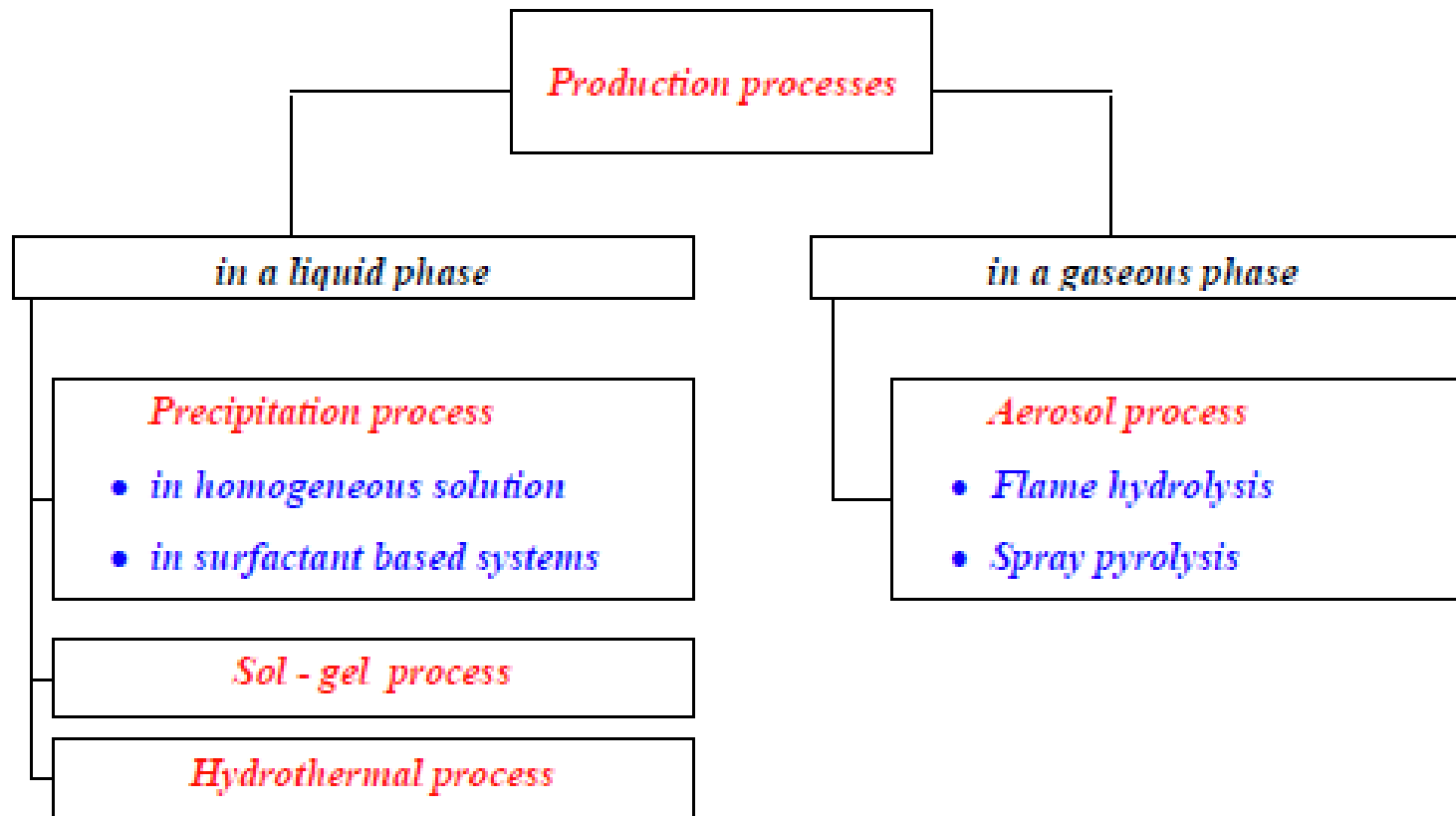
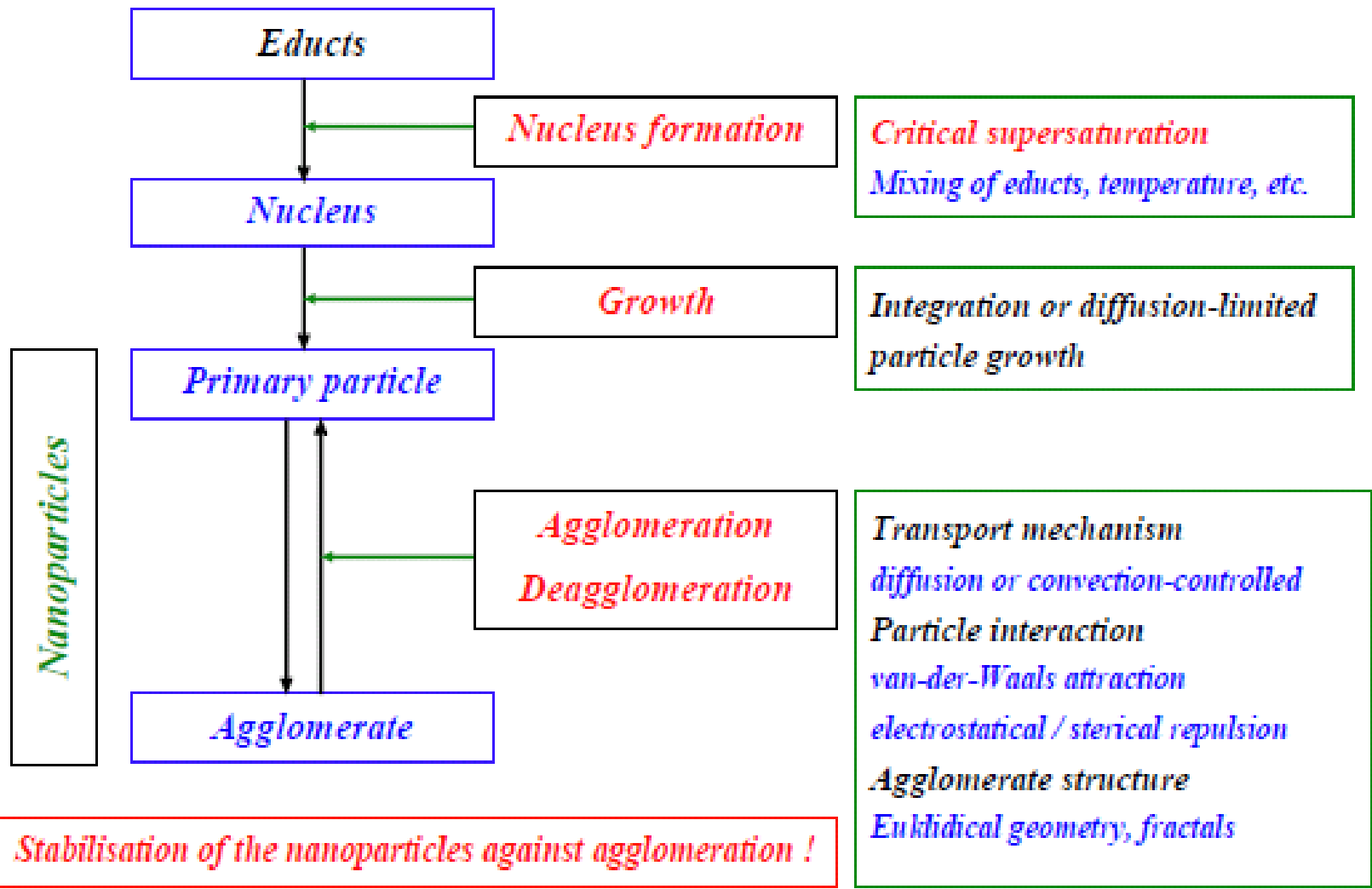


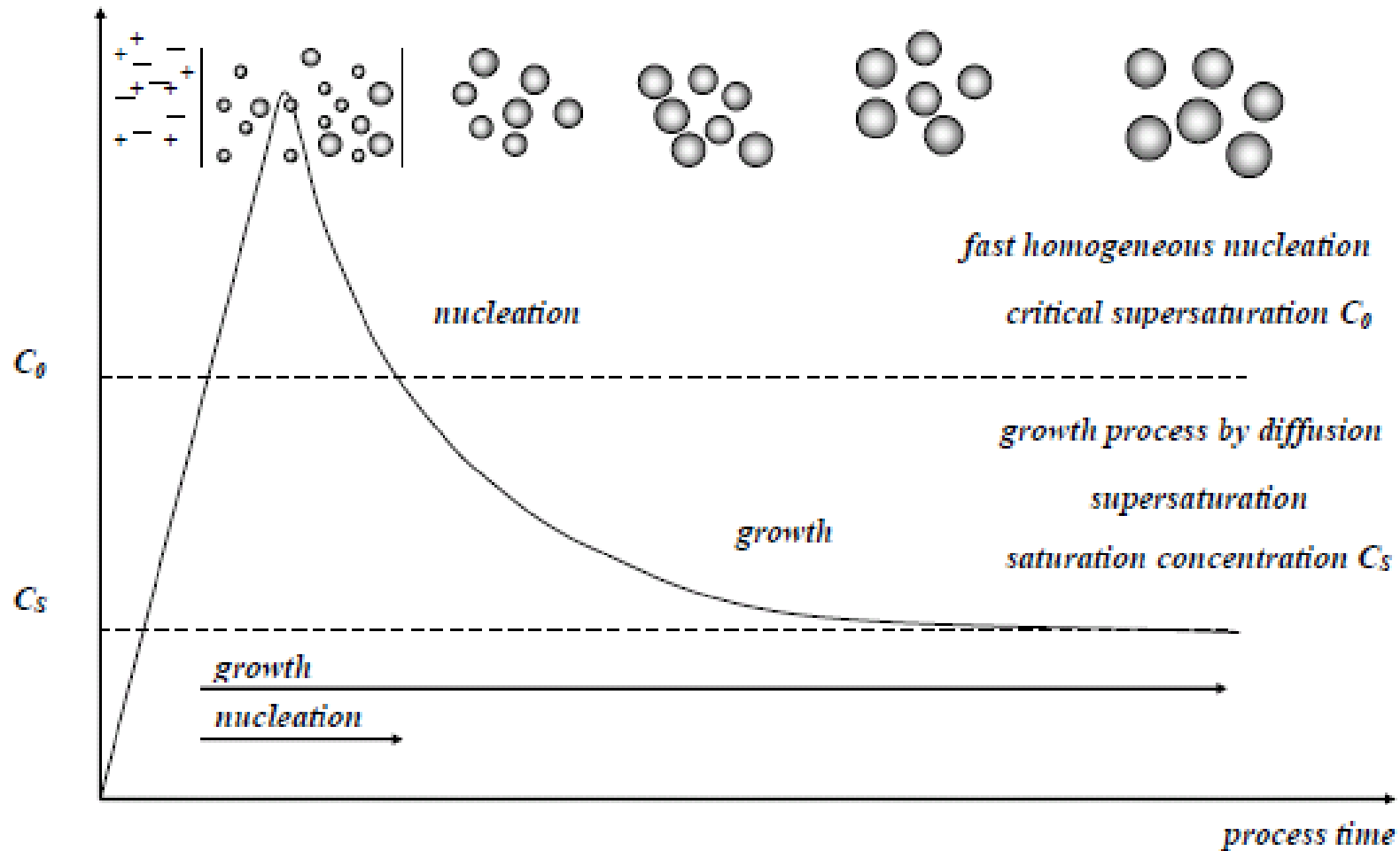
Course „NP in the environment“ - NP preparation

Processes for the production of nanoparticles

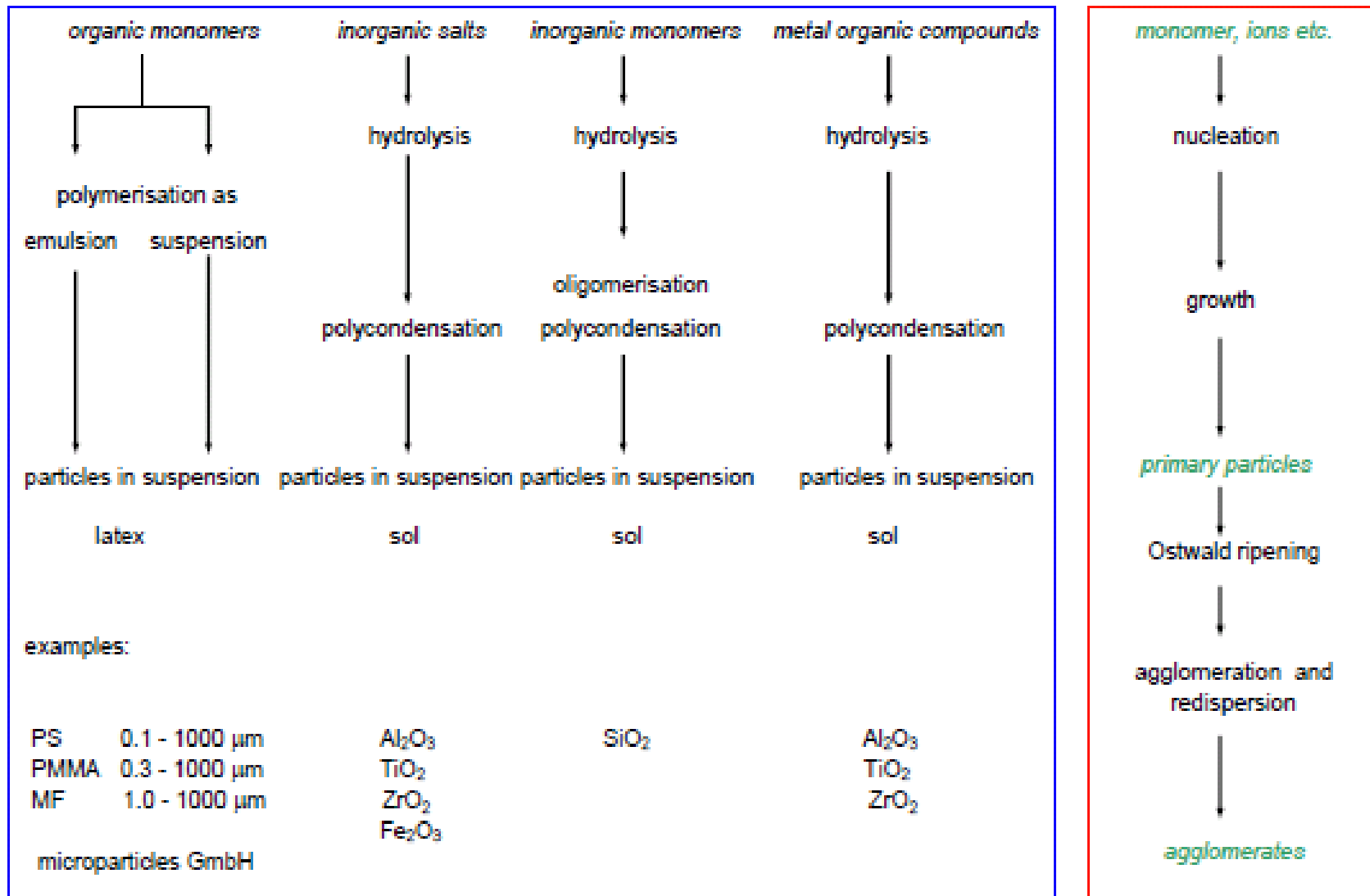




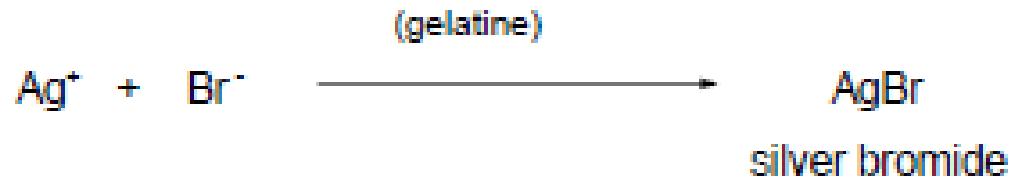
Mechanisms of formation of monodispersed hydrosols, Model of LaMer and Dinegar (1950)



