PAUL SCHERRER INSTITUT

Lesson 5

Ceramics and colloids

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Powder synthesis
Thermodynamic in solutions

Reference books

Books

1. Les Traité des Matériaux, Volume 16 « Les Céramiques »
   J. Barton, P. Bowen, C. Carry & J.M. Haussonne
2. The Colloidal Domain – D. F. Evans & H. Wennerström, Wiley,1999.(Chp. 1.4-1.6)

Summary

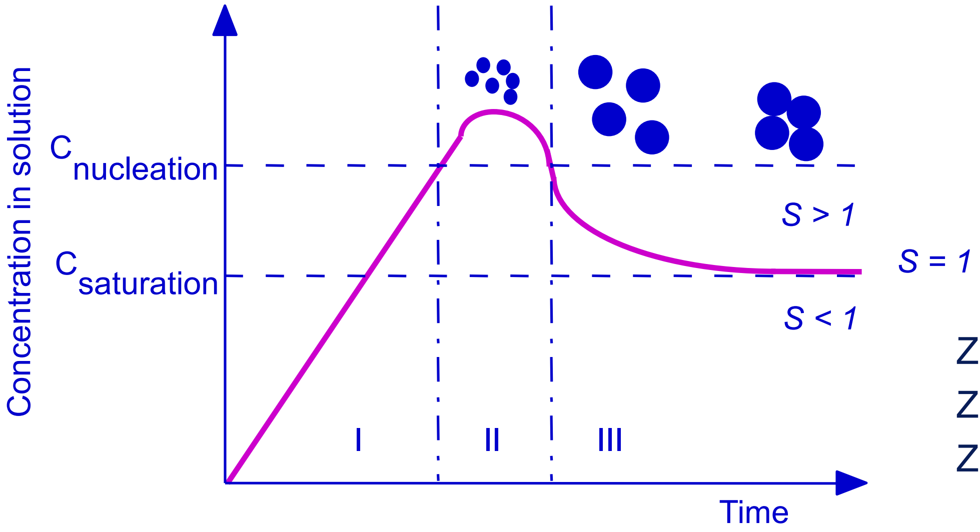
- Recall from previous lesson (4-5)
- Thermodynamic of precipitation (6-12)
- Introduction to the non-classical view (13-14)
- Examples (15-19)
- Speciation (20-23)
- Brownian Motion (24-25)
- Take away messages (26)

Powder (ceramic) synthesis by precipitation

- For metal oxide: precipitation of an appropriate salt (e.g. nitrate, chloride) and thermal decomposition in air (in some case direct precipitation of the metal oxide, e.g. TiO_2)
- For non-oxide (e.g. Si_3N_4) thermal treatment under controlled atmosphere (N_2, N_2/H_2, ….)
- [For metals: direct metal formation (e.g. Ag, Au) or synthesis in organic solvents (e.g. Ni, Co) or metal oxides thermally treated under reducing atmosphere (H_2/Ar)]
- Size&shape of the ceramic (e.g. metal oxide) are (almost) determined by the precipitate size&shape, therefore
- The evolution of the precipitation process is fundamental

$$S_R = \frac{C_l}{C_s}$$

= 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)

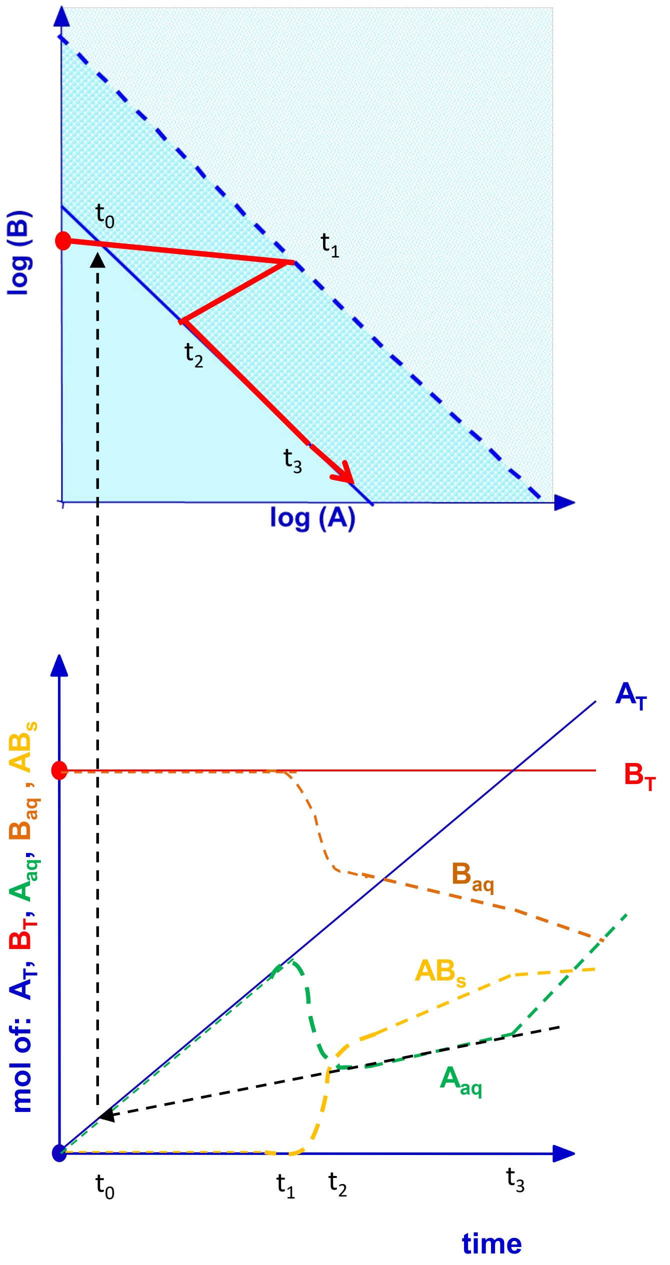


Zone I: The activity is to low to induce nucleation
Zone II: Nucleation = Formation of nuclei
Zone III: Crystal growth and eventually aggregation

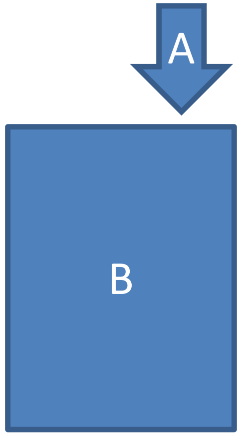
Everything clear? Questions?

