Contents

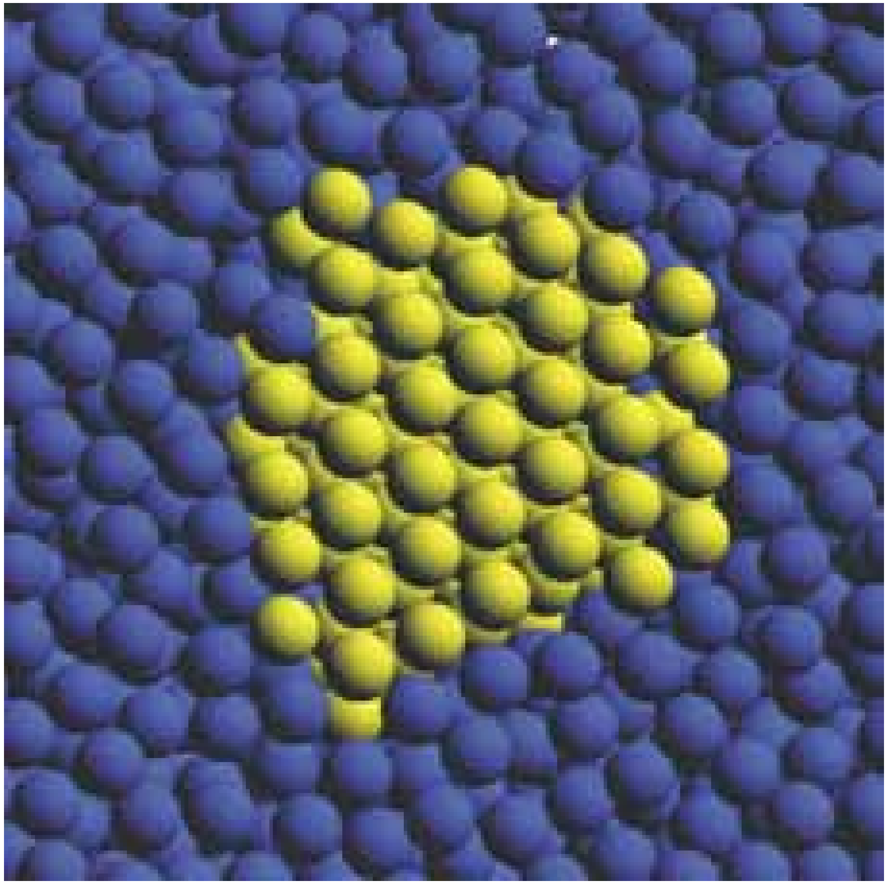
- **Classical Nucleation Theory & Variations**

- **Variations on a Theme (Monodispersity):**
  - ***'Stöber' Synthesis***

- **Conclusions**

Absolute Crystal Nucleation Rates for Hard-Sphere Colloids

Randomly stacked critical nucleus

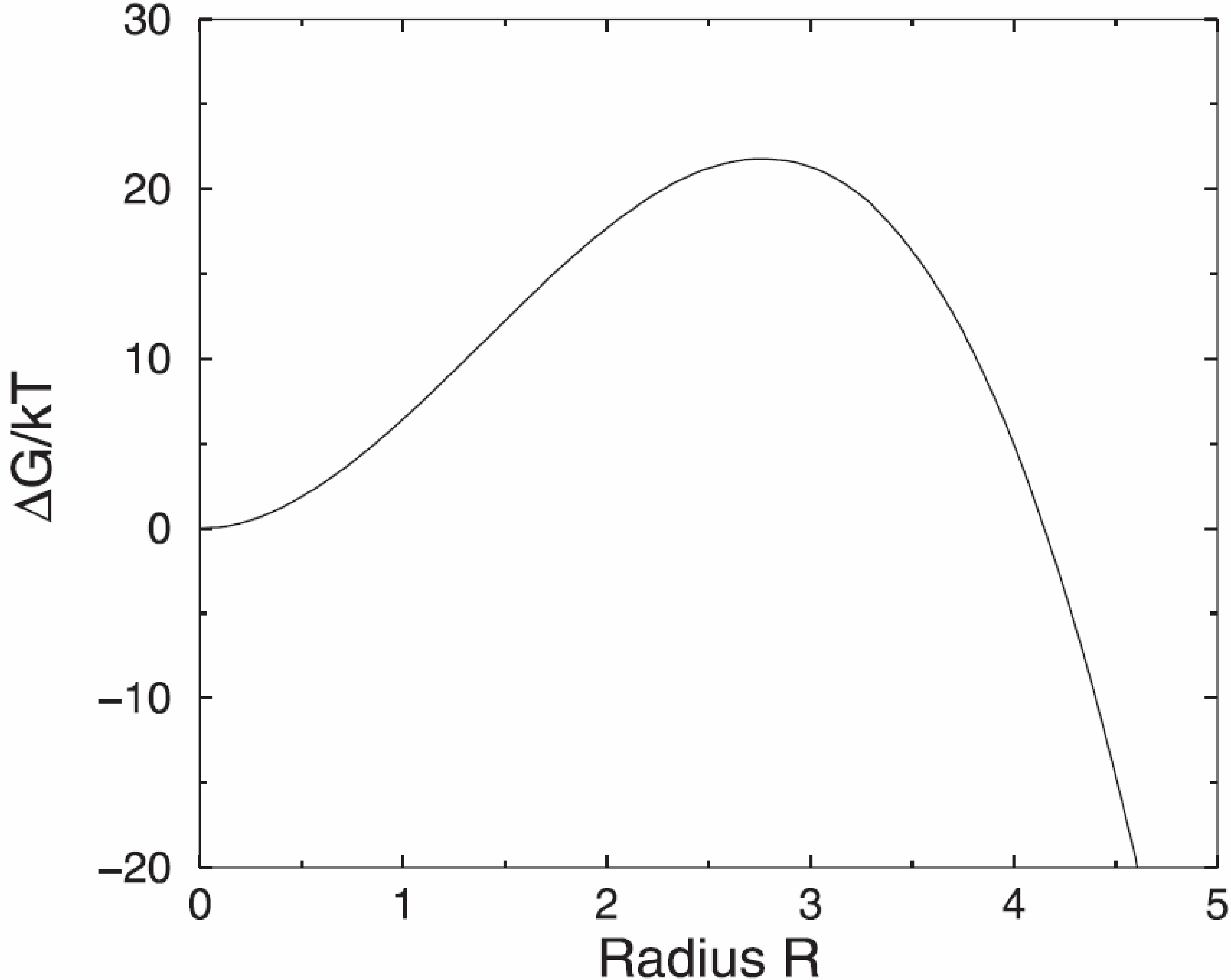


$\phi = 0.52$

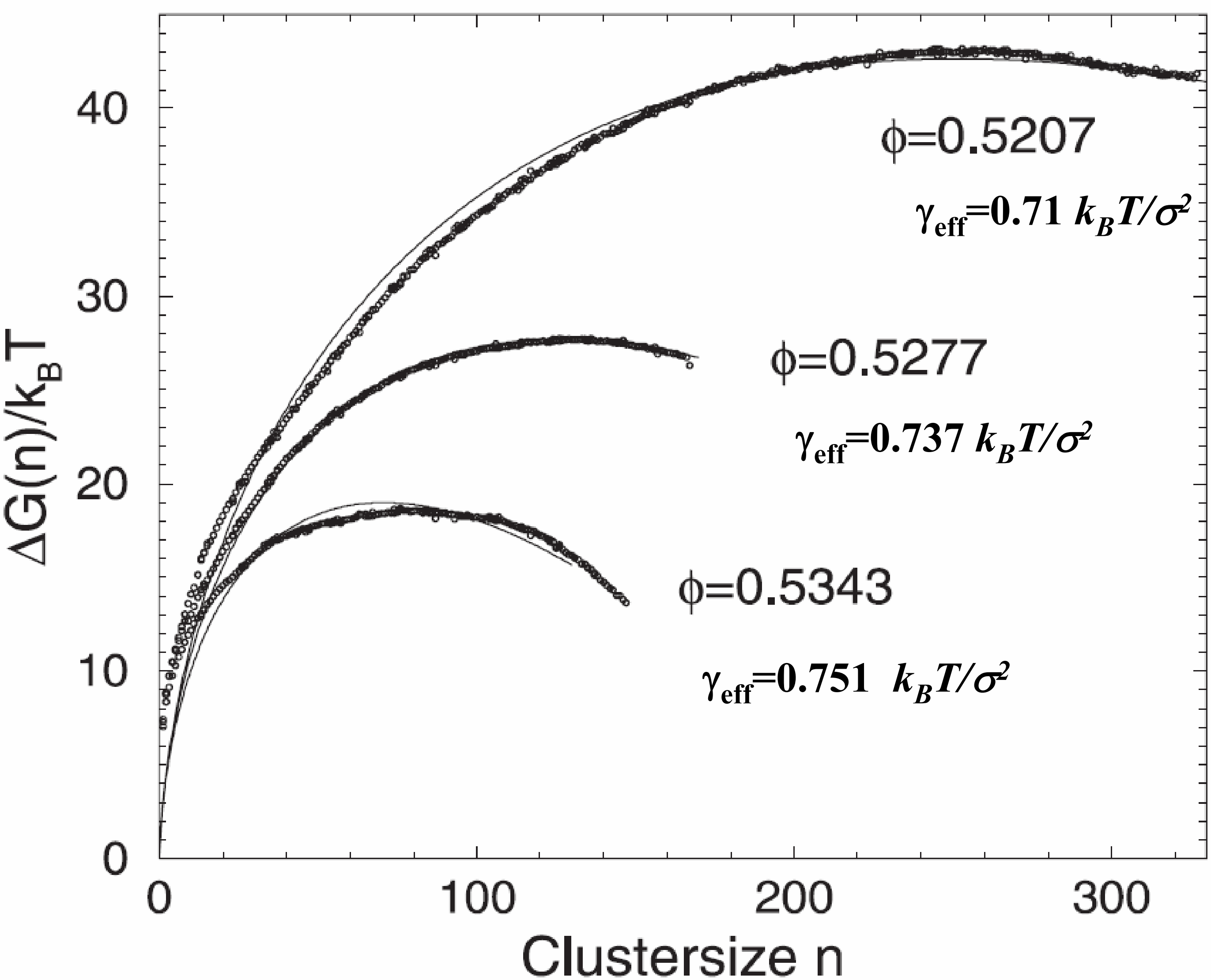
Monte Carlo Simulations with Umbrella sampling through a biasing potential

Auer & Frenkel, *Nature*, **409**, 1020 (2001)

Classical Nucleation Theory (*CNT*)



Critical Nucleus Size



DielectroPhoretic Forces

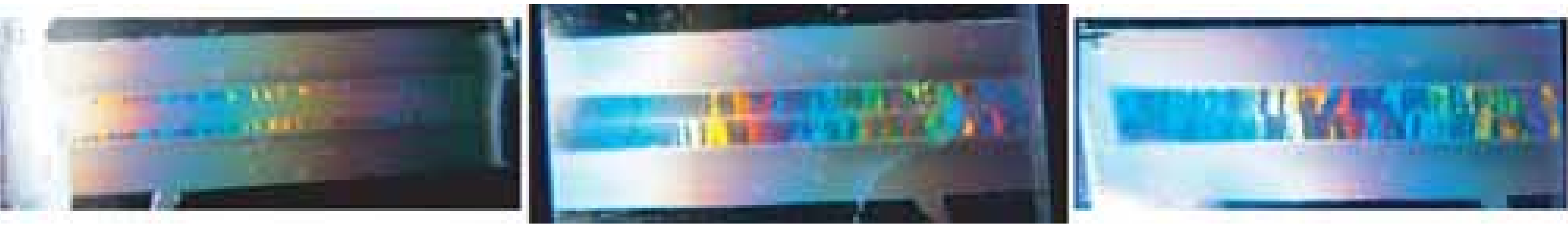
Dipole in a homogeneous electric field does not experience a force, in an inhomogeneous field its motion it does: Dielectrophoretic Force

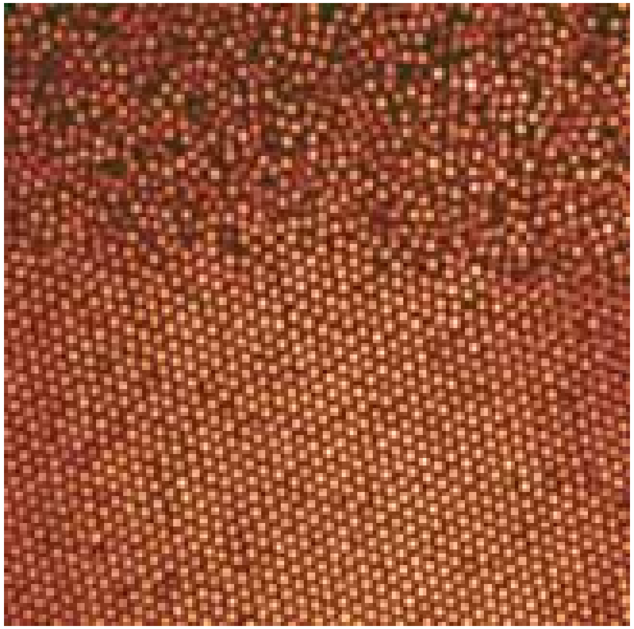
$$F_d = \frac{4\pi a^3}{c}\left(\frac{m^2-1}{m^2+2}\right)\bullet\nabla E^2$$

Using gradients in the electric field and let those balance against the osmotic pressure and gravity allows for field induced changes in the volume fraction in small volumes: A DieletrocPhoretic Bottle

DielectroPhoretic Bottle: *Slow Rate*

Field Strength 80 V/mm, 12 days crystallization, 4 mm width
1 MHz 1 mm thick



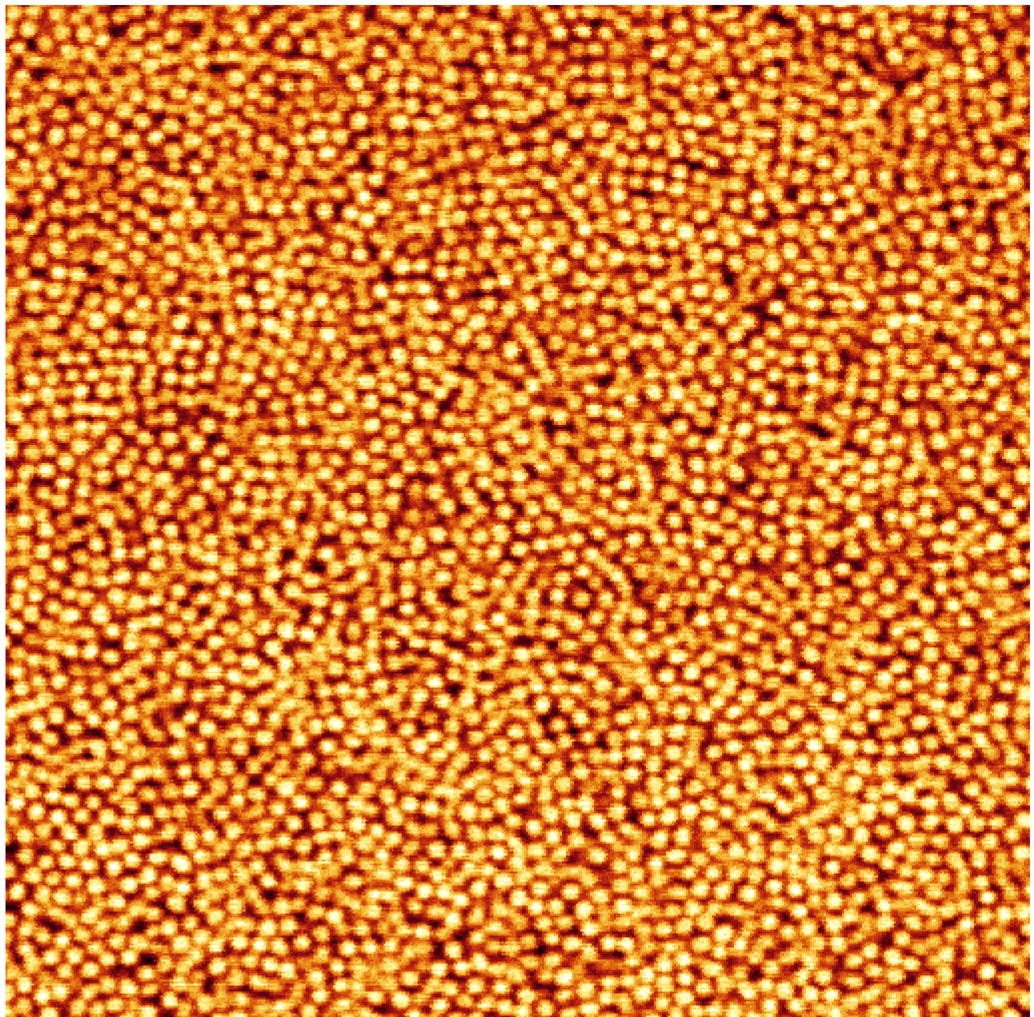


PHS-PMMA
2 μm diameter, CHB/cDec: density matched,
TBAB 'saturated' → 'almost' HS

NO Crystallization in control without E!

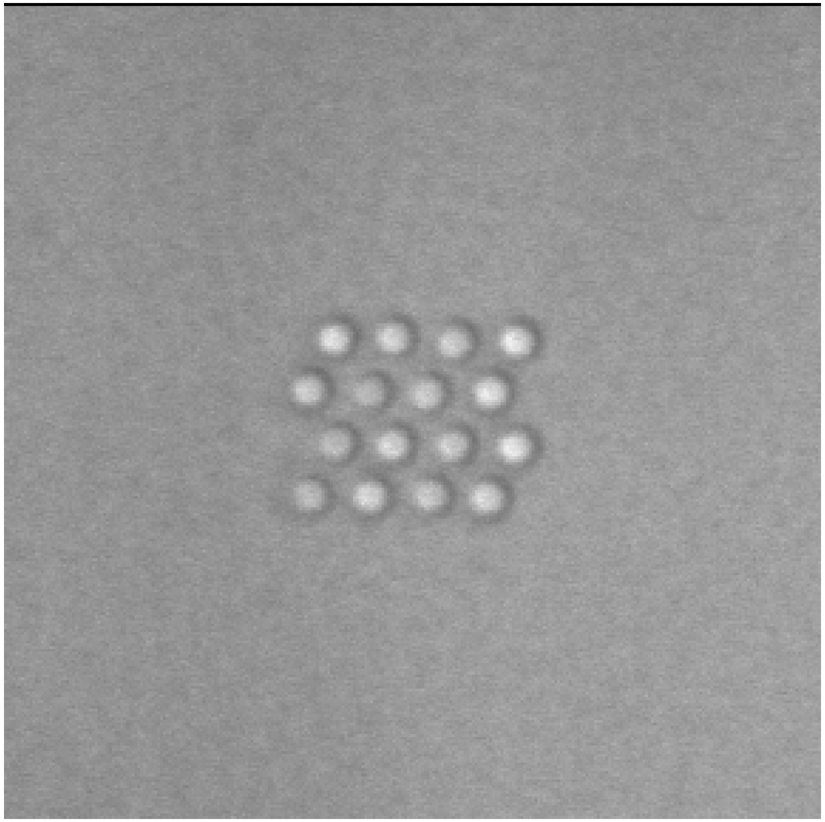
Heterogeneous Crystal Growth, Wall Induced!

Heterogeneous Crystal Growth, Random Crystal Orientation!