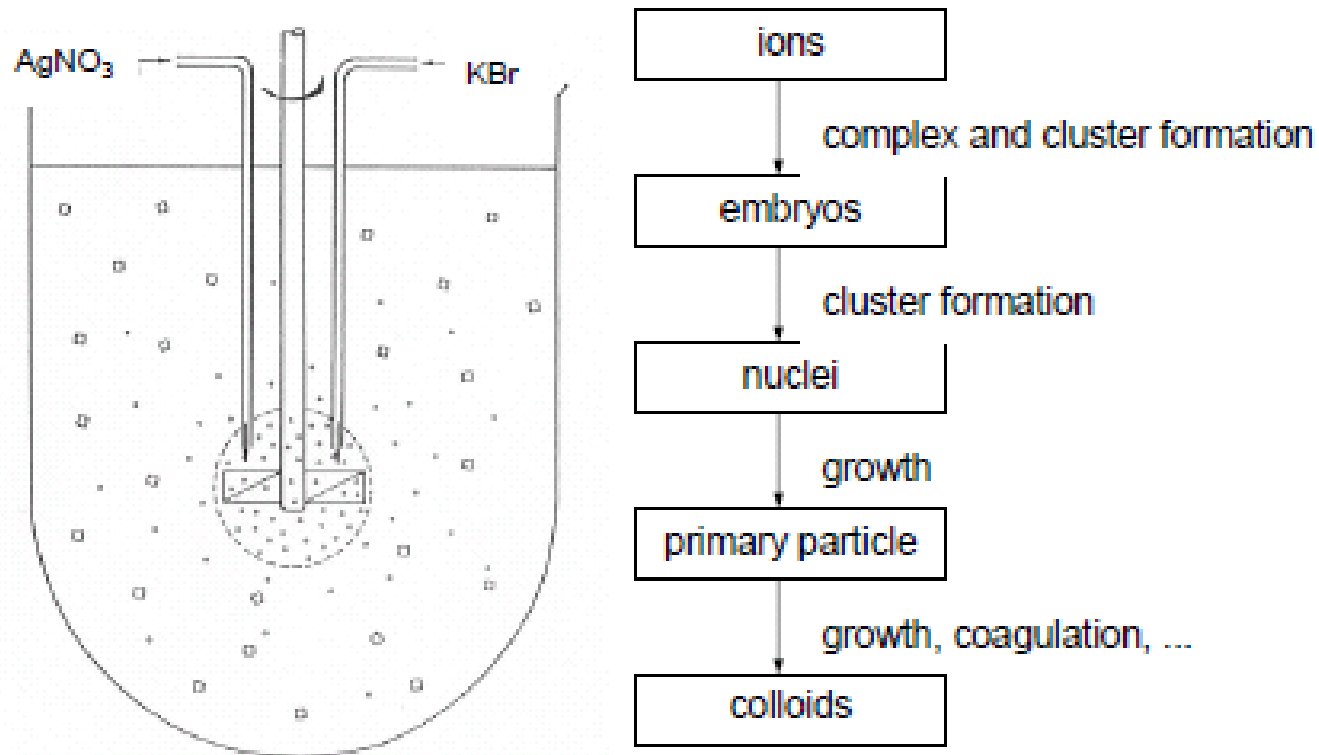
Different approaches to synthesize nanoparticles in liquids



Precipitation – in homogeneous solution, synthesis of silver bromide

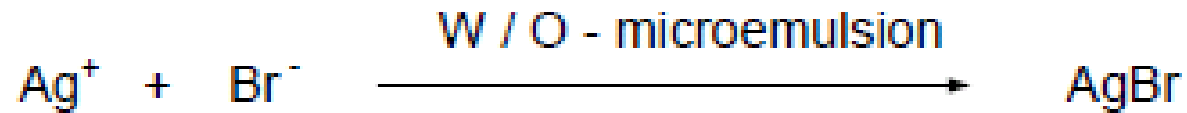


Controlled double jet precipitation technique, nucleus formation, followed by growth reaction and Ostwald ripening

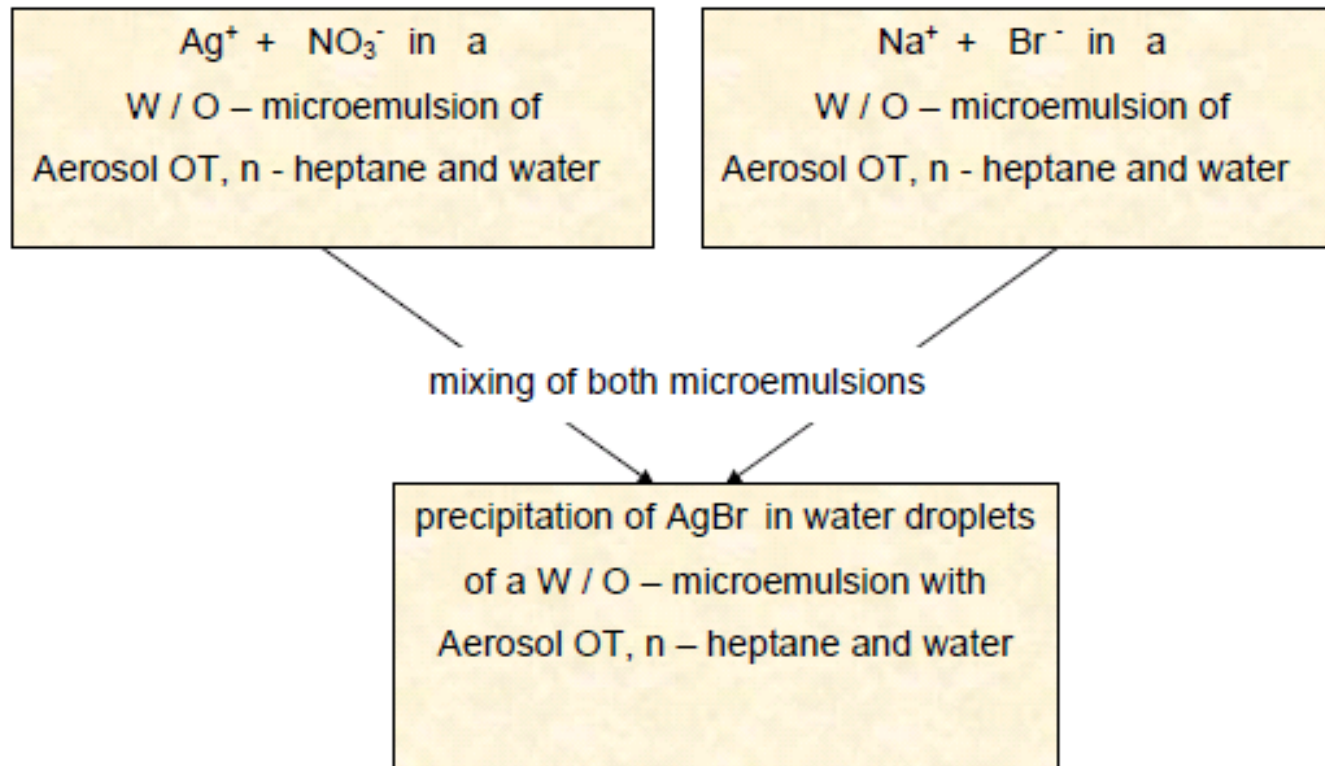


AgBr : 7 nm - 60 nm, particle system dependent
a lot of syntheses on a laboratory scale

Precipitation – in surfactant systems, synthesis of silver bromide



Principle of precipitation in surfactant systems (microemulsions, emulsions etc.)



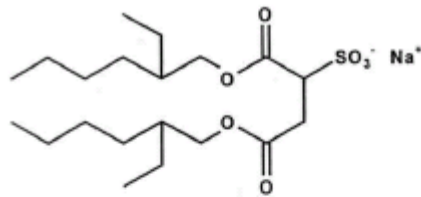
particle sizes: dependent of particle and microemulsion system

advantage: particle size can be controlled by droplet sizes in the microemulsion system

variety of syntheses on a lab scale

disadvantage: particles have up to 80 % of organic compounds

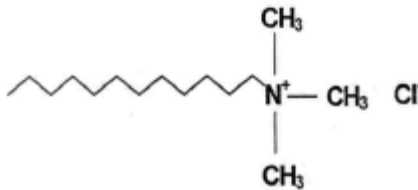
Some surfactants



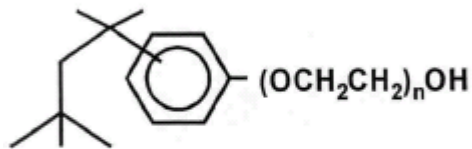
Aerosol OT
Sodium(bis-2-ethylhexyl)sulfosuccinate
(CMC = $2,5 \cdot 10^{-3}$ mol/l; 25°C, H₂O)



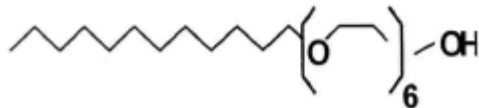
SDS
Sodium dodecyl sulfate
(CMC = $8,1 \cdot 10^{-3}$ mol/l; 25°C, H₂O)



Dodecyltrimethylammoniumchloride
(CMC = $1,7 \cdot 10^{-2}$ mol/l; 25°C, H₂O)

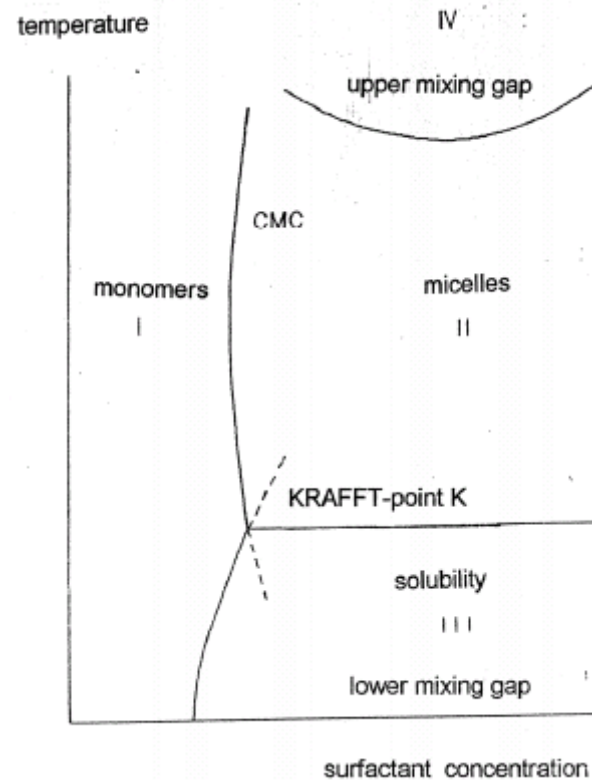


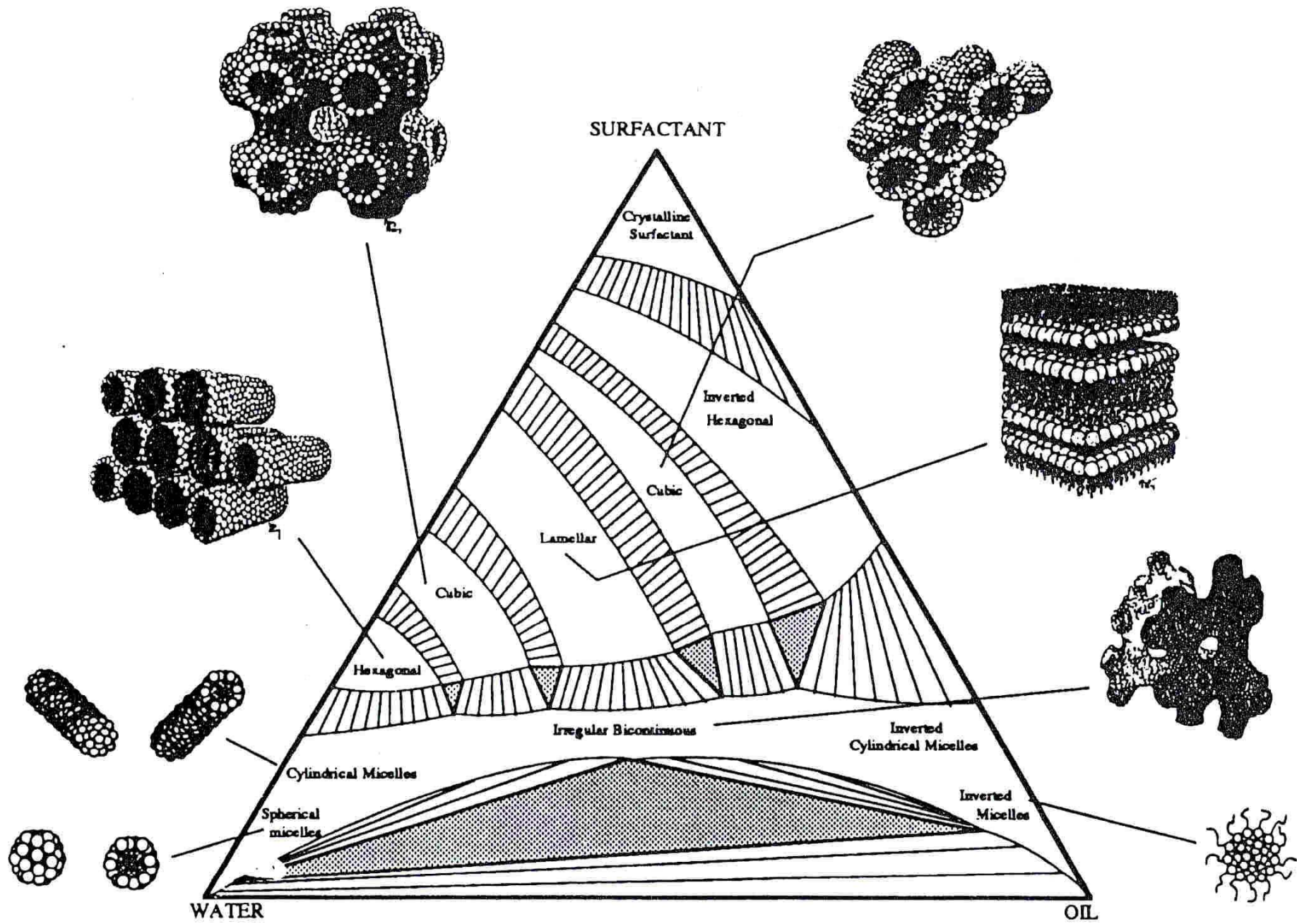
Triton[®]X-100
tert.-Octylphenylpolyethylenglykol
(n=9..10; CMC = $3,16 \cdot 10^{-4}$ mol/l; 25°C, H₂O)



