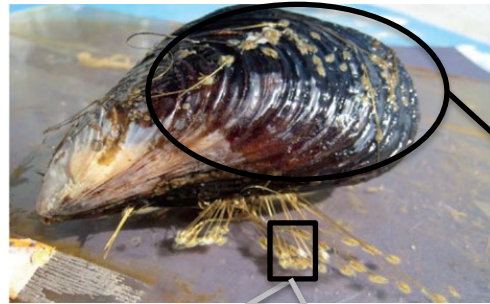
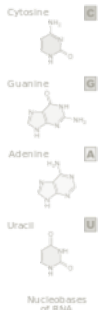


Course outline

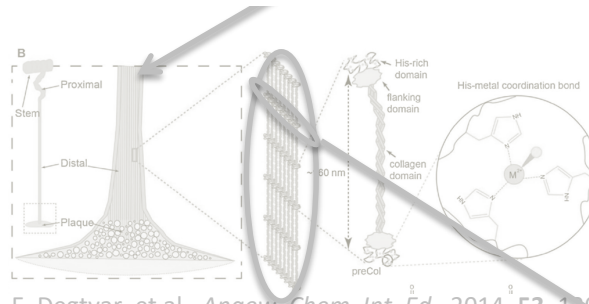


Introduction



Ordered materials

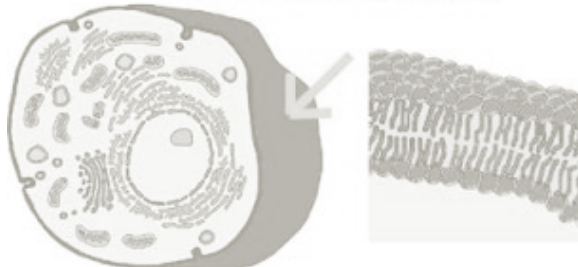
Thermotropic liquid crystals



E. Degtyar, et al., *Angew. Chem. Int. Ed.*, 2014, **53**, 12026-12044

Lyotropic liquid crystals

Cell Membrane

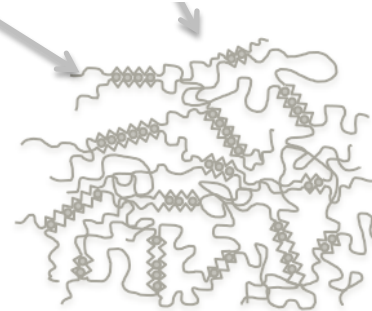


Disordered materials

Polymers

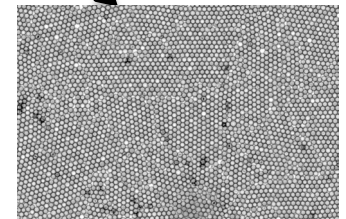


Gels



Colloids

Nanoparticles



Emulsions



Outline

- Introduction
- Particle motion
- Stabilization
 - electrostatic stabilization
 - steric stabilization
- Characterization
- Applications of particle dispersions
- Assembly of particles
- Colloidal crystals made of microgels
- Applications of colloidal crystals
- Agglomeration
- Applications of agglomerated particles

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Colloids

Colloid: Short synonym for colloidal system.

Colloidal: Either molecules or polymolecular particles that are dispersed in a medium and have at least one dimension between approximately 1 nm and 1 μm , or discontinuities in a system that are of this order.

The energy of inter-particle interactions is around $k_B T$.

		continuous phase		
		gas	liquid	solid
dispersed phase	gas			
	liquid			
	solid			

Colloids in our daily life

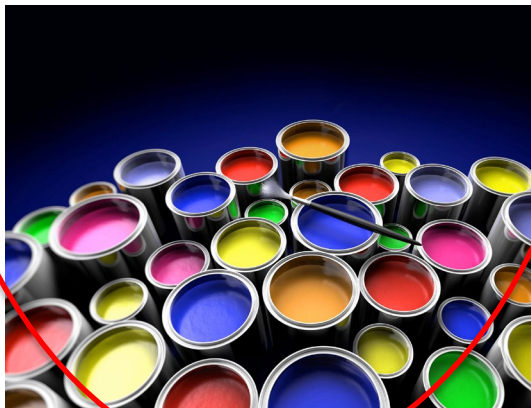
Dispersion: certain sun creams



Emulsion: mayonnaise



Polymer latex dispersion: paint

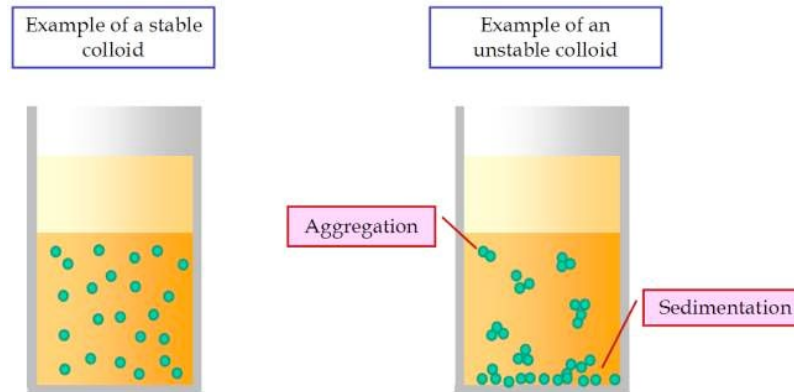


Emulsion: salad dressing



Dispersions

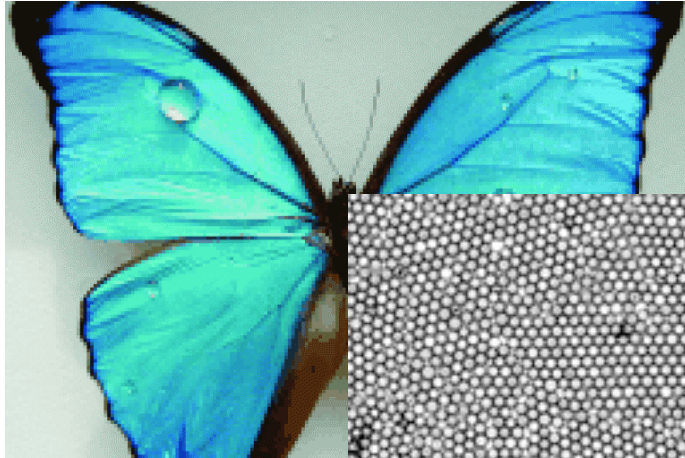
Dispersions are liquids containing particles.



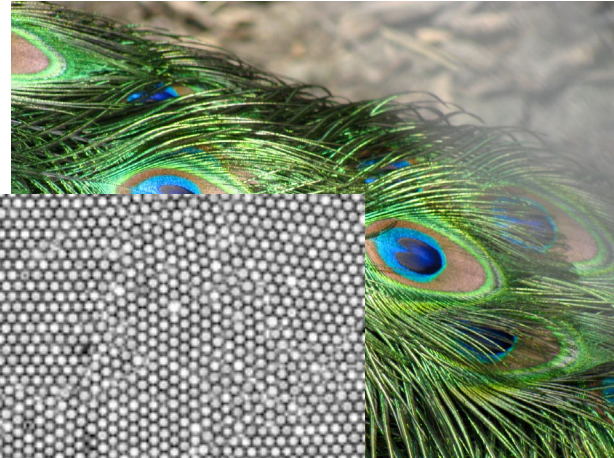
Examples of dispersions



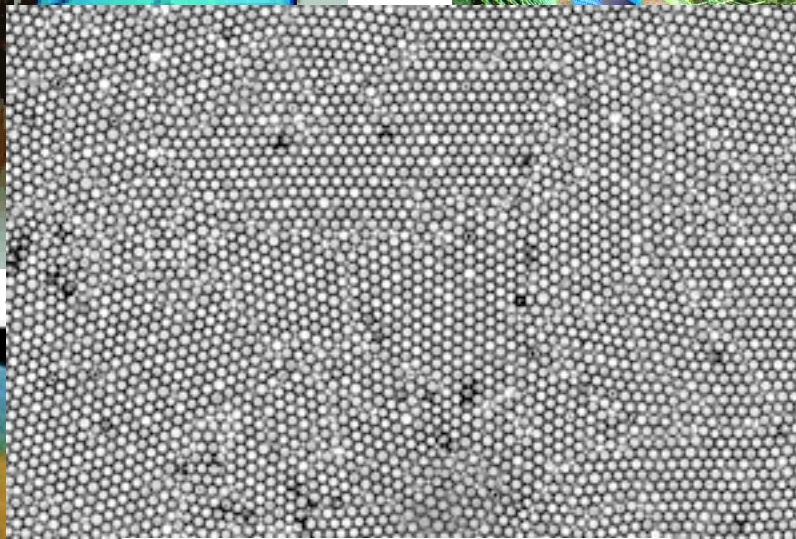
Colloids in nature



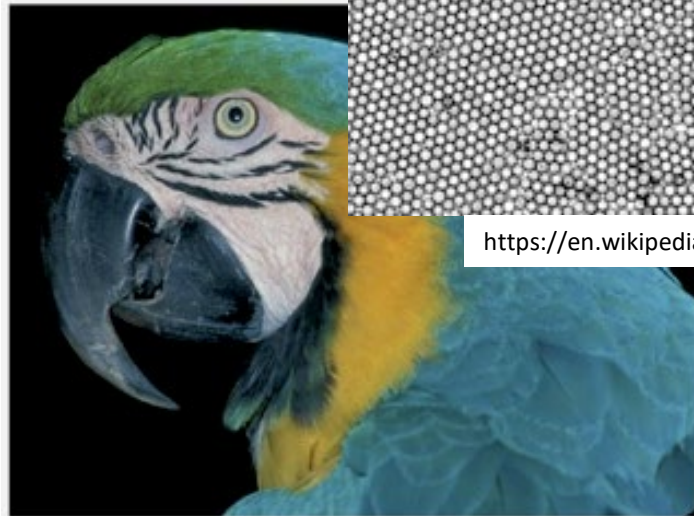
Z.-Z. Gu, et al., *Angew. Chem.*



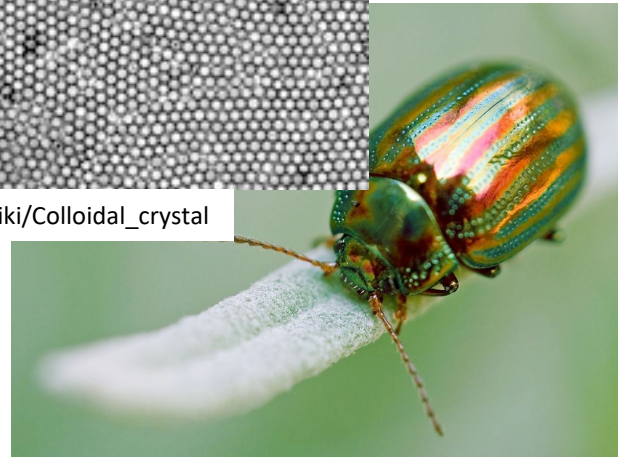
Structural_coloration



https://en.wikipedia.org/wiki/Colloidal_crystal



<http://photobiology.info/Ball.html>



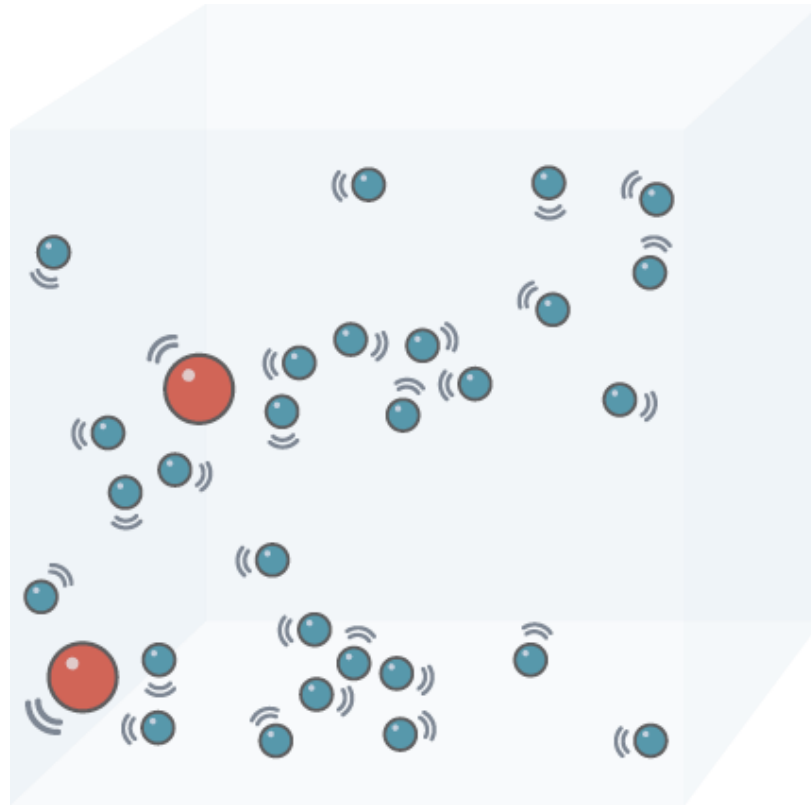
<http://www.scienceinschool.org/content/structural-colour-peacocks-romans-and-robert-hooke>

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Motion of particles

How fast do particles sediment?



<http://www.bbc.co.uk/education/guides/zgr2pv4/revision/5>

<https://www.youtube.com/watch?v=cDcprgWiQEY>

Particle motion

Forces that drive the motion of particles

Forces that drive the **destabilization** of dispersions:

gravitational force if $\rho_p > \rho_l$
buoyance force if $\rho_p < \rho_l$

$$F_b = \Delta\rho \frac{4}{3}\pi R^3 g$$

$$v_{sed} = \frac{2R^2 \Delta\rho g}{9\eta}$$

Force that contributes to the **stabilization** of dispersions:

drag force

$$F_d = 6\pi\eta Rv$$

l_{sed} : sedimentation length [m]
 m : mass of particle [kg]
 g : gravitational constant [N/kg]
 v_{sed} : sedimentation velocity [m/s]

Sedimentation speed of particles

$$v_{sed} = \frac{2R^2\Delta\rho g}{9\eta} \qquad v_{brownian} = \sqrt{\frac{2k_B T}{m}}$$

assuming $\Delta\rho = 1.6 \text{ g/cm}^3$:

r (nm)	v_{sed} (m/s)	v_{sed}	v_{brown} (m/s)
1	3.5×10^{-12}	13 nm/h	35
10	3.5×10^{-10}	1.3 $\mu\text{m/h}$	1
100	3.5×10^{-8}	125 $\mu\text{m/h}$	0.04
1000	3.5×10^{-6}	12.5 mm/h	0.001

The sedimentation of these colloids can be neglected compared to their thermal motion.

Do particles sediment?

Particles are considered to be Brownian if $l_{sed} > r_{particle}$.
In this case, sedimentation can be neglected.

The sedimentation length is calculated by equating the potential energy of a particle with its thermal energy.

$$l_{sed} = \frac{k_B T}{m^* g}$$

$$m^* = \frac{4}{3} \pi r^3 \Delta \rho$$

What is the sedimentation velocity for a grain of sand, 200 μm in diameter, $\rho_{\text{grain}} = 2200 \text{ kg/m}^3$, that is dispersed in water ($\rho_{\text{water}} = 1000 \text{ kg/m}^3$) ?

- A. 30 cm/s
- B. 3 cm/s
- C. 300 $\mu\text{m/s}$
- D. 30 $\mu\text{m/s}$
- E. 3 $\mu\text{m/s}$

$$\eta_{\text{H}_2\text{O}} = 1 \text{ mPas}$$
$$g = 9.8 \text{ N/kg}$$

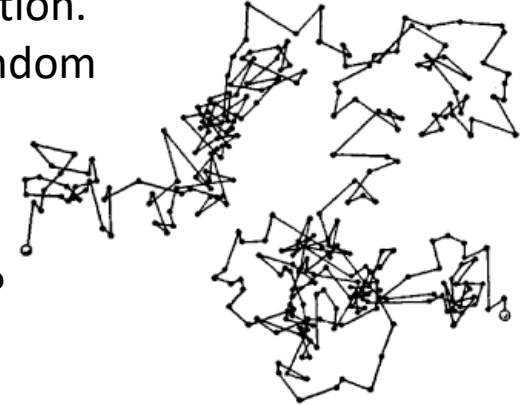
What is the sedimentation velocity for a virus, 50 nm in diameter, $\rho_{virus} = 1050 \text{ kg/m}^3$, that is dispersed in water ($\rho_{water} = 1000 \text{ kg/m}^3$) ?

- A. 70 mm/s
- B. 70 $\mu\text{m/s}$
- C. 70 nm/s
- D. 70 $\mu\text{m/s}$
- E. 70 fm/s

$$\eta_{H_2O} = 1 \text{ mPas}$$
$$g = 9.8 \text{ N/kg}$$

Brownian particles

Brownian particles are colloids that undergo Brownian motion. The motion path of particles can be described with the random walk model.



How far do particles move per time?

$$\lambda = \sqrt{2D_x t}$$

$$\lambda = \sqrt{6Dt}$$

How can we determine D ?

energy loss from viscous drag = thermal energy

$$6\pi\eta r_h D = k_B T$$

$$D = \frac{k_B T}{6\pi\eta r_h}$$

η : viscosity [Pas]

r_h : hydrodynamic radius of particle [m]

D : diffusion coefficient [m²/s]

λ : diffusion distance [m]

t : measurement time [s]

Which of the following statements about colloids is TRUE?

