



UNIVERSITY OF ROME "LA SAPIENZA"
NANOTECHNOLOGIES ENGINEERING

CHEMICAL PRECIPITATION

PRECIPITATION PROCESS

- ❑ The crystallization of poorly soluble solutes is called precipitation.
- ❑ The process is characterized by high supersaturation values, as a consequence of a chemical reaction that leads to the formation of a poorly soluble product.
- ❑ The formation of this very high supersaturation condition leads to a very high nucleation rate and a inhibited growth rate, followed by agglomeration and property changes of the formed crystals as a function of time

THE PROCESS

- ❑ Very high relative supersaturation values, in the range of thousands, that leads to a high, homogeneous nucleation rate.
- ❑ The nucleation rate may be as high as $10^{19} \text{ \#}\cdot\text{cm}^{-3}\cdot\text{s}^{-1}$.
- ❑ A very low growth rate, as a consequence of the quick consumption of the supersaturation by means of the ongoing chemical reaction.

THE PROCESS

- ❑ The mixing of the reactants that leads to the formation of the product by the chemical reaction is of great importance concerning the outcome of the process.
- ❑ An insufficient degree of mixing will lead to a reduced formation of nuclei, and as a consequence, a residue of the supersaturation will survive, leading to crystal growth and agglomeration phenomena.
- ❑ A sufficient mixing of the reactants will lead to the formation of many nuclei, in the range of $10^{11} - 10^{16}$ for each cm^3 , of nano or sub-micronic size, in a narrow range (thus giving rise to a product characterized by a narrow particle size distribution, PSD).
- ❑ The high kinetics will not allow to control the habit of the nuclei, that will form mostly spherical or irregularly shaped crystals.

PRECIPITATION OF NANOPARTICLES

- ❑ The precipitation process is of great interest to produce nanoparticles or nanocomposites.
- ❑ Field of interest are:
 - Ceramic materials for the production of pigments, solar creams, coatings.
 - Pharmaceutical products.
- ❑ There are other processes involving inorganic materials such as calcium carbonate, calcium sulfate and phosphates to assist environmental treatment processes.

SOLUBILITY AND SUPERSATURATION

- The driving force of the precipitation process is a high supersaturation value as a consequence of a quick chemical reaction of the reactants, generally both liquid or liquid/gas, giving a poorly soluble product.
- The precipitate co-exists in the bulk solution of the reactants in equilibrium conditions given by the product of solubility K_{sp} .
- For an electrolyte, $A_{v+} B_{v-}$, the supersaturation is expressed by the supersaturation ratio S , with $\pi = a_A a_B$ as a function of the activity values and $K_{sp} = a_{Aeq} a_{Beq}$ as a function of the relative solubilities, as:

$$S = \frac{\pi}{K_{sp}}$$

- The relationship can be approximated as $S = c/c_{eq}$, where c_{eq} is the solubility of the solute (product).

DIMENSION OF THE PARTICLES

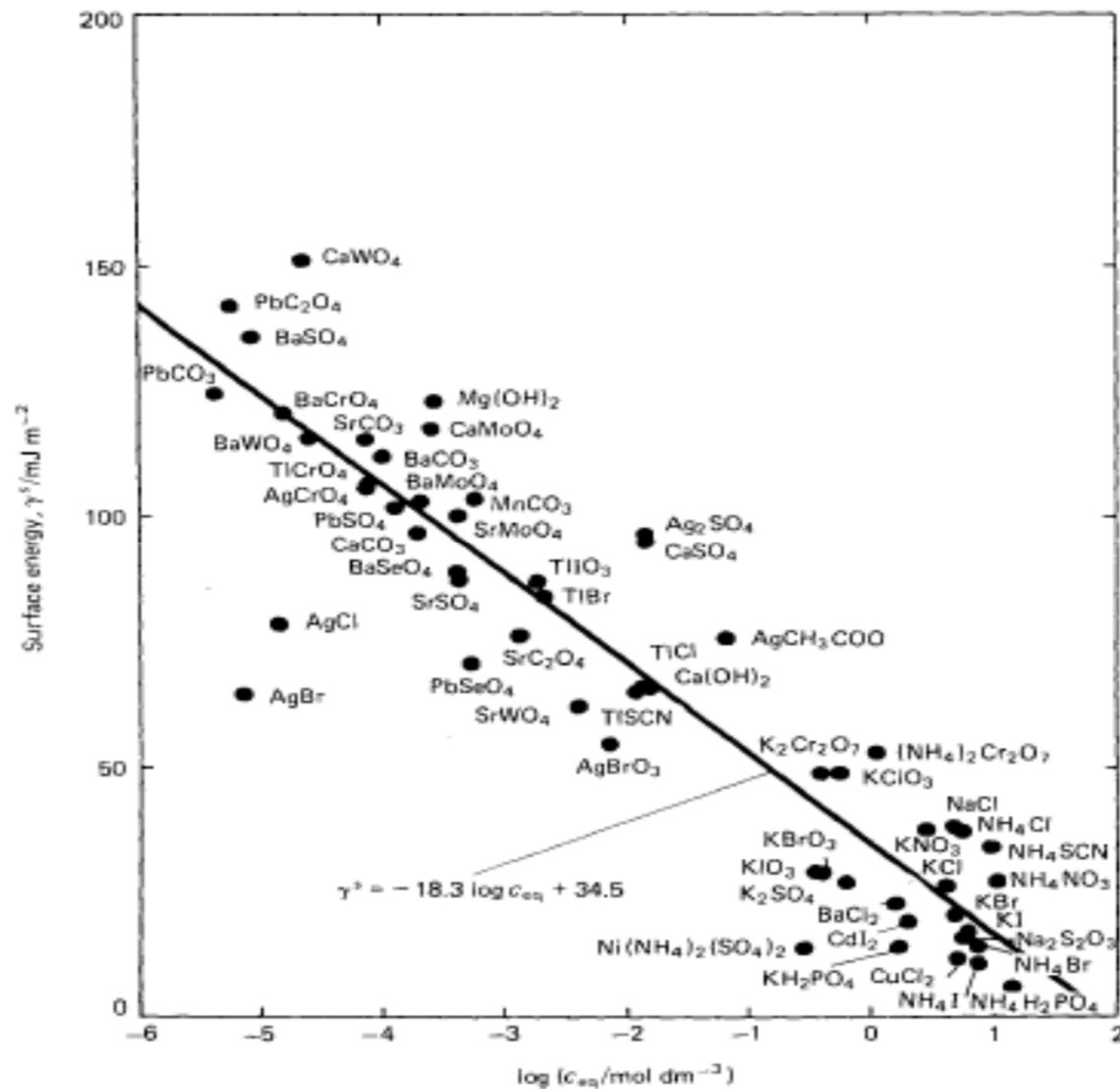
- For sub-micronic particles, the solubility of the crystals is affected by size and can be taken into consideration by using the Gibbs- Thomson equation:

$$\frac{\ln c_{eq}(r)}{\ln c_{\infty}} = \frac{2\sigma V_m}{RT r}$$

where σ is the edge (surface) energy, V_m the molecular volume, R the gas constant and T the absolute temperature.

- Only if the edge energy between solid and liquid is very high the solubility may sensibly change depending on size. For l'AgBr crystals of 50 nm the solubility may be 15 % higher than microparticles.

SOLUBILITY AND EDGE ENERGY



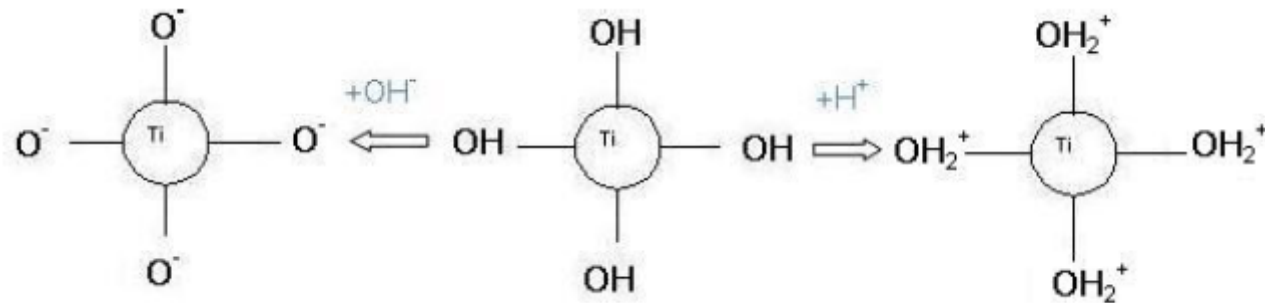
High edge energy \rightarrow low solubility

AGGREGATION OF PARTICLES AND SUSPENSION STABILITY

- The suspensions produced by precipitation may include a large number of nano, sub-micronic and microparticles of very high total surface. The chemistry of these surfaces as well as the stability of the colloids represent a great issue in respect to the suspension stability.
- The aggregation is given by the competition between repulsive and attractive forces.
- Attractive forces are physical ones, Van der Waals, and are proportional to the particle distance as d^{-2} .
- Repulsive forces are of electromagnetic origin, given by the electrical charge of the surfaces leading to the formation of the electric double layer.

ELECTIC CHARGE OF SURFACES

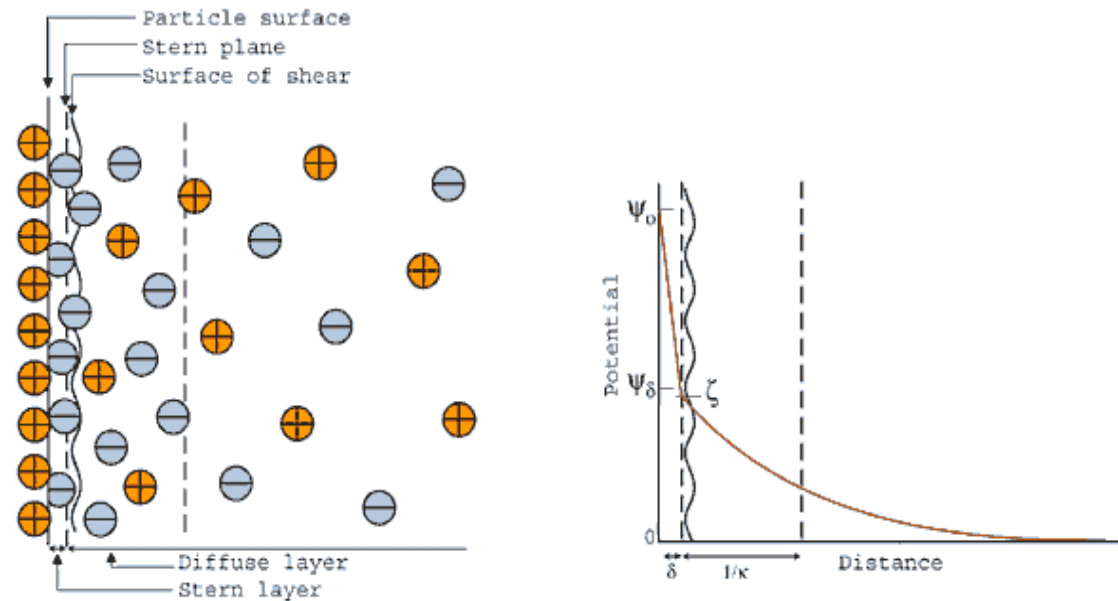
- Dispersed colloids in a solution have high edge energies, and in order to reduce this value, they tend to adsorb on the surface other ions (depending which ions are available in solution, acid or base)