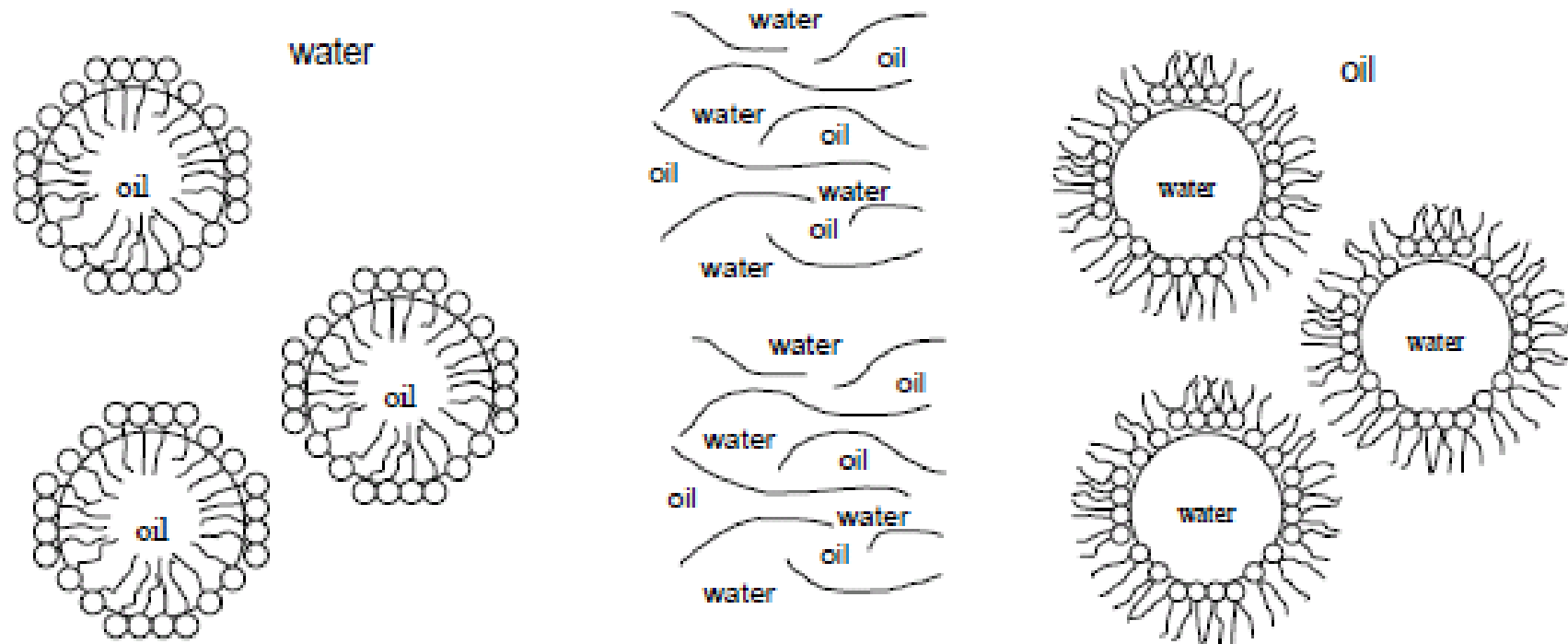
Dodecylhexaethylenglykoether
(CMC = $8,7 \cdot 10^{-5}$ mol/l; 25°C, H₂O)

Phase diagram of aqueous surfactant solution





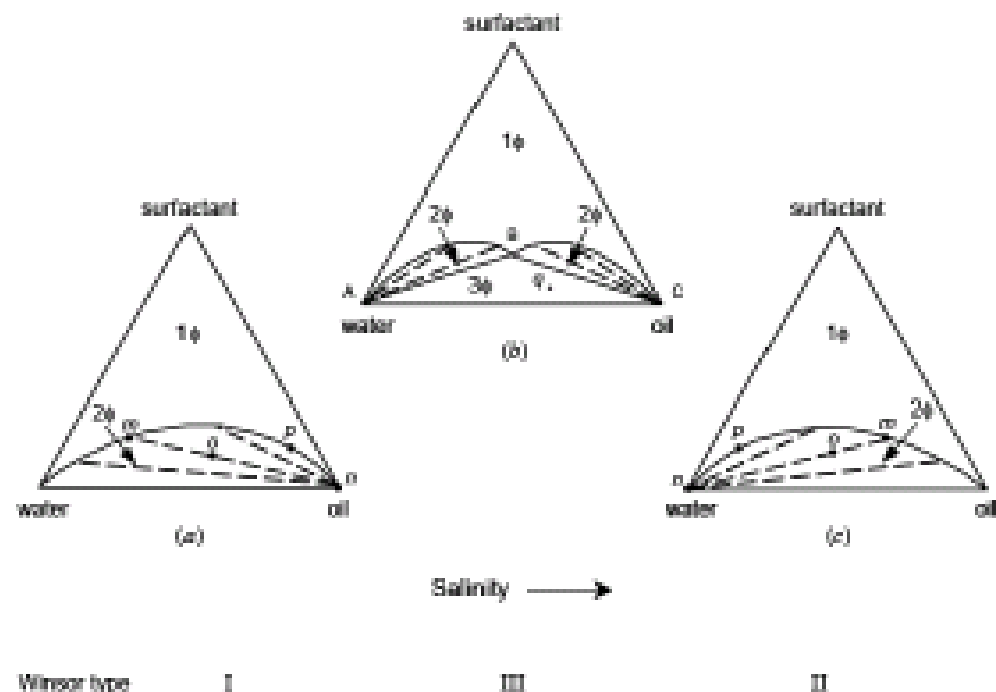
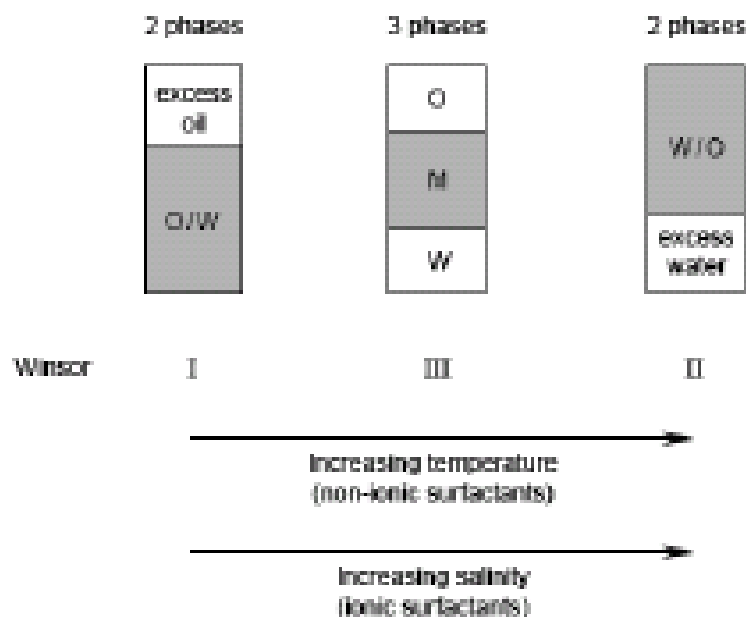
Structures of microemulsions



oil - in - water - microemulsion

bicontinuous microemulsion

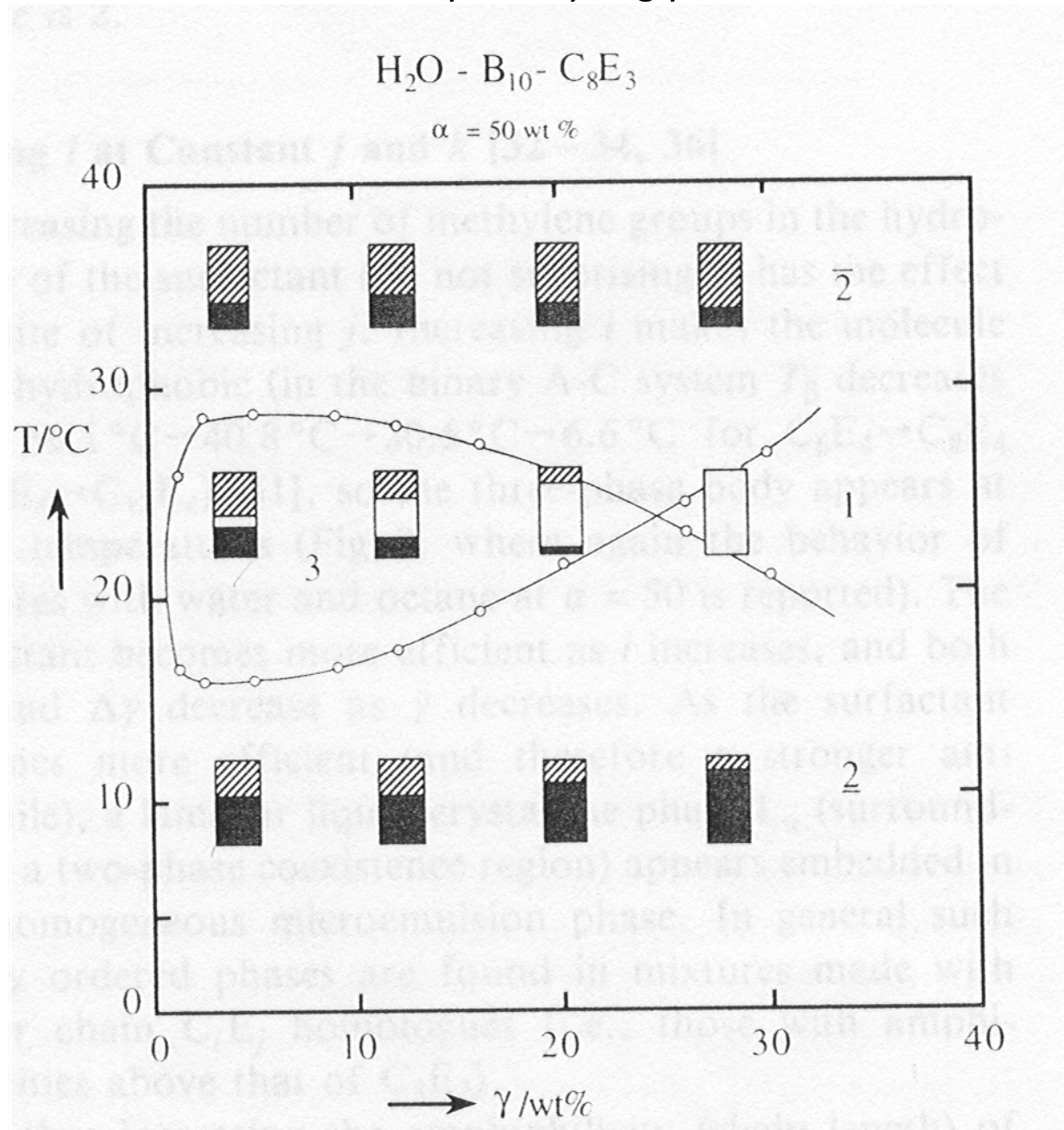
water - in - oil - microemulsion



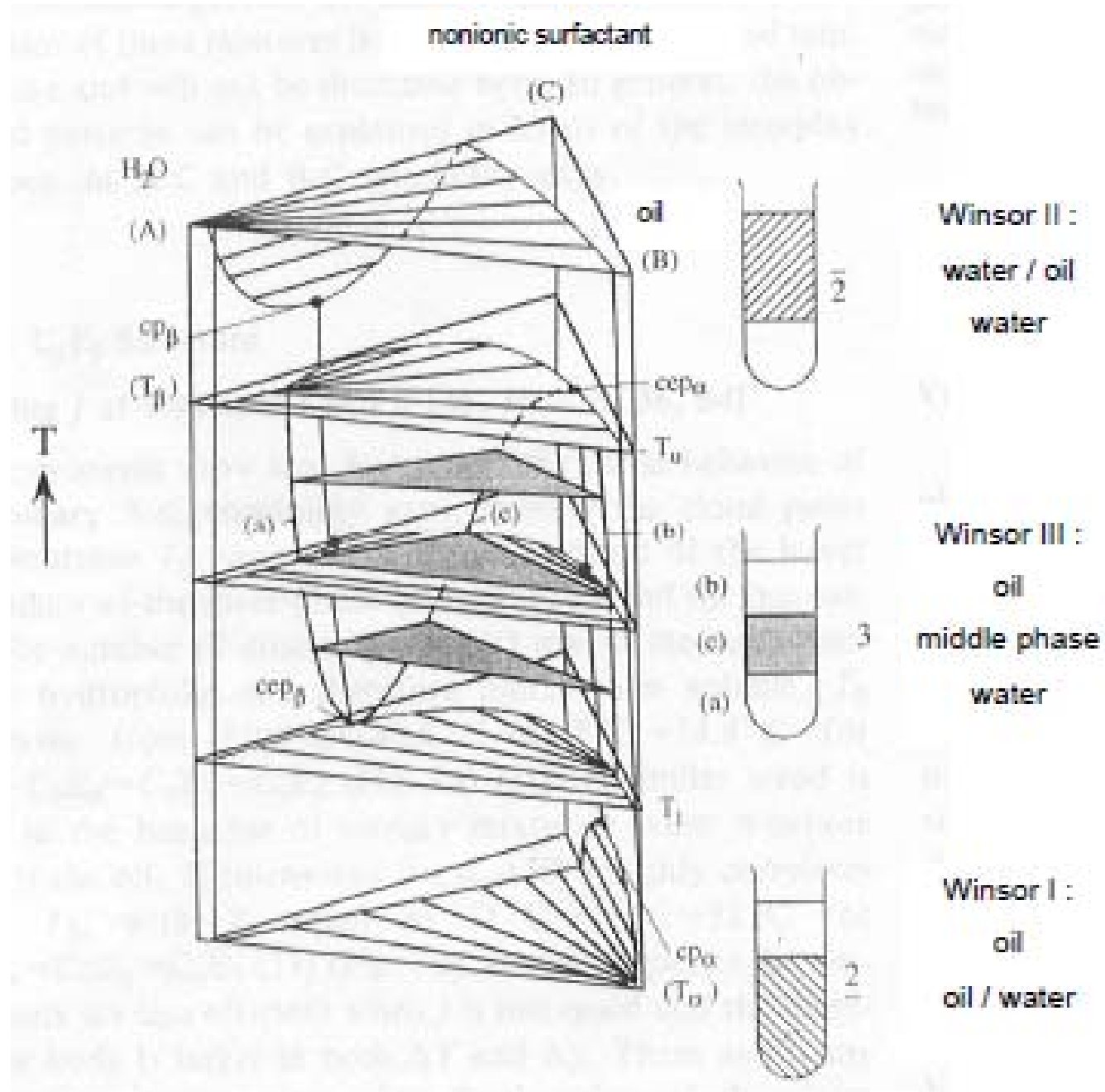
Winsor classification and phase sequence of microemulsions encountered as temperature or salinity is scanned for non-ionic and ionic surfactant respectively. Most of the surfactant resides in the shaded area. In the three-phase system the middle-phase microemulsion (M) is in equilibrium with both excess oil (O) and water (W).

Ternary diagram representations of two- and three-phase regions formed by simple water–oil–surfactant systems at constant temperature and pressure. (a) Winsor I type, (b) Winsor II type, (c) Winsor III type systems.

