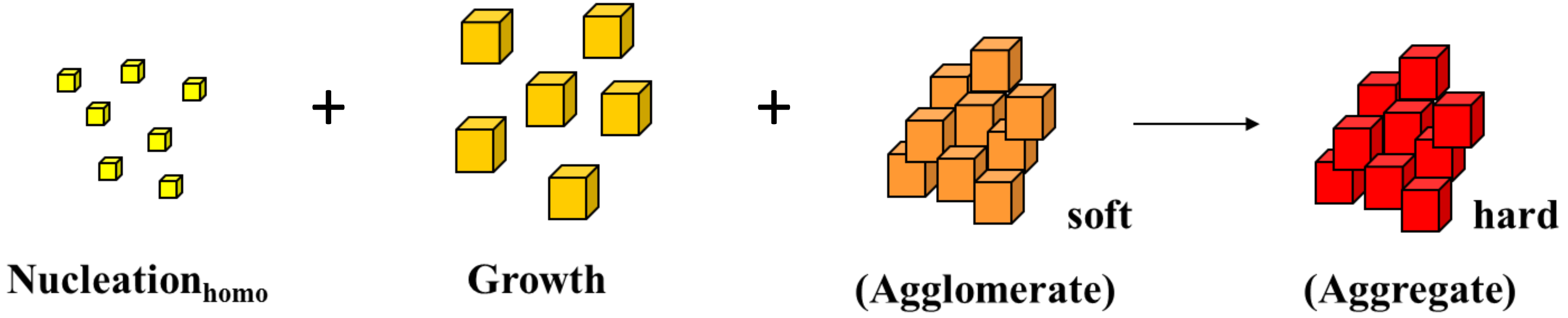
Zone III: Crystal growth and eventually aggregation


Model of LaMer and Dinegar (1950)

This partition of the precipitation in 3 zones (introduced in the ‘50) is a highly simplified view of a very complicated process, where the elementary sub-processes nucleation, growth, and aggregation can be convoluted. Such specific convolution defines the real **precipitation pathway** which is the object of an intense and controversial scientific research

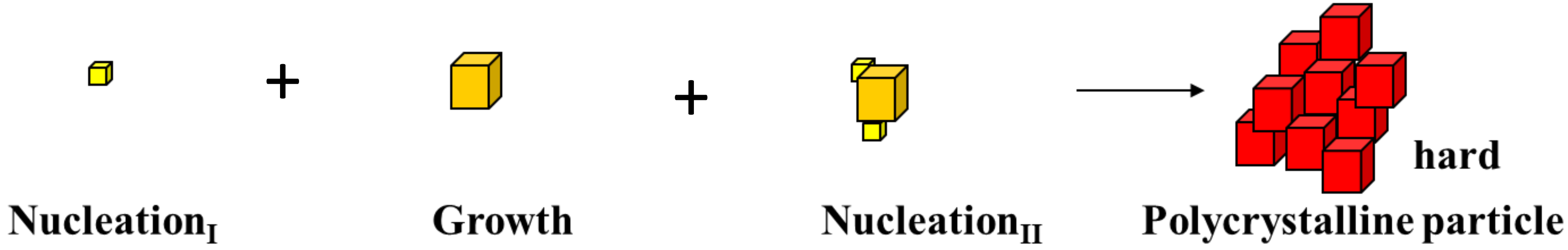
Two possible crystallization pathways…

Path 1: primary nucleation, growth, aggregation



Nucleation$_{homo}$ + **Growth** + **soft (Agglomerate)** → **hard (Aggregate)**

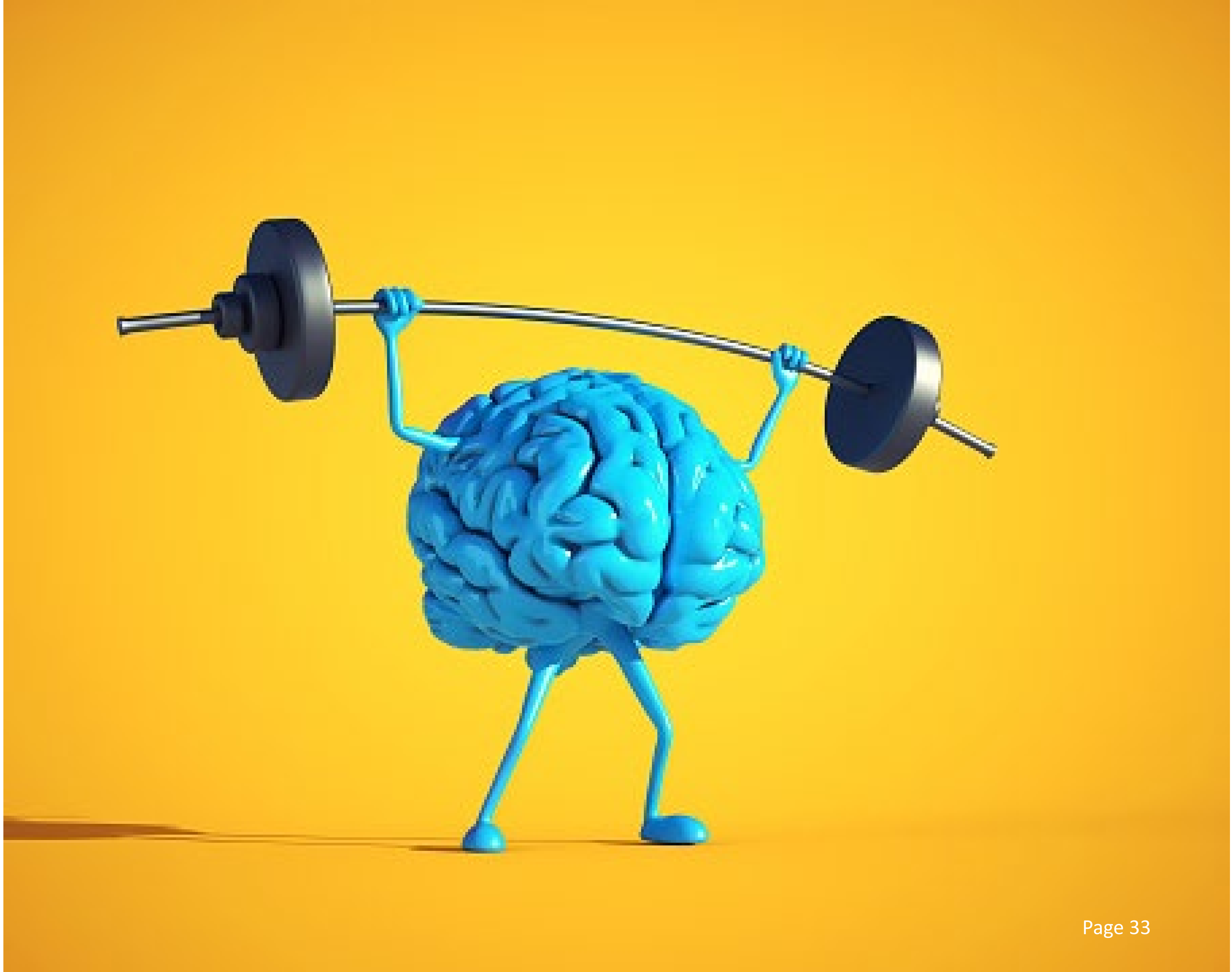
Path 2: primary nucleation, secondary nucleation, growth



Nucleation$_{I}$ + **Growth** + **Nucleation$_{II}$** → **hard Polycrystalline particle**

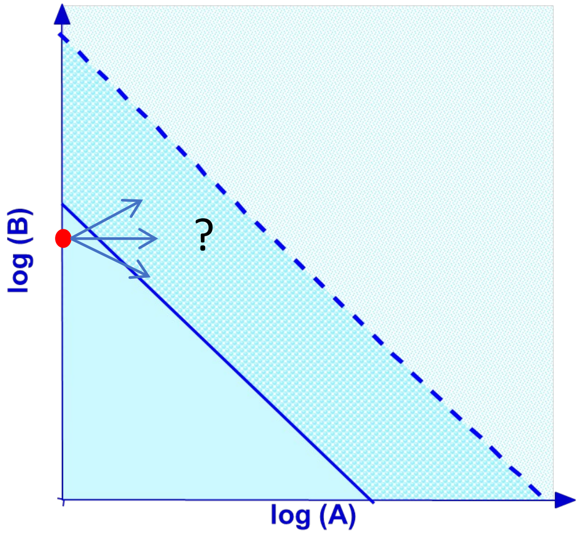
Two pathways, the same final result!

Exercise

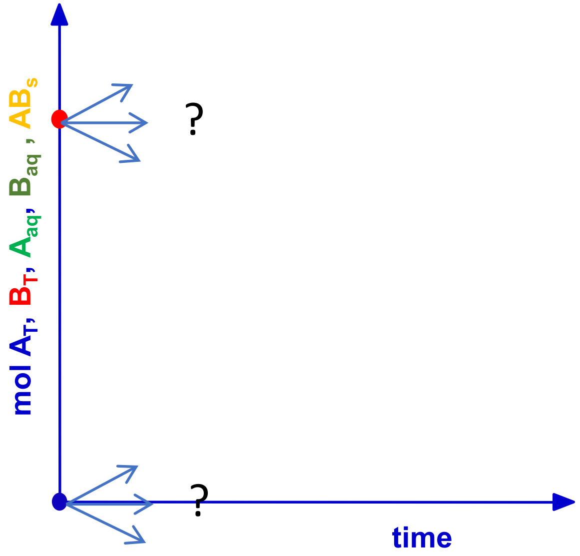


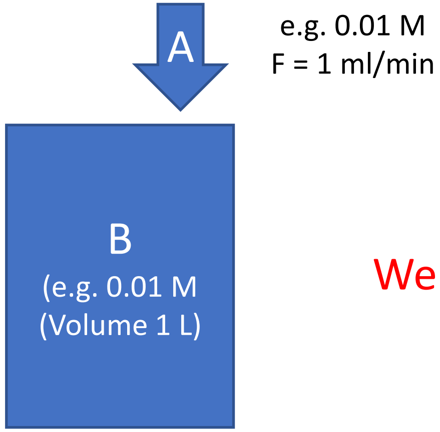
$A_{aq} + B_{aq} \leftrightarrows AB_S$ $Ba^{2+} + SO_4^{2-} \leftrightarrows BaSO4$

Conc [mol/L]
(A_{aq} and B_{aq})



mol




A
e.g. 0.01 M
F = 1 ml/min

B
(e.g. 0.01 M
(Volume 1 L)

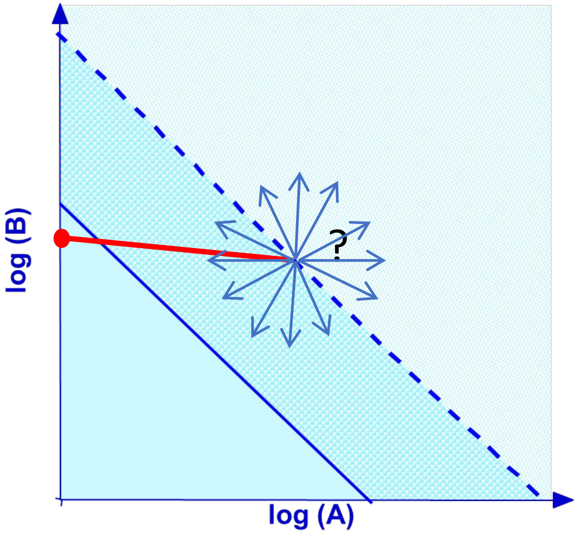
We can measure A_{aq}

Two chemical species: A_{aq} and B_{aq}
One solid species: AB_s

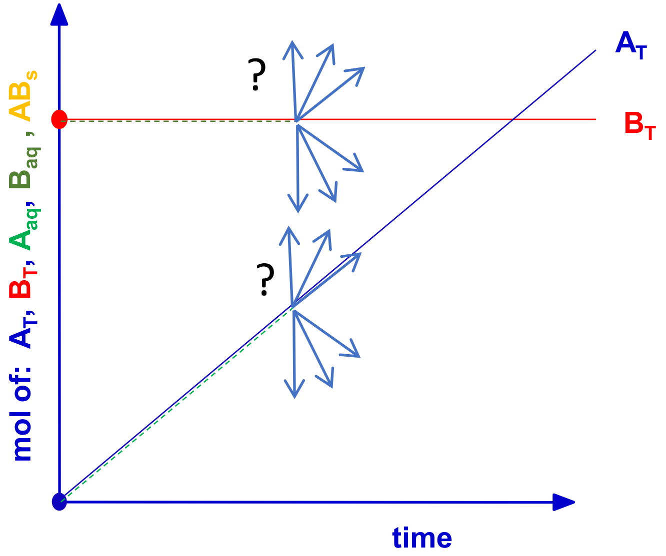
Mass balance:
$A_{tot} = A_{aq} + AB_S$
$B_{tot} = B_{aq} + AB_S$

In the presence of solid:
$A_{aq} x B_{aq} = Ksp_{AB}$

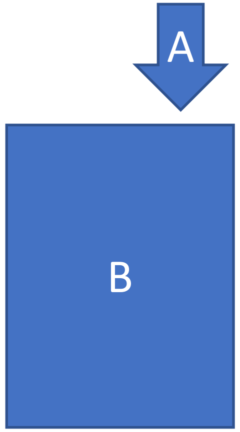
Conc [mol/L]
(A_{aq} and B_{aq})



