Multidisciplinary approach to NPs characterization

Doctoral School, MSE-674

1st Edition

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PSI-Villigen, 7th-9th January 2025

Table of Content (room OFLG/402)

9:15 – 10:45 Section 1.1

a) Introduction to NPs synthesis

b) Introduction to materials characterization

10:45 – 11:00 Coffee break

11:00 – 12:30 Section 1.2

c) Introduction to colloidal stability

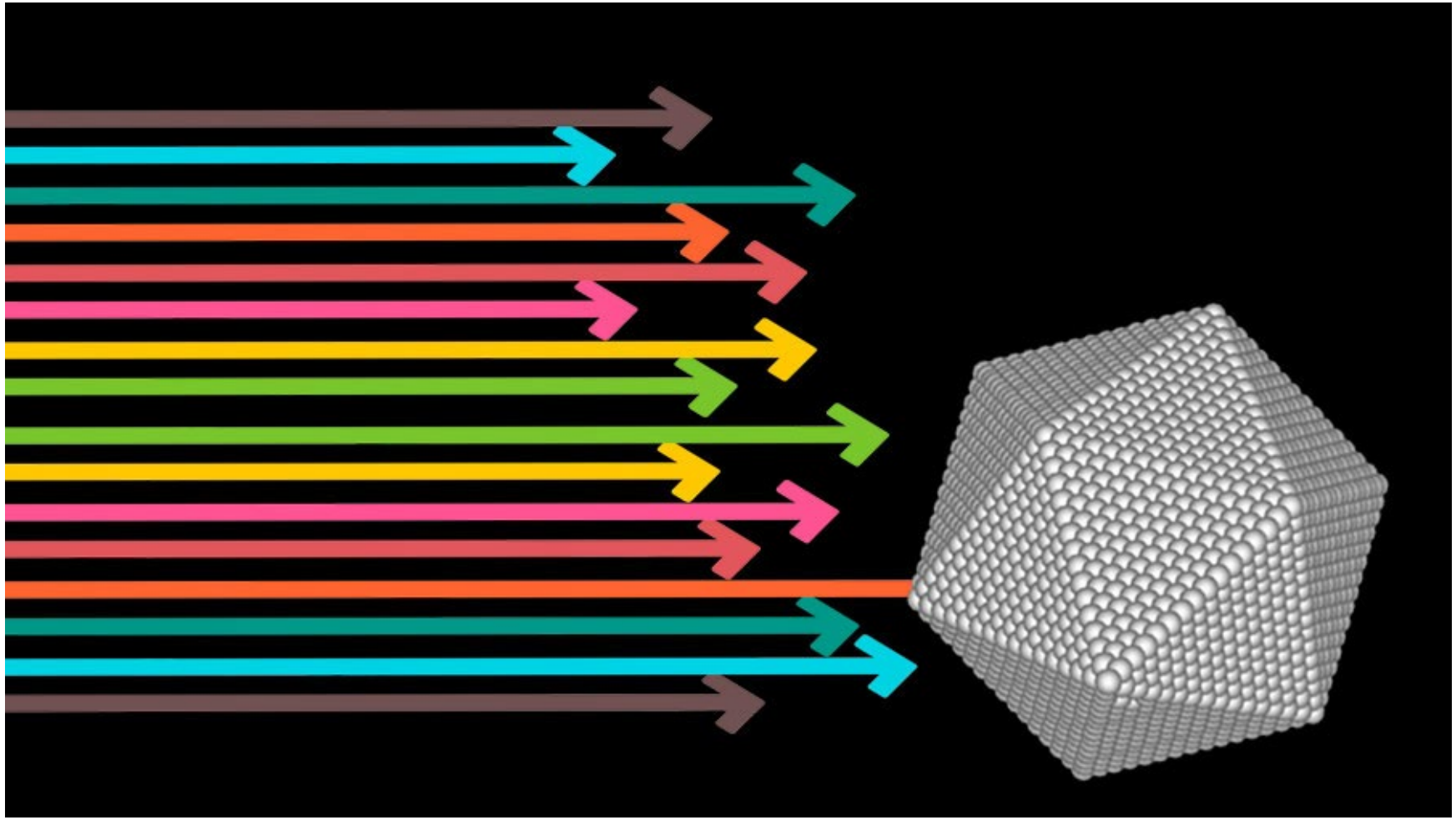
d) PSD via DLS: theory and practice

12:30 – 13:30 Lunch (OASE)

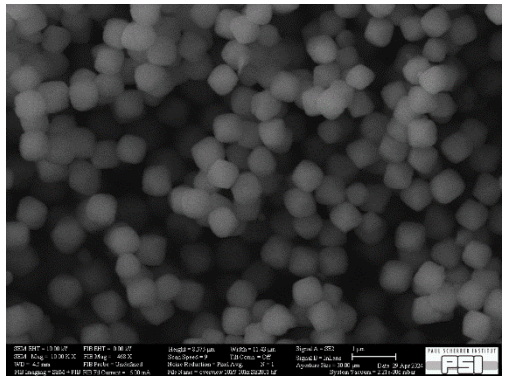
Introduction to NPs synthesis

Introduction to powder characterization

Introduction to NPs synthesis



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



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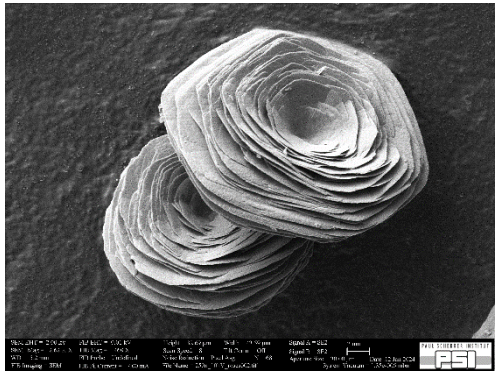
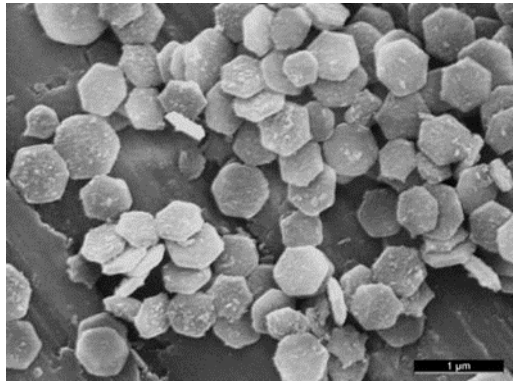
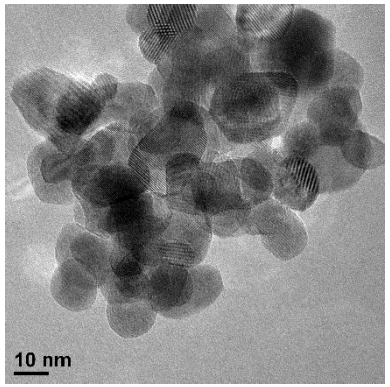


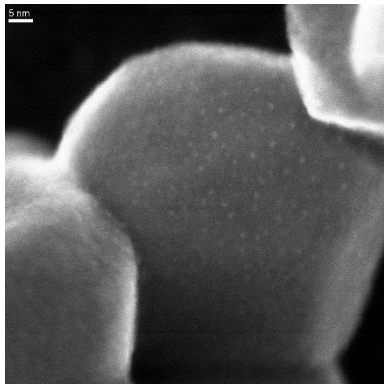
Calcium Aluminum Sulphate



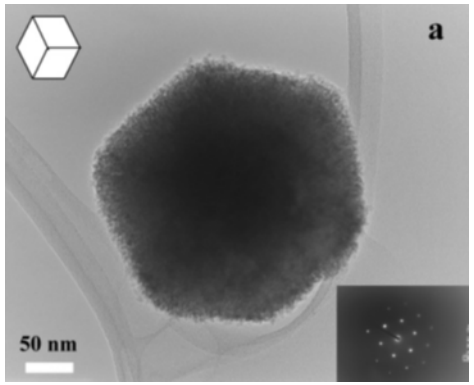
β-tricalcium phosphate



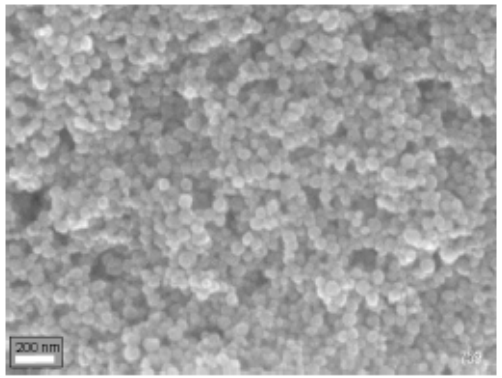
$Ce_{(x)}Zr_{(1-x)}O_2$



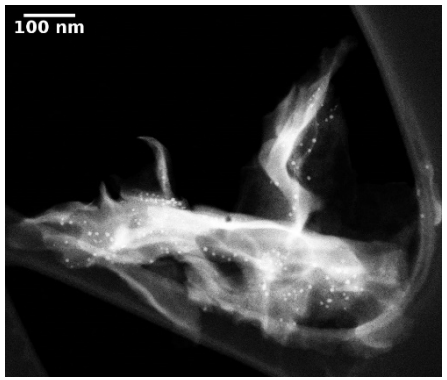
Pt @ CeO_2



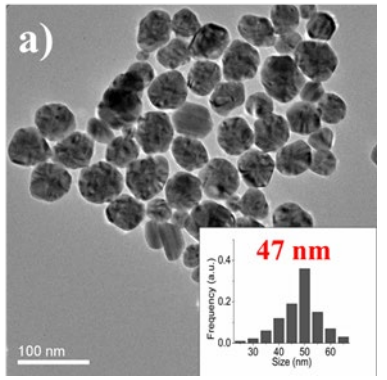
$SrTiO_3$



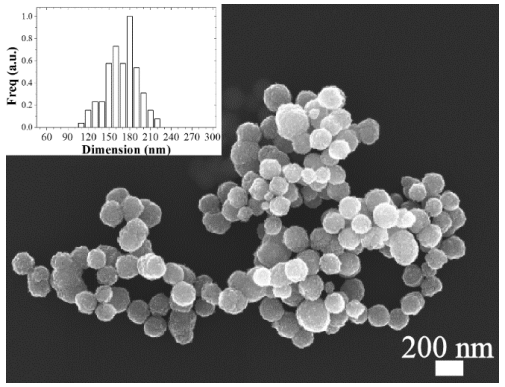
$BaTiO_3$



Ni-Co alloy in C-S-H



Ag



Ni

Material synthesis strategy: 7 magic rules

PSI

I

II

III

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….

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

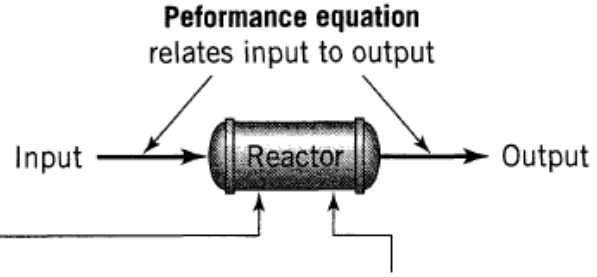
Back to school!

Scale up strategies

Chemical Reaction Engineering

Third Edition

Octave Levenspiel
Department of Chemical Engineering
Oregon State University



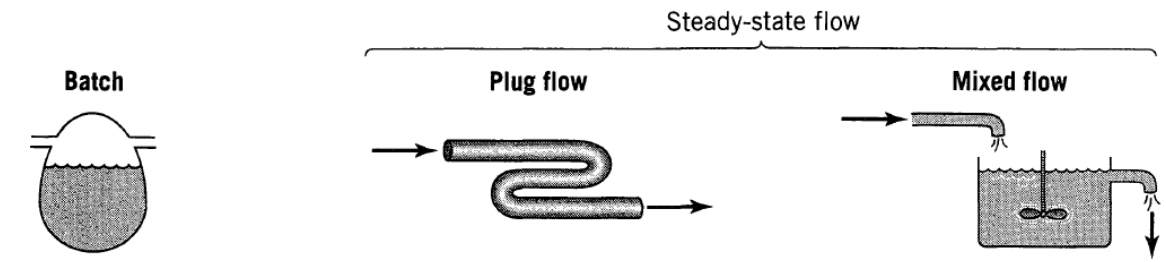
Contacting pattern or how materials flow through and contact each other in the reactor, how early or late they mix, their clumpiness or state of aggregation. By their very nature some materials are very clumpy—for instance, solids and noncoalescing liquid droplets.

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.



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.

Supersaturation (S) can be induced in systems in several ways:

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

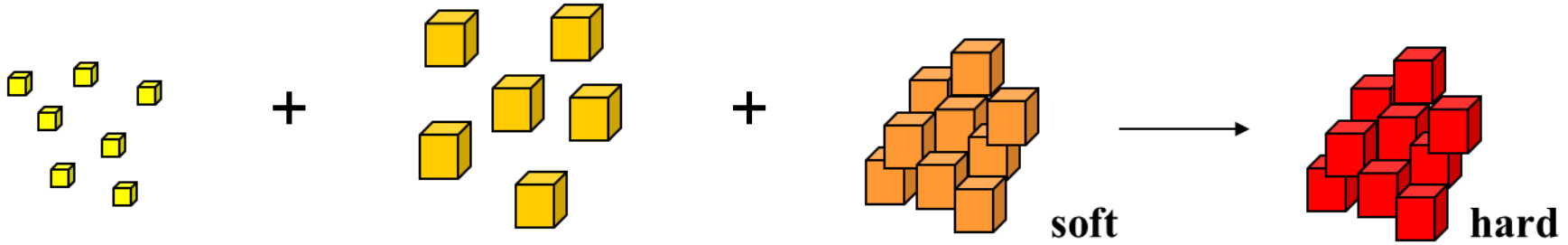
1. Temperature change (with thermodynamic and kinetic effects);
2. Mixing of solutions (same solvent, e.g. water);
3. Add another solvent (variation of dielectric constant of the solvent);
4. Induce a pH change (adding acid or alkaline solution, or consequence of another induced reaction);
5. Evaporation;
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 (e.g. size & PSD)

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

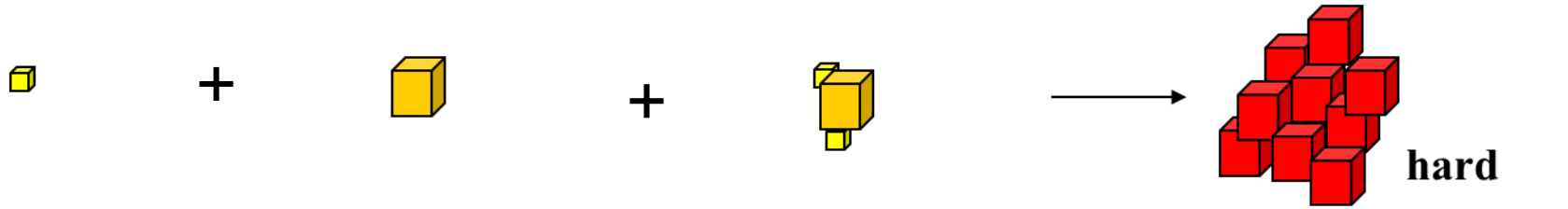
Two possible solid formation pathways…

Path 1: primary nucleation, growth, aggregation



Nucleation$_{homo}$ **Growth** **(Agglomerate)** **(Aggregate)**

Path 2: primary nucleation, secondary nucleation, growth



Nucleation$_{I}$ **Growth** **Nucleation$_{II}$** **Polycrystalline particle**

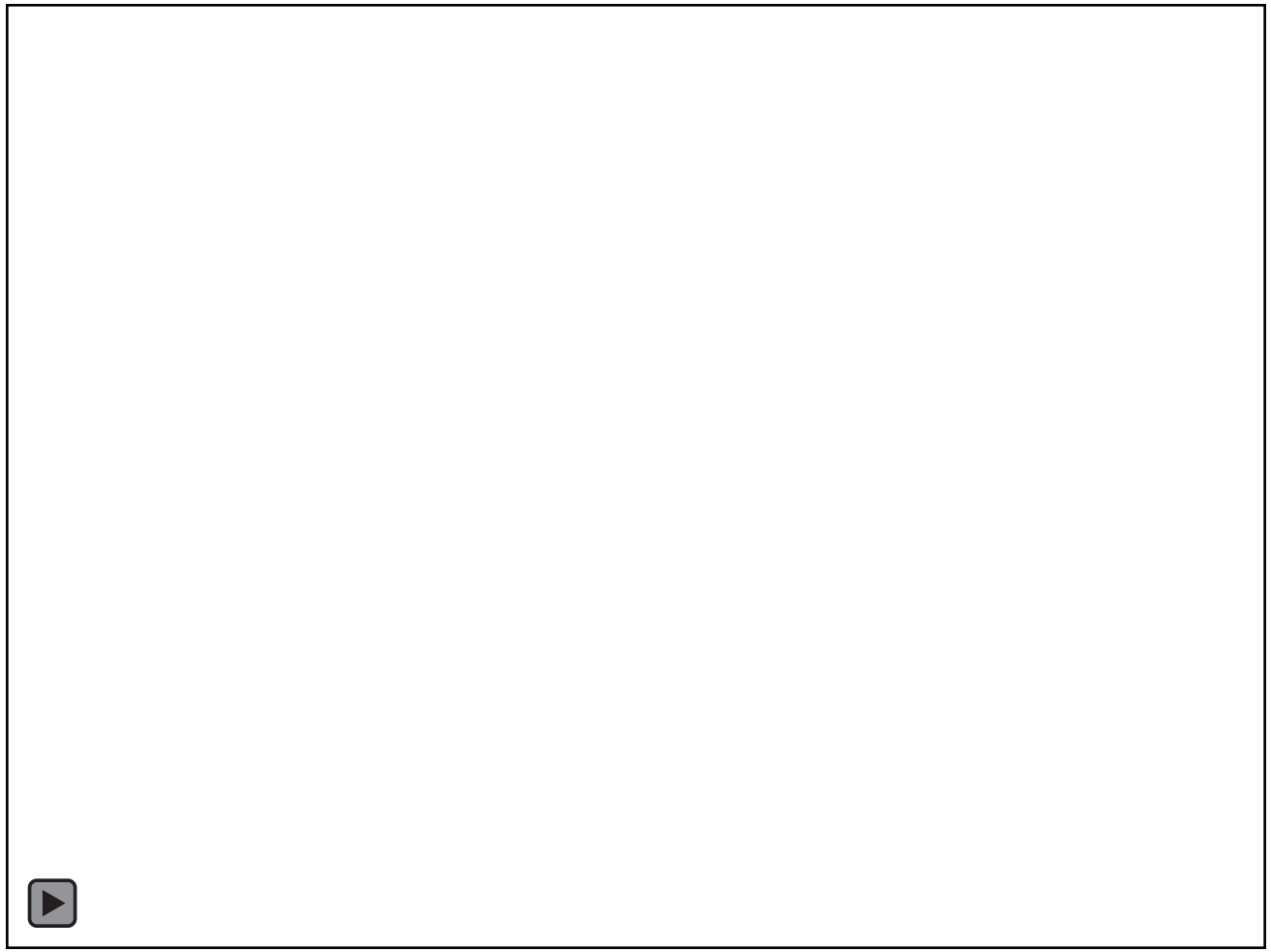
Two pathways, the same final result!

Modelling Nucleation of organic crystal…

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

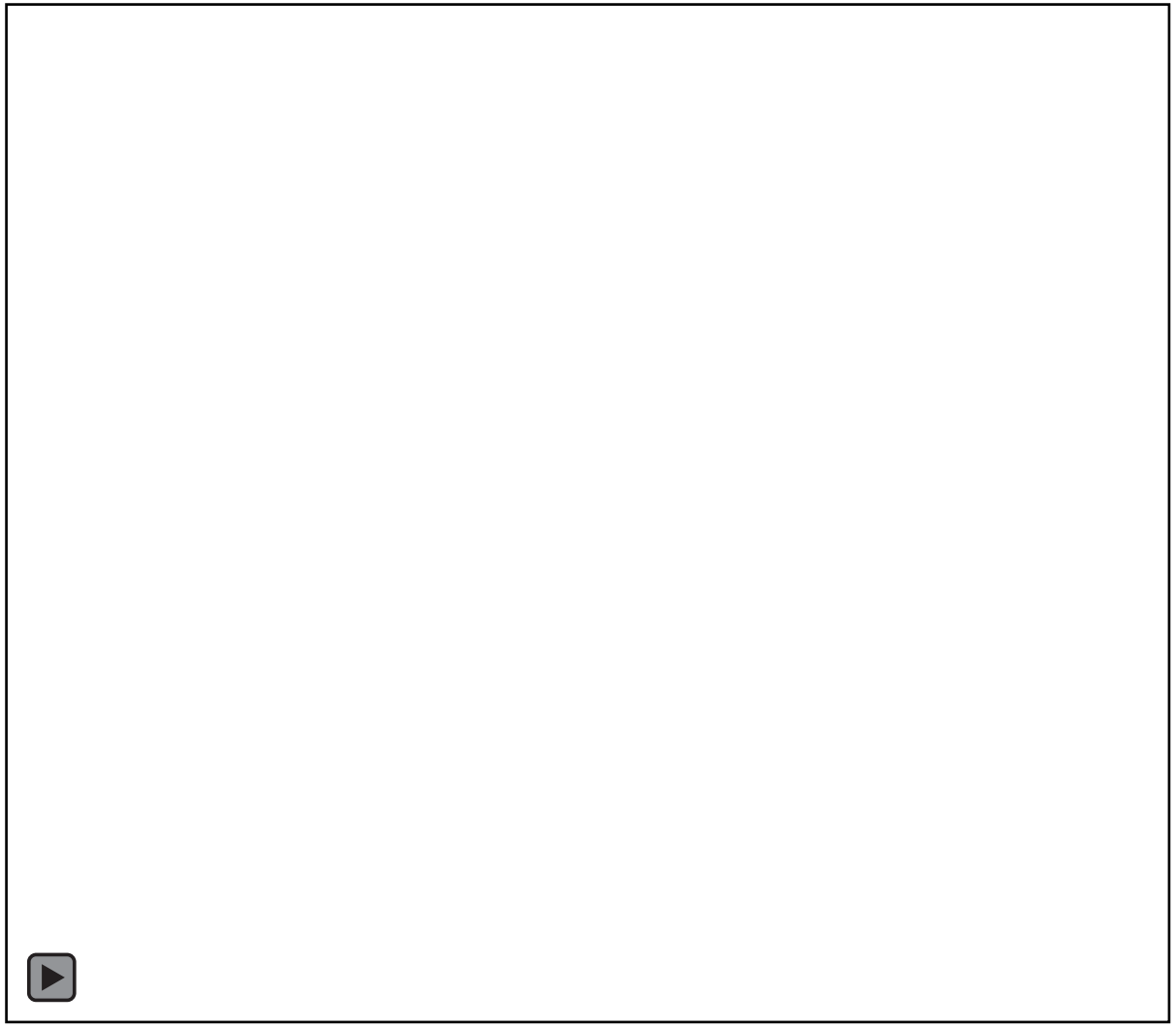
Nucleation from calculation model

Increasing S over time:

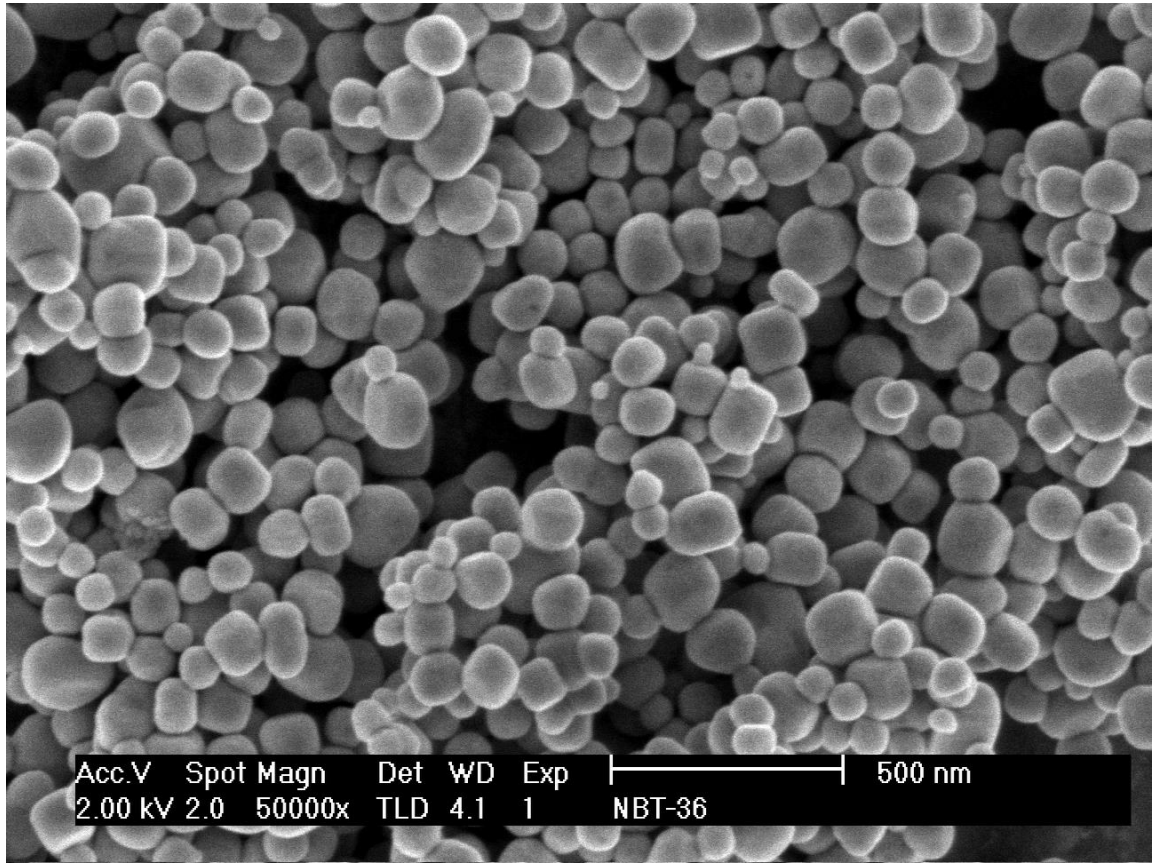


*R. Sear - Department of Physics, University of Surrey, Guildford, Surrey GU2 7XH, United Kingdom – r.sear@surrey.ac.uk