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

Molar amount



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



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:
$A_{aq} x\, B_{aq} = Kps_{AB}$

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Thermodynamics: Gibbs free energy

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

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

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 φ>0 transformation from 1 to 2 is a spontaneous process whereas when φ<0 the process is thermodynamically unfavourable and it does not occur[4] (at the macroscopic scale[3]).

[4] Is this correct?

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[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}

Thermodynamics: Gibbs free energy

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.*

Supersaturation can be induced in systems in several ways such as by a temperature change or as a consequence of mixing of two solutions.

Thermodynamics: Gibbs free energy

1

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

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 an 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!

Thermodynamics: Gibbs free energy

Decreasing the size of the solid the definition of “surface” and its properties are rather ambiguous. The surface tension should be a function of size.

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 weak point of the theoretical framework. We will see later which implication it has and to which extent we have to take into account of this approximation.

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[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

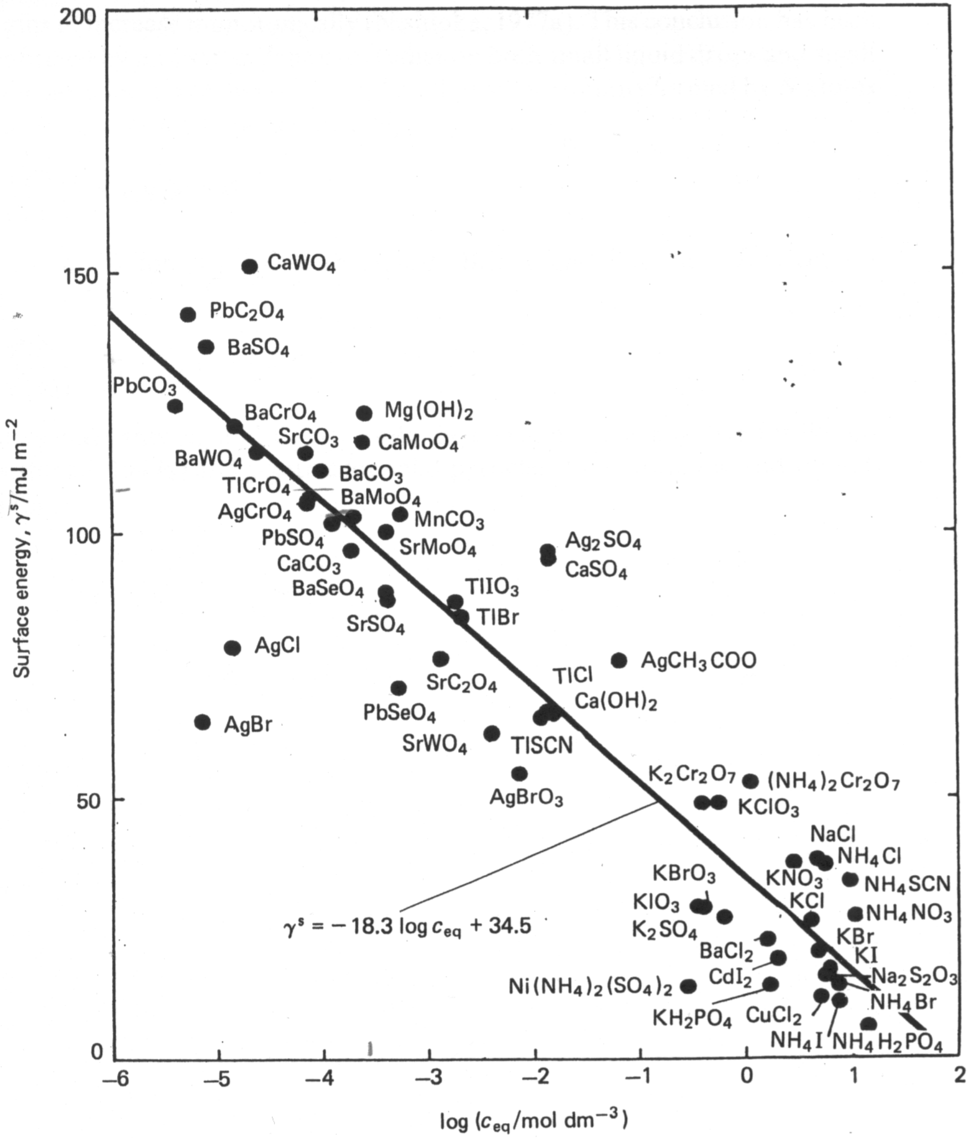
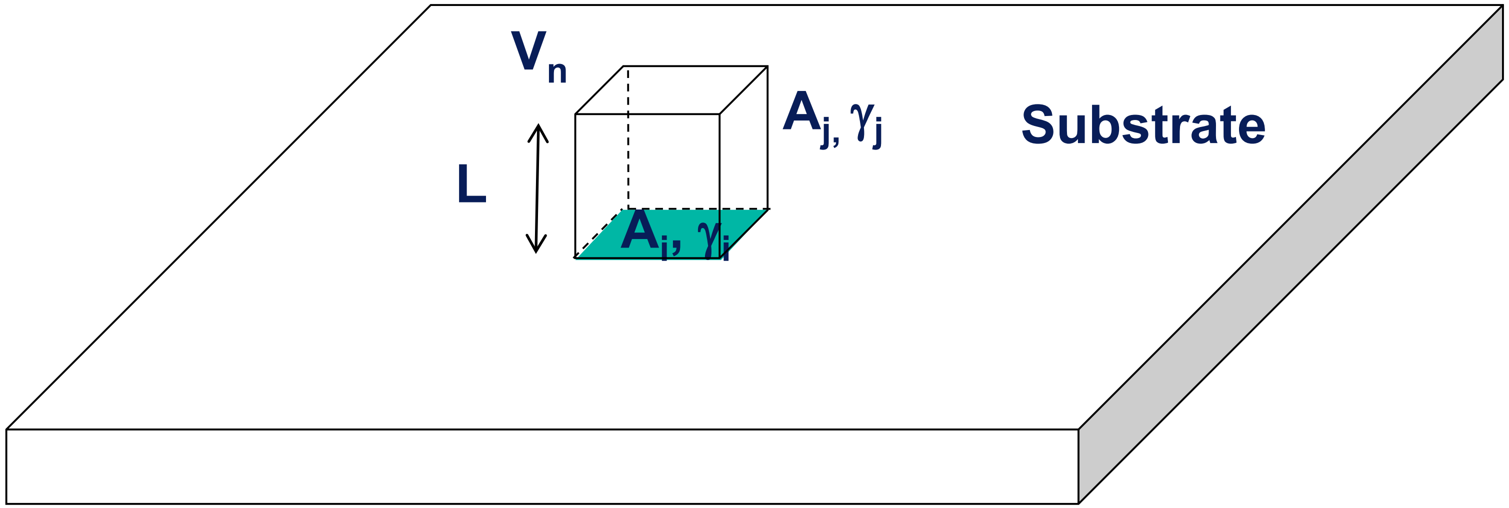