Molar amount



$A_{aq}+B_{aq} \leftrightarrows AB_S$



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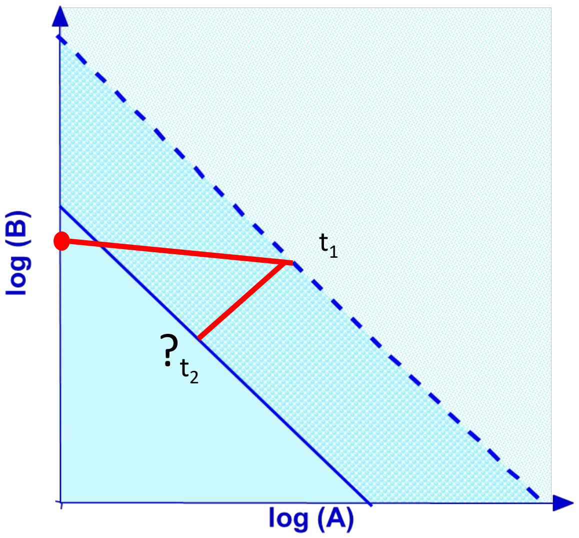
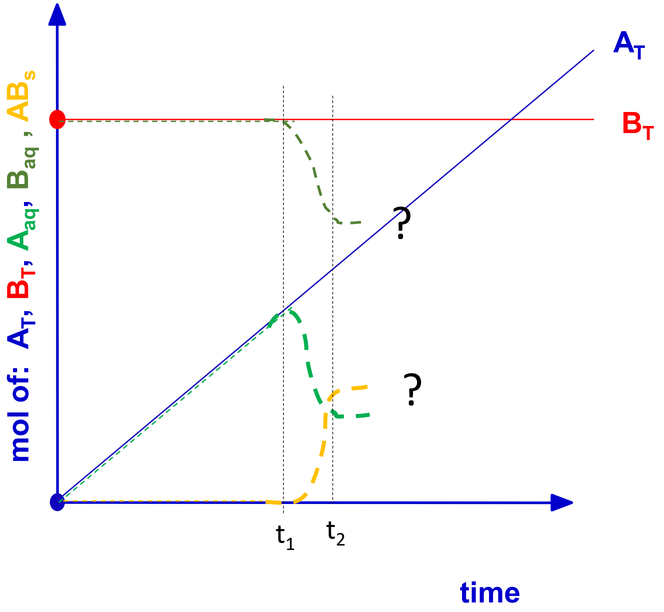
Conc [mol/L]
(A_{aq} and B_{aq})



Molar amount



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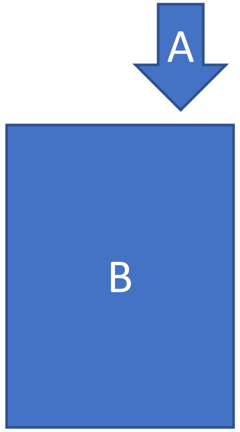

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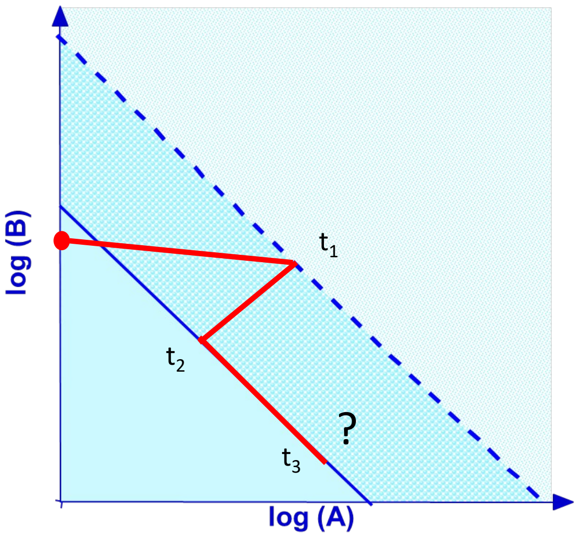
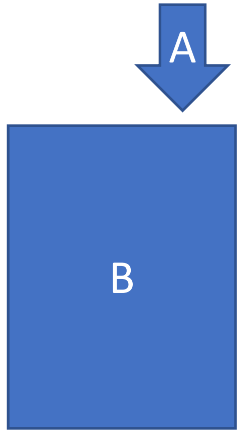
In the presence of solid:
$A_{aq} \times B_{aq} = Ksp_{AB}$

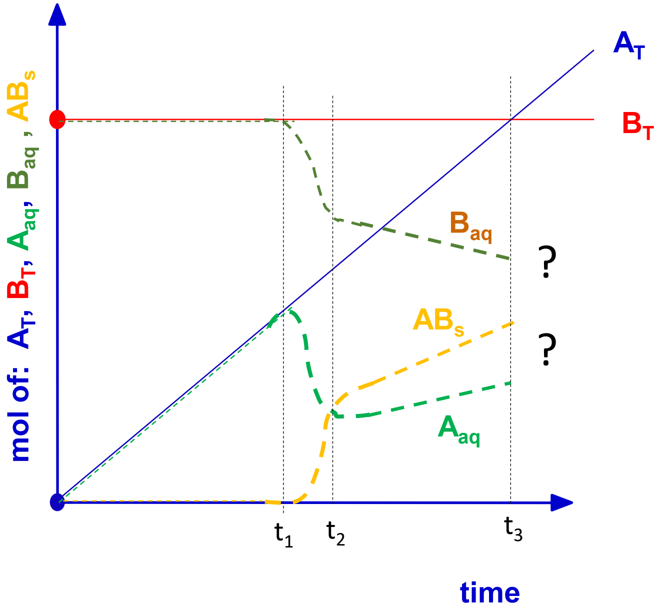
$A_{aq}+B_{aq} \leftrightarrows AB_S$

Conc [mol/L]
(A_{aq} and B_{aq})





Molar amount



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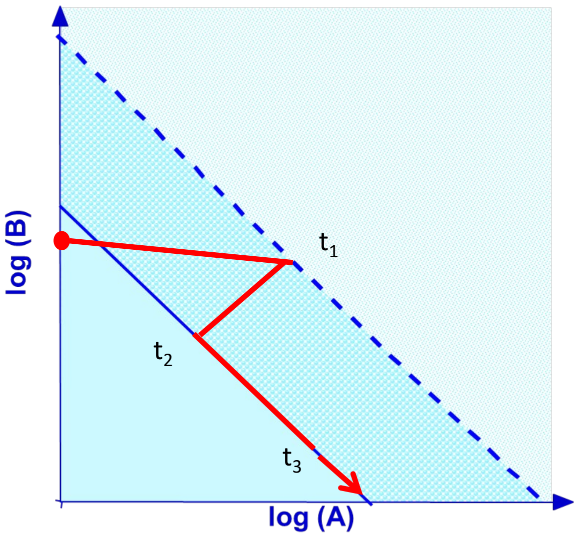
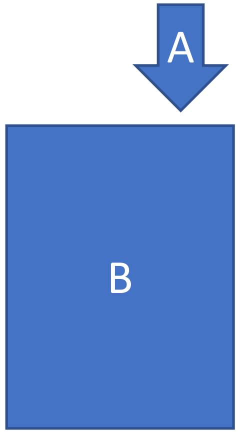
In the presence of solid:
$A_{aq} x\ B_{aq} = Ksp_{AB}$

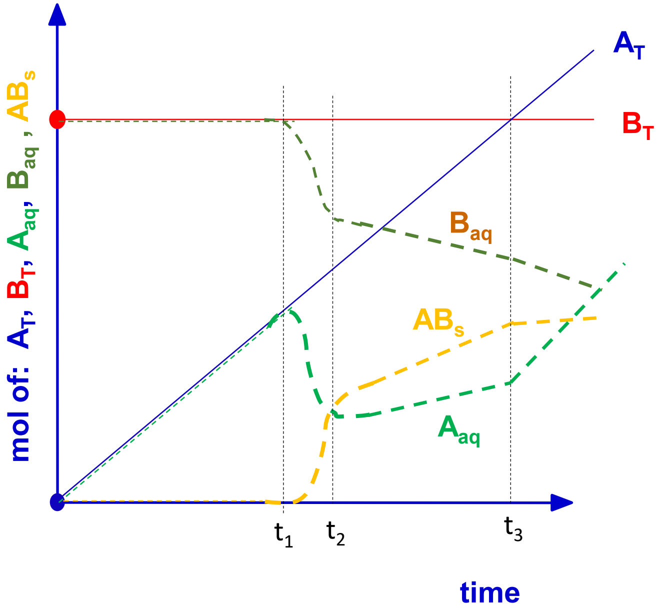
$A_{aq}+B_{aq} \leftrightarrows AB_S$

Conc [mol/L] (A_{aq} and B_{aq})





Molar amount



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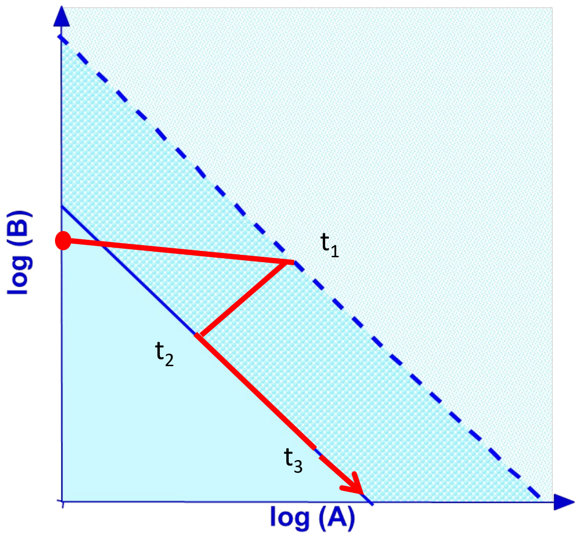

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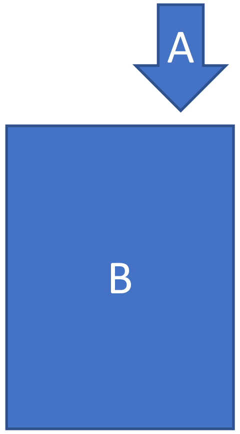

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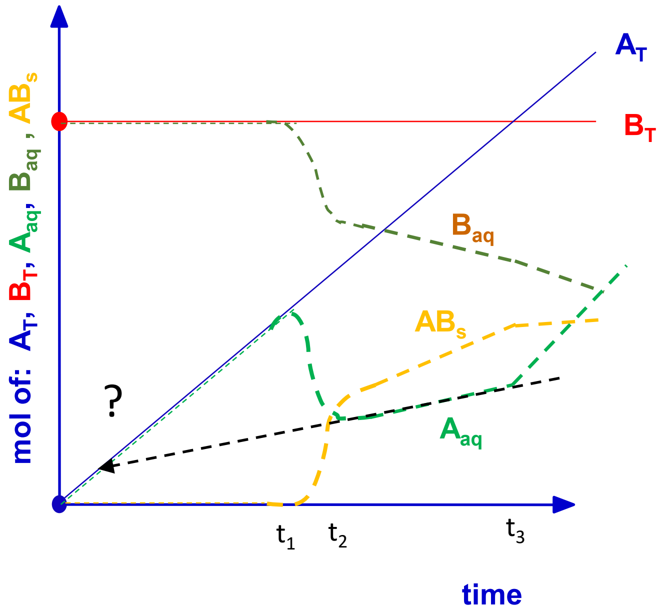

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In the presence of solid:
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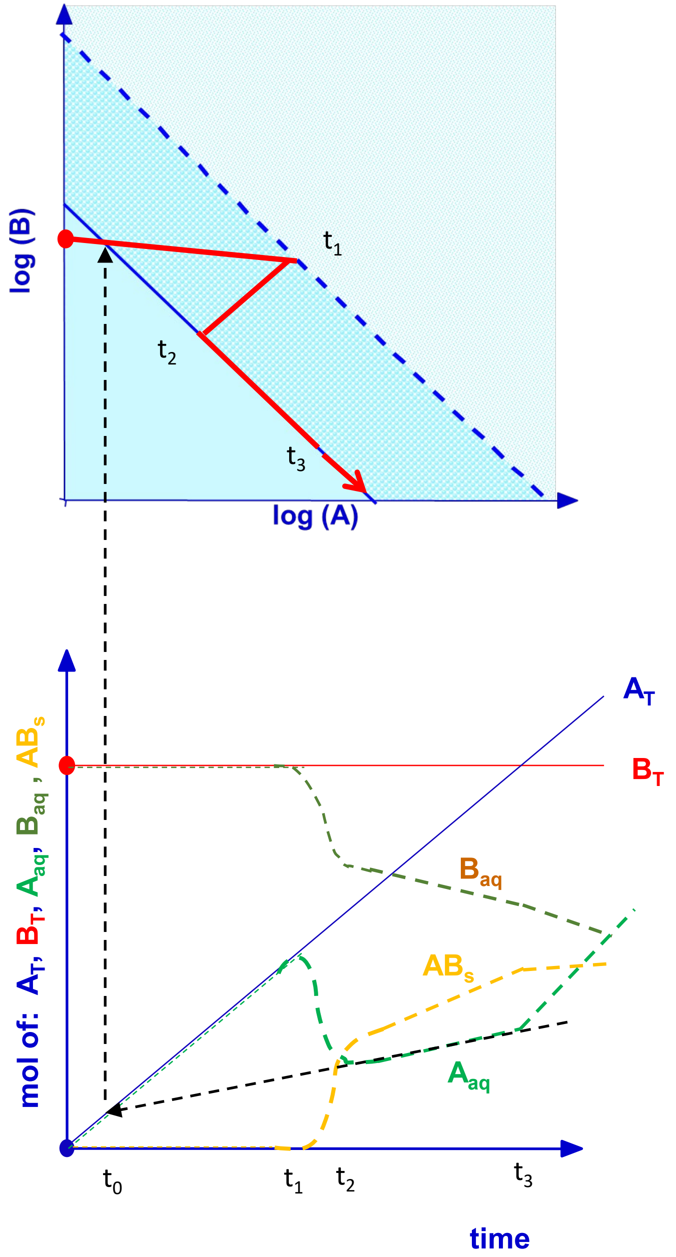
Conc [mol/L]
(A_{aq} and B_{aq})

