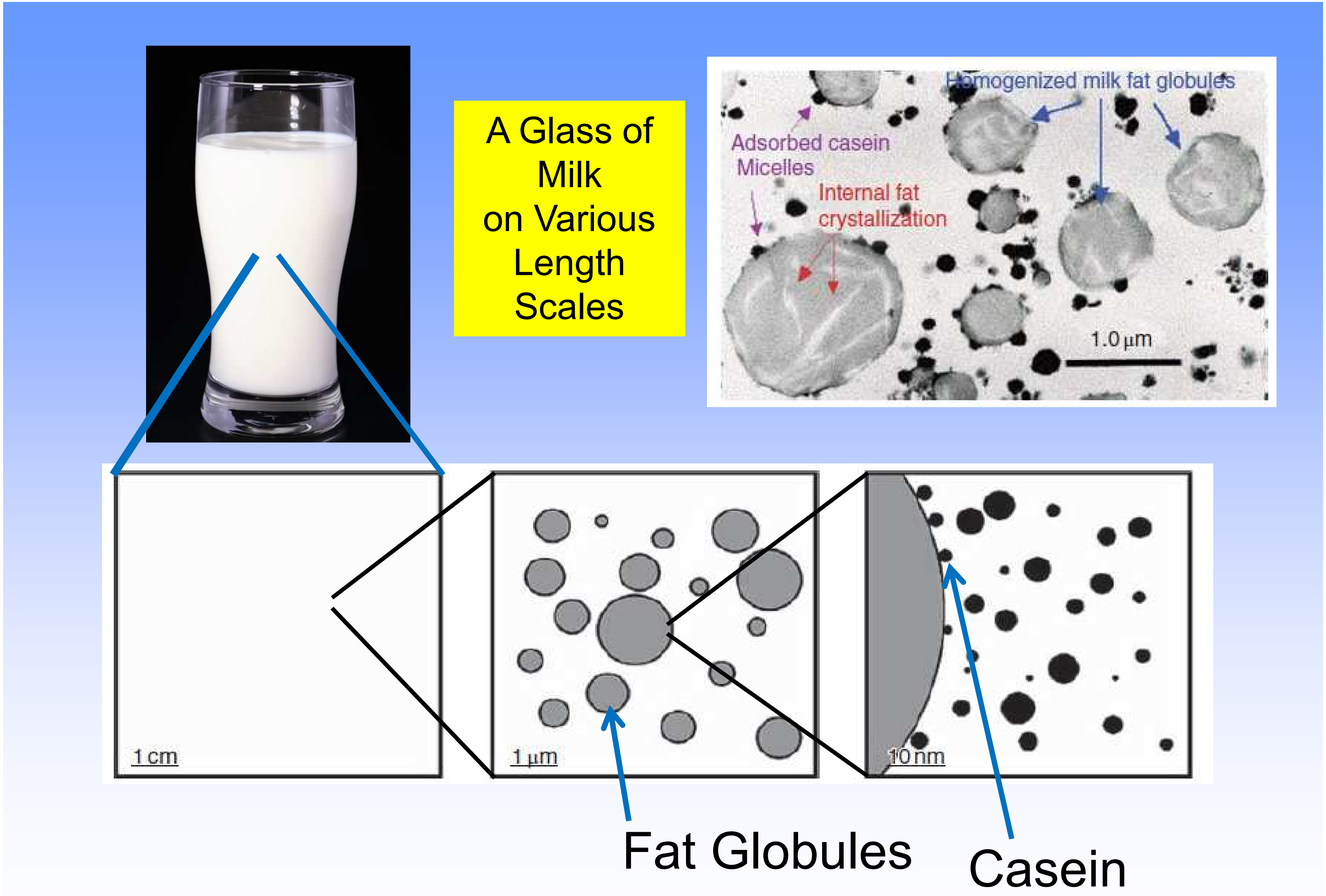
Stability of Colloids, Emulsions, Bubbles and Foams:

DLVO and Beyond



Kontogeorgis & Kiil, *Introduction to Applied Colloid and Surface Chemistry*-John Wiley & Sons (2016)

Emulsions

Emulsions are dispersed systems composed of immiscible or partially miscible liquid phases. The word emulsion comes from the Latin "to milk".

Emulsions are often dispersions composed of an oil (O) and water (W) and are thus typically classified as oil-in-water (O/W) or water-in-oil (W/O) emulsions, although more complex combinations are well known (such as W/O/W emulsions).

Emulsions are relatively static systems with rather large droplets (diameter of about 1 μm), but are typically thermodynamically unstable that will eventually phase separate. Hence, they require emulsifiers, most often mixed surfactants (or other substances, e.g., synthetic polymers, proteins or nanoparticles).

Kontogeorgis & Kiil, *Introduction to Applied Colloid and Surface Chemistry*-John Wiley & Sons (2016)

The Art of Making Emulsions

Making emulsions is sometimes more of an art than a science and we encounter less than "scientific" terms such as "skin feel", "creaminess", "oilyness", "shelf life" etc.

The work, W, required to make an emulsion is:

$$W = \gamma \Delta A$$

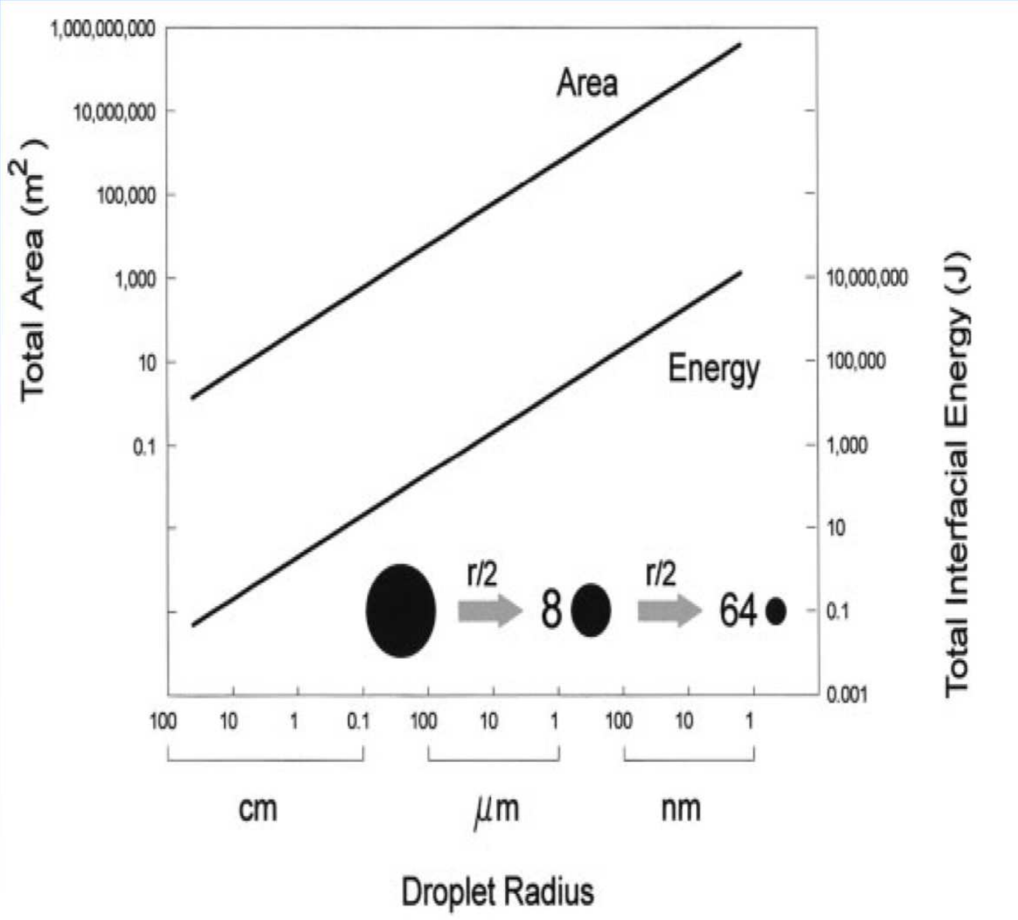
where γ is the interfacial tension and ΔA is the change in surface area .

Kontogeorgis & Kiil, *Introduction to Applied Colloid and Surface Chemistry*-John Wiley & Sons (2016)

Interfacial Tension and Energy Required for Dispersion

Work of creating surface or interface = γA

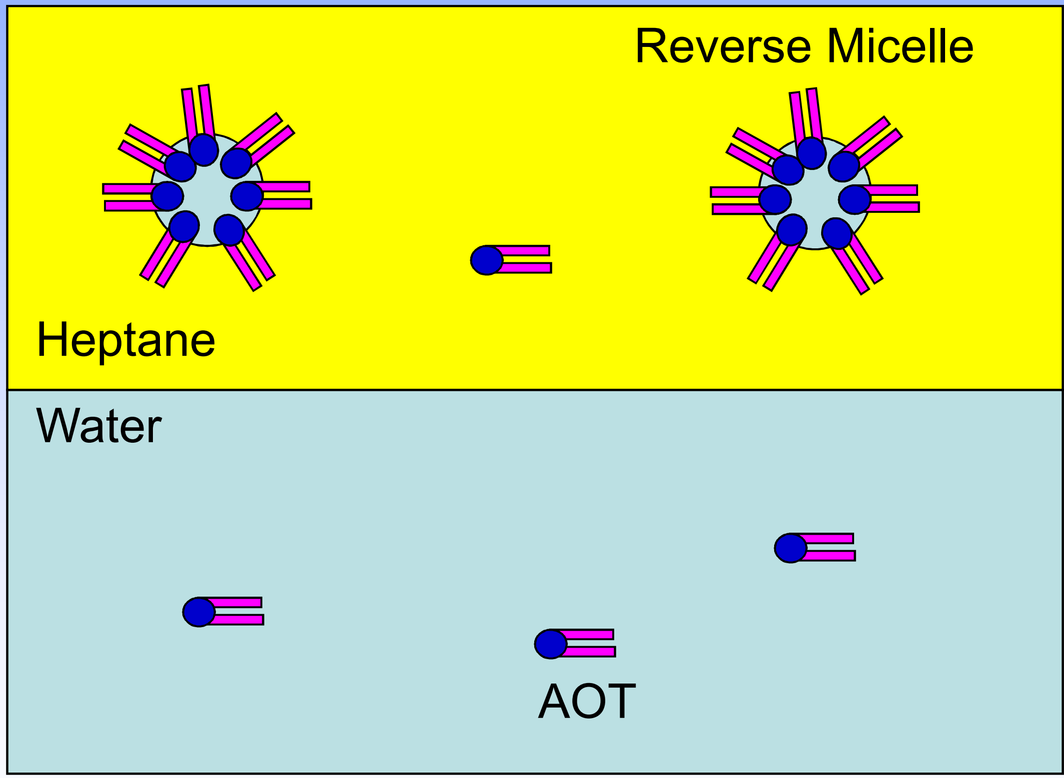
For dispersal of one barrel of oil in water:



Methods of Preparing Emulsions

- Spontaneous
- Non-Spontaneous
  - Mechanical (Stirring or Shaking)
  - Ultrasonic Irradiation
  - Extrusion
  - Shear
  - Inversion

Spontaneously Formed AOT-Water-Heptane Winsor Type II (W/O) Microemulsion



The size of the water pool depends on the added salt concentration.

Characterization of Emulsions:

Type (W/O, O/W, O/W/O, W/O/W, bicontinuous)

Conductivity (high if water the continuous phase, low if oil)

Rheology (Viscosity)

Interfacial Tensions

Drop Size

Size Distribution

Opacity (refractive index matching/mismatching)

Stability (temperature, salt, acid/base, additives, centrifugation, shear)

Demulsification

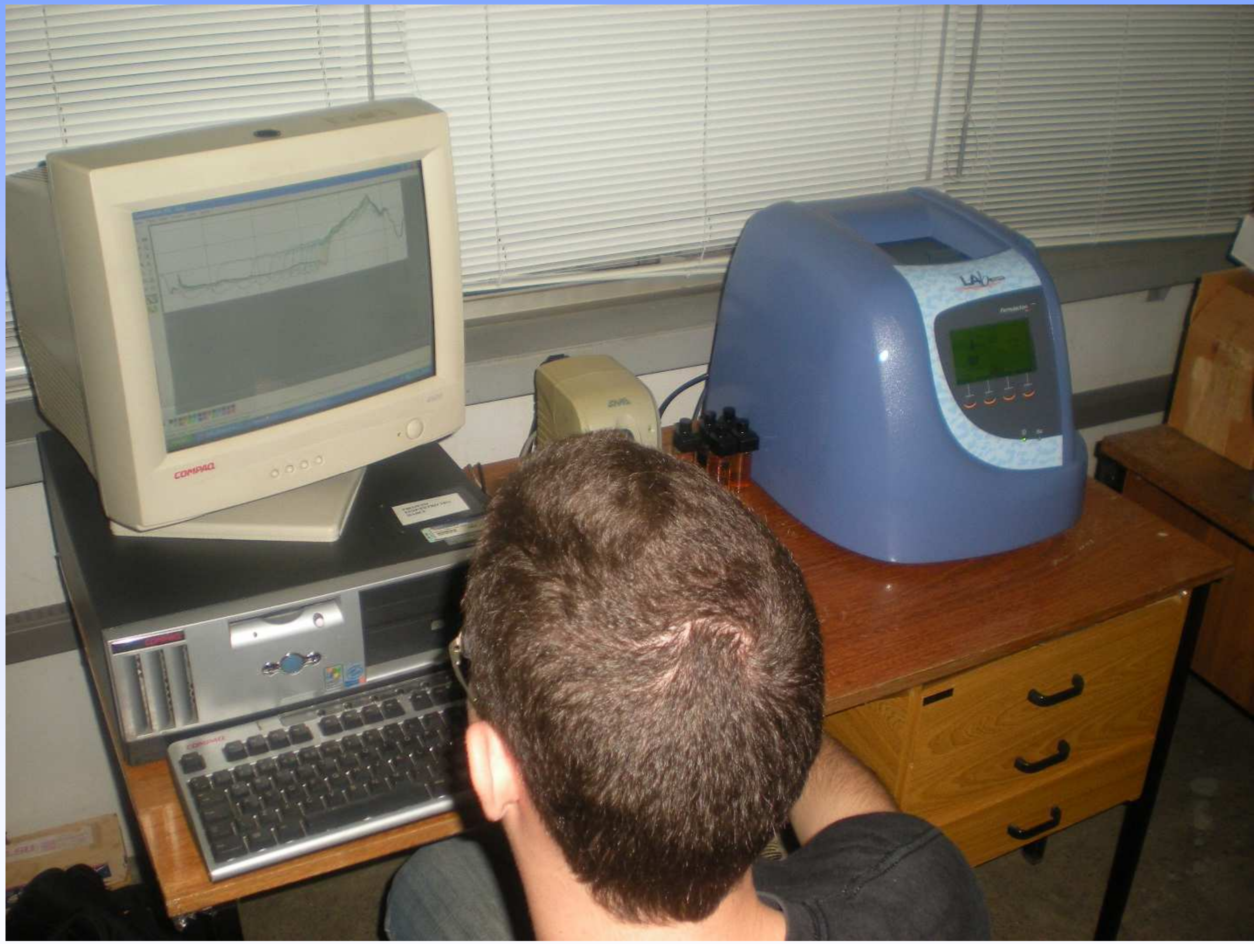
Sterically Stabilized

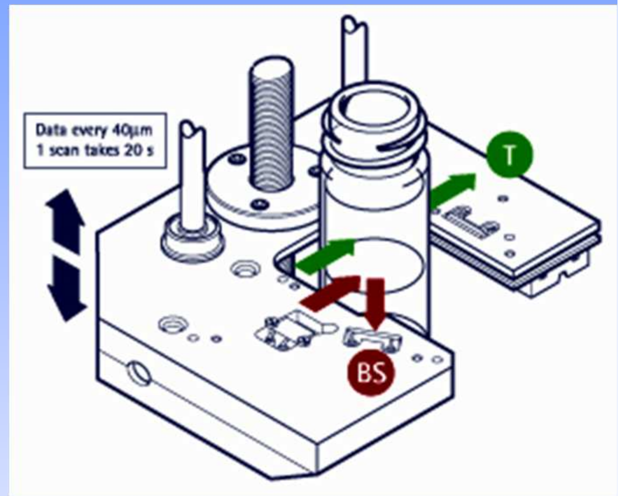
Electrostatic Field (desalting crude oil)
Centrifugal Force (creaming/sedimentation)
Extrusion (pores that collect dispersed phase)
Additives (demulsifiers)
Temperature (Phase Inversion Temp.)
Freeze-Thaw (freeze the aqueous phase)
Ostwald Ripening

Electrostatically Stabilized

Reduce Zeta Potential (Salt)
Reduce Surface Charge Density (additives)

Turbiscan for Studies of Emulsion Stability





Transmission

Back Scatter

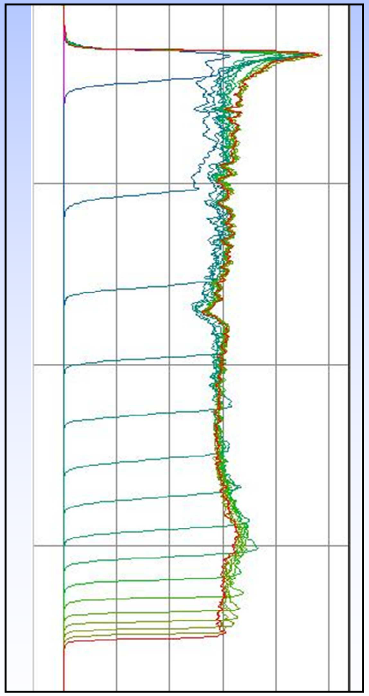
http://www.formulaction.com

Tubiscan Kinetics of Milk Flocculation

(powdered milk emulsion in water following addition of vinegar)

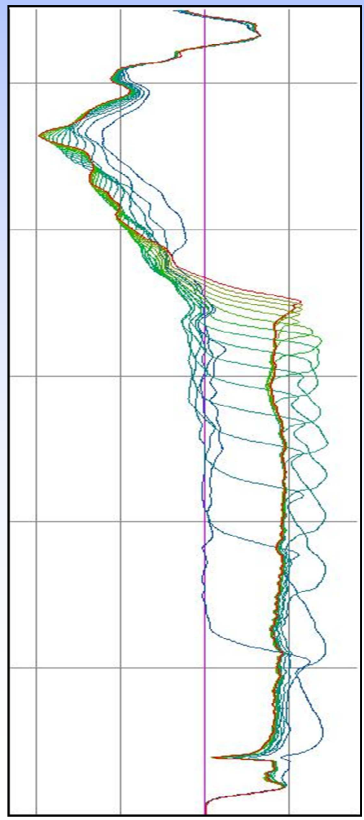
Transmission

(850 nm)



Back Scatter

(850 nm)



Factors Affecting Emulsification:

- Oil phase
- Water/Oil Ratio
- Detergent (Emulsifier)
- Co-surfactants
- Salt
- Temperature

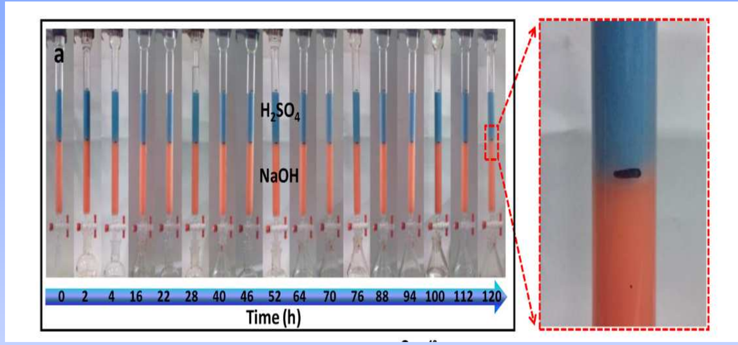
Water-in-Oil or Oil-in-Water Emulsions?

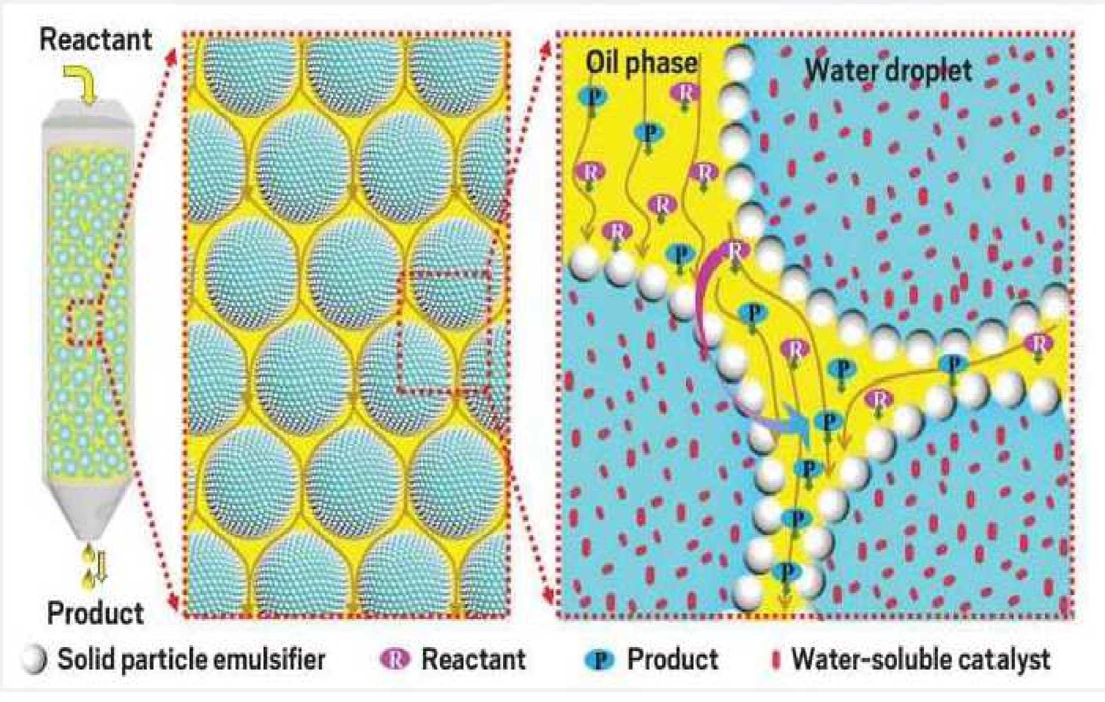
W/O Emulsions Disadvantages

- Higher cost of goods than o/w systems
- More difficult to manufacture and clean up
- Inherently less stable due to lack of cohesive double layer effect
- Often give a greasy occlusive skin feel

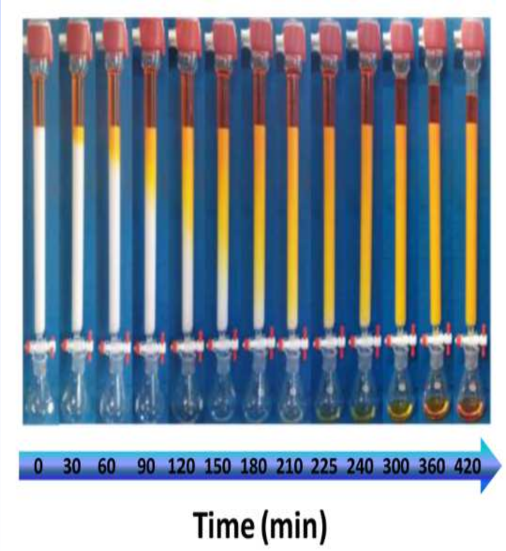
Pickering Emulsions: Emulsion Droplets Stabilized by Colloidal Particles. Flow System for Continuous Biphasic Catalysis

Water Droplets are Stationary:



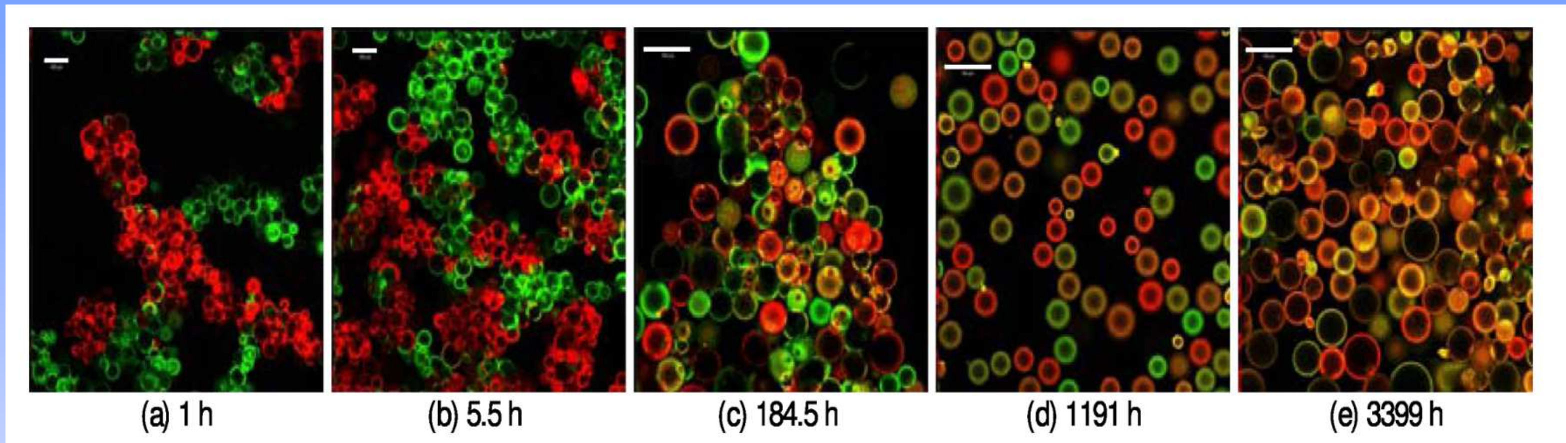


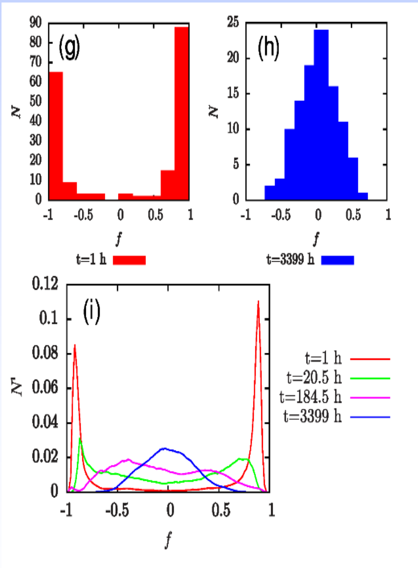
Continuous Oil Phase Flows down the Column:

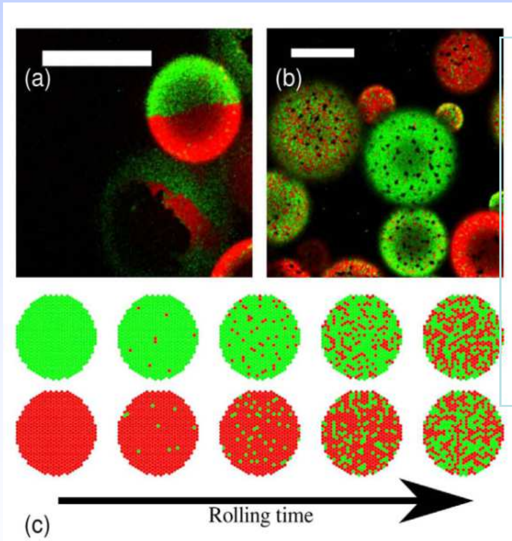


Zhang et al., J. Am. Chem. Soc. **2016**, *ASAP* (DOI: 10.1021/jacs.6b04265)

Pickering Emulsions: Emulsion Droplets Stabilized by Colloidal Particles. Particle Exchange Mechanisms using Colored Particles







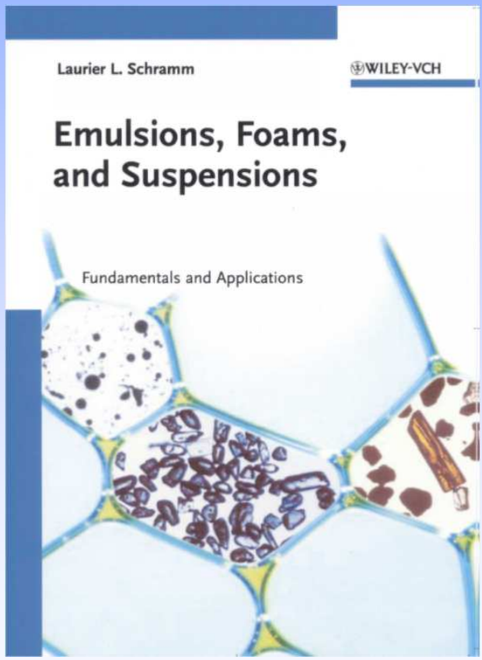
Transport Mechanisms:

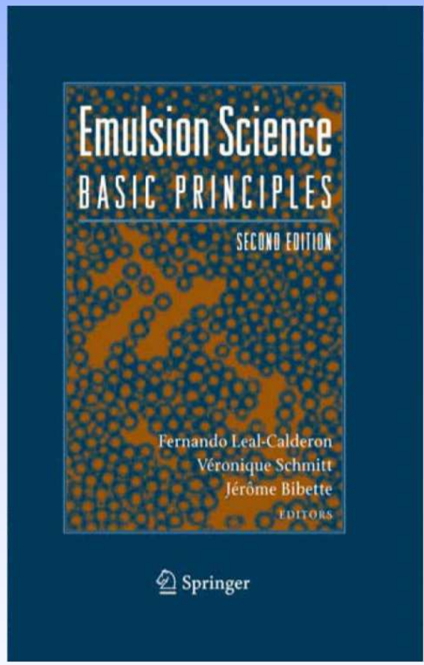
Major: Interdroplet Contact Transfer (Interfacial Fusion-Fission)

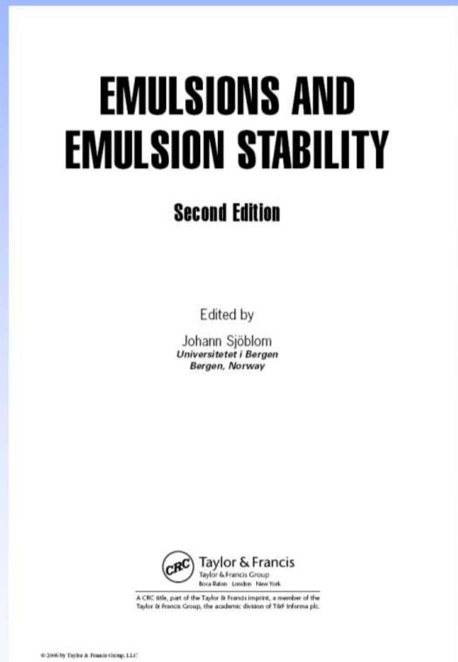
Very Minor: Free Particle Migration

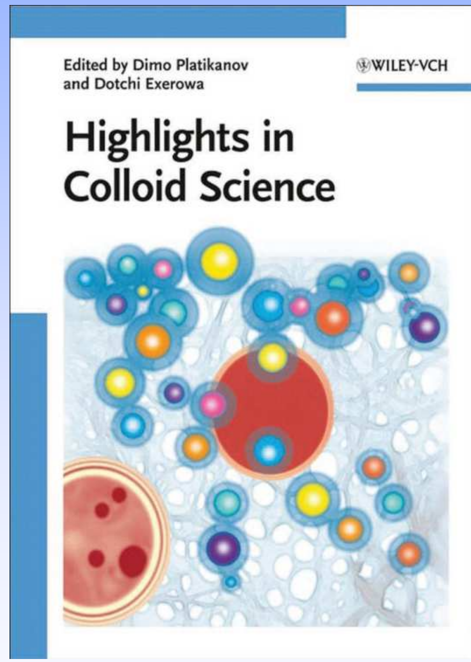
French et al., Scientific Reports **2016**, 6:31401 (DOI: 10.1038/srep31401)

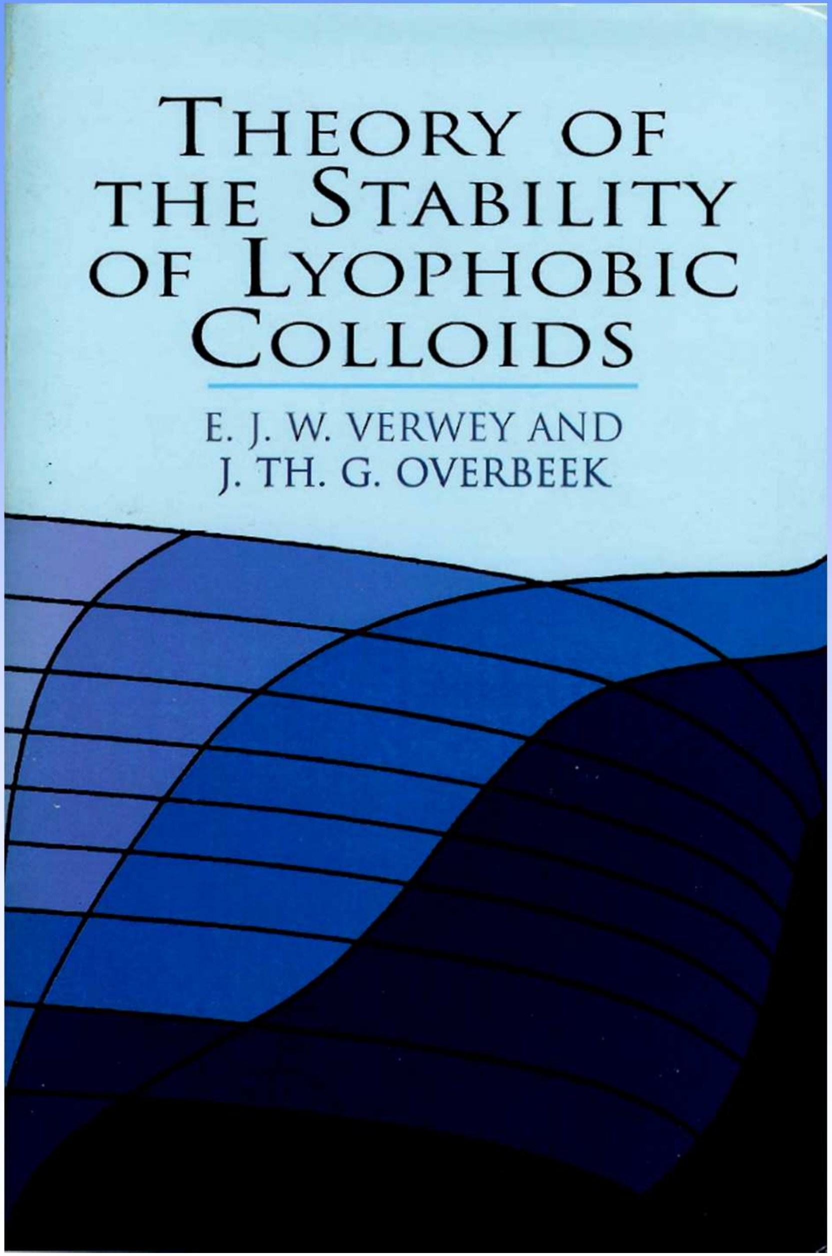
Bibliography
Emulsions











Colloid Stability

DLVO Theory

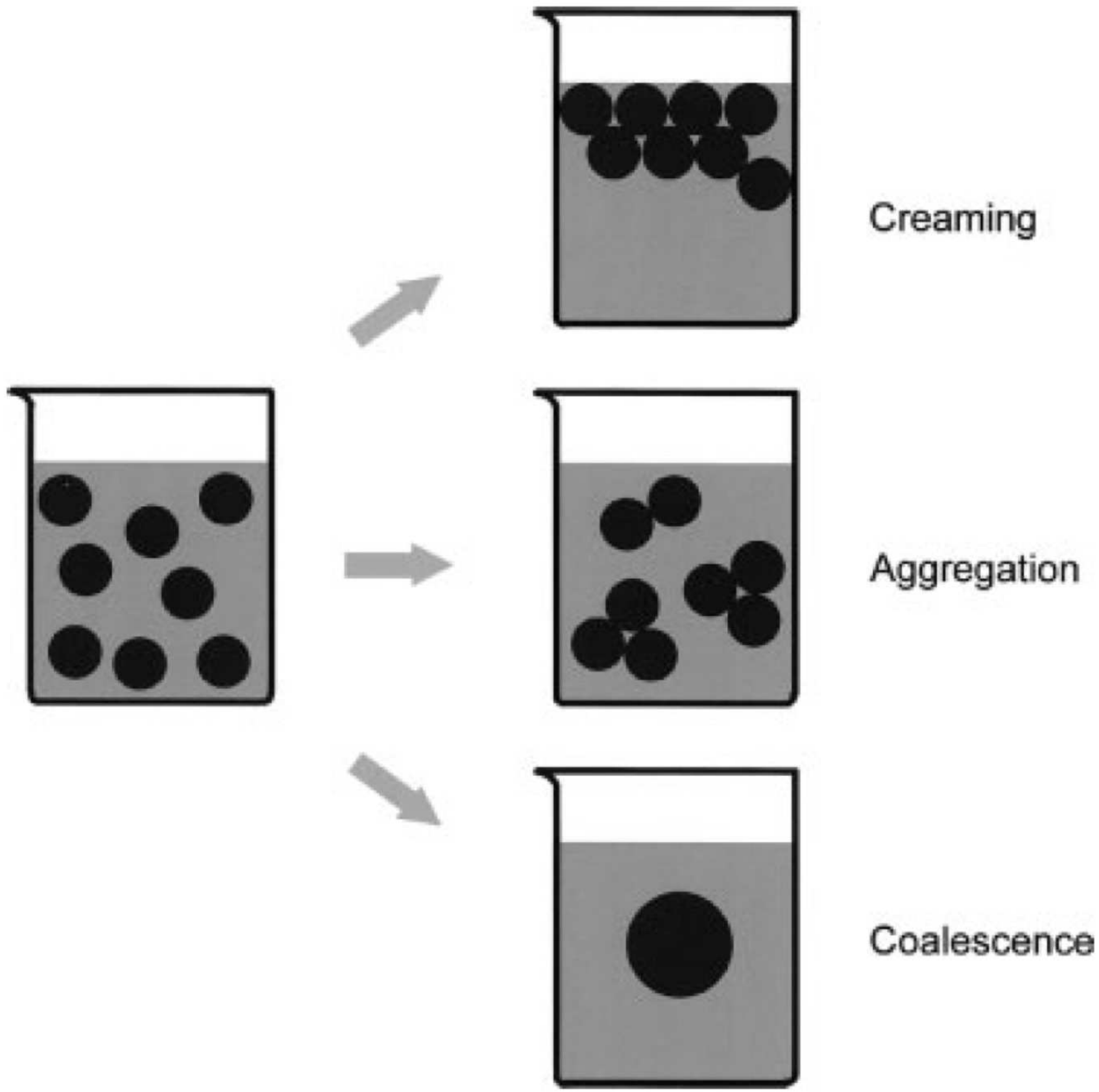
Derjaguin

Landau

Verwey

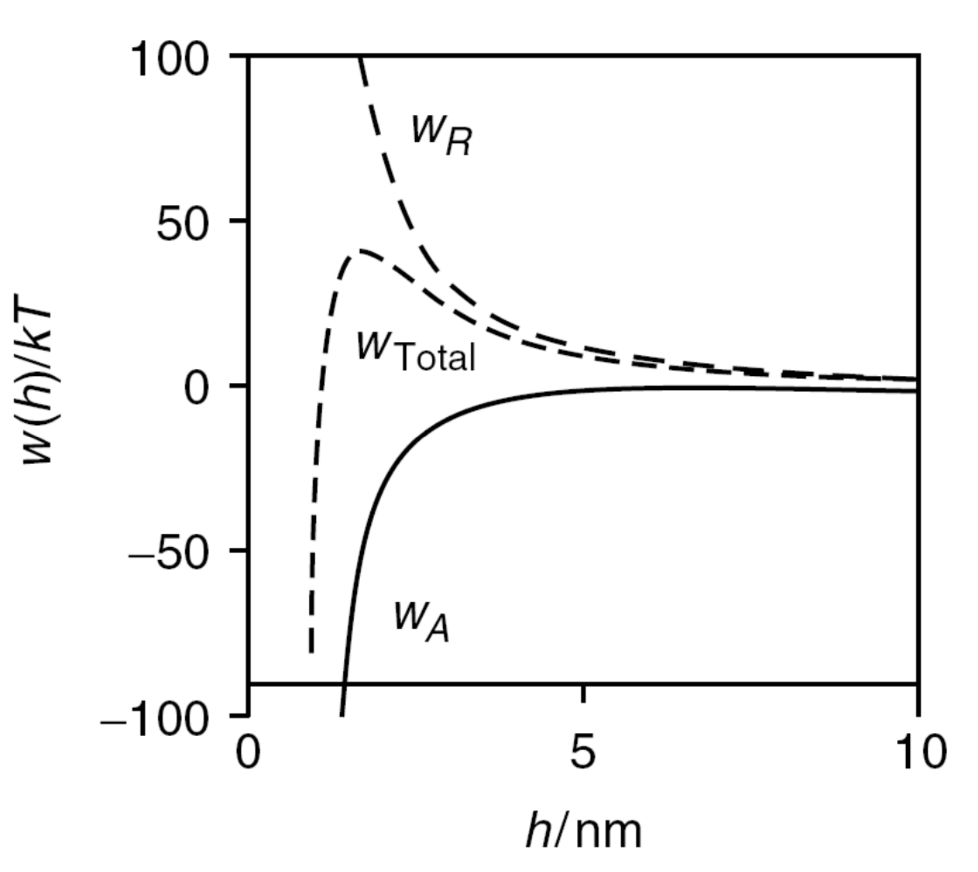
Overbeek

Creaming, Aggregation and Coalescence:



Colloid Stability (DLVO):

Repulsive at Large Distances, Attractive at Short Distances



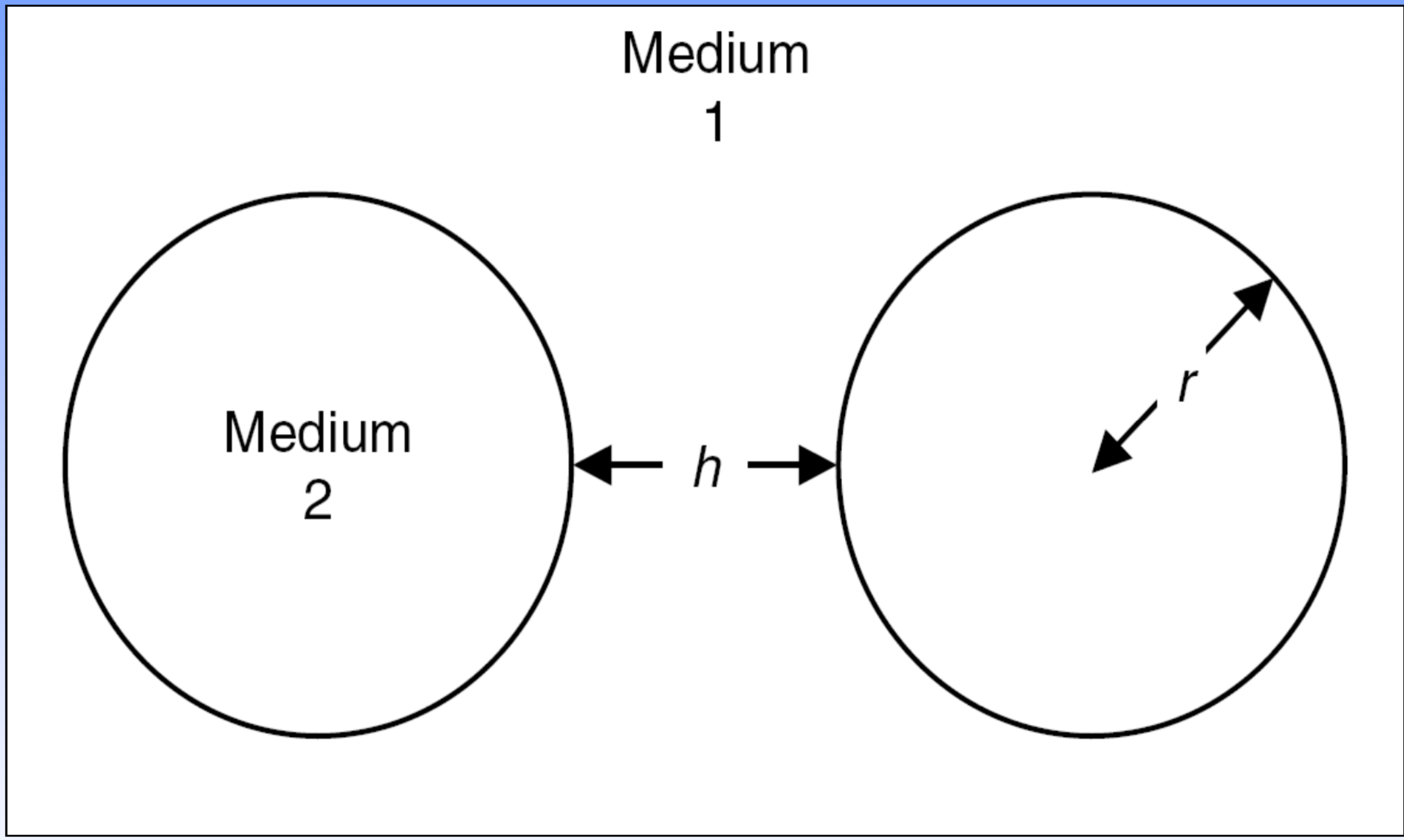
Metastable.

Floculation or Coalescence upon raising the temperature or lowering the barrier (salt, addition of acid, etc.).

