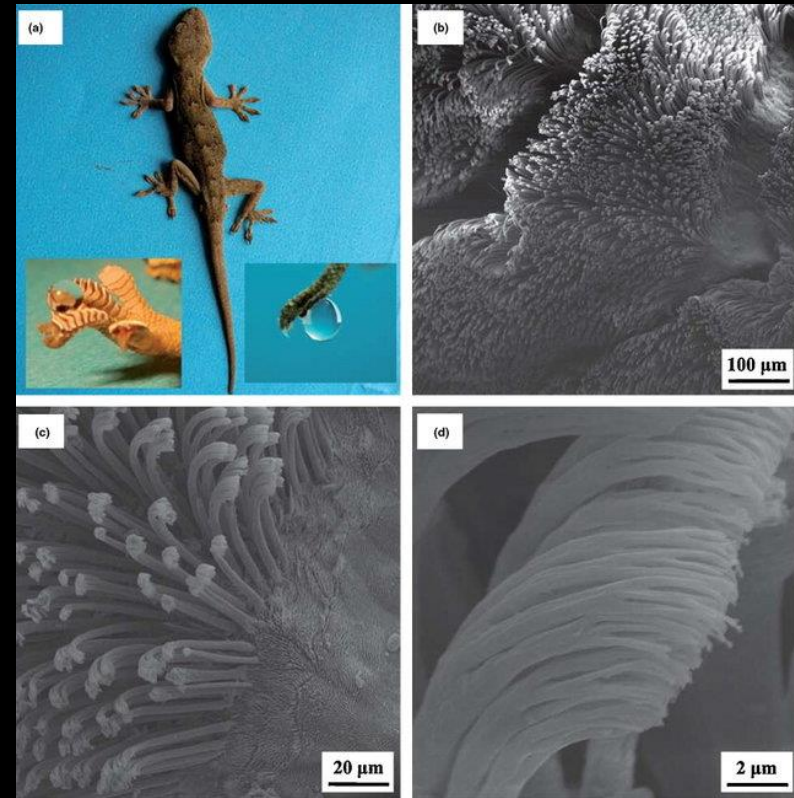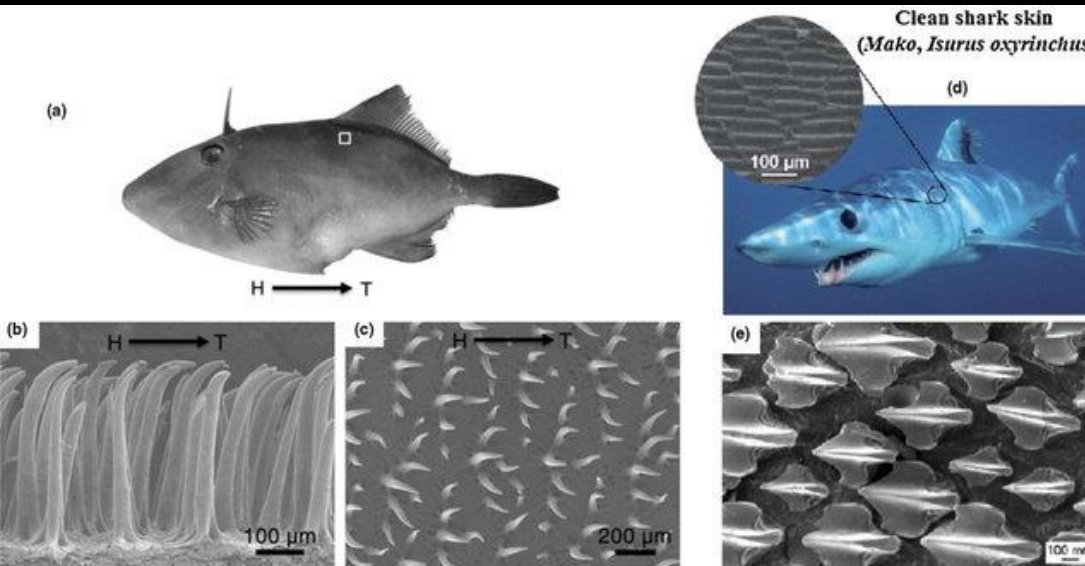# Physical Chemistry of Colloids

Mater. Today **2015**, *18, 273*

Lecture 5, *March 20, 2019*

Manos Anyfantakis
Physics & Materials Science Research Unit

Previously in ColloidsPhysChem...(I)

surfactants in solution
the hydrophobic tail is surrounded
by an 'iceberg' of structured water

adsoprtion to (LG or LS) interface

$$\Delta G_{ad} = \Delta H_{ad} - T\Delta S_{ad}$$

- 'iceberg' water molecules released into
  the solution → large ΔS increase

- ΔH_{ad}: often small; either < 0 (tail-tail vdW
  attractions) or > 0 (electrostatic head repulsion)

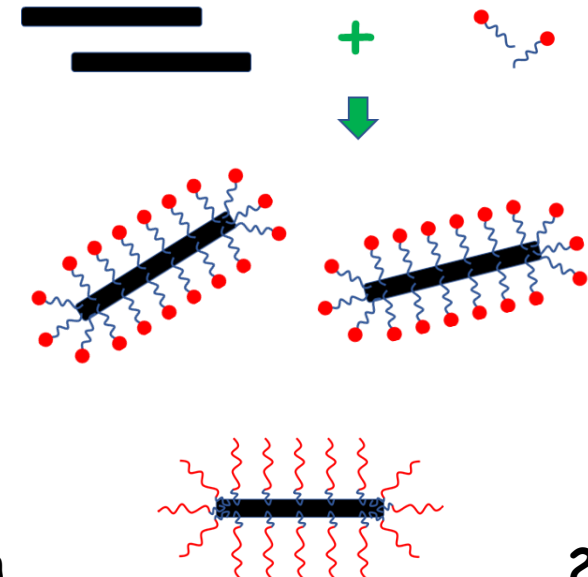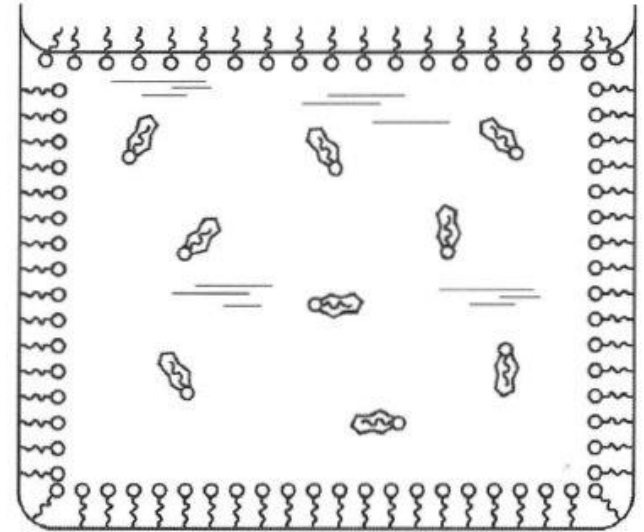ΔG_{ad} large & negative → adsorption favorable