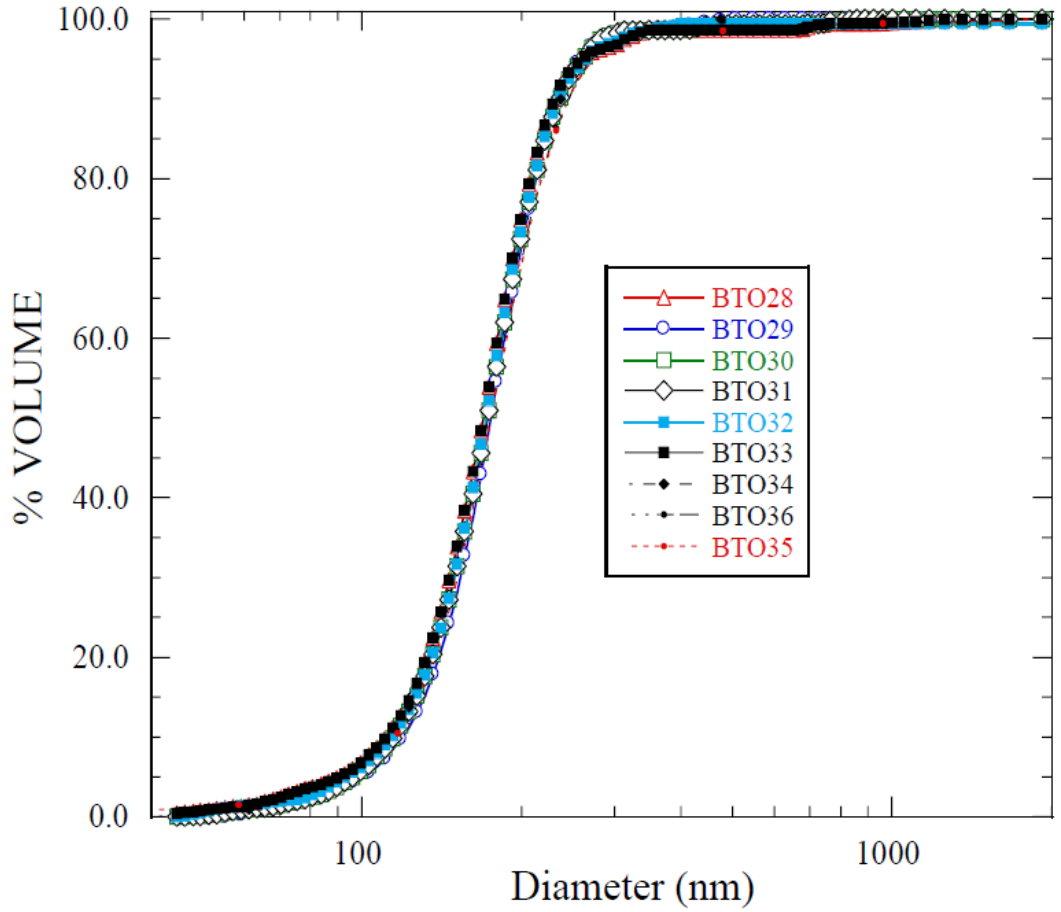
2D Nucleation + Growth



Reproducibility…



PSD, X-ray photocentrifuge



Barium titanate, 9 bathes, 3 operators

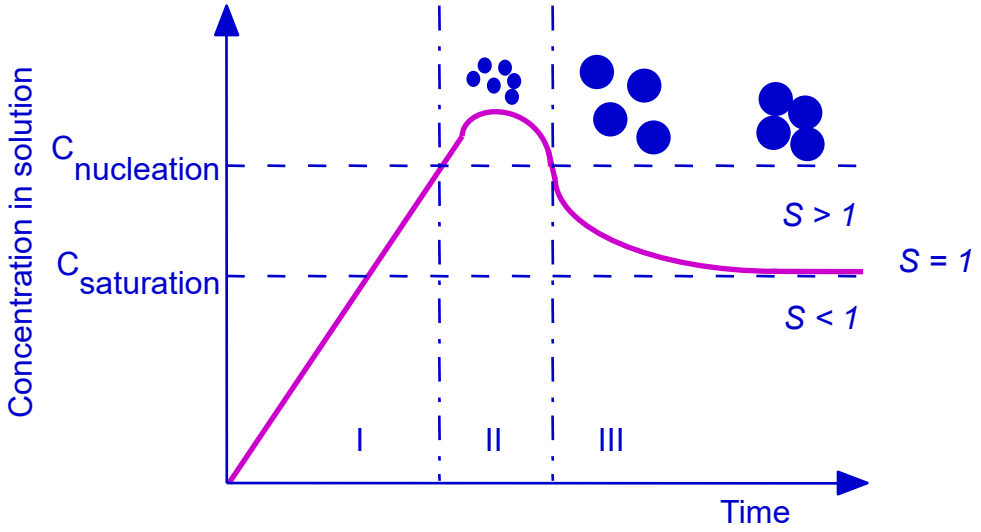
Evolution of a precipitation process

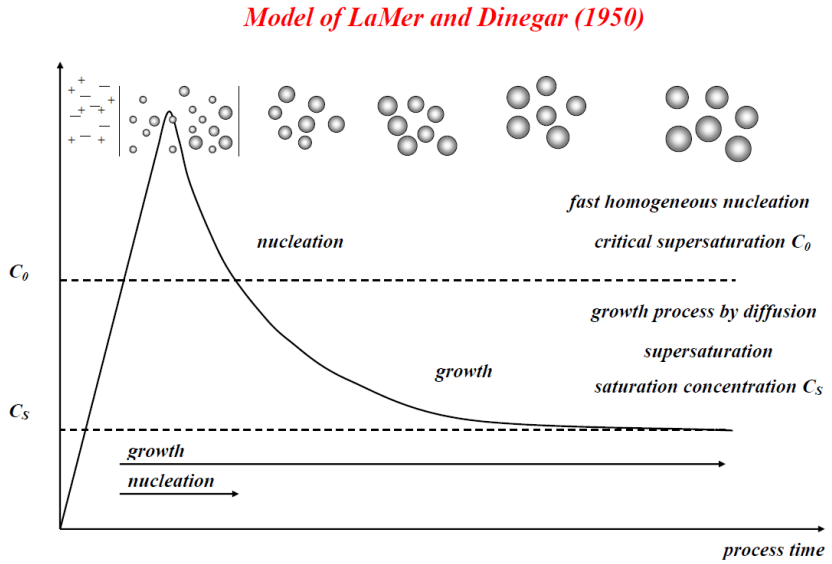
$$S_R = \frac{C_l}{C_s}$$

= 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)





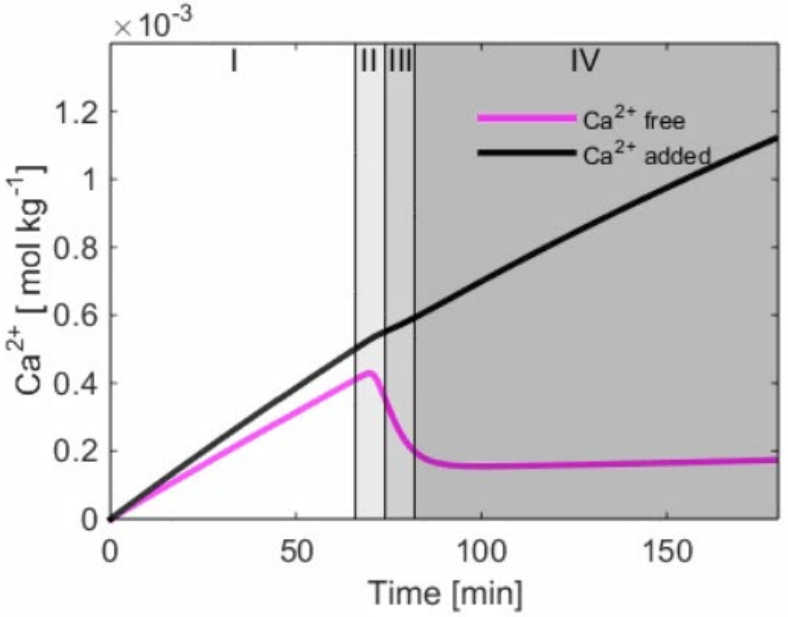
Zone I: The activity is to low to induce nucleation

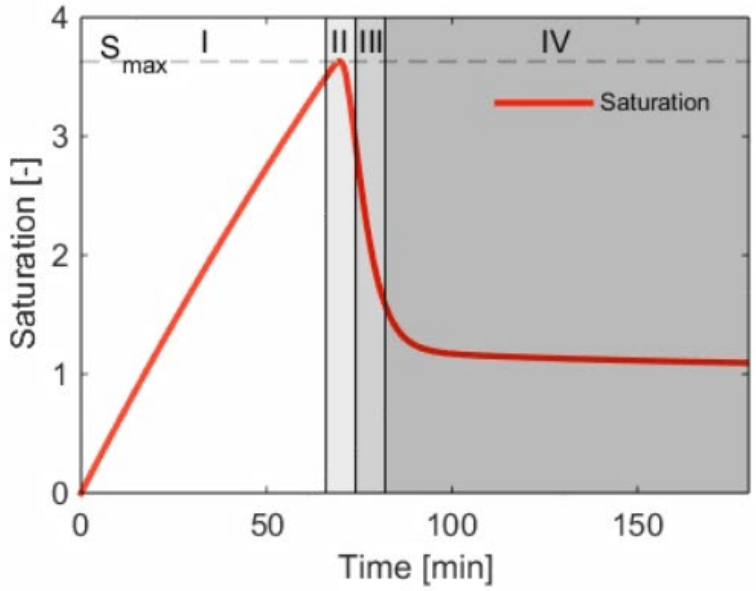
Zone II: Nucleation = Formation of nuclei

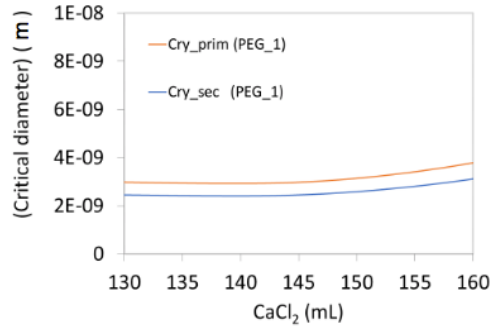
Zone III: Crystal growth and eventually aggregation

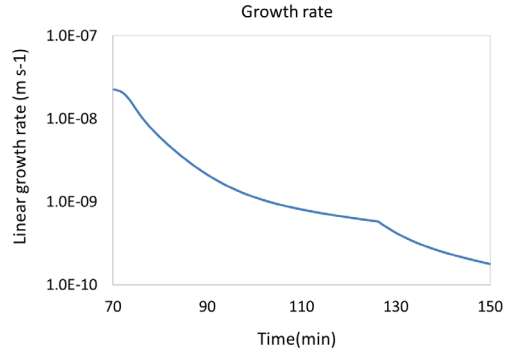
This partition of the precipitation in 3 zones (introduced in the ‘50) is a highly simplified view of a very complicated process, where the elementary sub-processes nucleation, growth, and aggregation can be convoluted. Such specific convolution defines the real **precipitation pathway** which is the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

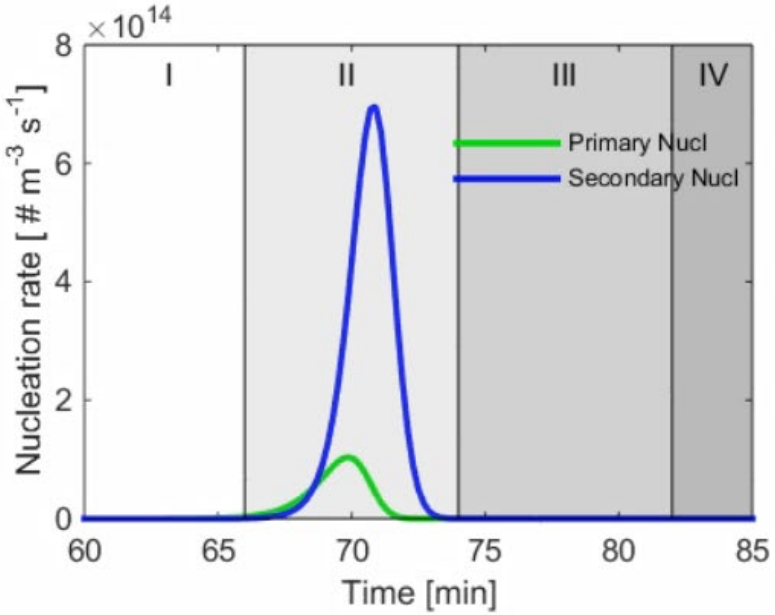
Example of precipitation modelling ($CaCO_3$)

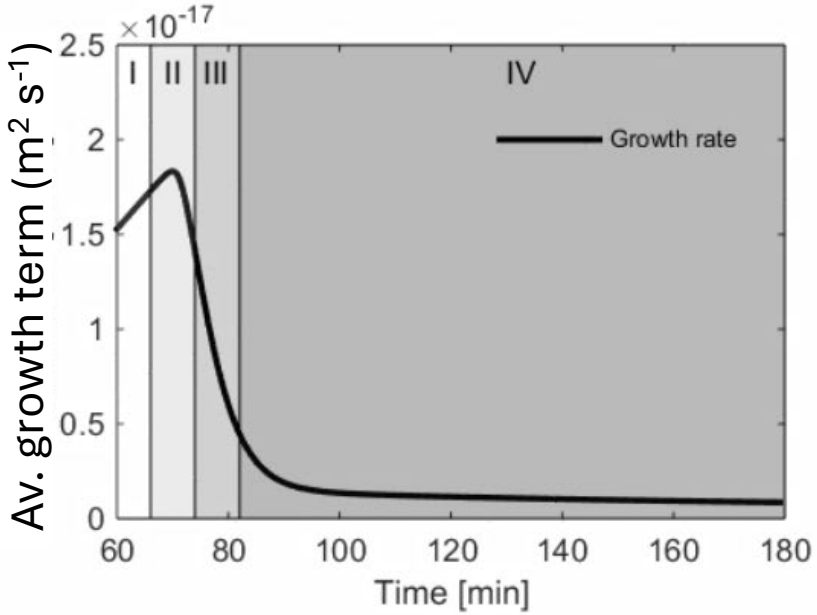












Linear growth rate (m s^{-1})=
Av. growth term (m^2 s^{-1}) / size (m)

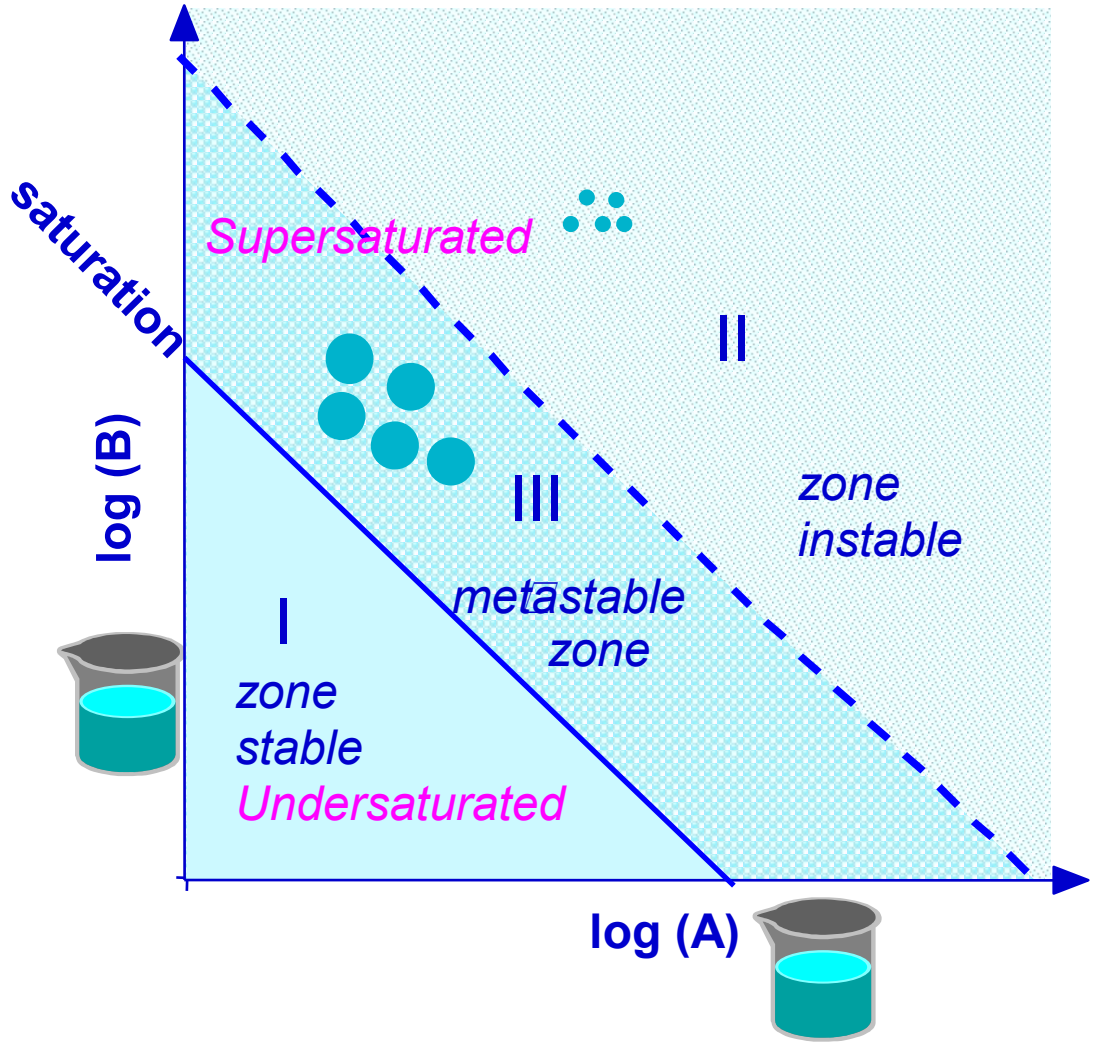
For particle 2 nm
= 2 10^{-9} m
Growth rate ≈ 10 nm/s

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)

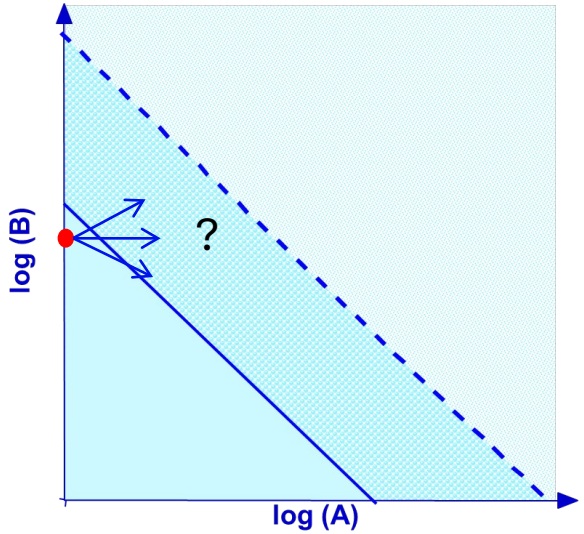
II Nucleation = formation of “solid entities” (embryo)

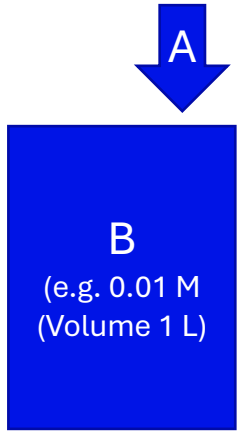
III Crystal growth and eventually agglomeration

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

$Ba^{2+}+SO_4^{2-} \leftrightarrows BaSO4$

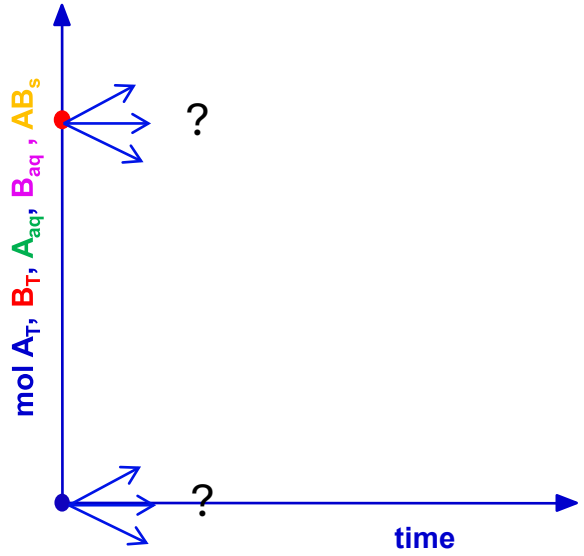
Conc [mol/L]
(A_{aq} and B_{aq})





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

mol

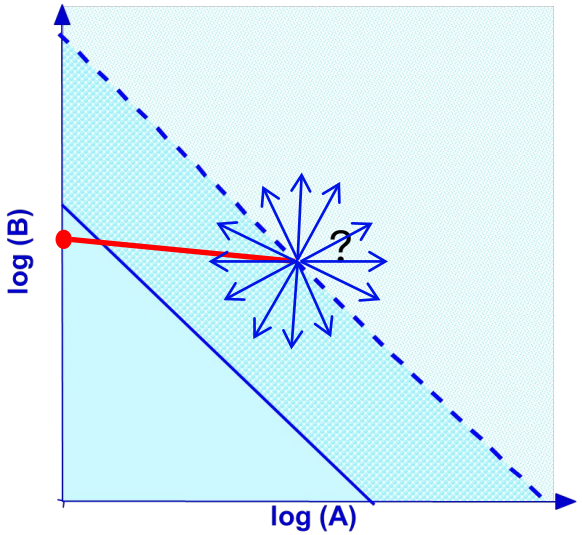


Two chemical species: A_{aq} and B_{aq}
One solid species: AB_s

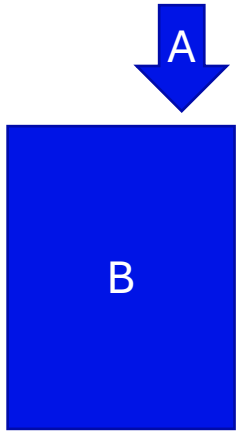
Mass balance:
$A_{tot} = A_{aq} + AB_S$
$B_{tot} = B_{aq} + AB_S$

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

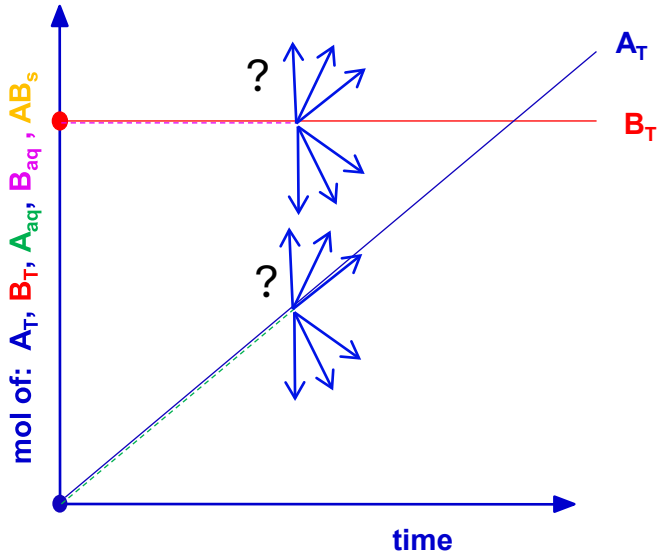
Conc [mol/L]
(A_{aq} and B_{aq})



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



Molar amount



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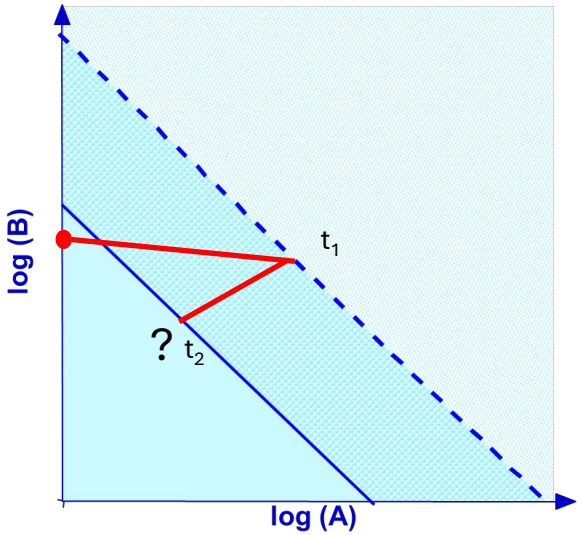

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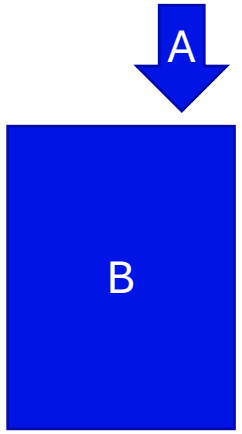

