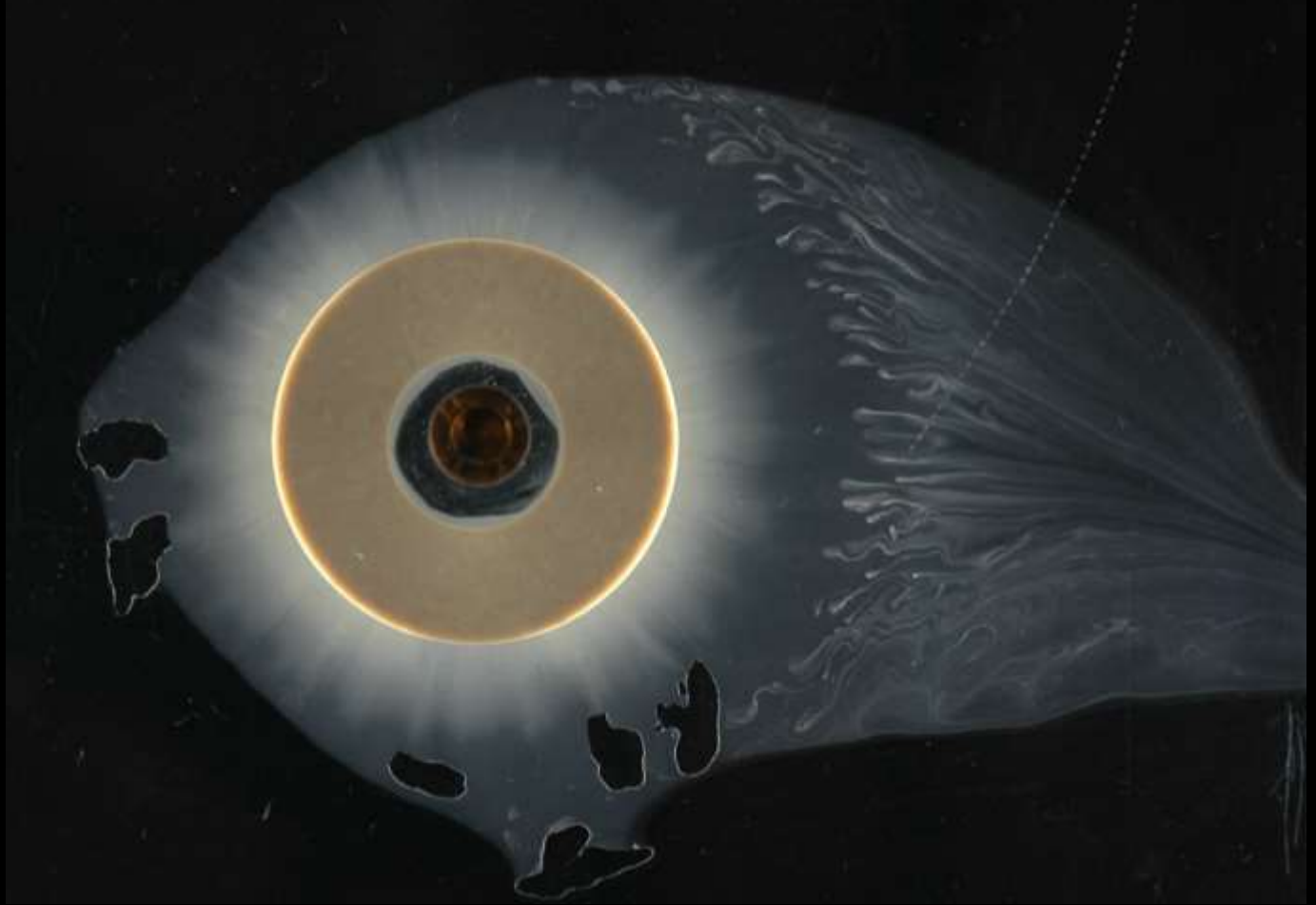
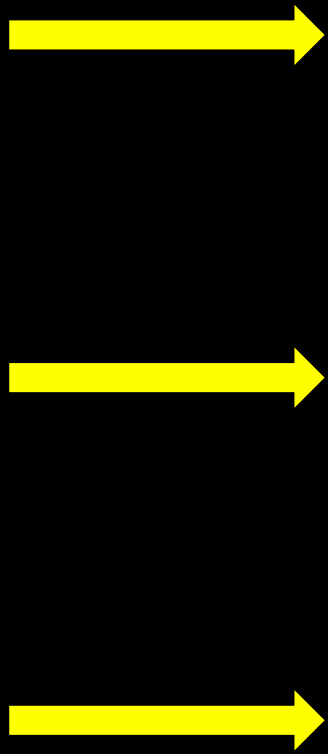


