Università degli Studi di Trieste
Dipartimento di Ingegneria e Architettura
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Scienza e Tecnologia dei Materiali Ceramici

Modulo 2: Materiali Nanostrutturati

- Lezione 4 -

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Previous lecture: Review

- Basic nanostructures: overview
- Nanoparticles
  - Stabilization approaches

This lecture: Content

- Basic nanostructures: overview
- Nanoparticles
  - Steric stabilization approaches
  - Colloidal synthesis of nanocrystals of binary compounds
  - Colloidal synthesis of metal nanoparticles
  - Kinetics of nucleation and growth in colloidal suspensions
  - Optoelectronic properties
  - Applications

Where are we?

3. Fabbricazione

- Approcci “bottom-up”:
  - Building blocks (nanocristalli: wells and films, wires, dots; carbon based nanostructures: fullerenes, graphenes, etc.)
  - Proprietà dei building blocks
  - Metodi di fabbricazione (deposizione di film, aerosol, sospensioni colloidali, epitassia controllata, etc.)
  - Assemblaggio (self assembly bioassistito, self assembly via polimeri, eterostrutture, Marangoni, ...)

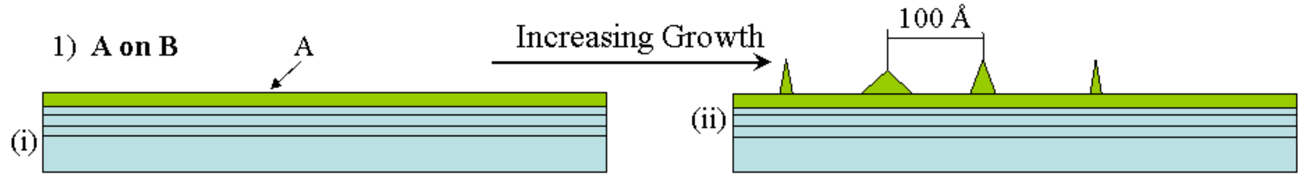
- Approcci “top-down”
  - Litografia, ball milling, ion implantation, thin film layers + thermal treatment, etc.

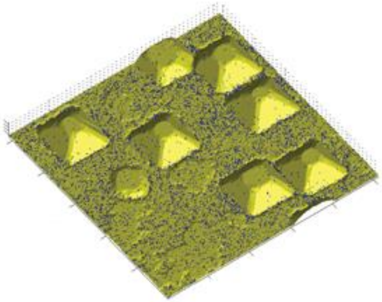
Approaches to nanoparticle synthesis

Nanoparticles:	nano-sized particles, crystalline or amorphous (1-200 nm)
Nanocrystals:	single crystal nanoparticles
Quantum dots:	nanoparticles where quantum confinment effects are important

