



Jean-François Dufrêche

Ions at Interfaces

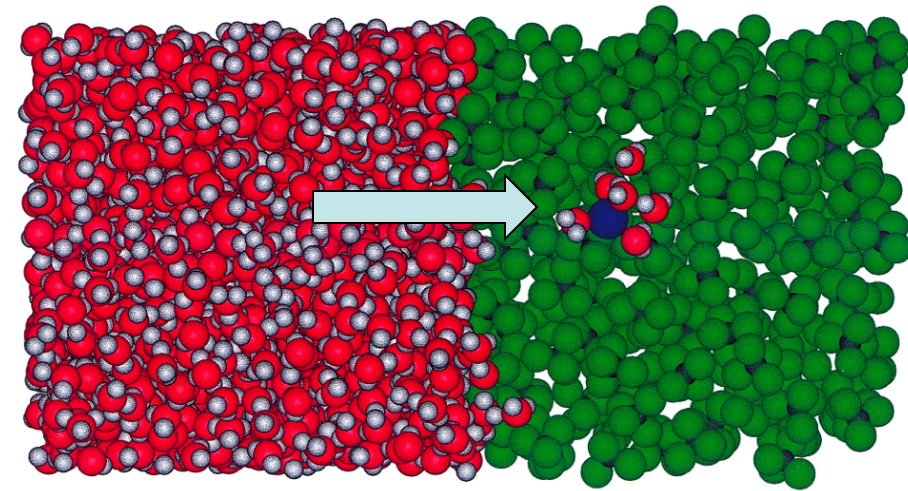


2014-2015



Separation chemistry: liquid/liquid and solid/liquid interfaces

- ☞ liquid/liquid extraction
- ☞ diffusion in porous media (solid/liquid)



Charged interface:

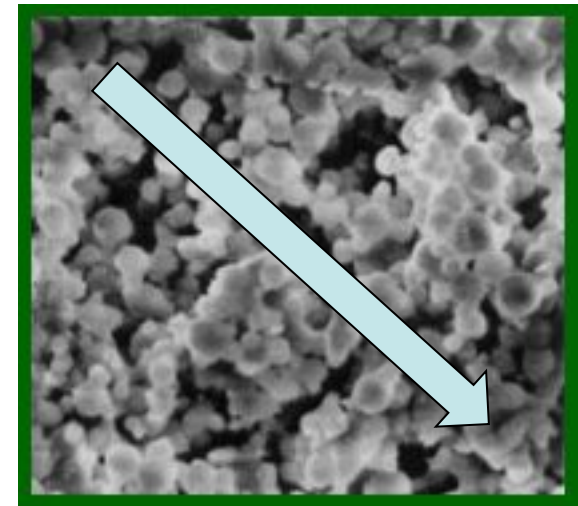
Non neutral interfaces: the two surfaces are charged

Ex : solid/liquid

$Q_{\text{solid}} \neq 0$

$Q_{\text{liquid}} \neq 0$

(but $Q_{\text{solid}} + Q_{\text{liquid}} = 0$)

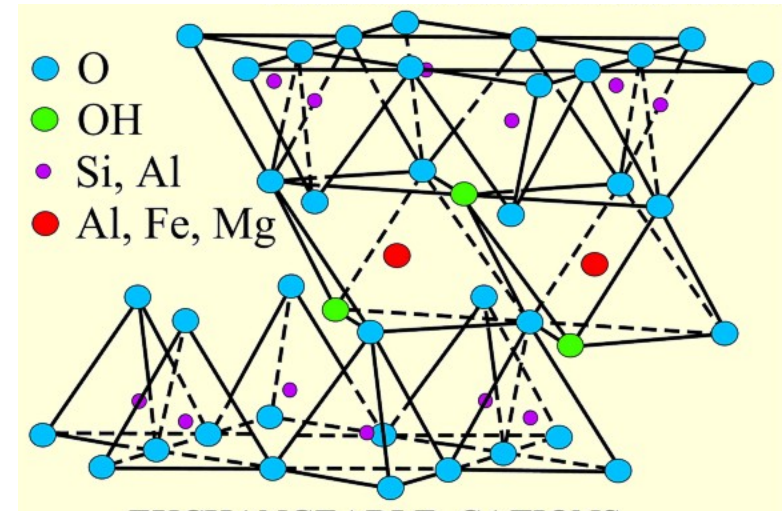




Origin of the charge

Desequilibrium in the volume charge

- ionic solids
- excess or defects of cation / anions
- Ex : AgI, clays, etc...

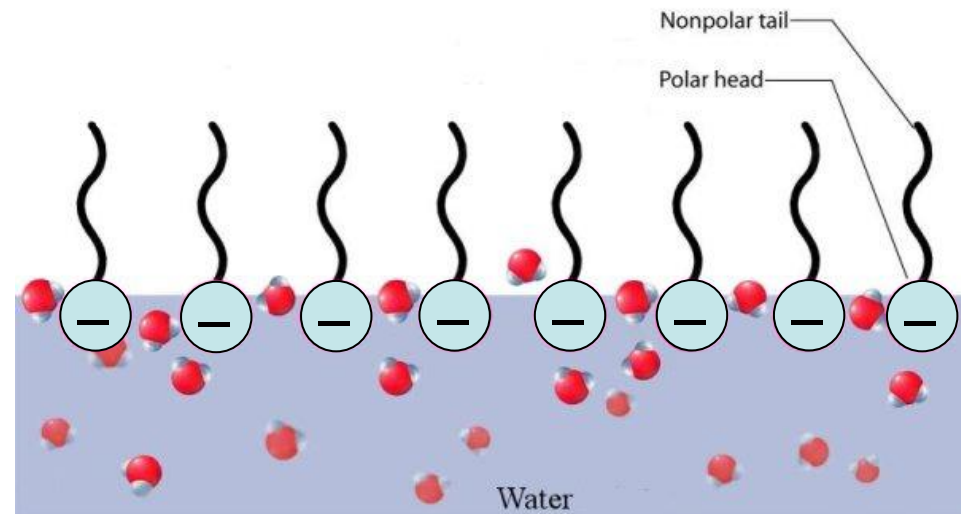


Surface chemistry

- Groups $\text{Si-OH} \leftrightarrow \text{Si-O}^- \leftrightarrow \text{SiOH}_2^+$
- Depends on the pH
- localised charge

Charged surfactant at the interface

- mobile charge





A very old story

Hermann Ludwig von Helmholtz
(1821-1894)

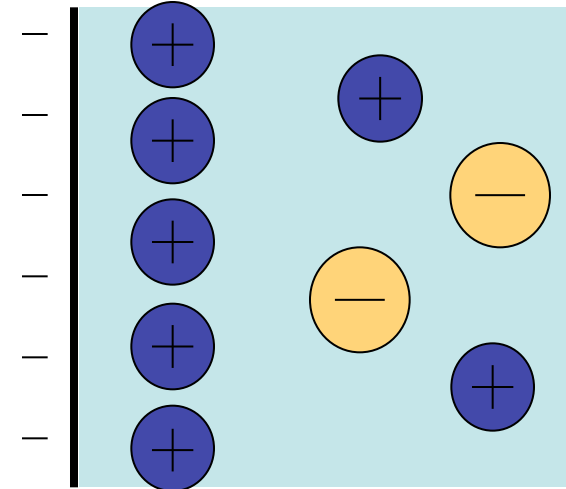


Electrical Double Layers (EDL)
are similar to capacitors !