Molar amount



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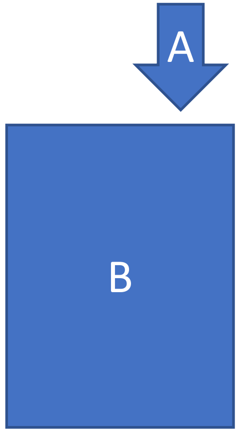

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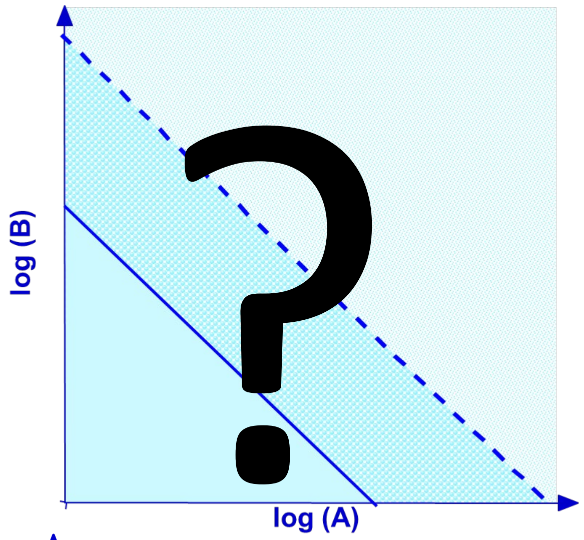
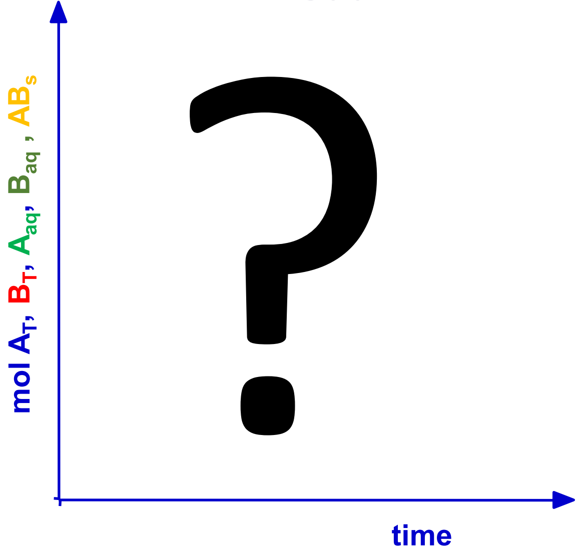


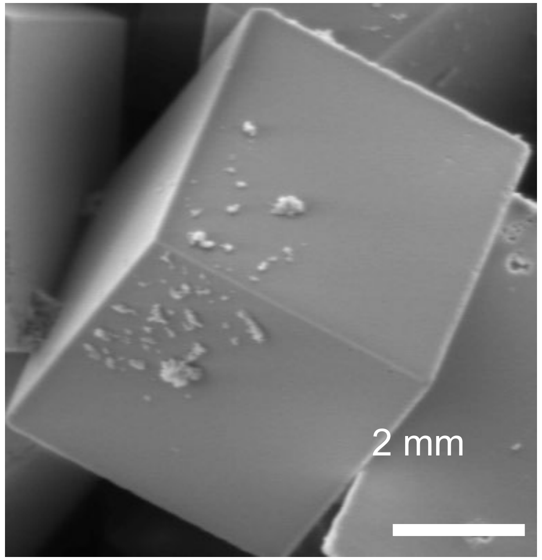


What does it happen if we change:

- Conc of B;
- Conc of A;
- pH (in case of speciation);
- Temperature;
- Flow rate of A;
- Volume of B;
- Material of the reactor
- Stirring speed;
- If we stop A at e certain point in time;
- Operator…

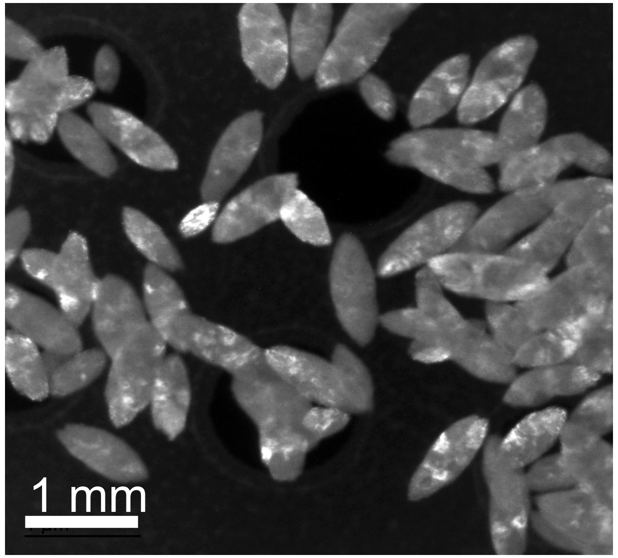
Even if the chemicals are defined (A and B), every change may defines new precipitation pathway. Thus, a different solid may be obtained.
Different means: size (&PSD), shape, stoichiometry, phase, amount, powder in suspension or on the reactor wall, …

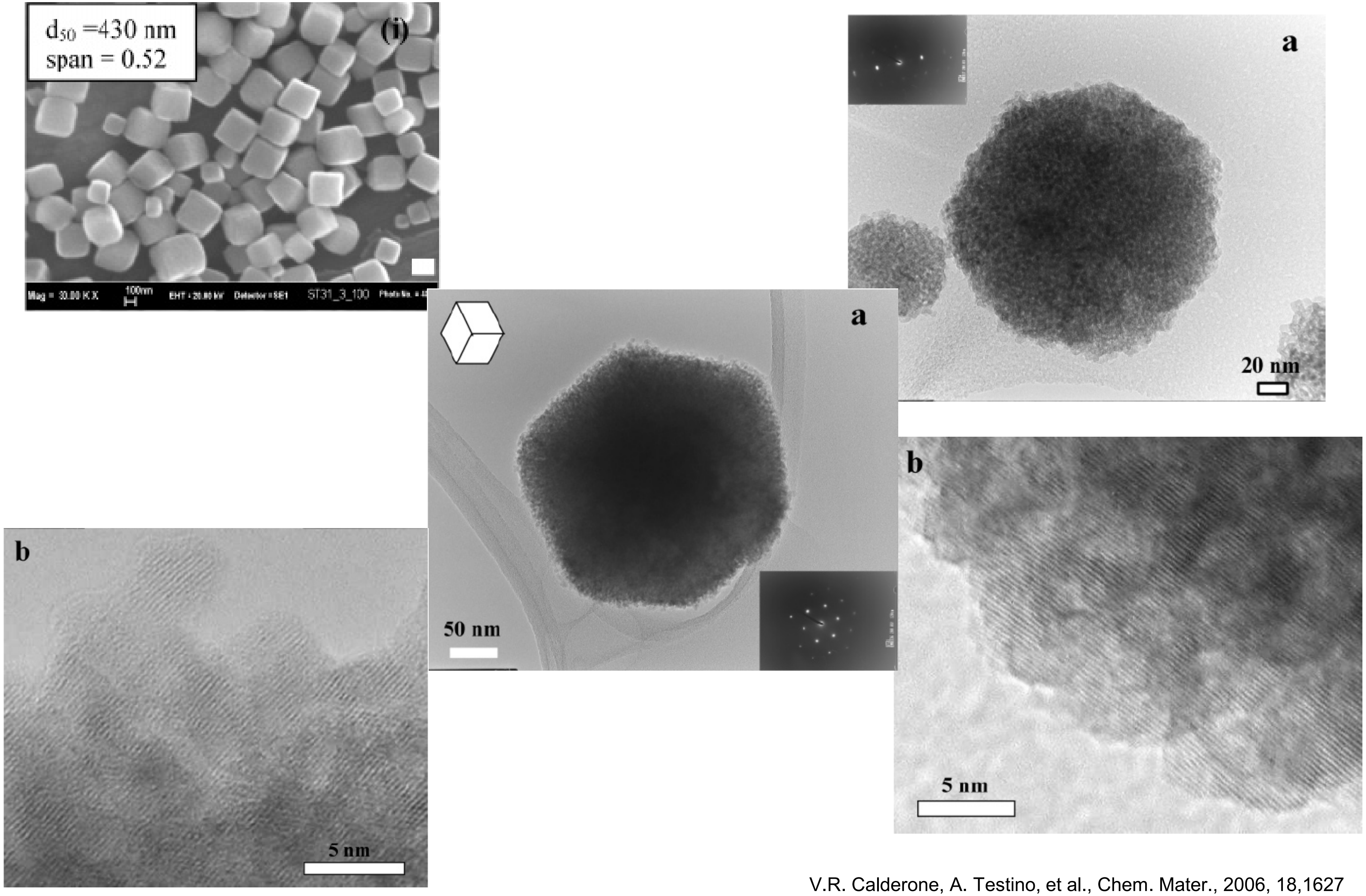
Examples Monocrystal - Polycrystal



- Calcite Monocrystal

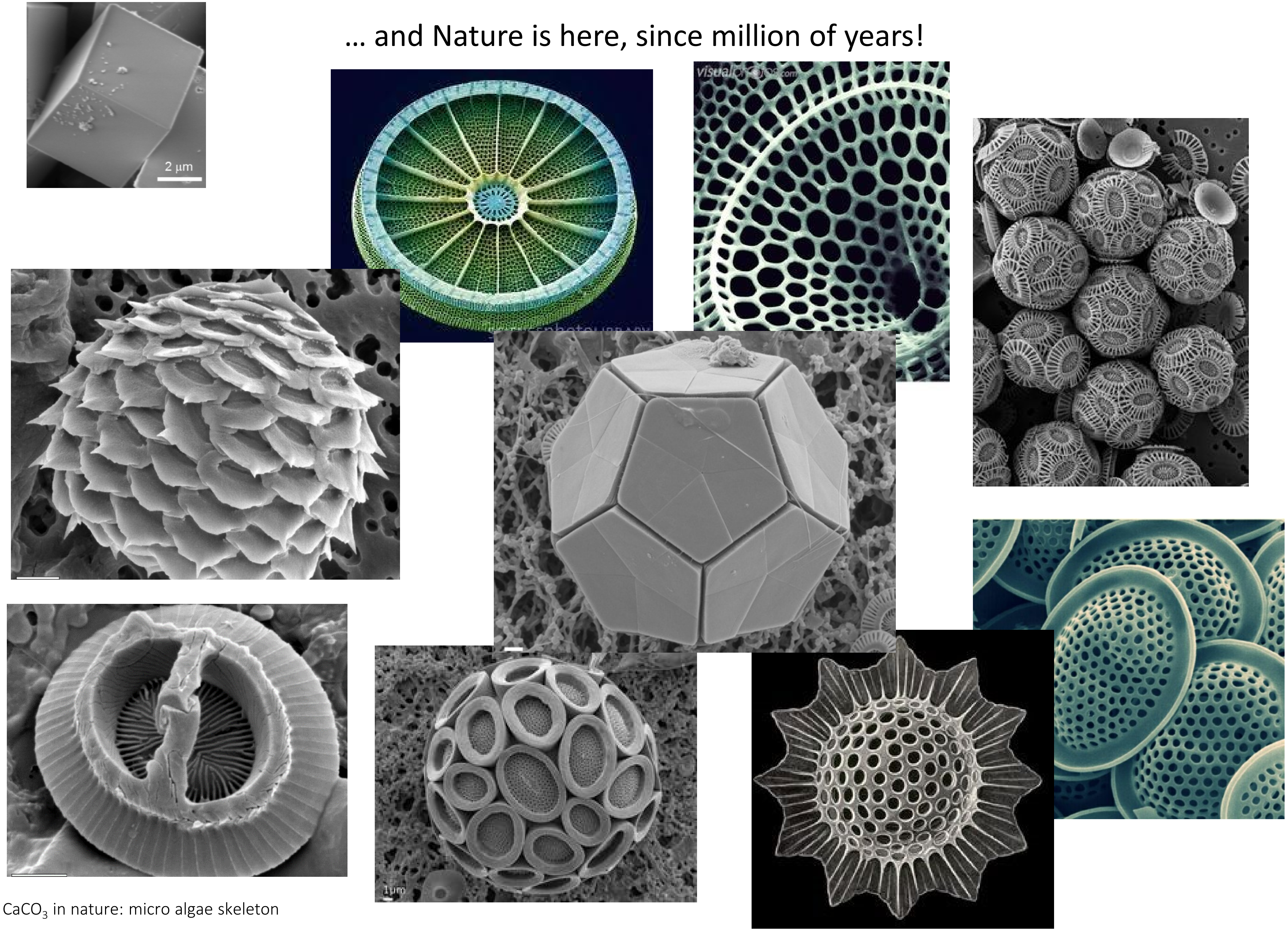
- Calcite - Polycrystal





V.R. Calderone, A. Testino, et al., Chem. Mater., 2006, 18,1627

Anyway, we are here…



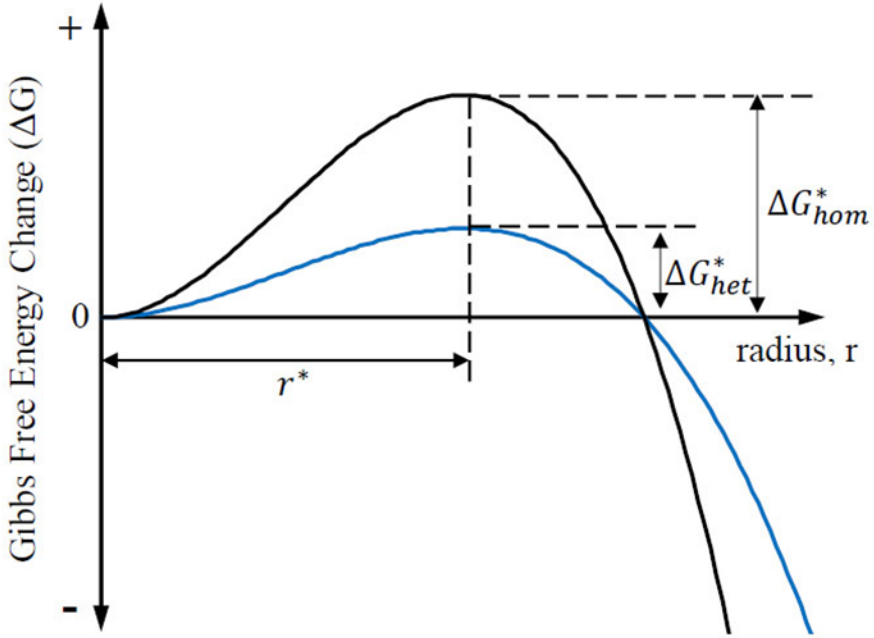
… and Nature is here, since million of years!