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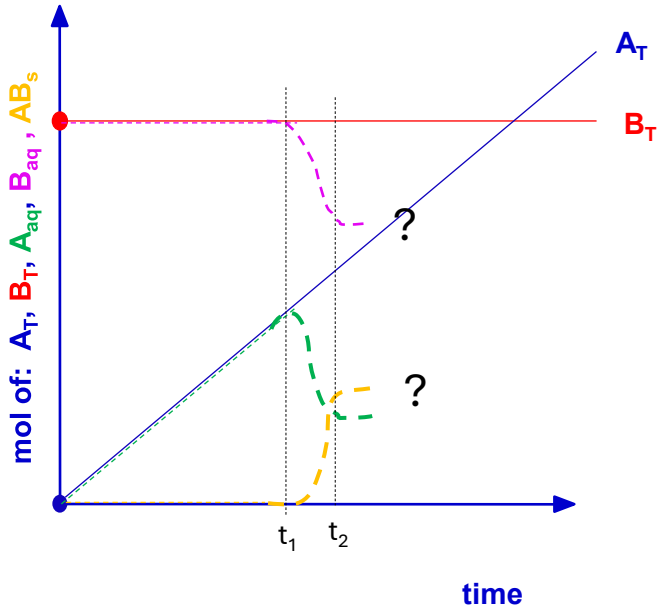

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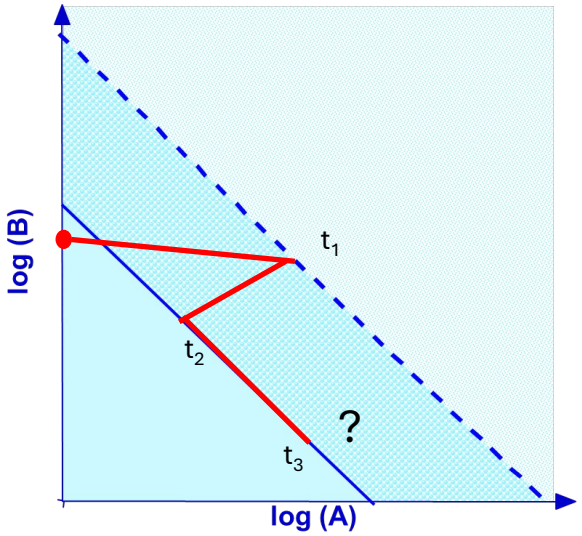

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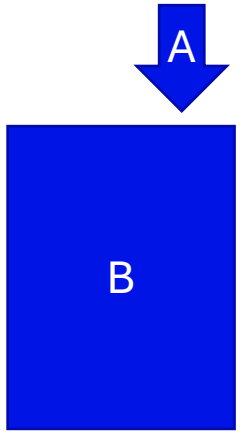

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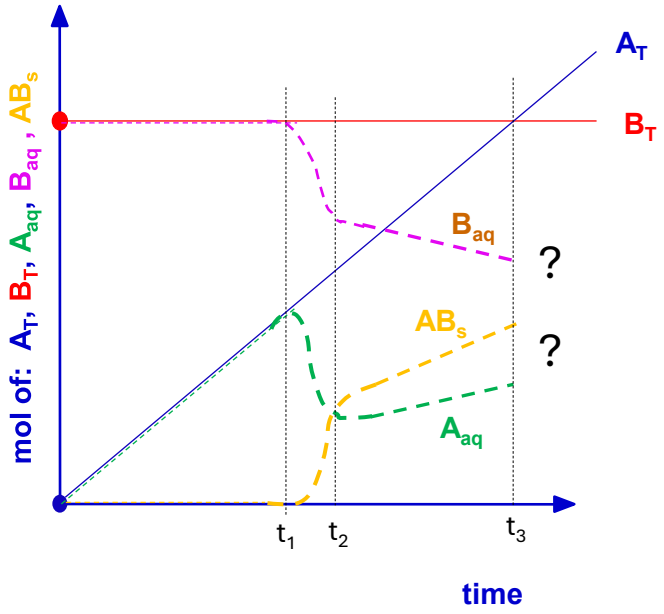

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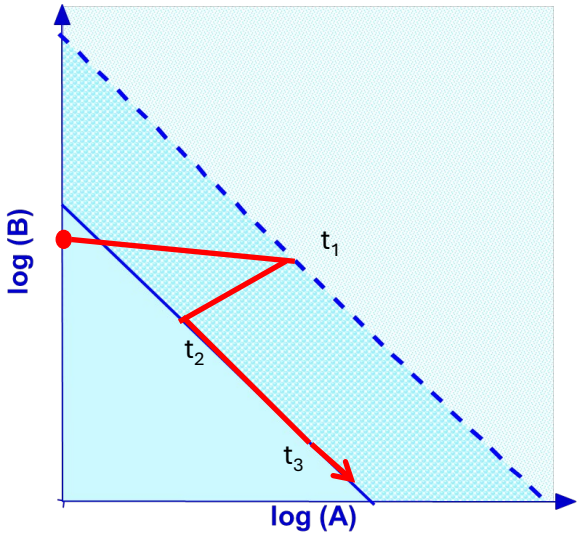

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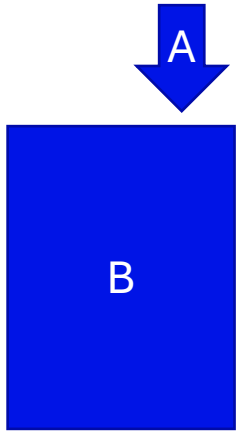
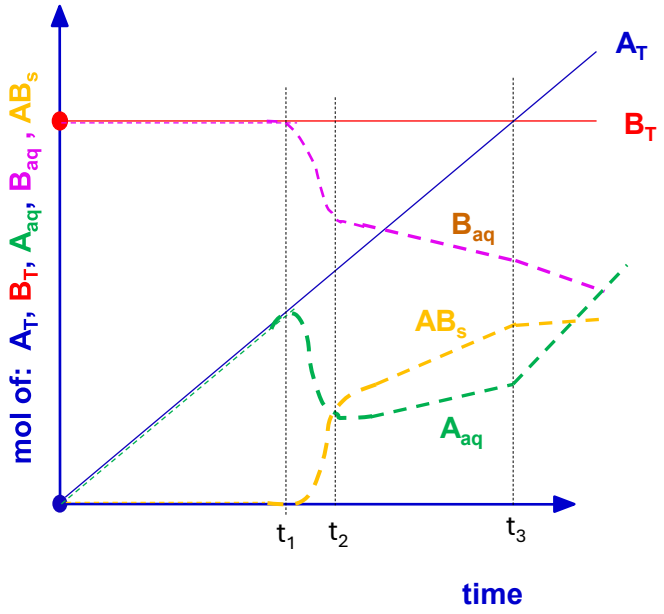


Molar amount

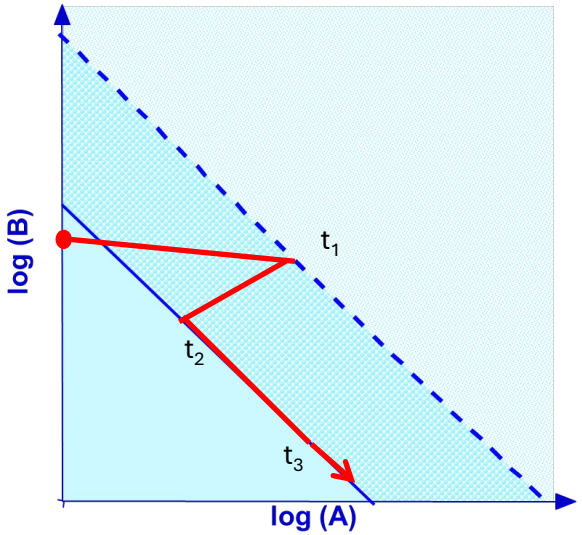


Two chemical species: A_{aq} and B_{aq}
One solid species: AB_s

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})



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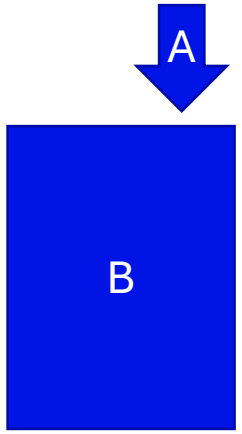

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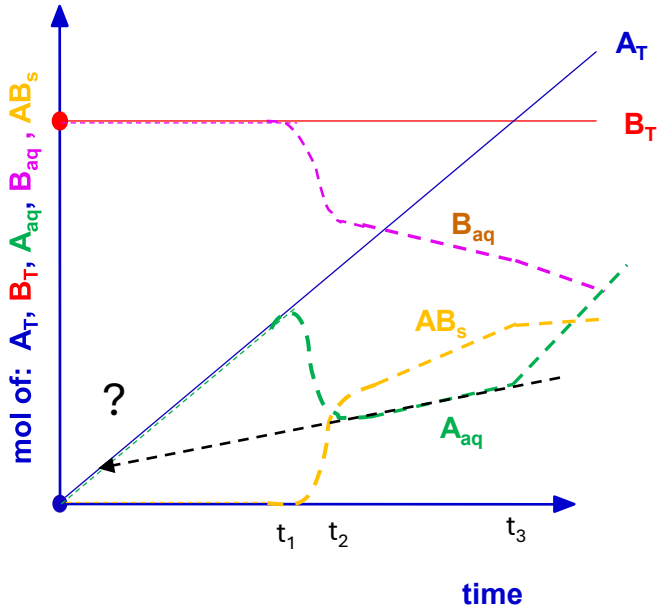

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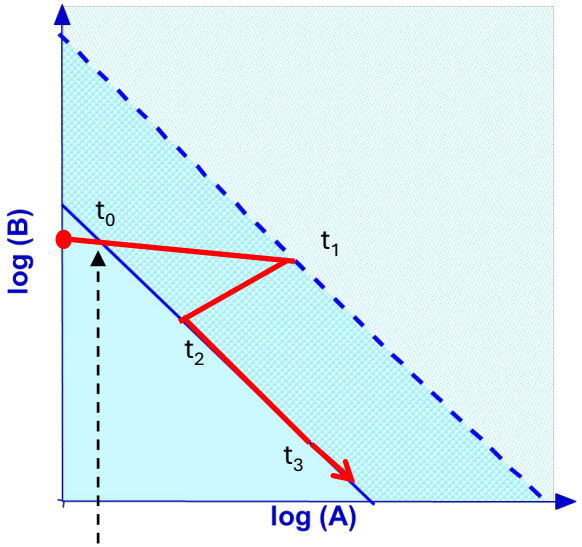
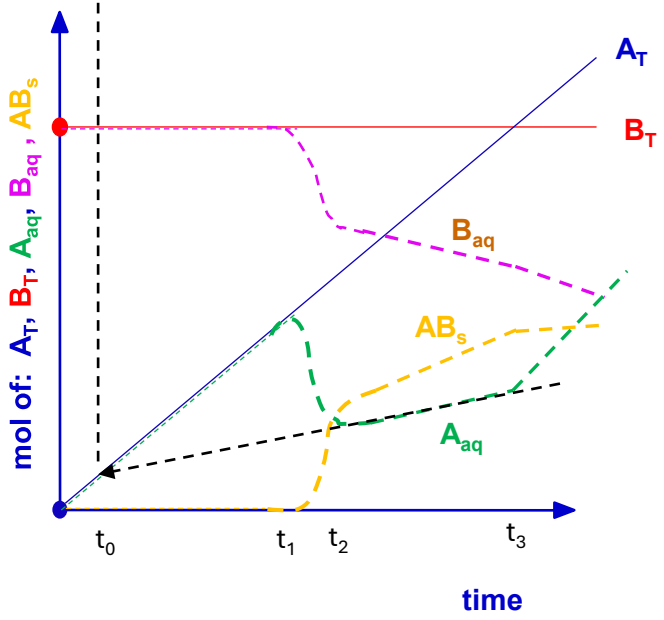


Molar amount



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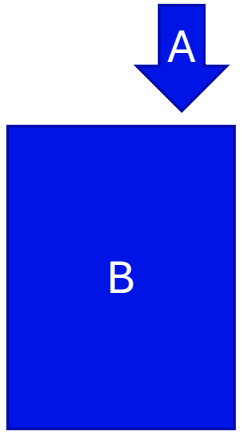

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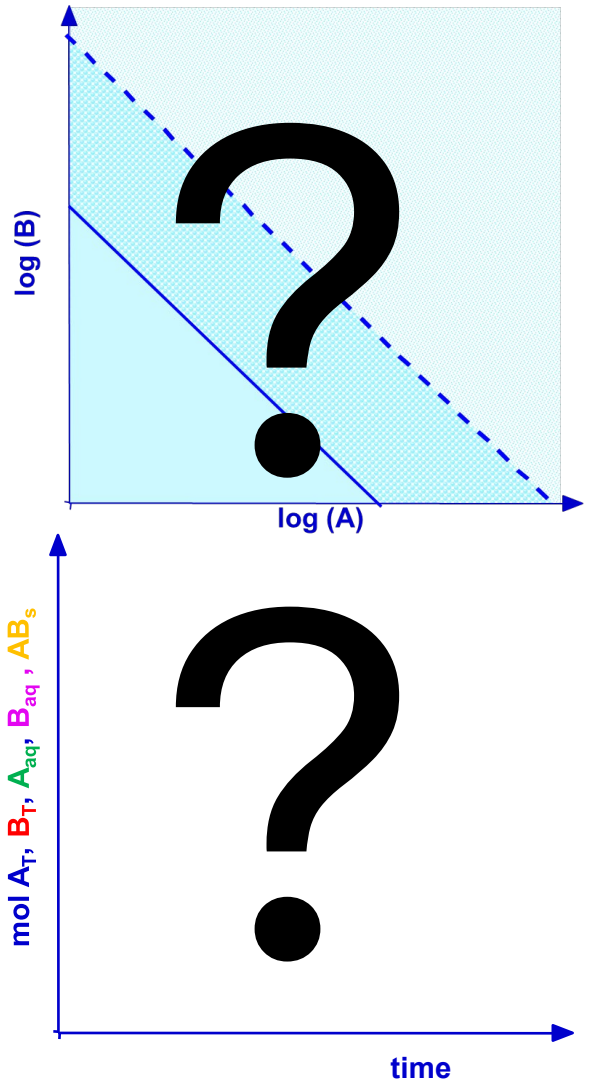


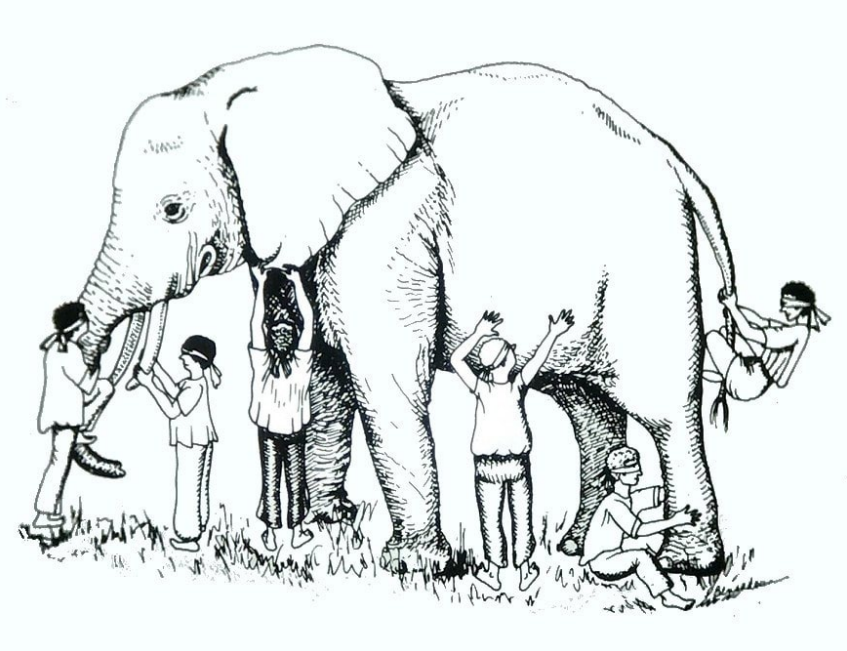
What does it happen if we change:

- 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, …

Introduction to powder characterization

Complementary techniques: it is just the minimum requirement



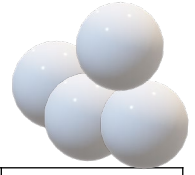
Do not be blind…

Minimum requirements for a generic materials

1. Diffraction (X, n) (LR, HR)
2. SSA and poreSD (e.g., N_2 sorption)
3. Density (e.g. He-pycnometry)
4. PSD (e.g. laser scattering methods)
5. Micrography (LR, HR)
6. Chemical composition (ICP, Local)
7. Spectroscopy (FTIR, Raman, XAS, NMR,…)

Example: multi-technique characterization

PSI

			Single crystal spherical particle	Internal close pores	Multi-domain	Open pores	Core-shell	Clusters segregation	(Partially) Amorphous	Different shape	Small aggregate	Aggregated particles
												
$/$$	Diffraction (X,n)	REFERENCE	☹	☺	☹	☺	😐	☺	☹	☺	☹
$$	SSA – PoreSD		☹	☹	☺	☹	☹	☺	☹	☺	☹
$	Density		☺	☹	☹	☹	☹	☺	☹	☹	☹
$	PSD		☹	☹	☹	☹	☹	☹	😐	☹	☺
$	Micrography (LR)		☹	☹	☹	☹	☹	☹	☹	☺	☺	☺
$$$	Micrography (HR)		☺	☺	☺	☺	☺	☺	☺	😐	😐	😐
$/$$	Chem. Comp (ICP)		☹	☹	☹	☹	☹	☹	☹	☹	☹	☹
$$$	Chem. Comp (Local)		☺	☹	☺	☺	😐	☹	☹	☹	☹	☹
$/$$	Spectroscopy		☹	☹	☹	😐	☺	😐	☹	☹	☹	☹

Colloidal Stability - Interparticle Forces

- Attractive

Van der Waals forces V_A

- Repulsive

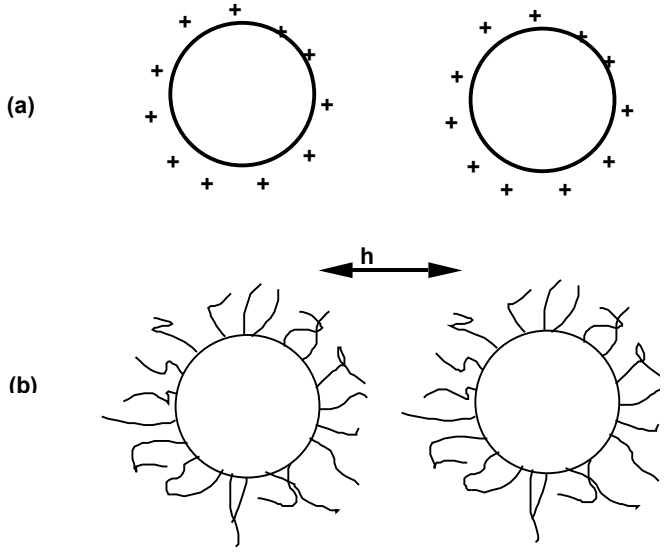
(a) electrostatic, V_E

charged surfaces

(b) steric repulsion, V_S

polymer adsorption

soluble polymers -



W. B. Russel, D. A. Saville, W. R. Schowalter - Colloidal Dispersions-Cambridge University Press (1990)

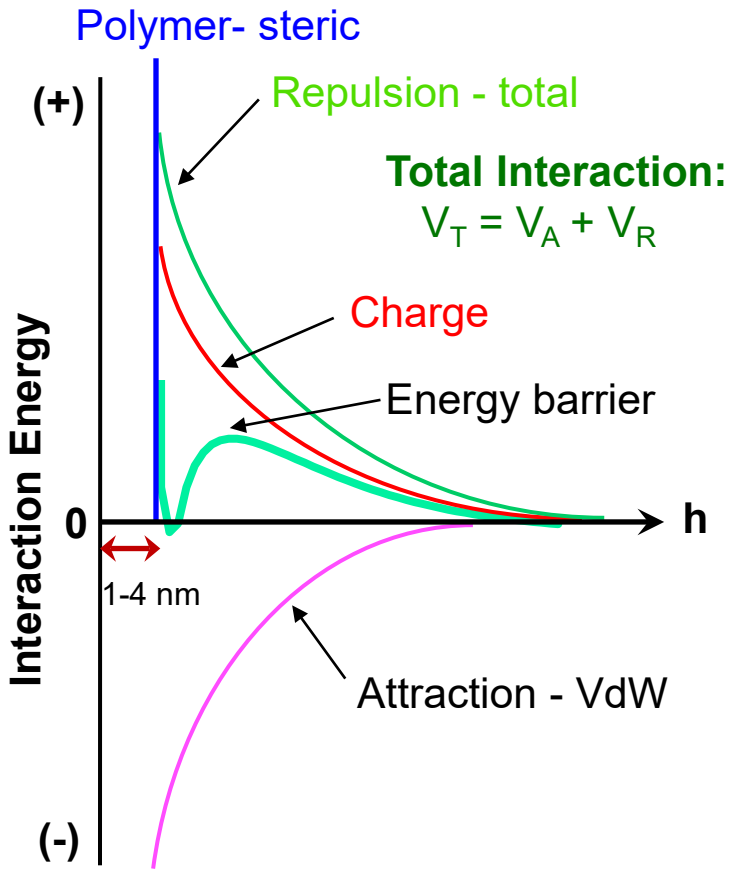
R.G. Horn, J. Am. Ceram. Soc., 73(5) 1117-35 (1990).

Overall Interaction Energy

- Total Interaction (Potential) Energy $V(h)_T$:
- DLVO theory
- Derjaguin/Landau and Vervey/Overbeck = algebraic sum….

$$V(h)_T = V(h)_A + \underbrace{V(h)_E (+ V(h)_S)}_{V(h)_R}$$

- Influences:
  - Rheology (flow of suspension)
  - Particle packing
  - Green body density
- Which in turn influences:
  - Sintering
  - Microstructure and
  - Properties



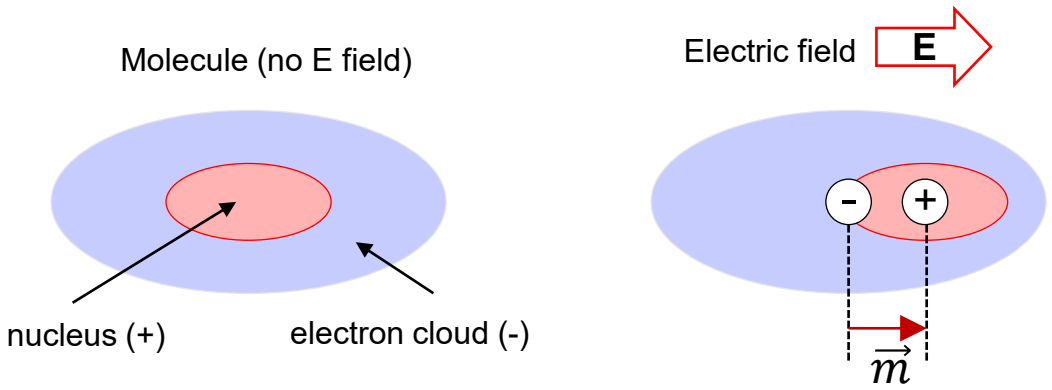
Attractive Forces - Intermolecular Forces

Van der Waals

- Always attractive between particles of the same nature
- Interaction between dipoles* (induced e.g. CH_4) or permanent (e.g. H_2O - hydrogen bond)

  3 types:
- Dipole - Dipole - interaction between permanent dipoles (Keesom forces)
- Dipole - Induced Dipoles – induced from permanent dipoles (Debye forces)
- Induced Dipole - Induced Dipole - instantaneous dipoles from electron cloud fluctuations (London or dispersion forces)

Material property - depends on dielectric and geometric properties of the system



Useful videos

*https://youtu.be/S8QsLUO_tgQ | https://youtu.be/nvJv6mCmk68 | https://youtu.be/ODnqtf3aAvw

Hamaker approach

Attractive Interaction Potential V_A

Hamaker Constant A, form factor H !!!

$$V_A(h) = - A \cdot H (h, shape)$$

Dispersion forces (instantaneous dipoles - induced dipoles)

Permanent Dipoles and Induced by permanent diploes

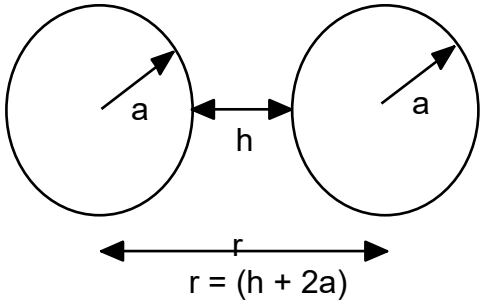
} Van der Waals

A - depends on dielectric properties (~ polarizability)

- particles and the continuous medium separating them,
- over the entire spectral range of electromagnetic waves.