Counter-ions: ions whose sign is the opposite of the solid surface
Counter-ions are stuck to the surface (Helmholtz layer)

U minimum

solid liquid



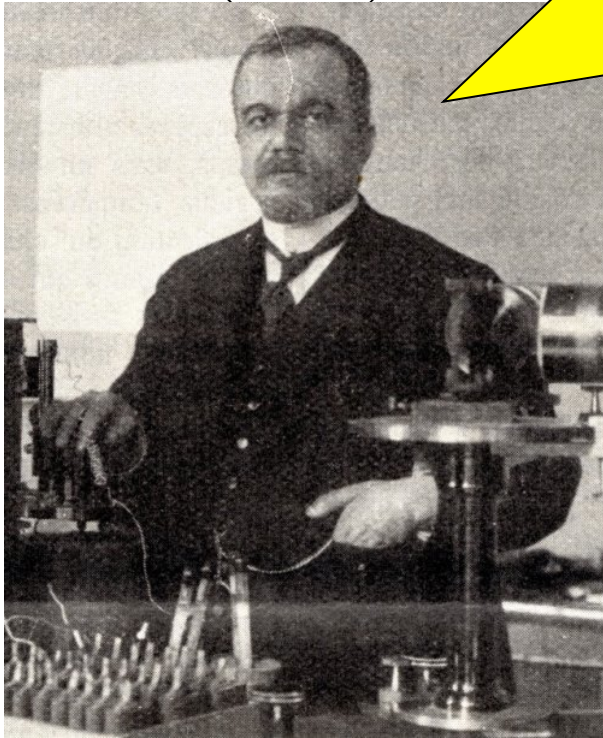
Helmholtz
Layer

Electrolyte
solution



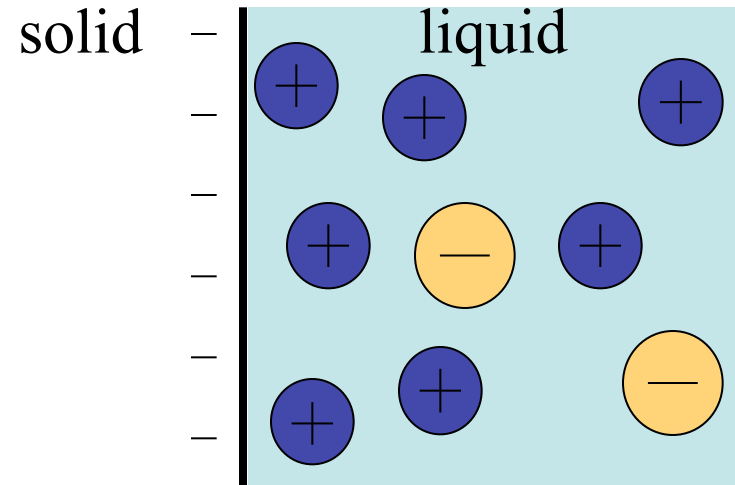
106 years ago...

Louis-Georges Gouy
(1909)



Thermodynamically, if T is known, we do not minimize U but $F=U-TS$

The electrostatic attraction of the counterions is somewhat counterbalanced by the thermal agitation



$F = U - T S$ minimum

Diffuse layer = effect of the temperature



Gouy-Chapman theory

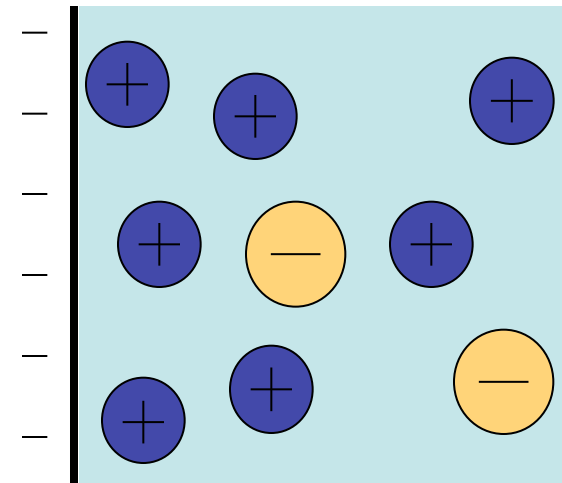
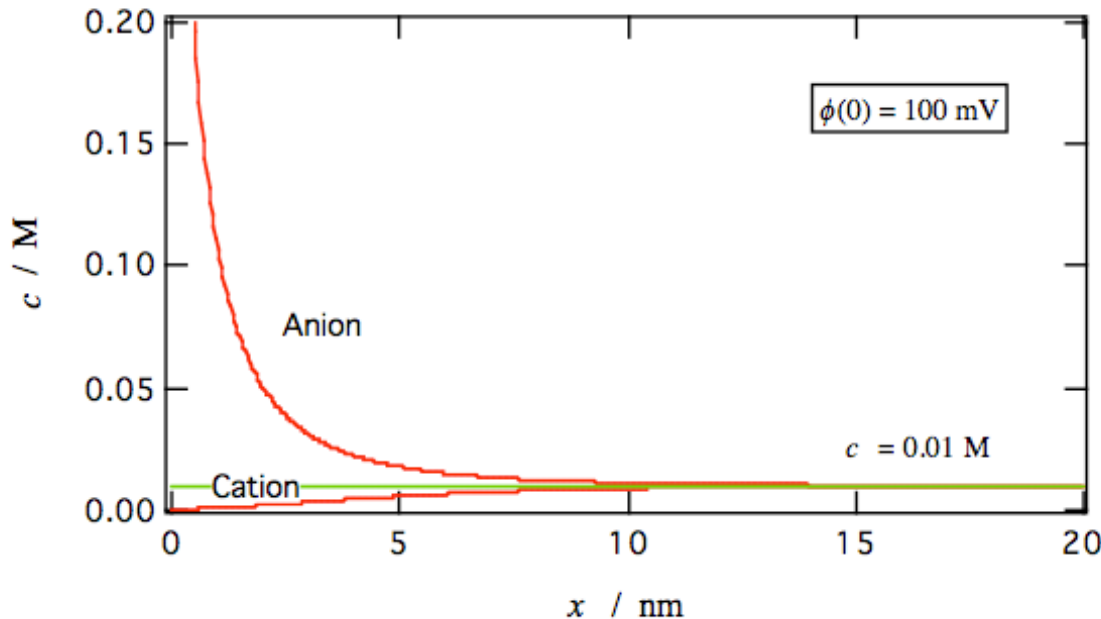
Ion distribution at the interface

95% of the calculations are still based on that approach

Poisson-Boltzmann Equation $C_i(x) = C_i^0 \exp\left(-\frac{q_i V(x)}{k_B T}\right)$

Boltzmann + Poisson equations:

$$\Delta V(x) = -\frac{\rho_{elec}(x)}{\epsilon_0 \epsilon_r} = -\frac{\sum_i q_i C_i(x)}{\epsilon_0 \epsilon_r}$$





Gouy-Chapman theory

Characteristic length of the EDL

Gouy length L_G

Size of the heavily condensed counterions

$$E_{electrostat}^{ion} = eV = e \frac{\sigma}{\epsilon_0 \epsilon_r} L_G \approx k_B T \Rightarrow L_G = \frac{\epsilon_0 \epsilon_r k_B T}{e \sigma}$$

Typically Angstrom. Condensed ions are in the first layer of the solvent molecules

Debye distance $L_D = \kappa^{-1}$

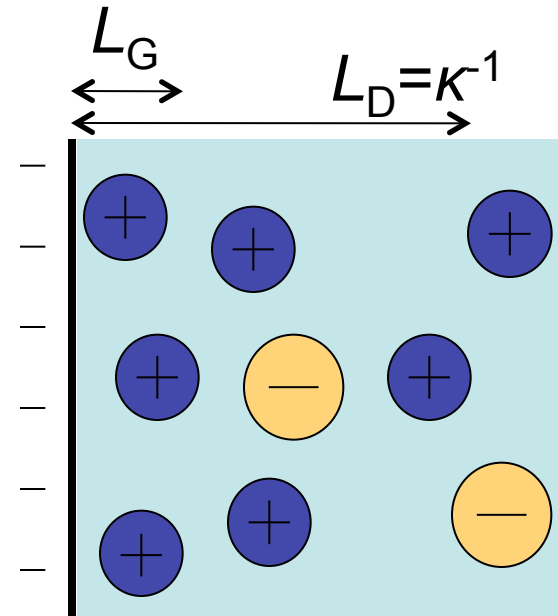
Size of the diffusion layer: distance

It takes to compensate the solid charge.