CaCO$_3$ in nature: micro algae skeleton

Take home messages

1. Nucleation and Growth are f(S), but to a very different extent;
2. Chemical speciation is fundamental to estimate correctly S;
3. The product strongly depends on the precipitation pathway.

Nucleation


+
-
0
Gibbs Free Energy Change (ΔG)
radius, r
r^*
ΔG^*_{hom}
ΔG^*_{het}

Nucleation

Energy needed to generate new solid volume, and the associated new surface is a function of the saturation ratio (S_R) and the surface tension (g) (Nielsen, 1964).

$$\Delta G = \underbrace{-\left(\frac{V}{V_m}\right)\cdot k_B T \cdot \ln(S_R)}_{\text{volume}} + \underbrace{\gamma \cdot A}_{\text{surface}}$$

Where:

- V: volume of the embryo;
- V_m: molecular volume of the solute (or building unit or growth unit)
- k_B: Boltzmann constant (1.38064852 × 10^{-23} m^2 kg s^{-2} K^{-1})
- T: temperature in K
- g : surface energy of the solid-liquid interface per surface unit (J m^{-2})
- A: surface

Nucleation – Critical size

- Volume and Surface contribution to the Gibbs free energy as a function of size (R) and geometrical factors (β_V and β_A)

$$\Delta G(R) = -\left(\frac{\beta_V R^3}{V_m}\right) \cdot k_B T \cdot \ln(S) + \gamma \cdot \beta_A R^2$$

$$V = \beta_V R^3$$

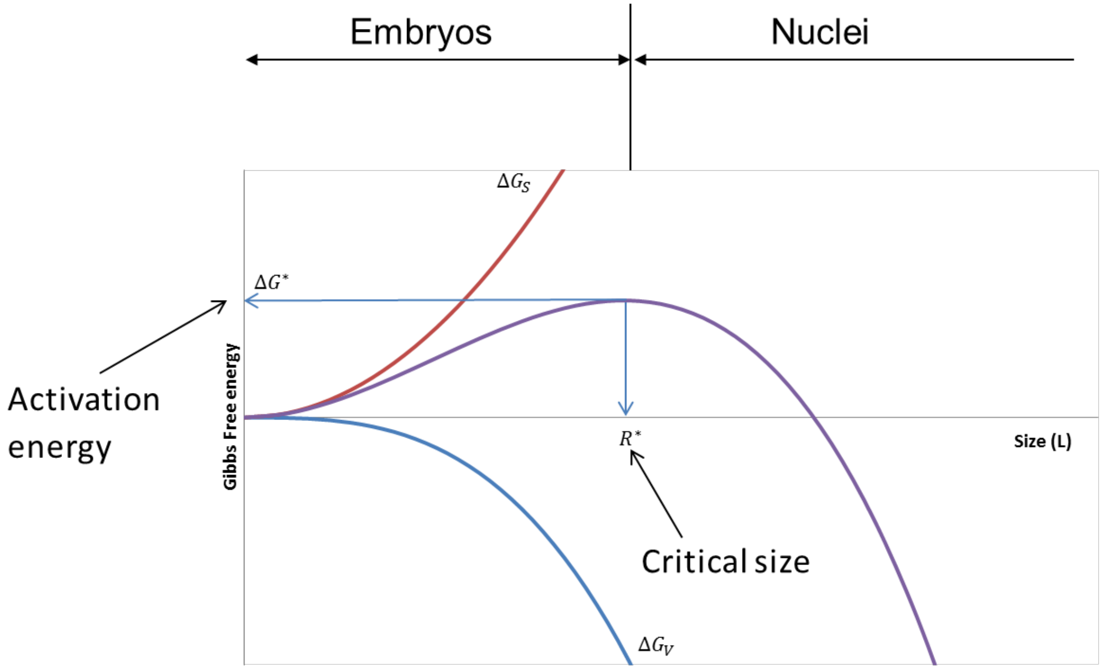
$$A = \beta_A R^2$$

$$\boxed{R^* = \frac{2 \cdot \beta_A \cdot \gamma \cdot V_m}{3 \cdot \beta_V \cdot k_B T \cdot \ln(S)}}$$

For spheres

$$\beta_V = \frac{4}{3}\pi$$

$$\beta_A = 4\pi$$



Exercise: how ΔG^* and R* can be deducted?

- Above the critical size, to a larger size corresponds a lower Gibbs free energy.
- Below the critical size…

… exercise. What does it mean?

(Nielsen, 1964)

Kinetic: nucleation (classical nucleation theory)

As already stated, according to the classical view, the elementary step in the formation of a nucleus can formally be described by the reciprocal "chemical reaction"

$$X_{(molec)} + X_{(r^*-molec)} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} X_{(r^*)}$$

The reaction rate is written as

$$\frac{dN(r^*)}{dt} = k_1 N(molec)\, N(r^*-molec) - k_{-1} N(r^*)$$

That can be approximated as:

$$J = \frac{dN(r^*)}{dt^{\mathrm{V}}} = \left\{ \frac{2D}{d^5} \exp\left(-\frac{\Delta G(r^*)}{k_B T} \right) \right\}$$

[# volume^{-1} time^{-1}]

$$J_{\mathrm{s}} = \frac{dN(r^*)}{dt} = \left\{ \frac{D}{d^4} \exp\left(-\frac{\Delta G(r^*)}{k_B T} \right) \right\}$$

[# surface^{-1} time^{-1}]

$$\Delta G^*_{3D} = \frac{4}{27} \frac{\nu^2 \gamma^3}{k_B^2 T^2 \ln^2(S)} \left(6 - \frac{\beta_{adh}}{\gamma} \right)^3$$

D: diffusion coefficient of the solute

d: molecular diameter ($\nu^{1/3}$)

Nucleation – type and rate – as function of S

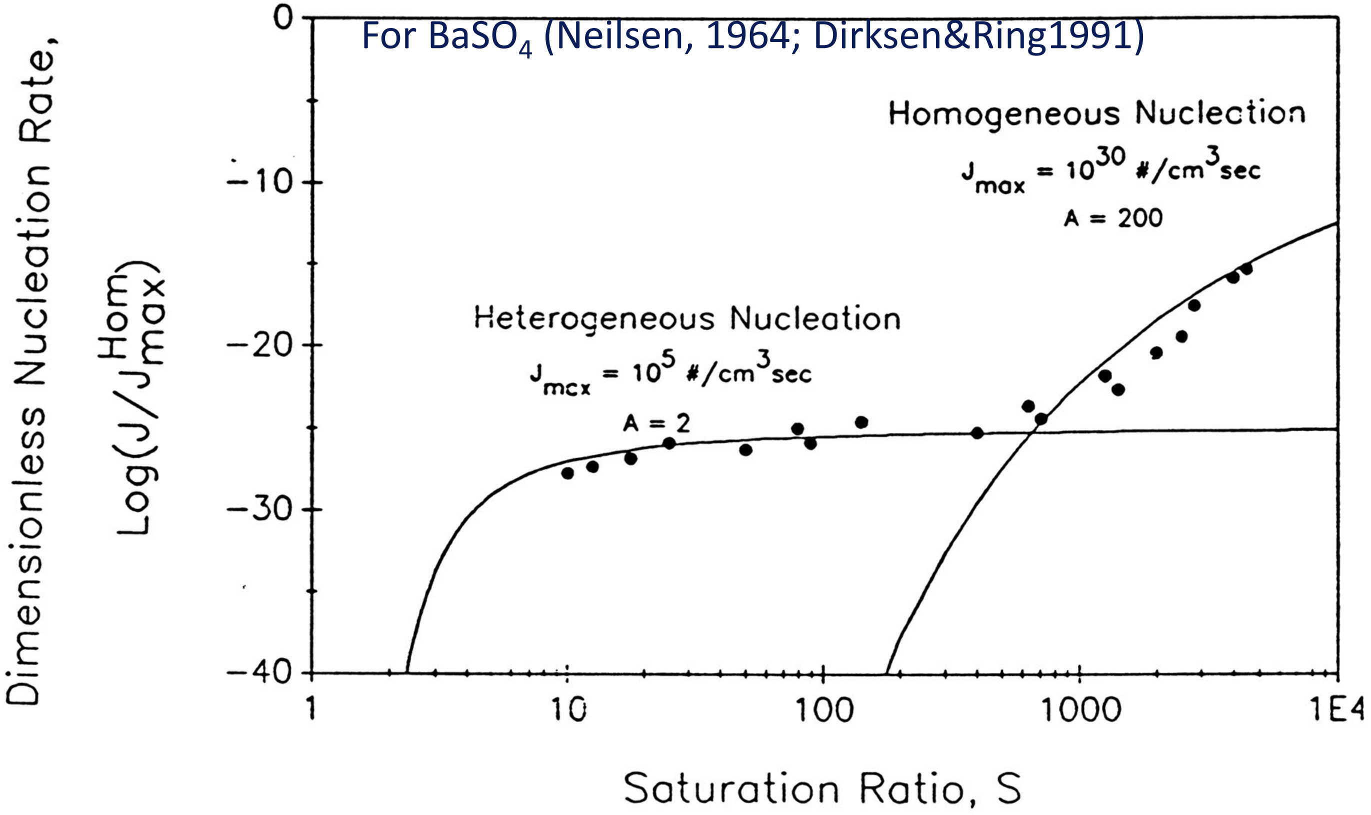
- Nucleation rate, J [# V^{-1} s^{-1}]. It is assumed that embryo grows by incorporation of growth units, one by one up to a critical size. $X_{(molec)} + X_{(r^*-molec)} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} X_{(r^*)}$

(Nielsen, 1964)

- J_{homo}, homogeneous nucleation rate: $$\boxed{\log\left(\frac{J_{homo}}{J_{homo}^{max}}\right) = \log(J) = -A\left[\log(S)\right]^{-2}}$$

where pre-exponential factor A or maximum nucleation rate, J_{homo}^{max}, can be estimated from the Einstein equation for diffusion (Eq. E1)

- J_{hetero}, heterogeneous nucleation: lower activation energy because of the lower γ → higher rate

