Previous Lecture

Basic Concepts:
Surface atom vs. bulk atom
Surface energy
Young-Laplace Equation

Stability of Nanomaterials

13TH SEPTEMBER 2017

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In this lecture

1. Ostwald Ripening
2. DLVO Theory
3. Examples of different sizes and geometries

After This Lecture You Can

Explain Electrical Double Layer

Predict the stability by DLVO theory or steric hinderance

Explain Ostwald ripening

Classify nanomaterials to 0D-3D

Nanomaterials Are Stable

- Glazing of pottery for hundreds of years

Metal salt (Ag, Au, etc.)
Vinegar, ocra, clay
- *mix on the top of glazed pottery*
- *Heat up to 600°C*

Ø *Nanoparticles embedded in the glazing*

- Michael Faraday's Au nanoparticles (1857)

http://www.rigb.org/our-history/iconic-objects

Au salt + citric acid -> Au nanoparticles

80-100°C for 30 min to 4 hours

Renaissance Artists Decorated Pottery with Nanoparticles, *ESRF Newsletter* 38 (2003) 4-5.

https://www.youtube.com/watch?v=qVhiwi6AvQM

Problems with Stability?

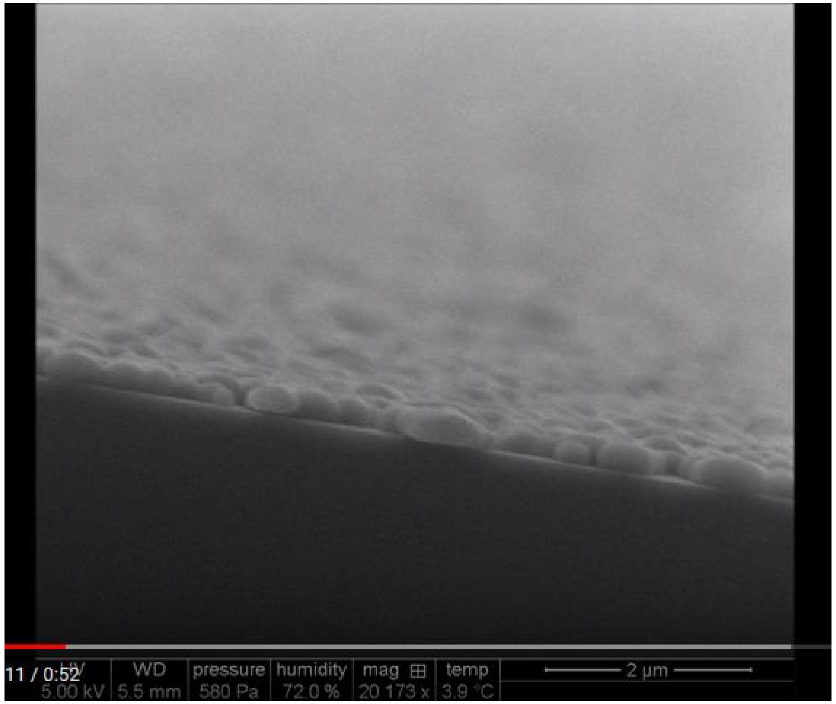
- Particle size(s)
  - "Dissolution"
  - Ostwald ripening
- Forces
  - "Precipitation"
  - DLVO theory

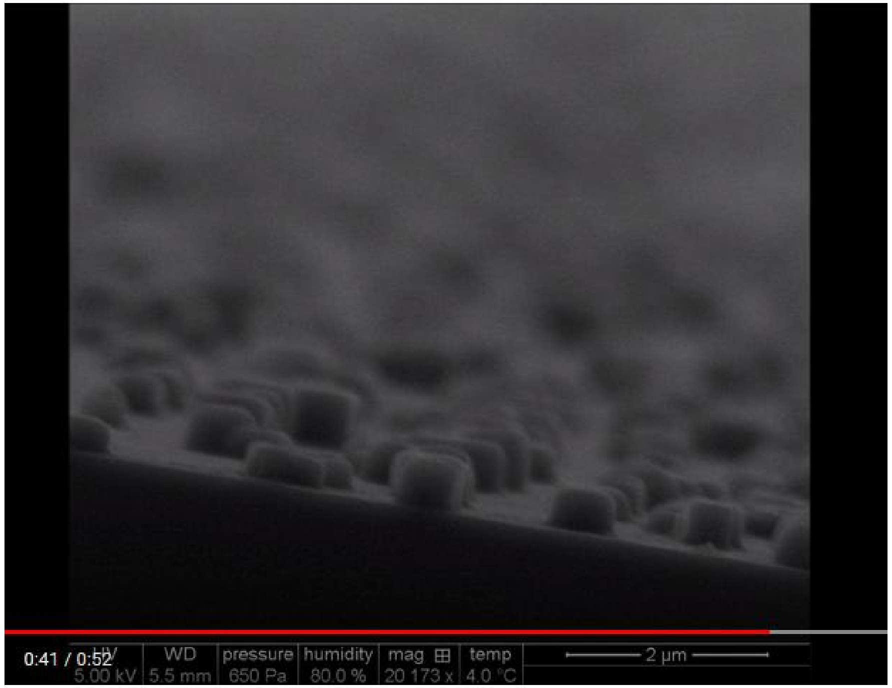
Ostwald Ripening

PART 1

Observation

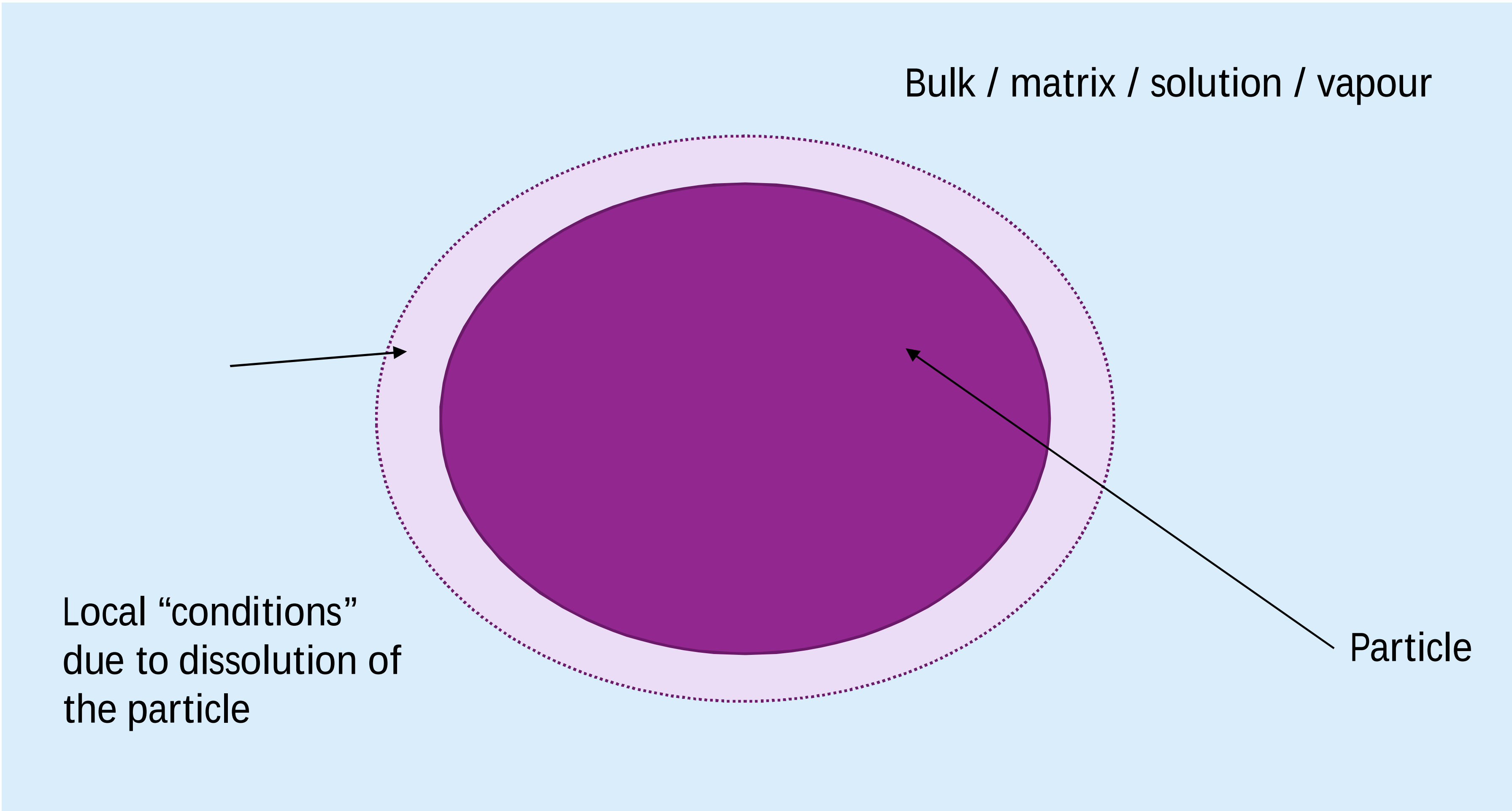
https://www.youtube.com/watch?v=hDWACXP833Y





Let’s first think only one particle

Dissolving small particles…



Dissolving small particles…

Ideal gas law for solid surfaces

Flat surface: $\boldsymbol{\mu_v - \mu_\infty = -kTlnP_\infty}$

Curved surface: $\boldsymbol{\mu_v - \mu_c = -kTlnP_c}$

v →vapour, c →curved surface and ∞→ flat surface

k Boltzmann's constant

T temperature

P equilibrium vapour pressure

Dissolving small particles...

Ideal gas law for solid surfaces

Flat surface: $\boldsymbol{\mu_v - \mu_\infty = -kTlnP_\infty}$

Curved surface: $\boldsymbol{\mu_v - \mu_c = -kTlnP_c}$

Remember Young-Laplace from Lecture 1: $\Delta\boldsymbol{\mu} = \boldsymbol{\gamma\Omega\left(\frac{1}{R_1} + \frac{1}{R_2}\right)}$

Combining these three equation

(flat – curved = $\boldsymbol{\Delta\mu}$)

$$\boldsymbol{\mu_c - \mu_\infty = kTln\left(\frac{P_c}{P_\infty}\right) = \Delta\mu = \gamma\Omega\left(\frac{1}{R_1} + \frac{1}{R_2}\right)}$$

Dissolving small particles…

$$\mu_c - \mu_\infty = \Delta\mu = kTln\left(\frac{P_c}{P_\infty}\right) = \gamma\Omega\left(\frac{1}{R_1} + \frac{1}{R_2}\right)$$

$$ln\left(\frac{P_c}{P_\infty}\right) = \frac{\gamma\Omega\left(\frac{1}{R_1}+\frac{1}{R_2}\right)}{kT}$$

Dissolving small particles…

$$\ln\left(\frac{P_c}{P_\infty}\right) = \frac{\gamma\Omega\left(\frac{1}{R_1}+\frac{1}{R_2}\right)}{kT}$$

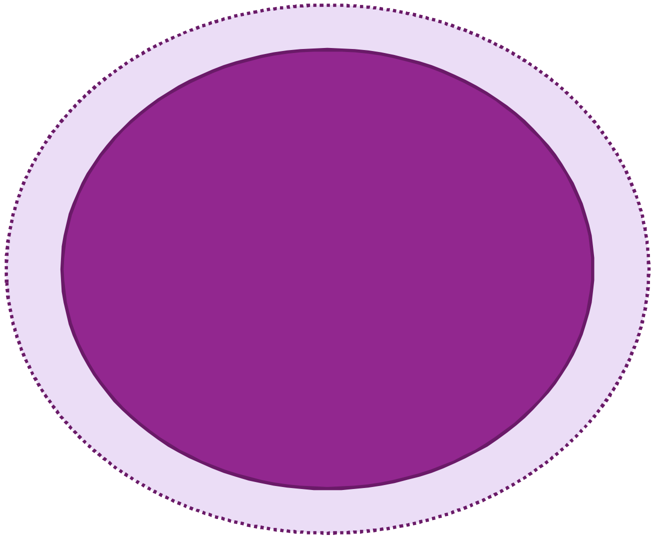
Discuss: What does this equation mean?

Dissolving small curved particles…

Kelvin equation

$$\boldsymbol{ln}\left(\frac{P_c}{P_\infty}\right) = \frac{\gamma\Omega\left(\frac{1}{R_1}+\frac{1}{R_2}\right)}{kT}$$

Smaller the particle radius, larger the ln term → Larger ln term means larger P_c, i.e. higher pressure at vapour must be achieved before equilibrium is reached



Partial pressure

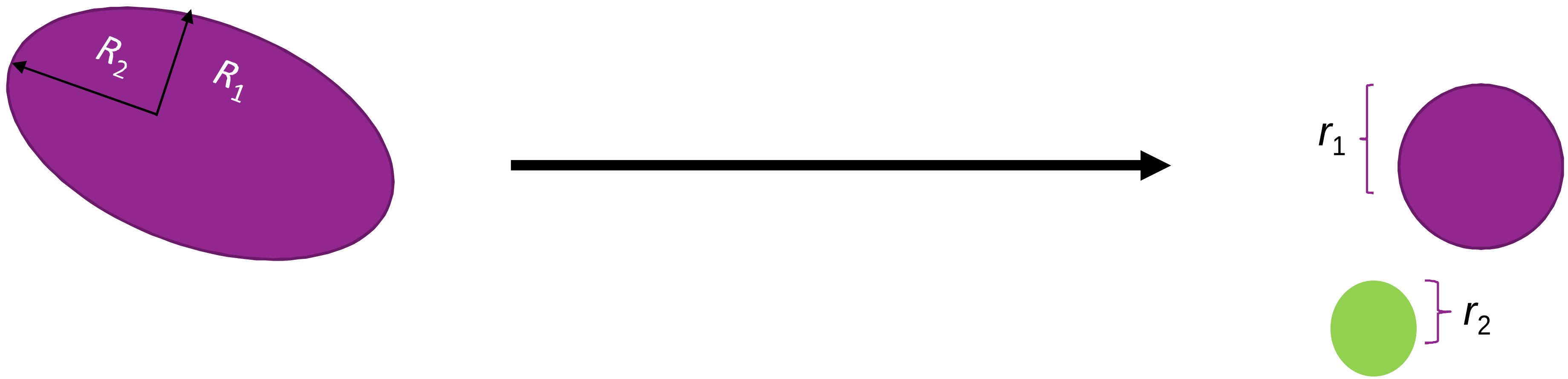
$$ln\left(\frac{P_c}{P_\infty}\right) = \frac{\gamma\Omega\left(\frac{1}{R_1} + \frac{1}{R_2}\right)}{kT}$$

Solubility

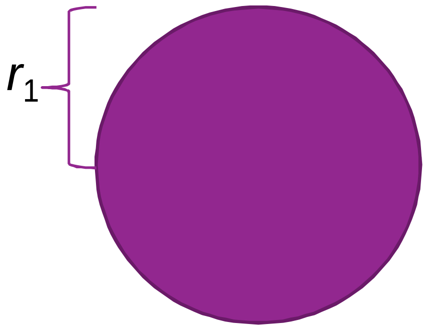
$$ln\left(\frac{S_c}{S_\infty}\right) = \frac{\gamma\Omega\left(\frac{1}{R_1} + \frac{1}{R_2}\right)}{kT}$$

Due to this, small particles tend to “dissolve”

But how about if we have different size of particles?