Depends on the ionic force

$$I = \frac{1}{2} \sum C_i Z_i^2$$

$$\kappa^2 = 4\pi L_B \sum_i C_i Z_i^2 \Rightarrow L_D = A \times I^{-1/2}$$





Gouy-Chapman theory

- ⇒ valid for **monovalent electrolyte** (i.e. 1/1 ex NaCl) in water if the solid **charge is not too important...**
- ⇒ At any case, **far away from the interface** $V(x)$ and $C_i(x)$ are proportional to **$\exp(-\kappa x)$** (but κ is sometimes different from the Debye inverse length)
- ⇒ globally gives correct results if the parameters are **renormalized** (**effective charges, effective potential**)
- ⇒ Relatively **simple** calculations

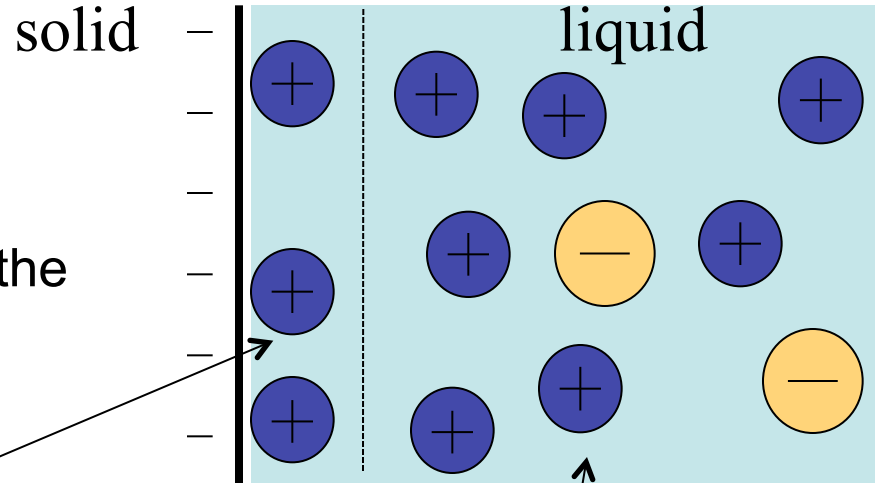


Stern layer

Otto Stern
(1888 -1969)



Add a layer !

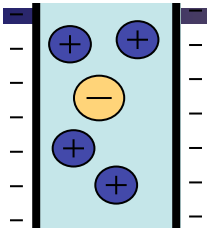


Stern model

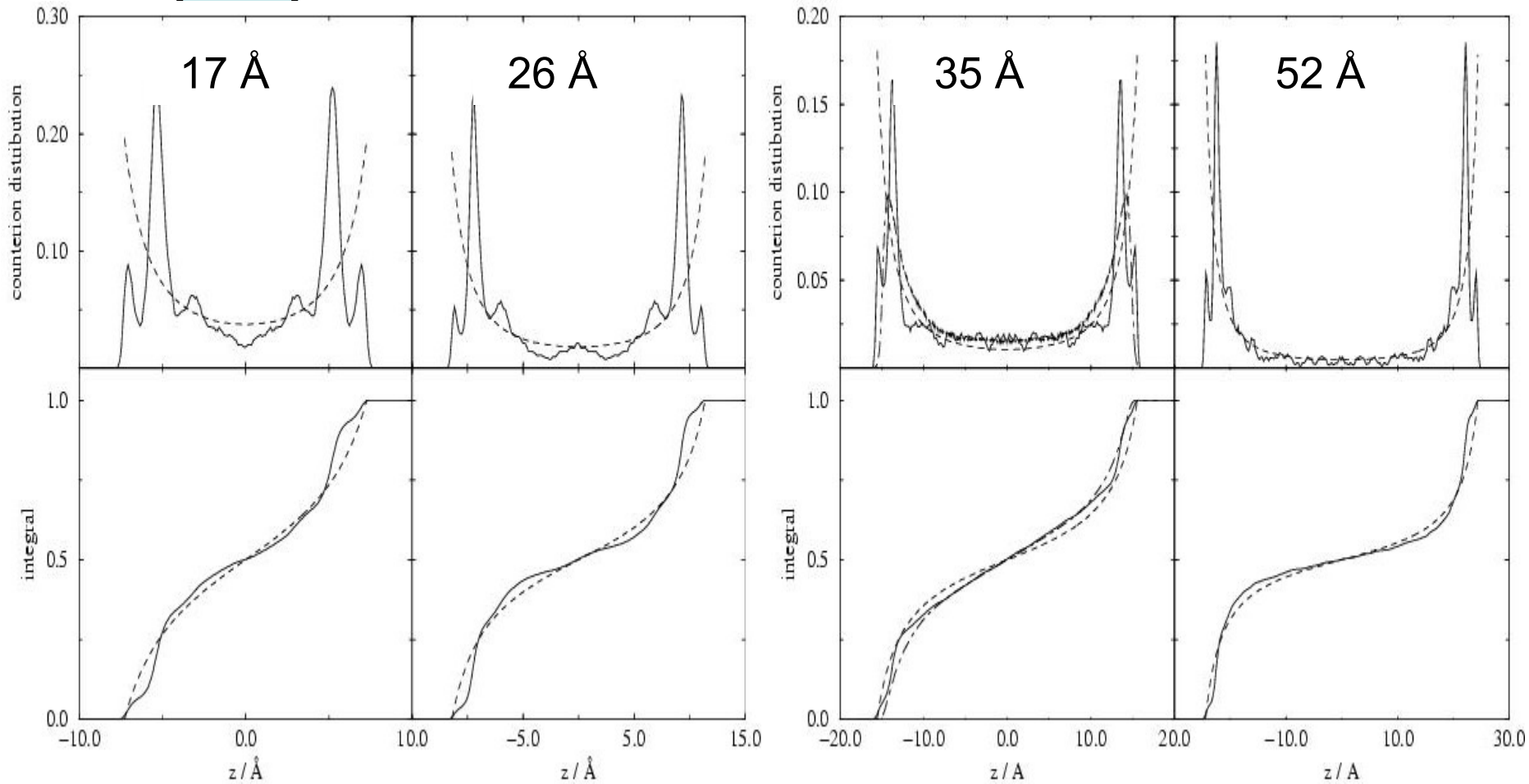
- first layer of ions different from the diffuse layer
- « triple layer » model
- unknown value → fitting (very convenient for modelling !)

