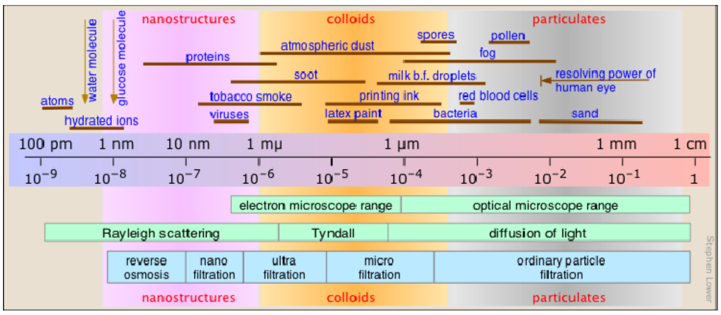
INTERFACIAL PROPERTIES

1

Colloid systems

Dispersed systems with where the size at least in one dimension is between 1 nm and 500 nm
Systems where surface plays a dominant role



https://chem.libretexts.org/Textbook_Maps/General_Chemistry/Book%3A_Chem1_(Lower)/07%3A_Solids_and_Liquids/7.10%3A_Colloids_and_their_Uses
https://www.youtube.com/watch?v=sAtAqsrala0
https://www.youtube.com/watch?v=kNGlL8gBQ7U

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Classification by physical state of the dispersion and dispersed medium

Dispersed phase	Dispersion medium	Type of colloid	Example
Solid	Solid	Solid sol	Some coloured glasses, and gem stones
Solid	Liquid	Sol	Paints, cell fluids
Solid	Gas	Aerosol	Smoke, dust
Liquid	Solid	Gel	Cheese butter, jellies
Liquid	Liquid	Emulsion	Milk, hair cream
Liquid	Gas	Aerosol	Fog, mist, cloud, insecticide sprays
Gas	Solid	Solid sol	Pumice stone, foam rubber
Gas	Liquid	Foam	Froth, whipped cream, soap-lather

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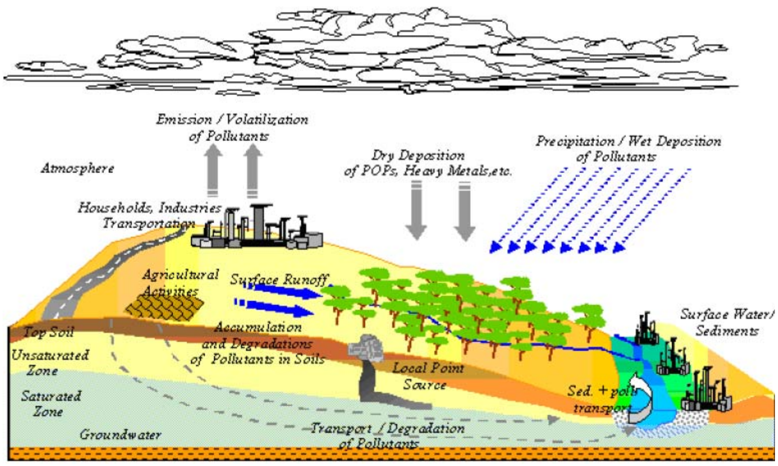
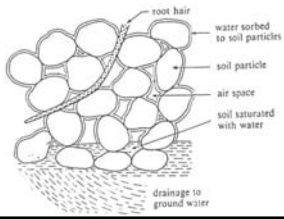
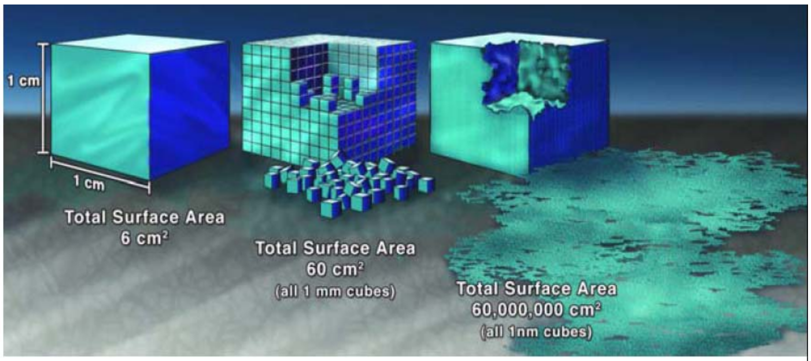