Figure 2.3 Experimentally determined surface energy, γ^s, as a function of equilibrium solubility, c_{eq}

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



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

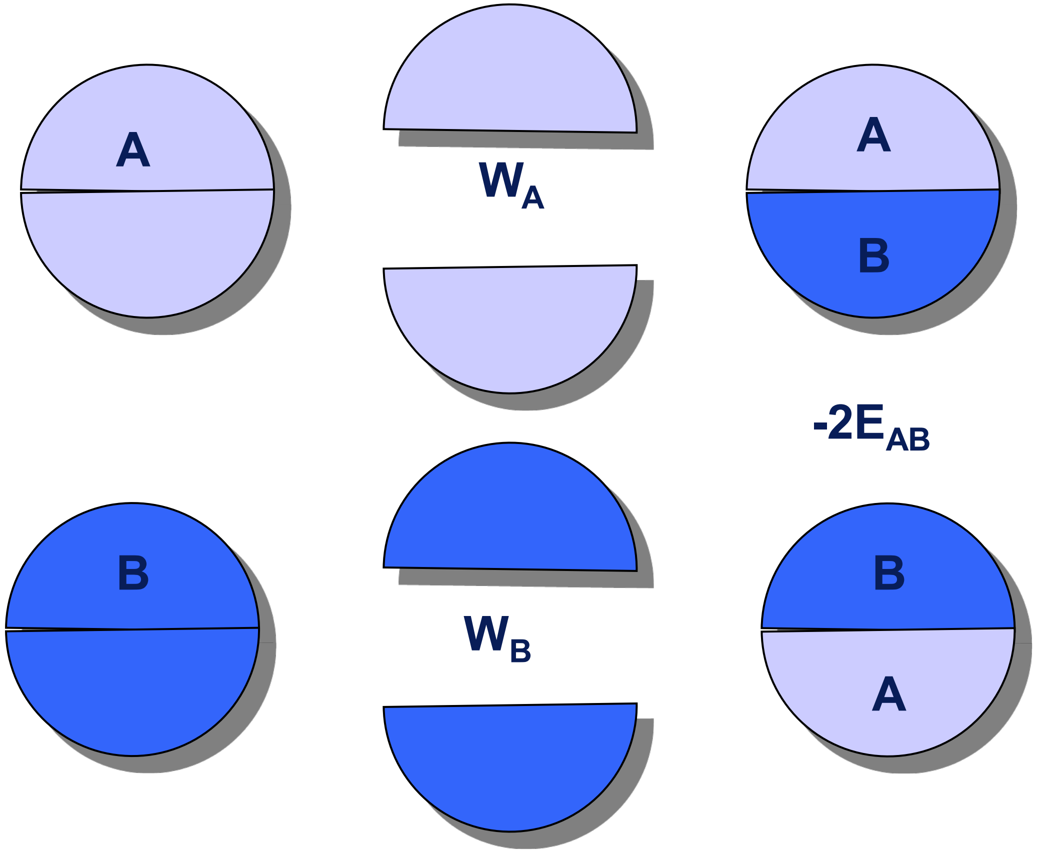
Also ΔG_I is a surface contribution!

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 solid 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.

Thermodynamics: Energy of Adhesion

$$\Delta G_I = \oint_{A_i} \left(\gamma_i + \beta_{adh} \right) dA$$



$$W_{AB} = W_A + W_B - 2E_{AB}$$

$$\gamma = \frac{W}{2S}$$ **(Born-Stern approx.)**

$$\gamma_{AB} = \gamma_A + \gamma_B - \beta_{adh}$$

β_{adh}= specific adhesion energy. Work required to generate new surface between A and B per unit of area.

$$0 < \beta_{adh} < \gamma_A + \gamma_B$$

No affinity **Maximum affinity**

Can be $\beta_{adh} > \gamma_A + \gamma_B$?
What does $\beta_{adh} = \gamma_A + \gamma_B$ mean?
What does $\beta_{adh} = 0$ mean?

Classical vs. Non-Classical

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

Classical **nucleation** 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.

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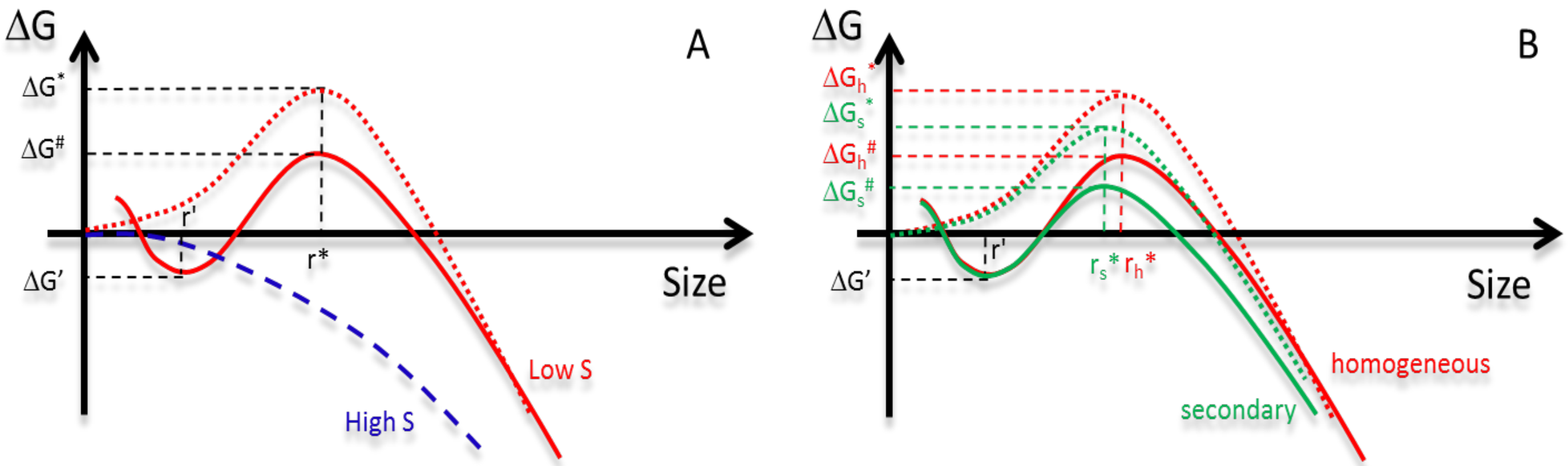
Classical vs. Non-Classical Nucleation Theory

Recall:
Week 4, slide 11



Schematic representation of Gibbs free energy landscapes.