Phase behaviour of microemulsions, pseudo binary phase diagram of a microemulsion system consisting of water, n – decane and n - hexyltriethylglycolether



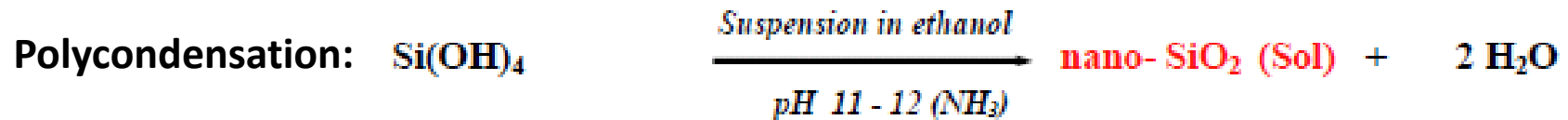
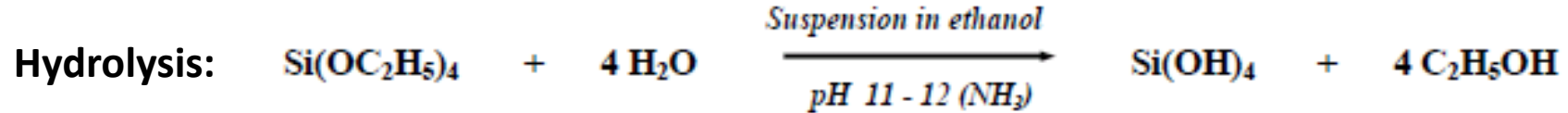
Phase diagram for a ternary system consisting of water - oil - nonionic surfactant



Process: Sol - Gel - Synthesis - Precipitation

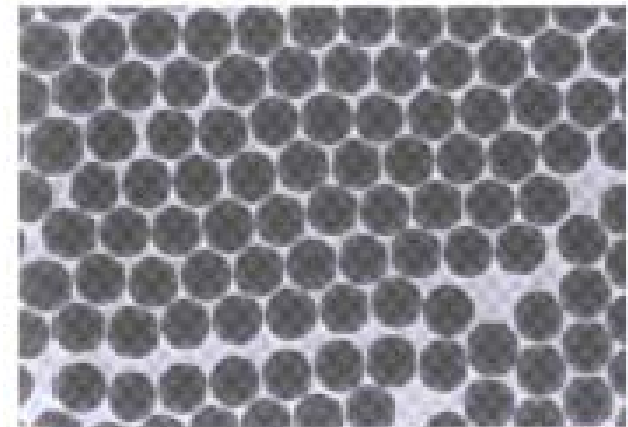
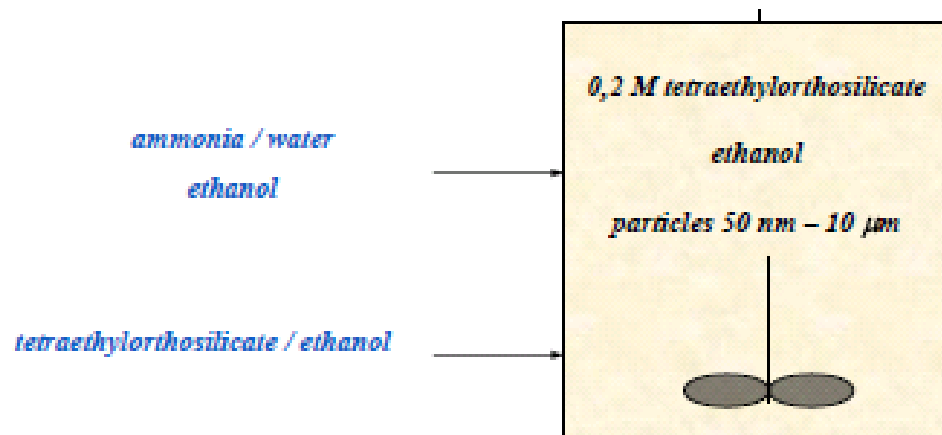
Chemical reactions: Hydrolysis - Polycondensation

Preparation of silica nanoparticles



Principles: Nucleation, nucleus growth, Ostwald ripening, (agglomeration)

Controlled double jet precipitation (CDJP)



Transmission electron microscopy (TEM) image of Stöber particles

Products: titanium (IV) –oxide, aluminium oxide, zirconium (IV)-oxide
nuclear power materials ThO₂, UO₂, PuO₂

(W. Hintz)

Growth mechanisms of particles

Reaction – limited cluster aggregation RLCA

Reaction rate : Hydrolysis \gg polycondensation

pH of suspension : pH in an acid range

Formation of polymer - like networks, porous particle with small pores

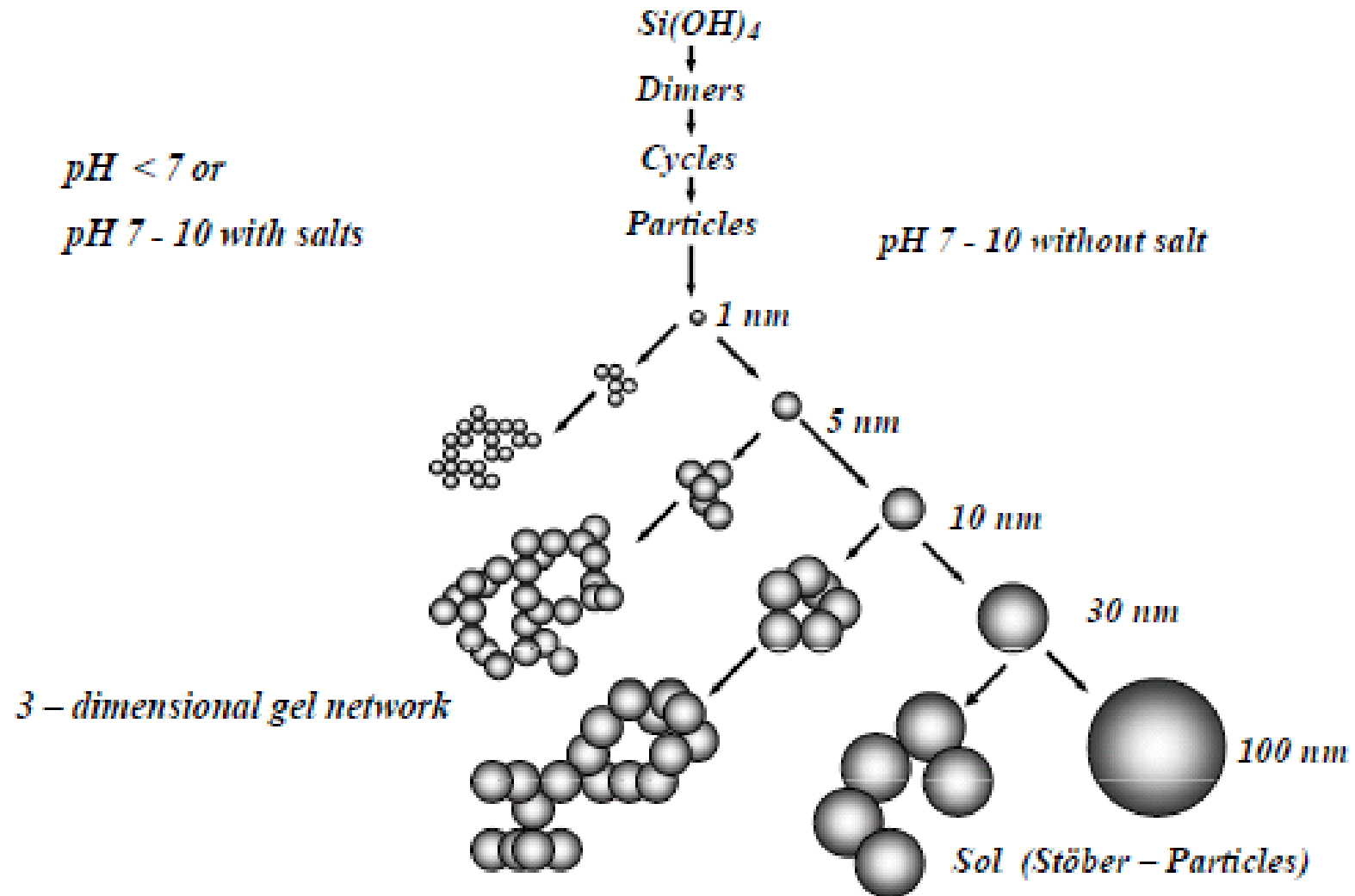
Reaction – limited monomer cluster growth RLMC (Eden growth)

reaction rate : Hydrolysis \ll polycondensation

pH of suspension : pH in an alkaline range

Formation of large, nonporous particles, colloidal gel with large pores

Morphology of silica nanoparticles

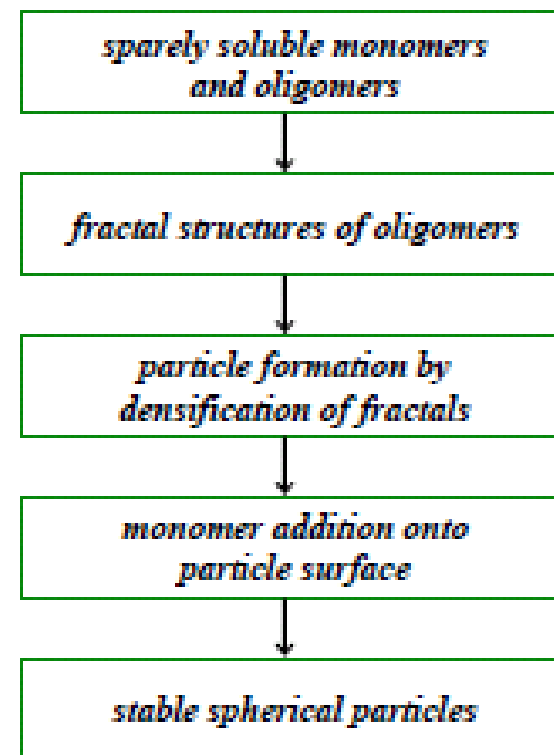
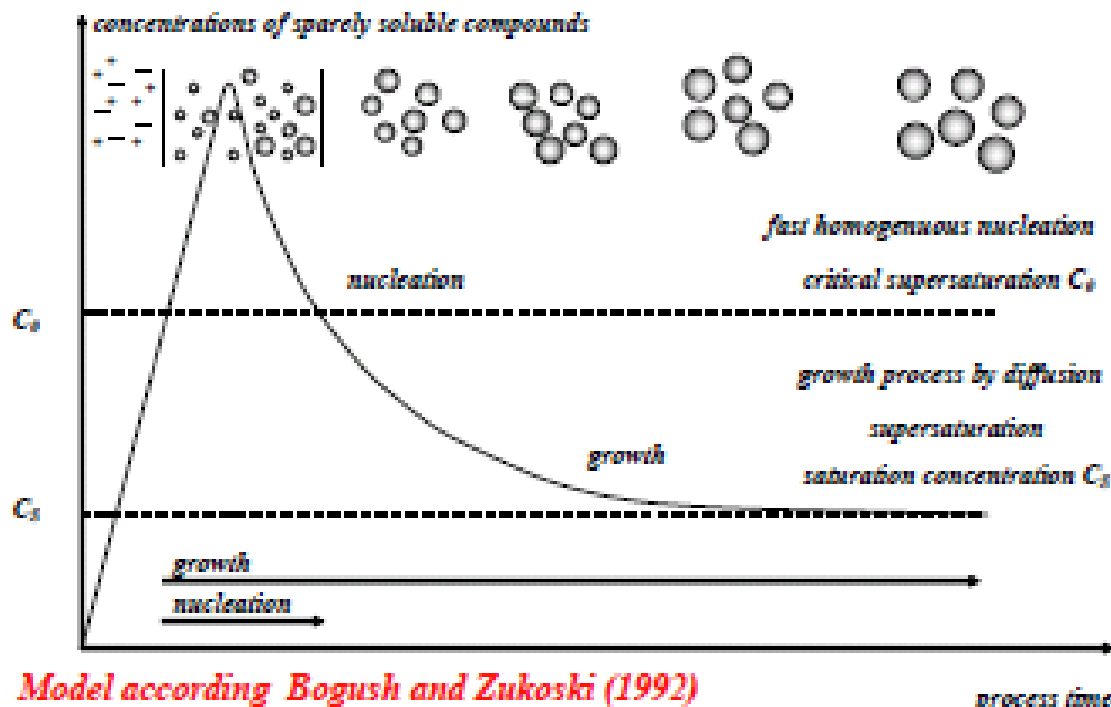


Brinker, C.J.; Scherer, G.W. : Sol-Gel-Science, The Physics and Chemistry of Sol-Gel-Science, Academic Press, San Diego, 1990

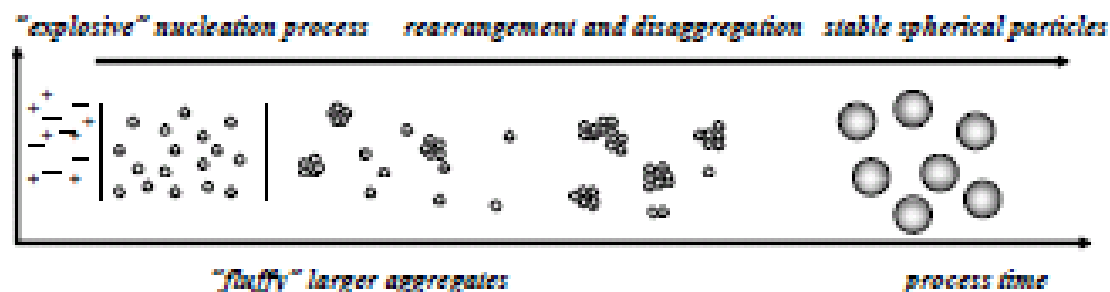
(W. Hintz)

Stöber process for generating monodisperse silica particles particle formation models

Model according LaMer and Dinegar (1950)



Model according Bogush and Zukoski (1992)



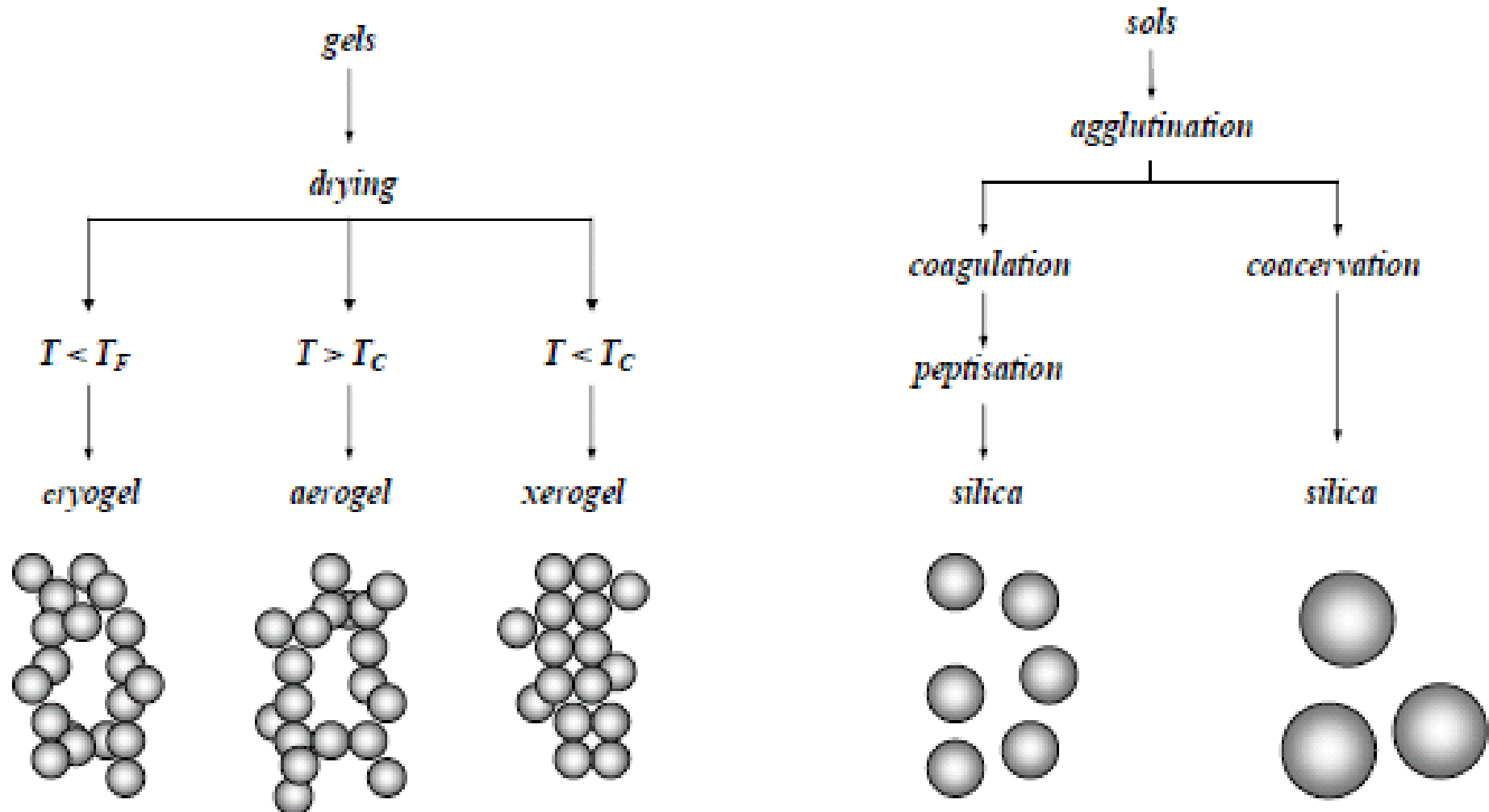
Model according Bailey (1992)

V.K. LaMer, R.H. Dinegar, Theory, production and mechanism of formation of monodispersed hydrosols, J. Amer. Chem. Soc. 72(1950) 4847-4854

