TECNOLOGIA DOS MATERIAIS CERÂMICOS

IV – RHEOLOGY OF CERAMIC SLURRIES

RAW MATERIALS

DOSAGE

ADITIVES

GRINDING AND/OR DRY MIX

GRIDING AND/OR WET MIX

ADITIVES

WASTE

CLASSIFICATION

WASTE

GRANULATION

SPRAY DRYING

PRESSING FILTER

PRESSING

PLASTIC FORMING

SLIP CASTING

DRYING

FINISHING

SINTERING

Clay plasticity

http://scmwaterproofporous.blogspot.pt/2010/10/clay.html

http://www.dezeen.com/2010/07/07/j olly-project-by-ian-mcintyre/

→ One of the characteristics of a clay is that when mixed with water it forms a coherent mass that is capable of being molded to any desired shape, i.e. it is **plastic**. It will be noted that any other substance, even when finely powdered, do not possess this property and are non-plastic, e.g. sand, flint, chalk, etc.

→ If sufficient water is added to clay, a **suspension** (or **slip**) is formed; on removal of some of the water, a putty-like mass or **paste** is formed. This unique characteristics of clay in contact with water are due to its **colloidal properties**.

What is a colloid?

→ Three of the fundamental states of matter are solids, liquids and gases. If one of these states is finely dispersed in another then we have a **colloidal system**. These materials have special properties that are of great practical importance.

→ There are various examples of colloidal systems that include aerosols, emulsions, colloidal suspensions and association of colloids.

What is a colloid?

Classification of colloids

Colloids consist of one or more phases, with some characteristic dimensions between ~ 10 nm – 1 μm, dispersed in an external phase.

	External phase		
Dispersed phase	**Gas**	**Liquid**	**Solid**
Gas	-	Foam	Solid foam
Liquid	(Liquid) Aerosol	Emulsion	(Solid) Emulsion
Solid	(Solid) Aerosol	Sol, colloidal dispersion	Solid suspension

Colloids with a liquid external phase can also be classified on the tendency of the dispersed particles to aggregate:

Lyophilic: dispersed particles tend to stay dispersed throughout the external phase
Lyophobic: dispersed particles tend to spontaneously aggregate

There are various examples of **colloidal systems** that include **aerosols**, **emulsions**, **colloidal suspensions (**also named **colloids** or **sols)** and **association of colloids**.

What is a colloid?

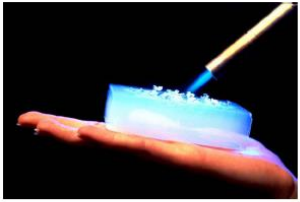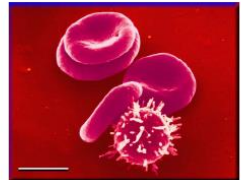## Colloids

Foams

Milk

Fog, smoke

image: consciousnutrition.com

Aerogel

Blood

Paints

Examples of colloidal dispersions

Food industry
- Dairy products
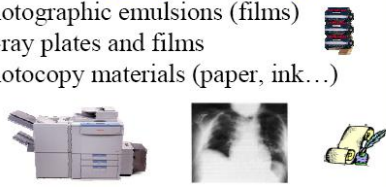- Dressings
- Chocolate
- …

Côte d'Or

Pharmaceutics and cosmetic
- Water-insoluble pharmaceutics
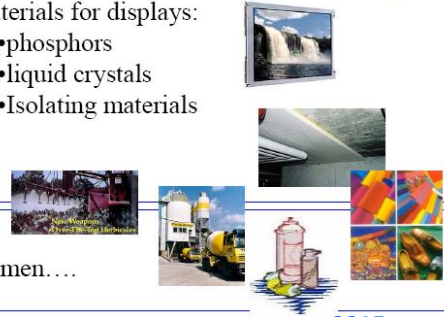- All kind of gels, emulsions and cosmetics

Photographic industry
- Photographic emulsions (films)
- X-ray plates and films
- Photocopy materials (paper, ink…)

Electrical an Electronic industry
- Materials for displays:
  - phosphors
  - liquid crystals
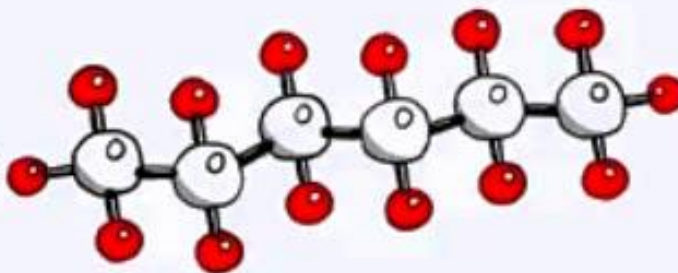 - Isolating materials

Other
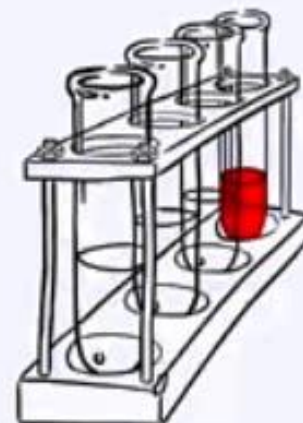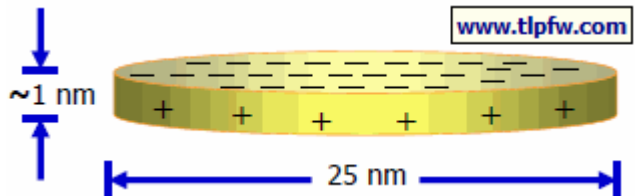- Agrochemicals, paints, dyestuffs, cement, bitumen….

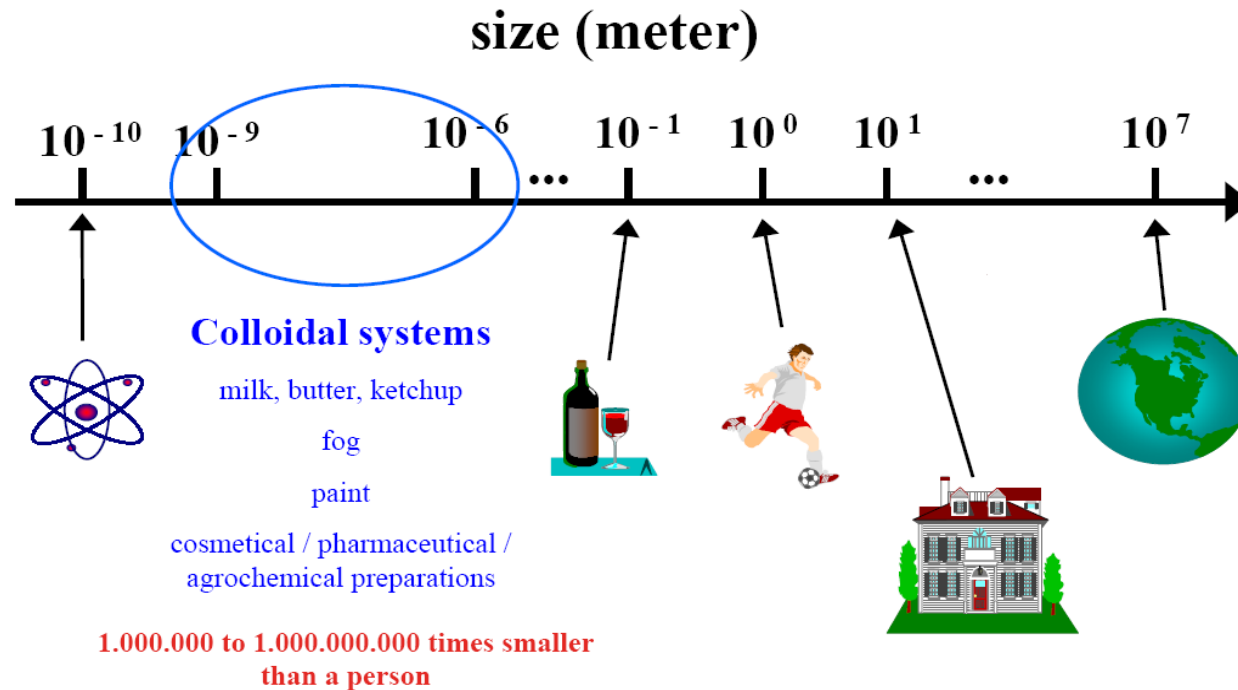Emulsions

What is a colloid?

→ We may define a **colloid** (**colloidal suspension** or **sol**) as a binary system, where a **non-continuous disperse phase** is **suspended in a liquid continuous phase**. The phase dispersed is divided to such a degree (**smaller than 1 μm in diameter**) that its surface properties are predominant.

What is a colloid?

Colloid science … ?

size (meter)

10^{-10} 10^{-9} 10^{-6} ... 10^{-1} 10^{0} 10^{1} ... 10^{7}

Colloidal systems

milk, butter, ketchup

fog

paint

cosmetical / pharmaceutical /
agrochemical preparations

1.000.000 to 1.000.000.000 times smaller
than a person

•The **dimensions** of the dispersed phase lie in the **range 1 – 1000 nm**, i.e. between **10 Å** and **1 μm**.

• It is not necessary for all three dimensions to lie below 1 μm, since colloidal behavior is observed in systems containing fibers in which only **two dimensions** are in the **colloid range**. In other systems, such as clays and thin films, only **one dimension** is within the **colloidal range.**

• Colloids in which the particle size is **below ~10 nm** (nanomaterials) often require **special consideration**.

What is a colloid?

Colloid science

To mix or not to mix, that is the question !

alcohol + water
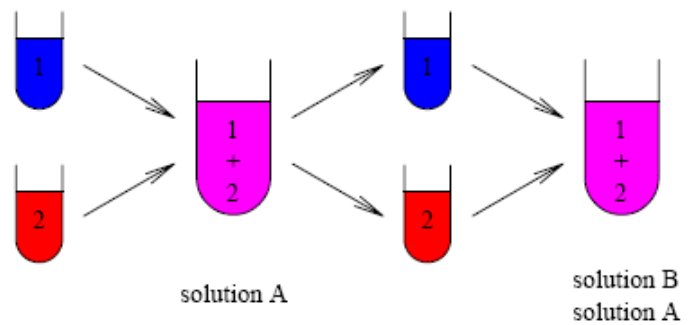mixable

oil + water
unmixable
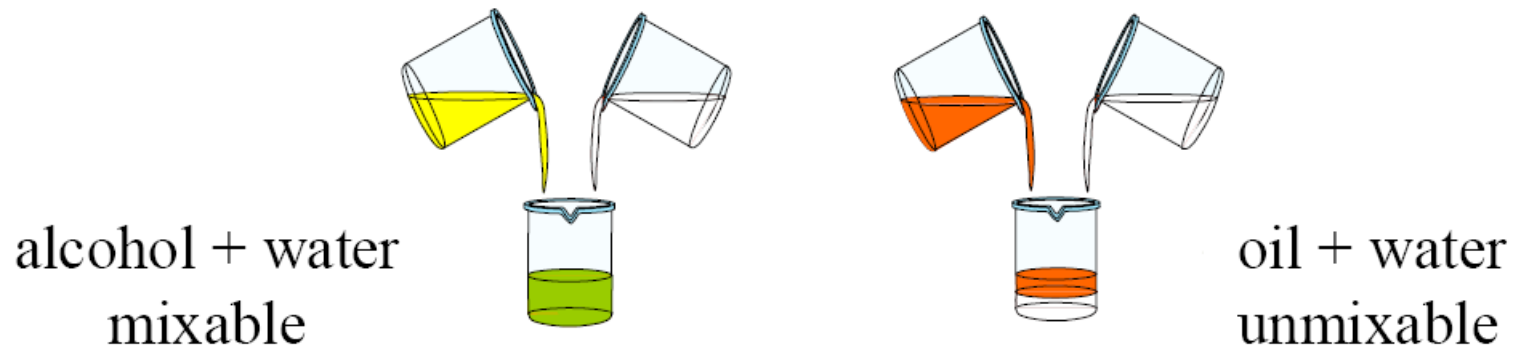
A colloid scientist wants to:

1. mix the unmixable → colloidal dispersions
2. keep it mixed → colloid stability

What is a colloid?

TO MIX OR NOT TO MIX?

SOLUTIONS

solution A

solution B
solution A

DISPERSIONS

dispersion A

dispersion B
≠ dispersion A

Mixing is **SPONTANEOUS**.

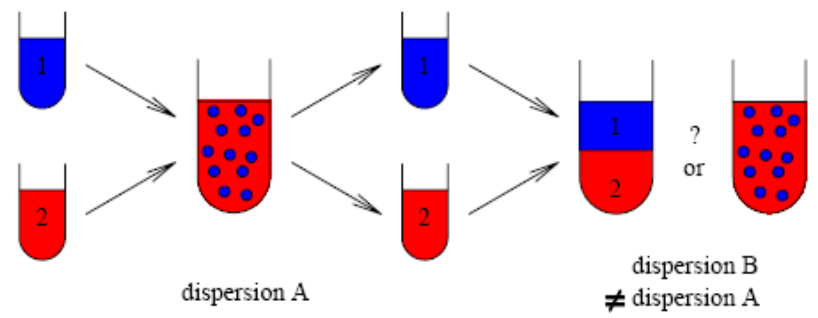Mixtures are

THERMODINAMICALLY STABLE

Inhomogeneities on molecular

level.

Mixing is **NON-SPONTANEOUS**.

Mixtures are

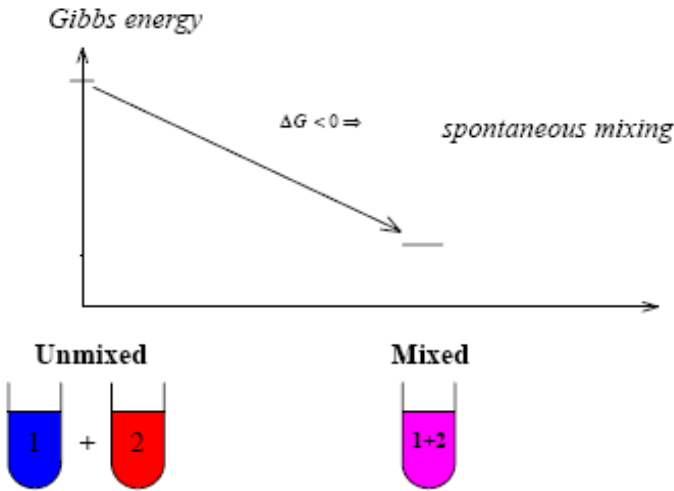**THERMODINAMICALLY METASTABLE.**

Inhomogeneities on length scales

large compared to molecular

dimensions.

What is a colloid?

Solutions are thermodinamically STABLE

Dispersions are thermodinamically METASTABLE

Gibbs energy

$\Delta G < 0 \Rightarrow$ spontaneous mixing

Unmixed   Mixed

1 + 2   1+2

Gibbs energy

$\Delta G < 0 \Rightarrow$ direction of spontaneous change

Unmixed   Mixed

1 + 2   1+2

A most important physical property of **colloid dispersions** is the tendency of particles to **aggregate**.
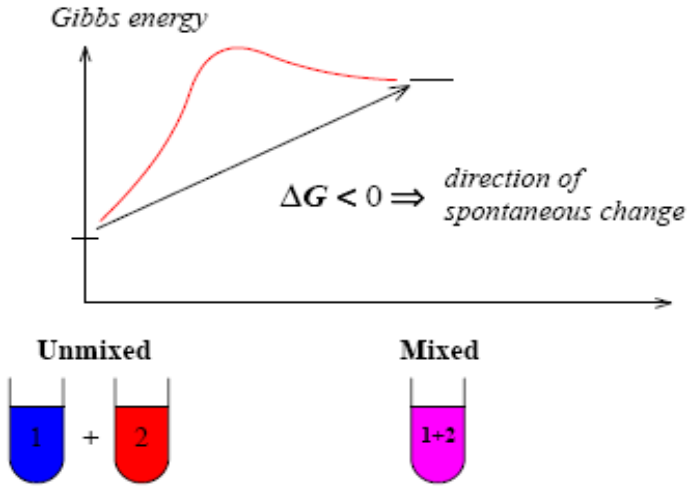
SLOW KINETICS ⇒ KINETIC

Protect sols against aggregation / flocculation / coalescence by **repulsive interactions**.

What is a colloid?

i. Coalescence

Good Emulsion

ii. Flocculation

iii. Creaming

iv. Breaking
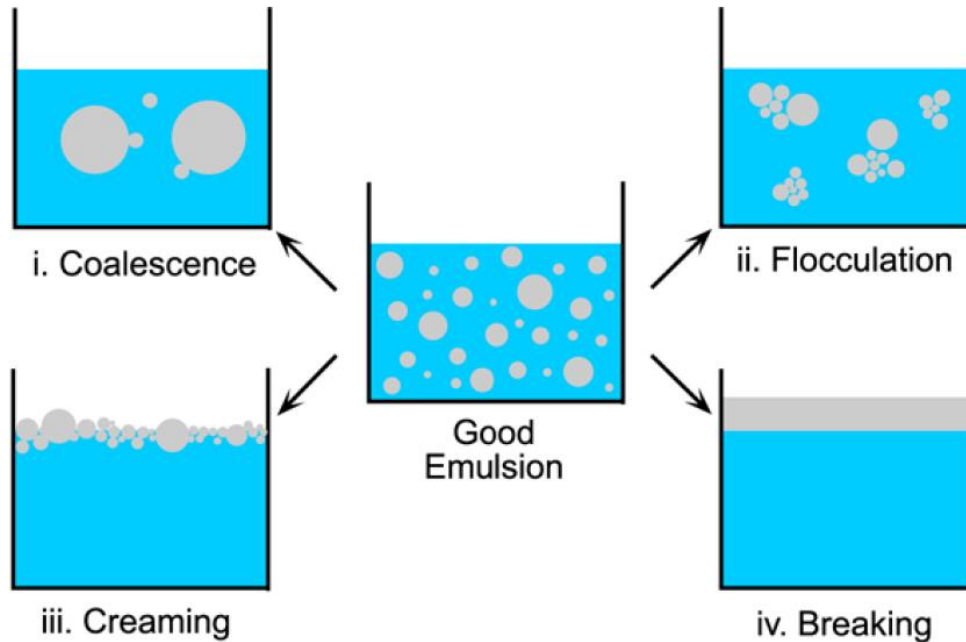
In certain circumstances, the particles in a dispersion **may adhere** to one another and form **aggregates** of successively increasing size, which **may settle** out under the influence of **gravity**!

An initially formed **aggregate** is called a **floc** and the process of its formation **flocculation**. The floc may or may not **sediment** or **phase separate**.

If the aggregate changes to a much denser form, it is said to undergo **coagulation**.

An aggregate usually separates out either by **sedimentation** (if it is more dense than the medium) or by **creaming** (if it is less dense than the medium).

The terms **flocculation** and **coagulation** have often been used interchangeably. Although **coagulation is irreversible** whereas flocculation can be **reversed** by the process of **deflocculation**.
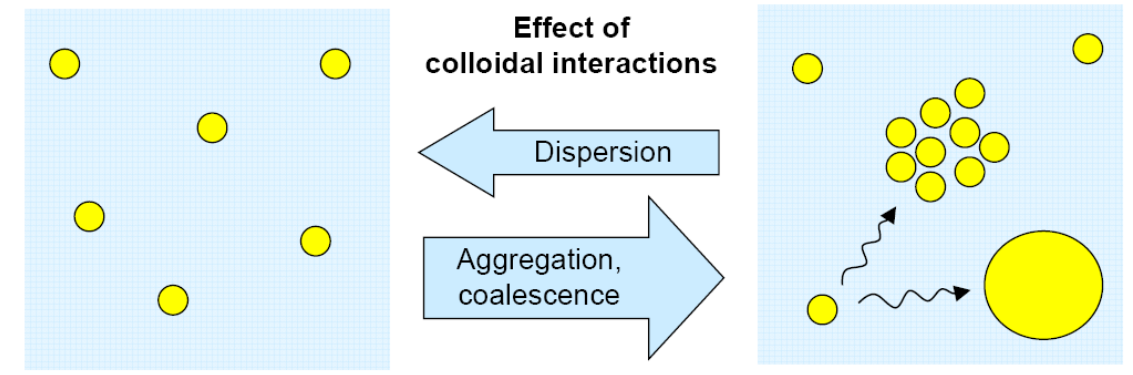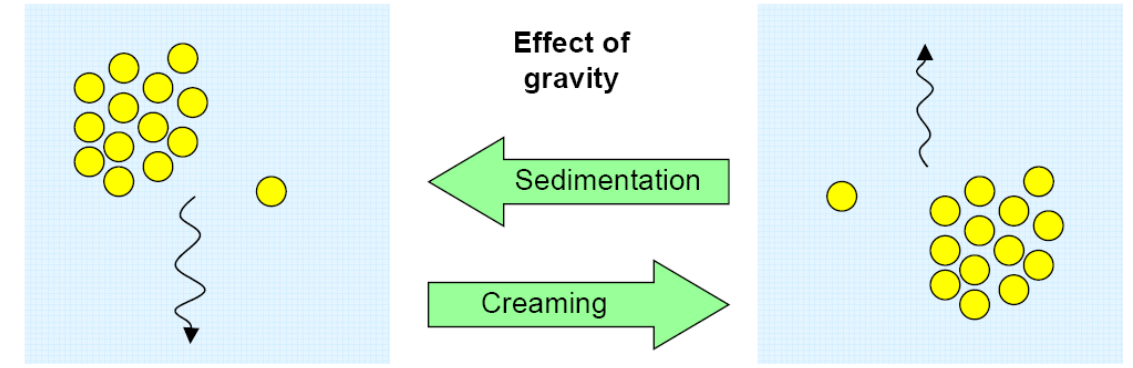
What is a colloid?
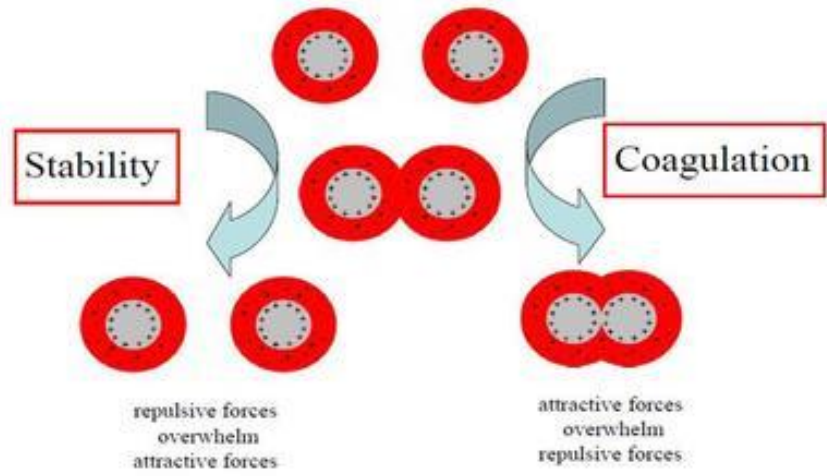
Dispersion phase **more dense** than the medium

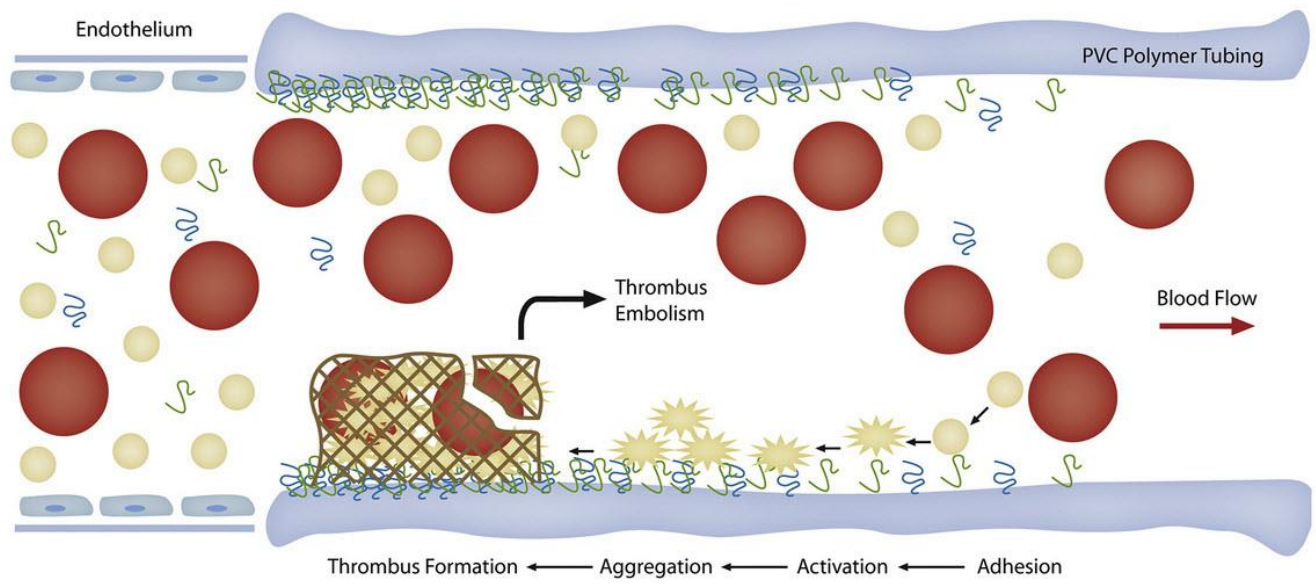Dispersion phase **less dense** than the medium

Stability of colloids

Sedimentation due to gravity

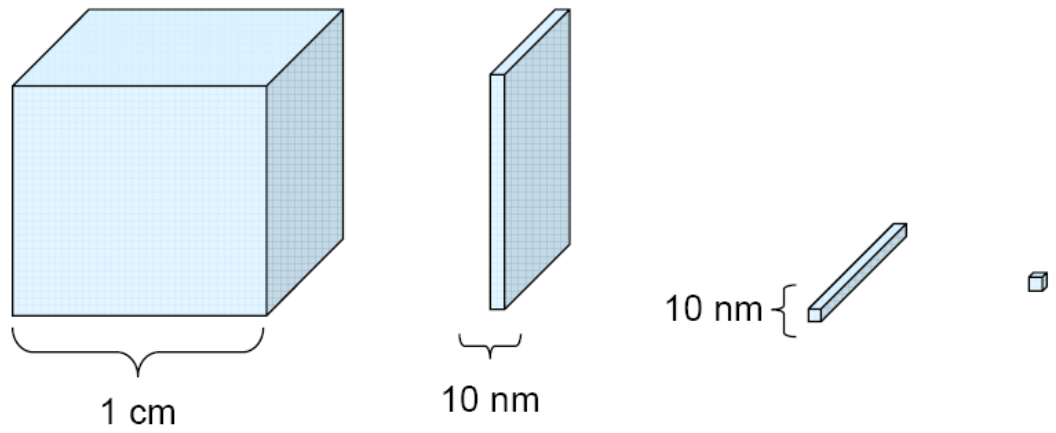**Creaming** due to attractive forces

What is a colloid?