application: aqueous dispersions of hydrophobic NPs

particles aggregate if not stabilized
(hydrophobic effect)

addition of surfactant
→ surfactants adsorb on NP surface
→ hydrophilic coating around the NPs
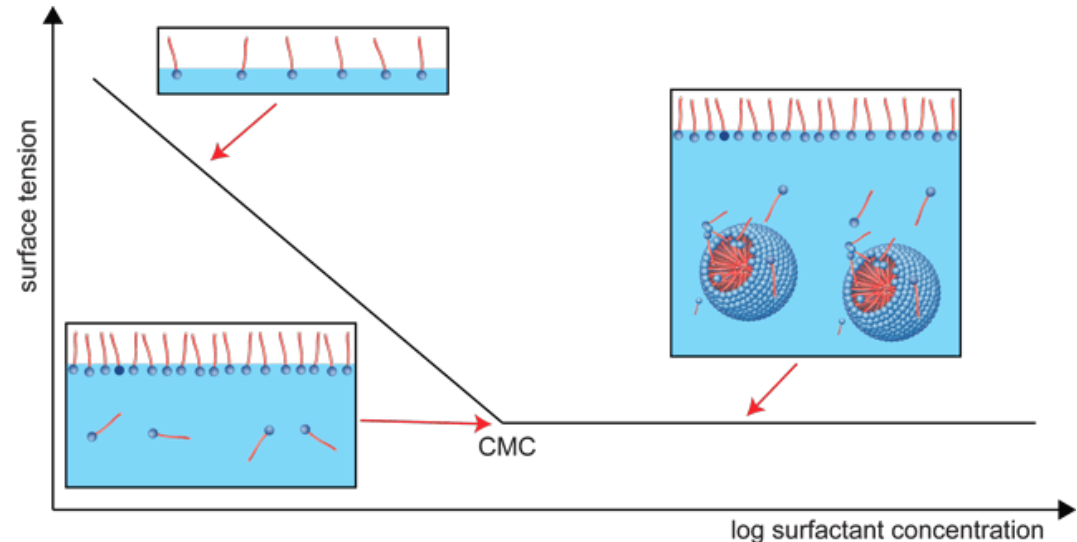→ repulsive forces between NPs preventing aggregation

Previously in ColloidsPhysChem...(II)

**low [surf.]:** *some* water molecules replaced by surfactants

hydrocarbon tails interact *via* London forces (weaker than H-bonding) → σ is reduced

σ decrease stronger with more surf. adsorbed @ the interface

interface saturation: addition of more surfactant does not decrease σ further

micelle self-assembly: spontaneous formation of aggregates to minimize contact of apolar chains with the polar solvent (hydrophobic effect)
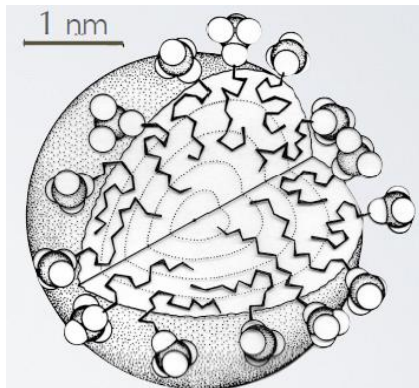
From Robert J. Hunter, 'Foundations of Colloid Science', Oxford University Press, 2002
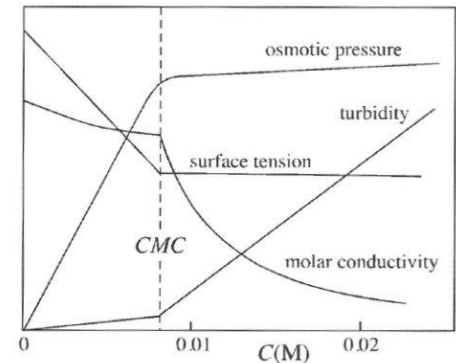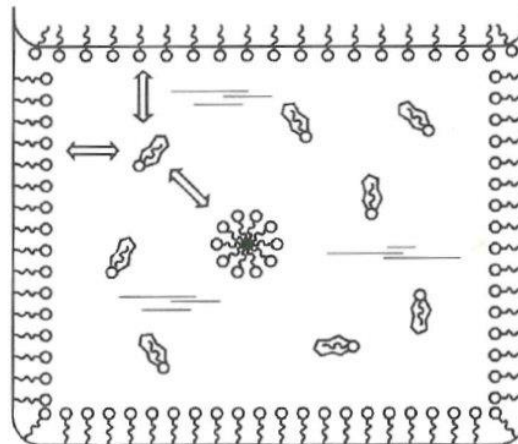

Fig. 3-20: Schematic diagram of physical property changes of aqueous solutions of sodium dodecyl sulfate at 25°C as a function of concentration.

Previously in ColloidsPhysChem…(III)

surfactants to form a space-filling sphere
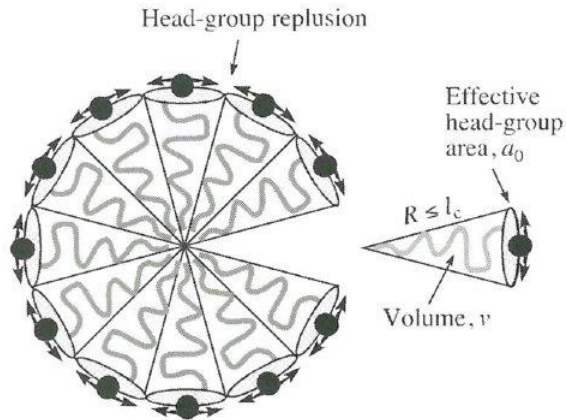→ geometric constraints on heads & tails

Fig. 3-31: Micelles as shape-filling structures, depend upon the size and shape characteristics of the monomer.