- In order to keep neutrality, the particle will form a second layer which includes ions of opposite charge with respect to the first one.

Z-POTENTIAL

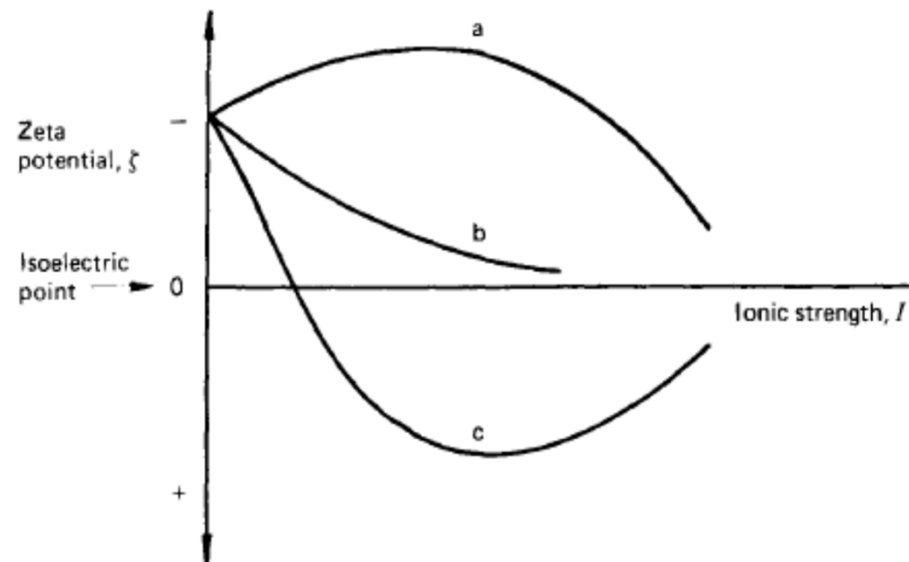
- The difference of electric potential between these two layers is called Z-potential. The first layer is strongly adsorbed on the particle (Stern layer), whereas the second one attaches more freely on the first layer surface, thus “following” the particle at best.



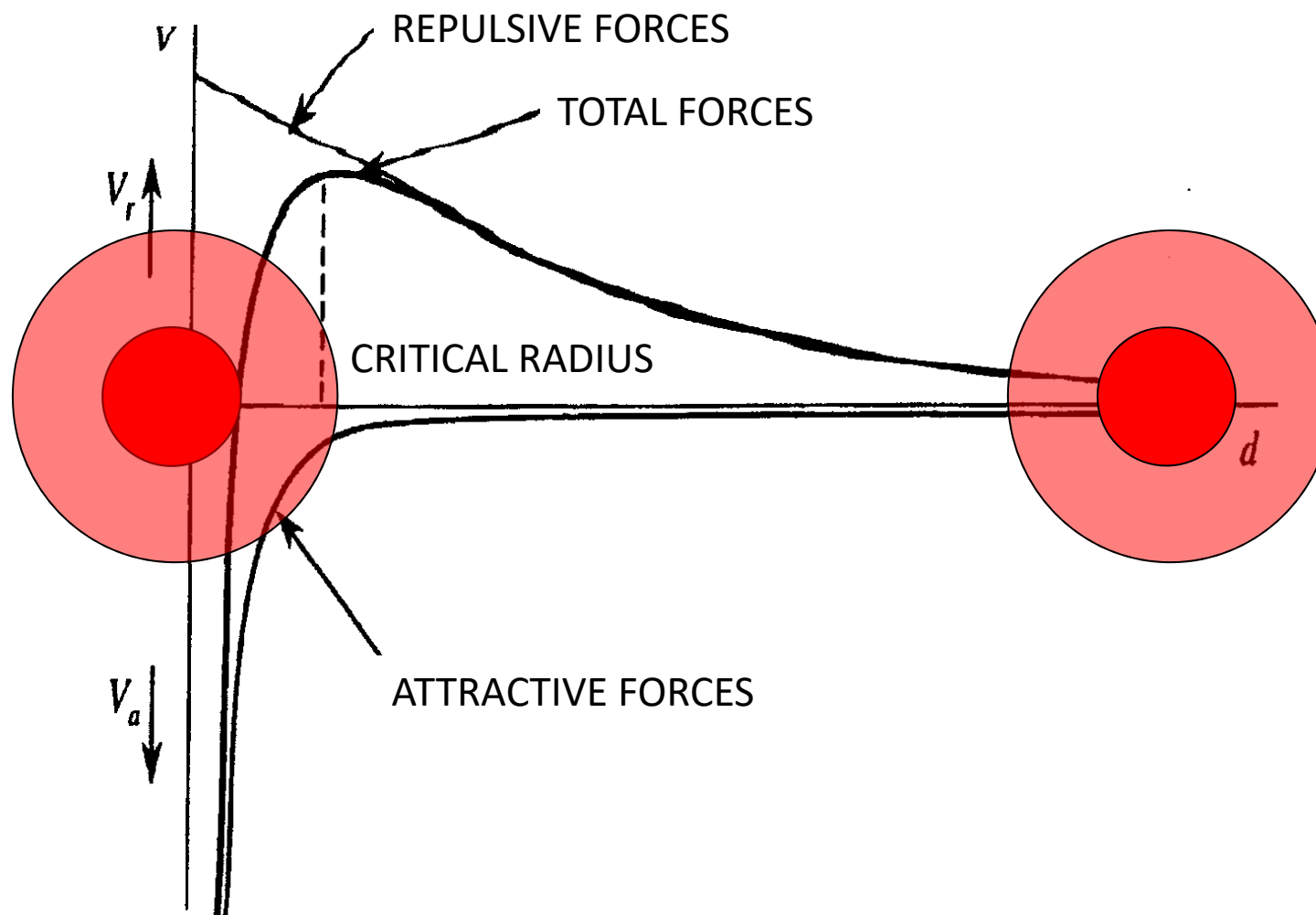
- Scheme of the electric double layer (left) and electric potential (right), being Ψ_0 = the initial value of the potential of the particle and Ψ_δ = the effective potential observed (Z-potential)