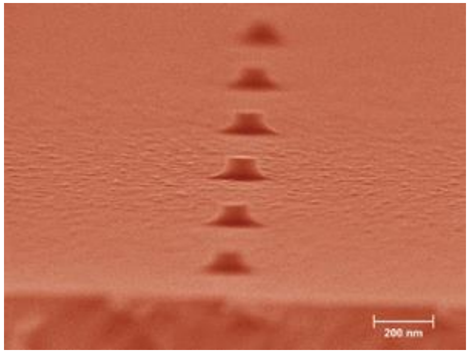
Approaches to nanoparticle synthesis

- **Self-assembled nanocrystals**

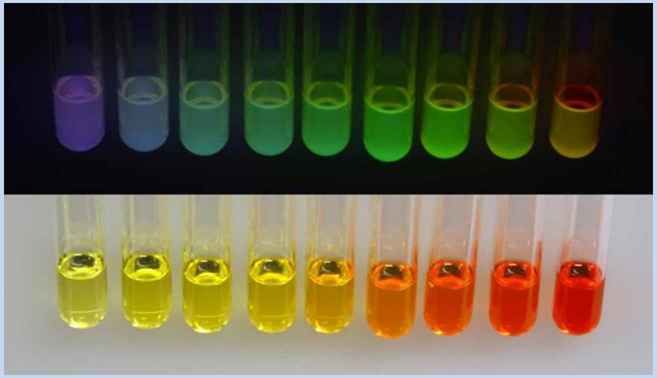


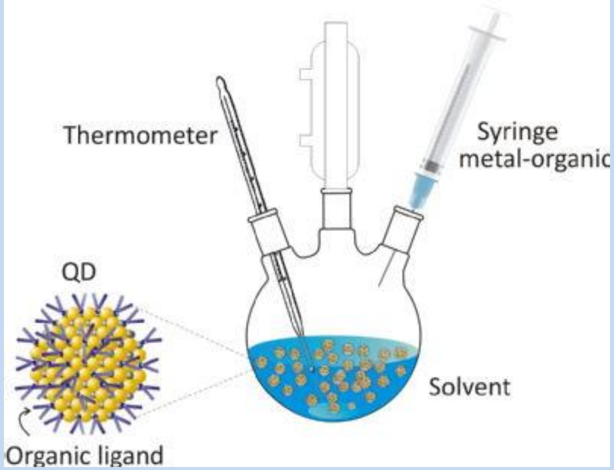


- **Lithography**



- **Colloidal nanocrystals**





Example: Colloidal synthesis of CdSe

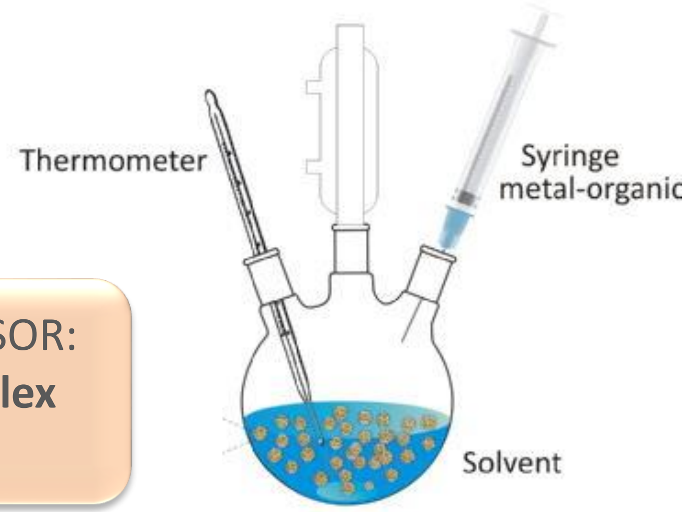
Cd + Se ⟶ **CdSe**

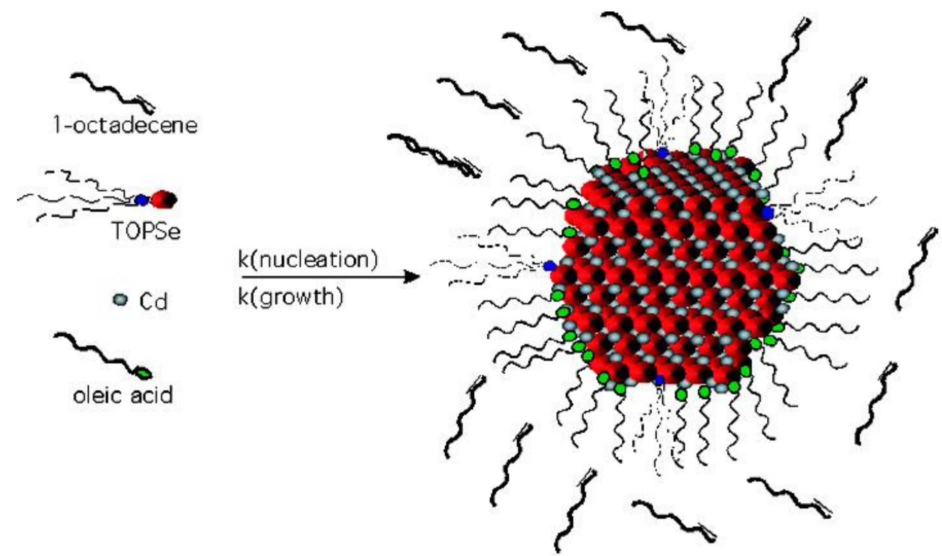
CADMIUM PRECURSOR:
Oleic Acid +
Cadmium complex
in solvent

