

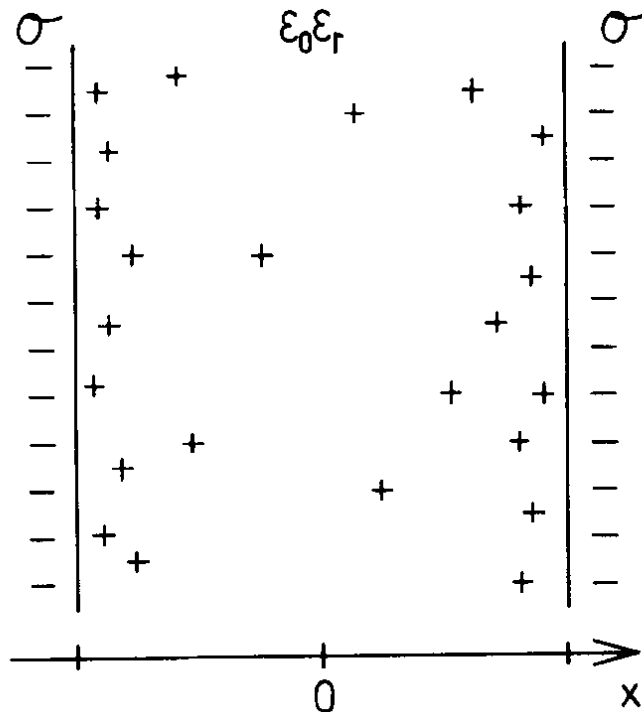
Appendix 3

# Models of clay colloid formation and stability

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# Electrostatics of charged layers



Model system of infinite planar uniformly charged surfaces with counterions and additional electrolyte In solvent (water).

Primitive model:

Solvent (water) represented by relative dielectric permittivity.  
Ions spherical, interacting according to Coloumb' s law, hard sphere at contact.

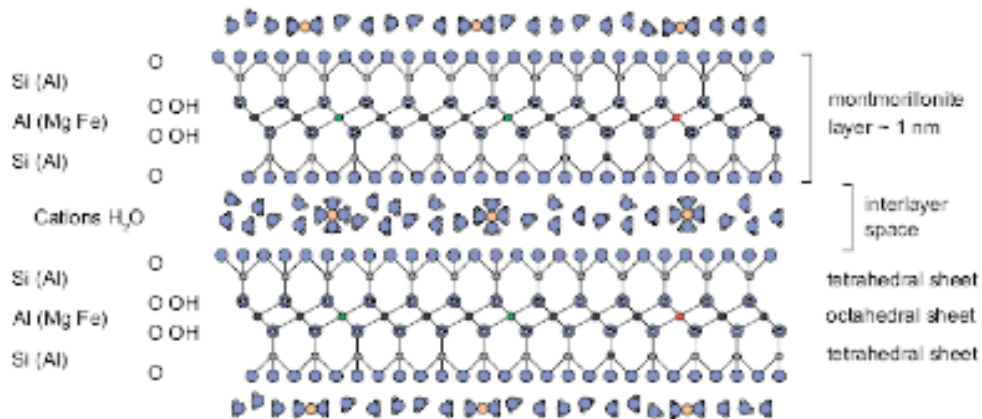
Theory in primitive model:

Poisson Boltzmann equation  
Monte Carlo computer simulations

Additional assumption:

Smearred uniform surface charge  
Perfectly flat surfaces.

# Swelling of layered structures



Degree of swelling is determined by:  
Forces between layers  
Chemical potential of solvent reservoir  
Possible equilibrium with solutes in external solvent.