THROMBUS EMBOLISM BY COAGULE FORMATION

http://www.kurzweilai.net/carbon-nanotubes-found-to-create-blood-clots-in-medical-devices

What is a colloid?

Surface matters

N	1	10^6	10^{12}	10^{18}
A_1 (cm²)	6	2	4×10^{-6}	6×10^{-12}
A_{tot} (cm²)	6	2×10^6	4×10^6	6×10^6

Colloidal systems are "all surface"

What is a colloid?

This is why surface chemistry plays such an important part in colloid science and why colloidal properties begin to become evident when the **particle size falls below 1 μm**.

Because of the range of dimensions involved in colloidal structures, the **surface-to-volume ratio** is extremely high and a **significant proportion of the molecules** in such systems **lie within or close** to the region of inhomogeneity associated with particle/medium **interfaces**. These molecules will have properties (e.g. energy, molecular conformation) different from those in the bulk phases more distant from the interface.

It is no longer possible to describe the whole system simply in terms of the sum of the contributions from the molecules in the bulk phases, calculated as though both phases had the some properties as they have in the bulk state.
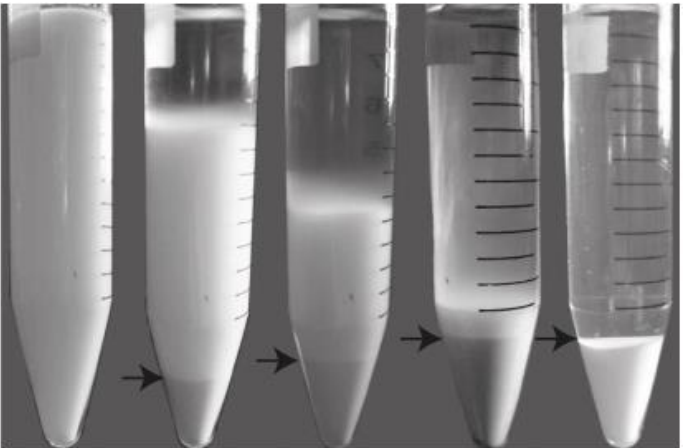
A significant and often dominating contribution comes from the molecules in the interfacial region.

Colloids properties: sedimentation

→ One important aspect of colloidal suspensions is their ability **to remain in suspension indefinitely**. For a spherical particle suspended in a liquid, **Stokes' Law** states that the **velocity of sedimentation**, **v**, is given by the equation:

$$v = 2r^2(d_1 - d_2)g / 9\eta$$

where
→ **r**-radius of particle
→ **d$_1$**-density of solid
→ **d$_2$**-density of liquid
→ **G**-acceleration due to gravity
→ **η**- viscosity of liquid

hard-sphere colloidal crystals and glasses

(a) after mixing — 2 3 4 5 6 7 8 9 10

(b) 1 day

(c) 4 days

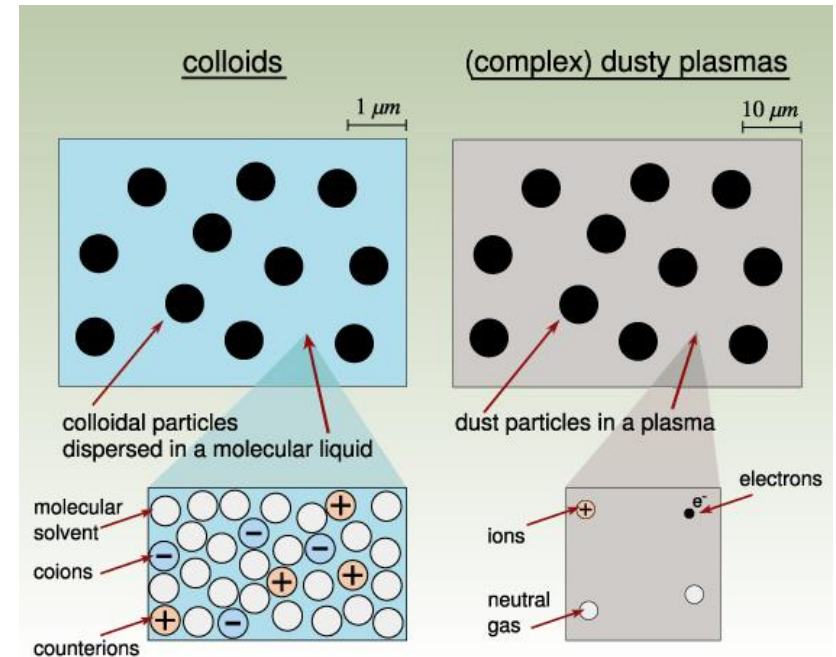| fluid $\phi < 0.494$ | fluid + crystal | crystal $\phi > 0.545$ | glass $\phi > 0.58$ |

Colloids properties: diffusion

→ However, small particles suspended in a liquid exert an outward pressure like gas molecules, resulting in a **diffusion effect** which opposes sedimentation. According to **Fick's law** of **steady state diffusion**, the amount **dw** of substance diffusing across unit area in time **dt** is given by the equation:

$$dw = -D \frac{dc}{dx} dt$$

→ where
→ **D**-diffusion coefficient
→ **Dc/dx**-concentration gradient

colloids   (complex) dusty plasmas

1 µm   10 µm

colloidal particles   dust particles in a plasma
dispersed in a molecular liquid

molecular solvent   electrons
coions   ions
counterions   neutral gas

→ For a constant temperature and viscosity, the constant **D** is proportional to **1/r**, where **r** is the radius of the particle diffusing.

Colloids properties: sedimentation vs. diffusion

→ Comparing **Stokes' law** with **Fick's law**, it is clear that the former, being a **square law**, rapidly becomes **very small for particles of colloidal size**, whilst the latter **increases rapidly as r decreases**.

$$v = 2r^2(d_1 - d_2)g / 9\eta$$

$$dw = -D \frac{dc}{dx} dt$$

→ Clearly there is a limiting size for r where **diffusion is sufficiently rapid to prevent any degree of sedimentation**; this becomes manifestly so when **r** is around **0.2 μm**.

→ Of course this has been oversimplified because it has been assumed that all particles are equal-sized spheres, acting as individual units; the possibility of interaction between the particles will be considered latter.

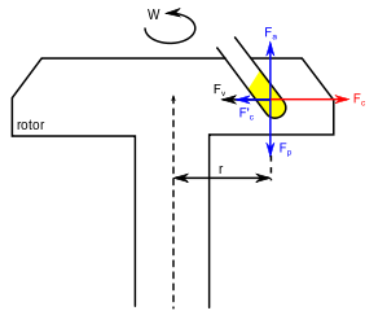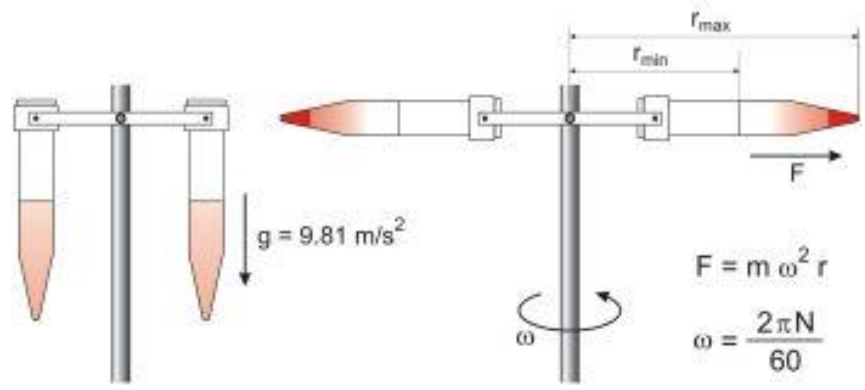# How to separate colloidal particles from the liquid medium: Centrifugation

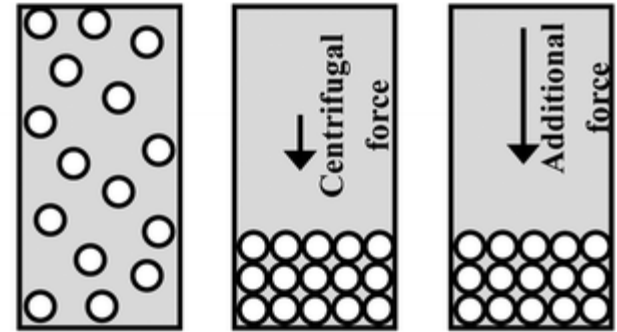Schéma des différentes forces s'appliquant
sur le composé à centrifuger

$$g = 9.81 \ m/s^2$$

$$F = m \, \omega^2 \, r$$
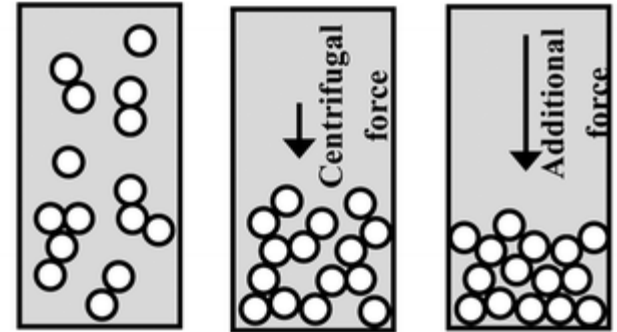
$$\omega = \frac{2\pi N}{60}$$

m = mass of particle

r = distance of particle from axis of rotation

ω = average angular velocity (rad/s)

N = revolution per minute, r.p.m.

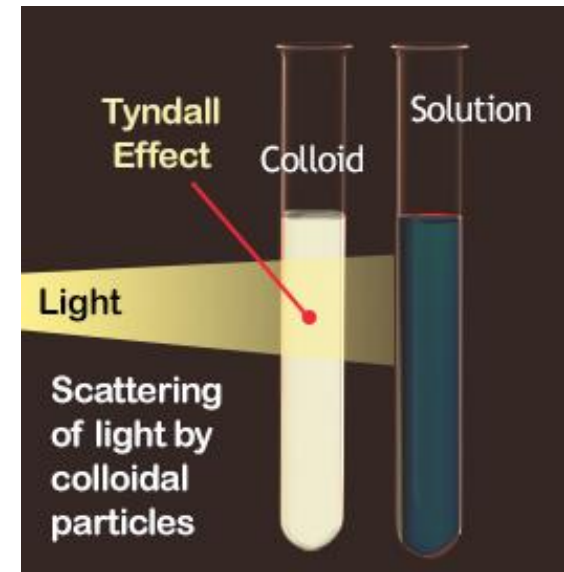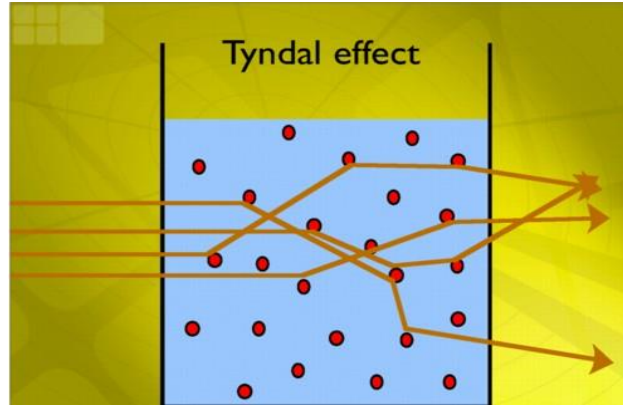(a) Stable particles

Centrifugal force

Additional force

(b) Aggregated particles

Centrifugal force

Additional force

Colloids properties: Tyndall effect

→ If a beam of light, viewed at right angles to its direction, is passed through a colloidal suspension, the light is **scattered by the particles**, rendering the path of the beam visible. If the beam of light is examined with a microscope, also set **at right angles to the beam**, the colloidal particles appear as bright points of light, though they are too small to be resolved, i.e., their shape cannot be discerned.

→ When examined in this way, the particles are seen to be rapid, random motion, known as **Brownian motion**. This is caused by molecules of the dispersion medium, which have a thermal motion dependent on the temperature, **striking the colloidal particles**, causing them to move in a similar way.

→ Clearly, since the velocity of a particle, for a given kinetic energy, will be inversely proportional to its mass, **only very small particles will acquire sufficient velocity for their motion to be detected**.

Colloids properties: electrokinetics
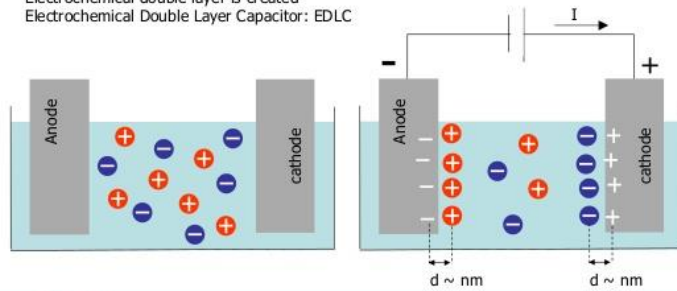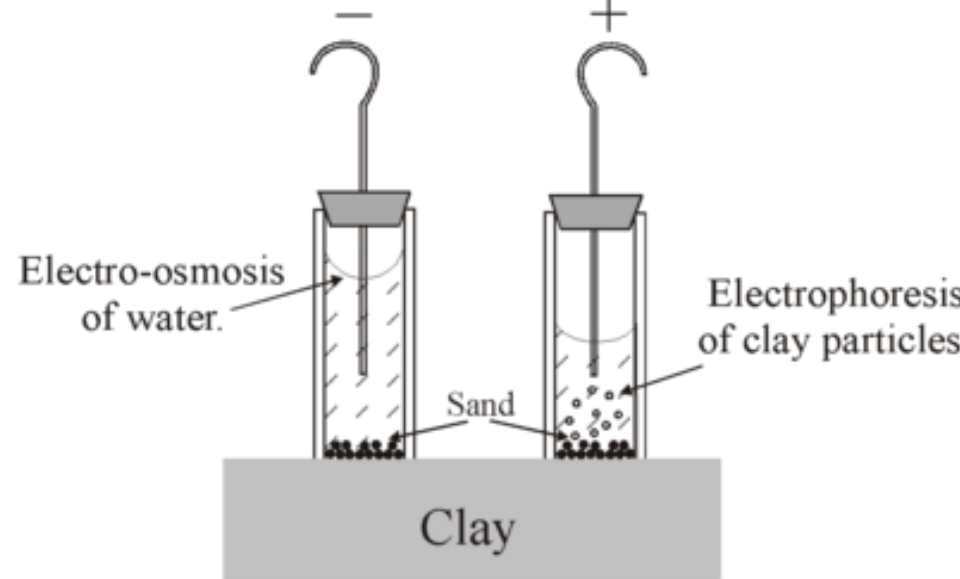
→ If two platinum electrodes, connected to a source of high potential (~200 V), are immersed in a colloidal suspension, a small current passes and the colloidal particles migrate towards one or other of the electrodes. This phenomenon is electrophoresis, and shows that **all colloidal particles carry an electric charge** (the charge is more often negative than positive and it may arise in a number of ways – see Ceramic Raw Materials and Ceramic Powders).

→ In the case of a clay suspension, as an example, the particles of clay migrate to the anode, showing that they are **negatively charged**. At the opposite electrode, the cathode, appear **the balancing ions**, or **counter-ions**, which of course are **positively charged**. With a natural clay, these ions will be a mixture of H, Ca, Mg, Na and K in various proportions, the metallic ions reacting with water to form hydroxides, the hydrogen appearing as the gas H_2.

Colloids properties: electrokinetics
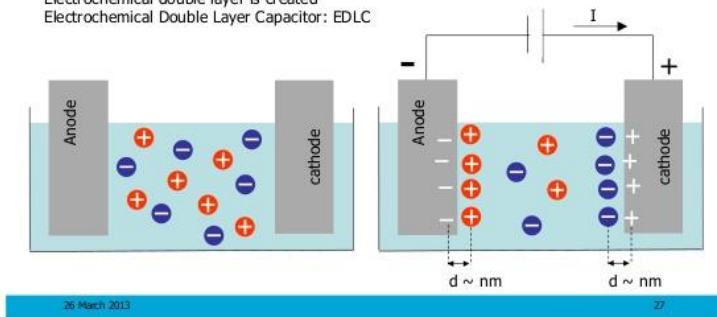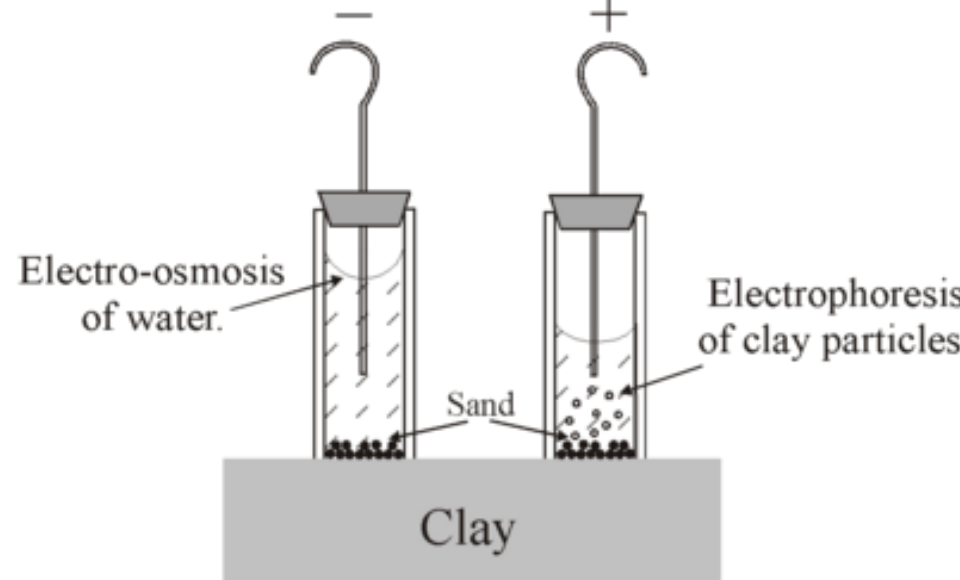
→ Charged particles in suspension will respond to an imposed potential difference, and the particle velocity is called **electrophoretic velocity**.

→ The **potential** at the **slippage plane** (or **shear plane**) is called **the zeta potential** ζ and can be calculated from the electrokinetic property. For the electrophoretic transport of no conducting particles,

$$\zeta = \frac{f_H \eta v_e}{\varepsilon_r \varepsilon_0 E}$$

→ where η is the viscosity of the electrolyte and v_e is the electrophoretic velocity for an imposed electrical field E. The ratio v_e/E is the electrophoretic mobility. The Henry constant f_H is equal to 1 when the product of the particle diameter a and k is > 100 and 2/3 when ak <1 (k from Gouy and Chapman model).

# How does a surface charges arise in Clays?

Exchangeable ions

→ Exchangeable ions present in clay minerals

  (see Ceramic Raw Materials and Ceramic Powders)

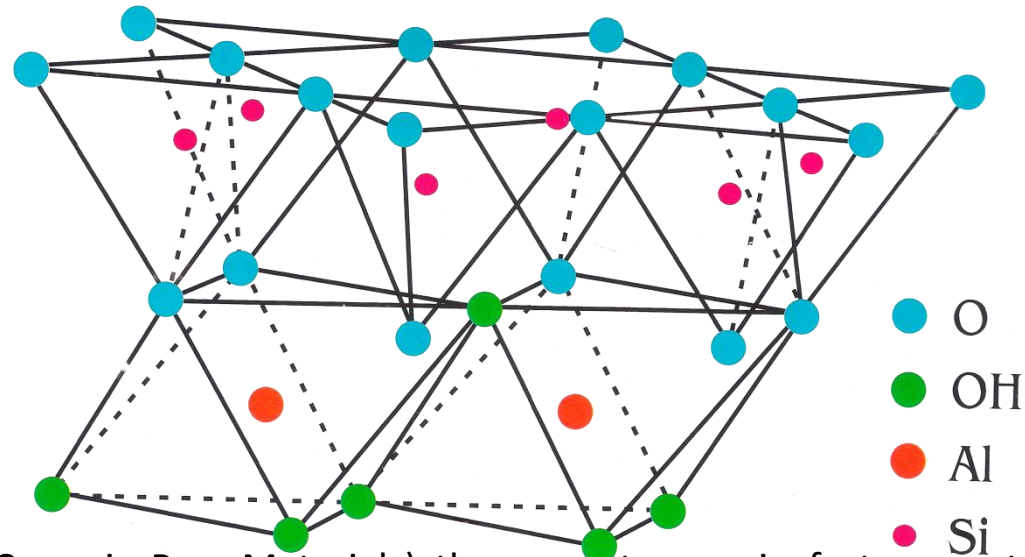 → i) either satisfy free valences at the crystal edges or

  → ii) balance inherent lattice charges due to isomorphs substitution

→ Therefore, the charge on the clay particles can develop only by diffusion of the exchangeable ion away from the solid surface when the clay is placed in water:

$$[Na\ clay] \rightarrow [clay]^- + Na^+$$
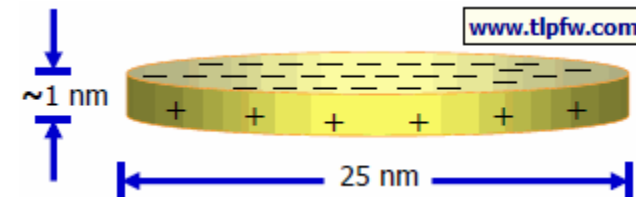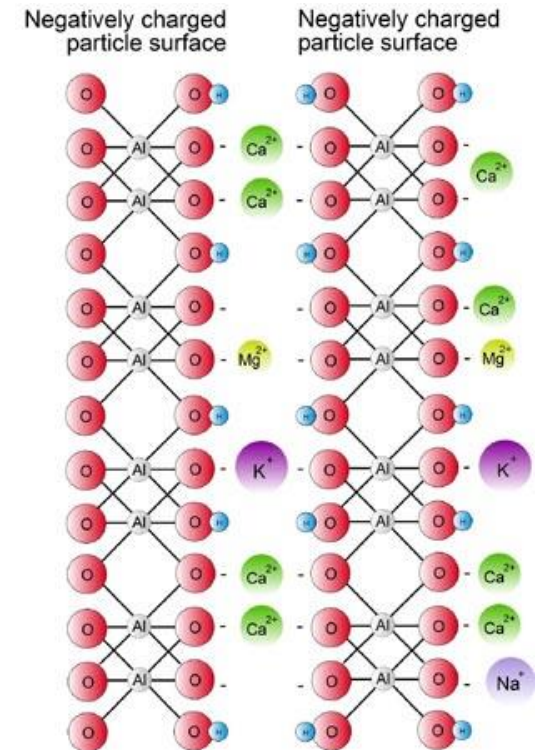
http://www.terragis.bees.unsw.edu.au/terraGIS_soil/sp_stability_indices.html

Colloids properties: cation exchange reactions

→ If a clay is placed in a solution of a given electrolyte, **an exchange** may occur between the ions of the clay and those of the electrolyte:

$$\text{X-clay} + Y^+ \leftrightarrow \text{Y-clay} + X^+$$

→ the reaction is balanced and the extend to which the reaction proceeds from left to right depends on:

    i) the nature of the ions **X** and **Y**

    ii) their relative concentration

    iii) the nature of the clay

    iv) any secondary reactions

→ Strong ionization and more charged colloidal particles ⇒ Deflocculation

Negatively charged particle surface   Soil solution

Colloids properties: cation exchange reactions


Legend:
- ● O
- ● OH
- ● Al
- ● Si

→ In **kaolinite minerals** (see Ceramic Raw Materials) there are two main factors contributing to cation exchange:

i) the oxygen and hydroxyl valences at the planar surfaces of the structure are completely satisfied. At the edges, however, there are aluminum, oxygen and hydroxyl ions with unsatisfied valencies or 'broken bonds', because the lattice is capable of extension indefinitely in the *ab* plane. This **surface charge** may be **equilibrated** by external ions, acting as counter-ion and **preserving electrical neutrality**. Note that this external ions do not form part of the structure, behaving as counter-ions and capable of being exchanged for other ions.

ii) in disorder kaolinites additional balancing cations are present because of the lattice substitutions.