SELENIUM PRECURSOR:
TOP-Selenio complex
in solvent

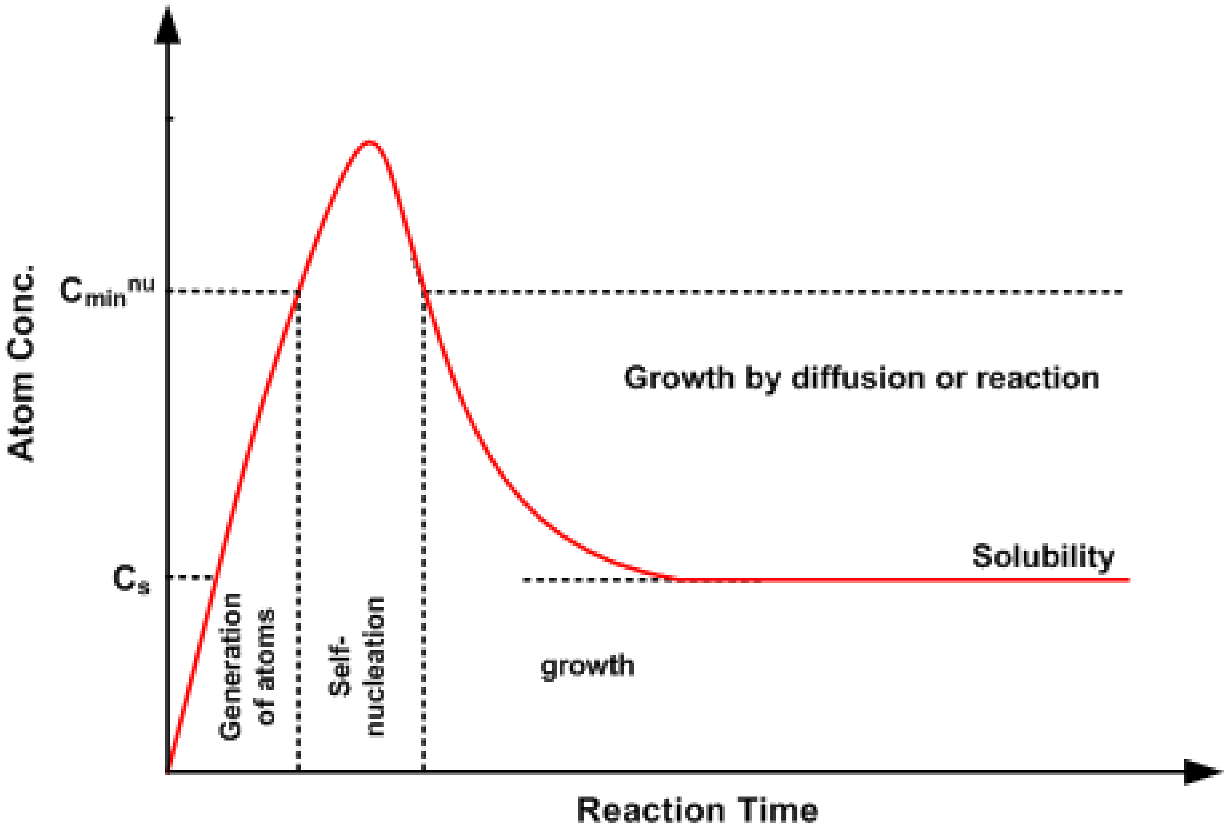
mixing

CdSe precipitation



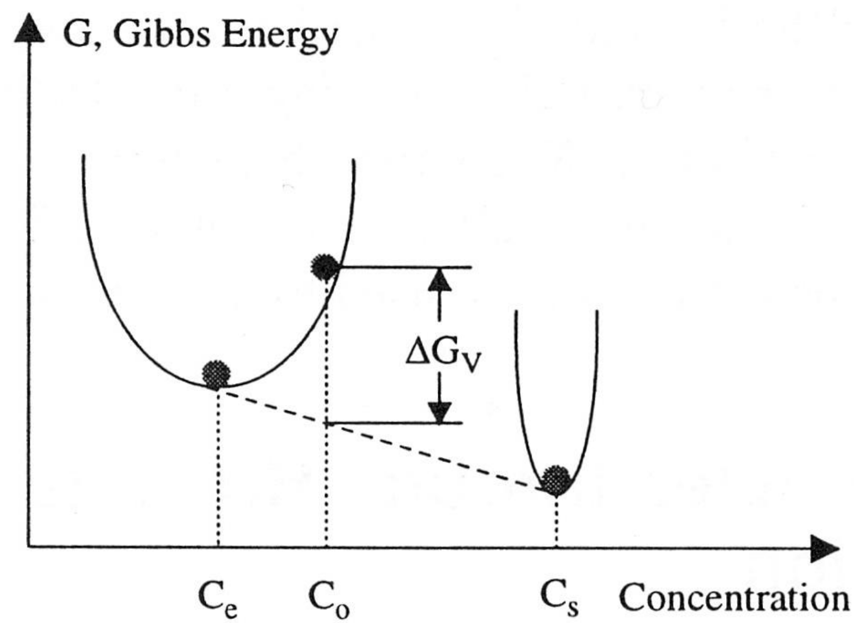


Synthesis of nanoparticles: Time evolution of concentration profile



Driving force

Supersaturation → High G
ΔG: driving force for nucleation and growth



Supersaturation

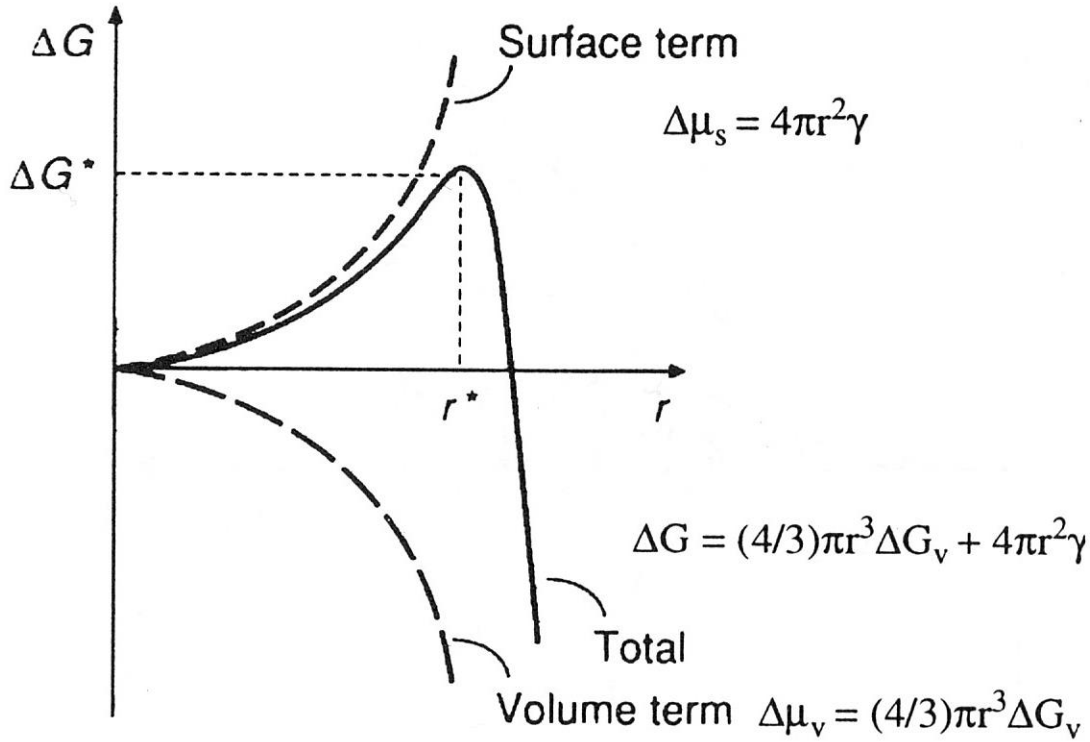
ΔG_v per unit volume in solid phase:

$$\Delta G_v = -\frac{kT}{\Omega}\ln(C/C_o) = -\frac{kT}{\Omega}\ln(1+\sigma)$$

C: solute concentration
C_0: equilibrium concentration (solubility)
k: Boltzman, Ω è il volume atomico, e
σ: supersaturation defined as $(C-C_0)/C_0$.

No supersaturation (s=0) $\rightarrow$ $\Delta G_v = 0$ $\rightarrow$ no nucleation
If $C > C_0$ ($s > 0$) $\rightarrow$ $\Delta G_v < 0$ $\rightarrow$ nucleation

Homogeneous nucleation



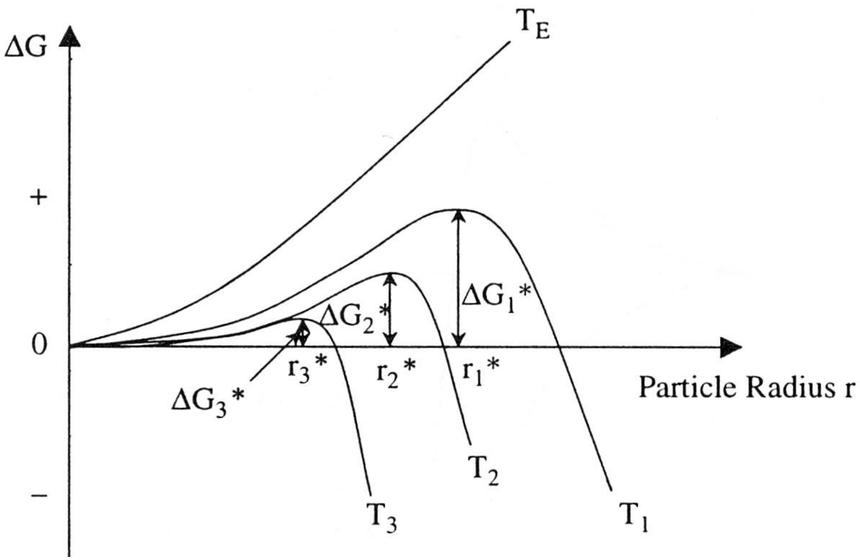
$$r^* = -2\frac{\gamma}{\Delta G_v}$$

$$\Delta G^* = \frac{16\pi\gamma}{(3\Delta G_v)^2}$$

Homogeneous nucleation

$$r^* = -2\frac{\gamma}{\Delta G_v}$$

Critical radius: minimum size attainable



Factors influencing r*:

- ΔG_V → supersaturation
- Surface energy →
  - Temperature
  - System chemistry (solvent, etc.)

