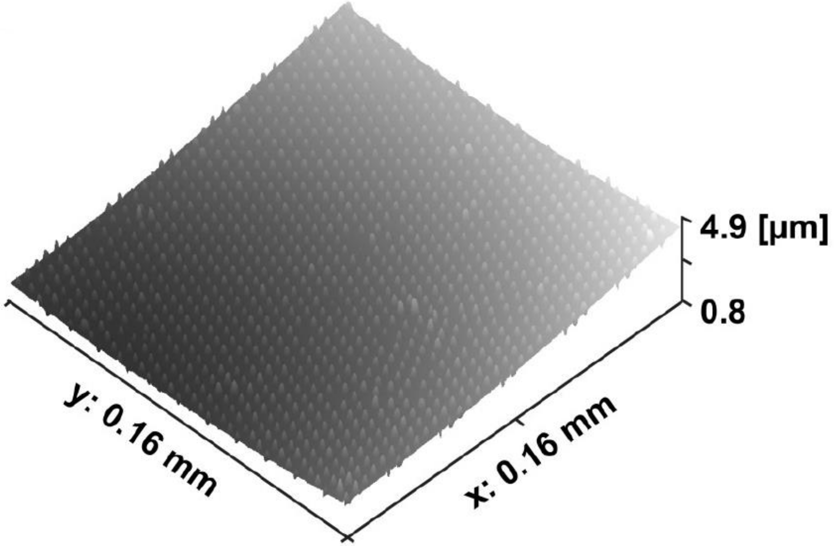
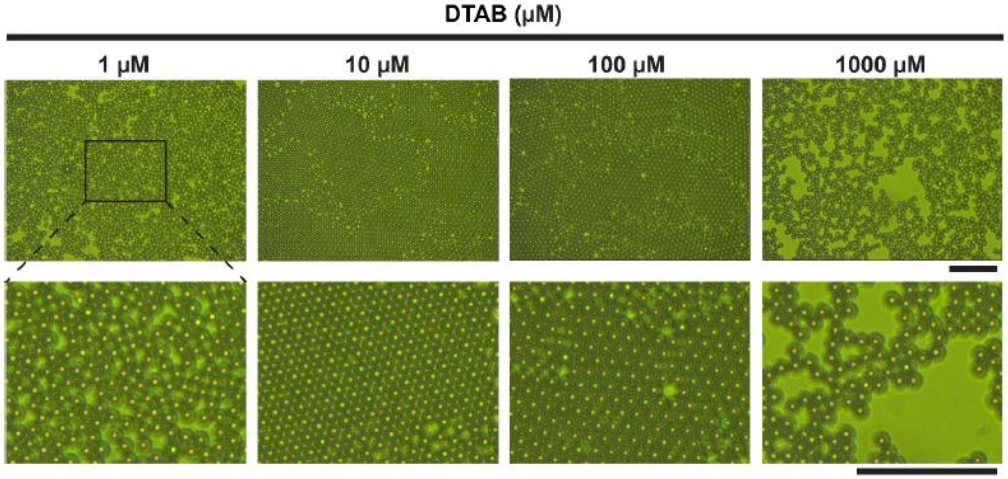
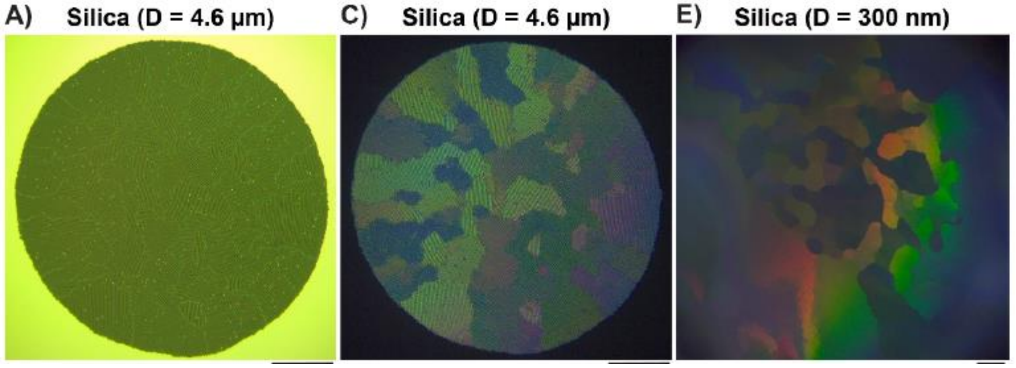
Physical Chemistry of Colloids

Langmuir **2018**, *34*, 15526





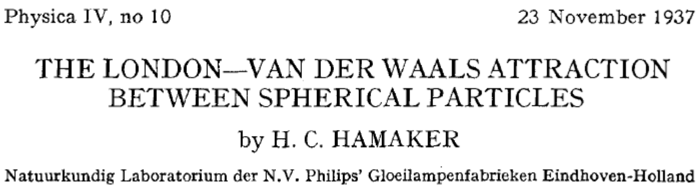


Lecture 9, *May 15, 2019*

Manos Anyfantakis
Physics & Materials Science Research Unit

Previously in ColloidsPhysChem…(I)

Hamaker theory (1937)
simple quantification of London type of vdW interactions between two macroscopic objects



Physica IV, no 10 23 November 1937

THE LONDON—VAN DER WAALS ATTRACTION BETWEEN SPHERICAL PARTICLES

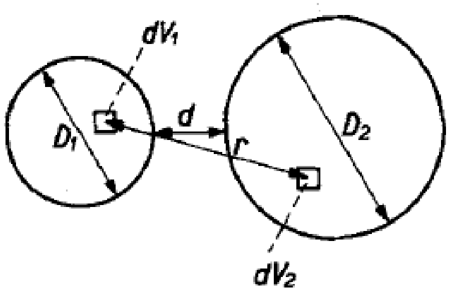
by H. C. HAMAKER

Natuurkundig Laboratorium der N.V. Philips' Gloeilampenfabrieken Eindhoven-Holland

basic assumption
interaction between two bodies approximated by summing the interactions between every pair of molecules that make up the bodies

$$\Phi = \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1(\neq i)}^{N}\Phi^{ij}(r_{ij})$$

gross approximation: interaction of molecule 1 in particle A with molec. 2 in part. B unaffected by all other molec.!



potential between colloid particles calculated using two components:

$$\boxed{\Phi = A \cdot f(geometry)}$$

$$\boxed{A_{212} = \left[\sqrt{A_{11}} - \sqrt{A_{22}}\right]^2}$$

$$\boxed{A_{213} = \left(\sqrt{A_{22}} - \sqrt{A_{11}}\right)\left(\sqrt{A_{33}} - \sqrt{A_{11}}\right)}$$