Critical Packing Parameter

$$p = \frac{v}{a_0 l_c}$$

v: volume of apolar tail

a_0: area of polar head interfcace

l_c: max. length of apolar tail

Jacob Israelachvili
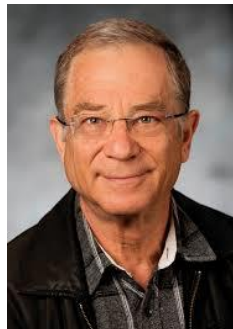
Critical Packing Parameter $(v/a_0 l_c)$	Critical Packing Shape	Structures Formed
< 1/3	Cone	Spherical micelles
1/3 – 1/2	Truncated cone	Cylindrical micelles
1/2 -1	Truncated cone	Flexible bilayers, vesicles
~1	Cylinder	Planar bilayers
>1	Inverted truncated cone or wedge	Inverted micelles

Previously in ColloidsPhysChem...(IV)

wetting
the ability of a liquid to maintain contact with a solid surface, resulting from intermolecular interactions when the two are brought together

wettability
the degree of wetting; determined by the balance between adhesive & cohesive forces

three-phase contact line
line where the solid (S), liquid (L) & gas (G) phases meet

contact angle (θ)

the angle that is formed between the tangent to the LG interface @ the contact line & the LS interface horizontal

- a quantitative measure of the liquid-solid interaction

- macroscopic quantity → integral result of long-range intermolecular forces in the three phases

dataphysics-instruments.com

Young's equation
- force equilibrium @ contact line

$$\sigma_{SG} = \sigma_{SL} + \sigma_{LG}\cos\vartheta$$

- three interfaces → three σ normal to contact line, they minimize area
- assumes perfectly flat & rigid surface *(ideal surface)*
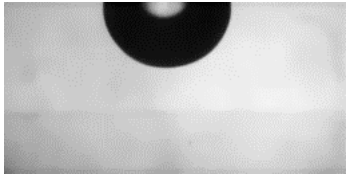- reality: *rough surfaces, finitely rigid* smooth surfaces

5
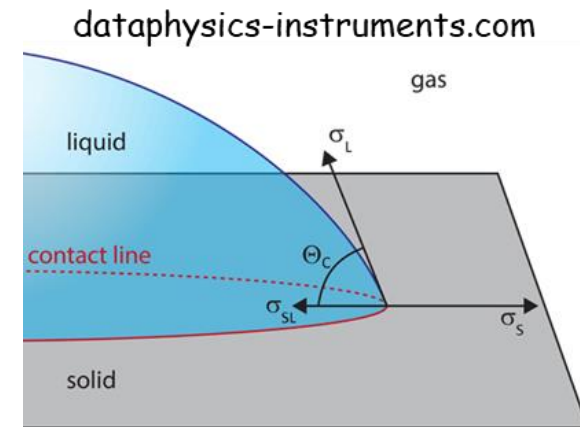
Spreading parameter & wetting regimes

wetting regimes based on the contact angle

complete wetting	partial wetting	partial non-wetting	non-wetting
$\theta = 0^o$	$0^o < \theta < 90^o$	$90^o < \theta < 180^o$	$\theta = 180^o$

nagelgroup.uchicago.edu
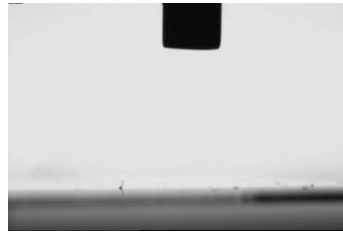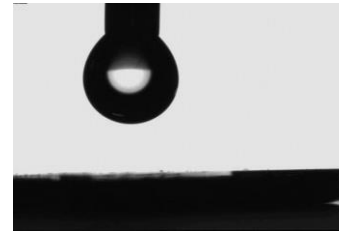
web.mit.edu/nnf/education/wettability/wetting.html
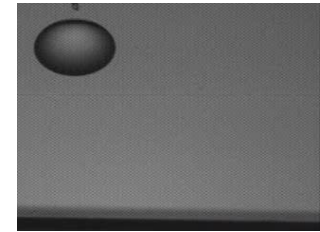
spreading parameter

$$S = E_{dry\ sub} - E_{wet\ sub}$$

$$S = \sigma_{SG} - (\sigma_{SL} + \sigma_{LG})$$

$E_{dry\ sub}$: surface energy (per unit area) of dry substrate

$E_{wet\ sub}$: surface energy (per unit area) of wet substrate

S≥0: complete wetting
- liquid spreads completely to lower its surface energy
- high σ_{SG} (e.g., clean glass, silicon) & low σ_{LG} (e.g. organic solvents) → favorable conditions

S<0: partial wetting
- drop forms a spherical cap with contact angle θ (@ equilibrium)
- *'mostly wetting'* & *'mostly non-wetting'* states

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Examples of contact angle values

Table 4-2: Contact angle values (liquids on solids against air)

Solid	Liquid	Contact angle (°)
Glass	Water	0
"	Benzene	0
Silica	Water	0
"	Acetone	0
"	Benzene	0
Anatase (TiO_2)	Water	0
Tin oxide (SnO_2)	Water	0
Barium sulfate	Water	0
Graphite	Water	86
"	Benzene	60
Stibnite (Sb_2S_5)	Water	84
"	"	38
Talc	Water	88
"	"	52
"	CH_2I_2	53
Hexadecyl alcohol	Water	50-72
Paraffin	Water	105
Teflon	Water	110
Glass	Mercury	135
Steel	Water	70-90

tables of θ are generally not found in literature; reason: *irreproducibility*

Contact angle hysteresis & its origin

simple experiments with sessile drops on
real surfaces give *irreproducible θ values*

addition/removal of liquid

youtube.com/watch?
v=1wh0VtnCIEs

- increasing $V_{drop} \rightarrow$ larger θ
- decreasing $V_{drop} \rightarrow$ smaller θ

drop on an inclined substrate

youtube.com/watch
?v=UWMwSppjv6s

- θ on upper (elevated)
  side < θ on lower side

What is the reason for the θ data irreproducibility?