Homogeneous nucleation

Rate of nucleation:

$$R_N = nP\Gamma = \left\{\frac{C_o kT}{3\pi\lambda^3\eta}\right\} \exp\left(-\frac{\Delta G^*}{kT}\right)$$

$$P = \exp\left(-\frac{\Delta G^*}{kT}\right)$$

$$\Gamma = \frac{kT}{3\pi\lambda^3\eta}$$

•n: number of species in solution per unit volume; (in homogeneous nucleation =C_0)

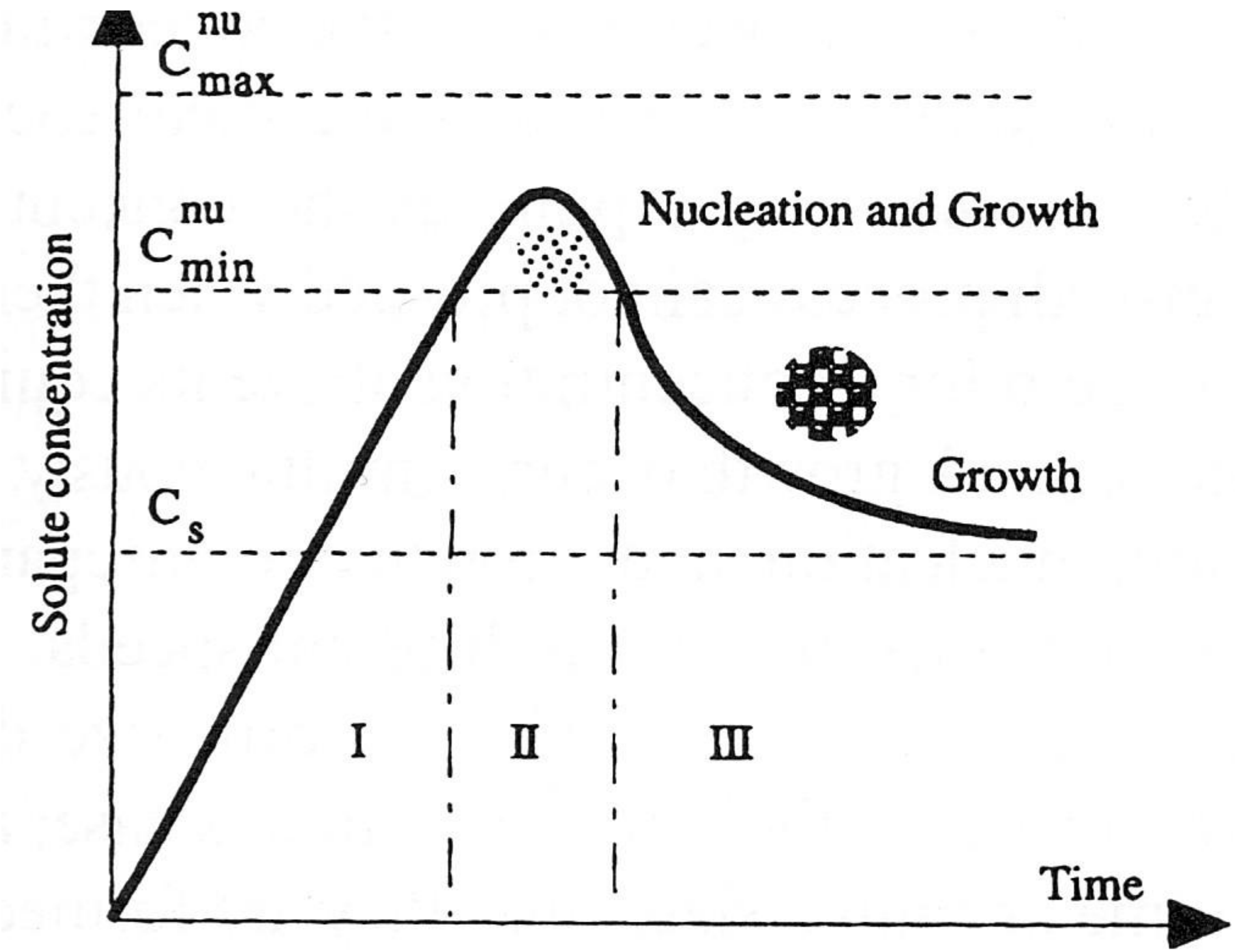
•λ: diameter of growth species

•η: viscosity of the solution

Large amounts of nuclei are favored by:

- High C_0
- High temperature
- Low viscosity
- Low ΔG^*

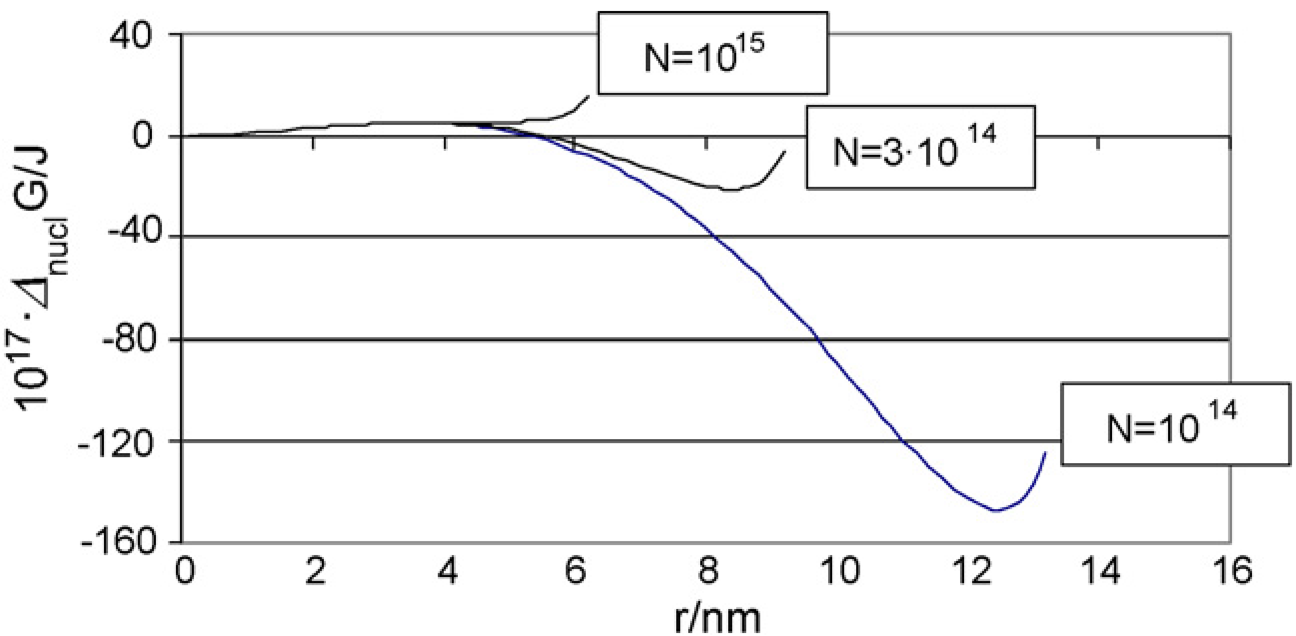
Homogeneous nucleation



Modified homogeneous nucleation

$$\Delta G = 4\pi r^2 \gamma_s + \frac{4}{3}\pi r^3 \Delta G_v$$

$$\Delta G_v = -\frac{RT ln S_{CdSe}}{V_{mol}}$$



Modified homogeneous nucleation

$$\Delta G = 4\pi r^2 \gamma_s + \frac{4}{3}\pi r^3 \Delta G_v$$

$$\Delta G_v = -\frac{RT lnS_{CdSe}}{V_{mol}}$$

$$C_{CdSe}V_{tot} = C_{CdSe\ 0}V_{tot} - n_{CdSe\ np}$$

cioè le moli di monomero in soluzione saranno quelle iniziali diminuite delle moli di CdSe nelle particelle. Queste vengono valutate mediante

$$n_{CdSe\ np} = \#_{np}\left(\frac{4}{3}\pi r^3\right)\frac{\rho_{CdSe}}{MW_{CdSe}}$$

il numero di nanoparticelle si ricava dalla nucleation-rate

$$R_n(t) \propto exp\left(-\frac{1}{T^3 ln^2 S(t)}\right)$$

$$\#_{np} = \sum_{t=0}^{end} R_n\,(t)$$

In alcuni casi, di ha una decrescita delle particelle. Quando la dimensione di queste raggiunge lo zero (regolata dalla growth-rate), il numero di nuclei viene ridotto.

La growth-rate invece deriva da

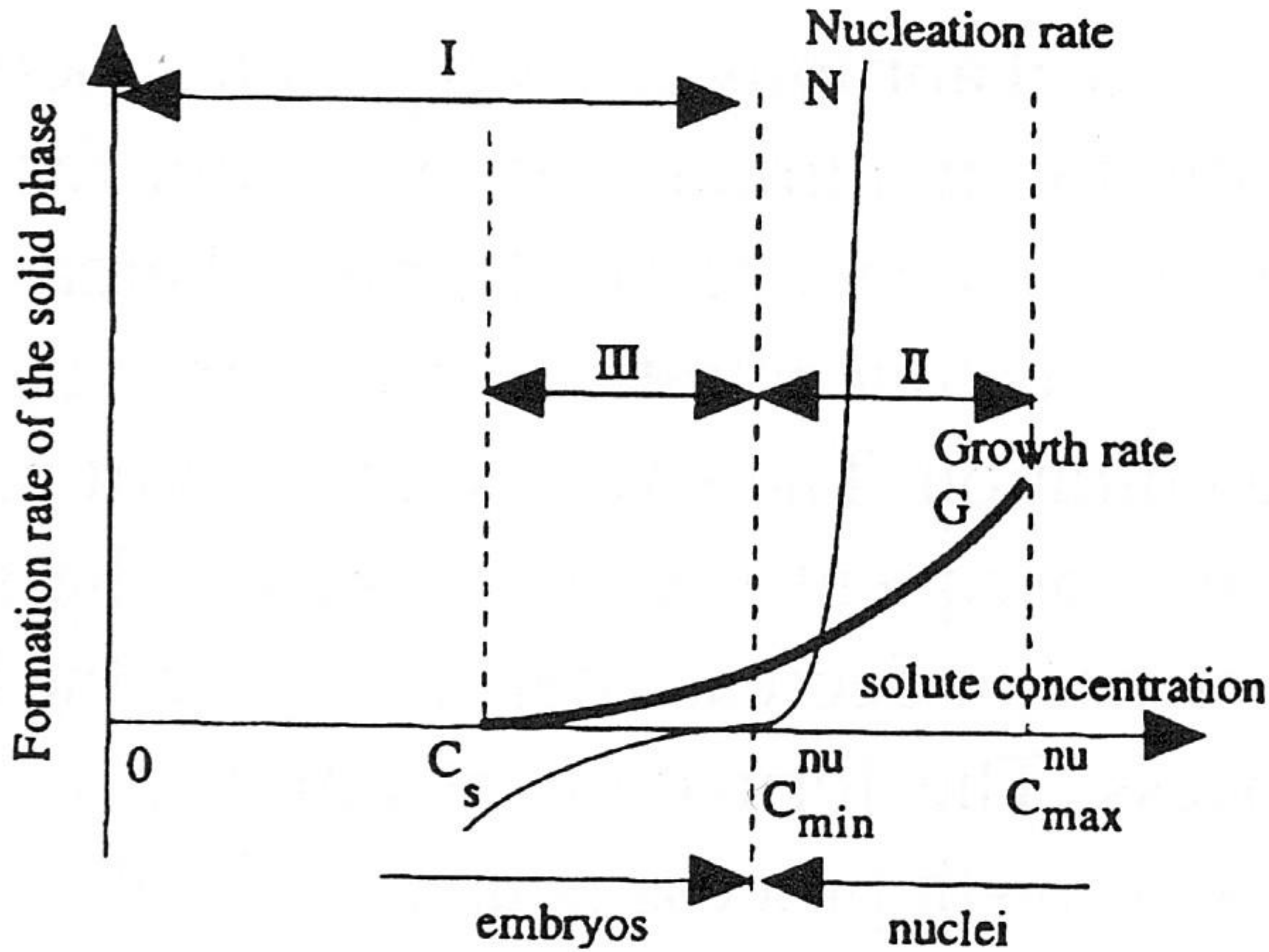
$$\dot{r} = \frac{dr}{dt} \propto \frac{1}{rr_c} - \frac{1}{r^2}$$