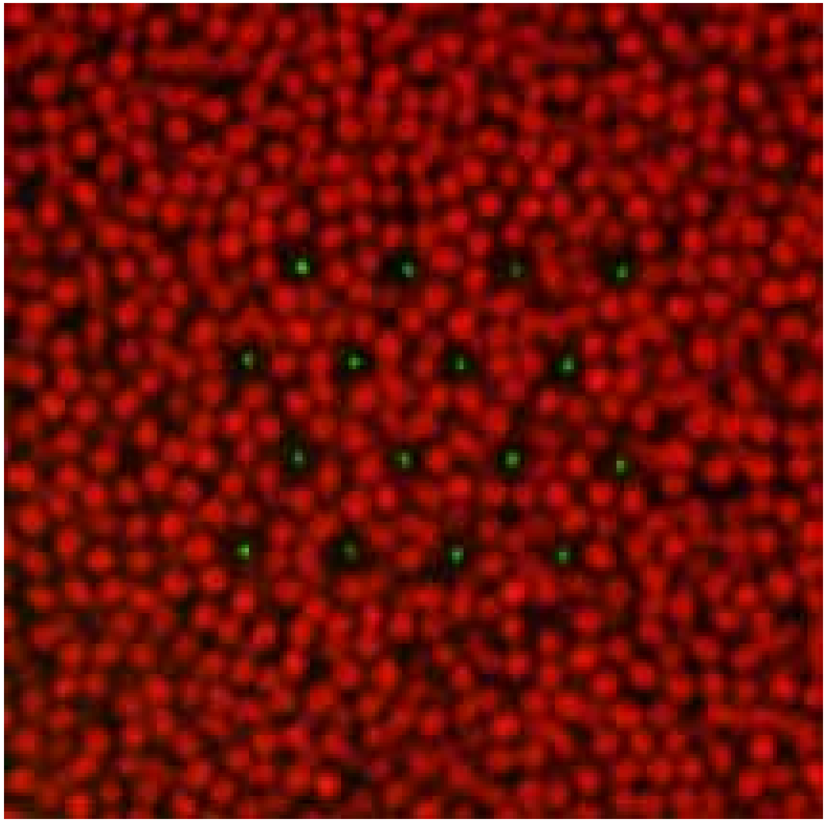


Density-Matched Tracer-Host Mixture

(PS-SiO_2-PMMA and PMMA)



Bright field

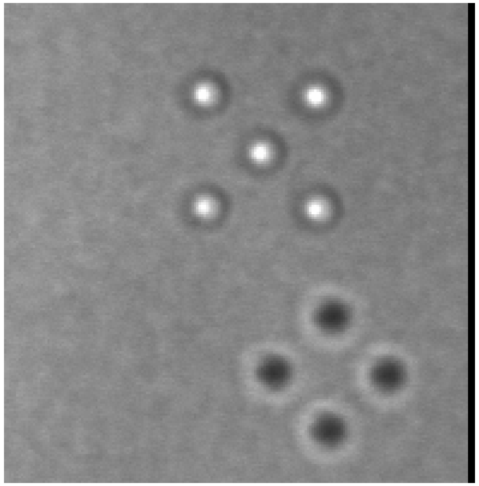


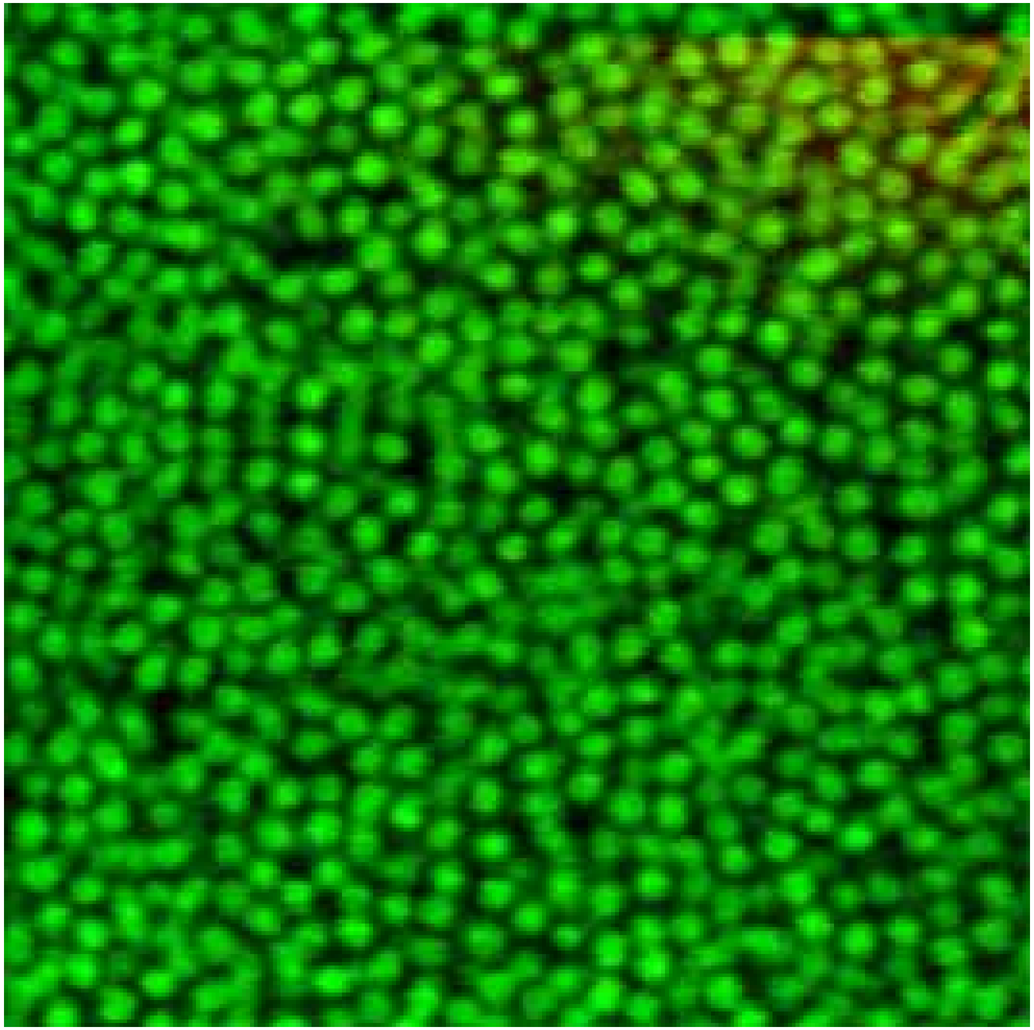
Combined fluorescence and reflection

Images
25x25 μm^2

3D Structures in a Concentrated Colloidal Dispersion

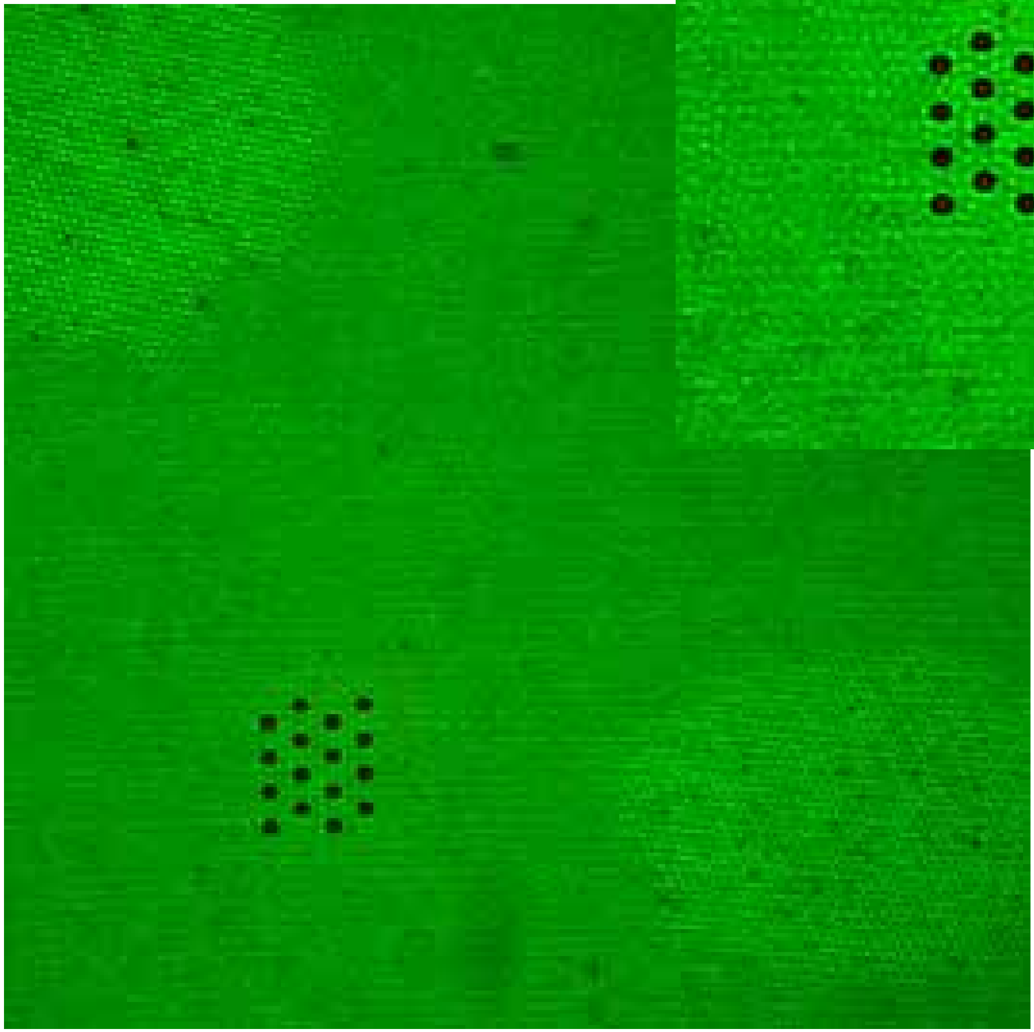
$\phi = 35\%$

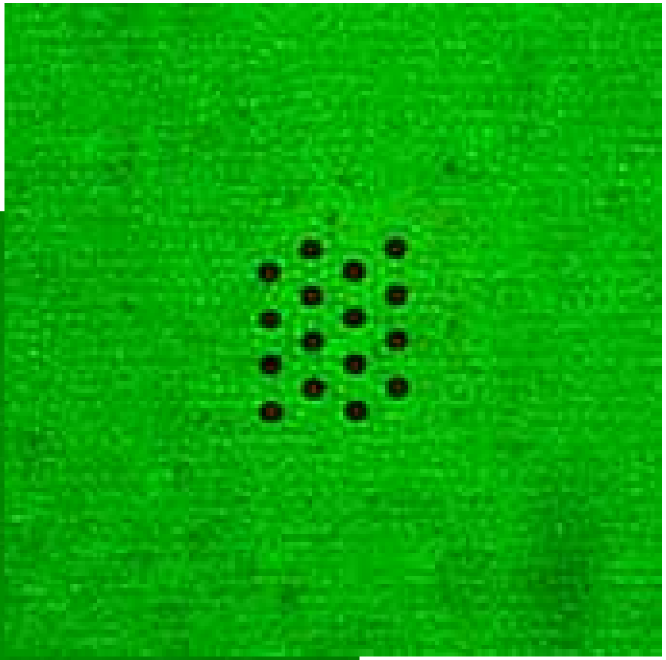




Confocal z-scan

Arrays at HS Fluid-Crystal Coexistence

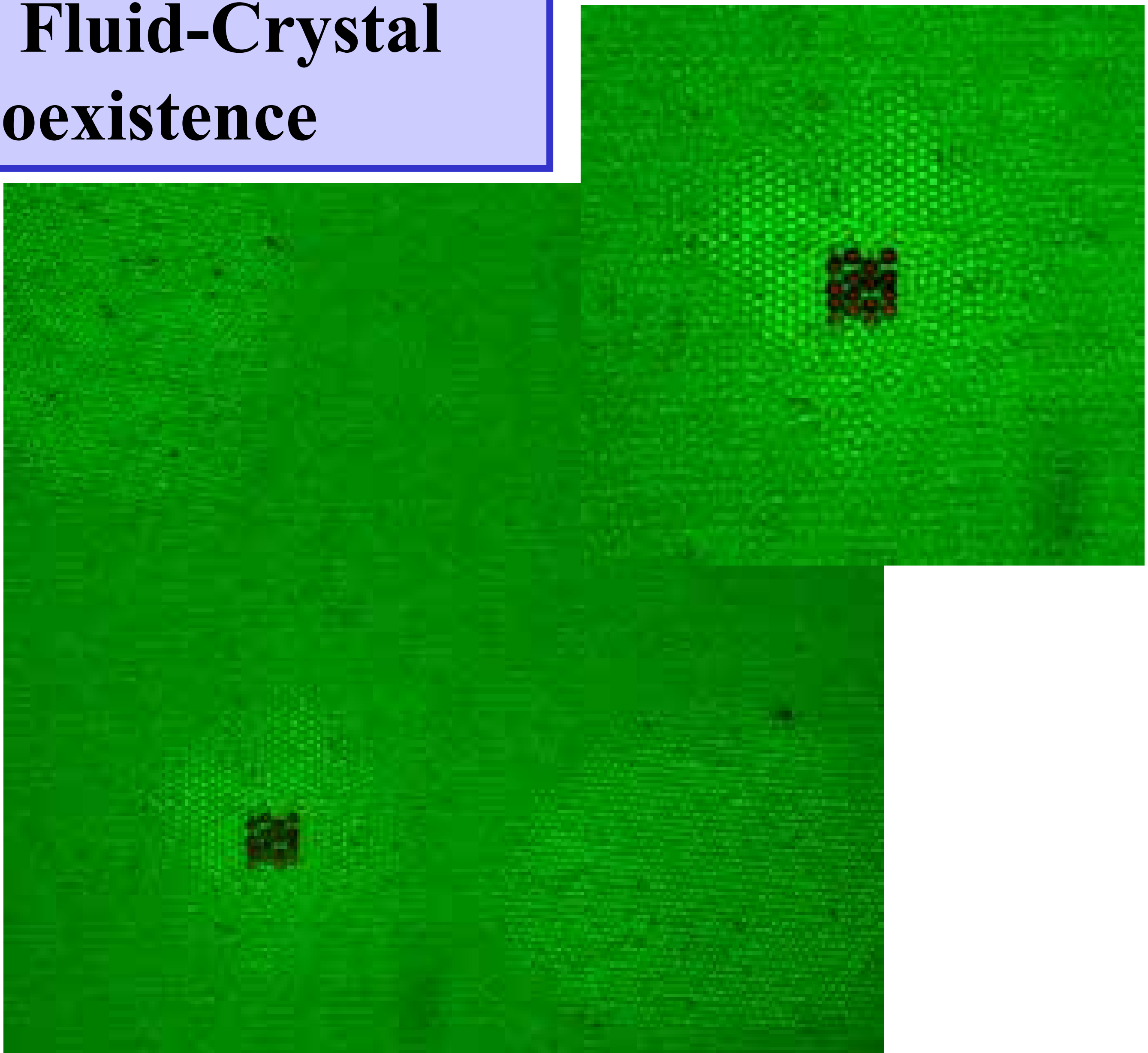




Averaged over 100 frames

Image 100x100 μm^2

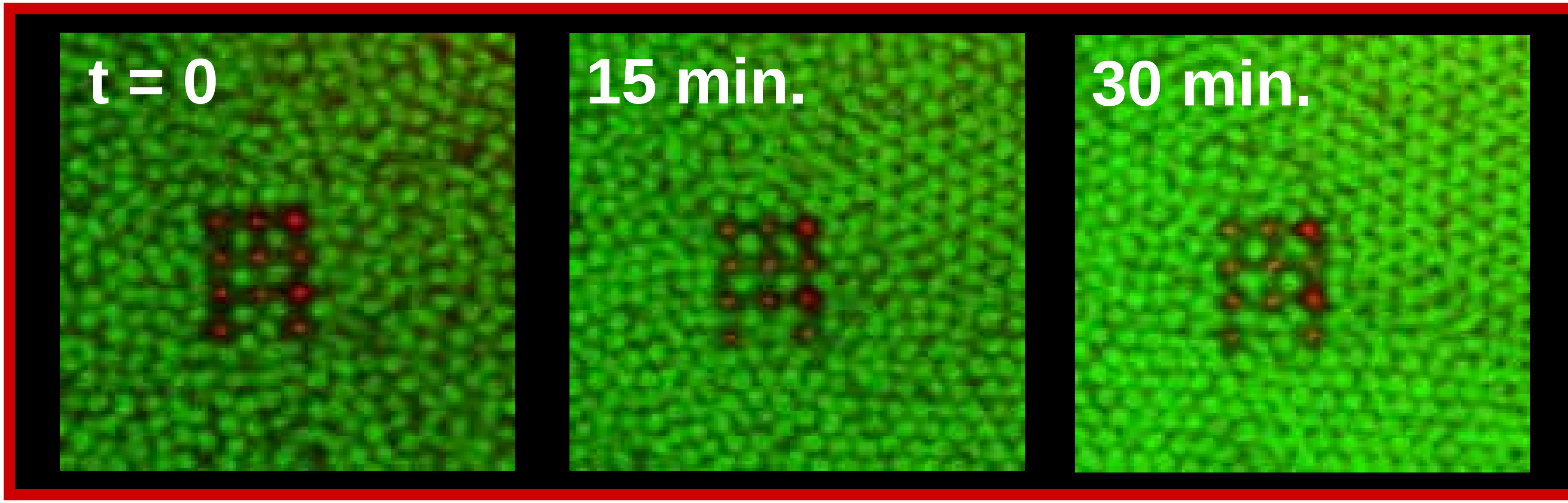
Arrays at HS Fluid-Crystal Coexistence



Averaged over 100 frames

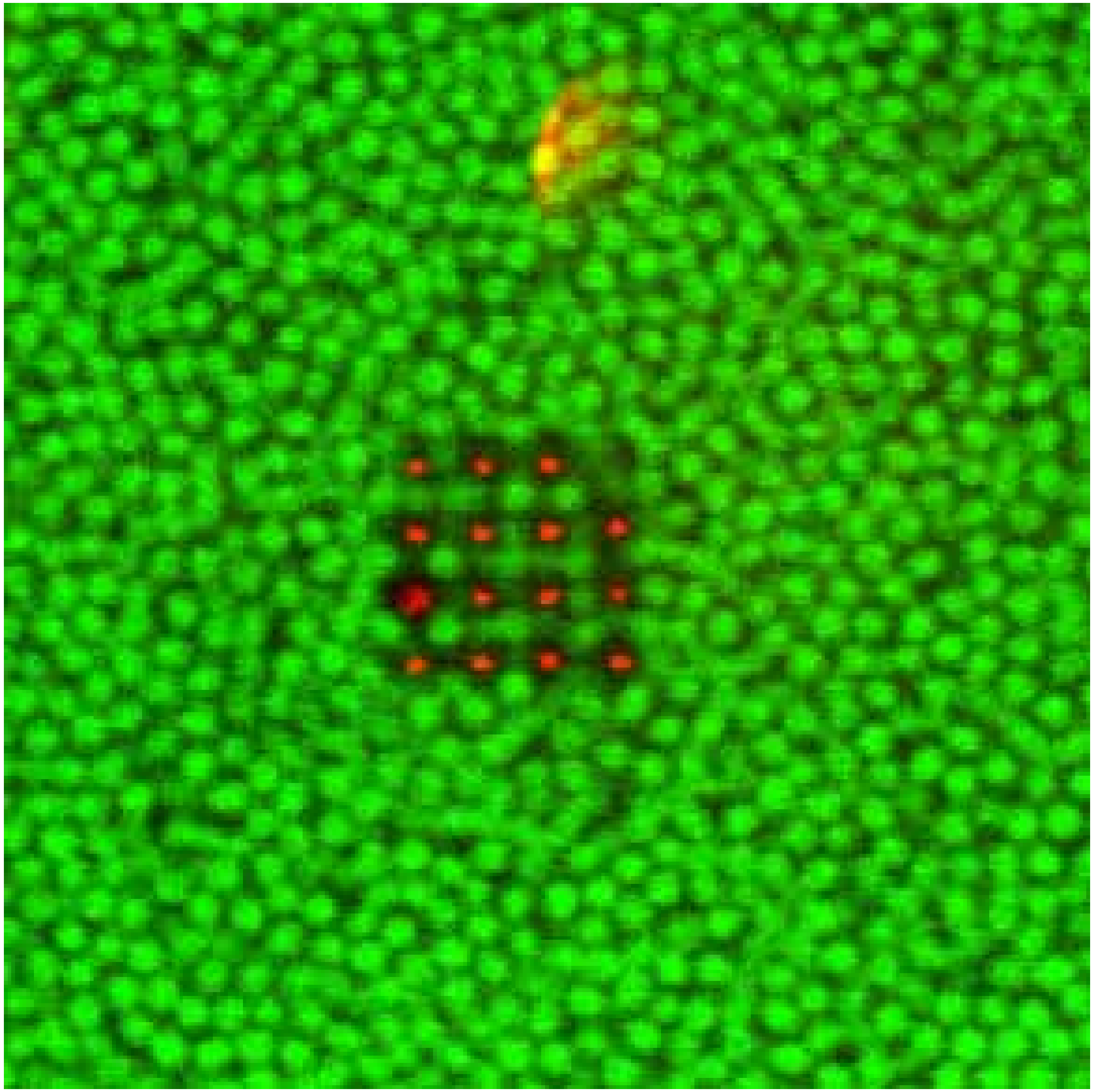
Image 100x100 μm^2

Tweezers *and* Dielectric Bottle

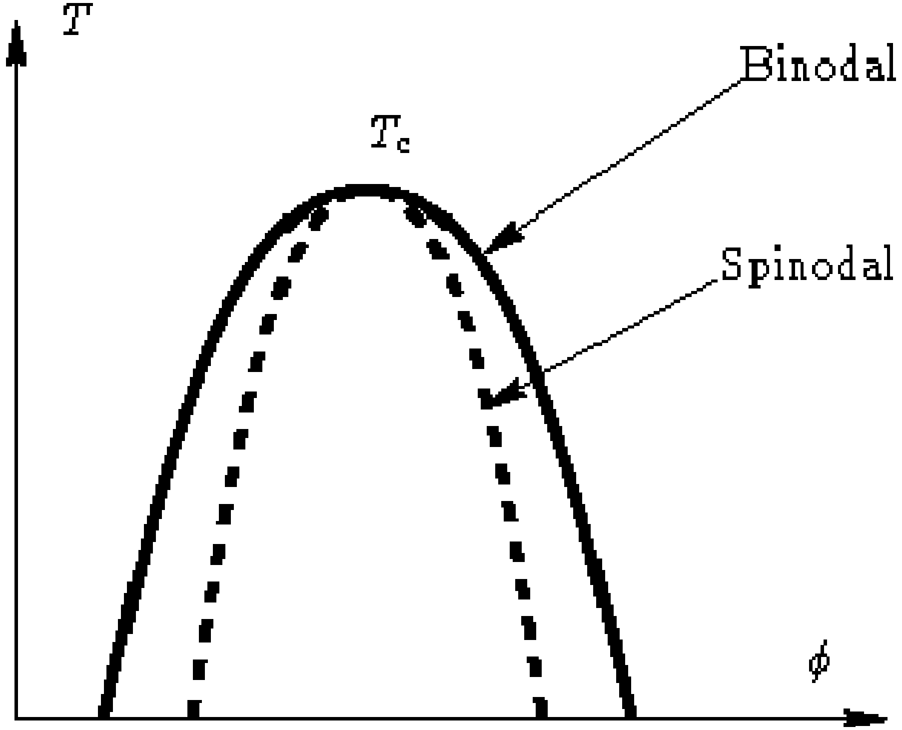


Success but no data (yet)!