- only uppermost layers of the substrate
  determine θ; coatings/contaminants important!

- difference between θ when liquid is advanced over
  ($θ_{adv}$) or receded from ($θ_{rec}$) the surface

contact angle hysteresis

$H = θ_{adv} - θ_{rec}$

origin of H

- surface roughness
- chemical heterogeneity

advancing angle receding angle

ramé-hart instrument co.

advancing and receding contact angles
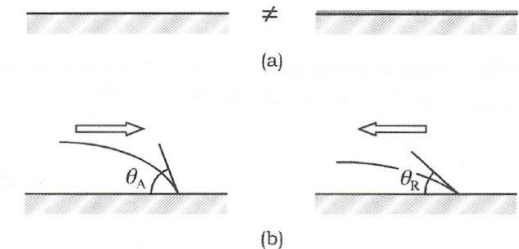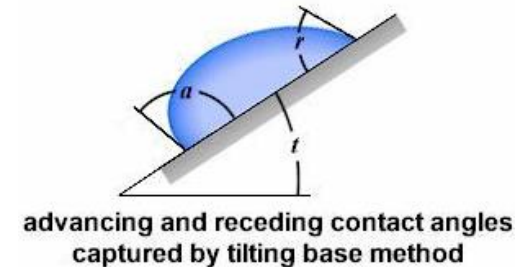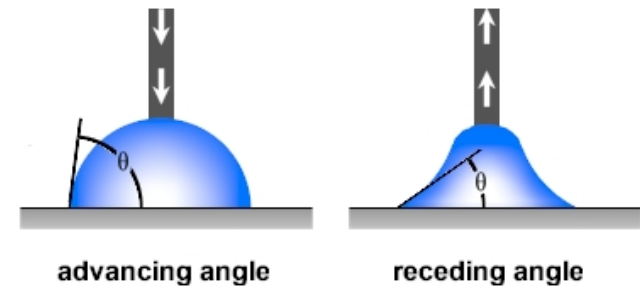captured by tilting base method

Fig. 4-7: "Irreproducible" contact angles: (a) Surface composition is different between nominally identical bulk solids, (b) Contact angle depends on whether liquid is advancing or receding across solid surface: hysteresis.
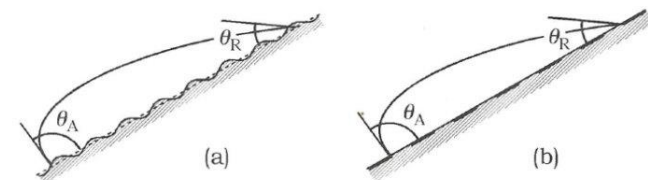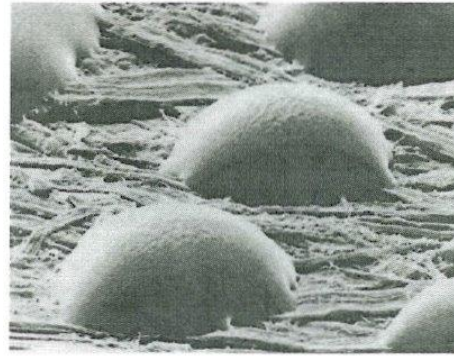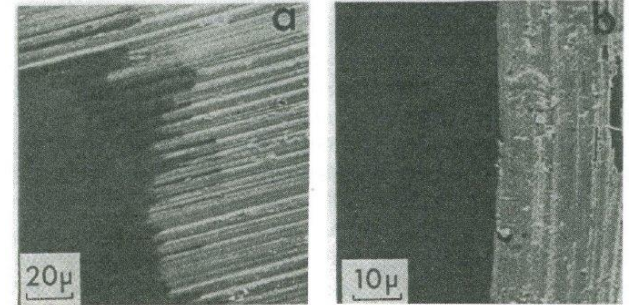
Fig. 4-9: Origins of contact angle hysteresis: (a) Surface roughness, (b) Surface chemical (energetic) heterogeneity.

Wenzel model for rough surfaces

real surfaces are generally both rough & energetically heterogeneous

solidified ink drops on bond paper

polyphenyl ether drop spreading on machined Al

Wenzel model

for rough surfaces: $A_{true} = r A_{smooth}$

r: rugosity factor (>1)

$$cos\theta_{app} = r\frac{(\sigma_{SG} - \sigma_{SL})}{\sigma_{LG}} = r cos\theta_0$$
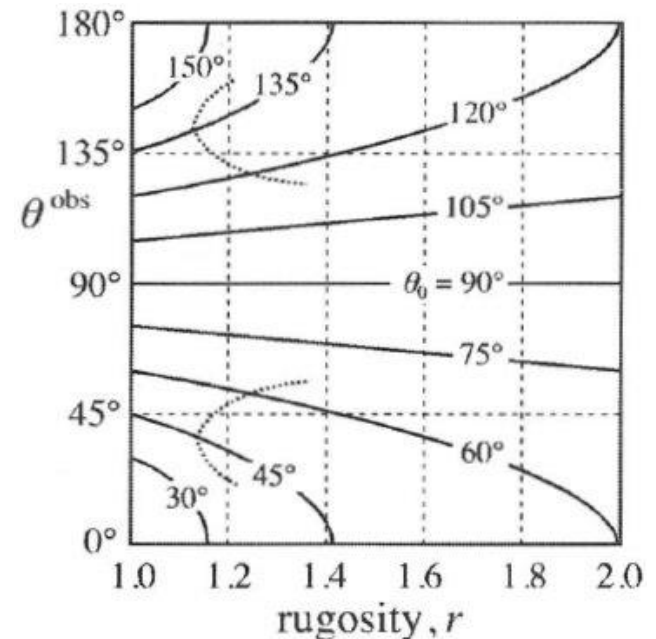
- *size scale of roughness small*
- *drop larger than roughness size scale*