Diffuse layer (GC approach)

Molecular nature of the solvent

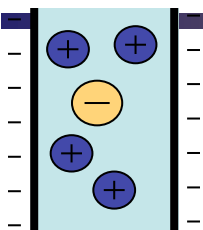


Counterions distributions around two charged sheets (clays)

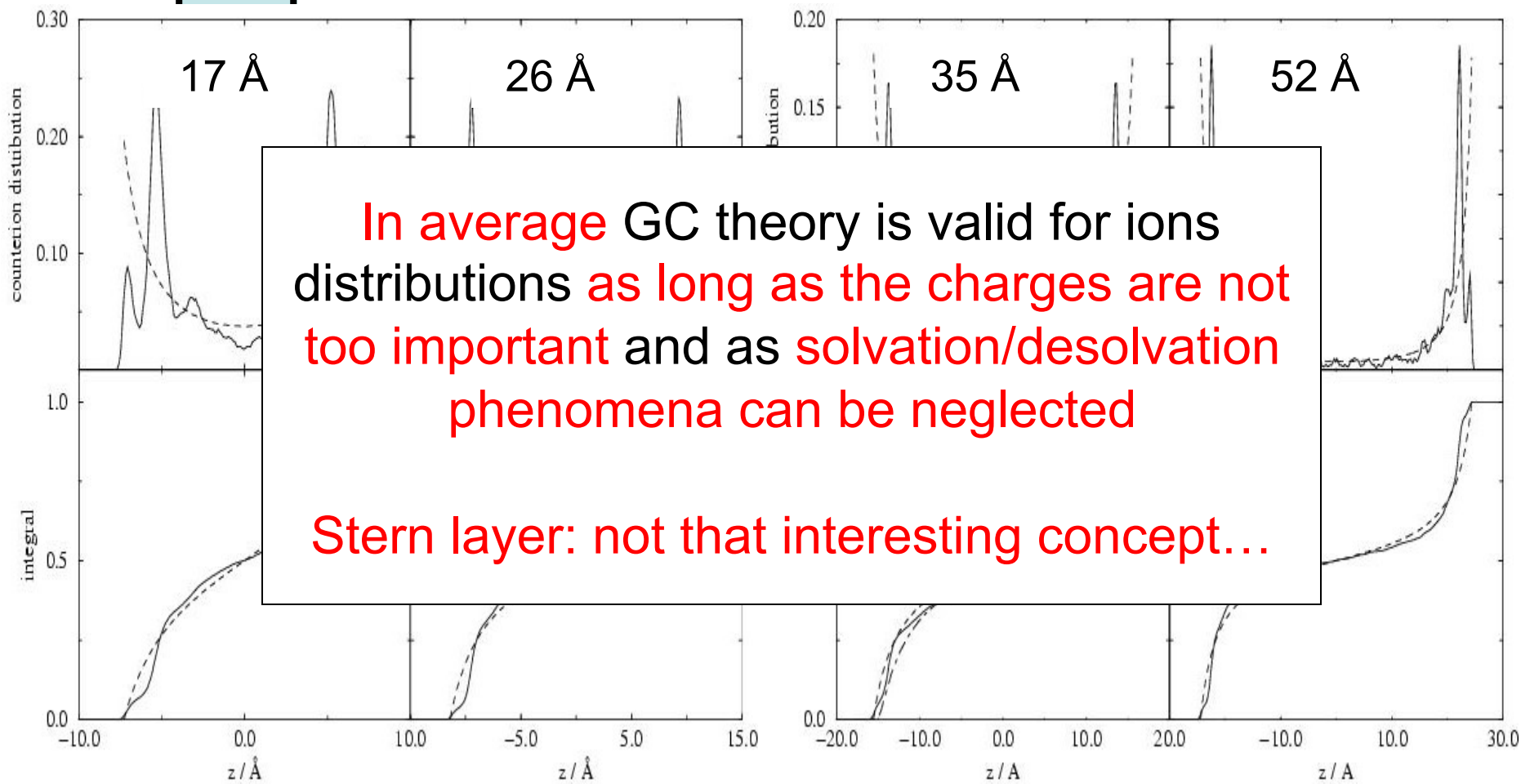


----- : Gouy-Chapman theory (PB equation) ——— Molecular model (Mol. Dyn.)

Molecular nature of the solvent



Counterions distributions around two charged sheets (clays)



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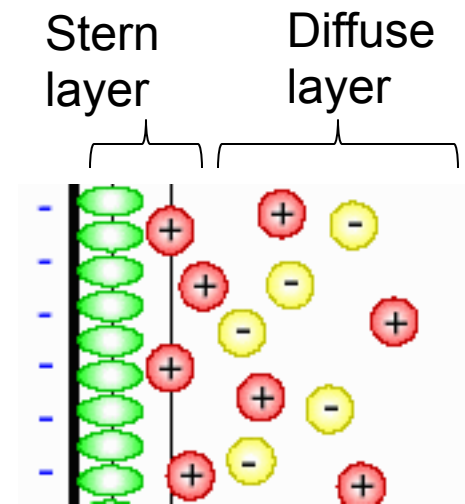
Poisson-Boltzmann (or Gouy-Chapman)

Specificity of ions

- ☞ only two parameters: charge and size with respect to the interface
- ☞ wrong at high ionic charge (typically if valency >2)
- ☞ neglect ion sizes whereas the concentration is very high !
- ☞ neglect the molecular nature of the solvent (desolvation)
- ☞ neglect polarisability forces (Van der Waals)
- ☞ Separation surface is fixed and it does not fluctuates

Stern layer

- ☞ all these effects are hidden in the Stern layer whose parameters can be fitted...

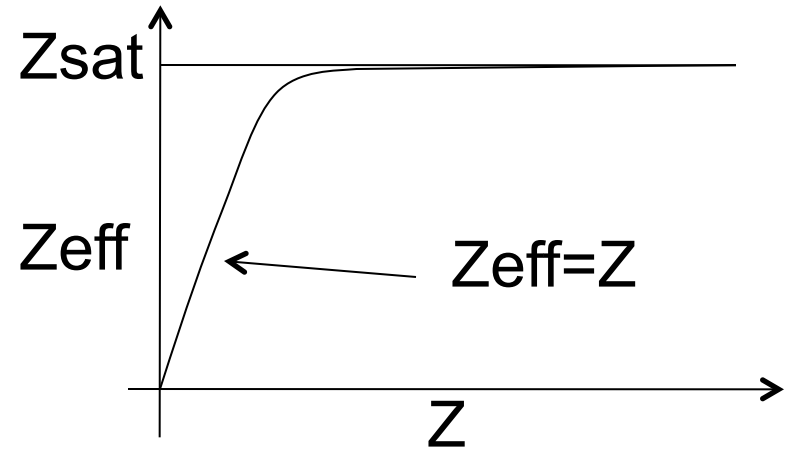
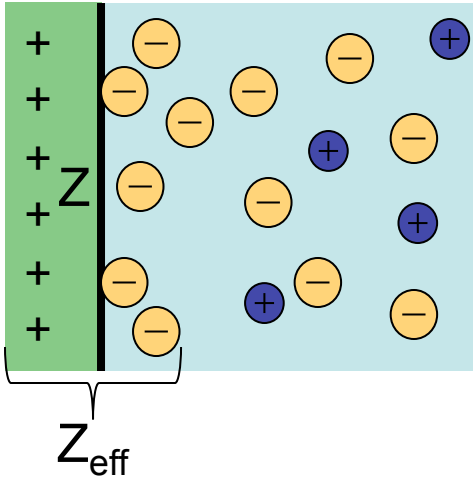