INFLUENCE OF TEMPERATURE ON SMECTITE CLAY GELS

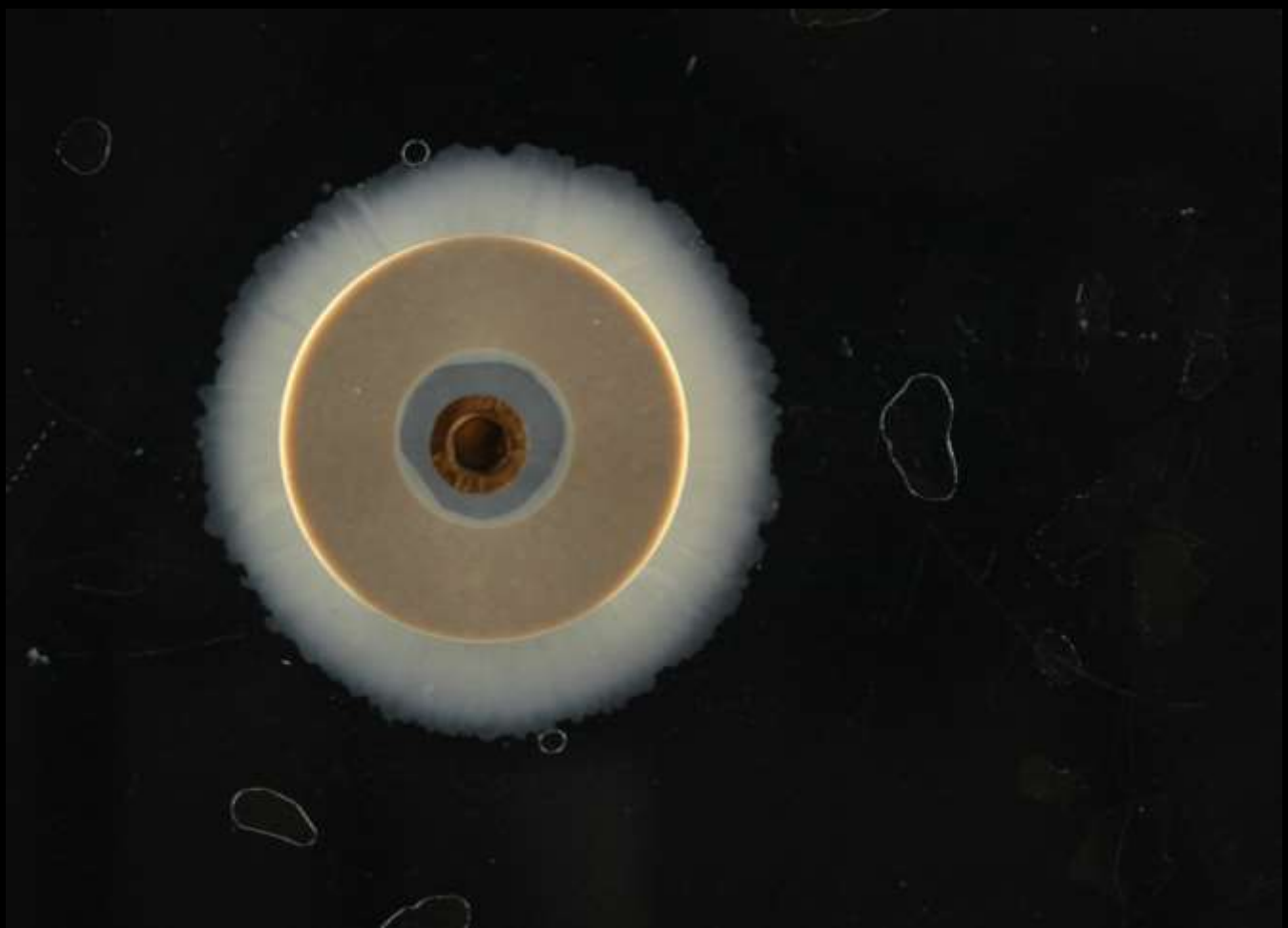
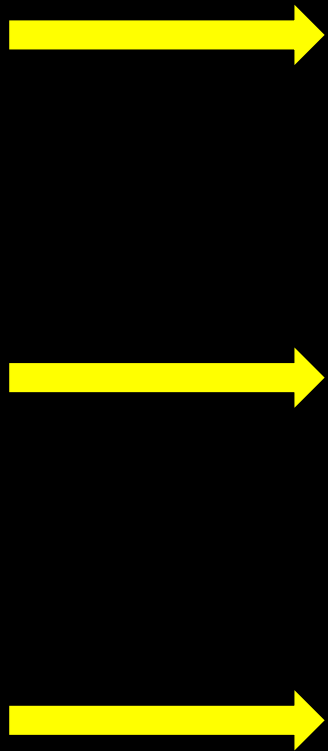
Emelie Ekvý Hansen
Magnus Hedström
Clay Technology AB