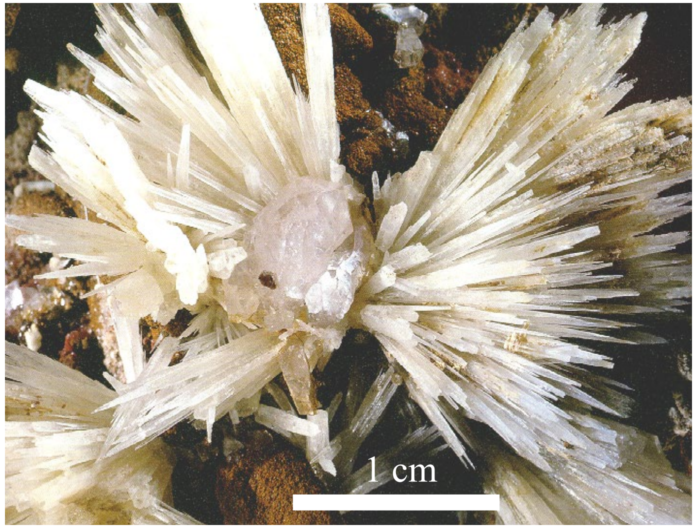
(A) In case of relatively low S (continuous line) a relative minimum may be depicted. The critical size and the size of metastable embryos are indicated as r* and r', respectively. For high S (dashed line) spinodal decomposition occurs and neither a metastability area nor a critical size can be argued. 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.