- a material property, the **Hamaker constant *A*,** accounting for properties of both particles & solvent
- **f (geometry):** geometries of the interacting particles & their **separation**

potential & force can be calculated using tabulated data & formulae
- **A** may be computed *ab initio* from molecular parameters
- **f (geometry)** has been calculated for various cases

Previously in ColloidsPhysChem…(II)

Lifshitz's approach

- released the Hamaker's assumption by treating interacting bodies as continua
- macroscopic body interactions due to fluctuating EM fields in gap between bodies
- macrosc. material property reflecting propagation & reception of EM energy: dielectric permittivity ε
- response of a material to an electric field depends on frequency (polarization does not change instanaeously)
- **ε'**: energy storage in material (polarization); **ε''**: absorption of energy → heat
- absorption peaks: key data used in Lifshitz's theory to calculate *A*

Calculation of *A* for interaction of media (e.g. particles) 1 & 2 accross medium 3

$$A = \frac{3k_BT}{4}\left(\frac{\varepsilon_1-\varepsilon_3}{\varepsilon_1+\varepsilon_3}\right)\left(\frac{\varepsilon_2-\varepsilon_3}{\varepsilon_2+\varepsilon_3}\right)+\frac{3h\nu_e}{8\sqrt{2}}\left[\frac{(n_1^2-n_3^2)(n_2^2-n_3^2)}{\{(n_1^2+n_3^2)(n_2^2+n_3^2)\}^{\frac{1}{2}}\left\{(n_1^2+n_3^2)^{\frac{1}{2}}+(n_2^2+n_3^2)^{\frac{1}{2}}\right\}}\right]$$

- *1st term (zero-freq. contribution): includes Debye & Keesom contributions*
- *2nd term: non-retarded dispersion energy contribution*

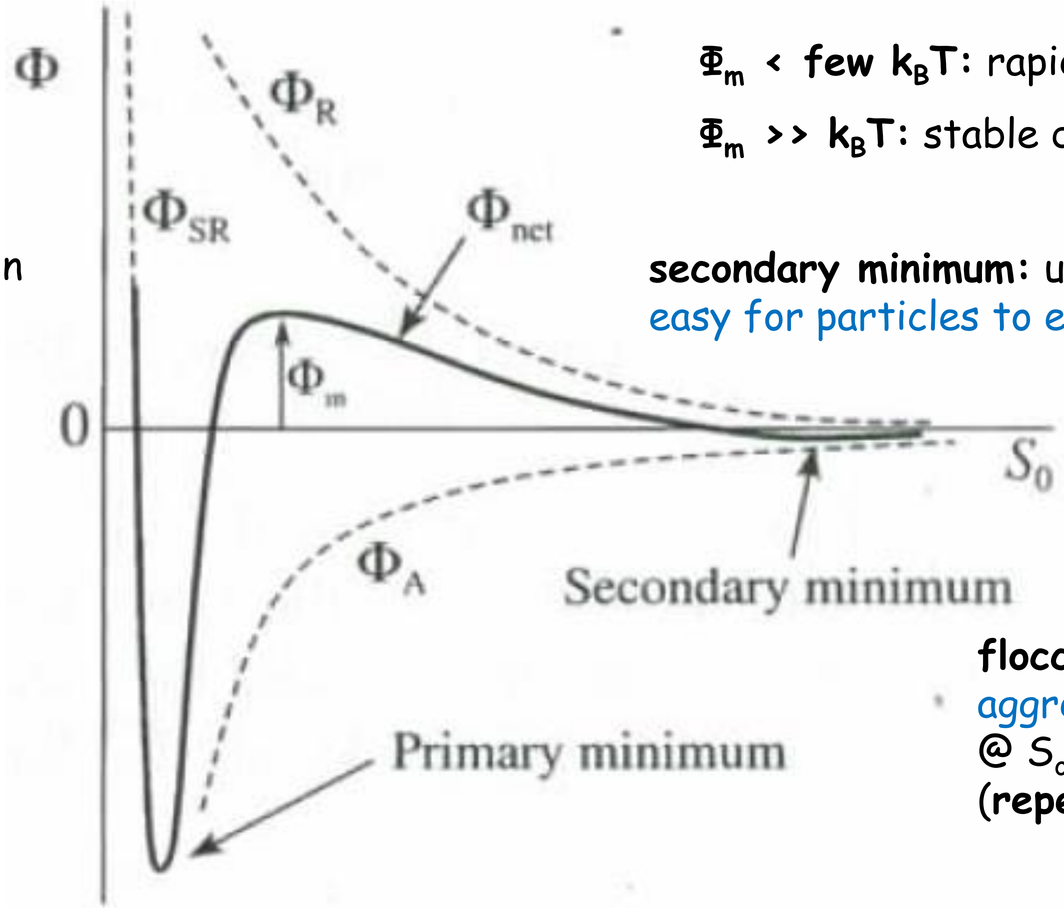
Key results

- for two identical bodies (**$\varepsilon_1 = \varepsilon_2$** & **$n_1 = n_2$**) → **A > 0, vdW atttractive**
- for two different bodies (**$\varepsilon_1 \neq \varepsilon_2$** & **$n_1 \neq n_2$**) → **A can be positive or negative**, depending on the medium (3) between them, **vdW attractive or repulsive**

Previously in ColloidsPhysChem…(III)

Brownian motion energy (~k_BT): means for particles to overcome the potential barrier & aggregate

aggregation probability: determined by Φ_m height (→ determines stability against aggregation)



Φ_m < few k_BT: rapid aggregation

Φ_m >> k_BT: stable dispersion

Φ_m: potential energy barrier to coagulation

secondary minimum: usually pretty shallow, easy for particles to escape once they are in

coagulation: irreversible aggregation of particles @ S_0 of primary min.

flocculation: reversible aggregation of particles @ S_0 of secondary min. (**repeptization** can occur)

primary minimum: depth determined by short term repulsion (not part of DLVO, could be due to tighly bound hydration layer)

Previously in ColloidsPhysChem…(IV)

influence of salt addition

- Φ_m decreases strongly with salt conc. C (compression & collapse of double layer)
- **critical coagulation concentration (CCC)** critical C (~ 400 mM): Φ_m → 0, rapid aggregation expected
- **coagulation criterion:** $\Phi_m = 0$ req.: $\Phi_{net} = 0$ & $d\Phi_{net} / dS_0 = 0$
- application of the above to analytical expressions of Φ_{net} yields CCCs ~ 50 - 250 mM for monovalent salts
- for high ψ_δ (> 100 mV), $CCC \sim 1/z^6$, independent of ψ_δ (Schulze-Hardy rule, explained by DLVO)