- A. Colloids are always smaller than 1 nm
- B. Colloids are always larger than 10 μm
- C. Colloids have at least one dimension between ~ 1 nm and 1 μm
- D. Colloids are not affected by Brownian motion

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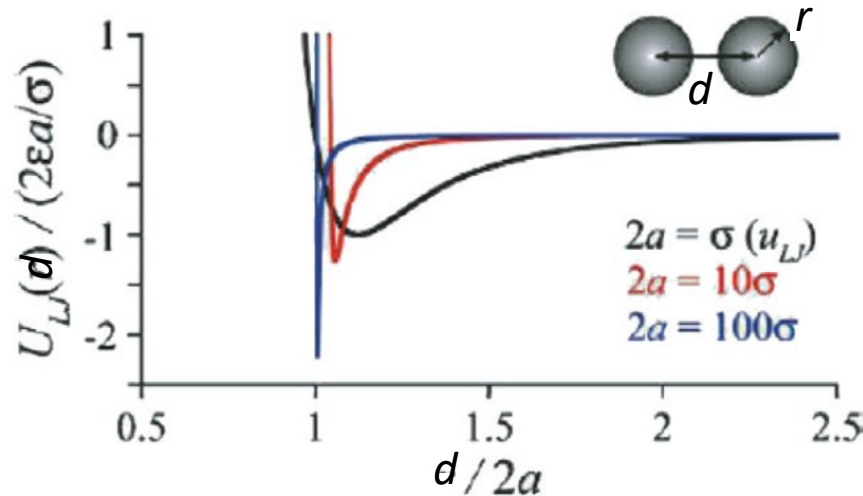
Forces in colloidal dispersions

Van-der-Waals forces:
$$U_{VdW} = -\frac{A}{12d} \frac{r_1 r_2}{(r_1 + r_2)}$$

note, for molecules:
$$U_{VdW} \propto \frac{1}{d^6}$$

A: Hamaker constant [J]
 r: particle radius [m]
 d: inter-particle distance [m]
 σ : characteristic distance at which $U(\sigma)=0$ [m]

Forces between colloids are much longer ranged than those between molecules.

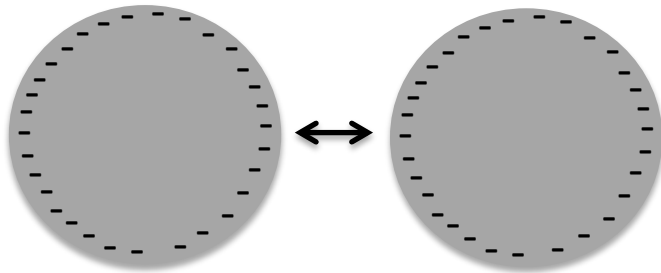


Rajagopalan, T.; et al., *Reports on Progress in Physics* **2013**, 76 (6), 066501

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Electrostatic stabilization



κ^{-1} : Debye screening length [m]
 c : ion concentration [molecules/m³]
 z : valency of ions [-]
 ϵ : dielectric permeability [-]
 e : charge of an electron [C]

$$U_{el} = U_{el,0} e^{-\kappa x}$$

$$\frac{1}{\kappa} = \sqrt{\frac{\epsilon_0 \epsilon_r k_B T}{e^2 \sum_i c_i z_i^2}}$$

Debye length:

The Debye length is the length scale over which charged colloids repel/attract each other.

Which factor does NOT influence the Debye screening length?

- A. Temperature
- B. Ion concentration
- C. Particle size
- D. Dielectric constant

DLVO interactions

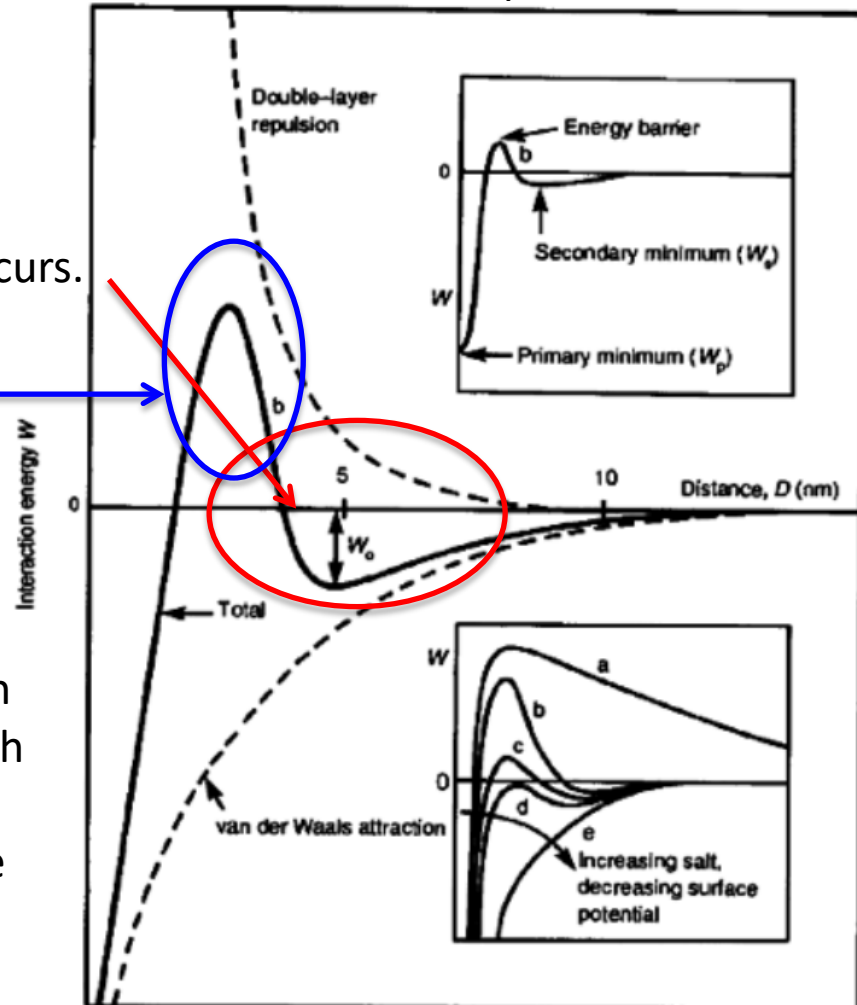
The DLVO theory describes the interactions between two charged surfaces that are contained in a liquid.

$$U_{DLVO} = U_{VdW} + U_{el}$$

Flocculation occurs.

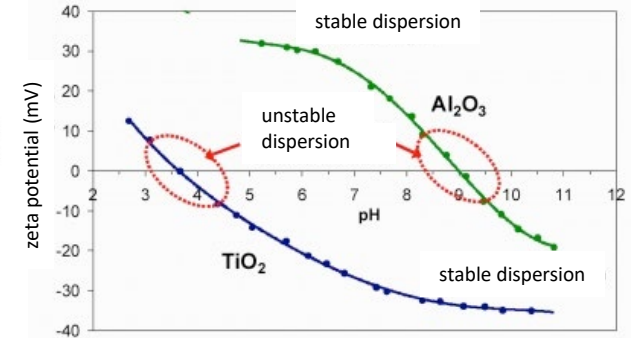
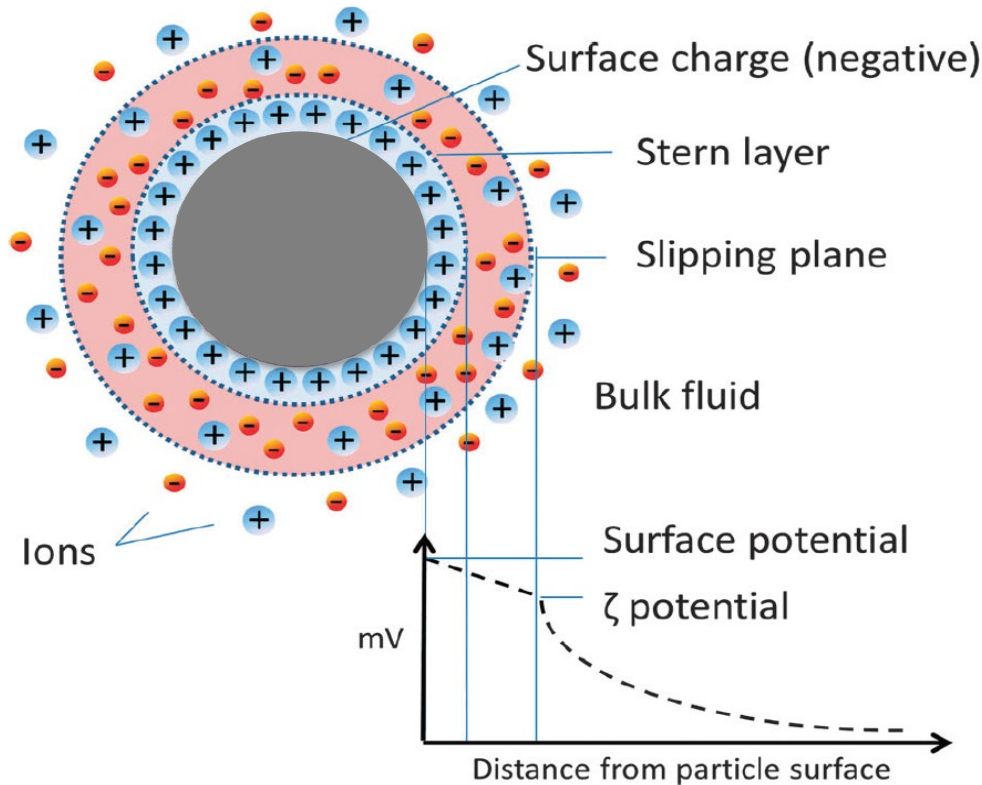
Kinetically trapped, metastable state which prevents aggregation.

The electrostatic stabilization works well in aqueous solutions with a low ionic strength at a pH far away from the point of zero charge (PZC) of the colloids because of the electrostatic repulsion forces.



Charge of particles

The zeta potential is the electric potential of the interfacial double layer at the slipping plane.

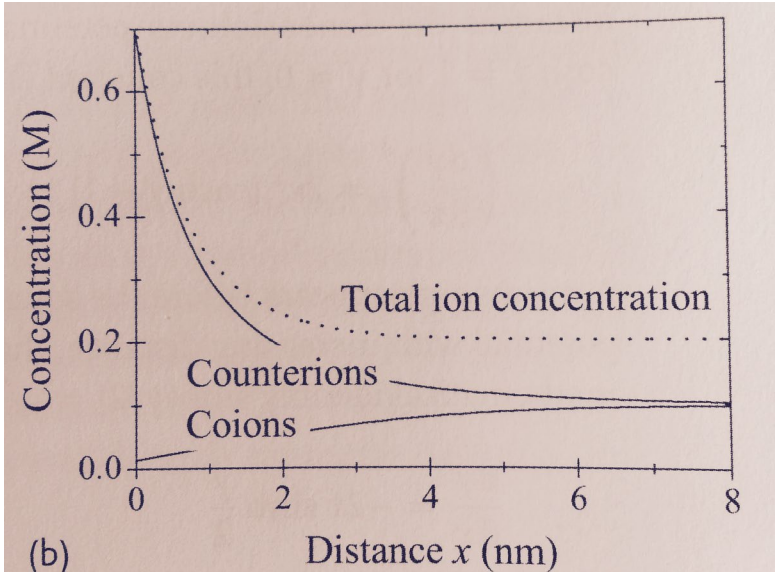
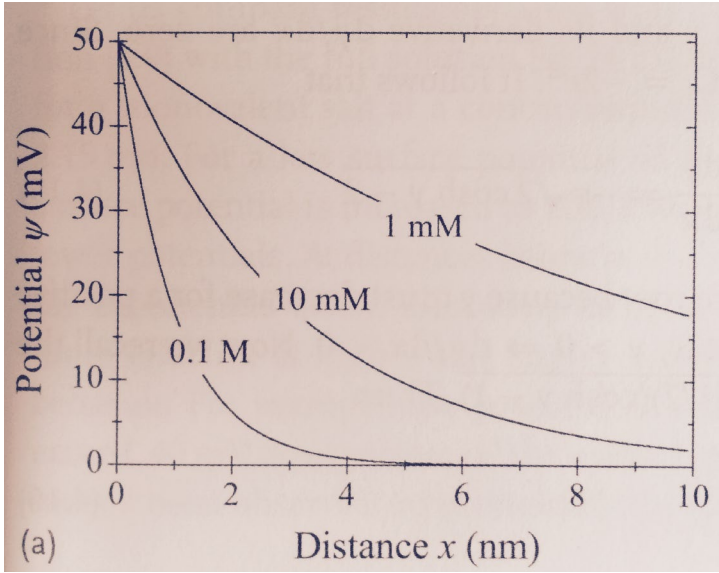
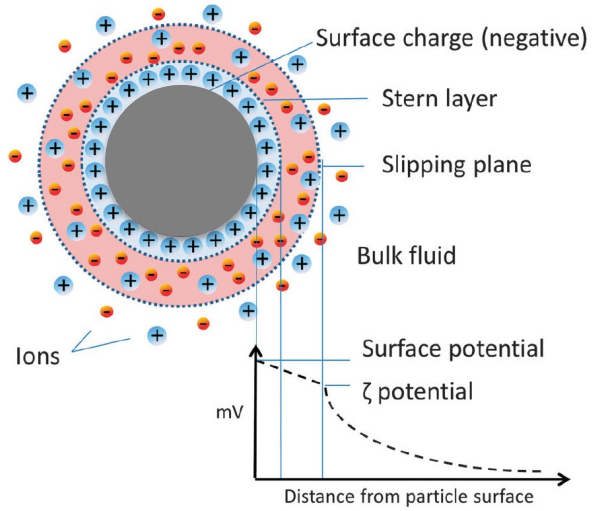


<http://www.quantachrome.nl>

Nominal composition	IEP (pH) ⁻¹
Sb_2O_5	0.3
Mo_2O_5	0.5
WO_2	1
SiO_2	2
$1.00 \text{ Na}_2\text{O} \cdot 0.58 \text{ CaO} \cdot 3.70 \text{ SiO}_2$	2-3
$\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6 \text{ SiO}_2$	3-5
ZrO_2	4-6
$\text{Ca}_5(\text{PO}_4)_3(\text{OH})$	7
$\text{Ca}_5(\text{PO}_4)_3(\text{F}, \text{OH})$	6
TiO_2	4.7
TiO_2	6.2
$\text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot 2 \text{ H}_2\text{O}$	4.8
$3 \text{ Al}_2\text{O}_3 \cdot 2 \text{ SiO}_2$	6-8
Cr_2O_3	7
Fe_2O_3	8-9
ZnO	9
Al_2O_3	7-9
CaCO_3	9-10
PbO	10.3
MoO_2	12
MgO	12

Ring, T. A. *Fundamentals of Ceramic Powder Processing and Synthesis*; Academic Press: San Diego, California, 1996

Influence of ions on the zeta potential



Zeta potential measurements



Force that drives the particle flow:

$$F = qE$$

Force that counteracts the particle flow:

$$F = 6\pi\eta vr \quad (\text{drag force})$$

In equilibrium, the two forces are balanced:

$$\frac{v}{E} = u = \frac{q}{6\pi\eta r}$$

Zeta potential:

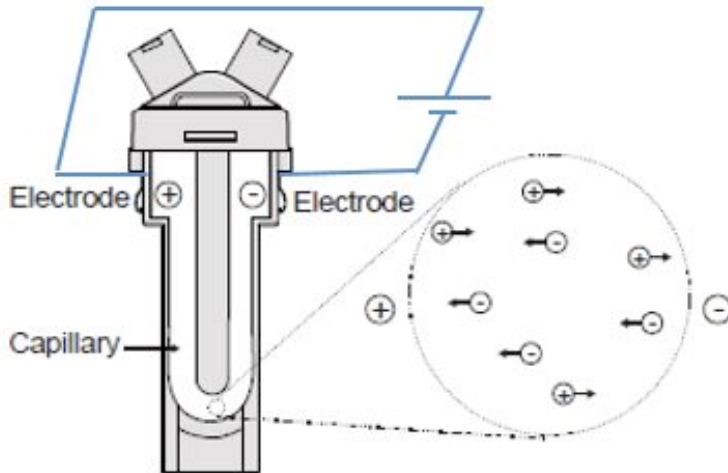
(can be derived from the Debye-Hückel theory)

$$\zeta = \frac{q}{4\pi\epsilon r} - \frac{q}{4\pi\epsilon \left(r + \frac{1}{\kappa} \right)}$$

in the limit $\kappa r \ll 1$

$$\zeta = \frac{3\eta u}{2\epsilon}$$

q : charge [C]
 E : electric field [V/m]
 η : viscosity [Pas]
 v : velocity [m/s]
 r : particle radius [m]
 u : mobility [m²/V/s]
 ζ : Zeta potential [V]
 ϵ : dielectric permittivity [-]



Which force is responsible for the stabilization of charged colloids in a dispersion?

- A. Van der Waals force
- B. Electrostatic repulsion
- C. Gravitational force
- D. Drag force

Charged particles with a radius of 100 nm are dispersed in an aqueous solution containing NaCl. What is the Debye screening length if the solution contains 0.1 mM NaCl?

- A. 40 μm
- B. 4 μm
- C. 400 nm
- D. 40 nm
- E. 4 nm
- F. 0.4 nm

$$\epsilon_0 = 8.85 \times 10^{-12} \text{ F/m}$$

$$\epsilon_r = 80$$

$$k_B = 1.38 \times 10^{-23} \text{ J/K}$$

$$T = 298 \text{ K}$$

$$e = 1.6 \times 10^{-19} \text{ C}$$

$$N_A = 6.02 \times 10^{23}$$

$$\frac{1}{\kappa} = \sqrt{\frac{\epsilon_0 \epsilon_r k_B T}{e^2 \sum_i c_i z_i^2}}$$

Charged particles with a radius of 100 nm are dispersed in an aqueous solution containing NaCl. What is the Debye screening length if the aqueous solution contains 1 M NaCl?