Minerals vs. Powders

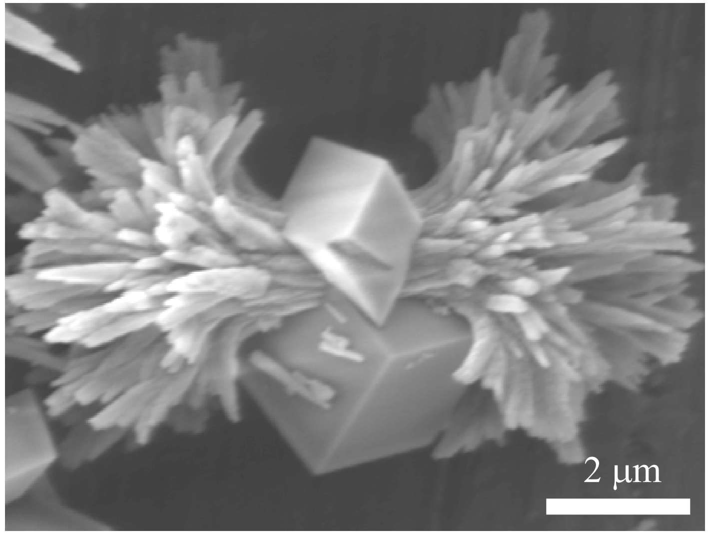
Minerals

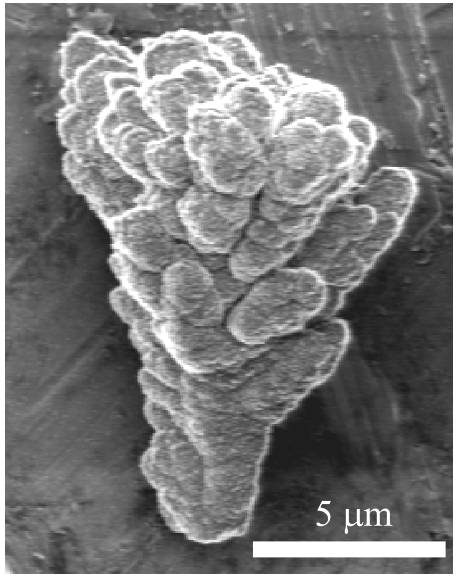
≈ 100 years



Powders

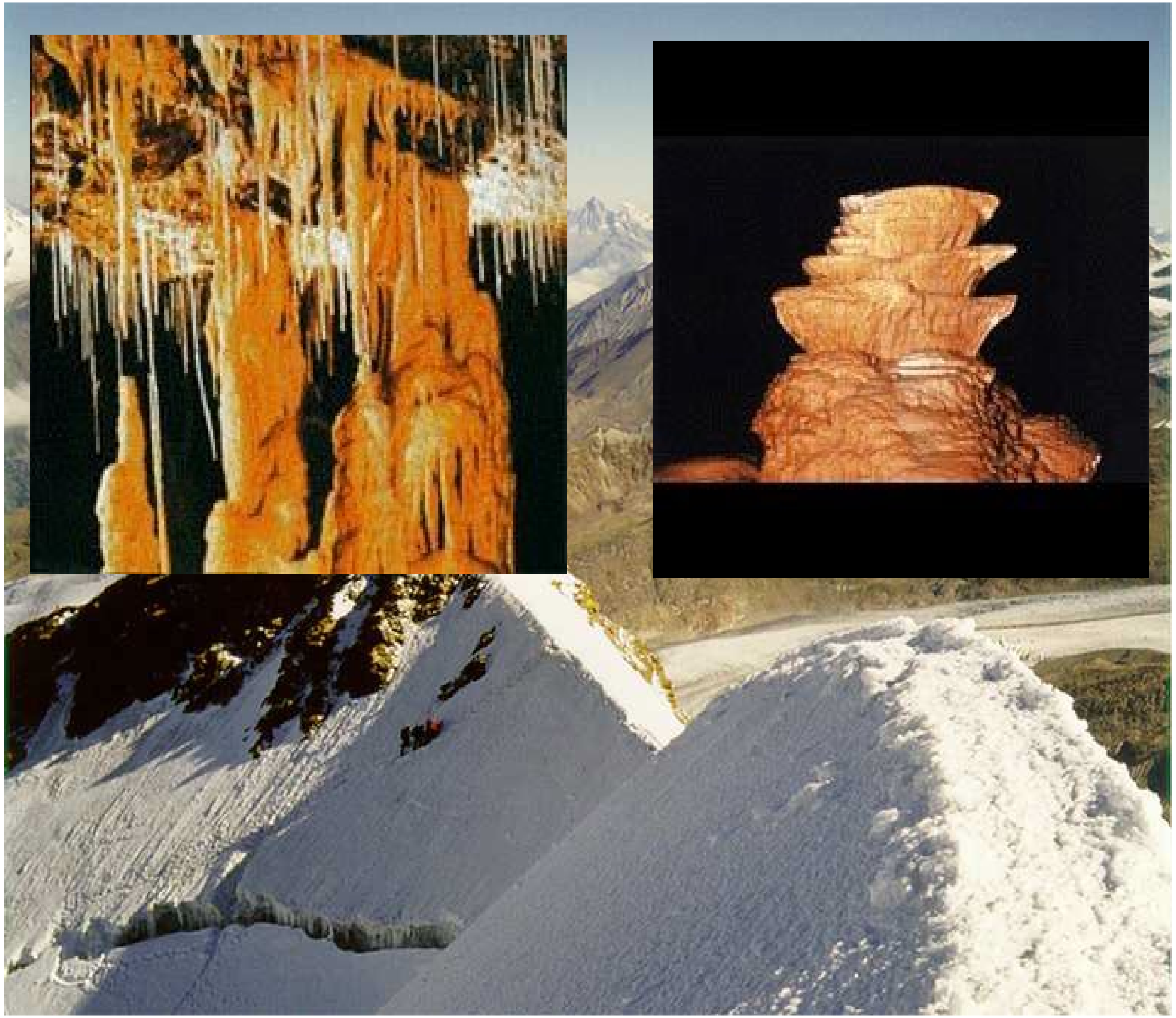
≈ 10 minutes





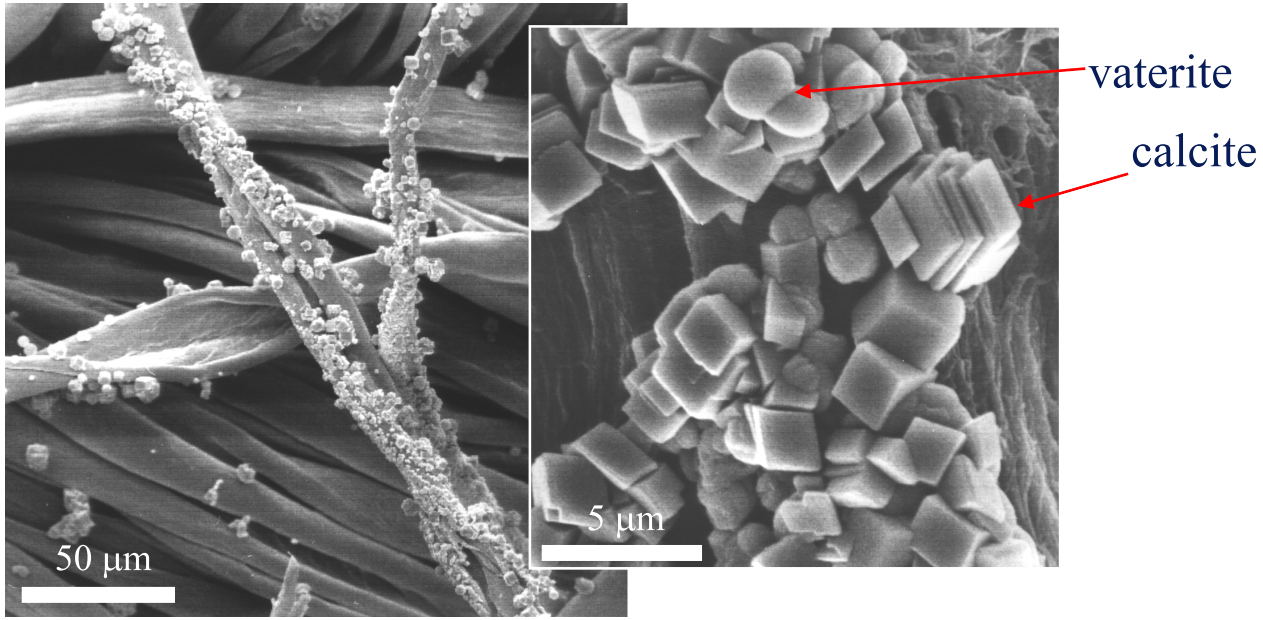
- Time
- Size

Natural forms of Calcium Carbonate – $CaCO_3$

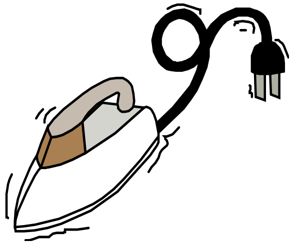


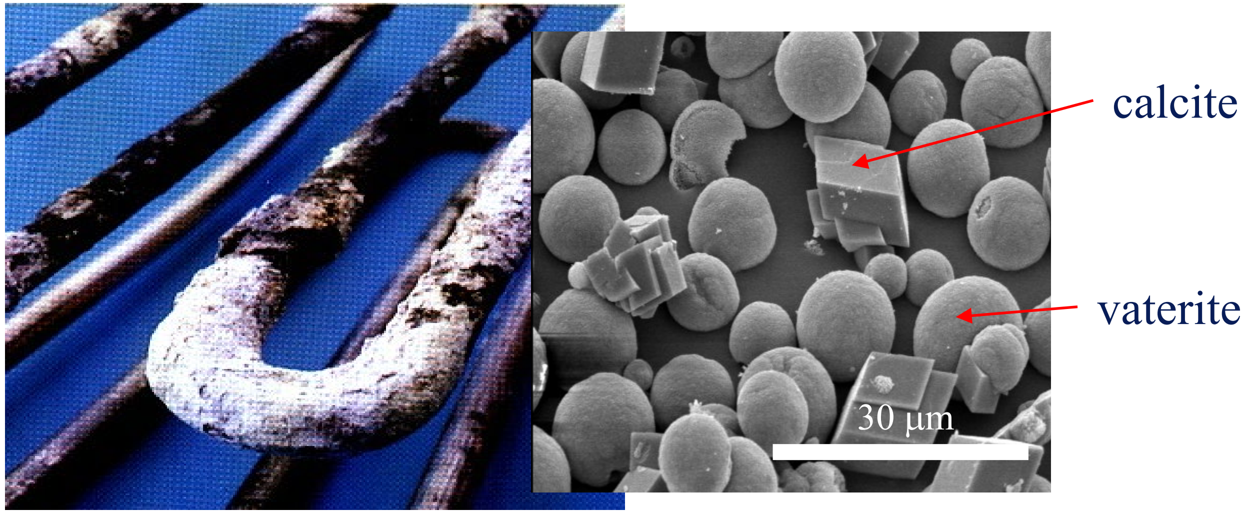
Calcium carbonate – unwanted precipitation