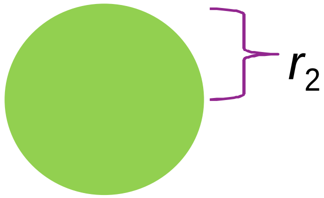


For simplicity, let’s think only spherical particles

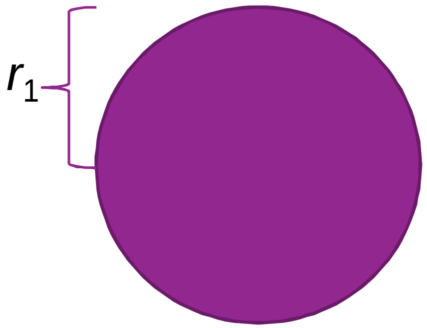


$$\mathit{ln}\left(\frac{S_{c,large}}{S_{\infty}}\right) = \frac{2\gamma\Omega}{r_1 kT}$$

$r_1 > r_2$



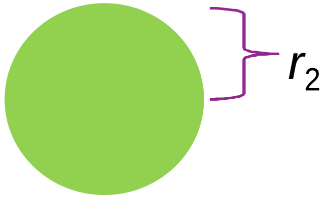
$$\mathit{ln}\left(\frac{S_{c,small}}{S_{\infty}}\right) = \frac{2\gamma\Omega}{r_2 kT}$$



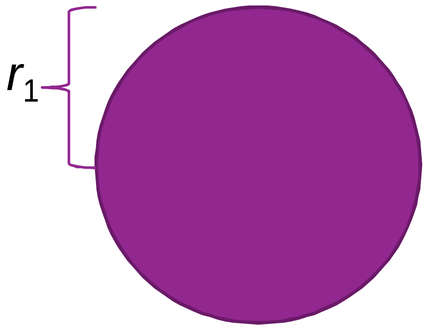
$$\ln\left(\frac{S_{c,large}}{S_{\infty}}\right) = \frac{2\gamma\Omega}{r_1 kT}$$

$r_1 > r_2$

$\rightarrow S_{c,\ small} >> S_{c,\ large}$



$$\ln\left(\frac{S_{c,small}}{S_{\infty}}\right) = \frac{2\gamma\Omega}{r_2 kT}$$



$$ln\left(\frac{S_{c,large}}{S_{\infty}}\right) = \frac{2\gamma\Omega}{r_1 kT}$$

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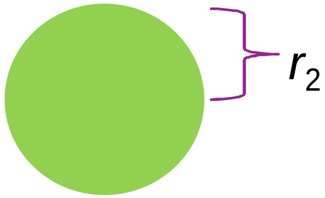
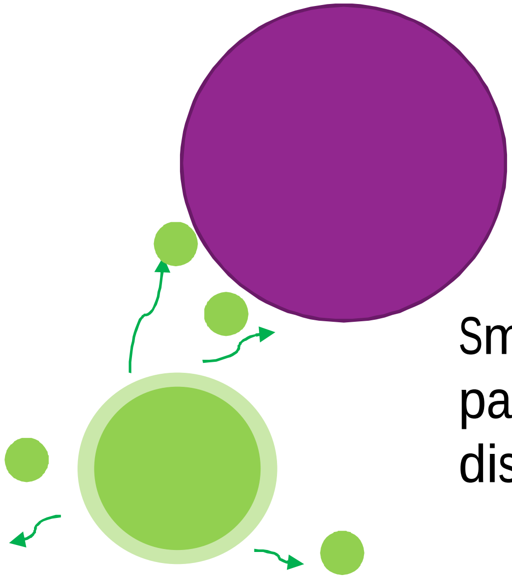
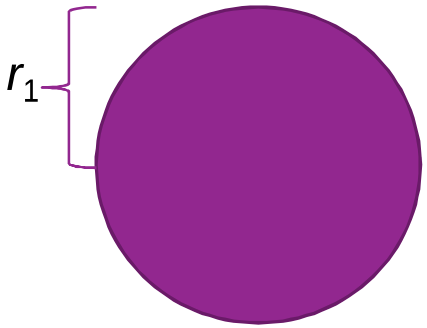


$$ln\left(\frac{S_{c,small}}{S_{\infty}}\right) = \frac{2\gamma\Omega}{r_2 kT}$$



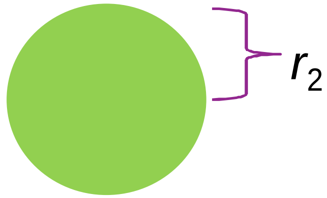
Smaller particle dissolves



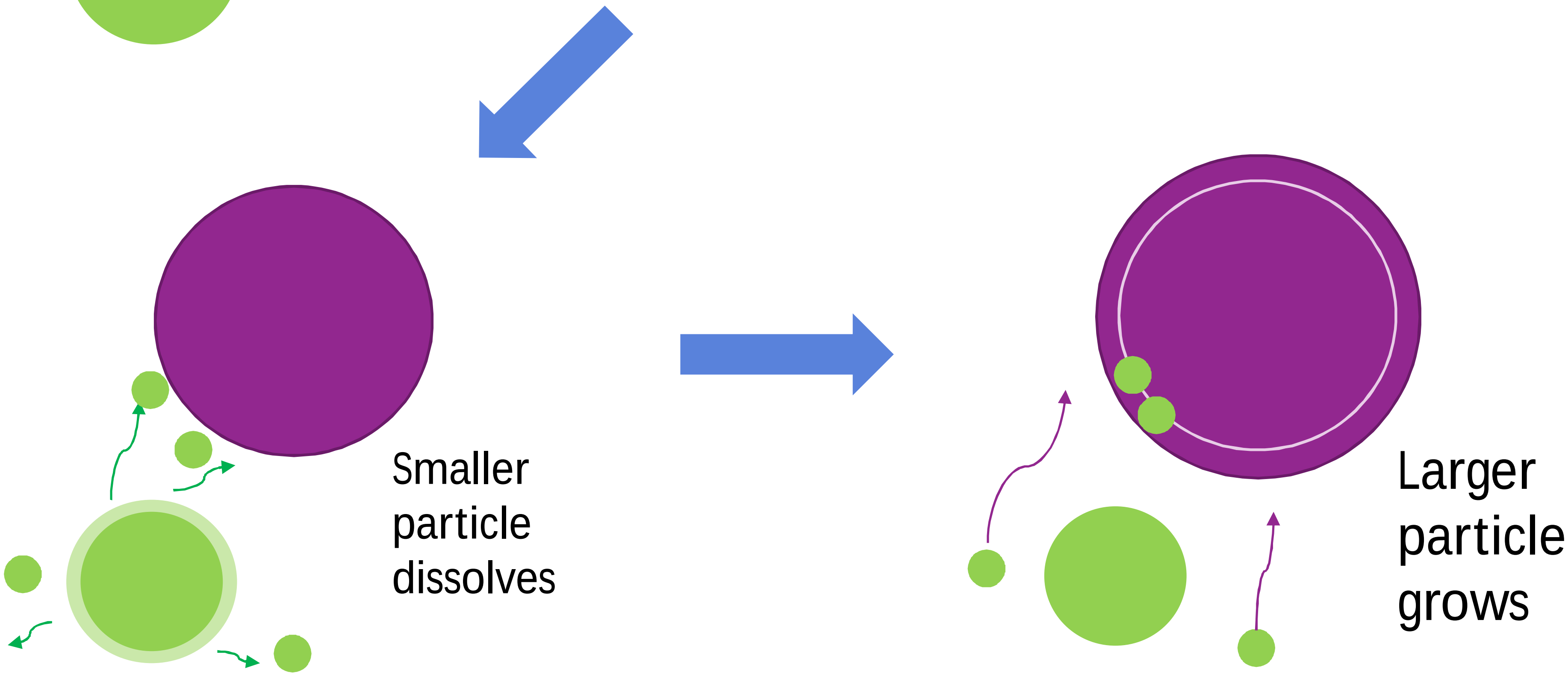
$$ln\left(\frac{S_{c,large}}{S_\infty}\right) = \frac{2\gamma\Omega}{r_1 kT}$$

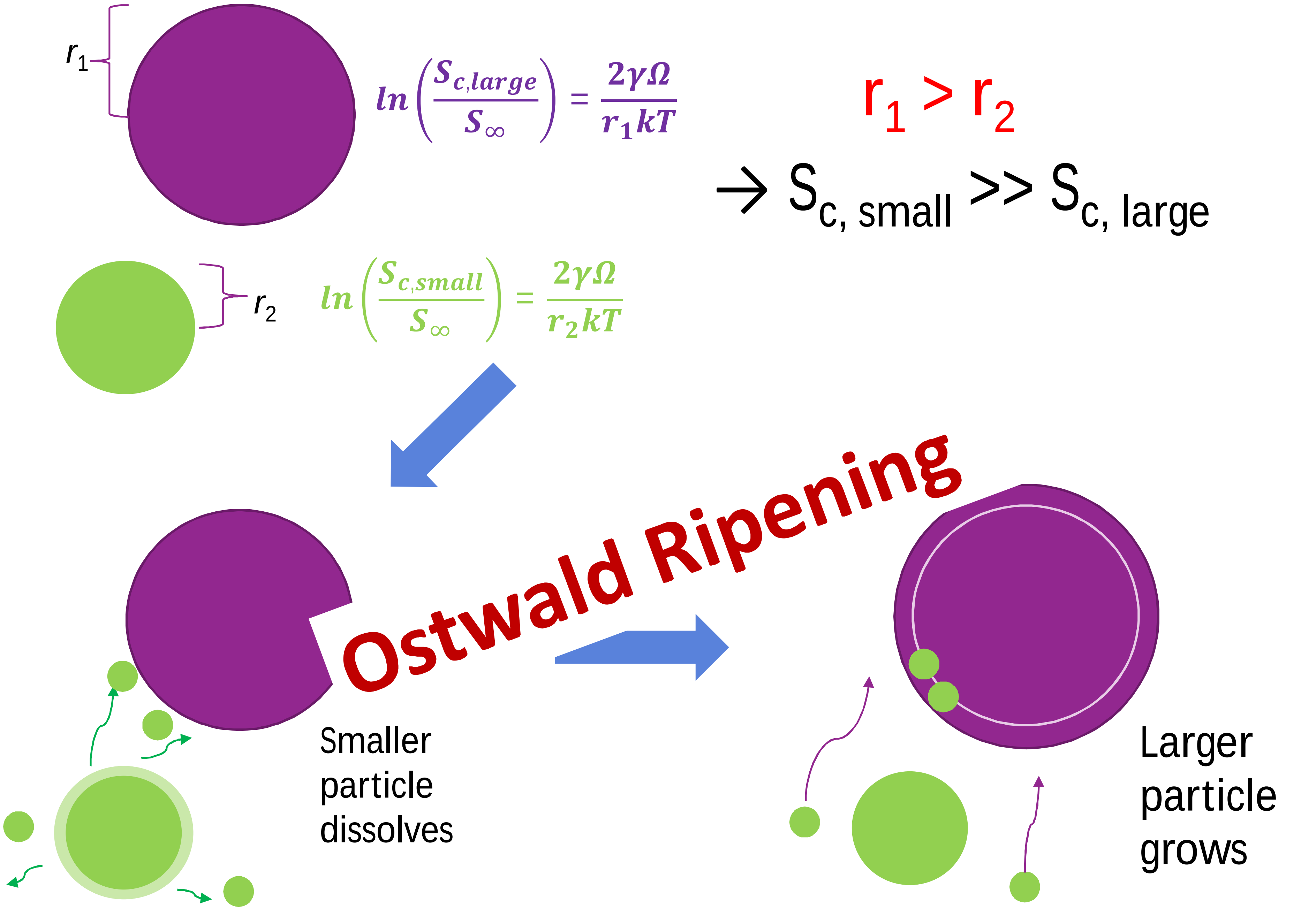
$r_1 > r_2$

$\rightarrow S_{c,\ small} >> S_{c,\ large}$



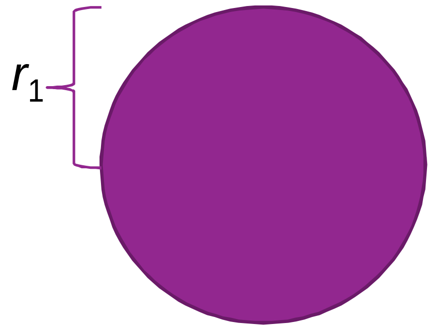
$$ln\left(\frac{S_{c,small}}{S_\infty}\right) = \frac{2\gamma\Omega}{r_2 kT}$$





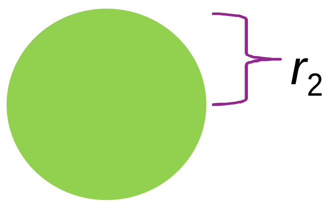
r_1
$ln\left(\frac{S_{c,large}}{S_\infty}\right) = \frac{2\gamma\Omega}{r_1 kT}$
$r_1 > r_2$
$\rightarrow S_{c,\ small} >> S_{c,\ large}$
r_2
$ln\left(\frac{S_{c,small}}{S_\infty}\right) = \frac{2\gamma\Omega}{r_2 kT}$
Ostwald Ripening
Smaller particle dissolves
Larger particle grows

Ostwald Ripening can also be considered from "concentration" around the particle

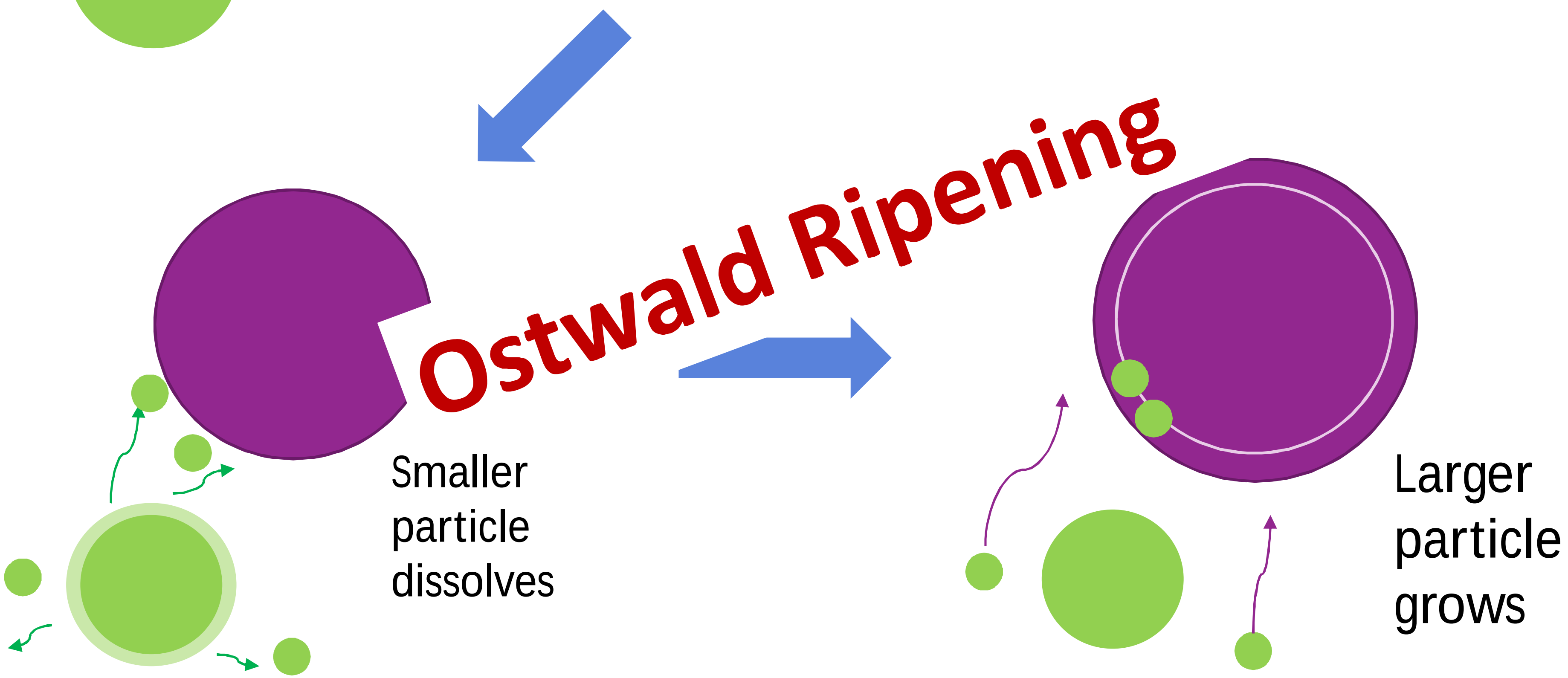


$$\ln\left(\frac{C_{c,large}}{C_0}\right) = \frac{2\gamma\Omega}{r_1 RT}$$

$\rightarrow C_{c,\ small} >> C_{c,\ large}$



$$\ln\left(\frac{C_{c,small}}{c_0}\right) = \frac{2\gamma\Omega}{r_2 RT}$$



Concept Check #1

Ostwald ripening

(a) is due to the higher solubility of smaller particles

(b) is due to lower solubility of smaller particles

(c) is due to lower vapour pressure of smaller particles

Concept Check #2

Ostwald ripening can take place

(a) slower at lower temperature

(b) when different sized particles are present in media

(c) only when different sized particles touch each other

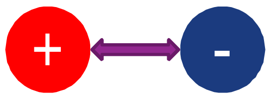
2^{nd} Part: DLVO Theory

Why some particles precipitate and why some stay in solutions?