For identical particles - size and chemistry in vacuum

$$A = \frac{3}{8} N^2 kT \sum_{n=0}^{\infty} \alpha^2 (i\xi_n)$$



N - number of molecules per unit volume of the material,

α is the polarizability of these molecules (dielectric constant), ξ_n is the electromagnetic frequency

Al_2O_3 in water is A ~36.7 x 10^{-21} J, under vacuum A ~ 152 x 10^{-21} J,

SiO_2 (silica) in water is A ~4.6 x 10^{-21} J, under vacuum A ~ 65 x 10^{-21} J

Van der Waals Forces - Measurement by AFM

Measurement of interparticle forces between the same material or different materials

A. Meurk, P. F. Luckham and L. Bergstrom, *Langmuir* **1997,** *13,* 3896-99

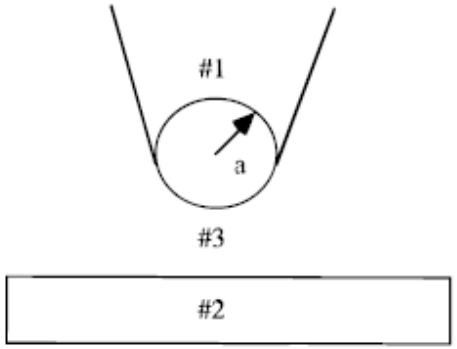
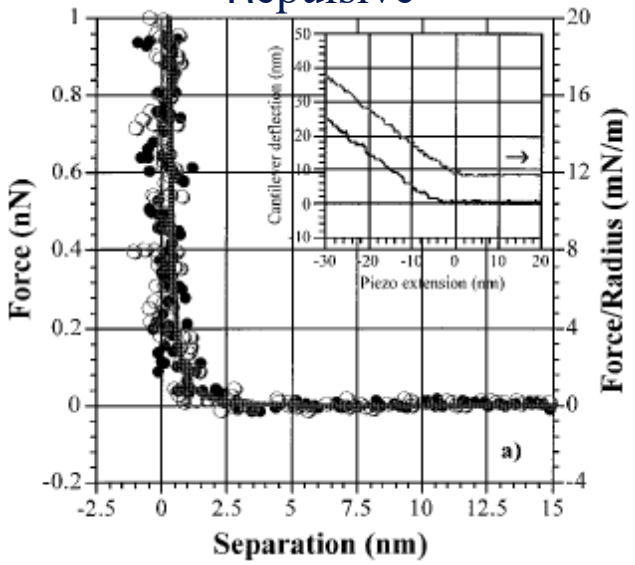


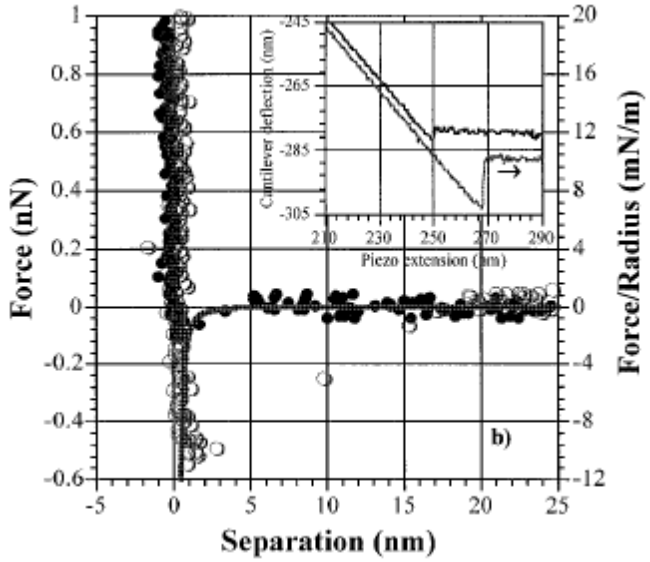
Table 2. Nonretarded Hamaker Constants

system (tip−medium−substrate)	A_{132}/ 10^{-20} J	resulting interaction
Si_3N_4−diiodomethane−β-Si_3N_4	1.0	attractive
Si_3N_4−1-bromonaphthalene−β-Si_3N_4	2.8	attractive
Si_3N_4−diiodomethane−SiO_2	−0.8	repulsive
Si_3N_4−1-bromonaphthalene−SiO_2	−0.2	repulsive

(a) Si_3N_4-diiodomethane-SiO_2 Repulsive



(b) Si_3N_4- diiodomethane-Si_3N_4. Attractive



filled circles denote approach, open circles denote retraction,

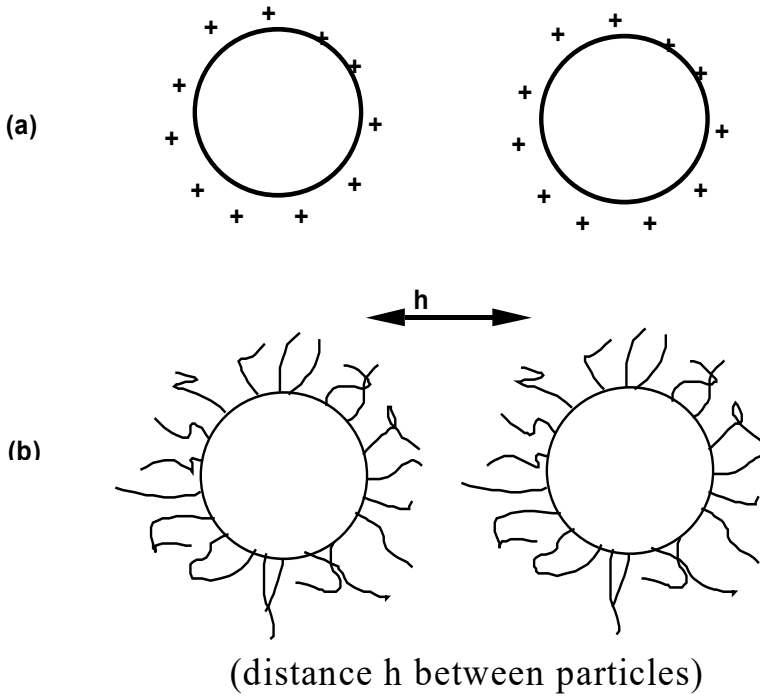
Repulsive forces

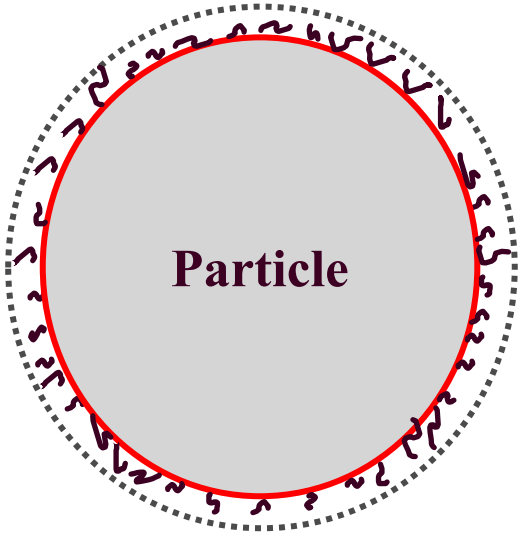
Electrostatic

- dissociation of species at the surface
- adsorption of charged species
- dissociated ions, molecules or polymers

Steric

- molecules - often adsorbed polymers





Formation of Charged Interfaces

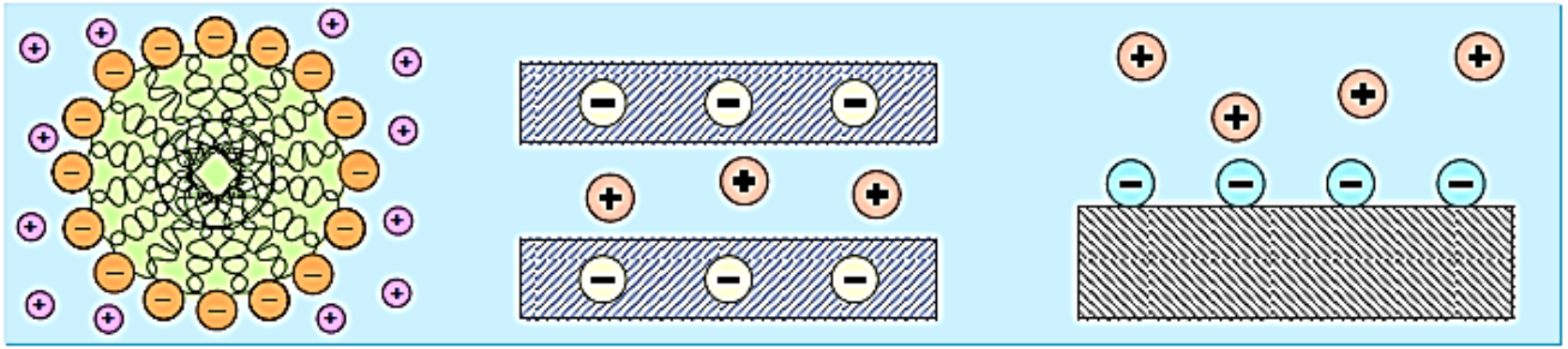
PSI

Ion adsorption at interfaces

- Mechanisms that can produce surface charges
- Colloidal particles formed from charged species: micelles of ionic surfactants (e.g. SDS);
- Polyelectrolytes (e.g., polyacrylate, alginate, etc.)
- Defects in crystal structure (substitution of Si^{4+} by Al^{3+} in clays)
- Presence of surface functional groups… titratable

  –OH, –COOH, $–NH_2$, $–SO_4H$, $–PO_4H_2$...
- Adsorption of charged species in solution (*Hofmeister* series):

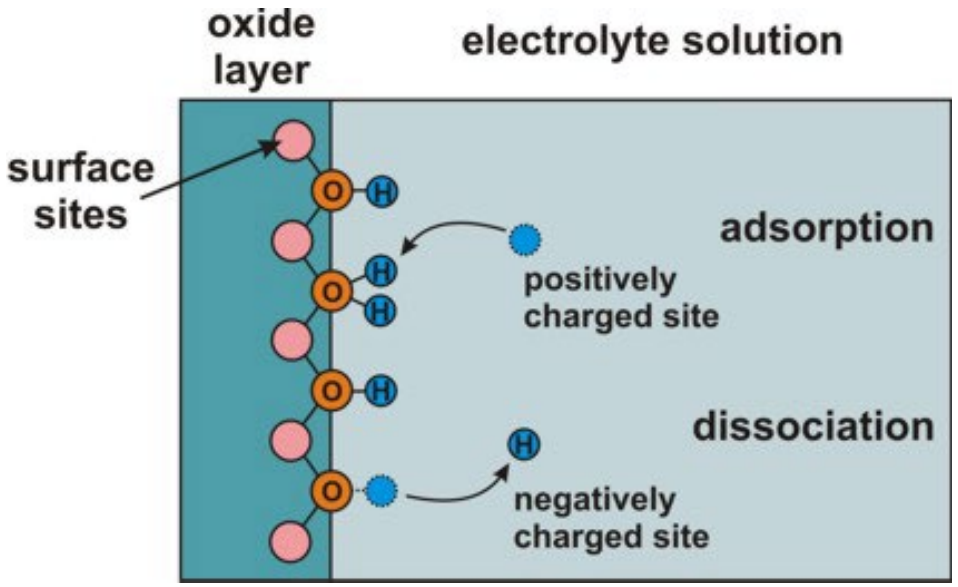
  $I^- > ClO_4^-$, $NO_3^- > Br^- > Cl^- > OH^- > F^-$, SO_4^{2-}

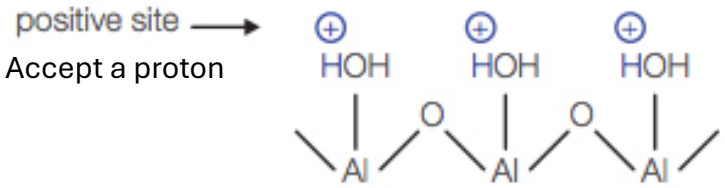


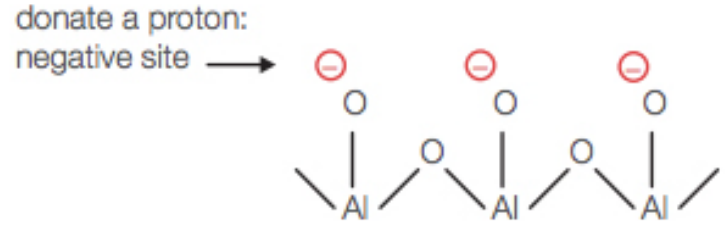
Micelle Clay sheet Anion adsorption

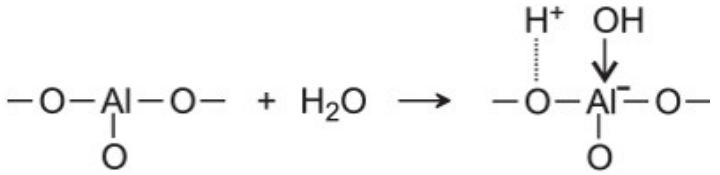
Surface charging – examples

- Surface of oxides in water often hydroxylated – termination metal-OH









Whether one has adsorption or dissociation depends on pH (concentrations of H + and OH- ions) and the chemistry of the metal-oxygen bond-hydroxide

Lewis acid: accepts a pair of electron

Brønsted acid: releases a H^+ (donor)

Lewis base: donates a pair of electron

Brønsted base: captures a H^+(acceptor)

Surface charging - Ion adsorption at interfaces

❖ "**potential determining ions** – pdi "- determines the potential of the surface

- e.g. Ca^{2+}... preferentially adsorbs on cement surface - surface charge changes from negative to positive
- NaCl... indifferent electrolyte ... no specific adsorption...does not influence potential
- HCl... H^+ Cl^- - **H^+** determines the potential ...
- NaOH...Na^+ OH^- - **OH^-** - determines the potential
- H^+ and OH^- determines the potential as a **function of pH**....
- De-protonation of a silanol group $-SiOH \leftrightarrow -SiO^- + H^+$

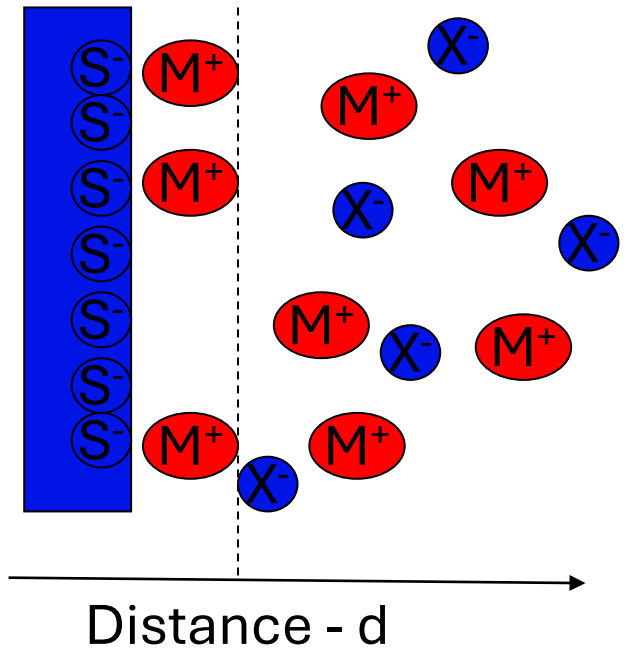
❖ Charge often determined by equilibrium process - 3 Free energy contributions

- Chemical interactions – short range – promote adsorption
- Electrostatic – longer range – limits surface charge – ordered localised arrangement
- Entropy – tends towards desorption – random uniform distribution of ions

Poisson Boltzmann equation – charged surface

Describes surface potential (Φ), ionic concentration (c), vs distance (d) from surface

Relationship between surface charge density (σ) and surface potential (Φ)



Poisson equations – charge density (ρ)

$$\varepsilon_0 \varepsilon_r \vec{\nabla}^2 \Phi = \rho_{(free-ions)}$$

$$\rho_{(free-ions)} = e \sum_i z_i c_i^*(\vec{r})$$

Boltzmann distribution

$$c_i^*(\vec{r}) = c_{i0}^* \exp\left(\frac{-z_i e \Phi}{kT}\right)$$

c^*_{io} - bulk value far from surface (Φ=0)

* Indicate that concentration is expressed as no. of molecules per m^3.

$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$: Laplace operator; e is the electric charge

Boltzmann contribution – charged surface

Electrostatic contribution tends to favour **ordered layer**

Entropy tends to generate **random** uniform distribution

Boltzmann distribution – effect of external field, Φ,

cf gravitational field - $m \times g \times h$ – density of air diminishes as we go up !!!

$$c_i^*(\vec{r}) = c_{i0}^* \exp\left(\frac{-z_i e\Phi}{kT}\right)$$

- c^*_{io}, concentration at Φ=0 i.e. in bulk solution far from interface ***(no. of molecules per m^3)***
- Combine Poisson Equations with Boltzmann distribution

$$\varepsilon_0 \varepsilon_r \vec{\nabla}^2 \Phi = \rho_{(free-ions)} \qquad \rho_{(free-ions)} = e\sum_i z_i c_i^*(\vec{r})$$

$\rho(r)$ volume charge density (C/m^3)

Poisson Boltzmann (PB) Equation – charged surface

- Ion distribution in an electrolyte outside a charged surface

$$\rho_{(free-ions)} \approx e\sum_i z_i c_{i0}^* \exp\left(\frac{-z_i e\Phi}{kT}\right)$$

$$\varepsilon_0\varepsilon_r\nabla^2\Phi = -e\sum_i z_i c_{i0}^* \exp\left(\frac{-z_i e\Phi}{kT}\right)$$

That is the PB equation describing the ion distribution in an electrolyte solution outside a charged particle

Assumptions made to arrive at PB – limitations

Potential generated by External charge – but ions also contribute

Ions are in motion dynamic – we take an average of many possible configurations to get an average potential

Mean Field Approximation to get a mean electrostatic potential

Approach can sometimes fail even qualitatively

Infinite plane solution – Guoy - Chapmann

To solve PB need geometry – infinite plane ⇨*d/dz*
Model of *Gouy (1910) - Chapman (1913) – diffuse layer of counterions outside the charged surface*

- *spatial distribution of* ions for an *infinite plane* evenly charged.
- the *Poisson –Boltzmann* equation simplifies to linear form

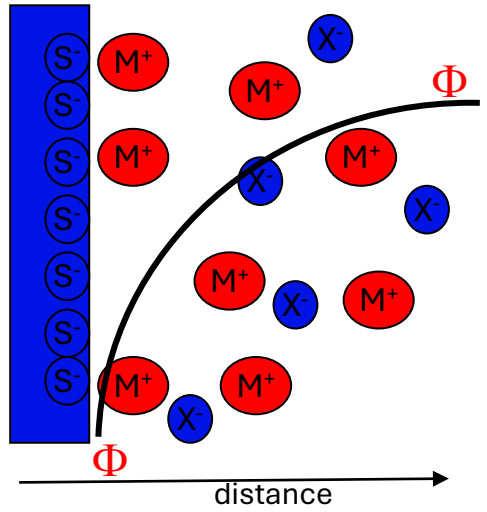
$$\nabla^2\Phi \rightarrow \frac{d^2\Phi}{dz^2}$$

Boundary conditions:

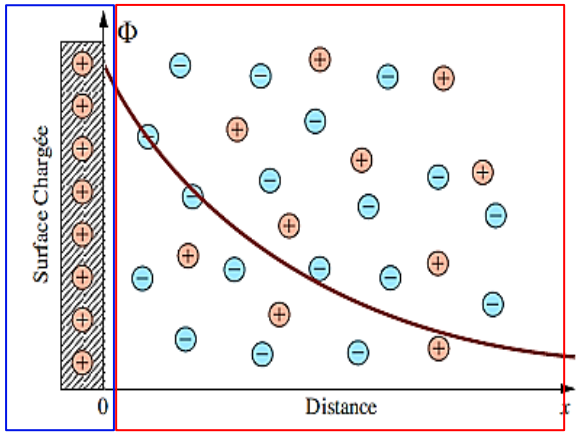
- Electroneutrality $d\Phi/dz = 0$ far from surface and
- c^*_{io}, represents bulk electrolyte concentration (no. ions/m^3)
- at surface behaves like capacitor $d\Phi/dz = -\sigma/\varepsilon_0\varepsilon_r$
- no charged species below surface i.e. z< =0, $d\Phi/dz = 0$

$$\left(\frac{d\Phi}{dz}\right)^2 = \frac{2kT}{\varepsilon_0\varepsilon_r}\sum_i c^*_{i0}\left[\exp\left(\frac{-z_i e\Phi}{kT}\right)-1\right]$$

♦ Square root of L.H.S. gives ± negative or positive surfaces

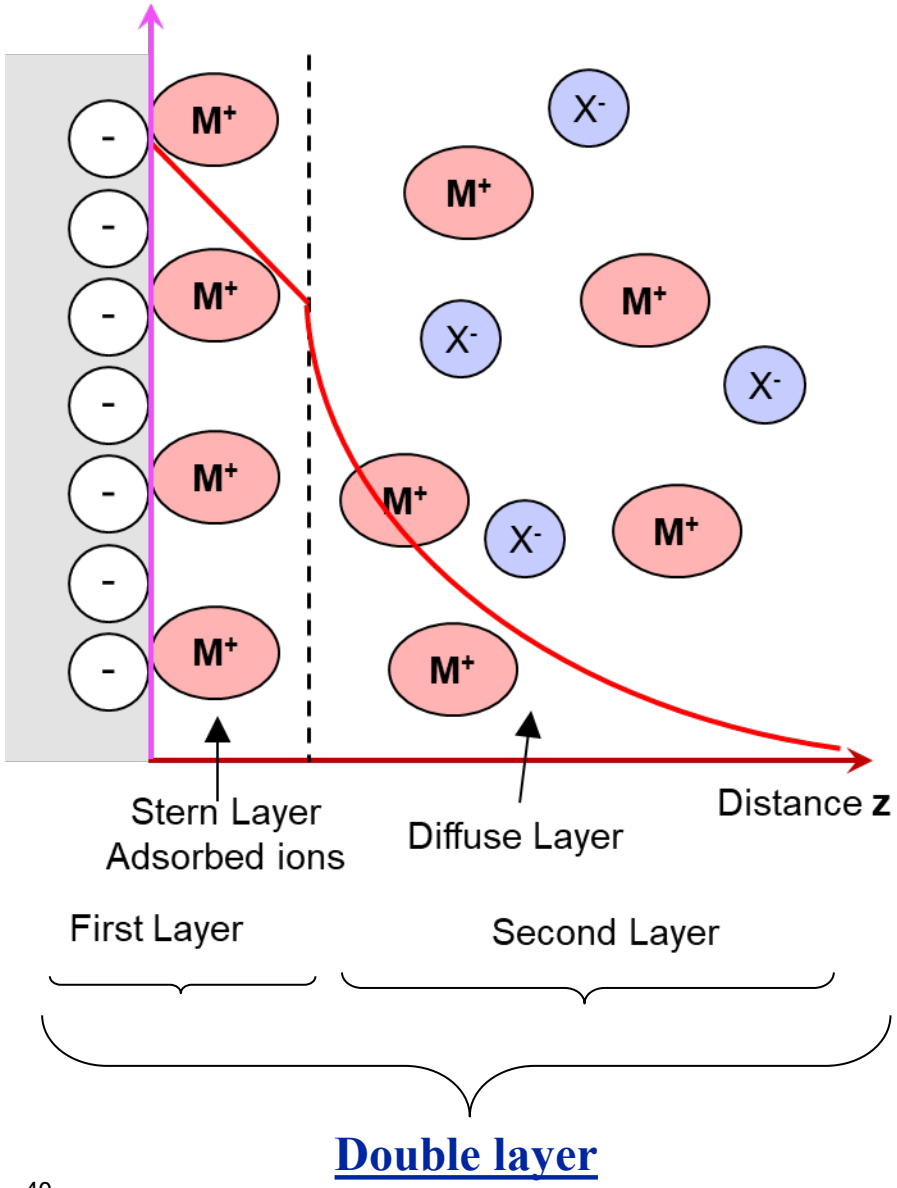


Diffuse layer of counterions



The charged surface, together with the diffuse layer of counterions forms an *electric double layer* .