Clay Colloids in Aqueous Systems, Berlin 3-4 Feb. 2016

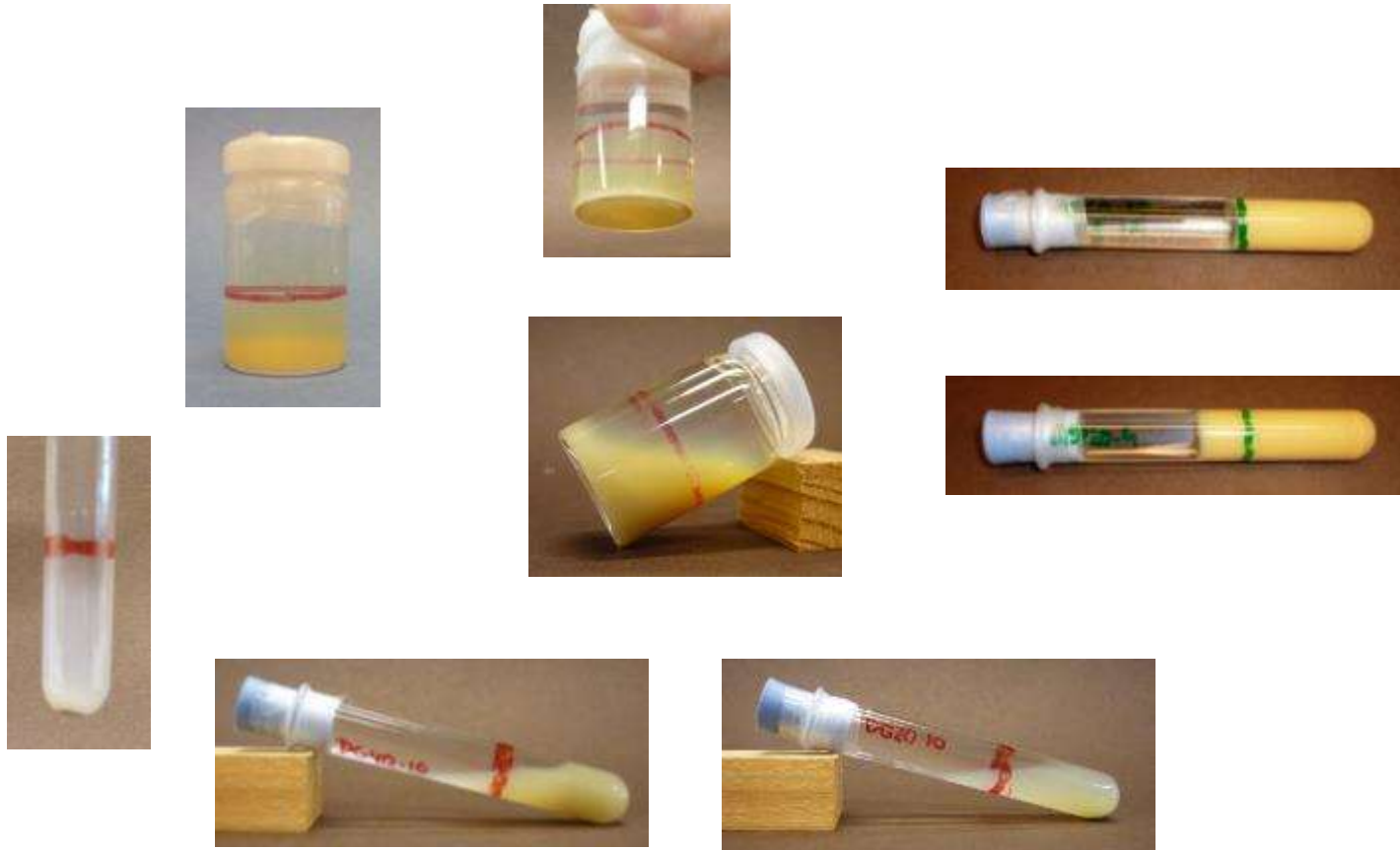
Erosion at low salinity



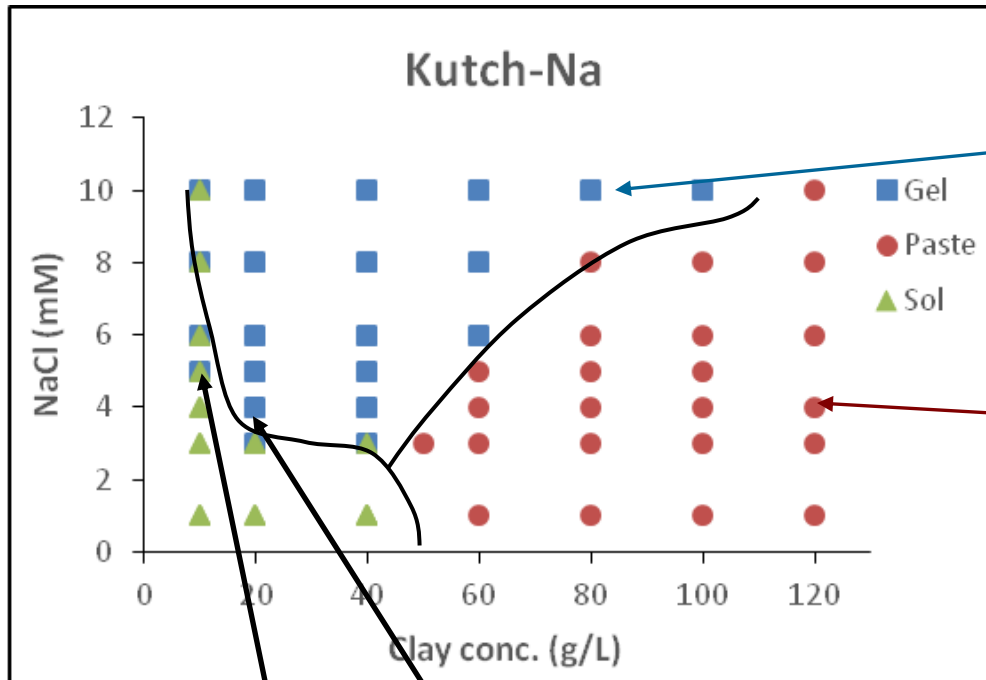
Formation of gel prevents erosion



Clay phases – from sol to gel



Phase diagram ionic strength, clay concentration



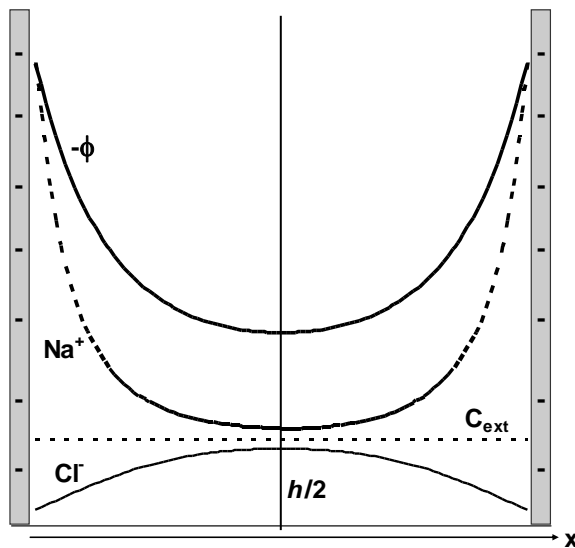
Immediate gelation

What forces cause gelation?