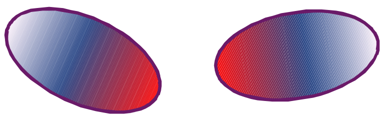
Electrostatic Stabilization

MAIN INTERACTION FORCES

- Repulsive forces
  - Electrostatic (negative-negative, positive-positive)



- Attractive Forces
  - Electrostatic (negative-positive)
  - Van der Waals



But how this actually works....

- Electrical Double Layer

Electrical Double Layer (EDL)

Surfaces become charged when in contact with a polar solution

For example:

- Electrode|solution
- Colloidal particle|solution

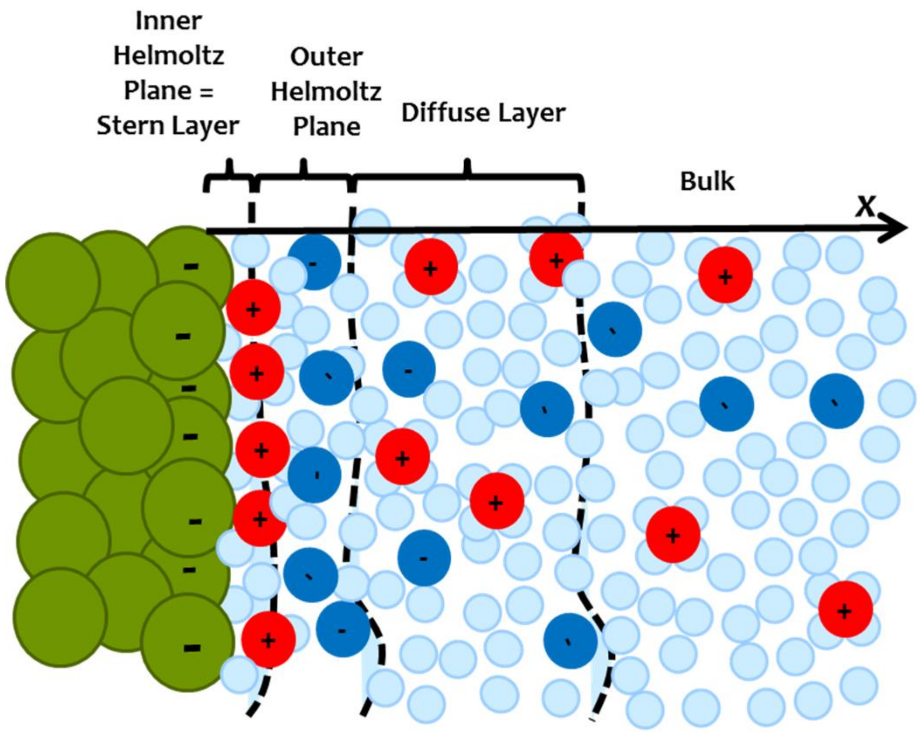
Theory of electrical double layer (EDL) tries to explain the distribution of ions (=potential distribution) nearby a charged surface

- In a polar solution

Electrical Double Layer

Electrical double layer (EDL) can be considred to be divided in three parts

1. Inner Helmholtz layer
   - Specifically adsorbed ions
2. Outer Helmholtz Layer
   - Non-specifically adsorbed ions
3. Diffuse layer
   - Ions moving due to electrostatic field and Brownin motion

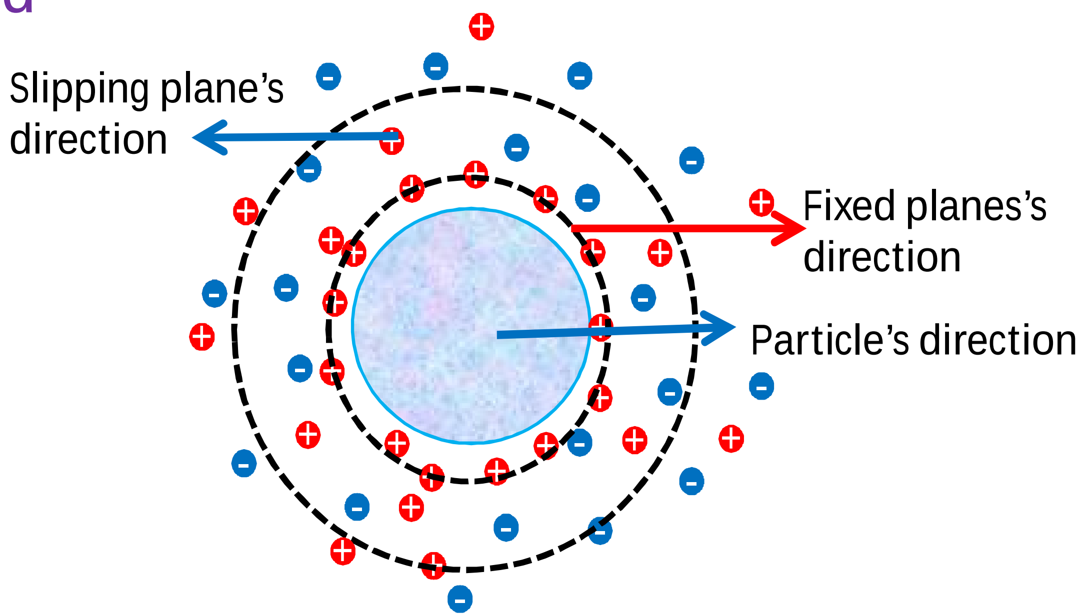


The borderline between layers is difficult to determine exactly

Electrical Double Layer

EDL can be also thought of consisting of two layers:

1. Fixed Layer (Stern Layer)
   - Adsorbed ions move with the particle in an electric field
2. Mobile Layer
   - Diffuse layer to the opposite direction as particle
     - Slipping plane



The borderline between layers is difficult to determine exactly

Potential Field in EDL: Poisson-Boltzman Equation

Poisson equation

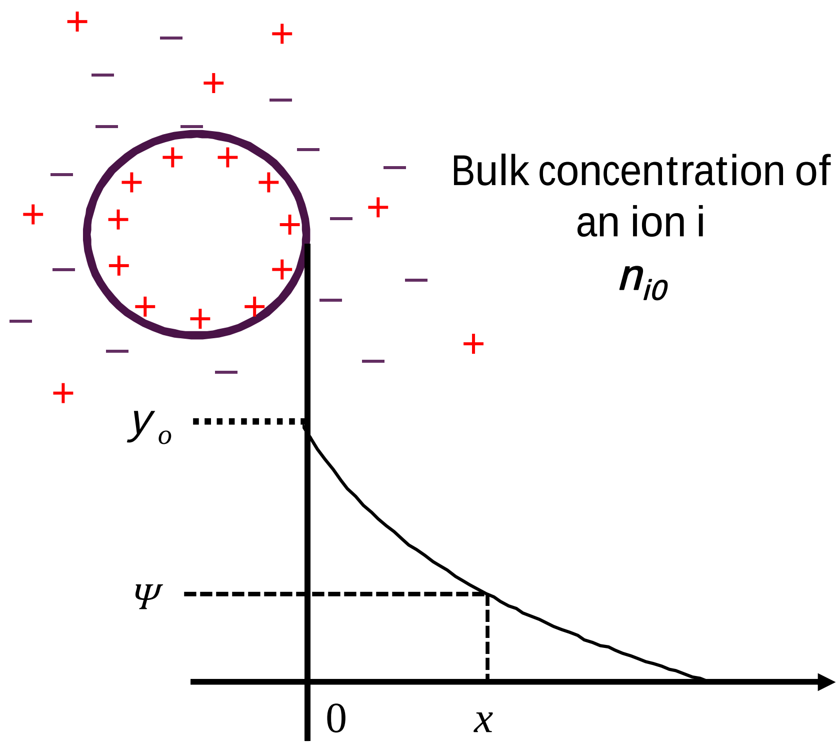
- non-linear dependence of the potential on the charge density

Boltzman equation

- what is the probability to find a particle at certain distance from the surface

Poisson-Boltzman equation

- how particles create an electrostatic field around a charged surface

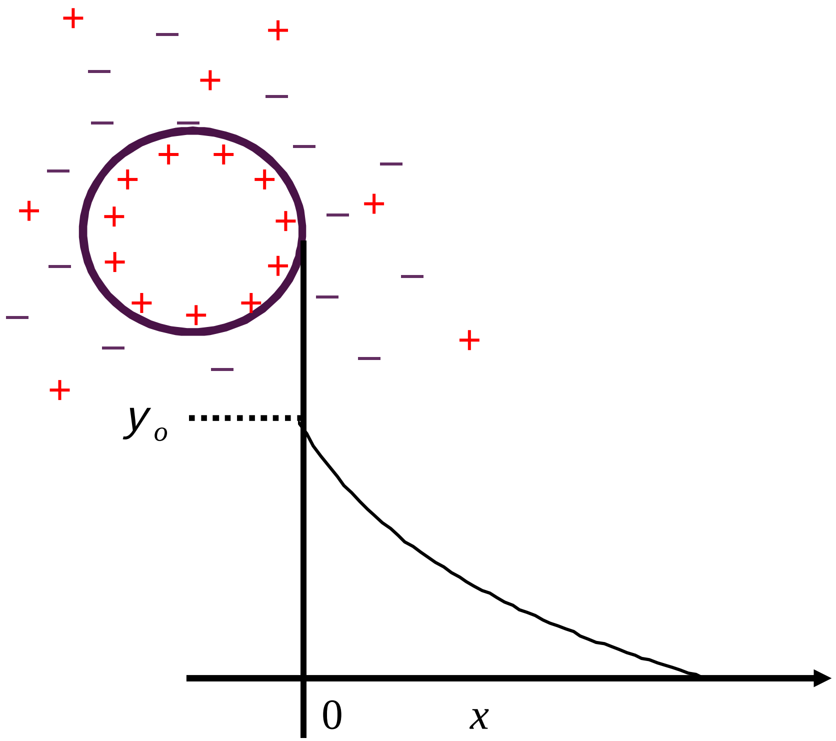


Solution of Poisson-Boltzman

$$\Psi = \Psi_0 \exp(-\kappa x)$$

where

$$\kappa = \left(\frac{e^2 \sum_i {z_i}^2 n_{i,0}}{\varepsilon k T}\right)^{1/2}$$



- Potential increases exponentially when approaching the surface
  - This equation is not valid extremely close to the surface

Thickness of EDL ≈ Debye length κ^{-1}

Debye length $\boldsymbol{\kappa}^{-1}$

- How far away from the surface the ions do "feel" the charged substrate

$$\boldsymbol{\kappa}^{-1}$$

$$= \left(\frac{e^2 \sum_i z_i{}^2 n_{i,0}}{\varepsilon kT}\right)^{-1/2}$$

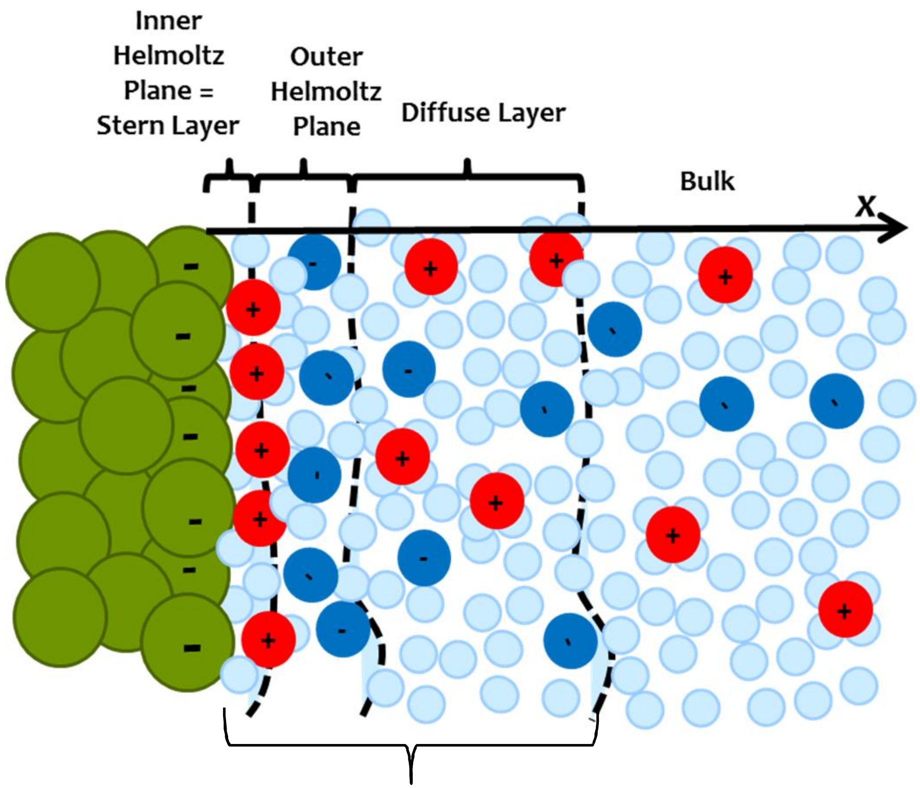
$$= \left(\frac{e^2 N_A \sum_i z_i{}^2 c_{i,0}}{\varepsilon kT}\right)^{-1/2}$$

$$= \left(\frac{F^2 \sum_i z_i{}^2 c_{i,0}}{\varepsilon RT}\right)^{-1/2}$$

$$= \left(\frac{F^2}{\varepsilon RT} I\right)^{-1/2}$$

where I is ionic strength

$[\kappa^{-1}]$ = [m]



Debye length $\boldsymbol{\kappa}^{-1}$

Concept Check #3

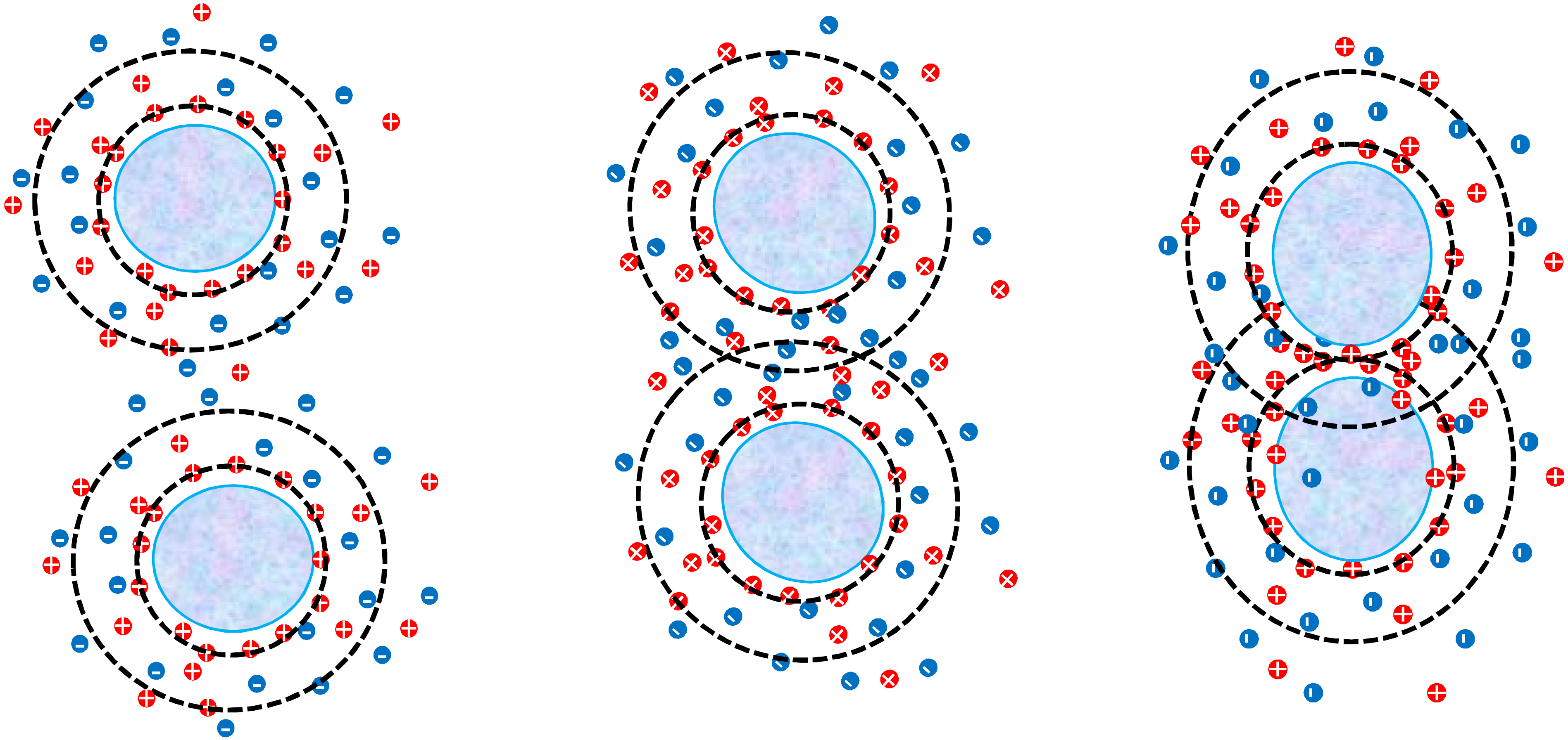
When the ionic strength of solution increases, the thickness of electrical double layer

1) Increases?
2) Decreases?
3) Stays constant?