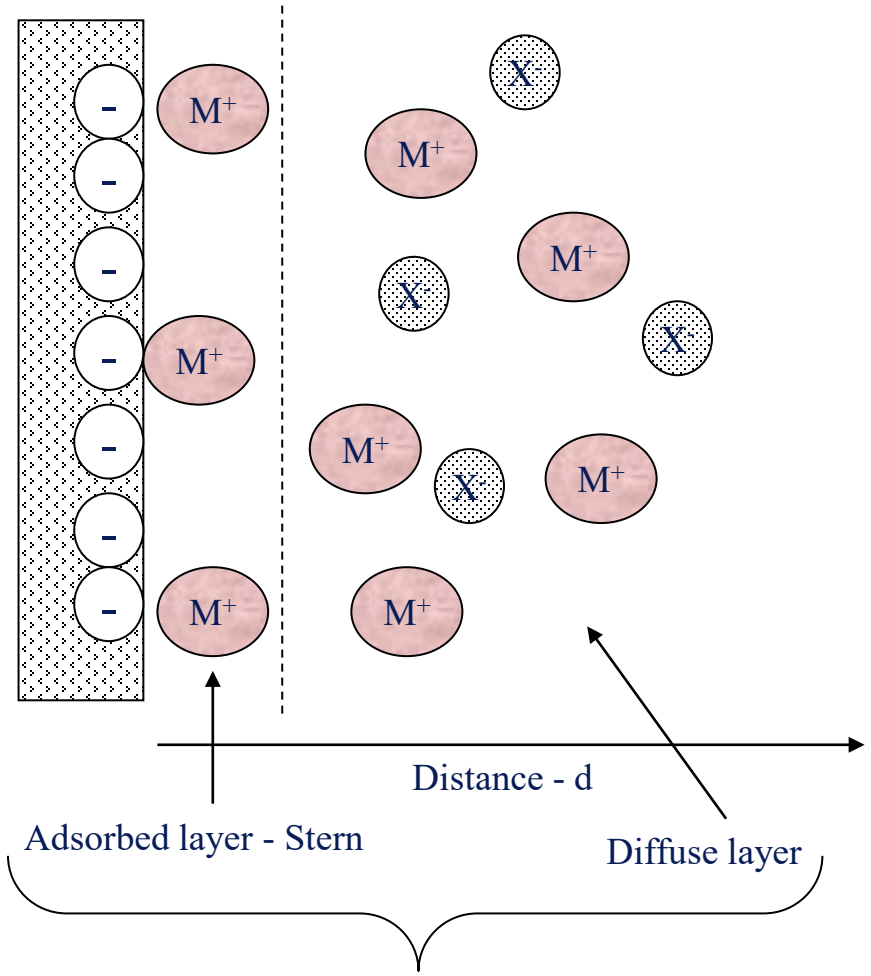
Double layer - Gouy and Chapman – Stern model



- Model of Gouy-Chapman - Treats ions as point charges
- Hydrated ions can adsorb (Helmholtz*). Water can also adsorb via hydrogen bonding
- Layer close to the surface – combined the diffuse layer model of Guoy-Chapman and adsorbed ions of Helmholtz ⇨ **Stern layer**.
- The limits of validity are for potentials of 200mV and ionic strengths of 1M.
- Surface and adsorbed layer – behaves as capacitor: linear decrease
- Exponential-like decrease of potential in diffuse layer

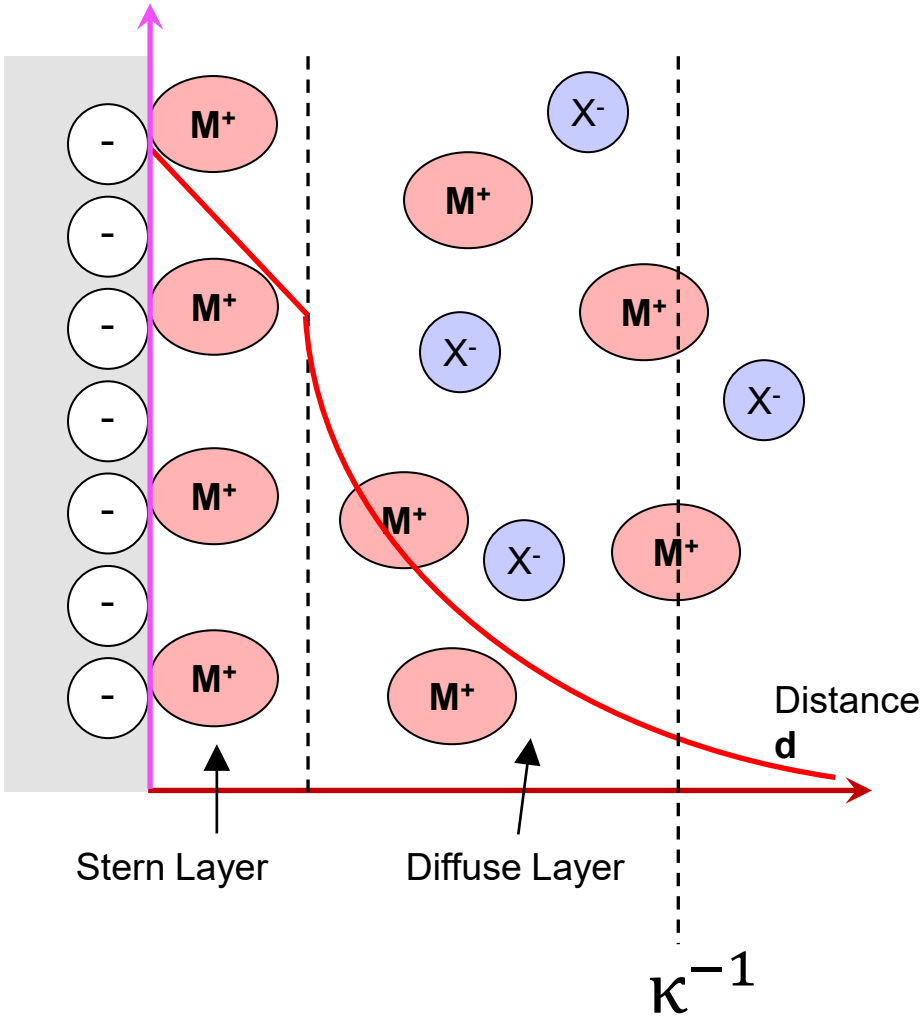
*https://en.wikipedia.org/wiki/Double_layer_(surface_science)

Double layer - Gouy and Chapman – Stern model



- Mean field approximation - i.e. average of many configurations of moving ions
- Limitations
  1. Ion-correlation effects due to highly polarizable layers - attractive
  2. Finite ion size - excluded volume effect - repulsive
  3. Image forces - "reflected" charge by surface gives "image in surface" - repulsive
  4. Surface charges discreet - not averaged as above - attractive
  5. Solvation forces - displacement / ordering of solvent - attractive, repulsive, oscillatory

Double Layer Thickness – Debye Length - κ^{-1}



$$\frac{1}{\kappa} = \left(\frac{\varepsilon_0 \varepsilon_r kT}{\sum_i (z_i e)^2 c_{i0}^*} \right)^{1/2}$$

- distance form the surface where the potential drops **by 1/e**
- Debye Length or
- Double layer (DL) thickness.

Debye length vs. ionic strength

- κ^{-1}
- Debye screening length or
- Double Layer thickness
- Effect size and rheology

$$\frac{1}{\kappa} = \left(\frac{\varepsilon_0 \varepsilon_r kT}{\sum_i (z_i e)^2 c_{i0}^*} \right)^{1/2}$$

	Electrolyte – Thickness (nm)					
Conc. (M)	*1:1*	*1:2*	*1:3*	*2:2*	*3:3*	
0.001	9,6	7,9	6,8	4,8	3,2	
0.01	3,0	2,5	2,2	1,5	1,0	
0.1	0,96	0,79	0,68	0,48	0,32	

Surface Charge density

- Gouy – Chapman Theory
  - Surface charge density, σ (C/m^2), as fn of surface potential, Φ,

$$\sigma = \left(8kTc_{i0}^{*}\varepsilon_0\varepsilon_r\right)^{1/2}\sinh\left(\frac{z_i e\Phi_0}{2kT}\right)$$

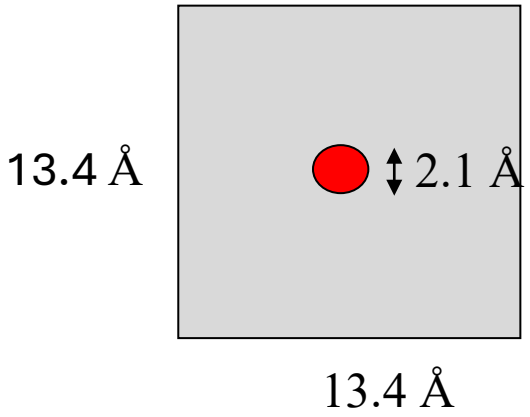
- Example
  - Φ_0 = -75 mV, c = 0.15M, NaCl, 25°C
  - σ = 0.09 C/m^2 means 1 unit charge per 180Å^2
  - Na^+ ~ 1 Å (radius) (+ solvation 2.1 Å)

(NB - c_{i0} - in number of molecules or ions / m^3)

Boundary conditions for integration

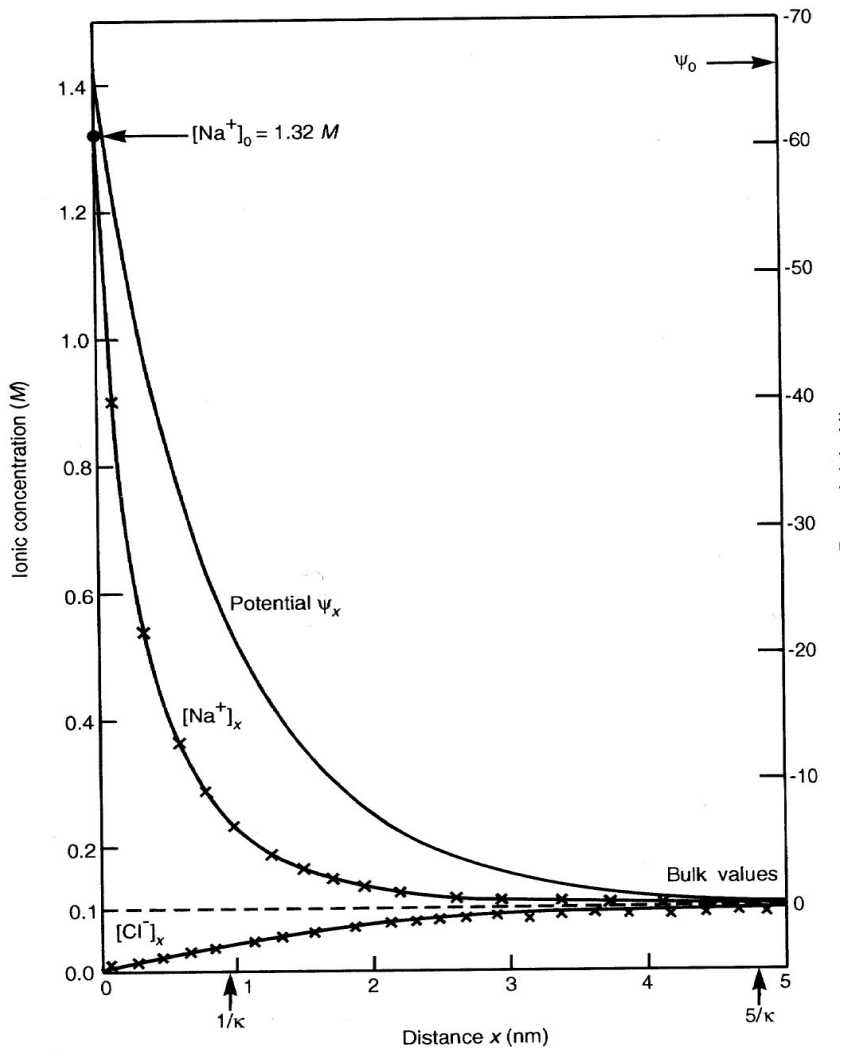
$$\left.\frac{d\Phi}{dz}\right|_{z\to\infty} = 0$$

$$\left.\frac{d\Phi}{dz}\right|_{z=0} = \frac{-\sigma}{\varepsilon_0\varepsilon_r}$$



See Z-pot later, which is bit smaller than Φ_0, and measurable.
A suspension of alumina in HNO_3 5 mM ≈ Z-pot 55 mV.

Ionic concentration and surface potential



Example – NaCl (0.1 M) - from Israelachvili*

- σ = 0.0621 C/m^2 (1e/2.6nm^2)
- Φ_0= -66.2 mV (from Graham)
- x in figure: Monte Carlo simulation

Counterion concentration very near surface (84% within 3Å) according to this Gouy–Chapman double layer approach

Concentration of ions at surface ~1-3M!

such high concentrations raise questions about assumptions for linearized Poisson- Boltzmann approach

Molecular modelling and numerical simulations (Monte Carlo) – show limitations**

*J. Israelachvili – Intermolecular & Surface Forces, 2nd edition, Academic Press, London, 1992

**Kerisit S, Cooke DJ, Marmier A, Parker SC , CHEMICAL COMMUNICATIONS (24): 3027-3029 (2005)

Surface potential measurement – zeta potential

- The experimentally determined surface potential is the zeta potential, ζ,
- Often calculated from a measure of electrophoretic mobility* (velocity per unit electric field) or
- Acoustophoretically$ by inducing a distortion of double layer, in an electric or acoustic field, leading to a differential movement between the charged particles and the continuous medium.
- The **zeta potential** thus determined does not correspond to the actual surface potential of the particles, but to the potential of an ill-defined plane beyond which the ions are not permanently bound to the particle, called the slip plane.

- The pH at which the zeta potential is zero is called the isoelectric point (**iep**)
- The pH when the surface potential is zero is called the point of zero charge (**pzc**)

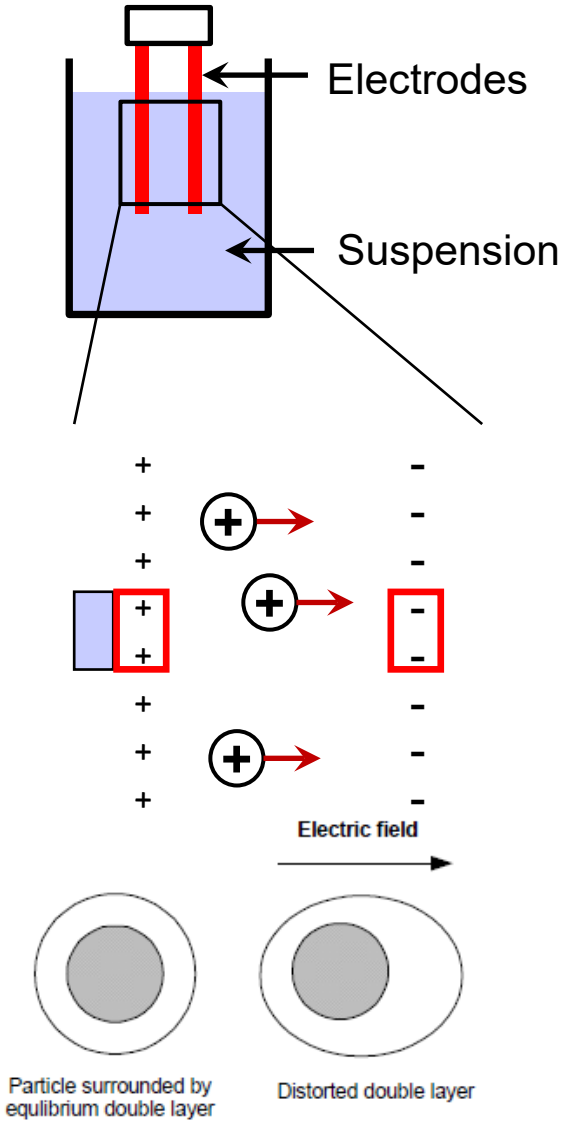


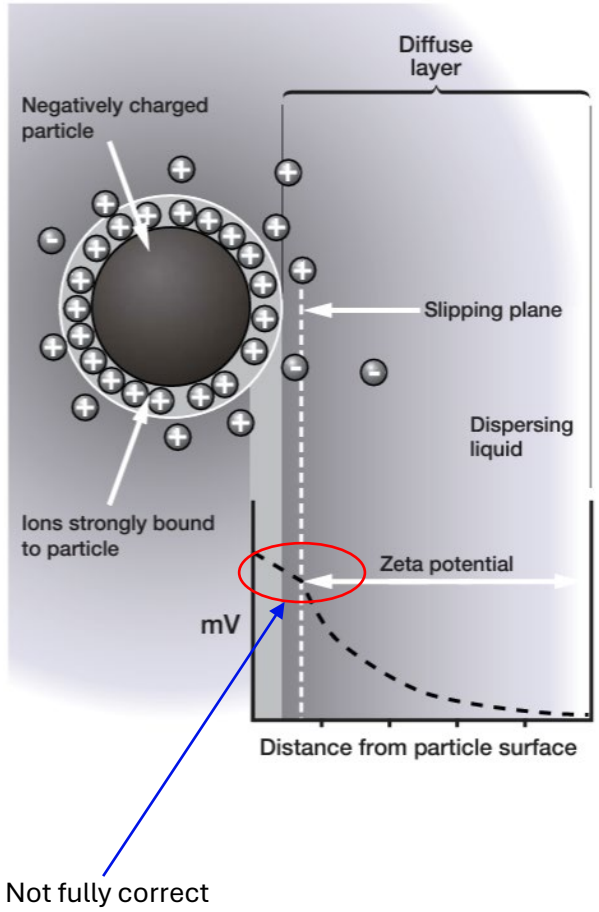
Figure 3: Distortion of double layer by applied electric field

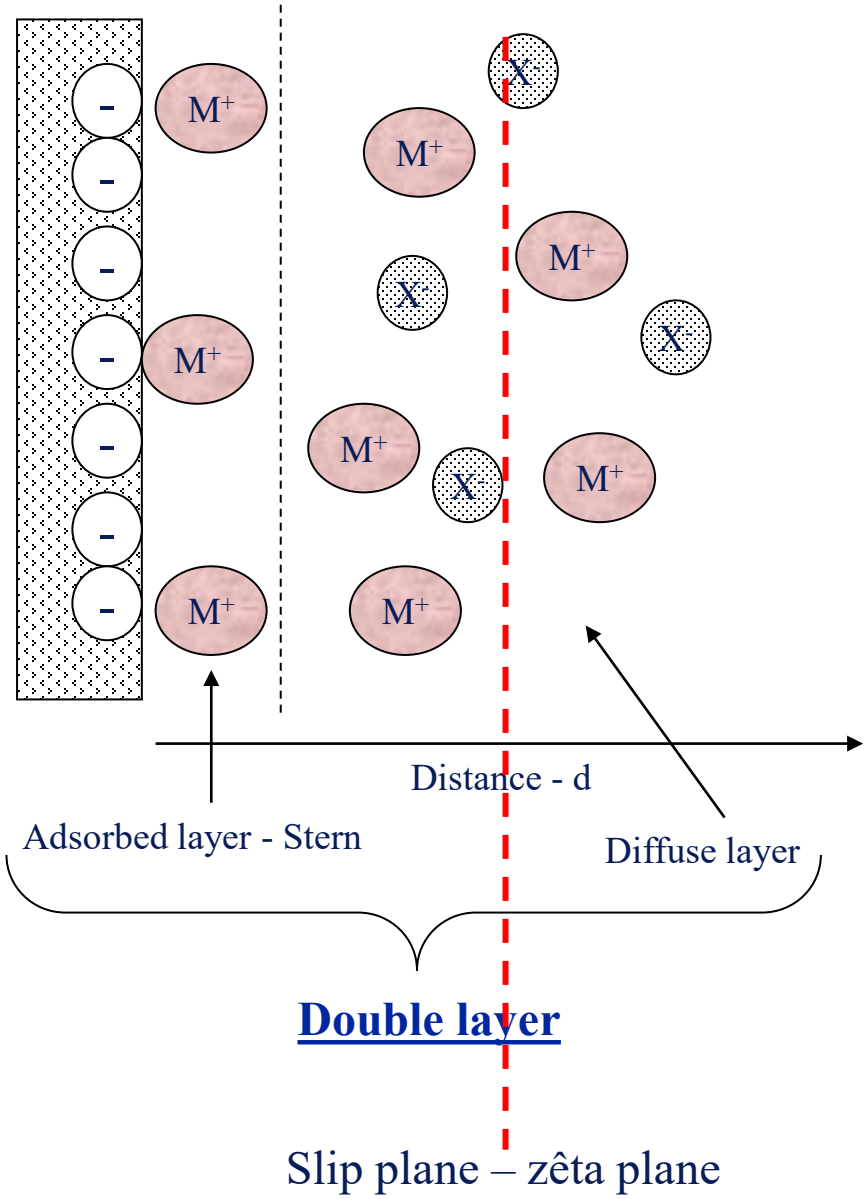
40 nm Al_2O_3 particle speed ≈ 2 m/s

* O'Brien, R.W. White, L.R. -J. Chem. Soc. Faraday Trans. 2, 74 1607 (1978)

$ O'Brien et al J.Coll.Inter.Sci., 173 406-418 (1995).

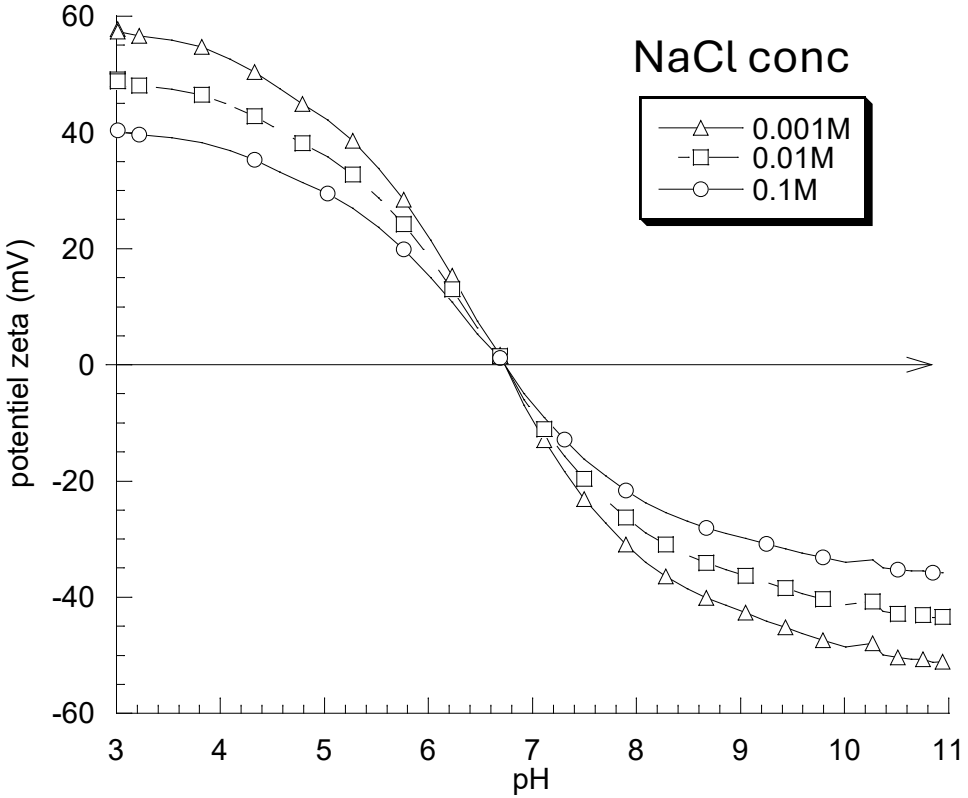
Double layer - Gouy and Chapman – Stern model





Surface potential measurement – zeta potential

Zeta potential as a function of pH with and ionic concentration for a TiO_2



Examples of iep

Powder	SiO_2	ZrO_2	TiO_2 rutile	TiO_2 anatase	Kaolin (edges)	Fe_3O_4	Fe_2O_3	Al_2O_3	ZnO_2	MgO
pH (iep)	2-3	4-5	4-5	6-7	5-7	6-7	6-9	8.5-9.5	≈9	12-13

Interaction Forces in Colloidal Systems

PSI

Interaction force

The *interaction force* between two colloidal particles expresses the variation of their *interaction potential G* according to their *distance* of separation *h* :

$$F = -\left(\frac{\partial G}{\partial h}\right)_T = -\left(\frac{\partial H}{\partial h}\right)_T + T\left(\frac{\partial S}{\partial h}\right)$$

The sign "-" is chosen so as to give a sign *positive* to a *repulsive force*.

Osmotic pressure

A particle in a solution undergoes a *force* linked to the *osmotic pressure* of the solution:

$$\frac{F}{Area} = -\frac{1}{Area}\left(\frac{\partial G}{\partial h}\right)_T = -\left(\frac{\partial G}{\partial V}\right)_T = -\frac{1}{V_{solute}}\left(\frac{\partial G}{\partial n_{solute}}\right)_T = \Pi_{osm}$$

"Area" is the surface of the particle.

Interactions between colloidal particles

The attractive / repulsive interactions between particles of a colloidal suspension in an electrolyte result from an *osmotic pressure difference* between the solution located *between* particles and *bulk* of the solution.

A direct effect of the formation of the double layer at a charged surface

Interaction Between Charged Surfaces

PSI

Identically charged surfaces

Semi-infinite plates separated by an electrolyte solution

When we bring together two identical charged surfaces, separated by an electrolyte solution

the overlap of their double layers produces a *repulsive* interaction.

For reasons of symmetry, we have:

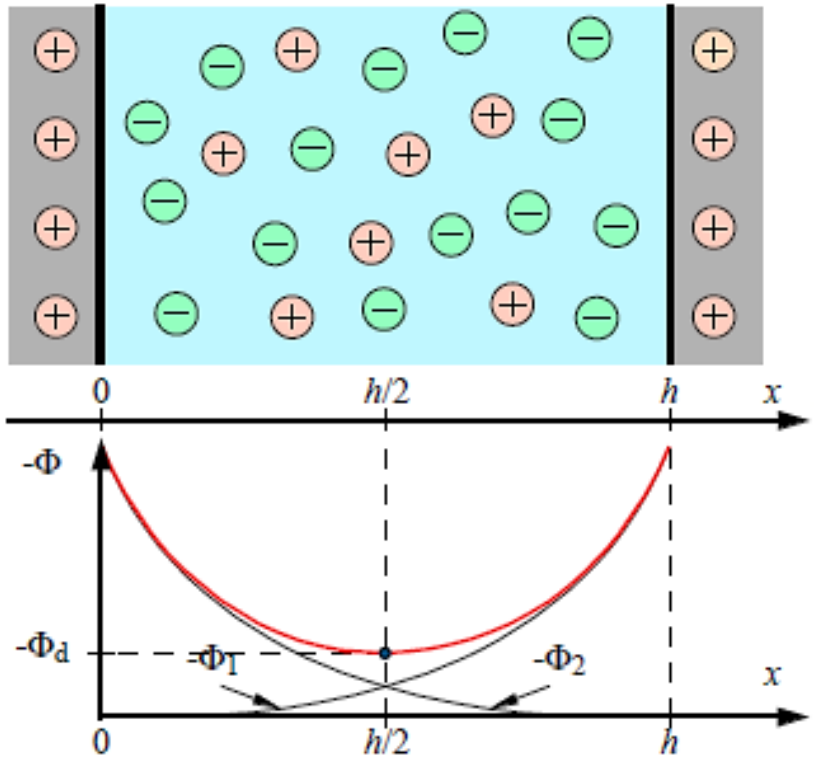
$$\frac{d\Phi}{dx}|_{h/2} = 0; \Phi(h/2) = \Phi_d$$

The ionic distribution between each charged surface

and the mid-plane (h/2) is identical giving :

$$\frac{F}{Area} = \Pi_{osm} = kT \sum_i c_i(h/2)$$

This equation also applies to *swelling of charged layered crystals such as clays* (e.g. montmorillonites, a 2:1 clay).