θ_0: intrinsic contact angle (Young)

effect of roughening

wetting liquid (θ_0 < 90º): wettability increases

non-wetting liquid (θ_0 > 90º): wettability decreases

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Cassie–Baxter model for chemically heterogeneous surfaces

Cassie & Baxter considered heterogeneous surfaces consisting of two types of patches with θ_1 & θ_2

$$cos\theta_{app} = \varphi_1 cos\theta_1 + \varphi_2 cos\theta_2$$

φ_1, φ_2: area fractions

case I: pores (filled with air) on surface

- vapor gaps: liquid does not wet the solid

- effective contact angles: θ_1, $\theta_2 = 180°$

$$cos\theta_{app} = \varphi_1 cos\theta_1 - \varphi_2$$

ultrahydrophobic surfaces ($\theta > 130°$) are based on such structures
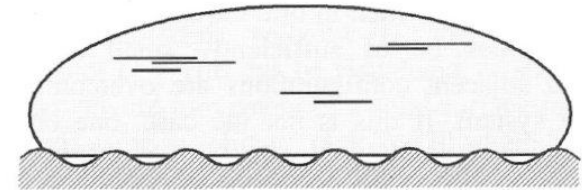
Fig. 4-16: A composite surface with unwetted gas pockets on the rough solid surface.

case II: pores pre-filled with wetting liquid

$$cos\theta_{app} = \varphi_1 cos\theta_1 + \varphi_2$$

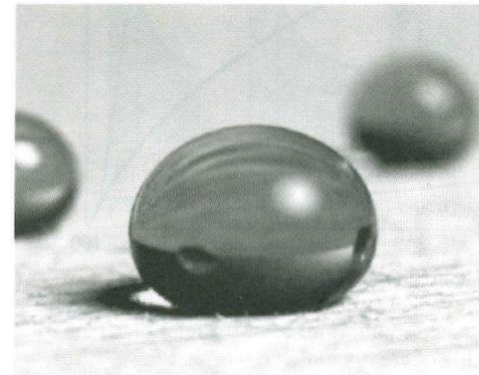- wetting out ($\theta \rightarrow 0°$) often observed

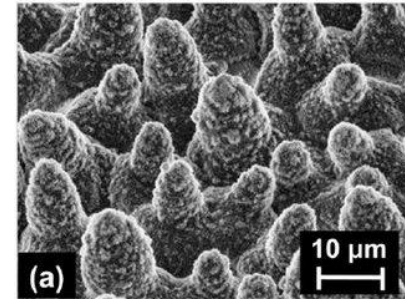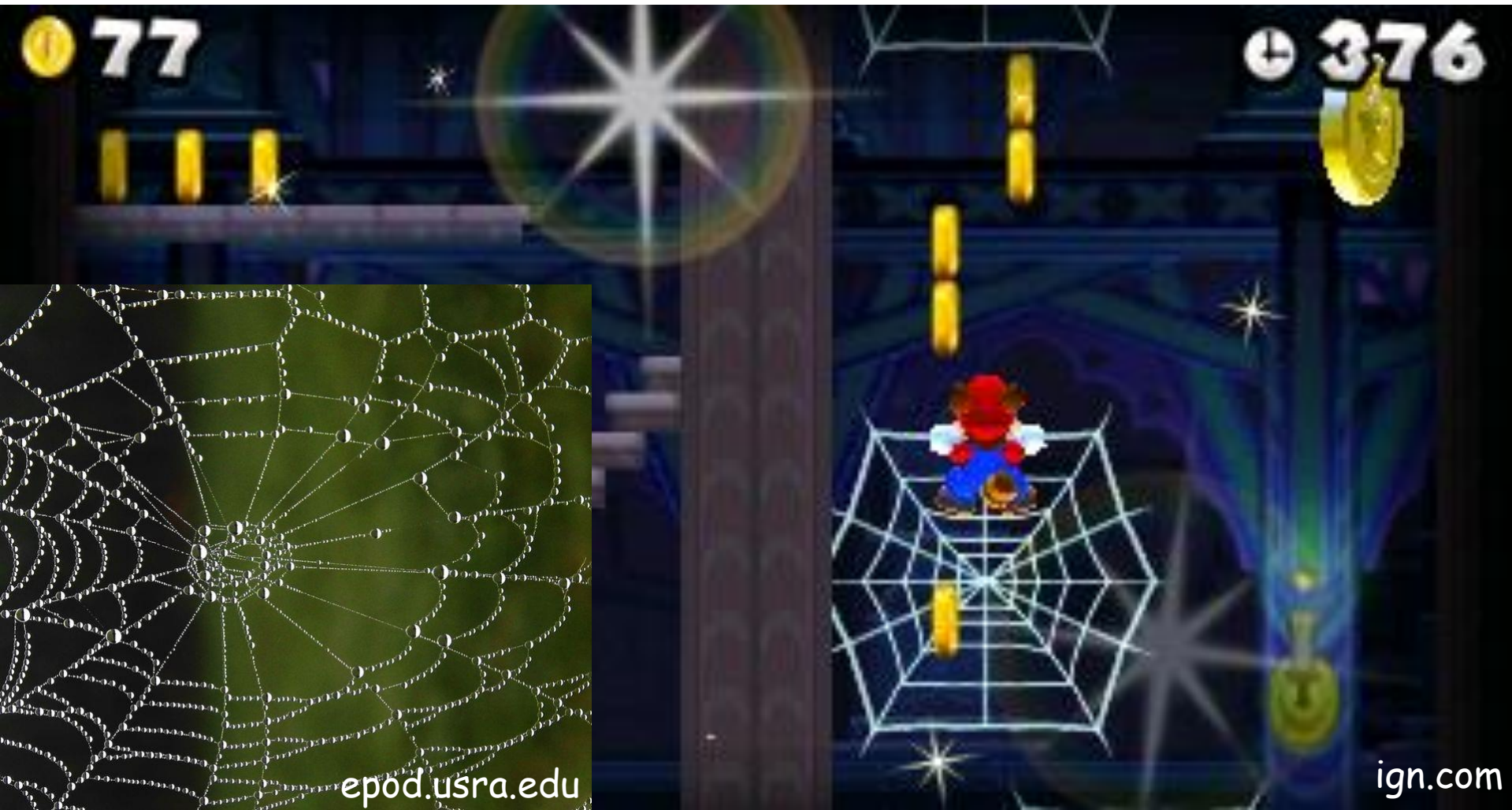Fig. 4-17: Water droplets on an "ultra-hydrophobic" surface created by coating wood with "Lotus Spray," an aerosol of hydrophobic nanoparticles. From [http://nanotechweb.org/cws/article/tech/16392/1/0611102.]