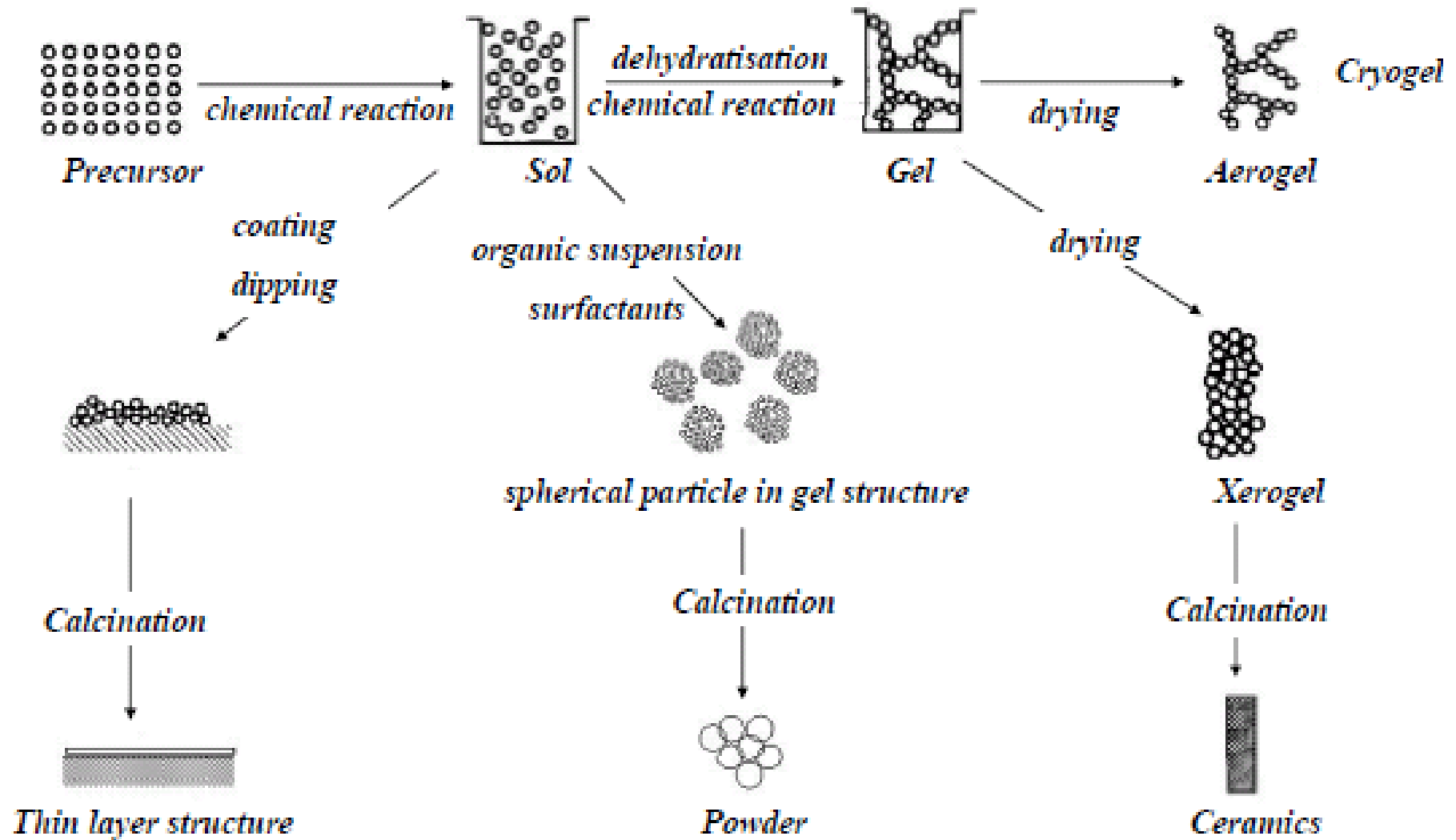
J.K. Bailey, M.L. Mecartney, Formation of colloidal silica particles from alkoxides, Colloids and Surfaces 63 (1992) 151-161

G.H. Bogush, C.F. Zukoski, Uniform silica particle precipitation: an aggregative growth model, J. Colloid Interface Sci. 142 (1992) 19-34

Influence of pH and drying conditions on the morphology of silica particles



Sol - gel processing

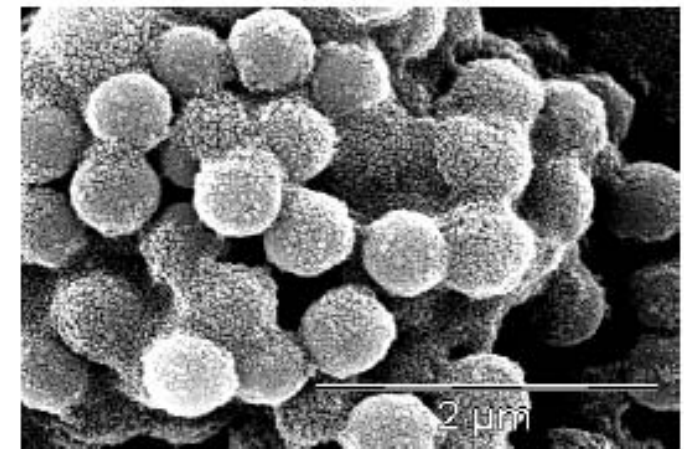
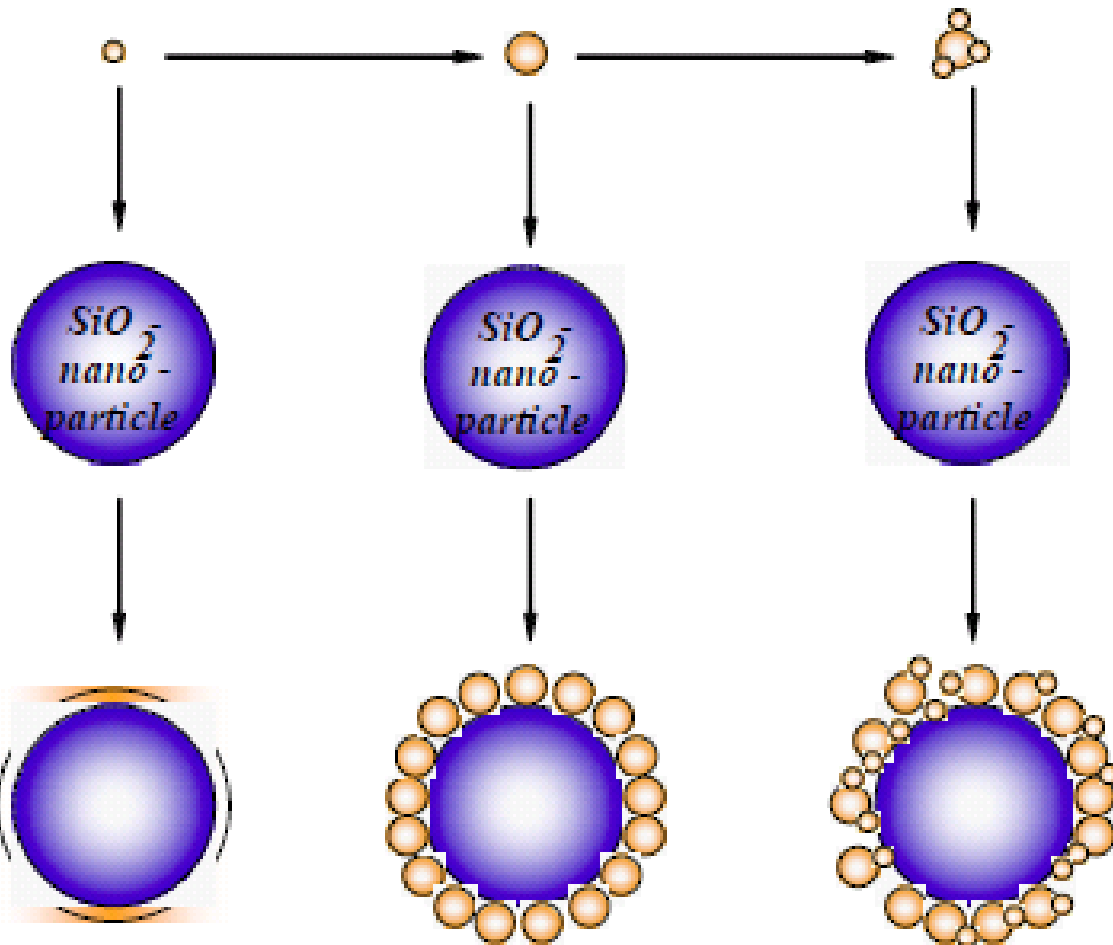


C.J. Brinker, G.W. Scherer: Sol-Gel Science, The Physics and Chemistry of Sol-Gel Processing, Academic press, San Diego, 1990

(W. Hintz)

Coating processes by TiO_2

precursor TiO_2 nanoparticle TiO_2 agglomerate



SEM image for coated 332 nm silica with 20 % (wt/wt)

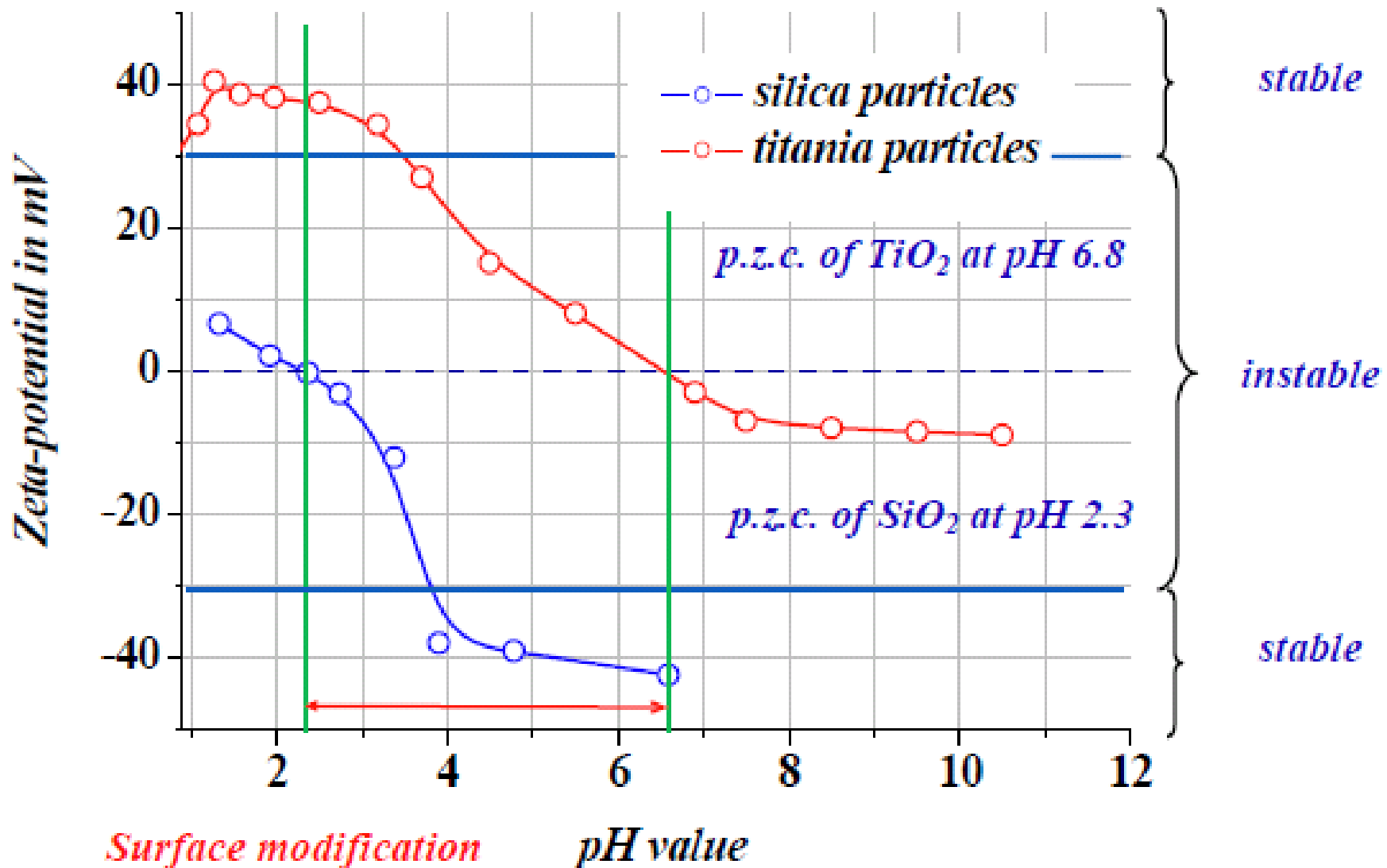
*dense, closed
 TiO_2 layer*

*homogeneous layer of
mono-disperse TiO_2*

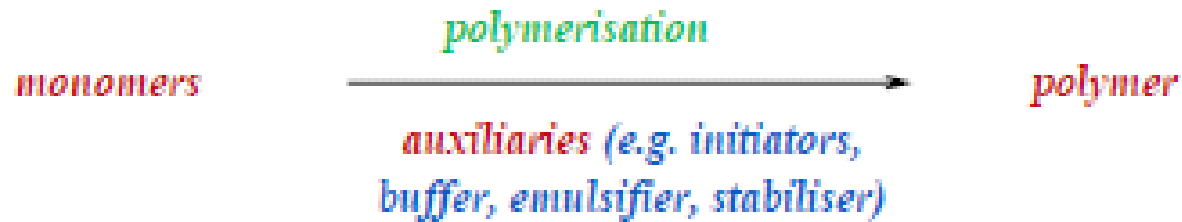
*heterogeneous layer of
polydisperse TiO_2 particles*