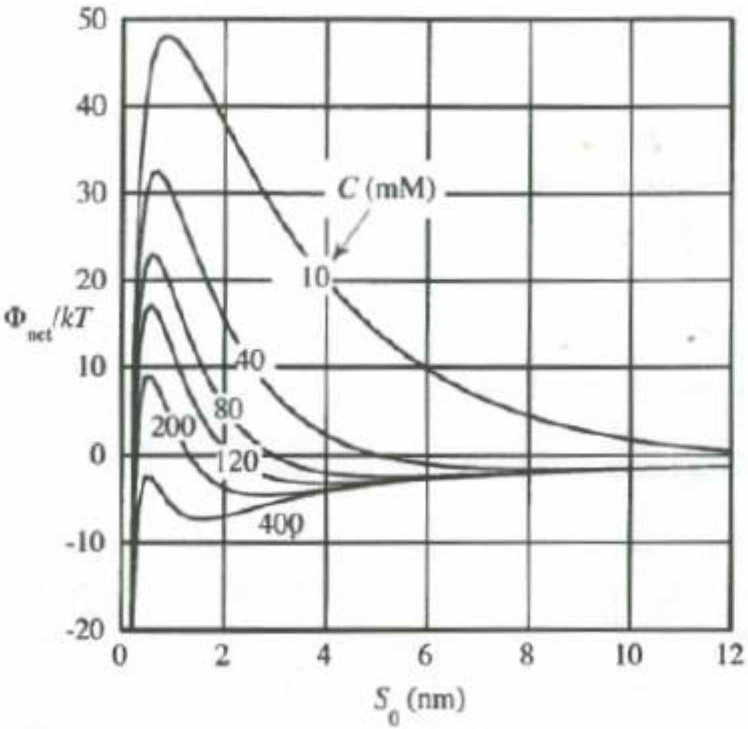
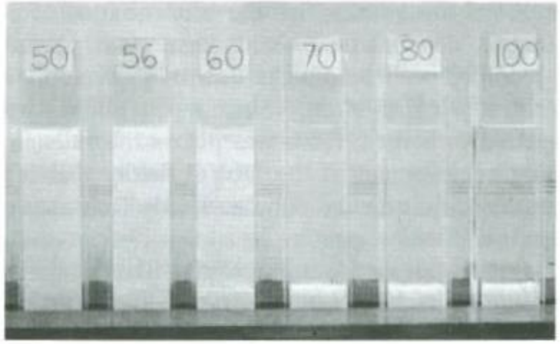


Fig. 7-8: The influence of indifferent electrolyte concentration on the total potential energy of interaction of two spherical particles: $a = 100$ nm, $T = 298$ K, $A_{212} = 0.849 \times 10^{-20}$ J, $z = 1$, $\psi_\delta = 30$ mV.

aggregation jar test to determine CCC

Fig. 7-10: Aggregation jar test series for As_2S_3 sol with 1-1 electrolyte concentrations in mM. The *CCC* appears to lie between 60 and 70 mM. From [Overbeek, J. Th. G., **Colloidal and Surface Chemistry, A Self-Study Subject, Part 2**, Lyophobic Colloids, p. 6.6, MIT, Cambridge, MA (1972).]



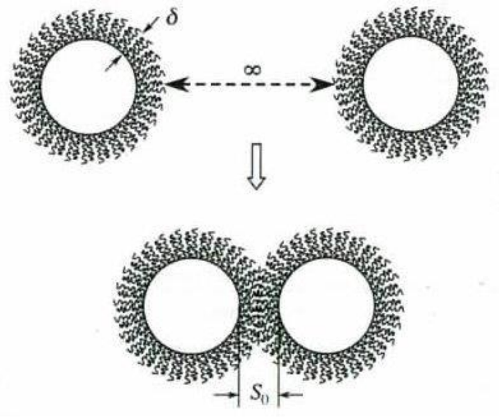
Steric stabilization of colloids

- *How is stability (against aggregation) achieved in aqueous media with high [salt] or non-aqueous solvents?*

Steric stabilization

-achieved by coating the particle surface with macromolecules (or other entities)

-very old method: Egyptians stabilzed pigment dispersions; Faraday used gelatin to stabilze Au sols



$$\Delta G_R = G_{S_0} - G_\infty$$

best steric stabilizers: block or graft copolymers that consist of both anchor groups & stabilizing moieties ("buoy" groups)


wsimag.com

requirements

- anchor groups attached (chemically/physically) to particles (→ no escape upon approach)
- anchor groups must be insoluble in the dispersion medium
- stabilizing groups must be as solvophilic as possible (need for large volume)
- stabilizing groups must have sufficient molar mass (provides needed adlayer thickness)

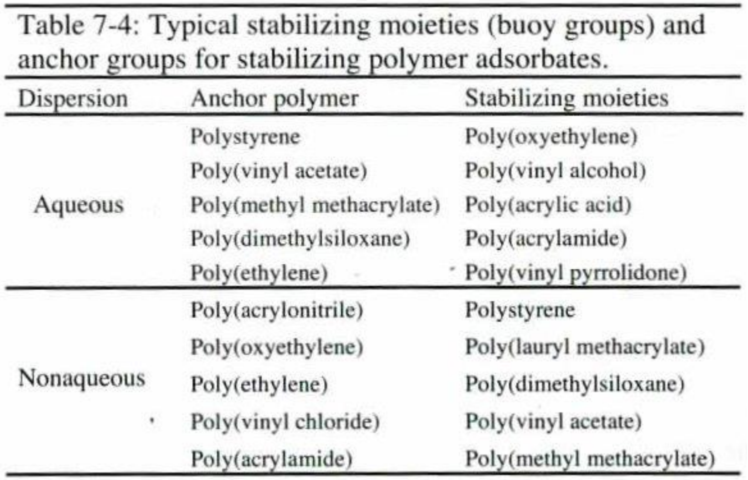


Table 7-4: Typical stabilizing moieties (buoy groups) and anchor groups for stabilizing polymer adsorbates.