Colloids properties: cation exchange reactions

→ Various theories of mechanisms by which cation exchange takes place have been proposed from time to time. Freundlich adsorption isotherm, Langmuir isotherm equation, Jenny and latter Gapon kinetic equations are some of the tentative to explain cation exchange reactions in clays.

→ Some of the foregoing models show agreement with experimental values over a limited range of concentrations, but **no universally applicable equation has been formulated**. Many equations that are satisfactory for exchange between cations of like valence break down when applied to unlike cations. Aluminum, which can fit into kaolinite or montmorillonite structures, is a particularly difficult ion to replace.
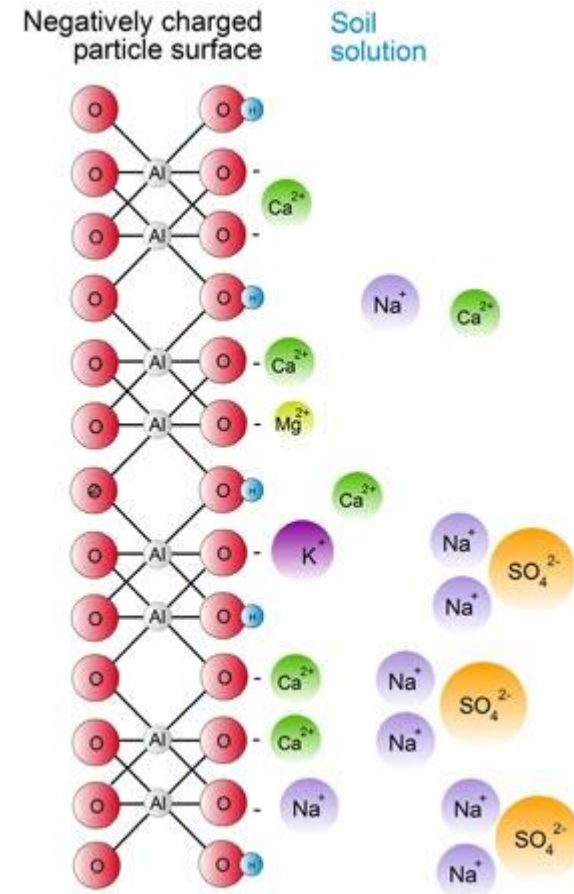
Colloids properties: cation exchange reactions
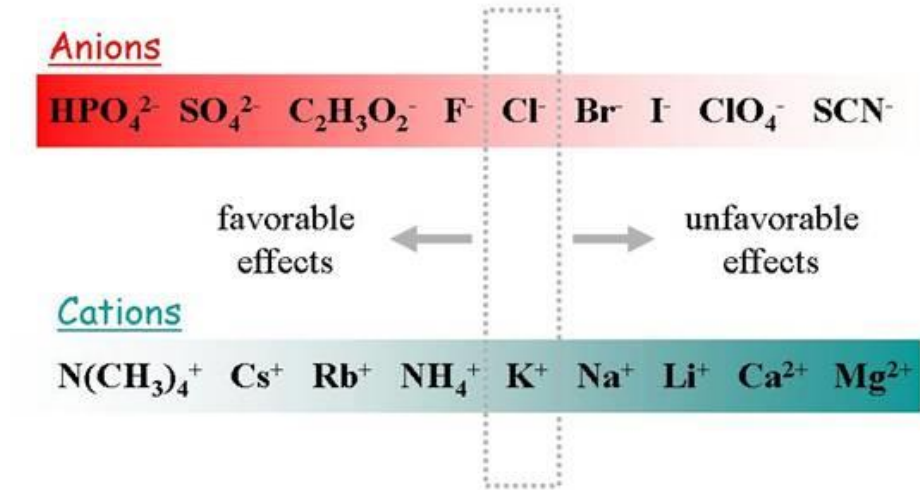
$\rightarrow$ Even for equivalent concentrations, **some cations are adsorbed more strongly than others**; if the cations are written in order of the readiness with which they are adsorbed, one obtains the **lyotropic** or **Hofmeister series**:

$$H > Al > Ba > Sr > Ca > Mg > NH_4 > K > Na > Li$$

Colloids properties: cation exchange reactions

strongly electropositive cations $\Rightarrow$ higher ionization

high charge, small cation radius (Na^+, K^+,…)$\Rightarrow$ high ionic potential

weak electropositive cations $\Rightarrow$ weak ionization

lower charge, higher cation radius (H^+, Ca^{2+}, Mg^{2+},…) $\Rightarrow$ lower ionic

potential

HOFMEISTER SERIES

Cations

| NH_4^+ | K^+ | Na^+ | Li^+ | Mg^{2+} | Ca^{2+} | guanidinium$^+$ |

SO_4^{2-} HPO_4^{2-} acetate$^-$ citrate$^-$ Cl^- NO_3^- ClO_3^- I^- ClO_4^- SCN^-

Anions

↑ surface tension
harder to make cavity
↓ solubility hydrocarbons
Salt out (aggregate)
↓ protein denaturation
↑ protein stability

↓ surface tension
easier to make cavity
↑ solubility hydrocarbons
Salt in (solubilize)
↑ protein denaturation
↓ protein stability

How does a surface charges arise in Clays?

pH

→ Oxides show unsaturation at their surface due to the incomplete coordination of atoms. When these oxide surfaces get in contact with water the surface becomes hydrated. In this process protons from the liquid phase are added to surface oxygen ions and create a neutral particle with OH groups at the surface. The surface charges are created subject to the pH of the suspension either by absorbing H^+ or OH^- ions or by dissociating the surface charged OH groups.

Acid environment
Me-OH$_2^+$

Alkaline environment
MeO$^-$
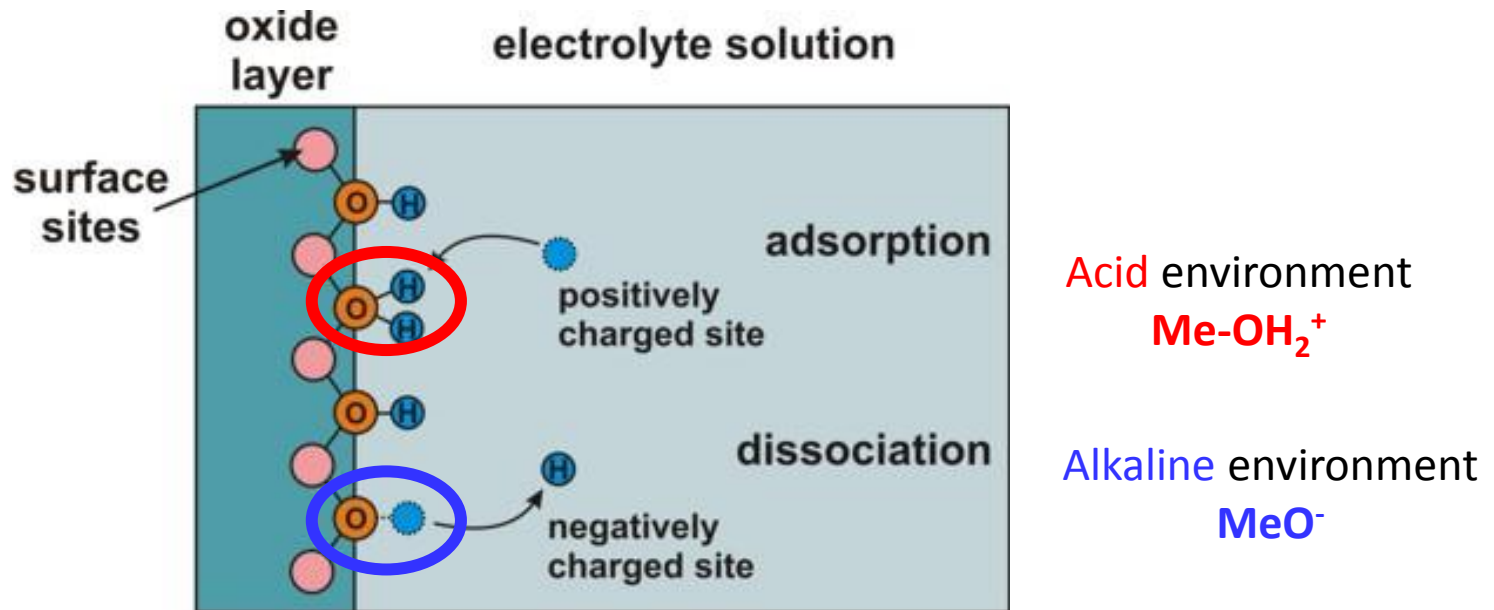
The surface charge of the particle is then compensated in the liquid phase by counter-ions, ensuring a condition of electrical neutrality in the system as a whole.

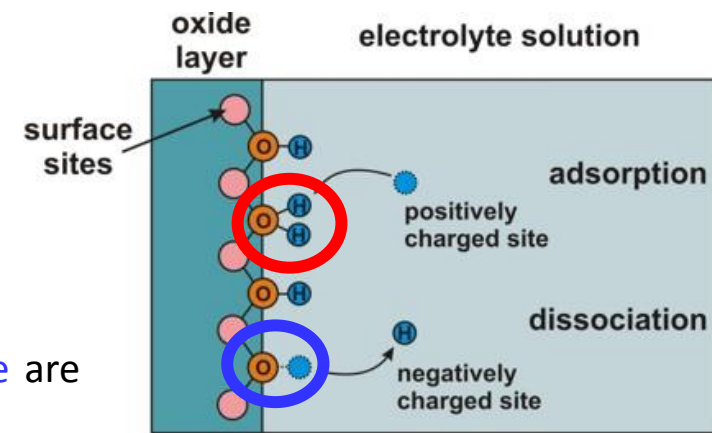# How does a surface charges arise in Clays?

pH

→ The processes appearing at the hydrated surface of an oxide are determined by the chemical reactions:

$$[Me\text{-}OH]_{(surface)} + H_3O^+_{(solution)} \overset{K_1}{\leftrightarrow} [Me\text{-}OH_2^+]_{(surface)} + H_2O \qquad \textbf{(in acid environment)}$$

$$[MeOH]_{(surface)} + OH^-_{(solution)} \overset{K_2}{\leftrightarrow} MeO^-_{(surface)} + H_2O \qquad \textbf{(in alkaline environment)}$$
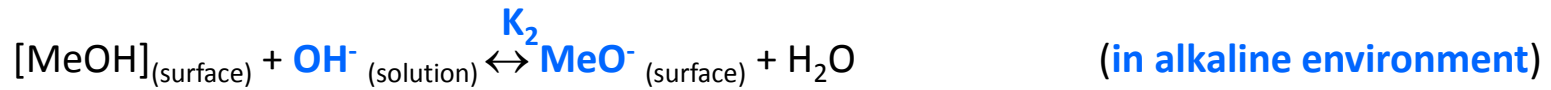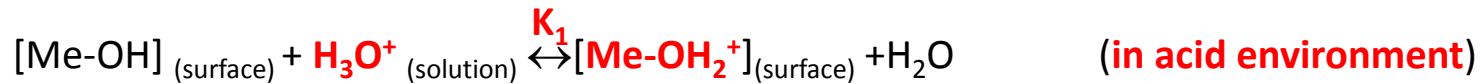
where **Me** is a metal ion at the surface, i.e., Ba^{2+}, Al^{3+}, Si^{4+}. By adding **H_3O^+ ions** the pH will be reduced as the uncharged surface absorbs protons and thus becomes **positively charged**.

The addition **of OH⁻ ions** separates hydrogen from the surface and produces a **negative surface charge** with pH values that are **higher than the point of zero charge (PZC) at the surface**.

How does a surface charges arise in Clays?

pH
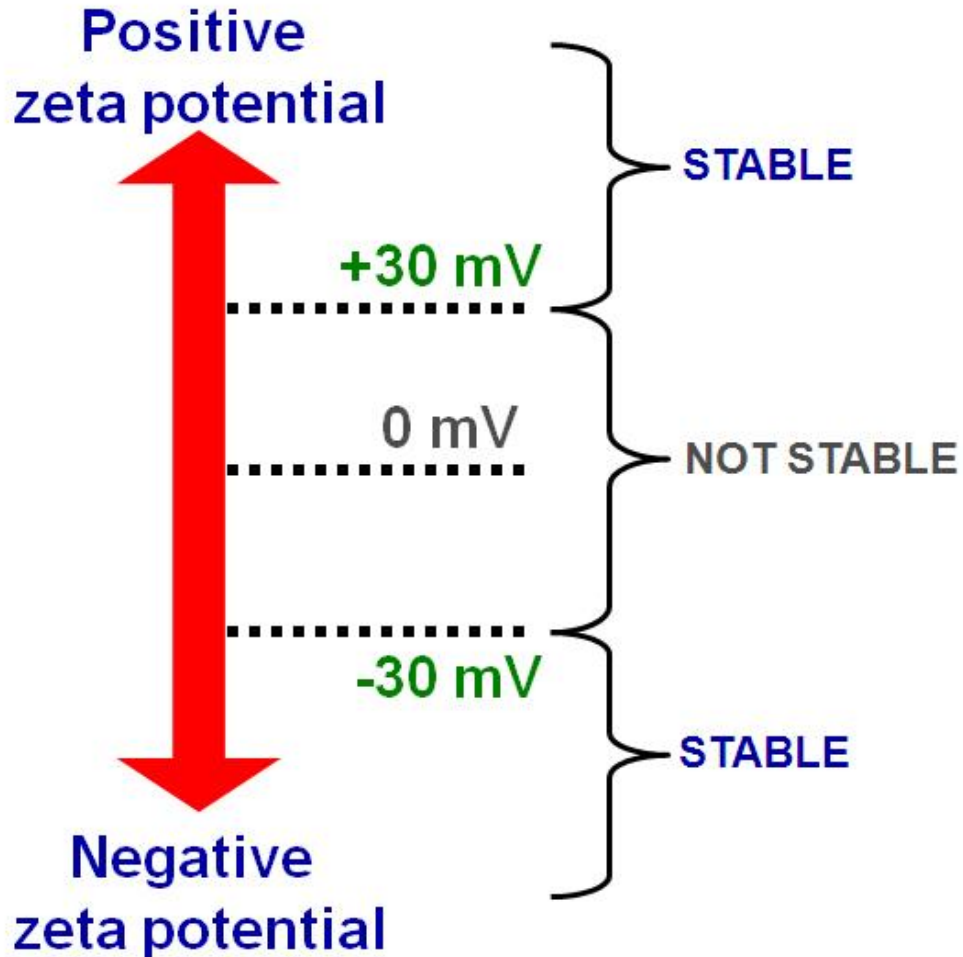
→ The **point of zero charge** (**PZC**) − frequently called **isoelectric point** (**IEP**) − of the surface reflecting the acid-base character is given by the two **pKs** of the previous reactions:
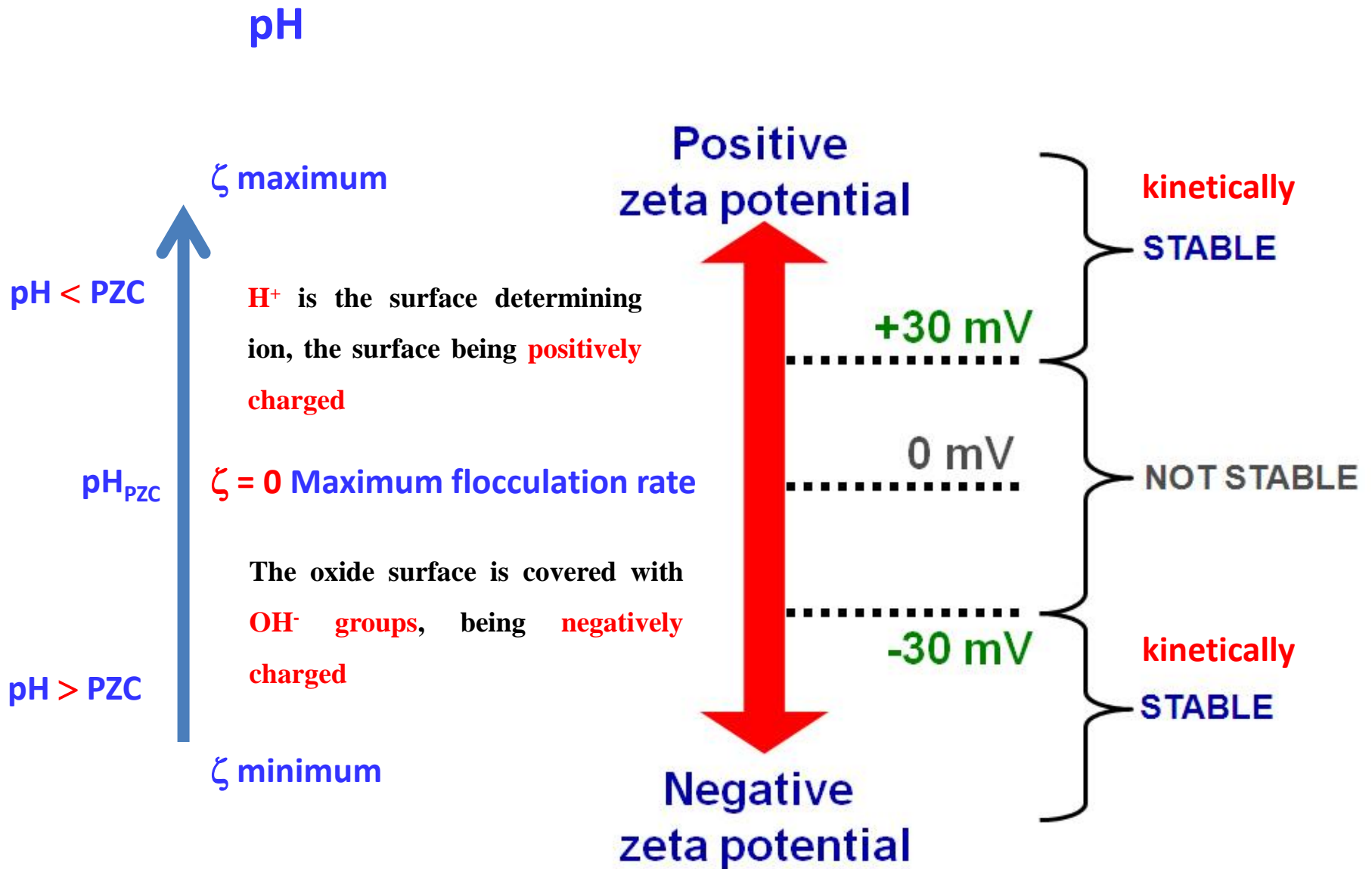
→
$$PZC = \frac{pK_1 + pK_2}{2}$$

→ According to the valence of the cation and the concentration of the oxygen ions the number of surface charges will vary and the point of zero charge will be shifted.

→ Ex. pure **alumina**, **PZC** lies at **pH = 9**

→   pure **silica**, **PZC** lies at **pH = 2**
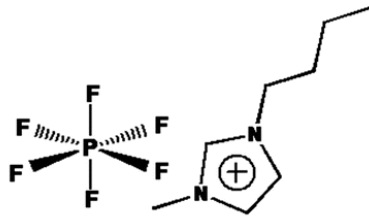
How does a surface charges arise in Clays?

pH

ζ **maximum**

pH $<$ PZC

H$^+$ is the surface determining ion, the surface being **positively charged**

pH$_{PZC}$ $\zeta = 0$ Maximum flocculation rate

The oxide surface is covered with **OH$^-$ groups**, being **negatively charged**

pH $>$ PZC

ζ **minimum**

Positive zeta potential

+30 mV

0 mV

−30 mV

Negative zeta potential

kinetically **STABLE**

NOT STABLE

kinetically **STABLE**

How does a surface charges arise in Clays?
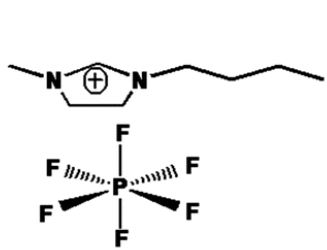
pH: examples

(a) E > PZC

(b) E ≈ PZC

(c) E < PZC

(d) E << PZC

2-

CPA

2+

PTA

Oxide Surface

pH<PZC   **PZC**   **pH>PZC**   pH
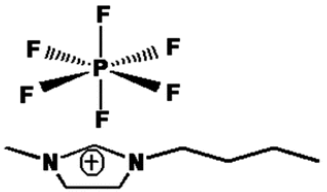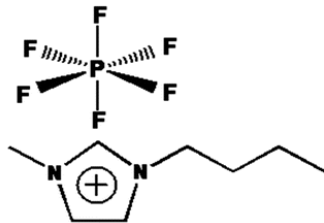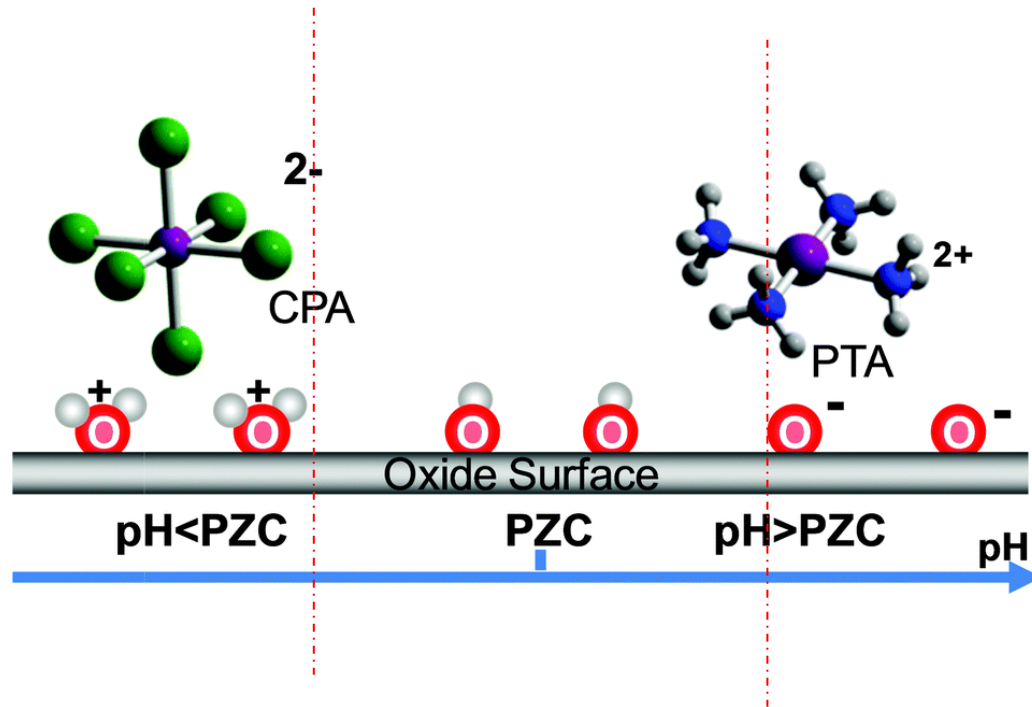
|ξ| ≥ 30 mV INCREASE ADSORPTION CAPABILITY!