- A. 40 μm
- B. 4 μm
- C. 400 nm
- D. 40 nm
- E. 4 nm
- F. 0.4 nm

$$\epsilon_0 = 8.85 \times 10^{-12} \text{ F/m}$$

$$\epsilon_r = 80$$

$$k_B = 1.38 \times 10^{-23} \text{ J/K}$$

$$T = 298 \text{ K}$$

$$e = 1.6 \times 10^{-19} \text{ C}$$

$$N_A = 6.02 \times 10^{23}$$

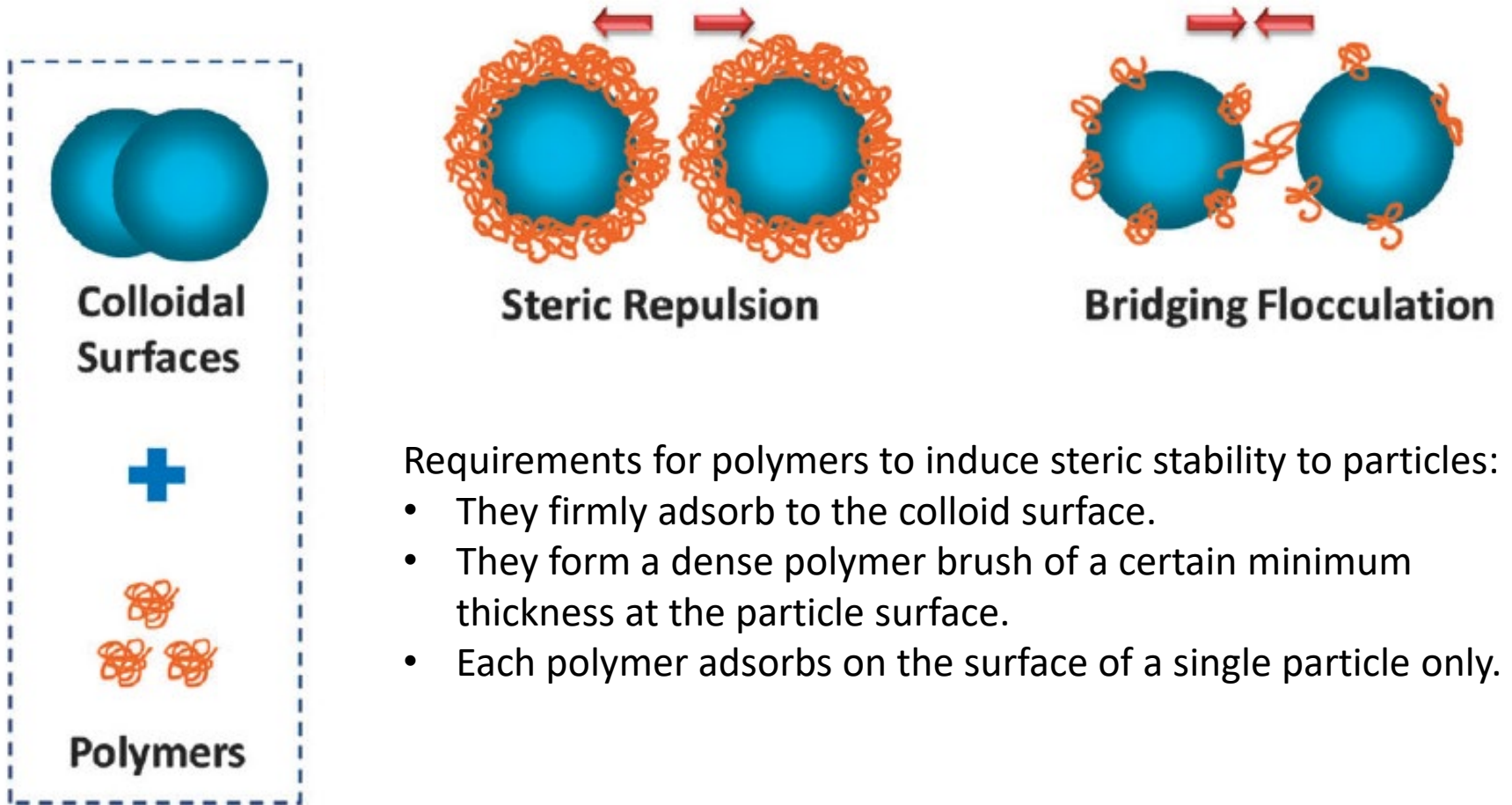
$$\frac{1}{\kappa} = \sqrt{\frac{\epsilon_0 \epsilon_r k_B T}{e^2 \sum_i c_i z_i^2}}$$

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Steric stabilization

Steric stabilization is the process by which adsorbed nonionic dispersants produce strong repulsion between particles in a dispersion.

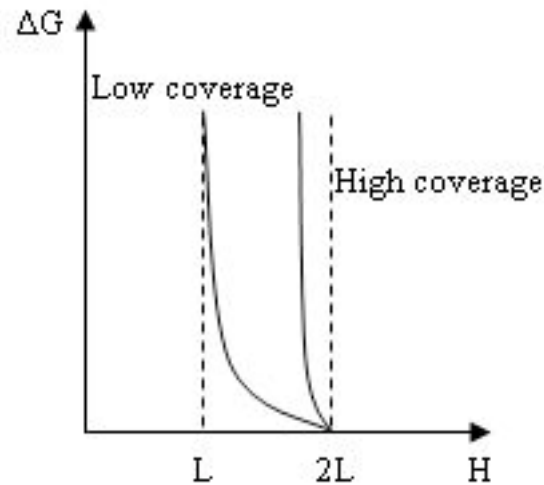
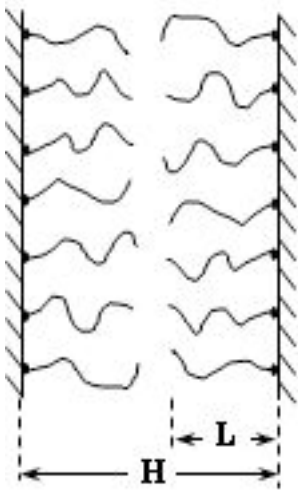


Thickness of the polymer brush

Sterically stabilized colloids are stable:

- in organic and inorganic media.
- under high ionic concentrations.

N : number of repeat units [-]
 l : length of a repeat unit [m]
 Γ : grafting density [molecules/m²]
 p_d : disjoining pressure [Pa]
 T : temperature [K]



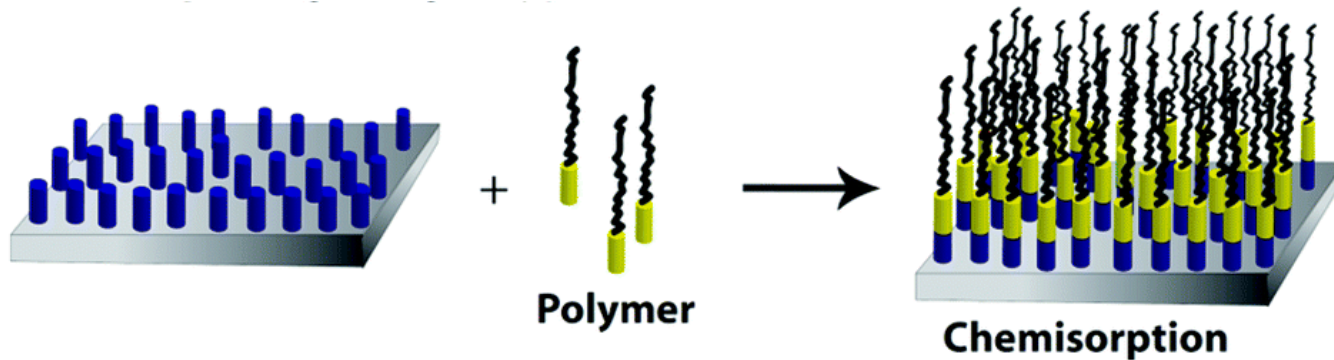
<http://depts.washington.edu>

What is L ?

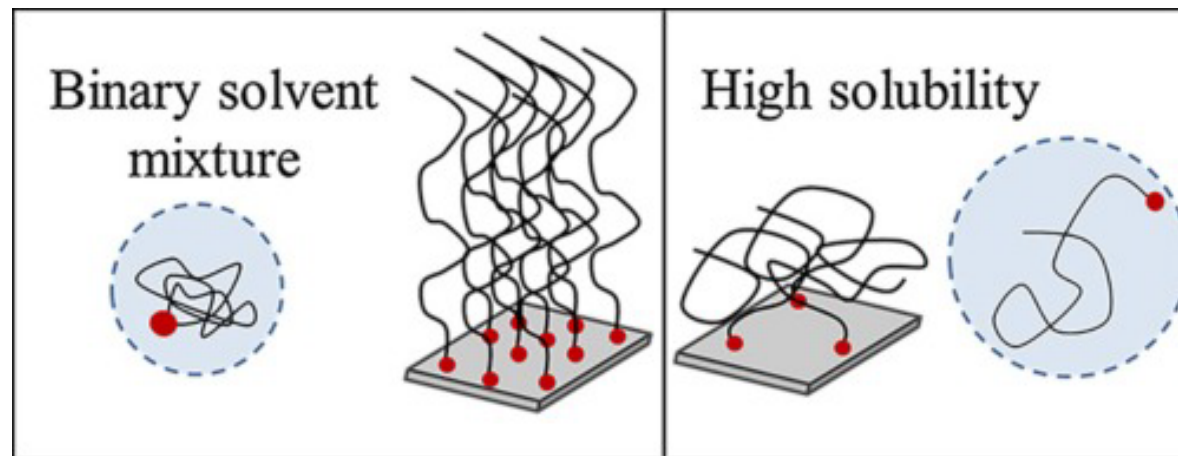
$$L_0 \approx Nl^{\frac{5}{3}}\Gamma^{\frac{1}{3}}$$

Maximizing packing density

How do you get to such a high grafting density?



Kocak, G.; Tuncer, C.; Butun, V. *Polymer Chemistry* **2017**, *8* (1), 144-176



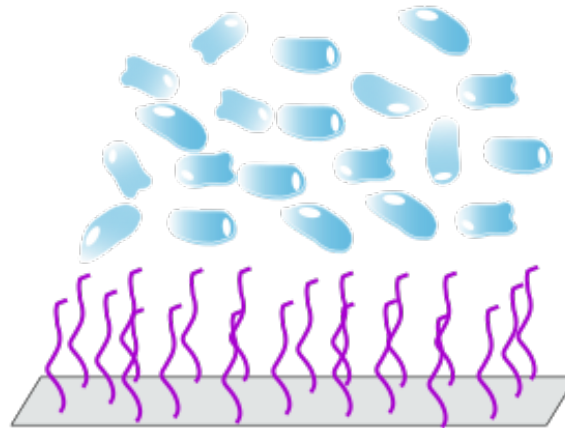
Arcot, L.; et al. *Applied Surface Science* **2015**, *341*, 134-141.

Cloud point grafting

Adsorption from poor solvent



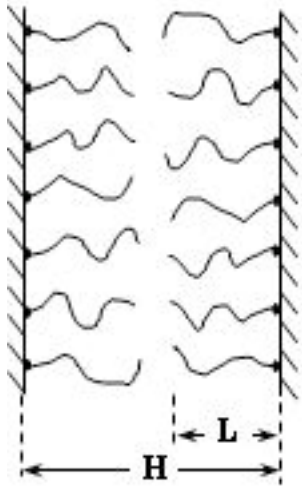
Swelling in good solvent



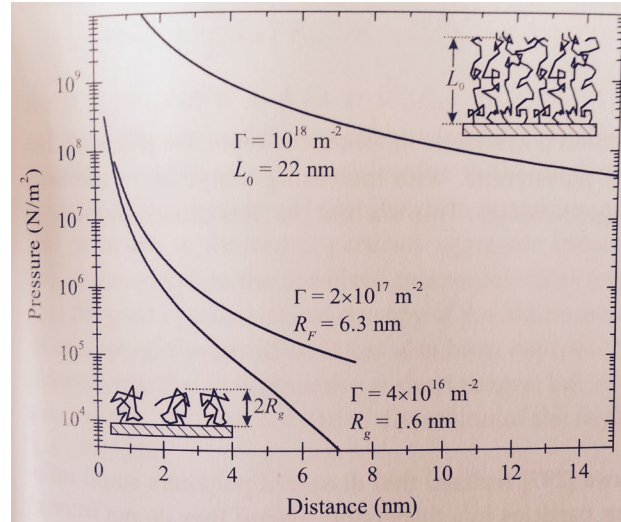
Cloud point grafting:

- Polymers are adsorbed from a poor solvent where they are collapsed.
- They adsorb at a high density because the steric repulsion is minimized.
- The substrate with the polymers adsorbed is transferred into a good solvent where the polymers swell.
- Because of the high packing density, the polymers cannot form coils but they must be rather extended thereby increasing the brush thickness.

Disjoining pressure



<http://depts.washington.edu>



N : number of repeat units [-]
 l : length of a repeat unit [m]
 Γ : grafting density [molecules/m²]
 p_d : disjoining pressure [Pa]
 T : temperature [K]
 L_0 : contour length [m]

for low grafting densities, $\Gamma < \frac{1}{4R_g^2}$

$$p_d \approx \frac{k_B T \Gamma}{x} \left(\frac{2\pi^2 R_g^2}{x^2} - 1 \right) \text{ for } x < 3\sqrt{2}R_g$$

$$p_d \approx \frac{k_B T \Gamma x}{R_g^2} e^{-\left(\frac{x}{2R_g}\right)^2} \text{ for } x < 3\sqrt{2}R_g$$

for high grafting densities, $\Gamma < \frac{1}{4R_g^2}$

$$p_d \approx k_B T \Gamma^{\frac{3}{2}} \left[\left(\frac{2L_0}{x} \right)^{\frac{9}{4}} - \left(\frac{x}{2L_0} \right)^{\frac{3}{4}} \right]$$

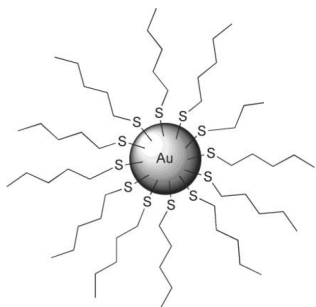
How can polymers be bound to colloids?

Polymers can be bound to particle surfaces through anchoring groups that have a high affinity to the particle surface.

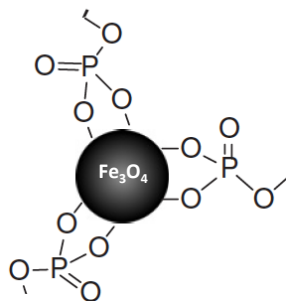
Au, Ag particles

many oxide particles:

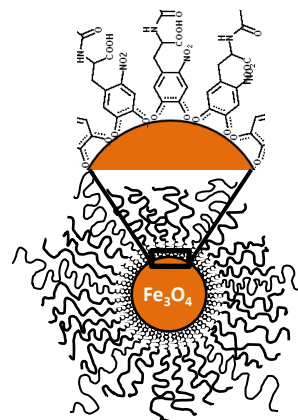
thiols $R-S-H$



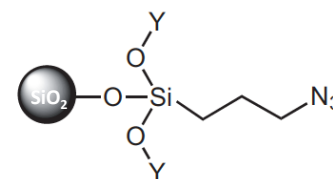
phosphates $R-O-P(=O)(OH)_2$



catechols $R_1-C_6H_2(OH)_2-R_2$



silanes $R-SiCl_2-O-Si(CH_3)_2-O-CH_3$



Roy, S.; Pericas, M. A. *Organic & Biomolecular Chemistry* **2009**, 7 (13)

Kobayashi, M., et al., *Science and Technology of Advanced Materials* **2006**, 7 (7)

Amstad, E., et al. *E. Nano Letters* **2009**, 9 (12)

Semsarilar, M.; Perrier, S. *Nat Chem* **2010**, 2 (10)

Polymeric particles:

Dispersants can be covalently bound to the particle surface.

The DLVO theory describes the balance between...

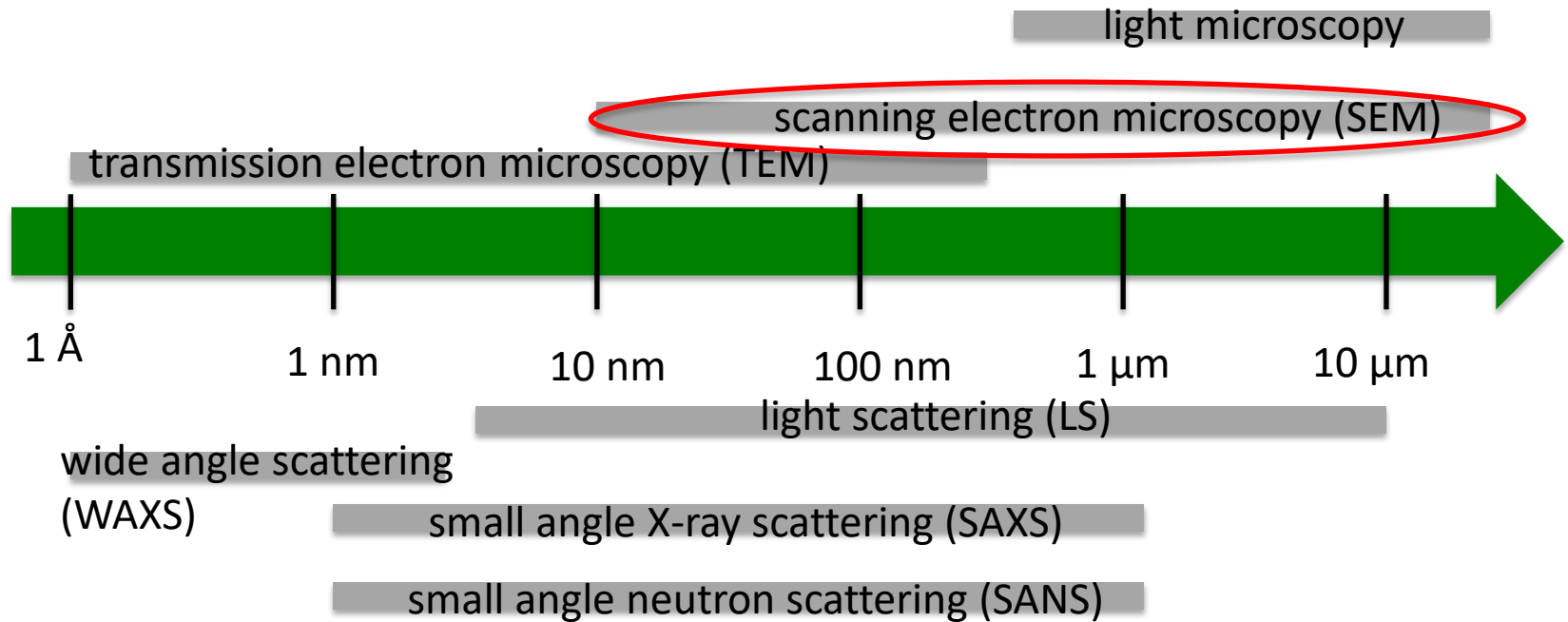
- A. Brownian motion and sedimentation
- B. Gravitational and buoyancy forces
- C. Van der Waals attraction and electrostatic repulsion
- D. Diffusion and convection