Dispersion	Anchor polymer	Stabilizing moieties
Aqueous	Polystyrene	Poly(oxyethylene)
	Poly(vinyl acetate)	Poly(vinyl alcohol)
	Poly(methyl methacrylate)	Poly(acrylic acid)
	Poly(dimethylsiloxane)	Poly(acrylamide)
	Poly(ethylene)	Poly(vinyl pyrrolidone)
Nonaqueous	Poly(acrylonitrile)	Polystyrene
	Poly(oxyethylene)	Poly(lauryl methacrylate)
	Poly(ethylene)	Poly(dimethylsiloxane)
	Poly(vinyl chloride)	Poly(vinyl acetate)
	Poly(acrylamide)	Poly(methyl methacrylate)

Steric stabilization of colloids (II)

repulsion (→ stability) exists only if **ΔG_R > 0**
upon particle approach (and layer overlap)

$$\boxed{\Delta G_R = \Delta H_R - T\Delta S_R}$$

$\Delta G_R > 0$ → $\Delta G_R < 0$: stability → instability

entropic stabilization (more common in non-aqueous media)

- large configurational S decrease due to loss of volume accessible to the polymer chains during interpenetration
- ΔH_R small & negative (monomer-solvent interactions slightly weaker than monomer-monomer & solvent-solvent interactions)

enthalpic stabilization (more common in aqueous media)

- occurs when ΔH_R relatively large & positive
- monomer-solvent interactions stronger than monomer-monomer & solvent-solvent interactions
- often observed in aqueous dispersions stabilized by hydrated polymers; associated with partial dehydration of chains upon interpenetration
- $\Delta S_R > 0$ (decrease in segmental S, larger increase in S of freed water)
- $\Delta H_R > \Delta S_R$ → $\Delta G_R > 0$
- dehydration picture cannot be complete: also in non-aqueous media; electrolyte can have a strong effect (→ association of water)

Steric stabilization of colloids (III)

T-dependent stability

- stability → catastrophic destabilization often within 1 – 2 °C
- Critical Flocculation Temp. (CFT): T @ which flocculation takes place
- aqueous *(non-aqueous)* dispersions often flocculated upon T increase *(decrease)*
- behaviour in sharp contrast to T-insensitive electrocratic dispersions

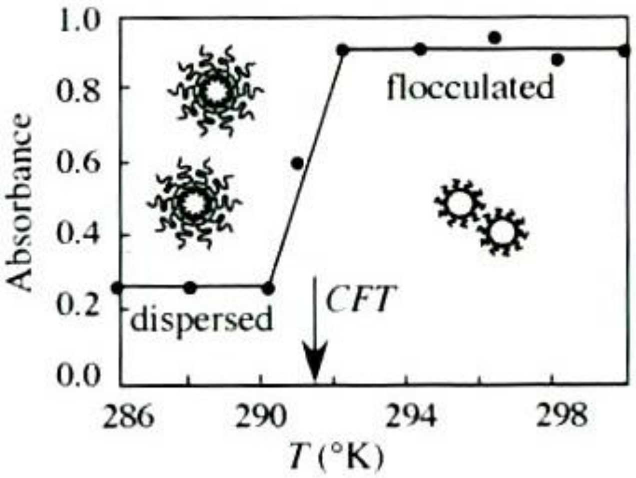


Fig. 7-24: Increase in turbidity of a poly(vinyl acetate) dispersion, stabilized by poly(ethylene oxide), on reaching the *CFT* in an aqueous electrolyte solution. After [Napper, D. H., *J. Colloid Interface Sci.*, **58**, 390 (1977).]

Reversible instability

- dispersions re-stabilized by re-heating/re-cooling, contrarily to electrocratic systems

Solvent-induced instability

- Critical Flocculation Vol: amount of (other) solvent req. for flocculation (solvency of stabilizing group reduced)
- reversible once original solvency conditions restored
- stability conditions depend only on nature of stabilizing moiety (good anchoring & total coverage provided)
- large stabilizers: stability independent of molecular weight

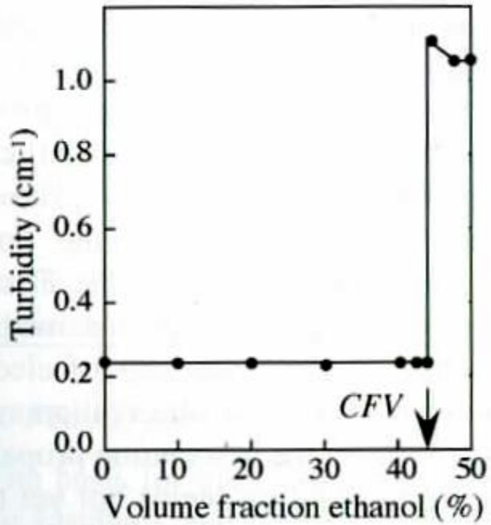
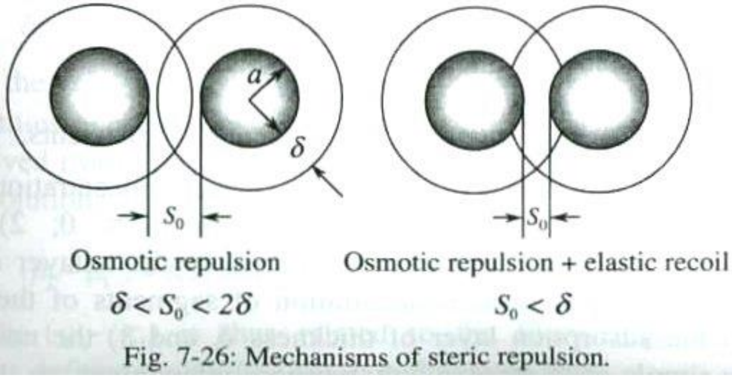


Fig. 7-25: Catastrophic onset of flocculation upon addition of non-solvent for stabilizing moieties (PSA). After [Napper, D. H., *Ind. Eng. Chem. Prod. Res. Develop.*, **9**, 467 (1970).]

Fischer theory of steric stabilization

Fischer theory (1958)

- polymer shells partially interpenetrate upon approach → osmpotic pressure difference *ΔΠ* between solvent molecules in interaction zone & those in external medium
- **δ < So < 2δ:**"external" solvent diffuses into the interaction zone → osmotic particle repulsion

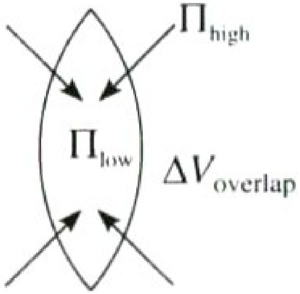


Osmotic repulsion $\delta < S_0 < 2\delta$

Osmotic repulsion + elastic recoil $S_0 < \delta$

Fig. 7-26: Mechanisms of steric repulsion.