Coffee break

epod.usra.edu

ign.com

Mario noticed that spider webs are very effective in capturing water in dewy mornings. Why?

chemistryworld.com/news/how-spider-silk-soaks-up-water/3001990.article

Critical surface tension & wetting series

θ measurements → information on the surface energetics of solids (Young's eq.)

high energy solids (e.g. metals)
- completely wet by most liquids
- S > 0 → $\sigma_{SG} - \sigma_{SL} > \sigma_{LG}$

low energy solids (e.g. polymers)
- intermediate wettability calls for quantitative characterization

- **Zisman plots:** $\cos\theta_{adv}$ of a given smooth solid vs. σ of different liquids

- σ_C: critical surface tension; at & below σ_C the solid is completely wet

- fluorinated surfaces have extremely low σ_C; close-packed -CF_3 practically unwetttable @ RT!

- wetting series based on atomic constitution (polarizability)
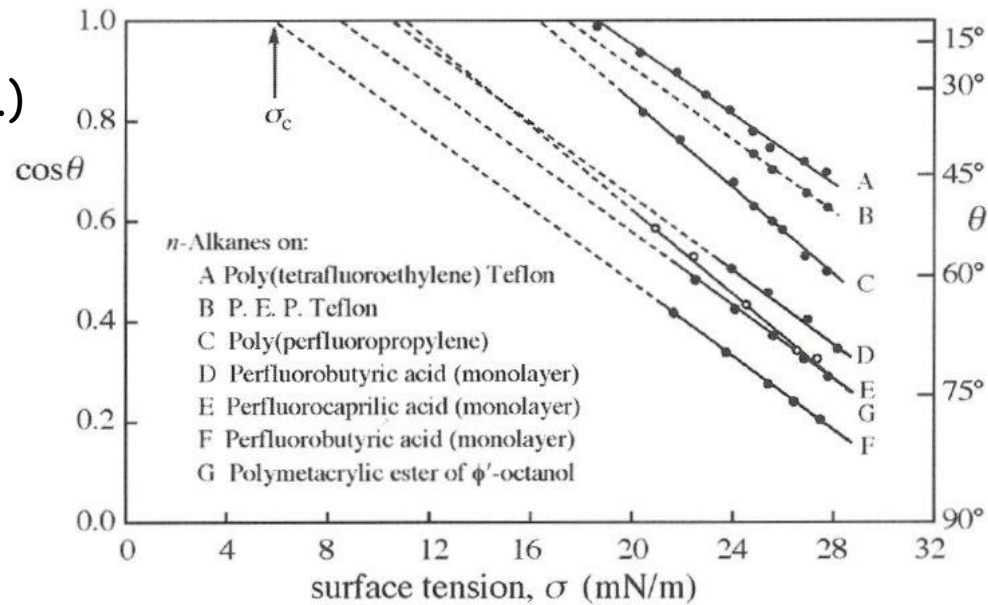 F < H < Cl < Br < I < O < N

n-Alkanes on:
A Poly(tetrafluoroethylene) Teflon
B P. E. P. Teflon
C Poly(perfluoropropylene)
D Perfluorobutyric acid (monolayer)
E Perfluorocaprilic acid (monolayer)
F Perfluorobutyric acid (monolayer)
G Polymetacrylic ester of φ'-octanol

Table 4-4: Critical surface tension of surfaces in terms of their chemistry. From [Osipow, L. I., **Surface Chemistry**, p.251, ACS Monograph Series No. 153, Reinhold, New York, 1962.]

| Surface	Chemical structure	σ_c (mN/m)
Perfluorolauric acid, monolayer	CF_3, close-packed	5.6
Perfluorobutyric acid, monolayer	CF_3, less closely packed	9.2
Perfluorokerosene, thin liquid film	CF_2, some CF_3	17.0
Polytetrafluoroethylene, solid	CF_2	18.2
Octadecylamine, monolayer	CH_3, close-packed	22.0
α-Amyl myristic acid, monolayer	CH_3 and CH_2	26.0
2-Ethyl hexyl amine, monolayer	CH_3 and CH_2	29.0
n-Hexadecane, crystal	CH_2, and some CH_3	29.0
Polyethylene, solid	CH_2	31.0
Naphthalene, crystal	⬡, edge only	25.0
Benzoic acid, monolayer	⬡, edges and faces	53.0
2-Naphthoic acid, monolayer	⬡, edges and faces	58.0
Polystyrene, solid	CH_2, some ⬡	32.8- 43.3
Polyethylene terephthalate, solid	⬡, CH_2, ester	43.0
Nylon, solid	CH_2, amide	42.5-46.0

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Surface treatment for changing wettability

several applications require the change wettability of solid materials

surface roughening (physical)

- can be achieved by sanding, plasma or chemical etching

- if $\theta_0 < 90^o \rightarrow$ wetting promoted
- if $\theta_0 > 90^o \rightarrow$ wetting hindered

surfactant addition (physical)

- decreases $\sigma_{LG} \rightarrow$ promotes wetting
- might increase/decrease σ_{SL} due to adsorption $\rightarrow$ promotes/hinders wetting
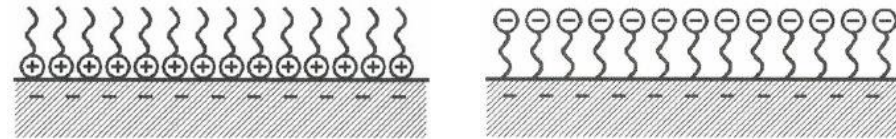
enrich surface with specific atoms (chemical)

- oxygen enrichment $\rightarrow$ promotes wetting
- treatment with plasma, corona discharge, flame; produce reactive radicals, limited permanence
- wet chemical treatment (strong bases or acids)