Example: Milk

Vinegar →

Interaction Between a Pair of Identical Colloid Particles of Radius *r* and Inter-Surface Separation *h*



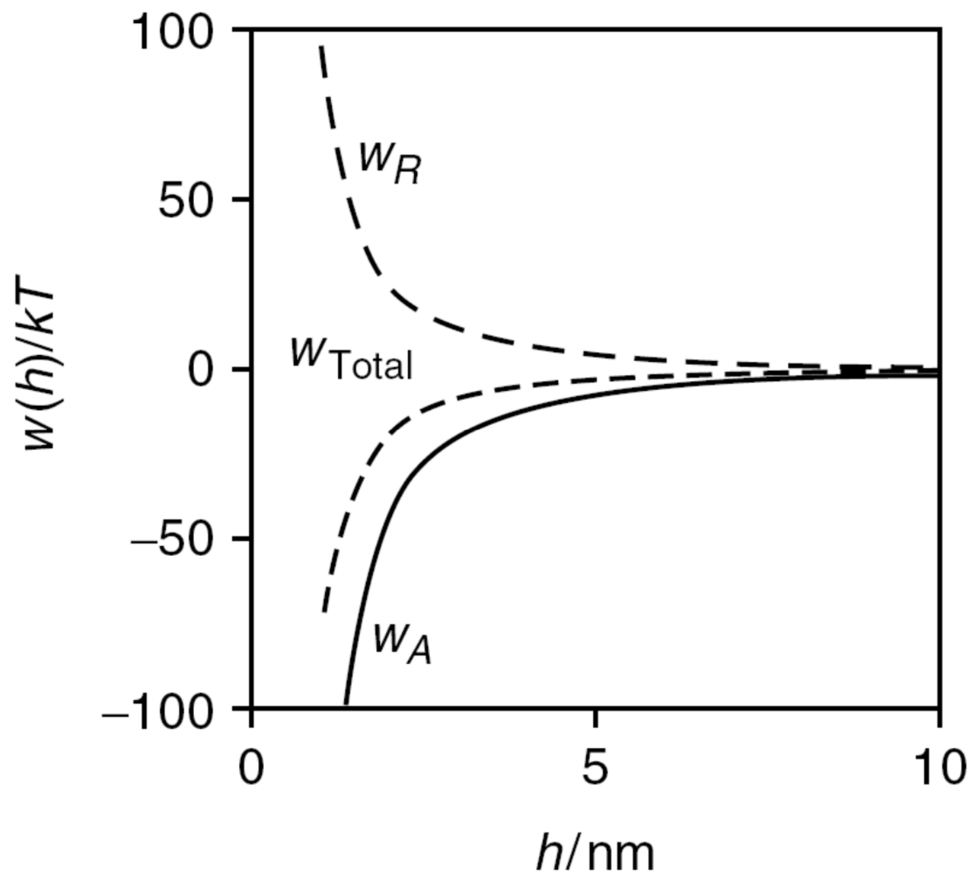
$$W_{Total} = W_{Attraction} + W_{Repulsion}$$

Attractive Intermolecular interactions ($W_{Attraction}$)

Electrostatic or Steric Repulsion ($W_{Repulsion}$)

Four Limiting Situations

1. Net Attractive at ALL Separations

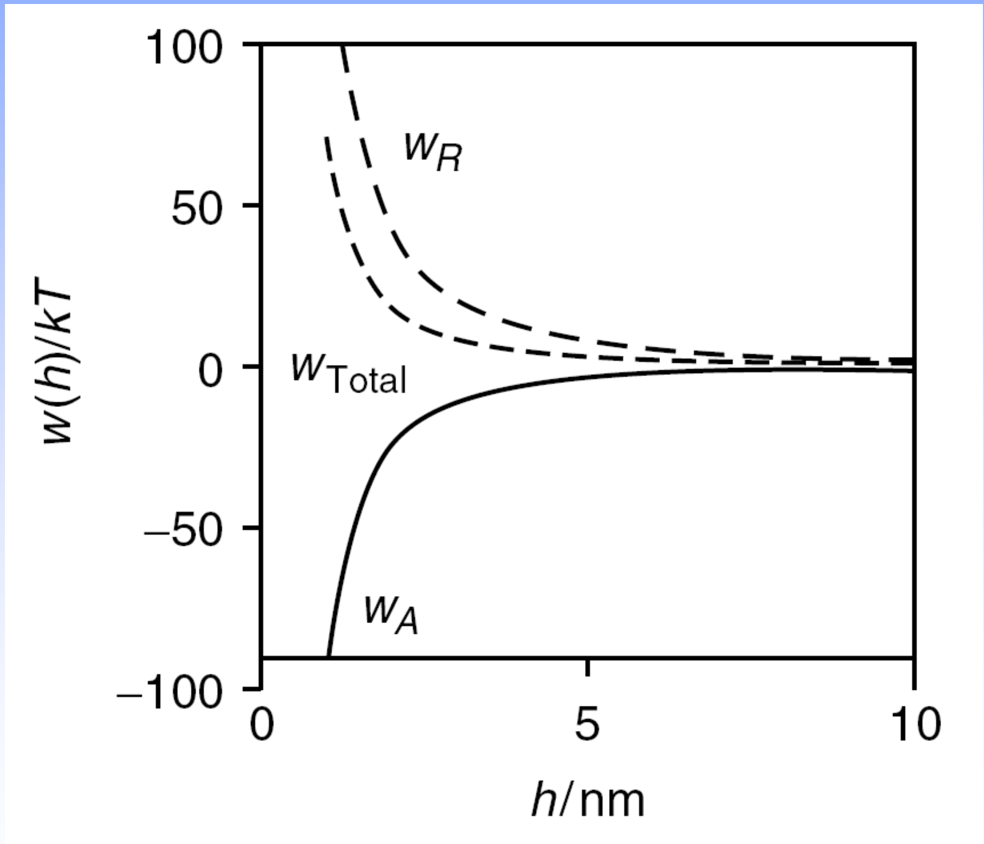


Intrinsically Unstable.

Fast Floculation or Coalescence.

Example: Olive Oil in Water with no stabilizers

2. Net Repulsive at ALL Separations

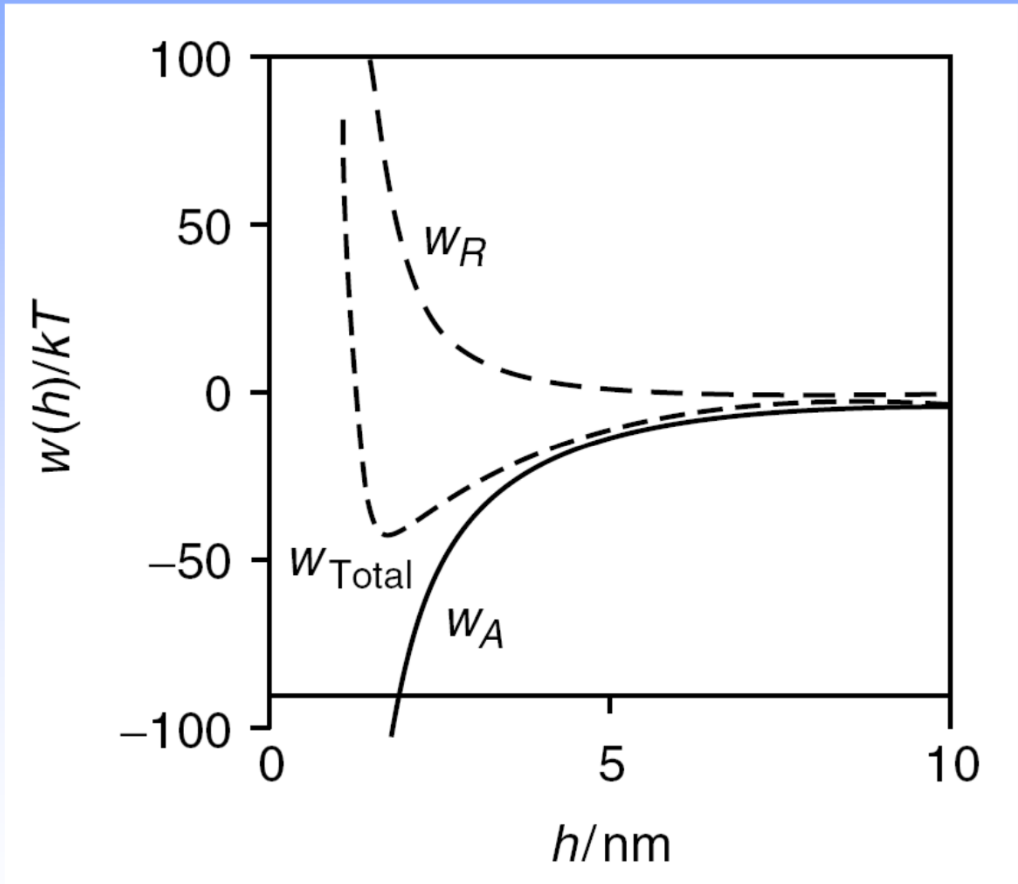


Intrinsically Stable.

No Floculation or Coalescence.

Example: Highly charged plastic spheres in water

3. Attractive at Large Distances, Repulsive at Short Distances

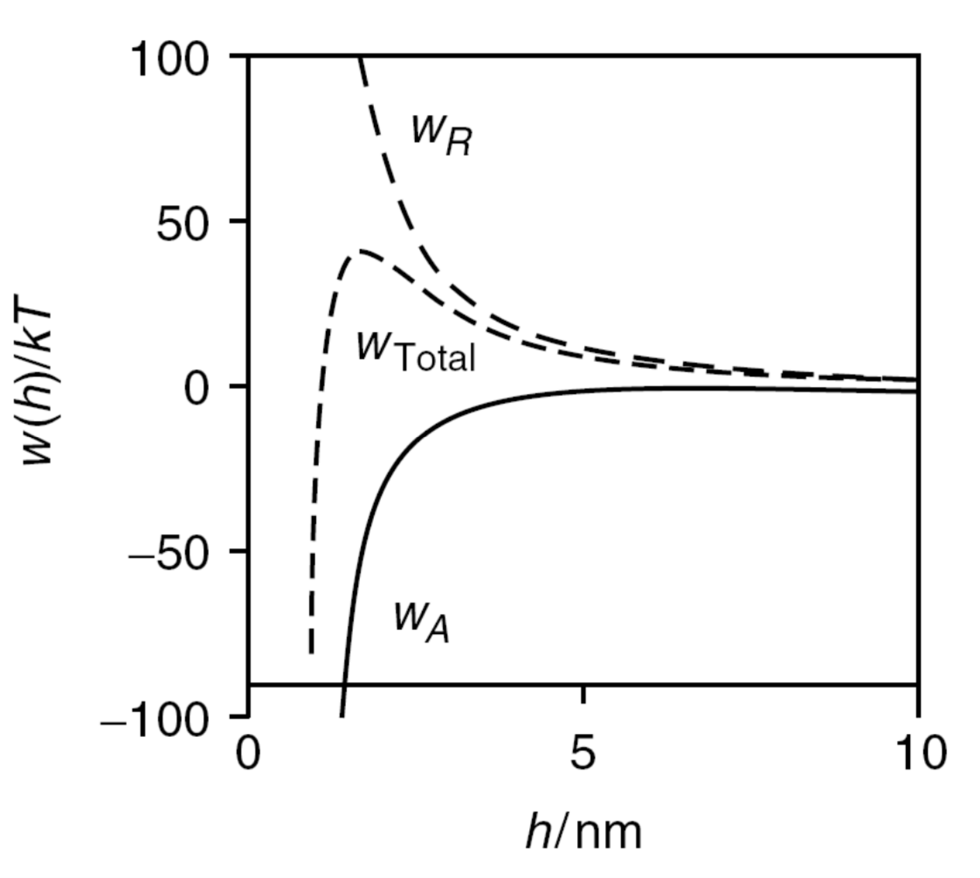


Metastable.

Rapid Floculation or Aggregation.

Example: Unstabilized Nanoparticles

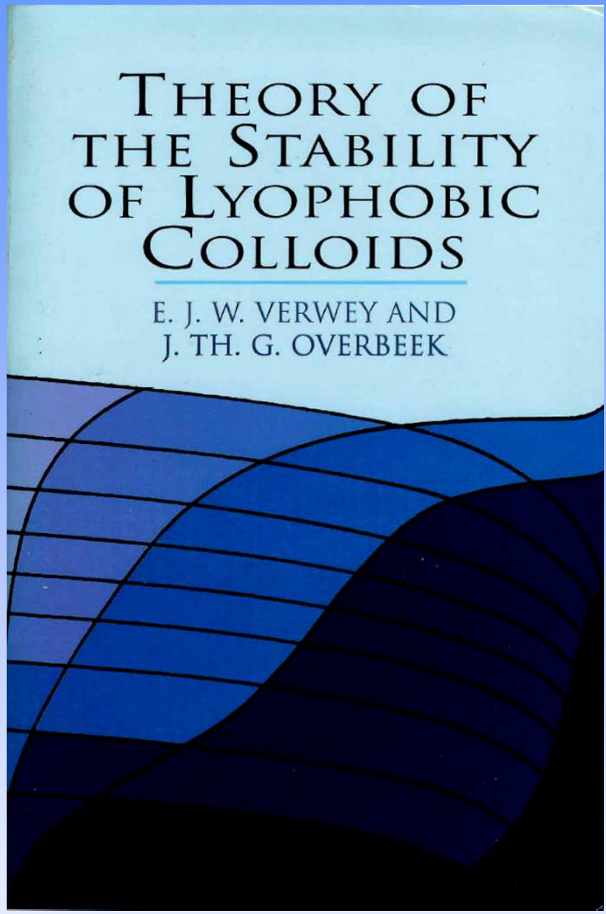
4. Repulsive at Large Distances, Attractive at Short Distances



Metastable.

Floculation or
Coalescence upon raising the temperature or lowering the barrier (salt, addition of acid, etc.).

Example: Milk

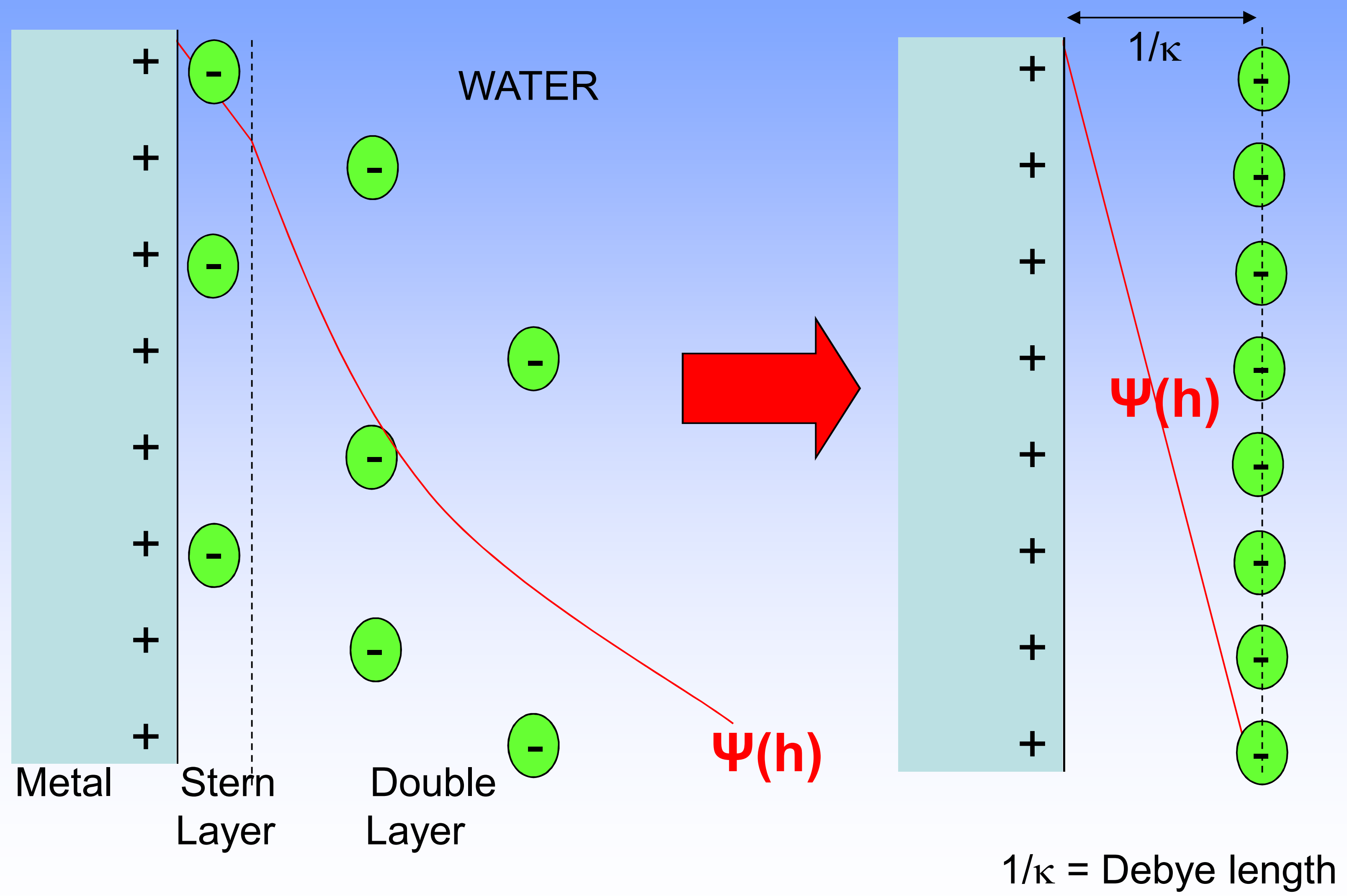


$$W_{Total} = W_{Attraction} + W_{Repulsion}$$

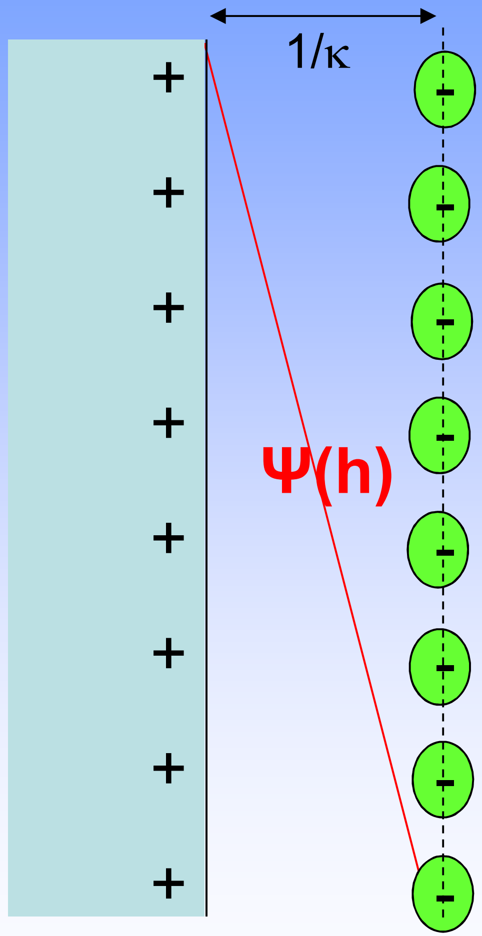
Attractive Intermolecular interactions

Electrostatic or Steric Repulsion

Classical Electrostatics: The Electrical Double Layer



Classical Electrostatics: The Debye Length

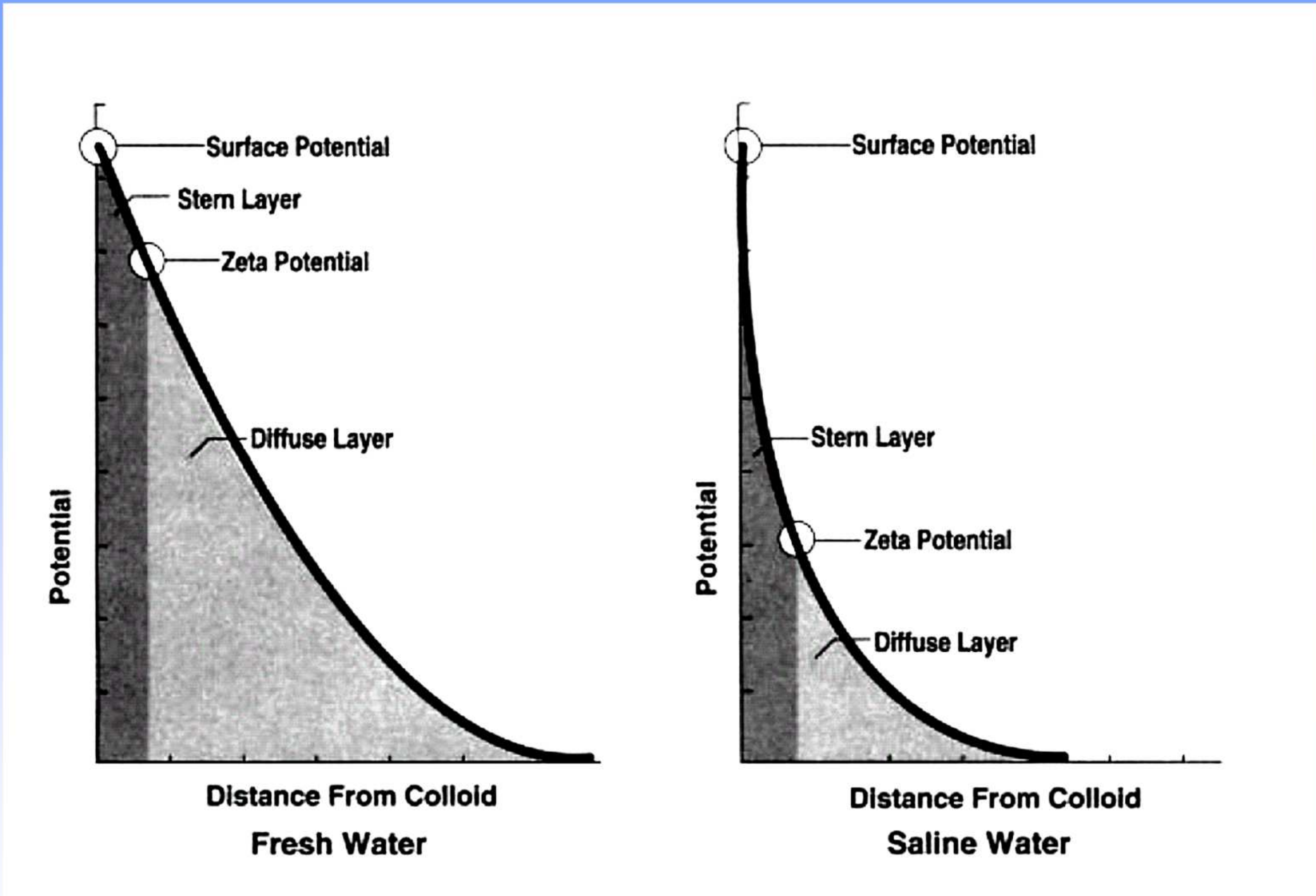


1/κ = Debye length

$$\kappa^{-1}(\mathrm{nm}) = \frac{10}{\sqrt{I(\mathrm{mM})}}$$

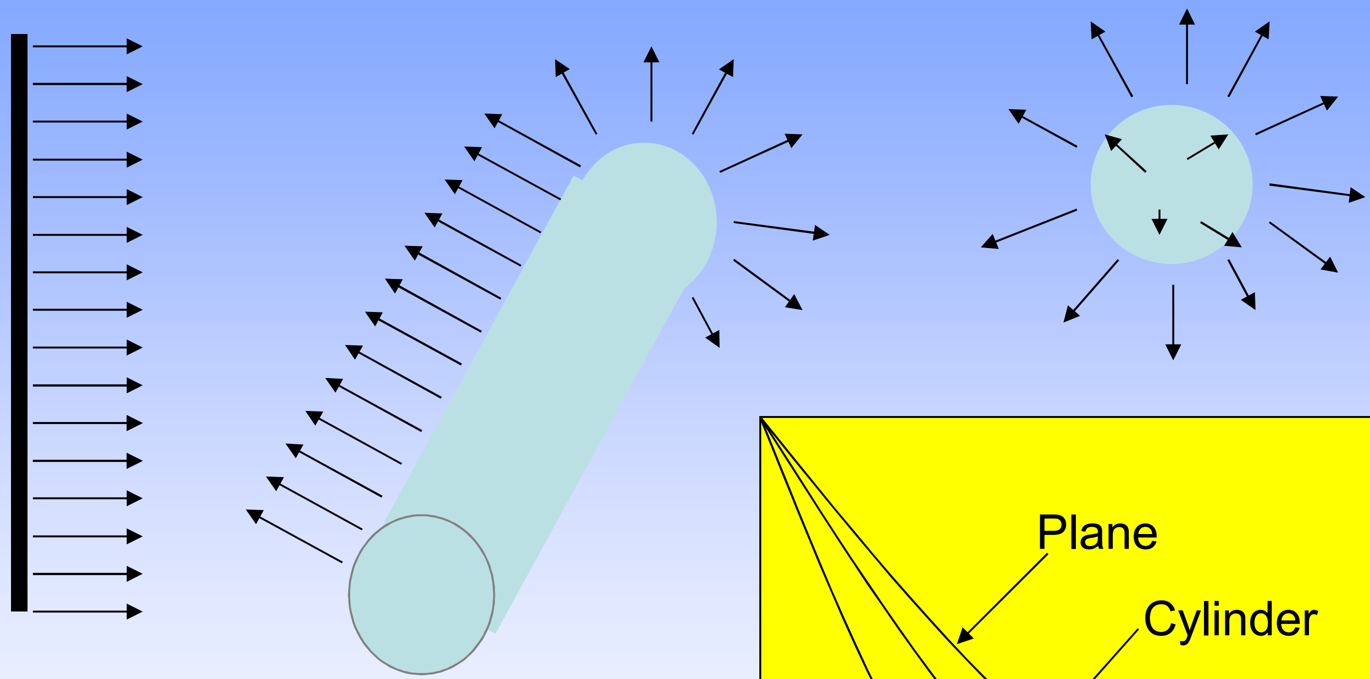
[NaCl (mM)	1/κ (nm)
1	10
10	3
100	1
1000 (= 1M)	0.3

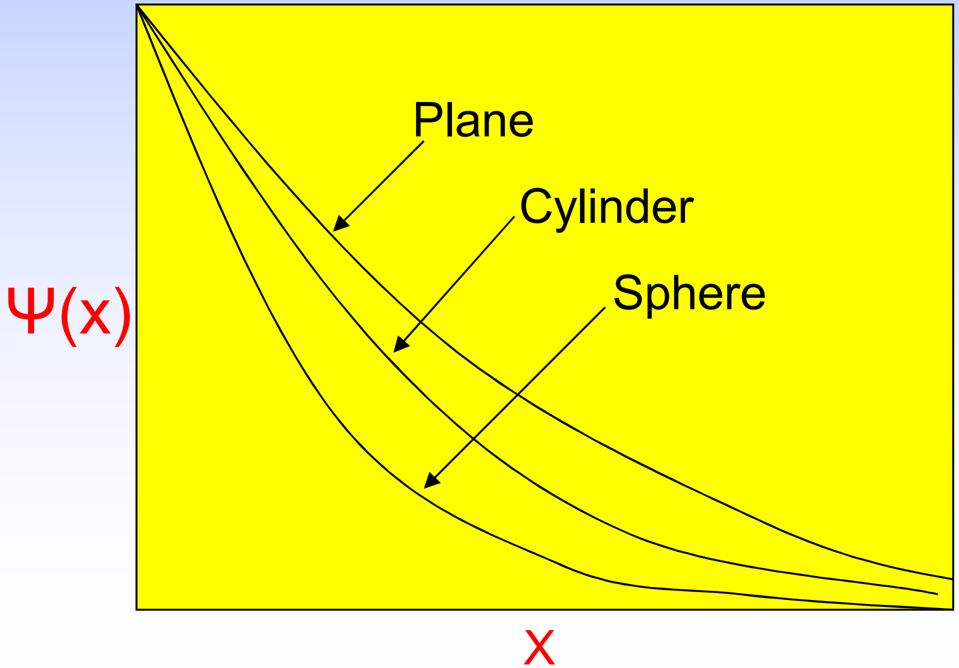
Effect of Electrolyte on the Electrostatic Potential



Nernst Equation: Ψ^o decreases 59 mV (= 2.303 x 26 mV) for each 10-fold increase in monovalent electrolyte concentration

Classical Electrostatics: The Poisson-Boltzmann Solution for a Charged Plane, Cylinder and Sphere





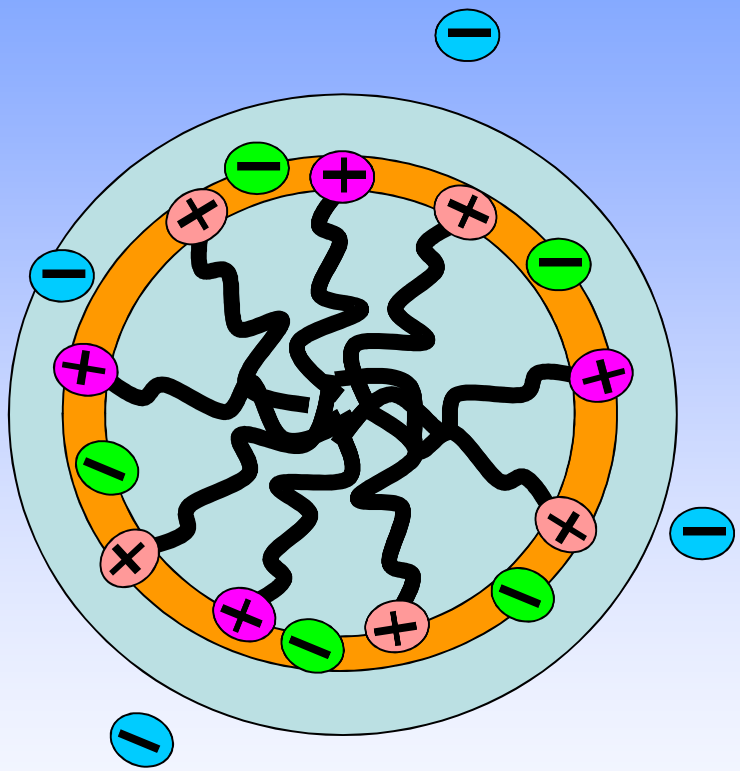
Plane:

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

Sphere:

$\Psi(x) = \Psi o \exp(-\kappa x)/[\kappa(r+x)]$

A "Real" Colloidal Interface



Non-Conducting Surface

Finite Ion Sizes

Ion and Water Penetrable
Interface

Stern-Layer or "bound" counterions (fraction Θ)

Double-Layer counterions

"Free" or Dissociated counterions (fraction α)

Counterion Selectivity

The Zeta Potential:

The effective potential at the shear surface (wherever that is...)

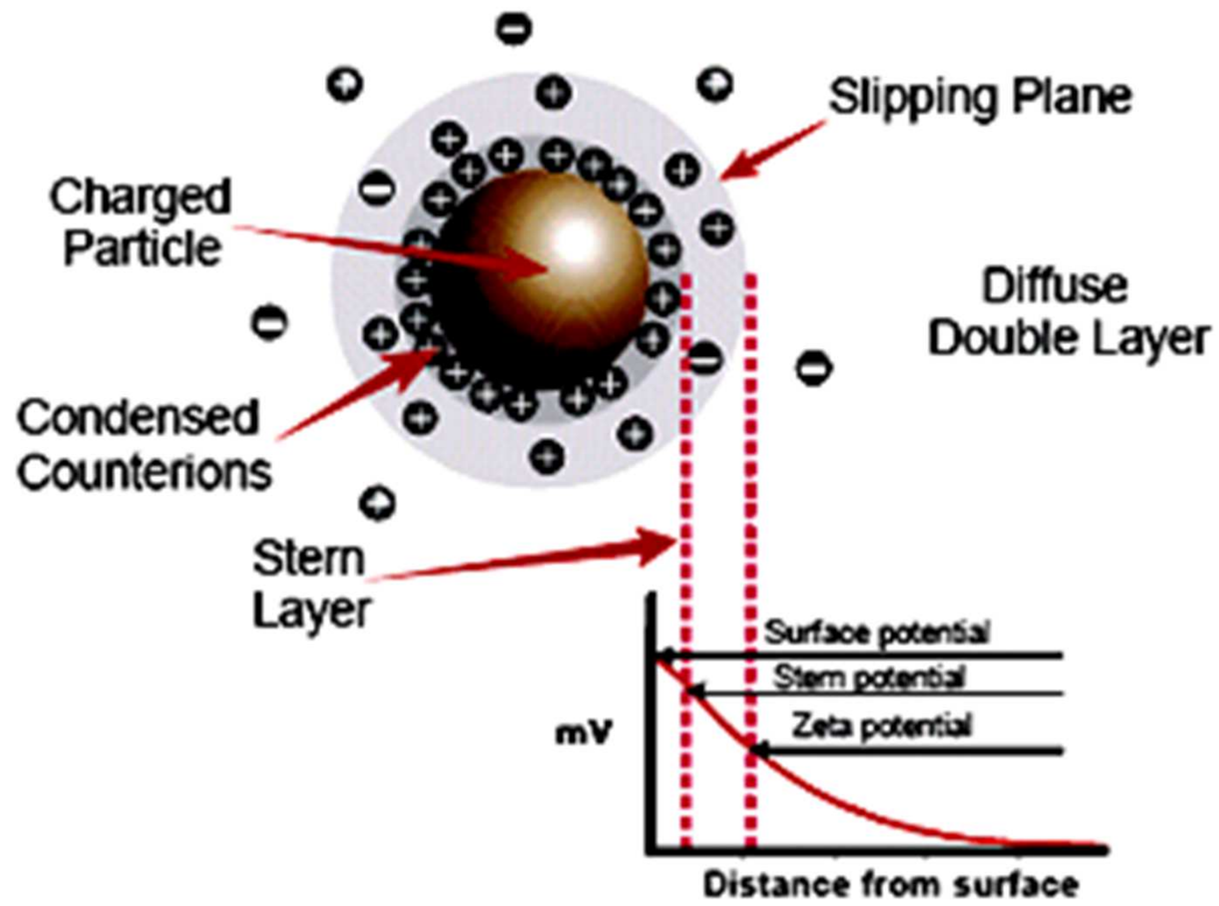
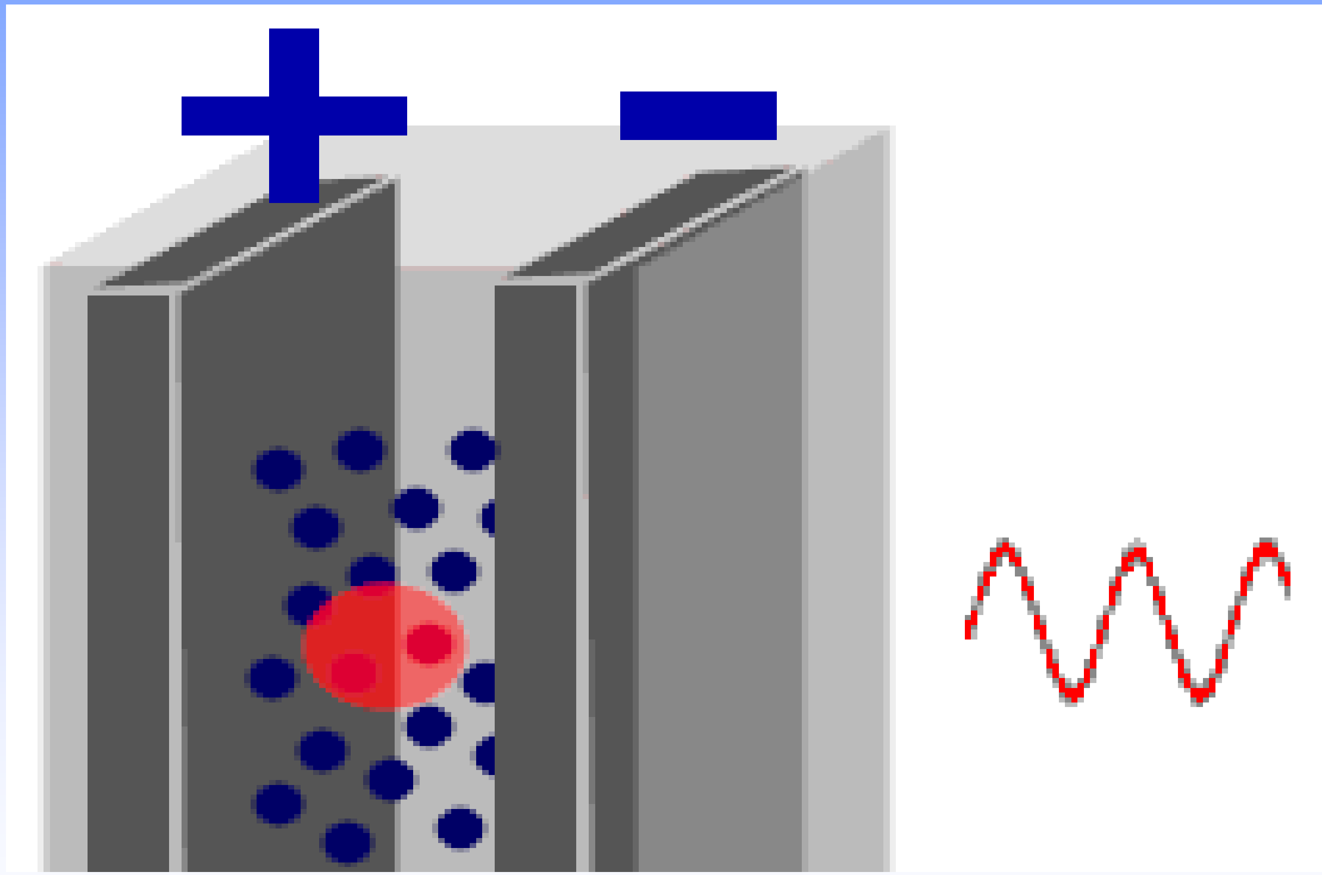


Figure 1: Schematic showing the distribution of ions around a charged particle.

Electrophoretic Mobility of Charged Particles

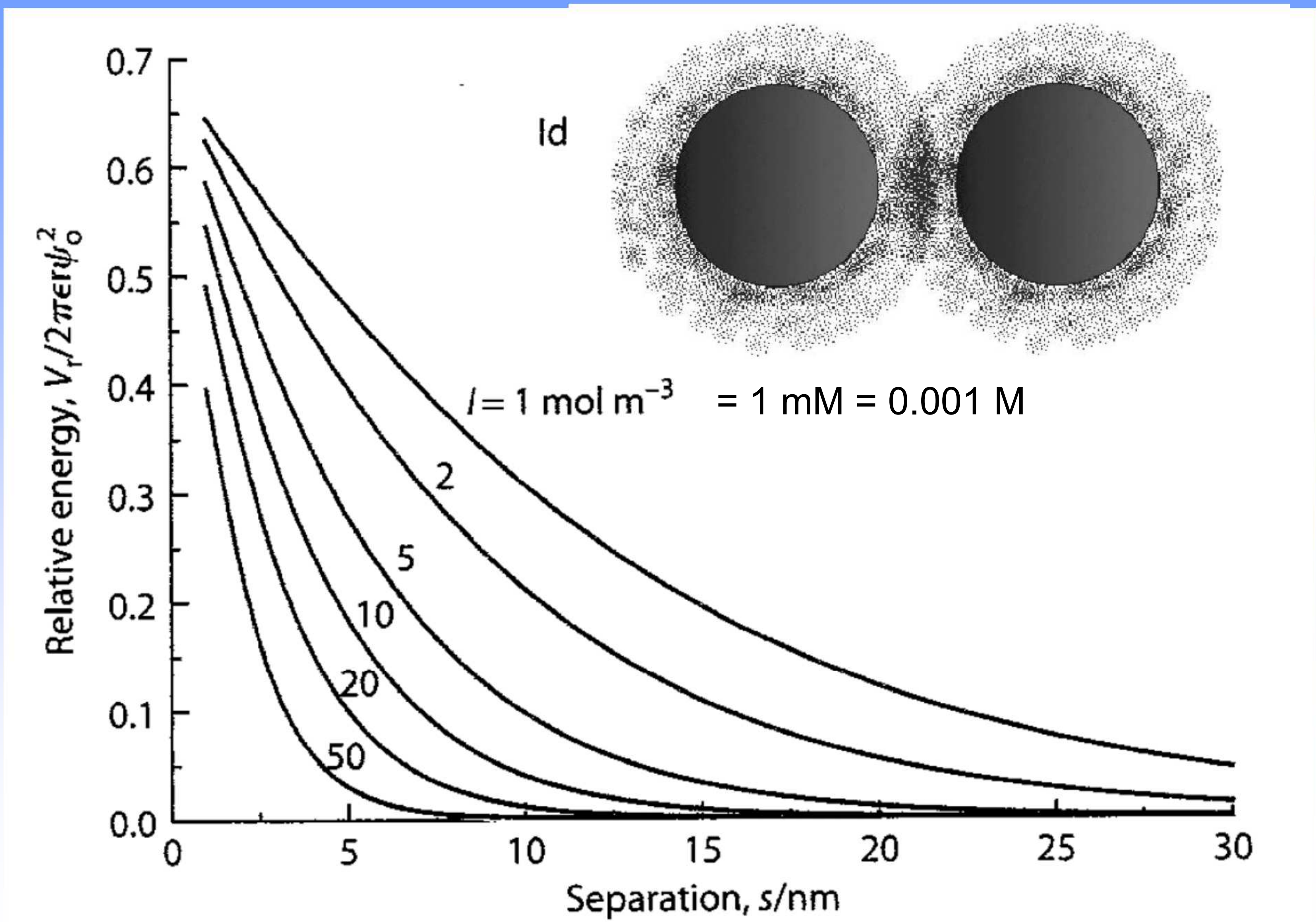
The Zeta Potential



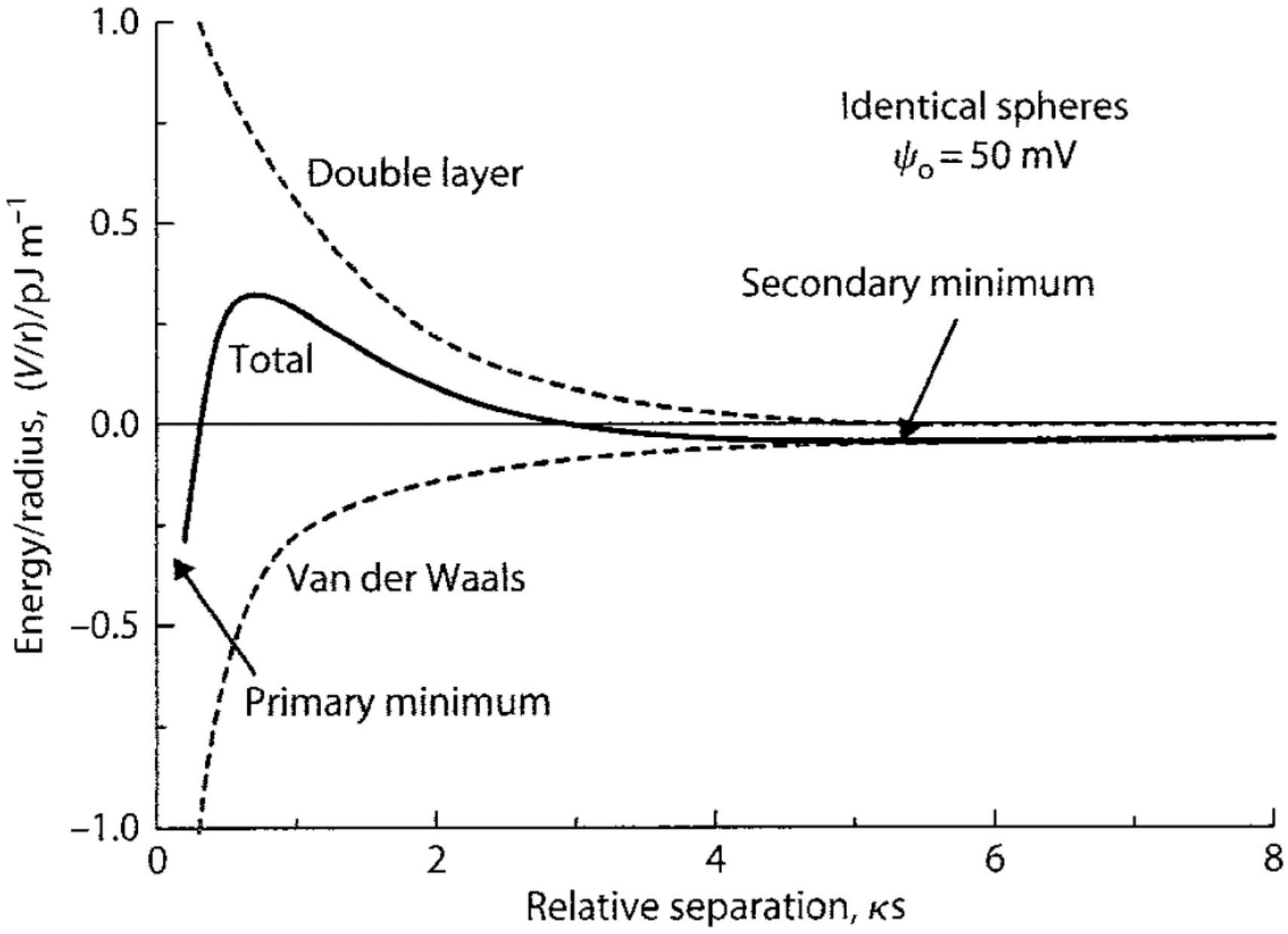
Electrophoretic mobility = $\mu_e = \varepsilon\zeta_{zeta}/\eta$