- **So < δ:** elastic recoil repulsion due to volume restriction



osmotic effect

$$\Delta G_R = \Delta\Pi \cdot \Delta V_{overlap} = \left(\Pi_{overlap} - \Pi_{ideal}\right) \cdot \Delta V_{overlap}$$

$$\frac{\Pi}{c_2} = RT\left(\frac{1}{M_2} + B_2 c_2 + B_3 c_2^2 + \cdots\right)$$

Virial expansion of van't Hoff's equation

M_2: molecular weight of solute

c_2: mass concentration of solute

assumptions

*-almost no solute in external medium, **$c_2 \approx 0$***

*-uniform [polymer segment] @ the adlayer, **$c_2 \approx 2c$***
*(**c**: average conc. in adsorption layer)*

*-only pairwise interactions (**B_3** & higher order neglected)*

$$\boxed{\Delta G_R = 2RTB_2c^2\Delta V_{overlap}}$$

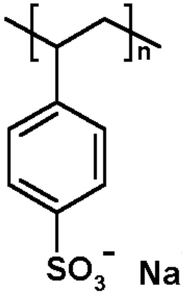
$B_2 > 0$: good solvent
$B_2 < 0$: bad solvent
$B_2 = 0$: θ solvent
$\boldsymbol{B_2 = f(T)}$

Electrosteric stabilization of colloids

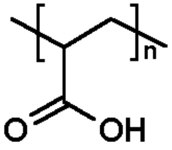
electrostatic & steric stabilization may act synergistically
→ ***electrosteric stabilization***

- involves charged polymers that are adsorbed onto particles
- achieved using i) polyelectrolytes or ii) neutral polymers (particle surface has already a double layer)

PSS



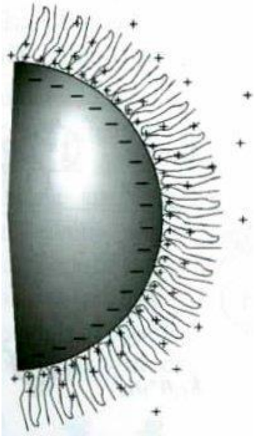
PAA



wikipedia

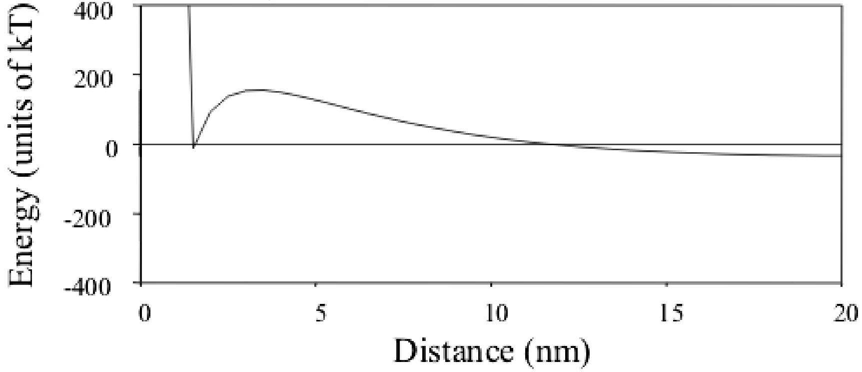
polyelectrolytes: polymers whose repeating units bear an electrolyte group which dissociates in water → charge

- polyelectrolytes anchor to surfaces of opposite charge
  → excess molar mass & charge → thick charged layer
- electrosteric stabilization may be achieved in non-aqueous solvents
- electrosterically stabilized colloids may be very robust:
  -electrostatic stabil. insensitive to T & solvent composition
  -steric stabil. insensitive to small [electrolyte] changes



treatment of electrosteric stabilization as the sum of electrostatic & steric components is an oversimplification:
adlayer infl. double layer; ions infl. adlayer

soft-matter.seas.harvard.edu



200 nm particles, A_{121} = 7x10^{-20} J, -100 mV ζ potential, 4 mM ionic strength, 1 nm polymer layer

Bridging flocculation

a very high molecular weight polymer (@ very low concentrations) may adsorb onto two or more particles @ the same time → aggregation

bridging flocculation important in wastewater clarification & paper making

first step

- a polymer (2) adsorbs onto a particle (1) → particle with one attached chain (1*)

second step

two processes compete

- "reaction" between particle 1* & particle 1 → bridging
- second polymer adsorbed onto particle 1* → no bridging

reconfirmation of adsorbed chain (→ thinner layer) prevents bridging

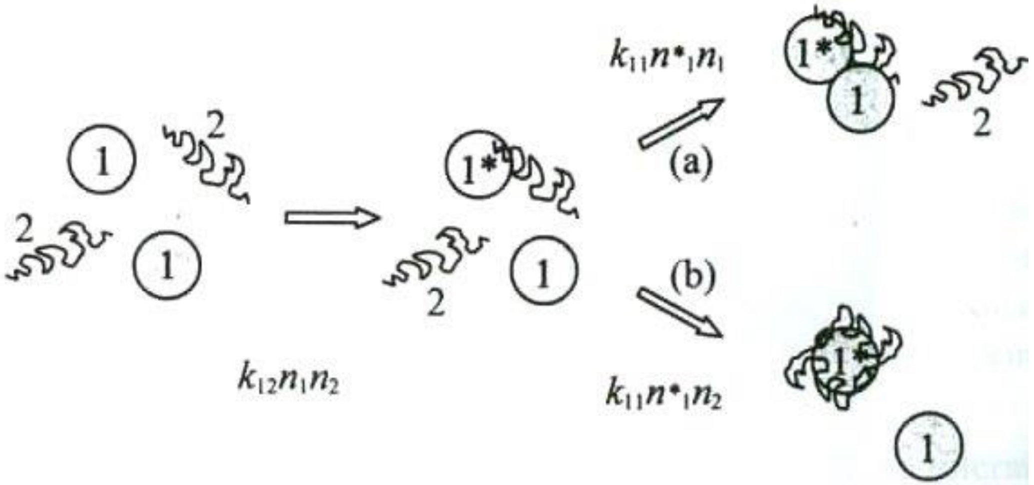


Fig. 7-30: Bridging flocculation. Polymer (2) adsorbs first to one particle (1) followed by adsorption to a second particle, as in route (a). In route (b), either the adsorbed polymer re-conforms, or a second polymer molecule adsorbs to the first particle.