Example: κ^{-1} for (1,1)-electrolyte

Concentration [mol/dm^3]	1/k [nm]
0.1	0.96
0.01	3.04
0.001	9.6
0.0001	30.4
® 0	® 100

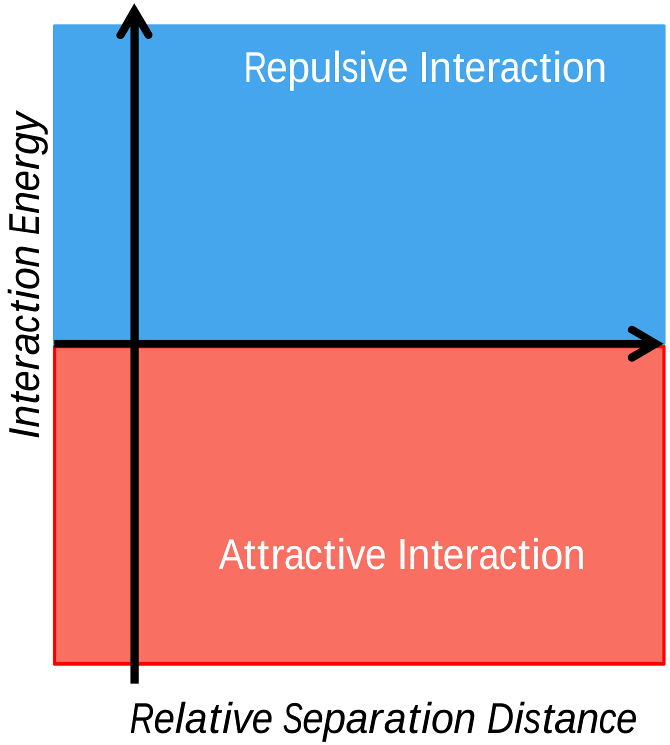
ØWhen ionic strength increases, thickness of the double layer decreases



How about other forces?

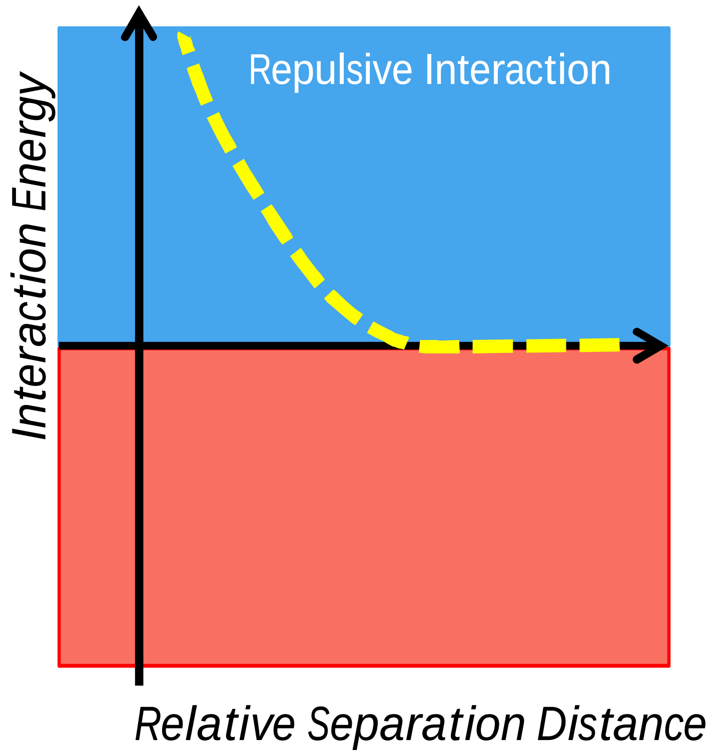
Let’s think forces between two particles in a solution.

DLVO* theory



** Derjaguin and Landau, Verwey and Overbeek*

DLVO theory

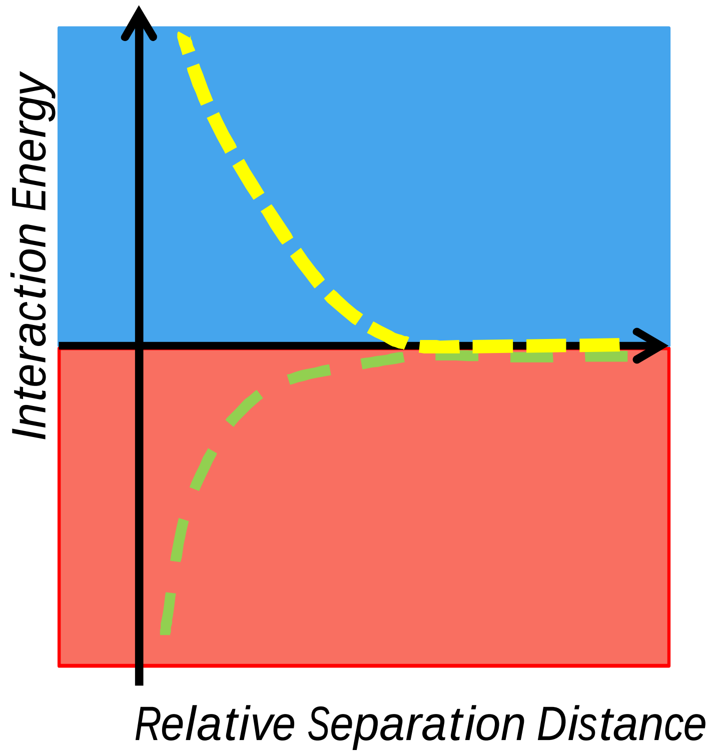


Net Interaction

=

Due to Repulsive forces

DLVO theory



Net Interaction

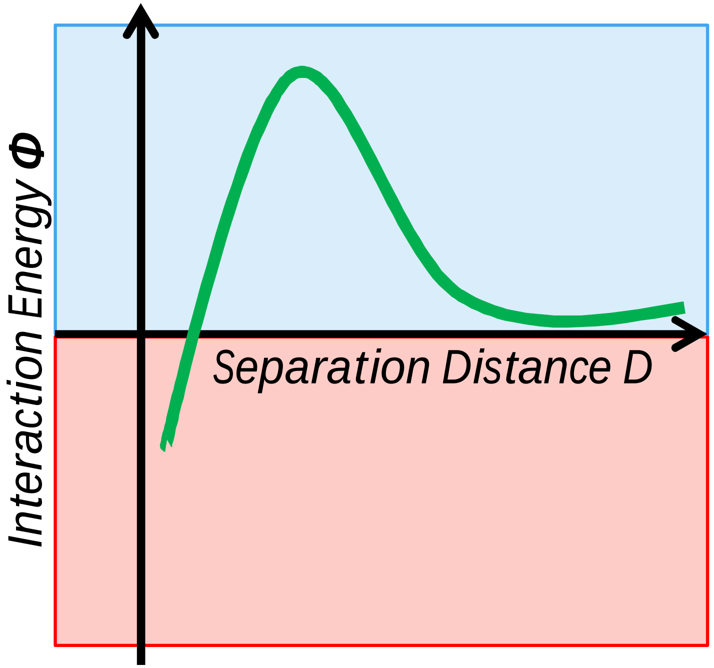
=

Due to Repulsive forces

+

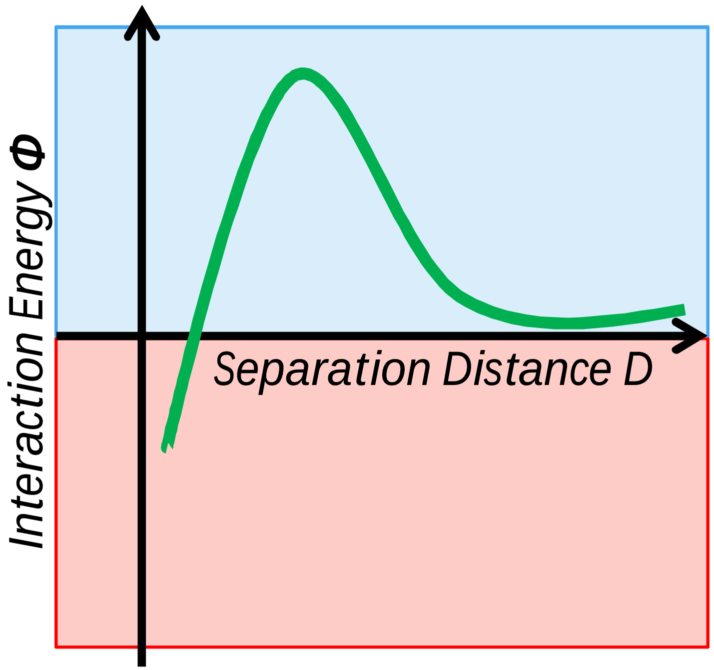
Due to Attractive forces

DLVO Theory



$$\boldsymbol{\Phi = Attractive + repulsive}$$

DLVO Theory



$$\boldsymbol{\Phi = \Phi_E + \Phi_{VdW}}$$

Electrostatic energy

$$\Phi_E = 2\pi\varepsilon_r\varepsilon_0 r E^2 e^{-\kappa D}$$

Where

$$\kappa = \sqrt{\frac{F^2 \sum_i c_i z_i^2}{\varepsilon_r\varepsilon_0 RT}}$$

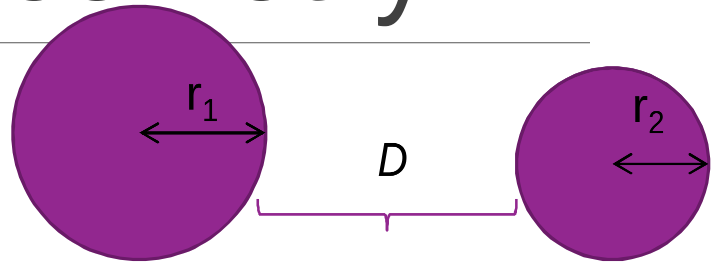
Van der Waals

$$\Phi_{VdW} = -\frac{A r_1 r_2}{6D(r_1 + r_2)}$$

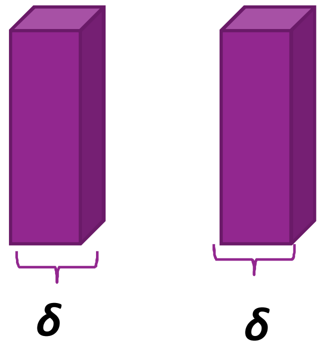
r=radius
E = potential
ε = permittivity; $_r$=relative, $_0$= vacuum
F = Faraday's constant
c_i = concentration of ion *i*
z_i = charge of ion i
R = gas constant
T = temperature
A = Hamaker constant
r_1 = radius of particle 1
r_2= radius of particle 2

VdW Depends on Geometry

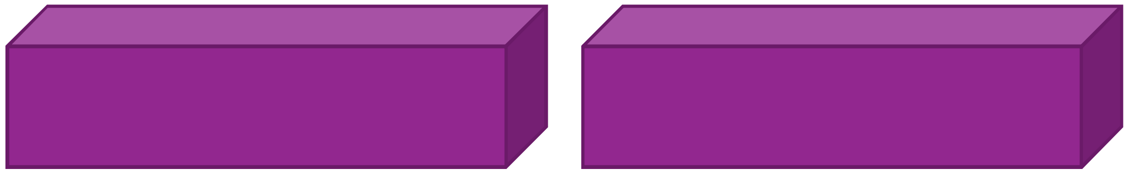
$$\Phi_{VdW} = -\frac{Ar_1 r_2}{6D(r_1+r_2)}$$



$$\Phi_{VdW} = -\frac{A}{12\pi}\left[D^{-2} + (2\delta + D)^{-2} + (\delta + D)^{-2}\right]$$