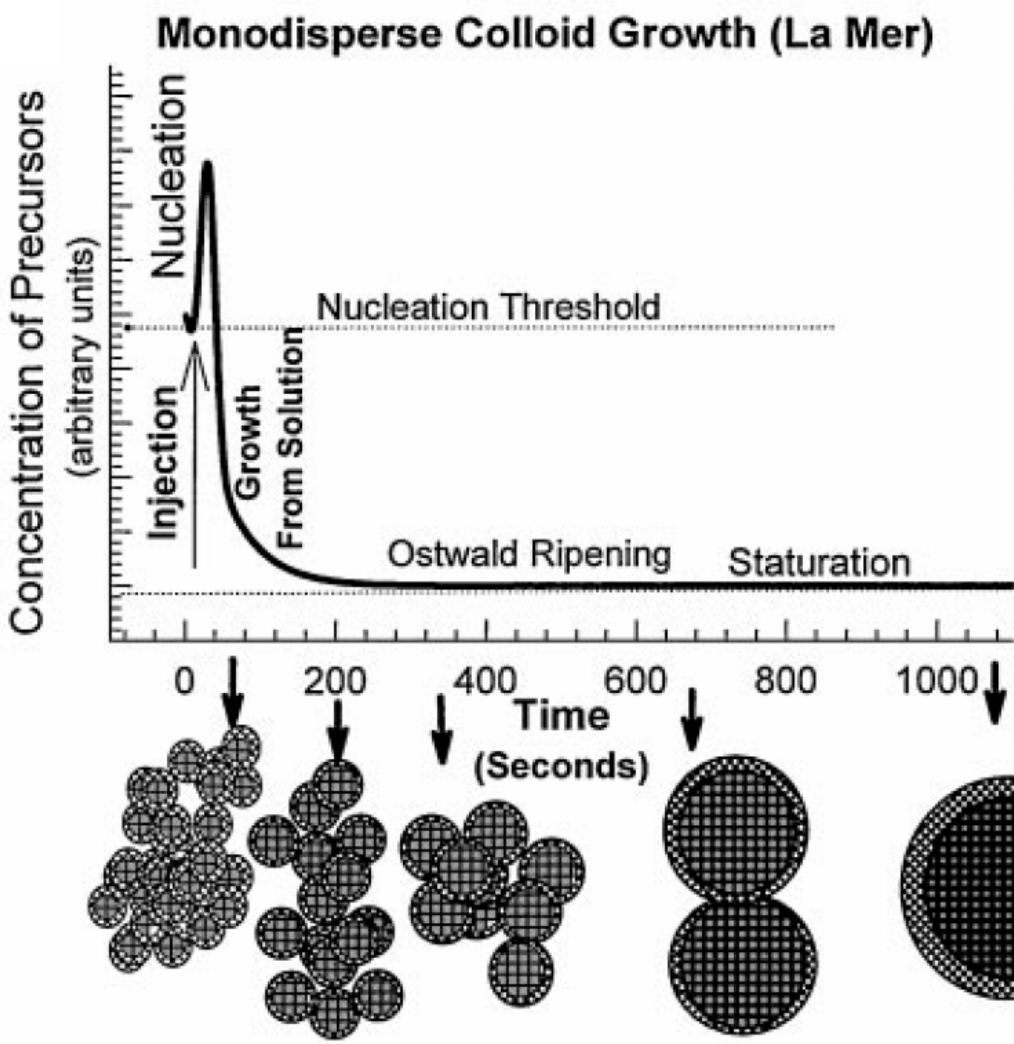
Tweezers *and* Dielectric Bottle

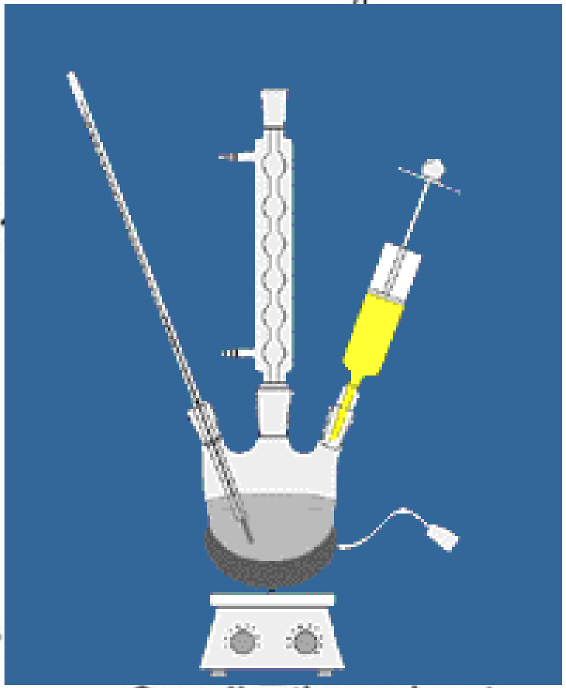


Spinodal Decomposition: *Nucleation & Growth*



Homogeneous Nucleation: *NanoCrystals*





Coordinating solvent
Stabilizer at 150-350C

Monodispersity through Growth

$$\frac{dV_p}{dt} \propto k_c R^{\alpha} c_h$$

$\alpha = 1$ **diffusion limited growth**

$\alpha = 2$ **surface reaction limited growth**

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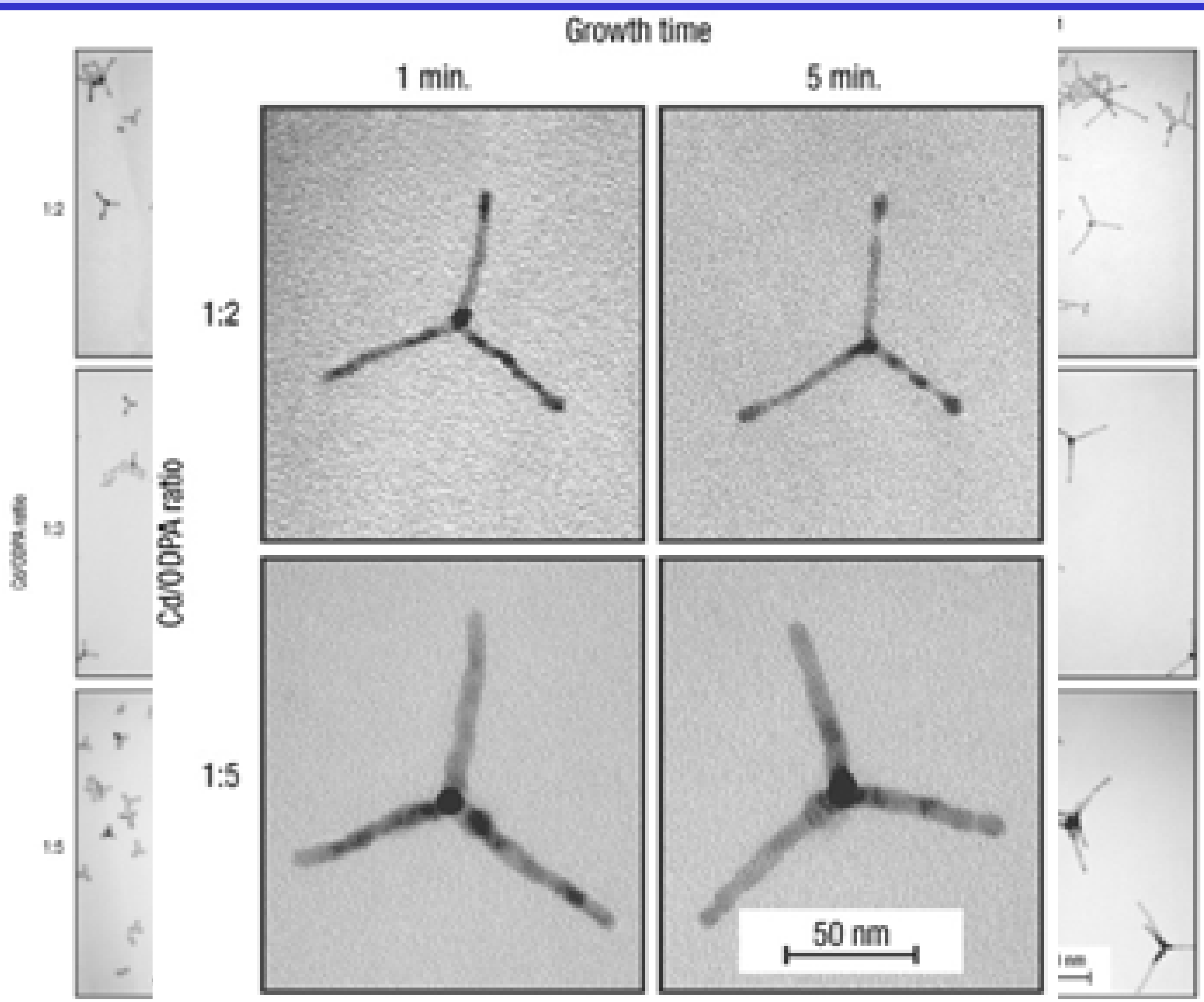
Multistage Nucleation and Growth

CdSe several μm in Size

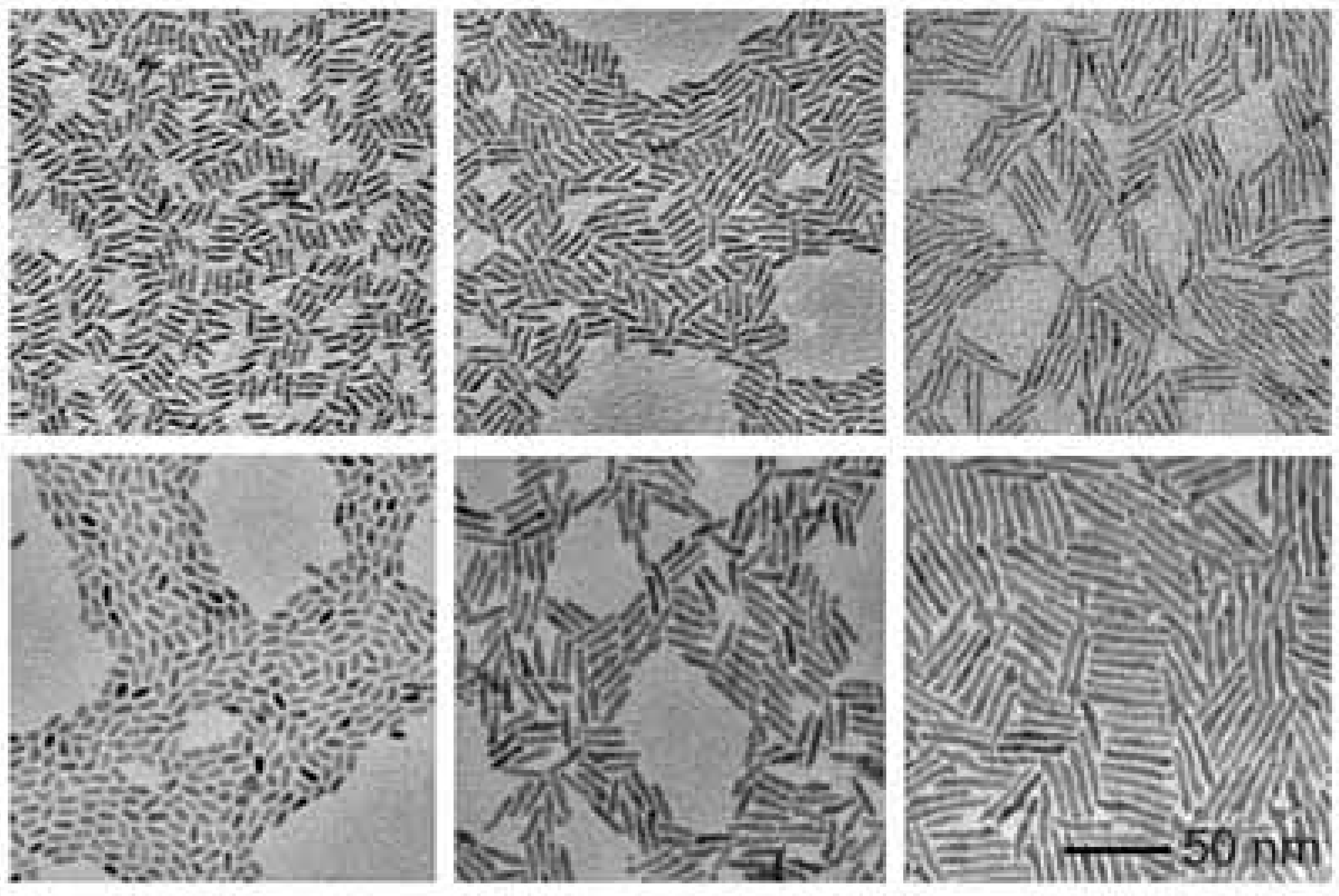
Polytypism in Nucleation & Growth



CdTe TetraPods

Alivisatos et al.
Nature Materials **2**, 382 (2003)

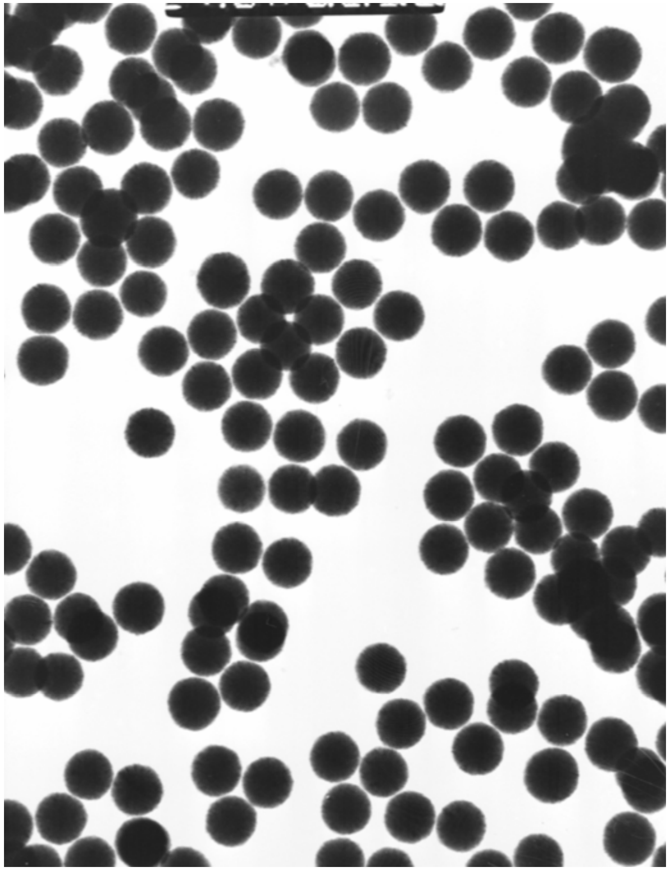
Colloidal NanoCrystals with Shape Control

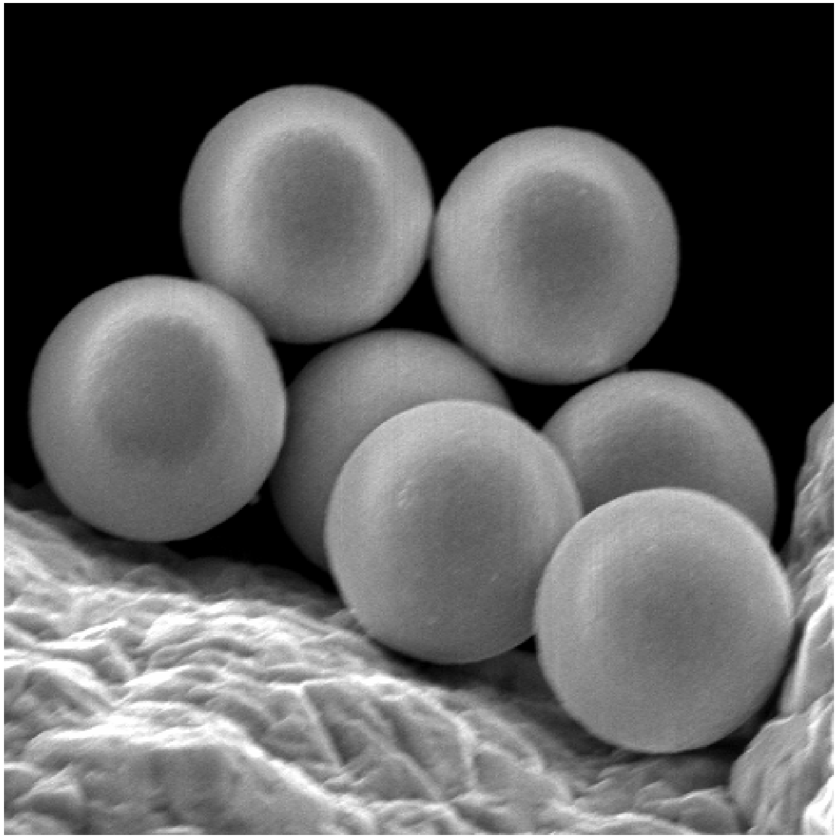


CdSe Nano Crystals with Shape Control Form LC phases

Alivisatos et al., *Nano Lett.*, **1**, 349 (2001)