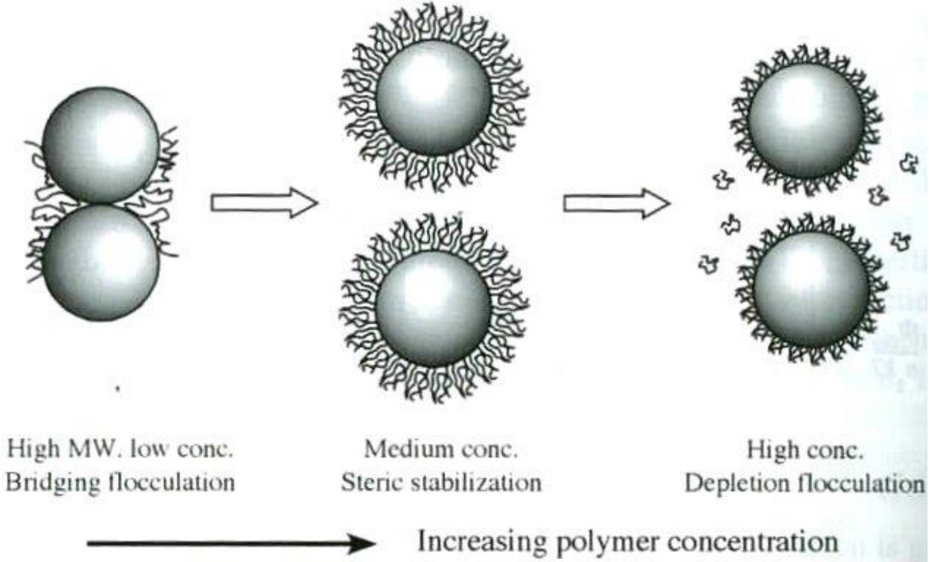
bridging favored when:
- [polymer] is as low as possible
- polymer has very high molecular weight (> 10^6 g/mol)

Coffee break


babyherogames.com


pngkey.com

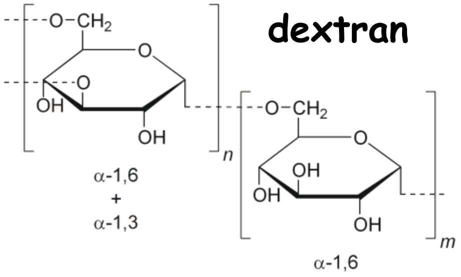
Mario is wondering:
"If I add polymer to a colloidal dispersion, which type of all those interactions should I expect?"



Depletion attraction

Depletion interactions arise when non-adsorbing polymers are added to colloidal dispersions

- neutral polymers (e.g. polysaccharides), polyelectrolytes/like-charged surface
- available surfaces already saturated with adsorbed polymers → free polymer



dextran

wikipedia

➢ When no (more) polymer adsorption is possible, free chains are excluded from a zone near the surface with thickness ~ ***R$_g$*** of polymer

two particles (with depletion layers) approaching so that polymer is excluded from the region between them
→ ***ΔΠ*** → flow toward this region → **attraction**

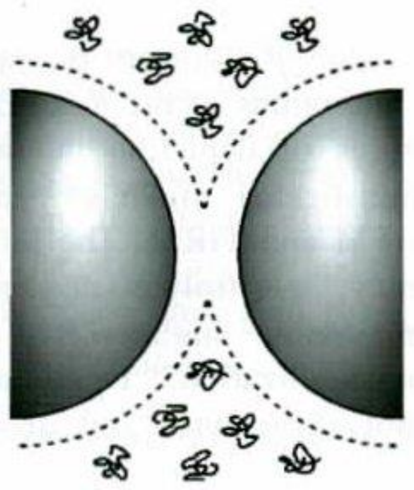


Fig. 7-31: Effect of free (unadsorbed) polymer: "depletion flocculation."

simple treatment

- non-adsorbed entities act as hard spheres with radius = ***R$_g$***
- completely excluded from depletion zone

$$\Delta G_{\mathrm{dep}} = -\left(\Pi_{\mathrm{soln}} - \Pi_{\mathrm{overlap}}\right)\Delta V_{\mathrm{overlap}} = -\Pi_{\mathrm{soln}}\,\Delta V_{\mathrm{overlap}} \qquad \Pi_{\mathrm{overlap}} = 0 \qquad \Pi_{\mathrm{soln}} = n_2 \mathrm{k_B} T$$

$$\Delta G_{\mathrm{dep}} = \Phi_{dep} = -\frac{2}{3}\pi n_2 \mathrm{k_B} T\left(R_g - \frac{S_0}{2}\right)^2\left(3a + 2R_g + \frac{S_0}{2}\right)$$

n_2: polymer number concentration in solution

Depletion attraction (II)

$$\Delta G_{\mathrm{dep}} = \Phi_{dep} = -\frac{2}{3}\pi n_2 \mathrm{k_B} T \left(R_g - \frac{S_0}{2}\right)^2 \left(3a + 2R_g + \frac{S_0}{2}\right)$$

- describes depletion interaction features in reasonable agreement with advanced models & experimental data (SFA, AFM, TIRM)
- depletion attraction between colloidal particles increases strongly with decreasing polymer size
- at particle separation ***S_0*** = 2***R_g*** → no attraction
- ***R_g*:** accounts for influence of T, molecular weight, solvency, & salt content
- depletion effects can also occur due to the presence of surfactant micelles or a second stable colloidal suspension (of smaller particles)

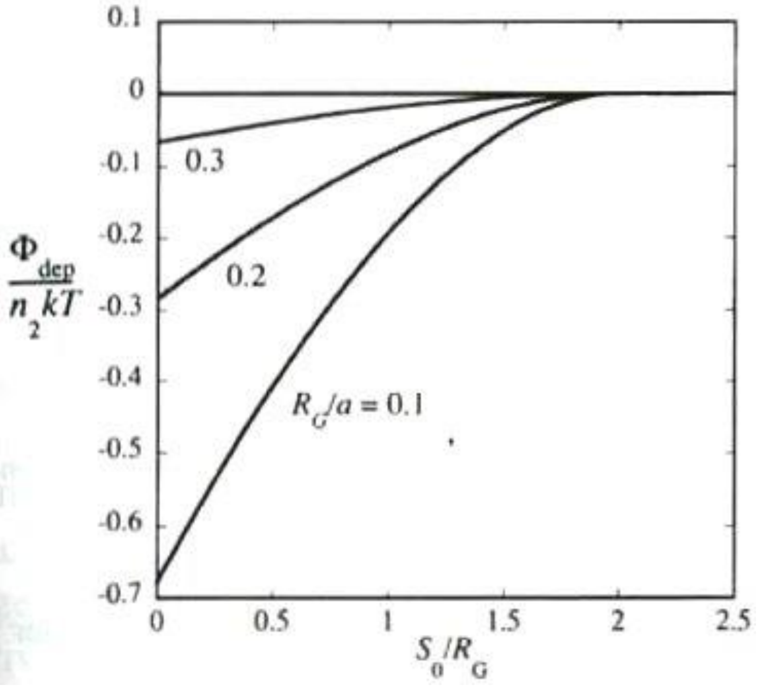


Fig. 7-32: Normalized deletion interactions plotted for different values of the free polymer size to the particle size.