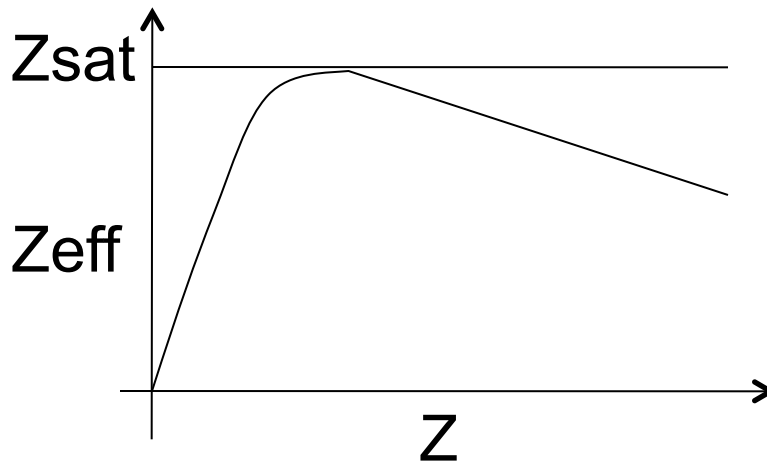
Ionic correlation effects (high valency 2 or 3)

Effects of the ionic correlations (highly charged ions)

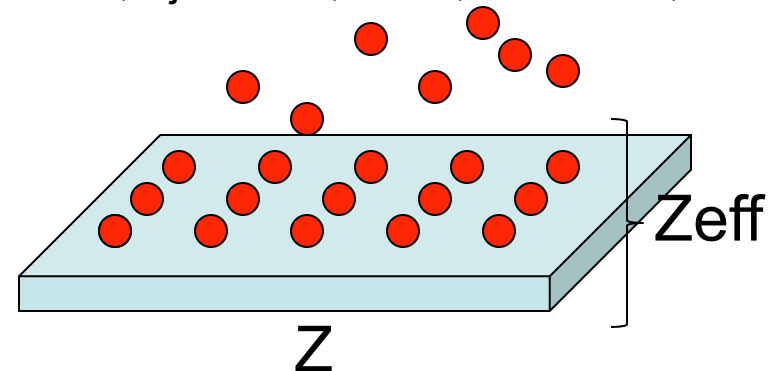
Effective charge (Z_{eff}) of the surface as a function of the natural charge (structural charge Z)



Electrolyte 2-2 or 3-3. Correlation effects



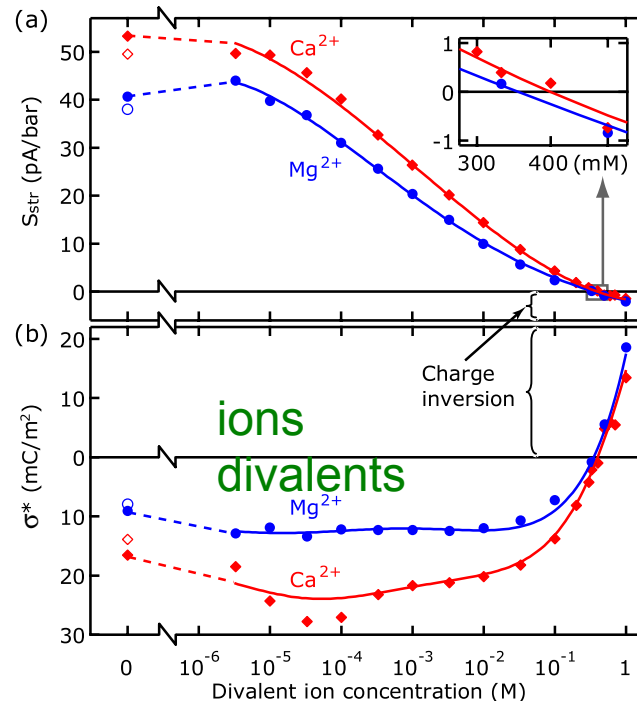
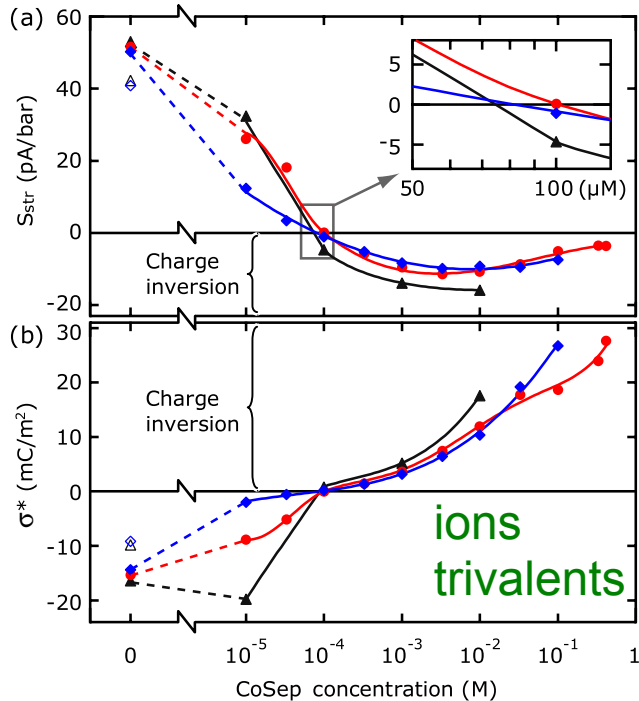
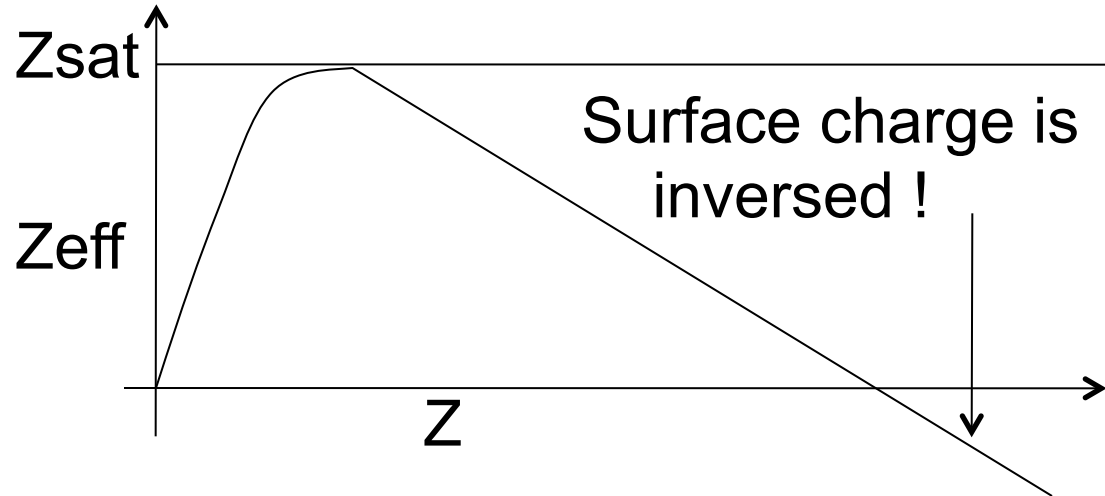
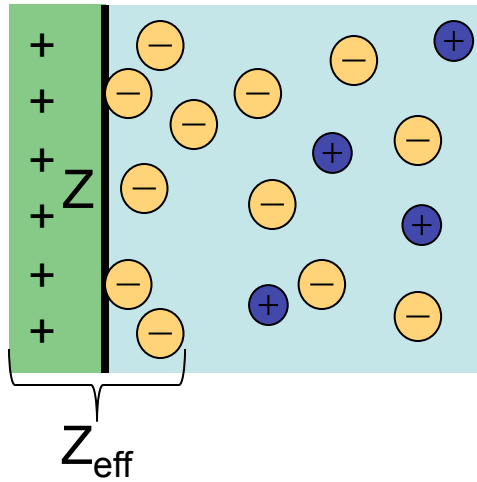
cf Alexander, Kjellander, Levin, Skhlovskii, etc