Hetero-agglomeration process for coating silica particles with titania

Zeta-potential of silica and titania particles in dependence of the pH value

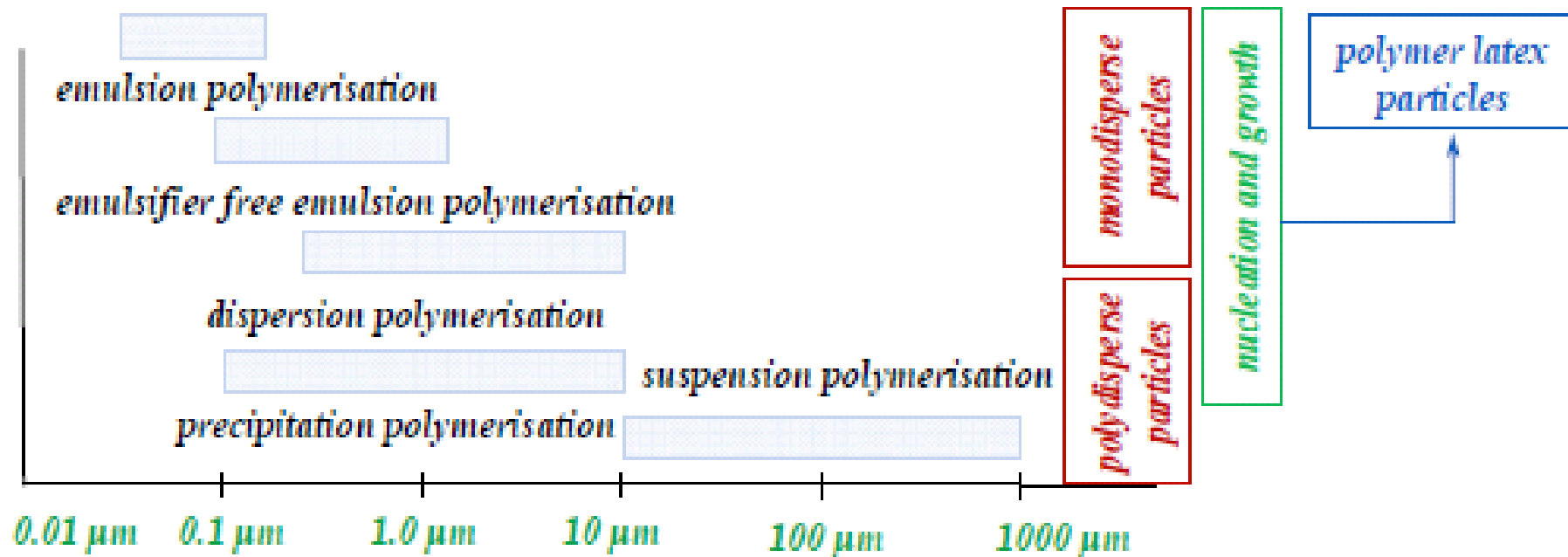


Heterogeneous polymerisation techniques of particle formation

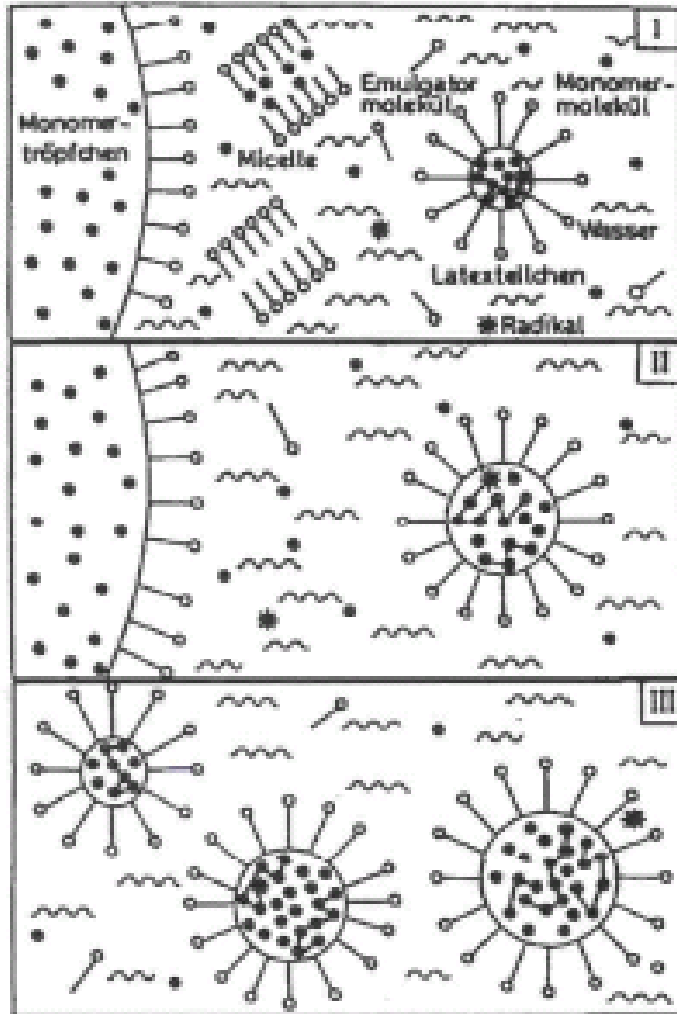


Homogeneous systems: bulk polymerisation, solution polymerisation → bulk polymeric mass

Heterogeneous systems: emulsion polymerisation, suspension polymerisation, dispersion polymerisation, precipitation polymerisation, miniemulsion polymerisation → latex particles



Emulsion polymerisation process



I) Particle formation (Nucleation)

Period of Inside the O/W emulsion, there are micelles (5-10 nm), surfactant stabilized monomer droplets (1-10 μm), and initiator (e.g. hydrochloric acid, γ , OH-). Monomer is (a) solubilised inside micelles, and sparsely dissolved in water. Initiator forms monomer ions, with the in water sparsely soluble monomer (N-butyl-2-cyanoacrylate) oligo-ions. These oligo-ions are stabilized by surfactant (swollen micelles), or solubilised in monomer containing micelles. Polymerisation starts; formation of small latex particle.

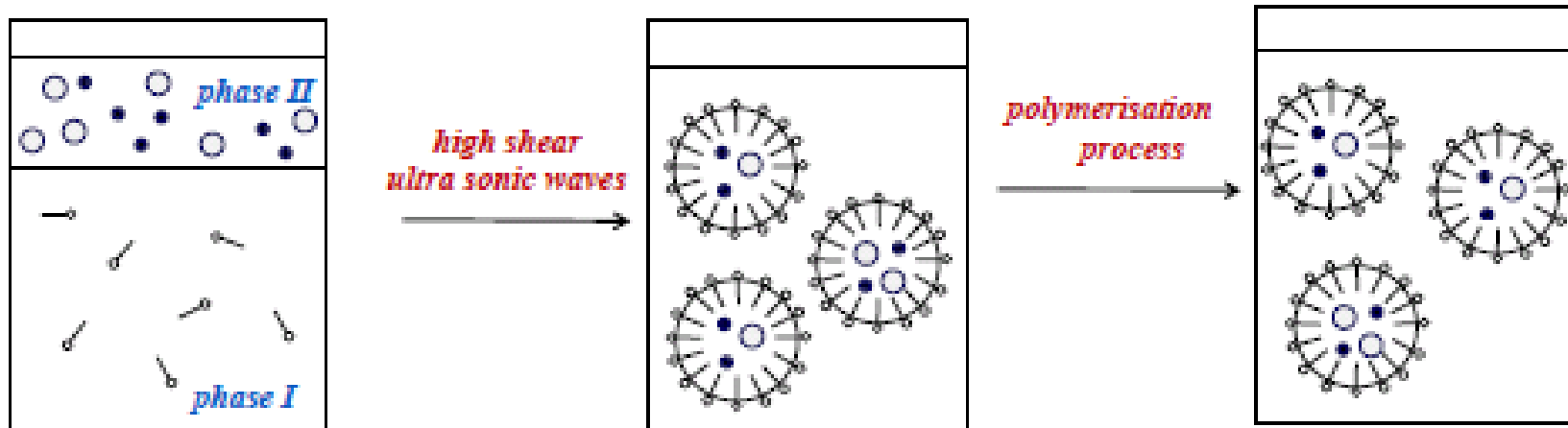
II) Period of growth

Latex particles grow until monomer droplets in emulsion are gone. Increasing surface area of the latex particle adsorbs more surfactant molecules, no micelles. Disappearance of droplets.

III) Period of final polymerisation

Remnants of monomers in the latex particles (50-300 nm) are polymerized

Polymerisation process in mini-emulsions



phase I: water
surfactant
initiator

phase II: oil
monomer

nanodroplets:
kinetically stable
small (100 - 500 nm)
homogeneous in size

nano-reactors: 100 - 500 nm
polymer particle is 1:1 copy
of nanodroplets

Laplace pressure:

$$\Pi_L = \frac{2 \cdot \sigma}{r}$$

Shear rate to rupture:

$$\dot{\gamma} = \frac{\sigma}{r \cdot \eta_r}$$

Physical characteristics of emulsion droplets

<i>radius</i> <i>in nm</i>	<i>Laplace pressure</i> <i>in MPa</i>	<i>shear rate to rupture</i> <i>in s⁻¹</i>
10	2.0	10 ⁸
100	0.2	10 ⁸
1,000	0.02	10 ⁷
10,000	0.002	10 ⁶

micro-emulsion: thermodynamically stable emulsion (oil, water, surfactant, co-surfactant)

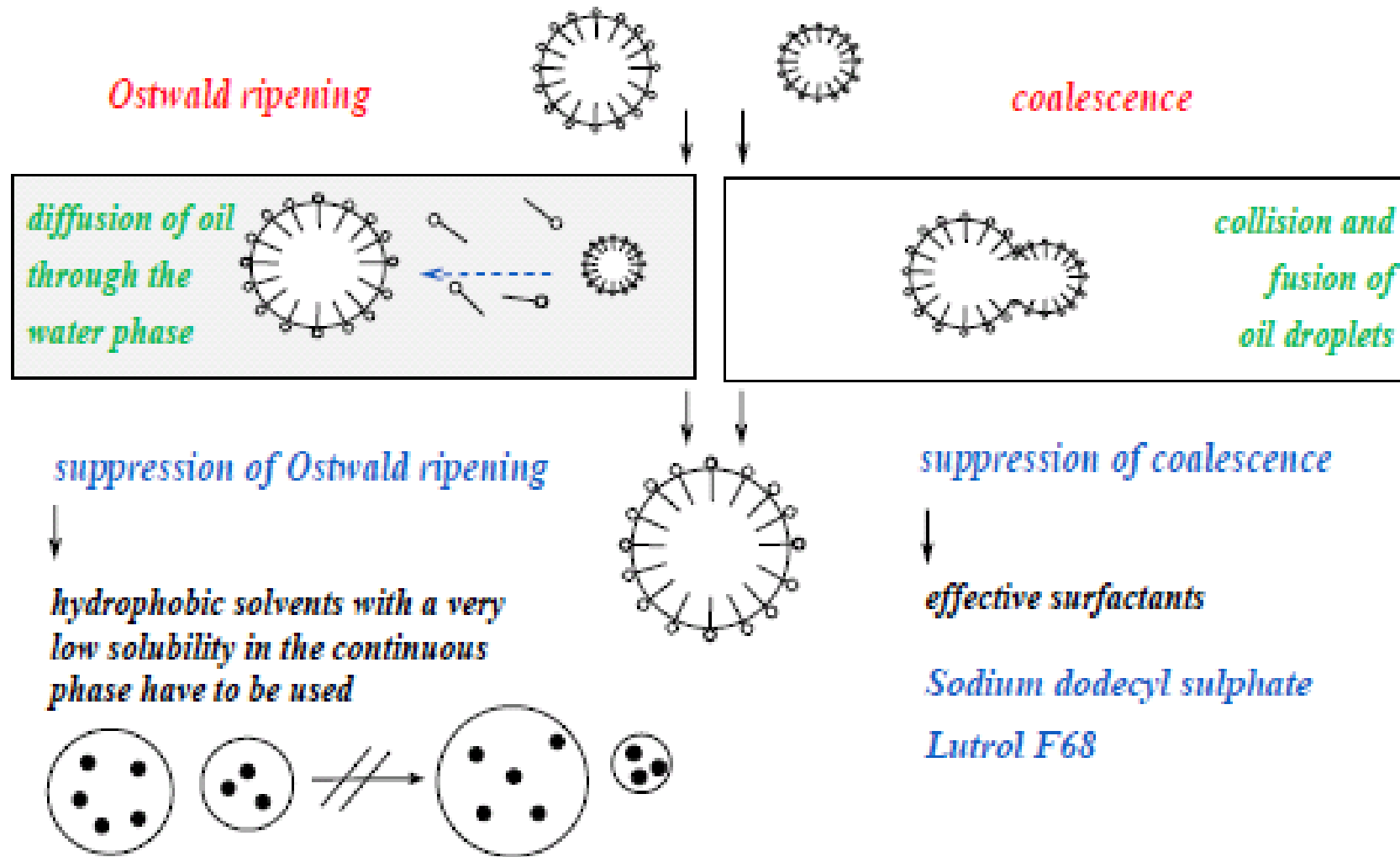
only kinetically stable emulsion:

nano-emulsion (1 - 100 nm)

mini-emulsion (100 - 1,000 nm)

macro-emulsion > 1.0 μm

Growth of mini-emulsion droplets

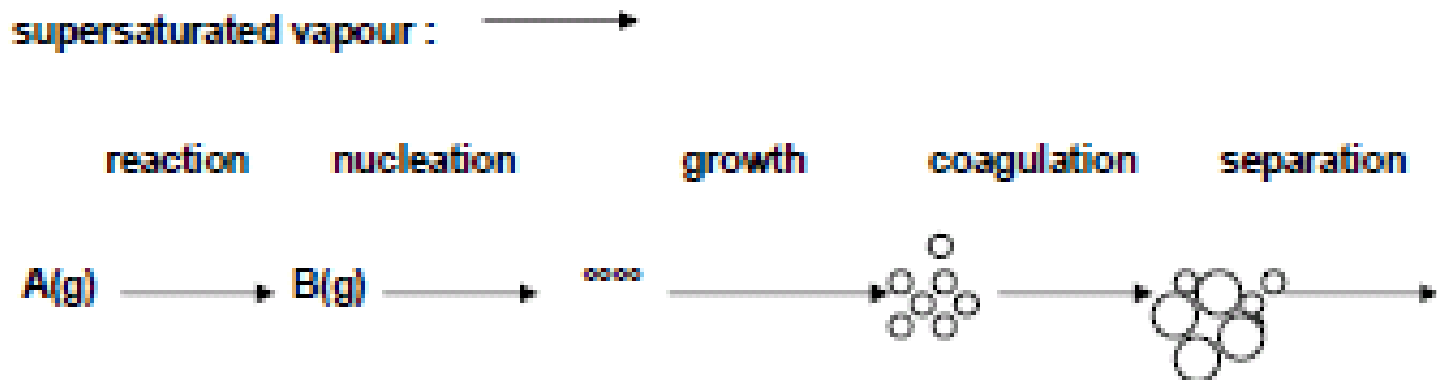


Forces: same chemical potential in each droplet - osmotic pressure vs. Laplace pressure

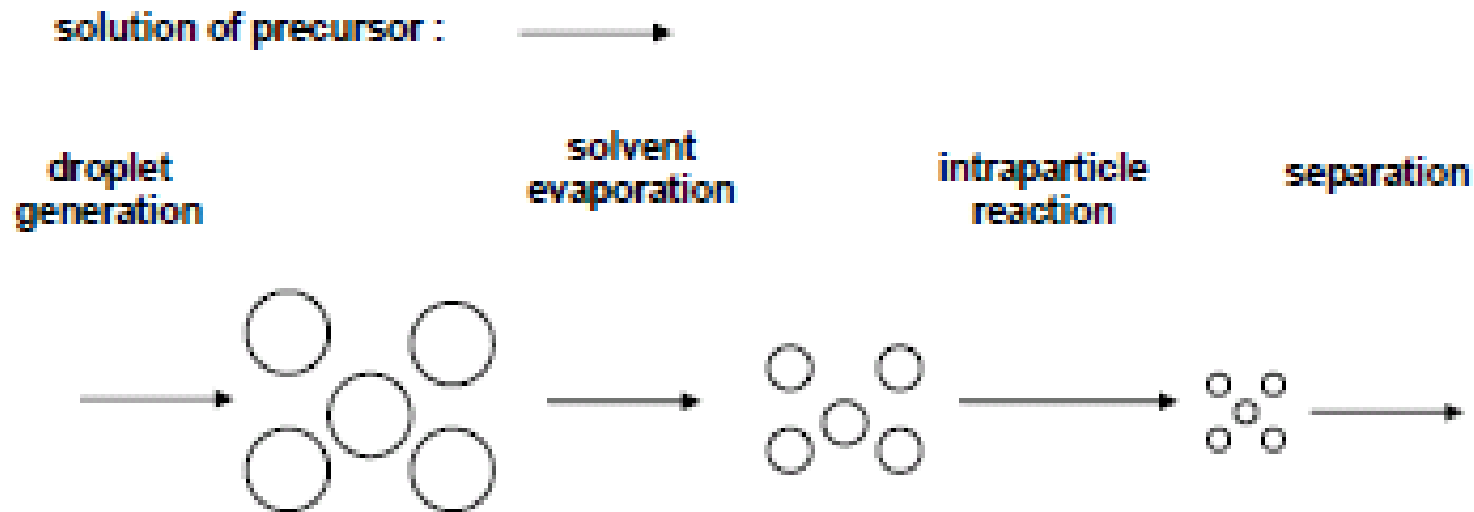
Aerosol nanoparticle synthesis - Chemical and physical processes

Particle formation in aerosol processes

Gas to particle conversion (GPC)

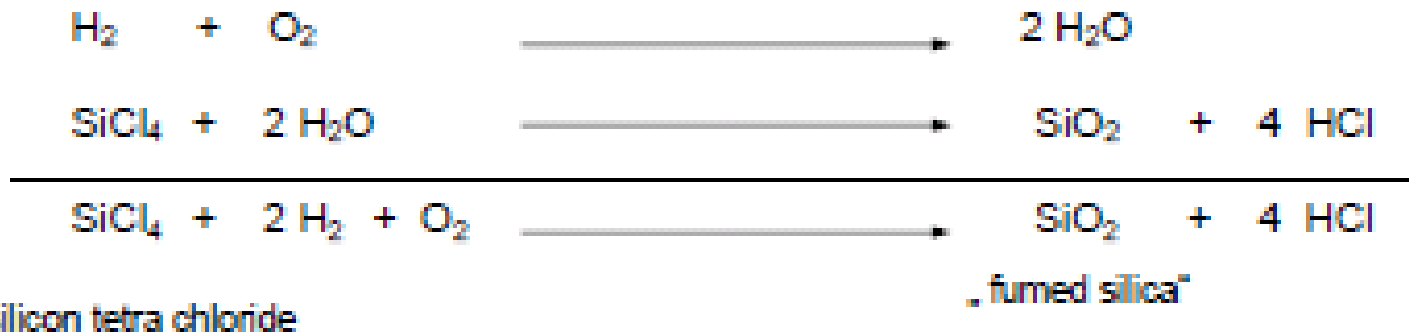


Particle to particle conversion (PPC)