POP= persistent organic pollutants



Particle size vs. surface

1 cube 1000 cubes 10^{21} cubes



Surface/volume

„God created space, and the devil created surface" Wolfgang Pauli

Specific surface area: A_S=area/mass; m^2/g

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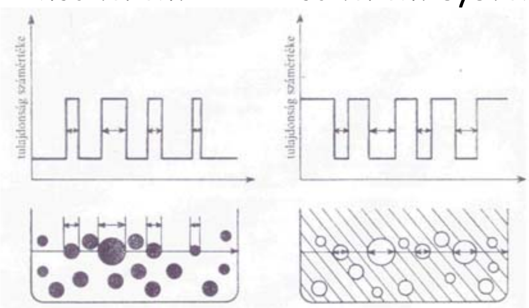
High surface area material

1. dispersion:

incoherent coherent systems



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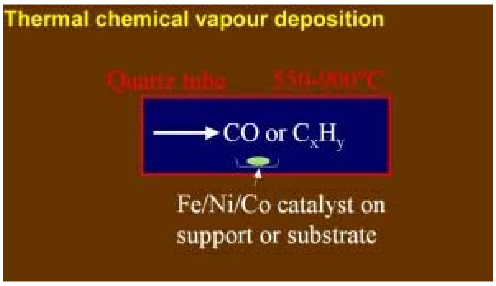
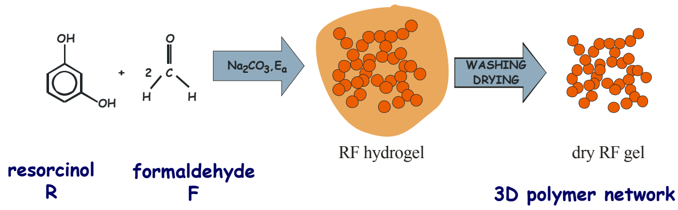
2. synthesis (bottom up)

~ chemical vapour deposition



~ sol/gel



polycondensation

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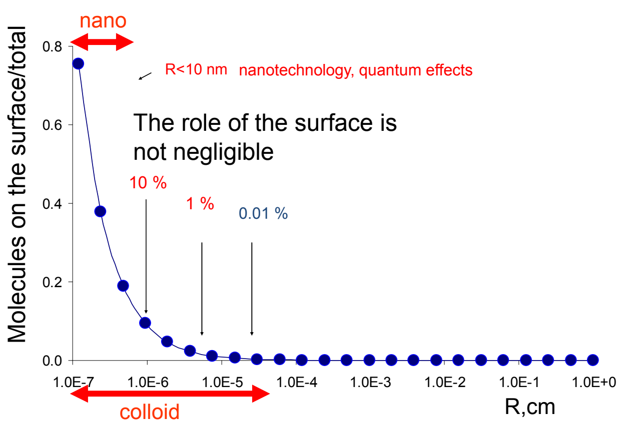
Surface molecules vs particle size



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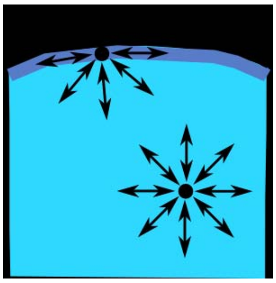
Molecules on the interface have excess energy

$$\gamma = \left(\frac{\partial G}{\partial A_S}\right)_{p,T}$$



Surface tension

$$dW_{surf} = \gamma dA_S$$

work/surface area; force/route

Depends on temperature

$$\gamma V_m^{2/3} = k_E (T_c - T - 6)$$

$$k_E = 2 \cdot 10^{-7} J / (K \cdot mol^{2/3})$$

Eötvös L.