Medium dielectric constant and viscosity

Effect of added electrolyte on the Double-layer interaction



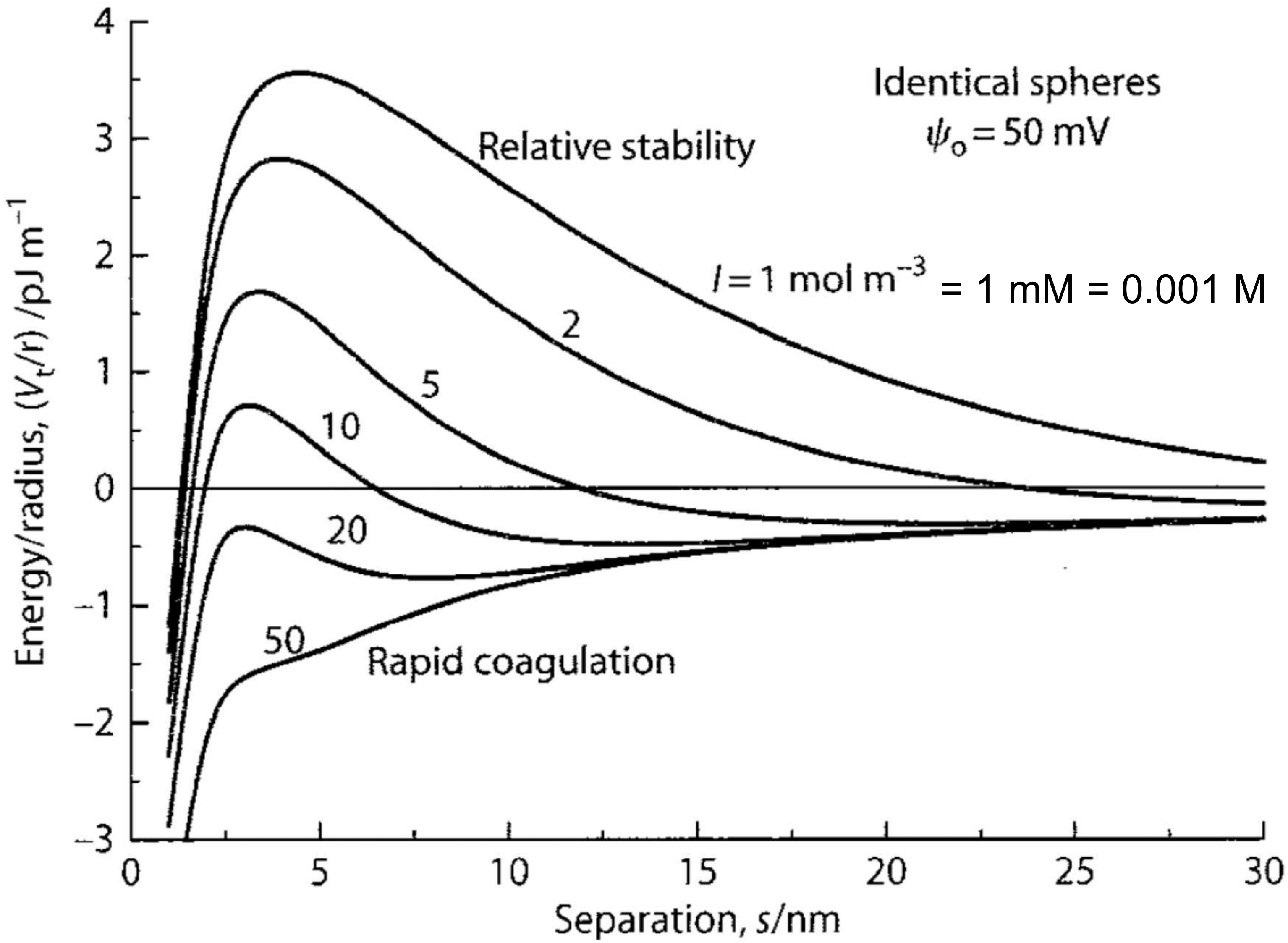
Effect of added electrolyte on the Colloidal interaction



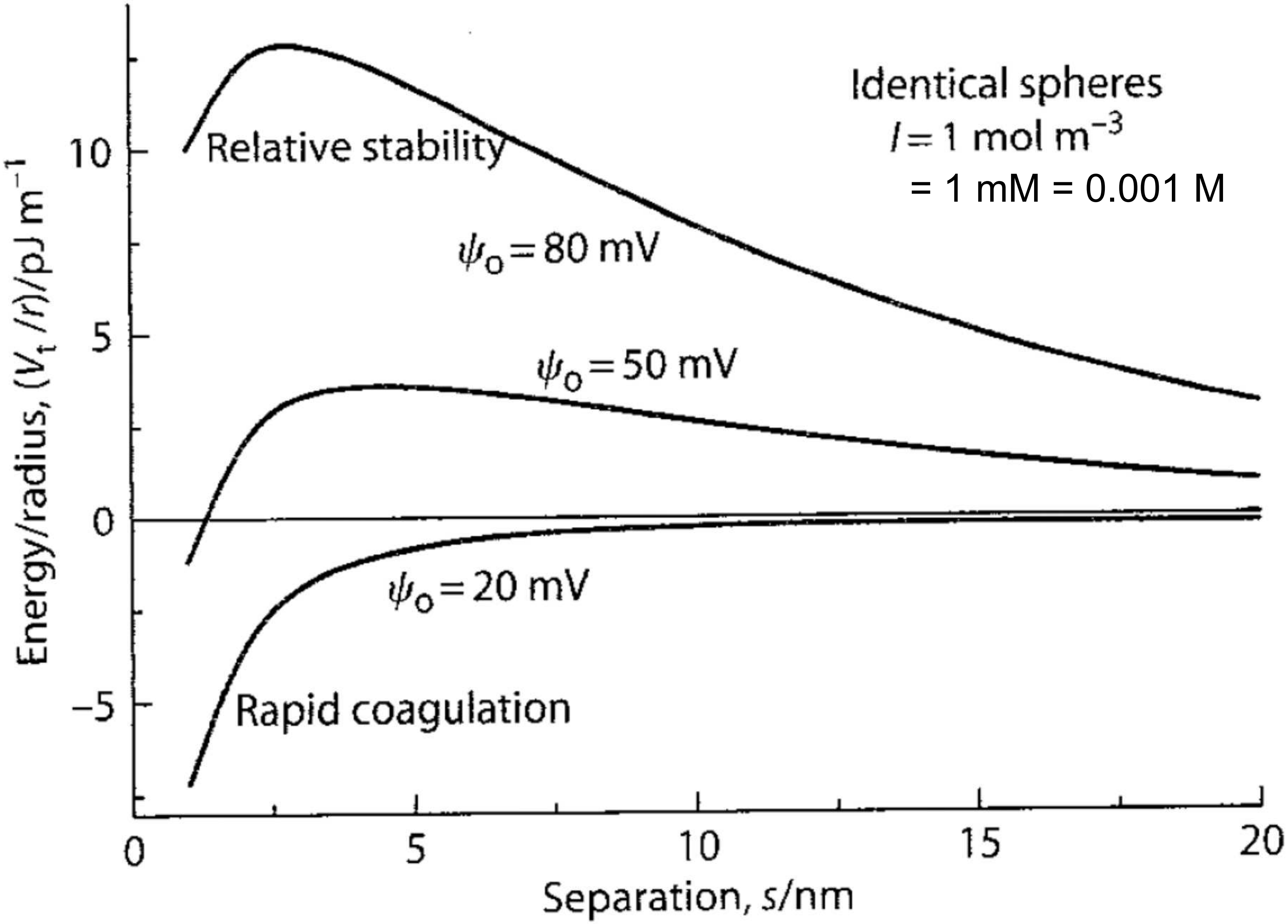
Stability Criteria based on the magnitude of the Zeta Potential

Stability characteristics		Zeta potential (mV)	
Maximum agglomeration and precipitation		+3 to zero	
Excellent agglomeration and precipitation		–1 to –4	
Fair agglomeration and precipitation		–5 to –10	
Agglomeration threshold (agglomerates of 2–10 particles)		–11 to –20	RT
Plateau of slight stability (few agglomerates)		–21 to –30	
Moderate stability (no agglomerates)		–31 to –40	
Good stability		–41 to –50	
Very good stability		–51 to –60	2 RT
Excellent stability		–61 to –80	3 RT
Maximum stability	– for solids	–81 to –100	4 RT
	– for emulsions	–81 to –125	5 RT

Effect of added electrolyte on the Interparticle interaction



Effect of added electrolyte on the Colloidal interaction



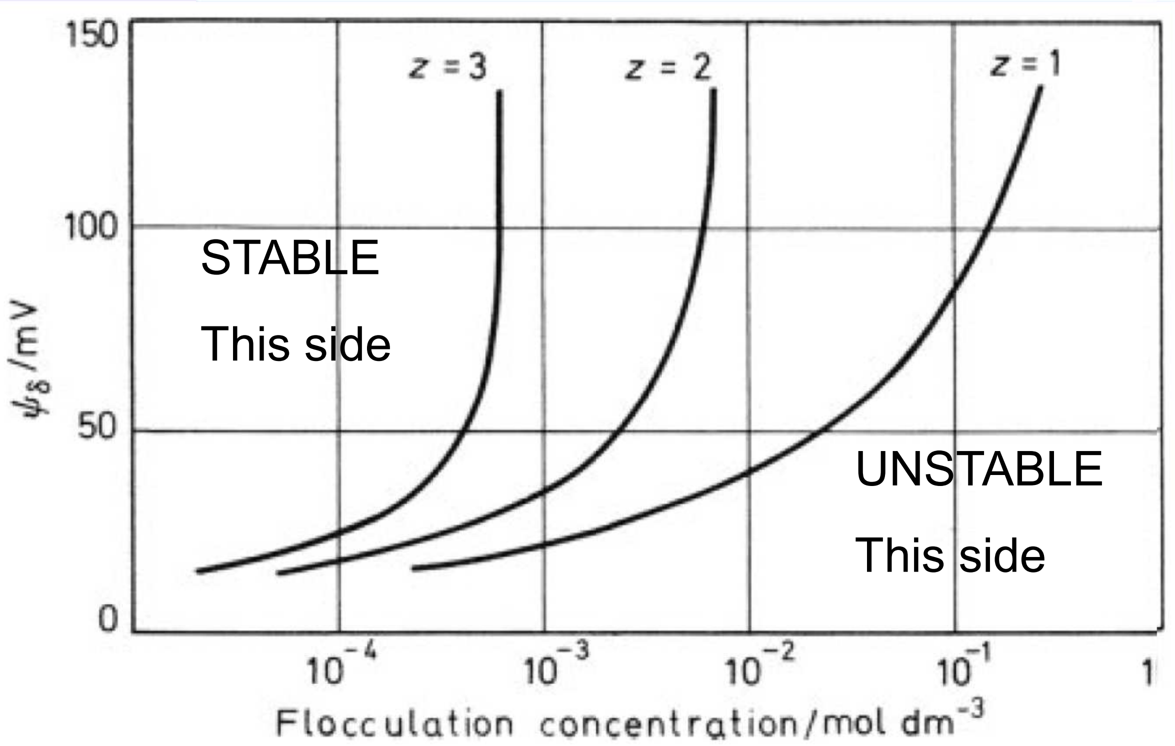
Effect of electrolyte valence on the Interparticle interaction

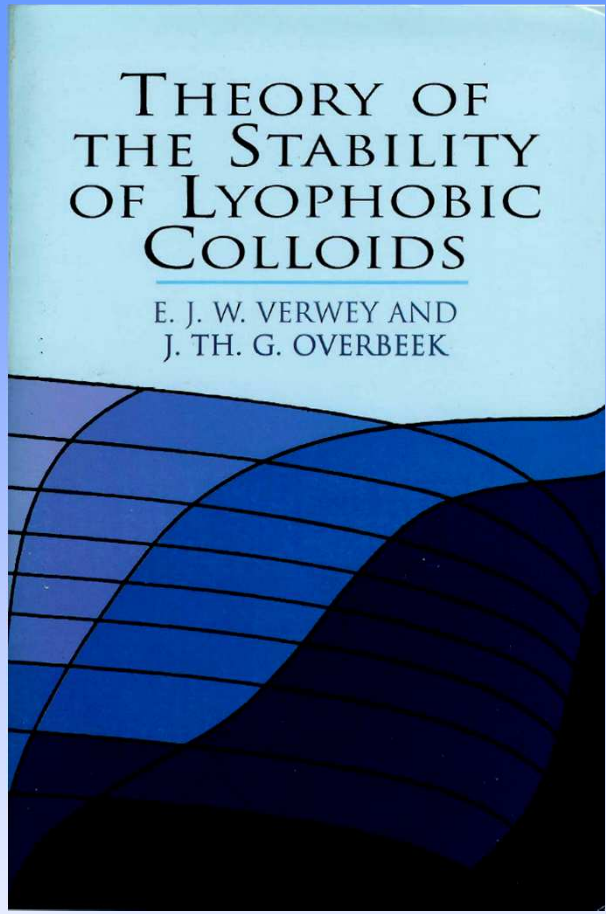
Schulze–Hardy Rule

critical coagulation concentrations (CCC)

vary inversely with the sixth power of the counter-ion charge

DLVO theory: $CCC\ (M) = (87.4 \times 10^{-40}) \ / \ (A^2 z^6)$



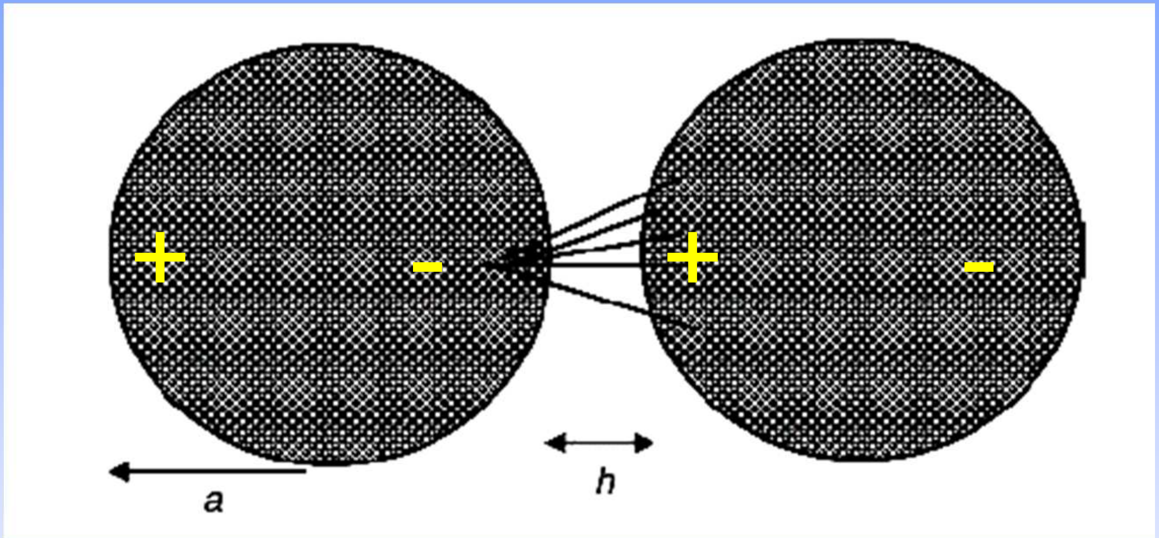


$$W_{Total} = W_{Attraction} + W_{Repulsion}$$

Attractive Intermolecular interactions ($W_{Attraction}$)

Electrostatic or Steric Repulsion ($W_{Repulsion}$)

Modeling van der Waals interactions



Permanent Dipole–Permanent Dipole (Dipolarity)

Permanent Dipole–Induced Dipole (Polarizability)

Induced Dipole–Induced Dipole (Dispersion interactions)

Hamaker Constants

Table 3.1 Hamaker constants for various materials

Particles	Hamaker constant ($J/10^{-20}$)	Media	Hamaker constant ($J/10^{-20}$)
Poly(tetrafluorethylene)	3.8	Water	3.7
Poly(methyl methacrylate)	7.1	Pentane	3.8
Poly(styrene)	7.8	Ethanol	4.2
Silica (fused)	6.5	Decane	4.8
Titanium dioxide	19.5	Hexadecane	5.1
Metals (Au, Ag, Pt, etc.)	~40	Cyclohexane	5.2

$$A = (\sqrt{A_{\text{particle}}} - \sqrt{A_{\text{medium}}})^2$$

General features of van der Waals interactions

1. The interaction between two oil droplets (or between two water droplets) is always attractive.
2. The strength of the interaction decreases with droplet separation, and the interaction is fairly long range ($w \propto 1/h$).
3. The interaction becomes stronger as the droplet size increases.
4. The strength of the interaction depends on the physical properties of the droplets and the surrounding liquid (through the Hamaker function).
5. The strength of the interaction depends on the thickness and composition of the adsorbed emulsifier layer.
6. The strength of the interaction decreases as the concentration of electrolyte in an oil-in-water emulsion increases because of electrostatic screening.

Modeling van der Waals interactions

van der Waals for an assembly of colloidal particles at close distance of approximation of the particles:

$$w_{\mathrm{VDW}}(h) = -\frac{A_{212}r}{12h}$$

van der Waals for molecules is proportional to r^{-6}.

w_{VDW} is much longer range for particles than for molecules

Note: w_{VDW} is net ATTRACTIVE at all ***h***

Hamaker function

$$A = A_{\nu=0} + A_{\nu>0}$$

“Static” Part (frequency independent)

$$A_{\nu=0} = \frac{3}{4}kT\sum_{s=1}^{\infty}\frac{1}{s^3}\left(\frac{\varepsilon_1-\varepsilon_2}{\varepsilon_1+\varepsilon_2}\right)^{2s}$$

Depends on DIelectric Constants of the particles and medium

(Permanent dipole interactions)

“Dynamic” Part (frequency dependent)

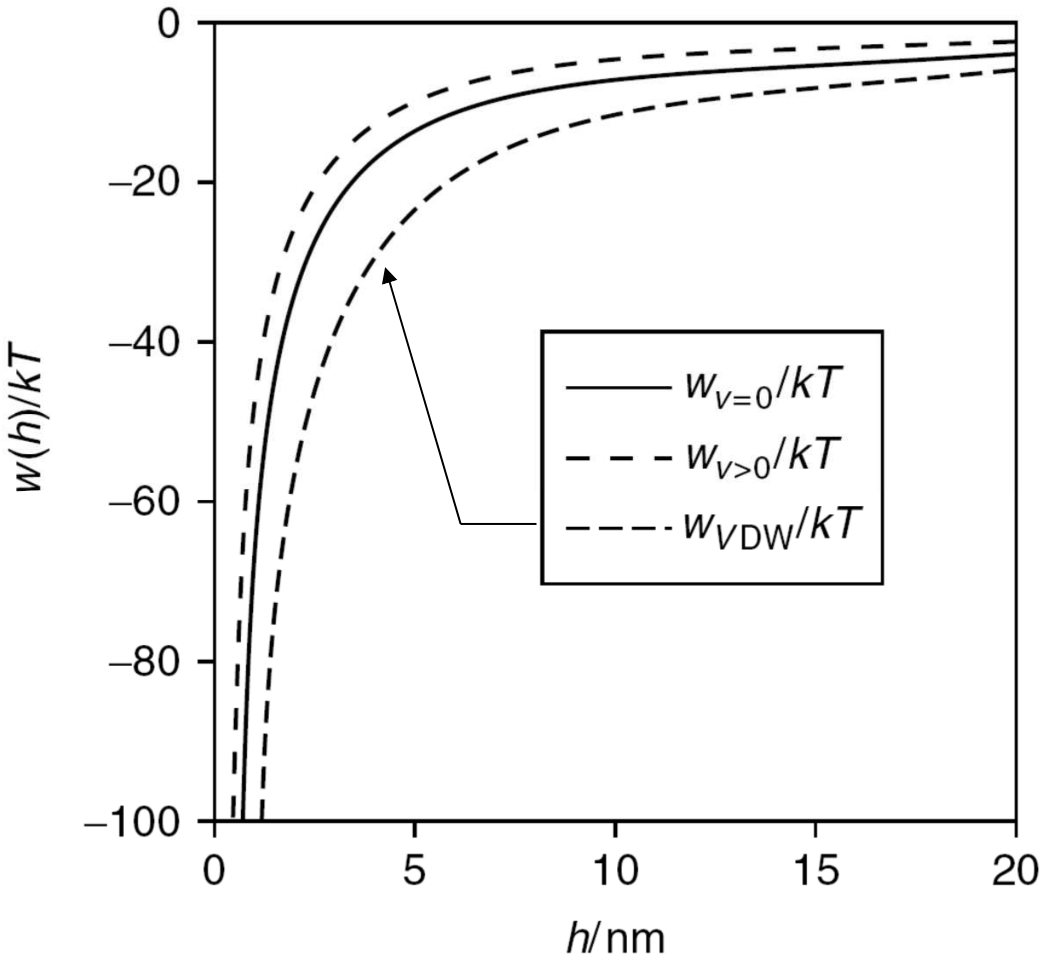
$$A_{\nu>0} = \frac{3h\nu_e}{16\sqrt{2}}\frac{\left(n_1^2-n_2^2\right)^2}{\left(n_1^2+n_2^2\right)^{3/2}}$$

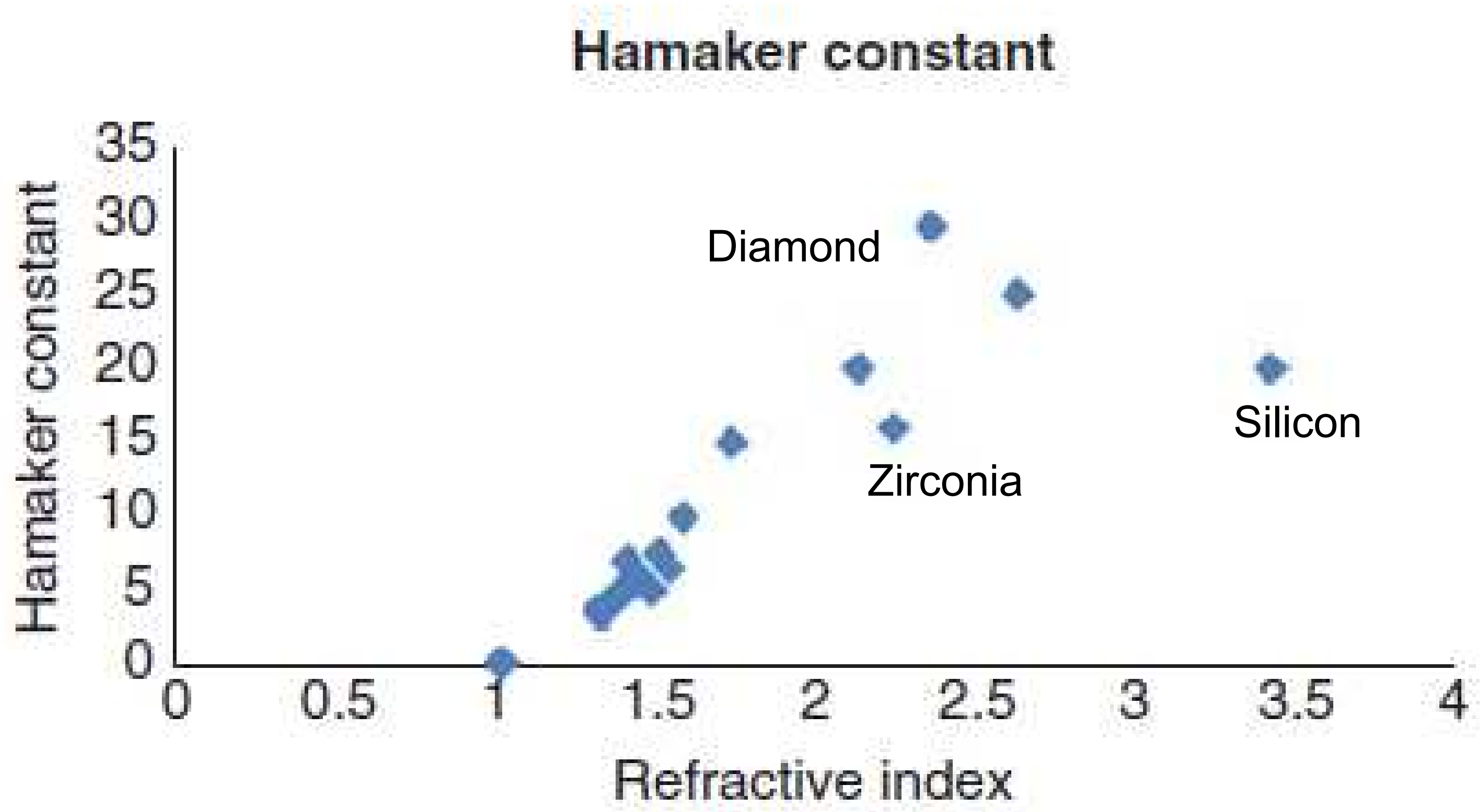
Depends on Refractive Indexes of the particles and medium

(Induced dipole interactions)

$$Hamaker\ function \quad A_{212} = A_{\nu=0} + A_{\nu>0}$$

Implies that: $w_{\mathrm{VDW}}(h) = w_{\nu=0}(h) + w_{\nu>0}(h)$

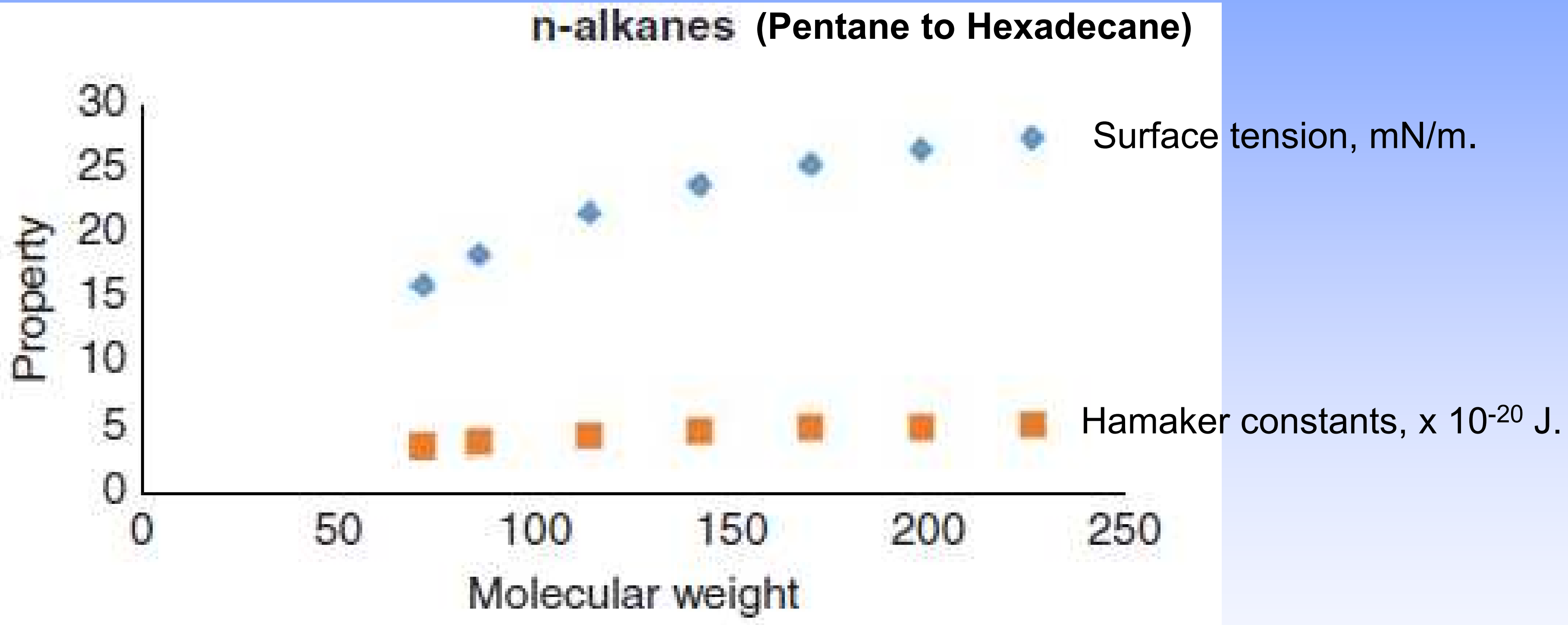




Hamaker constant for two identical particles interacting in air or vacuum (A_{11}) against the refractive index for 24 compounds. The Hamaker constant is given in 10^{-20} J.

Kontogeorgis & Kiil, *Introduction to Applied Colloid and Surface Chemistry*-John Wiley & Sons (2016)

Surface Tension of n-alkanes and Hamaker Constants

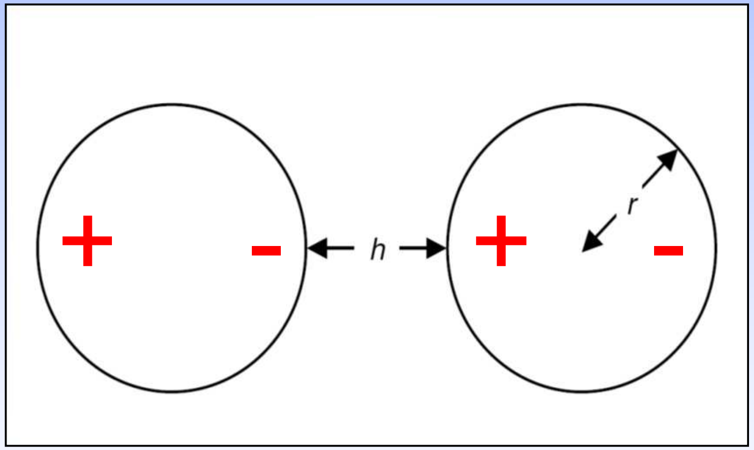


Kontogeorgis & Kiil, *Introduction to Applied Colloid and Surface Chemistry*-John Wiley & Sons (2016)

Modeling van der Waals interactions

The Corrections for Additional Phenomena

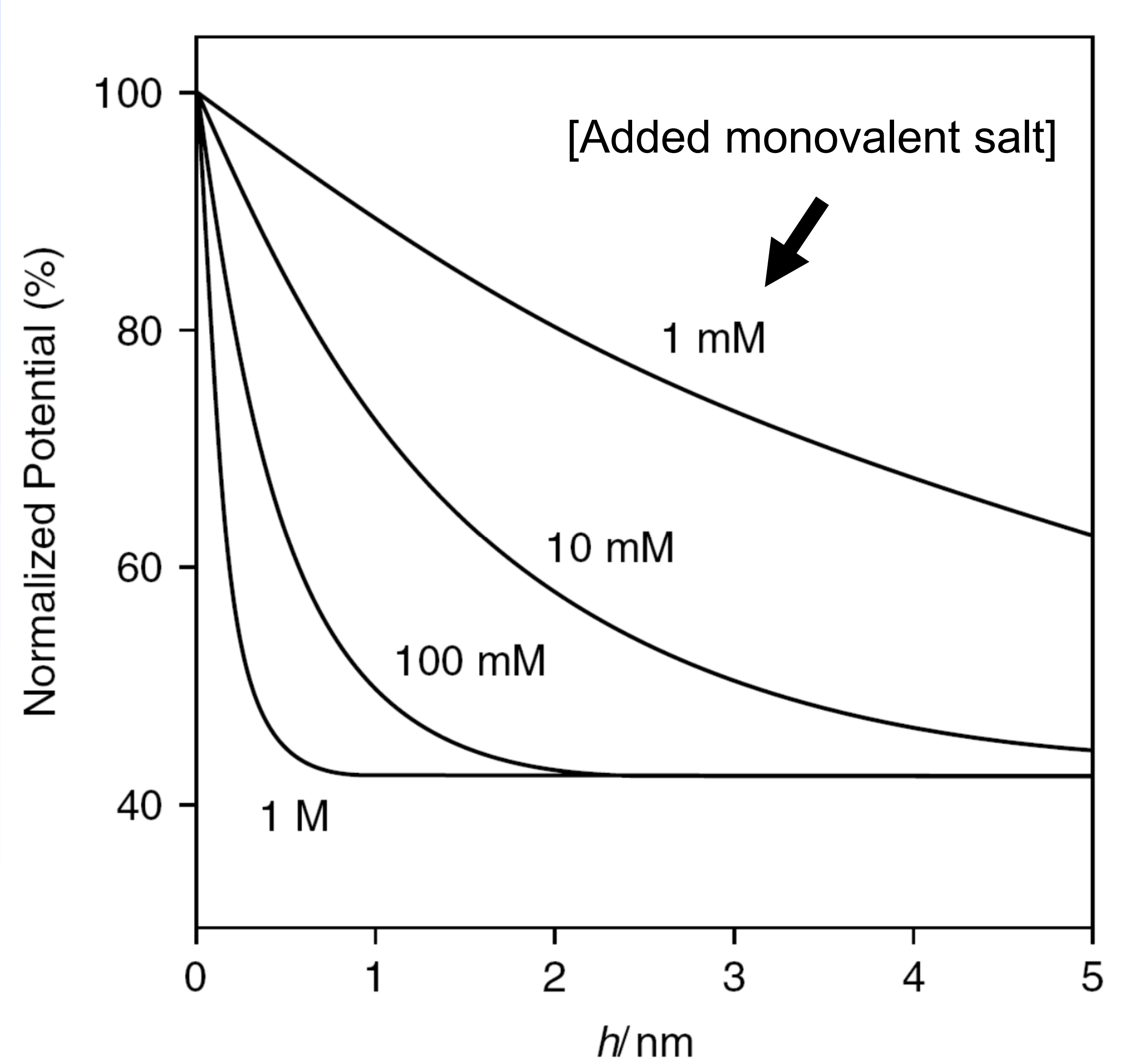
Electrostatic screening effects



$$A_{v=0} \times e^{-2\kappa h}$$

Electrolyte in the external medium (if water) screens the permanent dipole-permanent dipole interactions, incorporated via a dependence of $A_{\upsilon=0}$ on the inverse Debye Length κ.

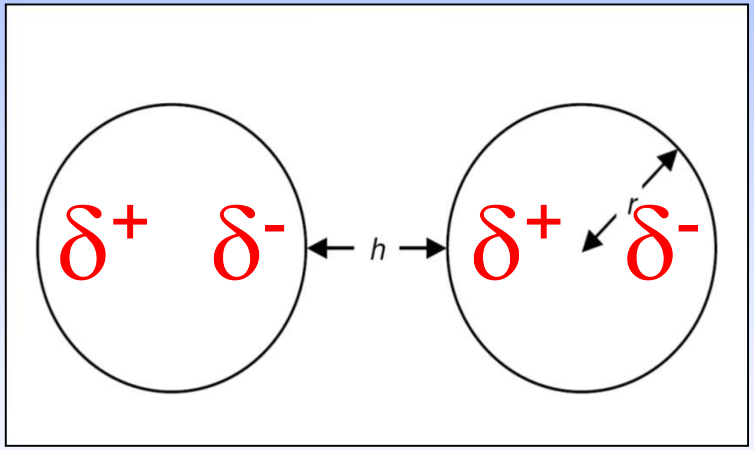
Influence of Electrostatic screening effects on the Work



Modeling van der Waals interactions

The Corrections for Additional Phenomena

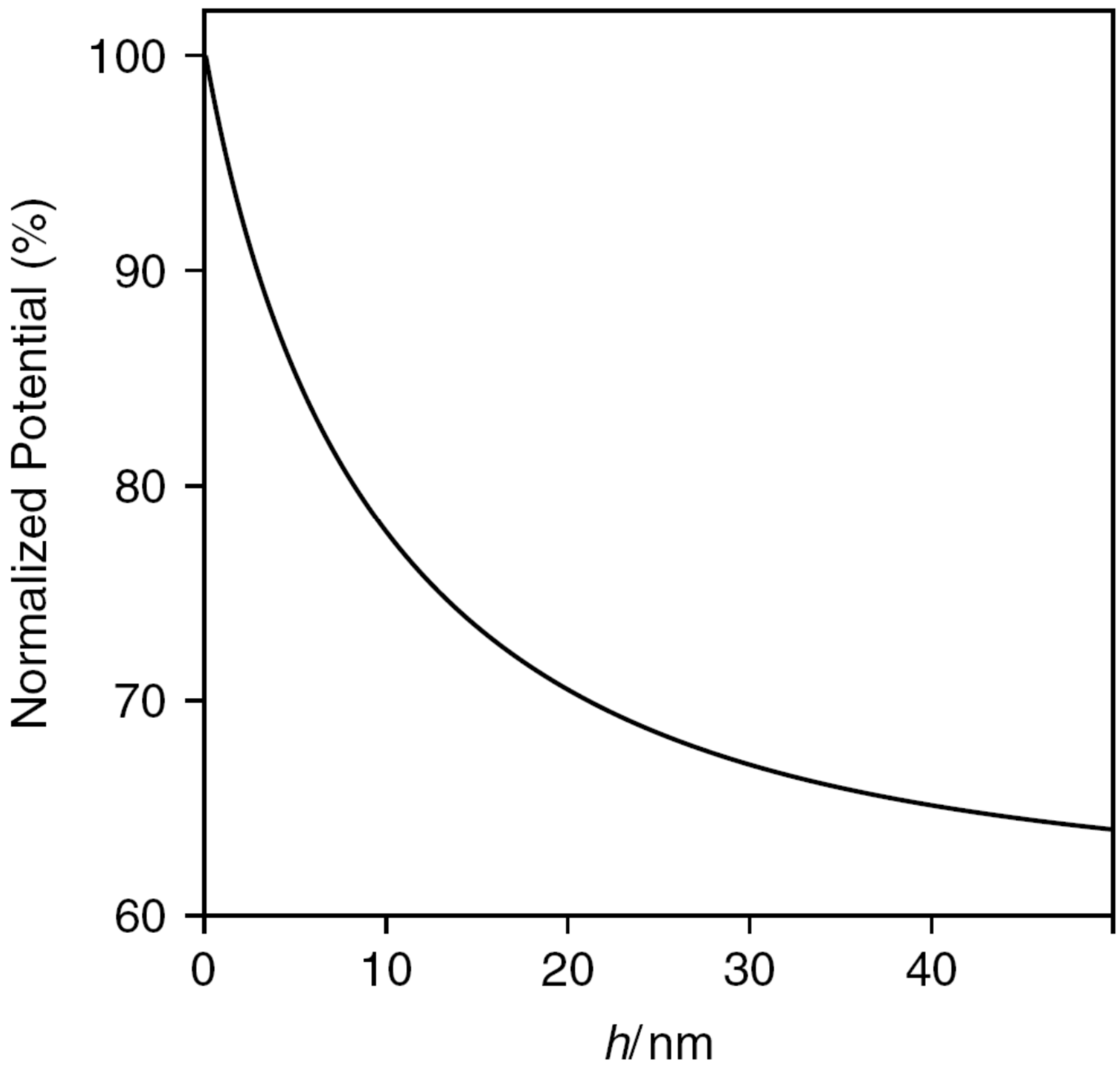
Retardation



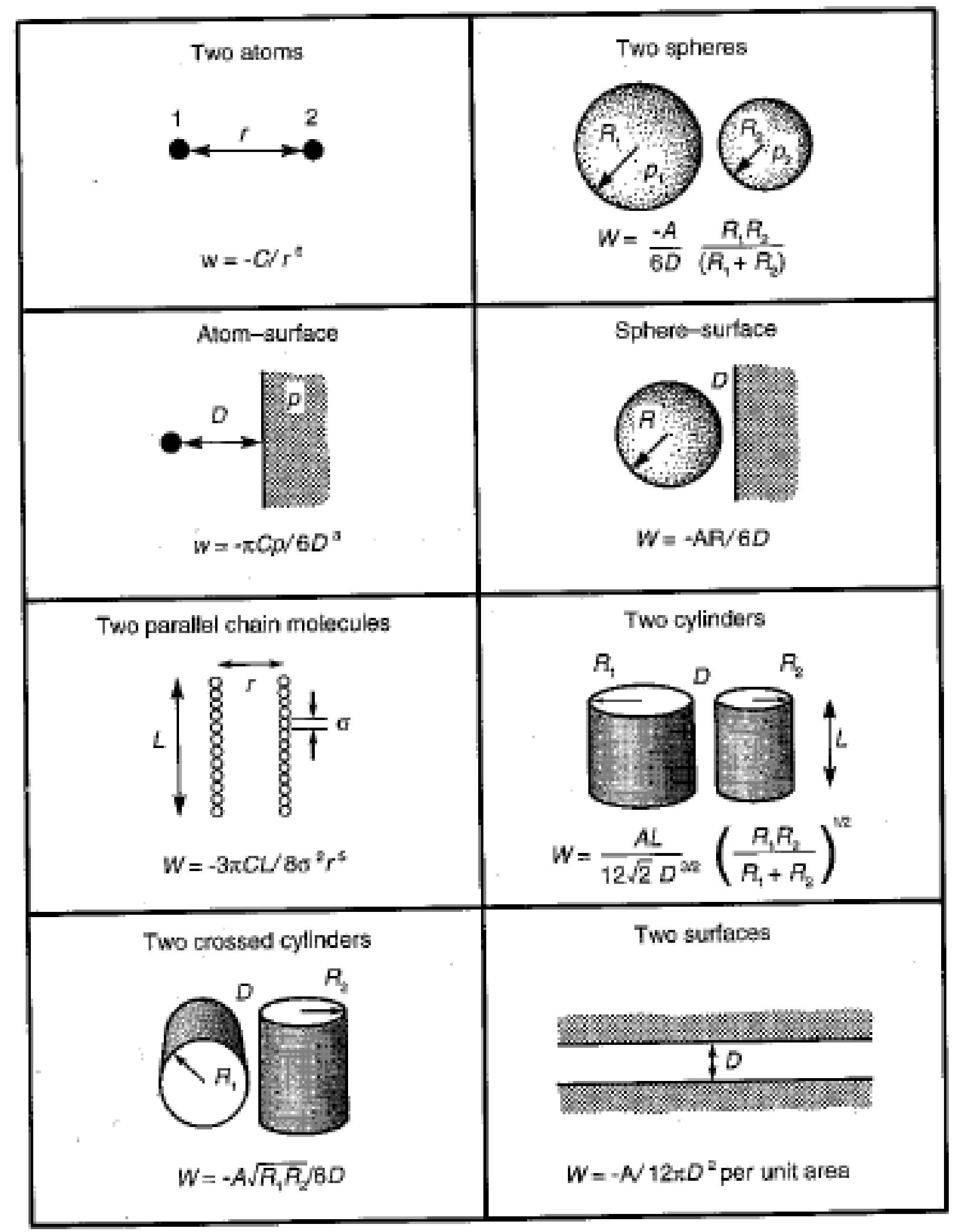
$$\frac{A_{v>0}}{(1 + 0.11h)}$$

The electrostatic field induced by particle 1 takes a finite time to reach particle 2, reducing the induced dipole interactions at larger separations.

Influence of Retardation on the Work



van der Waals interactions for other shapes

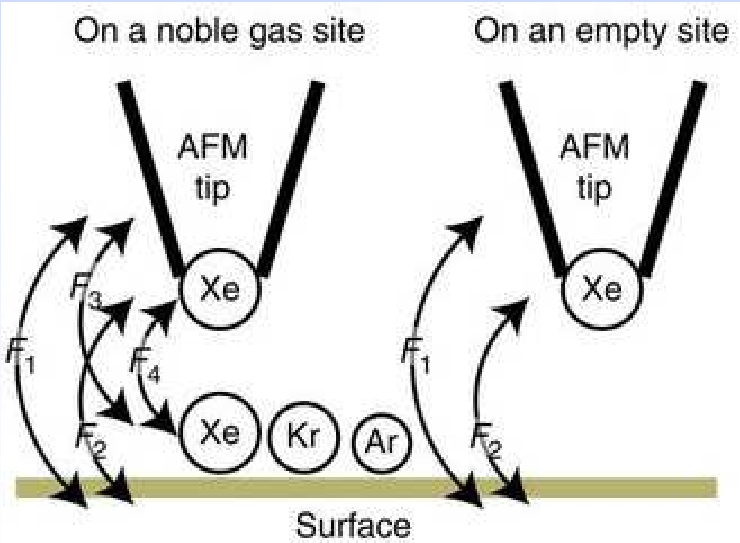


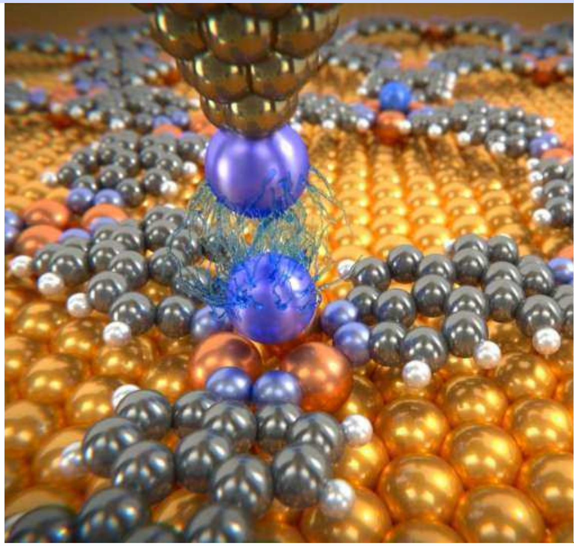
https://galileo.seas.harvard.edu/images/material/335/115/Israelachvili_ch11.pdf

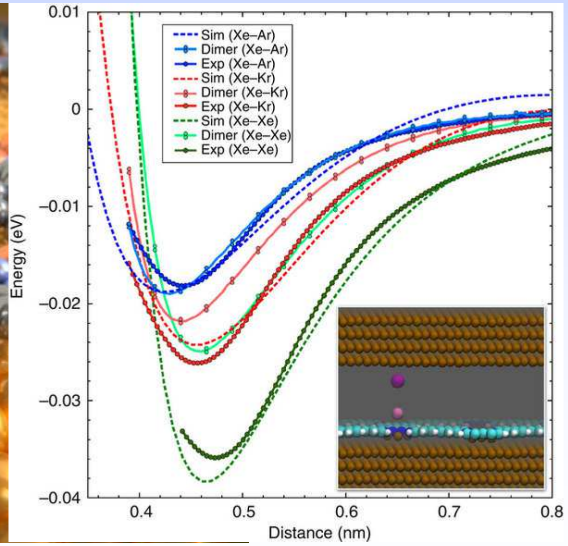
Direct Measurement of Surface Forces by Atomic Force Microscopy

Review: Theoretical Models for Surface Forces and Adhesion and Their Measurement Using Atomic Force Microscopy, Leite *et al*., *Int. J. Mol. Sci.* ***2012, 13, 12773-12856; doi:10.3390/ijms131012773***

Van der Waals interactions and the limits of isolated atom models at interfaces, Kawai et al., NATURE COMMUNICATIONS **2016**, *7,* 11559; DOI: 10.1038/ncomms11559







Recapitulating the

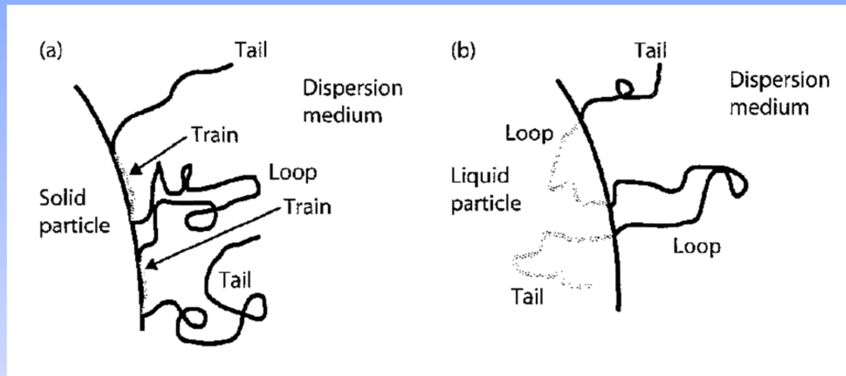
General features of van der Waals interactions

1. The interaction between two oil droplets (or between two water droplets) is always attractive.
2. The strength of the interaction decreases with droplet separation, and the interaction is fairly long range ($w \propto 1/h$).
3. The interaction becomes stronger as the droplet size increases.
4. The strength of the interaction depends on the physical properties of the droplets and the surrounding liquid (through the Hamaker function).
5. The strength of the interaction depends on the thickness and composition of the adsorbed emulsifier layer.
6. The strength of the interaction decreases as the concentration of electrolyte in an oil-in-water emulsion increases because of electrostatic screening.