How does a surface charges arise in Clays?

pH: examples

ξ MAXIMUM

POSITIVE SURFACE CHARGE

SiO_2

ξ MINIMUM

NEGATIVE SURFACE CHARGE

pH

$\xi = 0$

$|\xi| > 30$ mV

$|\xi| < -30$ mV

pH = 2

pH < 2

pH > 2

ISOELECTRIC POINT (PZT)

NULE SURFACE CHARGE

KINETICALLY STABLE SUSPENSION

KINETICALLY INSTABLE SUSPENSION

KINETICALLY STABLE SUSPENSION
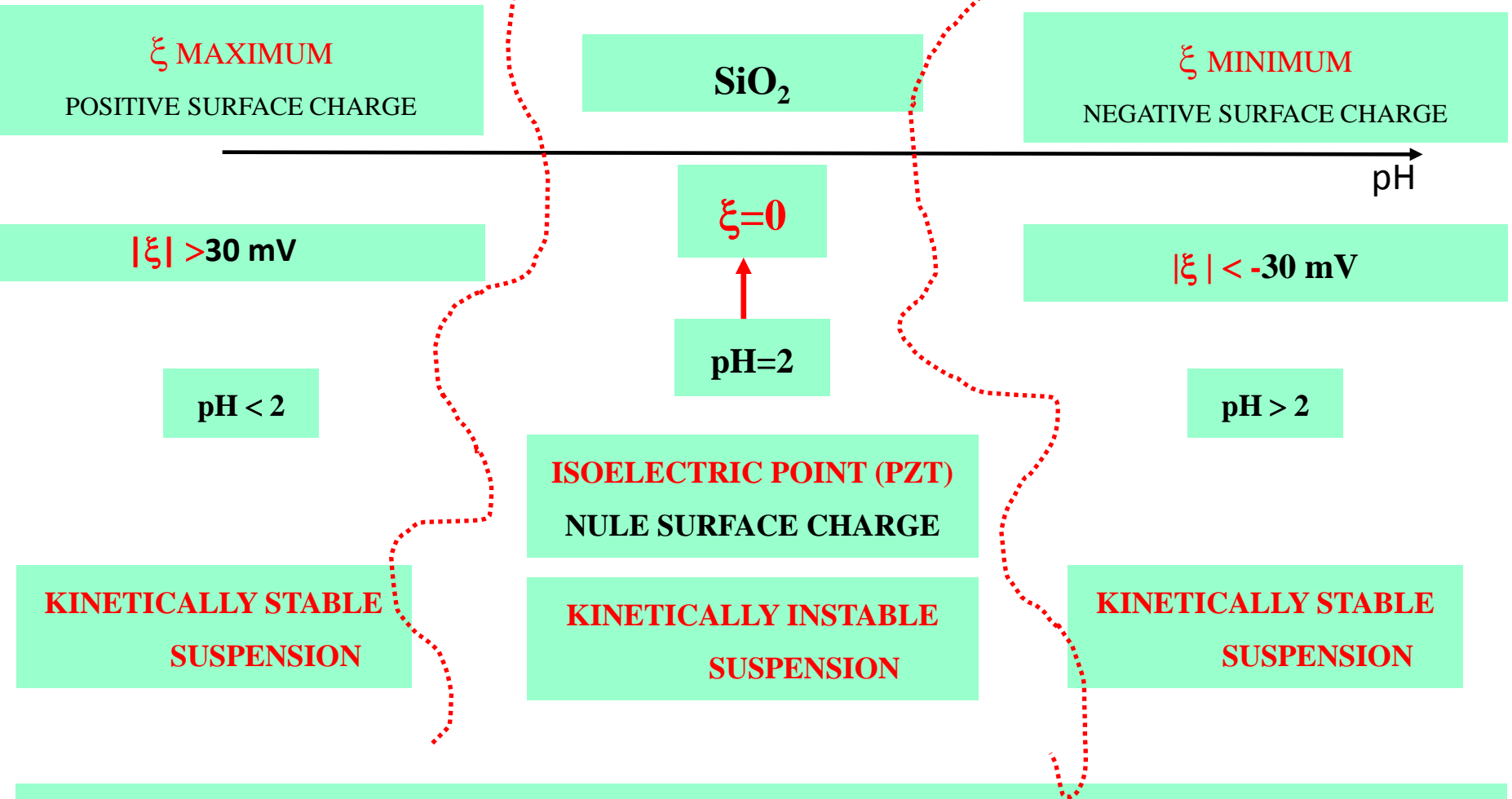
Floculation is maximum at PZT, point where electrophoretic velocity (and consequently **zeta potential**) **equals zero**.

Build up the diffuse electrical double layer

https://www.youtube.com/watch?v=HDQ8ct4md-8

Build up the electrical double layer (Helmholtz, Gouy, Chapman, Stern)
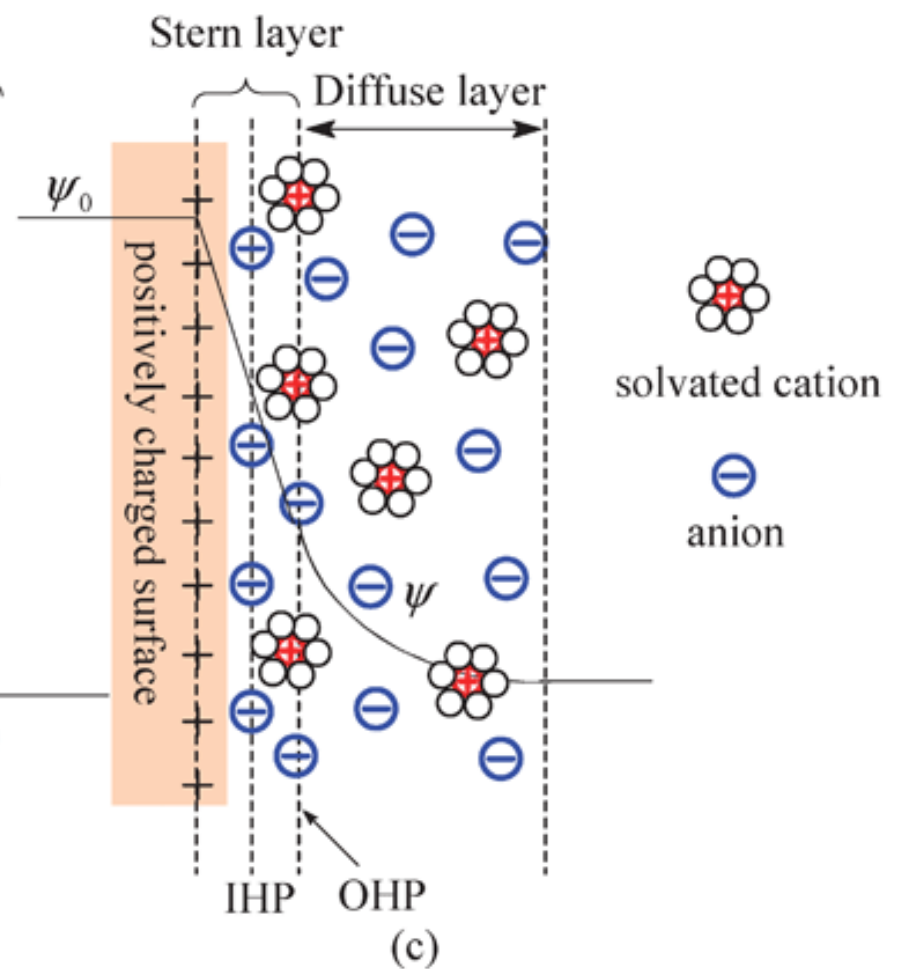
Helmholtz
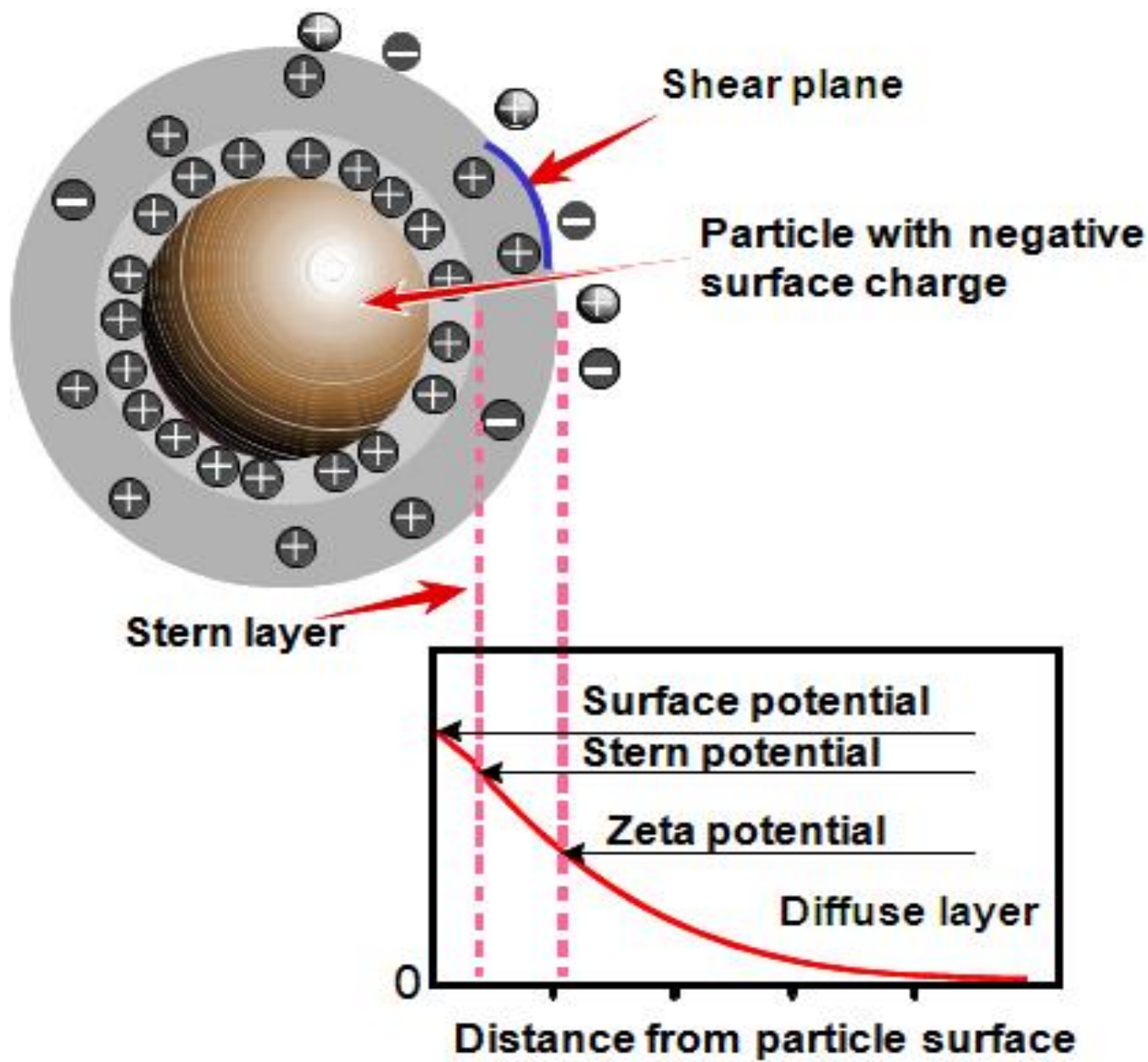**(1st model)**
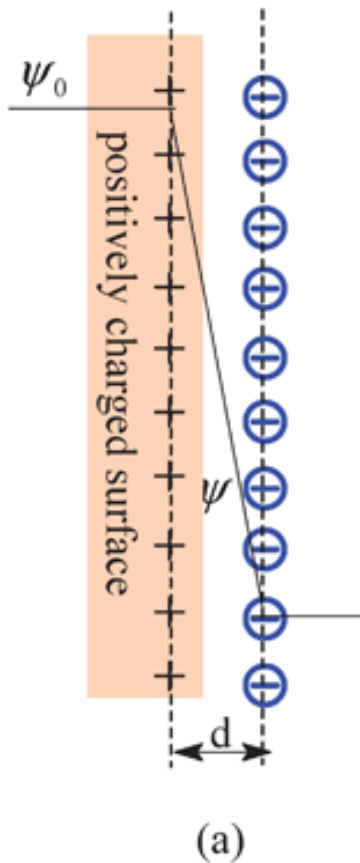
Gouy and **Chapman**
(2nd model)
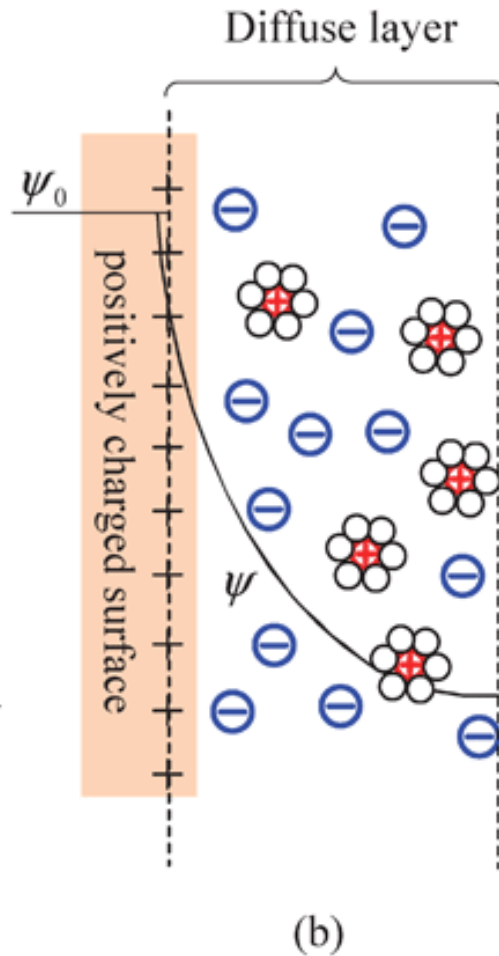
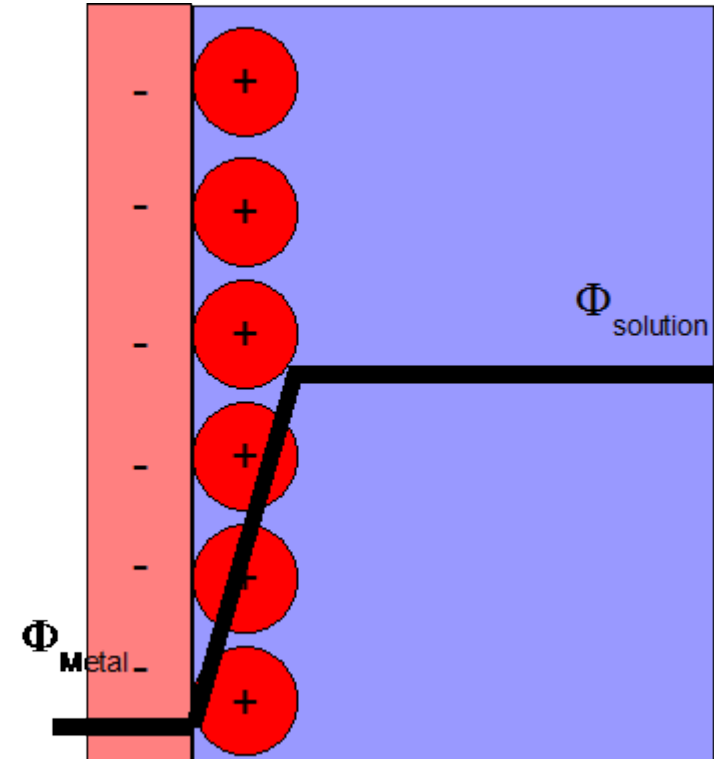**Stern**
(3rd model)

Colloidal stability: DLVO

Build up the electrical double layer (Helmholtz, Gouy, Chapman, Stern)

Helmholtz (1st model)

At the interface between powder particles and dispersion medium the solid particles are **surrounded by a layer of absorbed ions** that fit relatively tight to the particle surface.

Helmholtz (1st model) implied that **every negative charge of the particle was saturated by a counter ion**, but for steric reasons the counter ion will not (as a rule). That is why in the farer surroundings of the powder particles a so-called **diffuse electric double layer** is built up by a concentration gradient of counter-ions and polar molecules of the liquid.

The potential gradient is no sharp line, as a diffusion of counter-ions will be caused by the thermic movement of molecules.

Build up the electrical double layer (Helmholtz, Gouy, Chapman, Stern)

Gouy and Chapman (2nd model)

Gouy and **Chapman (2nd model)** independently derived a model for the potential gradient in the diffuse double layer based on a uniformly charged surface, an adjacent solution with uniform dielectric constant ϵ_R, and point charges.

Assuming that the charge distribution can be described by the Boltzman equation the result is the **concentration of counter ions N_i in the diffuse layer compared to the concentration of ions in the solution N_i^0.**

$$N_i = N_i^0 \exp\left(-\frac{U_i}{k_B T}\right)$$

The **potential energy of the ions U_i** is a function of the **valence z_i** of the ion, the **electron charge e^-** and **the electric point Ψ** at the respective position:
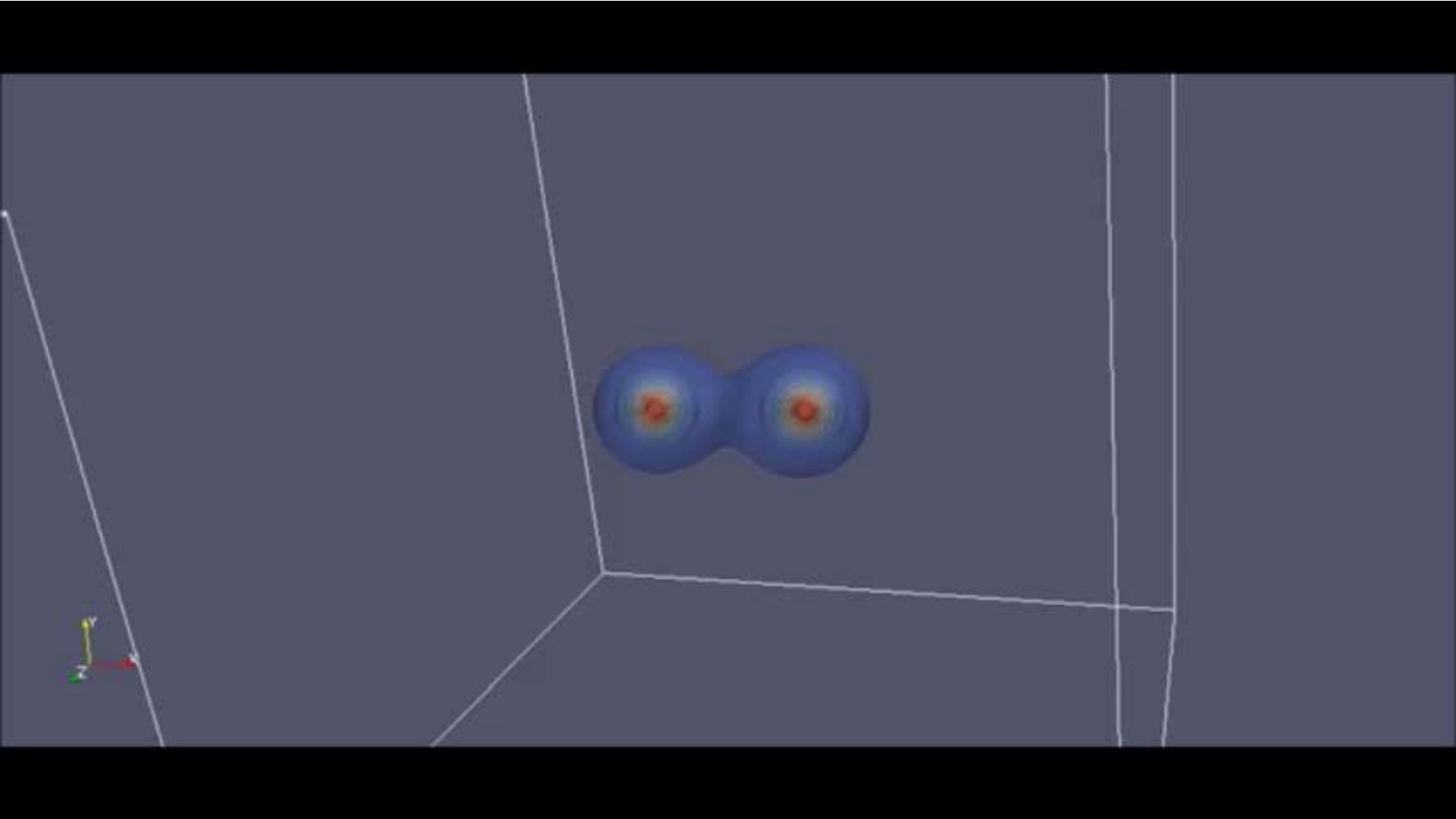
$$U_i = z_i e\, \psi$$

For a **surface potential $\Psi_0 \leq 100$ mV** is:

$$\psi = \psi_0 \exp(-kx)$$

Where **x** is the distance from the particle charged surface and the plane where $\Psi = \Psi_0/2.718$:

$$k = \left(\frac{e^2 \sum N_i^0 z_i^2}{\varepsilon k_B T}\right)^{1/2}$$

Build up the electrical double layer (Helmholtz, Gouy, Chapman, Stern)

Gouy and Chapman (2nd model)

The surface potential thus decrease exponentially in the first approximation with the distance from the particle surface.

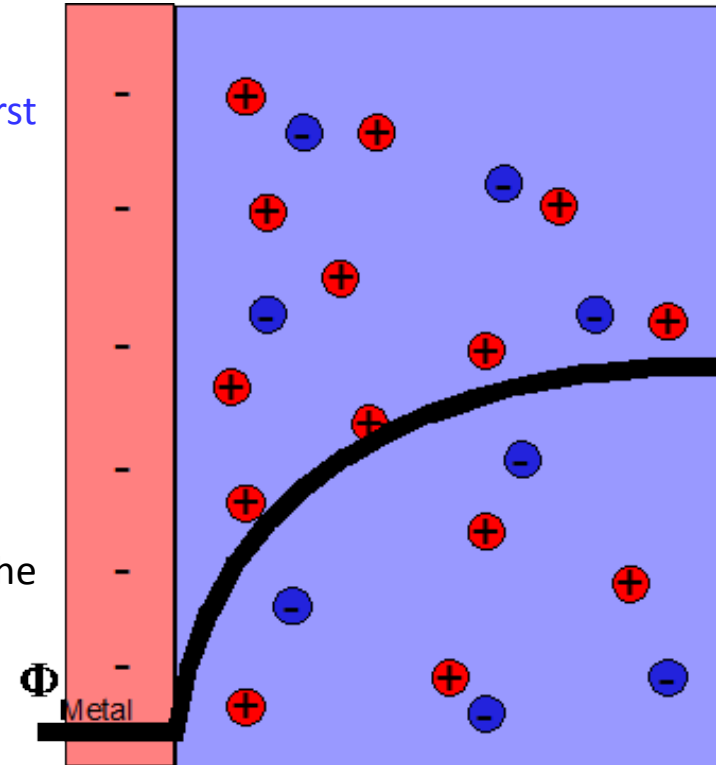**When x=k^{-1}, $\Psi= \Psi_0/2{,}718$**

From the ionic strength:

$$I = \frac{1}{2}\sum c_i z_i^2$$

(c_i= ionic concentration in mol/L) results the thickness of the diffuse electric double layer as:

$$k^{-1} = \left(\frac{\varepsilon_r \varepsilon_0 k_B T}{F^2 \sum N_i Z_i^2} \right)^{1/2}$$

Where **N$_i$** is the concentration of each ion type in the solution phase and **F** is the Faraday constant.