I due contributi all'energia libera (superficiale e volumetrico) quindi possono venire espressi dall'equazione

$$\Delta G_{np} = 4\pi r^2 \gamma_s - \frac{4\pi r^3}{3}\frac{RT}{V_m} ln\left(S_{CdSe\ 0} - \#_{np}\left(\frac{4}{3}\pi r^3\right)\frac{\rho_{CdSe}}{MW_{CdSe}C_{sol}V_{tot}}\right)$$

Va integrata su r. tutte le volte che vedo r in realtà dovrebbe essere l'integrale

Homogeneous nucleation



Growth

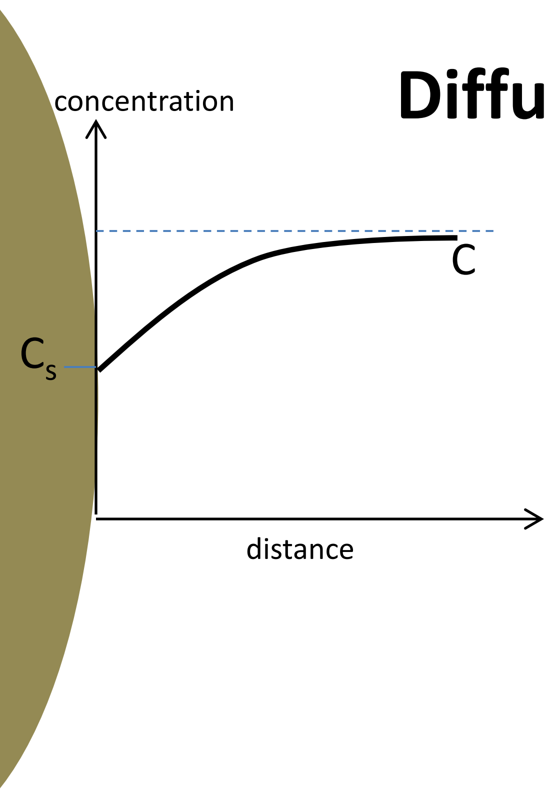
Growth of nuclei: two steps

1) Diffusion
   - Growth-species generation
   - Migration of growth-species to nuclei surface
   - Adsorption of growth-species to nuclei surface

2) Growth (irreversible incorporation of growth species into the surface)

Growth

Diffusion-controlled growth:



$$dr/dt = D(C - C_s)\frac{V_m}{r}$$

r: particle radius
V_m: monomer volume
D: diffusion coefficient

$$r^2 = 2D(C - C_s)V_m t + r_o^2$$

$$\delta r = \frac{r_o \delta r_o}{\sqrt{k_D t + r_o^2}}$$

where $k_D = 2D(C - C_s)V_m$.

As growth proceeds, size dispersion gets better

Diffusion-controlled growth favors the formation of uniformly dispersed particles

Growth

Growth controlled by surface processes:

Concentration of growth species is the same on the surface as in the bulk

Mononuclear growth (layer by layer): $\frac{dr}{dt} = k_m r^2$ (growth proportional to surface area)

→ $\frac{1}{r} = \frac{1}{r_o} - k_m t$

→ $\delta r = \frac{\delta r_o}{(1 - k_m r_o t)^2}$

As growth proceeds, size dispersion gets worse

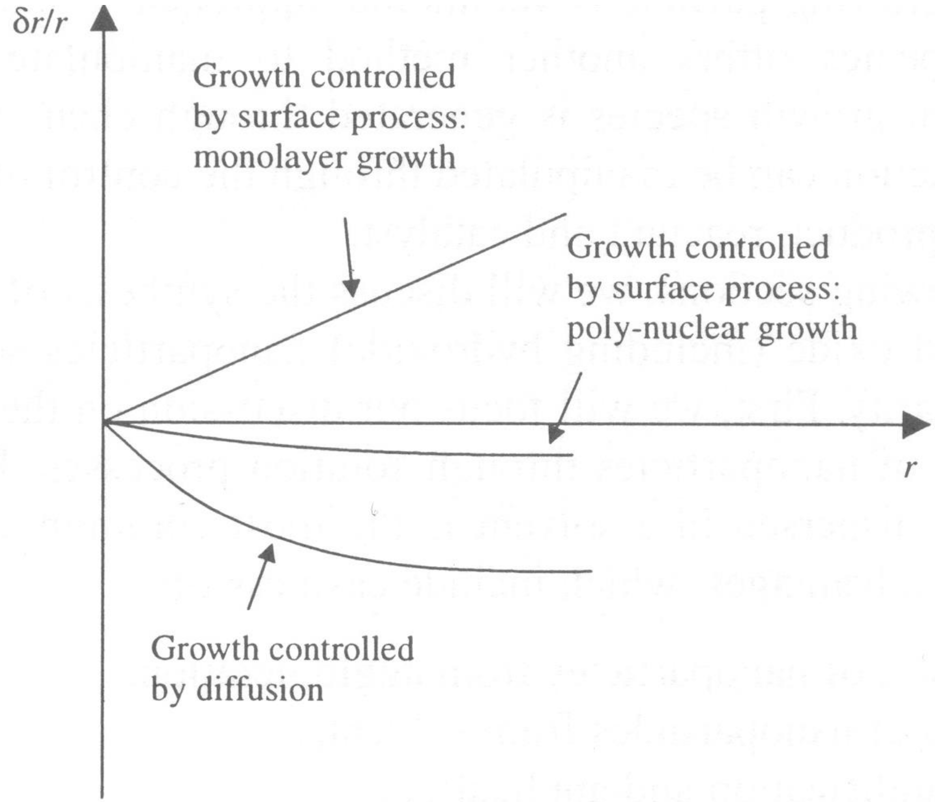
Polynuclear growth
(multiple layers grow simultaneously): $\frac{dr}{dt} = k_m$ (constant growth rate)