Colloidal Stability - DLVO Theory

Theory *DLVO*

The total interaction potential $V(h)$ is the algebraic sum of the repulsive potentials $V_R(h)$ (electrostatic) and attractive $V_A(h)$ (from *van der Waals*).

$$V(h) = V_R(h) + V_A(h)$$

The corresponding interaction force is therefore:

$$F = -\frac{dV}{dh} = -\frac{dV_A}{dh} - \frac{dV_A}{dh}$$

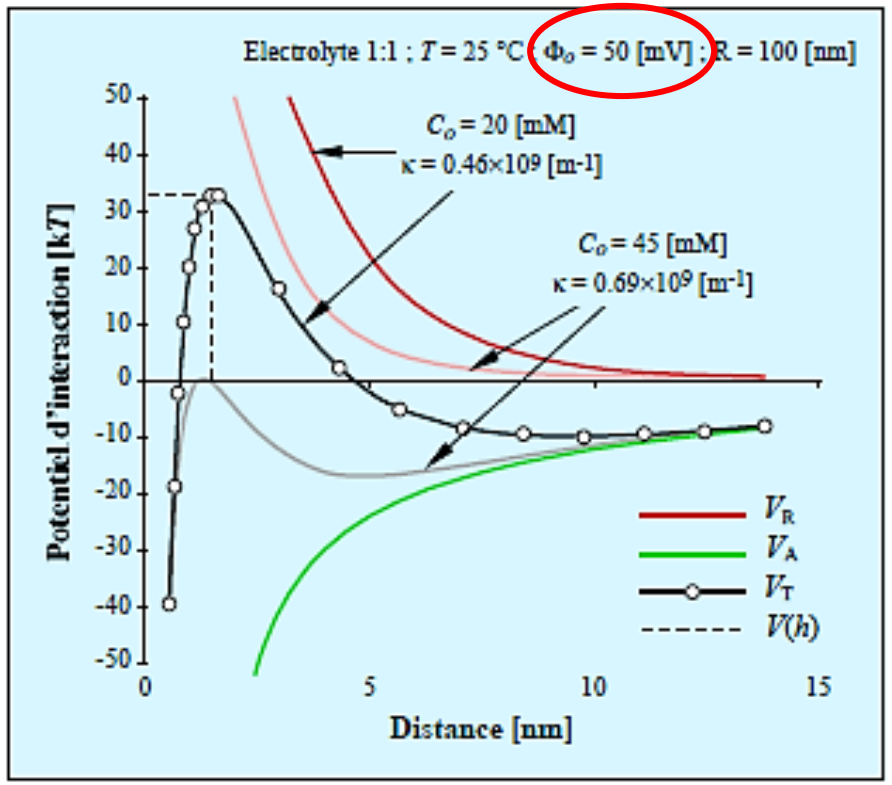
Theory developed by *B. Derjaguin* & *L. Landau*, and *E. Verwey* & *T. Overbeek*. 2 independent groups at the same time…. 1940's

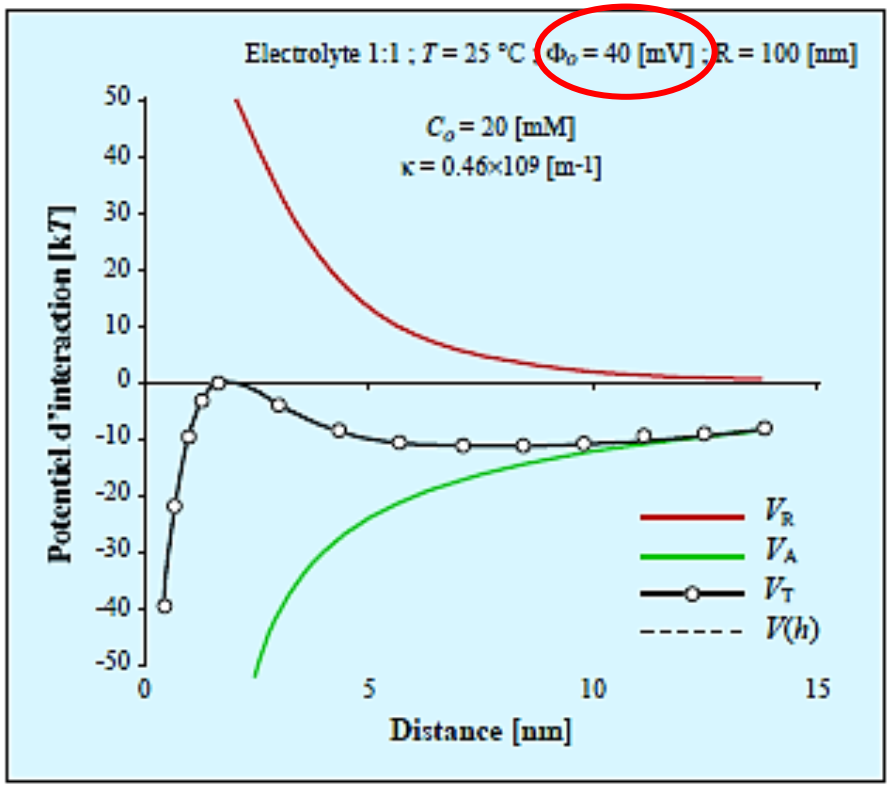
Colloidal Stability - DLVO Theory

Interaction between two identical **spheres for a symmetrical electrolyte (1: 1) e.g. NaCl**

The "electrostatic repulsion" component **decreases with increasing concentration** in the electrolyte of the solution.

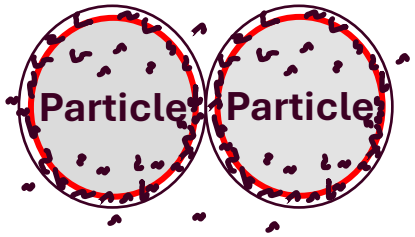
It is **very sensitive to the magnitude of the surface potential Φ_o**: the barrier decreases from 33 kT to 0 as potential decreases from 50 to 40 mV.





Adsorbed layer - repulsion

- Repulsion is felt when the polymer layers overlap
- The more these layers are extended the sooner the repulsion is felt and therefore the effect of the attractive van der Waals forces will be limited.



Theoretical approach

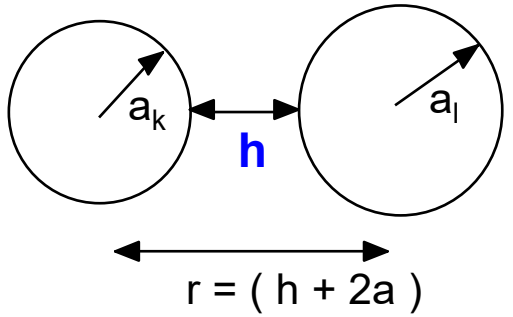
- Both enthalpy and entropy contribute to the force of repulsion.

Enthalpic

- an interpenetration of the polymers reduces the contact between the solvent and the polymeric chains (due to polymer-polymer contact).
- this changes the mixing enthalpy of the system giving our input enthalpy. (concentration gradient between bulk and interparticle space – osmotic pressure pushes particles apart)

Entropic

- as the adsorbed layer approach, each polymer can no longer adopt as many configurations as before – loss of disorder higher free energy – repulsion to avoid this – giving a repulsive entropic contribution.



Polymer conformation - Polyacrylic Acid on Alumina

PSI

PAA

$(-CH_2-CH(COOH)-)_n$

Example: polymer conformation

Adsorption of polyacrylic acid on alumina (Al_2O_3)

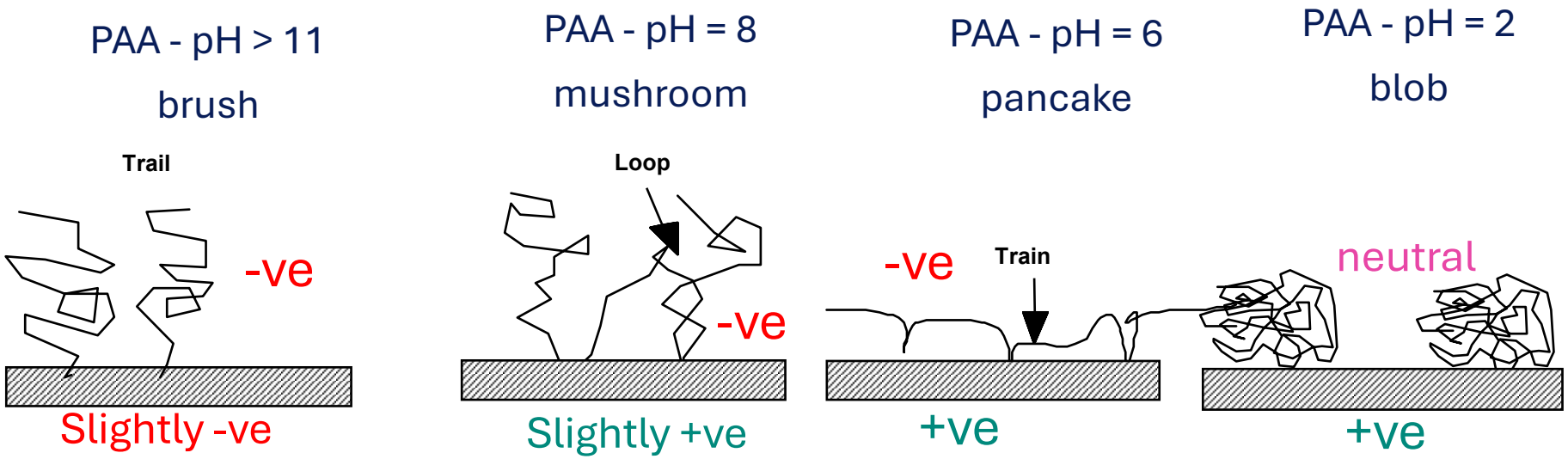
Isoelectric point - Al_2O_3, pH = 9,

PAA fully dissociated for pH> 6

Adsorbed layer thickness can be measured by Atomic Force Microscopy – AFM*

Or from atomistic modelling$

Steric and electrostatic contributions from carboxylate groups – electro-steric stabilization



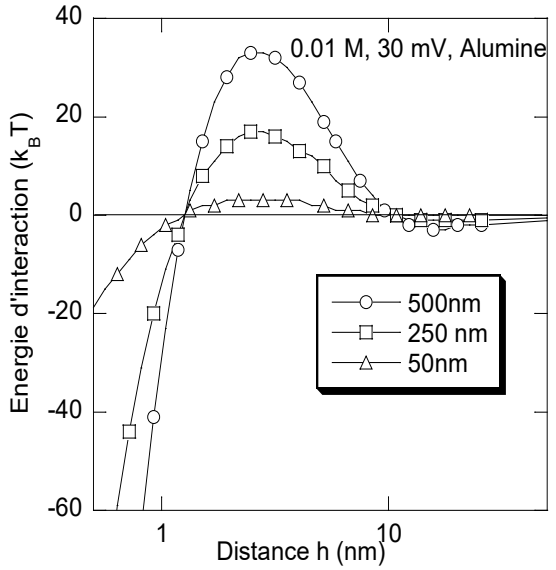
- *M. Palacios, P. Bowen , M. Kappl, HJ. Butt, M. Stuer, C. Pecharromán, U. Aschauer, F. Puertas "Repulsion Forces of Superplasticizers on Alkali Activated Slag Pastes" Materiales de Construcción, 489-513, 62 (308), 2012
- $U. Aschauer et al ",J.Coll.Inter.Sci. 346 (2010) 226–231

Assessment of colloidal stability

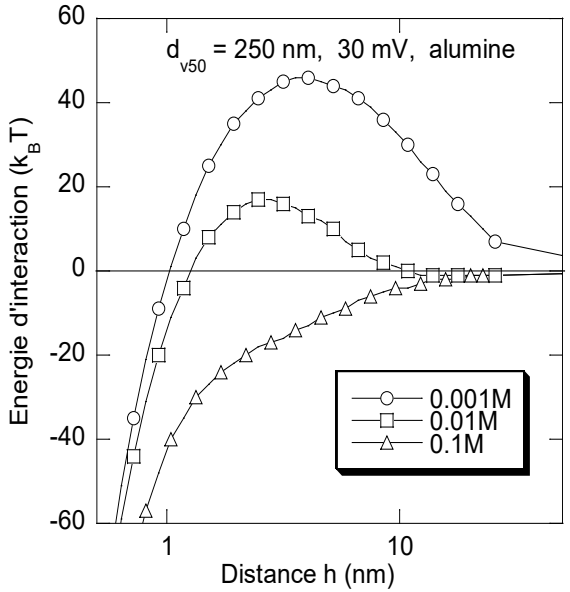
The examples above demonstrate:

- It is difficult to generalize the type of potential barrier that can stabilize a particle dispersion.
- A calculation of the interactions at play can clearly improve the understanding and the choice of a dispersing system.
- The development of computers greatly facilitates the use of this approach without having to resort to too simplistic modeling of the phenomena.
- Few studies correctly predict the order of magnitude of interaction potentials and the same for rheology – yield stress and viscosity.
- Qualitative agreement generally good, but difficult to quantify.
- There are several reasons for this
    - assumption of spherical particles and identical sizes
    - adsorbed layer thickness and conformation of the polymer (simulation , AFM)
    - unknown Hamaker constants,
    - hydrodynamic effects - soap in the bath!
- Facilitated by development of open access programs - e.g., *http://hamaker.epfl.ch*

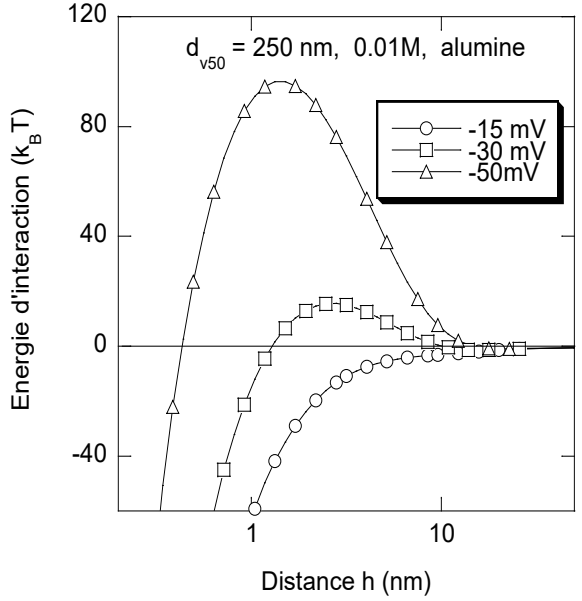
Interparticle potentials – summary - calculations – α Al_2O_3



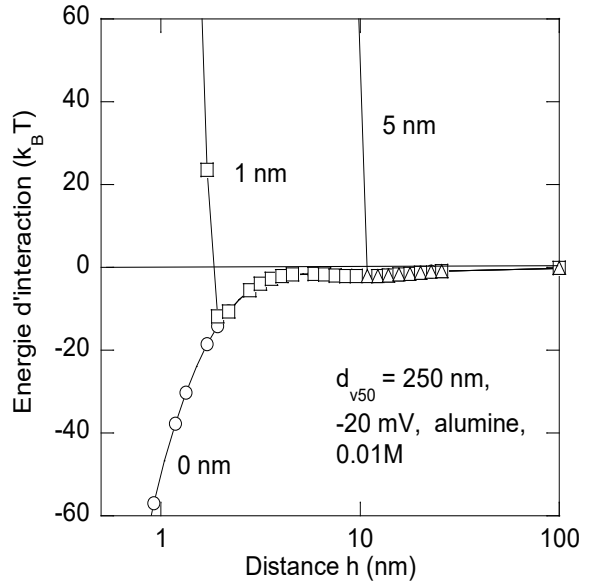
size



Ion conc



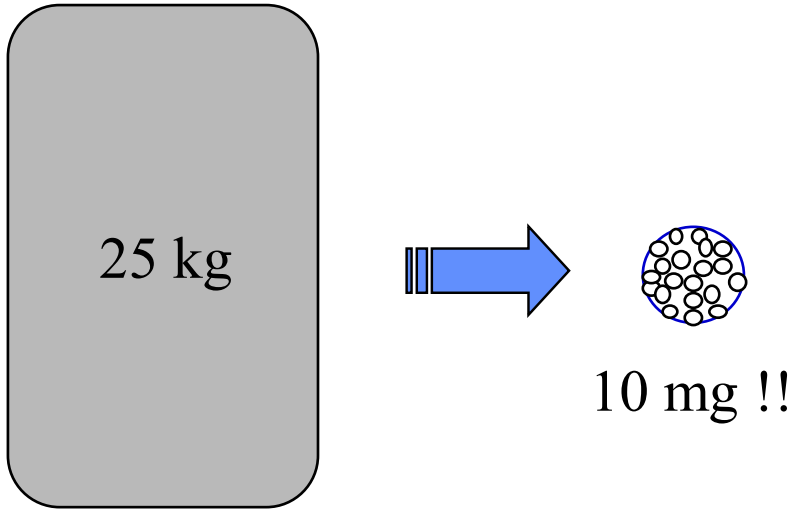
charge



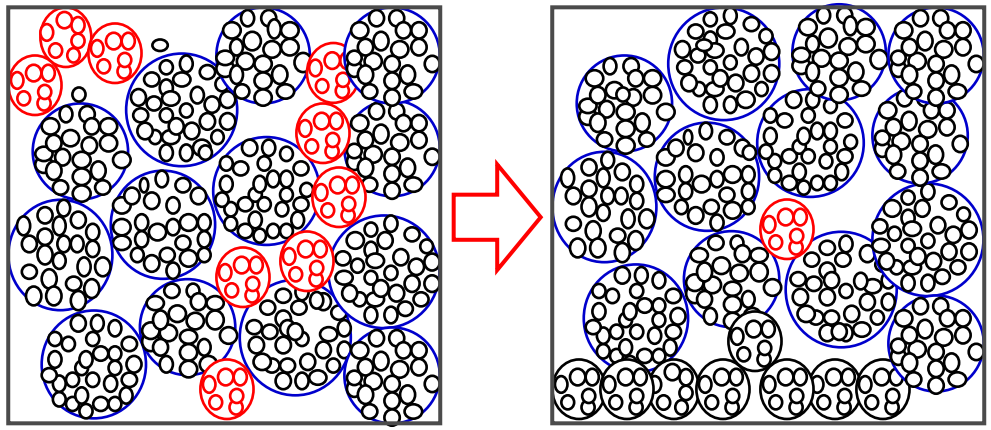
Adsorbed layer

Sampling

- Purchase 25 kg - 1000 kg
- Reproducible ceramic manufacturing process need
  - Constant powder quality
- Characterization use
- 50g – 10 mg
- Is our sample representative of the bulk lot?



- Possible segregation
- “Cornflakes/muesli” effect



Sampling - Golden Rules

Important that analytical sample representative of whole

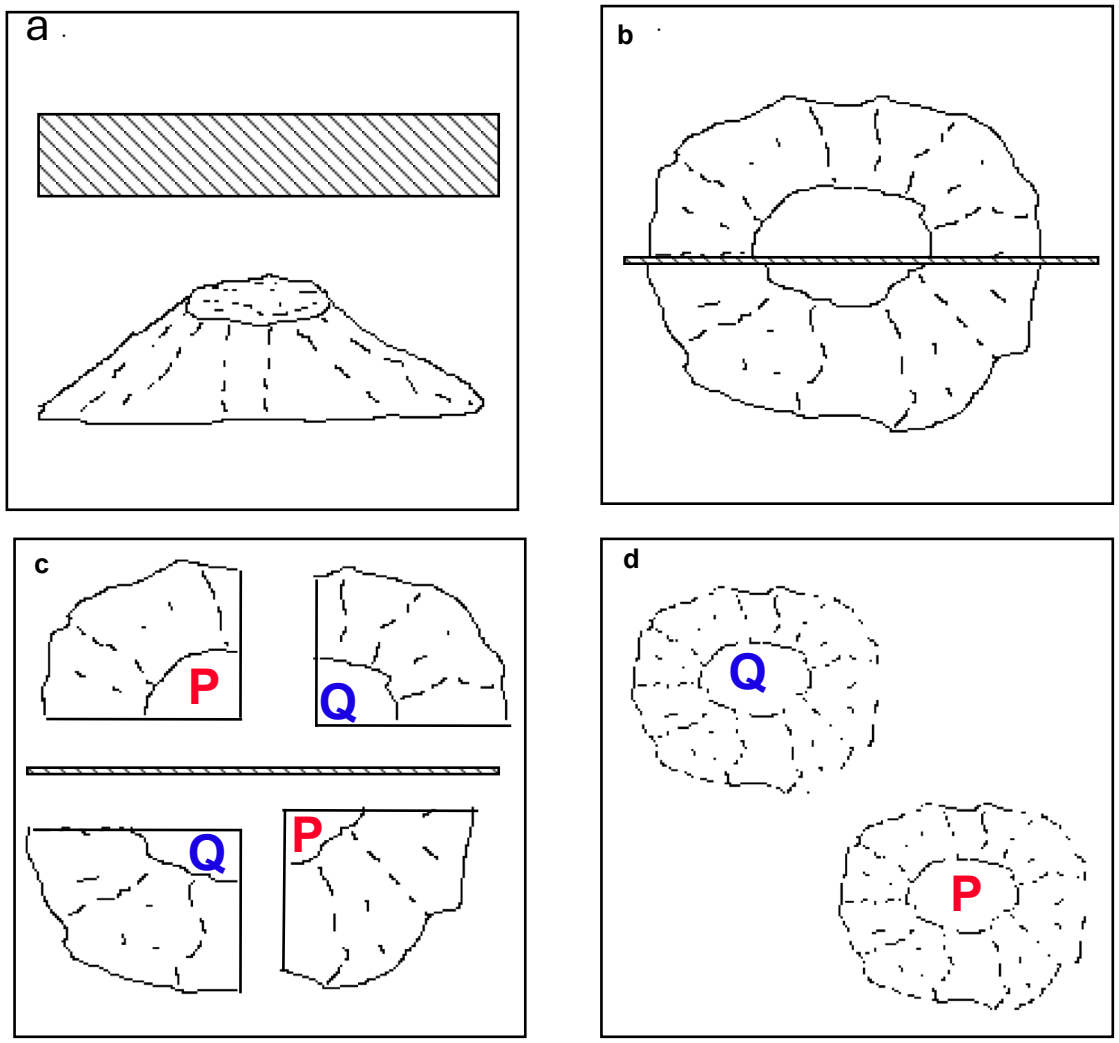
- "golden rules of sampling"* should be applied,
  - always sample a powder when it is in motion
  - take several small samples at different intervals rather than one larger sample

- Not always possible
  - other methods

Spinning Riffler or Rotary Sampler

*T. Allen, "*Particle Size Measurement*", Fifth edition, Chapman and Hall, New York, 1997.

Sampling - Cone and division into quarters



Very often -

– **Spatula in a pot**

– Mix pot first

– Take sample of medium

Sampling - Minimum number of samples

If we want to obtain a confidence level of 95% ($\pm$ X; $X = D_{bulk} - D_{sample}$)
of the median measured by our analytical technique, it is necessary to take n samples:

$$n = \left(\frac{t \cdot \sigma}{X}\right)^2$$

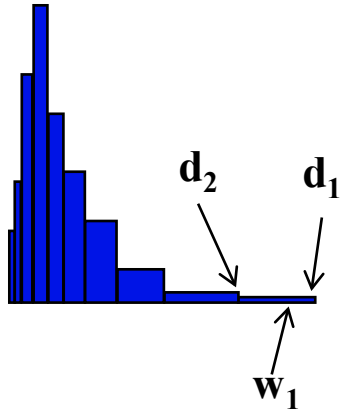
- t - t-distribution $t \approx 2$ for a confidence level of 95%
- σ is the standard deviation of the distribution of our sample

PSD on 16 samples taken at random a batch of powder unmixed. $\rightarrow \sigma$ calculation.
Then, 293 samples were needed for estimating a median of 3.1 µm of $\pm$ 0.1 (95% conf.)
With correct sampling using a rotary sampler: only 3 samples would have been needed.
Sampling form suspension: shaking/sonicate before sampling!

Sampling - Minimum weight

- Minimum weight ,W_m, needed to have a representative sample
  - no matter what precautions are taken on sampling
- Related to the particle size distribution of the powder in question

$$W_m = 0.5\left(\frac{\rho_p}{\sigma_i^2}\right)\left(\frac{1}{w_1}-2\right)\left(\frac{d_1^3-d_2^3}{2}\right)\times 10^3$$



- W_m minimum weight (g), σ_i^2 is the variance of the tolerated sample error
- ρ_p powder density (g/cm3), w_1 mass fraction of largest size class sampled
- d_1^3 maximum diameter of largest size class sampled (cm)
- d_2^3minimum diameter of largest size class sampled (cm)

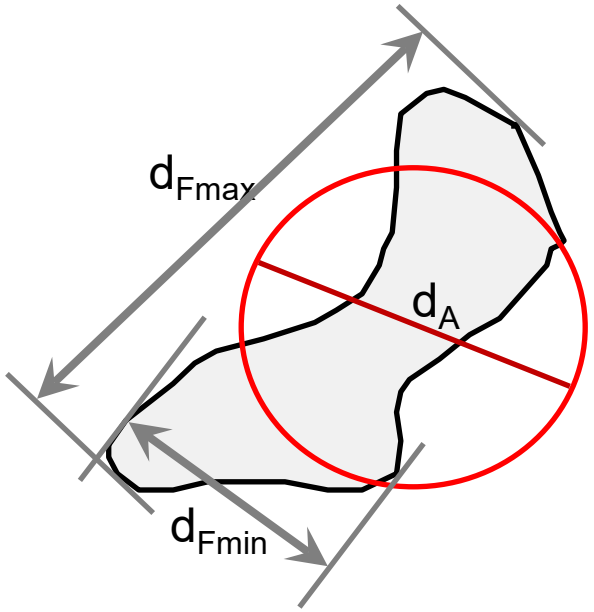
- e.g. for a sub-micron alumina (Alcoa A16SG) 0.3 mg is sufficient for σ_i 0.05 **but**
- For a glass spheres with a broad distribution from 10 to 1000 microns need 200g !!!!