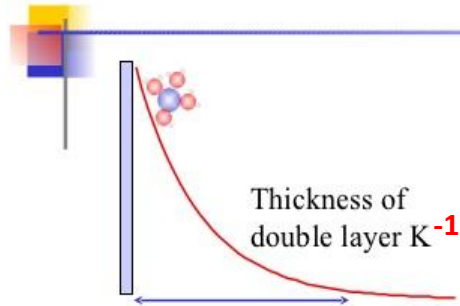**For water at 25ºC, a thickness of the diffuse electric double layer of 9,6 nm is calculated for 0.001 M 1:1 of a given electrolytic solution.**

Φ

Metal

Build up the electrical double layer (Helmholtz, Gouy, Chapman, Stern)

Gouy and Chapman (2nd model)

$1/2$

5.3 Thickness of Double Layer

Thickness of double layer K^{-1}

$$K^{-1} = \left(\frac{\varepsilon_0 \kappa \cdot kT}{2n_0 e^2 v^2} \right)^{1/2}$$

ε_0 : Permittivity in vacuum

κ : Relative permittivity

k : Boltzman constant

T : Temperature

n_0 : Cation concentration

e : Electron charge

v : Valence

$K^{-1}\uparrow$	repulsion force $\uparrow$	
$n_0\uparrow$	$K\downarrow$	repulsion force $\downarrow$
$v\uparrow$	$K\downarrow$	repulsion force $\downarrow$
$T\uparrow$	$K\uparrow$	repulsion force $\uparrow$(?)

κ decreases with increasing temperature

43

$\uparrow$ **concentration**

or

$\uparrow$ **valence of the counter-ions** ($\Leftrightarrow \uparrow$ **I**)

$\downarrow$**k^{-1}** ,

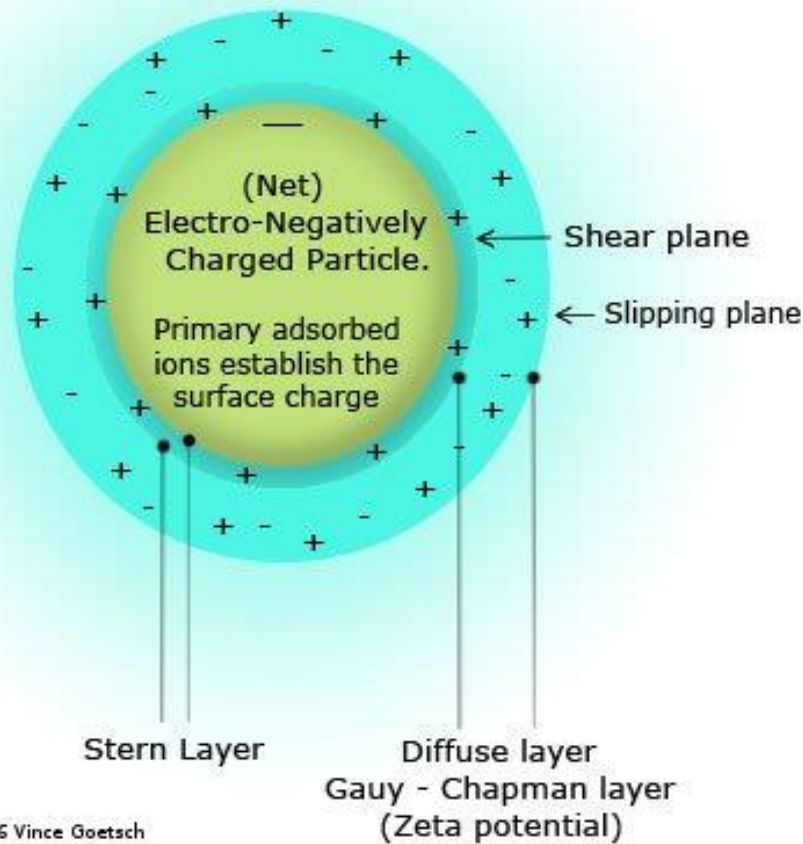(i.e.**compressing the double layer**)

For a given 0.01 M aqueous solution of 1:1 electrolyte, at 20ºC, the effective double layer thickness k^{-1} is calculated to be ~3 nm.

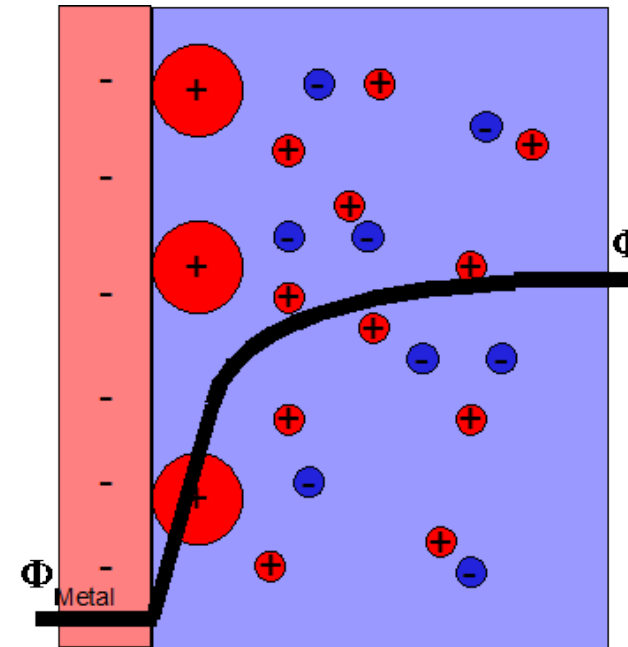The use of a liquid of a lower dielectric constant or T also compresses the double layer.

Double layer thickness is depend on the liquid medium, not on the colloidal particles!

Stern (3rd model)

(Net)
Electro-Negatively
Charged Particle.

Primary adsorbed
ions establish the
surface charge

← Shear plane

← Slipping plane

Stern Layer

Diffuse layer
Gauy - Chapman layer
(Zeta potential)

Copyright © 2006 Vince Goetsch

Φ

Φ Metal

Build up the electrical double layer (Helmholtz, Gouy, Chapman, Stern)

Stern (3rd model)

- $\uparrow$ I $\Rightarrow \downarrow$ k^{-1}
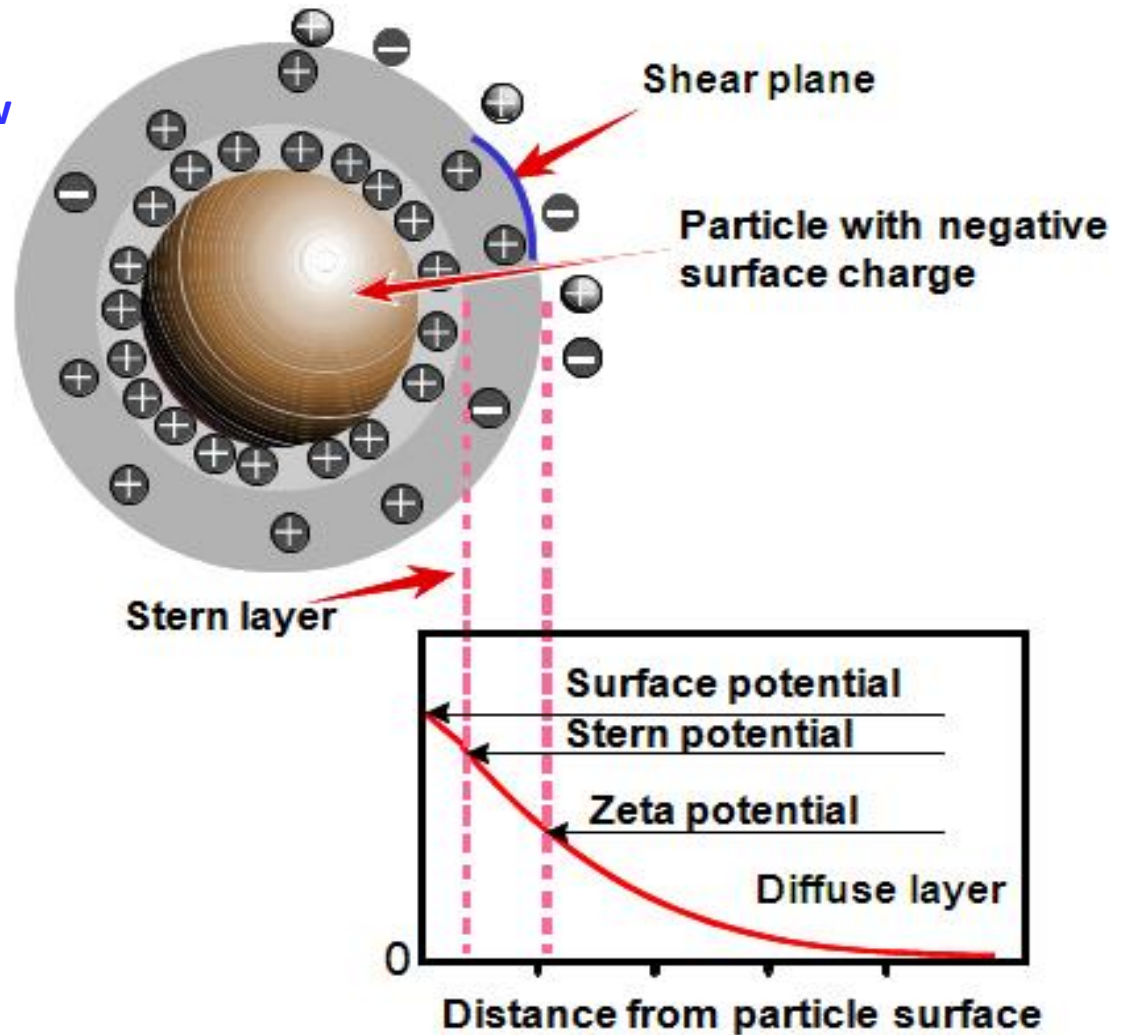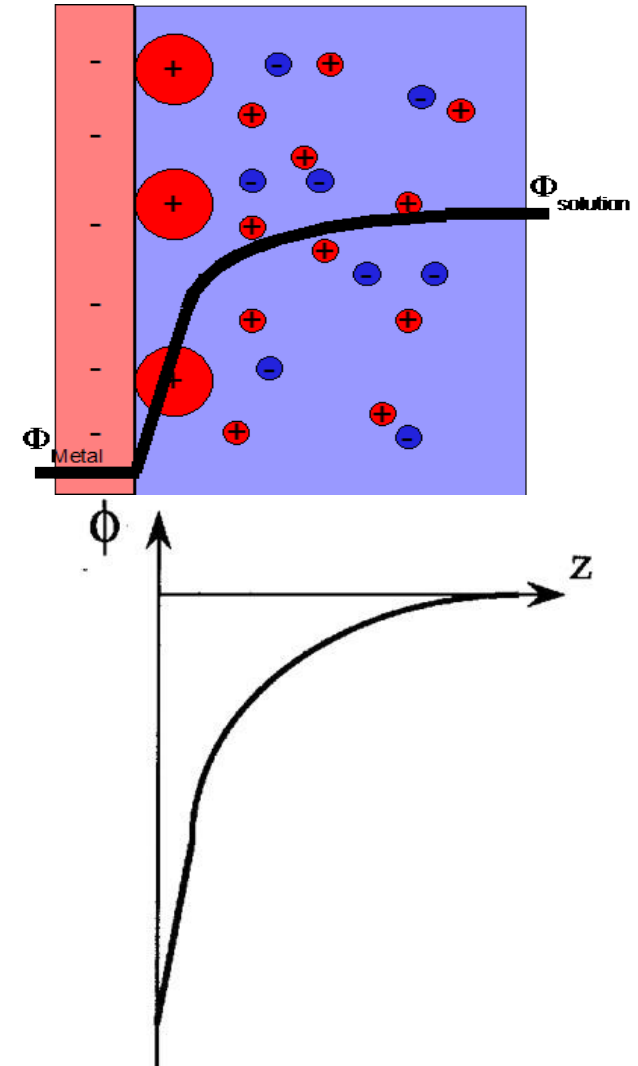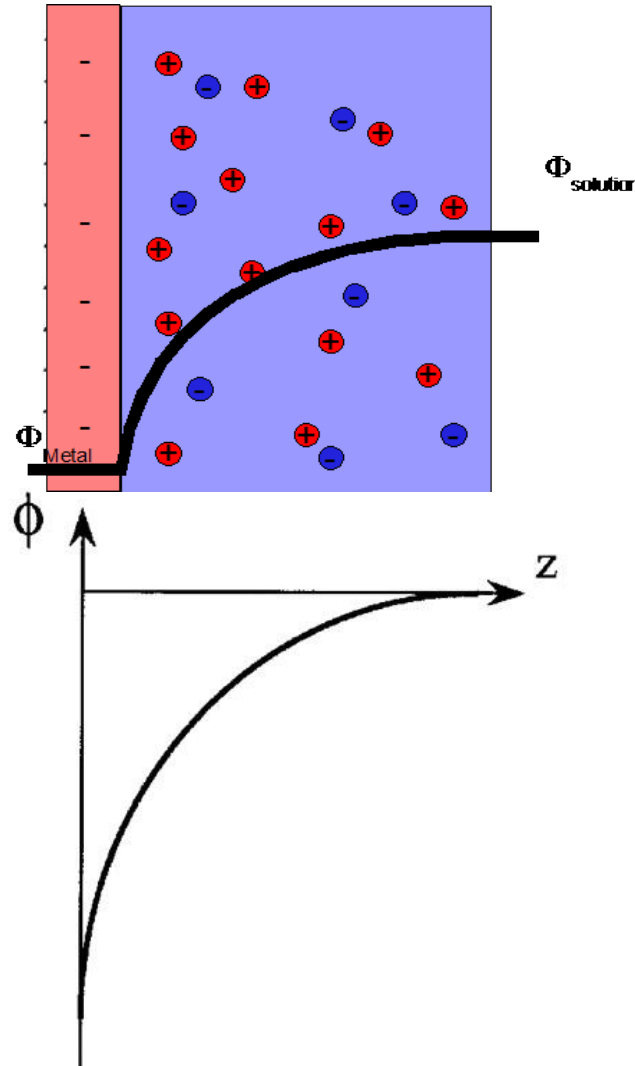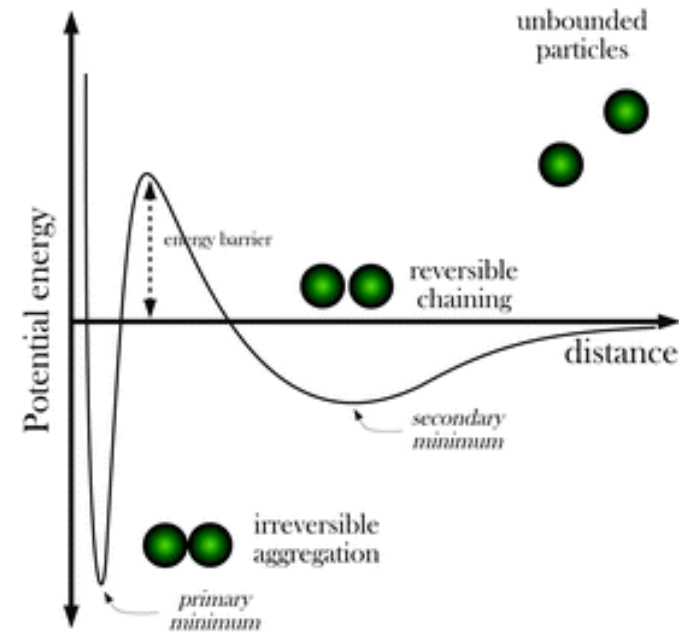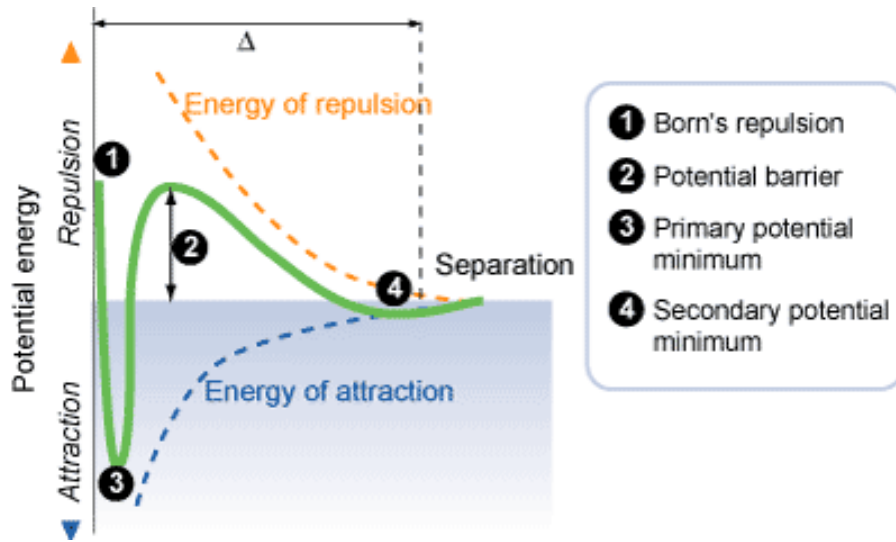- $\uparrow$ I (Stern layer saturated) **low**

⬇

V$_A$ >> V$_R$
Flocculation or Coagulation!

- $\downarrow$ I $\Rightarrow \uparrow$ k^{-1}
- $\uparrow$ I **high ζ**

⬇

V$_R$ >> V$_A$
Deflocculation!

Shear plane

Particle with negative surface charge

Stern layer

Surface potential
Stern potential
Zeta potential
Diffuse layer

Distance from particle surface

Build up the electrical double layer (Helmholtz, Gouy, Chapman, Stern)

Helmholtz

Gouy-Chapman

Stern

Colloidal stability: DLVO

- ❶ Born's repulsion
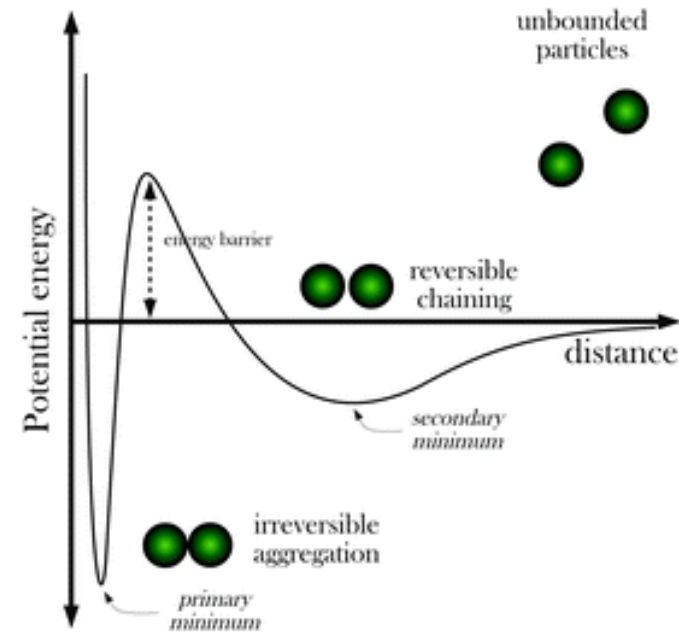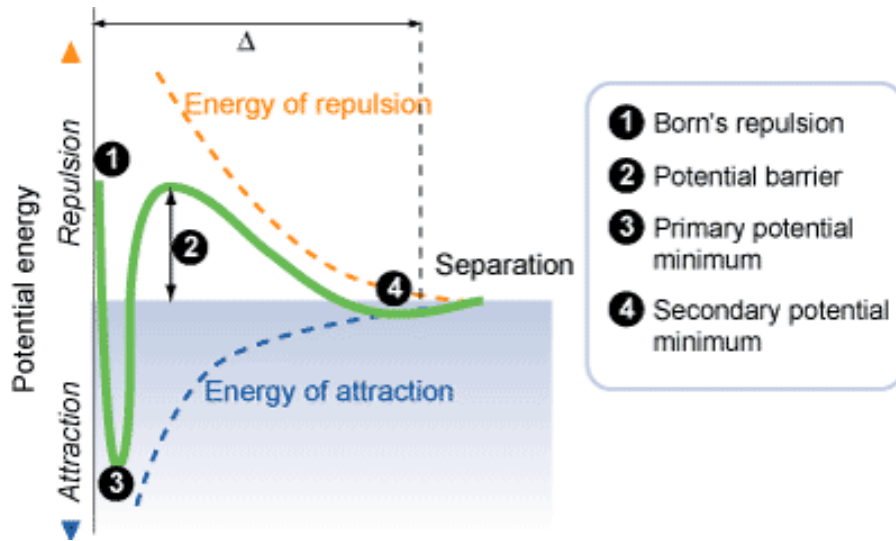- ❷ Potential barrier
- ❸ Primary potential minimum
- ❹ Secondary potential minimum
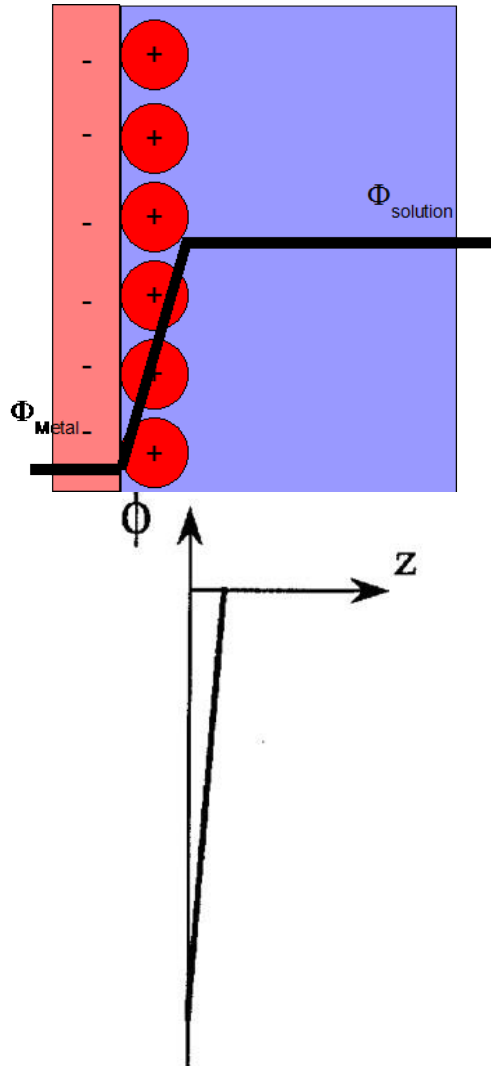
Powders suspended in a liquid spontaneously agglomerate unless they are **suitably deflocculated** by creating mutually repelling charged **double layers** or by physically preventing the close approach of particles due to the **steric hindrance** of adsorbed molecules. Electrical charging may stabilize slurries in polar liquids.