- fluorine enrichment $\rightarrow$ wetting hindered
- adsorption of polymers containing F
- treatment with silanes $Y-Si-(OR)_3$, $Y-Si-Cl_3$

$$-OH + (HO)_3-Si-Y \longrightarrow -O-Si-Y + H_2O$$

13
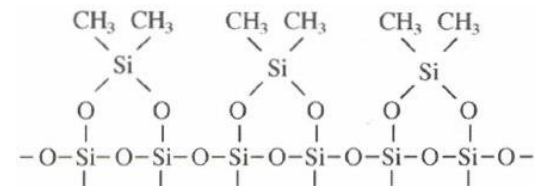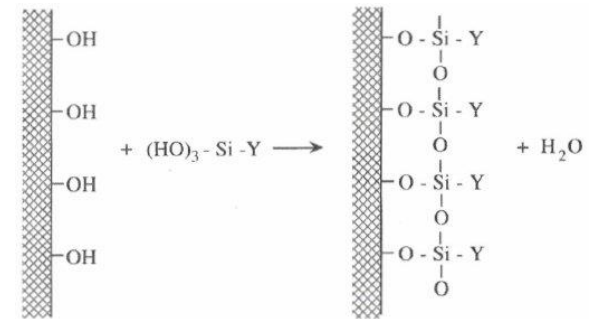
Charge separation at interfaces

interfaces divide electrically neutral bulk (solvent) phases
→ positive & negative charges separate in the direction normal to interface
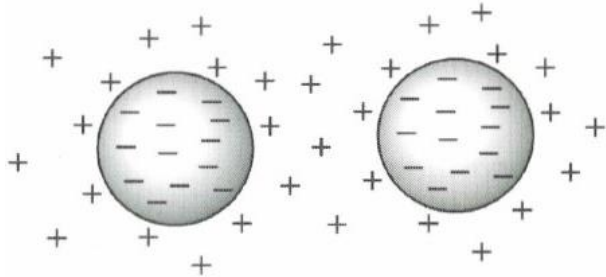

Fig. 1-3: Electrical charge separation at the interfaces of particles against their dispersion medium, water.

- no net charge in volume around the interface due to counterions
- locally, positive or negative charge dominates

electric double layer
the structure formed by surface charges & counterions @ the vicinity of an interface

electric double layer thickness
defined as the distance to charge neutrality (charged surface effectively screened out)

- water: thickness in the order of few nm
- non-aqueous media: much larger (lower ε_r)

  ➢ origin of electric charge separation?
  ➢ structure of electric double layer?
  ➢ electrostatic forces between surfaces?
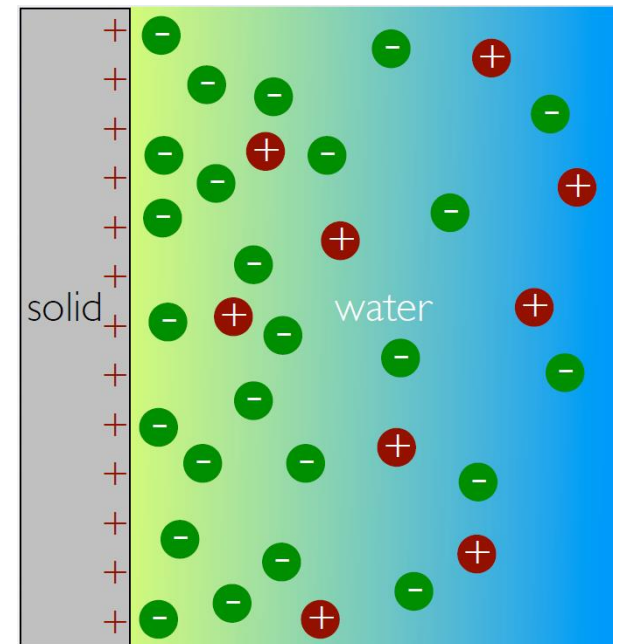
Origins of electric charge @ interfaces

preferential adsorption/desorption of lattice ions
ions of the surface lattice of crystalline colloidal
particles preferentially adsorb or desorb to the surface

example: AgI crystalline particles
- I^- ions adsorb to the surface more strongly than Ag^+
  → surface negatively charged
- equivalent: preferential desorption of Ag^+ into solution
- surface potential depends on [lattice ions] in solution;
  can be adjusted with $AgNO_3$ or KI

point of zero charge: bulk [ion] that will make
the potential zero (determined by titration)

Table 6-2: Ranges of *PZC*-values generally found
for representative mineral oxides (in terms of *pH*)*

Oxide	PZC range
α-Al_2O_3	8 – 9
Fe_2O_3	6 – 8
Fe_3O_4	6 – 8
MgO	10 – 12
MnO_2	2 - 4
SiO_2	2 – 3
SnO_2	3 – 4
TiO_2	6 – 7
ZnO	9 – 10
ZrO_2	5 – 7

* Approximate averages of values taken from [Kosmulski, M.,
Chemical Properties of Material Surfaces, Surf. Sci. Ser. 102,
Marcel Dekker, New York (2001).]

specific adsorption of (foreign) charged species
ions that are present in the system but are not an
integral part of the dispersed phase adsorb on surface

- ionic surfactants (hydrophobic effect)

- polyvalent ions of like or opposite
  charge adsorb via different mech. &
  can neutralize or reverse charge
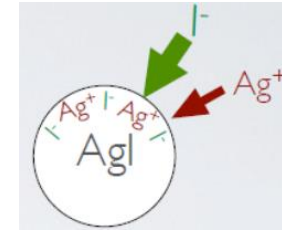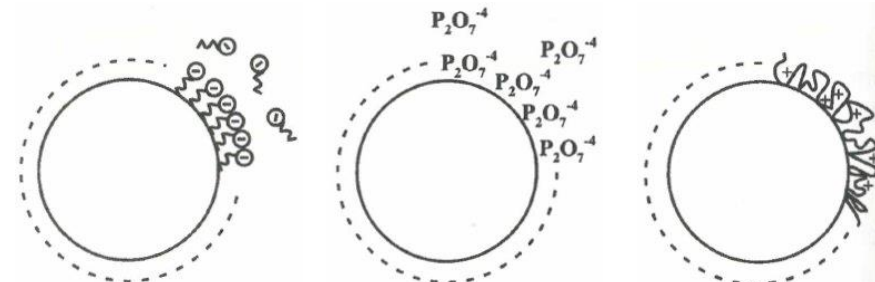
- polyelectrolytes (with hydrophob. groups)