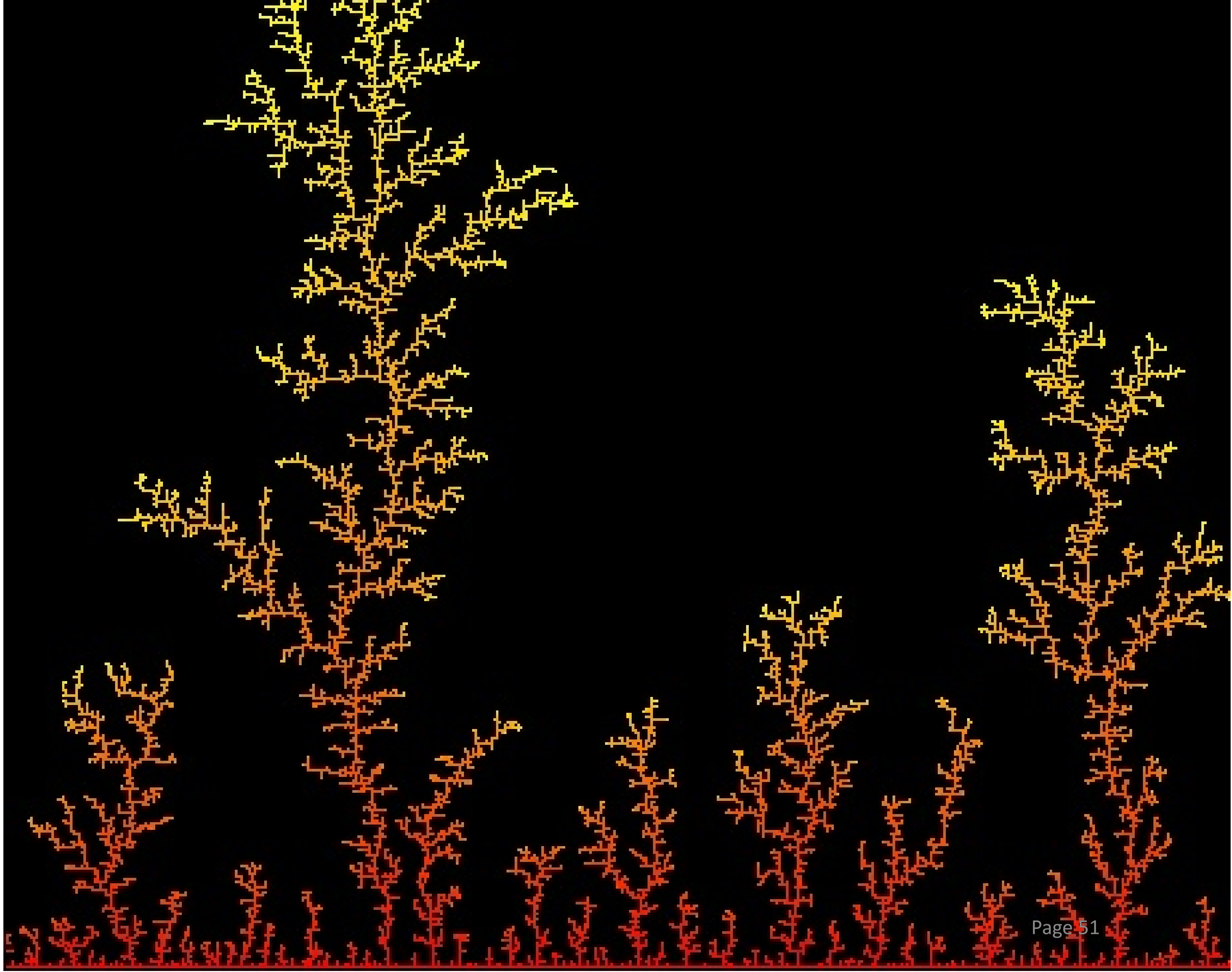


$$A = \frac{4}{27}\frac{\gamma^3\beta_A^3V^2}{\beta_V^2k_B^3T^3\ln(10)^3}$$

$$\boxed{J_{homo}^{max} = \frac{2D}{d^5}}$$ Eq. E1

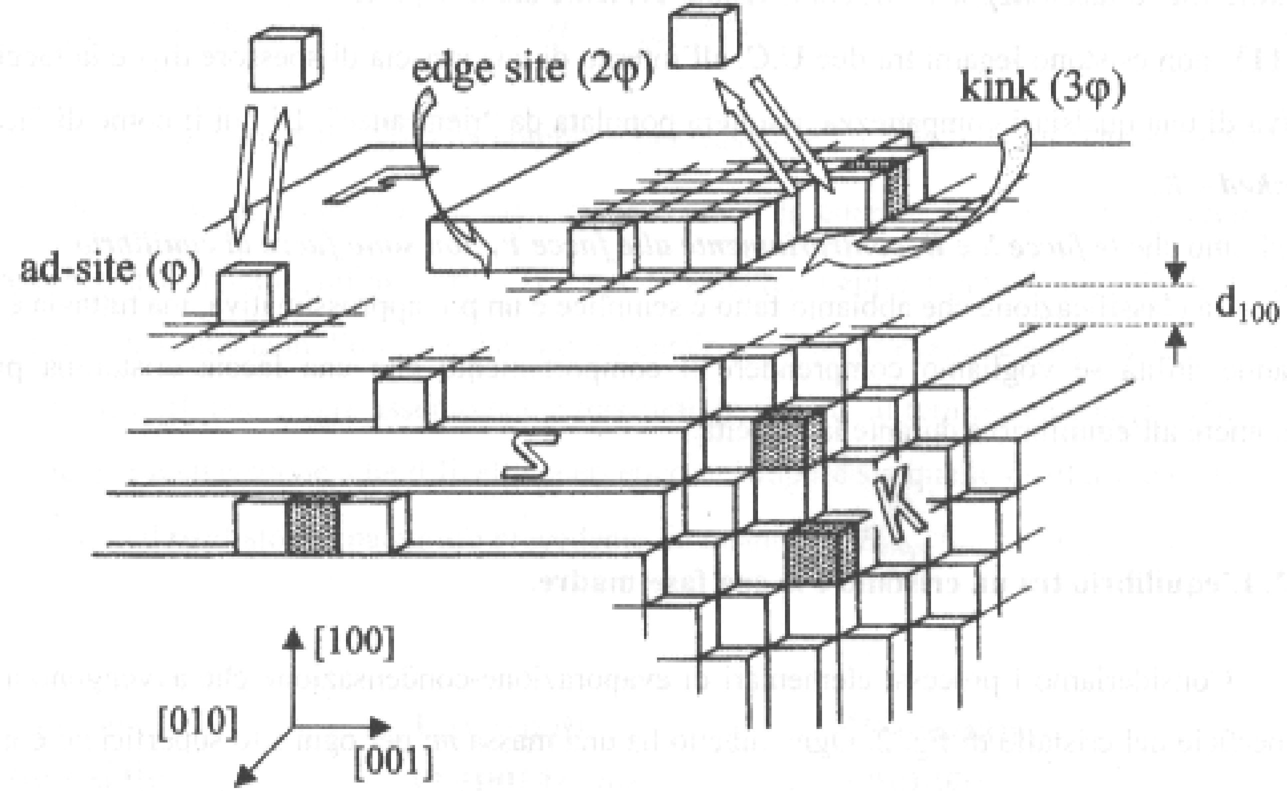
D: diffusion coefficient;
d: root-mean-squared displacement, estimated as the molecular diameter

Growth



Kinetic: Growth

Growth is a surface phenomenon and could depend on the structure of the crystalline surface which undergoes growing. According to the simplified visualization proposed by Hatman and Perdok, the crystalline surface is composed by K (kink), S (stepped), and F (flat) sites.



Growth: diffusion controlled

In the case of diffusion-controlled growth, the flux of solute J_D [mol L^{-2} t^{-1}] is

$$J_D = K_c\left(C_\infty - C_{eq}\right) = \frac{D}{\delta}\left(C_\infty - C_{eq}\right)$$

Mass tranf. coef.

and the linear growth rate [L t^{-1}] is

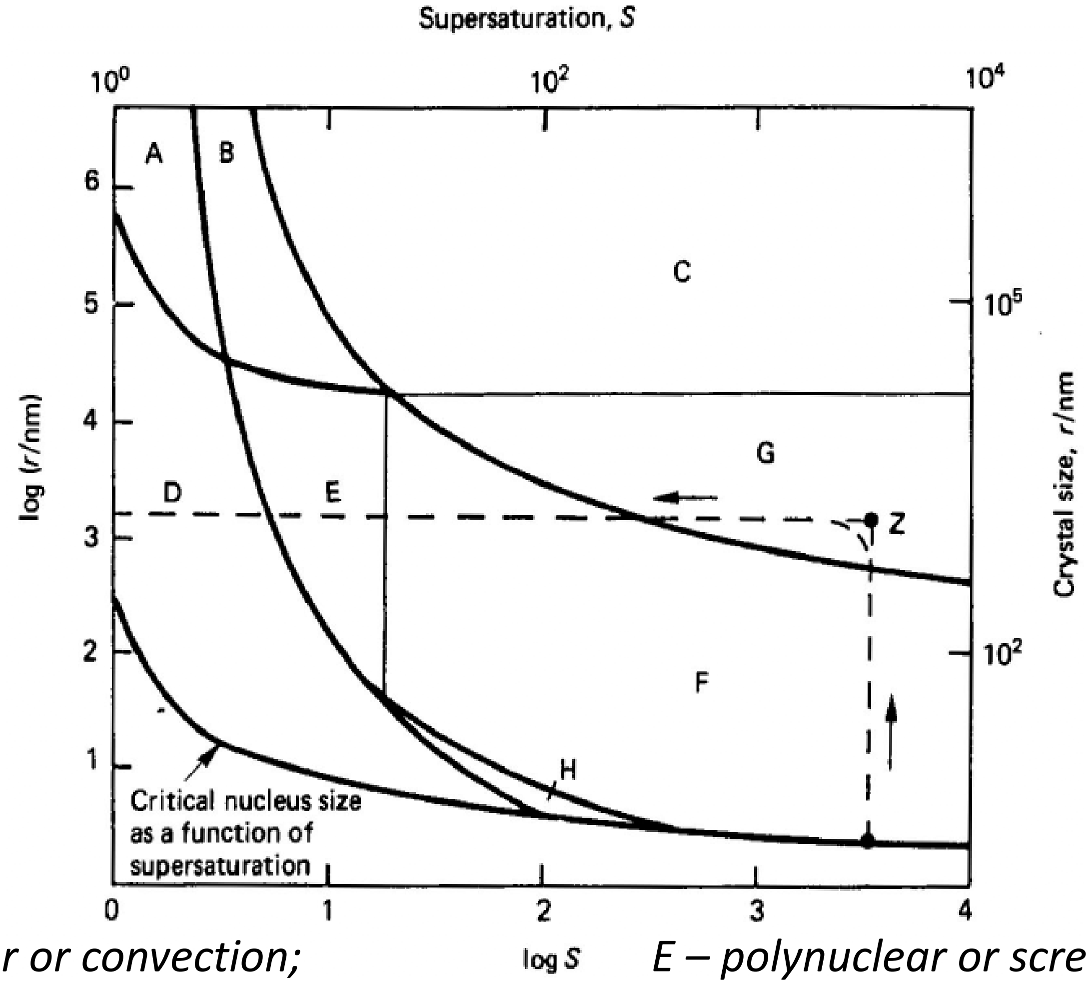
$$\boxed{G_D = \frac{dr}{dt} = J_D v_m}$$

v_m: molecular volume [L^3 mol^{-1}]

Eq1: For crystals smaller than 1μm the growth rate is typically controlled by Brownian diffusion and δ → r

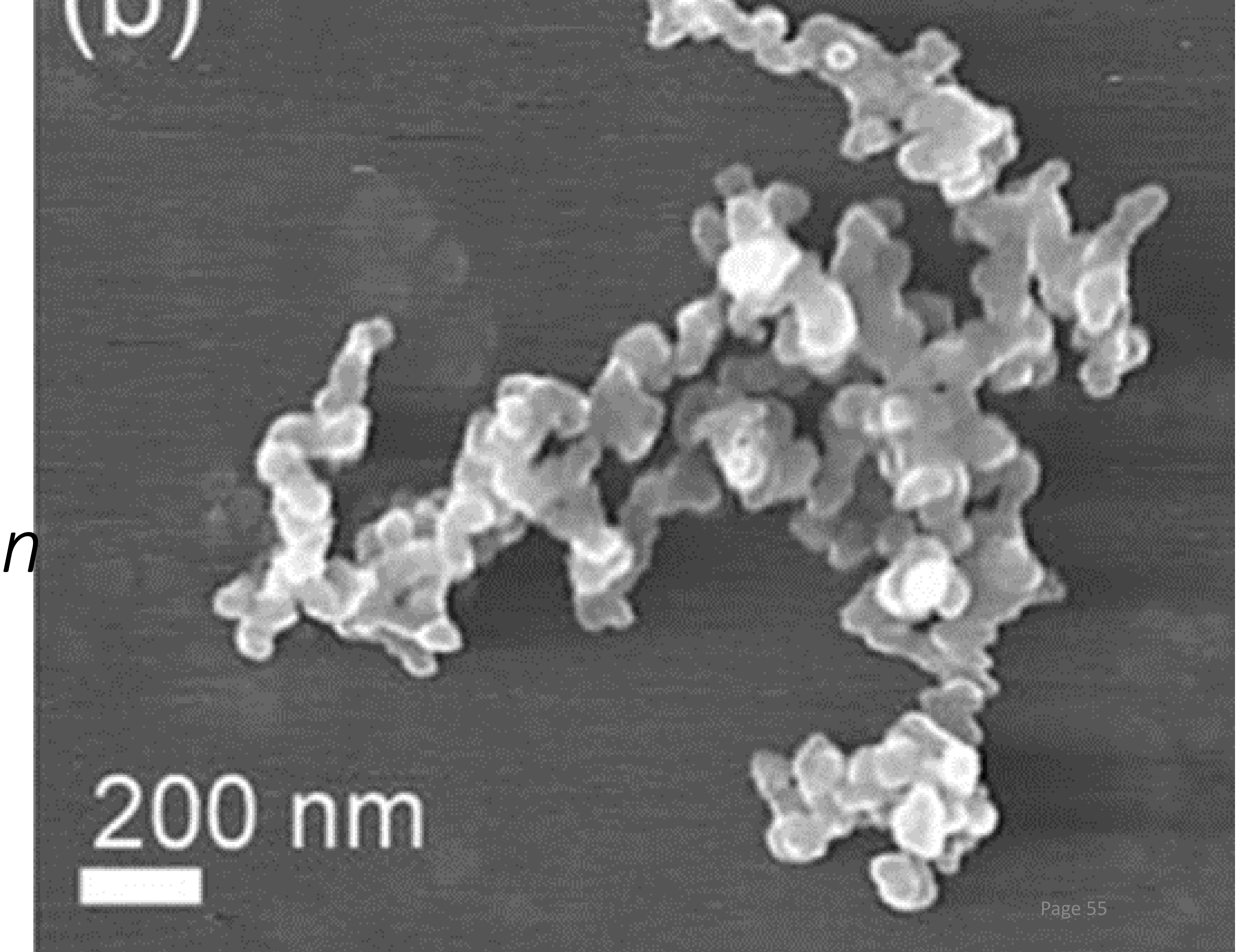
Crystallization Pathway (nucleation + growth)

Precipitation map for $BaSO_4$: controlling growth mechanism in the individual regions



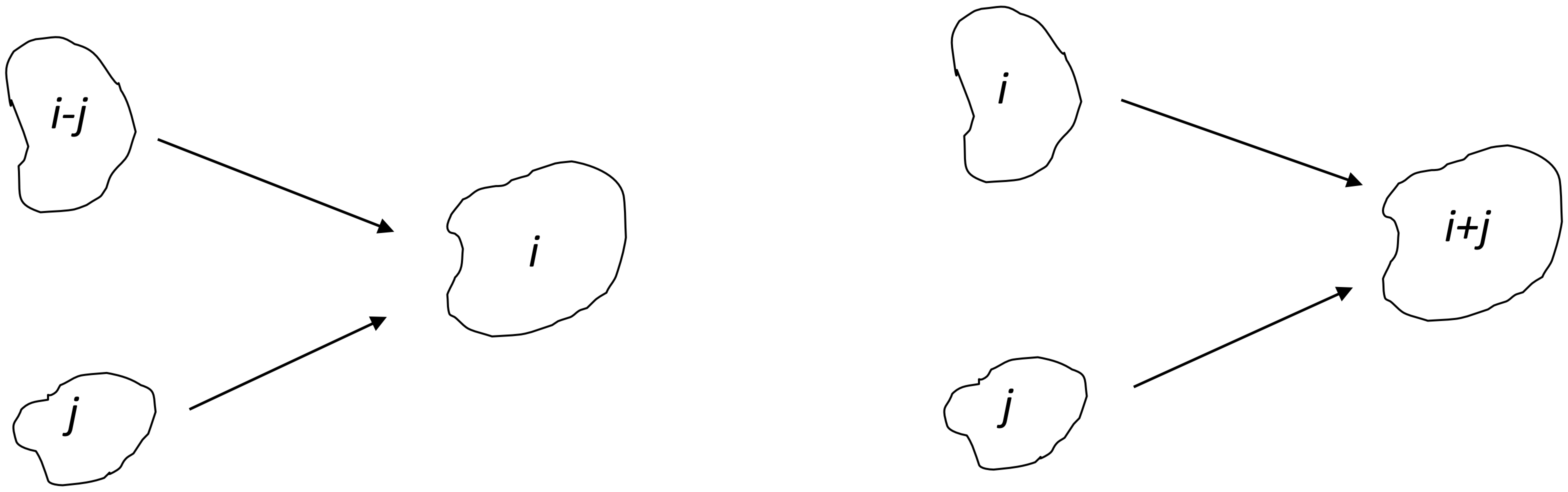
A –mononuclear or convection;
B – polynuclear or convection;
C – convection;
D – mononuclear or screw dislocation;
E – polynuclear or screw dislocation;
F – polynuclear;
G – diffusion;
H – mononuclear.