Aggregation of ZnS NanoXtals

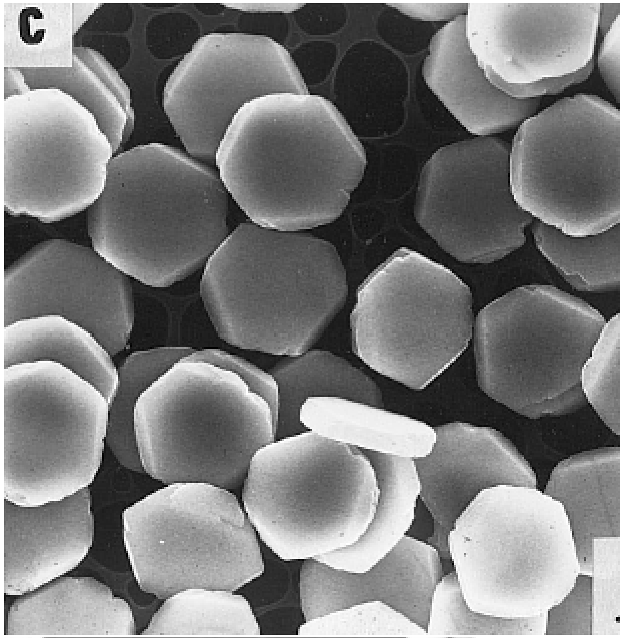


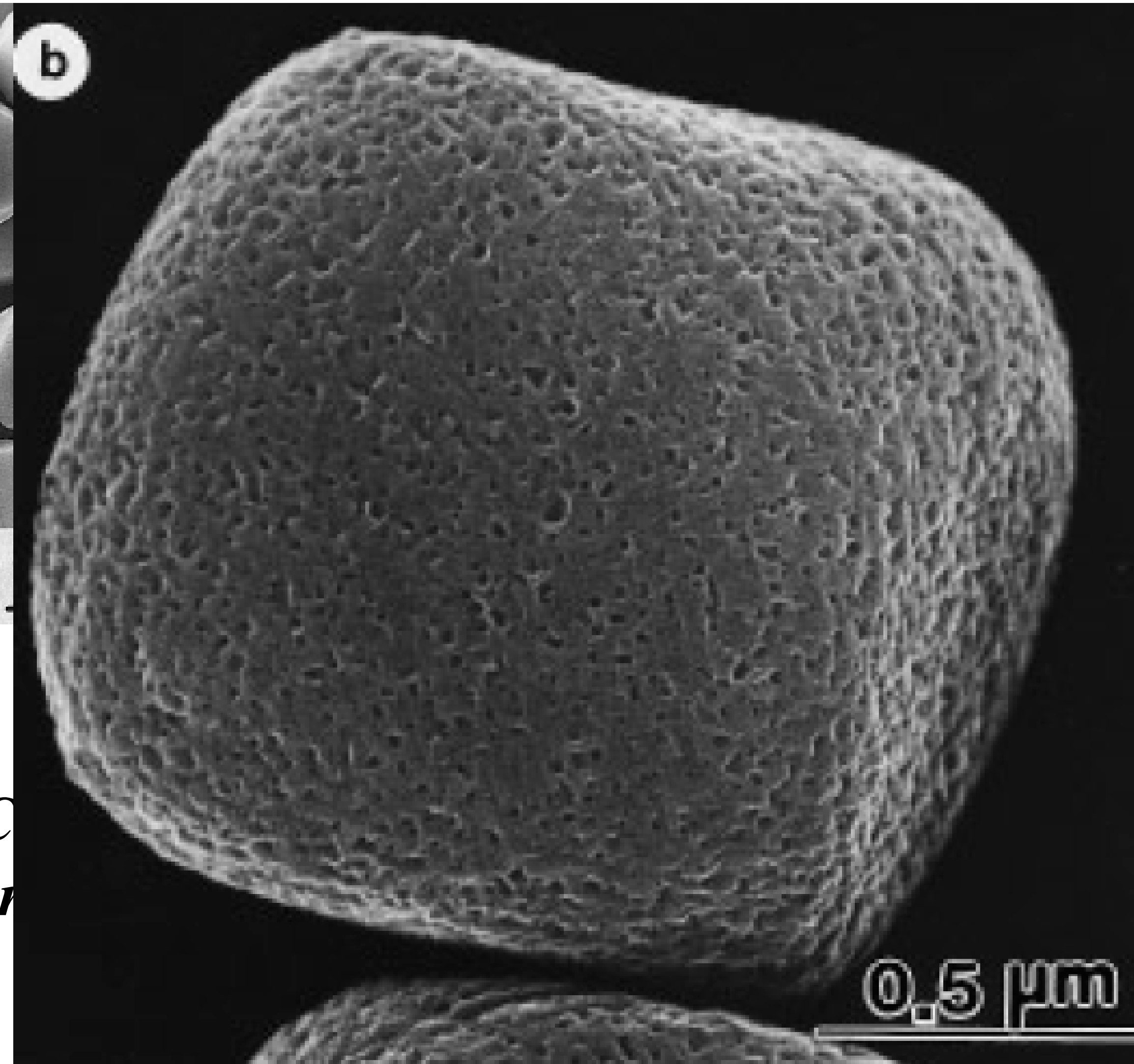


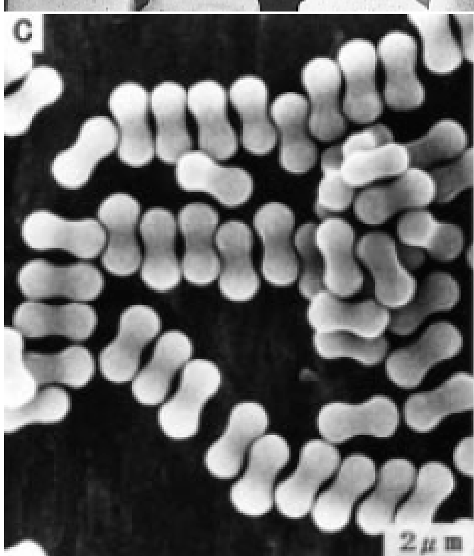
ZnS R = 103 nm $\delta \sim 3\%$

ZnS R = 1.4 μm $\delta \sim 1\%$

Monodisperse Hematite Fe_2O_3 Colloids

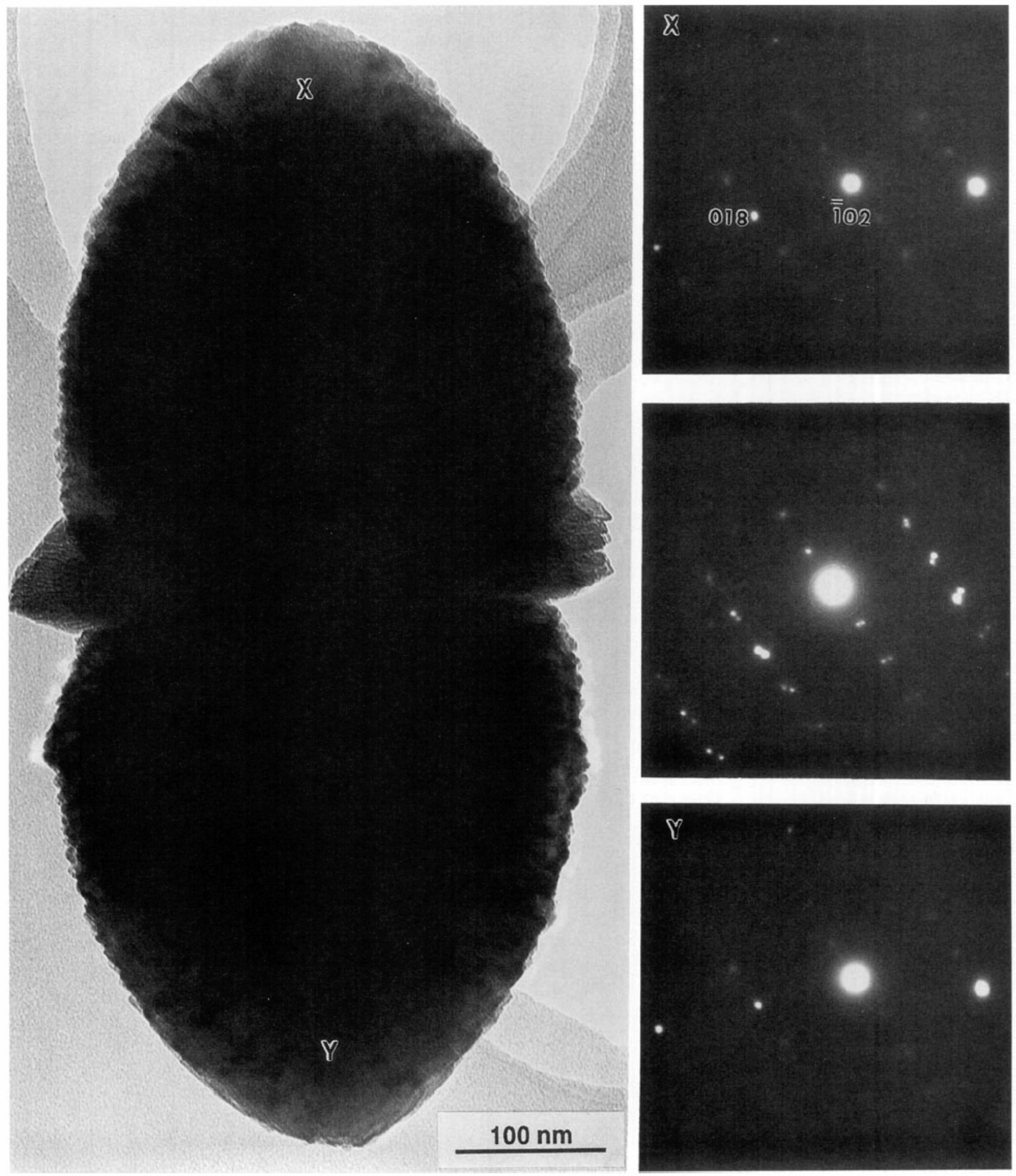






T. Sugimoto et al. *Chem. Eng. Technol*, ***26***, (**2003**)

Hematite: Aggregation of NanoXtals



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‘Silica’ from 4-AlkoxySilanes

General Scheme	Specific Example	Role
$R_xSi(OR`)_y$	$Si(OCH_2CH_3)_4$	Reagent
Alcohol	$HOCH_2CH_3$	Co-solvent
Water	H_2O	Reagent/Solvent
Amine	NH_3	Catalyst

Reactions:

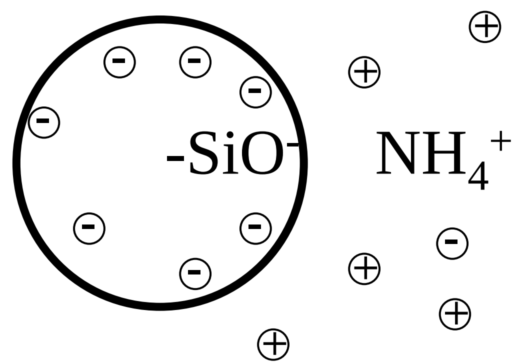
Hydrolysis (amine is catalyst)

$$-Si-OR + H_2O \leftrightarrow -Si-OH + HOR$$

Condensation (amine is catalyst)

$$-Si-OH + RO-Si- \leftrightarrow -Si-O-Si- + HOR$$

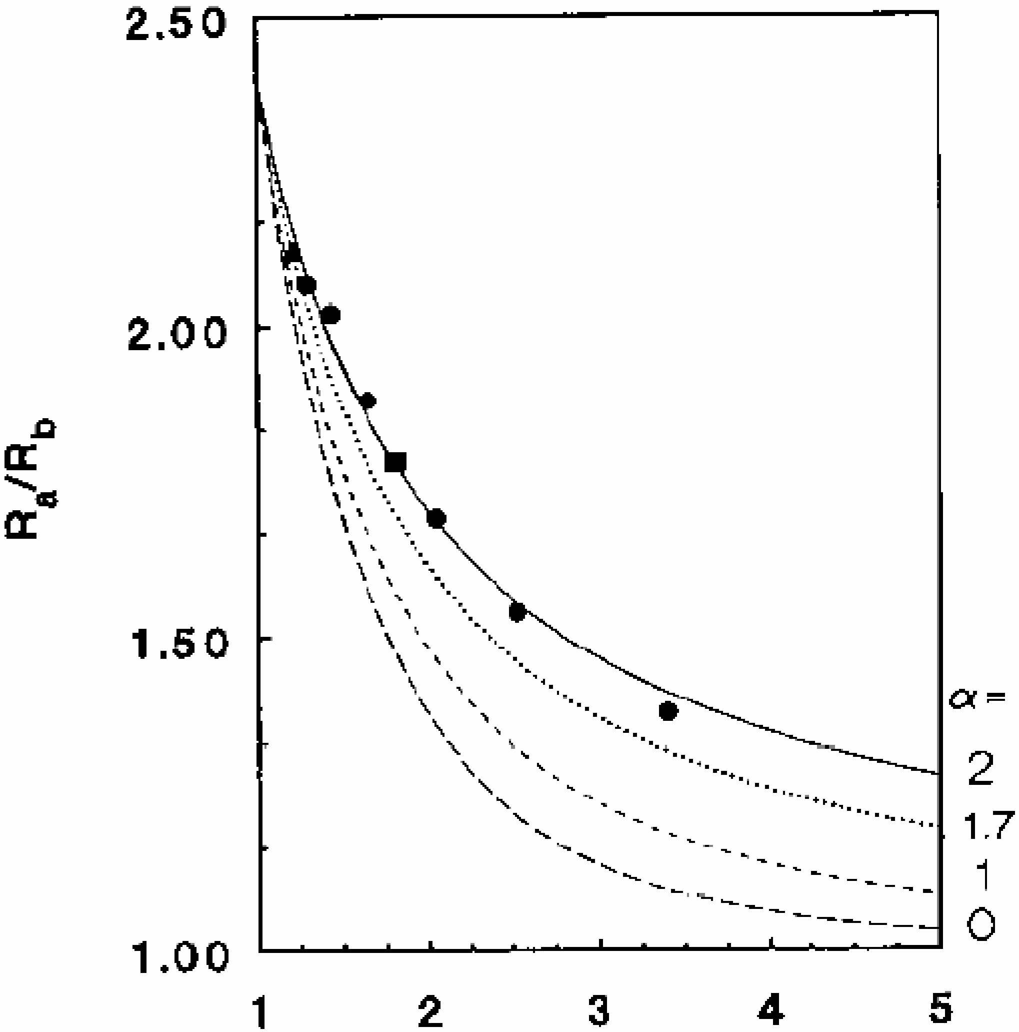
Dissociation



Stöber et al., *JCIS*, (1968) -> **Kolbe** (1956); **Sol-Gel -> NO Gel**

Silica Bidisperse Particle Growth

$$\frac{dV_p}{dt} \propto k_c R^{\alpha} c$$



$\alpha = 1$ **diffusion limited growth**

$\alpha = 2$ **surface reaction limited growth**

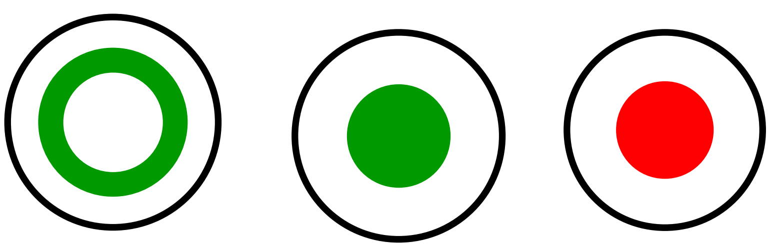
'Silica' from n-AlkoxySilanes (n<4)

- **Mechanism:**
  - *-Hydrolysis Rate Determining*
  - *-Initial Aggregation of 'Collapsed Polymers'*
  - *-Surface Reaction Limited Growth of 'Monomers'*
    - *-> Rel. Polydispersity $\propto$ 1/R*

***AvB, et al.**, JCIS, **154**,* **(1992); AvB, et al.,** *JNCS, 149* **(1993)**

- **Variations:**
  - *-Surface Coating with Coupling Agent* **R-Si(OEth)$_3$**
  - *-Seeded Growth*
  - *-Copolymerization with Coupling Agent*

AvB, et al.**, JCIS, **156**,* **(1993),** *Langmuir **8, (1993)
***10**,* **(1994)**



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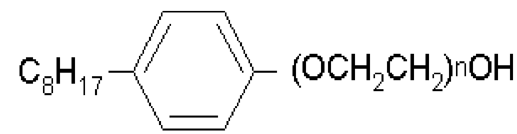
  - ***-In a μ-Emulsion***

- **Conclusions**

Silica in a W/O μ-Emulsion



n ~ 5

Components:

Cyclohexane (Cycl) — $(CH_2)_6$

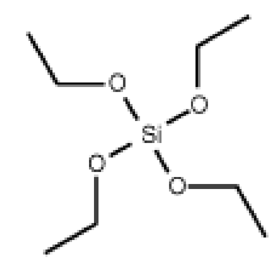
Polyoxyethylene nonylphenyl ether (NP5) — $4\text{-}(C_9H_{19})C_6H_4O(CH_2CH_2O)_{\sim 4}\ CH_2CH_2OH$

Ammonia (NH_3) — NH_3

Tetraethoxysilane (TES) — $Si(OCH_2CH_3)_4$

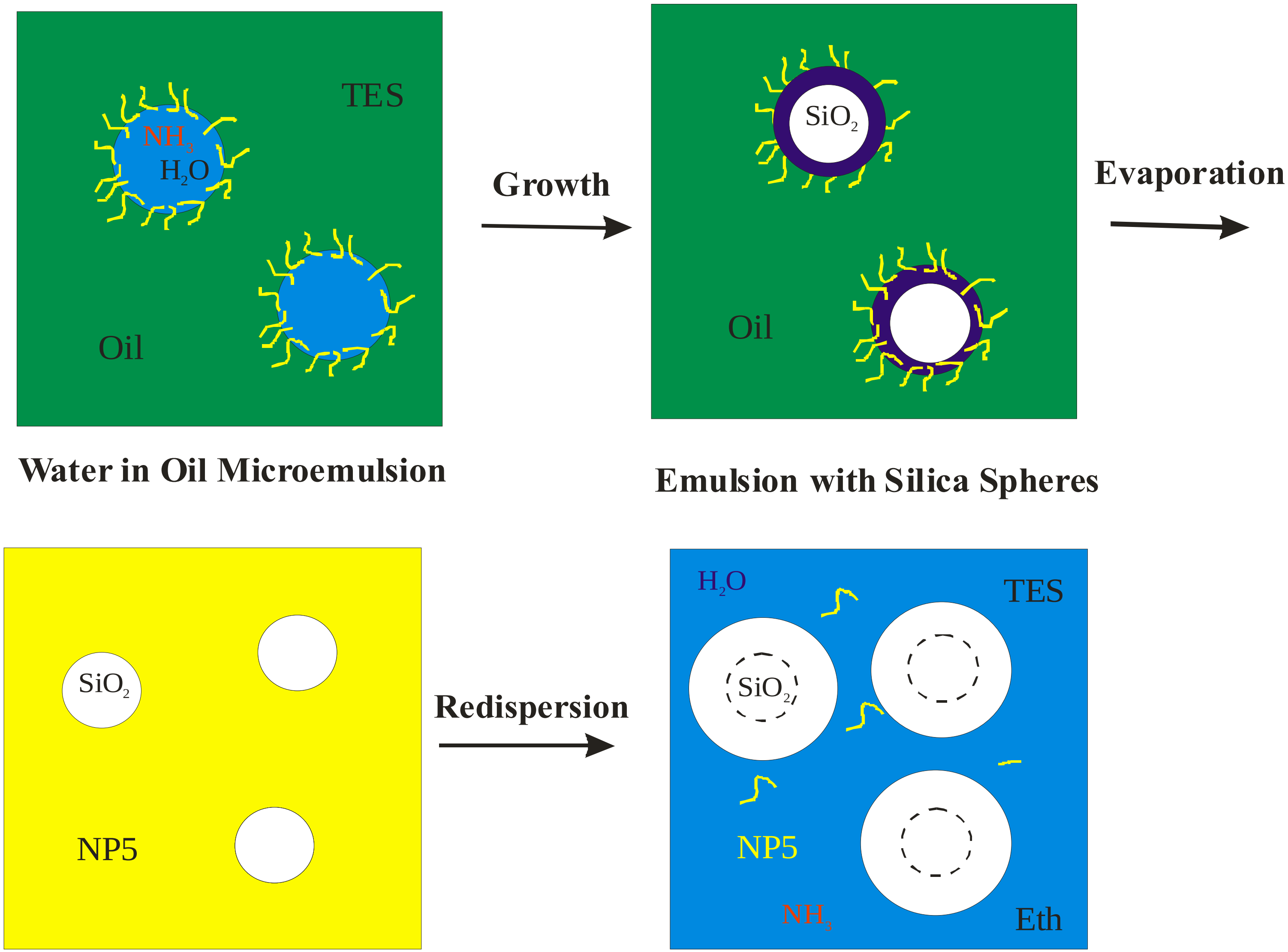
Water (H_2O) — H_2O

Ethanol (Eth) — H_3CH_2COH



Arriagada, et al., *Colloids Surf.*,**69**, 105 (**1992**).