The interaction of two particles with identical charged double layers was examined by Derjaguin and Landau and Verwey and Overbeek, and their combined theories are now referred to as **DLVO** theory.
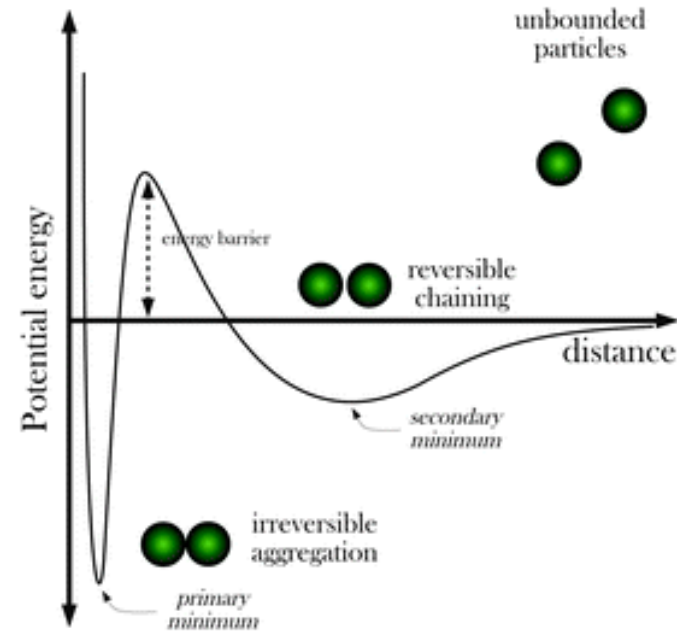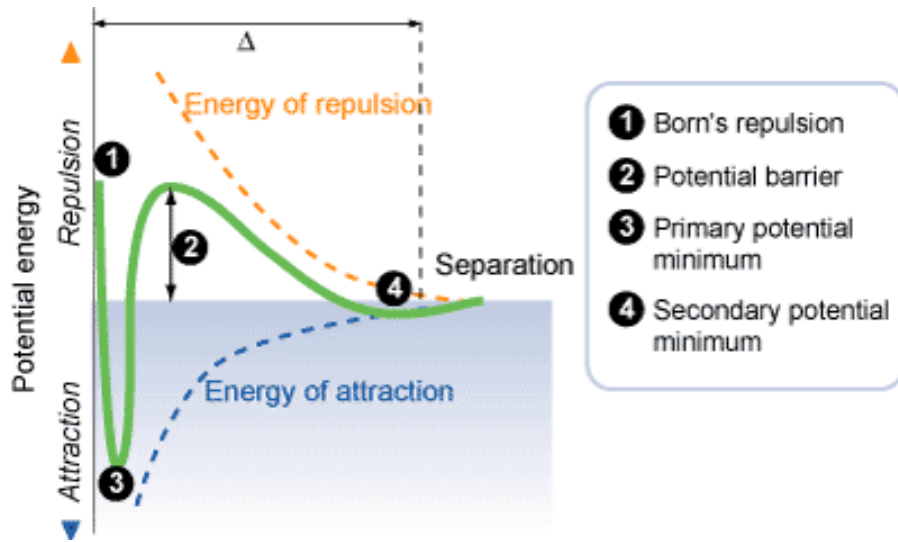
Colloidal stability: DLVO

- **1** Born's repulsion
- **2** Potential barrier
- **3** Primary potential minimum
- **4** Secondary potential minimum

The motivation force for coagulation is the ever-present **Van der Waals attractive force** which is a function of the dielectric constant of the medium and the mass and separation of the particles.

Repulsion is provided by the interaction of two electrical double layers. The form of the repulsion depends on the size and shape of the particles, the distance h between their surfaces, the double-layer thickness k^{-1} and ε_R of the liquid medium.

Colloidal stability: DLVO

Legend:
1. Born's repulsion
2. Potential barrier
3. Primary potential minimum
4. Secondary potential minimum

Van-der Waals attractive forces are the driving force for **coagulation** of the particles. For particles with diameter **d** and particles separation (**h**), the **potential energy for the attraction** is obtained by :

$$U_A = \frac{\left(\sqrt{A_2} - \sqrt{A_1}\right)^2 d}{24.h}$$

where **A_1** and **A_2** are the **Hamaker constants** for particles and dispersion medium, respectively.

Colloidal stability: DLVO

In order to avoid an agglomeration, **repulsive forces** have to react against the particle attraction. They depend on the size and shape of the particles, the distance h between their surfaces, the thickness of the double layer k^{-1} and the dielectric constant ϵ_r of the liquid medium.

According to **Coulomb law**, the potential energy of the repulsive forces is for **small particles** with relatively large double layer: **d/k⁻¹ <<1**

$$U_R = \frac{\varepsilon_r . d^2 . \psi_0^2}{4(h+d)} . \exp\left(-\frac{h}{k^{-1}}\right) \qquad \textbf{d/k}^{-1} \textbf{<<1}$$

and

$$U_R = \frac{\varepsilon_r . d . \psi_0^2}{4} . \ln\left[1 + \exp\left(-\frac{h}{k^{-1}}\right)\right] \qquad \textbf{d/k}^{-1} \textbf{>>1}$$

when the **particle diameter is much bigger** than the electric double layer, as it is normally the case for ceramic powder particles in aqueous suspension, i. e., **d/k⁻¹>>1**.

Colloidal stability: DLVO

DLVO theory

[Derjaguin & Landau (1941) / Verwey & Overbeerk (1948)]

Describes the stability of colloids with two contributions to the total energy:

1) Repulsion of the ionic double layers U_R

2) Van der Waals attraction between the colloidal particles U_A

Secondary minimum

Energy barrier

Primary minimum
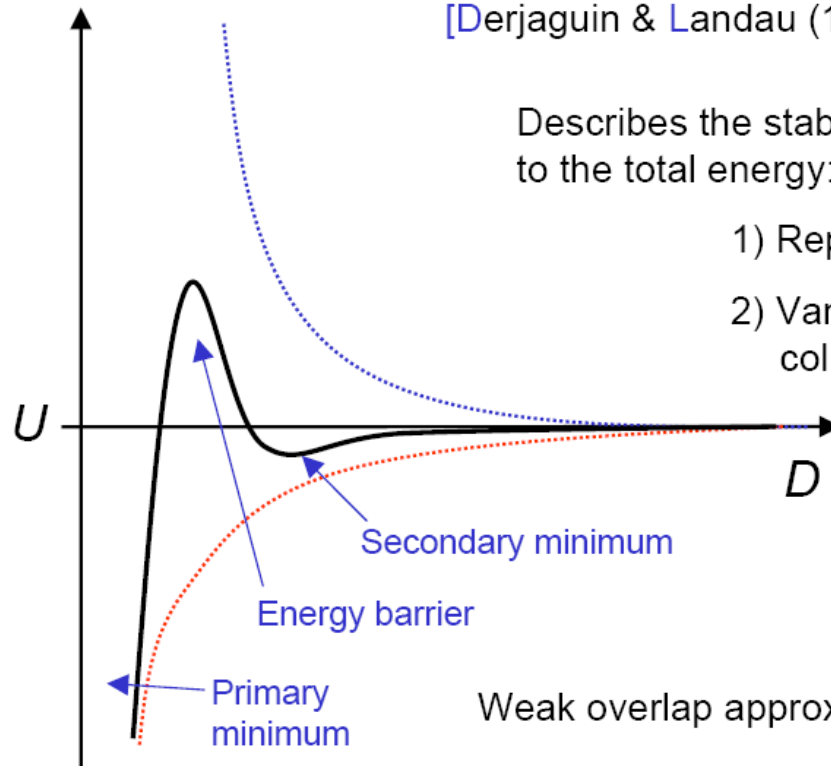
Weak overlap approximation:

$$U_{\text{DLVO}} = U_R + U_A$$
$$= (64\pi k_B T R c_0 \Gamma_0^2 / \kappa^2) e^{-\kappa D} - AR/12D$$

[J. Israelachvili, *Intermolecular & Surface Forces* (Academic Press, 1992)]

Colloidal stability: DLVO

The total interaction between two spheres

is the sum of the electrostatic repulsion and the dispersion attraction, DLVO theory:
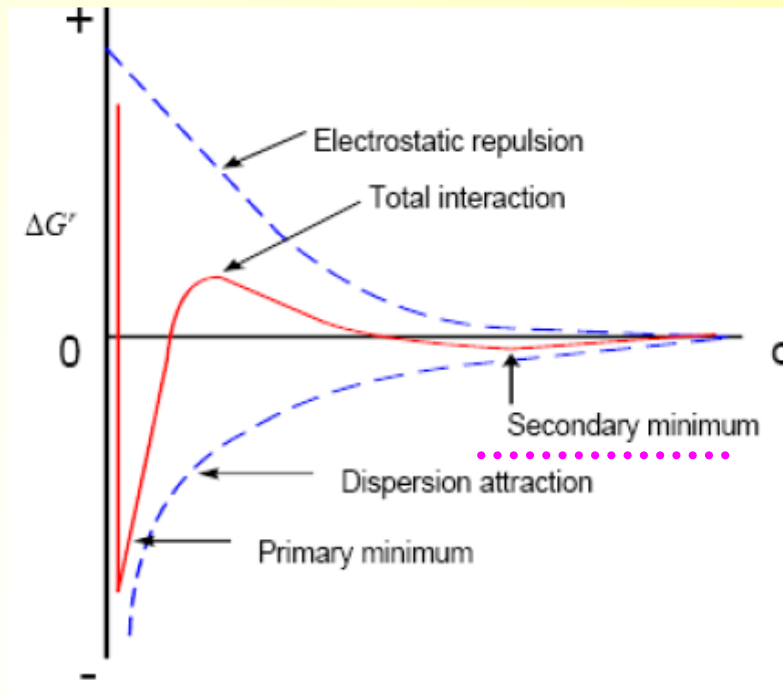
Notice the secondary minimum. The system flocculates, but the aggregates are weak. This may imply *reversible* flocculation.

$$V_T = V_A + V_R$$

$$V_A(H) \approx -\frac{Aa}{12H}$$

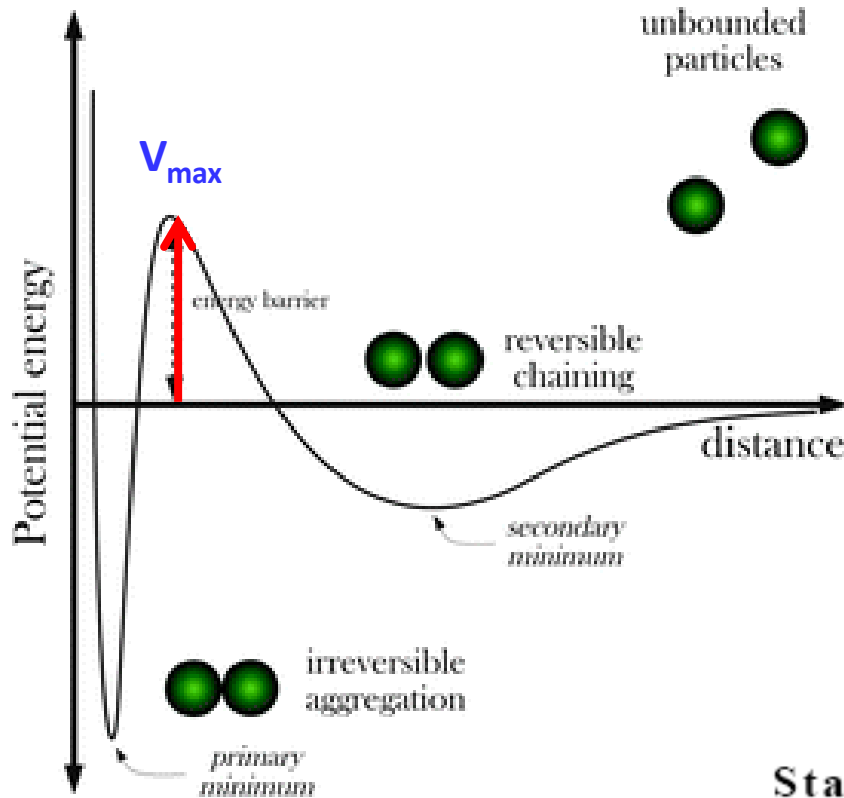$$V_R(H) \approx a(kT)^2 \gamma^2 z^{-2} \exp(-\kappa H)$$

The electrostatic stabilization is highly sensitive with respect to surface charge ($\zeta \sim \psi \sim$ pH) and salt concentration (κ, z).

$$\gamma = \frac{\exp\left[\dfrac{ze\psi_{St}}{2kT}\right] - 1}{\exp\left[\dfrac{ze\psi_{St}}{2kT}\right] + 1}$$

Colloidal stability: DLVO

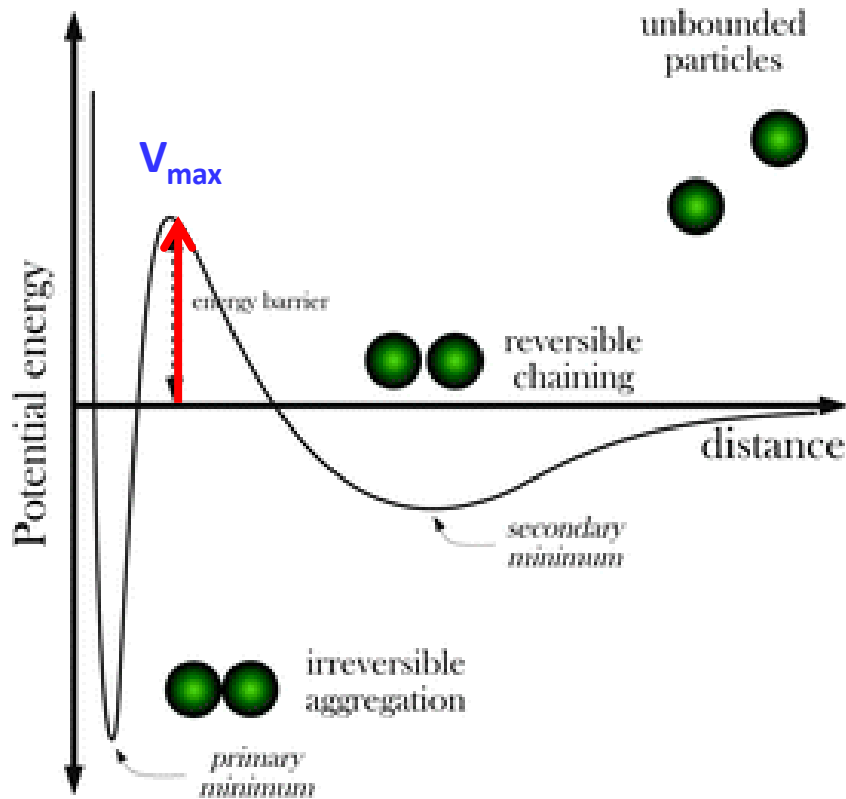Total interaction = sum of attractive + repulsive interactions

$$V_T(d) = V_A(d) + V_R(d)$$

Stability $V_{max} \gg kT$ kT = thermal kinetic energy

$V_{sec} > kT$ weak flocculation in secondary minimum (reversible)

Colloidal stability: DLVO

Factors affecting stability (electrostatic)

- V_{max} ↗ with particle size

- V_{max} ↗ with surface potential
  (in practice ζ potential)

  practical rule $|\zeta| \geq 25$ mV

  → ± 6 months stable

- Electrolyte (salt) concentration

  with C_{salt} ↗
  with z (charge number)

  → death of the dispersion !
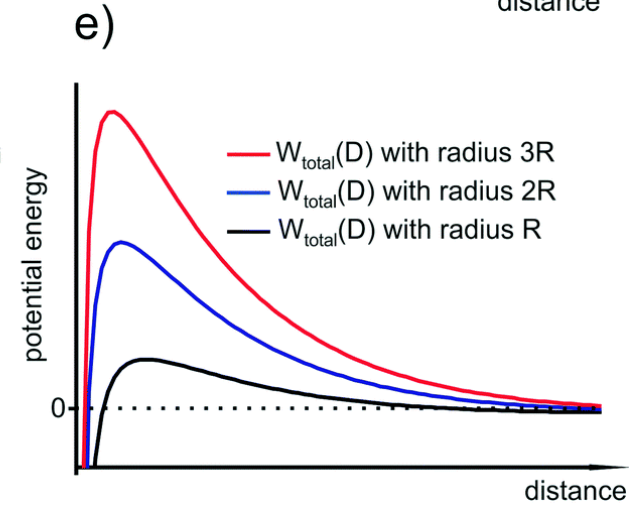 → desired in water purification

Colloidal stability: DLVO
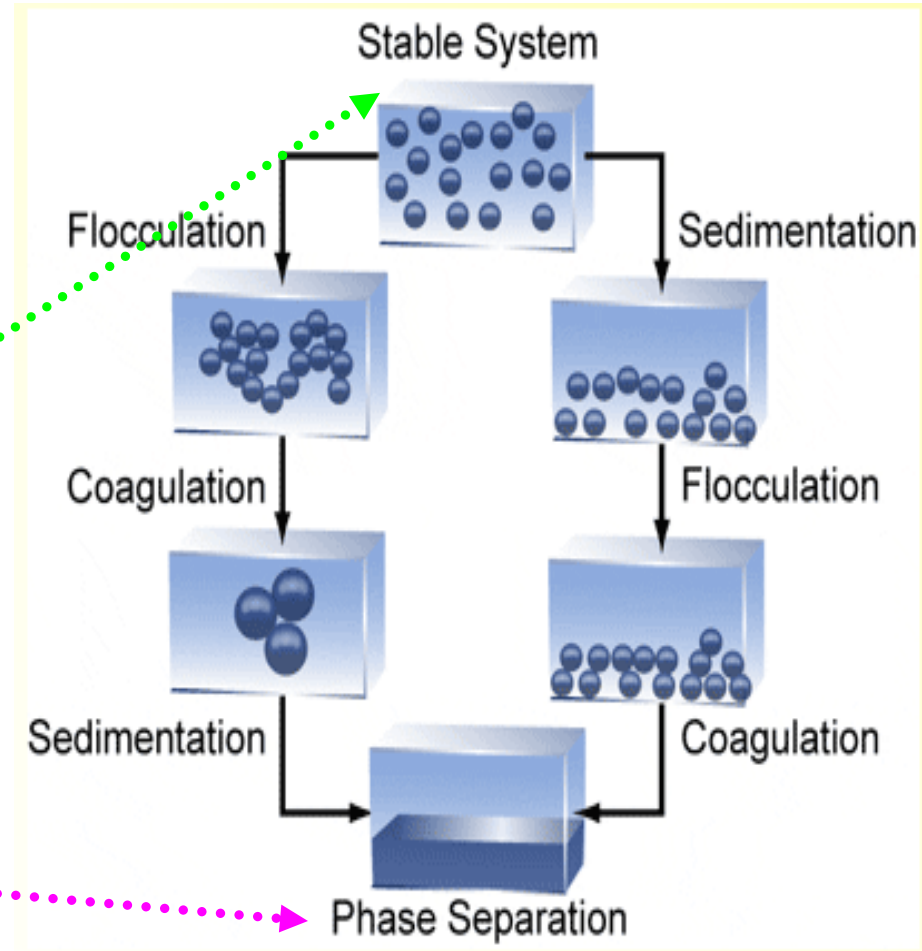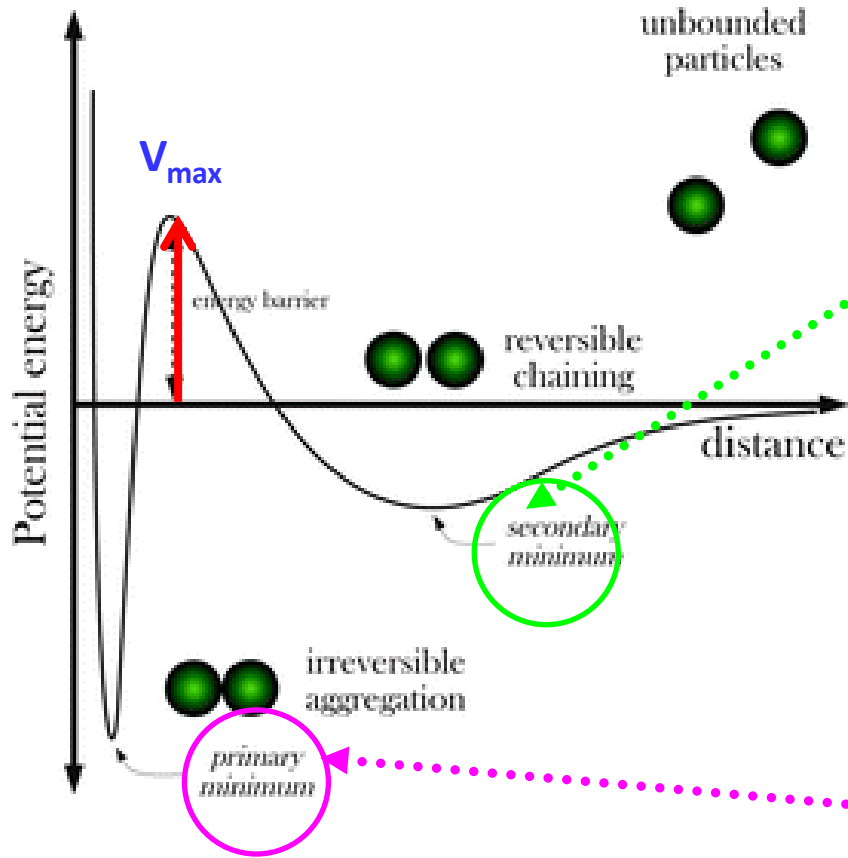
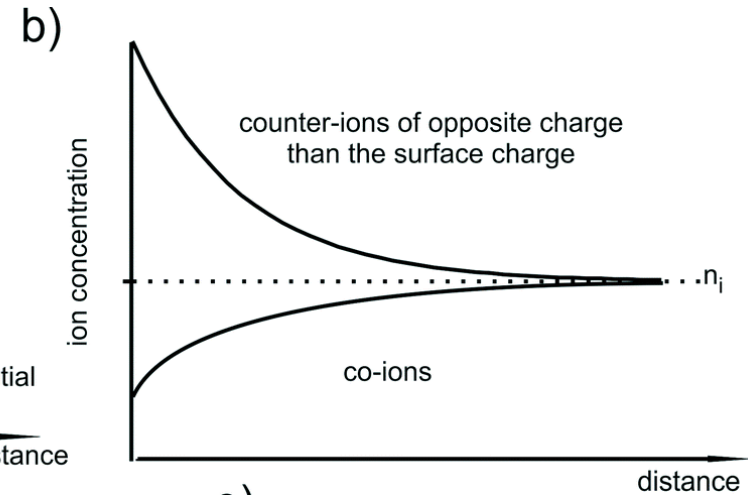# Colloidal stability: DLVO
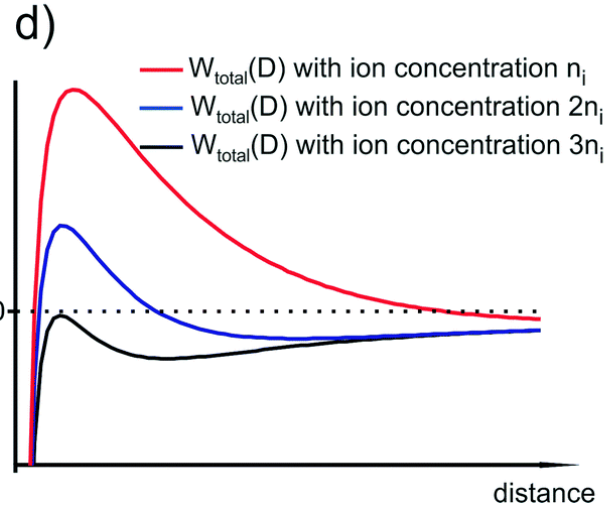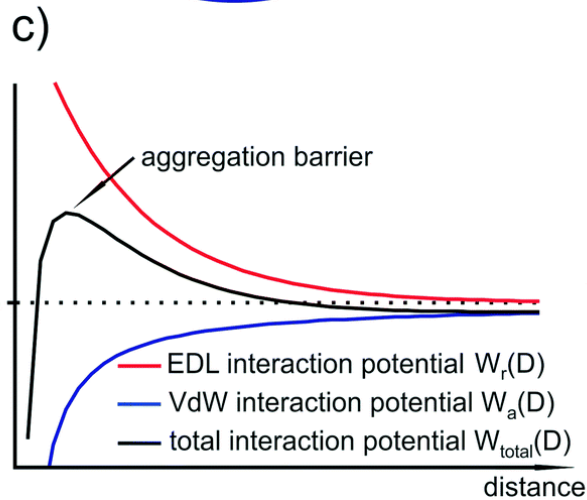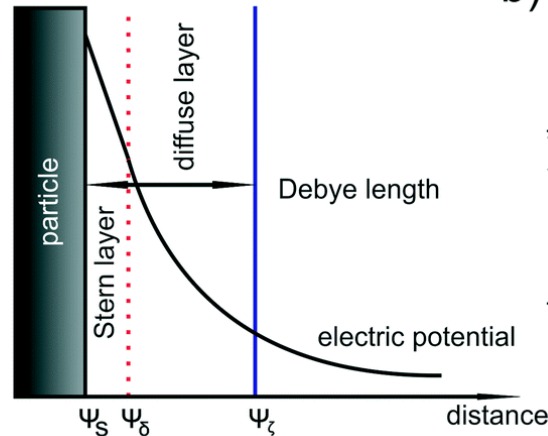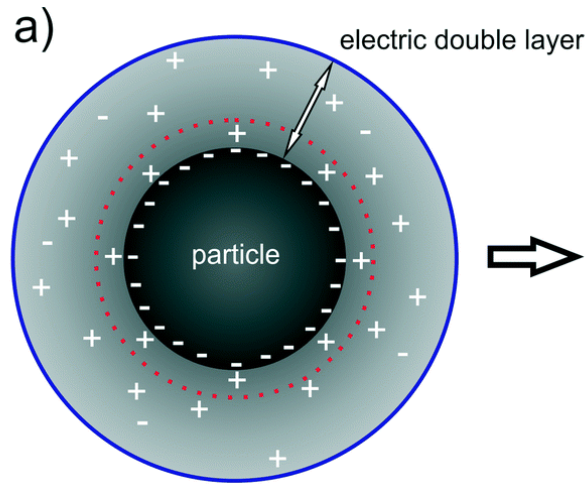
DLVO theory: general cases

1) Highly charged surfaces in dilute electrolyte, high energy barried, stable colloid.