- Tissues,clothes



- Heating elements





Precipitation ↔ Chemistry

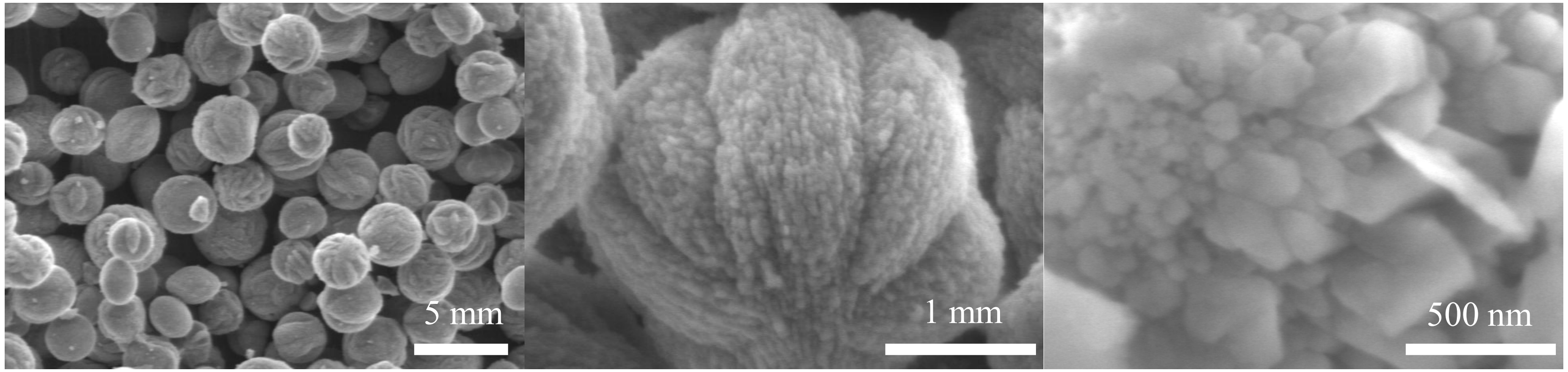
Example: calcium carbonate Applications - paper, tooth pastes, polymers (filler), pH-corrector, construction materials, black board chalk, paints, etc…

$$Ca^{2+} + CO_3^{2-} \leftrightarrows CaCO_3$$

- ➢ 3 crystalline structures (Calcite,Vaterite, Aragonite)
- ➢ 3 intermediate phases (Amorphous, Hexa-, Monohydrate)

⇒ Nucleation kinetics
⇒ Growth mechanism & kinetics

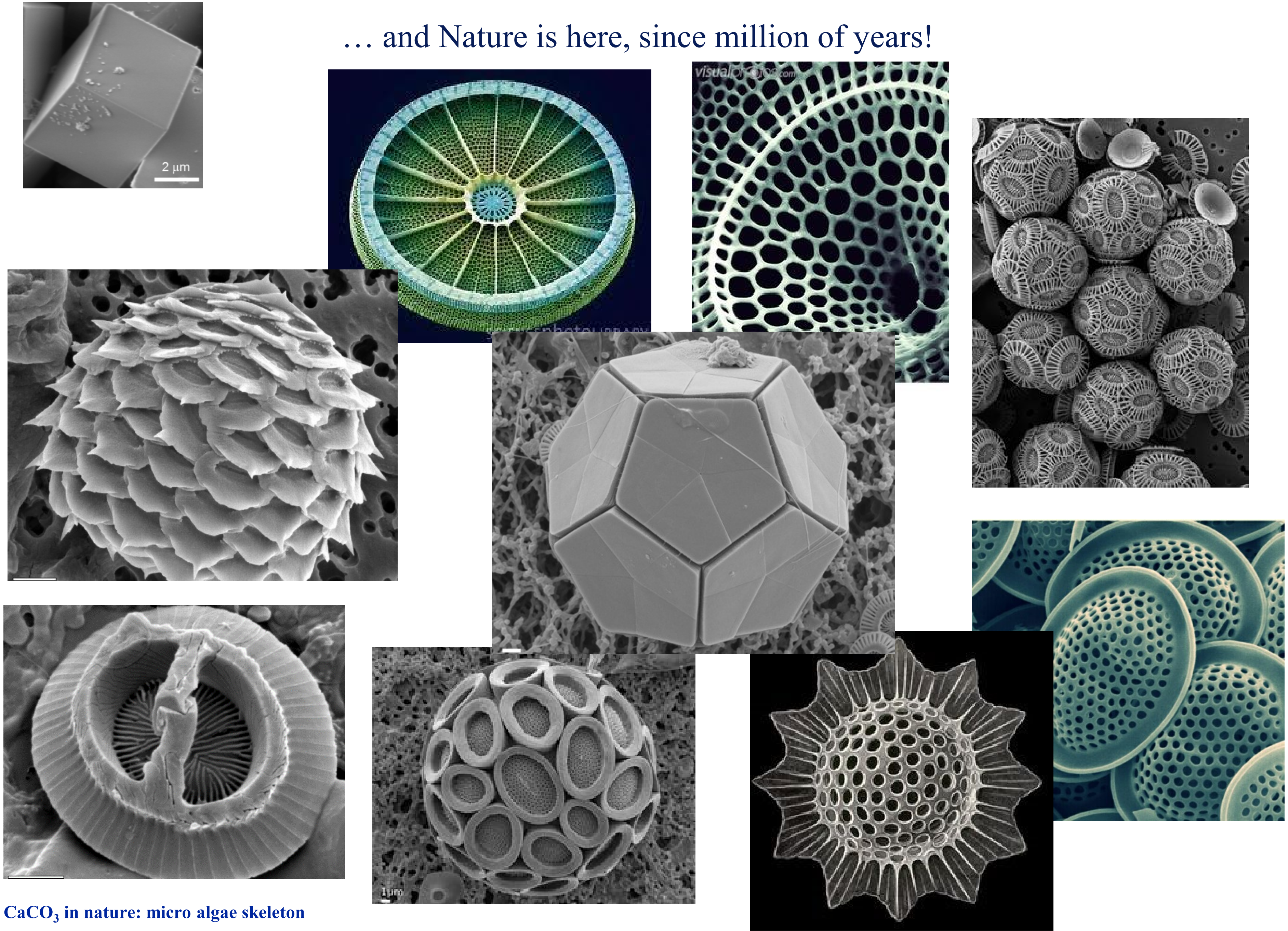
Normally only valid for simple nucleation – single crystal growth?