	$\gamma^{293\ K}$ mJ/m² or mN/m	interaction
He(l)	0,308 $^{2,5\ K}$	dispersion
n-hexane	18	dispersion
water	72	H-bridge
Hg(l)	472	metallic bond
$BaSO_4$	10³	ionic bond

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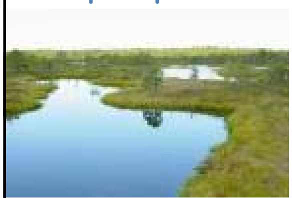
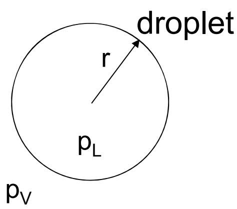
Phenomena related to surface excess energy

1. Vapour pressure over curved surfaces





Due to the surface tension: excess pressure within the droplet

$$p_L = p_V + \frac{2\gamma^{LV}}{r}$$

$$\Delta p = p_L - p_V$$

Young-Laplace

Bubble diameter (2*r*) (µm)	Δ P (Pa)	Δ P (atm)
1000	288	0.00284
3.0	96000	0.947
0.3	960000	9.474

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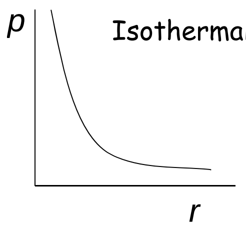
Liquid droplet

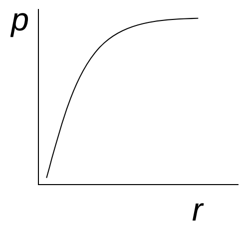
$$p = p_\infty e^{\frac{2\gamma V_m}{rRT}}$$

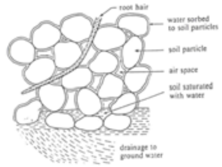


Isothermal distillation

Pore

$$p = p_\infty e^{\frac{-2\gamma V_m}{rRT}}$$





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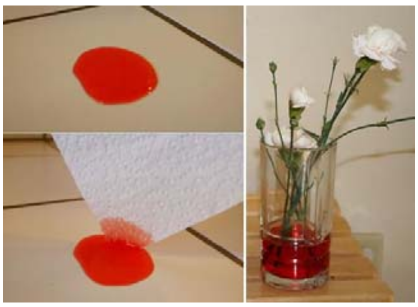
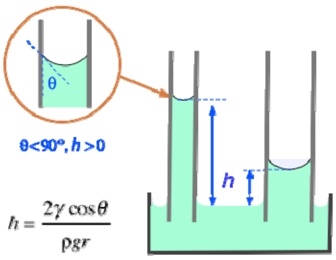
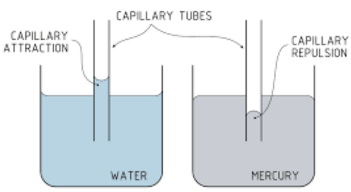
2. Capillary elevation





$$\Delta p_\gamma = \frac{2\gamma \cos\theta}{r} = h\rho g$$

$$\frac{2\gamma \cos\theta}{r} = h\rho g = \Delta p_{hydrost}$$



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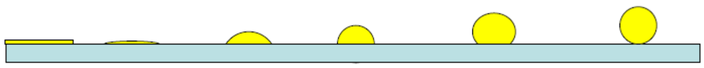
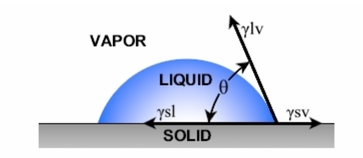
3. Contact wetting



θ Contact angle



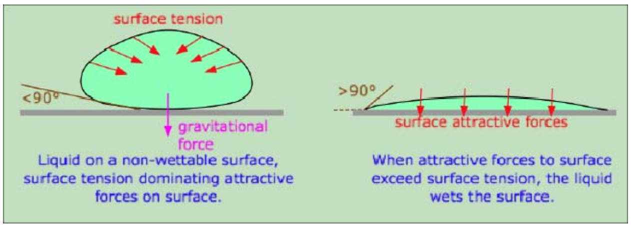
θ is the contact angle
γ^{sl} is the solid/liquid interfacial free energy
γ^{sv} is the solid surface free energy
γ^{lv} is the liquid surface free energy