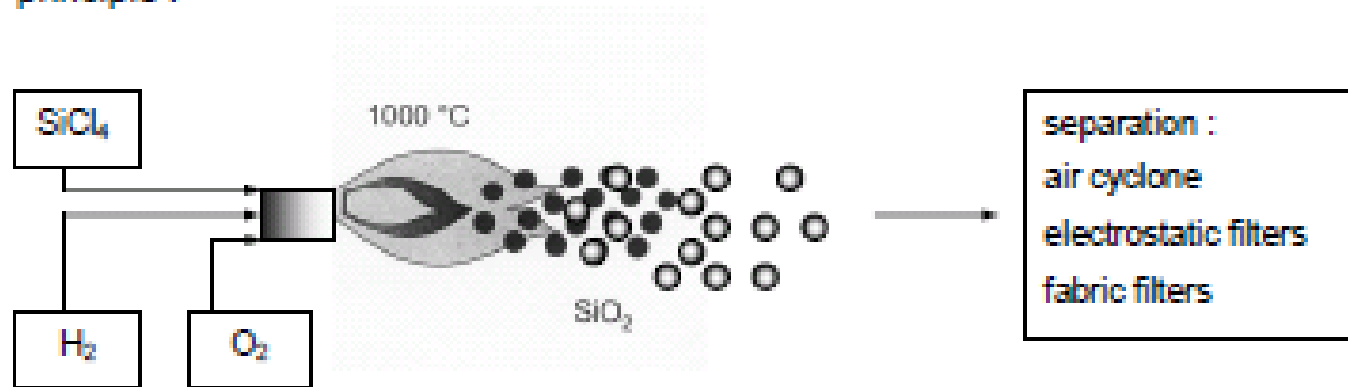
(W. Hintz)

Aerosol process - flame hydrolysis, Aerosil process Degussa 1942 - synthesis of silica



production in flame reactor

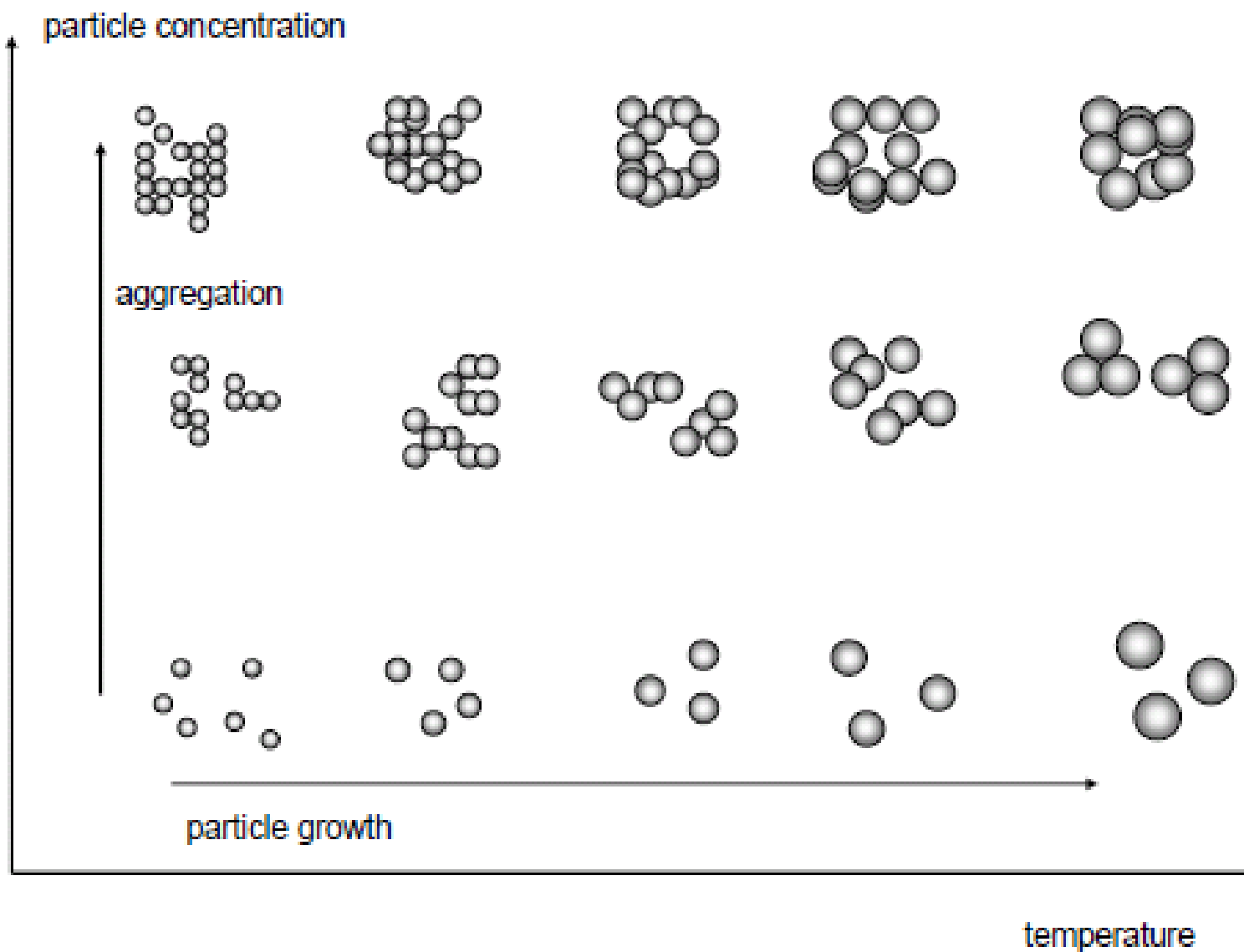
principle :



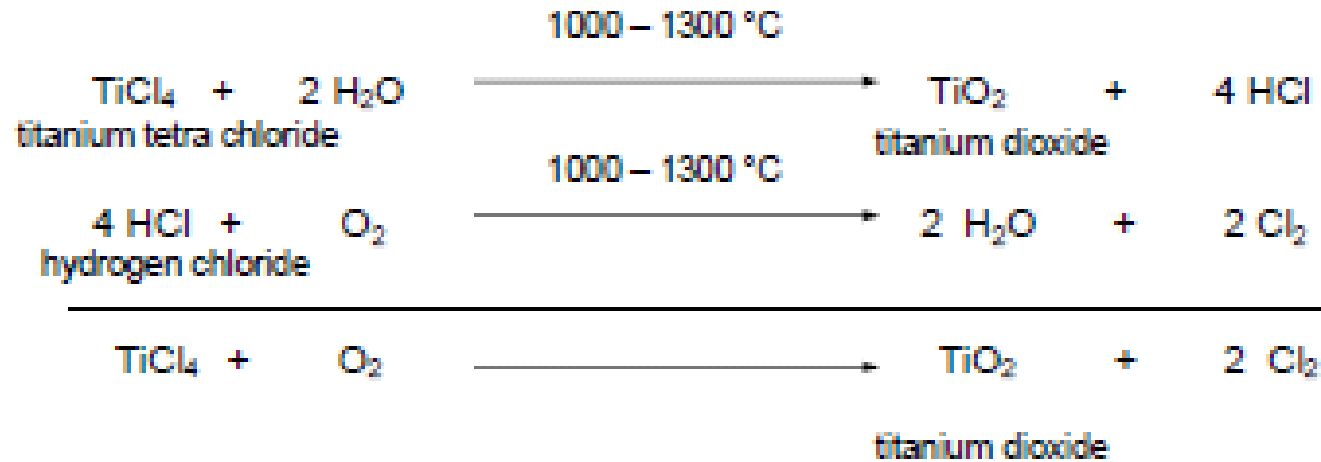
particle size range : primary particle size 7 – 40 nm, spherical, amorphous particle powder as agglomerated particles of high porosity
specific surface area 50 – 400 m^2 / g

Products : titanium dioxide , aluminium oxide, zirconium oxide, zinc oxide

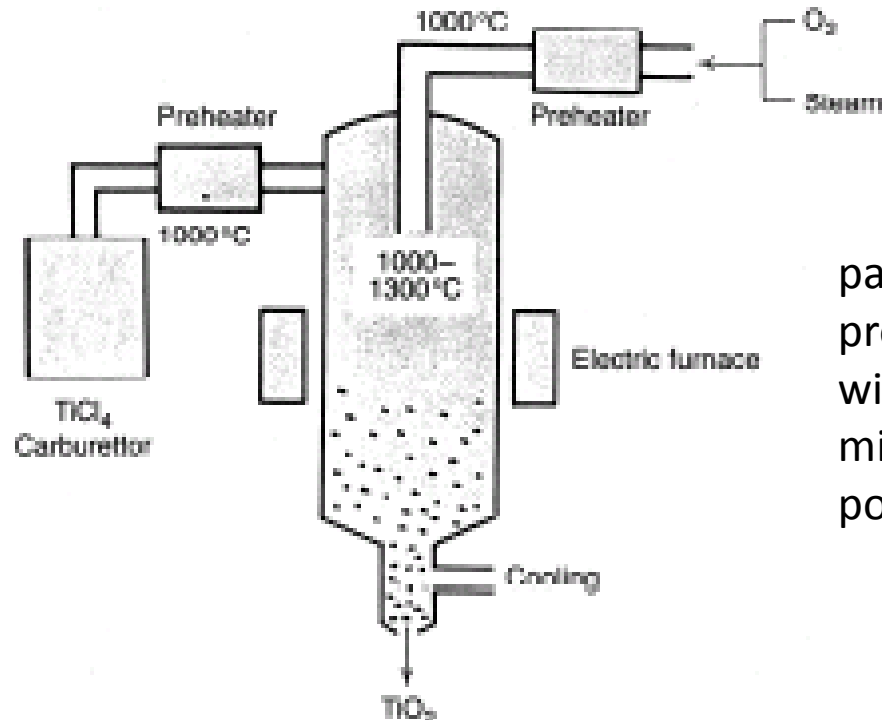
Particle morphology during flame hydrolysis



aerosol process - **flame hydrolysis**, synthesis of **titanium dioxide** - chlorine process

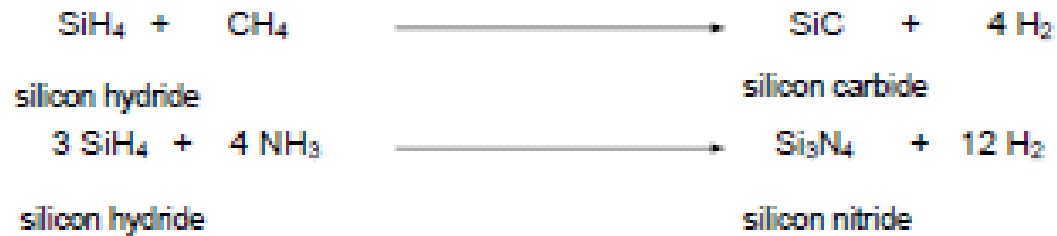


apparatus for titanium dioxide powder

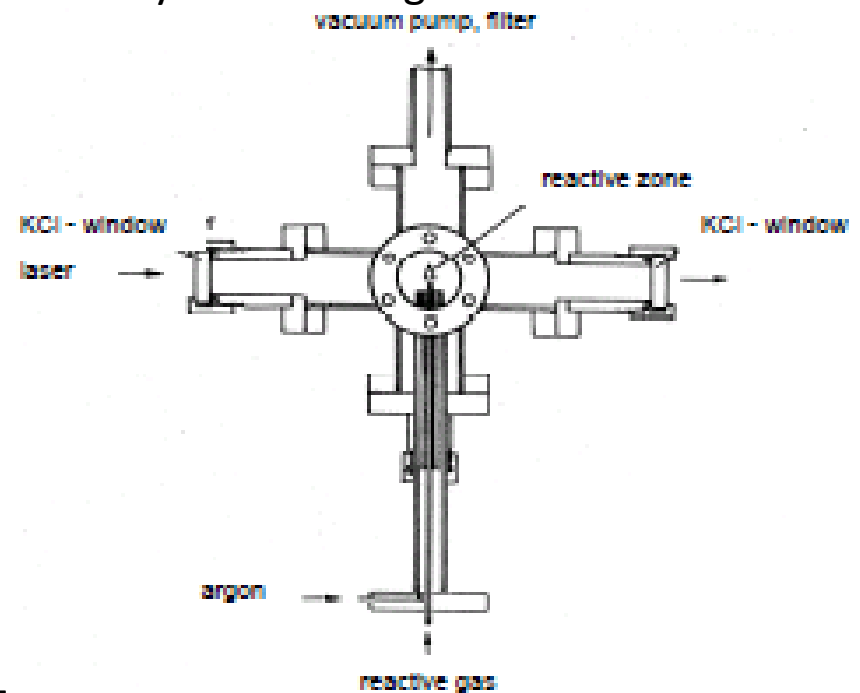


particle size : 100 - 400 nm, amorphous particles,
 product of anatase / rutile, part of rutile increases
 with temperature
 minimum aggregation and high dispersivity of
 powder

aerosol synthesis using laser light, synthesis of silicon carbide and silicon nitride



Reaction chamber for powder synthesis using a laser



advantage : particle of high purity , monodisperse particle size distribution, exact stoichiometry

disadvantage : precursor has to absorb laser light only on a laboratory scale, mass produced 1 – 100 g

Methods for powder generation with spray processes

methods	starting material	process steps
spray drying	suspension	solvent evaporation
spray drying	solution	solvent evaporation, crystallization
spray calcination	suspension	solvent evaporation, calcination
spray decomposition	solution of inorganic salts	solvent evaporation, calcination
spray hydrolysis	non aqueous solution or liquid metal compound	hydrolysis by water vapour, for solutions solvent evaporation
spray pyrolysis	solution or melt of metal organic salts	thermal decomposition, for solutions solvent evaporation
plasma evaporation of solutions	solution	solvent evaporation and nucleation / crystallization in a gaseous phase

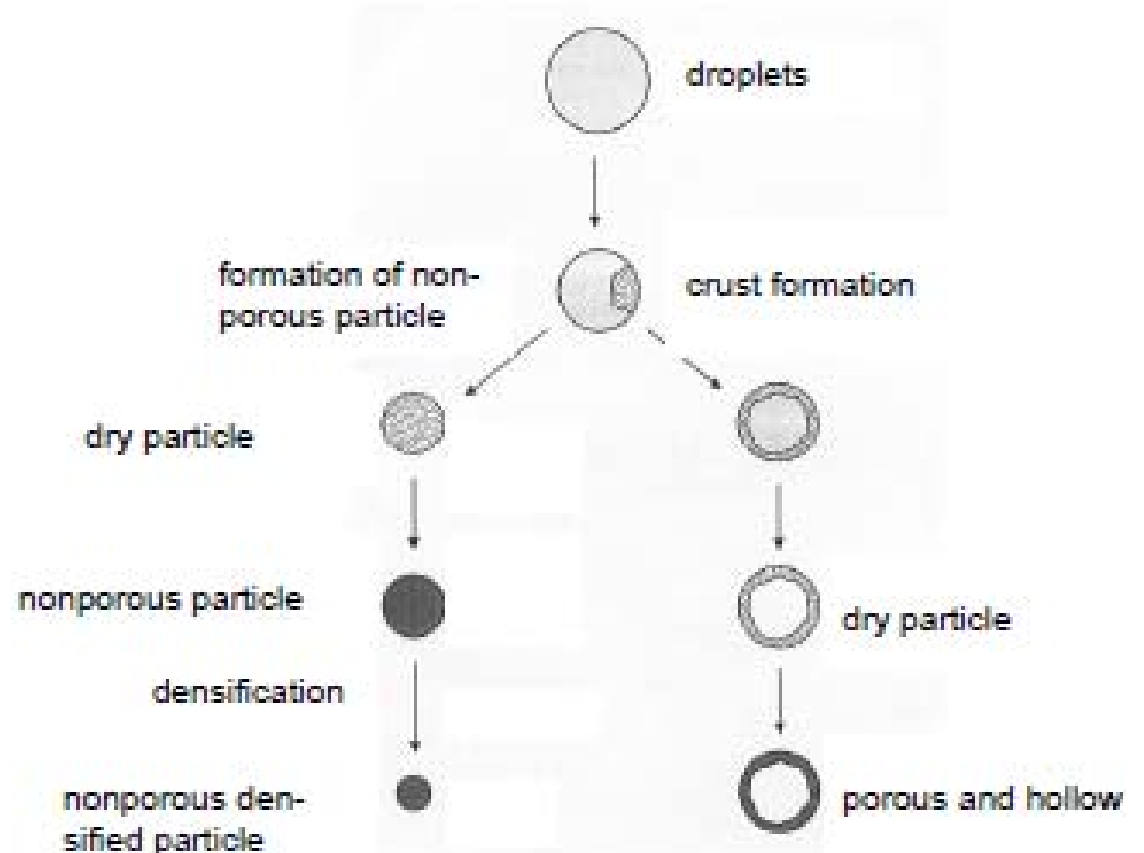
Spray hydrolysis



Particle :