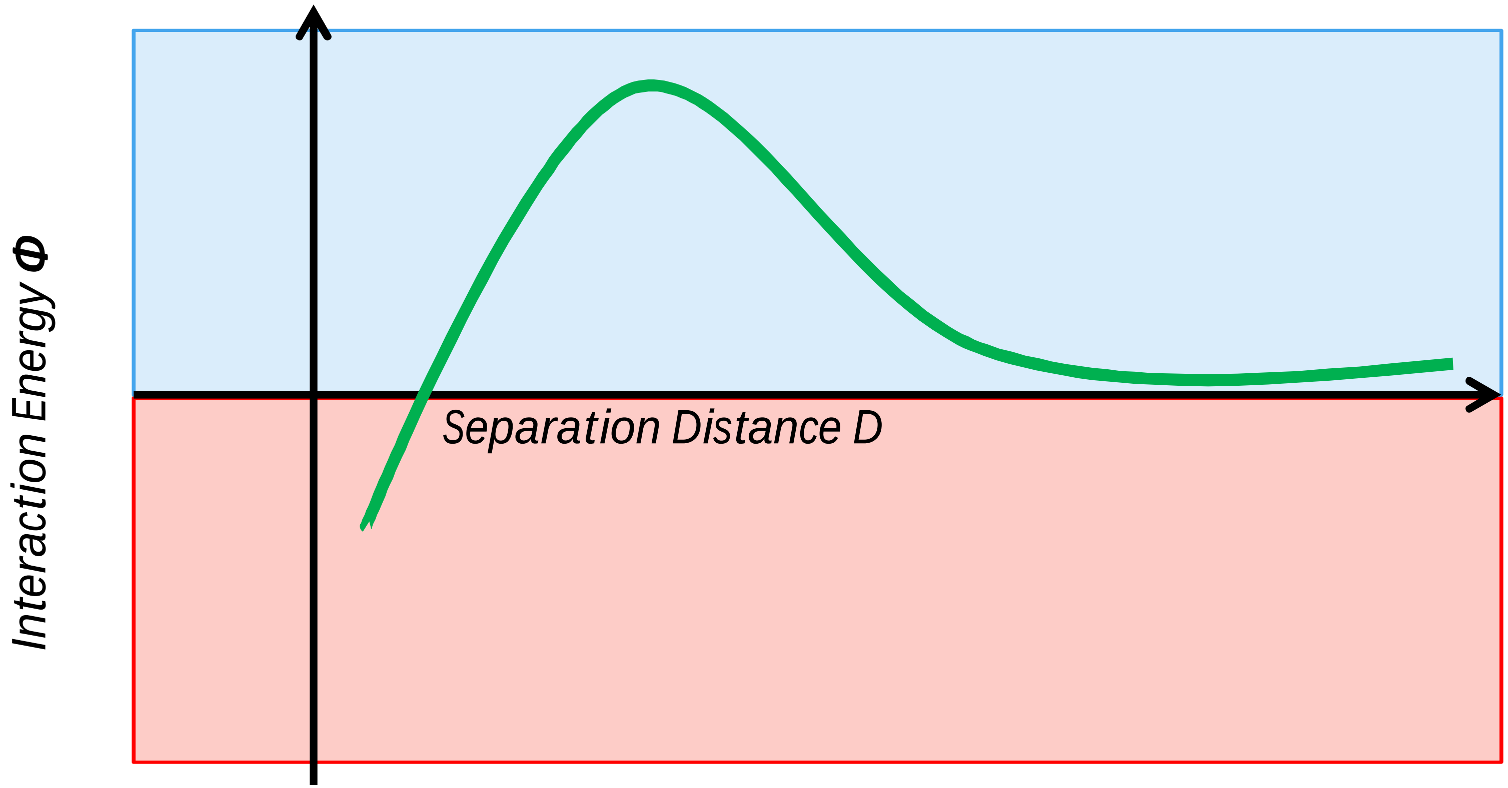


$$\Phi_{VdW} = -\frac{A}{12\pi} D^{-2}$$



D = separation distance

DLVO Theory



$$\Phi = \Phi_E + \Phi_{VdW}$$

Concept Check #4

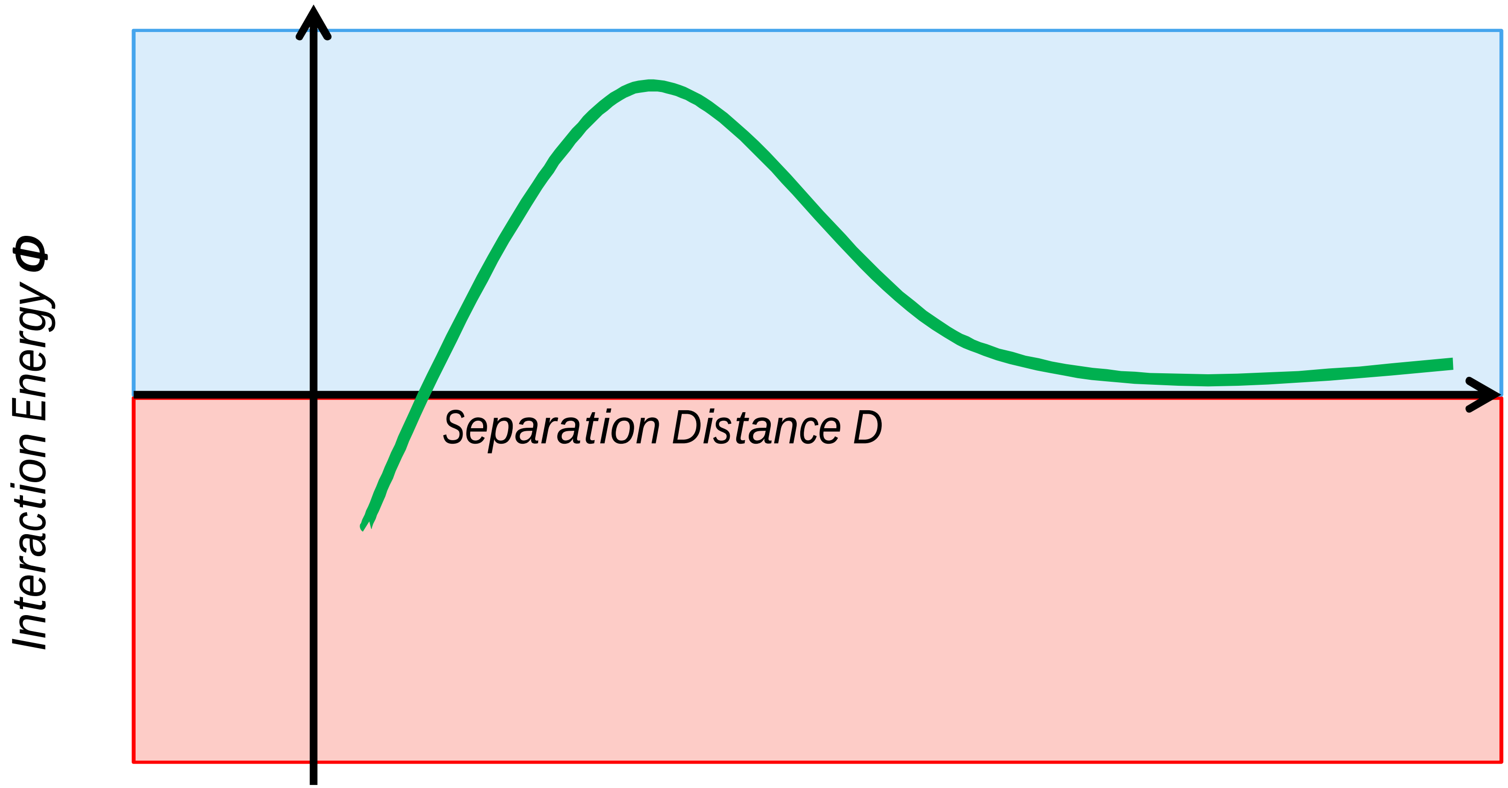
Based on DLVO theory

(a) particles aggregate when interaction energy is high

(b) particles are more likely to aggregate when the salt concentration decreases

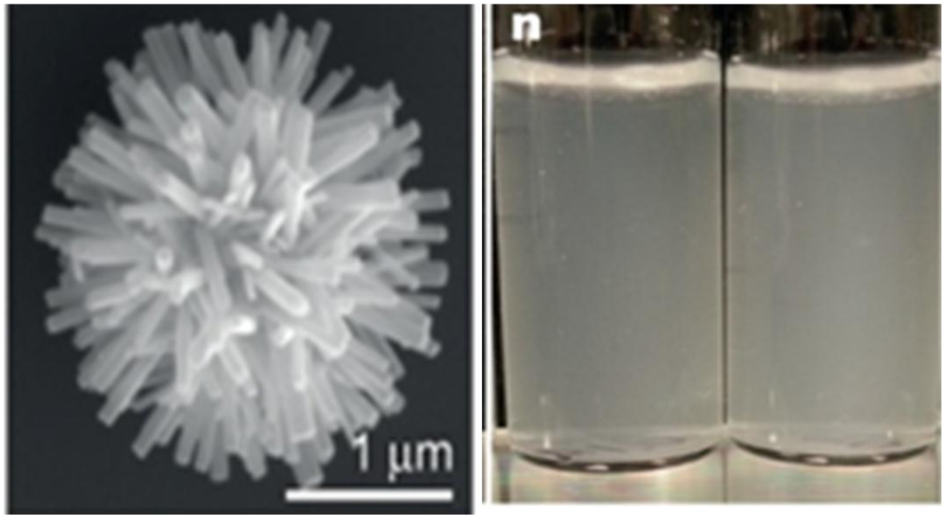
(c) particles are stable in a colloid due to electrostatic repulsion

DLVO Theory



$$\Phi = \Phi_E + \Phi_{VdW}$$

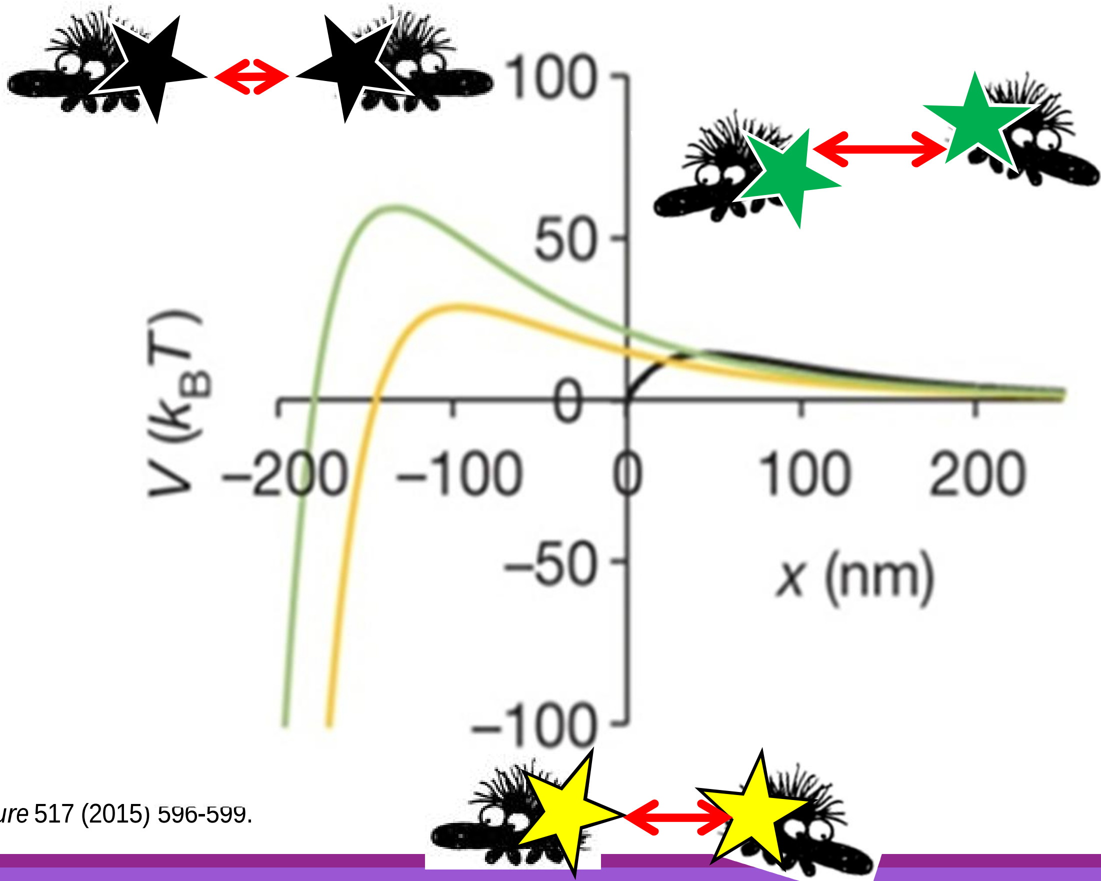
Hydrophobic Hedgehog Particles: Stable in Water??



J. H. Bahng, B. Yeom, Y. Wang, S. O. Tung, J. D. Hoff, N. Kotov, *Nature* 517 (2015) 596-599.

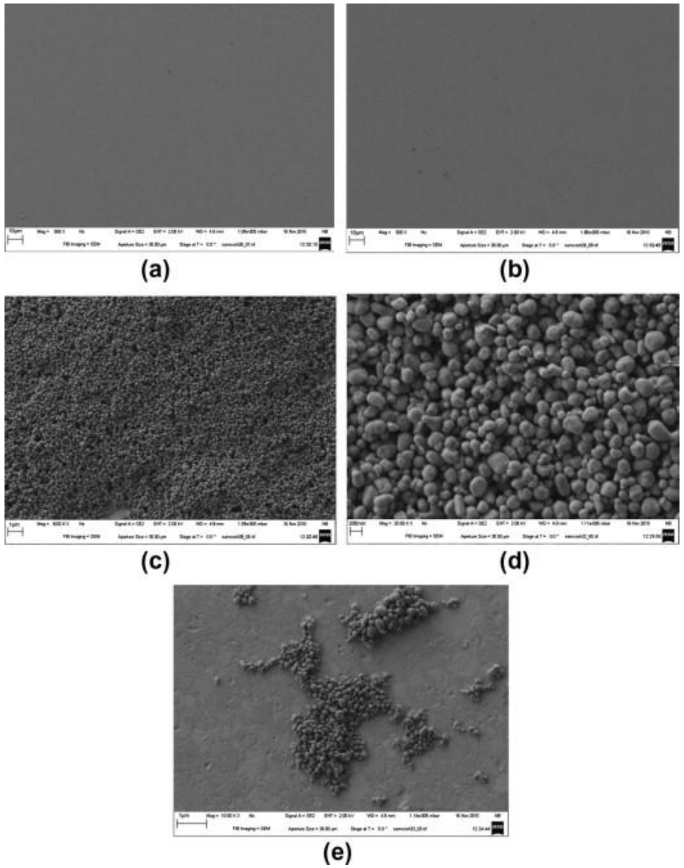
Hydrophobic Hedgehog Particles: Stable in Water

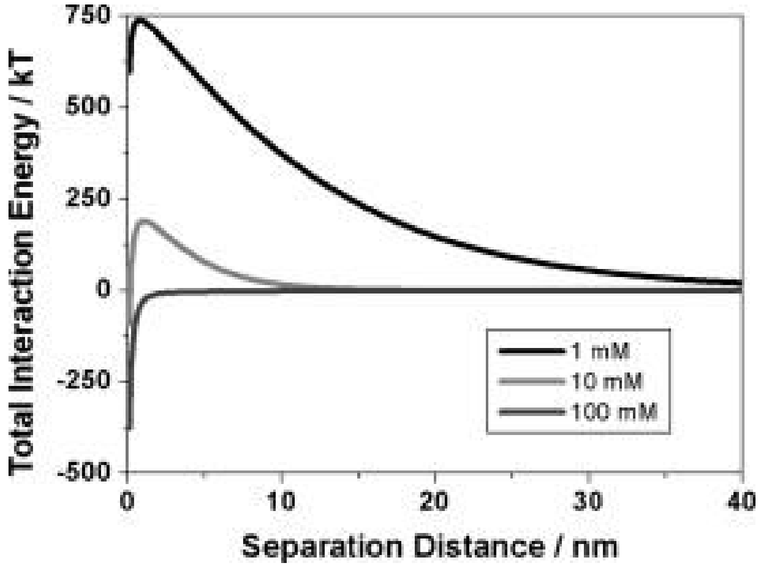
Smaller contact area with spikes



J. H. Bahng, B. Yeom, Y. Wang, S. O. Tung, J. D. Hoff, N. Kotov, *Nature* 517 (2015) 596-599.

TiO_2 Nanocontainers on Au QCM crystal





A. Pomorska, K. Yliniemi, B. P.Wilson, D. Shchukinc, D. Johannsmannd, G. Grundmeier, *Journal of Colloid and Interface Science* 362 (2011) 180-187 .

Other Routes to Stability

Steric Stabilization

Thermodynamical stabilization

Ø Based on Gibb's energy minimization of polymers in solvents

1. Polymer reduces ΔG by expanding in a solvent
   à Good solvent
2. Polymer reduces ΔG by coiling up in a solvent
   à Poor solvent

This is also dependent on *T*

Flory-Huggins Θ temperature (or Θ T)

Steric Stabilization

Flory-Huggins ***ϴ*** *temperature (or* ***ϴ*** *T)*

When $T = \Theta$, no change in Gibb's energy even if polymer conformation changes

$$\Delta G_{mixing} = \Delta H - T\Delta S$$

$$\boldsymbol{\Delta G_{mixing} = RT\,(n_1 ln\phi_1 + n_2 ln\phi_2 + n_1\phi_2\psi_{12})}$$

n_1 = number of solvent moles

n_2 = number of solute (polymer) moles

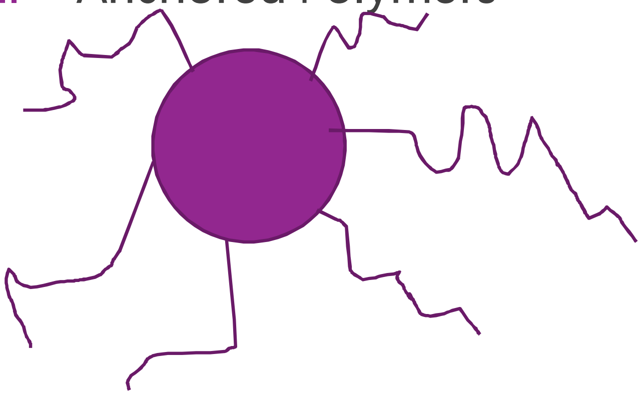
ϕ_1= volume fraction of solvent

ϕ_2= volume fraction of solvent

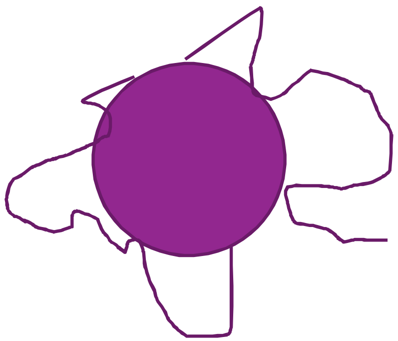
ψ_{12}= free energy parameter (incl. entropy)