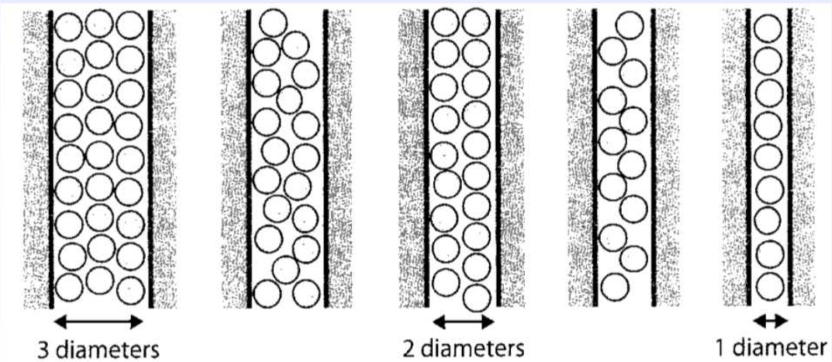
Limitations of DLVO theory

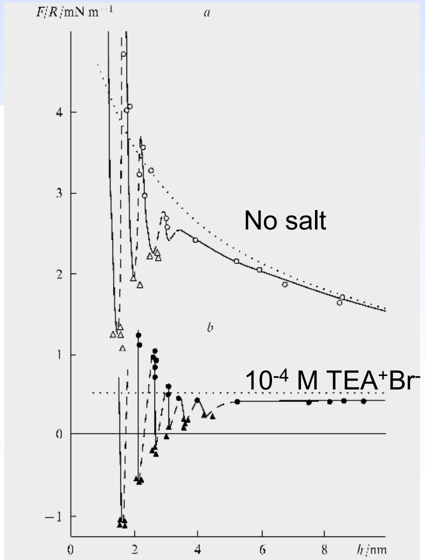
- Limited to Aqueous Media

- No Steric or Other Non-Electrostatic Stabilization



- Ignores Structuring of Solvent or Solvation





Mica surfaces with propylene carbonate.

Expt. ————————

Hamaker – – – – – – -

Limitations of DLVO theory

Specific Ion effects:

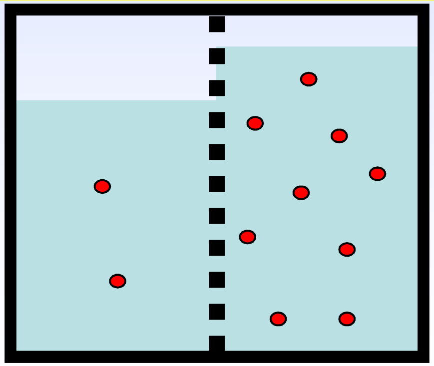
VOLUME 87, NUMBER 16 PHYSICAL REVIEW LETTERS 15 OCTOBER 2001

Specific Ion Effects: Why DLVO Theory Fails for Biology and Colloid Systems

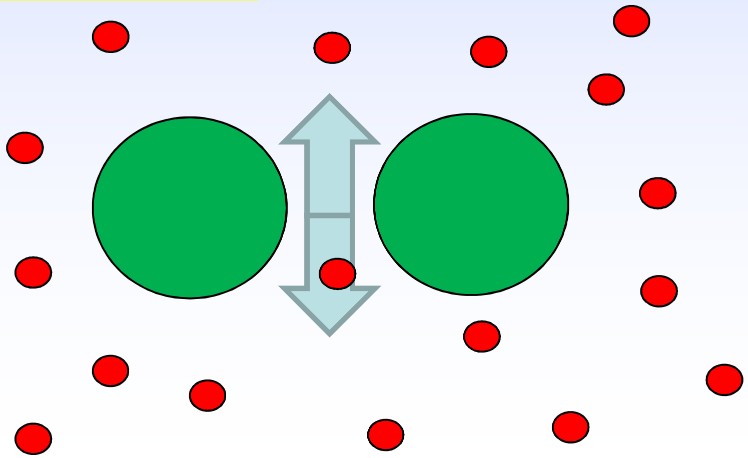
M. Boström, D. R. M. Williams, and B. W. Ninham*
Department of Applied Mathematics, Research School of Physical Sciences and Engineering, Institute of Advanced Studies, Australian National University, Canberra, Australia 0200
(Received 30 May 2001; published 1 October 2001)

The classical Derjaguin-Landau-Verwey-Overbeek theory that underpins colloid and surface science is shown to be flawed, especially at biological salt concentrations. This is in part because the dispersion forces acting on the ions are ignored. When these are included properly very different results are obtained. These results have substantial implications for biological and for ordinary colloid systems at moderate salt concentrations.

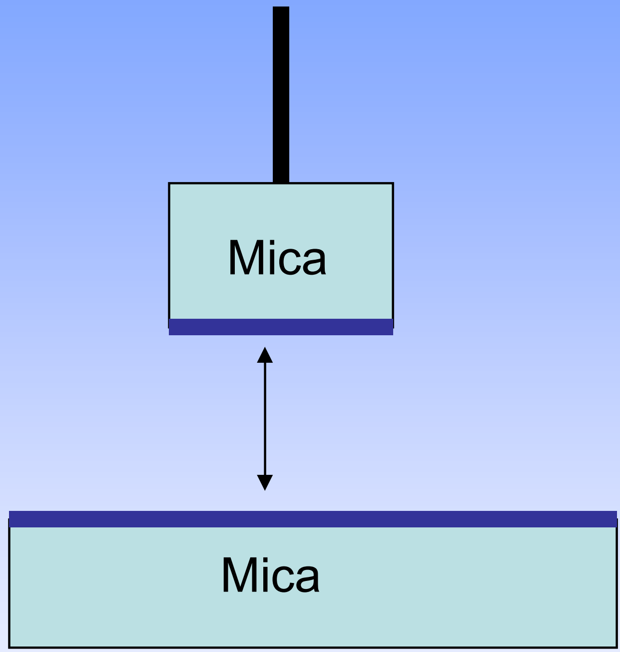
Depletion Forces (Osmotic Flows):



$\pi = \Delta c\ RT$



Measuring Surface Forces (SFA)



Direct force measurements between layers coated or adsorbod onto molecularly flat mica surfaces – Can measure both repulsion and attraction

Limitations of DLVO theory

Structuring of Solvent or Solvation

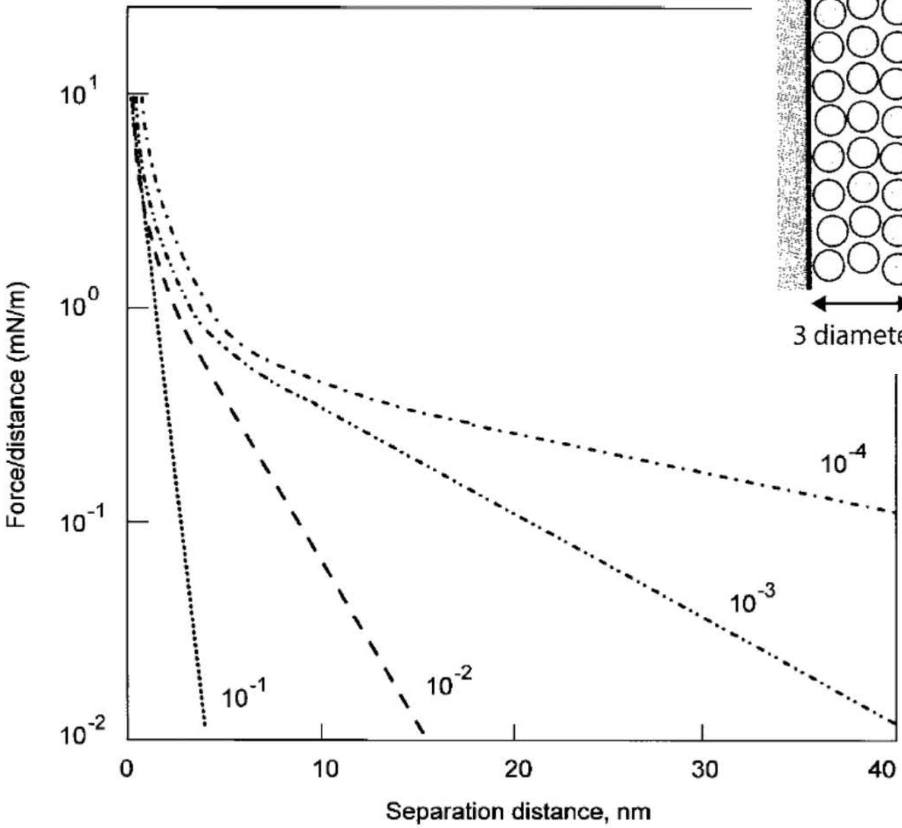
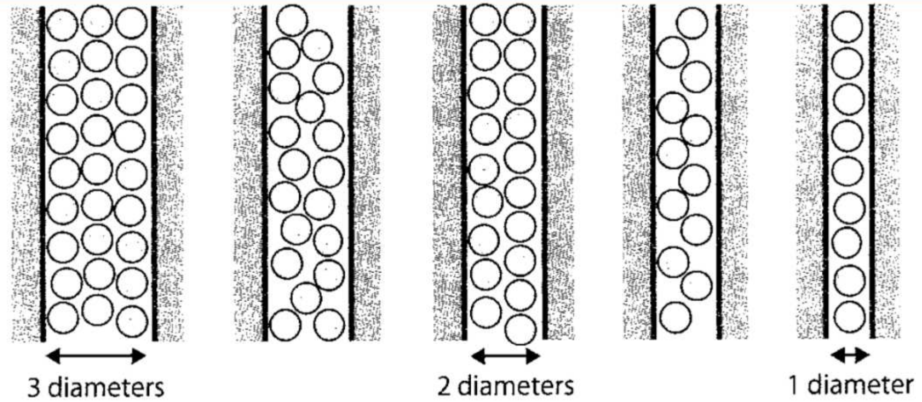
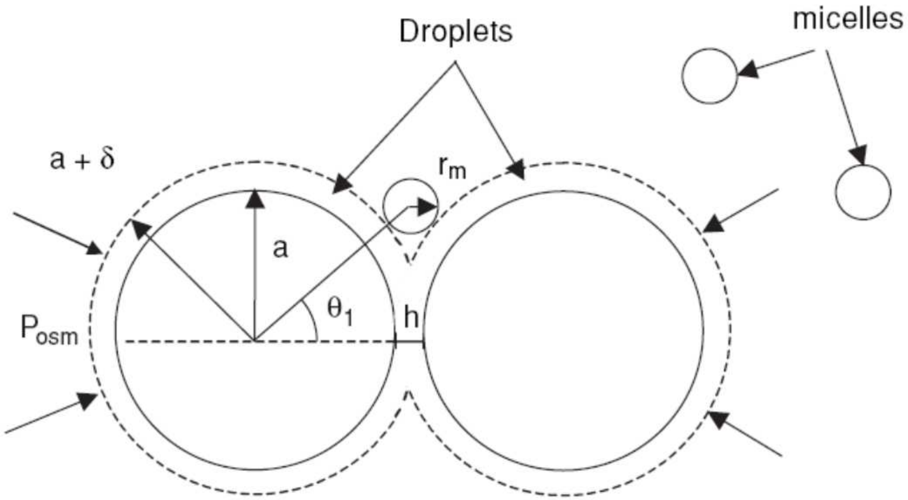
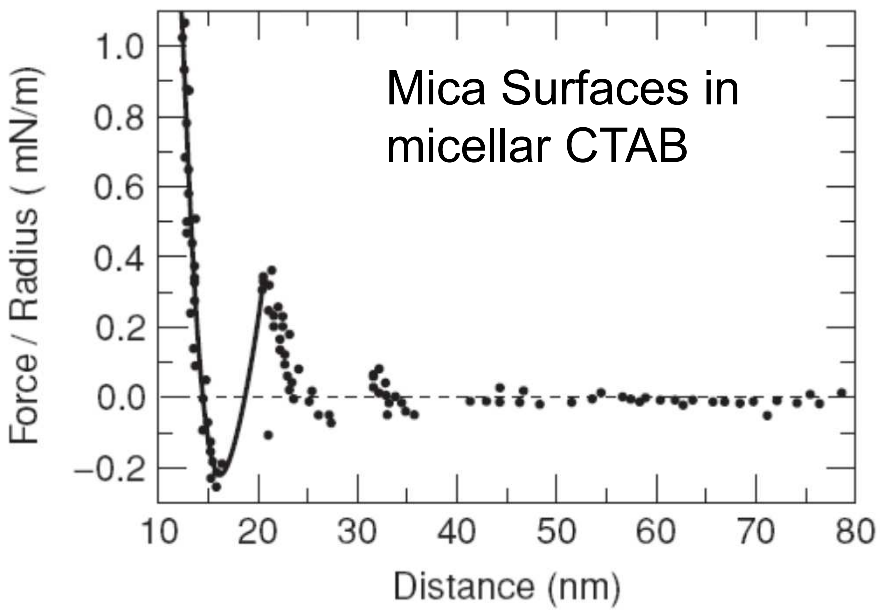


Figure 5.12 Illustration of force curves between silica surfaces in aqueous solutions of sodium chloride at various molar concentrations. At short range there is a strong repulsion which is not accounted for in the standard DLVO theory, due to hydration forces. Drawn based on data in Horn [284].



The Attractive "Depletion Force" between detergent-charged droplets





The depletion attraction has an entropic origin:

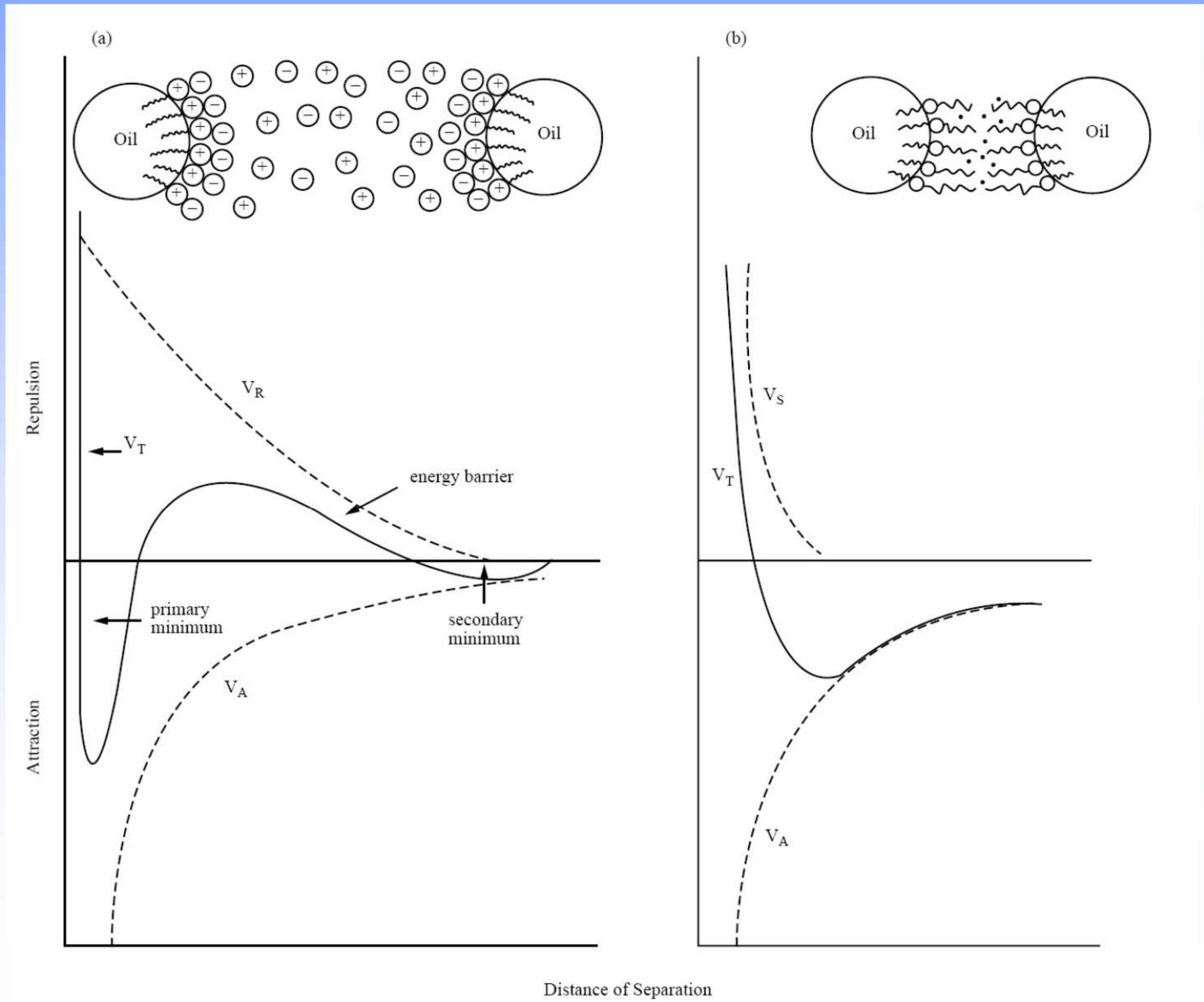
If two large oil droplets approach one another, micelles or polymer coils are excluded from the region in between, leading to an uncompensated osmotic pressure within the depleted region.

The so-called depletion interaction scales with the osmotic pressure π_{osm} of the micelles or polymer coils and also with the depleted volume in between the two large oil droplets.

Preferred over dispersion for charged colloids.

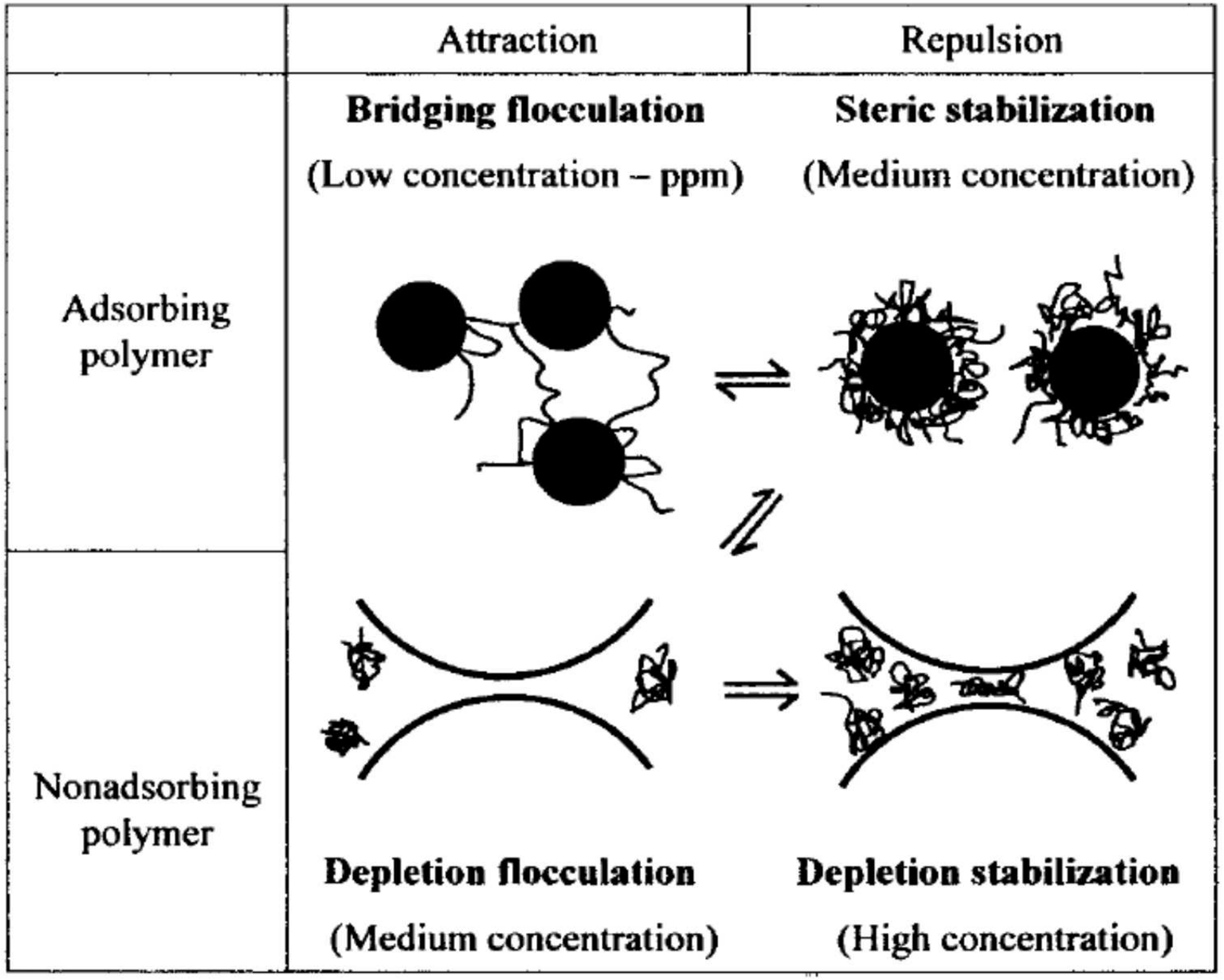
Limitations of DLVO theory

Electrostatic vs. Steric Stabilization of an Oil-in-Water Emulsion



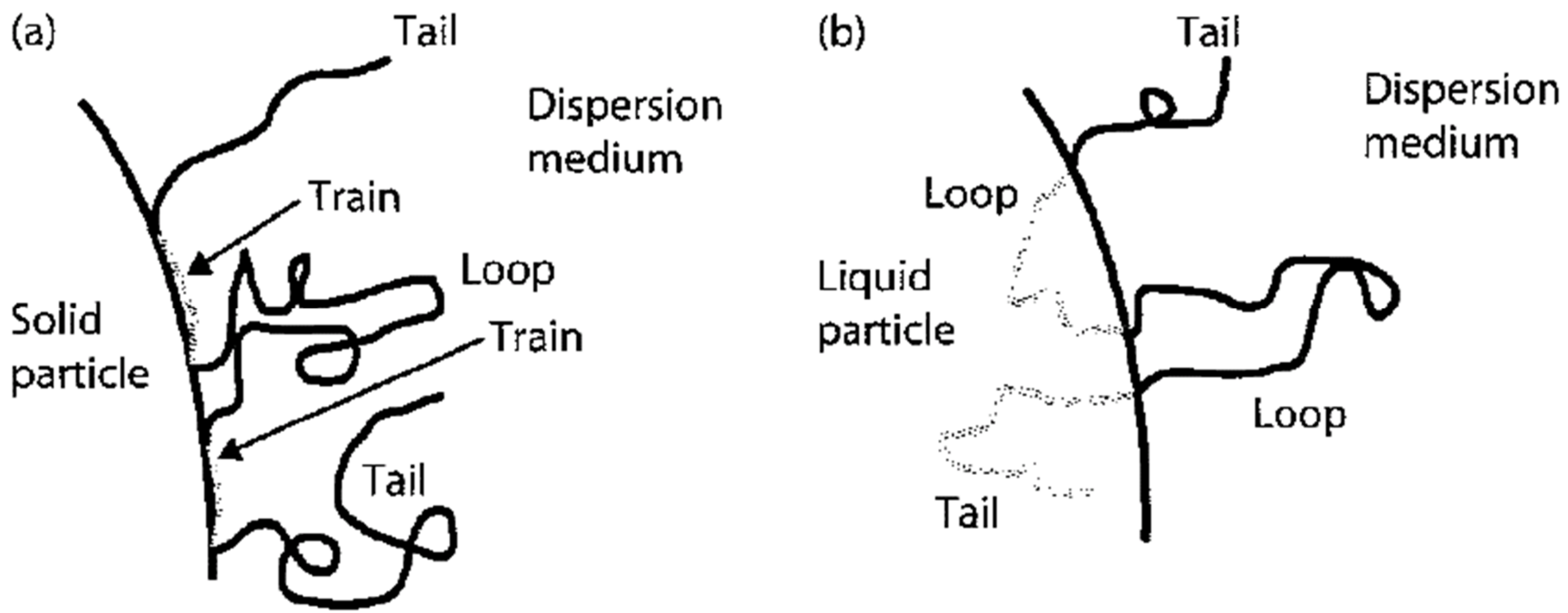
Limitations of DLVO theory

Steric or Other Non-Electrostatic Stabilization or Destabilization



Limitations of DLVO theory

Steric or Other Non-Electrostatic Stabilization or Destabilization



Limitations of DLVO theory

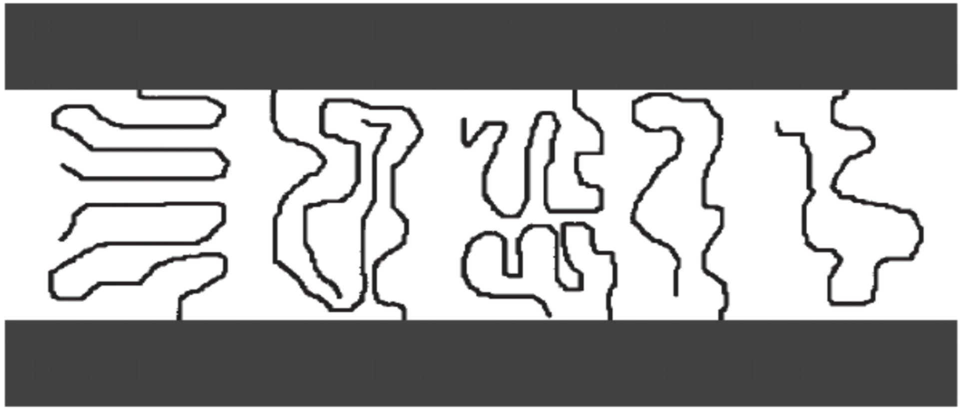
Steric or Other Non-Electrostatic Stabilization or Destabilization

Steric Stabilization

In principle, steric stabilization can result from any of the following :

- undulations of the interface(s)
- peristaltic fluctuations as two interfaces approach each other,
- overlap of the head-groups of adsorbed surfactants at the interface(s), and/or
- molecular-scale protrusions of surfactant or polymer chains.

Of these, the last is probably the most common.

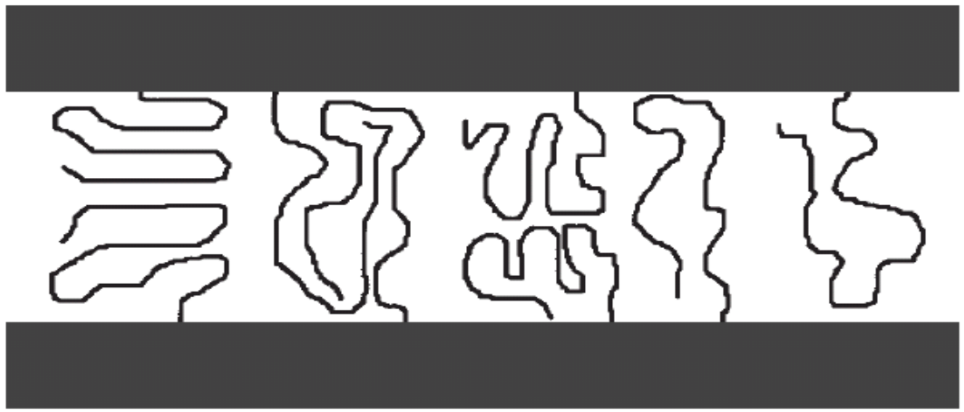


Limitations of DLVO theory

Steric or Other Non-Electrostatic Stabilization or Destabilization

Protective Agents:

- they can increase double layer repulsion if they have ionizable groups;
- the adsorbed layers can lower the effective Hamaker constant;
- an adsorbed film may necessitate desorption before particles can approach closely enough for van der Waals forces to cause attraction; or
- approaching particles may simply cause adsorbed molecules to become restricted in their freedom of motion (volume restriction).

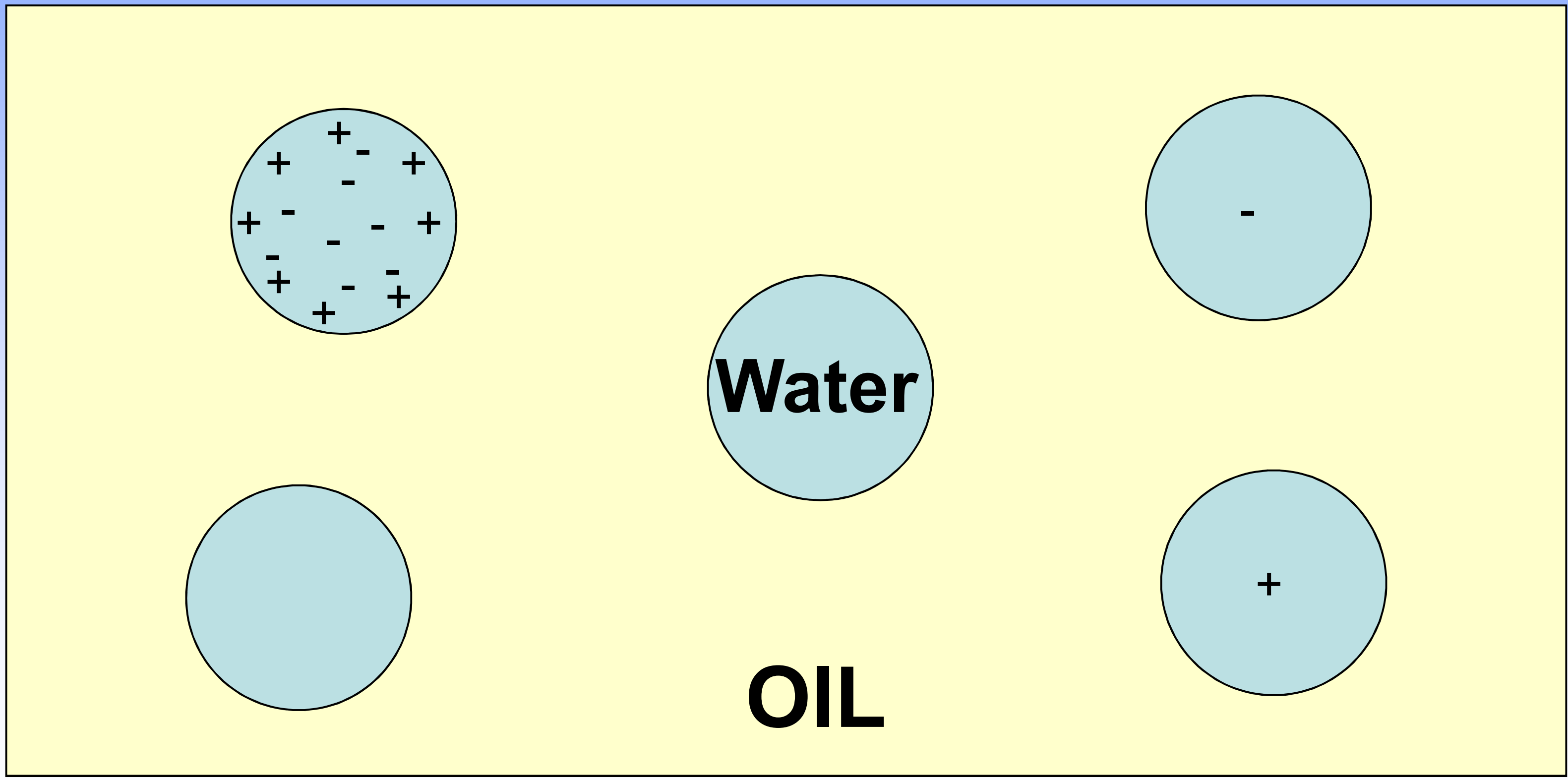


Increasing Emulsion Stability:

- Low interfacial tension – low interfacial free energy makes it easier to maintain large interfacial area.
- High surface viscosity and/or mechanically strong interfacial film – this acts as a barrier to coalescence and may be enhanced by adsorption of fine solids, or of close-packed surfactant molecules.
- Large electric double layer and/or steric repulsions – these repulsions act to prevent collisions and aggregation, and therefore coalescence.
- Small dispersion force attraction – this decreases the rate of aggregation and coalescence.
- Small volume of dispersed phase – this reduces the frequency of collisions and aggregation. Higher volumes are possible, for close-packed spheres the dispersed phase volume fraction would be 0.74, but in practice the fraction can be even higher.
- Small droplet size, if the droplets are electrostatically or sterically interacting.
- Small density difference between the phases – this reduces the rate of creaming/sedimenting and therefore collisions and aggregation.
- High bulk viscosity – this reduces the rates of creaming and coalescence.

Ion Distributions in Non-Aqueous Colloidal Solutions (Water-in-Oil Emulsion)

Gauss' Law + Lack of Solvation of Ions in the Oil Phase
+ Strong Electrostatic Attraction (Low Dielectric Constant)



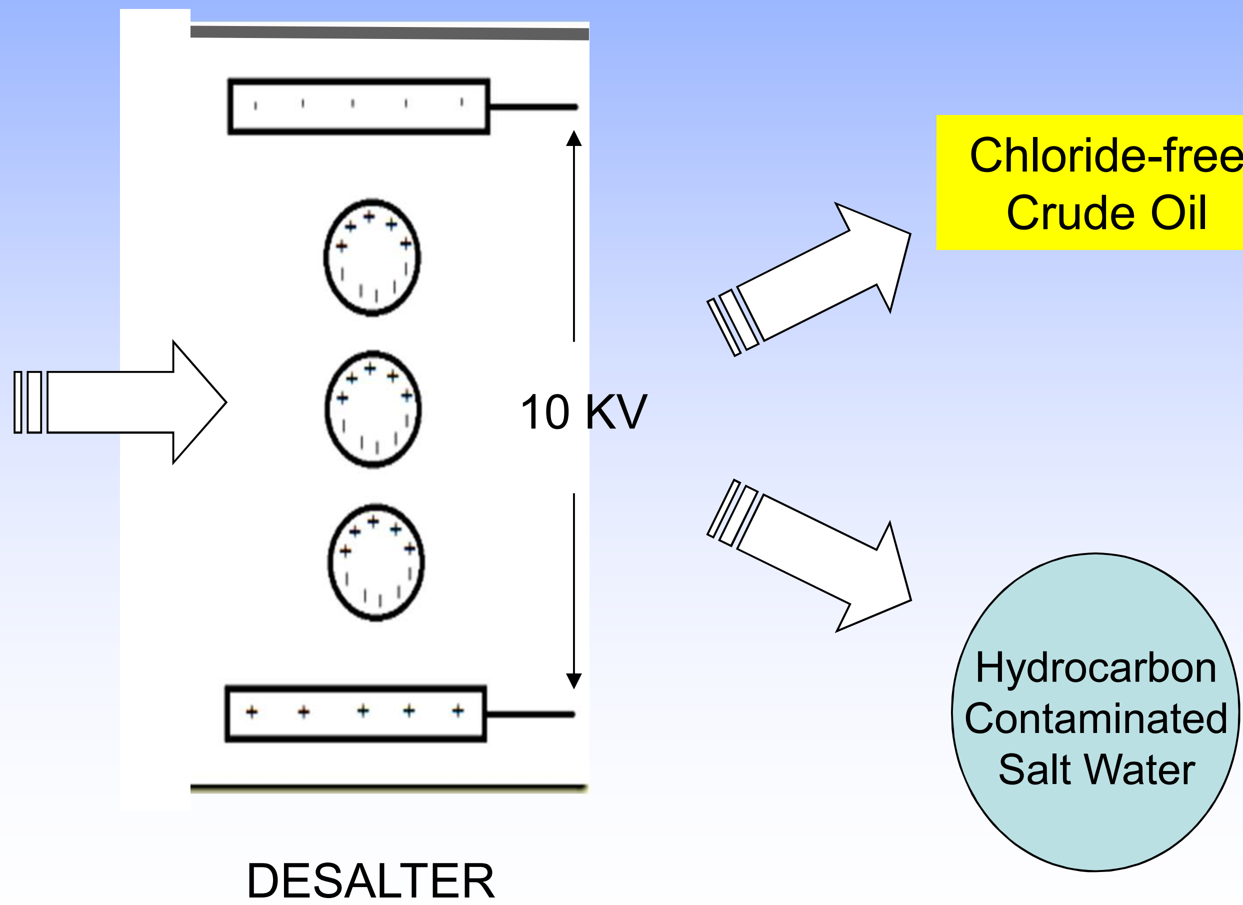
DLVO Not Applicable - No Real Electrostatic Stabilization.

Desalting Crude Oil (Water-in-Oil Emulsion)

Gauss' Law + Lack of Solvation of Ions in the Oil Phase + Strong Electrostatic Attraction (Low Dielectric Constant)

Add 3-5% water and

Heat the crude oil to ca. 100-170° C. to reduce viscosity and surface tension.



Bubbles and Foams

Soap Bubbles

I'm Forever Blowing Bubbles
by William Stephen Coleman

Boy Blowing Bubble
by Edouard Manet

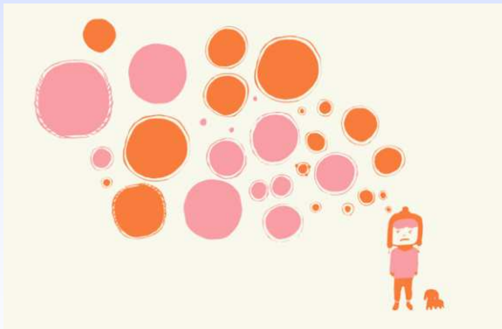
Two Boys Blowing Bubble
by Adriaen Hanneman

Still Life with a Boy Blowing Soap Bubbles
by Karel Dujardin

Soap Bubbles
by Jean Baptiste Siméon Chardin

Bubbles
by John Everett Millais

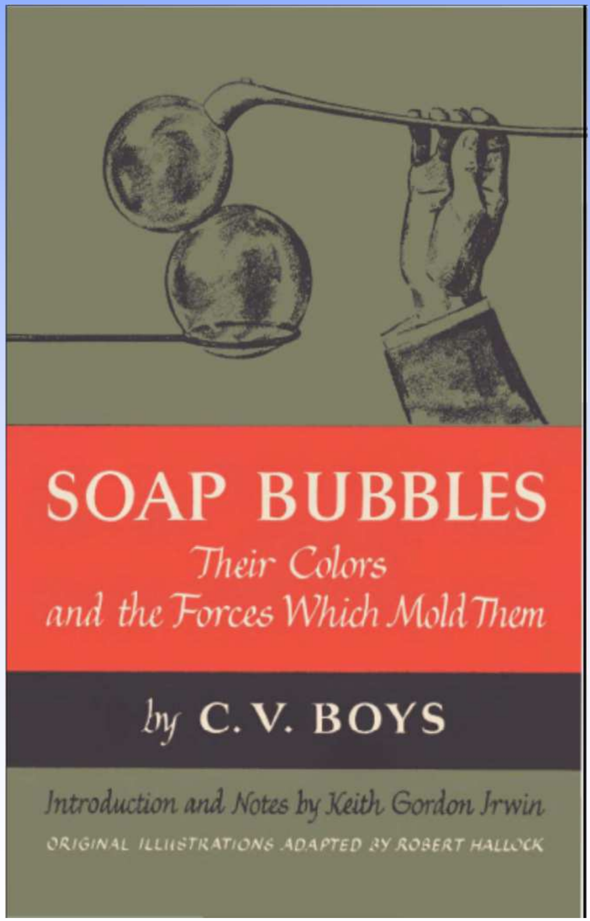
Bubble Boy
by Sreenivasa Ram Makineedi

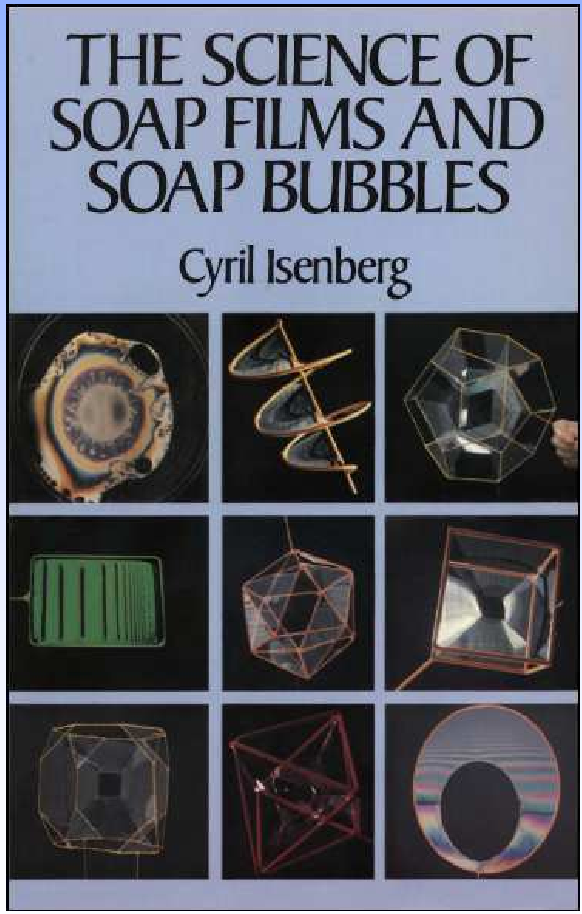


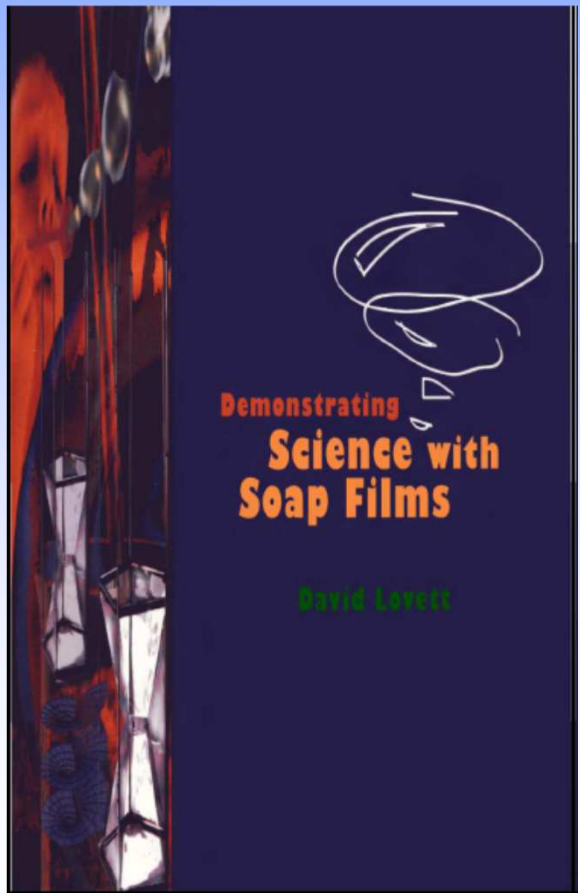
Bubble Boy
by Terri Fry Kasuba

http://www.ramblingsfromutopia.com/2012/06/diy-painting-with-bubbles.html

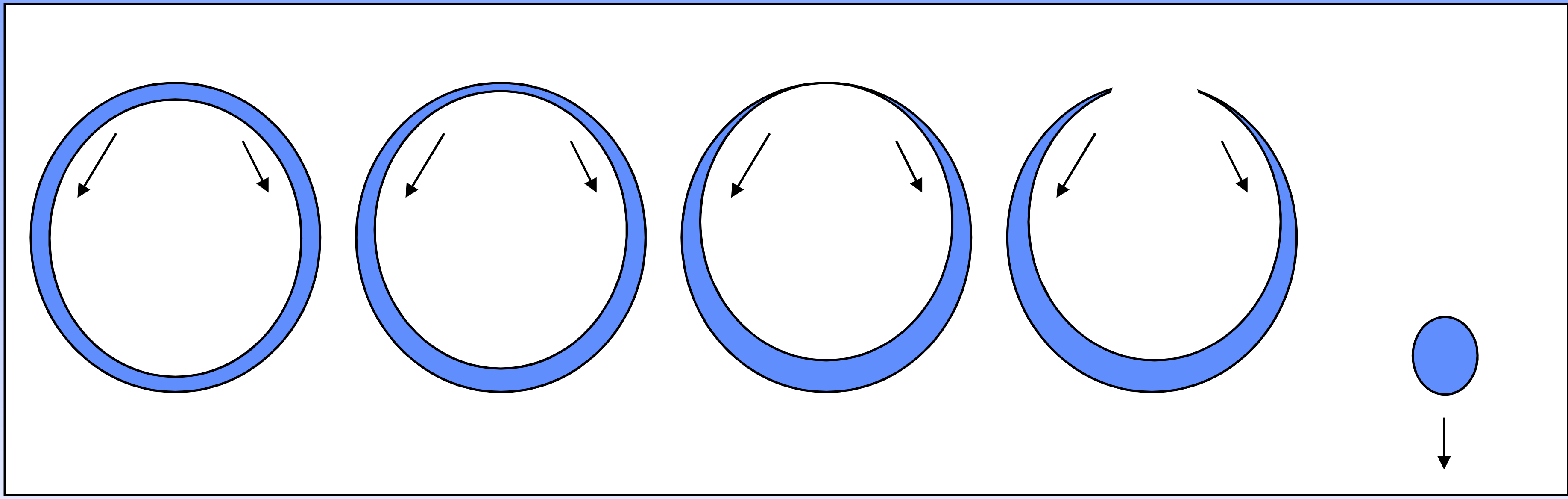
Soap Bubble Science



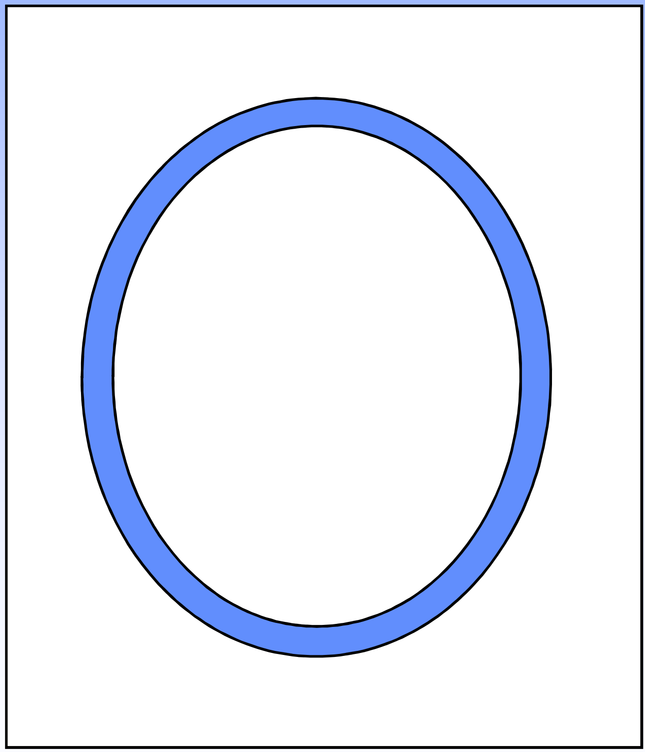


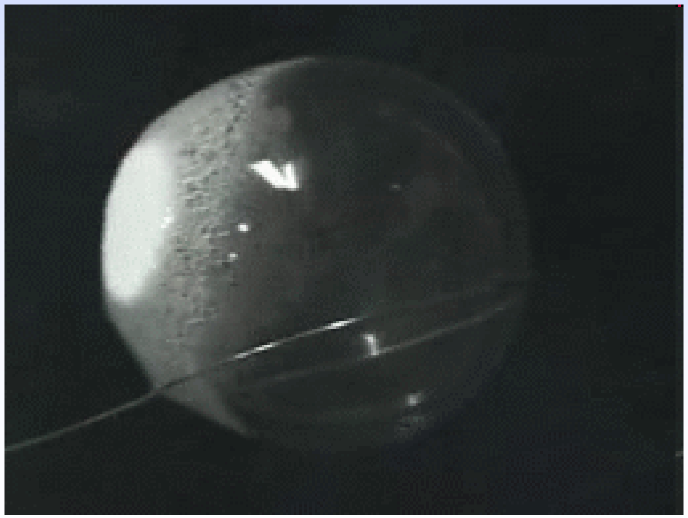


Water Bubbles are unstable (on the Earth)