$\gamma_{SV} = \gamma_{SL} + \gamma_{LV}\cos\theta$

$\gamma_{SV} - \gamma_{SL} = \gamma_{LV}\cos\theta$

Young equation

spreading θ = 0



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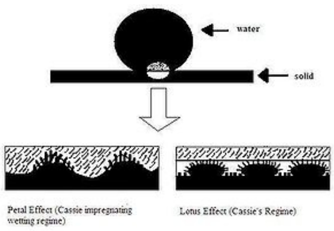
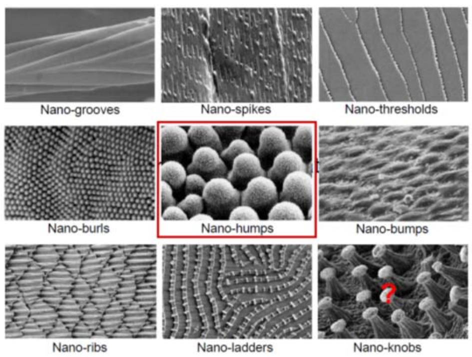
How can we influence contact angle (wetting phenomenon)?

1) Surface treatment
2) Liquid properties
3) Surface roughness





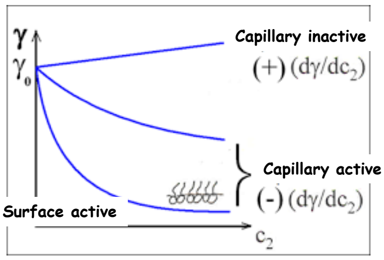
1) Surface treatment

e.g., waxing
de-greasing
smoothing/roughing

2) Liquid properties

change the solvent

change the composition of the solvent



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Surface active materials: surfactants

Amphiphilic character

LIOPHILIC (hydrophilic) LIOPHOBIC (hydrophobic)

Cassification: according to the charge of the organic (nonpolar) chain

Anionic	R-COO^- Me^+	Pl. soaps (salts of carboxylic acids)
Cationic	R-$N^+(CH_3)_3$ X^-	Quaternery ammonium salts
Non-ionic	R-Z-$(CH_2$ -CH_2 -$O)_n$ H	Z = O, S, NH

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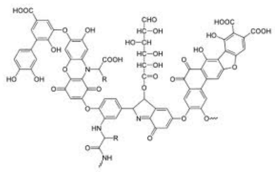
Natural surfactants

e.g.. – humic acid



- proteins

Natural foam

Environmetal catastrophy

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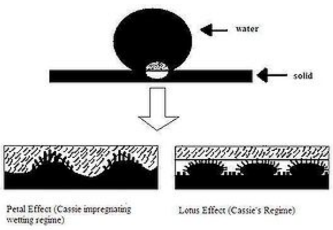
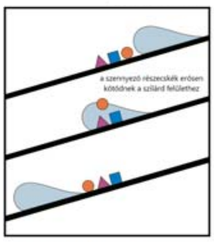
3) Surface roughness

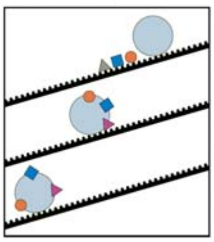


Lotus-effect: self-cleaning ability of microstructured, hydrophobic (water repellent) surfaces

Mechanism



Smooth surface



Rough hydrophobic surface

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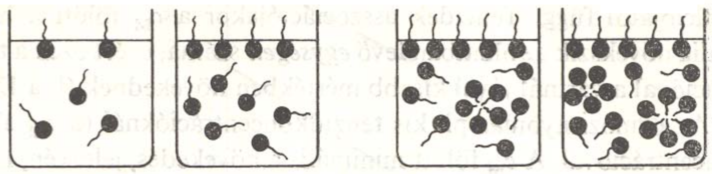
Aqueous solution of surfactants in action

T=const.

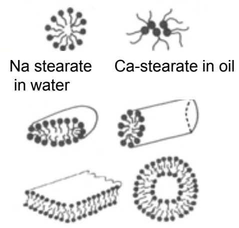


c_M Critical micelle concentration

surfactant concentration

surface tension

decreases constant



Surace excess concentration, mol/m^2

$$\Gamma = -\frac{c}{RT}\frac{d\gamma}{dc}$$

even more than 100 molecules may form a micelle

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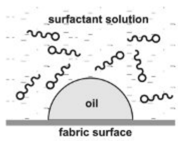
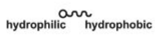
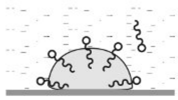
Mechanism of washing

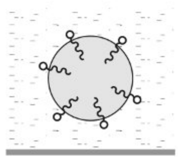


The surfactant contains molecules with hydrophilic and hydrophobic portions.