Z-POTENTIAL

- The value and sign of the Z-potential ζ are a function of the ionic strength, that is the ion type and concentration. If the concentration of these ions is high, the stability will reduce since they will reach by a greater amount the Stern layer.



ζ will reach a (a) maximum value in presence of mono- or bivalent ions, (b) tend to zero in presence of bivalent ions or (c) cross a minimum in presence of bi- and trivalent ions.

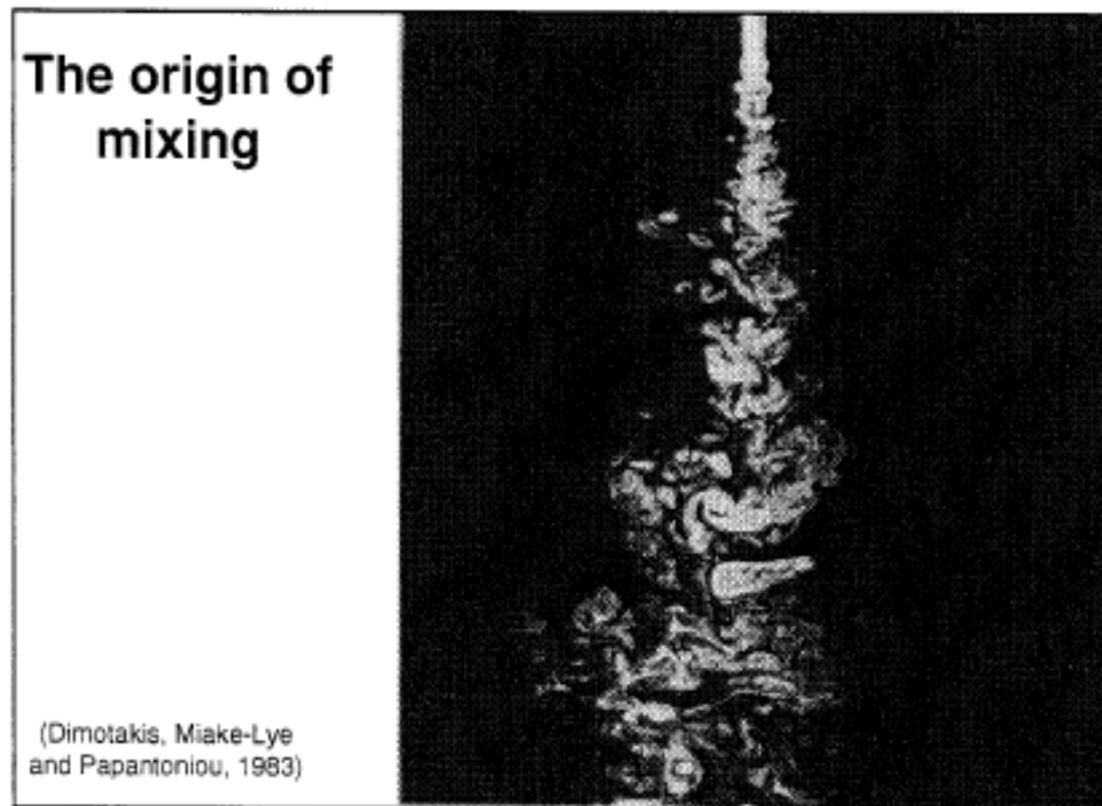


STABILITY

- If the Z-potential value is **outside** the range of ± 30 mV, the suspension is stable, that is agglomeration will not occur as a consequence of the presence of sufficient repulsive forces.
- A process leading to the stabilization of a suspension by repulsive forces is called electrostatic stabilization.
- Another way to stabilize suspensions without addition of ions is by polymers or macromolecules, capable to position themselves between the particles and forming a net in the bulk thus holding the particles at a certain distance (gelatin, surfactants). This latter process is called steric stabilization.