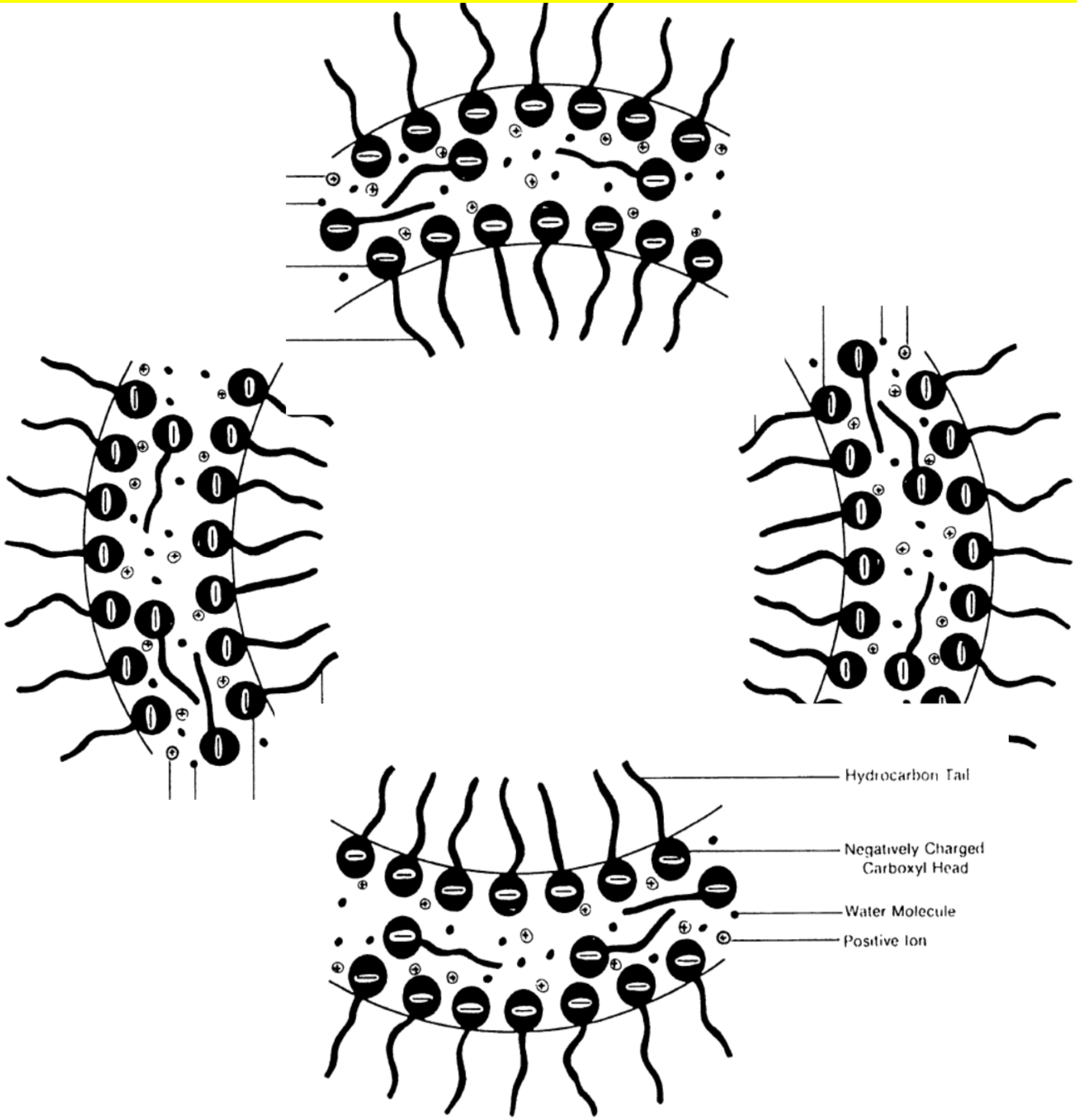
Water bubbles are "stable" (in outer space)



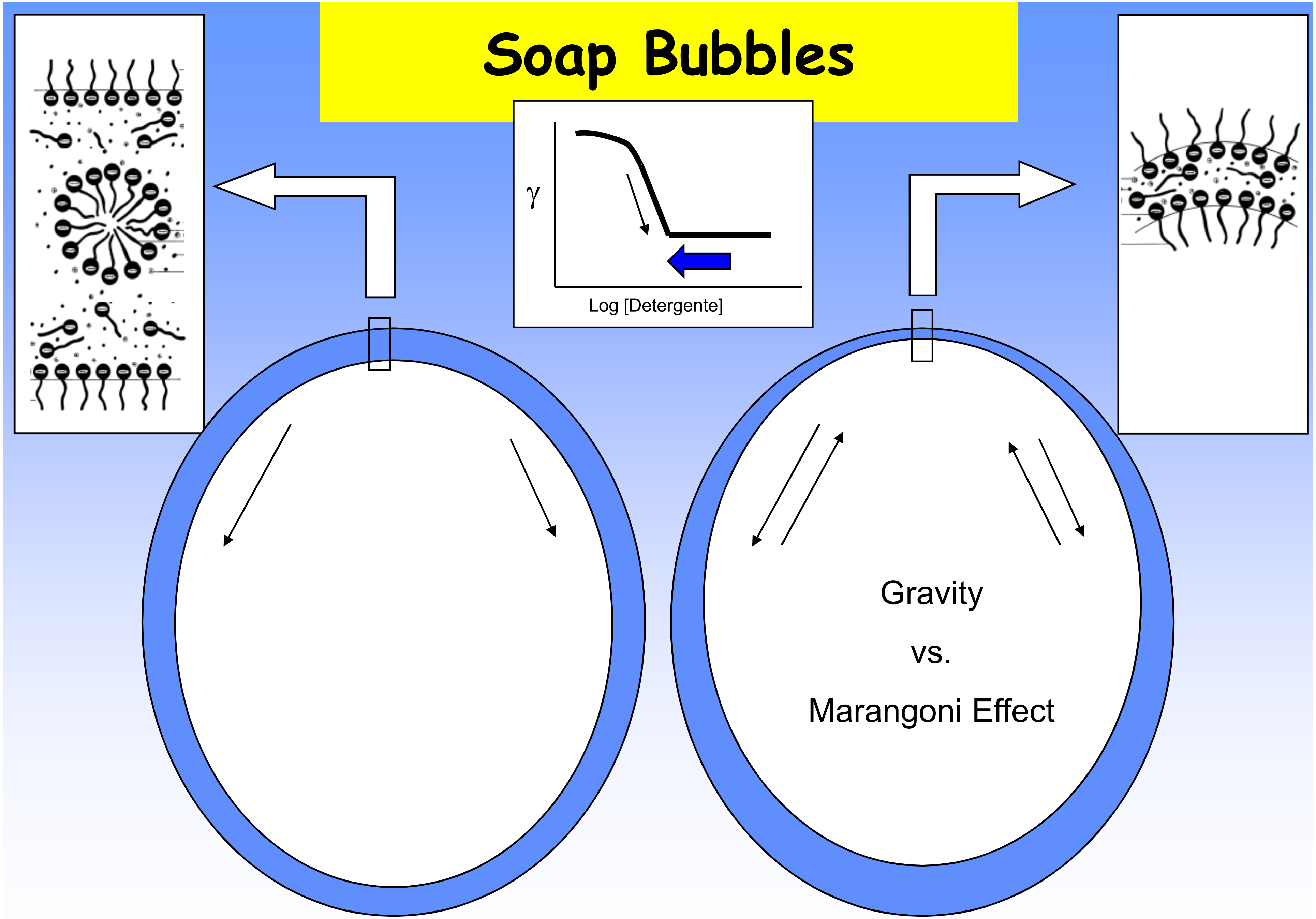


http://science.nasa.gov/PPOD/y2003/15apr_plopfiz.htm

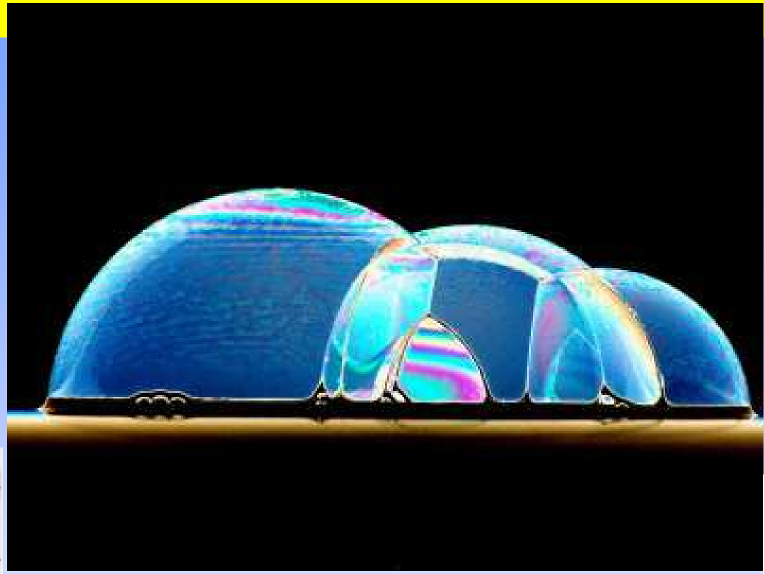
Soap Bubbles

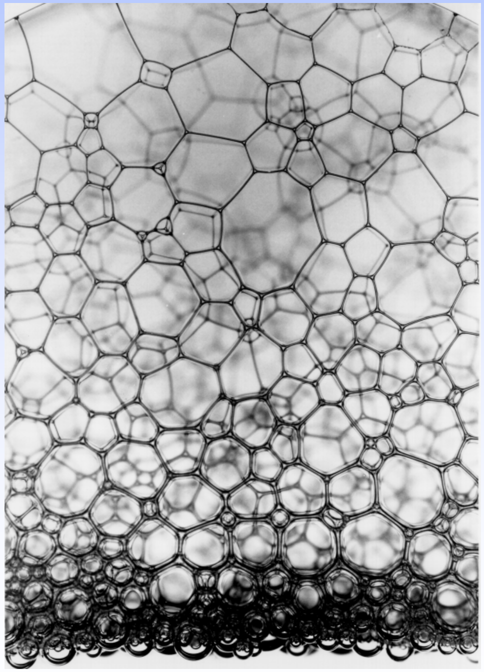


Soap Bubbles



Soap Bubbles in Foams

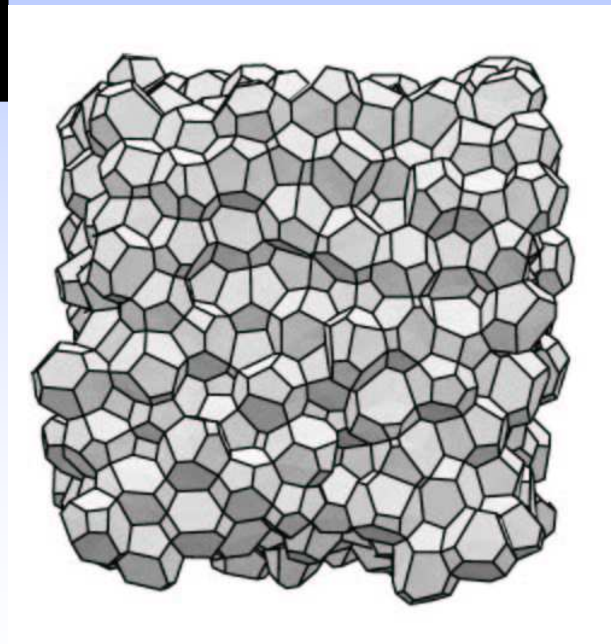




http://www.physics.ucla.edu/~dws/images/foamgrad_300.gif

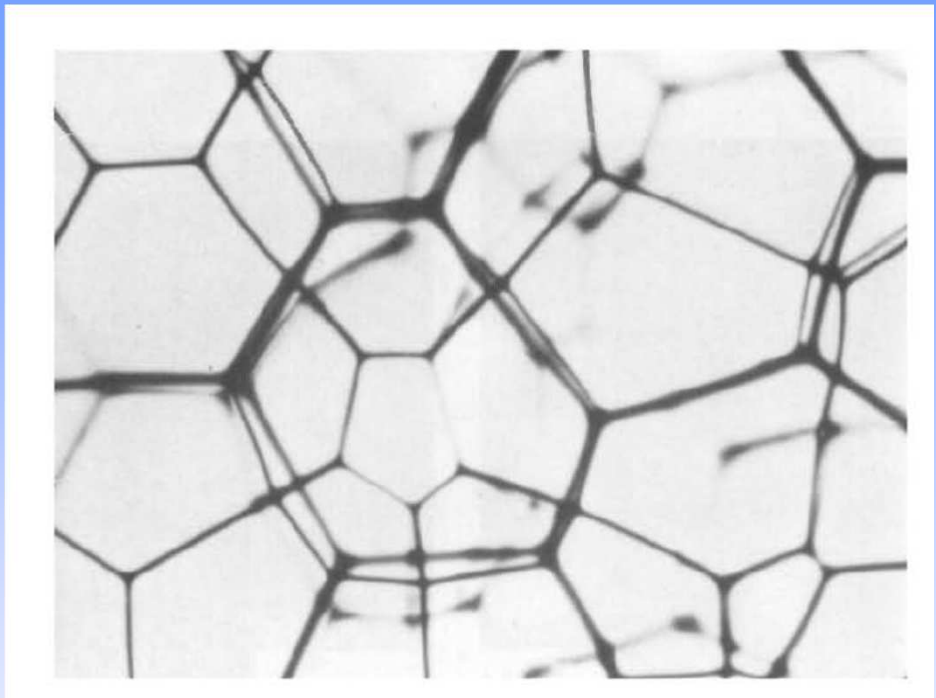
Plateau Borders

Minimum surface area or surface free energy of the foam



http://www.smu.edu/~/media/Site/Dedman/Departments/Math/Foam1.ashx

Soap Bubbles –Plateau Borders



4 13 A foam containing polyhedral cells

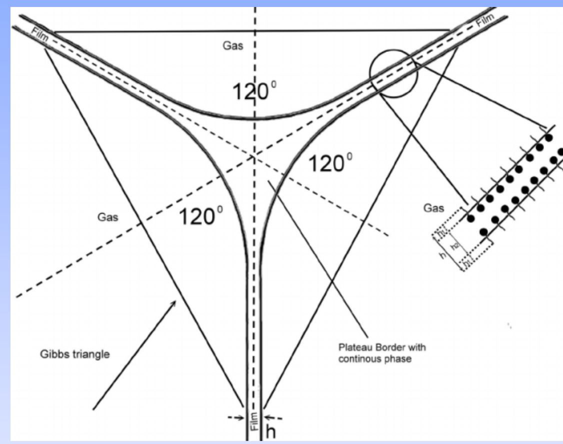
The phenakistiscope was invented almost simultaneously in November or December 1832 by the Belgian physicist Joseph Plateau and the Austrian professor of practical geometry Simon Stampfer.

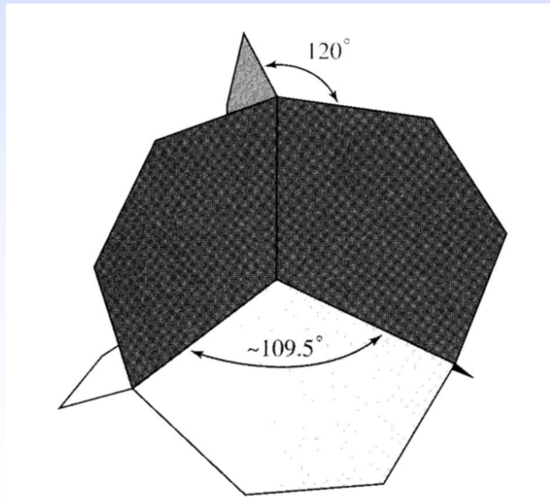
--

Plateau's Laws

In the nineteenth century, the Belgian Joseph Plateau introduced the laws of minimum surface area that are necessary for equilibrium and that define the shapes of foams.

1. Soap films are made of entire (unbroken) smooth surfaces. The mean curvature of a portion of a soap film is everywhere constant on any point on the same piece of soap film.
2. Soap films always meet in threes along an edge called a **Plateau border**, and they do so at an angle of arccos(−1/2) = 120°.
3. These Plateau borders meet in fours at a vertex, and they do so at an angle of arccos(−1/3) ≈ 109.47° (the tetrahedral angle).





Plateau's Laws

In addition to the Young-Laplace Equation, in the nineteenth century, the Belgian Joseph Plateau introduced the laws of minimum surface area that are necessary for equilibrium and that define the shapes of foams.

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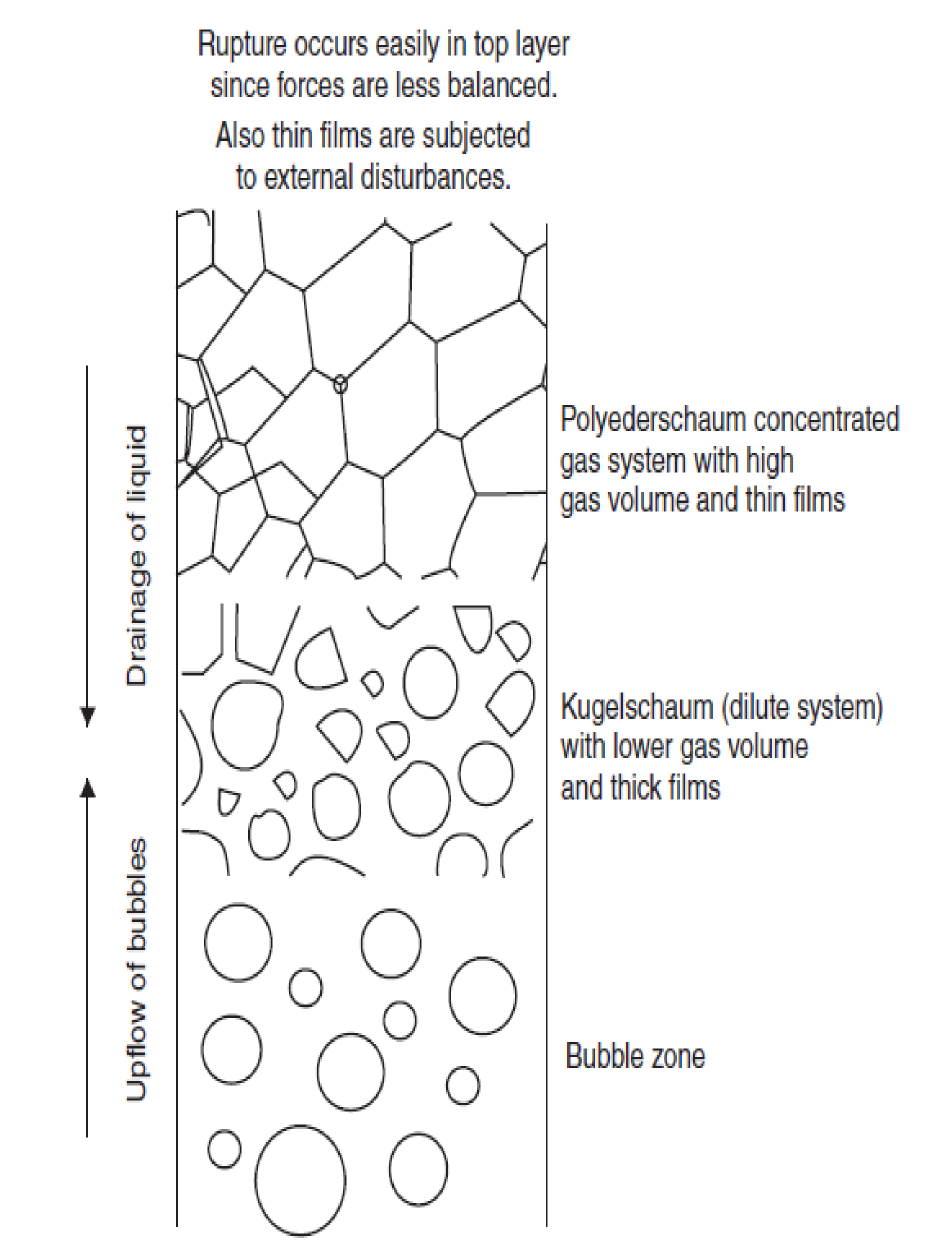
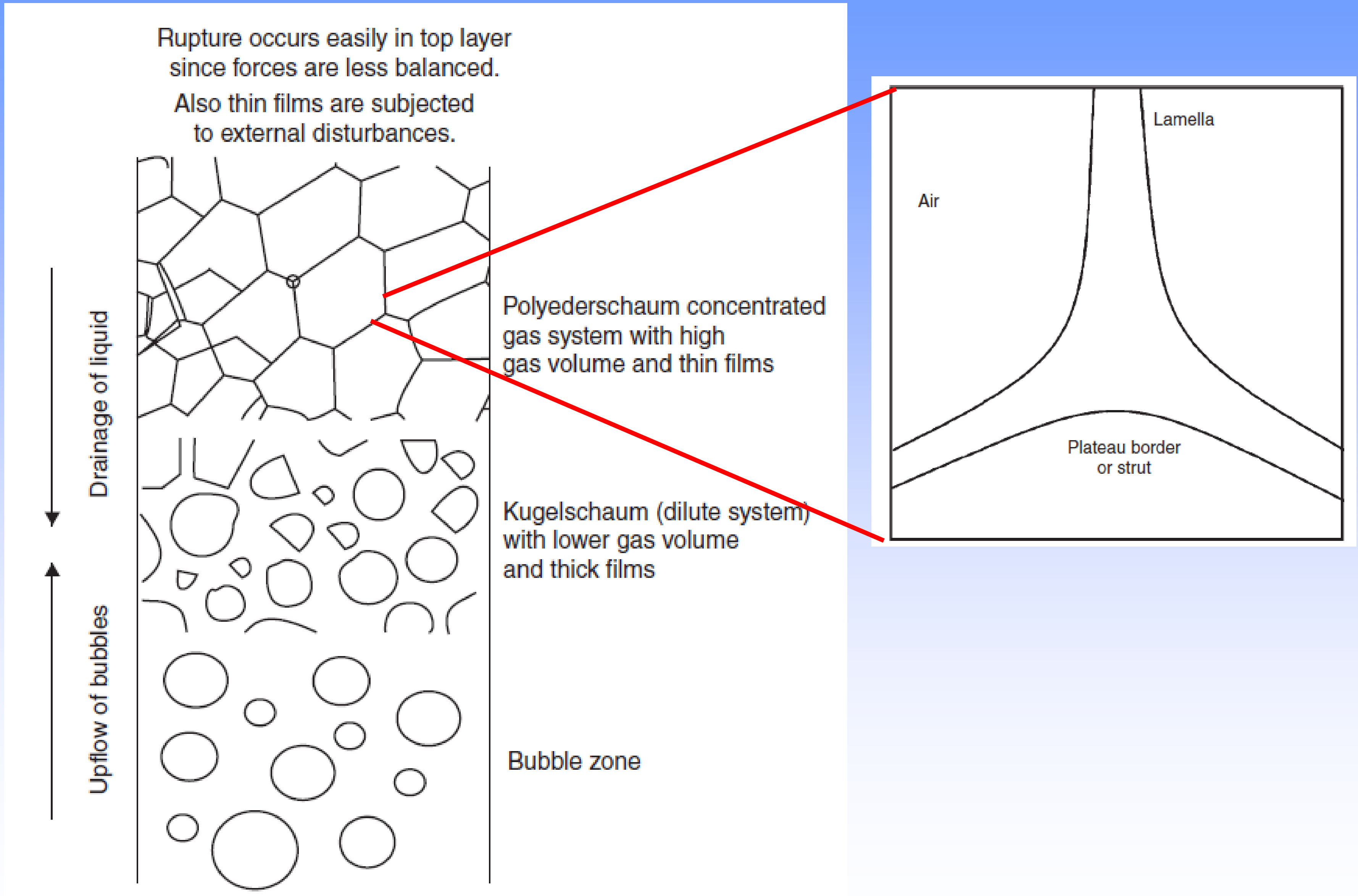
Foam structure during formation and drainage in a vertical column with gas injected from below.

"Polyederschaum" or polyhedral foam has a high gas content (>70 vol.%). The liquid in the polyhedral foam structure is distributed between the inter-bubble films and the Plateau borders (i.e., the channels that form where the films meet).

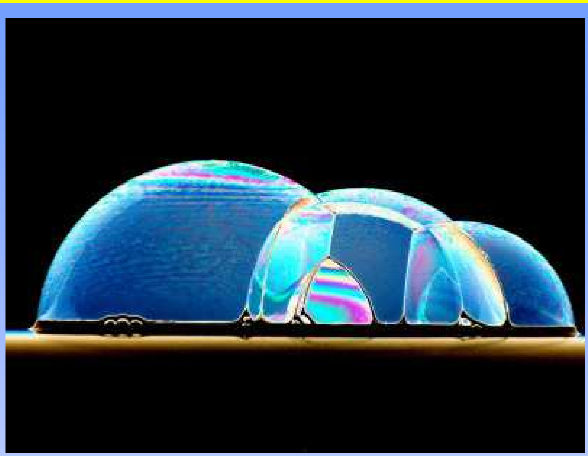


Kontogeorgis & Kiil, *Introduction to Applied Colloid and Surface Chemistry*-John Wiley & Sons (2016)



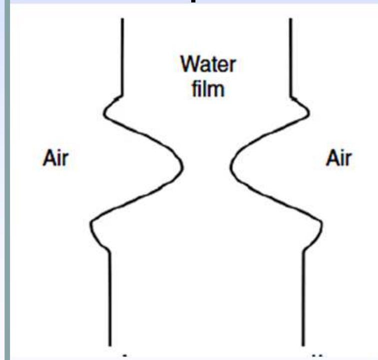
Kontogeorgis & Kiil, *Introduction to Applied Colloid and Surface Chemistry*-John Wiley & Sons (2016)

Increasing Foam Stability:



- Low surface tension – makes it easier to form and maintain large interfacial area.
- Low gravity drainage – decreases the rate of film thinning.
- Low capillary suction – decreases the rate of film thinning.
- High surface elasticity – counteracts the effect of surface perturbations.
- High bulk viscosity – reduces the rate of film thinning.
- High surface viscosity – reduces the rate of film rupture.
- High electric double layer repulsion – increases disjoining pressure and reduces the rates of film thinning and rupture.
- High steric repulsion – reduces the rates of film thinning and rupture.
- Low dispersion force attraction – decreases the rates of film thinning and rupture.

Surface Waves leading to the rupture of a soap film



Stability of Shaving Cream Foam

12 hrs Later

The Ross-Miles Foaming Test

In the Ross-Miles test, a dilute solution of surfactant is dropped from a fixed height into a pool of the same dilute solution and the volume of foam produced is measured

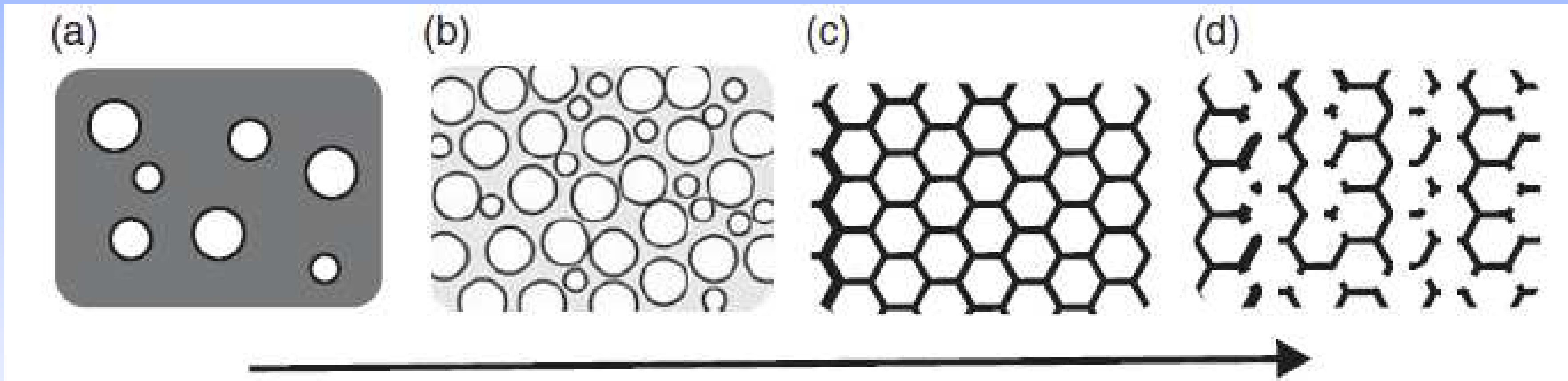
Extremes of Foam Stability

Unstable or transient foams have lifetimes of seconds.

Metastable (or permanent) foams can gave lifetimes measured in days or longer and can withstand ordinary disturbances (Brownian fluctuations), but may collapse from abnormal disturbances (e.g., evaporation or temperature gradients).

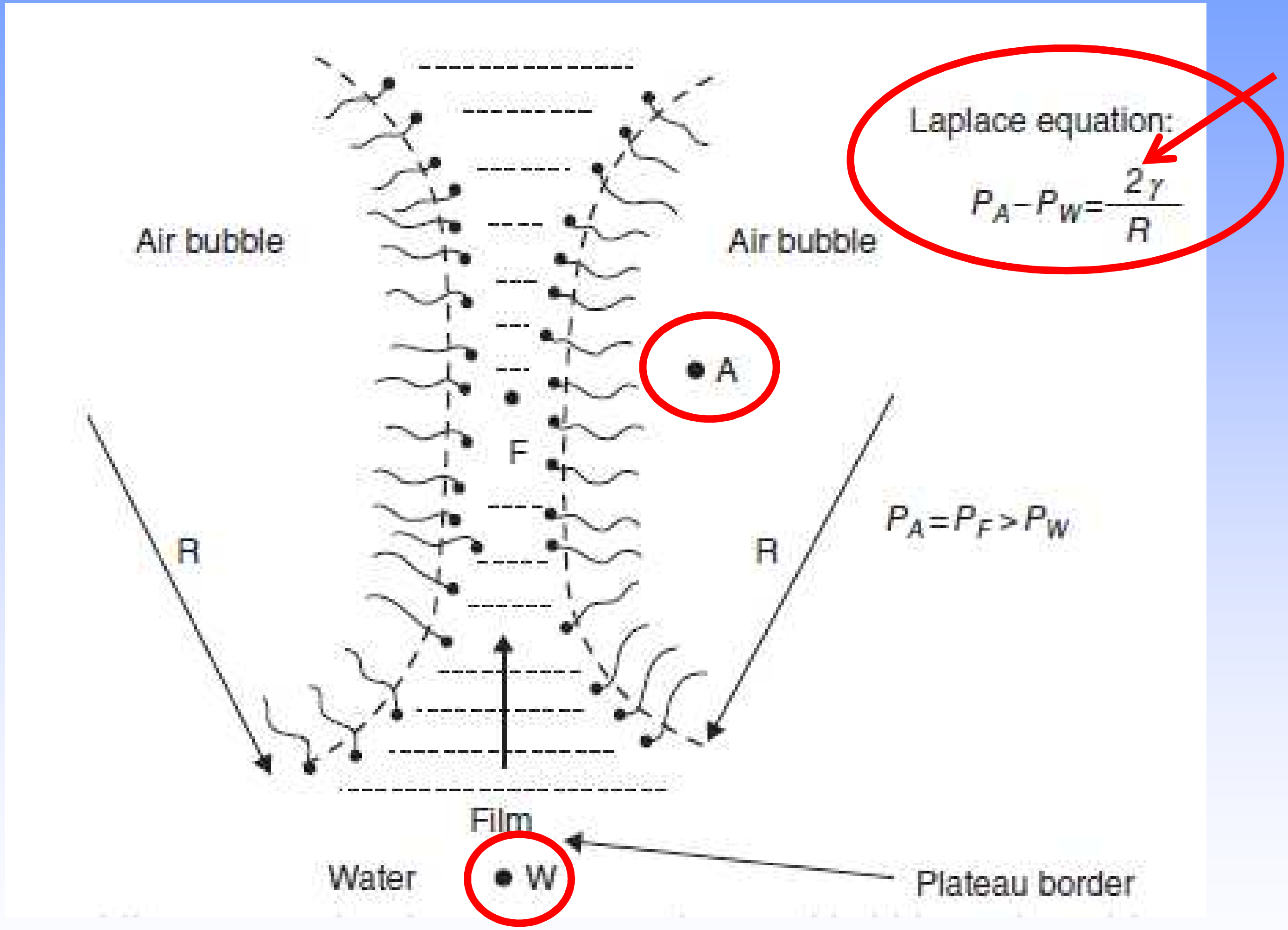
Kontogeorgis & Kiil, *Introduction to Applied Colloid and Surface Chemistry*-John Wiley & Sons (2016)

Destabilizing Foams



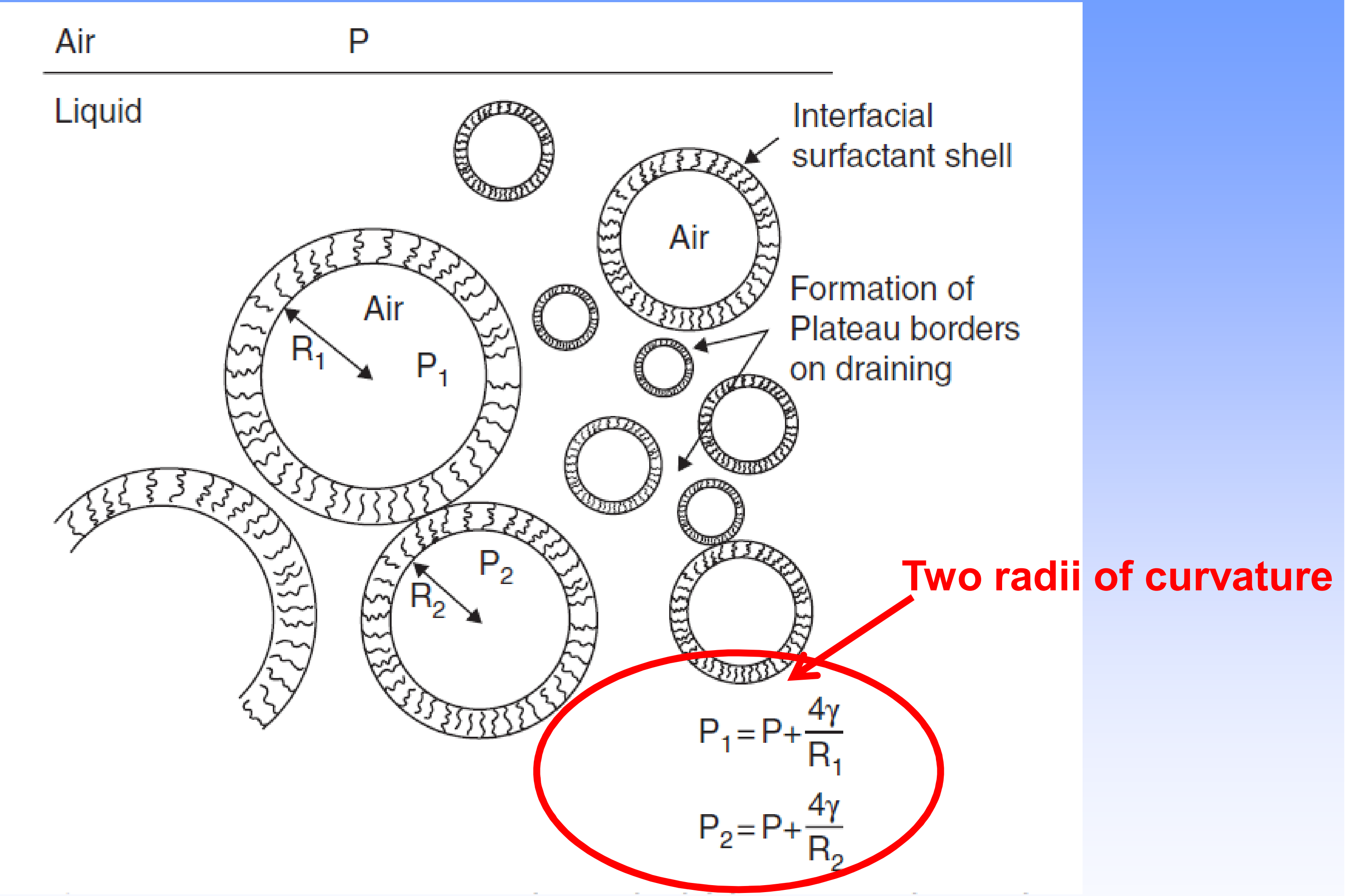
Kontogeorgis & Kiil, *Introduction to Applied Colloid and Surface Chemistry*-John Wiley & Sons (2016)

Laplace Pressure Difference between the Bubbles and the Aqueous Phase



Kontogeorgis & Kiil, *Introduction to Applied Colloid and Surface Chemistry*-John Wiley & Sons (2016)

Laplace Pressure Difference between the Air Bubbles in the Foam

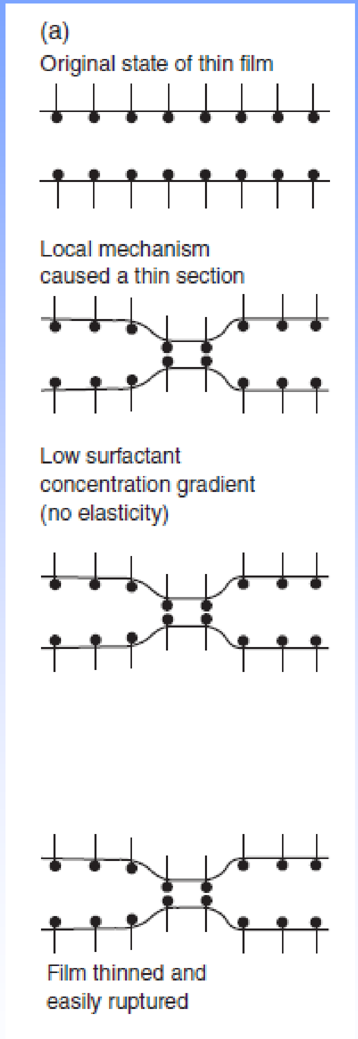


Higher Pressure in Smaller Bubbles means that Bubbles will tend to grow in size and become more uniform with time due to gas diffusion.