Gel formed within 18 h

Colloid stability

- Conditions for sol to be stable
- Range of repulsion extend beyond distance where attraction is $\sim kT$ or less



DLVO theory

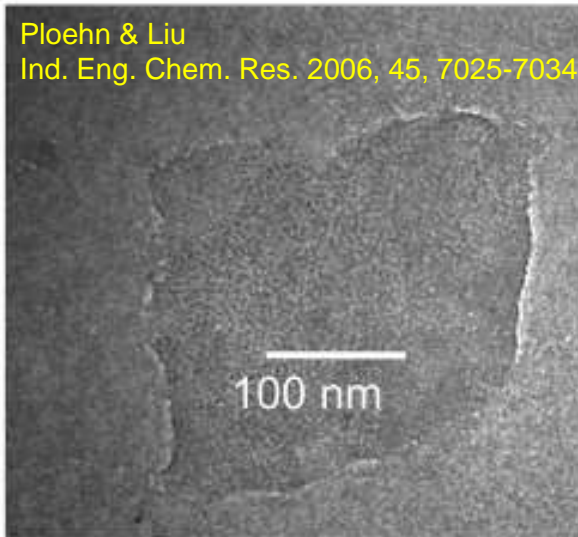
Parallel clay layers

Poisson-Boltzmann: osmotic repulsion

van der Waals attraction: Hamaker

van der Waals $\sim kT$

Ploehn & Liu
Ind. Eng. Chem. Res. 2006, 45, 7025-7034



$$\frac{F_{\text{vdW}}}{\text{area}} = -\frac{A_H}{6\pi} \left(\frac{1}{h^3} + \frac{1}{(h+2\delta)^3} - \frac{2}{(h+\delta)^3} \right)$$

$$\frac{U_{\text{vdW}}}{\text{area}} = -\frac{A_H}{12\pi} \left(\frac{1}{h^2} + \frac{1}{(h+2\delta)^2} - \frac{2}{(h+\delta)^2} \right)$$

$$A_H = 5kT \sim 2 \cdot 10^{-20} \text{ J}$$

$$\text{area} = 10^5 \text{ nm}^2$$

$$\delta = 1 \text{ nm}$$

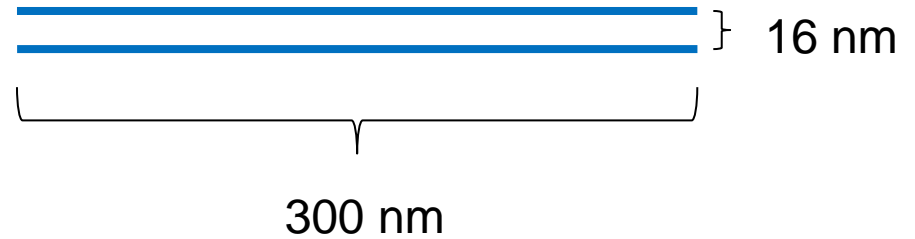
$$h = 16 \text{ nm} \rightarrow U_{\text{vdW}} = -1kT$$

van der Waals $\sim kT$

$$A_H = 5kT$$

$$\text{area} = 10^5 \text{ nm}^2$$

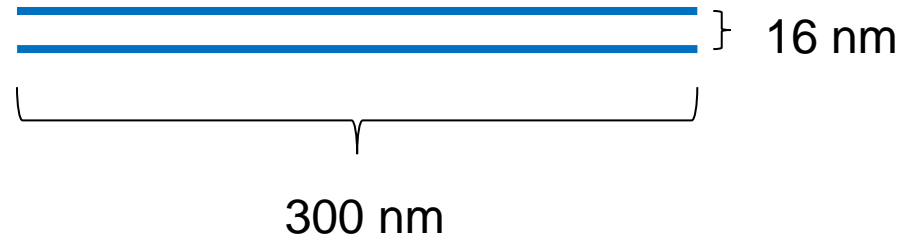
$$h = 16 \text{ nm} \rightarrow U_{\text{vdW}} = -1kT$$



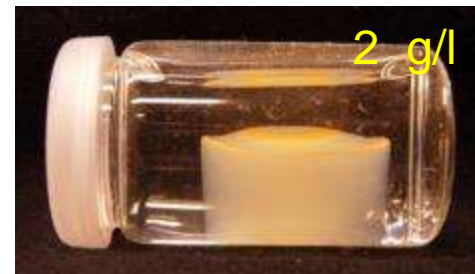
Volume fraction $\phi_c = 1/17$
160 g clay/l

van der Waals insignificant for gelation

$$A_H = 5kT$$
$$\text{area} = 10^5 \text{ nm}^2$$
$$h = 16 \text{ nm} \rightarrow U_{\text{vdW}} = -1kT$$