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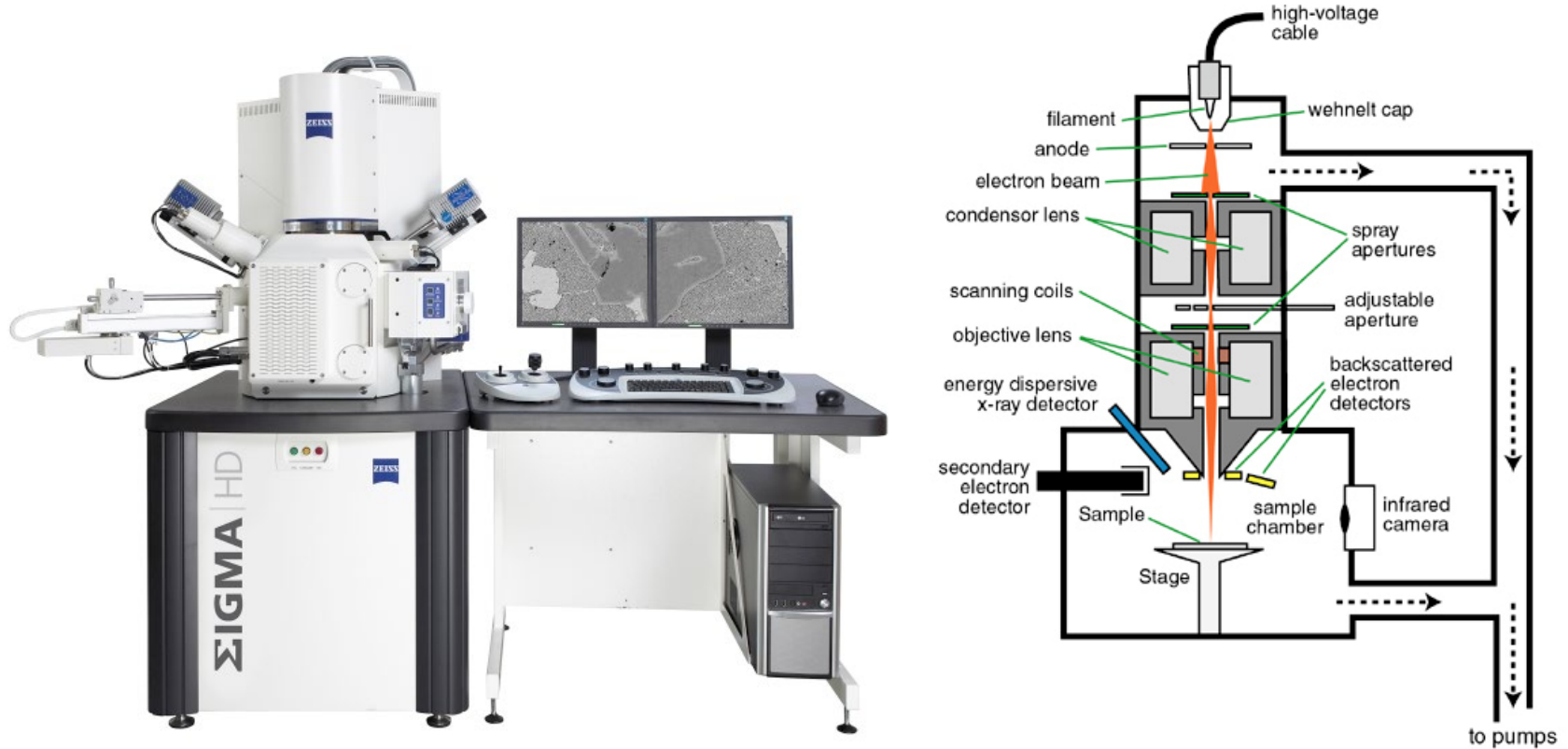
Characterization of colloids

I. Microscopy



II. Scattering

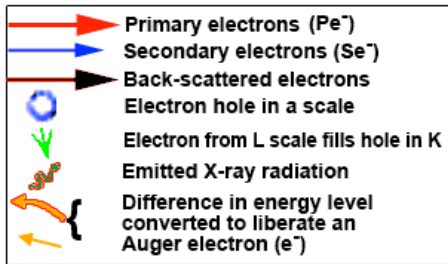
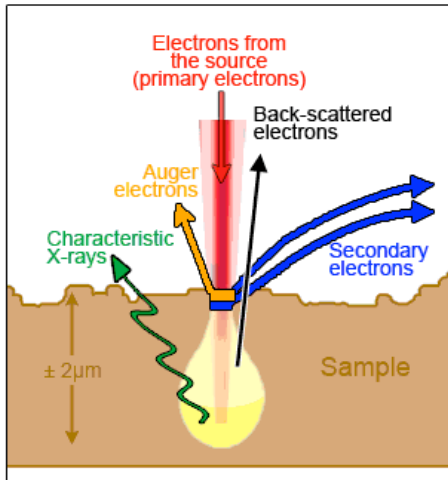
Scanning electron microscopy (SEM)



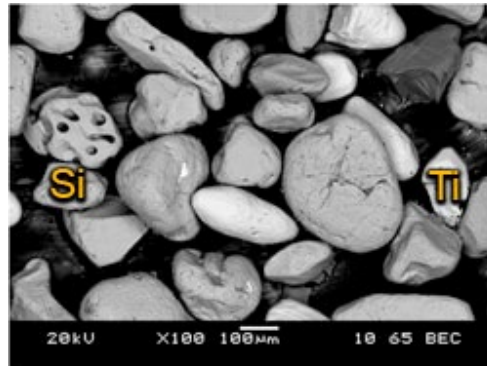
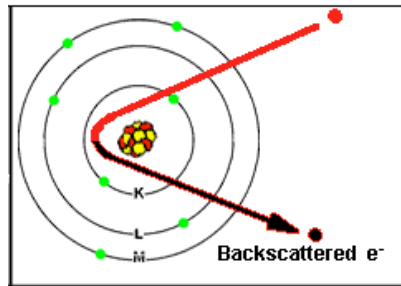
Good for

- measuring the particle size (down to ≈ 10 nm)
- visualizing the surface topology
- characterizing the chemical composition with electron dispersive X-ray spectroscopy (EDS)

SEM: Detectors

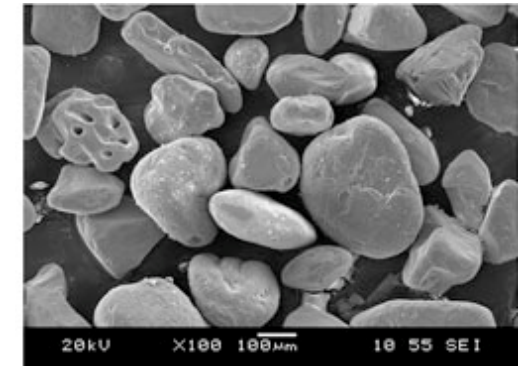
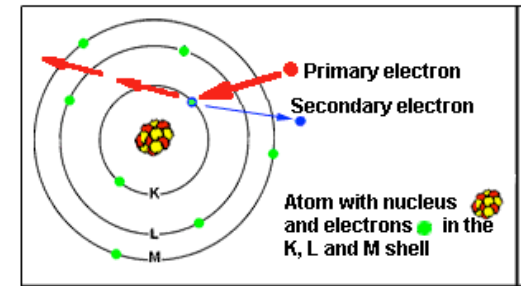


Backscattered Electrons (BE)



Atoms with high Z numbers backscatter more efficiently such that surfaces made from these molecules appear brighter. Electrons localized up to 200 nm below the surface can be detected.

Secondary Electrons (SEs)

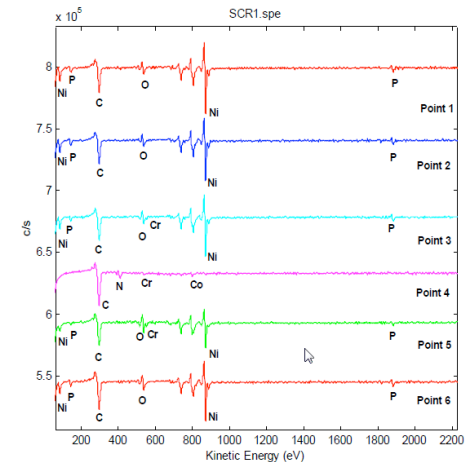
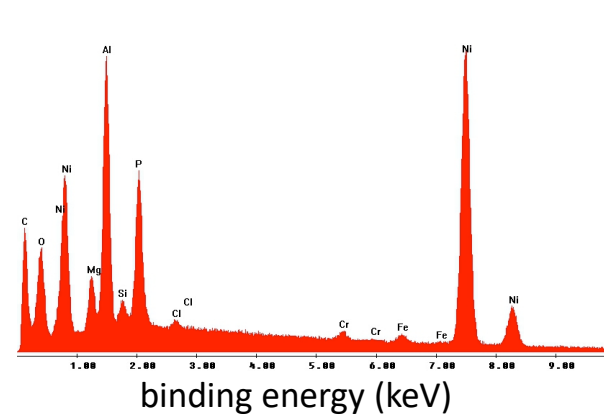
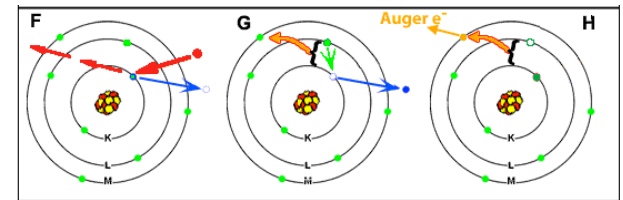
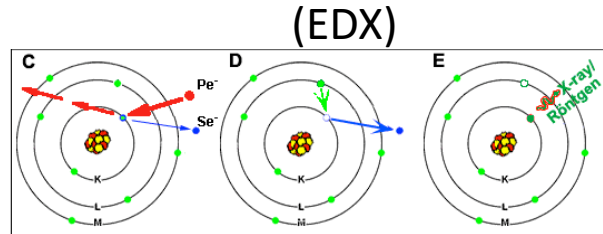
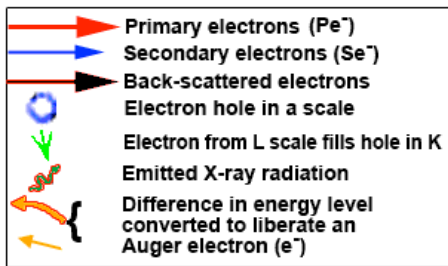
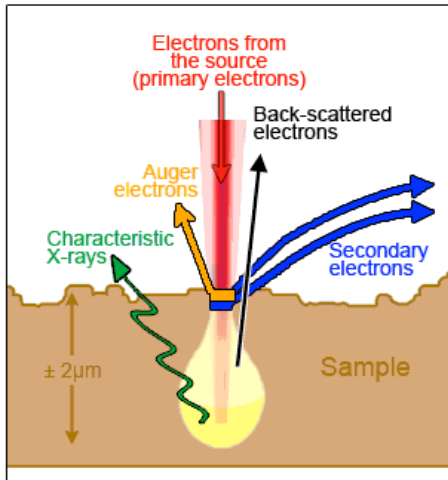


Low energy of SEs: Only the SEs located within a few nm from the surface can be ejected from the sample. Hence, only the surface is imaged.

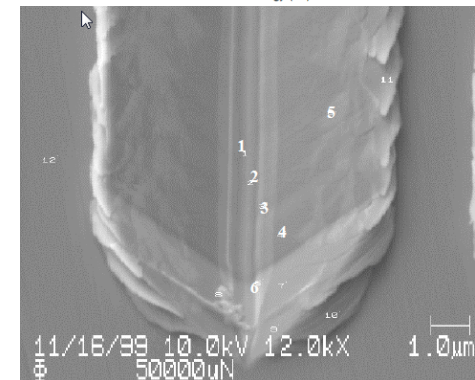
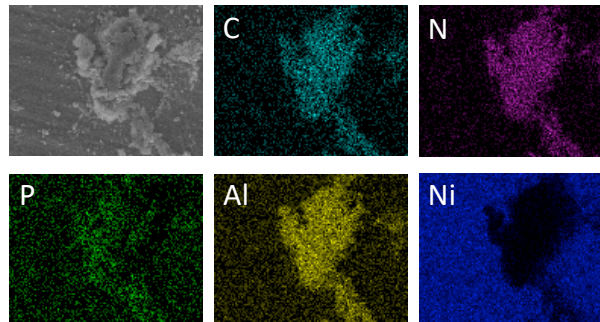
SEM: Detectors

Energy Dispersive X-ray Analysis

Auger Electrons

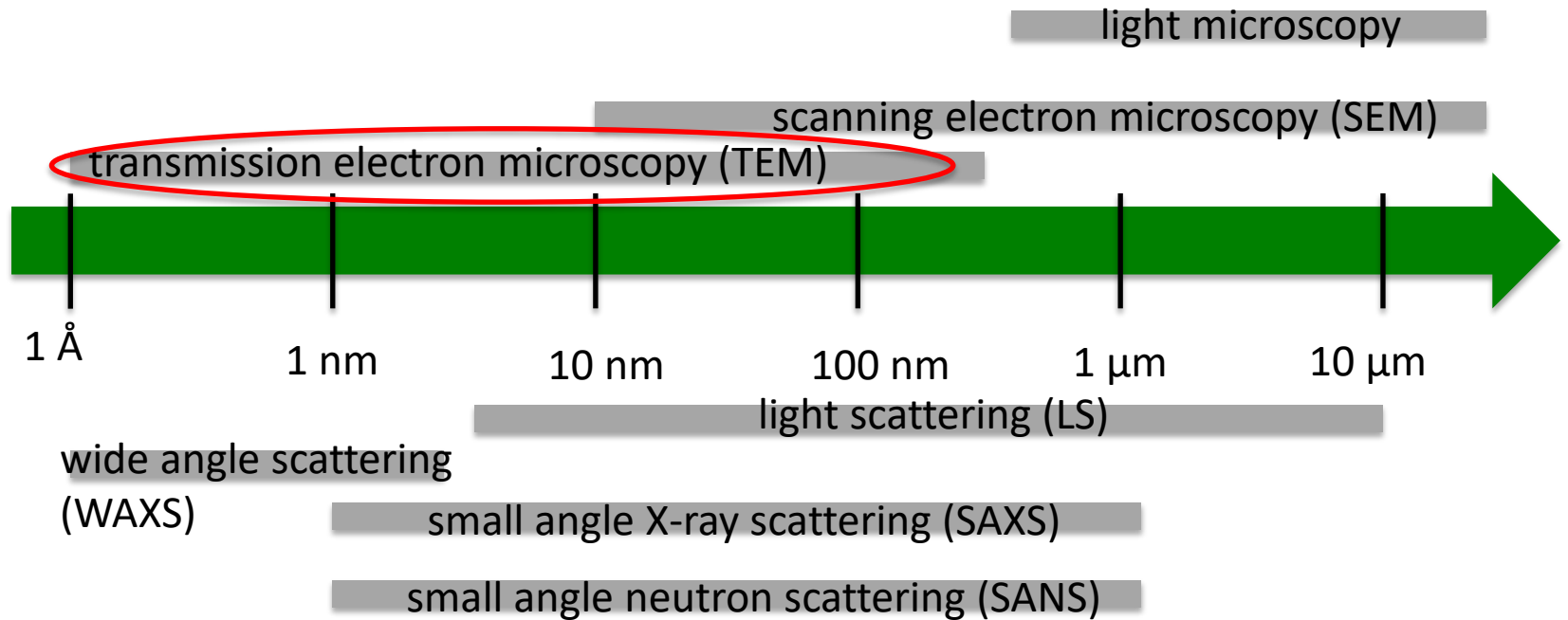


mapping



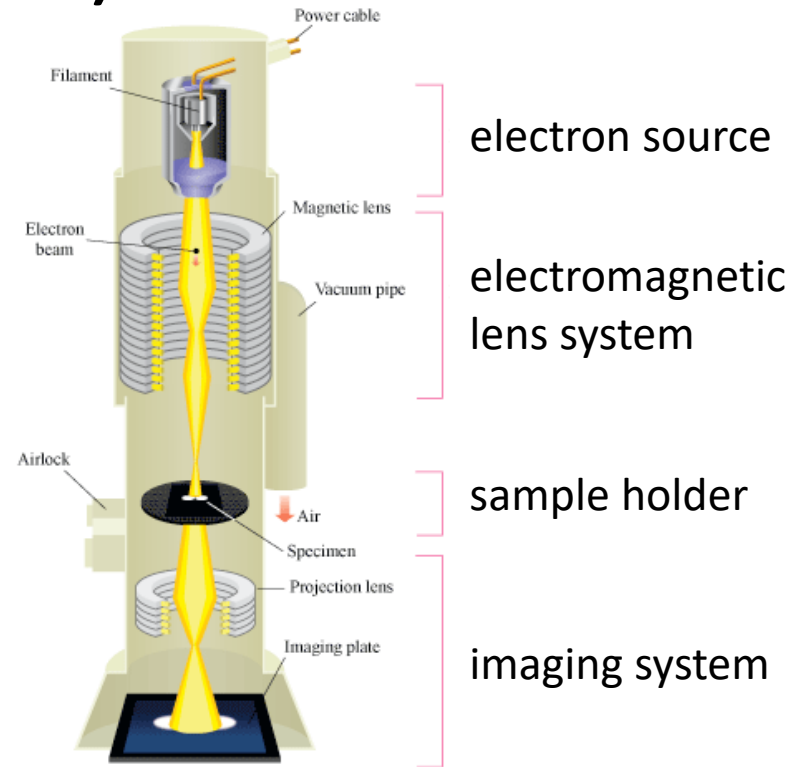
Characterization of soft materials

I. Microscopy



II. Scattering

Transmission electron microscopy (TEM)



Good for:

- measuring the size and morphology of nanoparticles
- determining the crystal structure
- visualizing the arrangement of block-copolymers at surfaces

Electron microscopy course taught by
Alexander Duncan
Cécile Hebert

In which mode would you operate the light microscope to visualize aggregates of gold nanoparticles contained in cells?

- A. bright field
- B. dark field
- C. polarized light

What technique would you use to determine if the core of a TiO_2 nanoparticle is crystalline?

- A. Bright field light microscopy
- B. dark field light microscopy
- C. SEM
- D. TEM

What detector would you use to determine the bulk chemical composition of a microparticle with SEM?