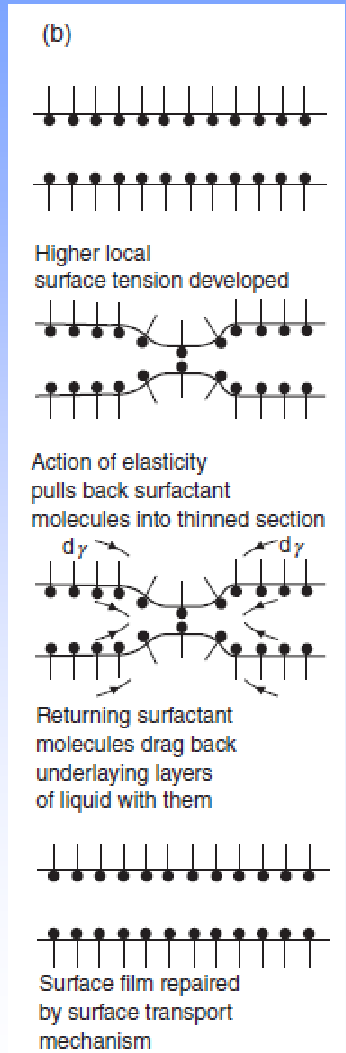
Kontogeorgis & Kiil, *Introduction to Applied Colloid and Surface Chemistry*-John Wiley & Sons (2016)

Surface Concentration and Surface Elasticity

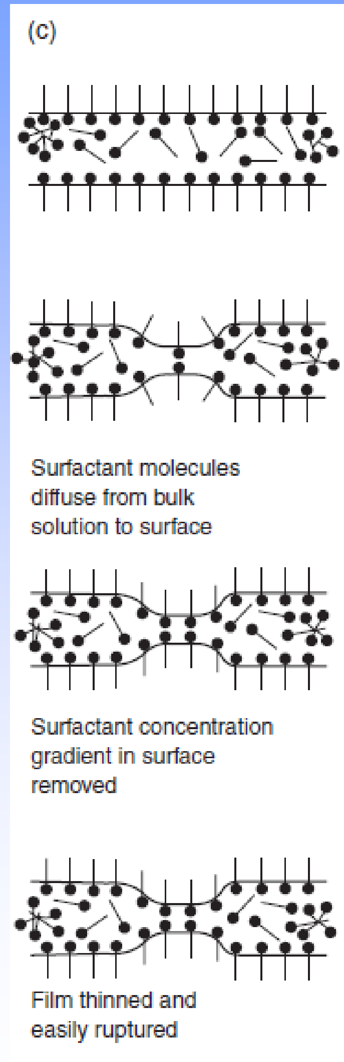
Too Low



Just Right

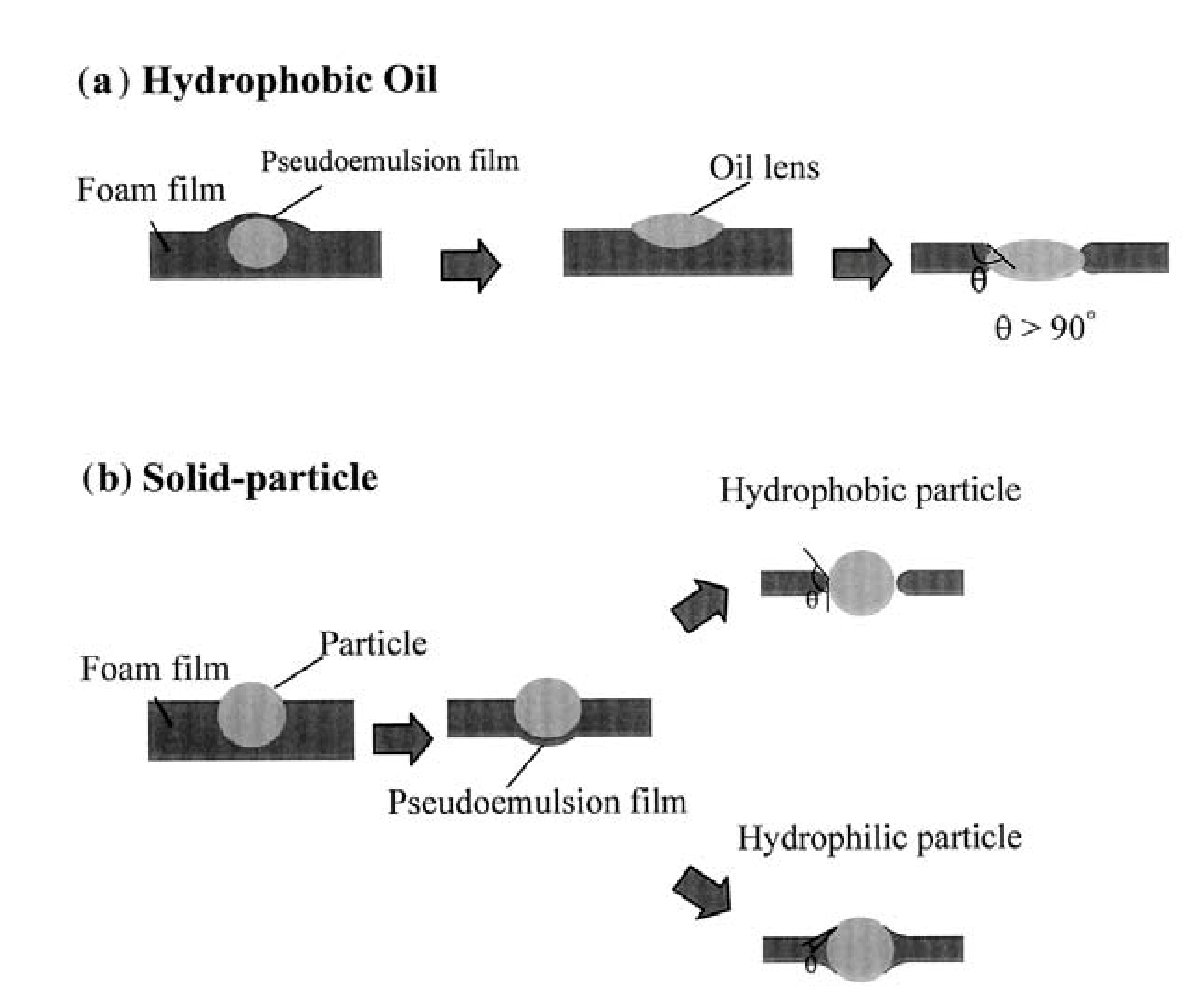


Too High



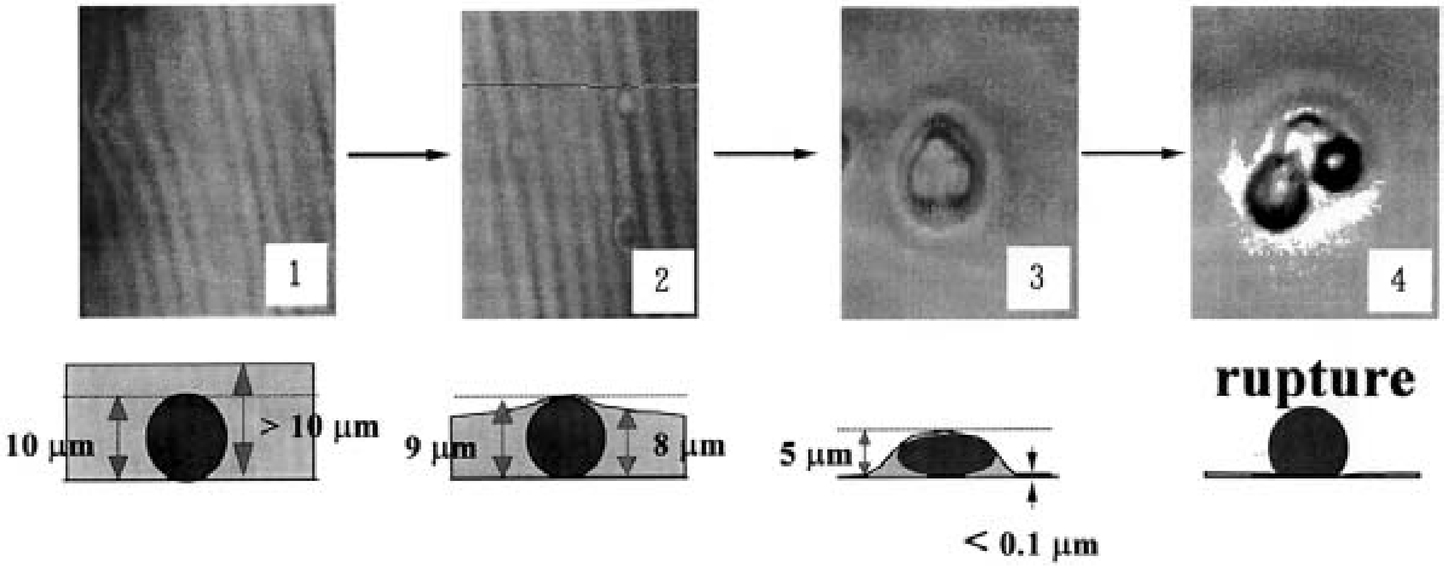
Kontogeorgis & Kiil, *Introduction to Applied Colloid and Surface Chemistry*-John Wiley & Sons (2016)

Anti-Foaming Mechanisms



Stanley Hartland, Surface and Interfacial Tension Measurement, Theory, and Applications (Surfactant Science)-CRC Press (2004)

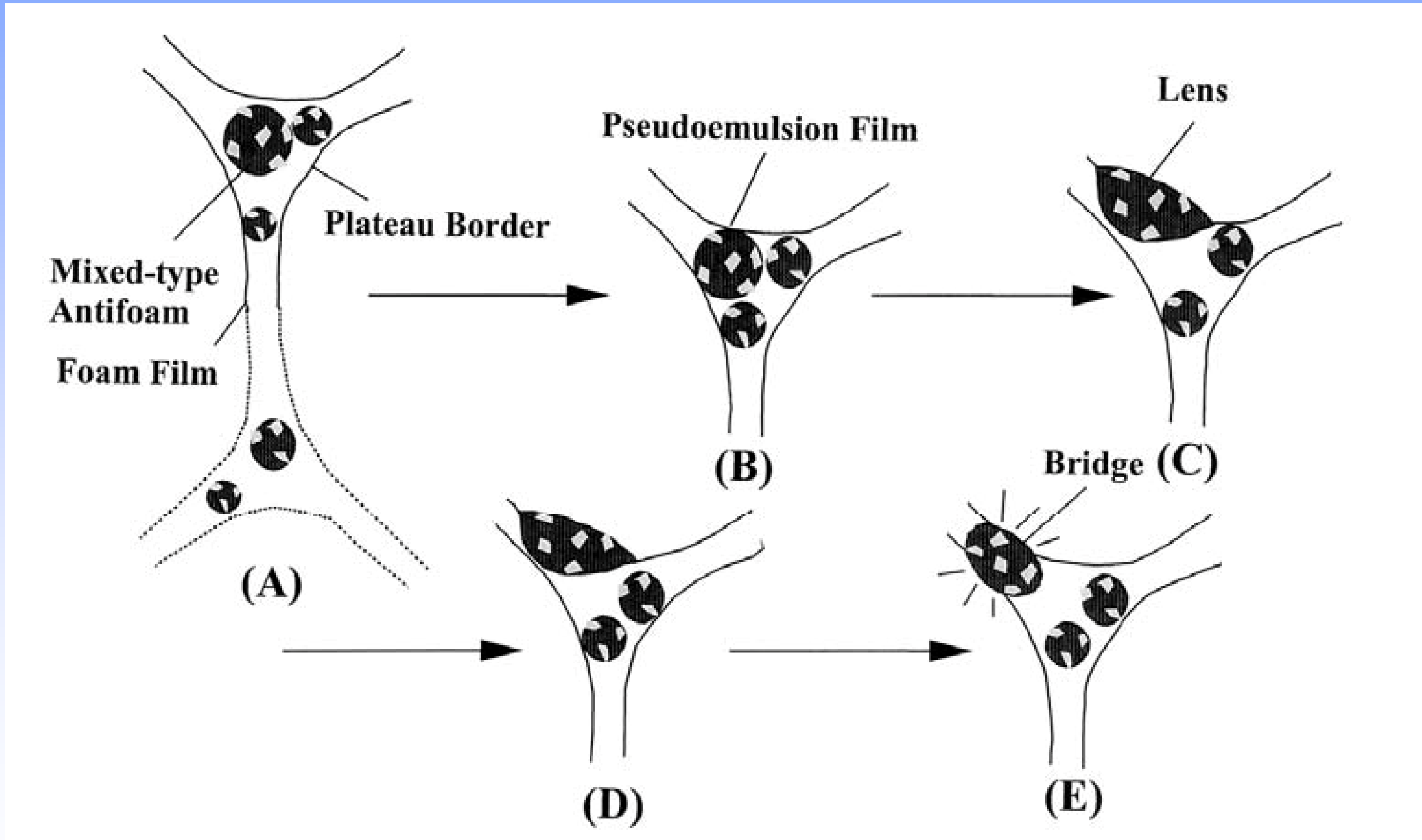
Direct Observation of Anti-Foaming



Stanley Hartland, Surface and Interfacial Tension Measurement, Theory, and Applications (Surfactant Science)-CRC Press (2004)

Anti-Foaming Mechanisms

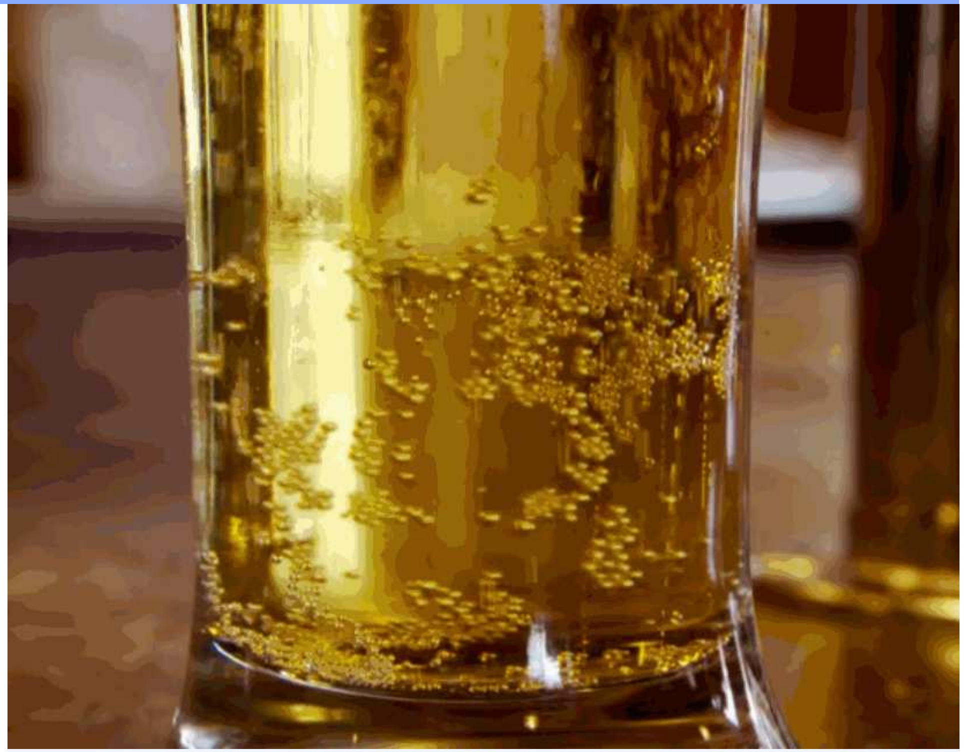
Mixed Type Anti-Foam:



Stanley Hartland, Surface and Interfacial Tension Measurement, Theory, and Applications (Surfactant Science)-CRC Press (2004)

Would Anti-Faming Agents Solve the Problem?

The Perfect Beer in a New, Perfectly Clean Glass vs. the Usual Situation



Nucleation and the Laplace Pressure

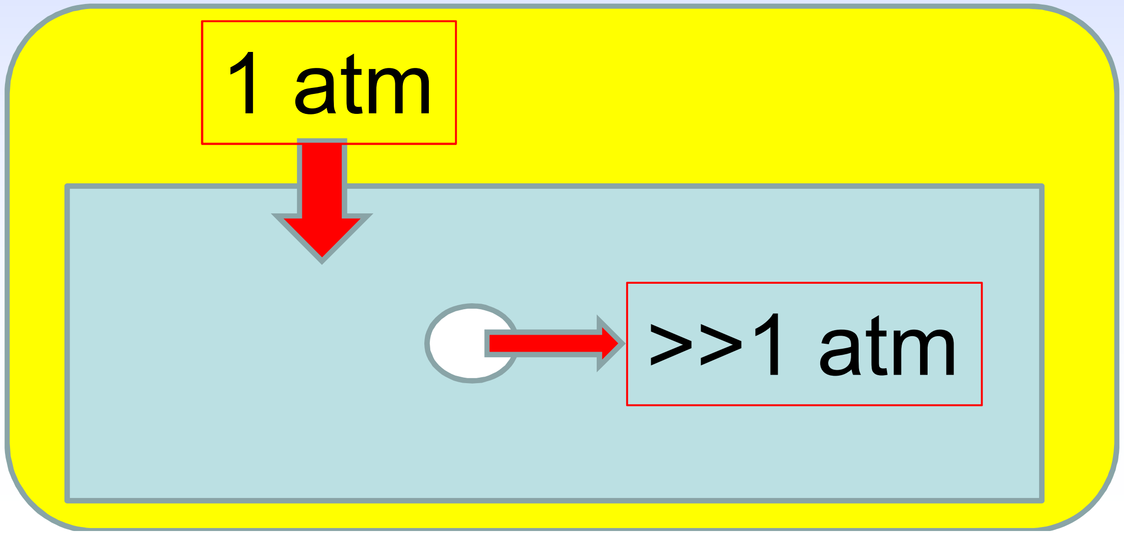
Nanobubbles

The Young–Laplace equation:

Bubble Size:

R_C	ΔP
10 µm	0.15 bar
1000 nm	1.5 bar
100 nm	15 bar
1 nm	1500 bar

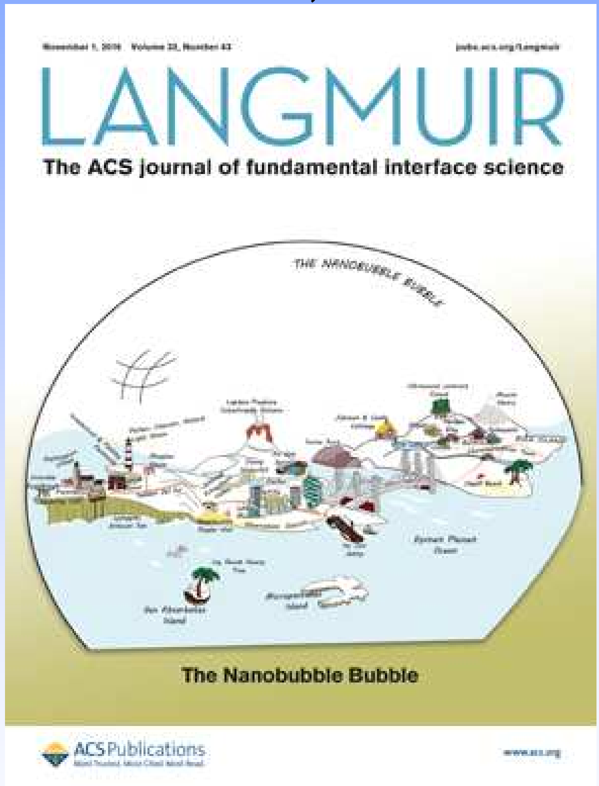
Nanobubbles (1.5 bar – 1500 bar)



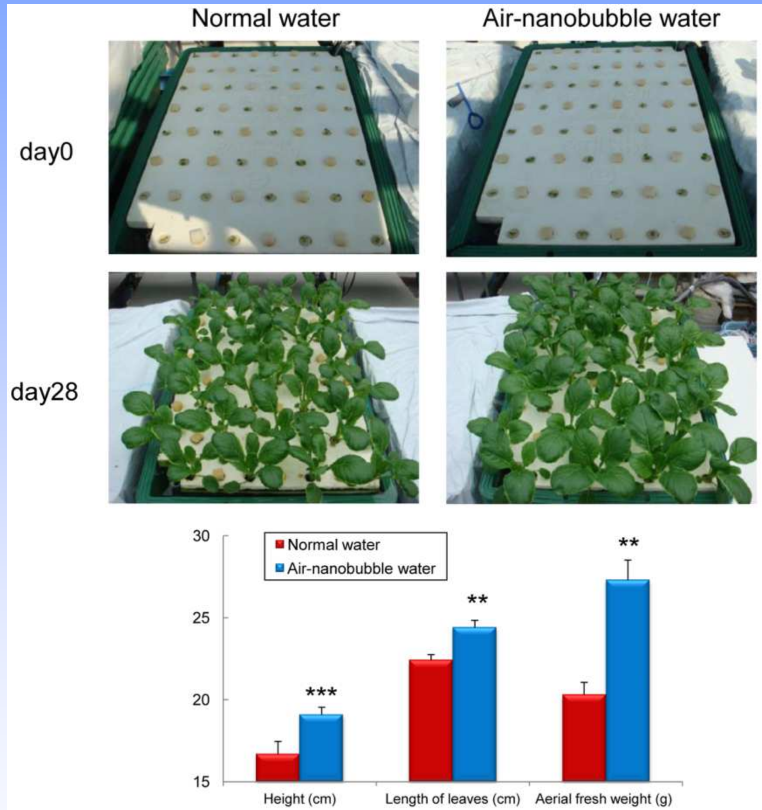
Nanobubbles are intrinsically unstable, but Brownian motion can impede bubble rise. Theory predicts nanobubble lifetimes of seconds – but experiment indicates substantially longer lifetimes!

Nanobubbles

Nanobubble Special Issue
November 1, 2016
Volume 32, Issue 43



A History of Nanobubbles, Muidh Alheshibri, Jing Qian, Marie Jehannin and Vincent S. J. Craig, *Langmuir*, **2016**, *32*, 11086–11100.
DOI: 10.1021/acs.langmuir.6b02489



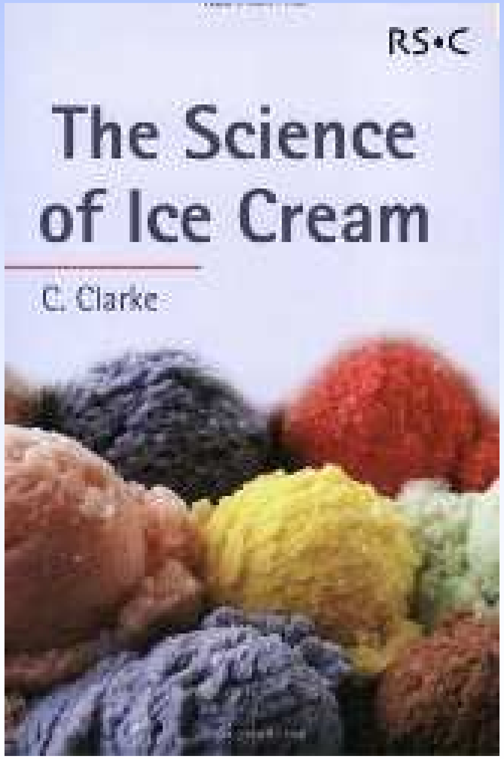
Oxygen and Air Nanobubble Water Solution Promote the Growth of Plants, Fishes, and Mice, Ebina et al., *PLOS ONE*, **2013**, *8*, e65339.

Practical Applications of Emulsions and Foams

Food Products and Agriculture
Biology and Medicine
Personal Care Products
Mining and Mineral Processing
Petroleum Industry
Environmental Remediation
Manufacturing and Materials Science
Metal Processing
Emerging Areas of Application.

Ice Cream

Why is Ice Cream sold by volume and not by weight in the grocery store?



Ice Cream

Composition:

50 vol % air

25 vol % ice

25 vol % "cream"

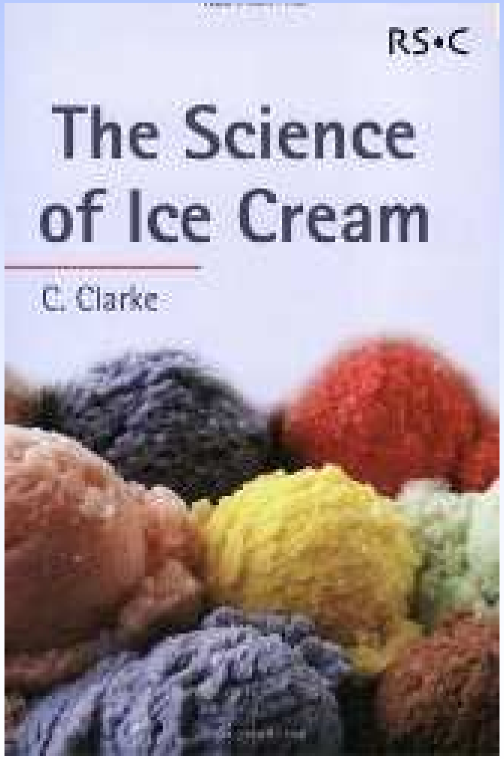
3 parts milk fat

2 parts milk solids

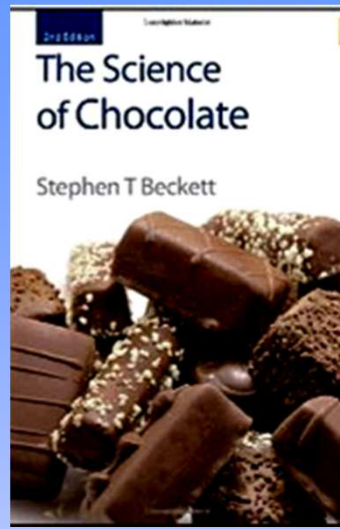
2 parts sugars

1 part corn syrup solids

0.1 part stabilizers/emulsifiers



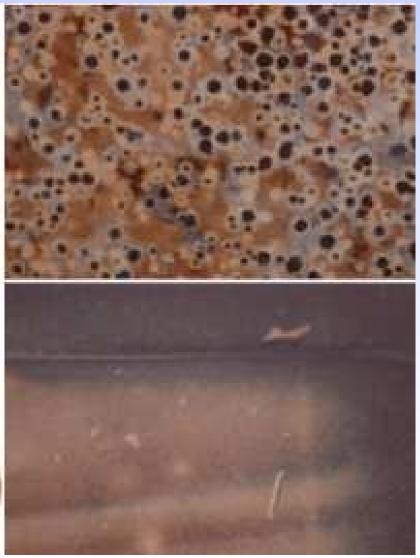
Other Interesting Foods



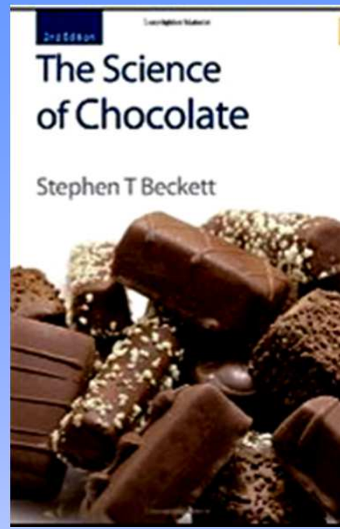
Chocolate:

Solid in oil emulsion.

Bloom (separation of cocoa butter due to crystallization of fat or crystallization of sugars).



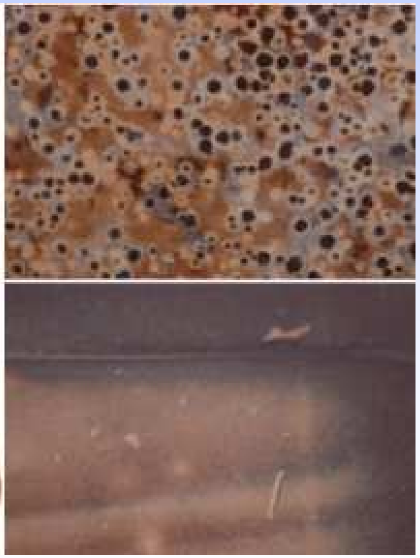
Other Interesting Foods



Chocolate:

Solid in oil emulsion.

Bloom (separation of cocoa butter due to crystallization of fat or crystallization of sugars).



Practical Applications of Emulsions and Foams

Agricultural Emulsions for Fungicides and Pesticides

Figure 13.7 Illustration of processes influencing the performance of a crop protection product. Spray droplets impact a leaf surface, and create a foliar deposit from which a pesticidal agent can move into the leaf or contact the fungal or insect pest. From Rodham [865]. Copyright 2000, Elsevier.

Solubiity, wetting and adhesion are considerations,
as well as stability, dilution, toxicity and biodegradability.

Application of Emulsions in Environmental Remediation

In-Situ Soil Remediation with Emulsions

Surfactant-Enhanced In-Situ Chemical Oxidation (S-ISCO™)

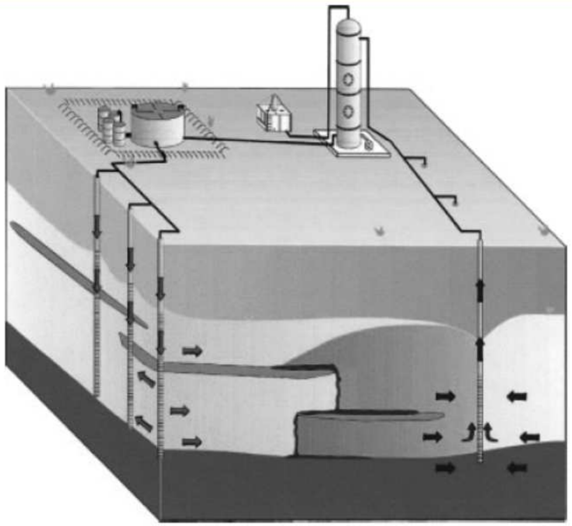


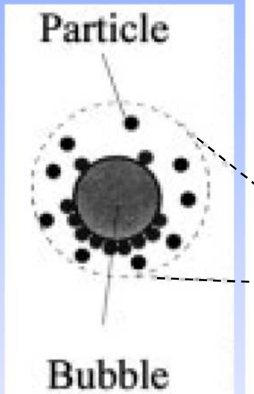
Figure 9.2 Illustration of an *in situ* surfactant flood for the displacement and production of DNAPL contaminants from a contaminated subsurface zone. From Battelle [538]. Copyright 2002, Naval Facilities Engineering Command.

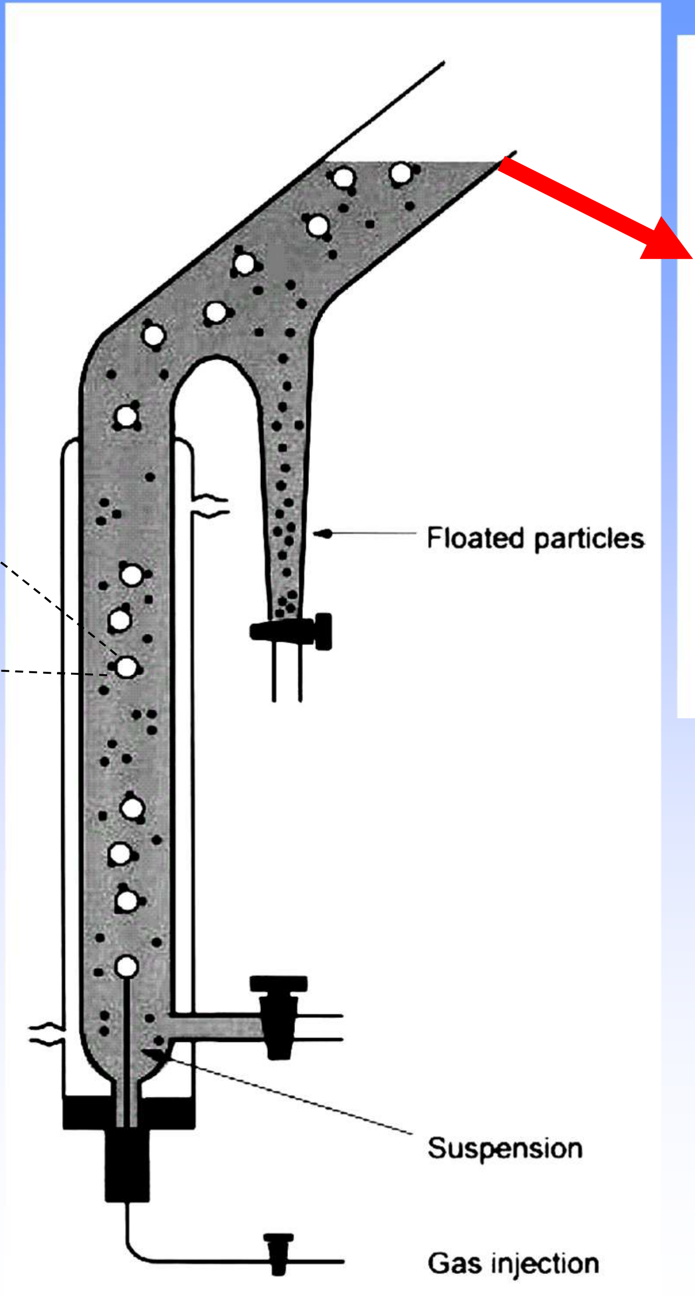
Figure 9. Soil Boring Photologs Comparing Pre- and Post-Treatment using the S-ISCO™ Process

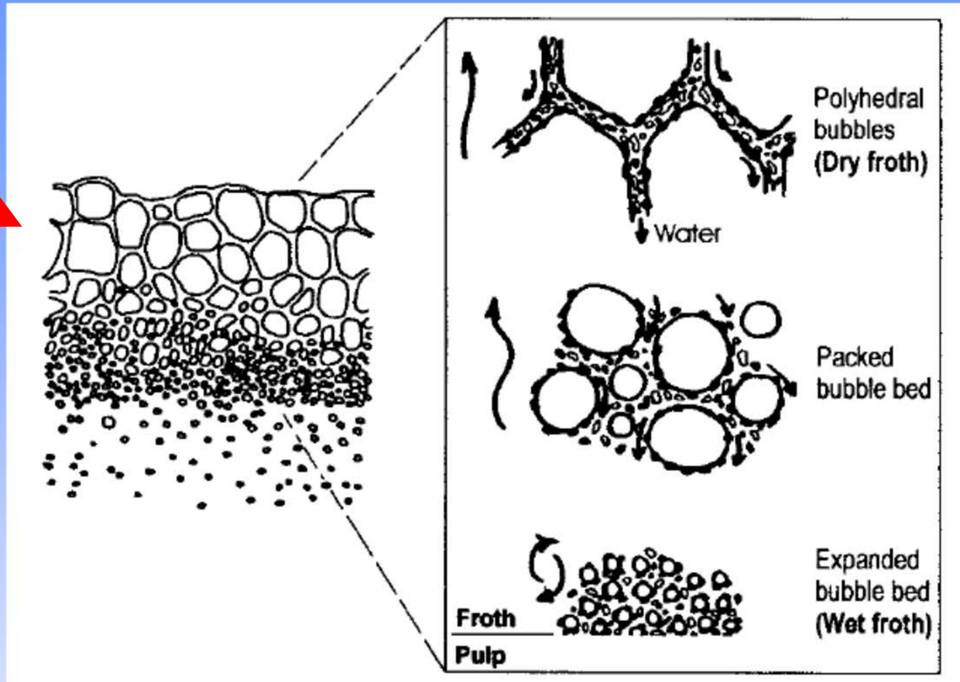
Persulfate + Verusol (emulsion) +Fe(II)-EDTA

http://www.verutek.com

Foam Flotation of Minerals and Ores







Contact angle

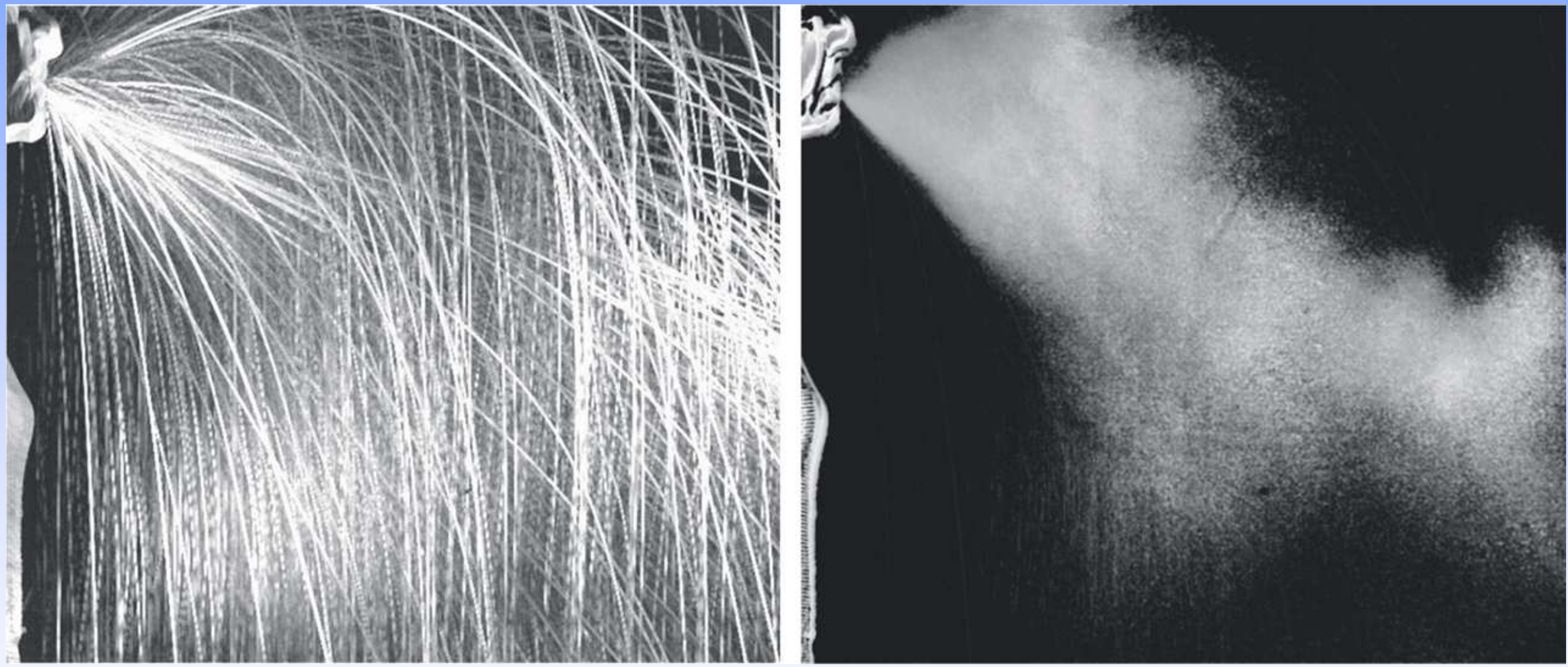
Surfactant surface coverage

Zeta potential

Surface Film rheology

Size and mass of particles

Achoo.Following a sneeze, high-speed video and image processing visualized a waterfall of large droplets (left) and a lingering cloud of small droplets (right) that can spread pathogens farther.



Elizabeth Pennisi Science 2014;343:1194-1197

Practical Applications of Emulsions and Foams

Emerging Areas of Application

<u>Smart Materials:</u>

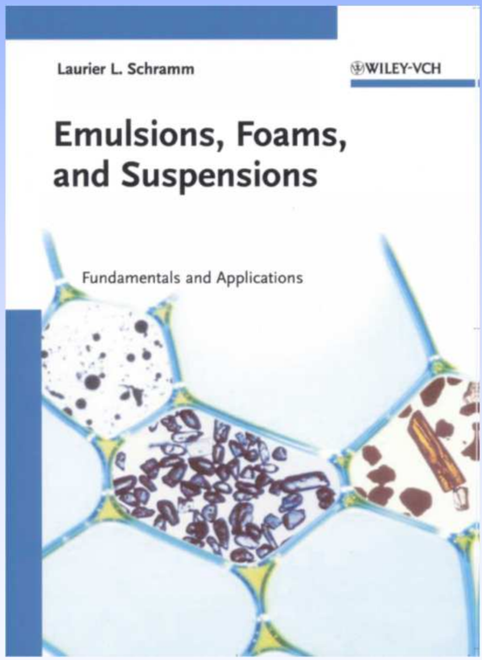
- Magneto-Rheological Materials
- Electro-Rheological Materials
- pH, temperature, solvent (hydrogels)

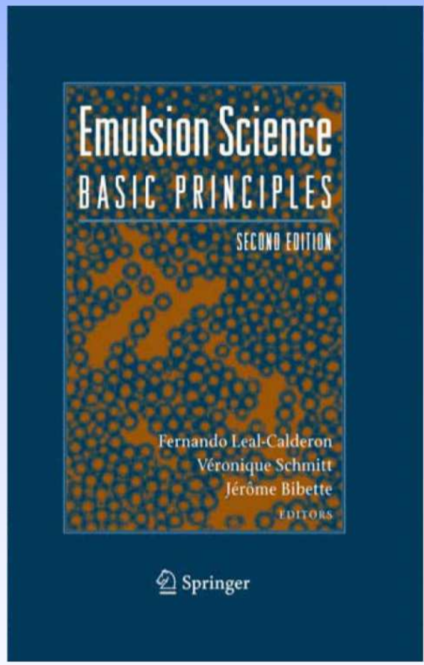
<u>Nanodispersions:</u>

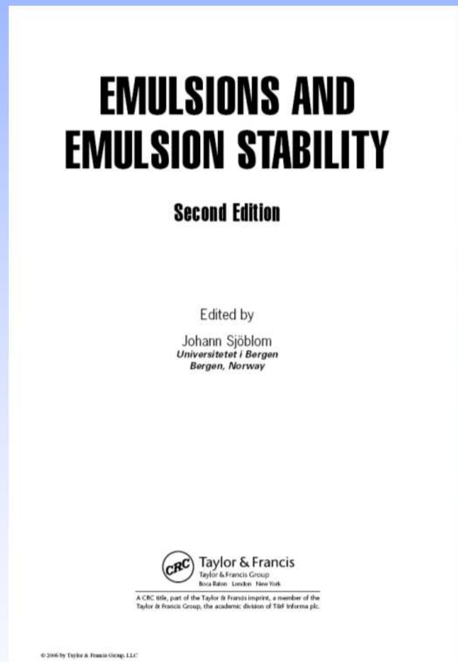
- Microemulsions for Preparation of Nanoparticles
- Microemulsions for Wetting, Dispersion and Stabilization of Nanoparticles

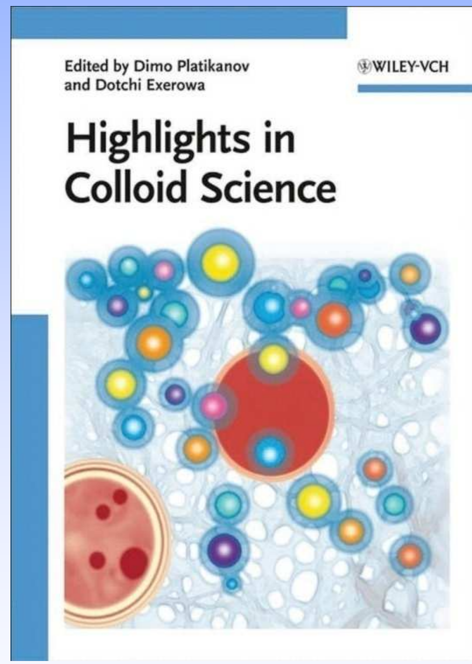
<u>Combating Chemical and Biological WMD</u>

Bibliography

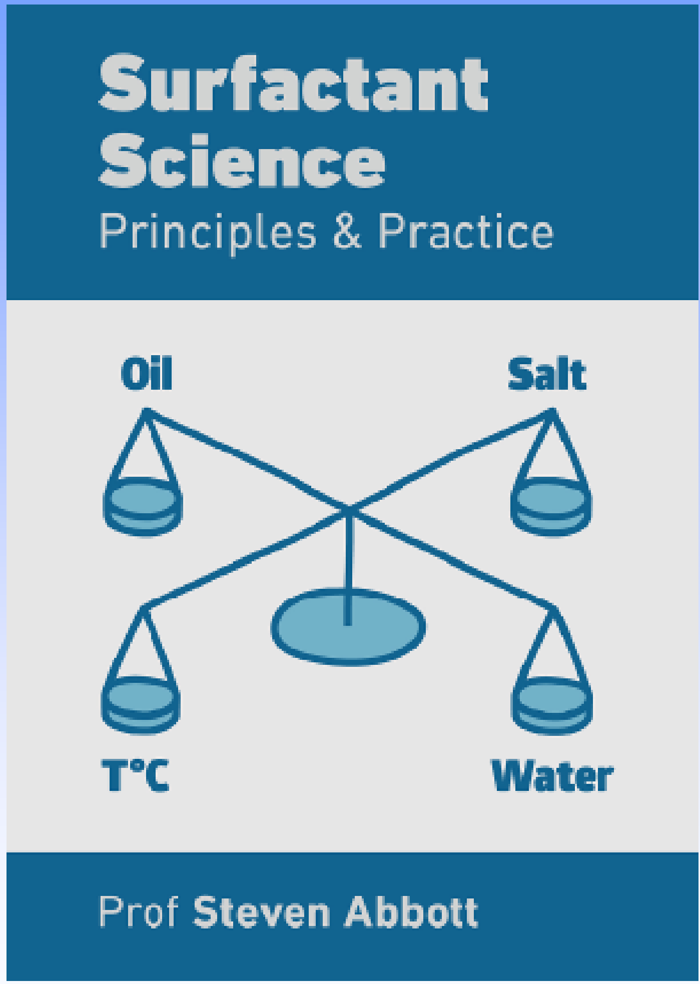








Bibliography



www.stevenabbott.co.uk

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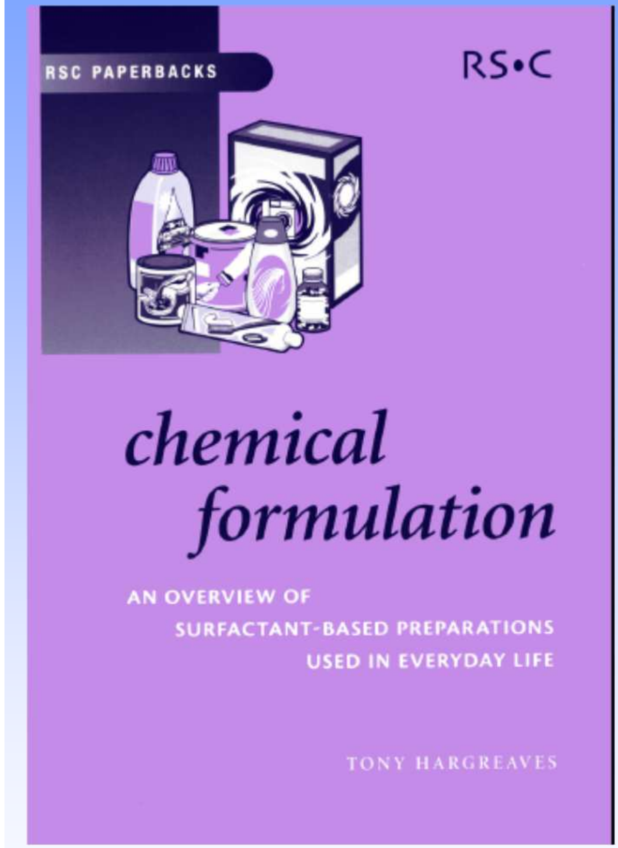
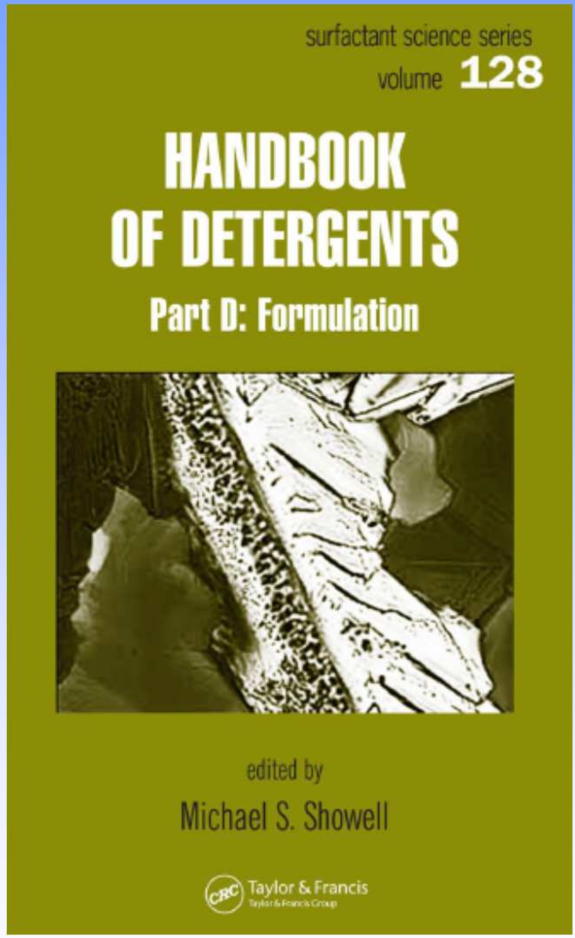
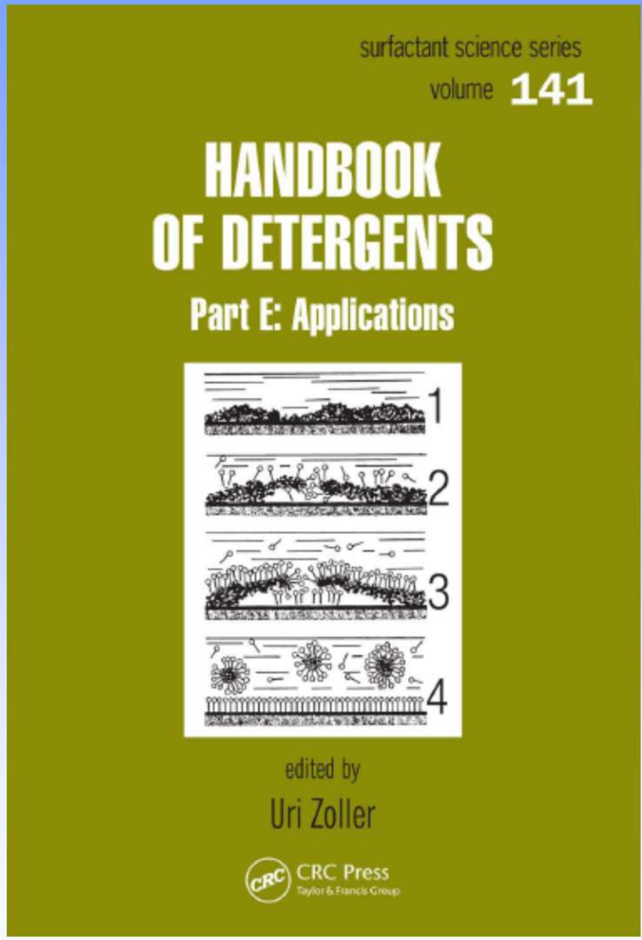
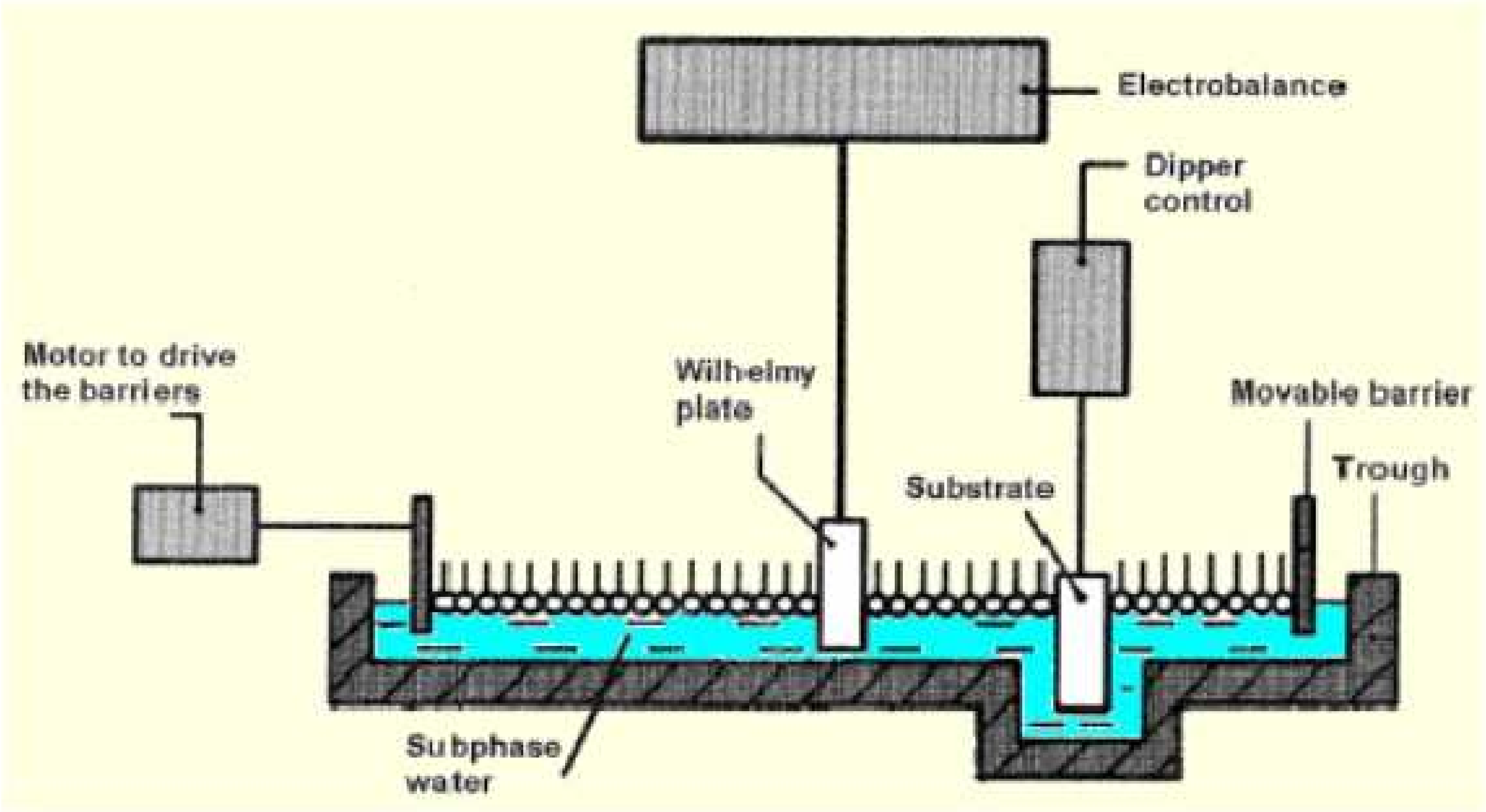