→ $r = k_p t + r_o$

→ $\delta r = \delta r_o$

As growth proceeds, size dispersion stays constant

Growth



To obtain monodispersed nanoparticles:

Use diffusion-controlled growth via:

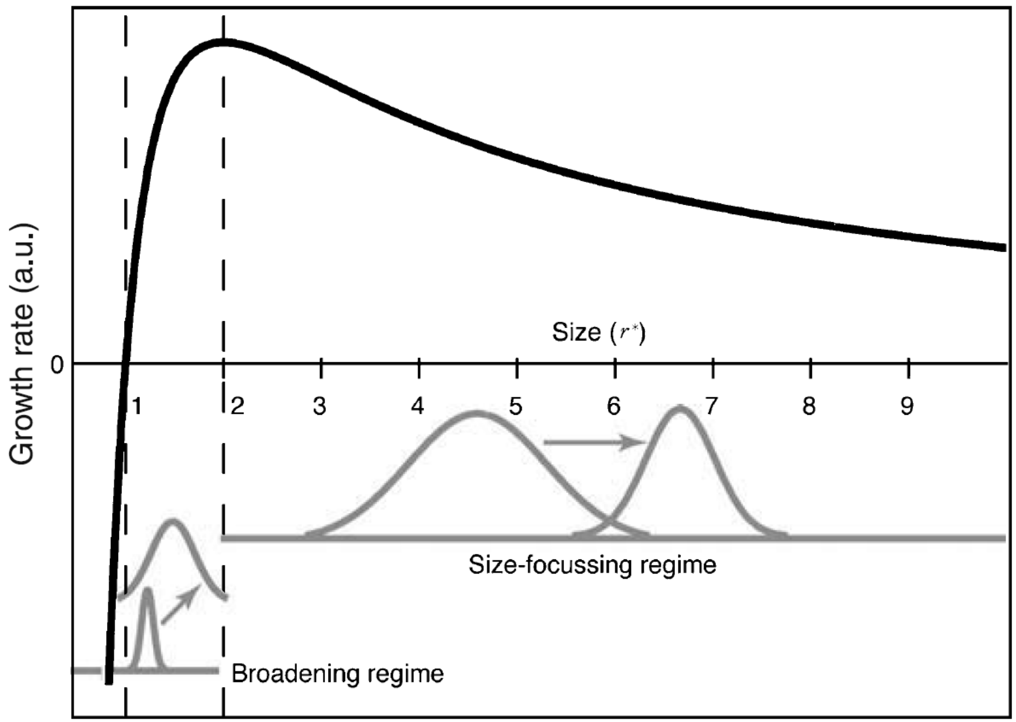
- low concentration
- high viscosity
- diffusion barrier at the surface
- controlled supply via chemical reactions

Growth:
Diffusion-controlled regime + Size-induced dissolution

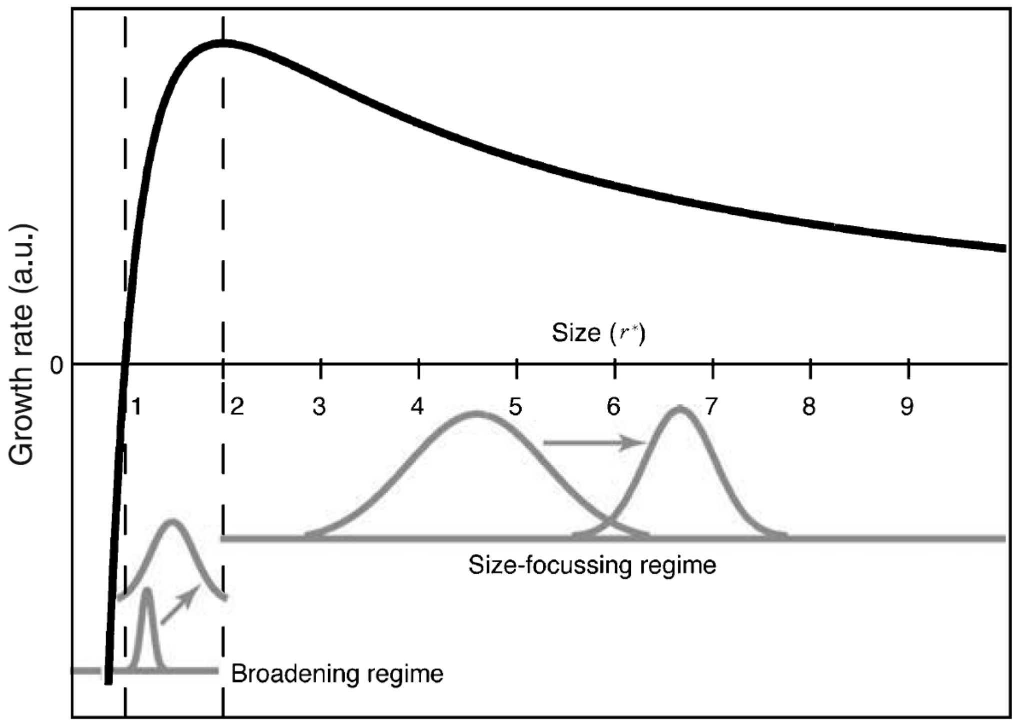
$$\frac{dr}{dt} = \frac{2\gamma D C_\infty \Omega^2}{k_B T}\frac{1}{r}\left(\frac{1}{r^*} - \frac{1}{r}\right)$$

Derives from the diffusion-limited growth regime, considering Gibbs-Thompson

γ	surface energy
D	diffusion coefficient
C_∞	bulk solubilty
Ω	monomer volume
r*	critical radius