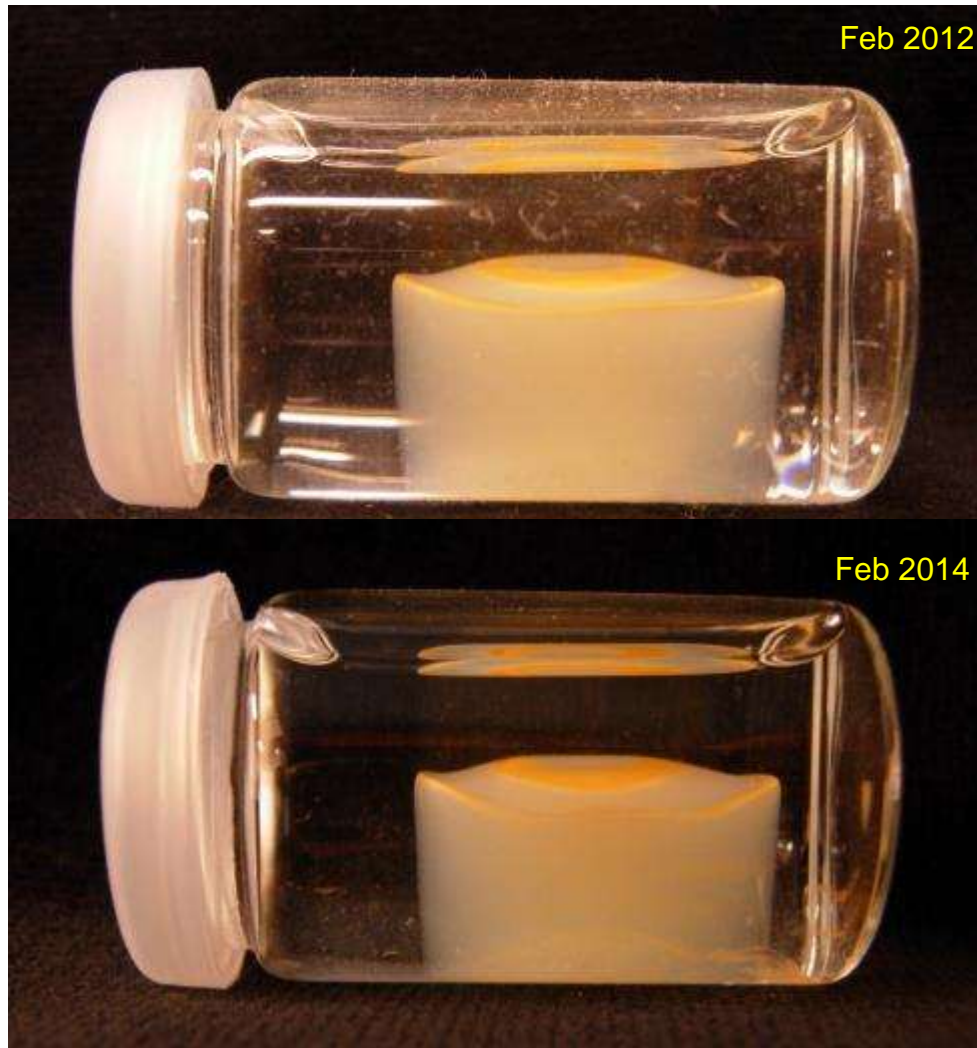


Volume fraction $\phi_c = 1/17$
160 g clay/l

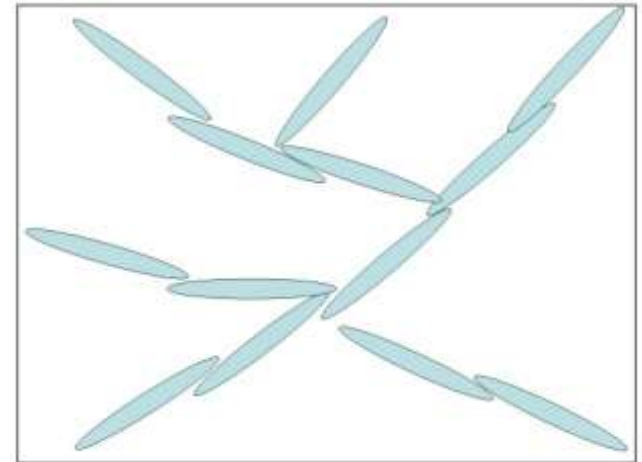


Conclusion: Gelation is not caused by van der Waals interaction

Structure of smectite gels



Proposal

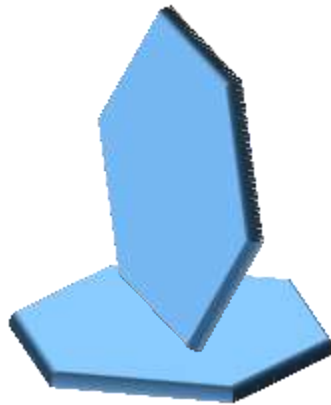


~1400 nm of water between clay layers
Diameter of typical clay platelet 100-500 nm