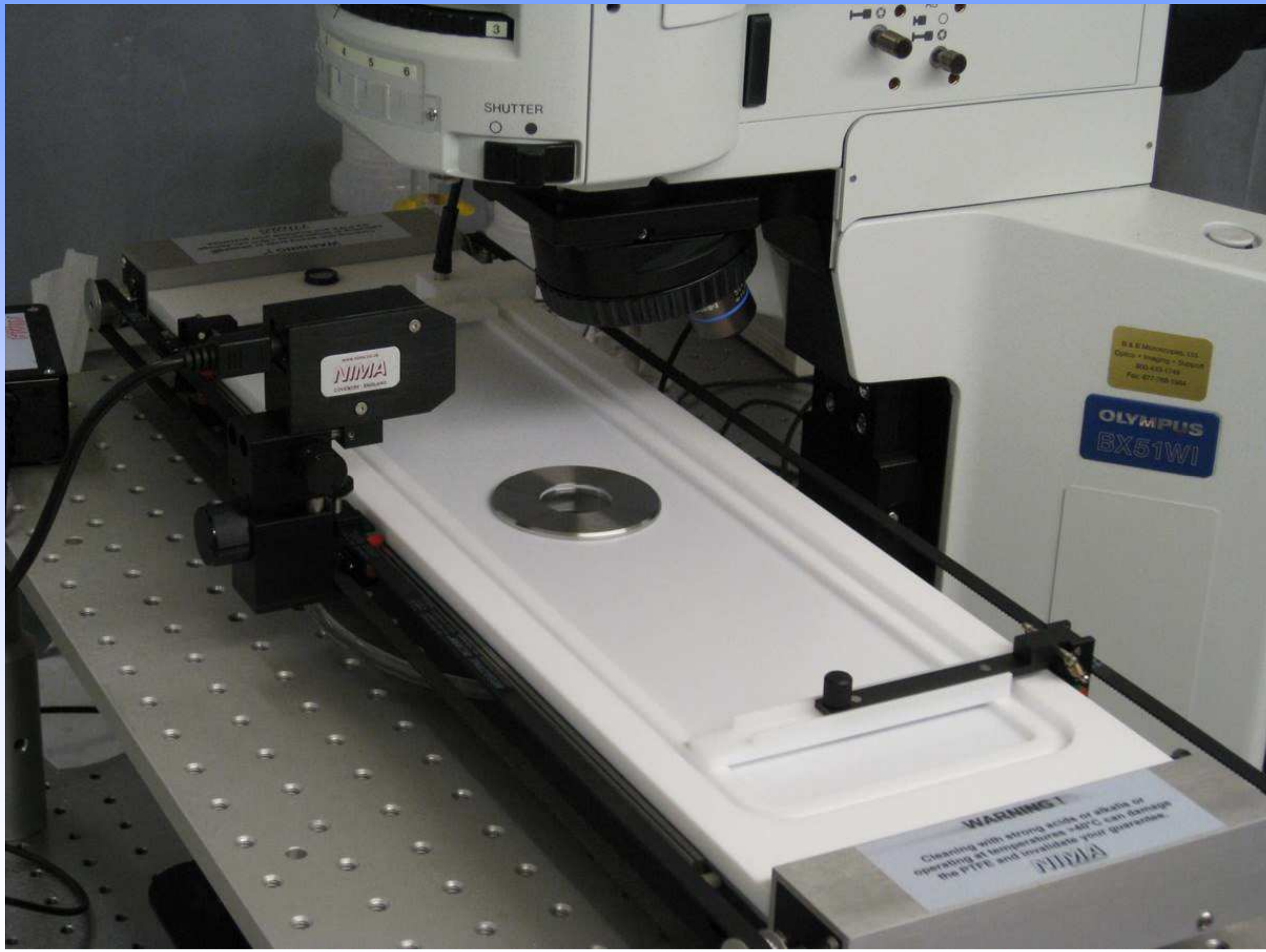


Monolayers, Micelles, Reverse Micelles, Vesicles and Microemulsions

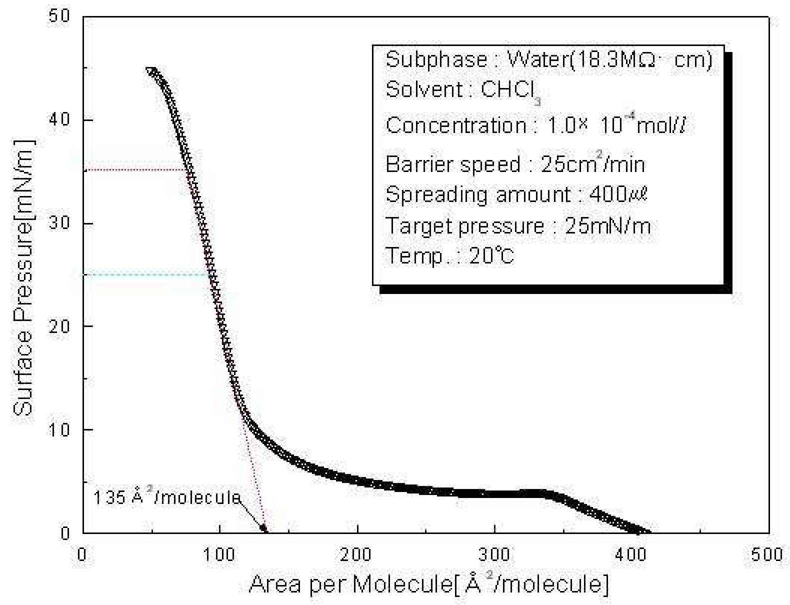
Fabrication of Langmuir –Blodgett Film

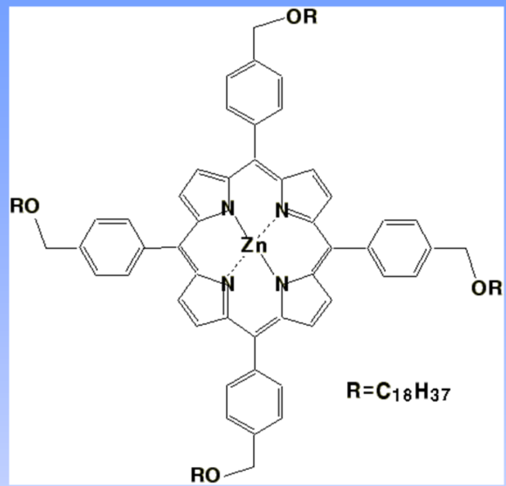


A Commercial Monolayer Trough

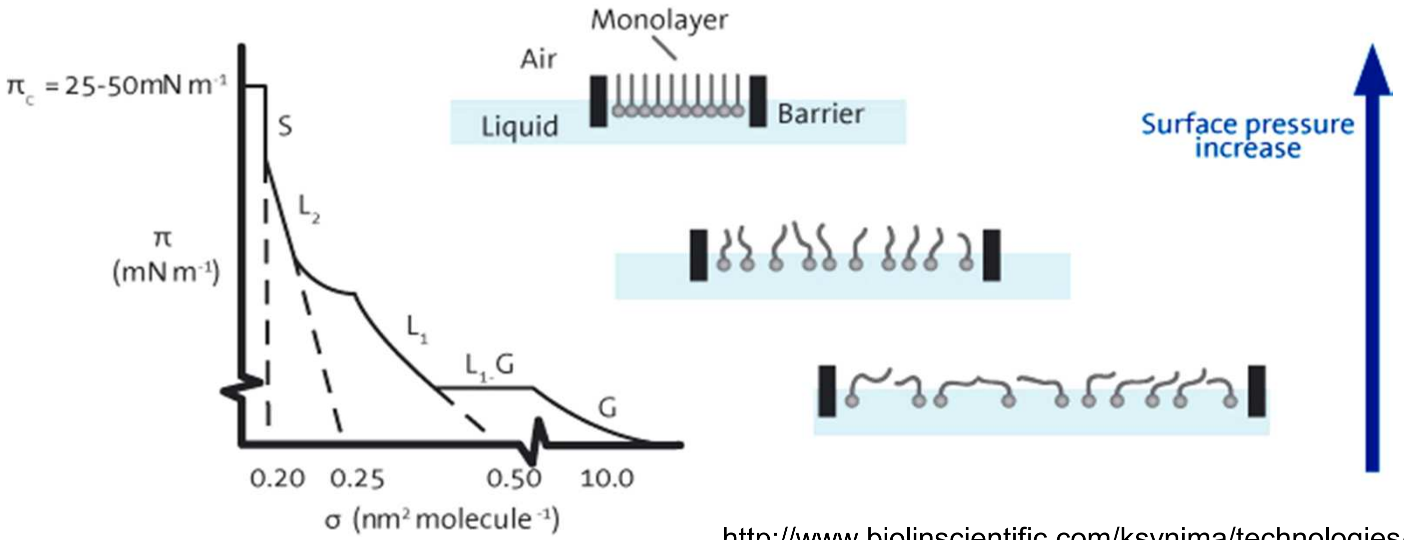


π-Area Isotherm of an Insoluble Monolayer of a Porphyrin Derivative



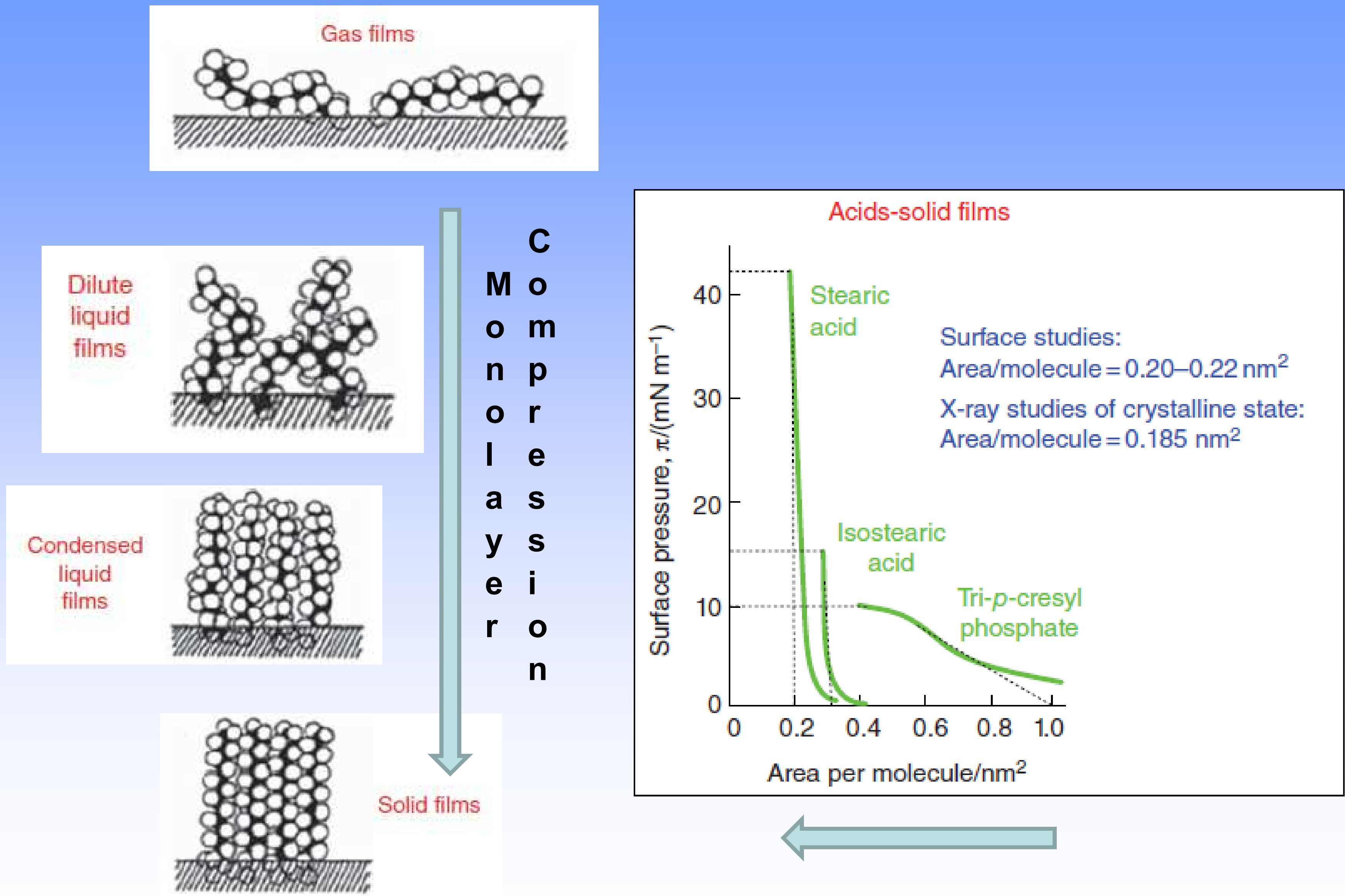


http://www.foresight.org/Conference/MNT9/Papers/Koo/



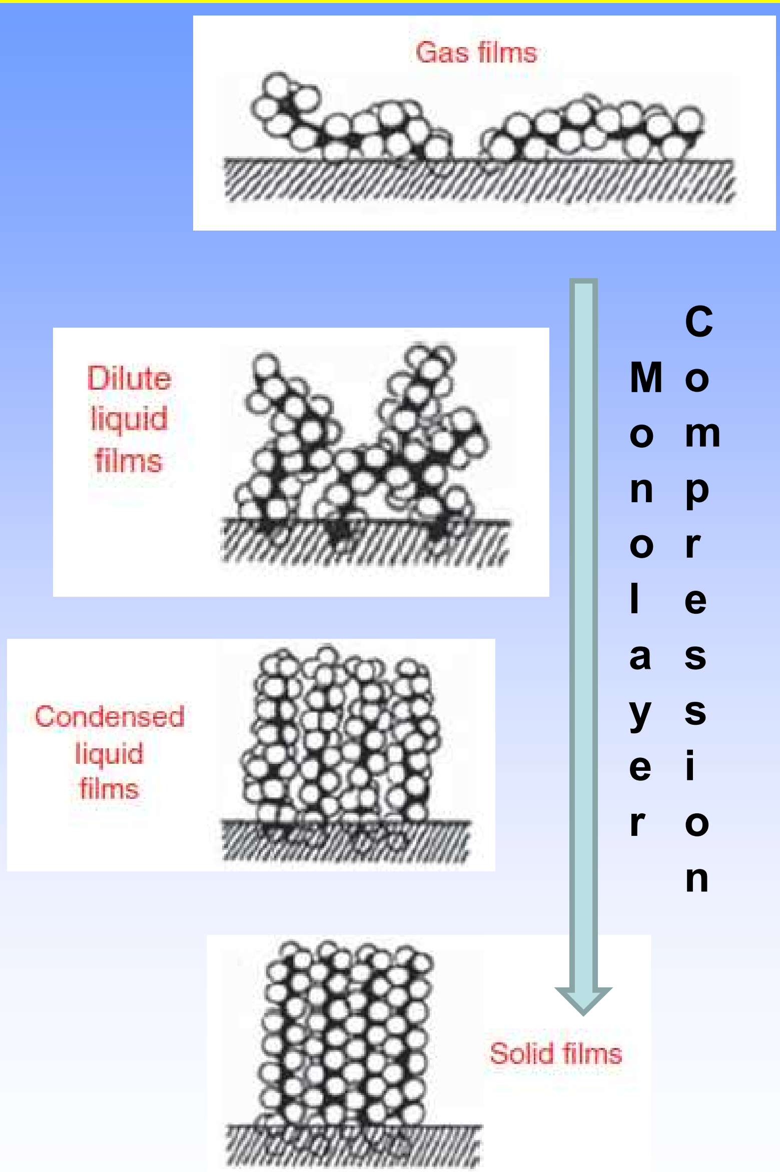
http://www.biolinscientific.com/ksvnima/technologies/

Insoluble Monolayers at the Air/Water Interface:



Kontogeorgis & Kiil, *Introduction to Applied Colloid and Surface Chemistry*-John Wiley & Sons (2016)

CTAB Monolayers at the Air/Water and Oil/Water Interfaces:

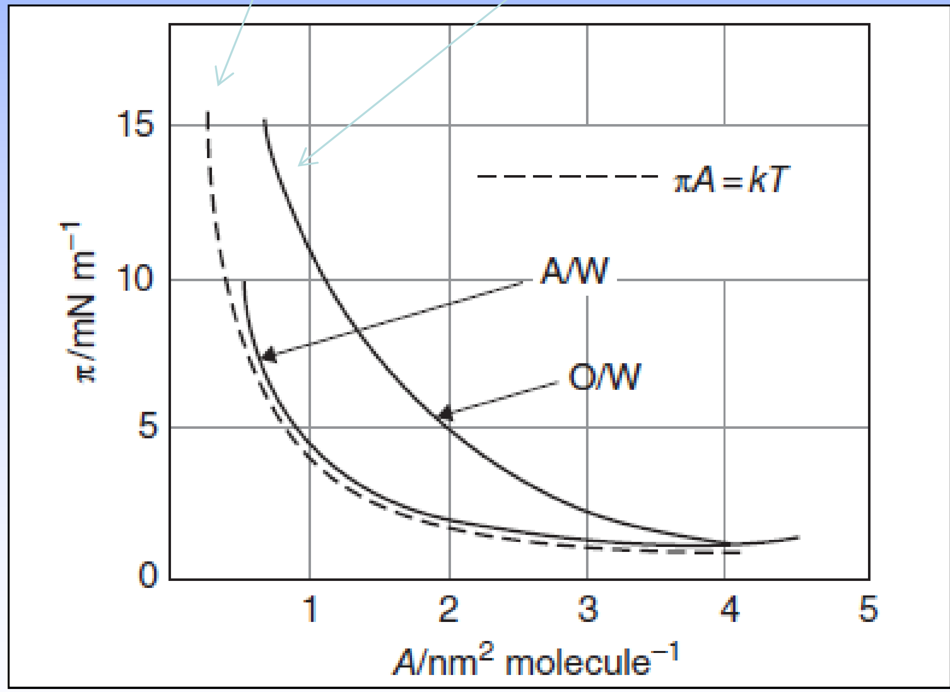


Monolayer Compression

CTAB: $CH_3(CH_2)_{15}\text{-}NMe_3^+\ Br^-$

Chain attraction

Headgroup repulsion



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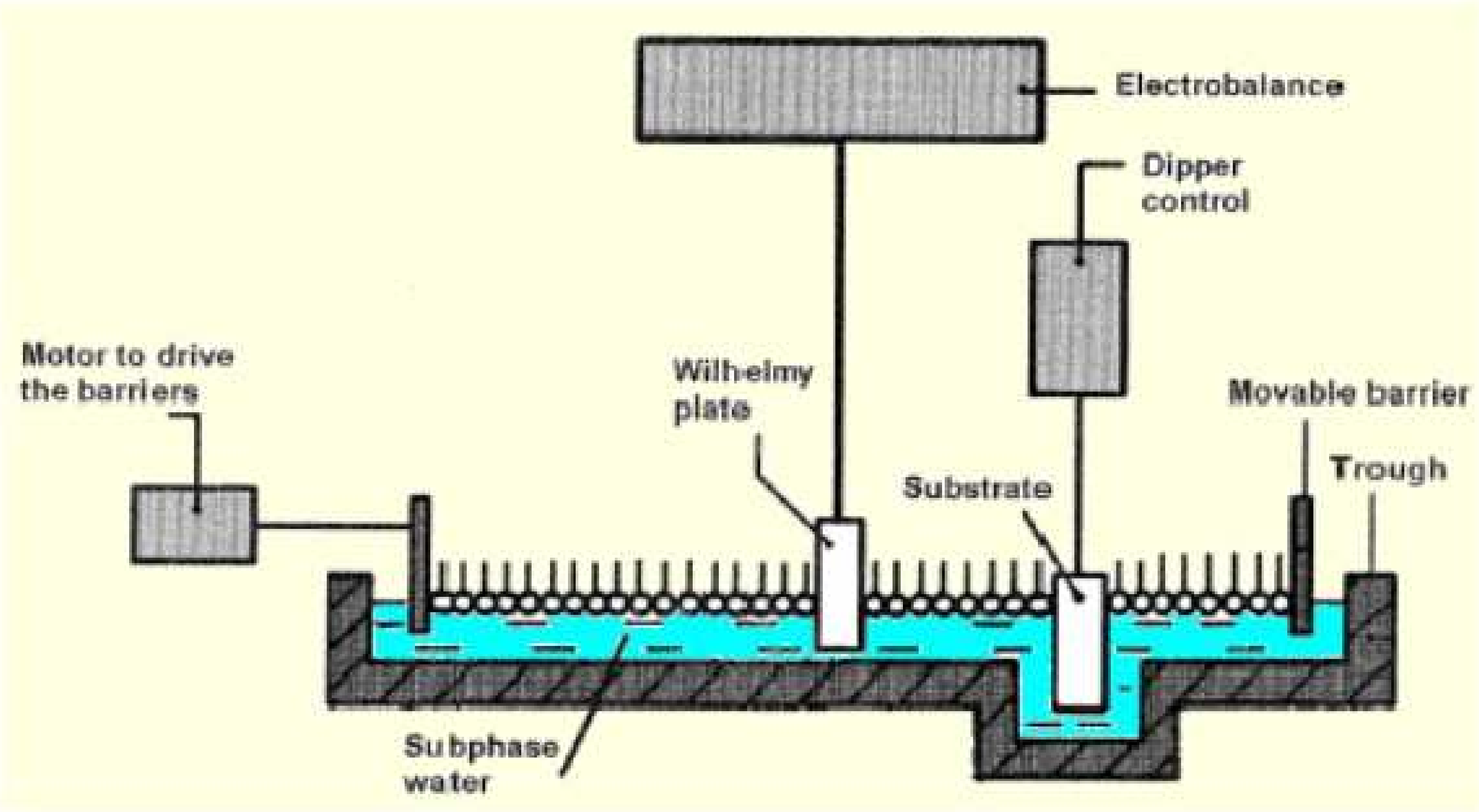
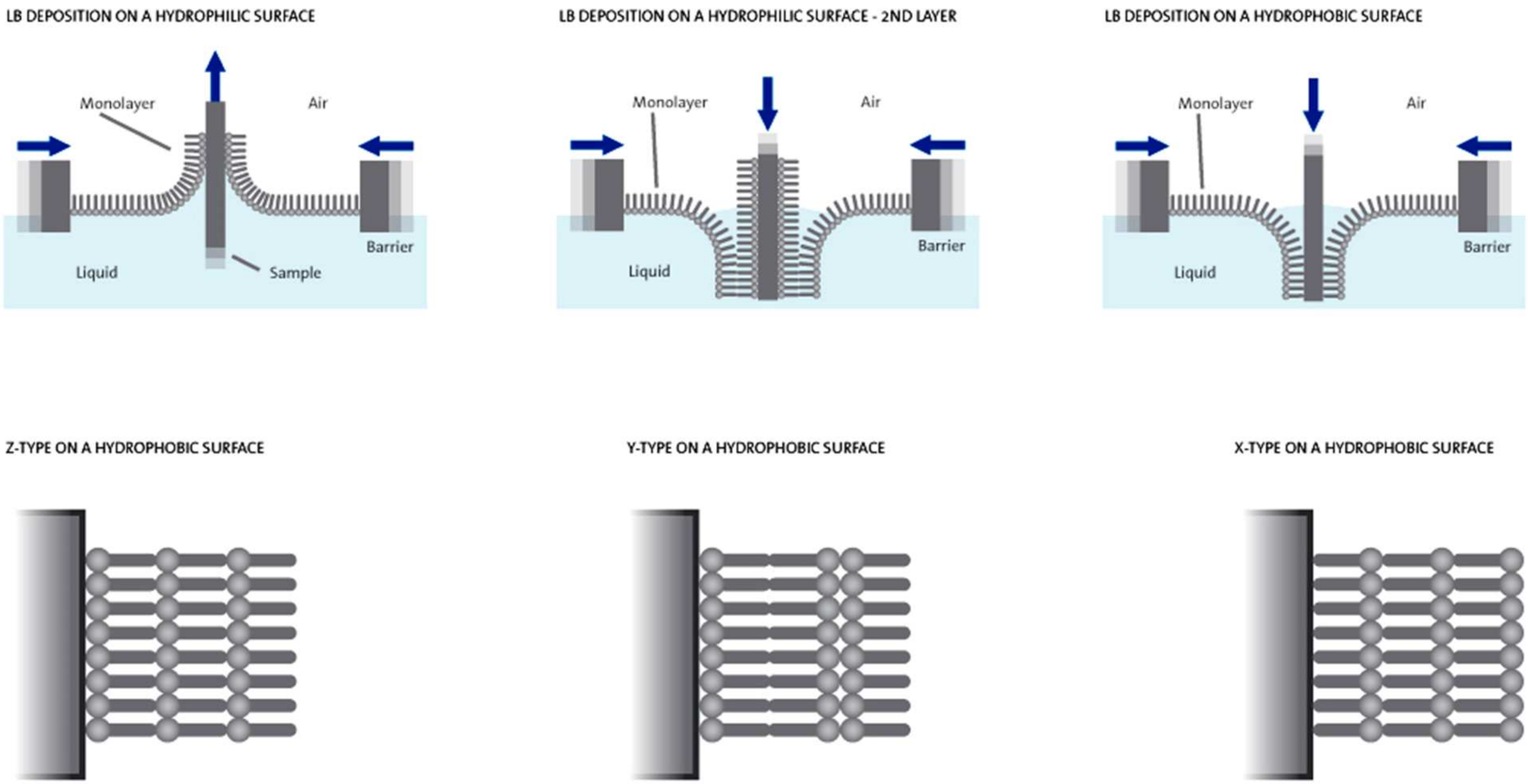
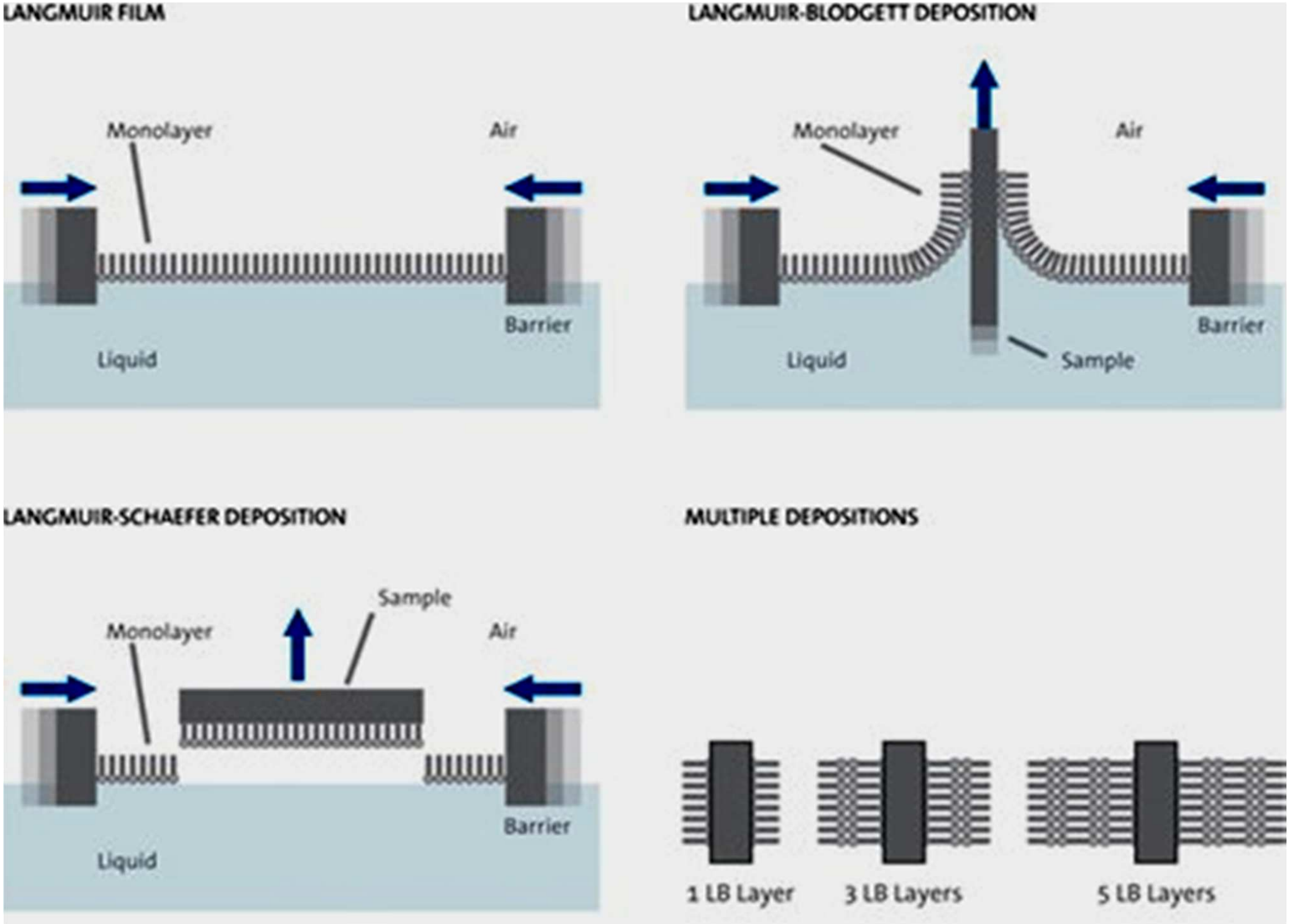


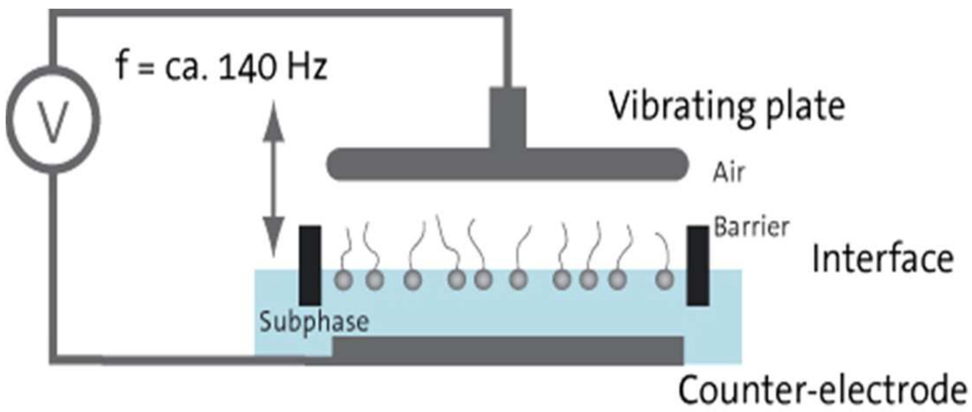


http://www.biolinscientific.com/ksvnima/technologies/



http://www.biolinscientific.com/ksvnima/technologies/

Surface Potential Measurement (Capacitance)



$\Delta V = \mu_n / \varepsilon \cdot \varepsilon_0 \cdot A$

with

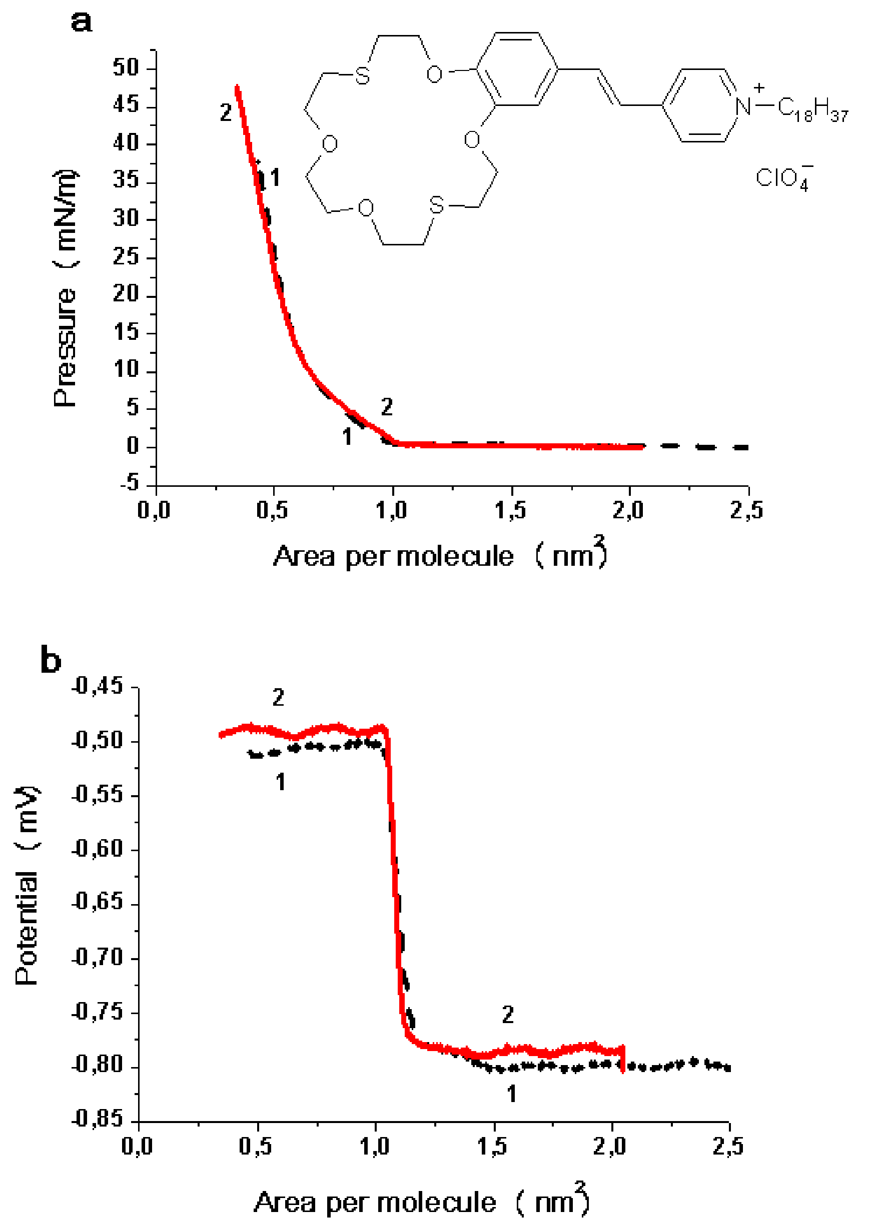
ε = subphase permitivity (e.g. here water)
ε_0 = air permitivity
A = area per molecule
μ_n = vertical component of the dipole moment

Other Techniques:
Brewster Angle Microscopy, Rheology, FTIR-Reflection Spectroscopy, Ellipsometry, Fluor

http://www.biolinscientific.com/ksvnima/technologies/

Comparing Surface Pressure-Area and Surface Potential-Area Isotherms

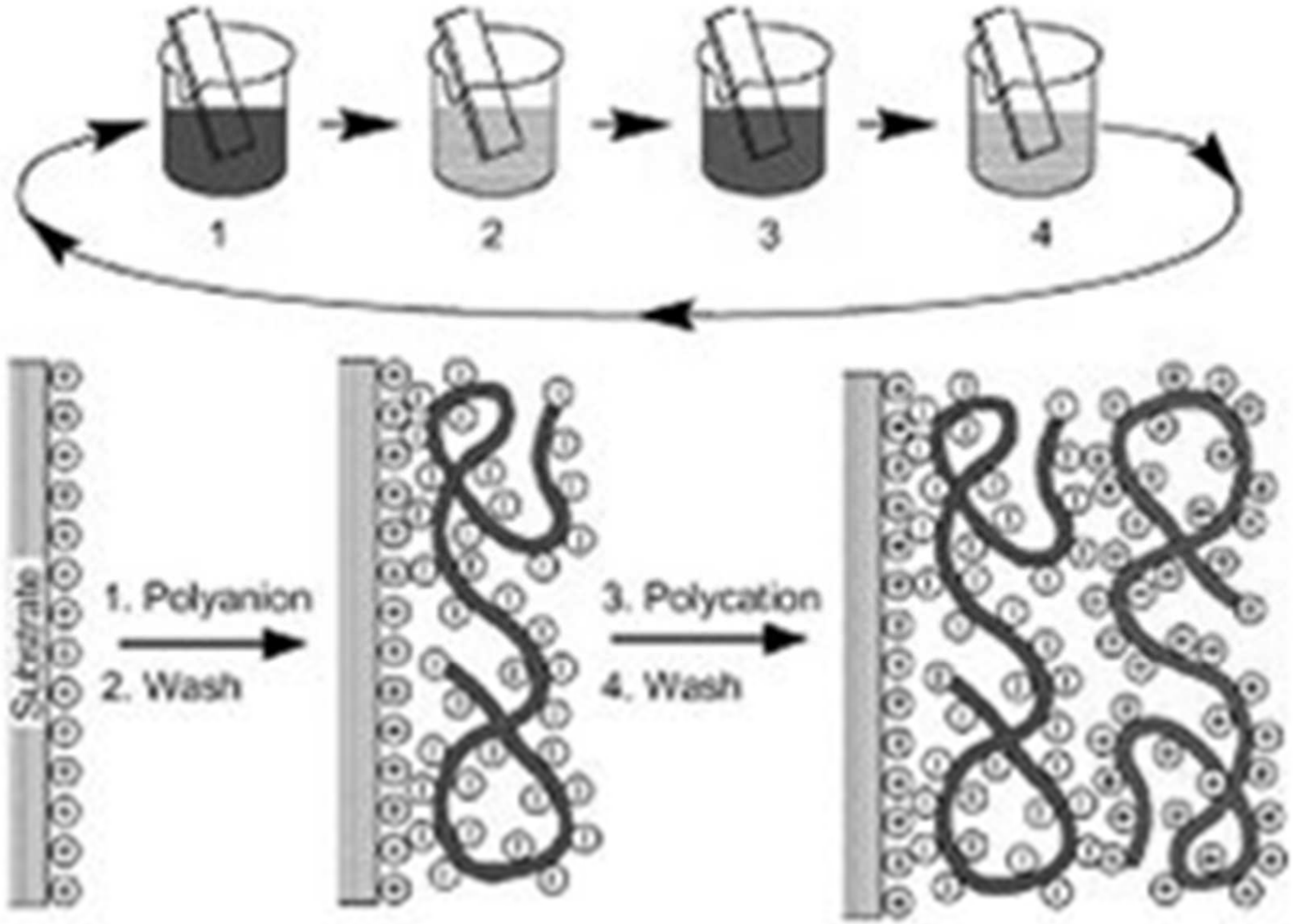
Nanoscience and Nanotechnology Research, 2013, Vol. 1, No. 1, 9-12
Available online at
http://pubs.sciepub.com/nnr/1/1/3