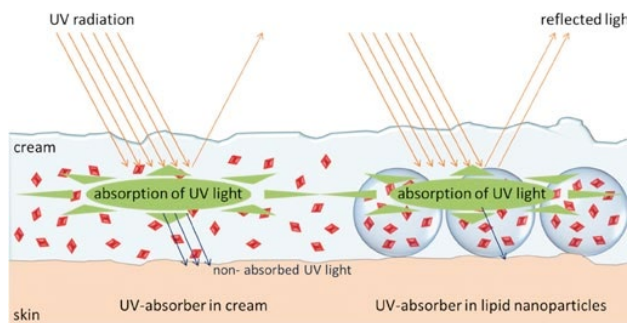
- A. Secondary electron detector
- B. Backscattered electron detector
- C. Electron dispersive X-ray detector
- D. Auger electron detector

Outline

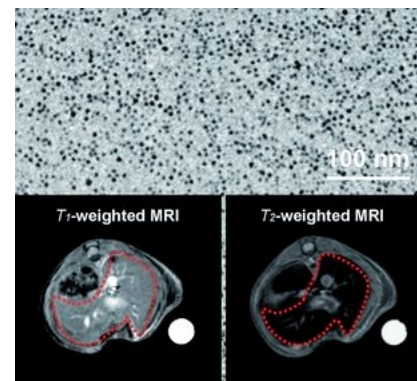
- Introduction
- Particle motion
- Stabilization
 - electrostatic stabilization
 - steric stabilization
- Characterization
- **Applications of particle dispersions**
- Assembly of particles
- Colloidal crystals made of microgels
- Applications of colloidal crystals
- Agglomeration
- Applications of agglomerated particles

Applications of sterically stabilized particles

UV light absorber

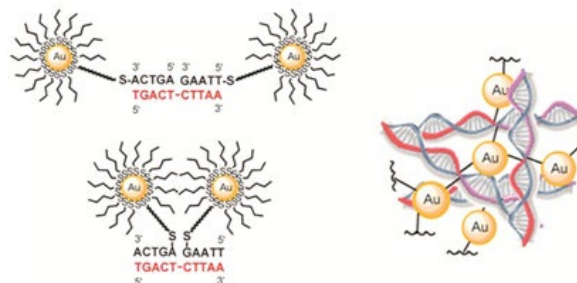


Magnetic resonance imaging contrast agents



Li, Z. et al. *Adv. Funct. Mat.* **2012**, 22 (11)

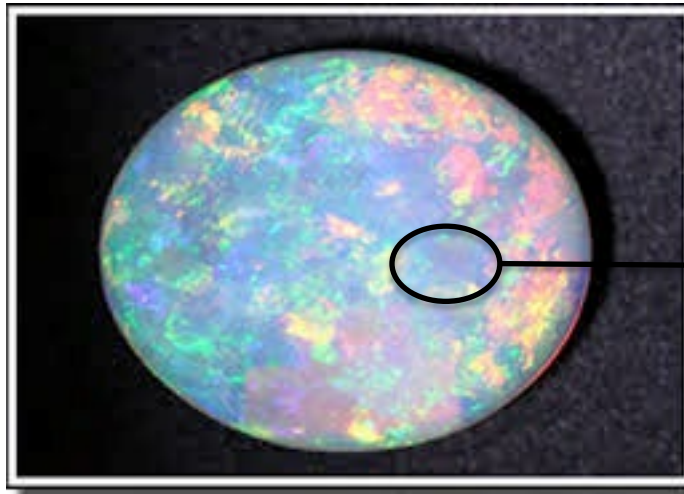
Labels that specifically bind to certain substances/objects



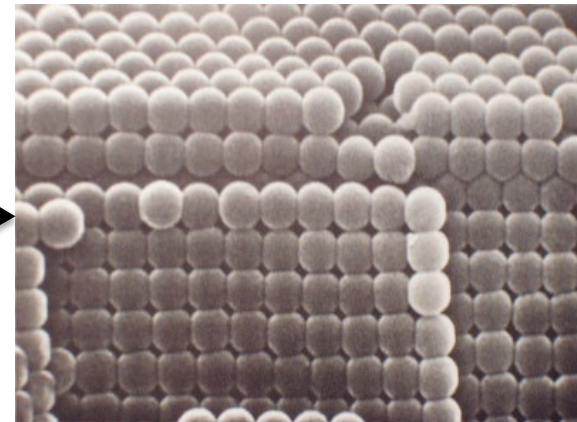
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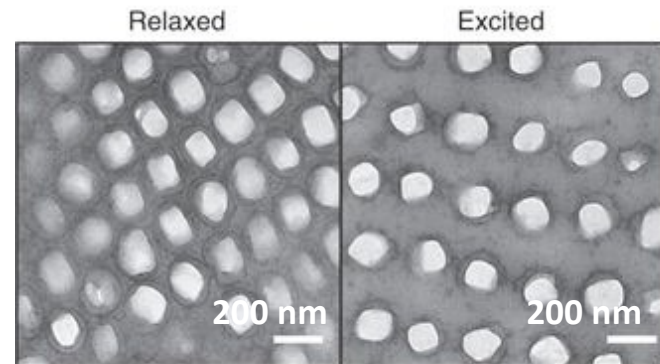
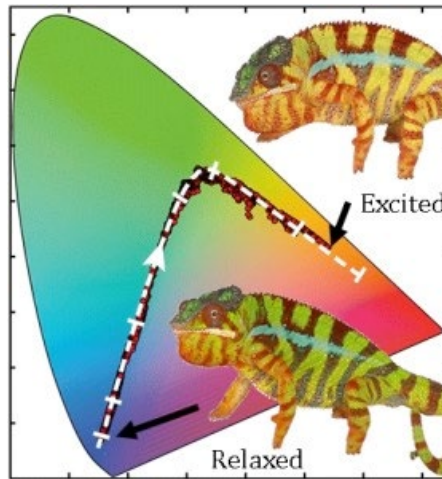
Structural colors



SiO₂ particles



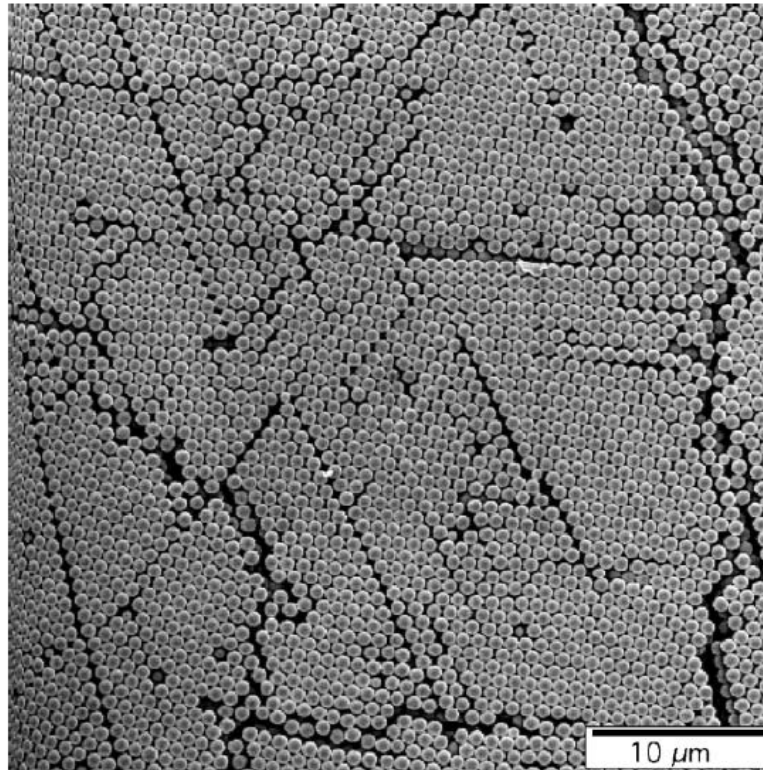
guanine crystals



J. Teyssier, *et al.*, *Nat. Comm.*, 2015, 6, 6368

Colloidal crystals

Colloidal crystals are ordered arrays of colloid particles.



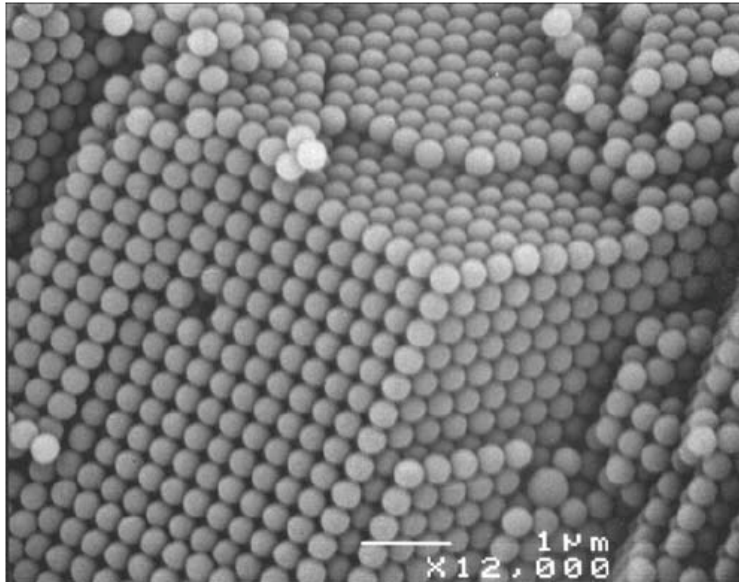
Lytle, J. C.; et al. *Journal of Materials Chemistry* **2004**, *14*, 1616.

Colloidal crystals form if the interaction energy gained by assembling particles into colloidal crystals exceeds the energy penalty that is caused by the decrease in entropy.

Maximum packing density

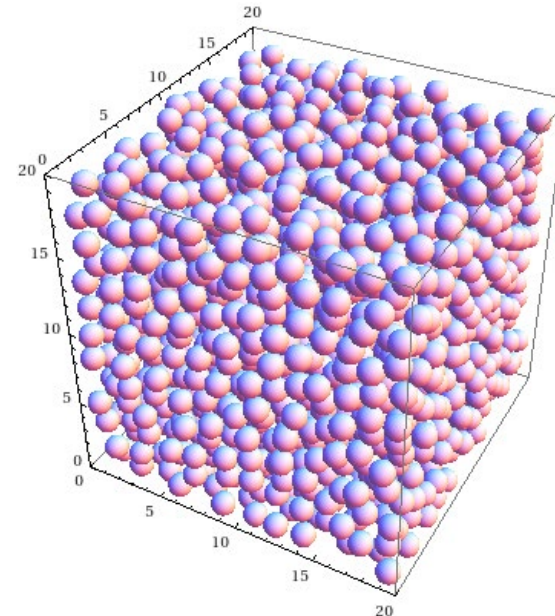
For hard spheres:

The maximum packing density that can be achieved if hard spheres are arranged into a close packed structure is **0.7404**.



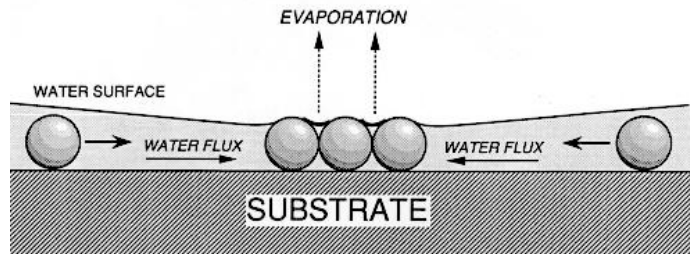
A. Imhof, in *Nanoscale Materials*, Springer US, Boston, MA, 2003,

The maximum volume fraction that can be achieved if hard spheres are randomly arranged is around **0.63**.



Assembly of colloids on surfaces

Direct assembly on solid surfaces

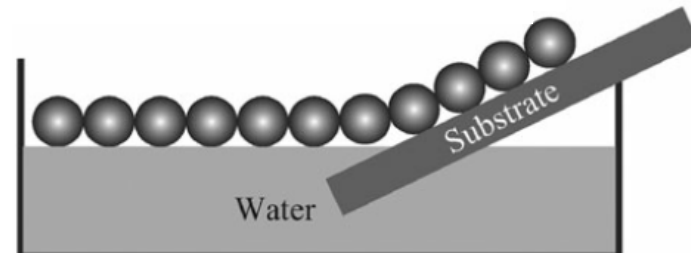


http://crystal.che.ncsu.edu/colloidal/2_3_2Dwetdyn.html

Requirements:

- The substrate must be wetting.
- The particle-surface interactions must be small.

Liquid interface mediated assembly

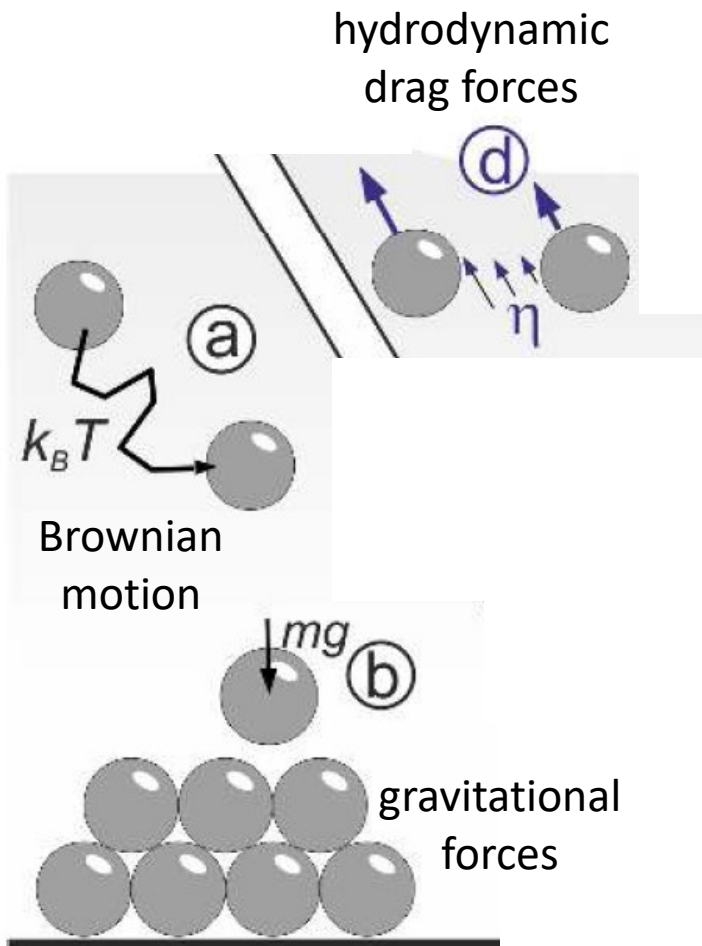


Lee, S.; et al., *S. Physical Chemistry Chemical Physics* **2009**, *11* (19), 3628-3633

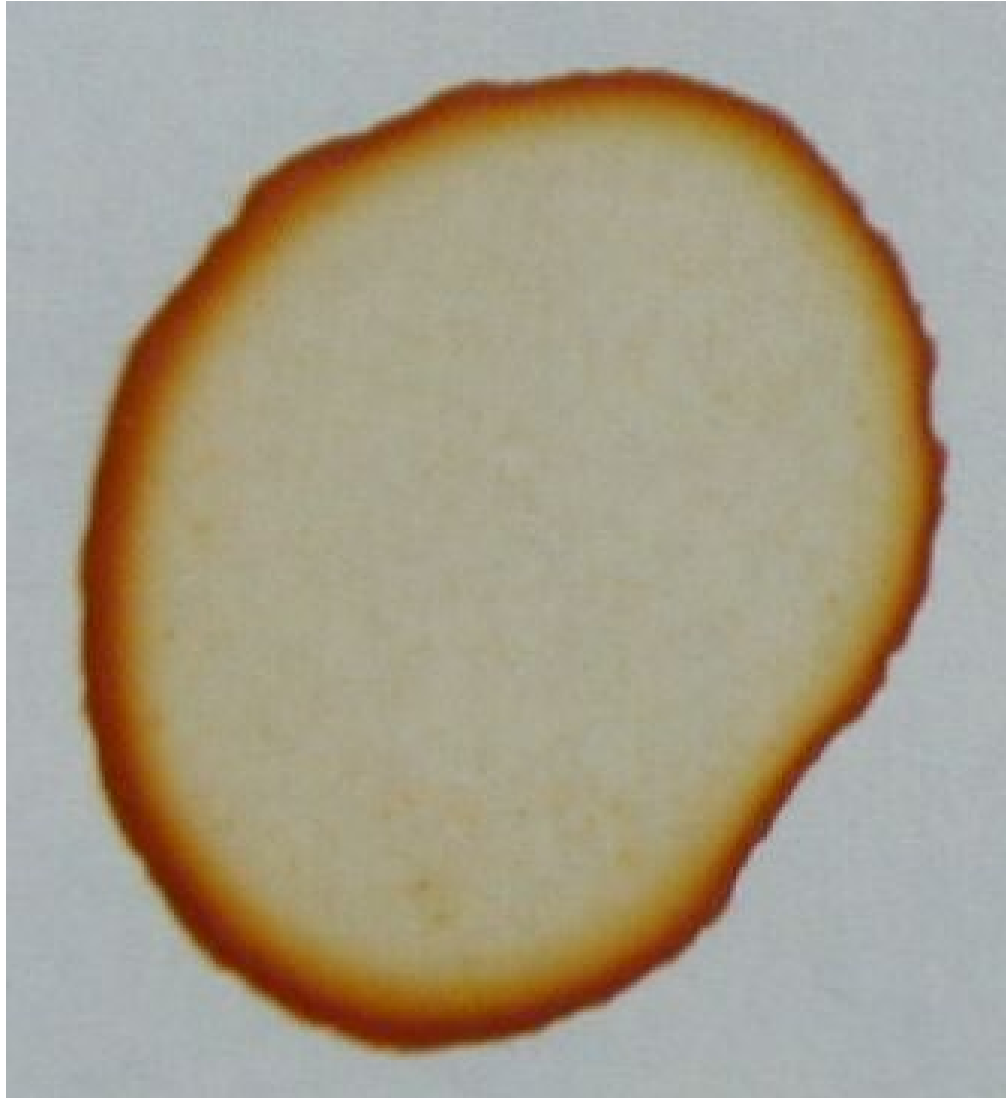
Which inter-particle interactions are NOT involved in the direct assembly of particles into colloidal crystals?