Silica in a W/O μ-Emulsion



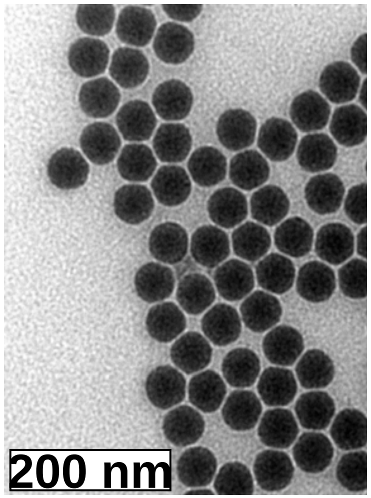
Water in Oil Microemulsion

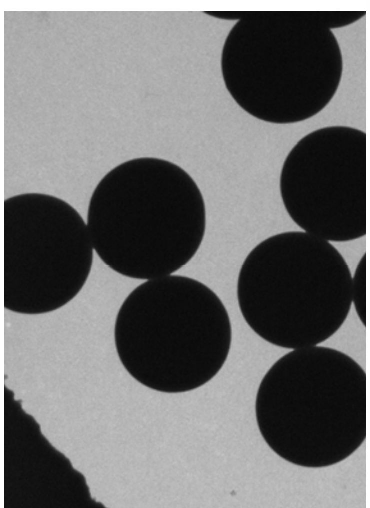
Emulsion with Silica Spheres

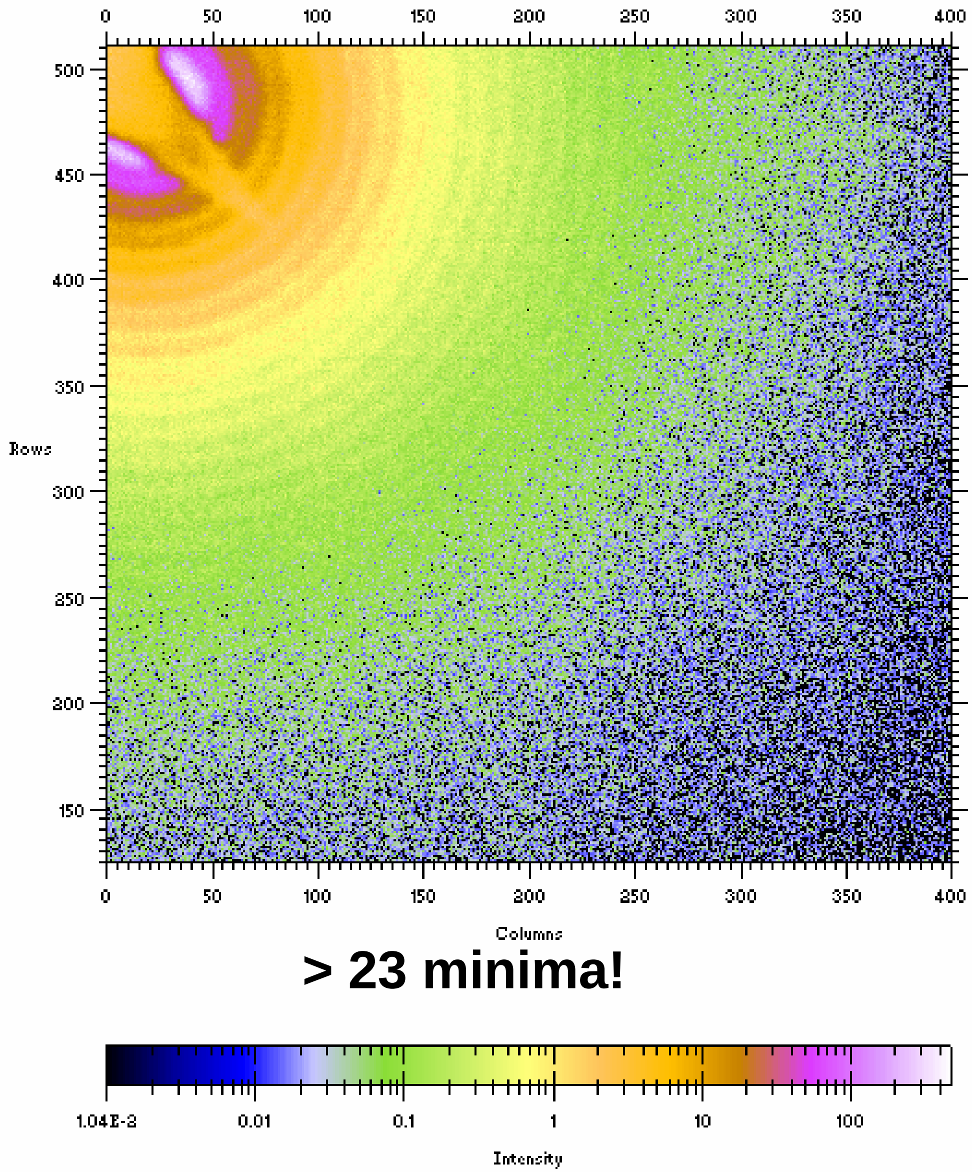
Silica Spheres Dispersed in Non-ionic Surfactant

Further Growth by Seeded Stöber Proces

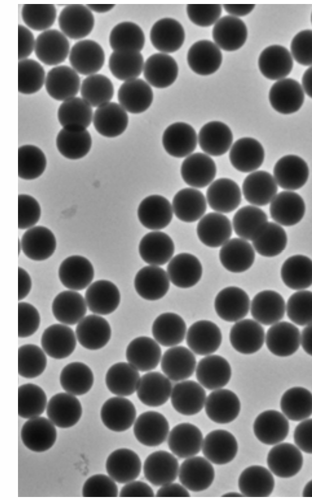
Silica Seeds From W/O μ-Emulsion







> 23 minima!

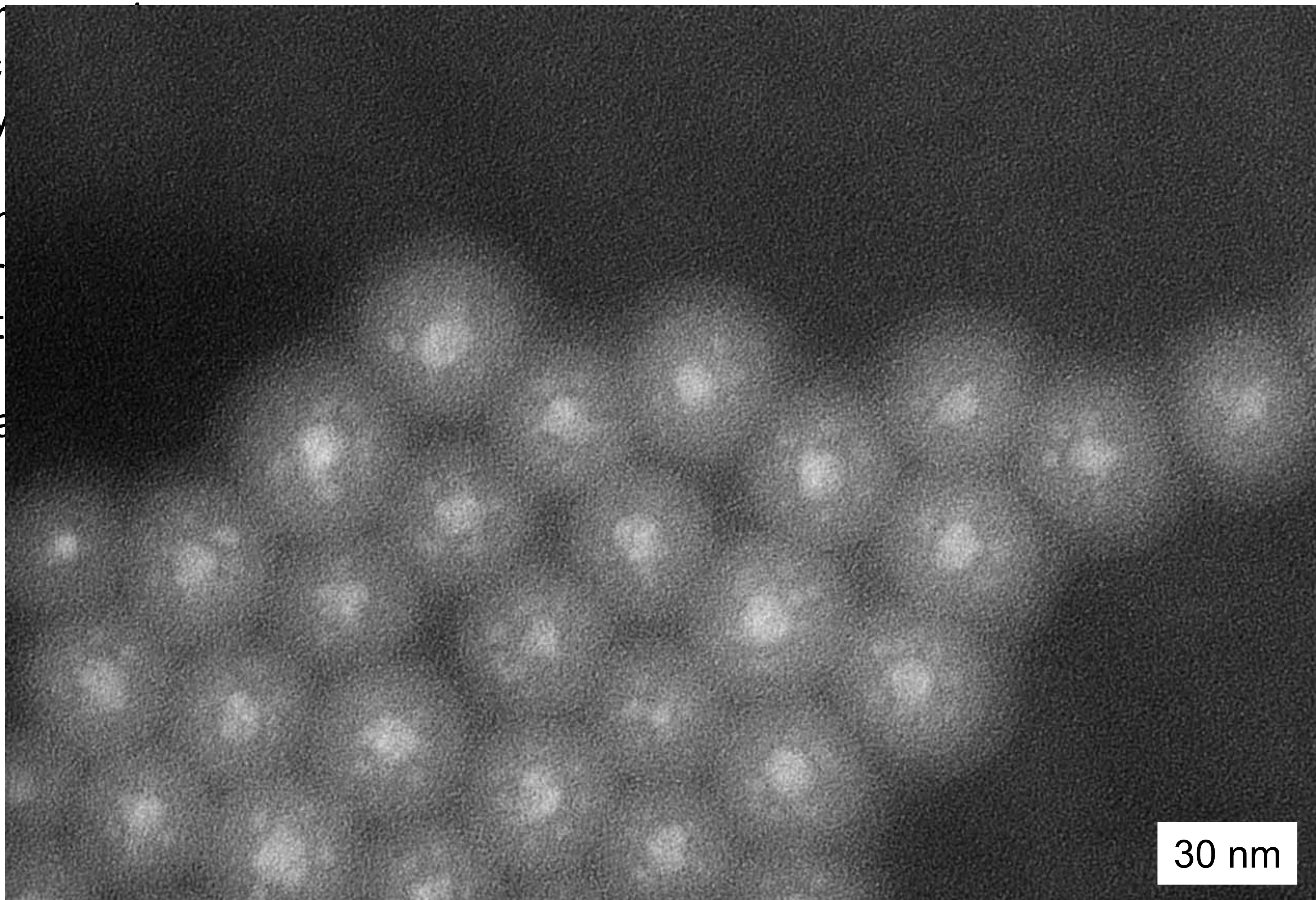


olloids!

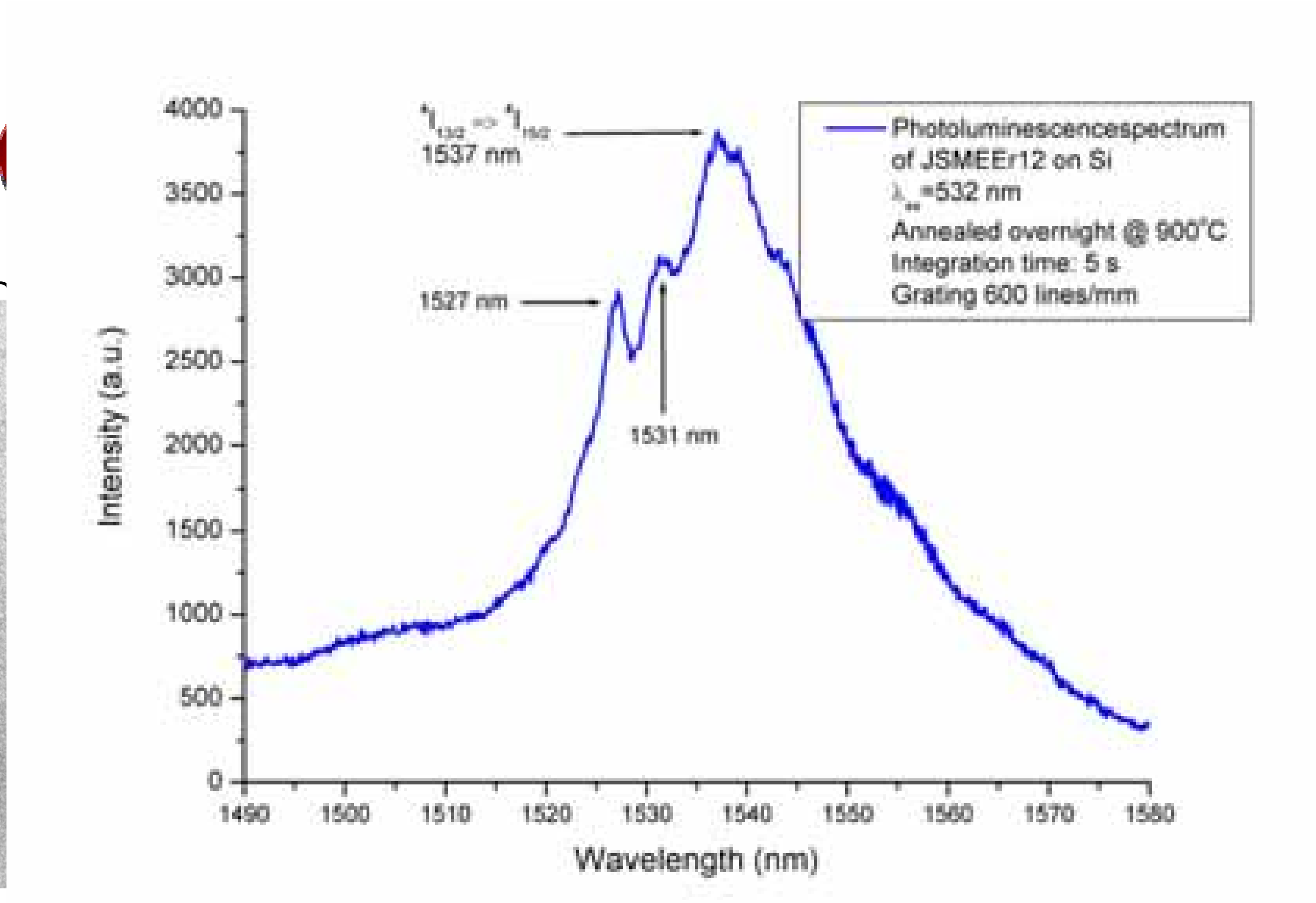
m, δ = 3%

ZnS-in-Silica in a W/O μ-Emulsion

Com
Cyc
Poly
H$_2$OH
Amr
Tetr
Wat itions)
Etha



QD/Ag/RE-in-Silica in a W/O μ-Emulsion



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  -***'Stöber' Synthesis (Coupling Agents)***

  -In a μ-Emulsion

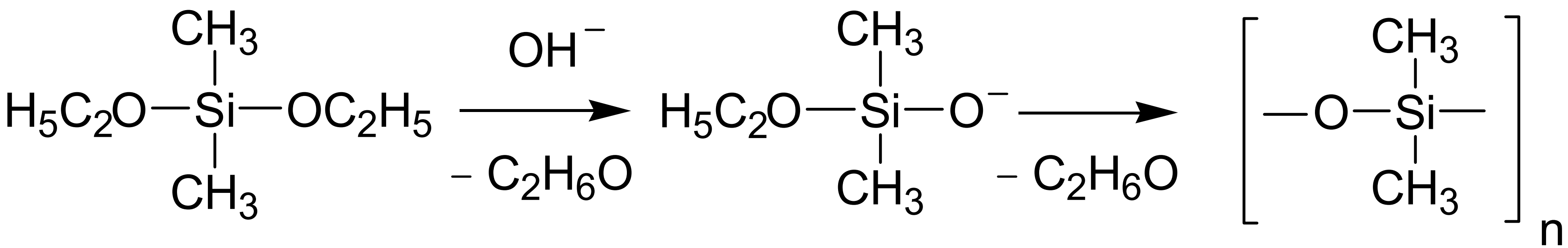
  -n=2 -> Emulsion -> Shells

- **Conclusions**

Monodisperse O/W Emulsion

DMDES
dimethyldiethoxysilane

Base-catalyzed (ammonia) hydrolysis and polymerization

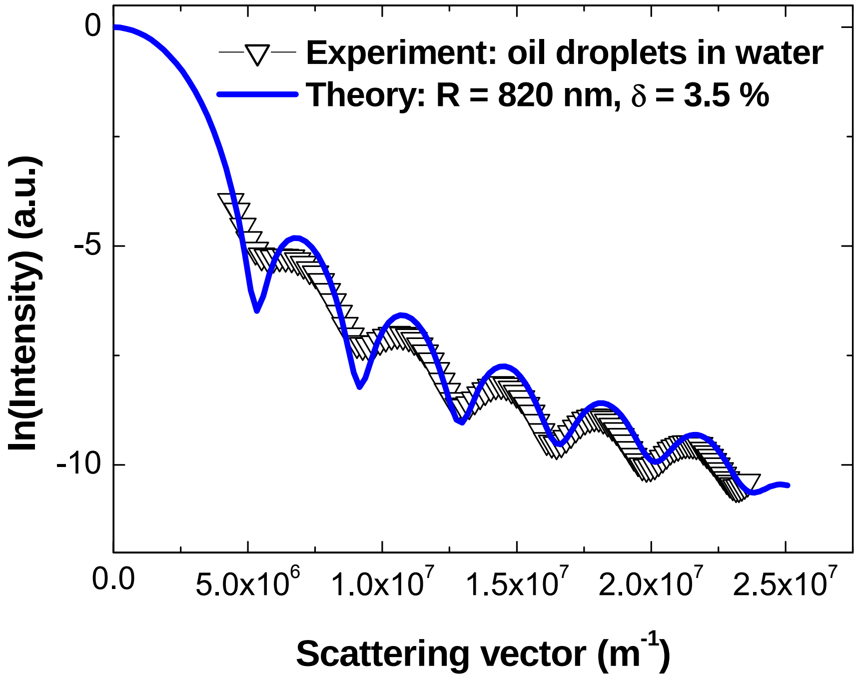


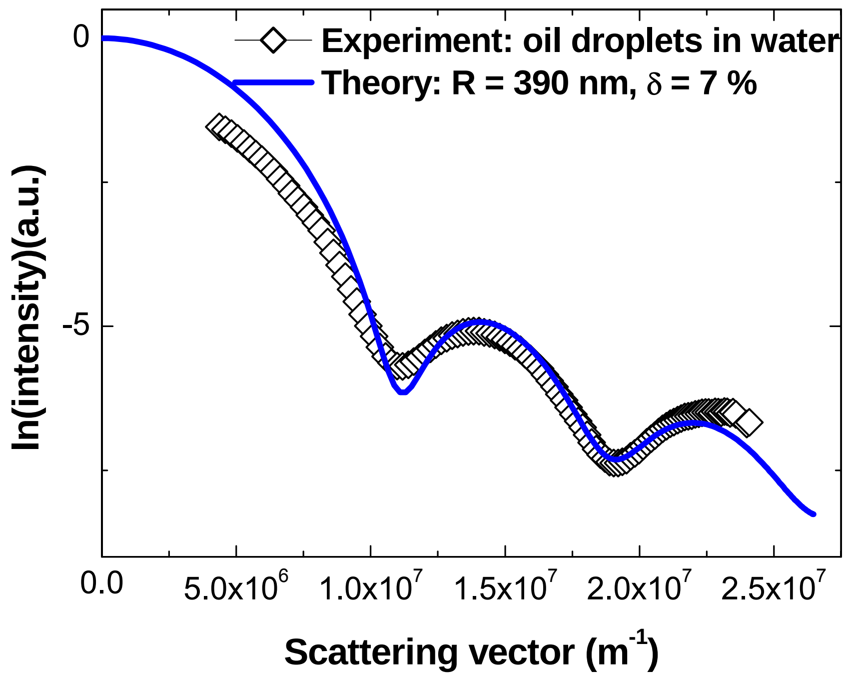
PDMS
‘poly’dimethylsiloxane
(silicone oil)

‘Stöber-Like Mechanism’