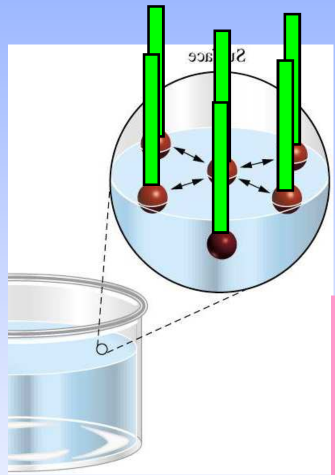
The Langmuir Trough

Langmuir Trough-ZVPS6TokX68_x264

Layer-by-Layer self assembly



Detergents e Tensoatives



Hydrophobic
Hydrophílic

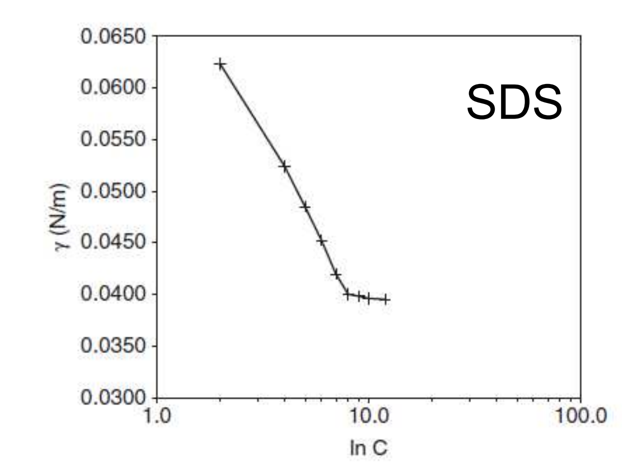
$CH_3(CH_2)_{11}$-OSO_3^- Na^+
SDS

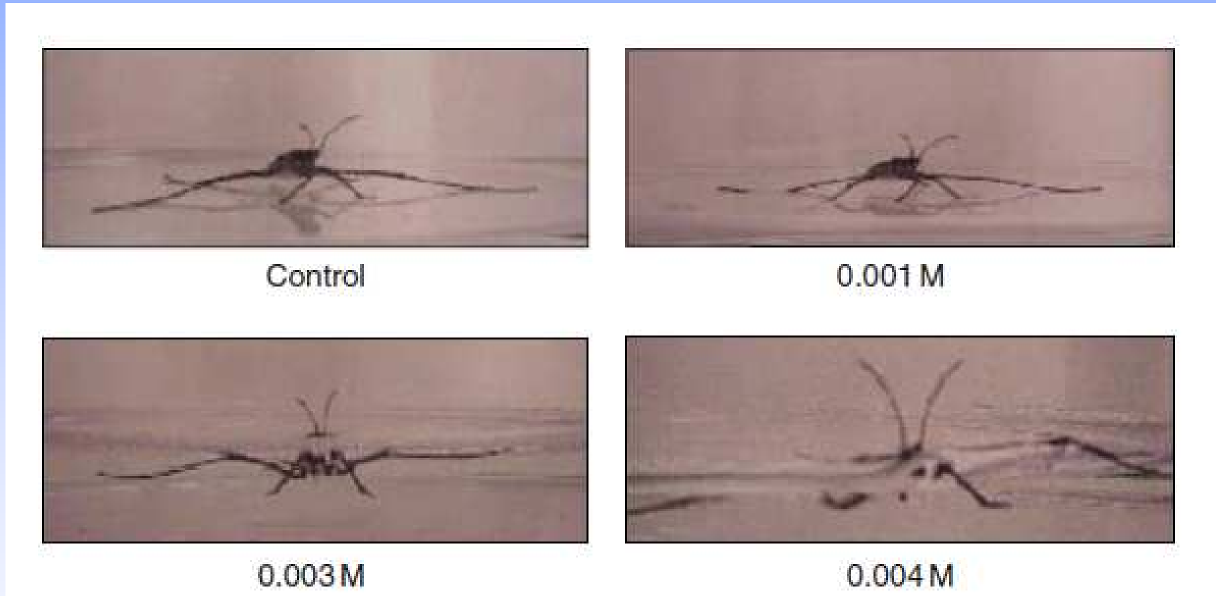
$C_{12}H_{25}$-Phenyl-SO_3^- Na^+ SDBS

$C_{18}H_{37}$-NMe_2^+ Cl^- DODAC

$C_{18}H_{37}$ Cream
Rinse/Fabric Softener

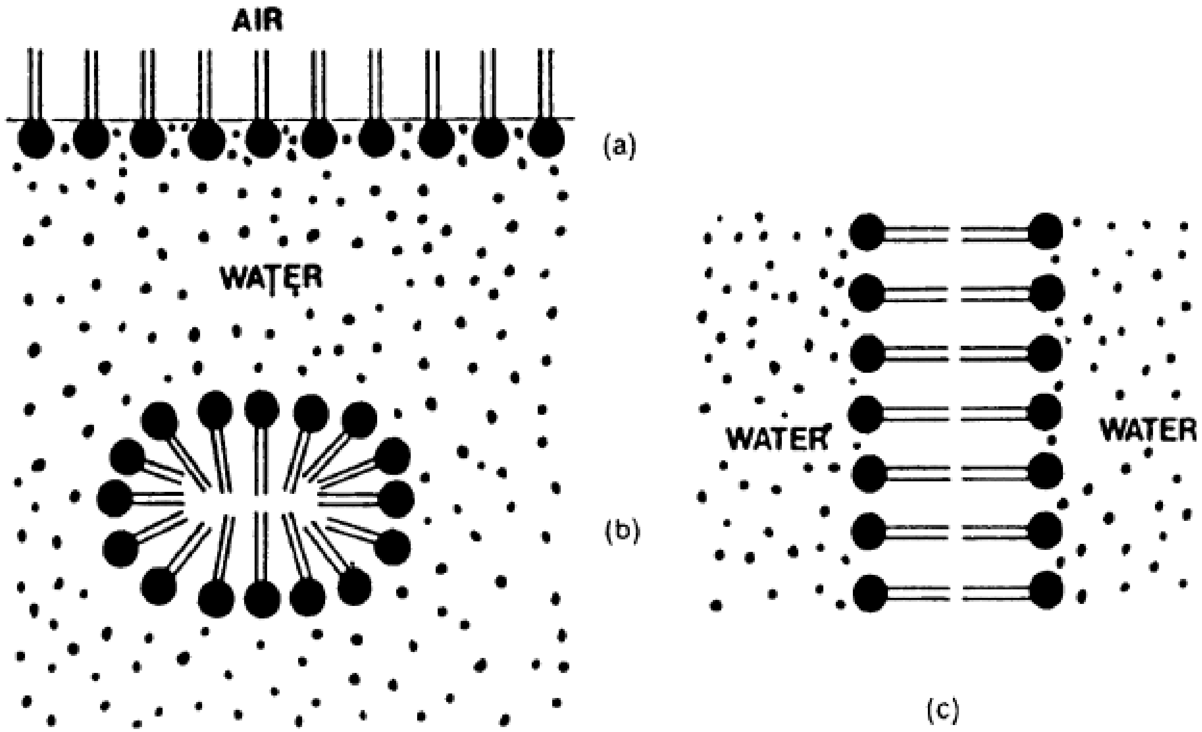
Sinking a Water Strider



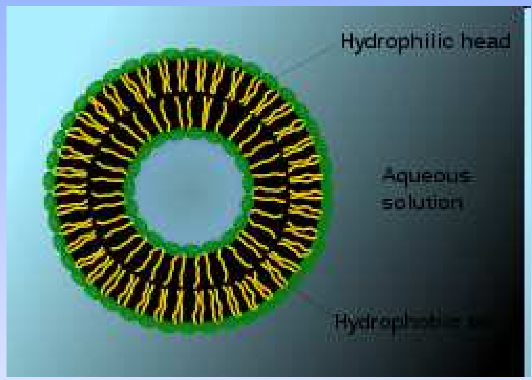


Kontogeorgis & Kiil, *Introduction to Applied Colloid and Surface Chemistry*-John Wiley & Sons (2016)

Monolayers, Micelles and Bilayers

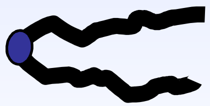


Vesicles and Bilayers



Lipid Vesicles

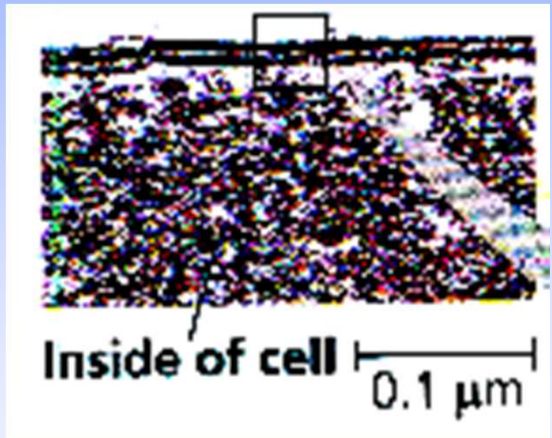
Form Micelles

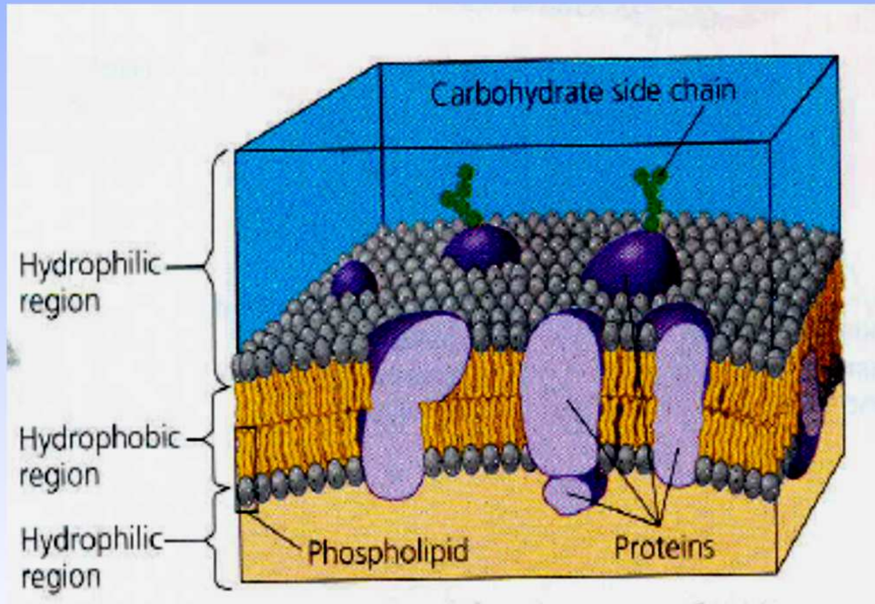


Form Vesícles

Packing (Radius of Curvature)

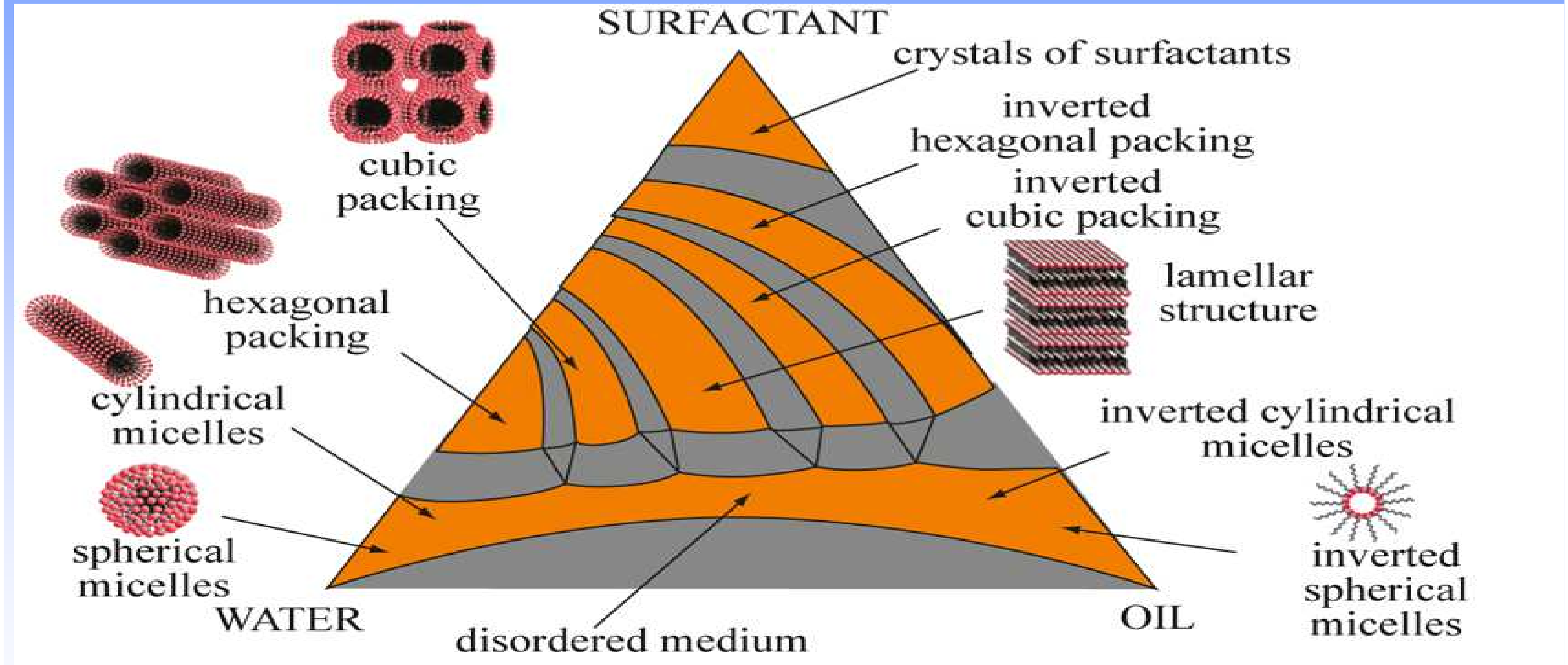
Bilayers as Models of Biological Membranes





(b) Structure of the plasma membrane

The Universe of Emulsions and Microemulsions

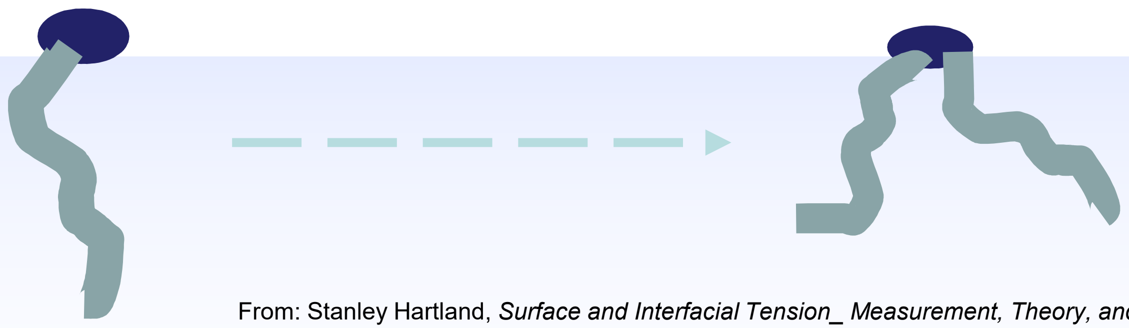


http://eng.thesaurus.rusnano.com/upload/iblock/a32/amfi1.jpg

The Critical Packing Parameter and the Preferred Geometry of Surfactant Aggregates

$$\frac{\text{Hydrocarbon chain volume}}{\text{head group area} \times \text{hydrocarbon chain length}} = v_{\text{chain}} / (a l_{\max})$$

CP P:	$<1/3$	$1/3$–$1/2$	$1/2$–1	>1
…ed geometry	Spherical micelles	Cylindrical micelles	Bilayers, discs, lamellar structures	Reversed micelles



From: Stanley Hartland, *Surface and Interfacial Tension_ Measurement, Theory, and Applications*, CRC Pres

The Critical Packing Parameter (CPP):

$$\mathrm{CPP} = \frac{V_{surf}}{\alpha_0 l_c}$$

V_{surf} denotes the tail chain (or chains) volume.

l_c is the critical tail chain length

α_0 is the head-group area at the head-tail interface

Approximate expressions for straight chains:

$$V_{surf} = (0.0274 + 0.0269n)m$$
$$l_c = 0.154 + 0.1265n$$

where n is number of carbons in the chain and m the number of hydrocarbon chains.

The CPP depends significantly on salt, pH, temperature, double bonds and double chains. Salts can have a profound effect due to lowering of the effective head-group area, thus increasing the CPP.

Calculating the Critical Packing Parameter, CPP

$$\mathrm{CPP} = \frac{V_{surf}}{\alpha_0 l_c}$$

Example:

SDS, Sodium Dodecylsulfate (n = 12 carbon chain)

$$V_s = 0.0274 + 0.0269n = 0.3502\ \mathrm{nm}^3$$

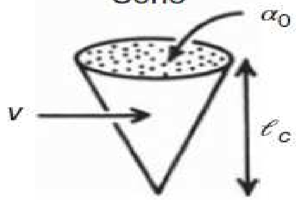
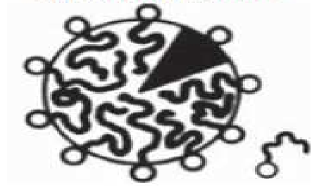
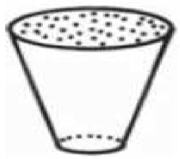
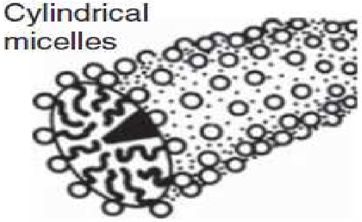
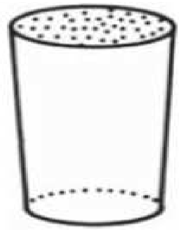
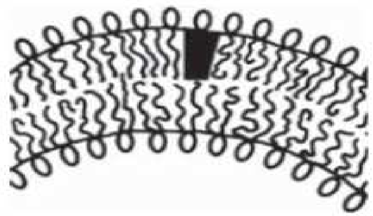
$$l_{max} = 0.15 + 0.1265n = 1.668\ \mathrm{nm}$$

$$\alpha_0 = 0.6\ \mathrm{nm}^2$$

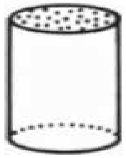
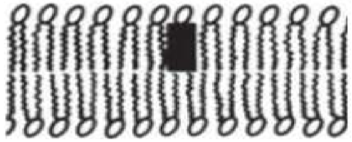
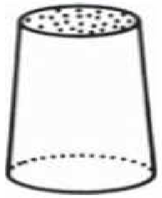
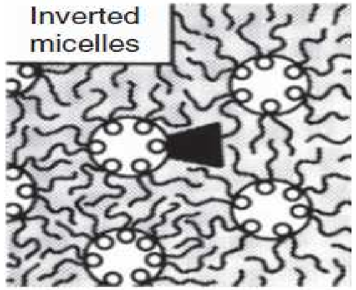
CPP = 0.35/(1.67x0.6) = 0.35 ≈ 1/3

$$N_{agg} = \frac{A_{micelle}}{A_{surfact}} = \frac{4\pi R^2}{\alpha_0} = \frac{4 \times 3.14 \times 1.668^2}{0.6} = 58$$

Predicting Aggregate Structure from the Critical Packing Parameter (CPP < 1):

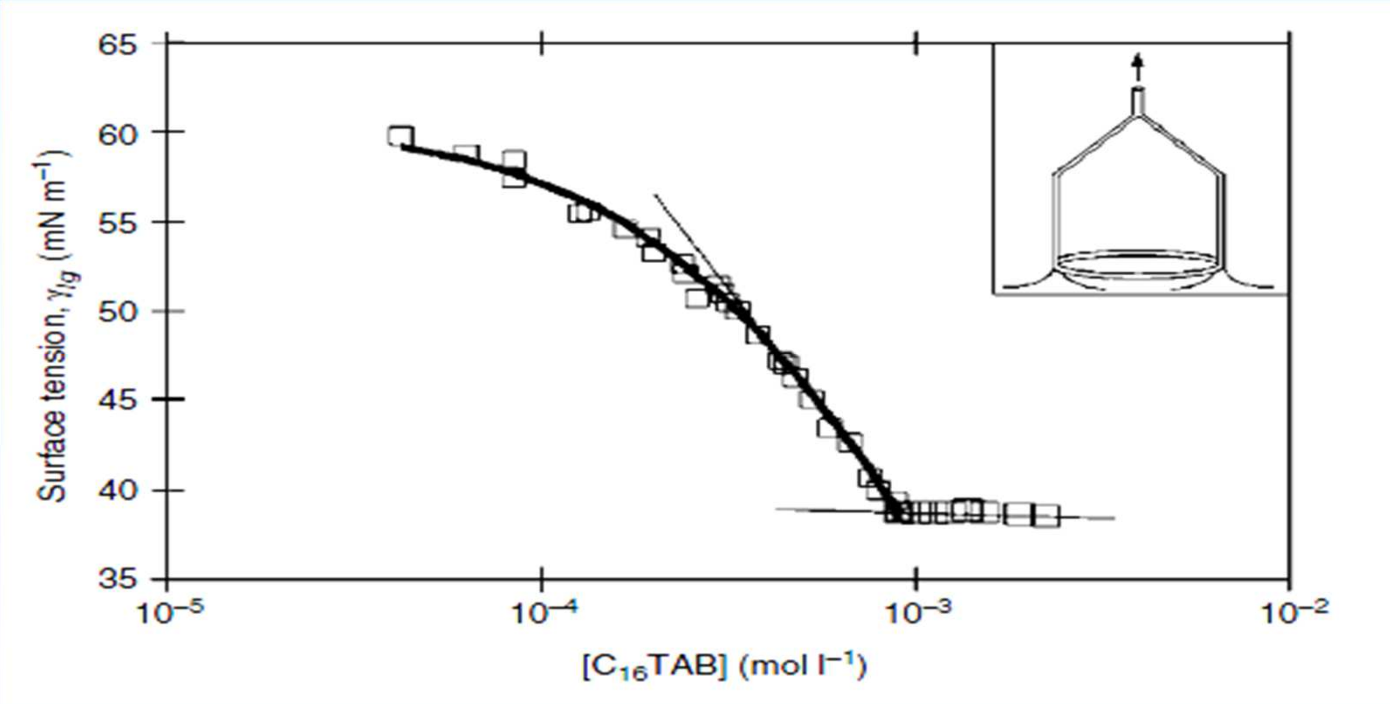
Lipid	Critical packing parameter *vlaolc*	Critical packing shape	Structures formed
Single-chained lipids (surfactants) with large head-group areas: *SDS in low salt*	< 1/3	Cone 	Spherical micelles 
Single-chained lipids with small head-group areas: *SDS and CTAB in high salt, nonionics*	1/3–1/2	Truncated cone 	Cylindrical micelles 
Double-chained lipids with large head-group areas,fluid chains: *Phosphatidyl choline (lecithin), Phosphatidyl serine, Phosphatidyl glycerol, Phosphatidyl inositol, Phosphatidic acid, sphingomyelin, DGDC[a] dihexadecyl phosphate, dialkyl dimethyl ammonium salts*	1/2–1	Truncated cone 	Flexible bilayers, vesicles 

Predicting Aggregate Structure from the Critical Packing Parameter (CPP ≥ 1):

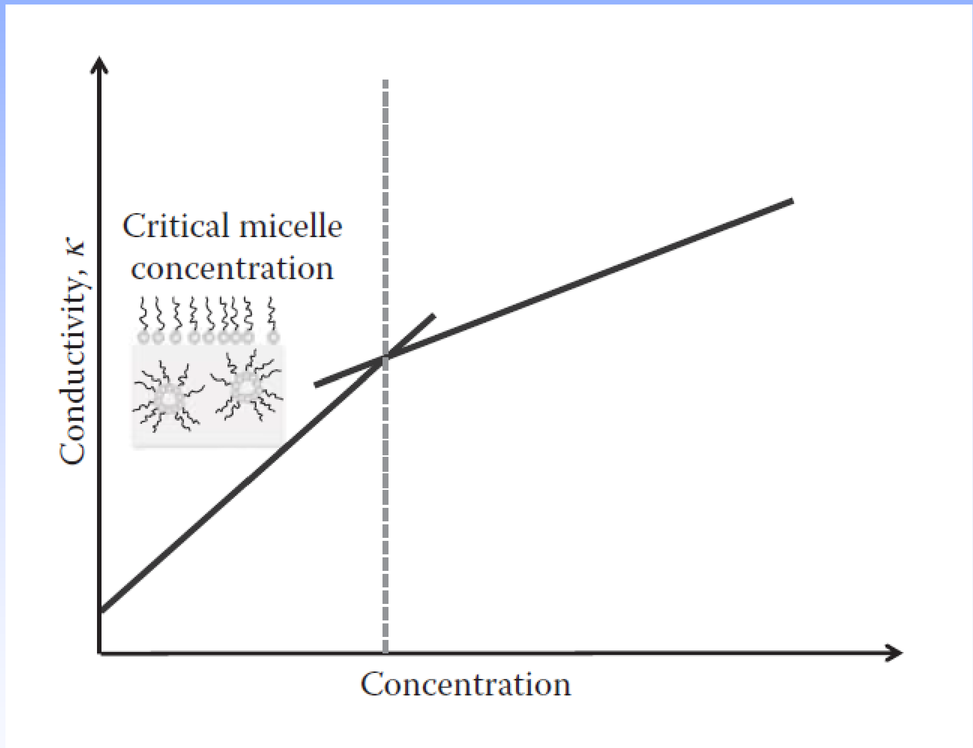
Lipid	Critical packing parameter *v/a₀l_c*	Critical packing shape	Structures formed
Double-chained lipids with small head-group areas, anionic lipids in high salt, saturated frozen chains: *phosphatidyl ethanolamine, phosphatidyl serine* + Ca^{2+}	~1	Cylinder 	Planar bilayers 
Double-chained lipids with small head-group areas, nonionic lipids, poly *(cis)* unsaturated chains, high T: *unsat. phosphatidyl ethanolamine, cardiolipin* + Ca^{2+} *phosphatidic acid* + Ca^{2+} *cholesterol, MGDG*[b]	>1	Inverted truncated cone or wedge 	Inverted micelles 

[a] DGDG, digalactosyl diglyceride , diglucosyl diglyceride.
[b] MGDG, monogalactosyl diglyceride,monoglucosyl diglyceride.
Reprinted from Israelachvili (1985), with permission from Elsevier.

Determining the CMC – Surface Tension

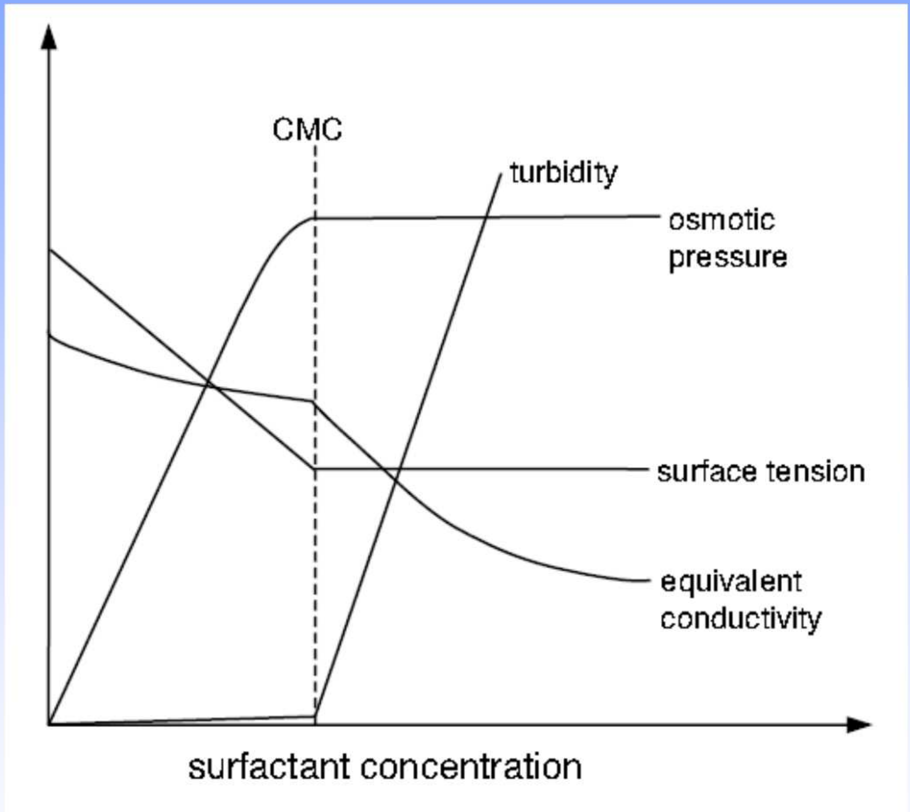


Determining the CMC – Conductivity (Ionic Detergents)



The ratio of the slopes above and below the CMC gives a rough estimate of the degree of micellar counterion dissociation (α)

Physical Techniques to Measure the CMC

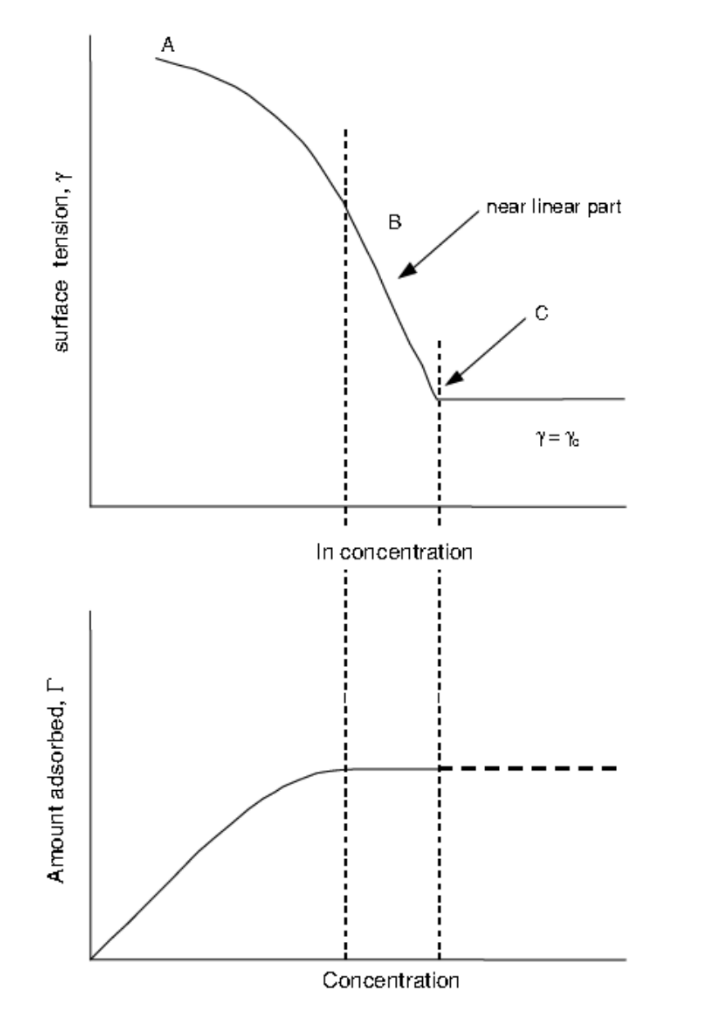


Other techniques:

Solubilization

Fluorescence Probes

Eastoe in Colloid Science, 2nd Ed., Wiley, 2010

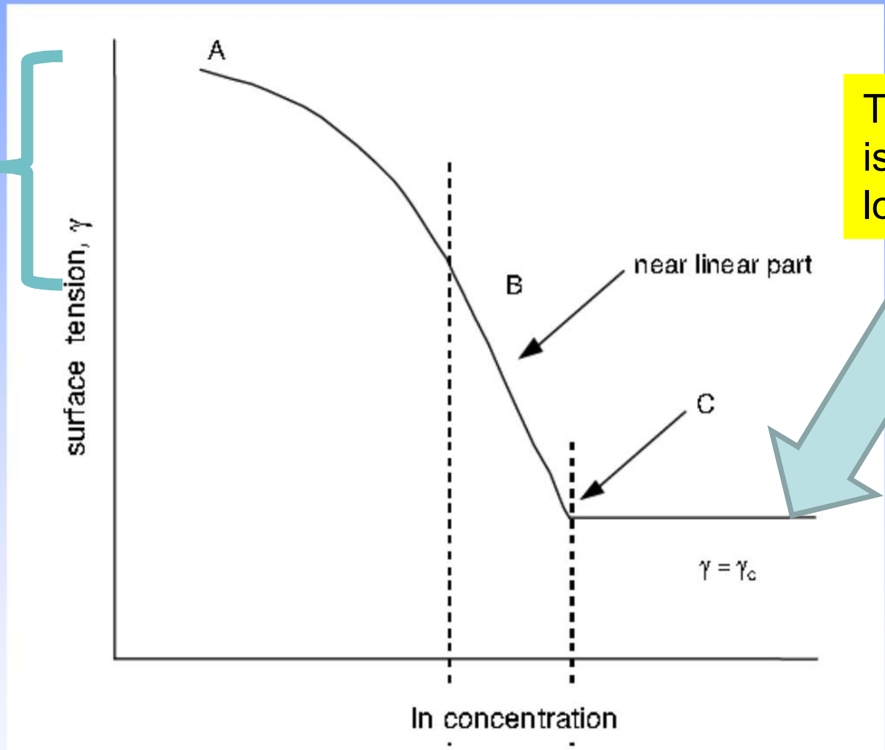


Typical Adsorption Isotherm of a Detergent below and above the CMC (at point c).

Corresponding Gibbs Surface Excess as a function of detergente concentration, Note that the the surface excess saturates before the CMC (at about point a).

Eastoe in Colloid Science, 2nd Ed., Wiley, 2010

The Surfactant Adsorption Efficiency



The **Effectiveness of Adsorption** is the maximum surface tension lowering.

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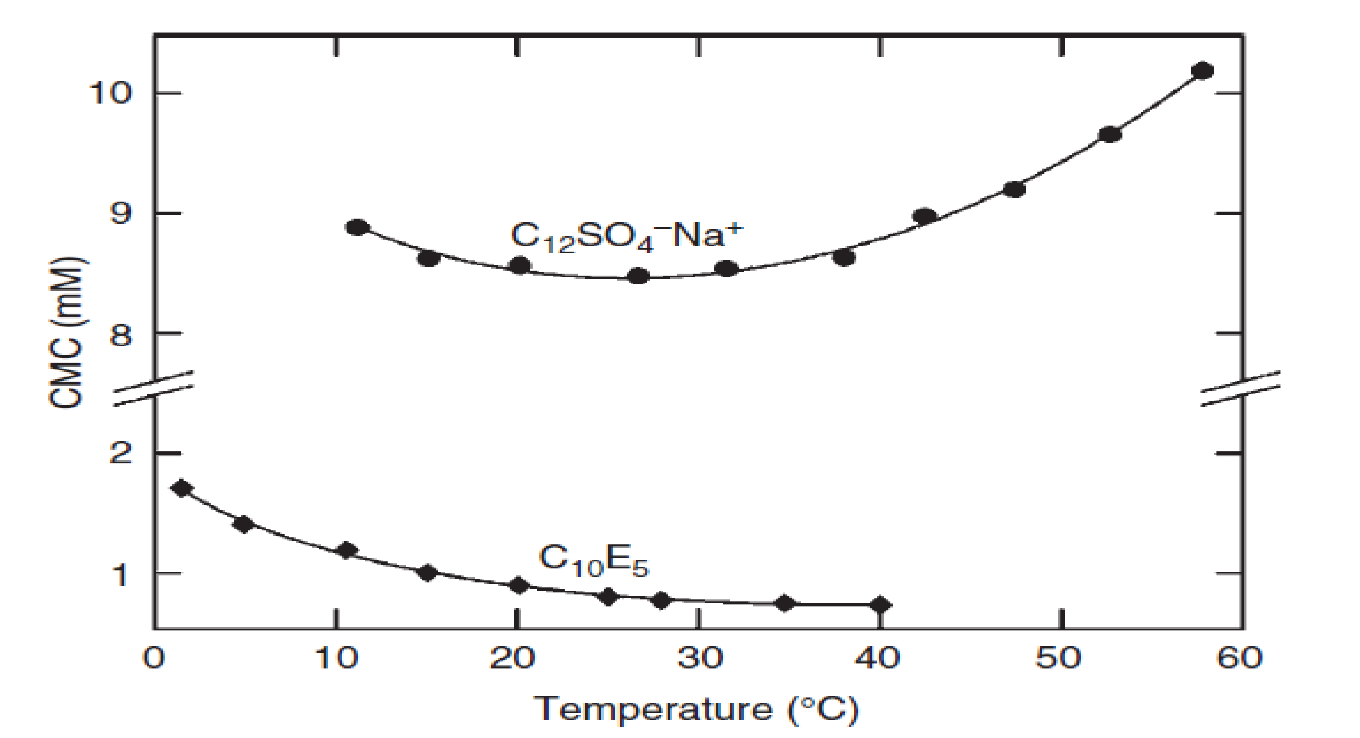
Temperature Dependence of the CMC:

Typically small, implying that the Enthalpy of Micellization is also small.



Thermodynamics of Micellization

$$\Delta G = RT \ln (CMC/55.5)$$

Surfactant	Gibbs energy change of micellization (kJ mol^{-1})	Enthalpy change of micellization (kJ mol^{-1})	Entropy change of micellization (J K^{-1} mol^{-1})
SDS	–21.9	+2.51	+81.9
$C_{12}E_6$	–33.0	+16.3	+49.3
Dodecyl pyridinium bromide	–21.0	–4.06	+56.9
N,*N*-Dimethyl-dodecylamine oxide	–25.4	+7.11	+109.0
N-Dodecyl-*N*,*N*-dimethyl glycine	–25.6	–5.86	+64.9

Spontaneous, Highly Cooperative

Dominated by the Change in Entropy upon Micellization

The Hydrophilic–Lipophilic Balance (HLB)

The HLB is an empirical parameter, with values below 8 indicating hydrophobic surfactants (emulsifiers) and values above 8 (or 10) hydrophilic surfactants.

The group contribution method of Davies and Rideal for estimating the HLB :

$$HLB = 7 + \sum_i n_i HLB_i$$

where n_i is the number of groups of each i type in the molecule. The i average HLB of mixed surfactants is calculated as the sum of the weight fraction x HLB for each surfactant.

Group	HLB	Group	HLB
$-SO_4Na$	38.7	-OH (free)	1.9
-COOK	21.1	-OH (sorbitan)	0.5
-COONa	19.1	Sulfonate	11
-N (tertiary amine)	9.4	CH, CH_2, CH_3	–0.475
Ester (sorbitan)	6.8	$-CH_2CH_2O$	0.33
Ester (free)	2.4	$-CH_2CH_2CH_2O$	–0.15
-COOH	2.1	$-CF_2, -CF_3$	–0.87
-O-	1.3		

Estimation of HLB by the Davies–Rideal method:

$$HLB = 7 + \sum_i n_i HLB_i$$

Group	HLB	Group	HLB
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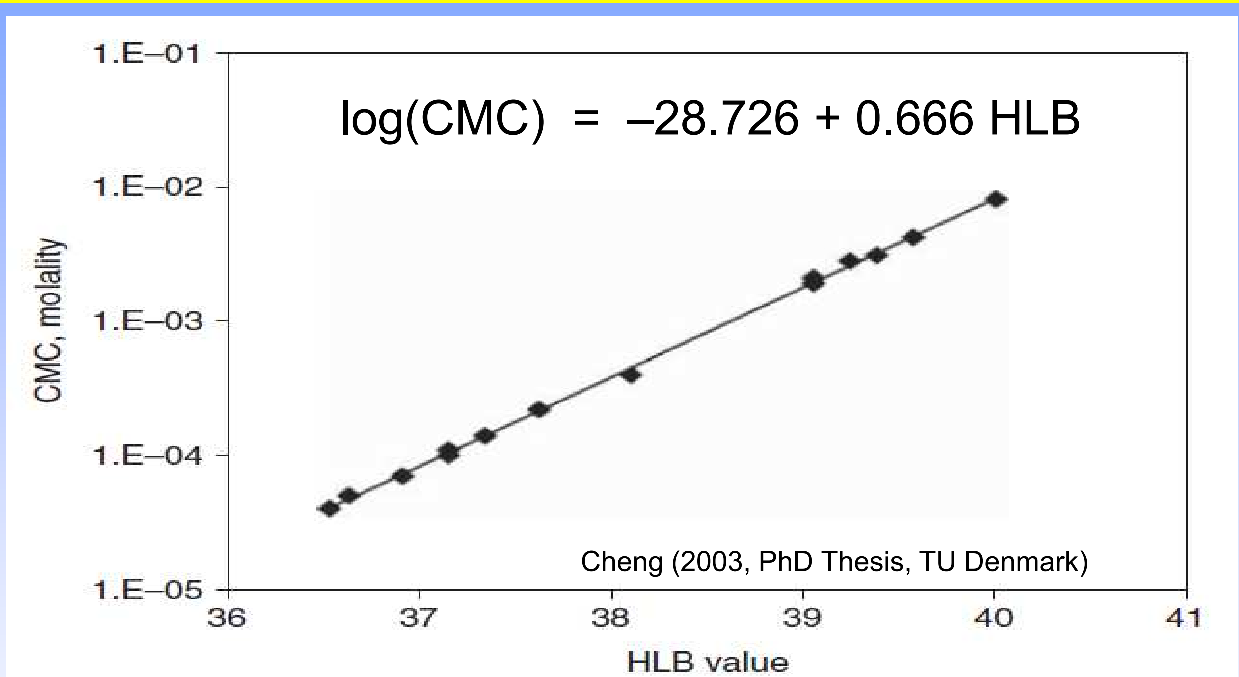
-COOH	2.1	$-CF_2, -CF_3$	–0.87
-O-	1.3		

$$HLB\ (C_{16}E_4) = 7 + 16(-0.475) + 4 \cdot 0.33 + 1.9 = 2.62$$
$$HLB\ (C_{12}E_{30}) = 7 + 12(-0.475) + 30 \cdot 0.33 + 1.9 = 13.1$$

Estimate of the HLB of a 50:50 mixture by weight:

Average HLB = 0.5 x 2.62 + 0.5 x 13.1 = 7.86

CMC of polyoxyethylene sodium alkyl sulfates ($C_nH_{2n+1}(OC_2H_4)_mSO_4^-Na^+$) as a function of the corresponding HLB values



Note: Sodium alkyl ether sulfates are widely used as detergents in consumer products due to their insensitivity to multivalent counterions (can be used in hard water without forming scum).

The Octanol-Water Partitioning Coefficient, K_{OW}:

$$K_{OW_i} = \lim_{x_i \to 0} \left(\frac{C_i^O}{C_i^W} \right)$$

where C_i is the concentration of compound i in water-saturated Octanol (O) or octanol-saturated Water (W).

Log K_{OW} can be estimated from group equivalents, calculated by numerous computer programs or estimated from the Abraham correlation:

Solubilization of organic molecules in micelles of SDS correlates reasonably well with log K_{OW}. In environmental studies, log(K_{ow}) values above 4 indicate potentially dangerous pollutants.

Mechanism(s) of Cleaning of Surfaces by Surfactants

Mechanism(s) of the Cleaning of Surfaces by Surfactants:

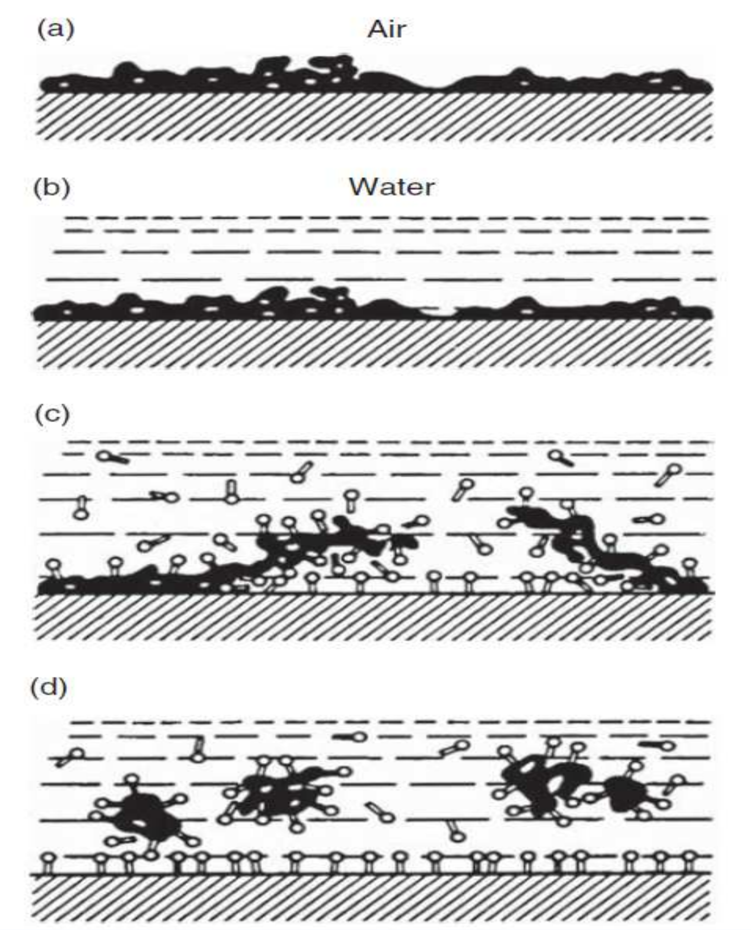
The solid substrate with the dirt prior to adding water and surfactants;

Wetting with water alone;

Decrease of adhesion in the presence of surfactants;

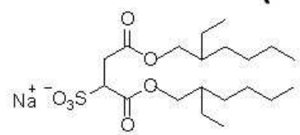
“Solubilization” or emulsification by the surfactant

Apud Shaw (1992).



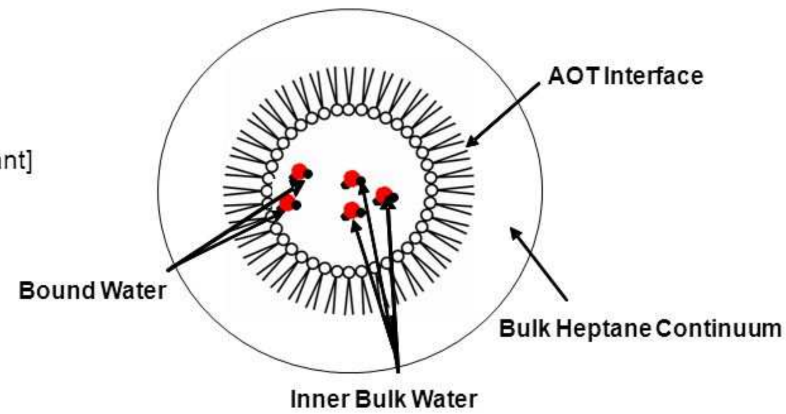
Reverse Micelles (W/O Microemulsions)

Surfactant Employed for Reverse Micelle Synthesis: Aerosol-OT (AOT)



Sodium bis(2-ethyl-hexyl)sulfosuccinate (AOT)

- Double chain amphiphile
- Able to form reverse micelles
- Able to solubilize water
- R value (w_o): [water]/[surfactant]



AOT Reverse Micelle

Molecular Dynamics Simulation of Hexagonal Close-Packed Micelle Formation

https://www.youtube.com/watch?v=lm-dAvbl330

Molecular Dynamics Simulation of Bilayer Formation

https://www.youtube.com/watch?v=lm-dAvbl330

Irving Langmuir GE film on surface chemistry 1939-METEzW1W9dg_x264