Steric Stabilization

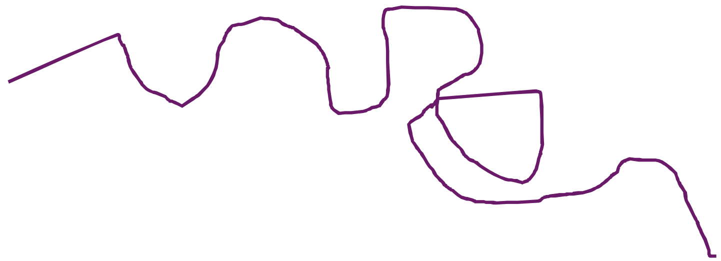
1. Anchored Polymers



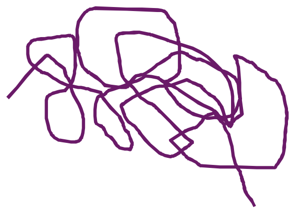
2. Adsorbed Polymers



1. Good Solvent

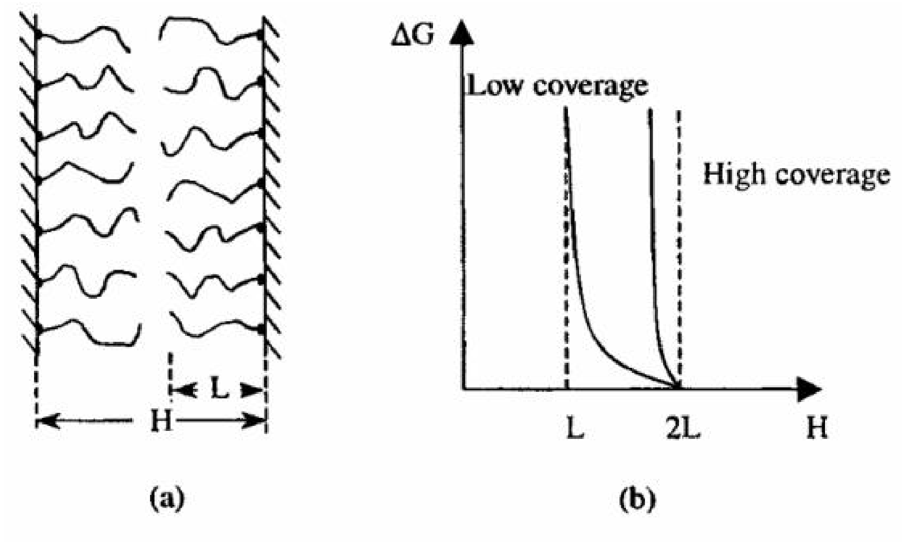


2. Poor Solvent

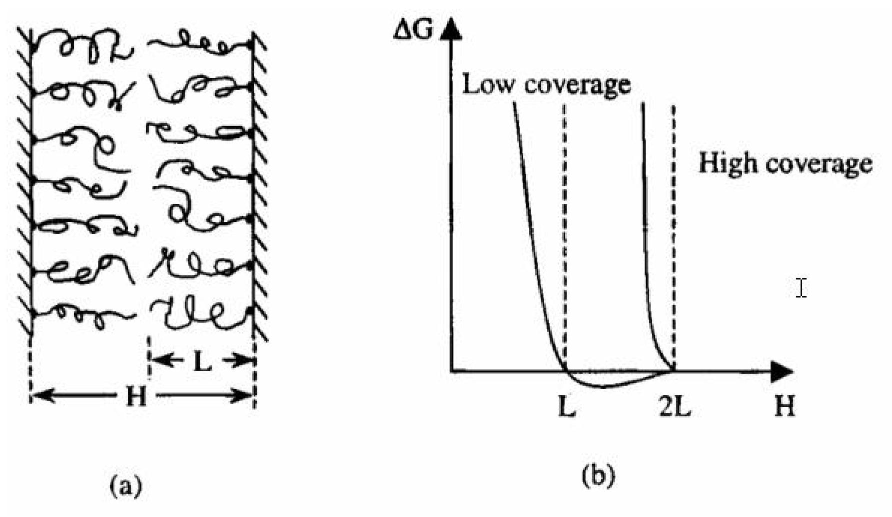


Solvent Type vs. Coverage

GOOD SOLVENT



POOR SOLVENT



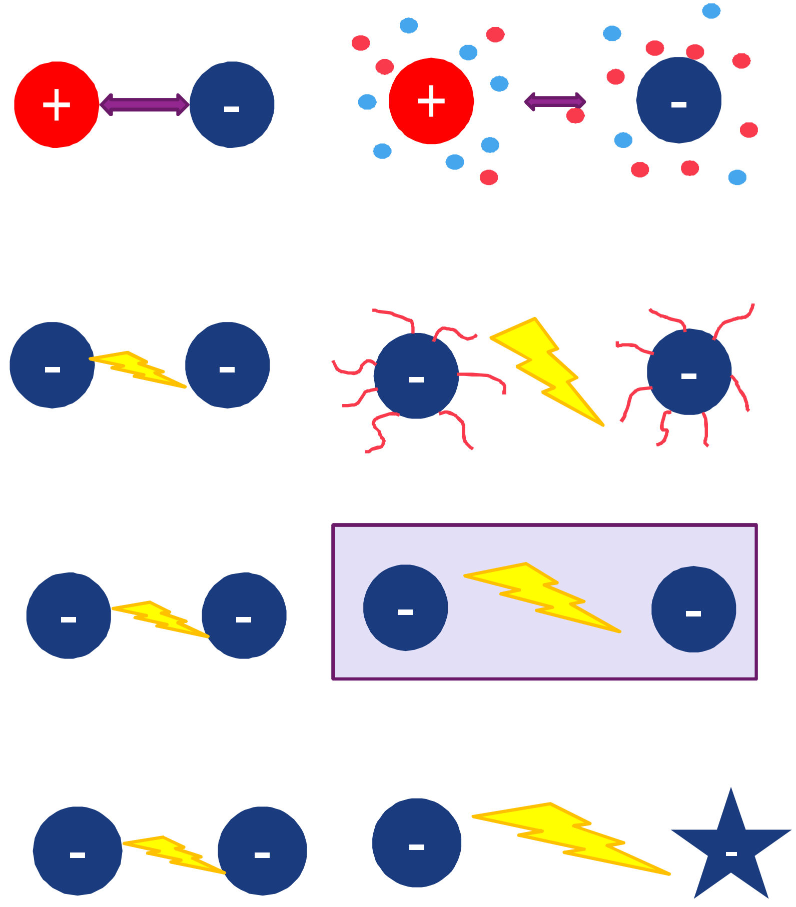
Images from: G. Cao, Y. Wang, Nanostrucures and Nanomaterials – Synthesis, Properties and Applications, 2^{nd} Ed. World Scientific, pp. 54-55.

Pair Discussion: How the following parameters affect (colloidal) stability?

1. Salt concentration in the solution
2. Adding surfactant/polymer on the nanoparticle surface (high coverage)
3. Changing the solvent
4. Changing the geometry

Pair Discussion: How the following parameters affect (colloidal) stability?

1. Salt concentration in the solution
   - Changes the electrostatic interactions
2. Adding surfactant/polymer on the nanoparticle surface (high coverage)
   - Changes the electrostatic and Van der Waals interactions
   - Steric hinderance
3. Changing the solvent
   - Changes the electrostatic and Van der Waals interactions
   - Affects steric hinderance
4. Changing the geometry
   - Changes Van der Waals interactions



3rd Part: Synthesis of Nanomaterials (aka Nanochemistry)

So many questions...

1. Where? To surface, in solution, as powder?
2. What size and shape?

Examples of self-assemblies – different geometries

0 dimensions: all dimensions on nanoscale (a dot)

- Quantum dots (semiconductor nanoparticles)
- Monolayer protected clusters (metallic nanoparticles with a capping layer)

1 dimension: two dimensions on nanoscale (a line)

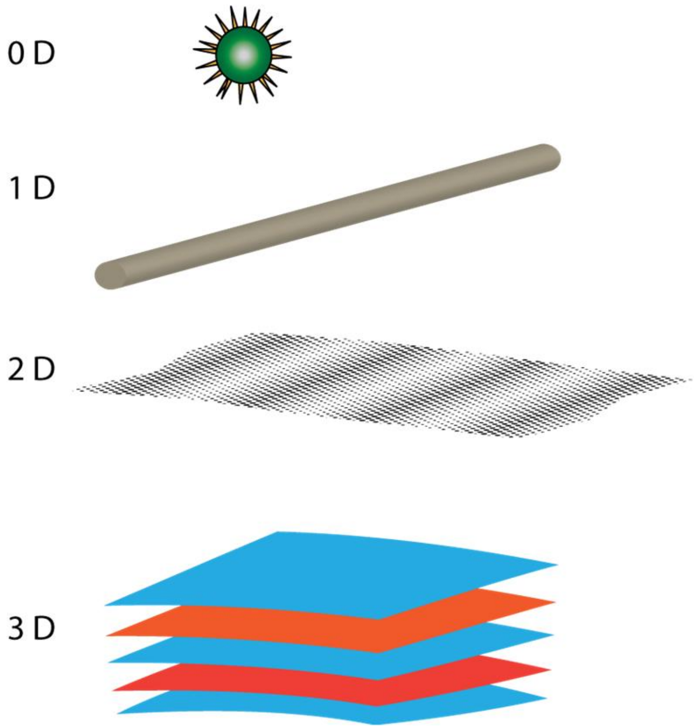
- Metal nanowires
- Carbon nanotubes
- Cellulose nanofibrils

2 dimensions: one dimension on nanoscale (a plane)

- Graphene
- Nanoclay platelets
- Self-assembled monolayers

3 dimensions:

- Layer-by-layer polyelectrolyte structures
- Viral capsides
- Nanocomposites



Nanochemistry is used to achieve these different geometries

BOTTOM-UP

"Building blocks joined together"

- Physical
  - Deposition by controlling the atmospheric pressure, ionic strength, temperature, concentrations
- Chemical
  - Synthesis, i.e. nucleation and growth via chemical reactions
  - In solutions & gases, at surface

TOP-DOWN

"Shaving of small pieces from a big block"

- Physical
  - Shaving
  - Grinding
  - Bombarding with ions, electrons (no reaction)
- Chemical
  - Dissolution
  - Pyrolysis (burning)
  - Bombarding with ions, electrons (causing a reaction)

BOTTOM-UP

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  - Deposition by controlling the atmospheric pressure, ionic strength, temperature, concentrations
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NANOCHEMISTRY

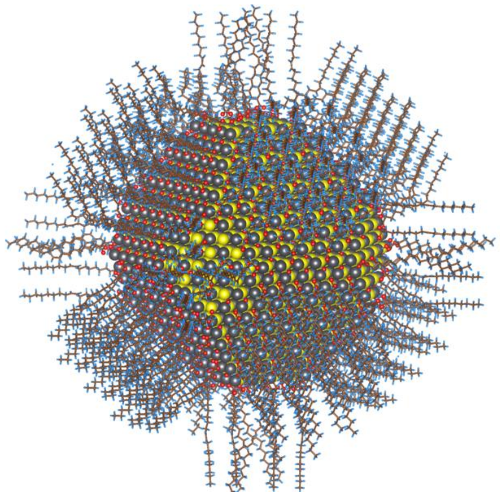
0D Nanomaterials

Nanoparticles

Quantum Dots

Inclusions

Example: Lead sulphide nanoparticle protected with oleic acid



Zherebetskyy et al., *Science* 344, (2014) 1380

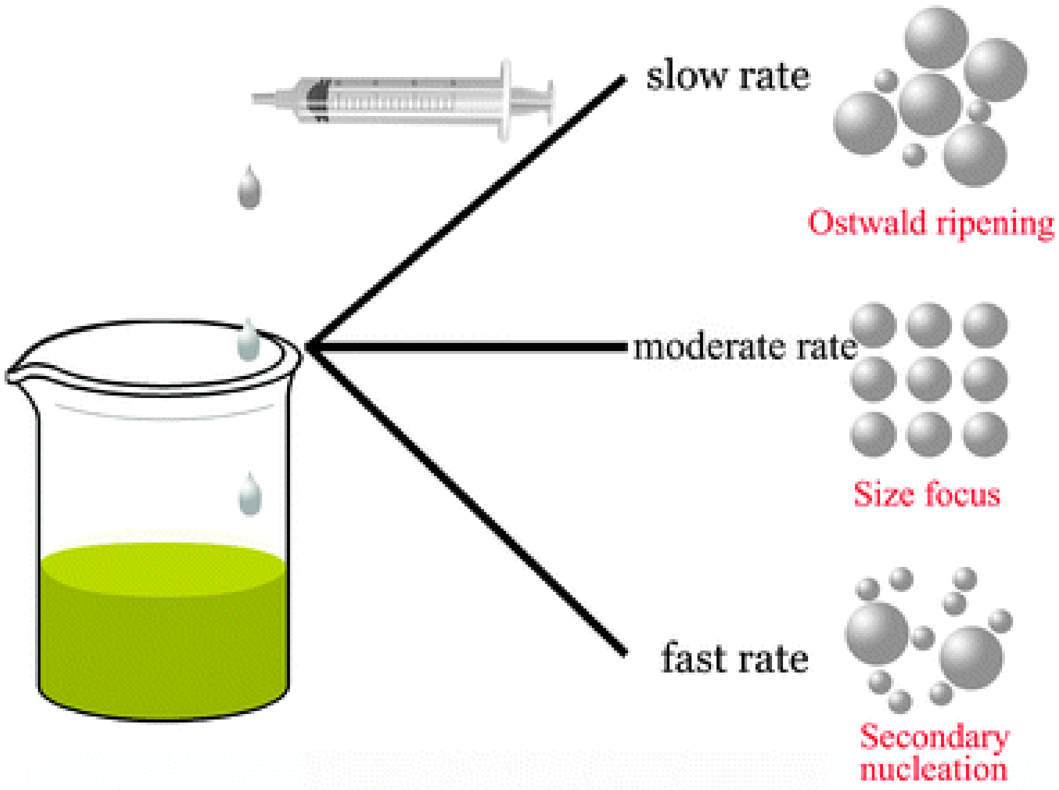
Example: Au NPs and Citric Acid

Example: Turkevic Method

https://www.tedpella.com/gold_html/goldsols.htm

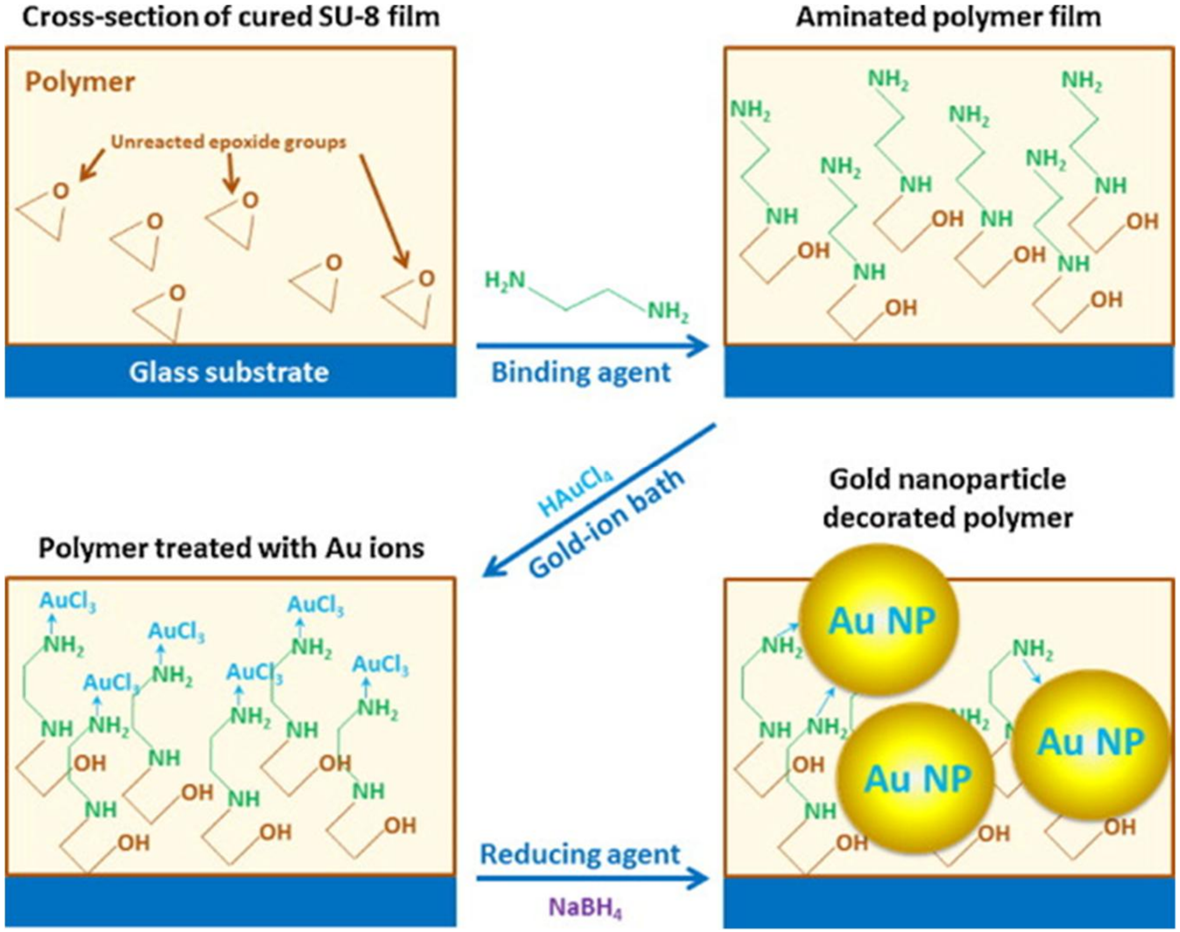
https://www.youtube.com/watch?v=SBkGZiTxHKE

Example: Seed-and-Feed



R. Zong, X. Wang, S. Shi, Y. Zhu, PCCP 16 (2014) 4236-4241.

Example: In-Situ at Surface



C J. Clukay, C. N. Grabill, M. A. Hettinger,A. Dutta, D. J. Freppon, A. Robledo, H. Heinrich, A. Bhattacharya, S. M. Kuebler, *Applied Surface Science* 292 (2014) 128-136.