Origins of electric charge @ interfaces (II)

ionization of surface functional groups
chemical functional groups of the dispersed phase
may lose or gain an H^+ → negative/positive charge

- common in polymeric particles with imbedded functional groups (e.g. from the initiator used)

- constant surface charge density

- sulfate groups: ionizable over ~ whole pH range

- weak acids (-COOH) or bases (-NH$_2$):
  degree of ionization = f(pH)

isomorphic substitution
mineral colloidal particles exchange one type
of ions in their lattice with another type
that has different valence but similar size

- clays: face charges negative & constant (isomorphic susbtitution); rims positive @ low pH

accumulation/depletion of e$^-$
- direct e$^-$ transfer from one phase to another
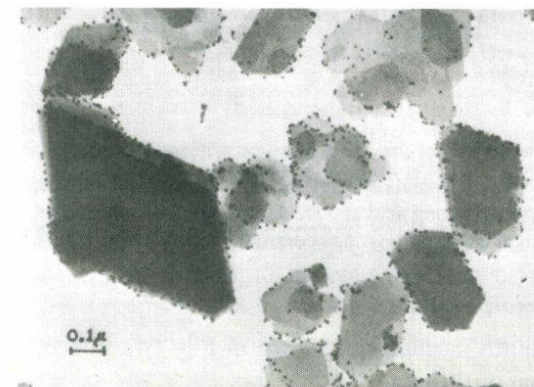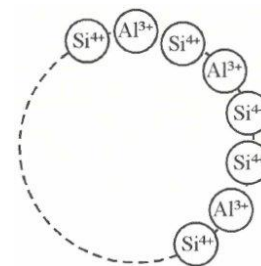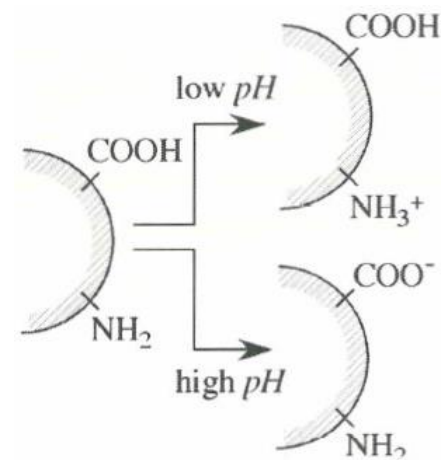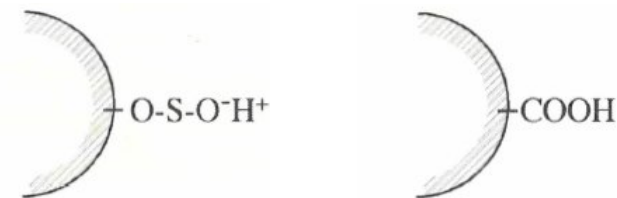- unoxidized metal/solution, O/W interfaces

Fig. 6-5: Electron micrograph of a mixture of a kaolinite and a negative gold sol. From [Van Olphen, H., **An Introduction to Colloid Clay Chemistry**, 2nd Ed., p. 95, John Wiley & Sons, New York, 1977.]

Interface charging in non-aqueous systems

electrostatic model of ion dissolution

- interaction of ions in a solvent is screened through solvent polarization

- polarization ~ relative dielectric permittivity ε_r (dielectric constant)

- *water:* $\varepsilon_r \approx 80$;   *alkane:* $\varepsilon_r \approx 2$ → water polarized more strongly

- attractive potential Ψ between two charges +q & -q @ distance r
  $$\Psi = \frac{1}{4\pi\varepsilon_r\varepsilon_0}\frac{q^2}{r}$$

- $\Psi \gg k_BT$ → charges strongly associate, dissolved state unstable

- $\Psi = k_BT$ → Bjerrum length: $\lambda_B = \frac{1}{4\pi\varepsilon_r\varepsilon_0}\frac{q^2}{k_BT}$ *distance between the ions req. for stable dissociation*

aqueous systems

- $\lambda_B \approx 0.7$ nm, about twice the thickness of hydration shell (easy to dissolve salts in water)

wikipedia

non-polar media

- $\lambda_B \approx 28$ nm

- for stable dissociation → ions must "hide" in a structure providing a shell of substantial thickness, which is very difficult

- ions "caged" inside or adsorbed onto large structures (reverse micelles, polymers, NPs)
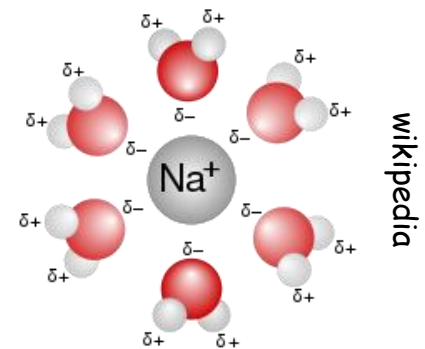
Models of the electric double layer

regardless of how charge separation is generated, a structure will be formed such that surface charge is neutralized by a layer of counterions in solution

Helmholtz model

- two adjacent monolayers of opposite charge ("molecular capacitor") @ distance δ

- δ: the hydrated radius of the counterions

- all of the potential drop occurs across δ

- surface charge density: $\bar{\sigma} = \dfrac{\varepsilon\varepsilon_0}{\delta}\psi_0$

Gouy-Chapman model

- counterion layer should be diffuse because thermal motion → uniform concentration

- equilibrium: balance between orienting effect of surface electric field & diffusion → high [counterion] near surface, ↓ with x

  assumptions
  - *ions point charges (they have no volume)*
  - *no specific adsorption of ions*
  - *ε_r of medium constant within the double layer*
  - *surface charge uniform over the surface*

Monolayer of counter-ions sufficient to neutralize surface charge

Potential ψ(x)