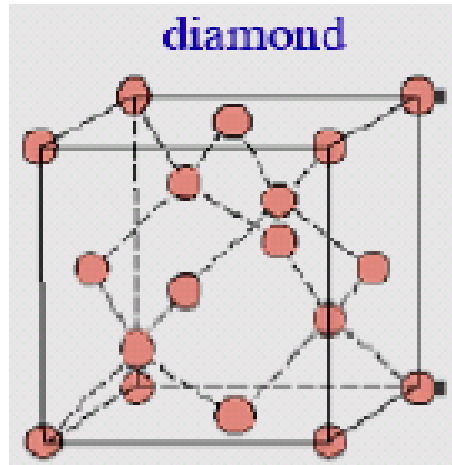
- mostly non agglomerated, spherical particle with high purity
- hollow and porous particle can be formed easily
- controlling of powder porosity by concentrations in droplets and by temperature gradients

Formation of nonporous and porous particle by spray hydrolysis

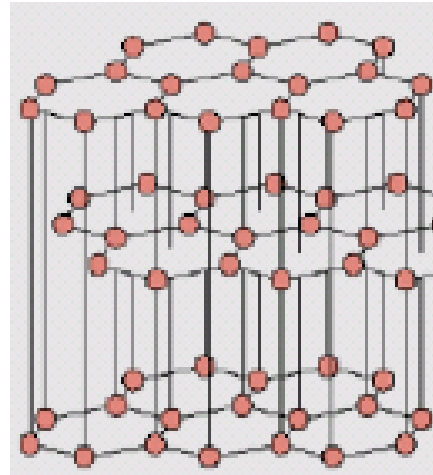


Carbon Nanotube: A Form of Carbon

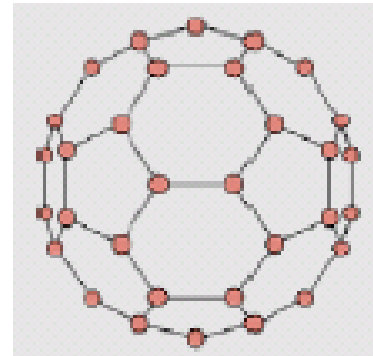
(metastable)



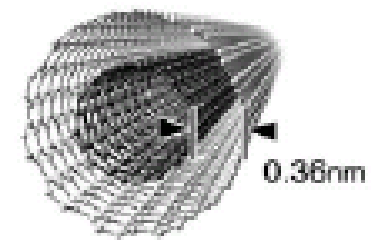
Graphite (stable)



Bucky ball
(metastable)



Nanotube = rolled sheet
of graphite



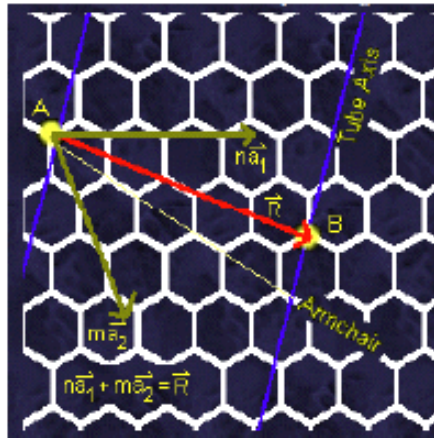
Smalley & Kroto, 1997 Nobel

Helical Microtubules of graphitic Carbon, Iijima, S, Nature, 354 (6348): 56-58 NOV 7 1991
Cited: >4000 times

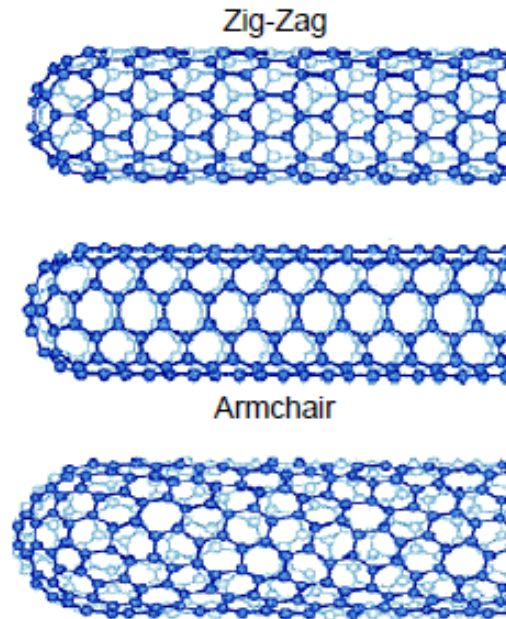
Accounts of Chemical Research (2002), 35(12). Entire issue is based on Nanotubes.

Dai, Hongjie. Carbon nanotubes: opportunities and challenges. Surface Science (2002), 500(1-3), 218-241.

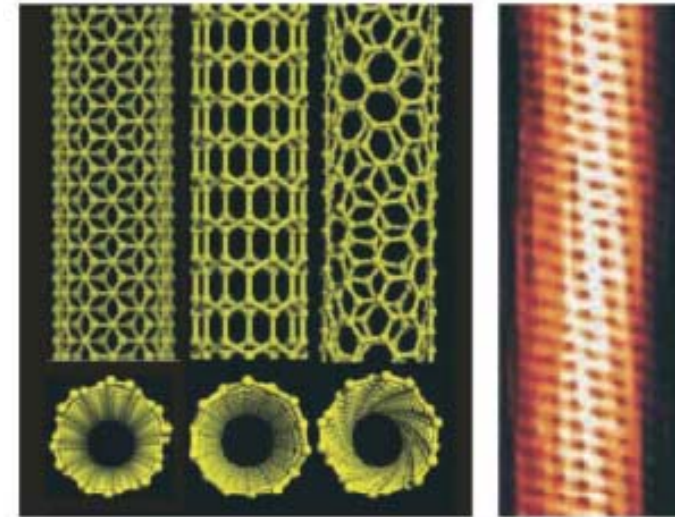
Different Types of Nanotubes



a1 zig zag vector
a2 reflection over armchair line

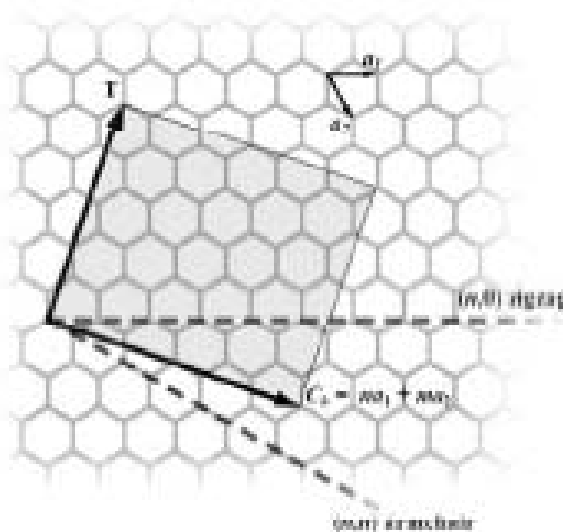


Chiral



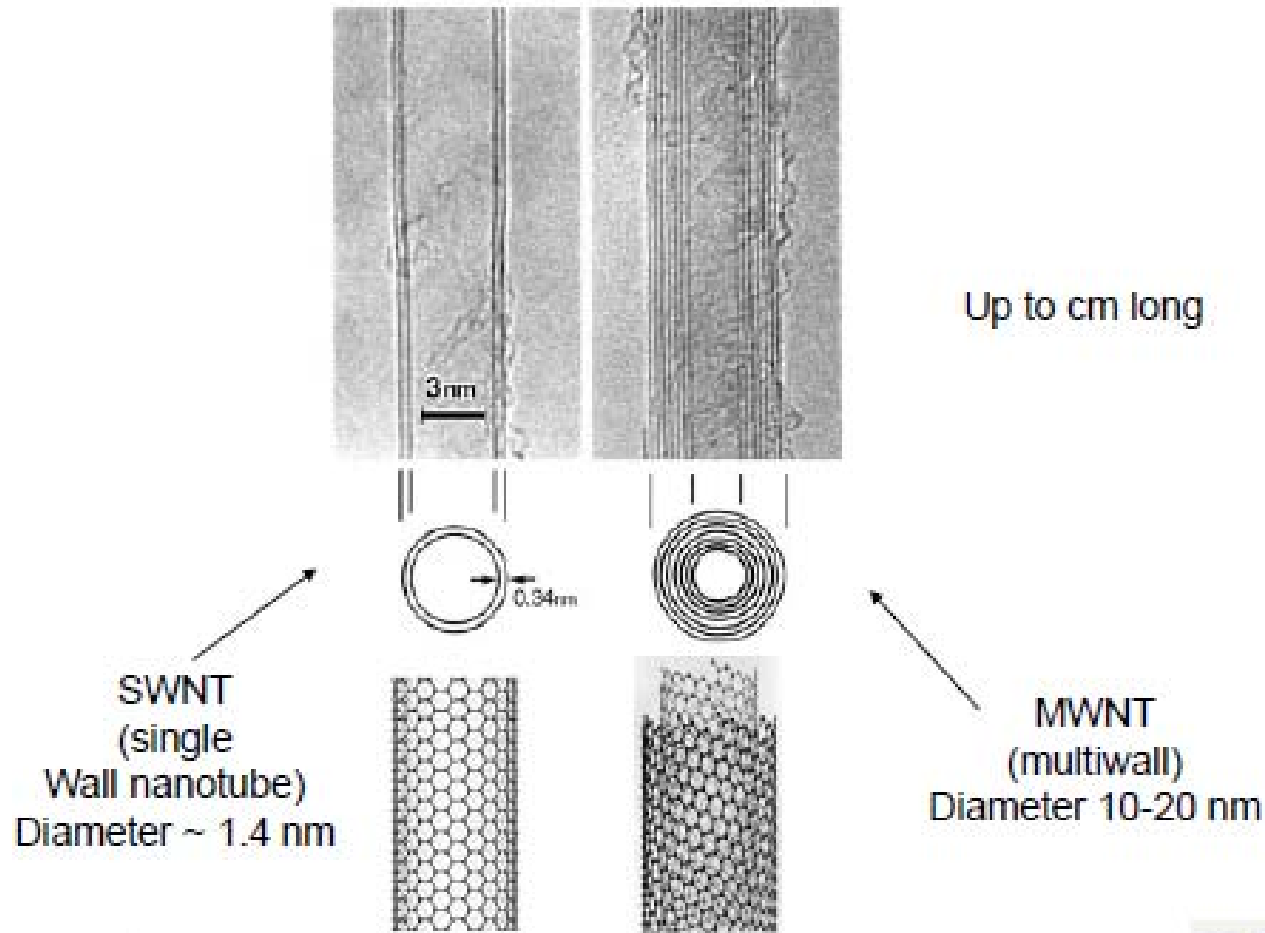
armchair Zig-Zag Chiral TEM Chiral

Science, 297, 2 Aug 2002



The (n,m) nanotube naming scheme can be thought of as a vector (Ch) in an infinite graphene sheet that describes how to 'roll up' to graphene sheet to make the nanotube. T denotes the tube axis, and a1 and a2 are the unit vectors of graphene in real space. It is based similar upon diagrams found in the literature (for instance, Odom et al. Topics Appl. Phys., 2001, 80, 173).

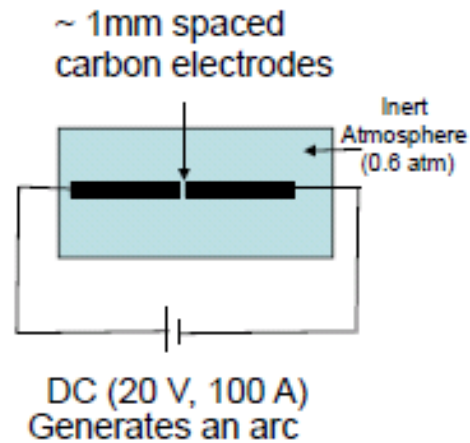
Single Wall and Multi Wall Nanotubes



Iijima, Sumio. Carbon nanotubes: past, present, and future. *Physica B: Condensed Matter* (2002), 323, 1-5.

Methods for Fabricating Nanotubes

Arc Discharge:



Metal doped electrodes (Fe, Co, Ni, Mo): SWNT

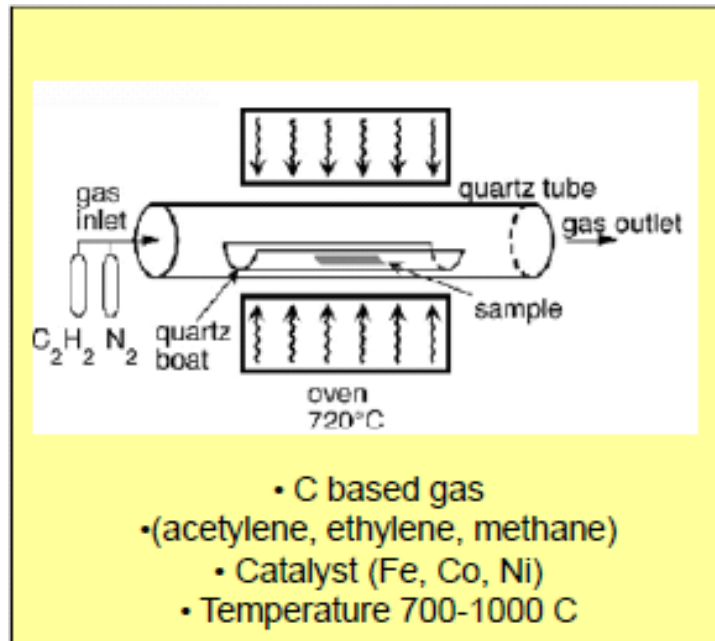
Pure graphitic electrodes: MWNT

During this process, the carbon contained in the negative electrode sublimates because of the high temperatures caused by the discharge. Because nanotubes were initially discovered using this technique, it has been the most widely used method of nanotube synthesis.

The yield for this method is up to 30 percent by weight and it produces both single- and multiwall nanotubes, however they are quite short (50 microns)

Methods for Fabricating Nanotubes

Chemical vapor deposition (CVD)



CO, Fe(CO)₅
Commercial process
97% Pure, 450 mg /hr

Purification of carbon nanotubes to get precise composition and size

- Oxidation: Damage to SWNT (closed structure less reactive) less than other carbon / metal compounds
- Acid treatment, Ultrasonication (Metal removal)
- Magnetic removal of catalysts
- Microfiltration (SNWT trapped), fullerenes solvated in CS_2
- Functionalization, Cutting using fluorination and pyrolysis
- Chromatography (HPLC-SEC)

Nano-clays – nanocomposite based on exfoliated clays