- A. Thermal energy
(Brownian motion)
- B. Drag forces
- C. Electrostatic
attraction forces
- D. Gravitational forces

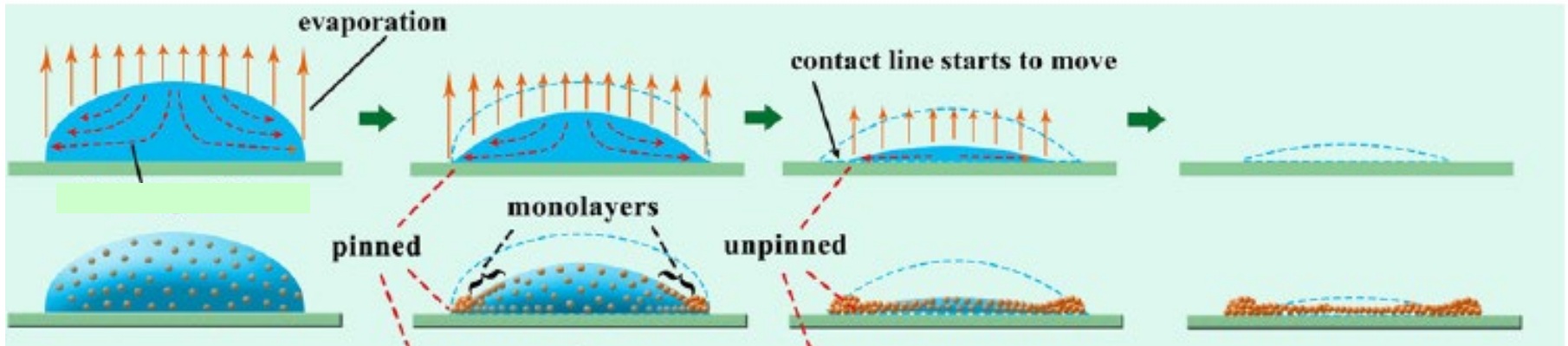
Inter-particle interactions



Direct assembly of particles on solid surfaces

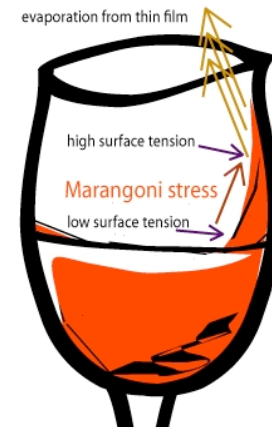


What drives the particle assembly?

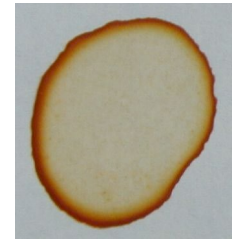


Tang, Y.; He, W.; Wang, S.; Tao, Z.; Cheng, L. *Nanotechnology* **2014**, *25*.

Marangoni effect: The Marangoni effect is a mass transport along an interface that is caused by gradients in the interfacial tension.



Coffee ring effect

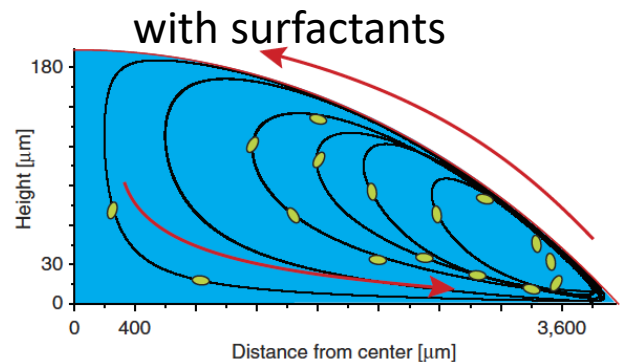
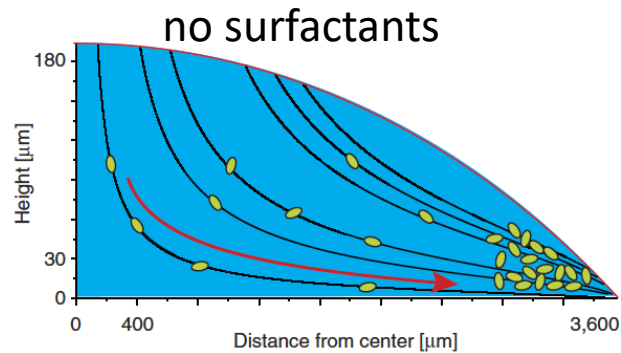


The coffee ring is caused by the Marangoni effect.

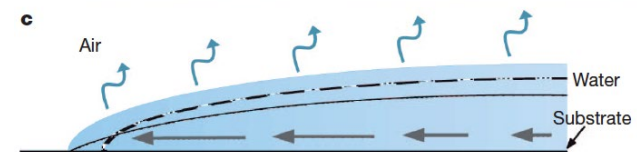
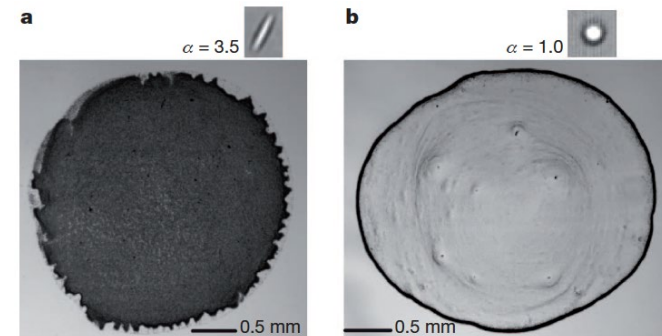
The coffee ring effect can be overcome using

- surfactants or
- anisotropic particles.

Effect of surfactants



Effect of anisotropic particles

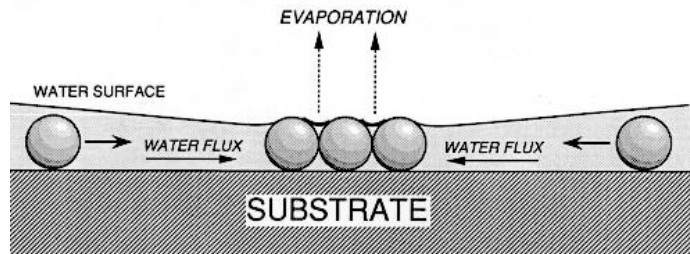


Yunker, P. J.; et al. *Nature* **2011**, *476* (7360), 308-311

The stronger adsorption of anisotropic particles at the air-liquid interface prevents particles from leaving this interface. Instead, they form a stable monolayer at liquid-air interface.

Assembly of colloids on surfaces

Direct assembly on solid surfaces

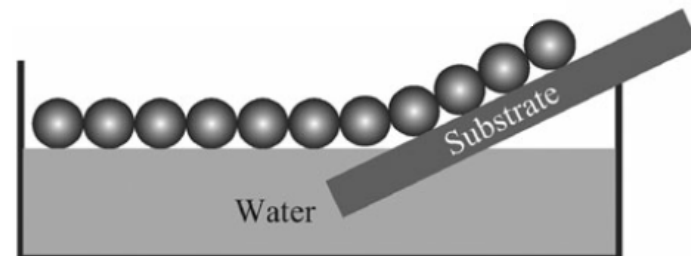


http://crystal.che.ncsu.edu/colloidal/2_3_2Dwetdyn.html

Requirements:

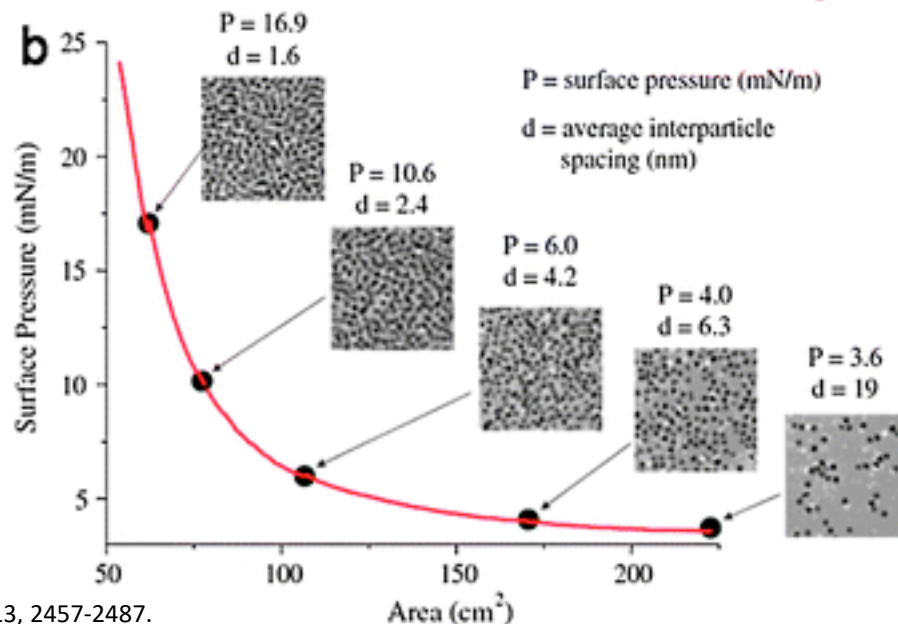
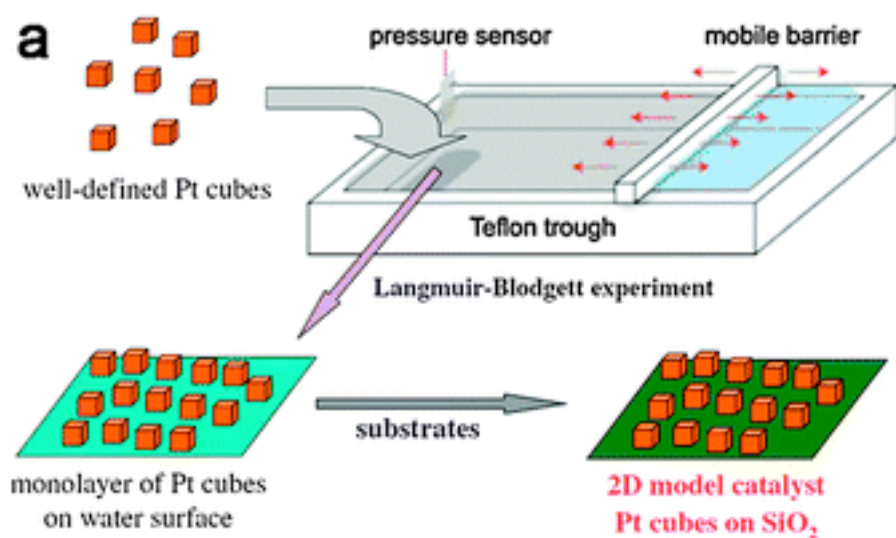
- The substrate must be wetting.
- The particle-surface interactions must be small.

Liquid interface mediated assembly



Lee, S.; et al., *S. Physical Chemistry Chemical Physics* **2009**, *11* (19), 3628-3633

Example: Langmuir-Blodgett films



C.-J. Jia and F. Schuth, *PCCP*, 2011, 13, 2457-2487.

Advantages:

- High order of particles.
- Large freedom in the choice of the substrate.
- Patterning over large areas is possible.

Disadvantages:

- It is a slow process.
- It is an experimentally complex process.

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- Agglomeration
- Applications of agglomerated particles

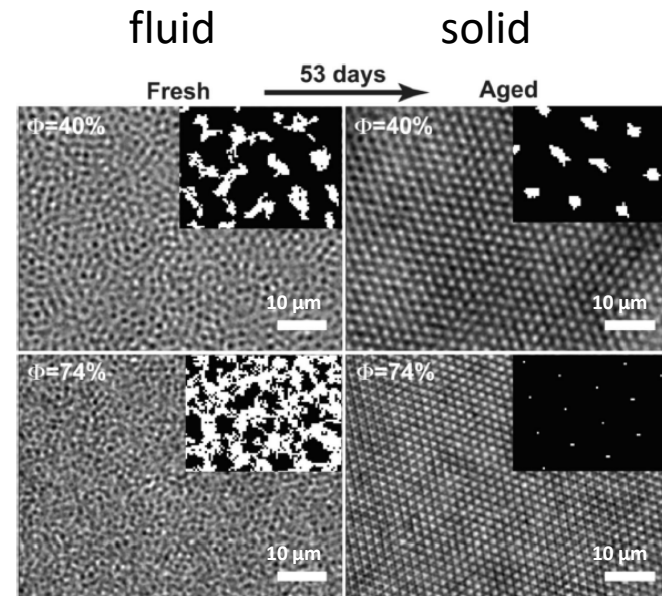
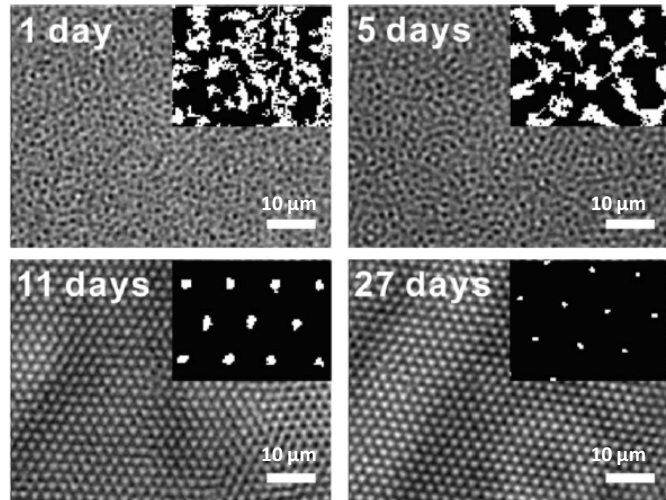
Crystallization of microgels

Microgels can be assembled into colloidal crystals if they are weakly attractive.

Dynamics of crystallization

$$d \approx 2 \mu\text{m}$$

Microgel concentration, $\Phi = 2 \text{ wt}\%$

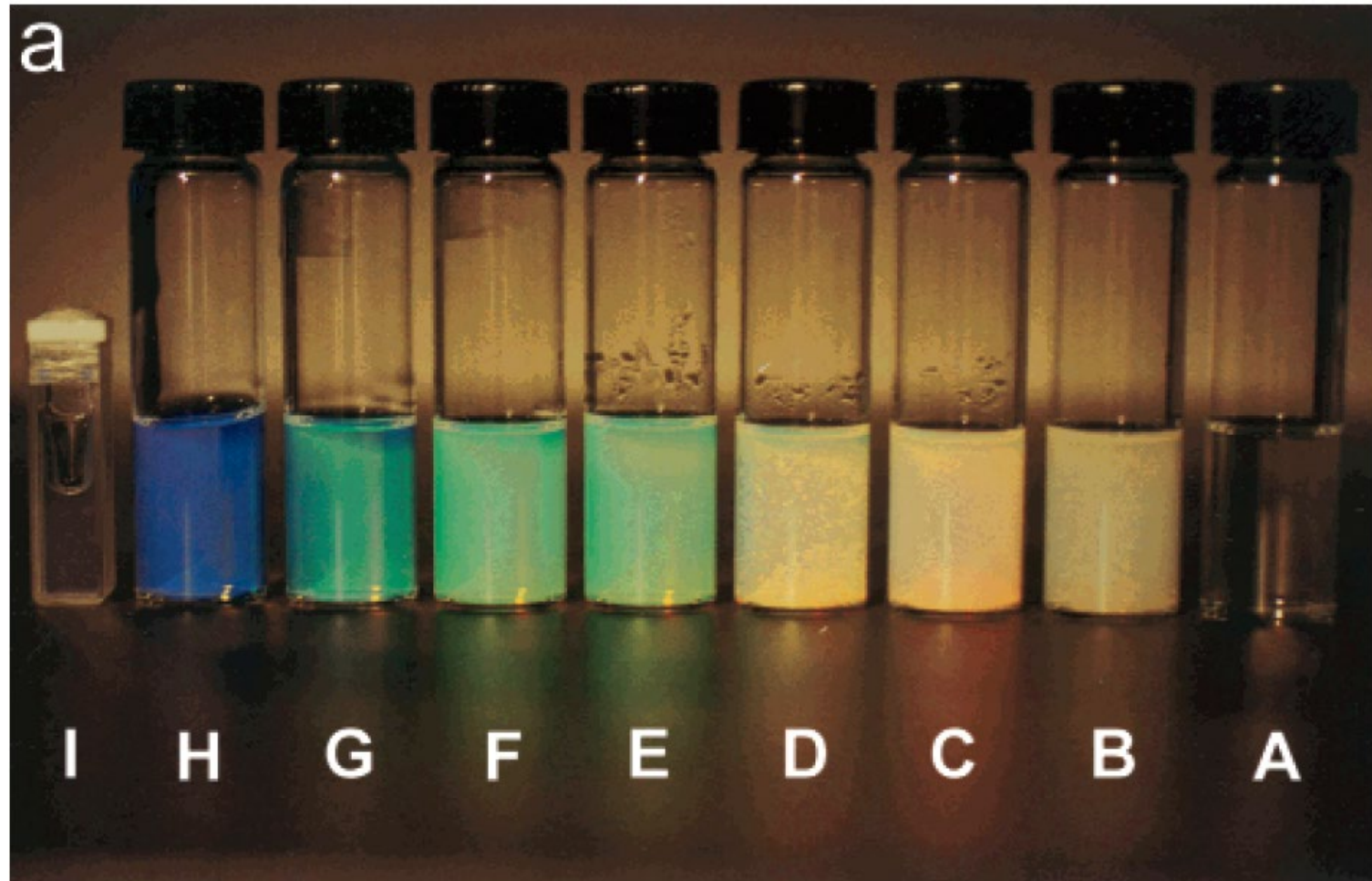


Meng, Z.; Cho, J. K.; Breedveld, V.; Lyon, L. A. *The Journal of Physical Chemistry B* **2009**, *113* (14), 4590-4599

The formation of colloidal crystals can take a long time.