Surfactant molecules are absorbed into the surface of the oil and so remove it from the fabric surface.



The surfactant molecules remain surrounding the oil once it has been removed, so helping to prevent its redeposition onto the cleaned surface.

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4. Adsorption

Consequence of the excess energy of the surface

Adsorption: enrichment on the surface

Desorption: removal of the adsorbed molecules

Spontaneous process leading to equilibrium

$$A+S \rightleftarrows AS$$

A: free molecule
S: surface site
AS: molecule bounded to S

It is an EXOTHERMIC process: $\Delta G = \Delta H - T\Delta S$

Application: e.g., water treatment, gas purification, gas seperation, chromatography

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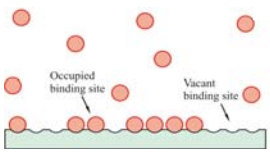
a) Gas/solid interfaces



To set up a model we need simplifying conditions: i) flat surface, ii) sites of equal energy, iii) limited to a single layer.

This is the Langmuir model

$$A(g) + S \rightleftharpoons AS$$

A: free molecule
S: surface site
AS: molecule bounded to S

N_t # of total available sites
N # of occupied sites

$$\Theta = \frac{N}{N_t}$$

coverage= occupied/total

$$v_a = k_a(N_t - N)p = k_a N_t (1-\Theta)p$$ Rate of adsorption

$$v_d = k_d \Theta N_t$$ Rate of desorption

equilibrium: $$v_a = v_d$$

$$k_a N_t (1-\Theta)p = k_d N_t \Theta$$

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$$k_a N_t (1-\Theta) p = k_d N_t \Theta$$

$$K = \frac{k_a}{k_d}$$

$$\Theta = \frac{K \cdot p}{1 + K \cdot p}$$

For macrosopic quantities:

$$\Theta = \frac{m^s}{m_m}$$

m^s material adsorbed on e.g., 1 g of solid material
m_m the maximum uptake in the single layer (monolayer capacity)

How we collect these data?

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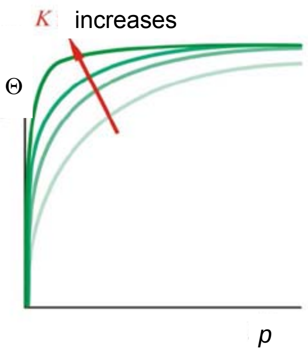
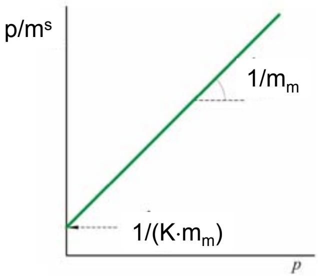
$$\Theta = \frac{m^s}{m_m} = \frac{K \cdot p}{1 + K \cdot p}$$

$$m^s = \frac{m_m \cdot K \cdot p}{1 + K \cdot p}$$ **Langmuir model**

How to determine the parameters? (K, m_m)





Linear form

if p→0 $m^s = K_H \cdot p$ **Henry**

$$\frac{p}{m^s} = \frac{1}{Km_m} + \frac{p}{m_m}$$

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Way to determine specific surface area of irregular/porous materials:

$$\text{Specific surface area} = \frac{m_m}{M} N_A a_s$$

a_s the area occupied by a single molecule on the surface

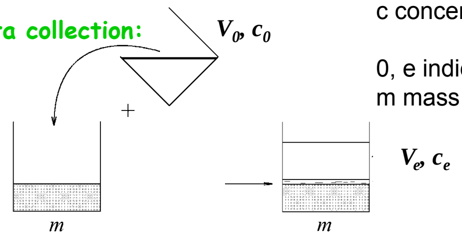
Standard procedure: determination of specific surface area from gas adsorption data; probe gas: N_2, 77 K
a_s=0.162 nm^2

b) Liquid solution/solid interfaces:

Interactions: surface site – dissolved material
surface site - solvent
solvent – dissolved material

V volume of the solution
c concentration of the dissolved material in the solution
0, e indices? Initial and equilibrium, resp.
m mass of the solid phase

Data collection:



Evaluation:

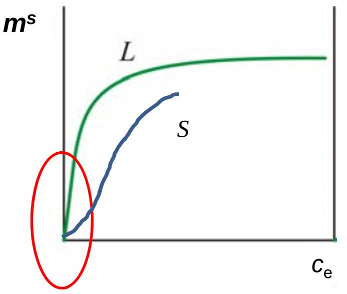
$$m^s = \frac{(c_0 - c_e)V_0}{m}$$

T=const. (isotherms)

Interpretation: solid surface + nonionic dissolved material

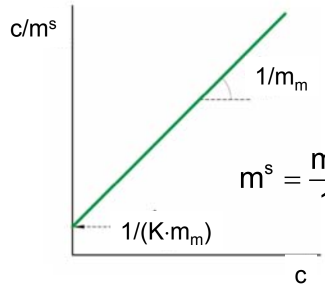
van der Waals/dispersion interactions

Types of the resulted isotherms



Modelling of L type

e.g. Langmuir



$$m^s = \frac{m_m \cdot K \cdot c}{1 + K \cdot c}$$

c→0 Henry

$$m^s = K_H \cdot c$$

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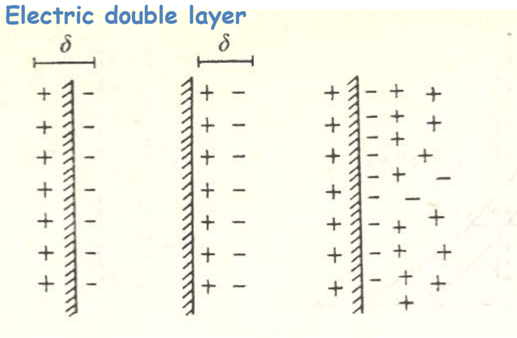
Ionic surfaces/ionic dissolved materials

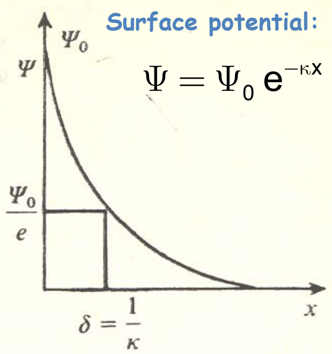
Typical interactions: Electrostatic forces (Coulomb) between surface, (counter)ions and solvent

Electric double layer



Surface potential:

$$\Psi = \Psi_0 \, e^{-\kappa x}$$



The (counter)ion determines the potential

δ Thickness of the layer
Stern-layer

Thermal motion
Diffuse double layer

in case of symmetrical electrolite:

$$\kappa = \text{const} \cdot z\sqrt{c}$$

z : # of charges

$1/\kappa$ fictive layer thickness

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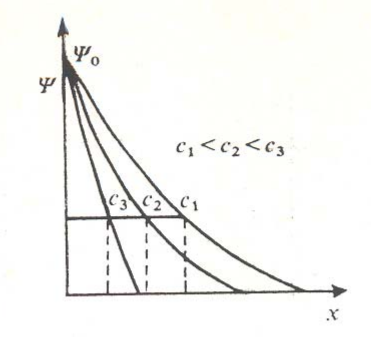
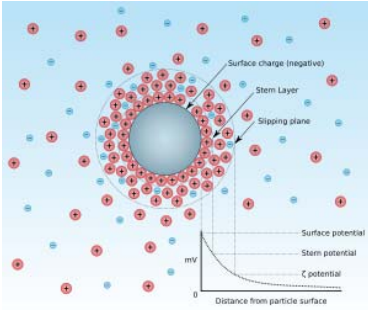
Influence of concentration on the layer thickness





The surface charge is able to stabilize the colloidal particles:

ζ - potencial (electrokinetic potential on the particle surface)

Zeta potencial [mV]	Stability
0 to ±5	fast sedimentation
±10 to ±30	instable
±30 to ±40	low stability
±40 to ±60	good
above ±60	excellent

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