*T. Allen, "*Particle Size Measurement*", Fifth edition, Chapman and Hall, New York, 1997.

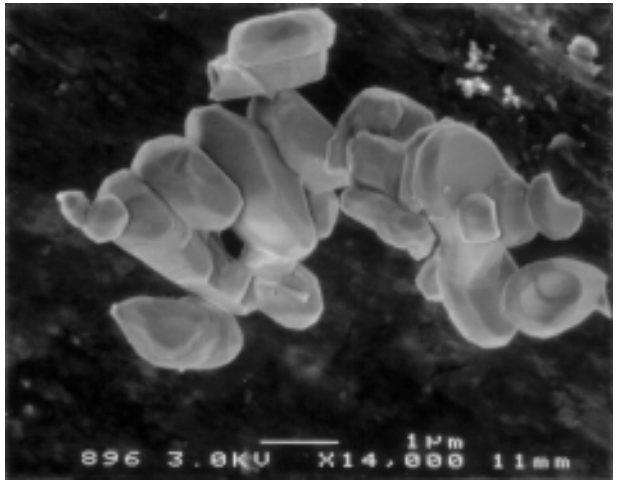
Different Particle Diameters

Diameter		Definition
Stokes diameter	d_{st}	Diameter of free-falling sphere which would fall at the same rate as the particle in a given fluid
Seive diameter	d_T	Minimum square aperture through which the particle will pass
Volume diameter	d_v	Diameter of the sphere with the same volume as the particle
Surface diameter	d_s	Diameter of the sphere that has the same surface area as the particle
Projected area diameter	d_A	Diameter of the circle which has the same area as the projected area of the particle
Feret's diameter	d_F	Distance between two parallel tangents which touch the outline of the particle projection
Average Feret diameter	d_{Fav}	Average Feret diameter from diameters measured over all anlges between 0 and180°
Maximum Feret dia.	d_{Fmax}	Maximum distance between two parallel tangents which touch the outline of the particle projection
Minimum Feret dia.	d_{Fmin}	Minimum distance between two parallel tangents which touch the outline of the particle projection

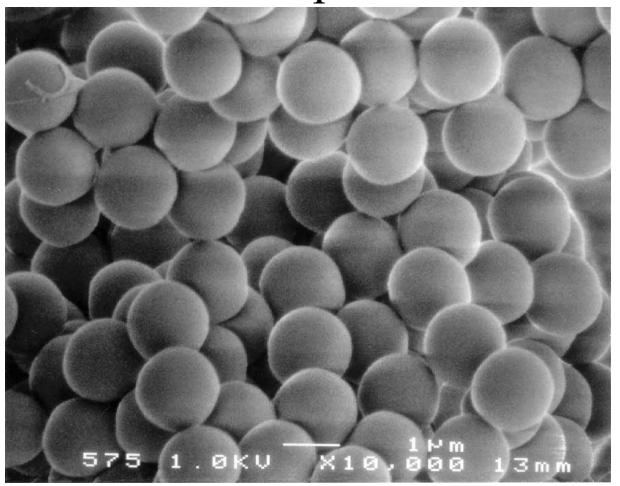
Diameters and distributions



Alumina – irregular shape



Silica - spherical



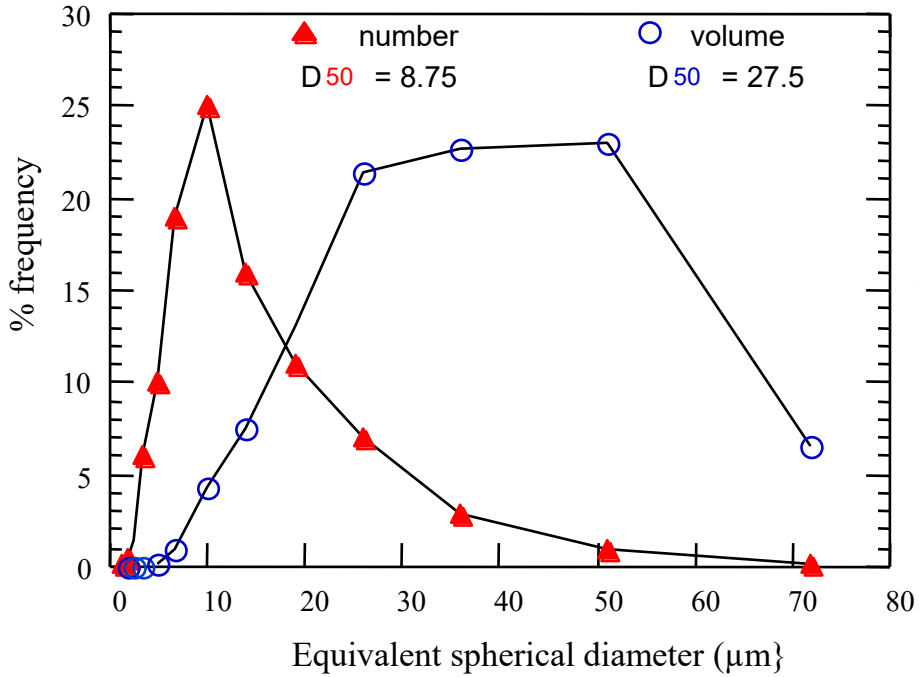
d_{Fmax} : Maximum Feret diameter
d_{Fmin} : Minimum Feret diameter
d_A : Equivalent circular diameter with same projected surface area as the particle

Sphericity (W_w):

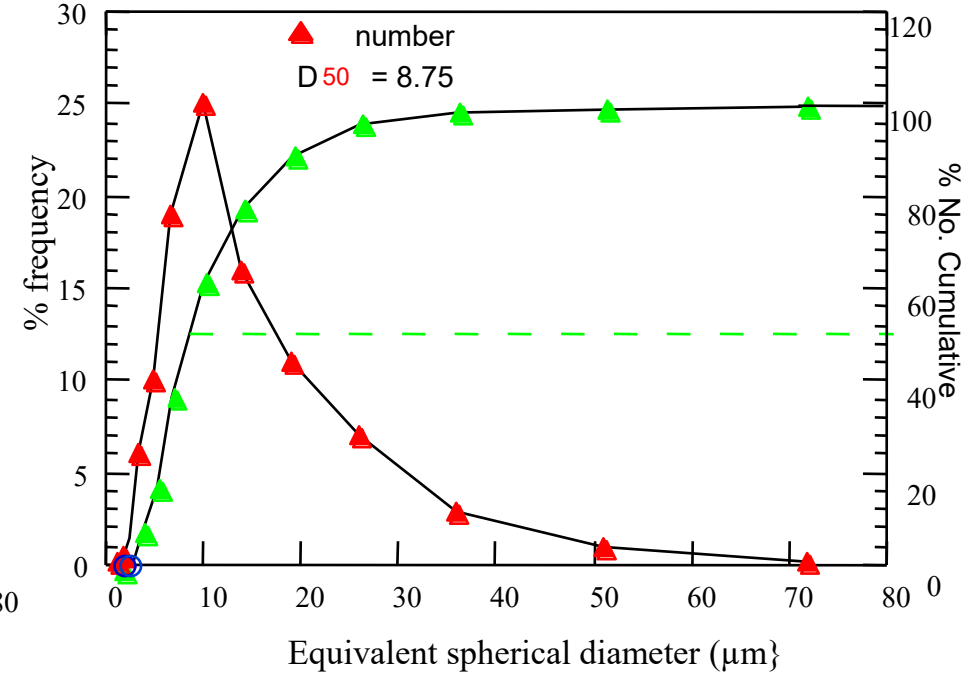
$$W_w = \frac{Specific\ surface\ area\ of\ a\ sphere\ with\ same\ volume\ as\ particle}{Specific\ surface\ area\ \text{of particle}}$$

Diameters and Distributions

- Number or volume - distribution base

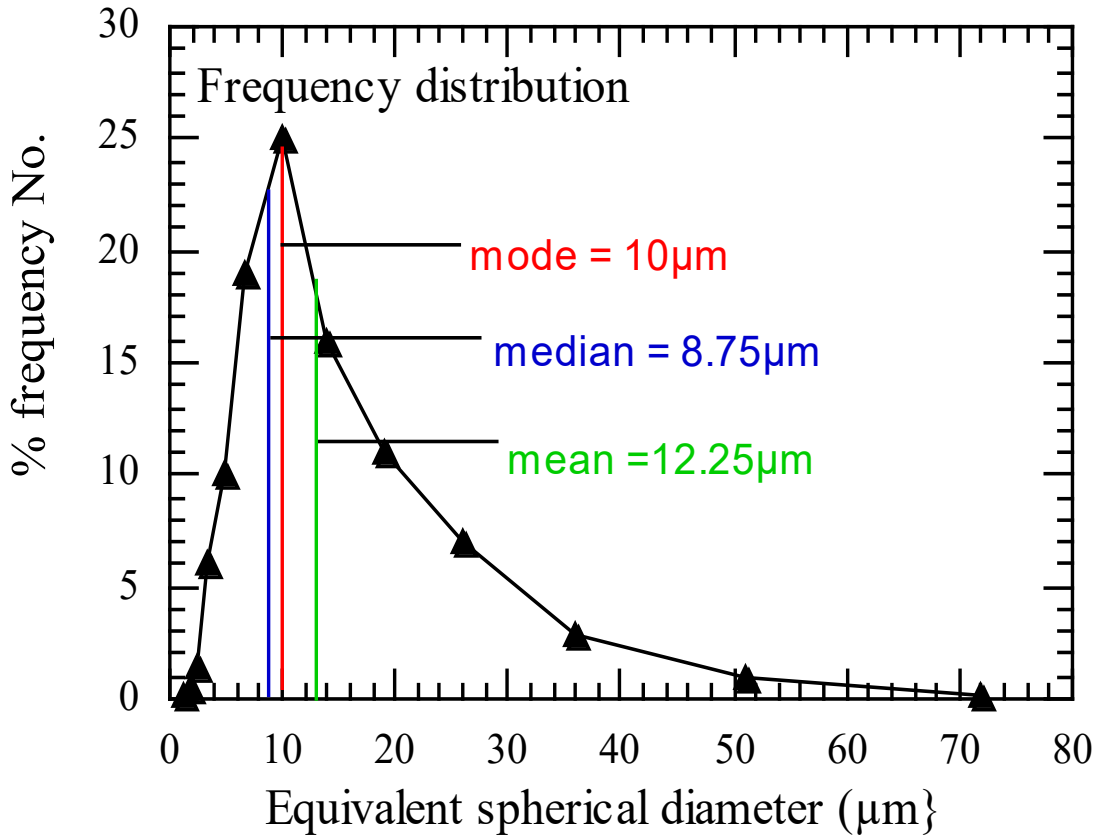


- Frequency or cumulative - Less than - Greater than



Distributions and Average Diameters

- Averages - central tendency -
- Mean - Mode - Median - for a normal distribution all are equivalent



Number - length

$$d_{nl} = \frac{\sum_{i=1}^{n} d_i N_i}{\sum_{i=1}^{n} N_i}$$

Number - surface

$$d_{ns} = \sqrt[2]{\frac{\sum_{i=1}^{n} d_i^2 N_i}{\sum_{i=1}^{n} N_i}}$$

Number - volume

$$d_{nv} = \sqrt[3]{\frac{\sum_{i=1}^{n} d_i^3 N_i}{\sum_{i=1}^{n} N_i}}$$

Length - surface

$$d_{ls} = \frac{\sum_{i=1}^{n} d_i^2 N_i}{\sum_{i=1}^{n} d_i N_i}$$

Surface - volume

$$d_{sv} = \frac{\sum_{i=1}^{n} d_i^3 N_i}{\sum_{i=1}^{n} d_i^2 N_i}$$

Volume - moment
(mass - moment)

$$d_{vm} = \frac{\sum_{i=1}^{n} d_i^4 N_i}{\sum_{i=1}^{n} d_i^3 N_i}$$

Specific Surface Area

$$d_{BET} = \frac{6}{S_{BET} \cdot \rho}$$

Distributions and Average Diameters – example - exercises

Silica powder – example - D_{n50} = 1.12µm
Narrow size distribution σ_{n50} = 0.55 µm

Diamètre cumulatif	Cumulatif	Diamètre fréquence	Fréquence
[µm]	[%]	[µm]	[%]
4.00	100.0	3.750	0.4
3.5	99.6	3.00	4.1
2.5	95.5	2.175	10.3
1.85	85.2	1.675	13.6
1.5	71.6	1.350	17.3
1.2	54.3	1.125	9.2
1.05	45.1	0.975	12.3
0.90	32.8	0.825	12.4
0.75	20.4	0.675	9.0
0.6	11.4	0.550	5.1
0.50	6.3	0.425	3.9
0.35	2.4	0.175	2.4

Number - surface

$$d_{ns} = \sqrt{\frac{\sum_{i=1}^{n} d_i^2 N_i}{\sum_{i=1}^{n} N_i}} = 1.41\mu m$$

Length - surface

$$d_{sl} = \frac{\sum_{i=1}^{n} d_i^2 N_i}{\sum_{i=1}^{n} d_i N_i} = 1.58\mu m$$

Number - volume

$$d_{nv} = \sqrt[3]{\frac{\sum_{i=1}^{n} d_i^3 N_i}{\sum_{i=1}^{n} N_i}} = 1.56\mu m$$

Surface - volume

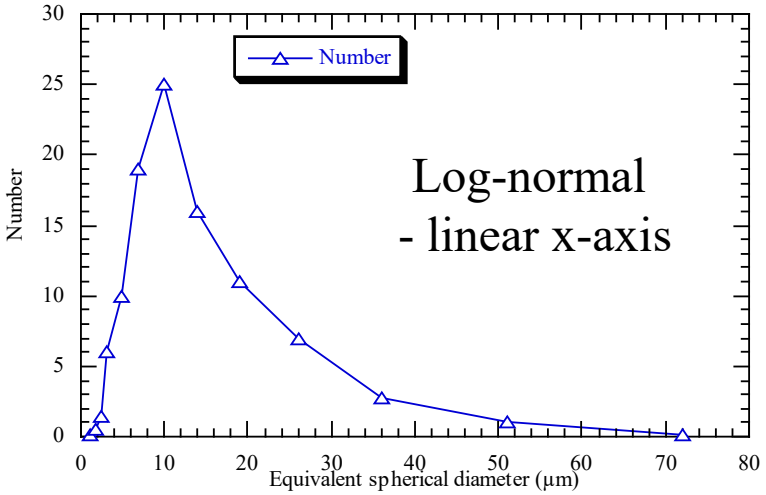
$$d_{vs} = \frac{\sum_{i=1}^{n} d_i^3 N_i}{\sum_{i=1}^{n} d_i^2 N_i} = 1.91\mu m$$

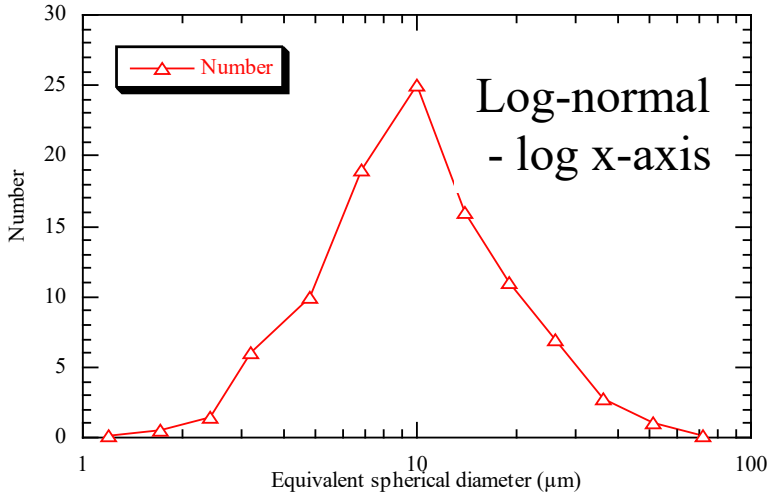
Volume - moment
(mass - moment)

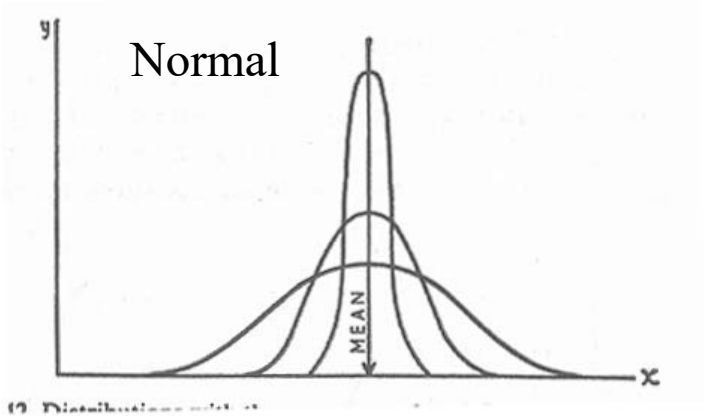
$$d_{4,3} = \frac{\sum_{i=1}^{n} d_i^4 N_i}{\sum_{i=1}^{n} d_i^3 N_i} = 2.21\mu m$$

CONCLUSION:
D_{43} = 2x D_{n50}……..
MUST DEFINE
DIAMETER

Types of distributions - graphical examples







At least, two quantities needed: mean and span

Good review: Yu & Standish, Powder Technology **62** 101-118 (1990), https://doi.org/10.1016/0032-5910(90)80073-8

Types of Distributions & Widths

Types of distributions*

- **Normal**

$$y = f(x) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{(x-\bar{x})^2}{2\sigma^2}\right]$$

- σ is the standard deviation

- **Log-normal** - x is simply replaced by ln x

- **Rossin Rammler** often used for milled or crushed materials

$$y = \frac{df(x)}{dx} = 100nbx^{n-1}\exp(-bx^n)$$

- n and b are material dependant constants

Widths of distributions

- Standard deviation- dispersion or width

$$\sigma_v = \sqrt{\left(\frac{\sum f_i (d_i - d_v)^2}{V}\right)}$$

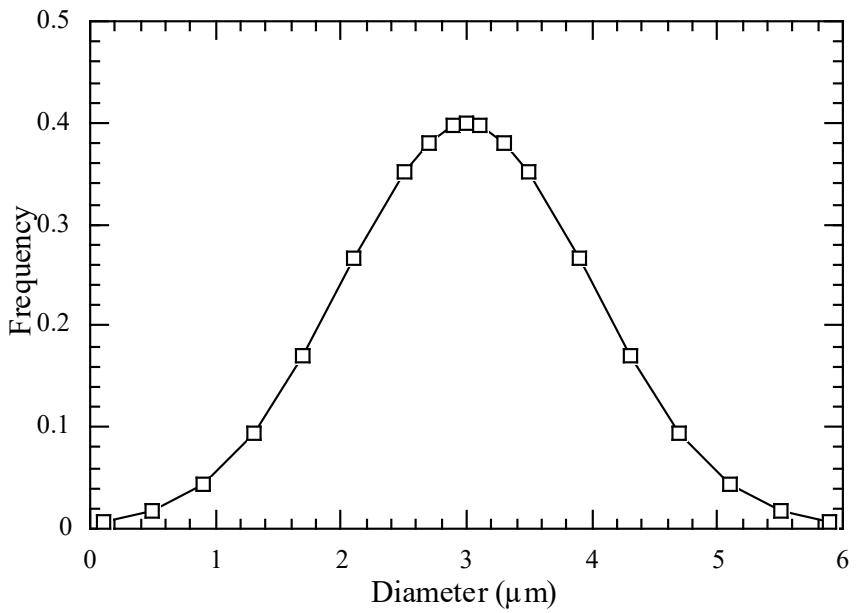
d_v: mean volume diameter
f_i: is the frequency of particles (as a volume) of that diameter
V: total volume for all of the diameter intervals

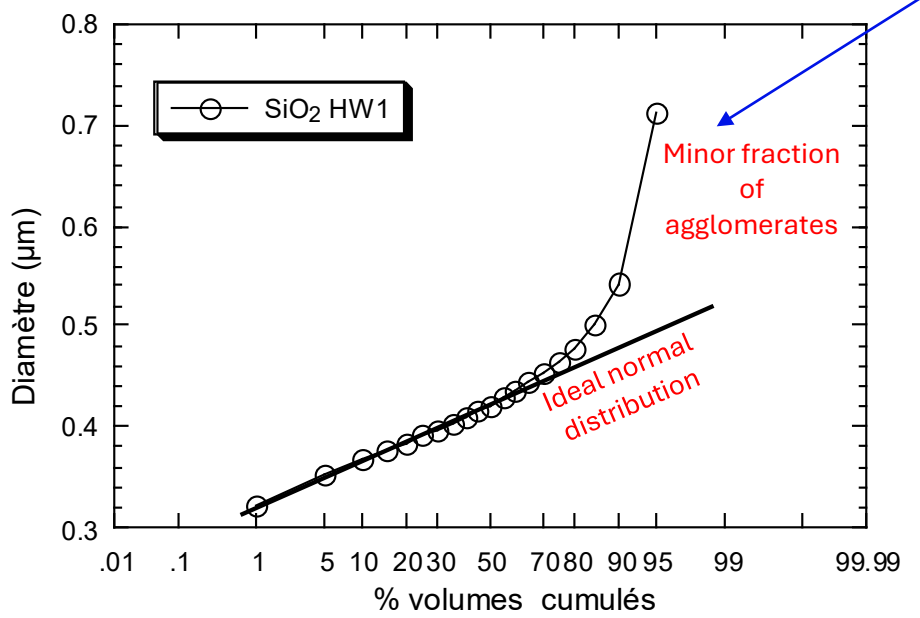
- Span = $(d_{90} - d_{10}) / d_{50}$

*T. Allen, "*Particle Size Measurement*", Fifth edition, Chapman and Hall, New York, 1997.

Normal Distribution

$$y = f(x) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{(x-\bar{x})^2}{2\sigma^2}\right]$$



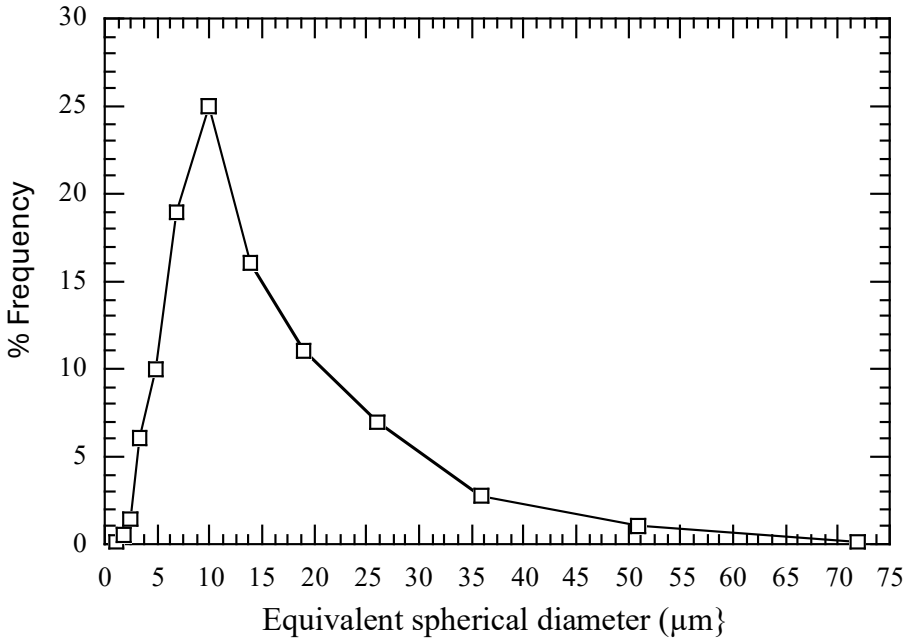


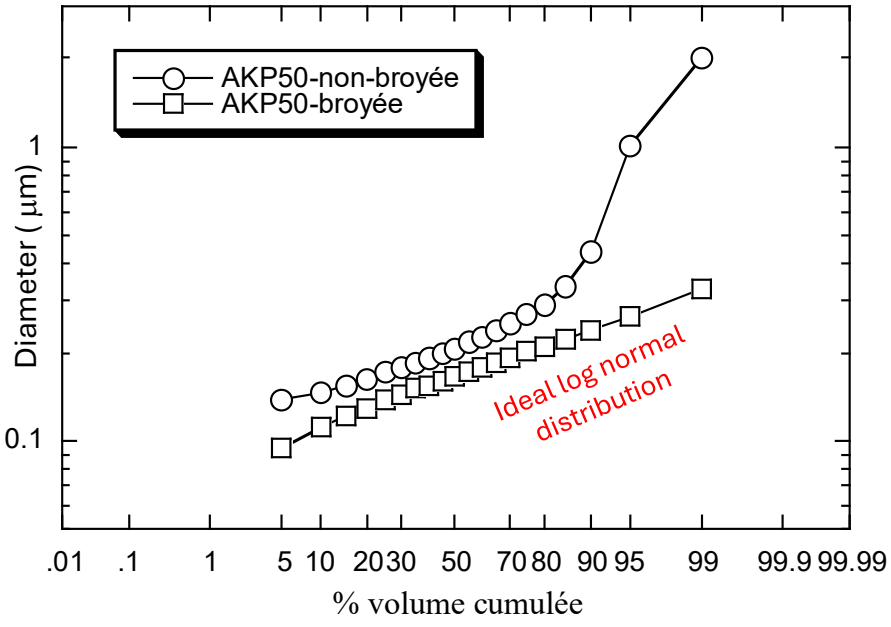
Small fraction of large particles: strong DLS signal!