Aggregation



Aggregation

The aggregation process can take place by collisions.



Birth of particle of size i

Death of particle of size i

$$\frac{1}{2}\sum_{j=1}^{i-1} f_{i-j,j} - \sum_{j=1}^{\infty} f_{i,j}$$

Second order "reaction"

$$f_{i,j} = \beta(i,j)\, n_i n_j$$

$$\beta_{i,j} = \frac{2k_B T}{3\mu}\frac{\left(R_i + R_j\right)^2}{R_i R_j}\frac{1}{\boxed{W_{ij}}}$$

It is a process that does not influence speciation

Aggregation

van der Waals attraction

$$V_{\mathrm{VDW}}(h) = -\frac{A_{12}\bar{r}}{12h}\left[\frac{1}{1+\frac{h}{2(r_1+r_2)}} + \frac{(h/\bar{r})}{1+\frac{h}{\bar{r}}+\frac{h^2}{4r_1r_2}} + \left(\frac{2h}{\bar{r}}\right)\ln\left\{\frac{h}{\bar{r}}\left(\frac{1+\frac{h}{2(r_1+r_2)}}{1+\frac{h}{\bar{r}}+\frac{h^2}{4r_1r_2}}\right)\right\}\right]$$

Hamaker coef.

Electrostatic repulsion

$$V_{\mathrm{E}}(R) = 4\pi\epsilon\epsilon_0\psi_0^{2}\left(\frac{2r_ir_j}{r_i+r_j}\right)^2\left(\frac{\exp(-\kappa(R-r_i-r_j))}{R}\right)$$

Surface potential

$$\kappa = \left(\frac{e^2}{\epsilon\epsilon_0 kT}\underline{\sum\rho_i z_i^{2}}\right)^{1/2}$$

Debye param.

Ionic strength

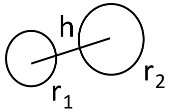
$$V_{ij}(R) = V_E(R) + V_{vdW}(R)$$

$$W_{ij} = (r_i+r_j)\int_{r_i+r_j}^{\infty}\frac{\exp(V_{ij}(R)/kT)}{R^2G(R)}\,\mathrm{d}R$$

$$\beta_{ij} = \underline{\frac{2kT}{3\mu}(r_i+r_j)(r_i^{-1}+r_j^{-1})}\frac{1}{W_{ij}}$$

Brownian kernel

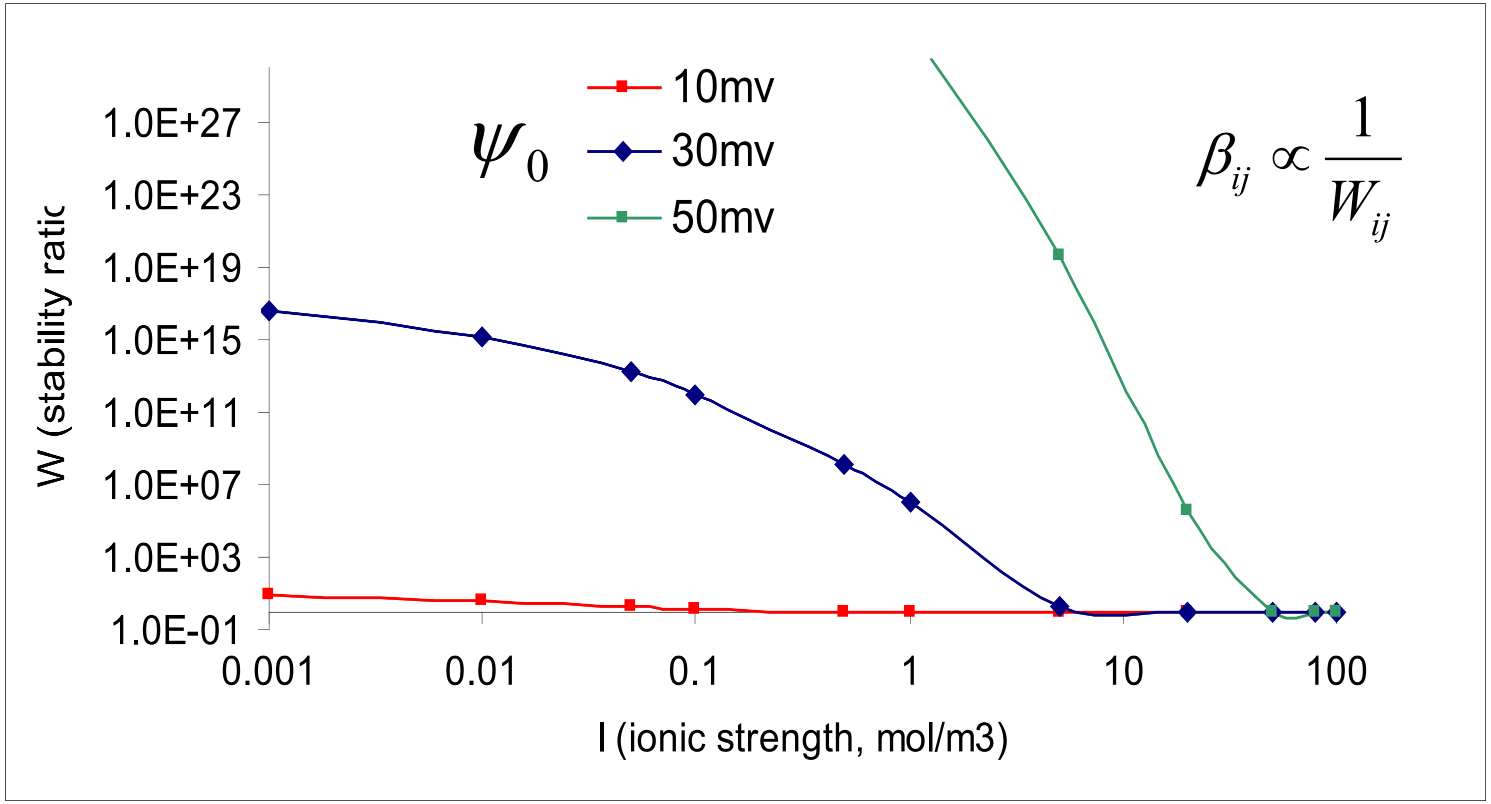
Stability ratio



h = R; r̄ = geom. av. = 2r1r2/(r1+r2)

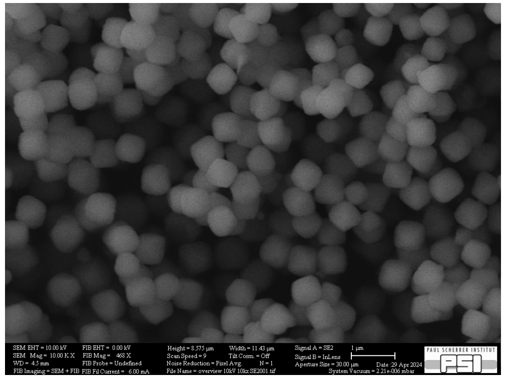
Aggregation

$r_i=r_j= 50$ nm T=298 K $A_{12}=10^{-19}$ J



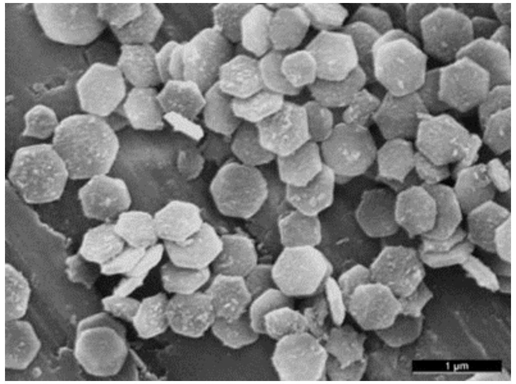
Increasing Ionic strength → aggregation rate increases

Powder synthesis via wet chemical route offers the possibility to produce high quality NPs. Selected examples.

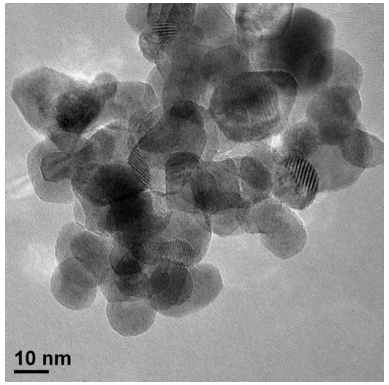


MOF 808

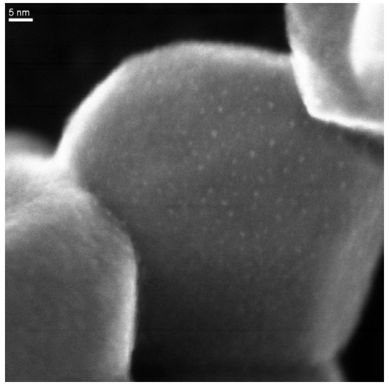
Calcium Aluminum Sulphate



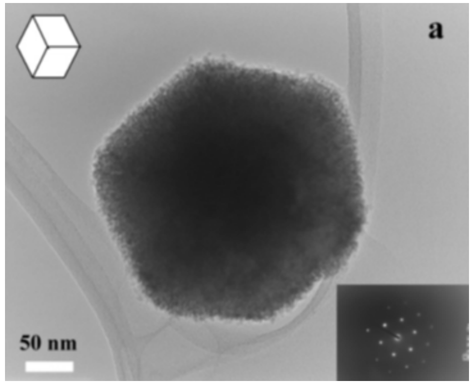
β-tricalcium phosphate



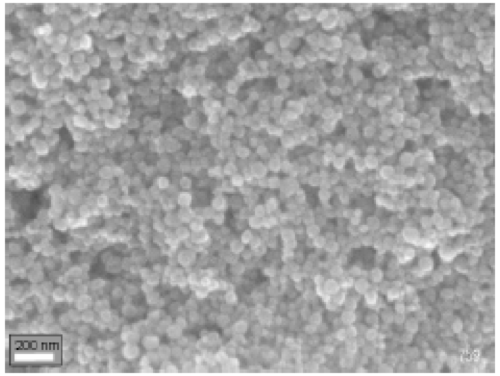
$Ce_{(x)}Zr_{(1-x)}O_2$



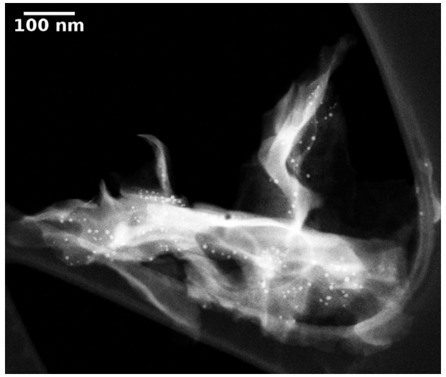
Pt @ CeO_2



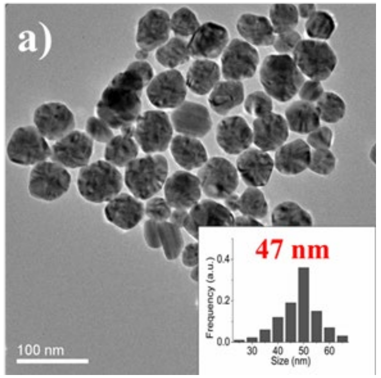
$SrTiO_3$



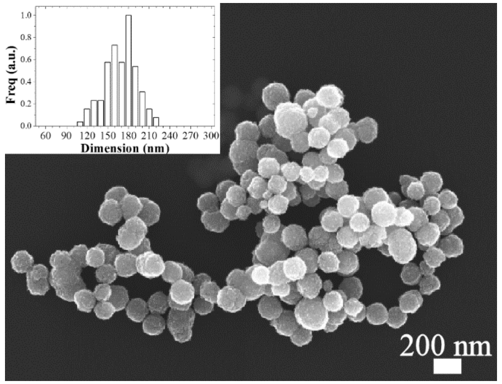
$BaTiO_3$



Ni-Co alloy in C-S-H

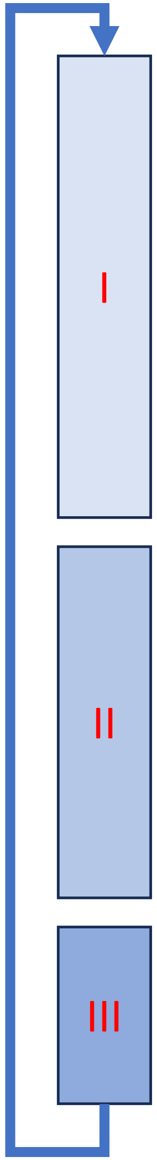


Ag



Ni

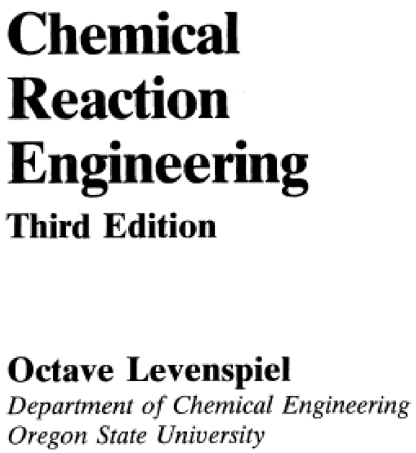
Material synthesis strategy: 7 magic rules