Obey, Vincent, J. Colloid Interface Sci. ***163****, 454 (1994)*

Monodisperse O/W Emulsion



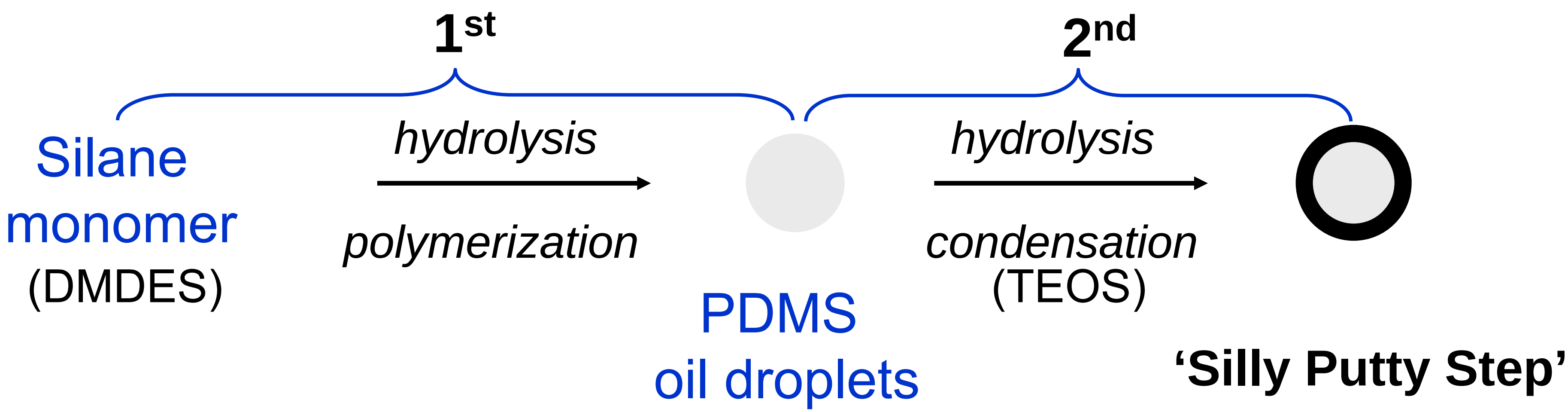


Monodisperse Elastomeric Shells

1st step: Templates
- oil droplets
- silicone oil-in-water emulsion

2nd step: Encapsulation
- solid shells
- cross-linked 'silica'

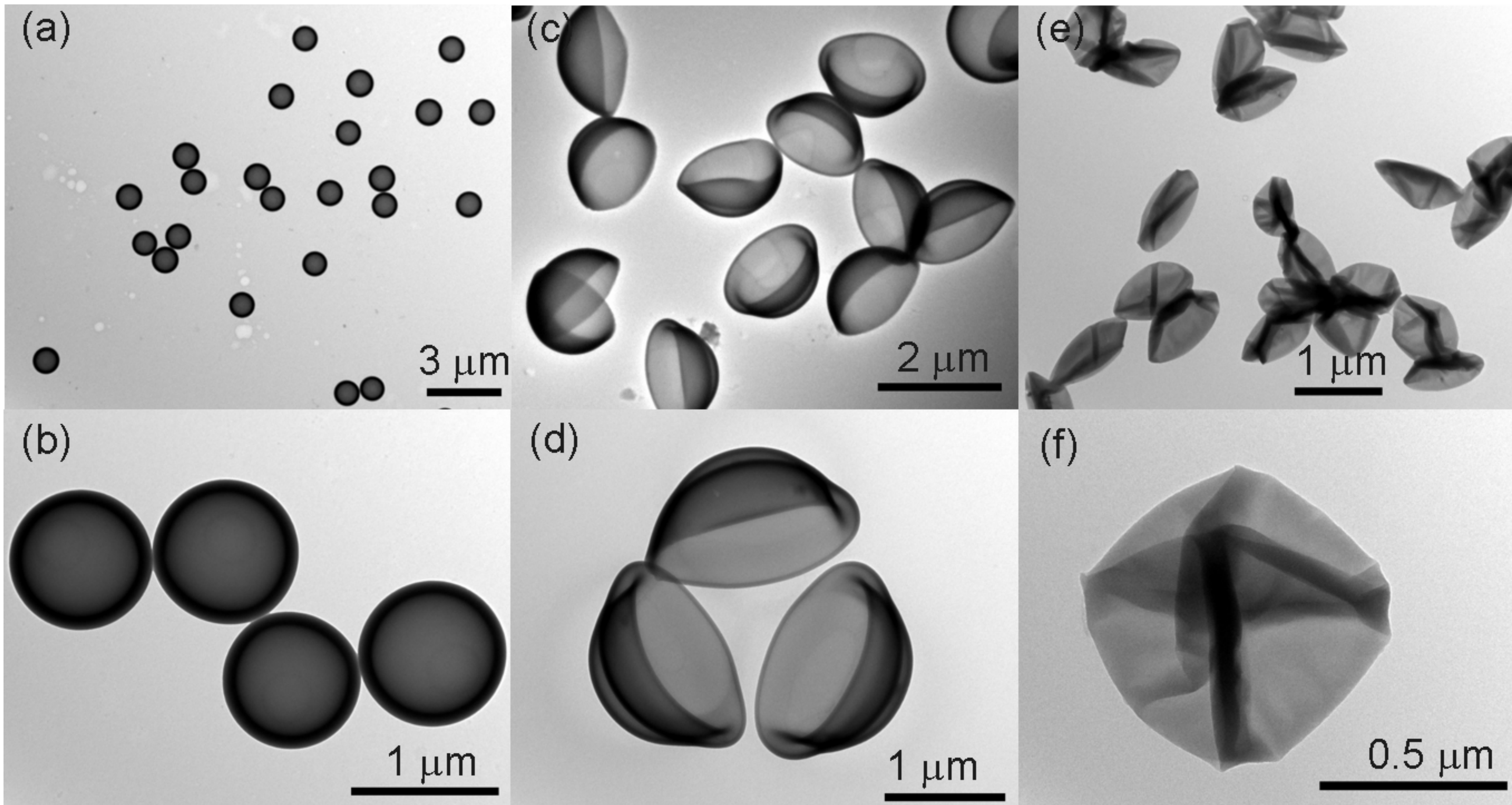
Template removal
- hollow shells



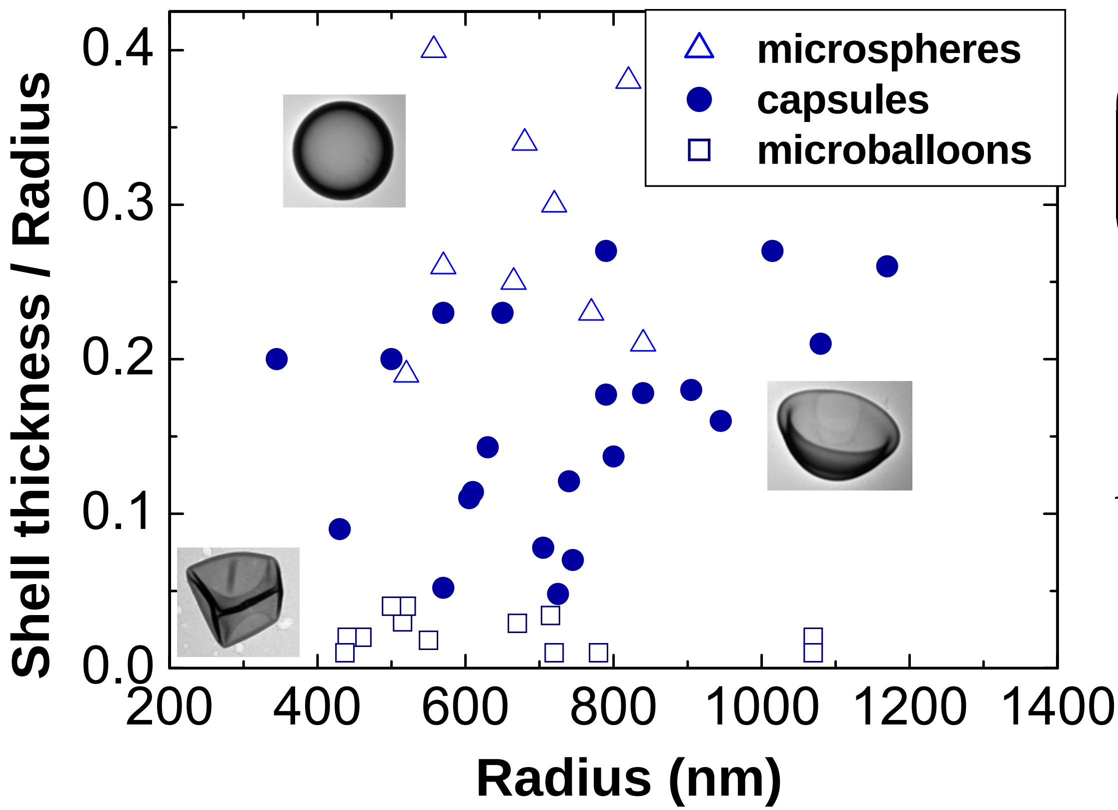
Zoldesi et al. Adv.Mater. ***17****, 924* **(2005)**

Monodisperse Elastomeric Shells: *Buckling*

Microspheres　　Microcapsules　　Microballoons



Buckling of Elastomeric Shells



$$\left(\frac{d}{R}\right)_c \approx 0.23 \qquad p_{eff} = \frac{\gamma}{a}$$

$$p_c = \frac{2E}{\sqrt{3(1-\sigma^2)}}\left(\frac{d}{R}\right)^2$$

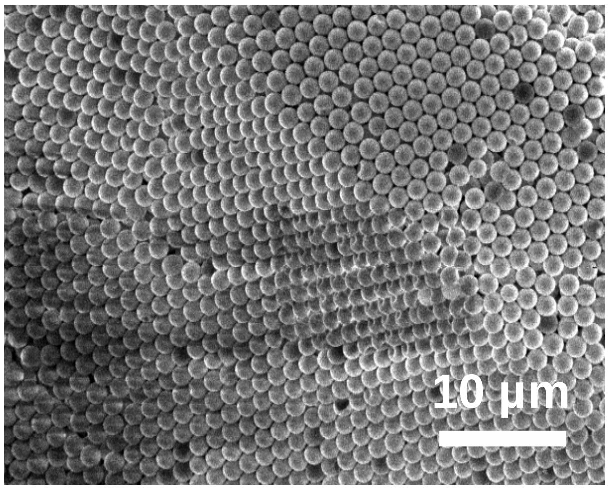
E -Young's modulus
σ - Poisson ratio
d - shell thickness
a - pore diameter

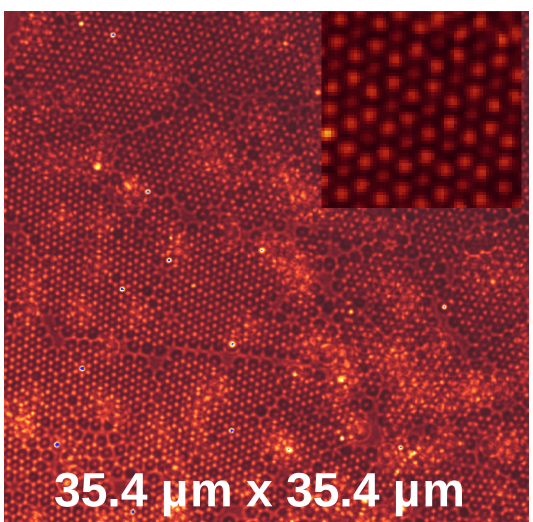
E = 0.109 +/- 0.027 GPa

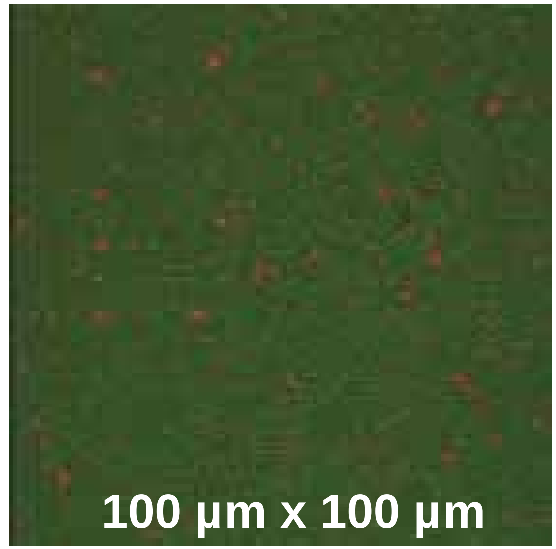
L.Landau, E.Lifshitz, Theory of Elasticity (1997)