Inversion of surface charge

And even sometimes



Streaming current

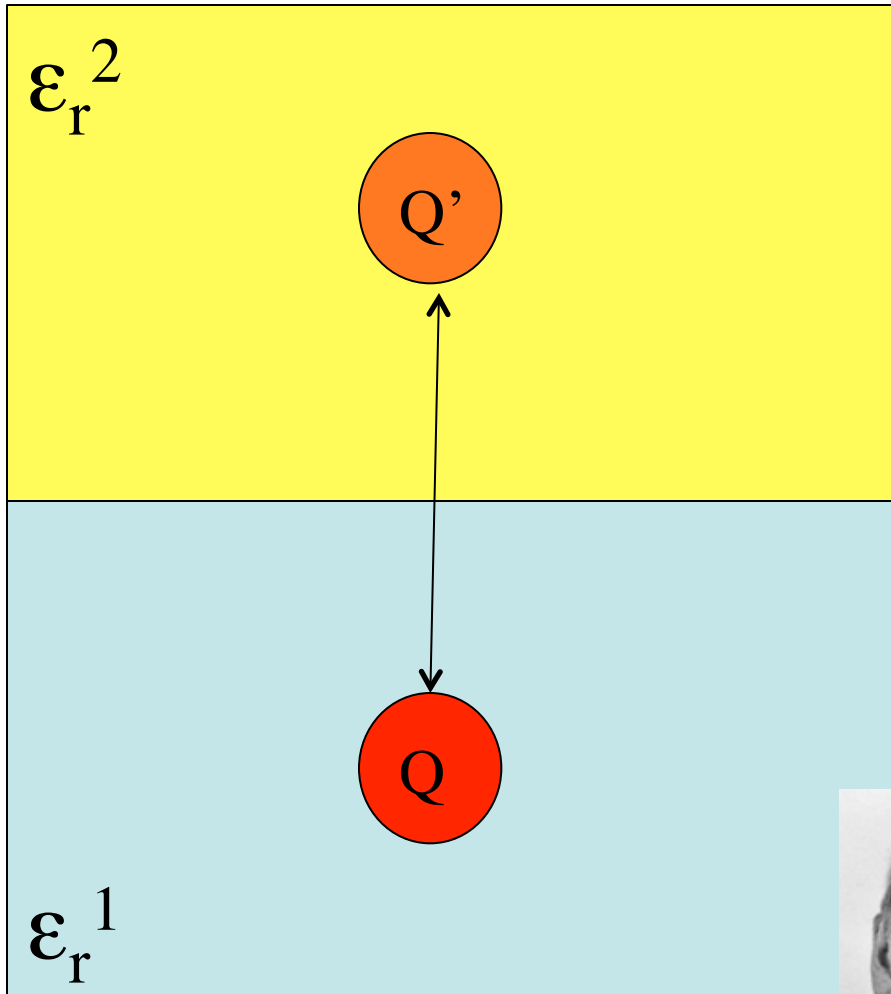
Effective charge

Exp: van der Heyden et al. PRL 2006



Polarisability of the solvents

Onsager and Samara



$$\epsilon_r^2 < \epsilon_r^1$$

Polarisability of the solvent

Ion close to the interface is expelled because of the solvent polarisation

Modelling: image charge Q'