Colloidal crystals made of microgels

PNIPAM microparticles, $d_h \approx 216$ nm

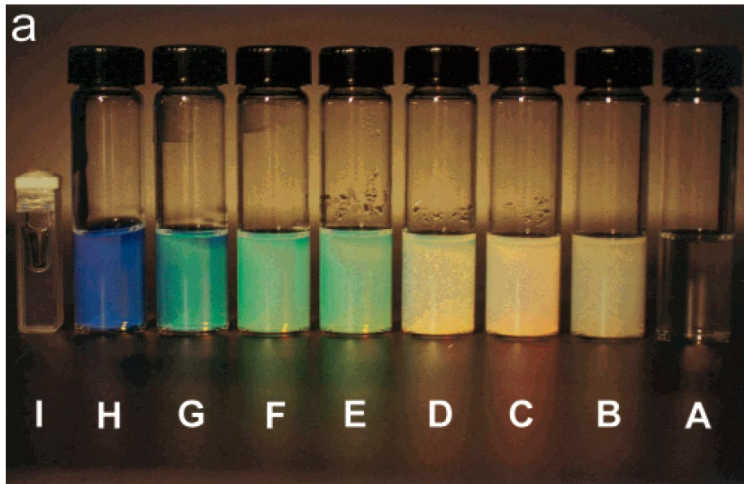


Why does the color of the dispersions change with the particle concentration?

- A. The absorption wavelength is a function of the polymer concentration.
- B. The mobility of the particles changes and thus also their scattering behavior.
- C. The effective diameter of the microgels and thus the interference pattern changes.
- D. Adjacent particles start to entangle, resulting in a bulk hydrogel

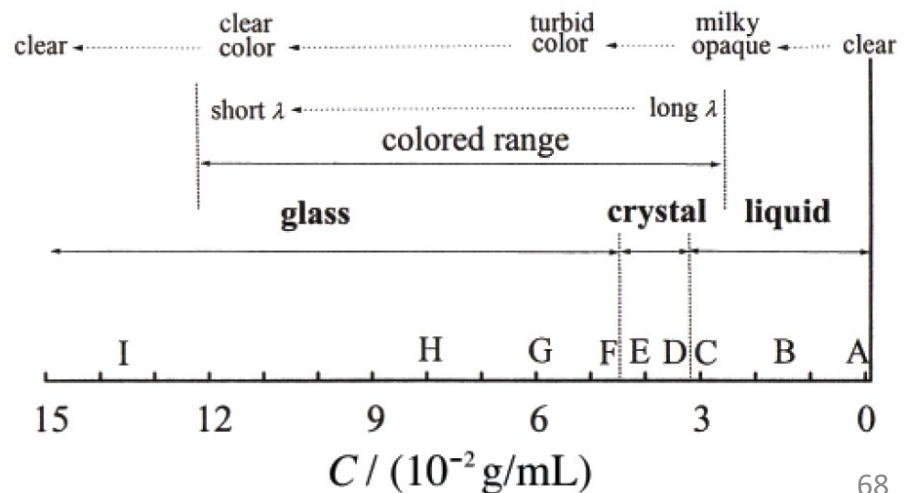
Colloidal crystals made of microgels

PNIPAM microparticles, $d_h \approx 216$ nm



	c (wt%)	c (vol%)
A	0.064	
B	1.47	50
C	3	59
D	3.4	
E	4.2	
F	4.6	61
G	5.95	
H	7.92	
I	13.7	

A-C: The scattering area increases.
 D, E: These samples are crystals. Their iridescent color is due to Bragg reflections.
 F-I: These samples are glasses. The inter-particle distance is determined by the particle size and results in the coloring of the samples. As the concentration increases, the particle size decreases and hence, the color is blue-shifted.



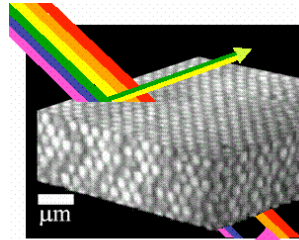
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Applications of colloidal crystals

Why have certain colloidal crystals colors?

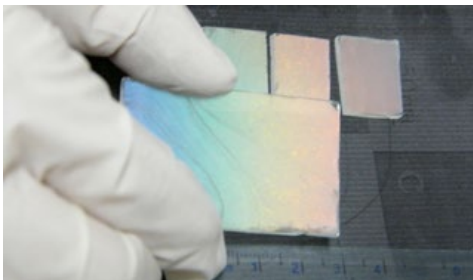
The size of colloids is between 1 nm and 1 μm . The wavelength of visible light is in this range. Hence, if only certain reflective wavelengths constructively interfere, the colloidal crystals appear to be colored.



<http://people.umass.edu/~dinsmore/softcmp.html>

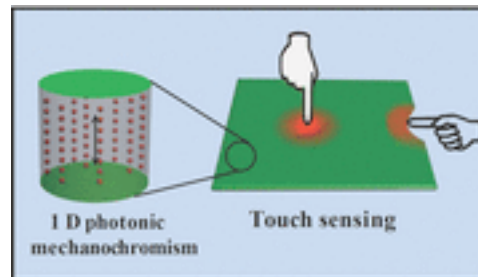
Examples:

colorant



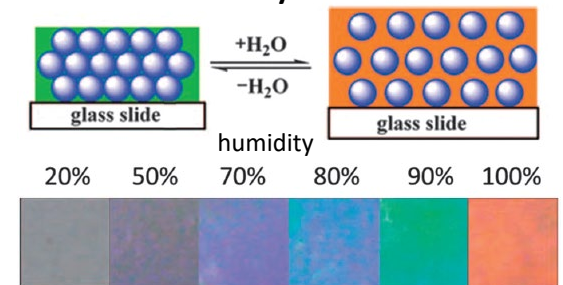
<http://clxy.snnu.edu.cn/jhzeng/res/rnews.html>

touch sensor



Wang, X.-Q., et al. *Advanced Optical Materials* **2014**, 2 (7)

humidity sensor



Tian, E., et al. *Journal of Materials Chemistry* **2008**, 18 (10), 1116-1122 70

Outline

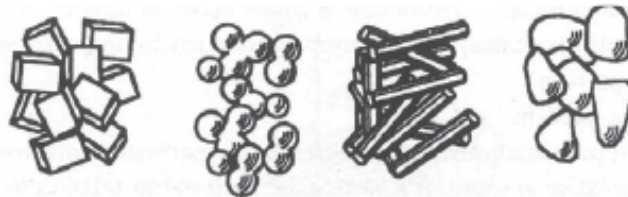
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Agglomerate vs. Aggregate

primary particle



agglomerate



aggregate



adhesion

sintered body
(crystal structure)

primary particles



agglomeration by
physical interactions
of primary particles
(agglomerate)



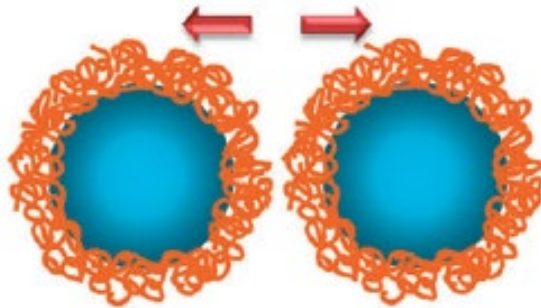
new formed particle
(aggregate)

Agglomerates are assemblies of primary particles whose total surface area does not differ appreciably from the sum of specific surface areas of each particle.

Aggregates are assemblies of primary particles whose total surface area differs appreciably from the sum of the specific surface areas of each particle.

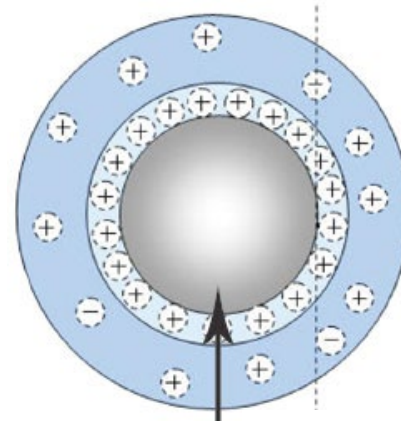
Agglomeration of particles

Sterically stabilized particles



Steric Repulsion

Electrostatically stabilized particles



Agglomeration can be caused through

- the addition of a poor solvent to collapse the polymers at the particle surface.
- physical or chemical removal of dispersants.
- the addition of non-adsorbing polymers that induce attractive depletion forces.
- the addition of salts. They screen charges at the particle surface thereby decreasing the Debye length.
- the addition of non-adsorbing polymers that induce attractive depletion forces.

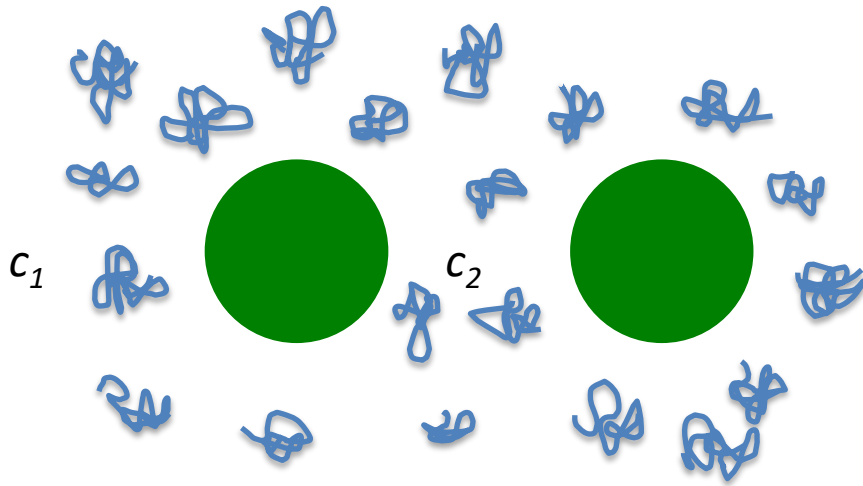
What are depletion forces?

Depletion forces

A **depletion force** is an attractive force that occurs between large colloidal particles, which are dispersed in a diluted solution containing depletants.

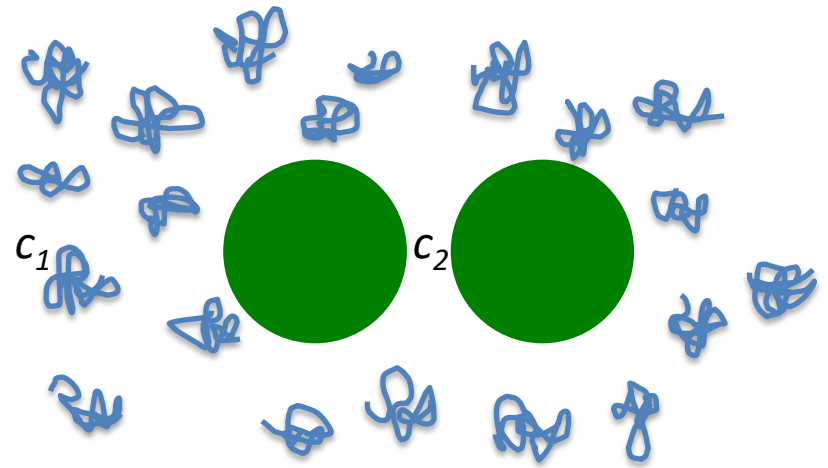
A **depletant** is a small solute that is preferentially excluded from the vicinity of particles.

Depletion forces are present if the distance between adjacent colloids is on the order of R_g of the depletant.



$$c_1 = c_2$$

There is no osmotic pressure and hence there are no depletion forces.



$$c_1 > c_2$$

There is an osmotic pressure, resulting in depletion forces.

Depletion force between two plates

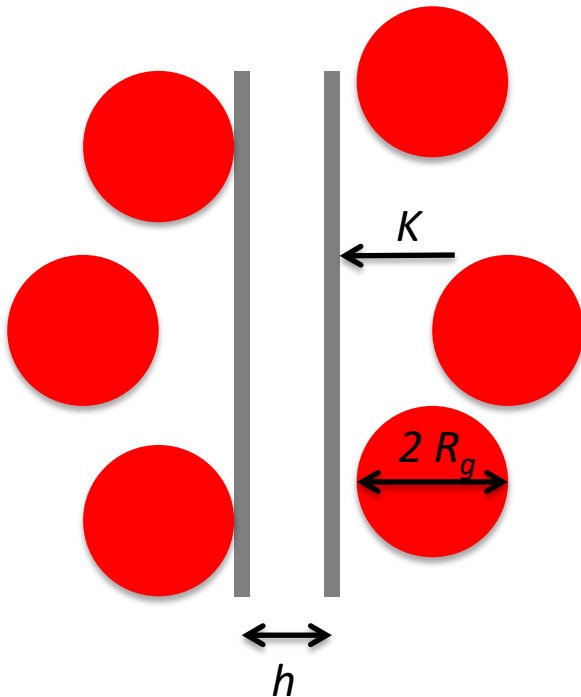
$$p_0 = n_b k_B T$$

p_o : osmotic pressure [Pa]

n_b : bulk number density of particles [particles/m³]

W : interaction potential [J]

R_g : Radius of gyration of the depletant [m]



$$p_0 = -n_b k_B T \quad h < 2R_g$$

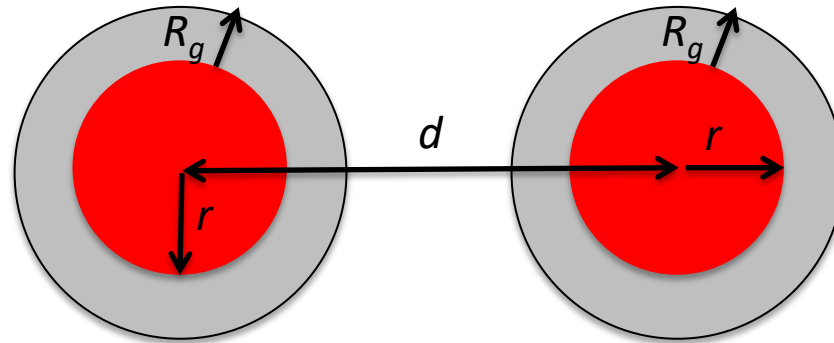
$$p_0 = 0 \quad h \geq 2R_g$$

$$p = -\frac{dW}{dh}$$

$$W(h) = -n_b k_B T (2R_g - h) \quad h < 2R_g$$

$$W(h) = 0 \quad h \geq 2R_g$$

Depletion forces between two spheres



for $h = d - 2r < R_g$

$$E_{dep} = -p_0 V_{dep}$$

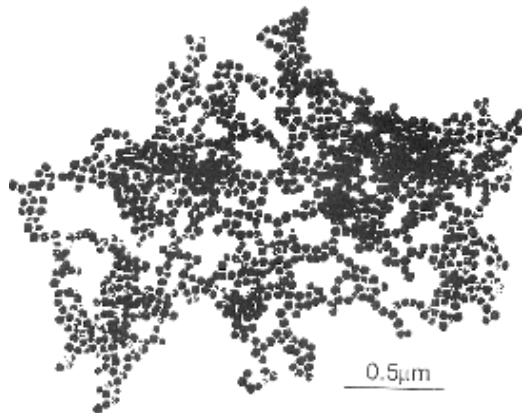
$$V_{dep} = \frac{4}{3}\pi(r + R_g)^3 \left(1 - \frac{3d}{4(r + d)} + \frac{d^3}{16(r + d)^3} \right)$$

Agglomeration

Diffusion limited agglomeration

Encountering particles stick irreversibly to each other.

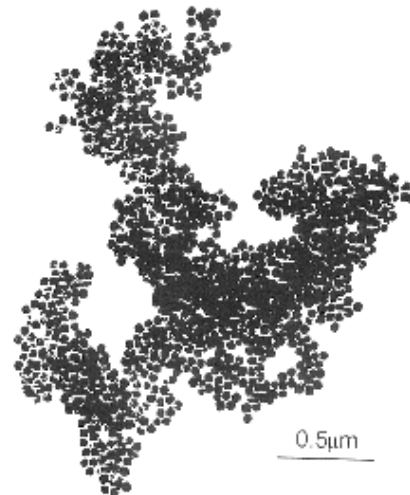
Diffusion limited agglomeration results in loose structures.



Reaction limited agglomeration

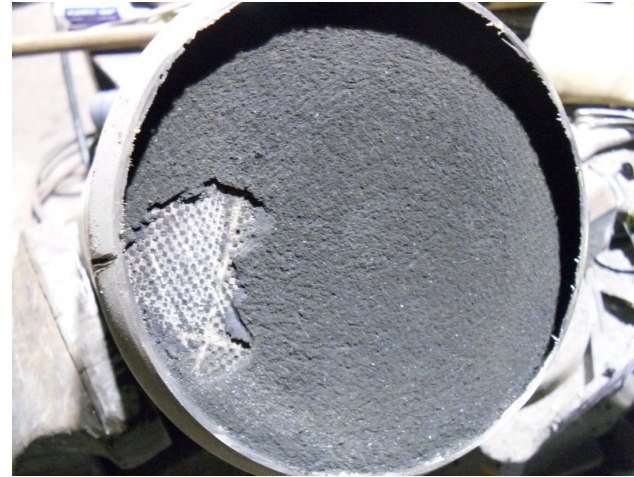
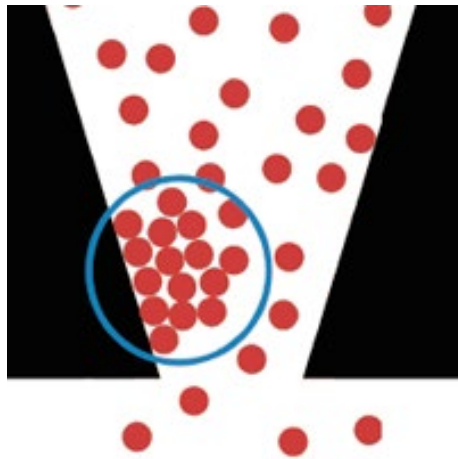
There is a finite probability for two encountering particles to stick to each other.

Reaction limited agglomeration results in dense structures.