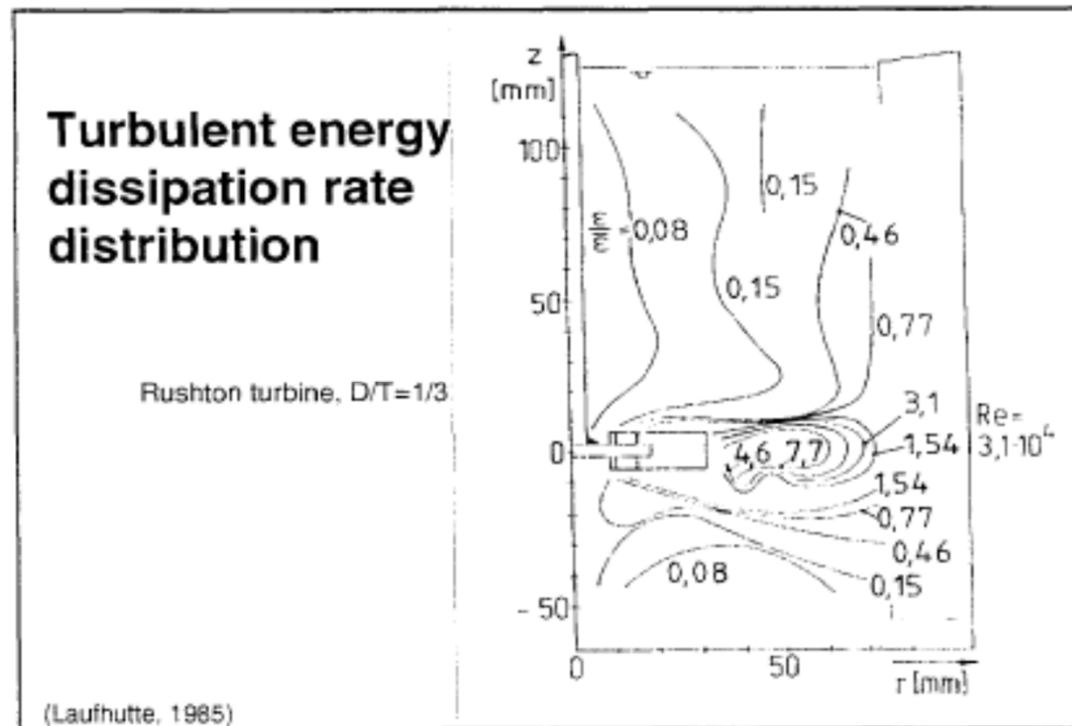
MIXING

- ✓ Mixing is a very complex process that requires several passages to complete.
- ✓ Mixing starts with the disintegration of the liquid in smaller, single volumes that will distribute throughout the reactor and becoming smaller each time.



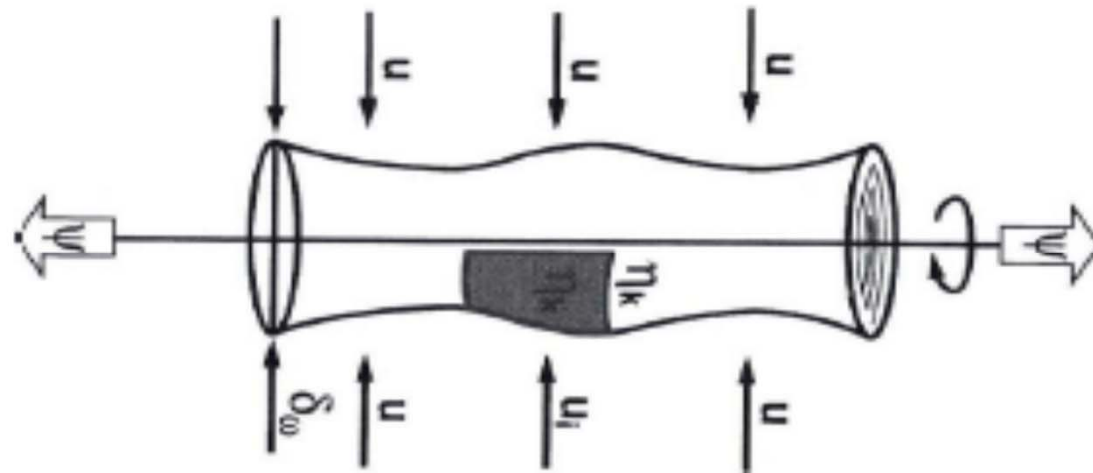
TURBULENCE

- In turbulent regimes, the liquid bulk is transported by means of single, spiral shaped groups of molecules sticking together and called “eddies”.
- The turbulence covers all the three dimensions and will form vortices, given by the fluctuations of the local liquid velocities as soon as motion energy is transferred by the mixing device.