Higher order concentration effects (ideal van't Hoff relaxed) & polymer-polymer interactions permitted

- depletion effect is just the short-range component of a general structural interaction producing longer range oscillatory effects
- repulsive component of such oscillations may be the cause of ***depletetion stabilization***, observed for higher [polymer]

Solvation forces

Structural (or solvation) force

- a different type of force observed experimentally (Surface Force Apparatus SFA, thinning of liquid films)
- oscillatory nature; require that molecules in the medium are able to establish at least medium-range order
- the result of packing constraints imposed on the ordering of solvent molecules (or other dispersed entities) upon approach of two surfaces
- surface roughness important: random microroughness → eliminates oscillatory component → monotonically decreasing repulsion

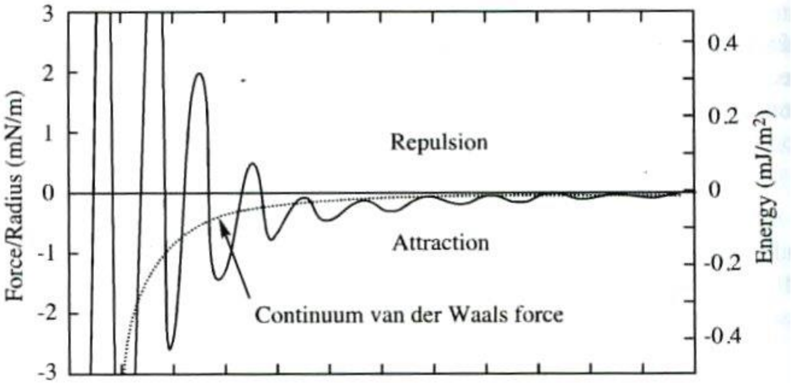
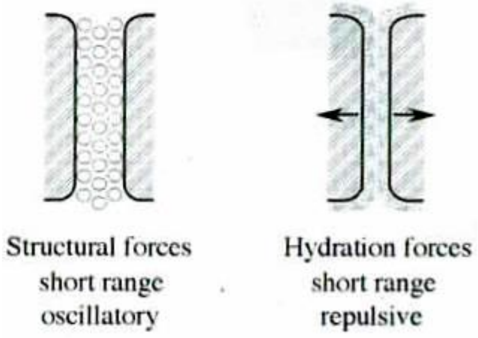


Fig. 7-2: Measured force between mica surfaces in Octamethylcyclotetrasiloxane (d ≈ 9Å). After [Horn, R. G., and Israelachvili, J. N., *J. Chem. Phys.*, **75**, 1400 (1981).]



aqueous media: *hydration force*

- repulsive, short-range force of exponential form
- degree of hydration depends on exchange of ions of diff. hydration degrees between solution & surface
- used to explain repeptization of electrocratic colloids & high [salt] required to coagulate hydrophilic particles

$$\Phi_{\text{hydration}} = A exp\left(-\frac{S_0}{\lambda_{hyd}}\right)$$

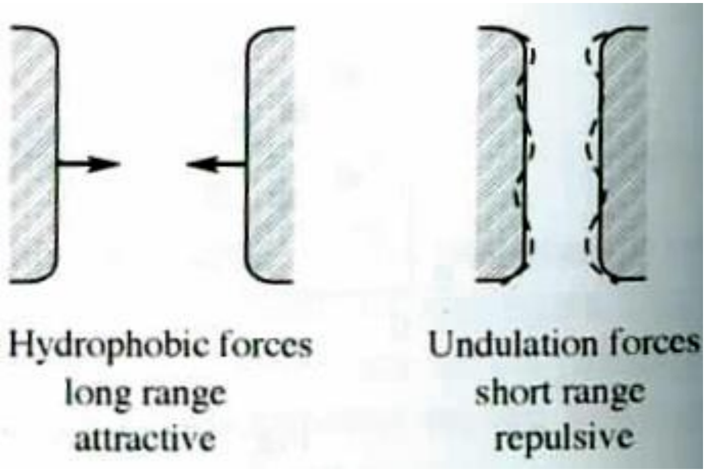
A: const. depending on hydration degree $\approx 3 - 30\ \mathrm{mJ/m^2}$

λ_{hyd}: decay length $\approx 0.6 - 1.1\ \mathrm{nm}$

Solvation forces (II)

hydrophobic interaction

- arises when either or both surfaces are hydrophobic (θ_{water} > certain value)
- hydrophobic surface incapable of forming H-bonds with water molecules
- resulting attractive force can be strong
- especially important for interaction between extended surfaces; importance for colloid stability not yet so firmly established



experiments for hydrophobic quasi-flat surfaces @ S ≤ 10 nm

$$\Phi_{\mathrm{hydrophobic}} = -B exp\left(-\frac{S_0}{\lambda_{phob}}\right)$$

B: constant depending on hydrophobicity degree $\approx 20-100\ \mathrm{mJ/m^2}$

$\lambda_{phob} \approx 1-2\ \mathrm{nm}$

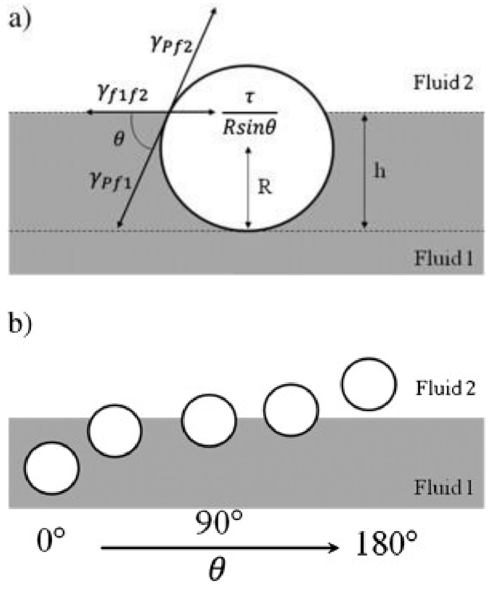
- hydrophobic effect can be large & long-ranged for low-curvature surfaces
- physical origin of hydrophobic attraction is a subject of controversy
- possibly due to nanobubbles residing on hydrophobic surfaces in contact with water (SFA, AFM & ellipsometry support this)
- observations indicate that for $\theta_{adv} > 66^o$ → hydrophobic behaviour
  $\theta_{adv} < 66^o$ → hydrophilic behaviour

Surface aggregation of colloidal particles

colloidal particles (< 10 μm) can aggregate when on interfaces; important in many process (flotation, anti-stick surfaces)

- ➢ a degradation pathway of otherwise stable dispersions

particles migrate to & get trapped @ interfaces (capillary trap) because they are not fully wet by either phase (contact angle > 0°)