2) Secondary minimum appears (typically > 3 nm), energy barried still too high, *kinetically* stable colloid

3) Lower energy barrier, slow coagulation

4) Energy barrier falls below $U = 0$, critical coagulation concentration, fast coagulation, unstable colloid

5) No energy barrier, strong attraction, very fast coagulation

MORE SALT
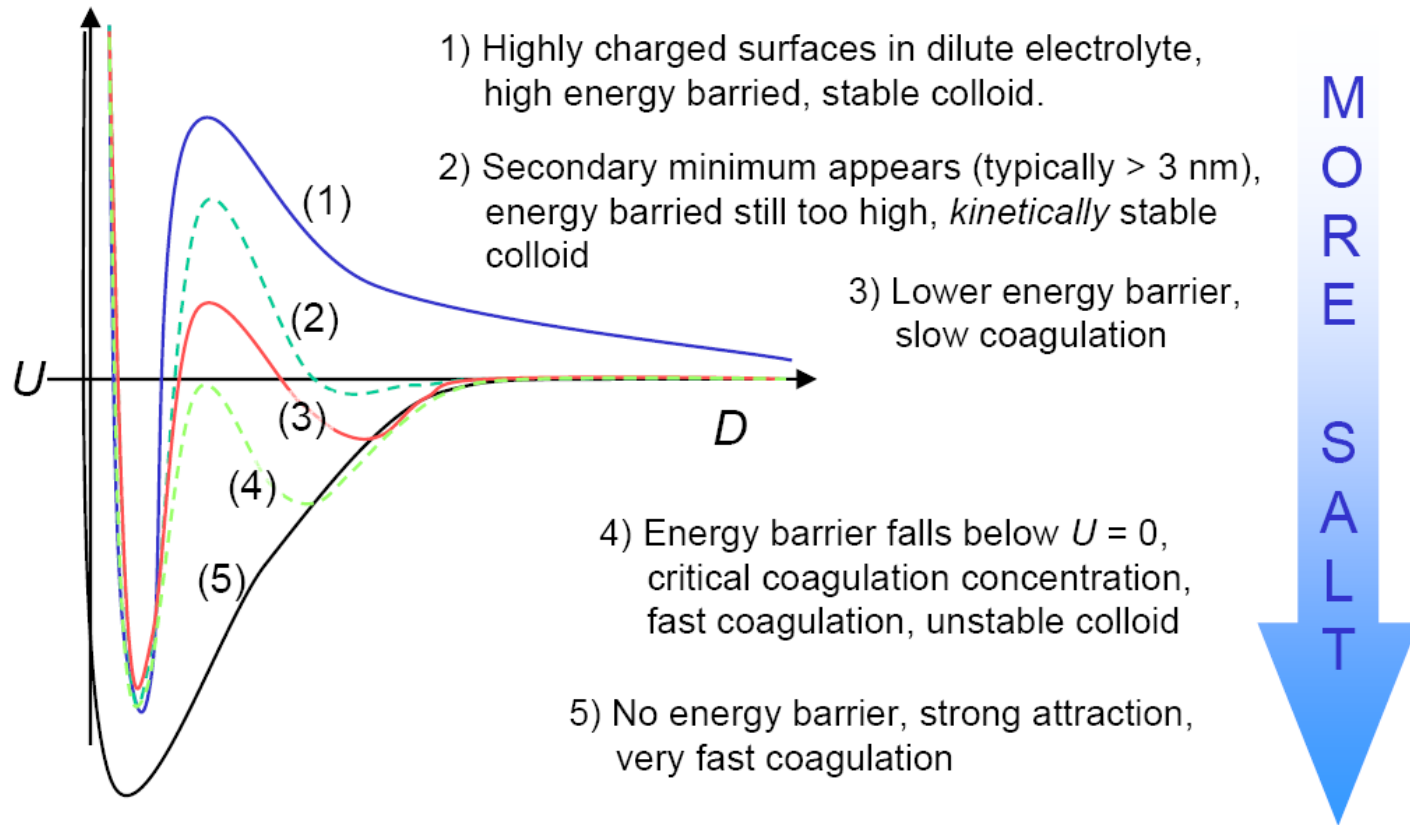
[J. Israelachvili, *Intermolecular & Surface Forces* (Academic Press, 1992)]

DLVO theory: limitations

Though the DLVO theory is a good theoretical starting point for studying the stability of colloidal systems, its basic formulation usually fails due to several reasons:

- **Ion correlations:** discrete nature of charge distribution at small separation

- **Steric effects** due to, e.g., polymer absorption
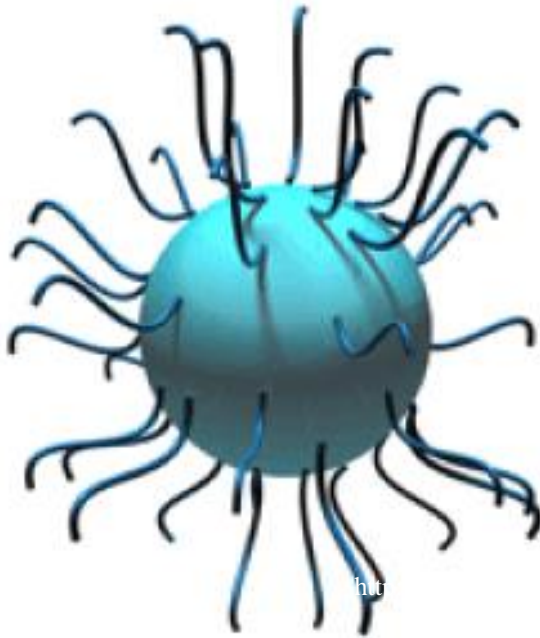
- **Depletion interactions**
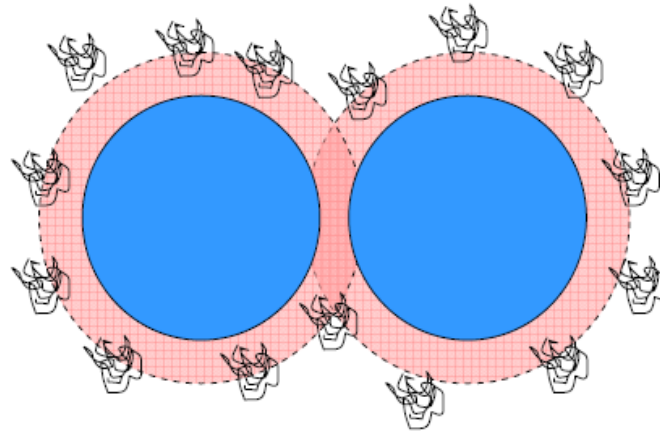
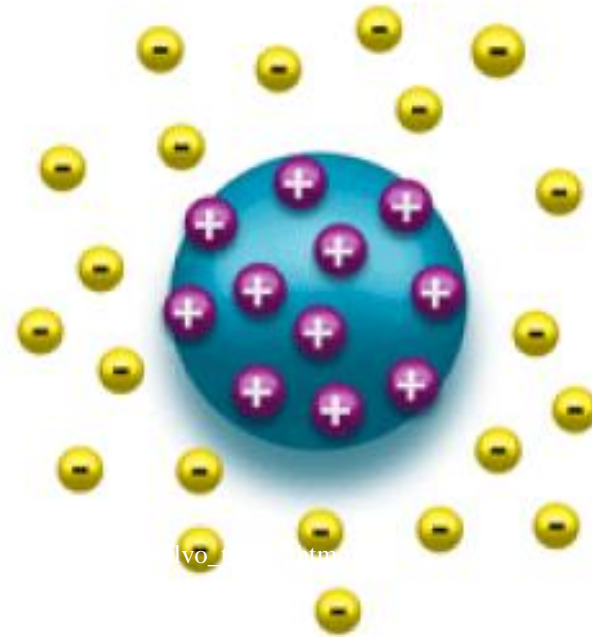

- **Stern layer:** hydrated ions of finite size

[J. Israelachvili, *Intermolecular & Surface Forces* (Academic Press, 1992)]

Colloidal stability: steric stabilization vs. electrostatic stabilization

THERE ARE **TWO MAJOR STABILIZATION MECHANISMS**:
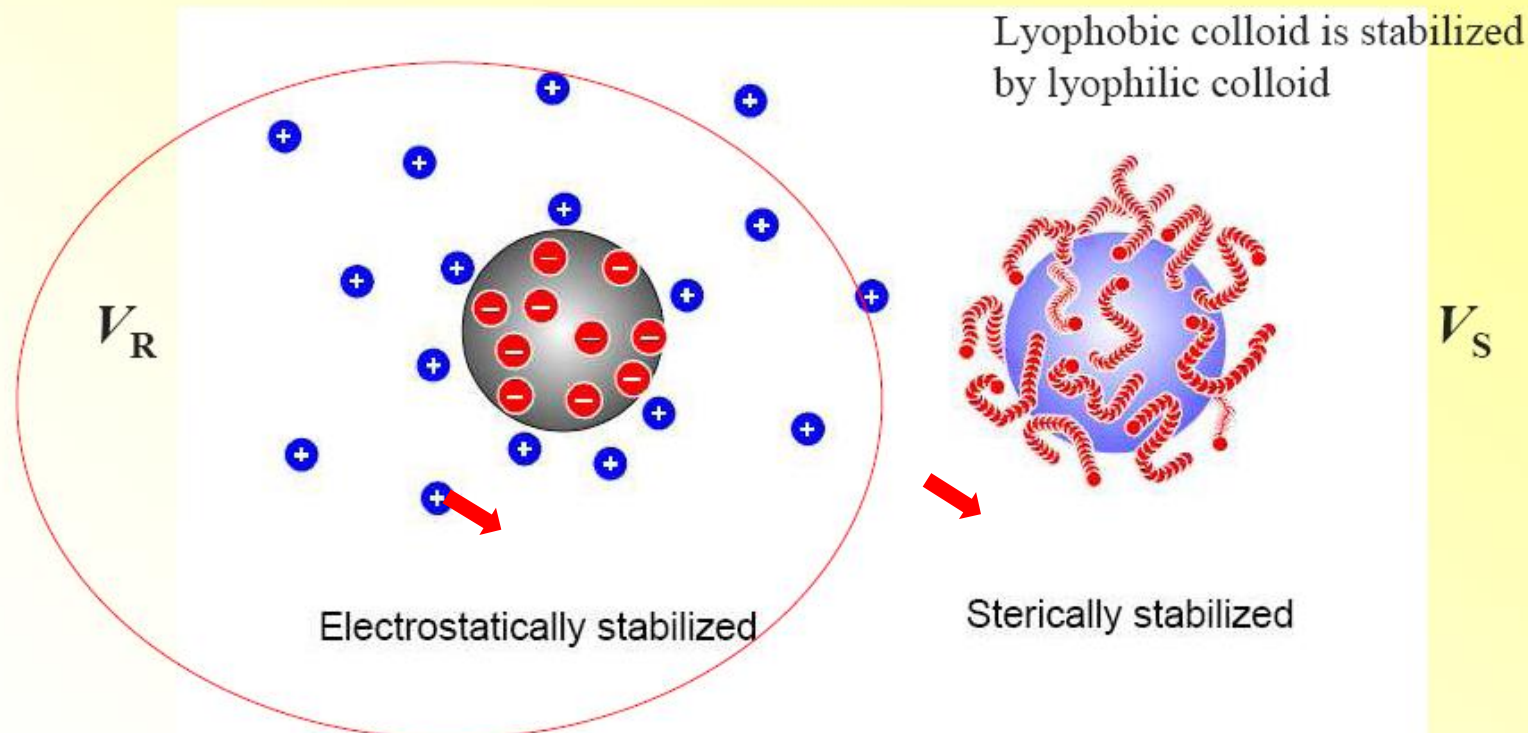

STERIC STABILIZATION

ELECTROSTATIC STABILIZATION

Colloidal stability: steric stabilization vs. electrostatic stabilization

THERE ARE **TWO MAJOR STABILIZATION MECHANISMS**:

Colloidal stability requires a **repulsion force**:
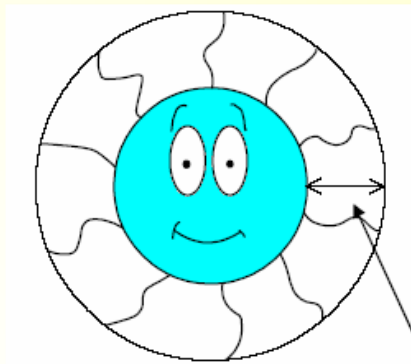
Lyophobic colloid is stabilized by lyophilic colloid

V_R

V_S

Electrostatically stabilized

Sterically stabilized

All particles naturally attract each other.

Electrical charges or attached polymer layers screen the attraction.

Colloidal stability: steric stabilization vs. electrostatic stabilization

Steric stability: lyophilic colloids as stabilizers

Protective action of adsorbed macromolecules (natural and synthetic)

$$V_S = V_M + V_{VR}$$
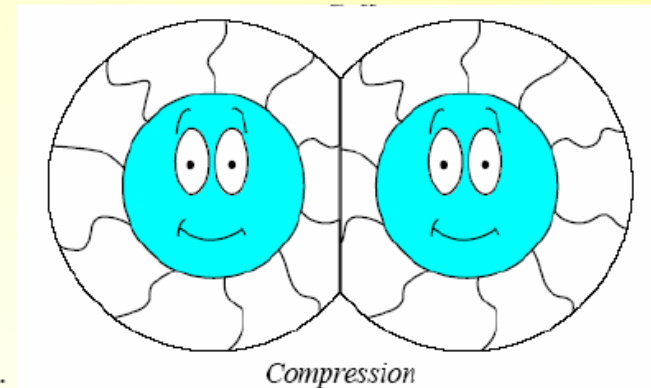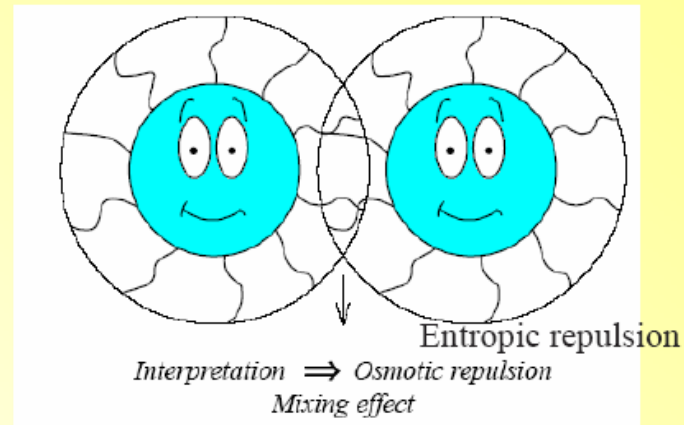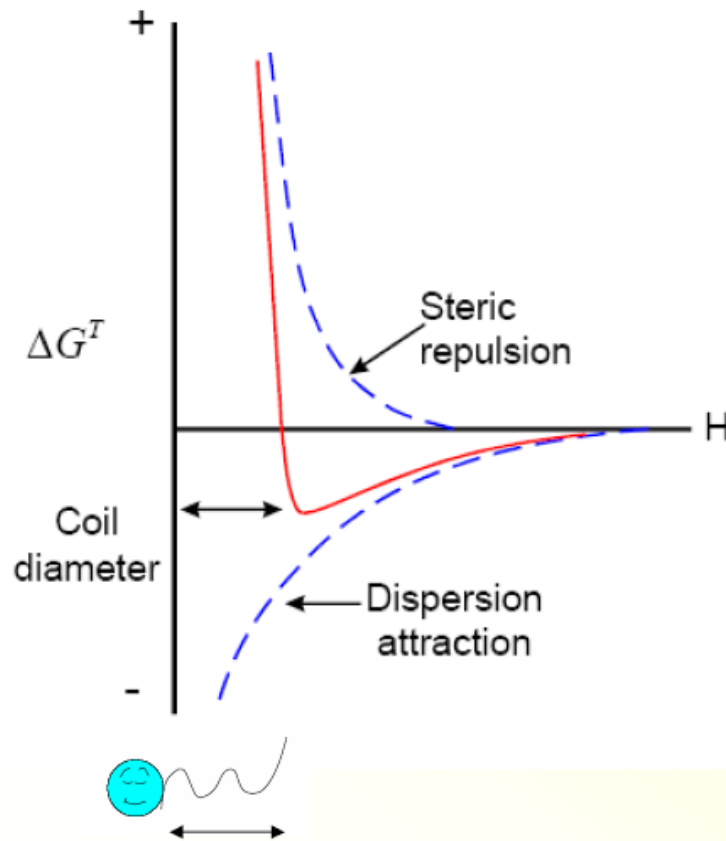
Two effects

V_M → Interpretation ⟹ Osmotic repulsion
Mixing effect
Entropic repulsion

V_{VR} → Compression

Polymer thickness

Work is required to push the particles closer together than their polymer layers keep them apart.

Colloidal stability: steric stabilization vs. electrostatic stabilization

Steric stabilization

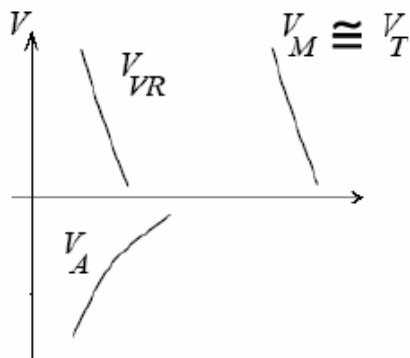Steric stabilization by surface bound polymers is:
1. not sensitive to surface charge and salt concentration
2. works also in non-aqueous media
3. (and works also in concentrated dispersions)

Disadvantage: more difficult to prepare.

$$V_T = V_A + V_S \qquad V_R = 0$$

Colloidal stability: steric stabilization vs. electrostatic stabilization
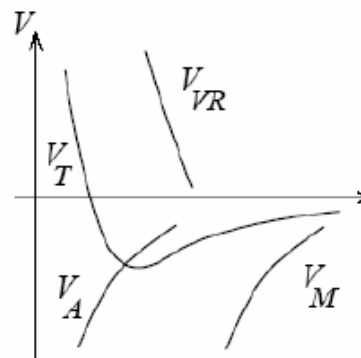

How to avoid coagulation

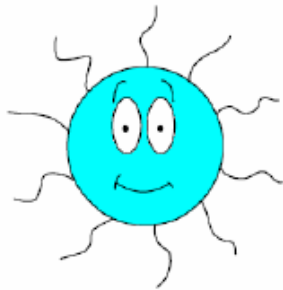Good solvent — Flory Huggins Parameter $\chi < 0.5$

Poor solvent — $\chi > 0.5$

The stabilizing polymer must be a **good solvent** environment

$$V_S = V_M + V_{VR}$$

$$V_T = V_A + V_S$$

Effect temperature!

Rheology of Clay-Water systems
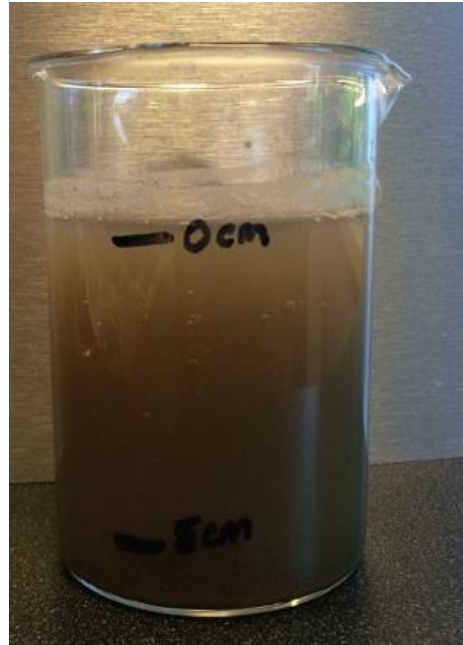
Rheology of Clay-Water systems

Newton's fluids
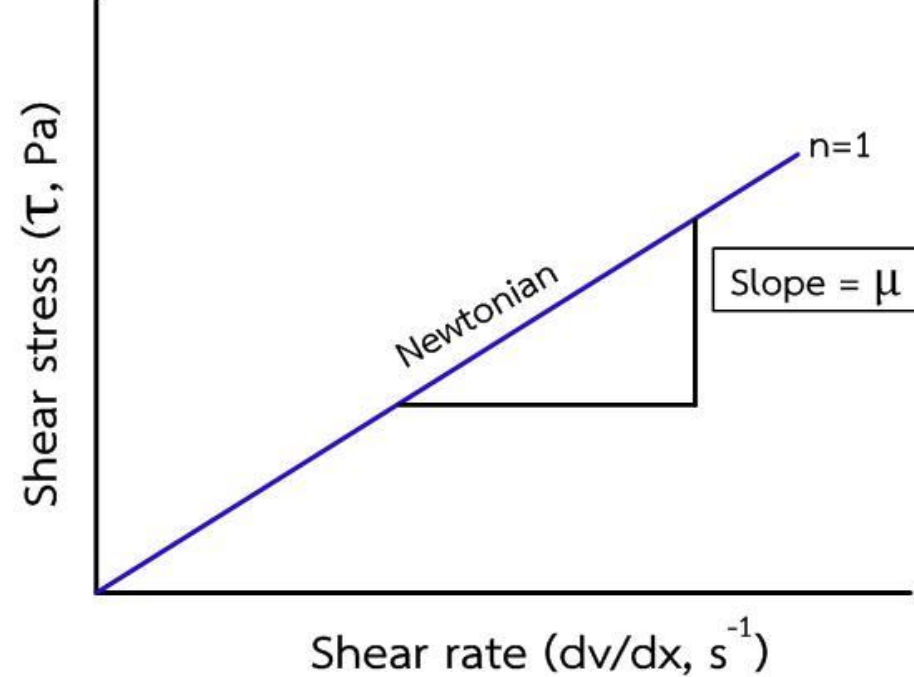
$f = \eta D$

The **viscosity** is a measure of the internal friction of liquid molecules counteracting the flow of the liquid.

If there is a linear relation between shear rate and shear stress we talk about **Newton's fluids**.

Pure liquids such as water, alcohol, glycerin, etc., at constant temperature, obey the Newton's law.

$$f = \eta D$$

where **f** = shear stress, **D** = shear rate and η = coefficient of viscosity.