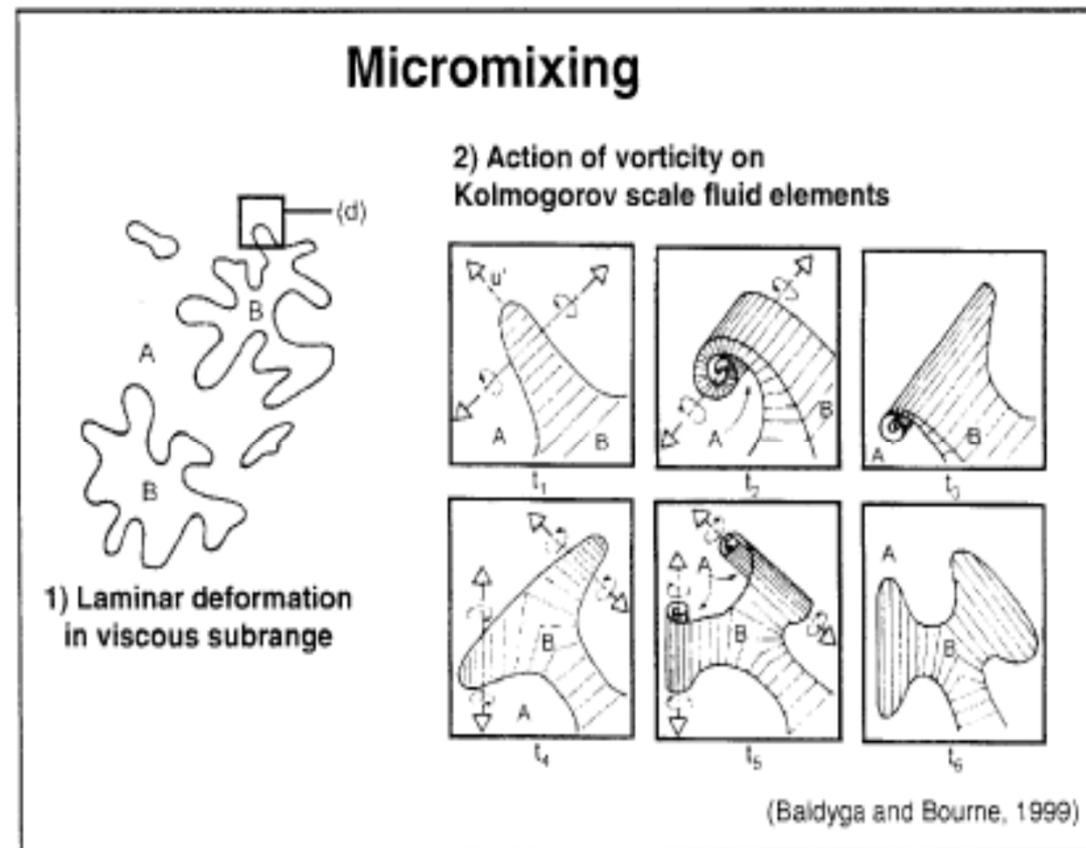
EDDIES

- The eddies will interact with the liquid, and by a spiral motion, will be divided in smaller ones.
- The mixing device transfers energy to the liquid to the bigger eddies, that will transfer energy to the smaller ones.
- The energy spent to the eddies formation will increase the internal energy of the fluid.



KOLMOGOROV SCALE

The smallest eddies that may form are given by the Kolmogorov scale, as a function of the viscous dissipation of the energy in the liquid, thus producing a specific eddies length.