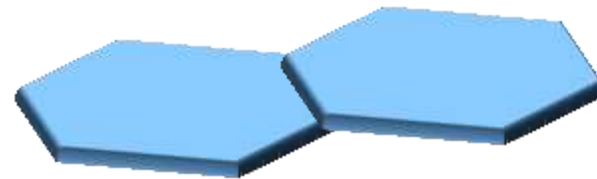
Hypothetical binding modes in gels

Face (-) – edge(+) attraction

T-shape

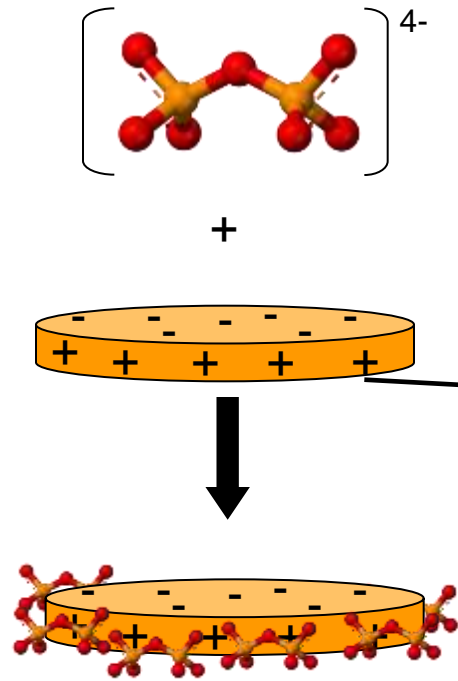


Overlapping coin

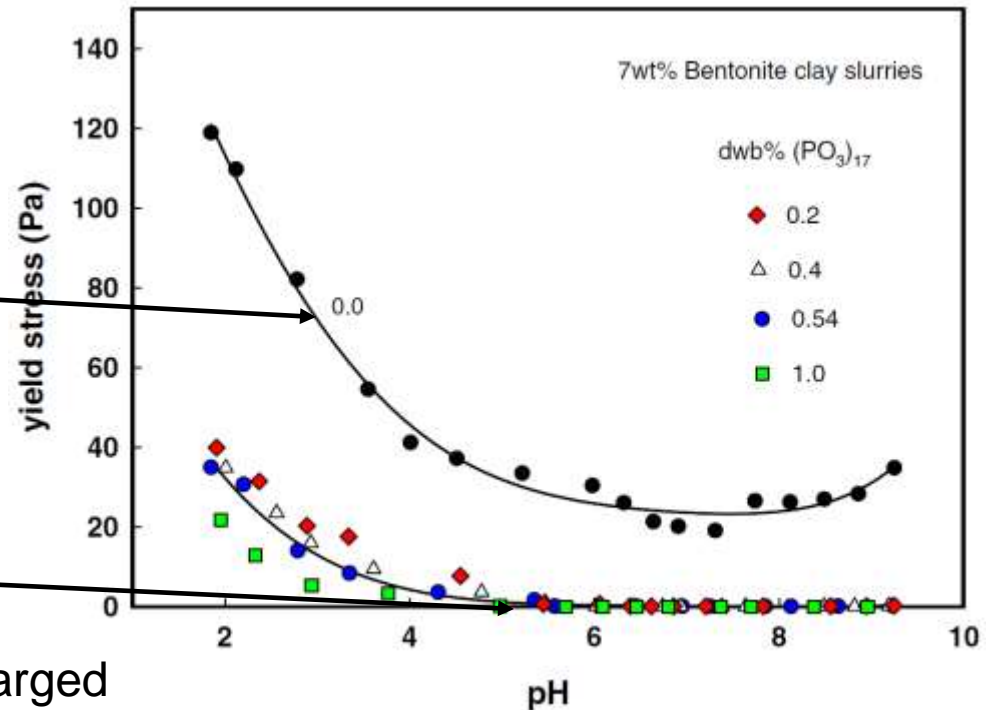


Edge(+) – face (-) interaction

Effect of polyphosphates



Yield stress in 7 wt% bentonite slurry

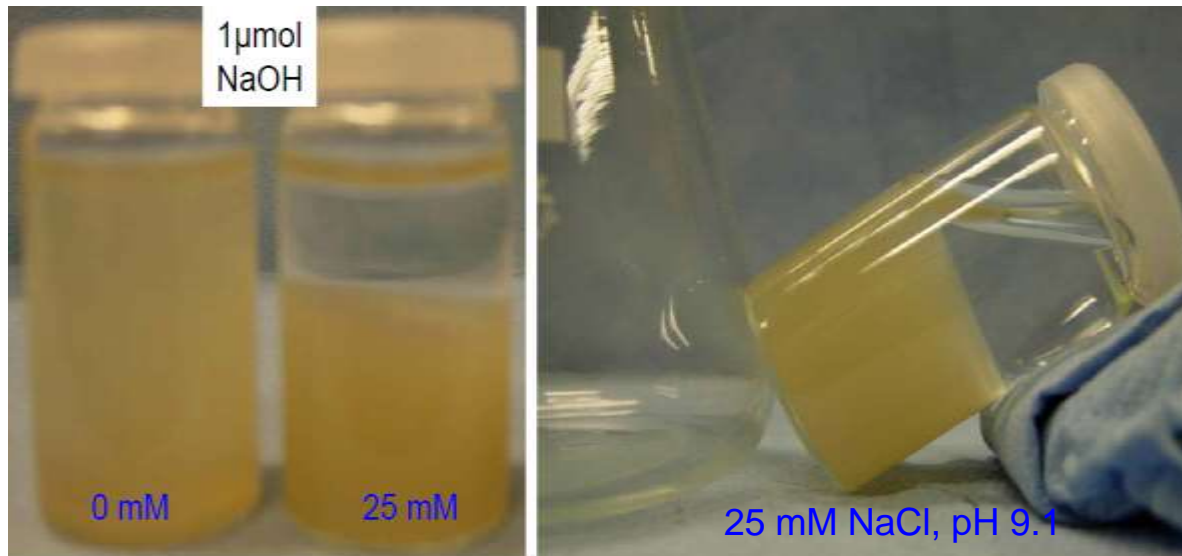
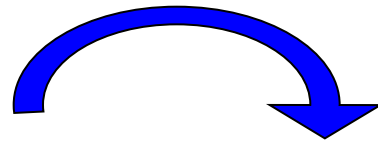


Goh., Leong, Lehane *Rheol. Acta.* **50**, 29-38 (2011).