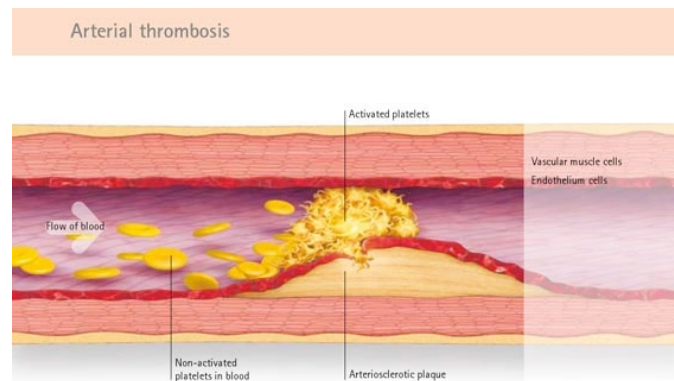
Agglomeration that induces clogging events

clogging of filters



<http://adetuning.co.uk/dpf/>

clogging of blood vessels



<http://pharma.bayer.com>

You disperse CaCO_3 particles or agglomerates in an aqueous solution (pH = 6) using two different approaches and let them sediment. The structure has the higher density if

- A. you take agglomerated particles
- B. you take individually stabilized and dispersed particles

Isoelectric point of $\text{CaCO}_3 \approx 8.5$

Rain washes fine clay particles (CaCO_3 particles approximately $0.15 \mu\text{m}$ in diameter) from the soil of a farmer into a river. Why do particles stay dispersed while they are in a stream of fast flowing fresh water? Because they are

- A. electrostatically stabilized
- B. sterically stabilized
- C. electrosterically stabilized

Isoelectric point of $\text{CaCO}_3 \approx 8.5$

What happens to clay particles when the river empties into an ocean?

- A. they sediment because they are too large
- B. they remain well dispersed
- C. they agglomerate and sediment
- D. they go to the liquid-air interface

Isoelectric point of $\text{CaCO}_3 \approx 8.5$

Delta formation

Colloids (clays) become unstable if they are suspended in water containing high salt concentrations and agglomerate.



Outline

- Introduction
- Particle motion
- Stabilization
 - electrostatic stabilization
 - steric stabilization
- Characterization
- Applications of particle dispersions
- Assembly of particles
- Colloidal crystals made of microgels
- Applications of colloidal crystals
- Agglomeration
- **Applications of agglomerated particles**

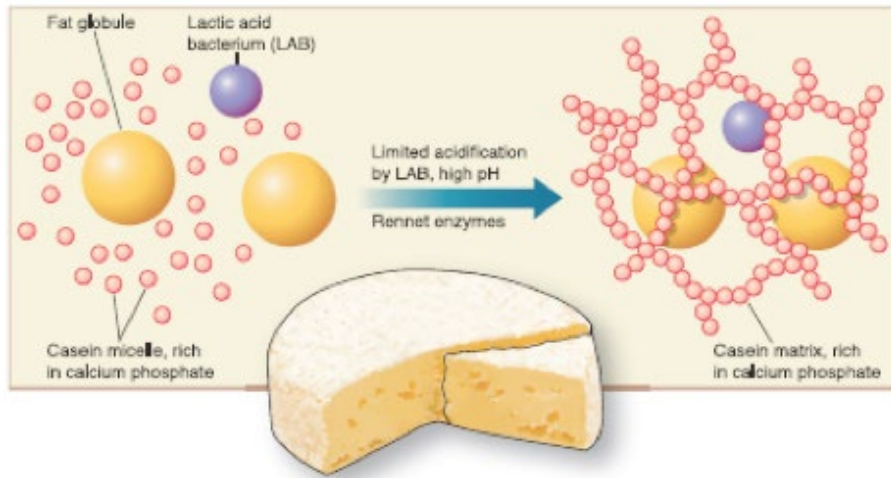
Agglomeration during cheese formation



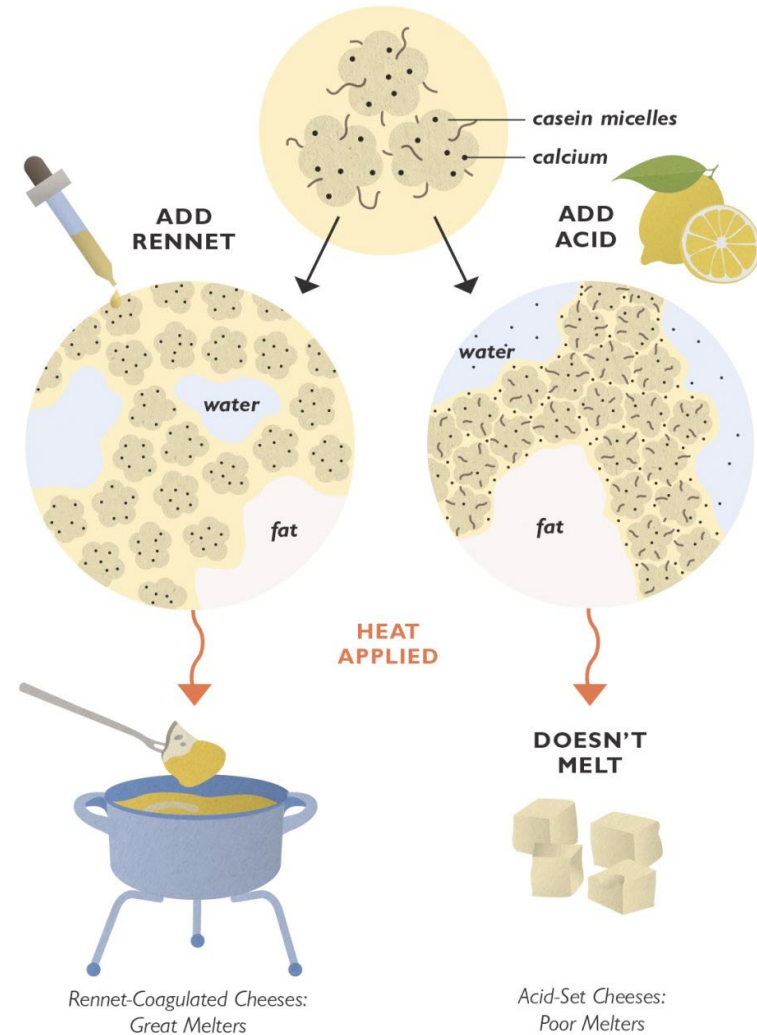
Sterically stabilized casein micelles begin to flocculate if the steric brush, made from casein, collapses due to changes in pH.



Cheese production

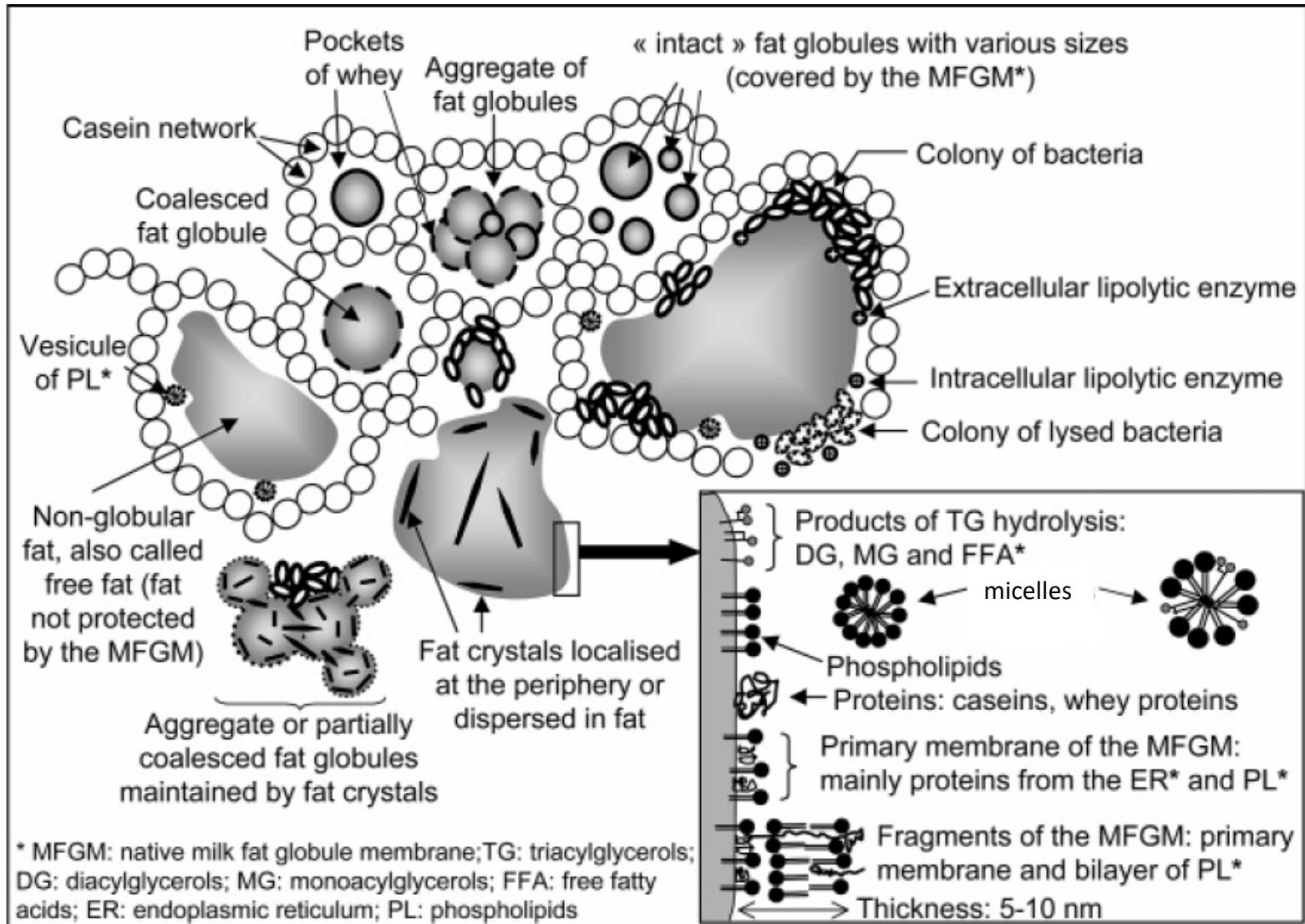


<http://slowfoodwellesleysnail.blogspot.ch/2014/01/wasiks-cheese-lecture.html>

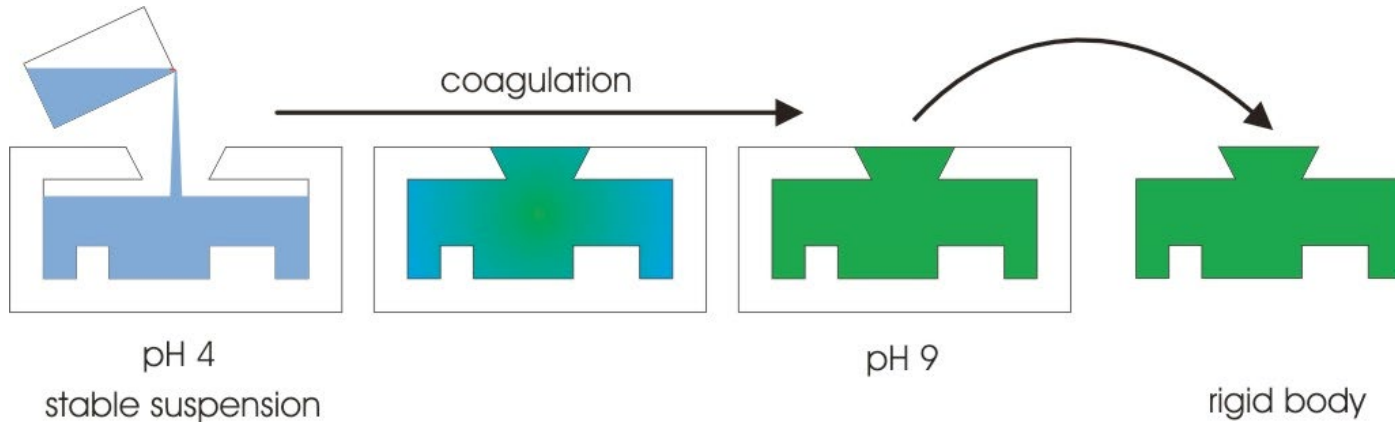
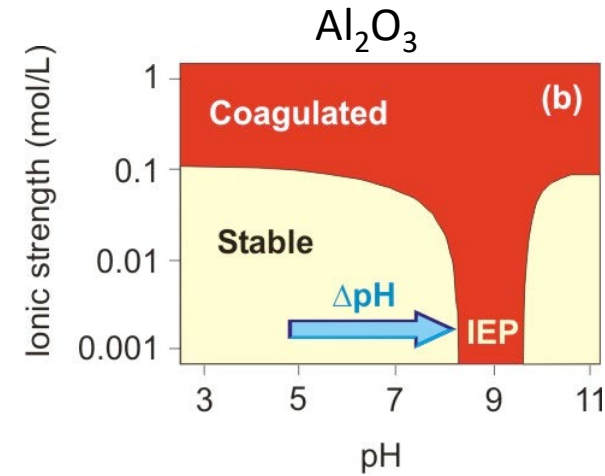
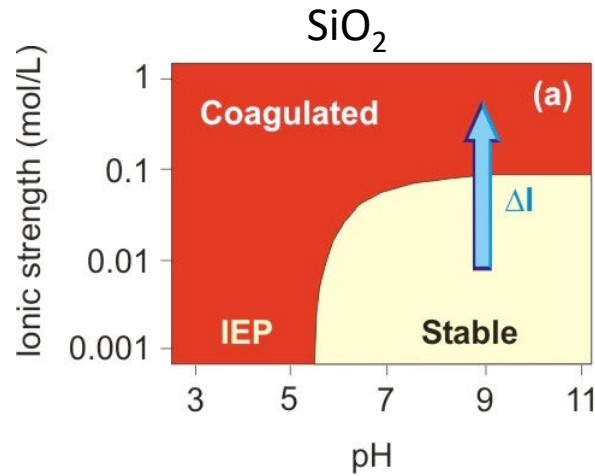
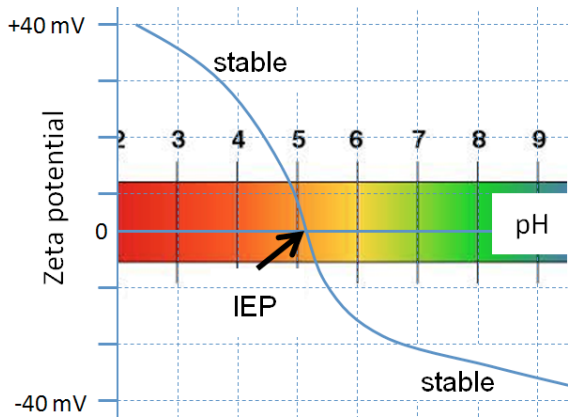


<http://luckypeach.com/guides/science-melting-cheese/>

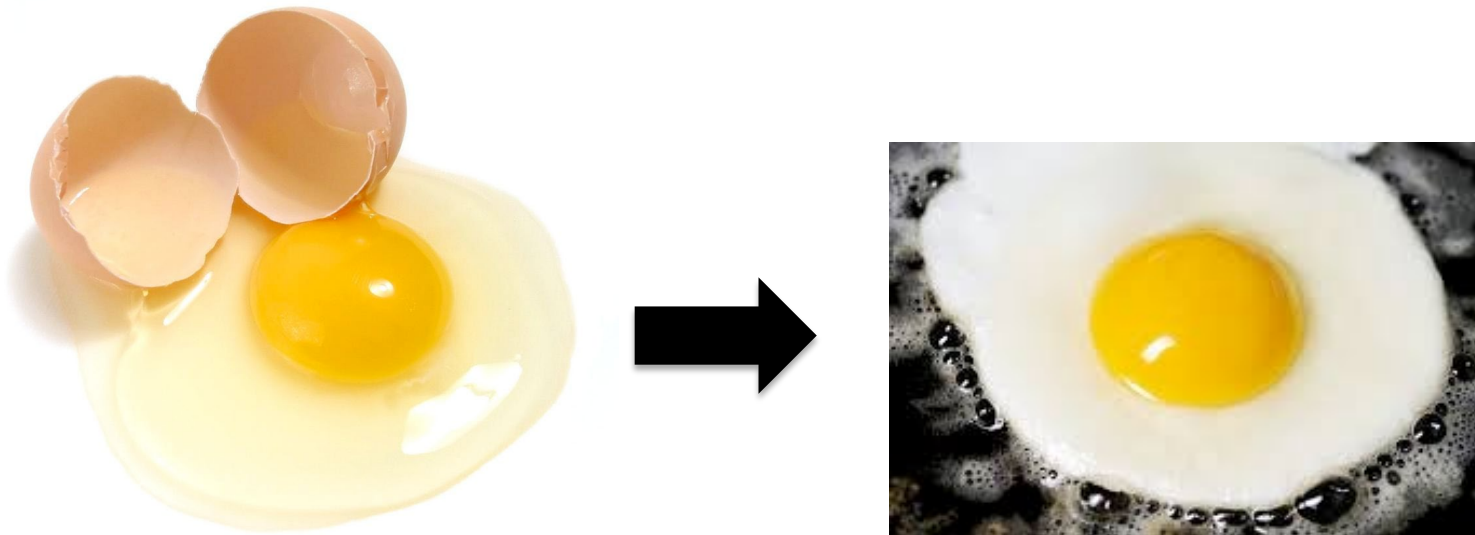
Emmentaler cheese



Direct coagulation casting

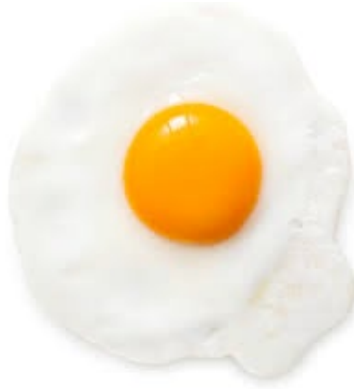


Colloidal gels



What happens during this transition?

Colloidal gels



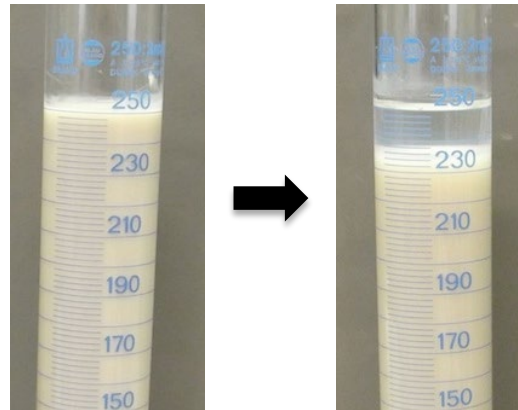
Colloidal gels



Why does this phase separation occur?

Syneresis

Syneresis is the collapse of a gel that is accompanied by the expulsion of liquid.



Syneresis is unwanted in yoghurts.



Syneresis is wanted during cheese production.



Application: 3D printing of structural colors