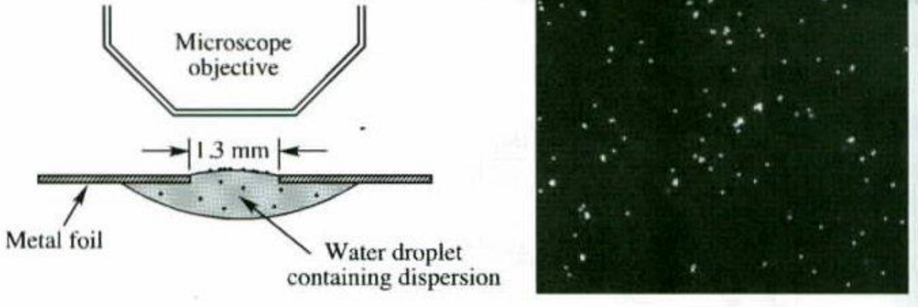
Curr. Opin. Colloid Interface Sci. **2014**, 19, 355

electrost.-stabilized particles @ the air-water interface

- Hamaker constant in air > one for particles in water → vdW attraction increased
- double layer only in water → electrostatic repulsion decreased

experiment: PS particles @ A-W interface

- θ_{part} = 102° → half-immersed
- particles arrived @ surface as singlets via diffusion
- doublets, triplets… over time
- aggregation onset @ [salt] ~ two orders of magnit. less than for bulk



(a) (b)

Fig. 7-22: (a) Schematic of sample cell for darkfield microscopic observations of particle adsorption and surface aggregation. (b) Observed aggregate population of 1-μm diameter PS primary particles at the surface of a 100 mM NaCl solution after 1.6 hr. Field of view shown: 160 μm. From [Williams, D. F., and Berg, J. C., *J. Colloid Interface Sci.*, **152**, 218 (1992).]

Evolution of structure of aggregates

after aggregates are formed, they grow & form different structures under diff. conditions

early-stage

- pairs of particles stick to each other to form doublets
- dominant even in dense dispersions

middle-stage

- aggreg. grow into structures, the form of which depends on aggregation rate

rapid aggregation

- particles stick @ initial point of contact → aggregates more open & occupy more volume
- fractal (self-similar) structures

slow aggregation

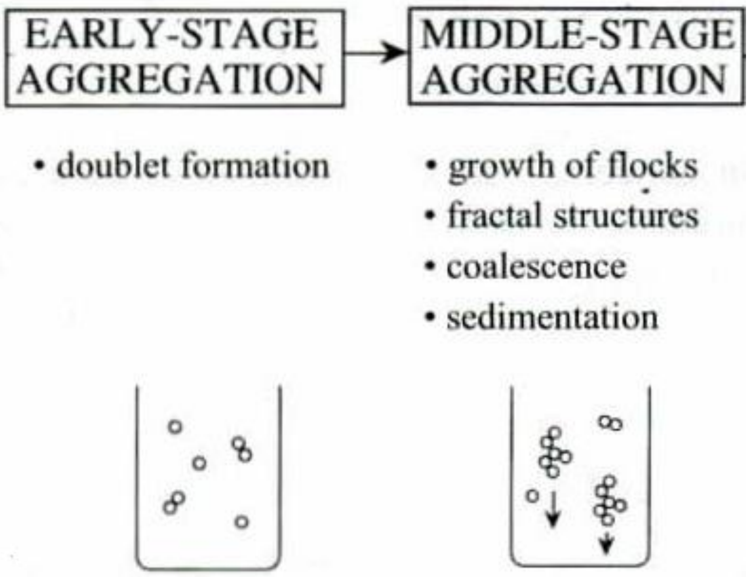
- particles can move & densify → denser flocks

electrocratic colloids

- rapid aggregation, voluminous structures

sterically stabilized & depletion attraction systems

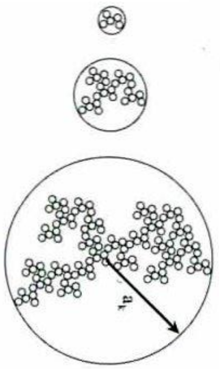
- individual particles can slide around one another & make the aggregate denser



EARLY-STAGE AGGREGATION → MIDDLE-STAGE AGGREGATION

- doublet formation

- growth of flocks
- fractal structures
- coalescence
- sedimentation



fractal aggegate

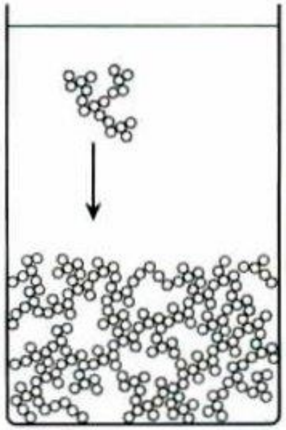


Fig. 7-41: Sediment structure obtained under conditions of rapid aggregation.

Evolution of structure of aggregates (II)

late-stage: structure of "particle assembly" depends on preceding events

gelation

- formation of very voluminous flocks due to rapid aggregation (attraction-driven)
- entire dispersion percolates into a network that can span the whole sample volume

glass transition

- [particle] increase: particles "pack" randomly, still liquid-like structure
- viscosity increases dramatically as transition is approached
- above glass transition: sample cannot equilibrate (frozen)
- colloids as model ("big atoms") for studying this univeral effect

Jeroen Appel, *PhD thesis* **2017**, Wageningen Univ. (NE)

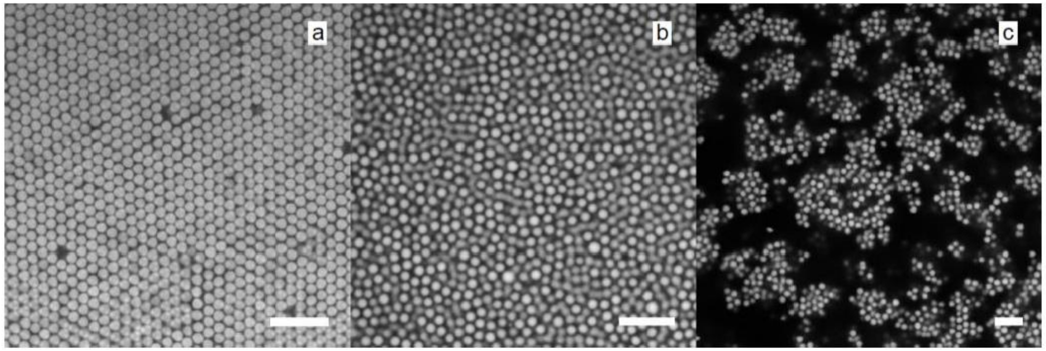


Figure 1.4: Confocal microscopy images of pTFEMA-pTBMA colloids in three different solid-like phases. A colloidal crystal (a), colloidal glass (b) and colloidal gel phase (c). Scale bars 10 μm.

crystallization

- occurs for colloids with size dispersity < 10% that are stable to aggregation (repulsion-driven)
- colloidal crystallization is an entropic effect

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