Size distribution control
- focusing and defocusing -



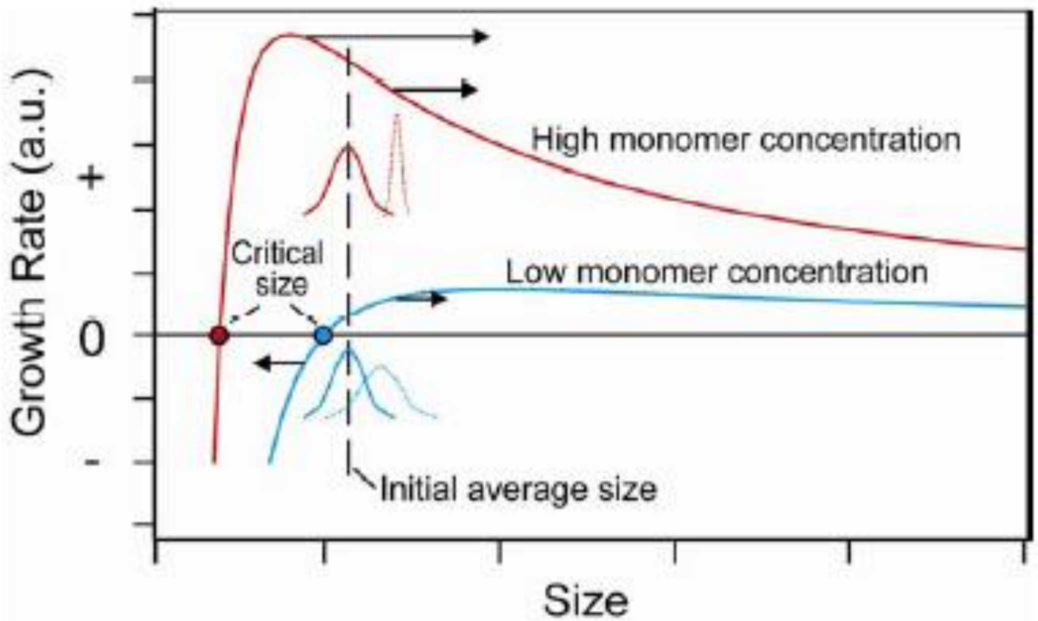
As synthesis proceeds:
Monomer concentration decreases
→ Critical radius increases

→ Growth regime evolves:

- Focusing $r_{min} > 2r^*$
- Broadening $r_{min} < 2r^*$
- Ostwald ripening $r_{min} < r^*$

r_{min} : radius of the smallest particle in the distribution

Size distribution control
- focusing and defocusing -

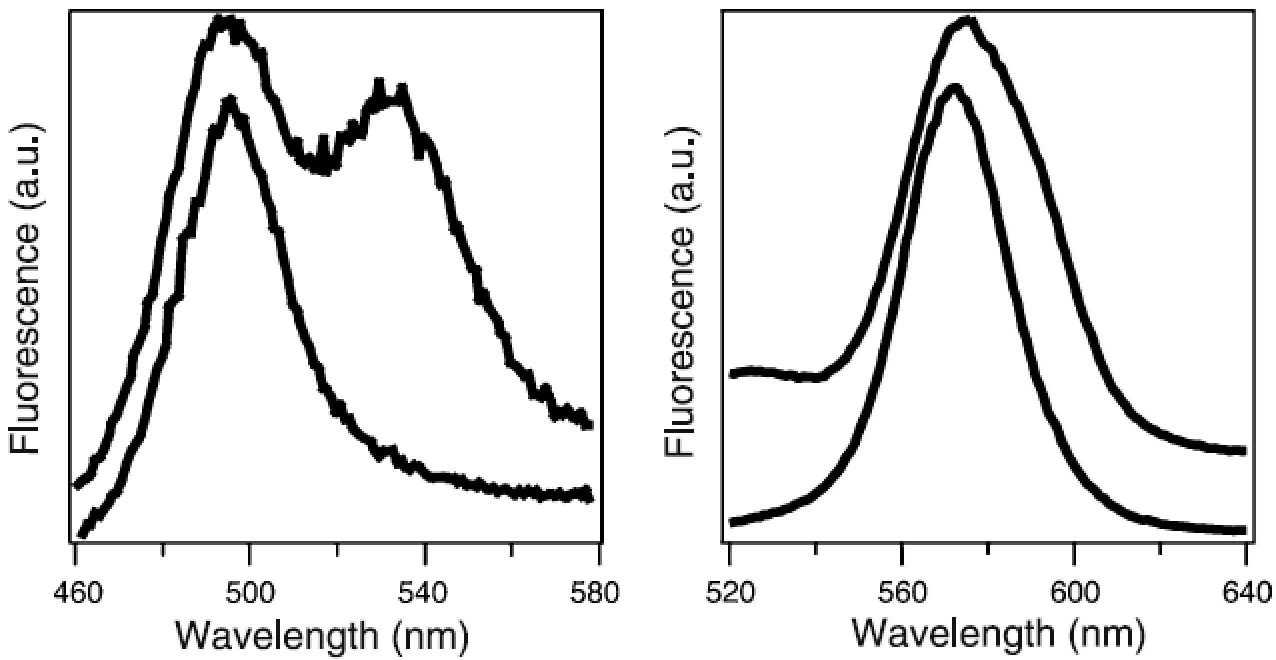


High monomer concentration (early synthesis stage):
Small critical size, all particles grow, small particles grow faster → focusing

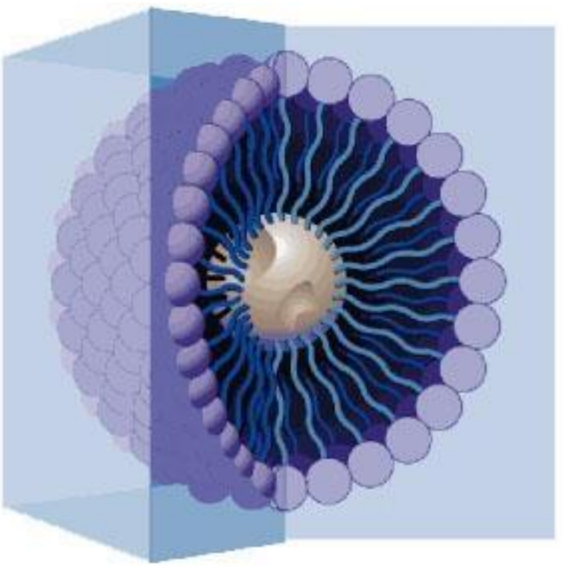
Low monomer concentration (later stage):
Large particles grow faster → defocusing (distribution broadening)

Size distribution control
- other strategies -

- Continuous monomer addition
- Size-selective precipitation:



Nanoparticles: alternative growth methods



Synthesis inside micelles

Aerosol methods

Growth termination

Spray pyrolisis

Template-based synthesis