Both edge and face negatively charged
gel → sol

Indirect “proof” of positive edge charge

Ionic strength determines gel formation



Birgersson et al. SKB-TR 09-34 (2009).

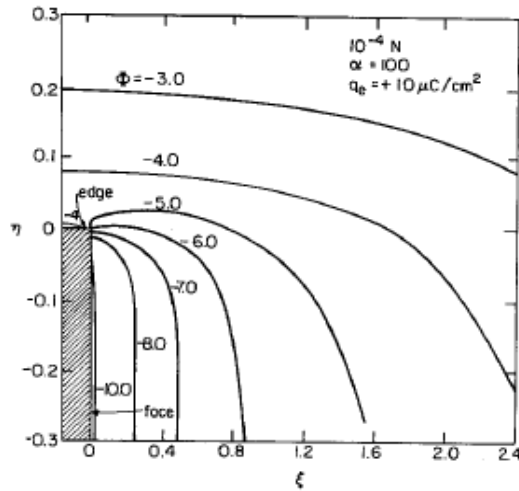
The nature of the clay edge charge must still be positive at high pH

Edge(+) – face(-) attraction

- Is it possible to demonstrate this hypothesis without modify the clay i.e. without pyrophosphate?
- Is there a way to test the concept of spillover of negative potential from faces to edge-region?

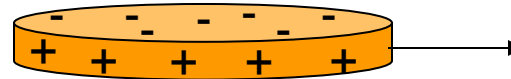
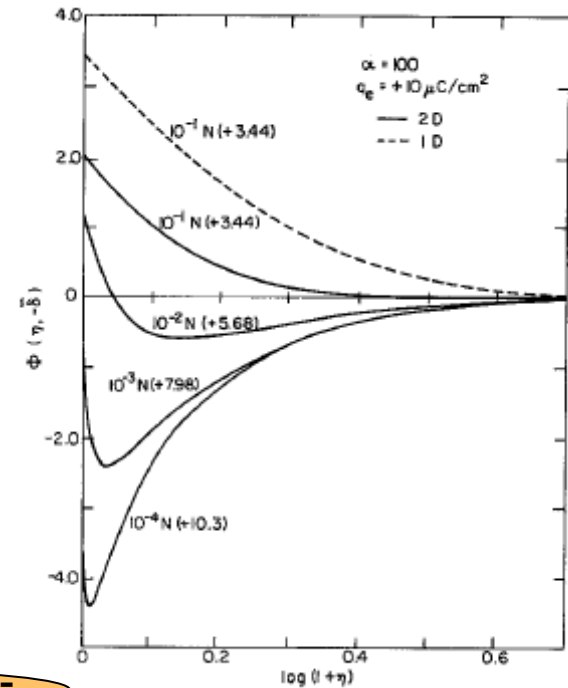
Spillover of diffuse double layers

Equipotentials around a montmorillonite particle



The positive potential near the positive edge is hidden due to spillover of negative potential from the face

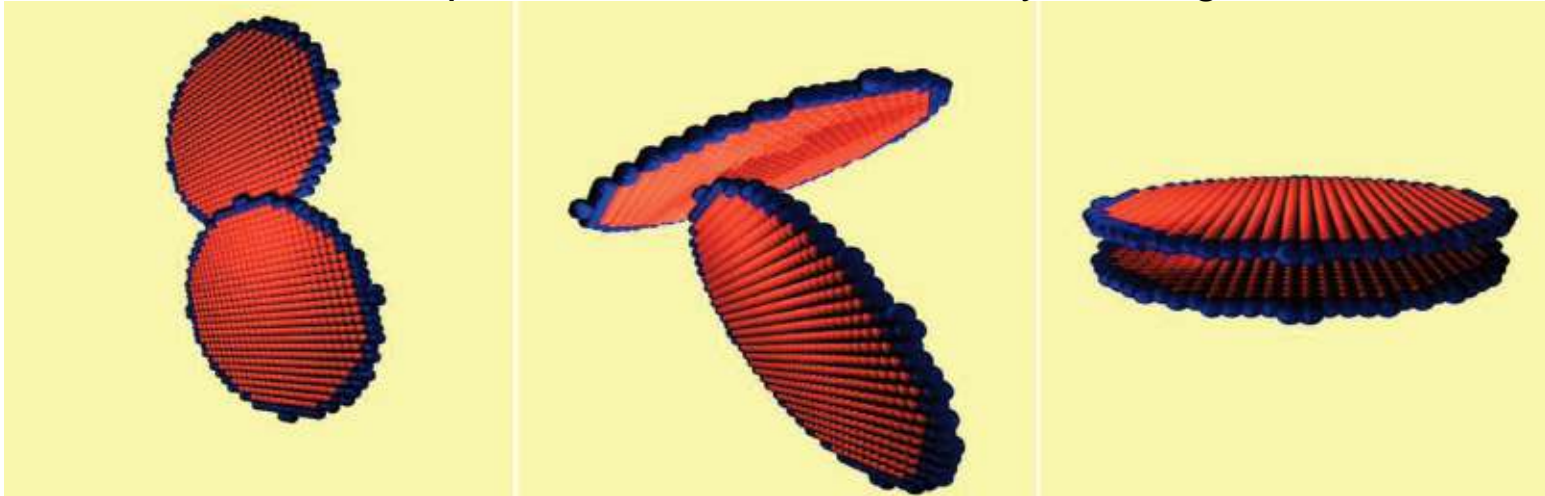
Electrostatic potential along the montmorillonite particle's midplane