$$Q' = \frac{\epsilon_r^2 - \epsilon_r^1}{\epsilon_r^1 + \epsilon_r^2} Q$$



Onsager and Samara

Molecular models

Big polarisable ions attracted by the interface

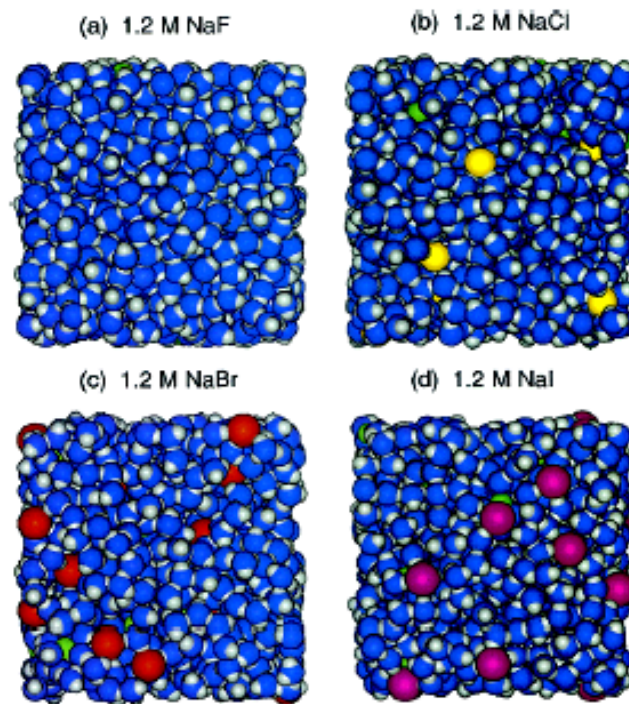
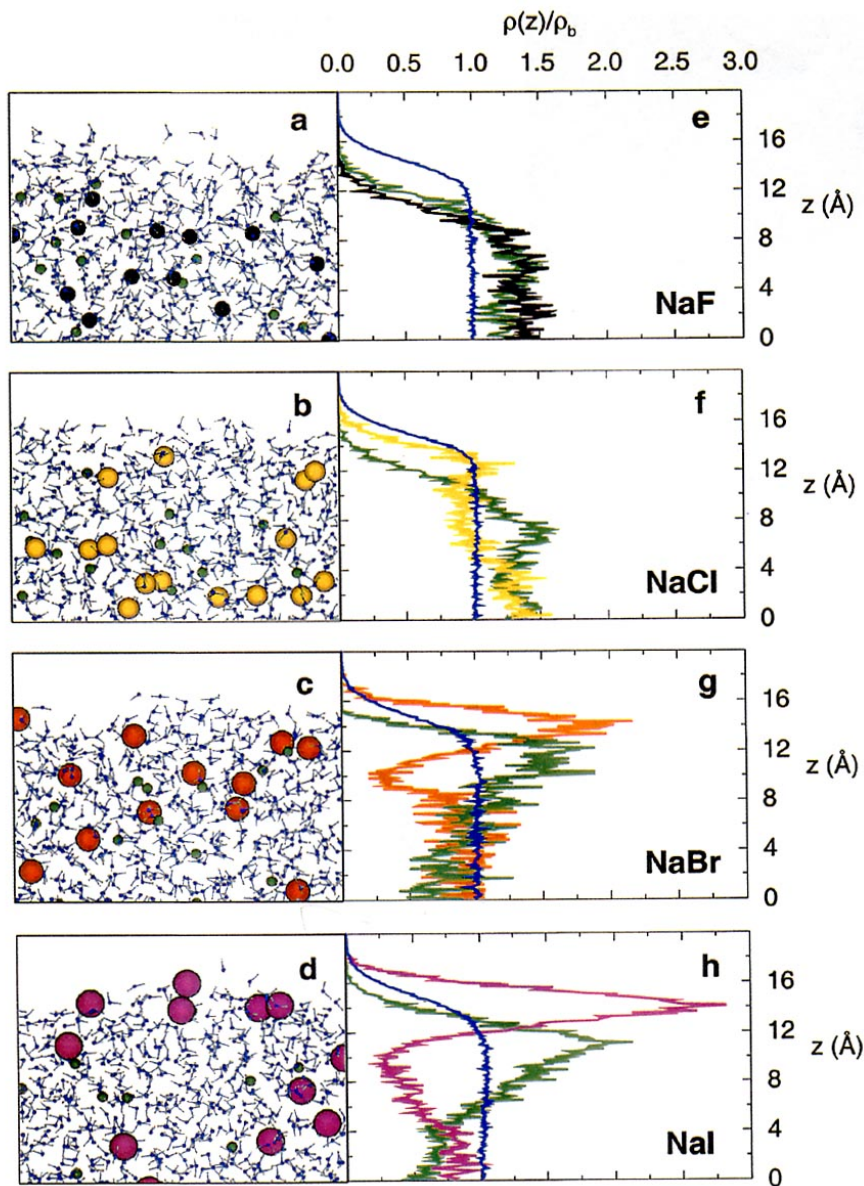
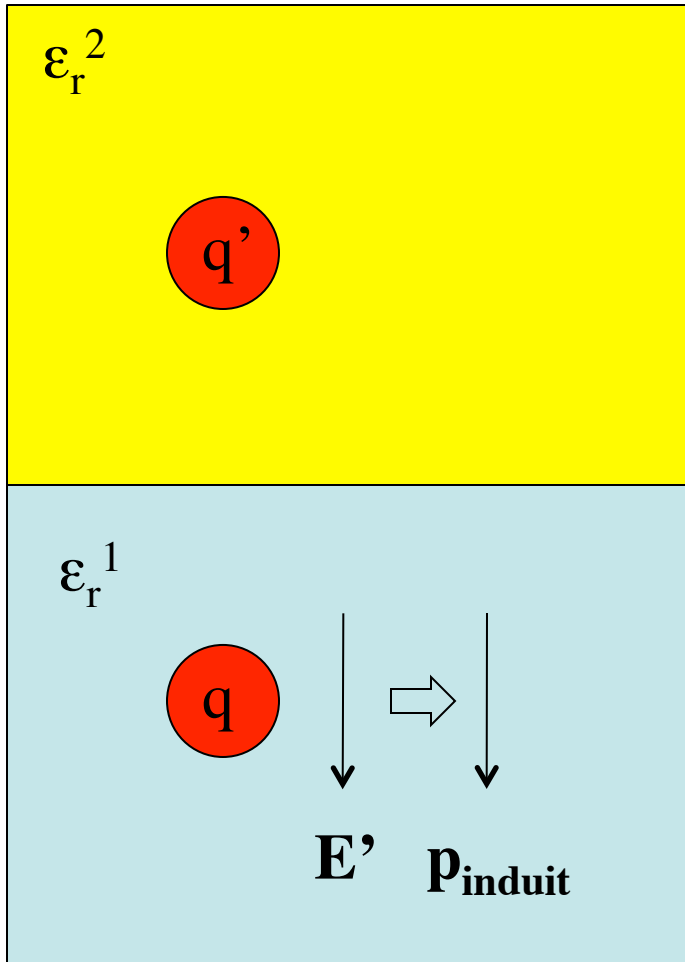


Figure 9. Snapshots viewed from the air side from MD simulations of the solution/air interfaces of 1.2 M sodium halide solutions: (a) sodium fluoride, (b) sodium chloride, (c) sodium bromide, and (d) sodium iodide. Coloring scheme: fluoride ion, black; chloride anion, yellow; bromide anion, orange; iodide anion, magenta; sodium cation, green; water oxygen, blue; water hydrogen, gray.



Polarisability of the ions

Ions attracted to a water/oil interface is it is polarisable



Effect due to the polarisation of the ions

The polarisation of the interface creates a dipolar moment on the ion which attracts it at the interface

Stabilizing effect

Depends strongly on the charge and polarisability of the ions

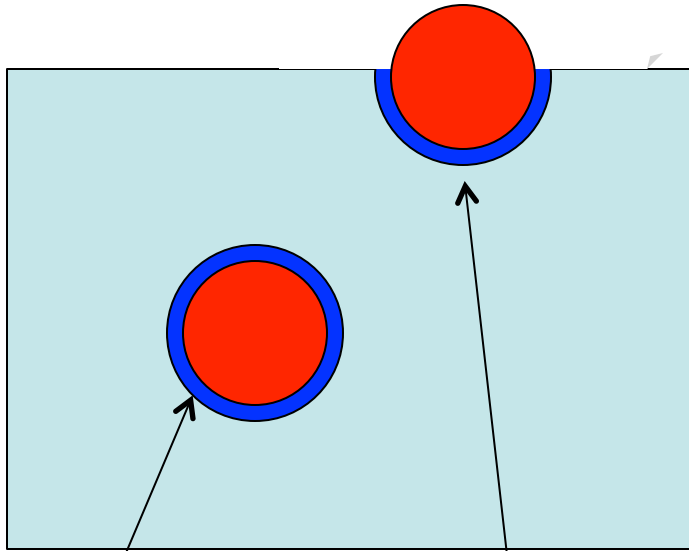
Numerically

$$G_{\text{image}} \approx k_B T \text{ for polarisable ions}$$



Depletion of big ions

A big size is enough to attract a big ion at the interface



Effect due to the solvent entropy

Can be calculated (Asakura et Oosawa potential)

Increases the polarisability attraction (big ions are polarisable)

Domain forbidden to the solvent because of the solvent molecule size

Smaller forbidden domain if the ion is at the interface
→ bigger solvent entropy
→ stable



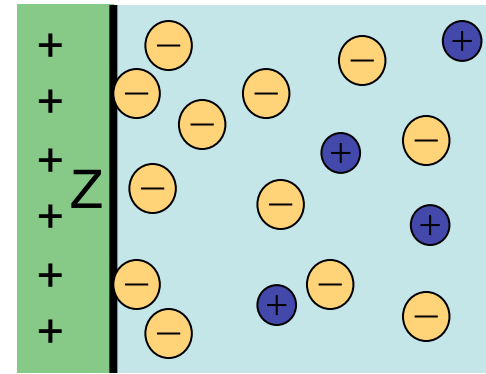
Brazilian Nuts effect



Role of the ion hydrated sizes

Size (hydrated diameter of the ions)

- Important role in solution (departure from ideality)



- **complex role** at interface

High ion concentration (condensed double layer):
enhance repulsion between counter-ions

Small ion concentration: +/- predominant → decreases
electrostatic attraction between + and - (add a
repulsion force between ion). EDL size is bigger.