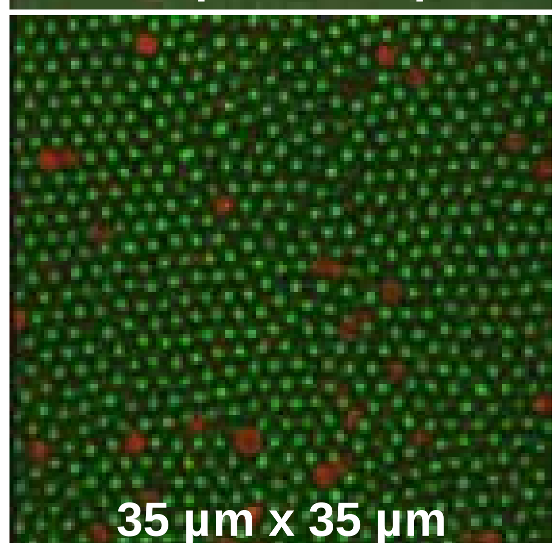
Monodisperse Elastomeric Shell

microspheres

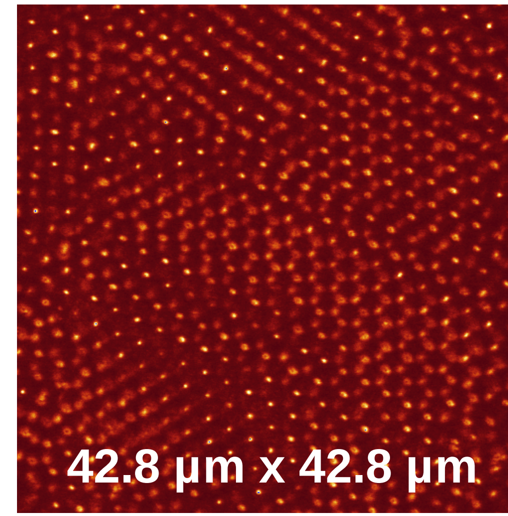


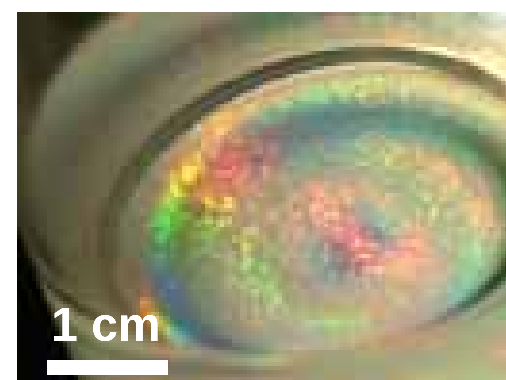




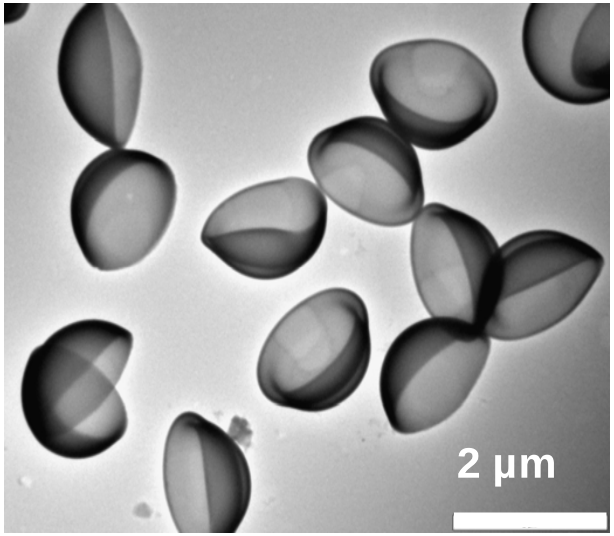


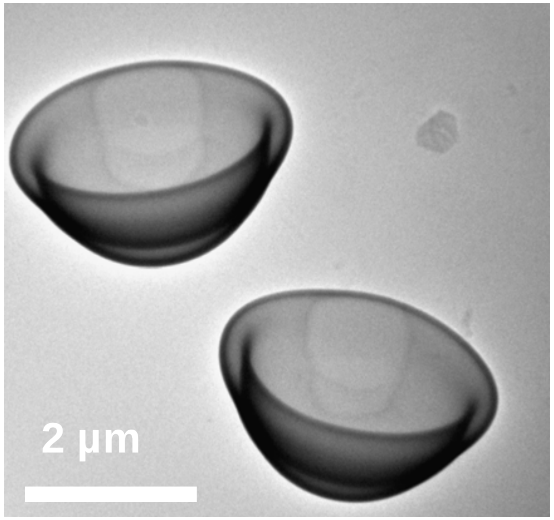
microcapsules

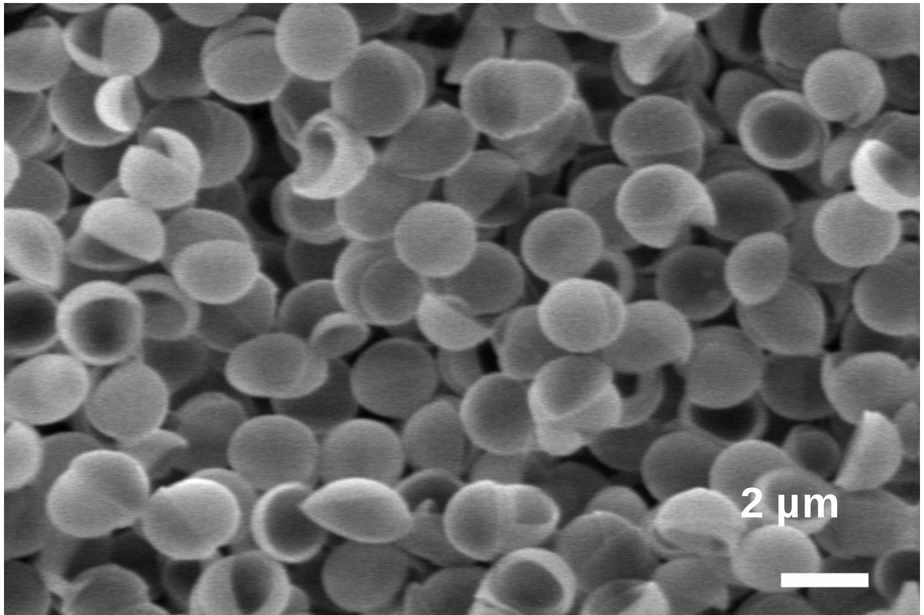




Shape Monodisperse Microcapsules

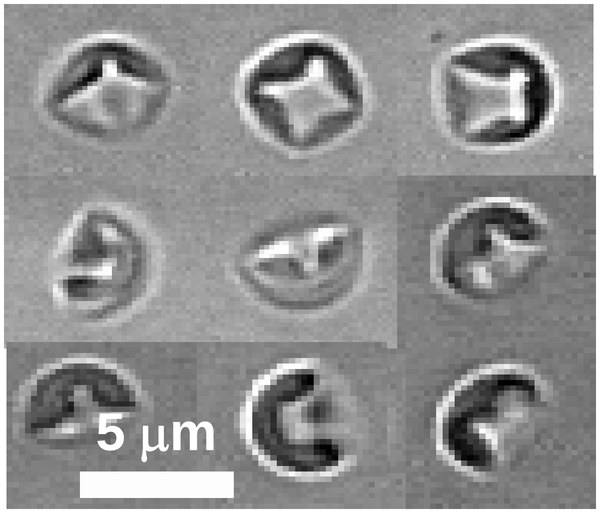




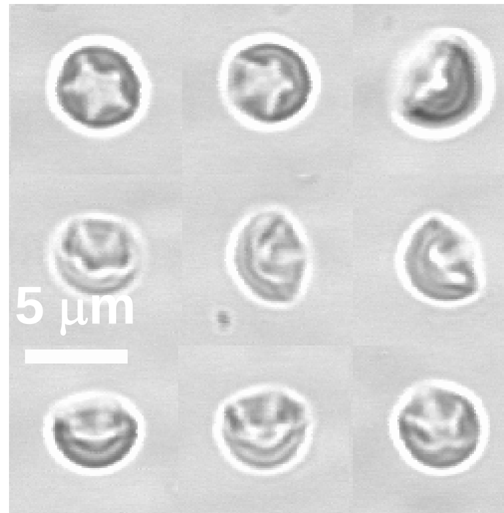


Shape Monodisperse Microcapsules

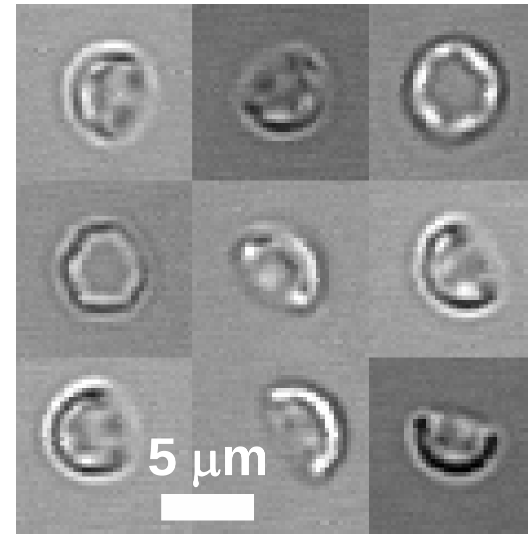
4 wrinkles



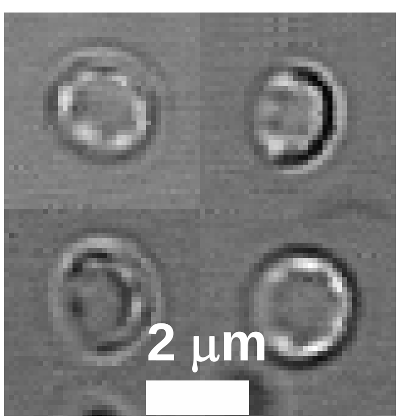
5 wrinkles



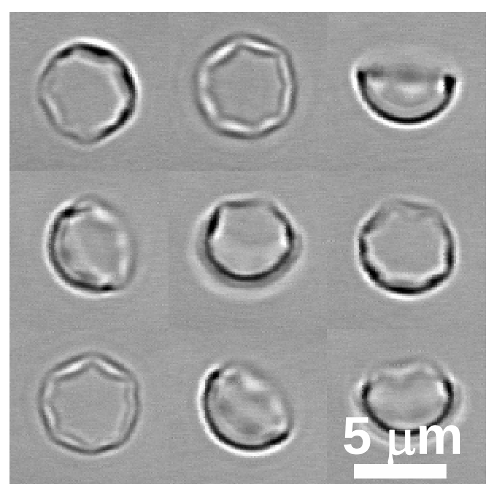
6 wrinkles



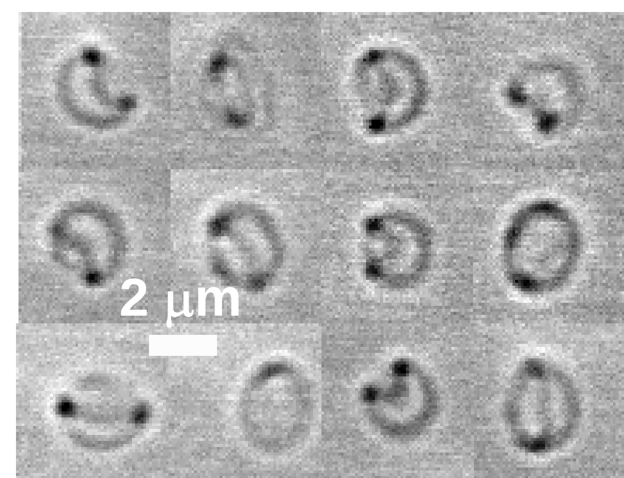
7 wrinkles



8 wrinkles



coffee seeds



Shape Monodisperse Microcapsules

Elastic energy : Bending energy + Stretching energy

$$\lambda = \left(\frac{k / A}{R^2} \right)^2 = \frac{1}{\sqrt{12(1-\sigma^2)}} \frac{d}{R}$$

k – bending constant
A – stretching constant (A=Ed)
σ - Poisson ratio

$\frac{1}{\lambda^2}$ - Föppl-von Kármán number

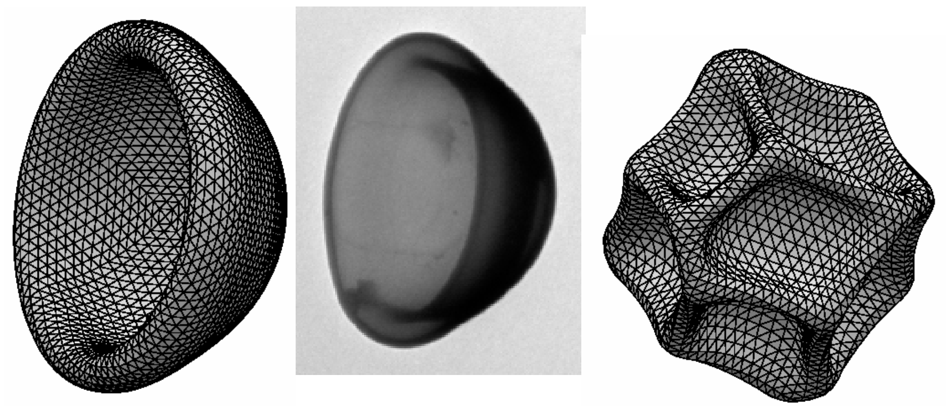
Procedure:

- Surface Evolver routines (*)
- Minimization of the energy
- Step by step decrease of the interior volume
  (ΔV/V – relative decrease of the internal volume)
- Spontaneous curvature c_0 first set to $c_0 = 0$ than to $c_0 = 1/R$

L.Landau, E.Lifshitz, *Theory of Elasticity* (1997)
*Tsapis et al., *Phys.Rev.Lett*. **94**, 018302 (2005)

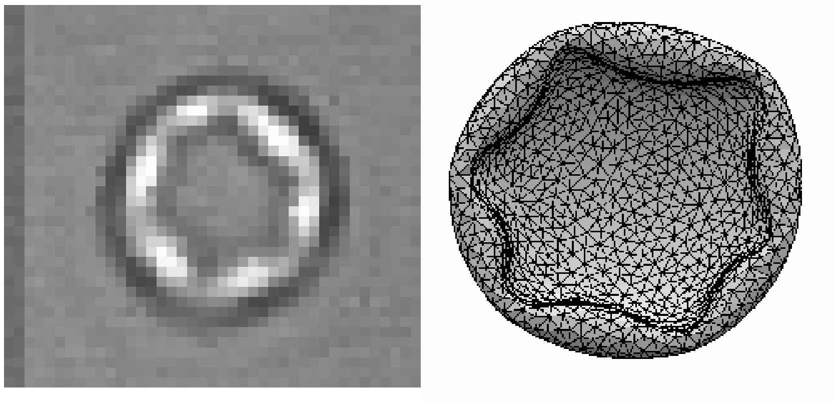
Shape Monodisperse Buckled Capsules

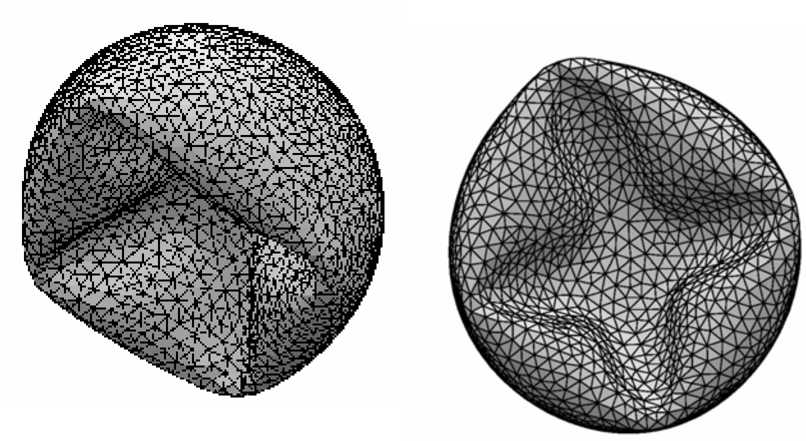
λ = 0.049, ΔV/V = 0.76



λ = 0.0116, ΔV/V = 0.36

λ = 0.015, ΔV/V = 0.67





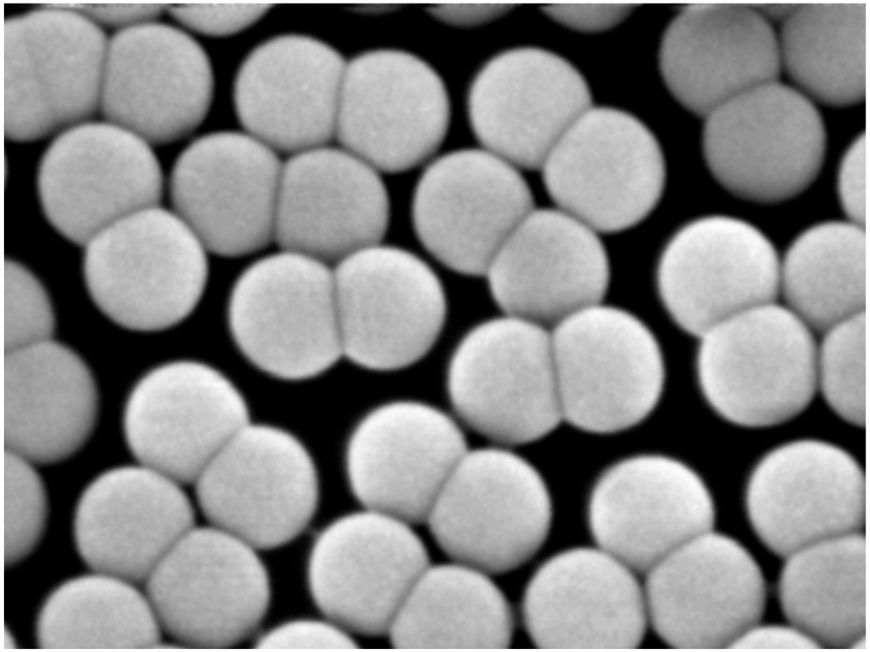
Contents

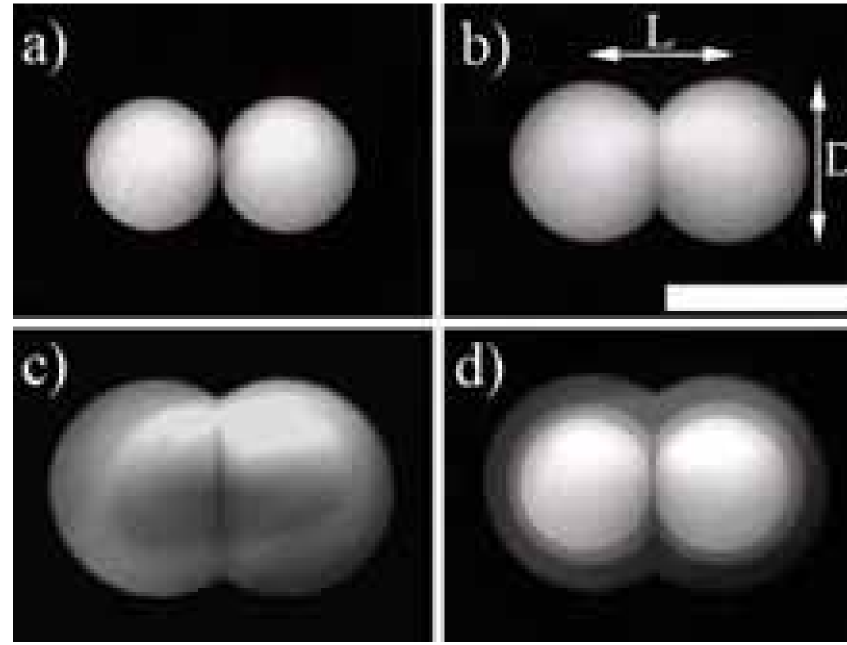
- **CNT & Variations**

- **Variations on a Theme (Monodispersity):**
  - *‘Stöber’ Synthesis (Coupling Agents)*
  - *In a μ-Emulsion*
  - *n=2 -> Emulsion -> Shells*
  - *’Controlled’ Aggregation*

- **Conclusions**

~40% Silica Dumbbells

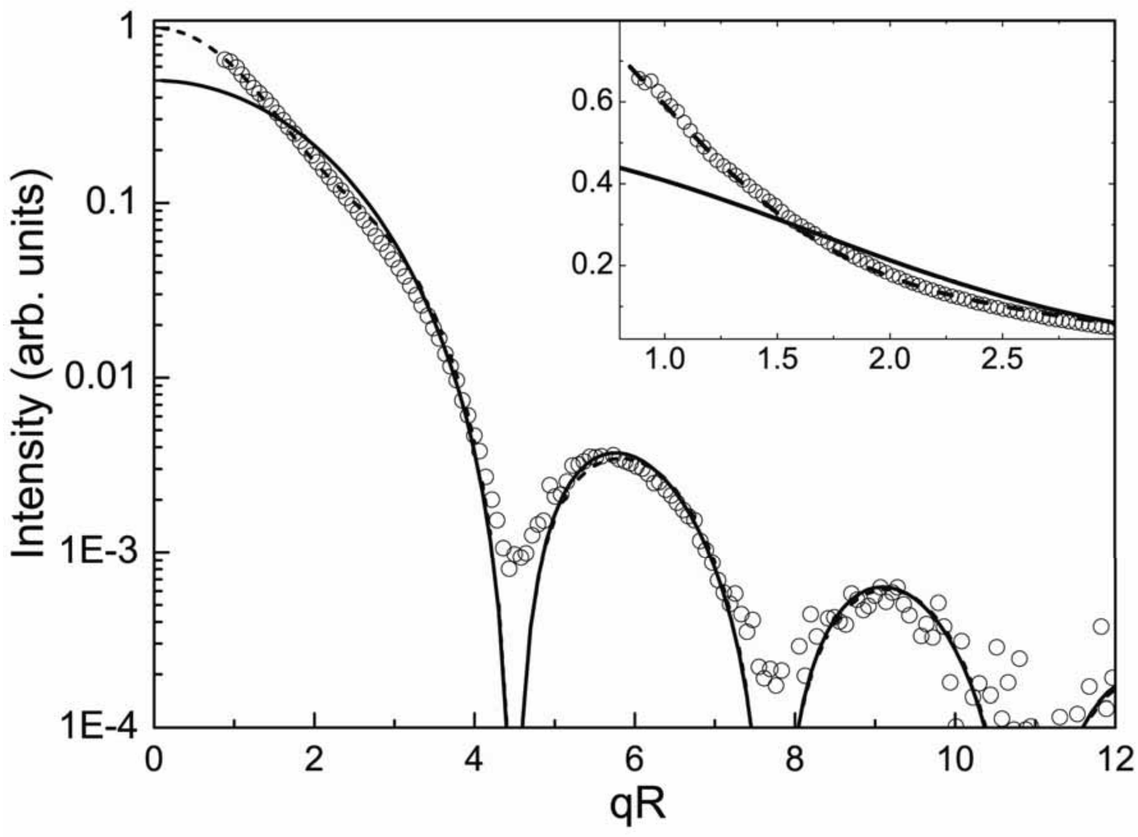


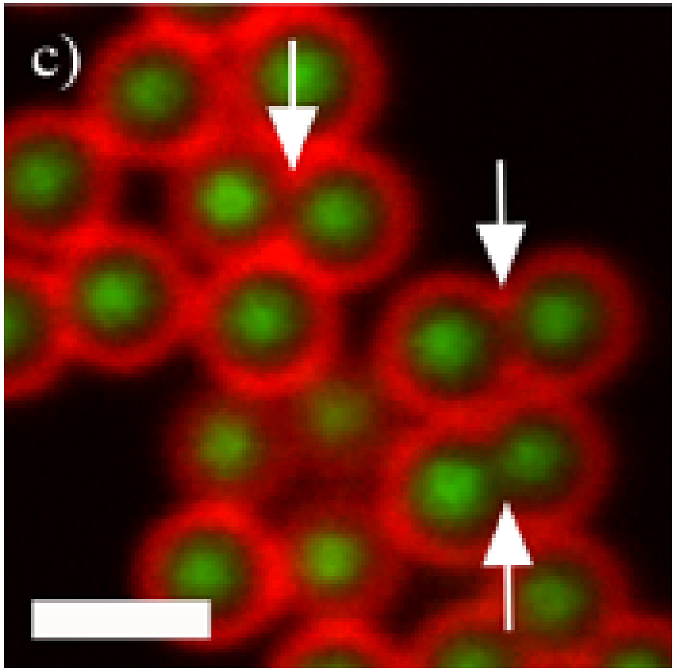


-Ionic Strength *and* Shear Induced ('Steady' State) -> 40% Yield (~1 μm spheres)

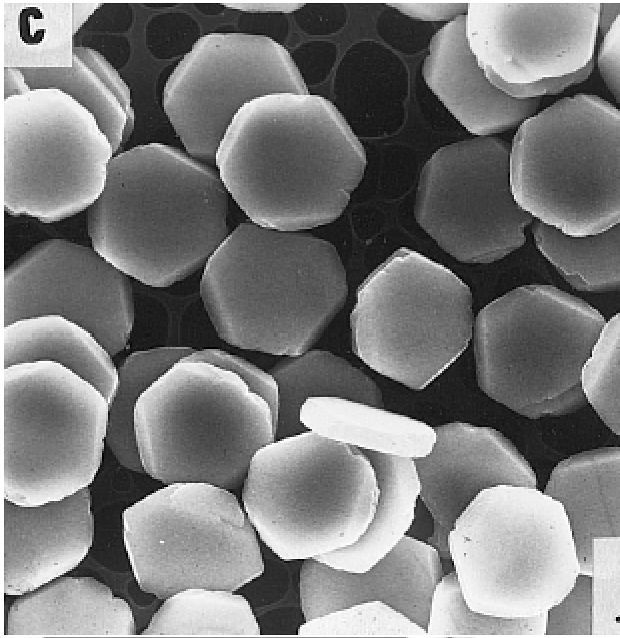
-Smaller Spheres: Ionic Strength & Depletion Induced -> 10% Yield