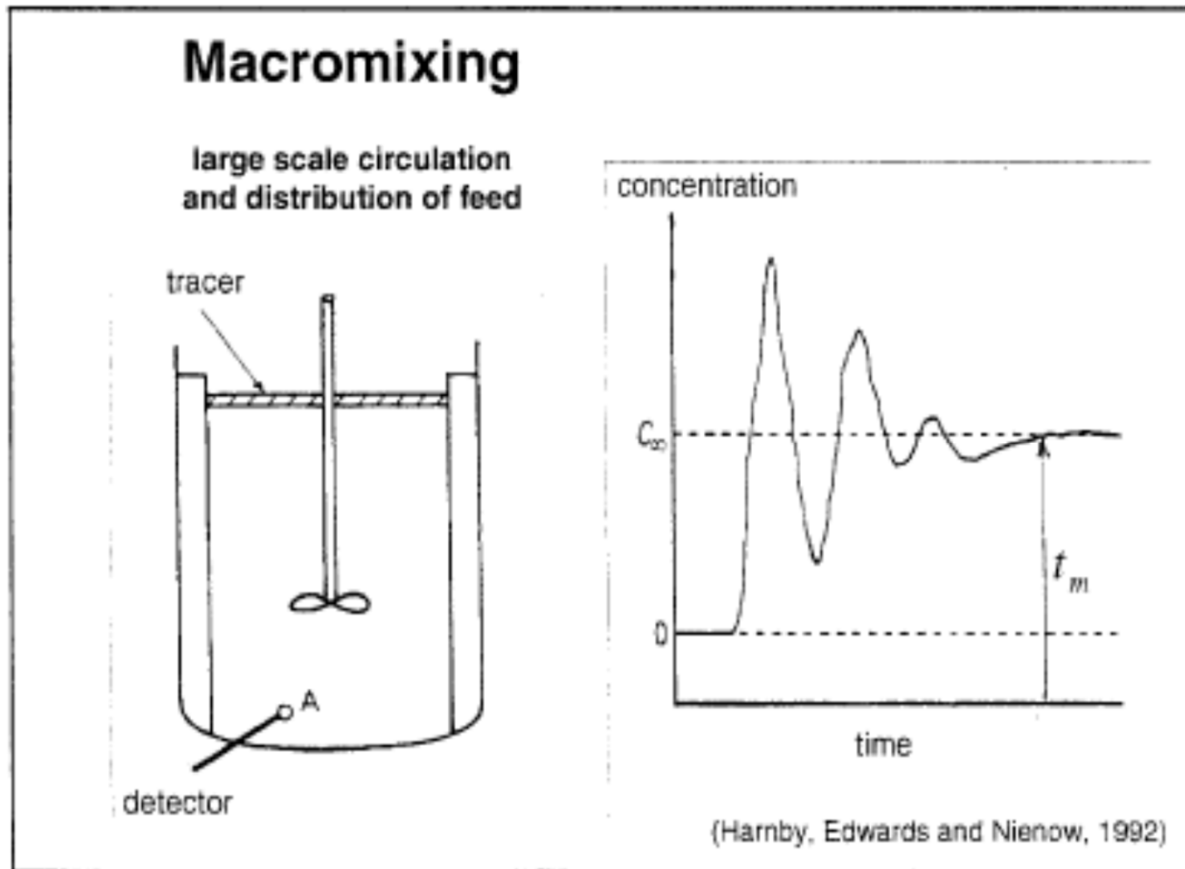
MACROMIXING, MESOMIXING AND MICROMIXING

Mixing is attained by three successive steps:

1. A liquid is dispersed in another one on macro scale, but at micro scale the two liquids are segregated (macromixing) .
2. Segregation of the liquids is still existing but of small entity, the contact surface is very high giving rise to convective mixing (mesomixing).
3. Mixing at molecular level, and segregation of phases disappears. The resulting liquid is homogeneous at molecular scale. (micromixing).

MACROMIXING

The characteristic time is in terms of seconds, and is a function of the equipment design.



$$\tau_c = \frac{V_c}{Q_c}$$

MICROMIXING

- Micromixing depends on the specific energy, not on the equipment. Therefore key to obtain micromixing conditions is the effective and quick energy transfer from the mixing device to the liquid. The micromixing time may be estimated starting from the Baldiga e Bourne (1986) equation:

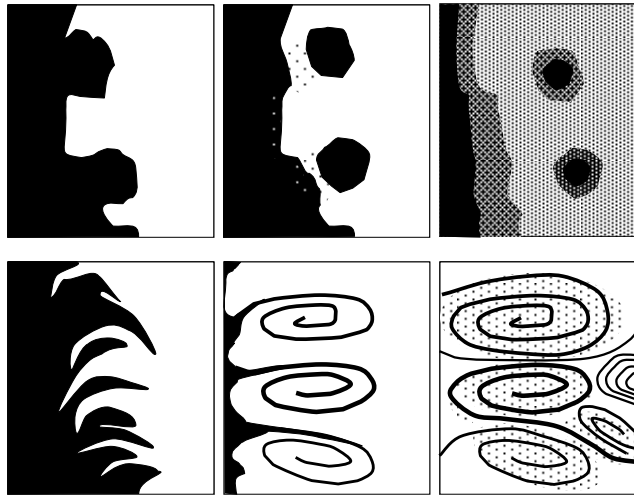
$$\tau_{\omega} \cong 12 \left(\frac{V}{\varepsilon} \right)^{0.5}$$

- The micromixing scale is that of Kolmogorov:

$$\lambda_k = \left(\frac{v_f^3}{\varepsilon} \right)^{1/4}$$

MICROMIXING

- Two mechanisms are possible: laminar distribution or turbulence erosion



- The chemical reaction will take place at the interphase, therefore high interphase surface leads to quick and massive reaction rates.

PRECIPITATION TIME

- The mixing and reaction times must be (in sum) faster than the nucleation time, in order to limit the precipitation process to perform nucleation:

$$t_m + t_r \ll t_{ind}$$

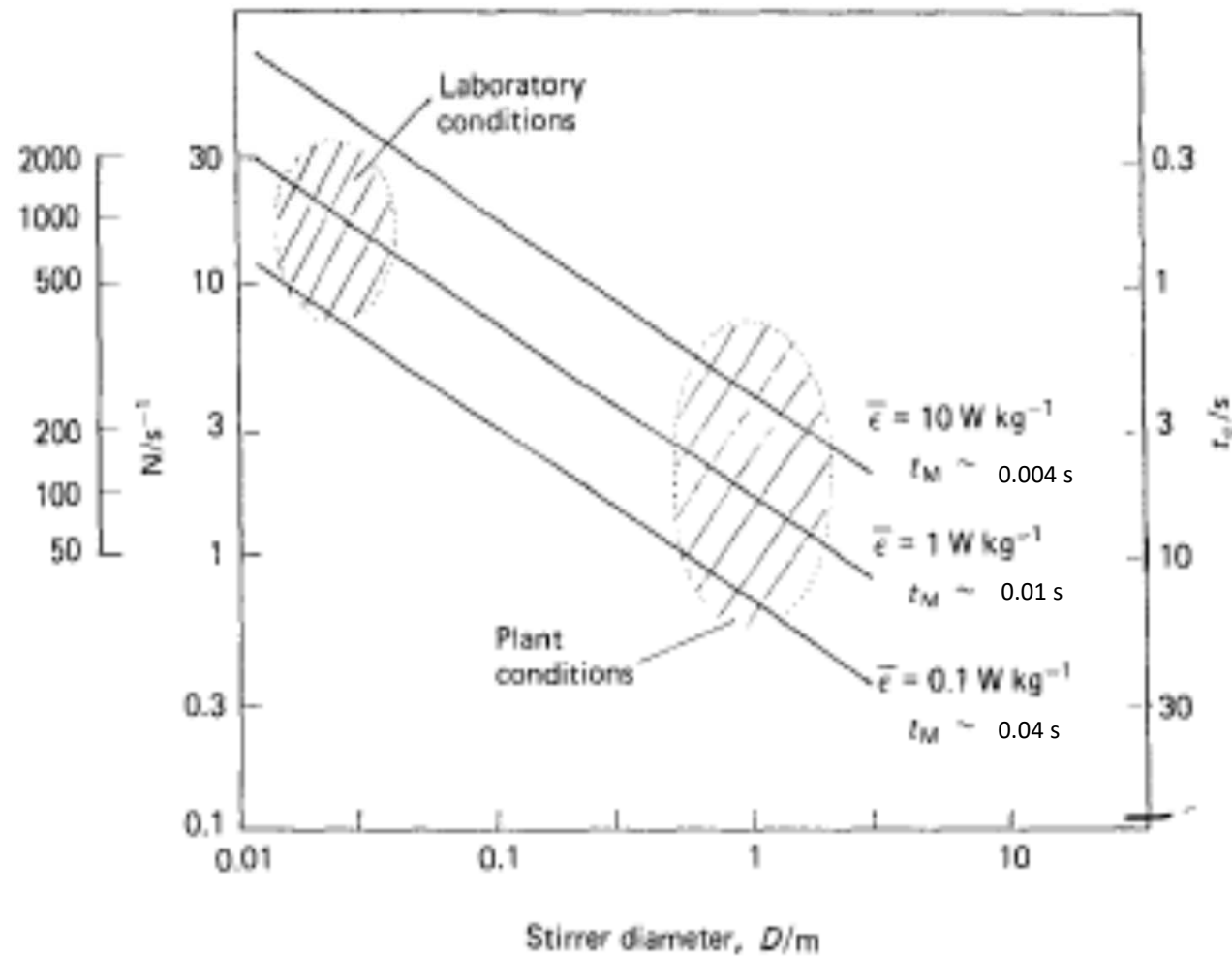
where t_m , t_r , t_{ind} is the time of mixing, reaction and (nuclei) induction.

- Since $t_r \ll t_{ind}$ following condition is generally sufficient to hold:

$$t_m \ll t_{ind}$$

MICROMIXING

- The mixing time given by a Rushton impeller, t_c , is:
$$t_c \cong \frac{V}{v_l} = \frac{V}{N_Q N d_T^3}$$

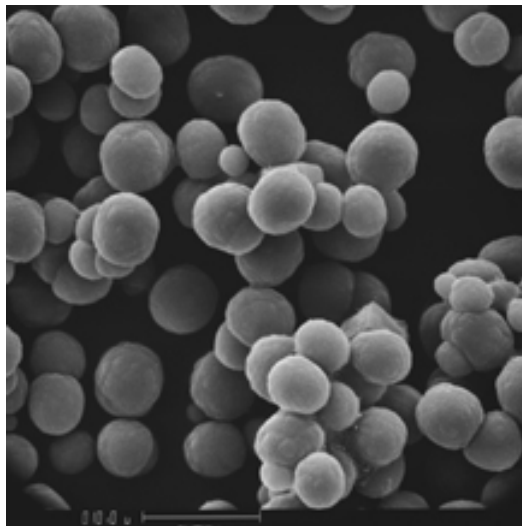


PROCESS INTENSIFICATION

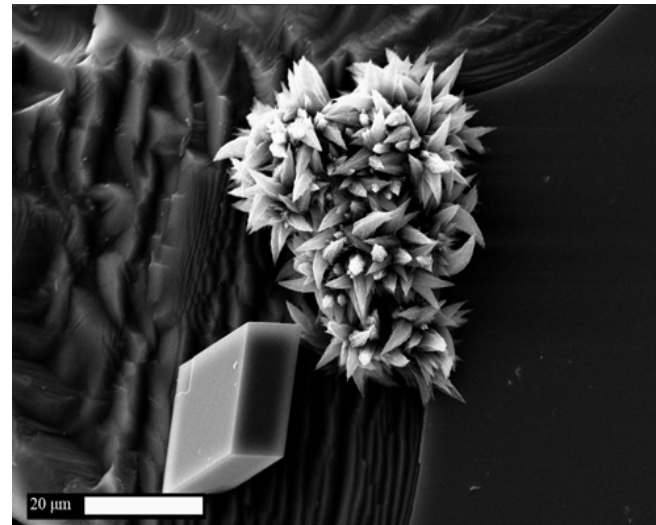
- Many processes aiming the production of nanoparticles will be operated at high supersaturation values, such as $S \cong 1000 \div 10000$, that will lead to induction times as low as milliseconds. Therefore, mixing times must be lower than this!
- Therefore, special equipment is required in order to achieve these very low mixing times such as T-mixers or SDR. The procedure to identify equipment capable to promote extreme operating conditions is called “**process intensification**”.

POLYMORPHISM

- The mixing is important even for the crystal phase and shape. As an example of an example, the precipitation of calcium carbonate at 30°C will lead to vaterite and/or calcite at low, aragonite at high mixing rates.



vaterite



calcite

aragonite