Rheology of Clay-Water systems

Non-Newton's fluids
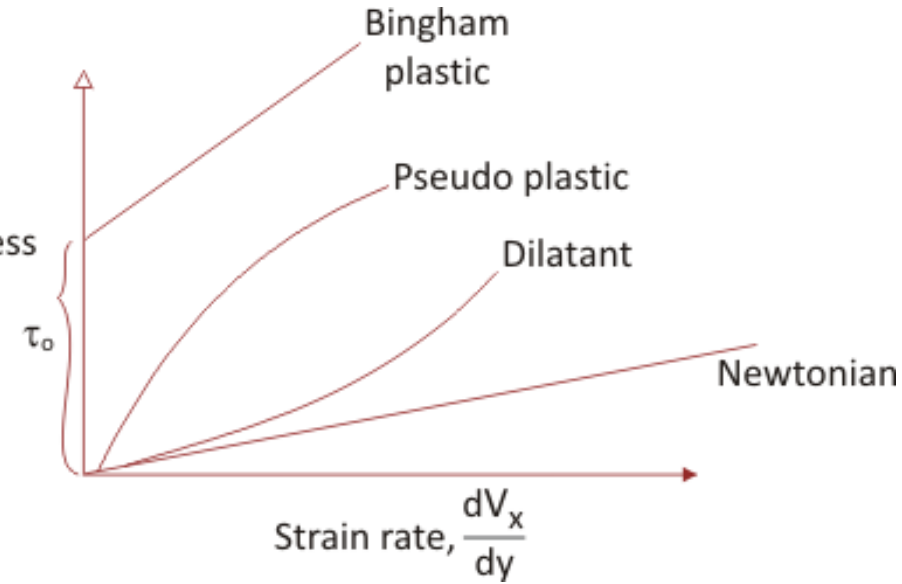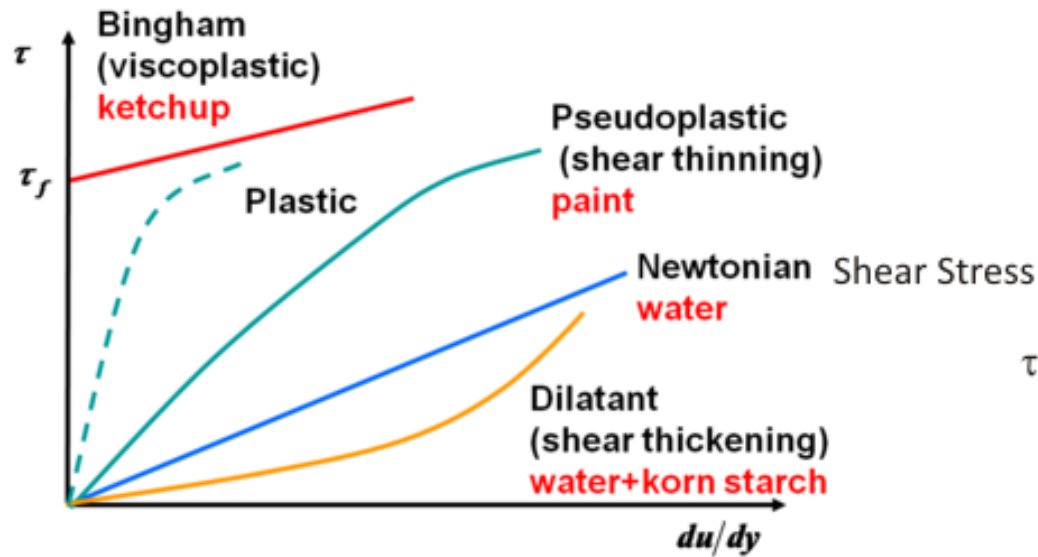
Suspensions in general do not obey Newton 'law and give a curve of some kind when stress is plotted against shear rate. The curve may be either convex or concave to the stress axis and may or may not pass through the origin.

In all such systems, **the value of η is not constant but varies with shear rate**.

Rheology of Clay-Water systems

Plastic fluids
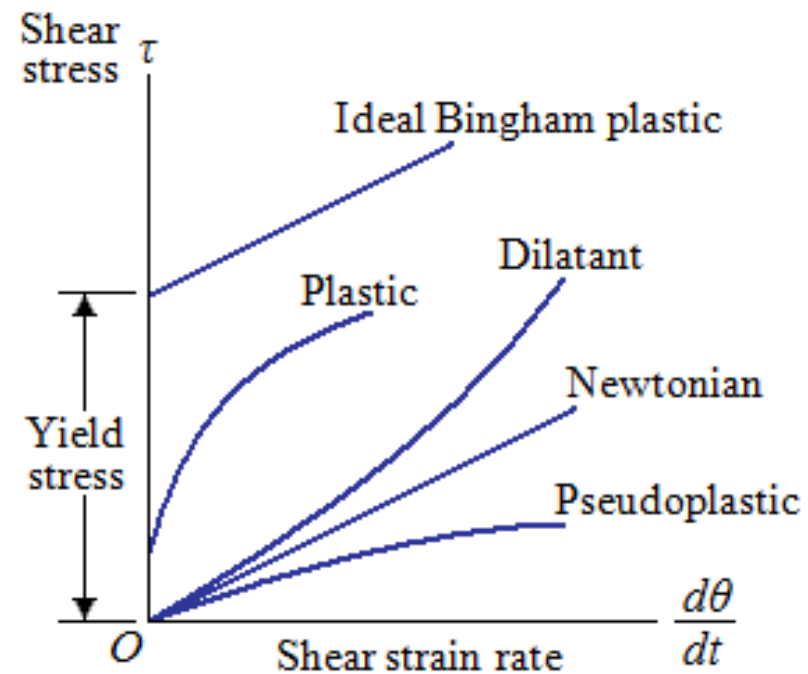
A **plastic** type of **flow curve** is given by the majority of water-clay suspensions and pastes in the flocculated state. An important characteristic of this curve is that it does not pass through the origin but intersects the stress axis at a point **f'**. This means that a definite minimum stress, called the **yield stress** or **yield value**, **f'**, has to be applied before the system begins to flow.

Rheology of Clay-Water systems

Pseudo- Plastic fluids
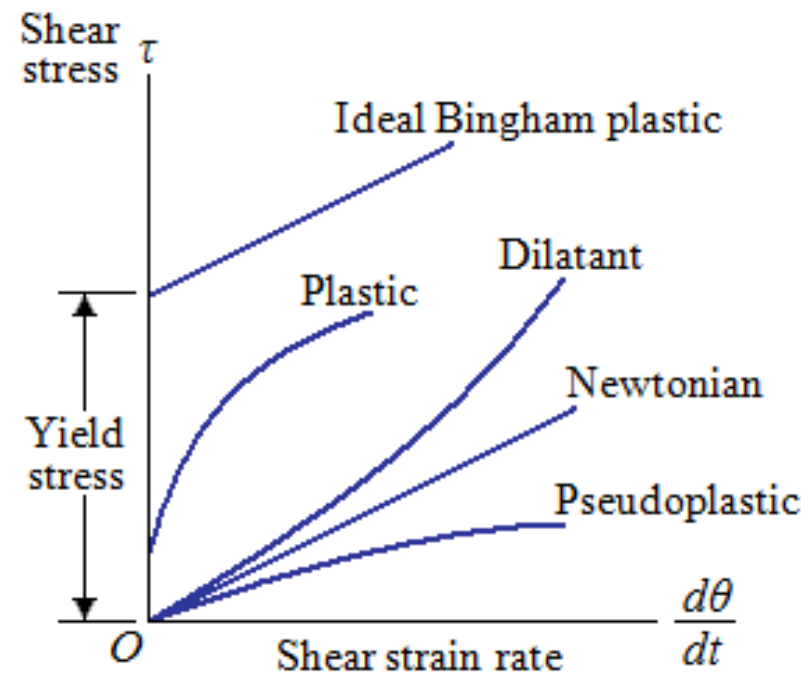
This is the term given to systems that give a flow curve similar in shape to plastic systems but having **no yield values**, i.e., the curve passes through the origin.

It is said to occur with suspensions of asymmetric particles that **tend to orientate themselves along the direction of shear**.

It may in practice be difficult to differentiate pseudo-plasticity from true plasticity.

Rheology of Clay-Water systems

Mechanisms of Plastic flow

In plastic and pseudo-plastic flows, the apparent viscosity of clay suspensions **decreases** with **increasing shear rate**. This behavior, and the existence of a yield value, is generally believed to be due to the **formation of an internal structure in the suspensions**.
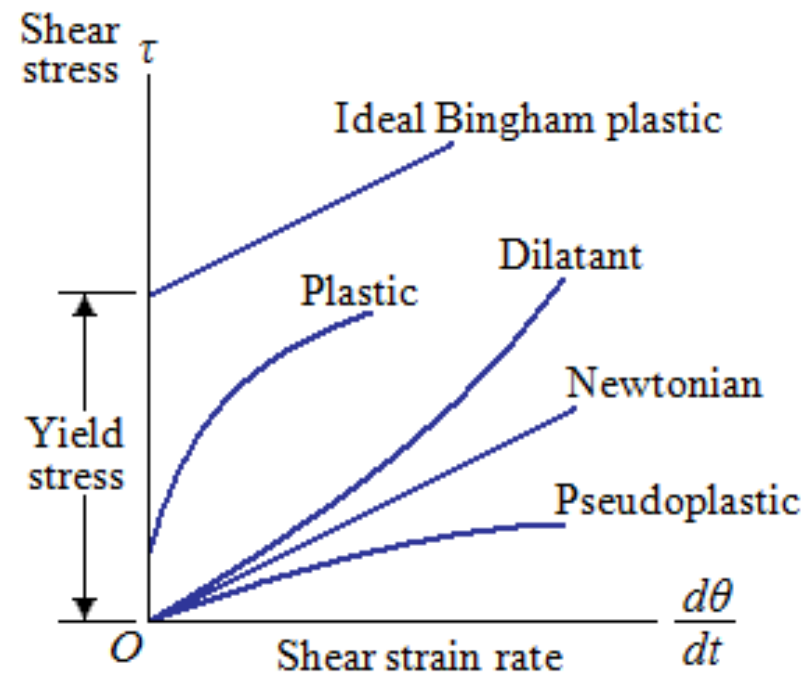
Flocculated systems have a strong tendency to form flocs or aggregates. In a suspension at rest therefore, a **3D network of particles** is formed which must be broken down before flow can occur: then the system possesses a **yield value**. Breakdown is not complete at commencement of shear; large aggregates still remain although the continuous structure has been destroyed. The effect of increasing the shear rate is to break down these aggregates progressively into their individual particles, thus reducing their mutual interference and thereby reducing the viscosity.

Rheology of Clay-Water systems

Bingham Plastic Model

Bingham's fluids
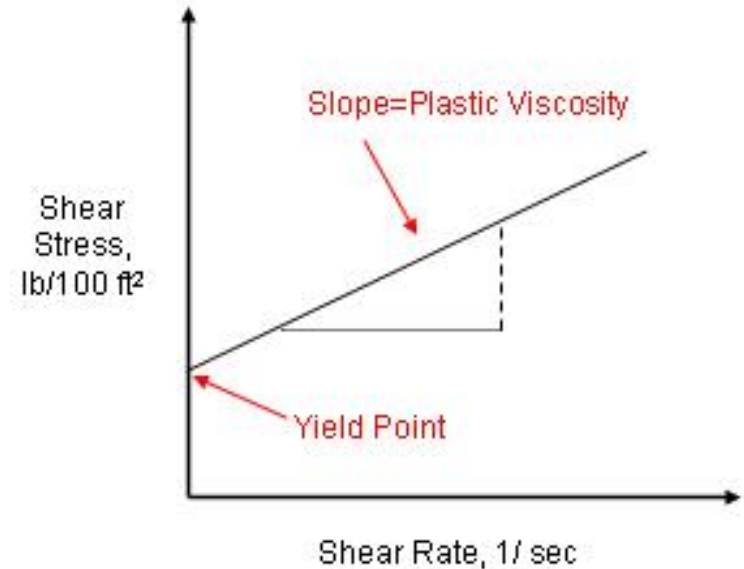
Occasionally, a system gives a stress-shear graph that is linear but **still shows a yield value**. In this instance the relationship between f and D may be written as:

$$f - f' = \eta_0 . D$$

where **f'** is the **yield value** and η_0 is a **constant**, sometimes called the **absolute viscosity**. Although few clay suspensions obey **Bingham's law** exactly, many approximate closely to it, only deviating at low shear rates. This behavior is common for flocculated clay suspensions, particularly at high concentrations.

Rheology of Clay-Water systems

Dilatancy
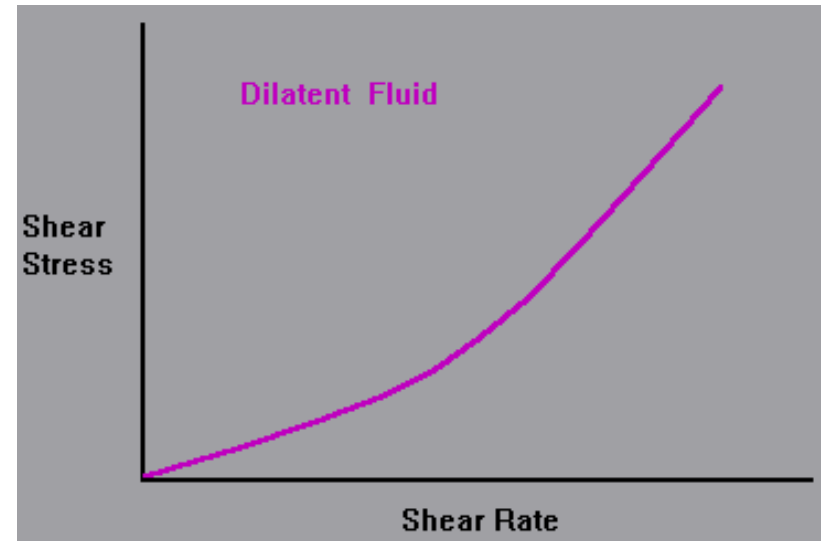
A limited number of systems exhibited **dilatant** behavior, giving a flow curve. This type of behaviour is shown mainly by non-plastic materials such as alumina, flint, quartz, etc.

Purely dilatant systems have no yield value and the viscosity of such systems **increases with increasing shear rate**.

The reason for dilatant behavior is not fully understood, but it may be due to the squeezing out of water from between the particles of the suspension at the places of greater shear; this is consistent with the observation that dilatancy is most marked with suspensions of coarse particles, which have little inter-particle cohesion.

Dilatancy is frequently observed in **deflocculated clay systems** at **high rates of shear**.

Rheology of Clay-Water systems

Thixotropy
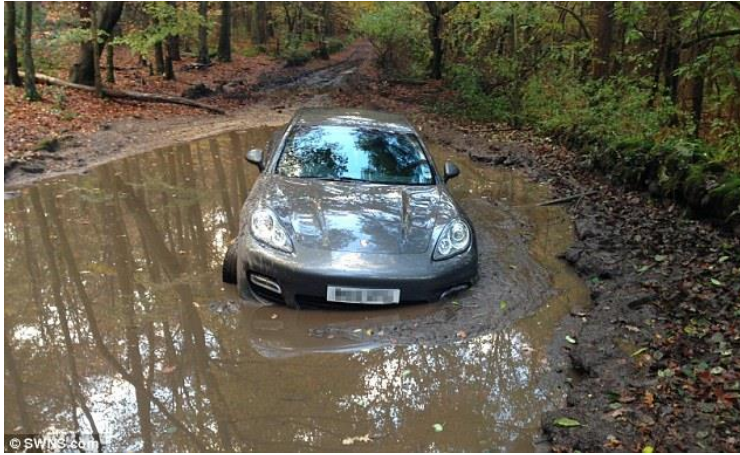
Many clay suspensions, if allowed to stand undisturbed for some time, are observed to thicken up, i.e. become more viscous; in extreme cases (e.g. clays treated with excess electrolyte) the vessel containing them may be inverted without causing the suspension to run out. On vigorous stirring, such suspensions become quite fluid again, reverting to their original condition when stirring ceases, and so on. This **reversible time-dependent** property is known as **thixotropy**. As might be expected, thixotropic slips show a reduction of viscosity with increasing shear rate; their flow curves usually show a yield value, with marked curvature in the region of lowest shear rate.

Sedimentary kaolinites treated with sodium carbonate in slight excess exhibit marked thixotropy; montmorillonites may have such a high degree of thixotropy that they form gels when undisturbed.

Rheology of Clay-Water systems

Thixotropy

Left graph — Viscous fluids:
Axes: τ — Shear stress (Pa) vs $\dot{\varepsilon}$ — Strain rate (s^{-1})
Curves: non-Newtonian Pseudo-Plastic ($n<1$); Newtonian; non-Newtonian Pseudo-Plastic ($n>1$)

$$\tau = \eta\,\dot{\varepsilon}$$
$$\tau = A\dot{\varepsilon}^{n}$$

Right graph — Plastic materials:
Axes: τ — Shear stress (Pa) vs $\dot{\varepsilon}$ — Strain rate (s^{-1})
Curves: Pseudo-Plastic ($n<1$); Bigham=viscoplastic; Pseudo-Plastic ($n>1$); ideal=elasticplastic; τ_0
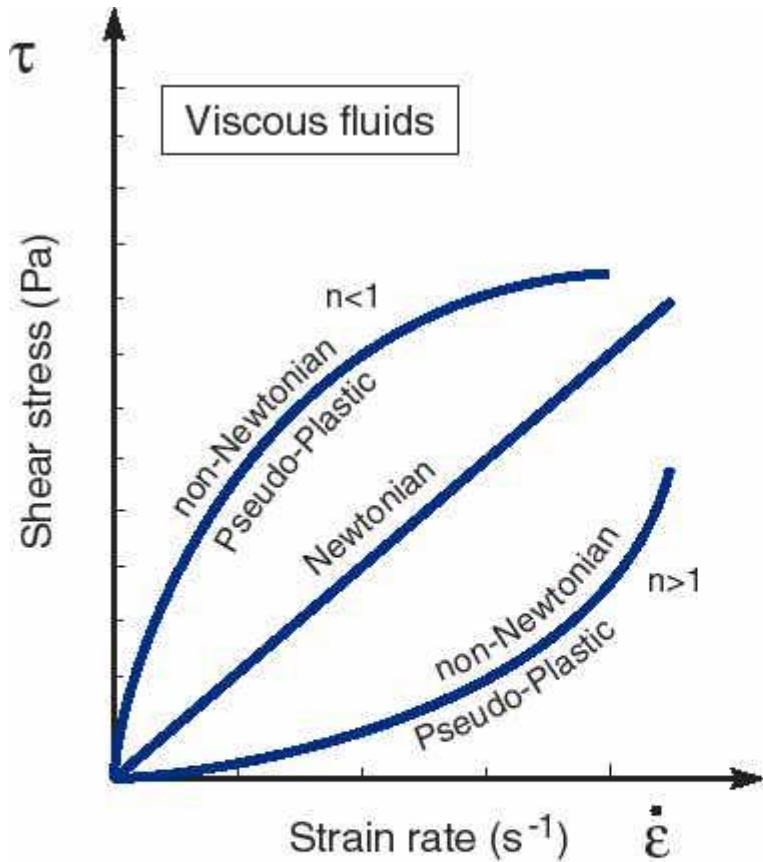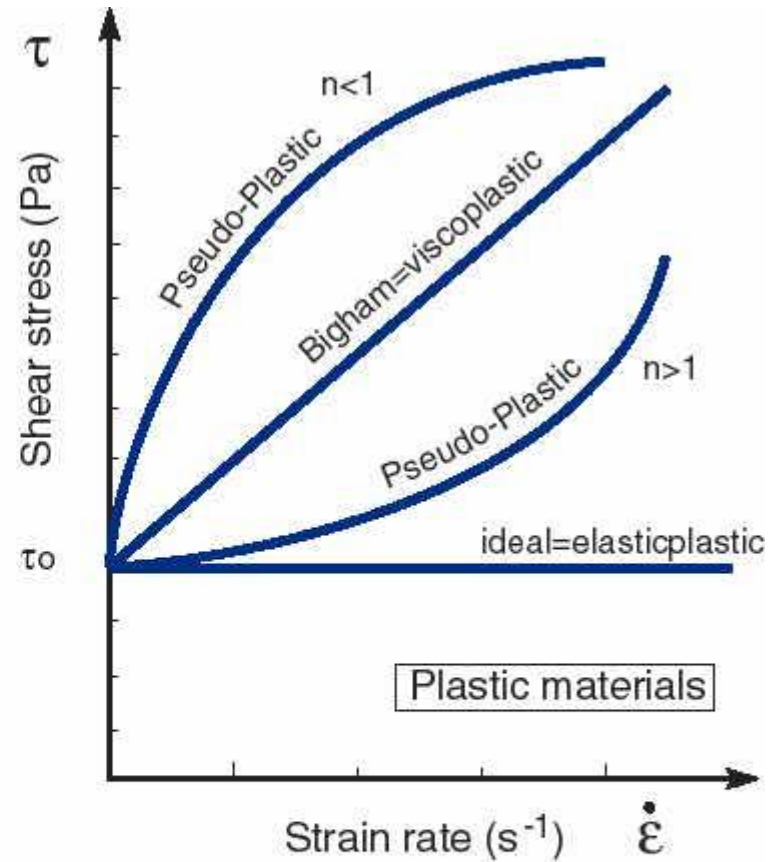
$$\tau = \tau_0 + \eta\,\dot{\varepsilon}$$
$$\tau = \tau_0 + A\,\dot{\varepsilon}^{n}$$

Viscosity is a measure of the resistance of a fluid to flow

Rheology of Clay-Water systems

Summary

ζ **High ($|\zeta| \geq 30$ mV), diluted suspension**

Isometric colloidal particles ·········· **Newtonian fluid** ··········· $\tau = \eta G$

(ex. spherical particles)

Anisometric colloidal particles ··········**Pseudo-plastic fluid** ··········· $\eta_a\downarrow$, G$\uparrow$
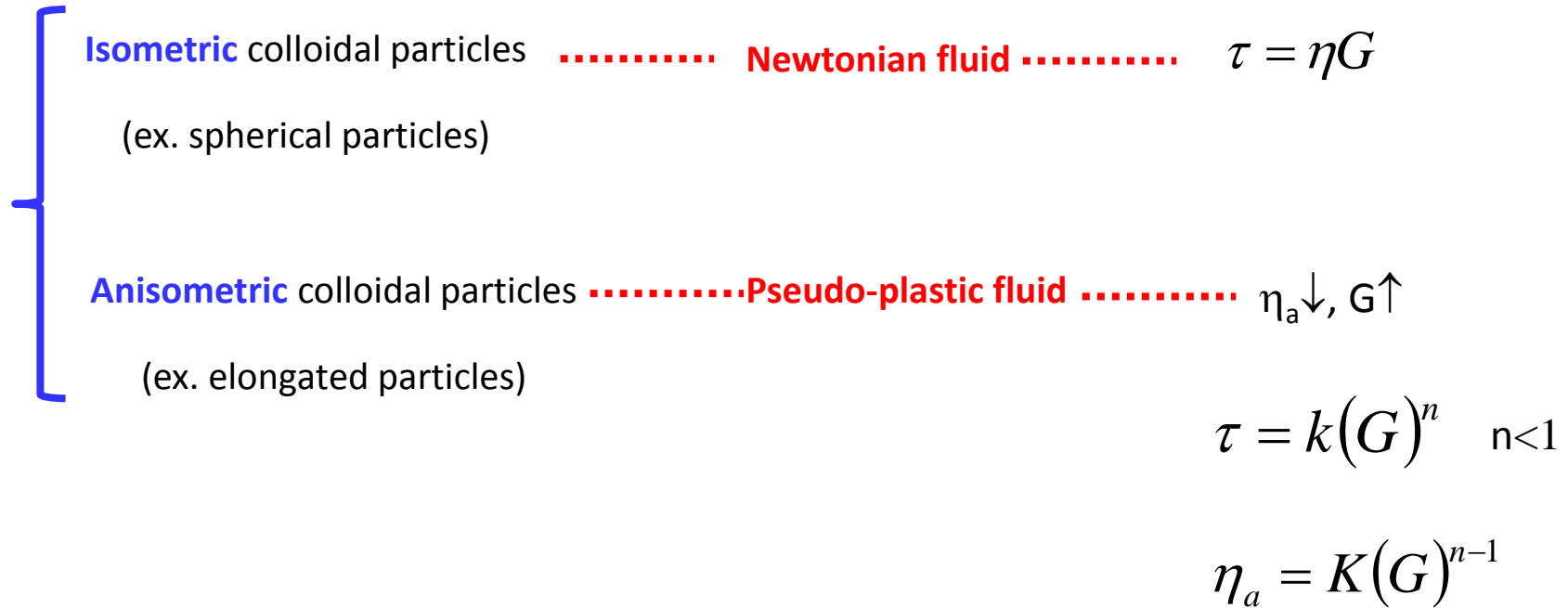
(ex. elongated particles)

$$\tau = k\left(G\right)^n \quad n<1$$

$$\eta_a = K\left(G\right)^{n-1}$$

ζ **High ($|\zeta| \geq 30$ mV), concentrated suspension**

High colloidal particles ·········· **Dilatancy** ············· $\eta_a \uparrow$, G$\uparrow$

concentration

Rheology of Clay-Water systems

Summary

ζ **Low (|ζ| < 30 mV), concentrated suspension**

Plastic/Newtonian fluid ⋯⋯⋯ $\tau = \eta G$

Pseudo-plastic fluid ⋯⋯⋯ $\eta_a \downarrow$, G$\uparrow$

Dilantancy ⋯⋯⋯ $\eta_a \uparrow$, G$\uparrow$

Yield point

Thixotropy

Further reading

- **The Coloidal Domain. Where Physics, Chemistry, Biology, and Technology.** Meet. D. F. Evans, H. Wennerstrom, Wiley-VCH (1999)

- **Sol-Gel Science. The Physics and Chemistry of Sol-Gel Processing**. C. Brinker George Scherer, Academic Press (2013)

- **Sol-Gel Materials. Chemistry and Applications**. J. D. Wright, N. A. J. M. Sommerdijk, Gordon and Breach Science Publishers (2001)

Rheology of Clay-Water systems

And now let's see how industry conform

ceramic raw materials!