1. **Literature survey**. It is not easy to find a material never prepared before… or at least something similar to start with. Get familiar with the published procedures to understand pros and cons
2. **Thermodynamic calculation**. There are several available software that allows to predict suitable conditions to produce a defined material
3. Estimate the **sensitivity** of the synthesis method to variation of concentration, pH, temperature, or any other experimentally controllable variable via **calculations**
4. Proceed with **experiments in small batch scale**, appropriate mixing, controlled temperature, monitor pH, and TAKES NOTES of everything is happening
5. Collect the solid and **characterize it**, and characterize it, and characterize it, and characterize it, and characterize it, and characterize it, and characterize it….
6. **Think**, write down, rationalize, discuss
7. **Restart** from 1 until the material is of acceptable quality and **<u>REPRODUCIBLE</u>** (!) in small scale
8. If needed, identify a **scale up** strategy.

Planned time: 1 year

Back to school!



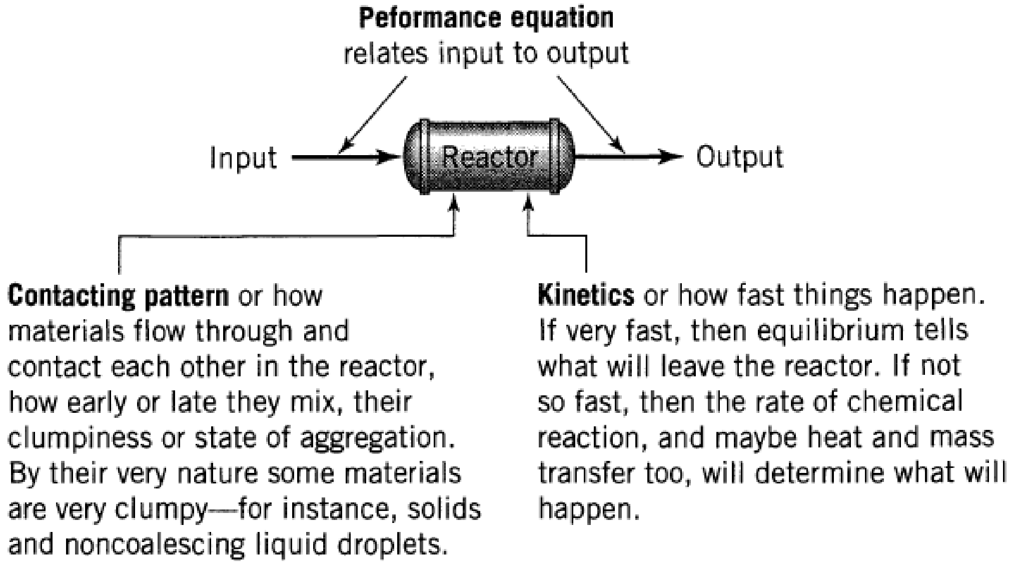
Chemical Reaction Engineering

Third Edition

Octave Levenspiel

Department of Chemical Engineering

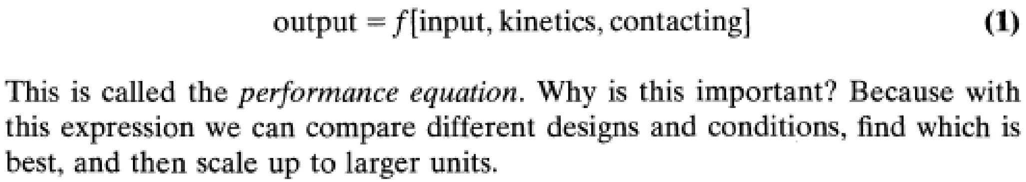
Oregon State University



Contacting pattern or how materials flow through and contact each other in the reactor, how early or late they mix, their clumpiness or state of aggregation. By their very nature some materials are very clumpy—for instance, solids and noncoalescing liquid droplets.

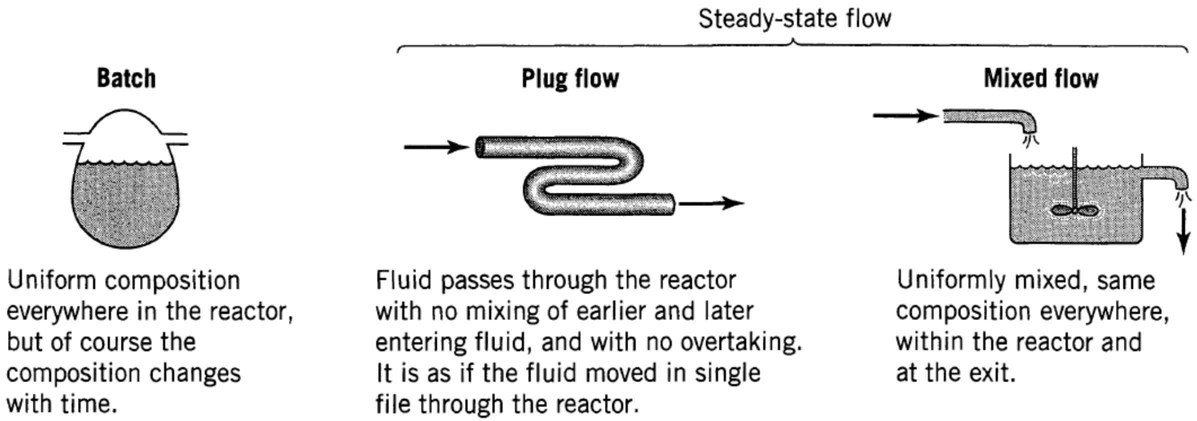
Kinetics or how fast things happen. If very fast, then equilibrium tells what will leave the reactor. If not so fast, then the rate of chemical reaction, and maybe heat and mass transfer too, will determine what will happen.

Figure 1.2 Information needed to predict what a reactor can do.



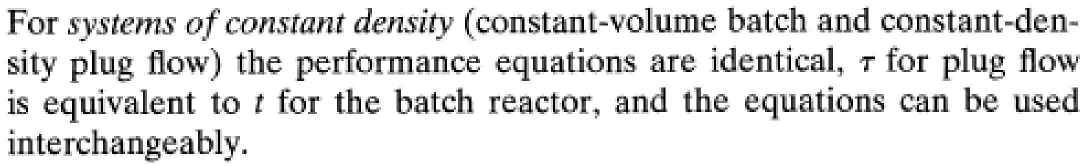
$$\text{output} = f[\text{input, kinetics, contacting}] \qquad \textbf{(1)}$$

This is called the *performance equation*. Why is this important? Because with this expression we can compare different designs and conditions, find which is best, and then scale up to larger units.



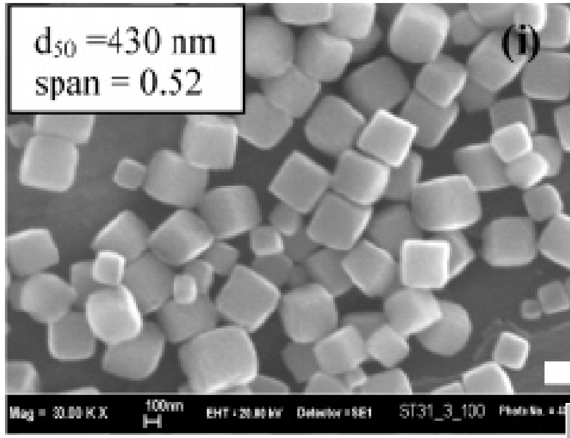
Batch	Plug flow	Mixed flow
Uniform composition everywhere in the reactor, but of course the composition changes with time.	Fluid passes through the reactor with no mixing of earlier and later entering fluid, and with no overtaking. It is as if the fluid moved in single file through the reactor.	Uniformly mixed, same composition everywhere, within the reactor and at the exit.

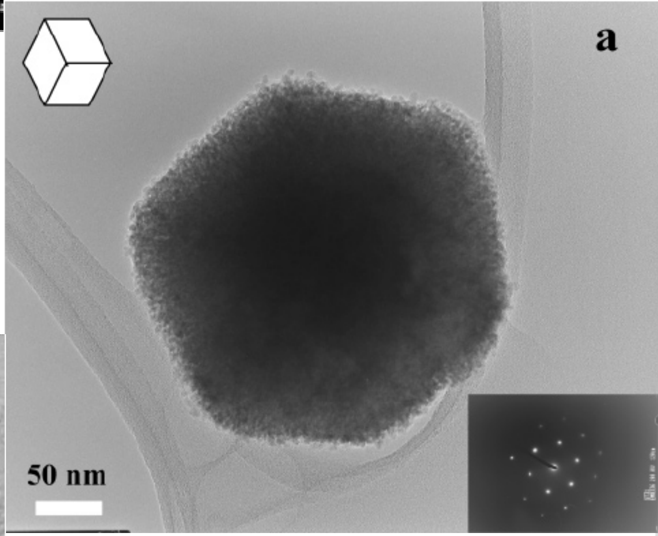
Figure 2.1 Ideal reactor types.

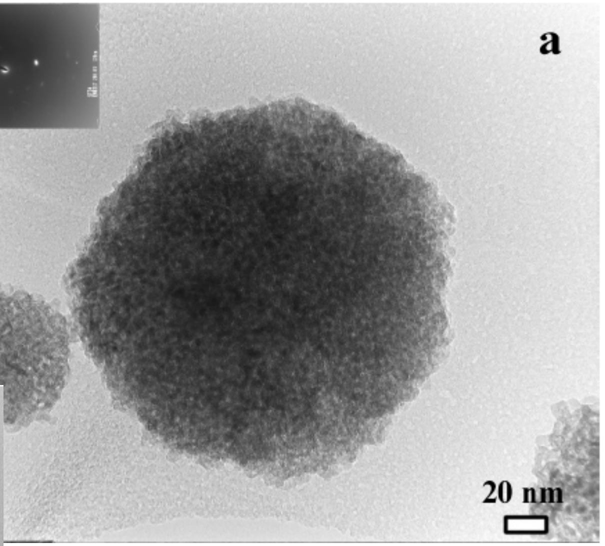


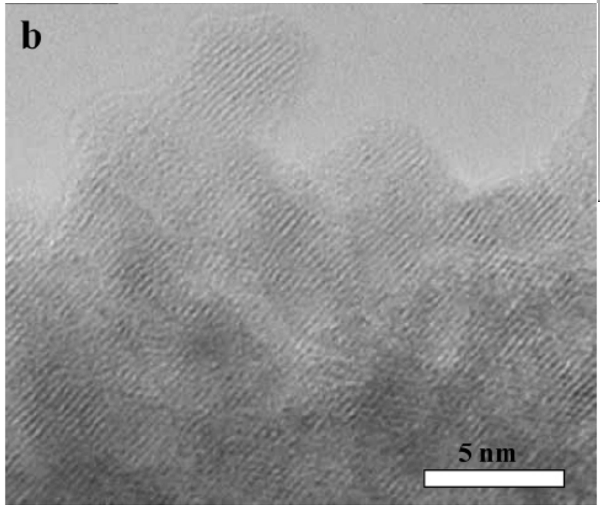
For *systems of constant density* (constant-volume batch and constant-density plug flow) the performance equations are identical, τ for plug flow is equivalent to t for the batch reactor, and the equations can be used interchangeably.