- **Sieved Powders** – narrow distributions – often follow a normal distribution

Log-Normal Distribution

$$y = f(x) = \frac{dF}{d(\ln x)} = \frac{1}{\ln \sigma_g \sqrt{2\pi}} \exp\left[-\frac{(\ln x - \ln \bar{x}_g)^2}{2 \ln^2 \sigma_g} \right]$$





Commercial ceramic powders, often follow a log-normal distribution (top-down processing, milled powders)

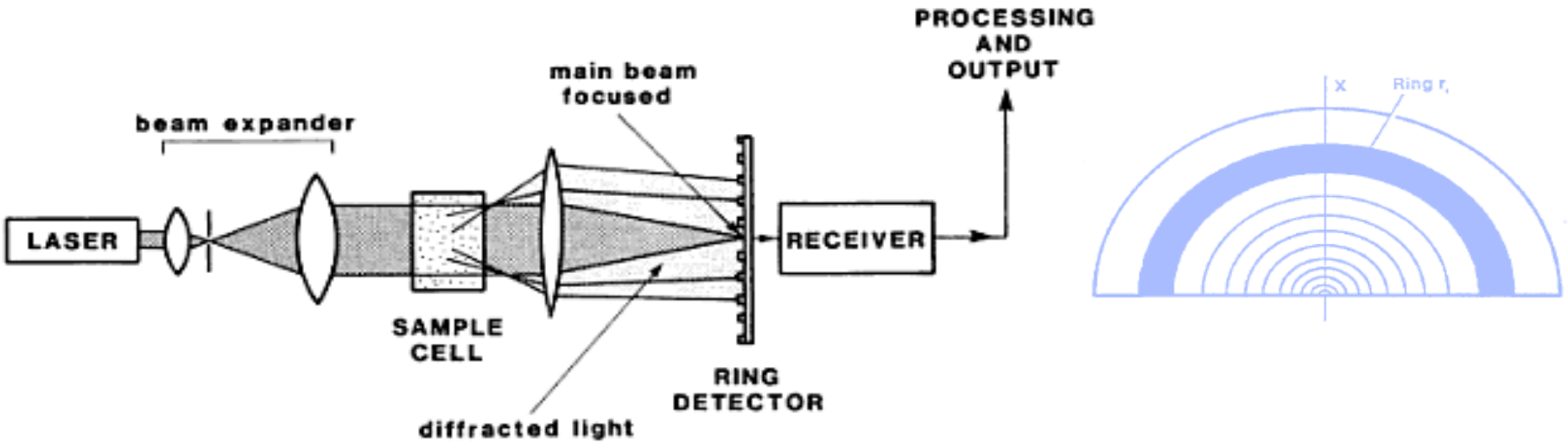
PSD: Current Methods - Brief review

`Method	Medium	Size (µm)	Sample (g)	Time*	Measured Dia.
Microscopy					
Optical	Liquid/gas	400-0.5	<1	S-L	Projected area
Electron	Vacuum	400-0.001	<0.1	S-L	Férèt
Sieving	Air	8000-37	50	M	Sieve
	Liquid	5000-5	5-20	L	
Sedimentation					Stokes
Gravity	Liquid	100-0.5	<5	M-L	Mass
Centrifuge	Liquid	300-0.02	0.01- 2	M	Projected area
Analytical Ultra Centrifuge		0.001…	<0.1	M-L	Hydrodynamic
Light Scattering					
Diffraction	Liquid/gas	3000- 0.05	<0.1-2	S	Volume
Dynamic	Liquid	0.5(1)-0.002	<0.1	S	Hydrodynamic
Tracking*	Liquid	>20nm	<0.001	M	Hydrodynamic
Electrical Sensing Zone (optical)	liquid	(1200) 250-0.4	<1	S-M	Volume
Gas Adsorption dBET	Gas/Vacuum	5-0.005	<5	L	Surface-Volume

Analysis times S = short (< 20 min); M = moderate (20-60 min); L = long (>60 min)

*H. Gaczyk, et al J.Aero.Med.&Pulm. Drug Deliv.(2014)

Laser Diffraction



- Variation of the light intensity, I, with angle from the forward direction, θ ,for light scattered by diffraction for a powder is given by

$$I(\theta) = I_0 \int_0^{\infty} f(R)\left(\frac{RJ1\alpha\theta}{\theta}\right)^2 dR$$

- Io is the incident light intensity, $\alpha = 2\pi\lambda/R$, λ is the wavelength of the light, R particle radius
- J1 a Bessel function. A review of the various approaches used to derive particle size from this formulation is well summarized by Azzopardi

*B.J. Azzopardi «Particle Size Analysis », Ed. Stanley-Wood, N.G. & Lines, R.W., p.108, Royal Society of Chemistry, Cambridge, (1992).
"Principles, methods and Application of Particle Size Distribution analysis" J. P. M. Syvitski. Cambridge Univ. Press. 1991

Laser Diffraction

- Resulting diffraction** pattern can be described by diffraction theory (Azzopardi)
- Particles < 1µm full Mie theory*** has to be used
- Superposition of the diffraction patterns from each size represented in our powder
- Initial size distribution is "guessed"
  - theoretical diffraction pattern computed and compared with the real data.
  - differences minimized using a least squares method
  - residual gives a guide as to how well the optical model correctly represents the data
  - calculates the volume distribution as a fundamental result
  - all other information is derived from this result assuming a spherical particle shape.
- Each producer believes his algorithm for data reduction best
- Accuracy – reproducibility - better than 5% whole distribution*
- Best for particles 4µm > x > 3000µm (down to 0.5 µm good, 0.1 µm possible)
- Fast <1 min! (Excluding sample preparation)

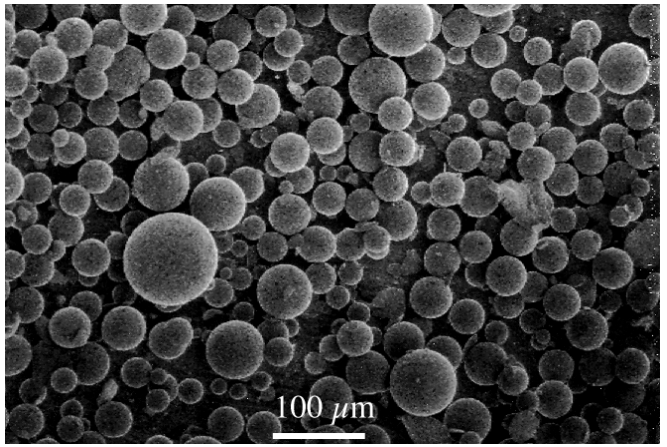
*M. Khalili et al "An Investigation to determine the precision for measuring particle size distribution by laser diffraction" World Congress on Particle Technology 4, Sydney 2002, Paper no 111

** diffraction theory or Fraunhofer *** combination of diffraction and scattering

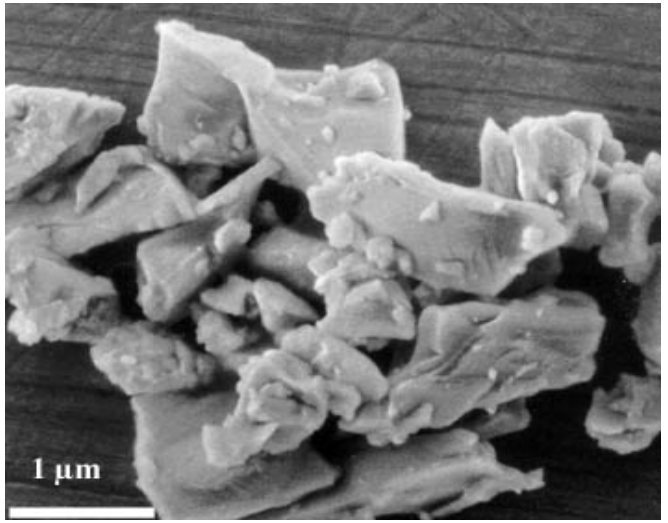
Particle Shape - Regular Geometries

- Most instruments give as an output
  - Equivalent Spherical Diameter (ESD)
  - Often normalized on volume
- ONLY spheres will give comparable results
- Non-spherical particles ESD always smaller than real size and method dependent (Jennings & Parslow)[1]
- Comparison of ESD's from different methods
  - Shape factor - lot of work on clay minerals
  - Morphology of particles studied not uniform
  - Difficult to compare Image Analysis and other methods

Theory



Reality



Never trust a PSD measurement without a micrograph!

[1] Proc. R. Soc. Lond. A 419, 137-149, 1988

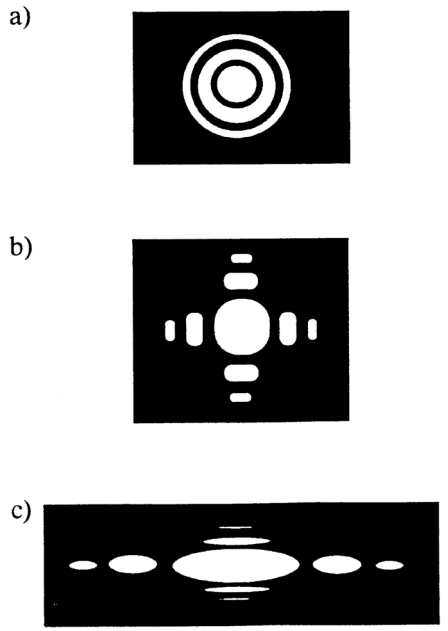
Laser Diffraction - Shape

- Shape limitation
  - non-spherical particularly elongated particles*
- Diffraction pattern need
  - X-Y resolution
- Gabas et al. show can get min max dimensions

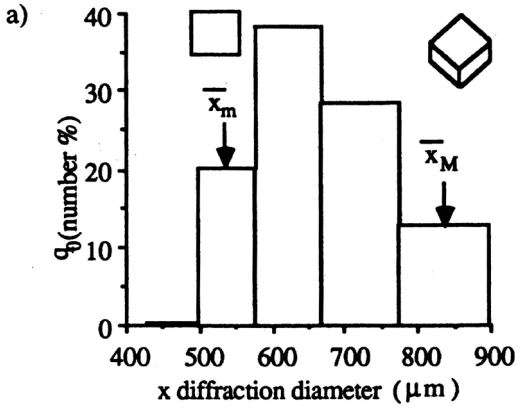
(a) Circular aperture

(b) Square aperture

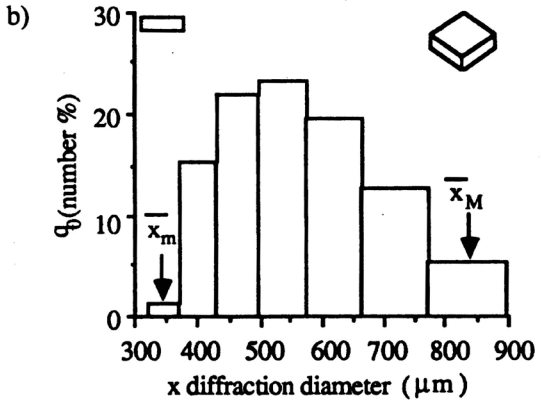
(c) Rectangular aperture



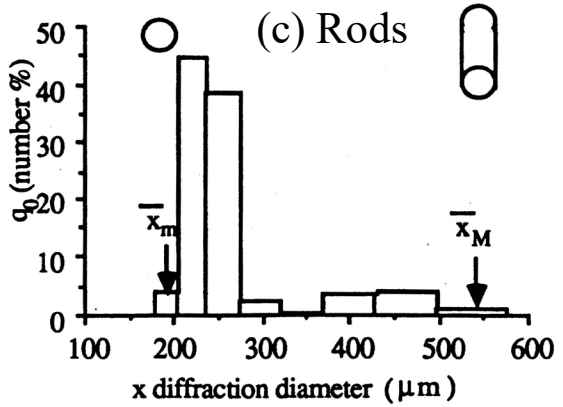
(a) Cubes



(b) Square plates



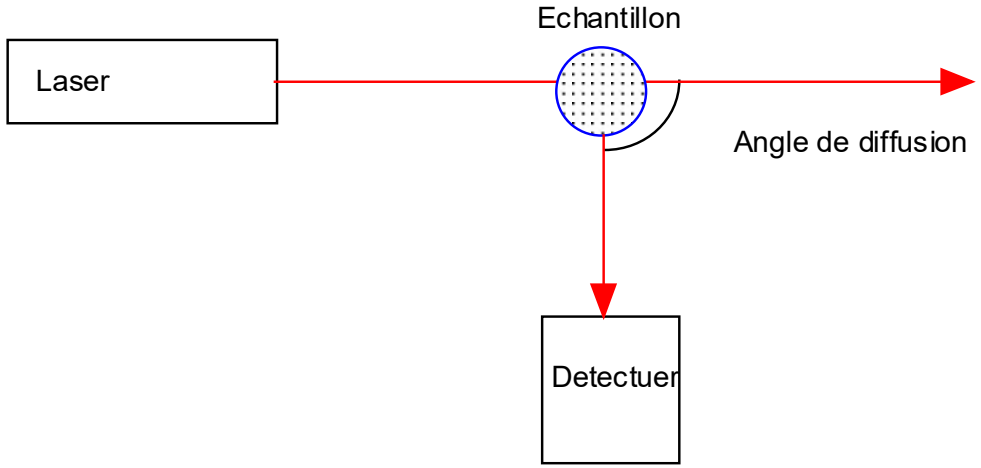
(c) Rods



*N.Gabas,N.Hiquily, C. Laguérie, Part.Part.Syst.Charact, II 121-126 (1994)

Photon Correlation Spectroscopy - PCS

- Dynamic light scattering (DLS) method or
- Photon correlation spectroscopy (PCS) or
- Quasielastic light scattering (QELS) (as it was first termed)



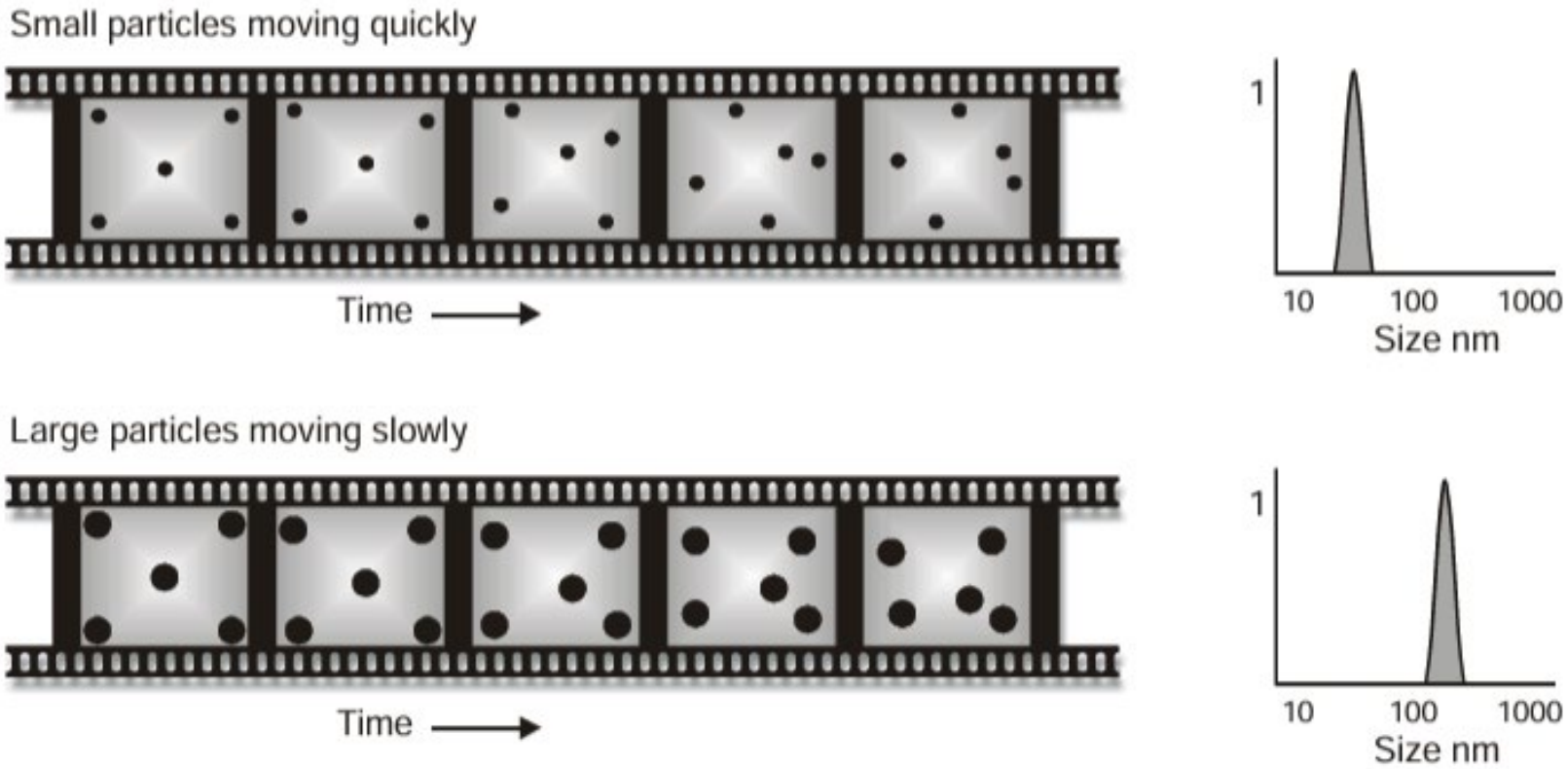
- Rayleigh limit $R << \lambda$

$$I = \frac{I_0 16\pi^4 R^6 [(n^2-1)(n^2+2)]^2}{r^2 \lambda^4}$$

- Io is the incident intensity,
- $n = n_1/n_o$ relative refractive index for
- particle of refractive index n_1
- suspending medium n_o ,
- R is particle radius,
- λ the wavelength of light in the medium
- r the distance between the scattering particle and the detector.

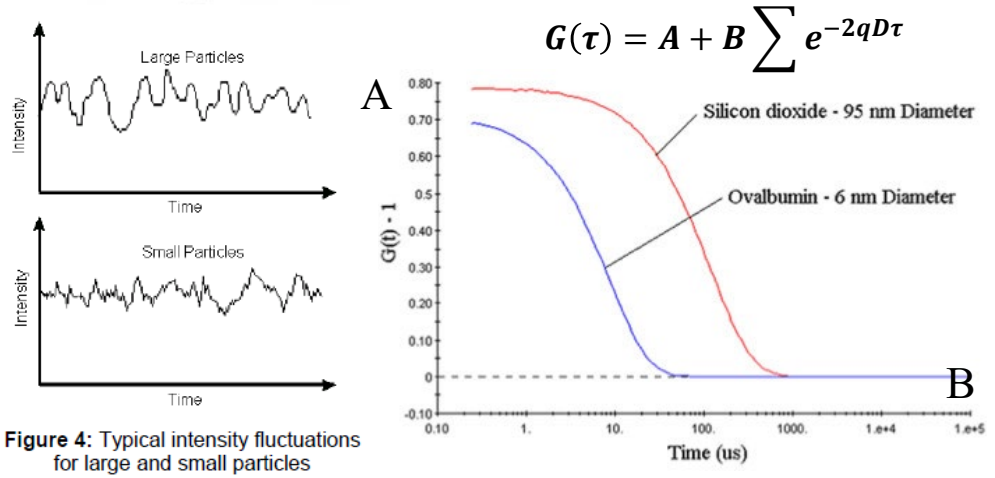
- Dependence of the scattered intensity
- Proportional R^6 : Particle only twice the size will give 64 times the intensity!

Dynamic particle movement tracking



Photon Correlation Spectroscopy - PCS

- Light scattered by particles*
  - Random thermal fluctuations - intensity of scattered light related - to diffusion coefficient D_t - d_h hydrodynamic diameter (=2R)
  - Auto Correlation Function (ACF) – relationship between scattered intensity at time t and t+δt,
- Very good - narrow distributions (steep slope in ACF)
  - < 300nm (>1μm sedimentation)
- Very quick (< 1 min)

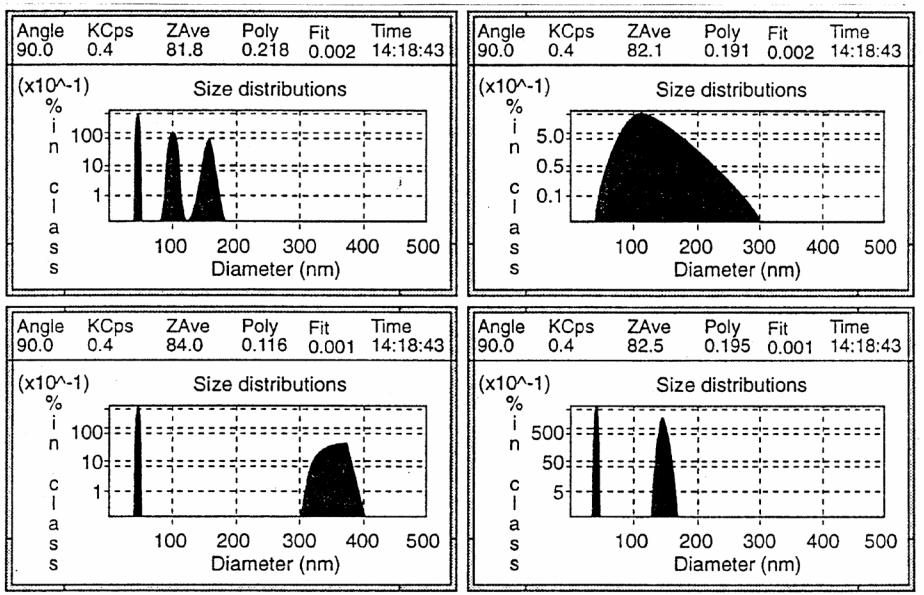


$$G(\tau) = A + B\sum e^{-2qD\tau}$$

Figure 4: Typical intensity fluctuations for large and small particles

q (n, λ)– scattering vector, A intercept, B baseline

- Samples with wider distributions
  - the polydispersity index (PI) gives an idea of the spread of the PSD under investigation;
  - however, the Laplace transform used in the analysis of the ACF is ill-defined
  - i.e. there is no unique solution



*B. Weiner in Particle Size Analysis, Eds. Stanley-Wood, N.G. and Lines, R.W., p.173, Royal Society of Chemistry, Cambridge, (1992)

Particle size description in documents

When describing particle size data or measurements in a document the following details should be quoted:

- Type and supplier of instrument used (e.g., laser diffraction, DLS, …)
- The base to which the distribution is normalized (number, volume…)
- How the sample was dispersed if using a suspension

Further details can be added such as:

- Refractive index of particle and liquid used for light scattering model
- Particle density for sedimentation methods
- Strength of ultrasonic treatment
- Volume of sample treated
- Concentration of suspension (g/ml)
- Pre-treatment for specific surface area measurements
- Any other special detail you have noticed is important for reproducible PSD measurement

Steps in measuring a PSD

Get any information possible from supplier (size and size method, purity, SSA)

- Get a suitable image
  - optical microscopy >10 μm
  - electron microscopy <5 μm (SEM, TEM)

- Choose suitable method based on size range:
  - 0.1 to 1000 μm – laser diffraction good point to start if not elongated
  - 10nm to 1000nm Disc centrifuge (X-ray for inorganic)
  - 2-500nm DLS – care when broad distribution, colloidal stability
  - < 5 nm 2D Analytical Ultra Centrifugation

- Complex shape: Image Analysis

Complementary methods: SSA, XRD, Zeta potential, imaging

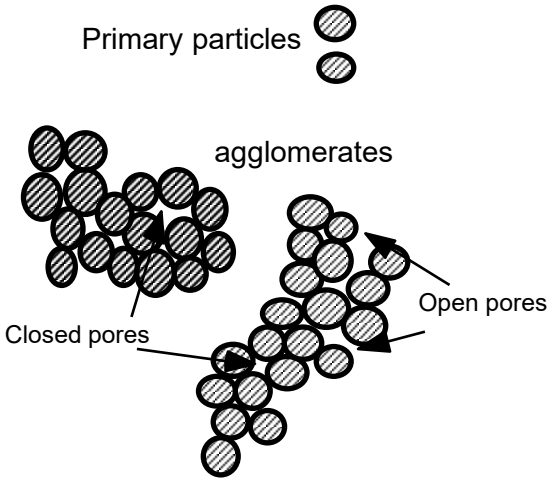
Density, Porosity, and Specific Surface Area

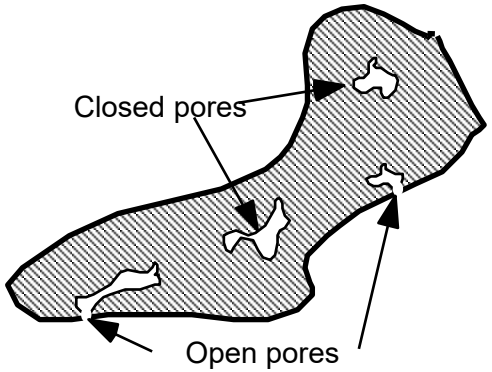
Powders - nanosized – aggregation – open porosity

Often thermal treatment during synthesis – possibility of closed pores

Density lower than – theoretical – calculated from crystal structure

High surface areas (HSA) and possibility of hydroxylated surface – e.g., hydrothermal $BaTiO_3$ – closed porosity formed while heating from 500 to 900°C





- Density (mass/volume) pure phase or powder from pycnometry, can use gas (helium) or a liquid (water, alcohol…)
- Apparent (bulk) density of a powder mass per unit volume - particles and interstitial porosity

Take home messages

1. Assess the synthesis method based on the specific application. Carry out preliminary TD calculation.
2. Consider multidisciplinary approach to NPs characterization.
3. Consider colloidal stability and assess the appropriate PSD measurement method.