1D Nanomaterials

Rods

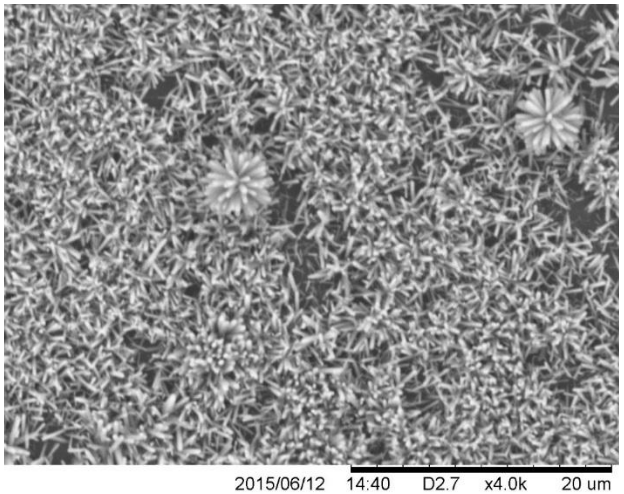
Tubes

Whiskers

Fibres or fibrils

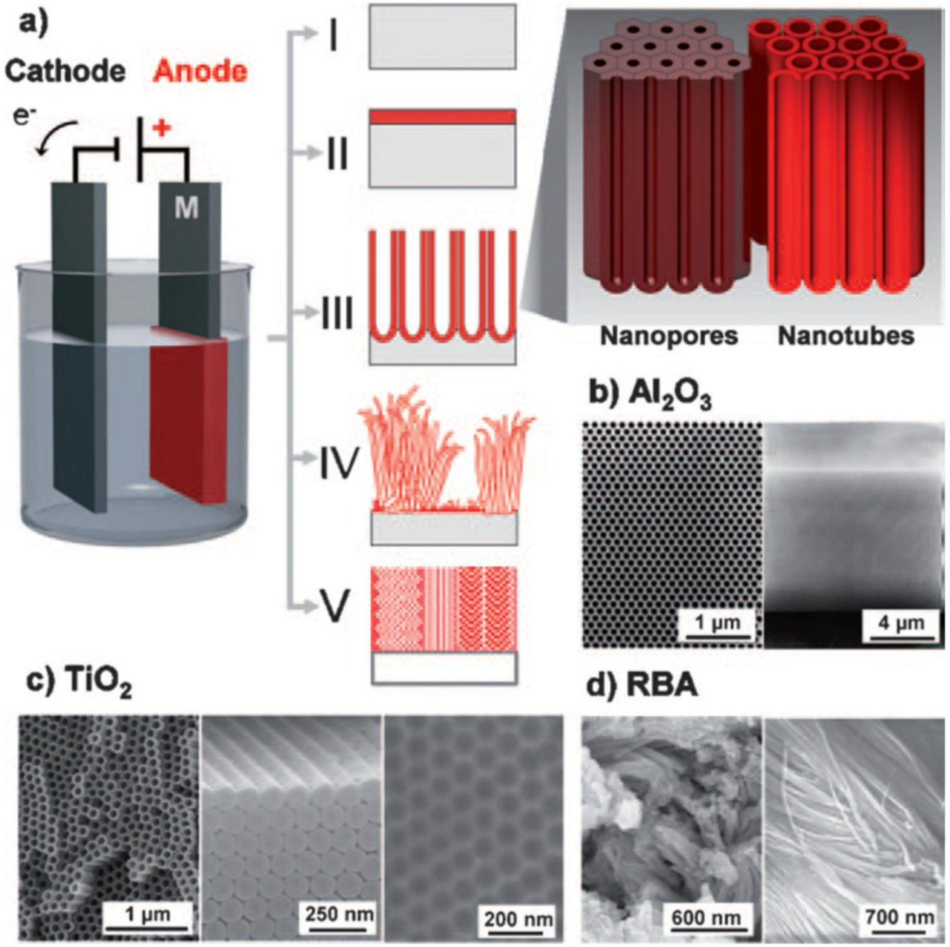
Wires

Example: ZnO Nanorods and Hedgehog Particles



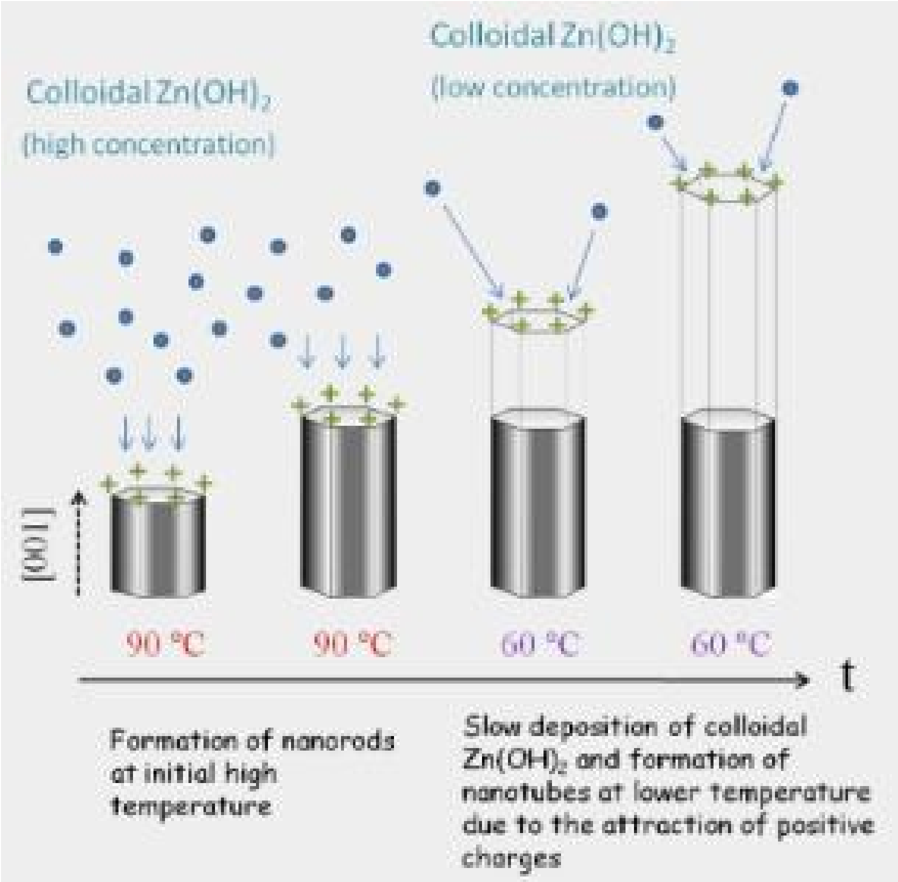
Authors: Manu Tehnunen, Kirsi Yliniemi, Sasha Hoshian, Sami Franssila

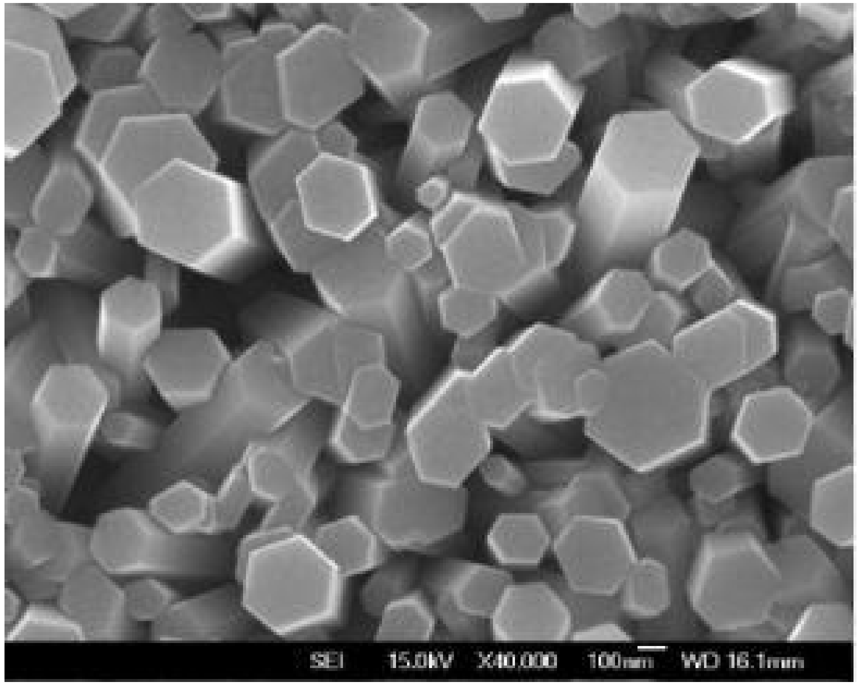
1D Nanomaterials: Nanotubes



P. Roy, S. Berger, P. Schmuki, *Angew. Chem. Int. Ed.* 50 (2011) 2904 – 2939.

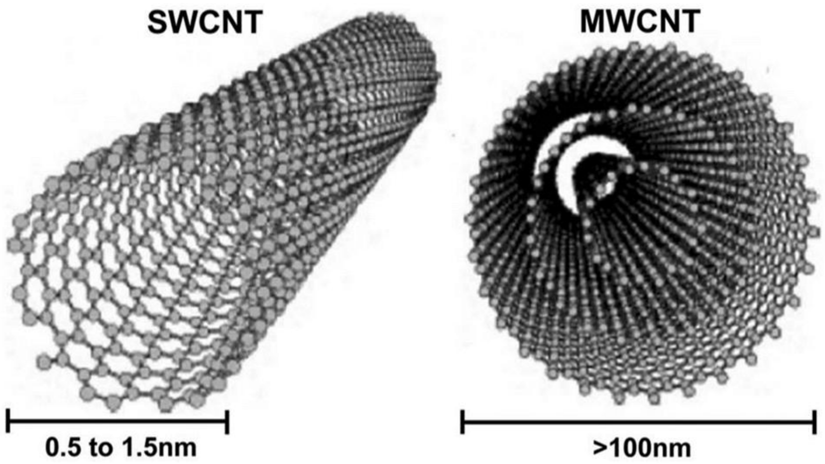
1D Nanomaterials: Nanorods

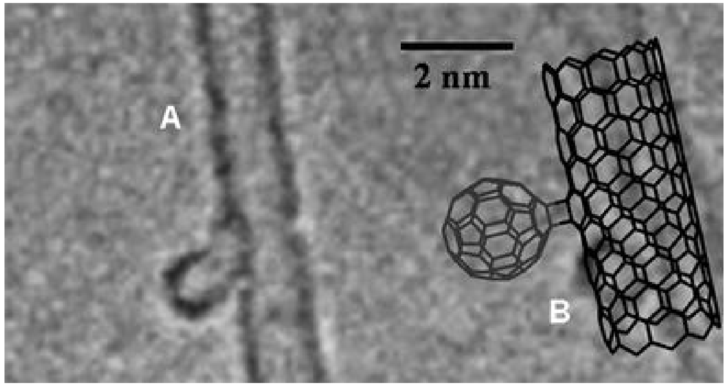




K.-W. Chae, Q. Zhang, J. Seog Kim, Y.-H. Jeong, G. Cao, *Beilstein J. Nanotechnol.* 1 (2010) 128–134.

Carbon Nanotubes (CNT) and Nanobuds (CNB)





P.A. Martins-Júnior et al. Journal of Dental Research 2013;0022034513490957

A. G. Nasibulin, P. V. Pikhitsa, H. Jiang, D. P. Brown, A. V. Krasheninnikov, A. S. Anisimov, P. Queipo, A. Moisala, D. Gonzalez, G. Lientschnig, A. Hassanien, S. D. Shandakov, G. Lolli, D. E. Resasco, M. Choi, D. Tomanek, E. I. Kauppinen, *Nat. Nanotechnol.*, 2 (2007), 156.