Kralj, D. et al, J. Cryst. Growth, 104, 1990

Anyway, we are here…

… and Nature is here, since million of years!



CaCO$_3$ in nature: micro algae skeleton

Equilibrium constant

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

Example: $(Ca_3(PO_4)_2)^0(aq) \rightleftarrows 3Ca^{2+}(aq) + 2P{O_4}^{3-}(aq)$ ➡ $K_{eq} = \dfrac{[Ca^{2+}]^3\left[P{O_4}^{3-}\right]^2}{[(Ca_3(PO_4)_2)^0]}$

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

Example: $BaSO_4(s) \rightleftarrows Ba^{2+}(aq) + S{O_4}^{2-}(aq)$ ➡ $K_{sp} = [Ca^{2+}]\left[S{O_4}^{2-}\right]$

- Squared brackets, [ ],indicate molar concentration;
- Equilibrium constant depends on temperature only;
- Molar concentrations are approximation of activities.

$$[C] = mol/L$$

$$K_{sp} = K_{sp}(T)$$

$$a_i = \gamma_i \cdot [C]_i$$

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

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

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

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

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

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

Hydrated ionic diameter

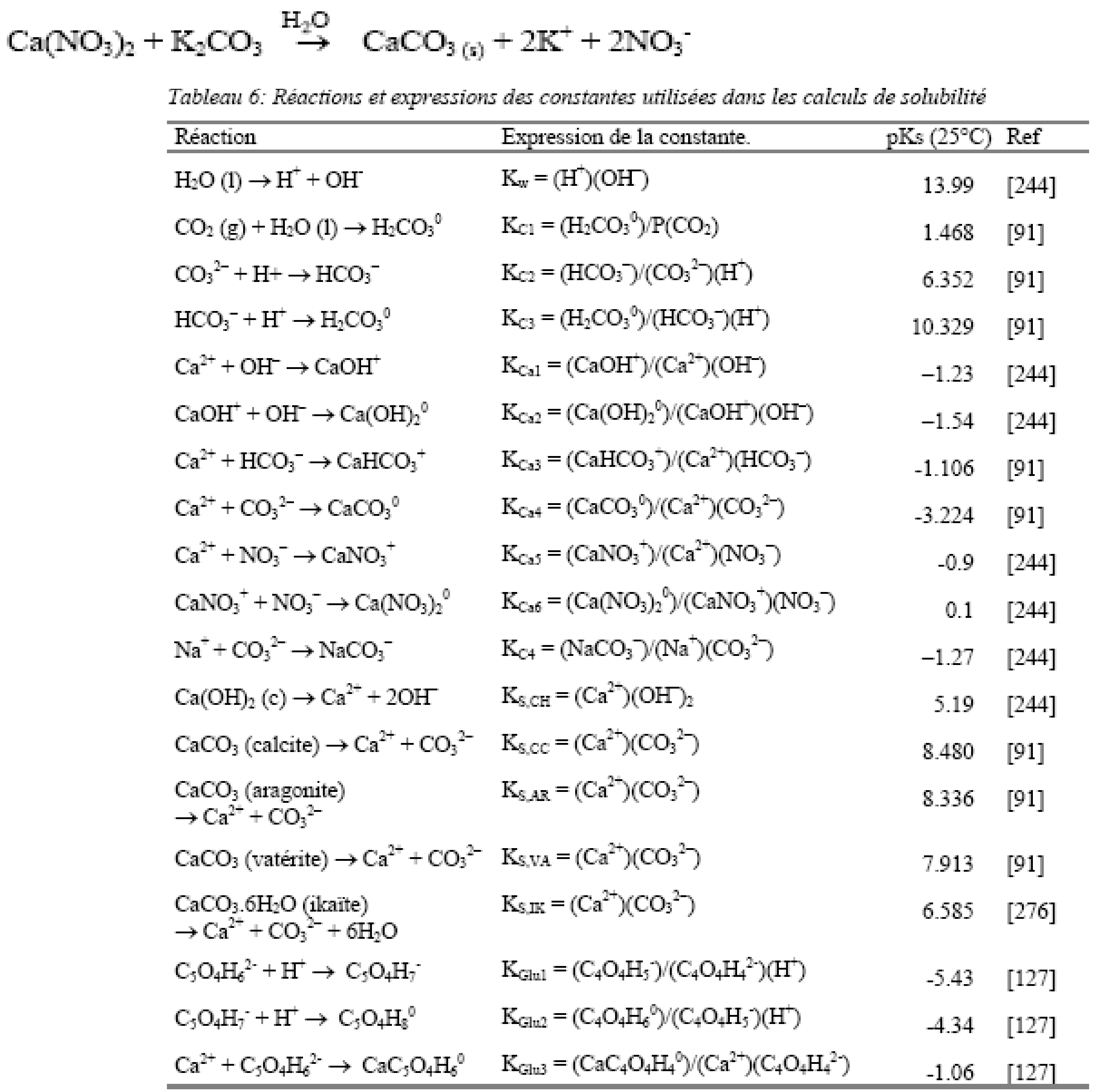
- Thermodynamique des solutions d'électrolytes