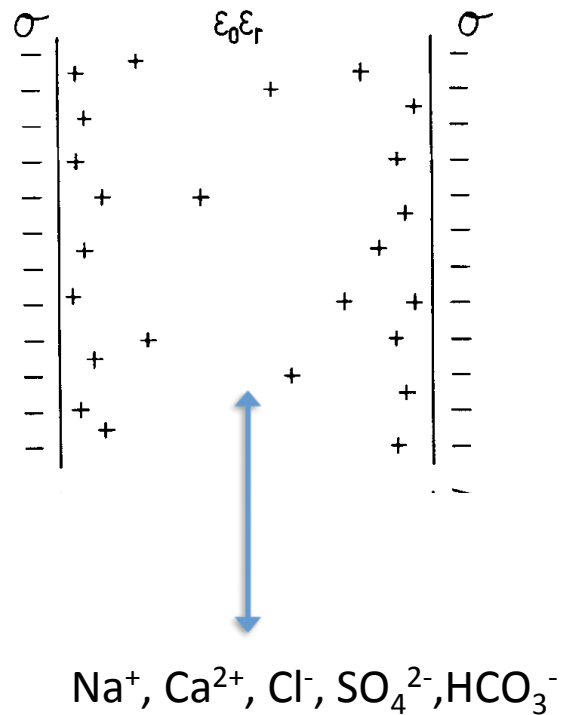
Figure 2.1 Structure of montmorillonite

Theory: DLVO-theory based on PB-equation for electrostatics (repulsion) and Hamaker constant description of van der Waals forces (attraction)

Observations for clays: Five scenarios

- i) No swelling in water or electrolyte (mica and many other clays minerals)
- ii) “crystalline swelling” i.e. swelling to distinct separations of one or two water layers
- iii) Swelling to a finite thickness (a few nanometers) of water layer
- iv) Finite swelling to a disordered arrangement of clay particles
- v) Indefinite swelling leading to a stable colloidal sol

# Ion exchange



Counterions and cations in the reservoir can exchange with ions in the layered clay.

Effect mainly determined by the charge of the ion and its concentration.

$\text{H}^+$ -ions shows large chemical specificity effects.

Over time exchange effects can lead to the transformation of a calcium clay to a sodium one or vice versa.

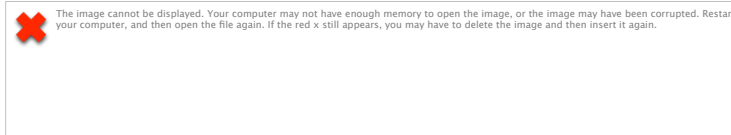
Multivalent ions are selectively picked up by clays.

Ion chemical potential is in PB approximation given by concentration at mid-plane and electrostatic potential at mid-plane (relative to bulk).

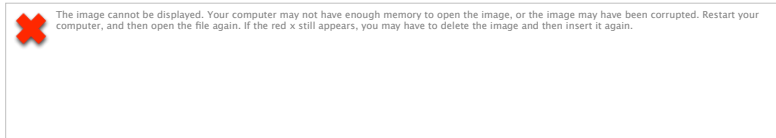
# Stability of sols

DLVO-theory:

electrostatic repulsion:



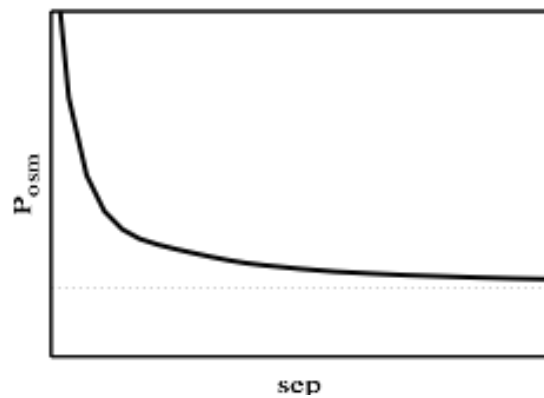
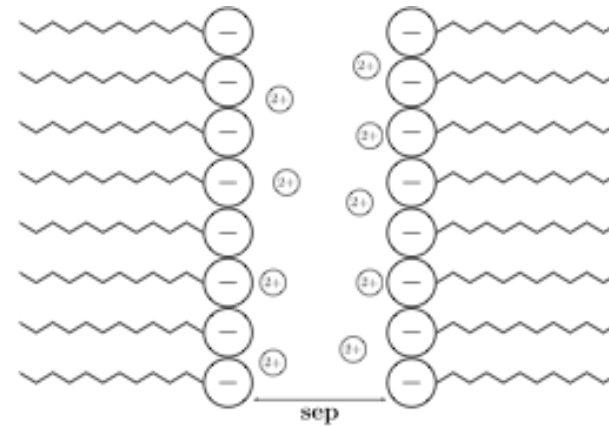
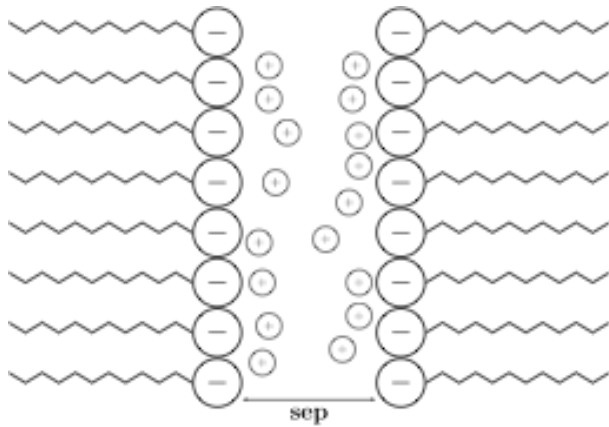
Van der Waals attraction:



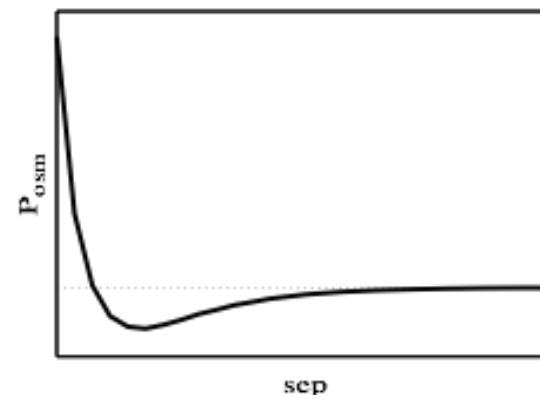
Ion correlations give  
electrostatic attraction

Attractive edge-side  
interactions can give  
“card-house” packing.

# Electrostatic interactions with correlations

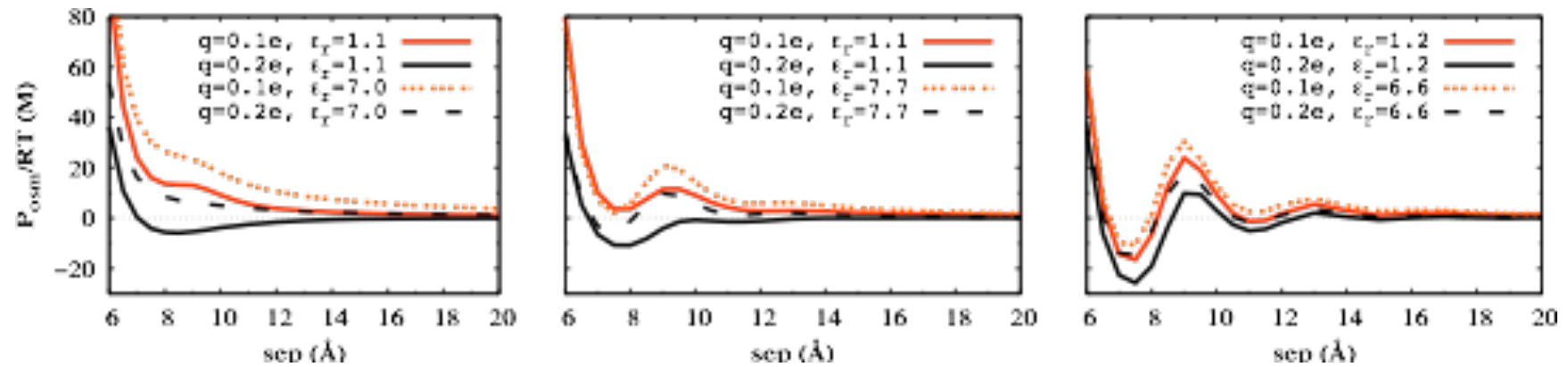


Monovalent counterions



Divalent counterions

# Ion correlations and solvent effects



Primitive model

Explicit solvent

lower density

higher density

# Reflections on the contents of reports provided by SKB

(report received 28/10 not included)

- Na-montmorillonite or bentonite erode when exposed to pure water
- Ca-montmorillonite or bentonite stays intact when exposed to pure water of solutions of  $\text{CaCl}_2$  or gypsum.
- Na-montmorillonite or bentonite does not erode when in contact with more concentrated NaCl-solutions. No real consensus on value of critical concentration.
- Presence of  $\text{Ca}^{2+}$  ions in NaCl-solutions narrows conditions under which erosion occurs. The reports don't give a satisfactory account of this effect.
- Role of interaction edge-side isn't fully investigated.