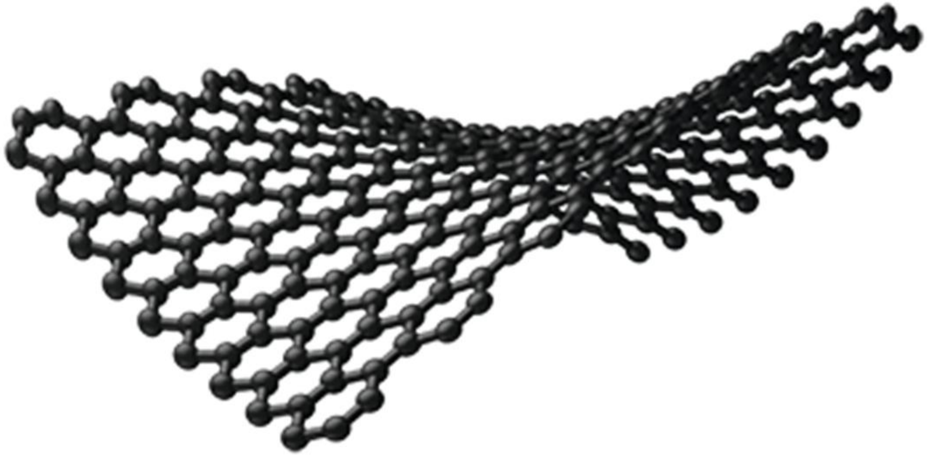
More in Lecture 4

2D Nanomaterials

Sheets and foils

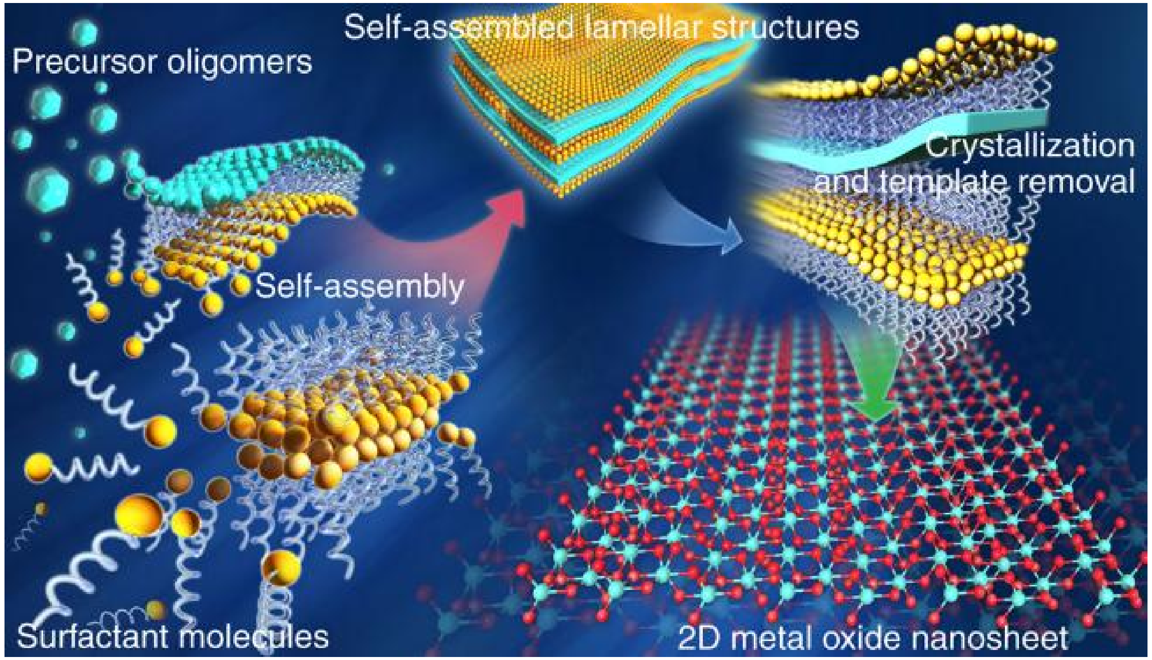
Nanoparticle Arrays

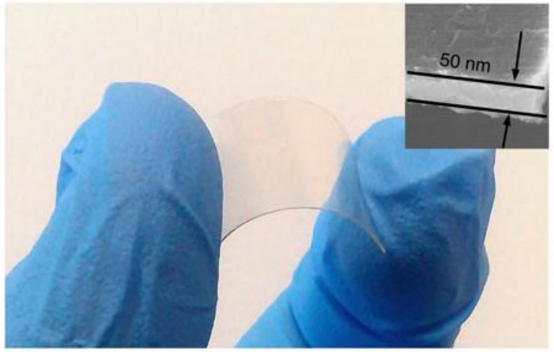
Example: Graphene

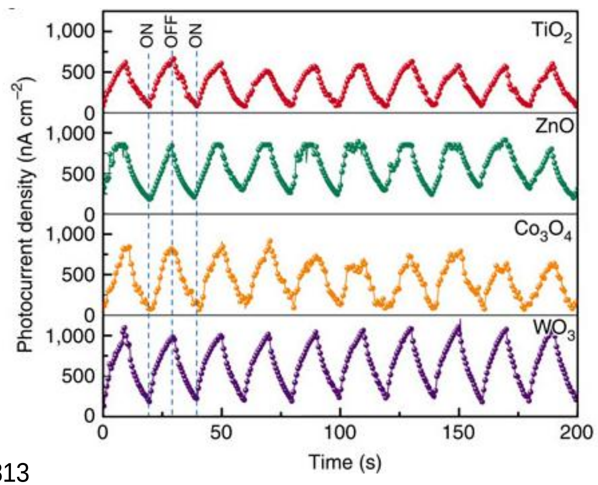


http://graphene-flagship.eu/?page_id=34#.Vc3BWmO8pio

Transition Metal 2D Sheets







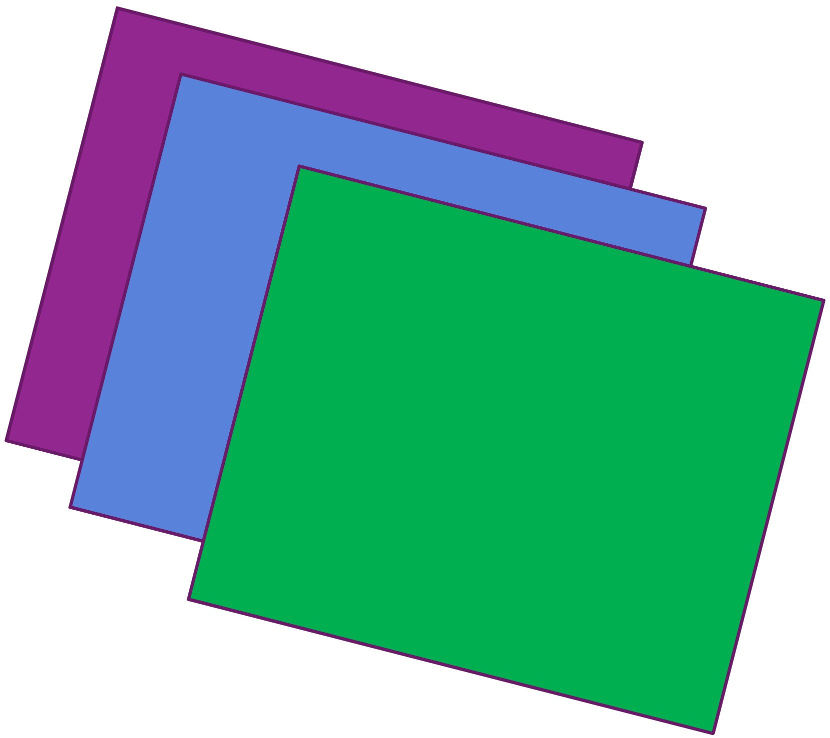
Z. Sun, T. Liao, Y. Dou, S. M. Hwang, M.-S. Park, L. Jiang, J. H. Kim, S. X. Dou, *Nature Comm.* 5 (2014) No. 3813

3D Nanomaterials

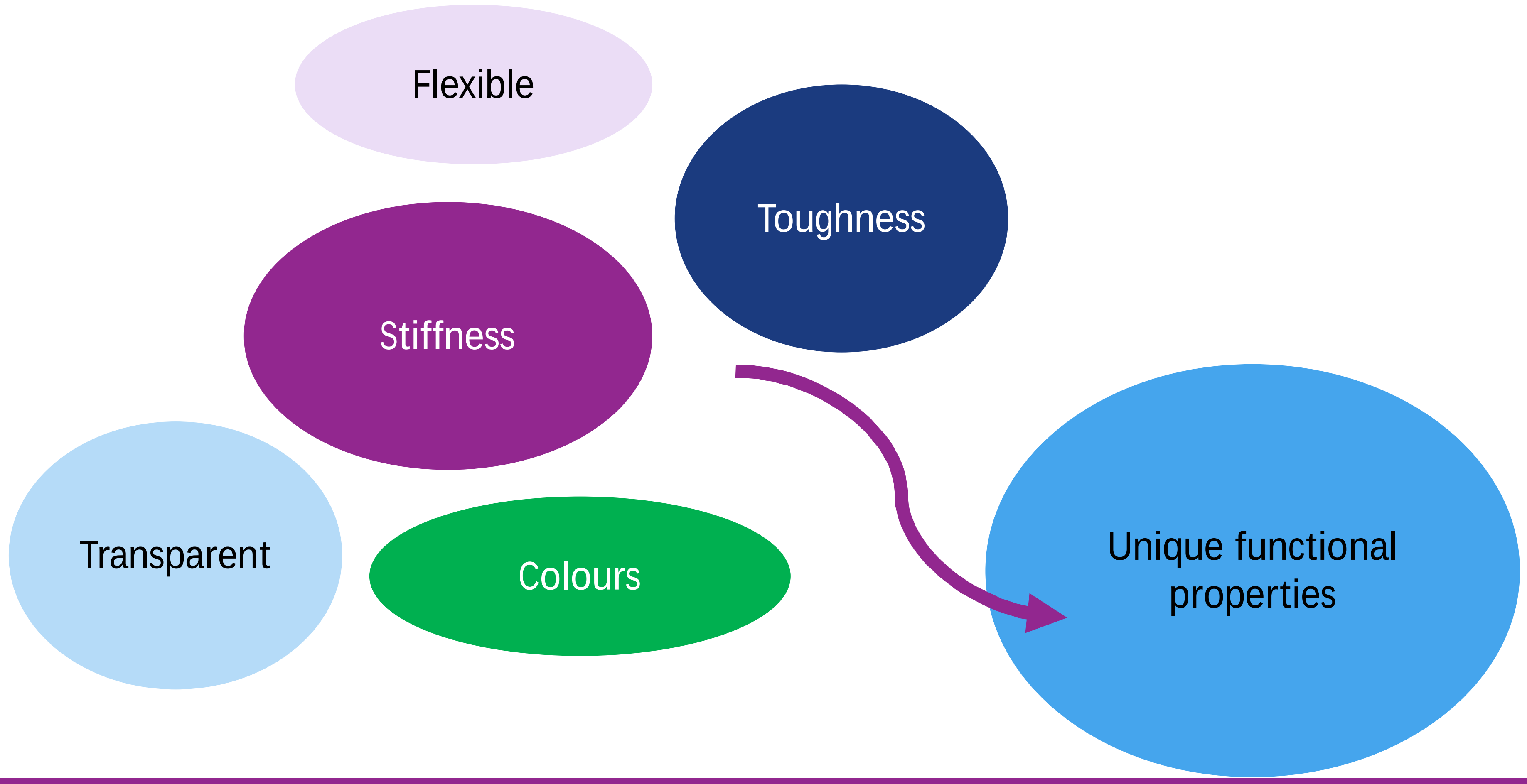
Composites

Layer-by-Layer Films

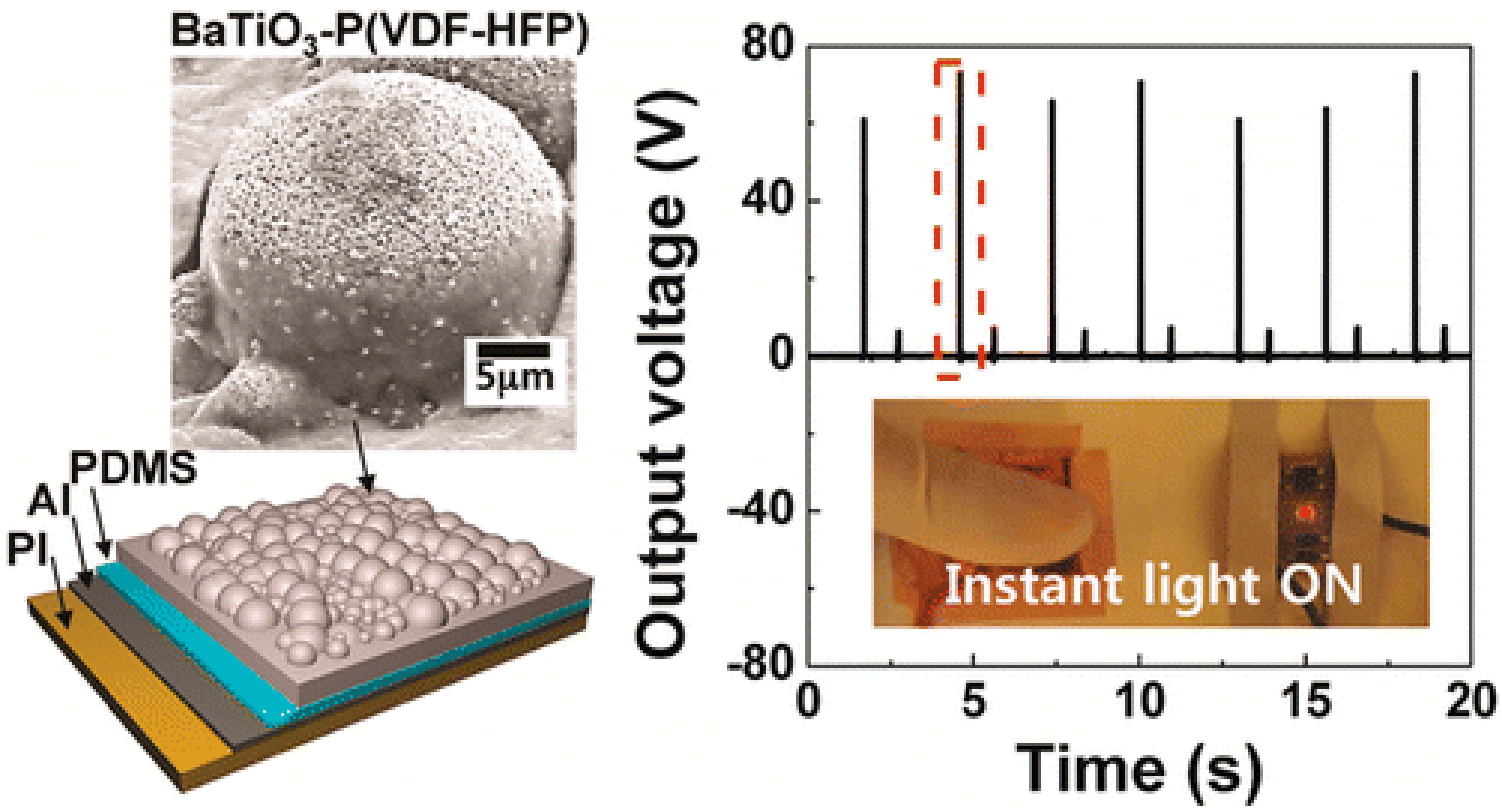
Self-assembled capsules



3D: Composites

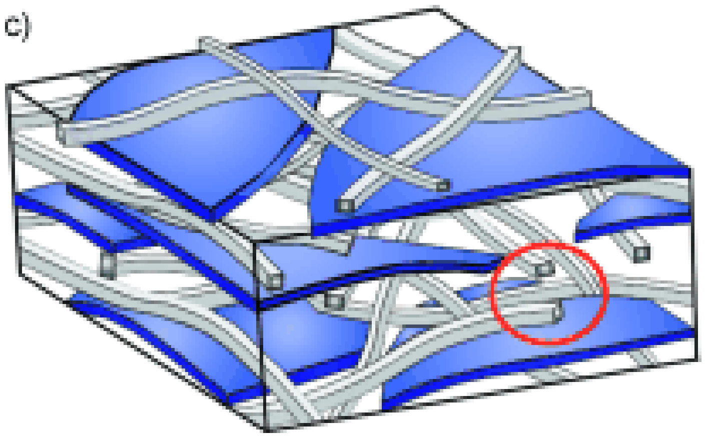


Composites



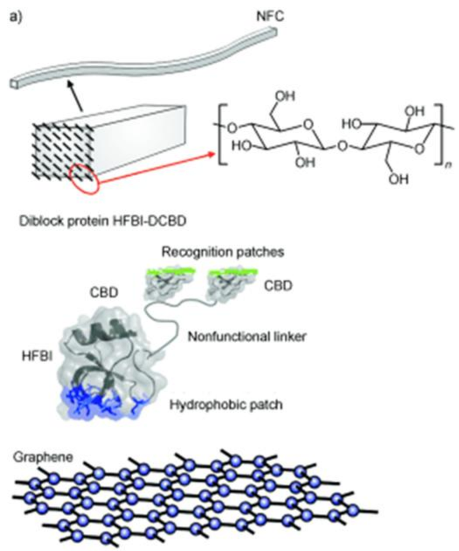
S.-H. Shin *et al.*, *ACS Nano* 8 (2014) 2766–2773.

Biomimetic Composites



<u>Self-assembly</u>

- Combining natural and synthetic materials
- Manipulating natural materials
  - Fusion proteins
  - Nanocellulose



Improving nanocellulose properties with graphene – binder = genetically engineered protein
Young's modulus: 20.2 Gpa
Strength: 278 MPa
Strain-to-failure: 3.1%
Work-of-fracture 57.9 kJm^{-2}

Reading Material

Basic Concepts

G. Cao, *Nanostructures and Nanomaterials – Synthesis, Properties and Applications*, 1^{st} Ed. (2004) World Scientific, pp. 32-62. (electronic)

OR

G. Cao, Y. Wang, *Nanostructures and Nanomaterials – Synthesis, Properties and Applications*, 2^{nd} Ed. (2013) World Scientific, pp. 38-75.

For Interested Reader: 0D-3D Materials

G. Cao, Nanostructures and Nanomaterials – Synthesis, Properties and Applications, 1^{st} Ed. (2004) World Scientific, pp. 32-205. (electronic)

OR

G. Cao, Y. Wang, Nanostructures and Nanomaterials – Synthesis, Properties and Applications, 2^{nd} Ed. World Scientific, pp. 61-266. OR

M.F. Ashby, P.J. Ferreira, D.L. Shodek, Nanomaterials, Nanotechno9logies and Design – An Introduction to Engineers and Architects (2009) Elsevier pp. 257-289

MORE ABOUT THIS TOPIC

CHEM-E4105 Nanochemistry & Nanoengineering

3rd Period (January-February 2017)

Prof. Mady Elbahri (Mat. Sci. & Chemistry)

Next Lecture

Self-Assembly