- Quelques valeurs de diamètres ioniques hydratés:

d [nm]	X
1.10	Sn^{4+}, Zr^{4+}
0.90	H^{+},Al^{3+},Fe^{3+}
0.80	Be^{2+},Mg^{2+}
0.60	Li^{+},Ca^{2+},Fe^{2+},Co^{2+},Ni^{2+},Cu^{2+},Zn2+
0.50	Ba$^{2+,}$Cd$^{2+,}$,Hg$^{2+,}$,S^{2-},CH$_2$(COO)$_2^{2-}$
0.45	CH$_3$COO^{-},CO$_3^{2-,}$P$_2$O$_7^{4-}$, Pb^{2+}
0.42	Na^{+},HCO$_3^{-}$, H$_2$PO$_4^{-}$
0.40	SO$_4^{2-}$,HPO$_4^{2-}$,PO$_4^{3-}$, HP$_2$O$_7^{3-}$
0.35	OH^{-}
0.30	K^{+},Cl^{-},Br^{-},I^{-}, NO$_3^{-}$
0.25	Ag^{+}, NH$_4^{+}$

Extrait de S. Kotrly et L. Sucha, « Handbook of Chemical Equilibria in Analytical Chemistry » Ellis Horwood Ltd, Chichester, 1985.

Precipitation – thermodynamic model - $CaCO_3$



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

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]

Several equilibrium reaction, not all relevant

Lower Ks = Lower solubility

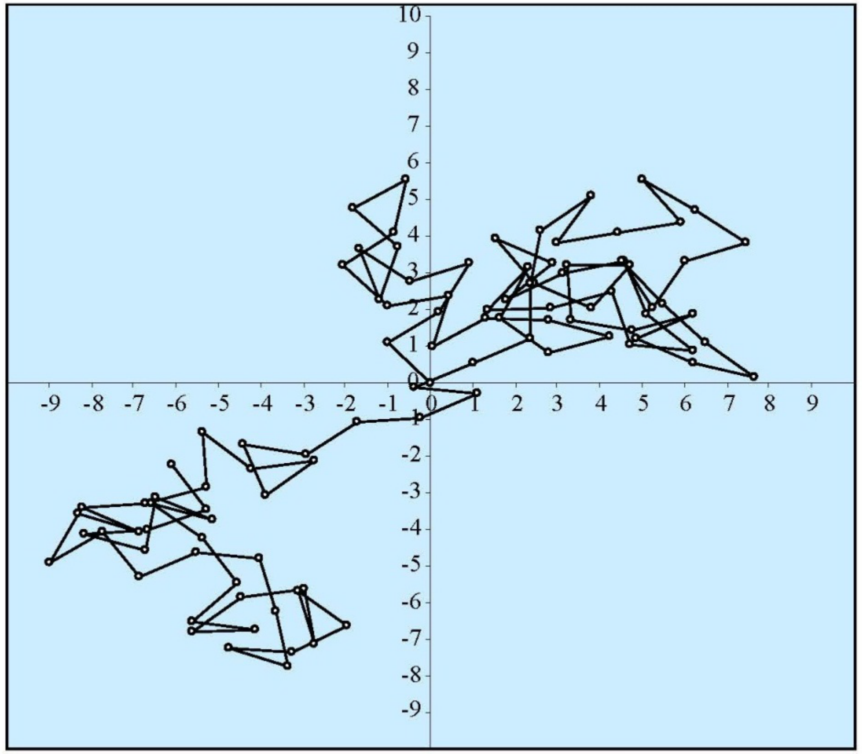
$p(x) = -\log_{10}(x)$

Brownian Motion

- <u>Thermal energy</u>

  At macroscopic level (e.g. 1 mole= 6.023 10^{23} molecules): **R*T***

  At molecular level: **k*T*** = average kinetic energy of molecules



- The average square displacement: random movement

$$\langle r^2 \rangle = \langle x^2 + y^2 + z^2 \rangle$$

$$\sqrt{\langle r^2 \rangle} = l_0 \sqrt{N_r} \qquad (1.6.4)$$

$\boldsymbol{N_r}$: number of elementary displacements

$\boldsymbol{l_0}$: average lenght of a elementary displacement

r^2 : average squared displacement

Brownian Motion

- <u>Diffusion</u>

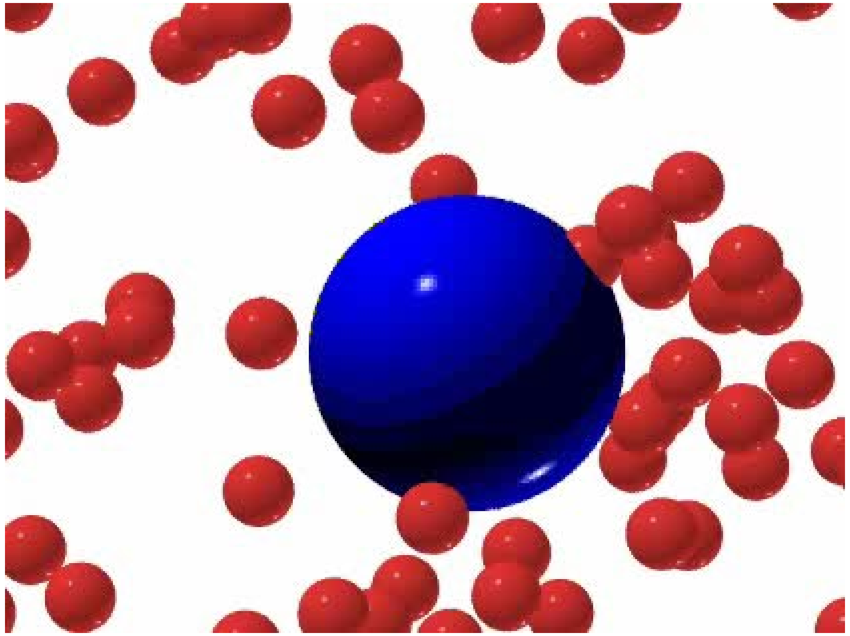
- Diffusion coefficient: definition

$$\langle r^2 \rangle = 6Dt$$

- Typical values *D*

D [m^2/s] at 25 °C :

Water (gas, 1 atm) : $3.4\ 10^{-5}$
Water (liq, 1 atm) : $2.8\ 10^{-9}$
Benzene (liq, 1 atm) : $2.2\ 10^{-9}$
Glucose (aq, 0.4 wt.%) : $0.67\ 10^{-9}$
Na^+ ion (aq) : $7.4\ 10^{-9}$
Ca^{2+} ion (aq) : $5.5\ 10^{-9}$



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!