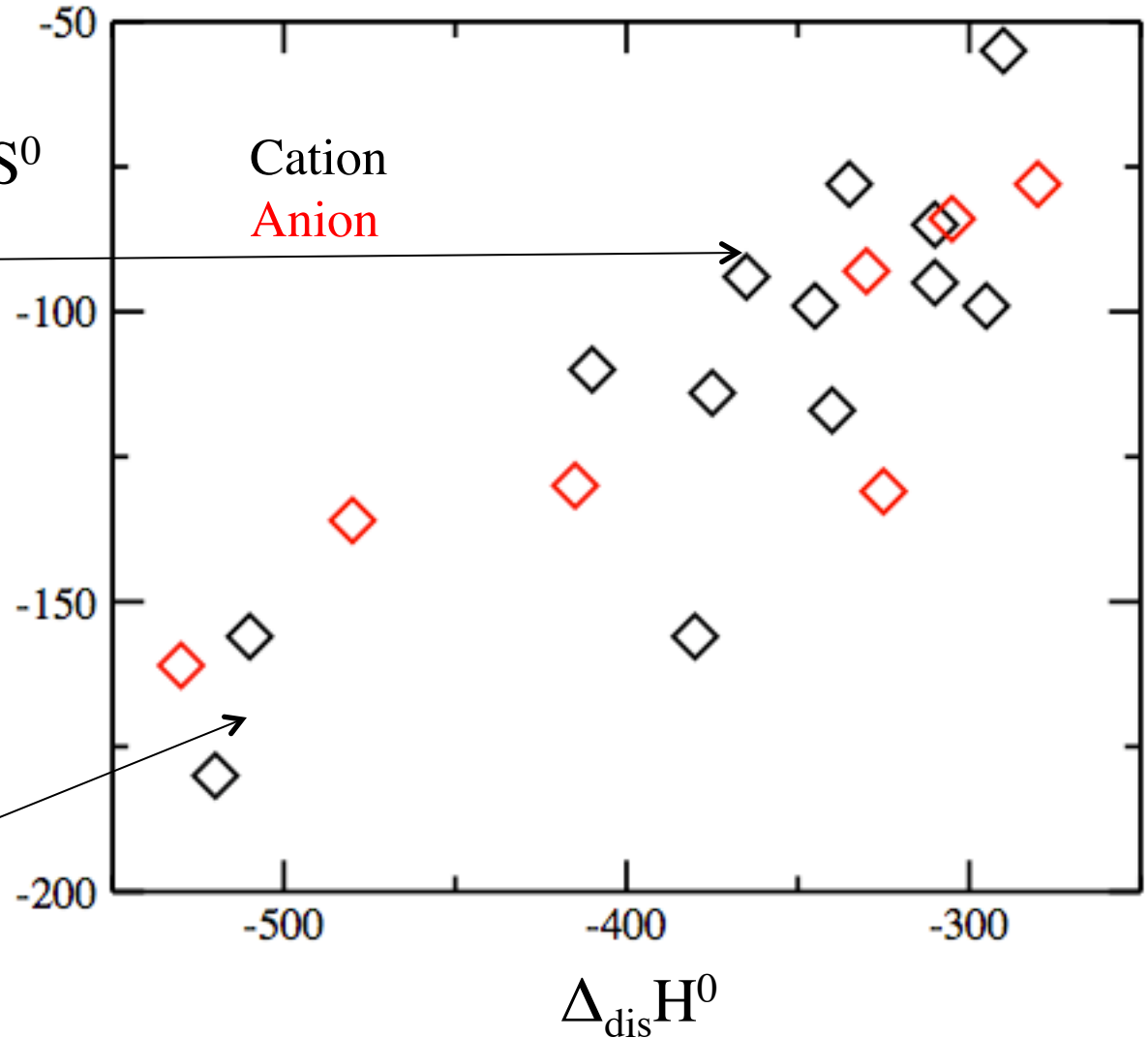
Size effects

Simple monovalent small ions

Big ions (ex I⁻)
low solvation
« Free » water
around these ions

$\Delta_{\text{dis}} S^0$

Cation
Anion



Small ions (ex Li⁺)
high solvation
Organized
solvation layer

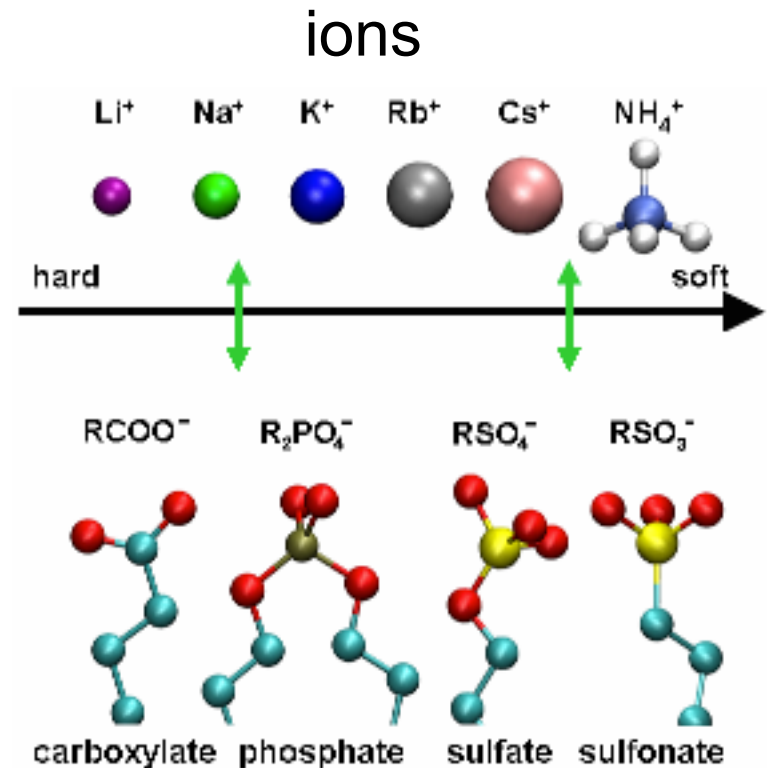


Corresponding rules

Small ions are preferentially associated to **small sites** (solvent expelled \rightarrow entropy gain)

Big ions are preferentially associated to **big sites** (they do not have to expell water to be associated)

solvation/desolvation
question : depends to the ion size compared to hte one of the interface site (hydrophobic/phillic force)

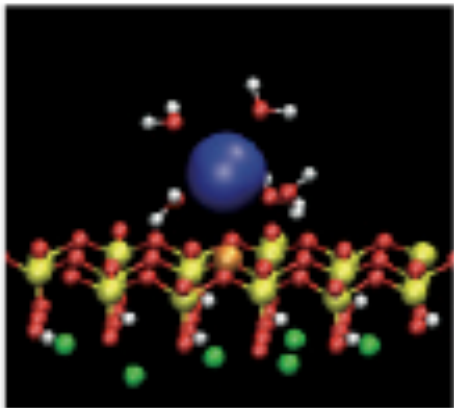


sites de surfaces

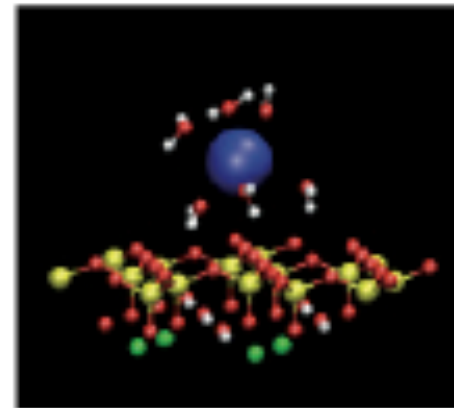


The Nature is not simple !

Molecular simulations of cations at a montmorillonite clay surface



Cs^+



Na^+

- **Cesium ions** are dehydrated because clay cavities exactly correspond to the ion size \rightarrow solvation by the surface instead of solvation by water
- **Sodium** (and further) ions stay solvated by water.

Beware of general laws...

Specific effects are subtle effects...