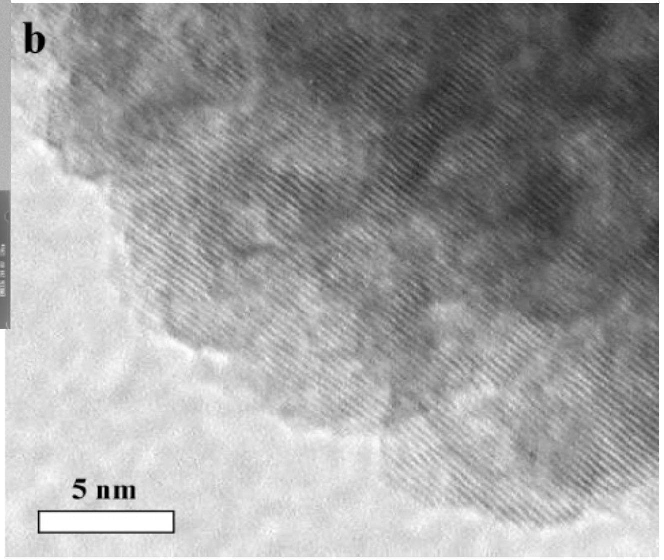
Examples Monocrystal – Polycrystal



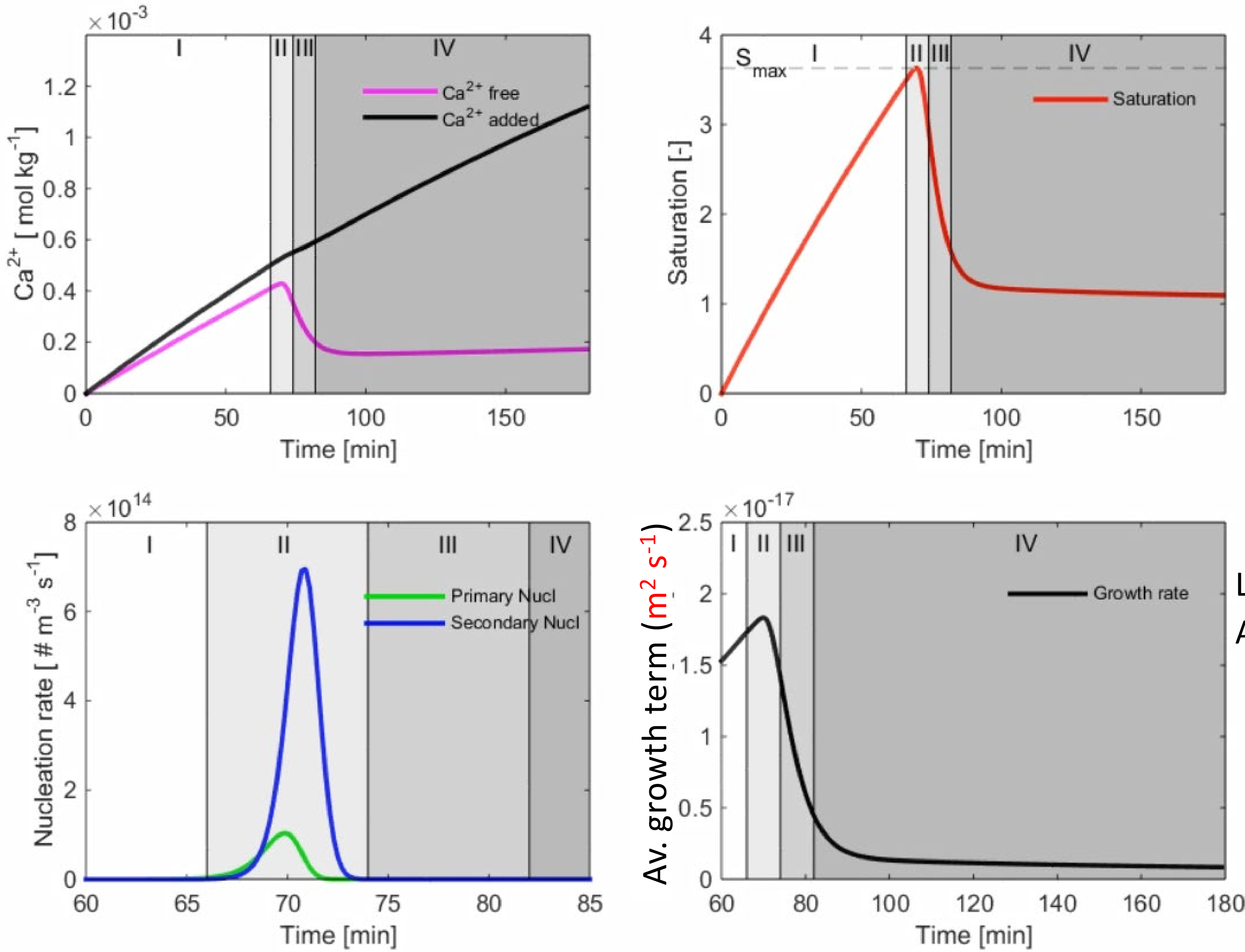


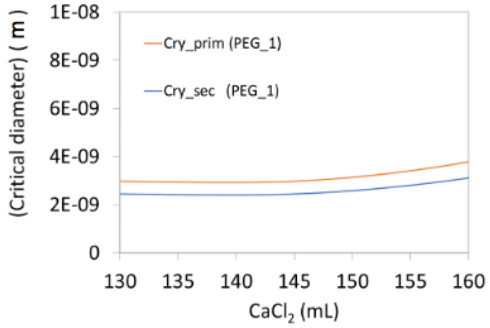


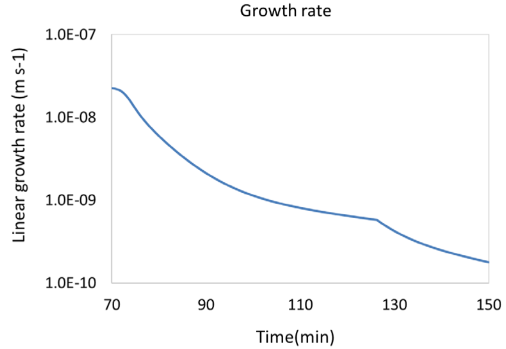




Example of precipitation modelling ($CaCO_3$)







Linear growth rate ($m\ s^{-1}$)=

Av. growth term ($m^2\ s^{-1}$) / size (m)

For particle 2 nm

= 2 10^{-9} m

Growth rate ≈ 10 nm/s

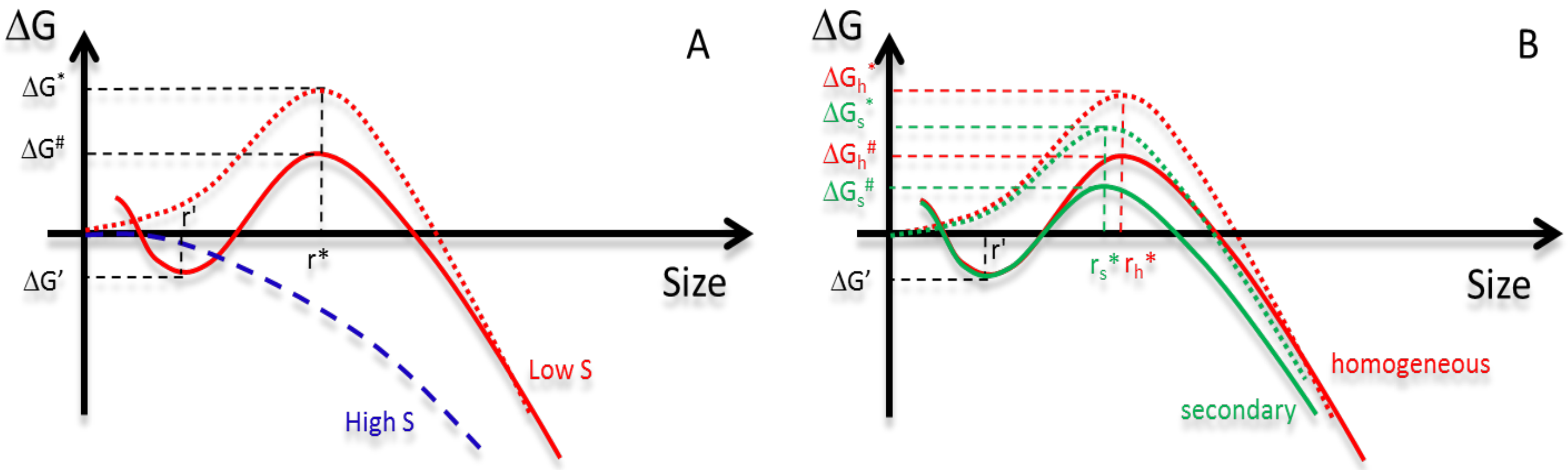
Classical vs. Non-Classical

Classical on **non-classical**? About what? Nucleation or Crystallization?

Classical **<u>nucleation</u>** means to assume valid some mathematical simplification, such as the *capillary approximation* and other constraints which is “hidden” into the so-called classical nucleation theory (CNT), as postulated by Gibbs (1876), formulated by Volmer and Weber (1925), corrected by Becker and Döring (1935), completed by Zeldovich (1943) and disseminated by Nielsen (1964).

What is **non-classical**? Every Gibbs free energy **landscape** which postulate the existence of stable or metastable entities (cluster or pre-nucleation clusters) before the critical size.

Classical vs. Non-Classical **Nucleation** Theory

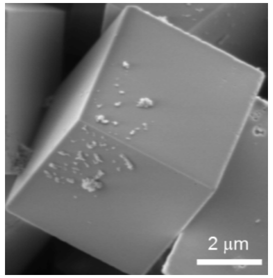


Schematic representation of Gibbs free energy landscapes.

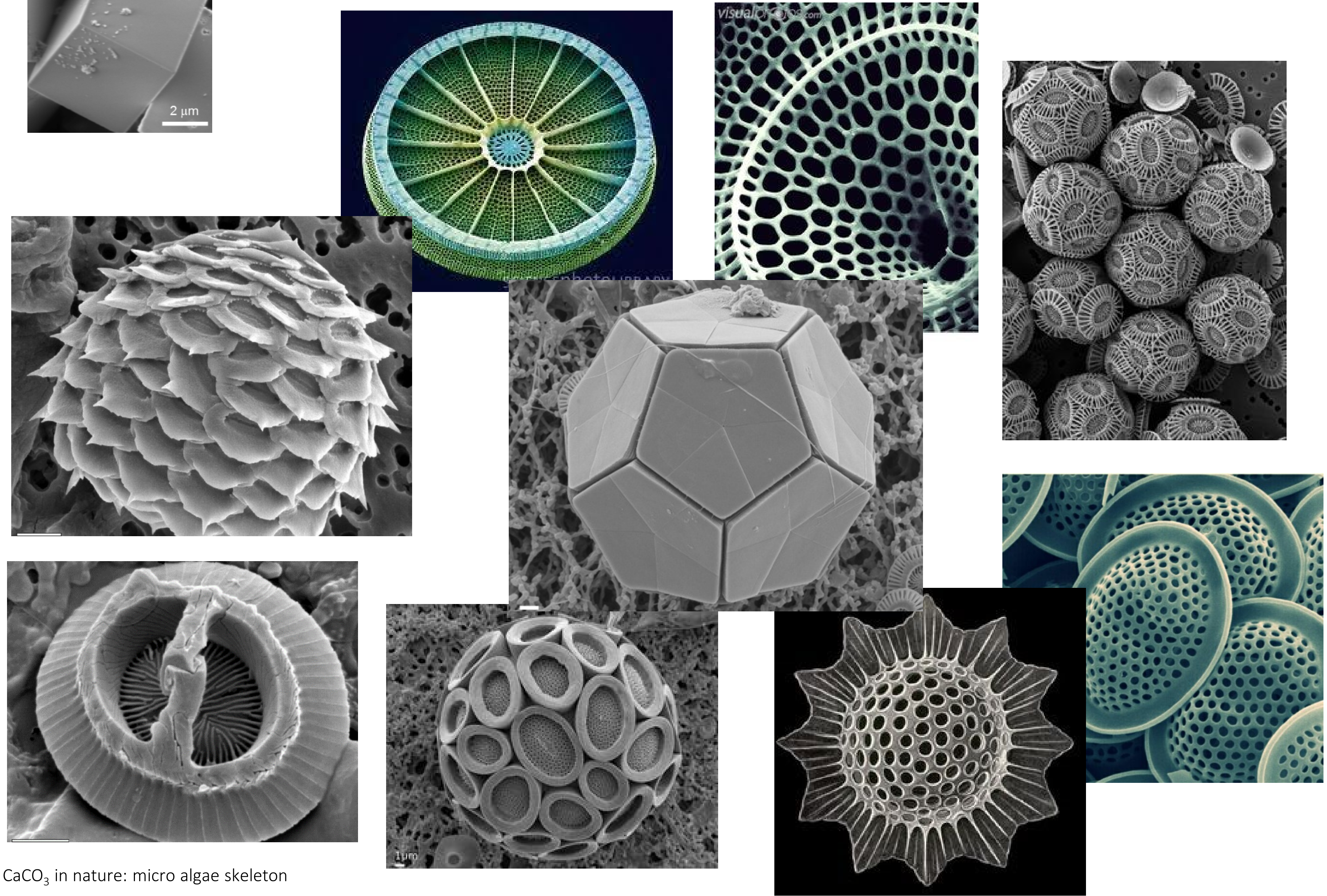
(A) In case of relatively low S (continuous line) a relative minimum may be depicted. The critical size and the size of metastable embryos are indicated as r* and r’, respectively. For high S (dashed line) spinodal decomposition occurs and neither a metastability area nor a critical size can be argued. The dotted line depicts the Gibbs free energy profile according to the **classical theory**.

(B) Homogeneous and “true” secondary nucleation Gibbs free energy landscapes. In the case of secondary nucleation, the coordinate of the critical size corresponds to a lower size and lower activation energy with respect to the homogeneous nucleation due to the contribution of the cohesion energy. Dotted and continuous lines depict the **classical** and **non-classical** landscape, respectively. This is just an example: by concept extension, any time the Gibbs free energy landscape is not according to the classical profile, can be noted as non-classical. Major complication: no mathematical framework!

Anyway, we are here…



… and Nature is here, since million of years!



$CaCO_3$ in nature: micro algae skeleton

Take away messages

1. Quality of ceramic depends on quality of powder; quality of powder depends on quality of precipitate;
2. Hydrothermal precipitation can lead directly to ceramic powders or…
3. A thermal treatment is needed to transform precipitates into ceramic powders;
4. Precipitation, even an apparent simple system such as $CaCO_3$, is a convolution of complex sub-processes;
5. A TD&K model is necessary to understand a precipitation process;
6. Size&phase can be controlled in different way, including by seeding;
7. Morphology of precipitated particle depends on relative interfacial energy of different crystal planes – equilibrium morphology dominated by surface with lowest interfacial energy;
8. Interfacial energy and morphology can be changed by specific adsorption of ions or organic molecules onto different crystallographic surfaces, nature do it every day!