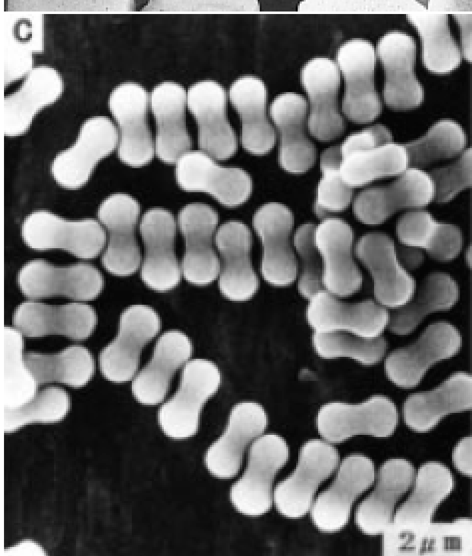
Silica Dumbbells



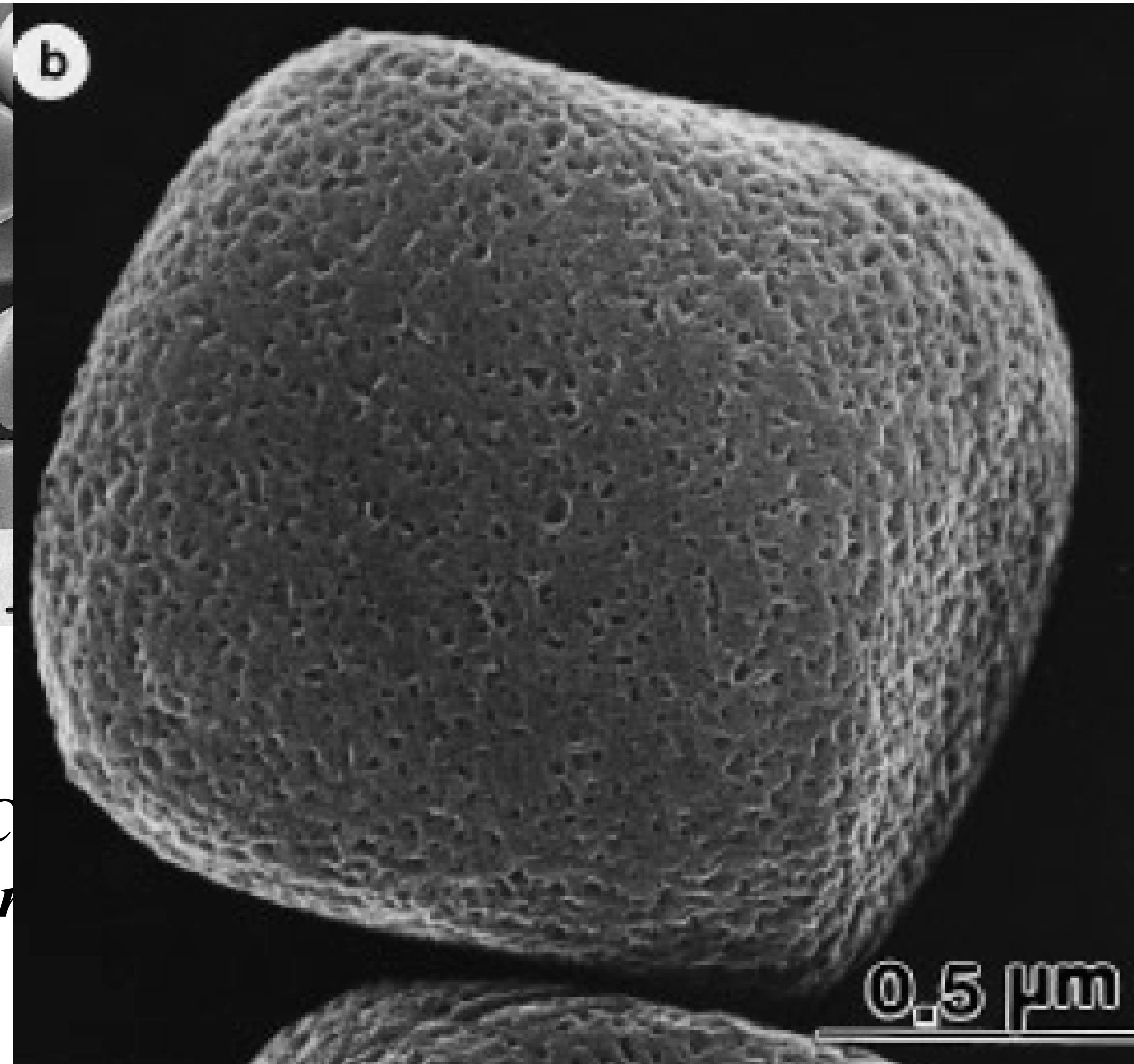


Monodisperse Hematite Fe_2O_3 Colloids



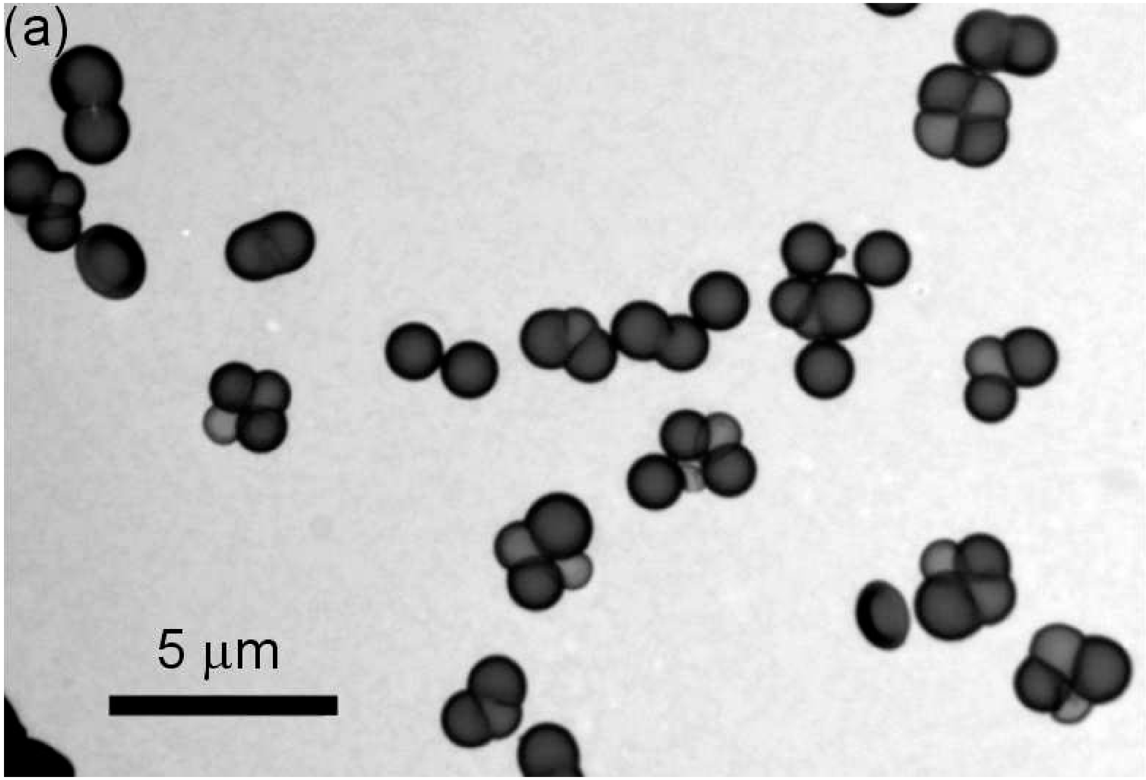


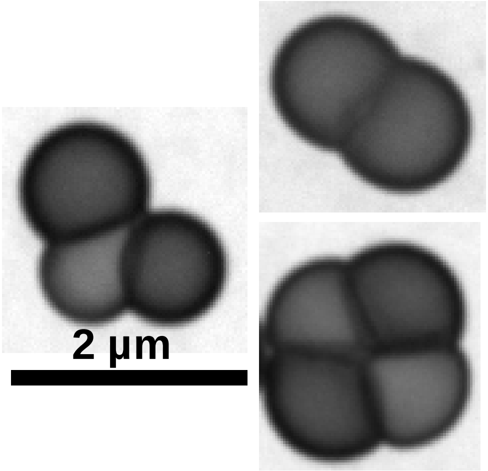
C
sr



T. Sugimoto et al. *Chem. Eng. Technol*, ***26*, (2003*)***

‘Aggregated’ Microcapsules





Higher n-mers -> Shape Constant!

Contents

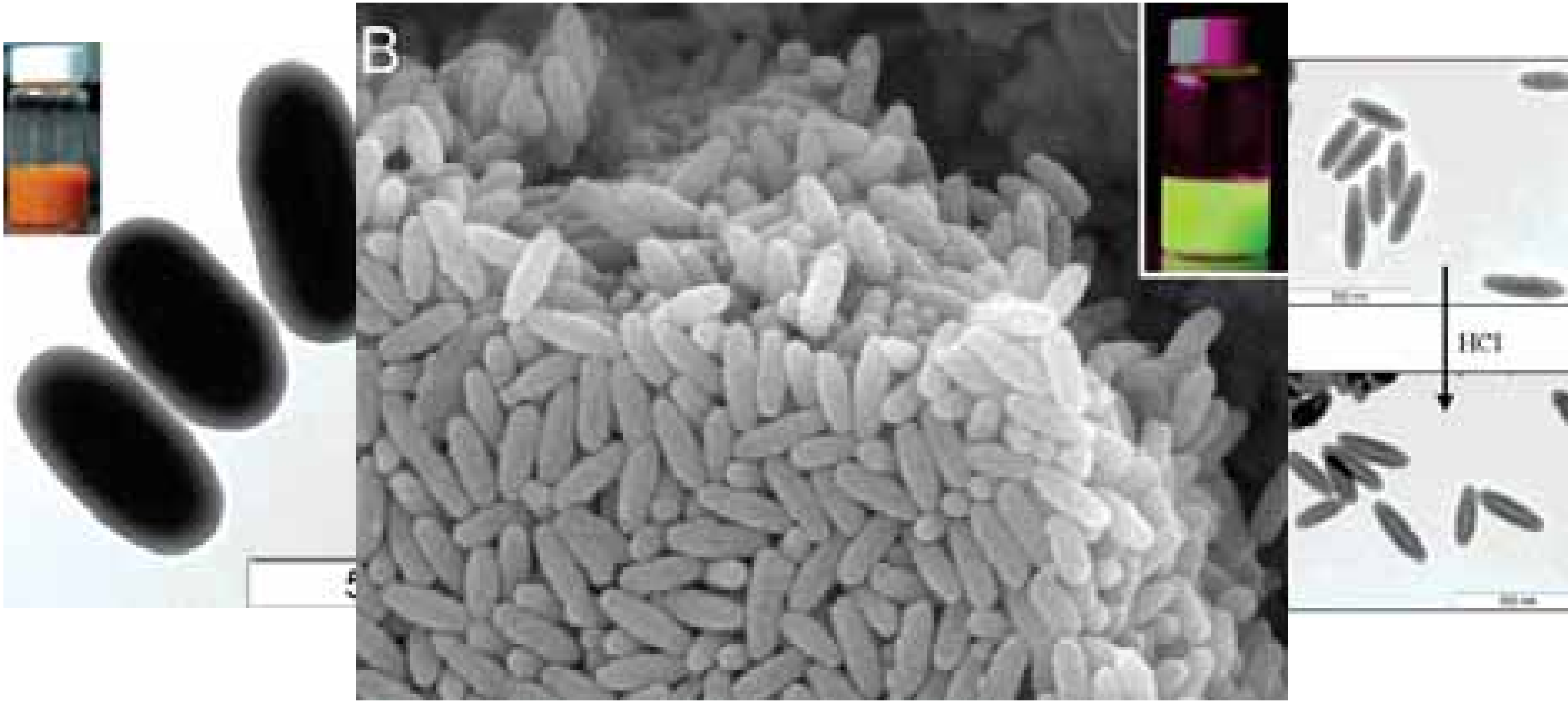
•**Introduction:** ***Colloids in the Next 100 Years***

•**Variations on a Theme (Monodispersity):**

- ***'Stöber' Synthesis (Coupling Agents)***
- ***In a μ-Emulsion***
- ***n=2 -> Emulsion -> Shells***
- ***'Controlled' Aggregation***
- ***Templating -> Shell -> Model Colloid***

•**Conclusions**

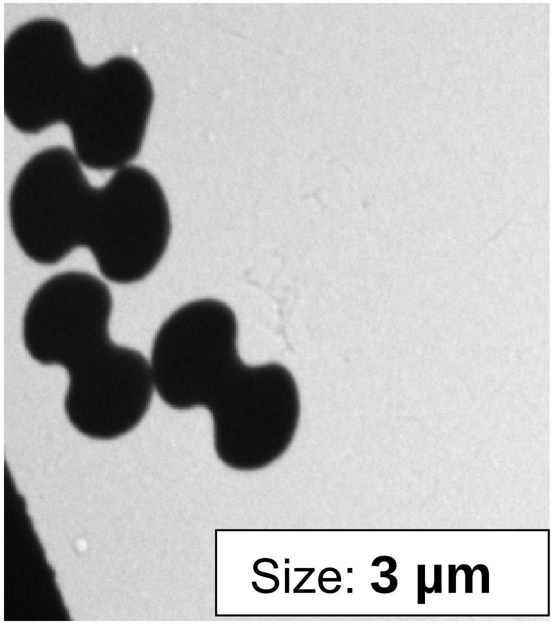
PVP Coating to Grow Silica

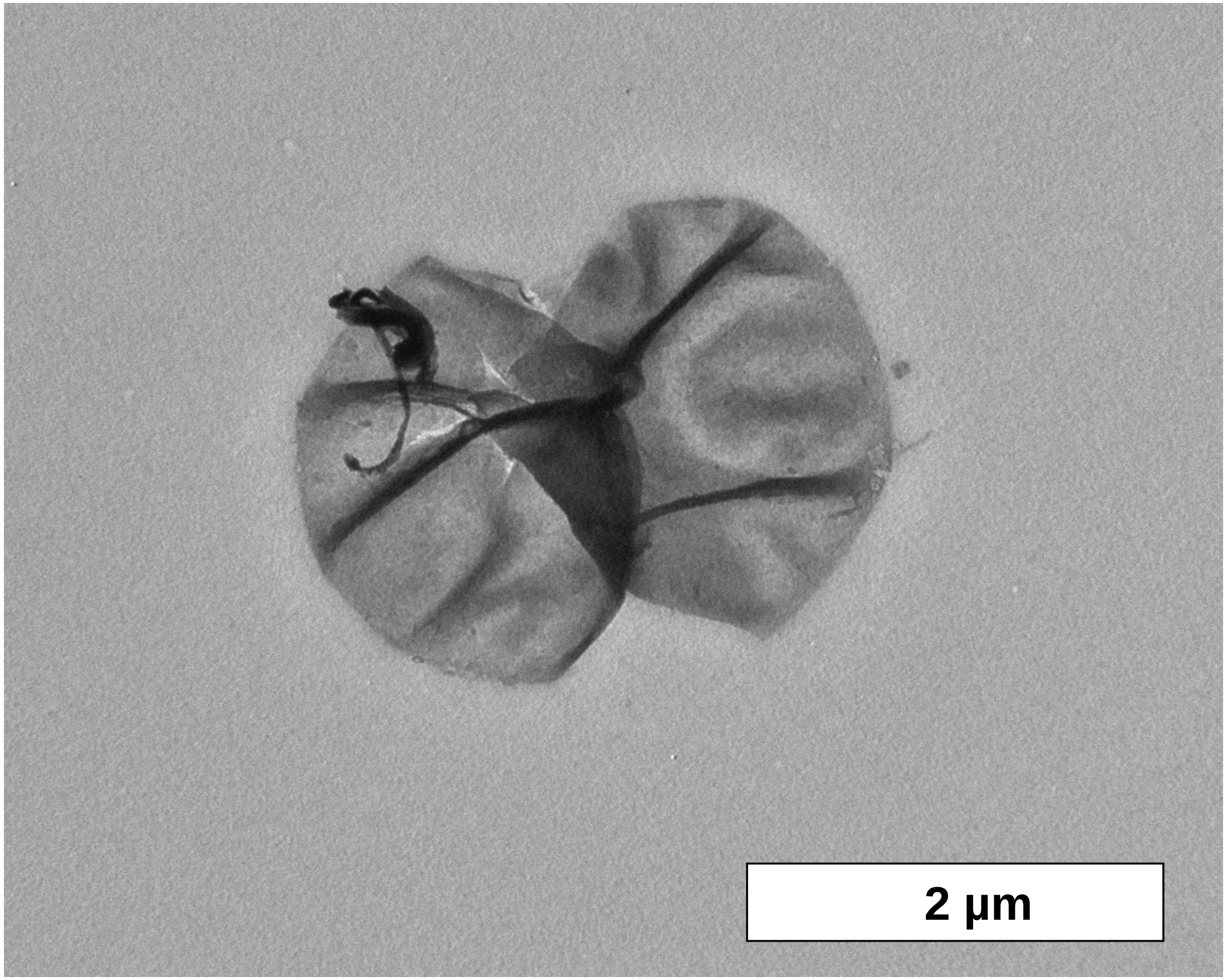


Porous Silica on Hematite -> Dissolve -> Fill -> Close Up!

Philipse, et al., *Langmuir* ***22, (2006)***

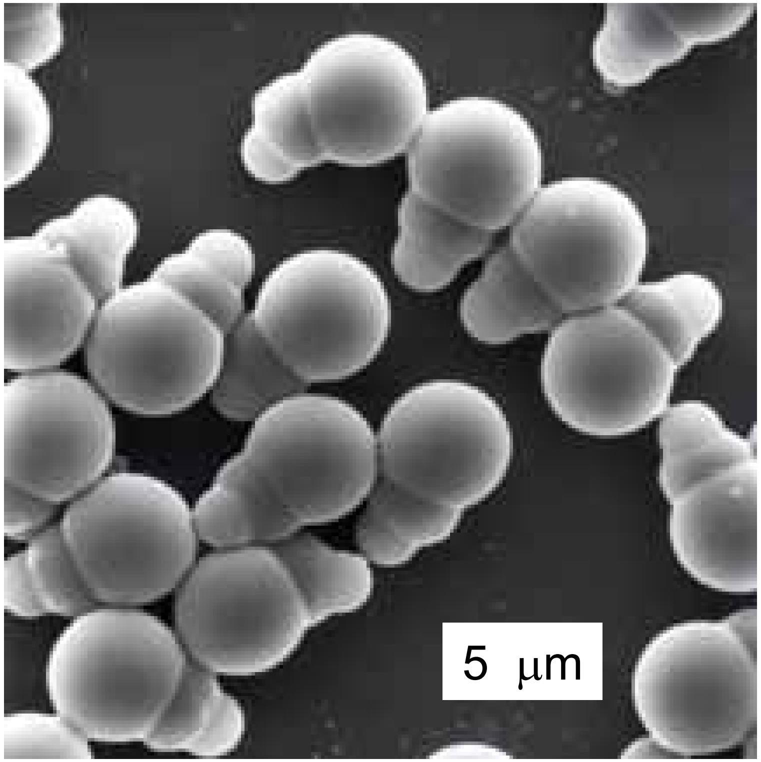
Silica around Hematite 'Peanut'

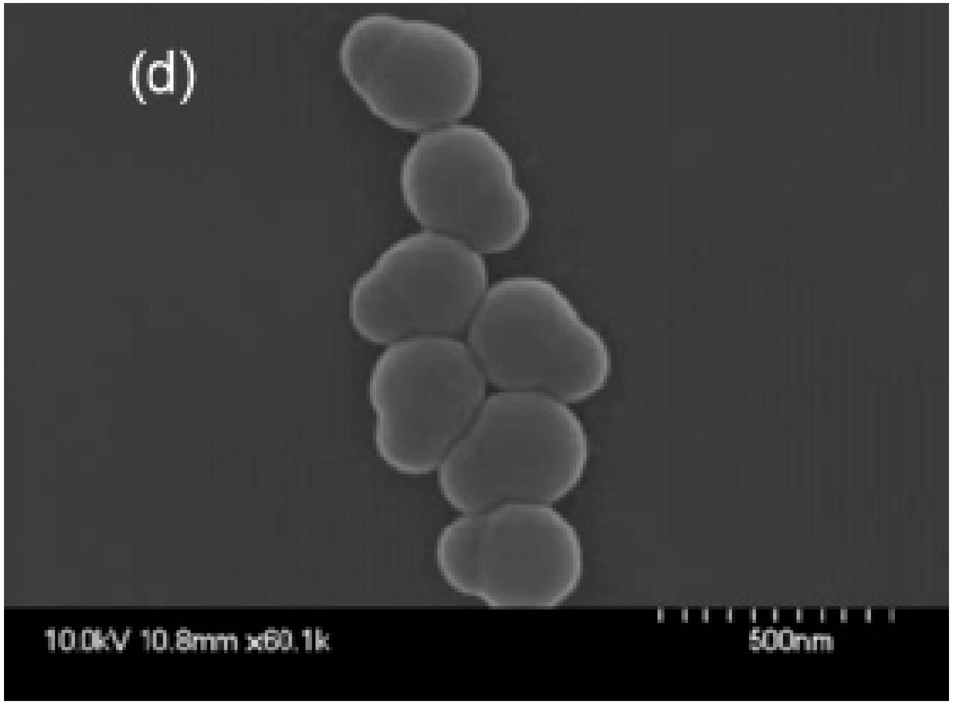




After Coating with PVP silica and Dissolution

Repeated Polymerization:
Wetting/Phase Separation





Sheu, et al.*J. Polym. Sci. A***28**, 629 (**1990**).

Mock et al., *Langmuir* ***22,*** 4037 ***(*2006*)***

PHSA-PMMA (core-shell) by Dispersion Polymerization