Poisson-Boltzmann calculation by
Secor & Radke, *J. Colloid Interf. Sci.* **1985**, 103, 237.

Monte Carlo: Screened Coulomb interactions + vdW

Laponite-like w.r.t. size and layer charge



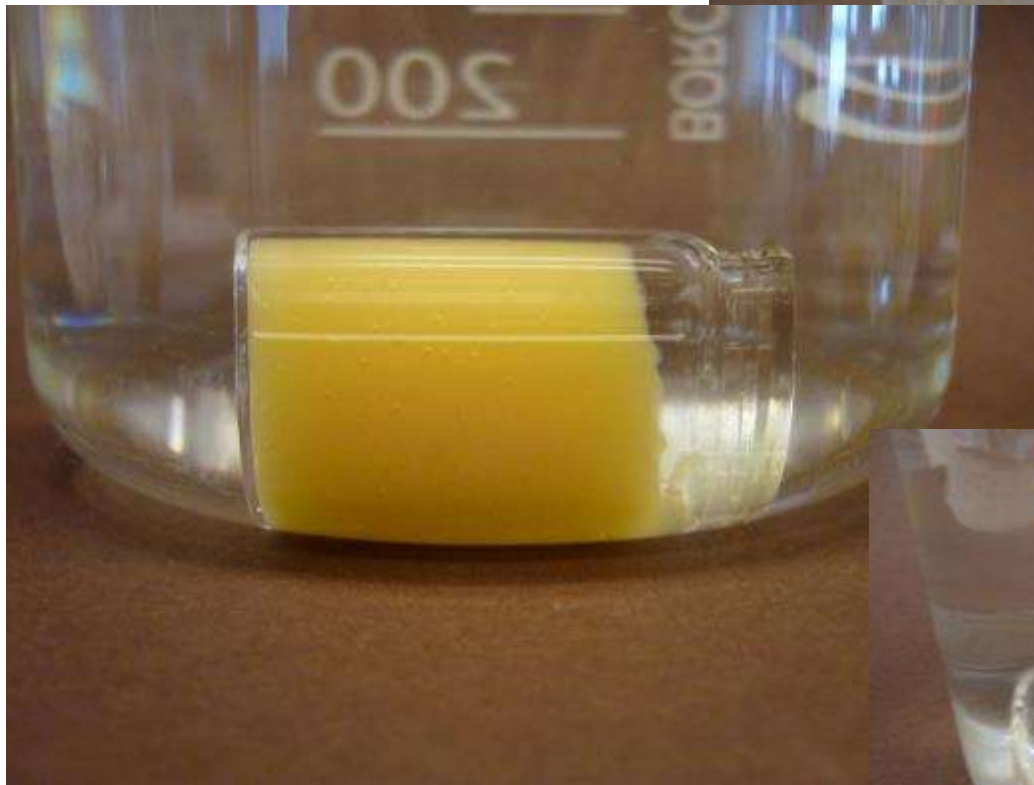
Jönsson, Labbez, Cabane Langmuir 24, 11406 2008.

Above ~200 mM most electrostatic interactions are screened and van der Waals dominates

Effect of screening due to excess NaCl

- Screening make the spillover smaller
- Screening applies both to positive and negative charge
 - Thus electrostatic attraction will also be weakened
 - Competition between spillover and weakened electrostatic attraction
- There might be a maximum strength of the gel at an intermediate NaCl conc.
 - at *sufficiently* high concentration van der Waals will be the important attraction
- Test this prediction/hypothesis by heating clay gels

Response to increased temperature



At the “transition” temperature

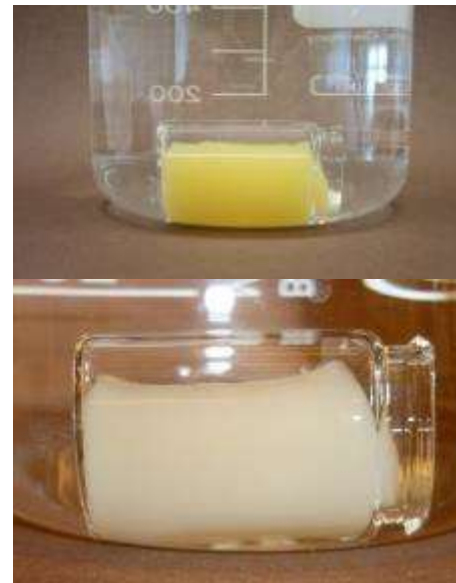
Melting

- Transfer from a gel to a liquid
- Loss of solid-like structure
- Exhibits a flow
- Return to gel on cooling



Deformation

- Retention of some solid-like structure
- Behaves partly as a liquid

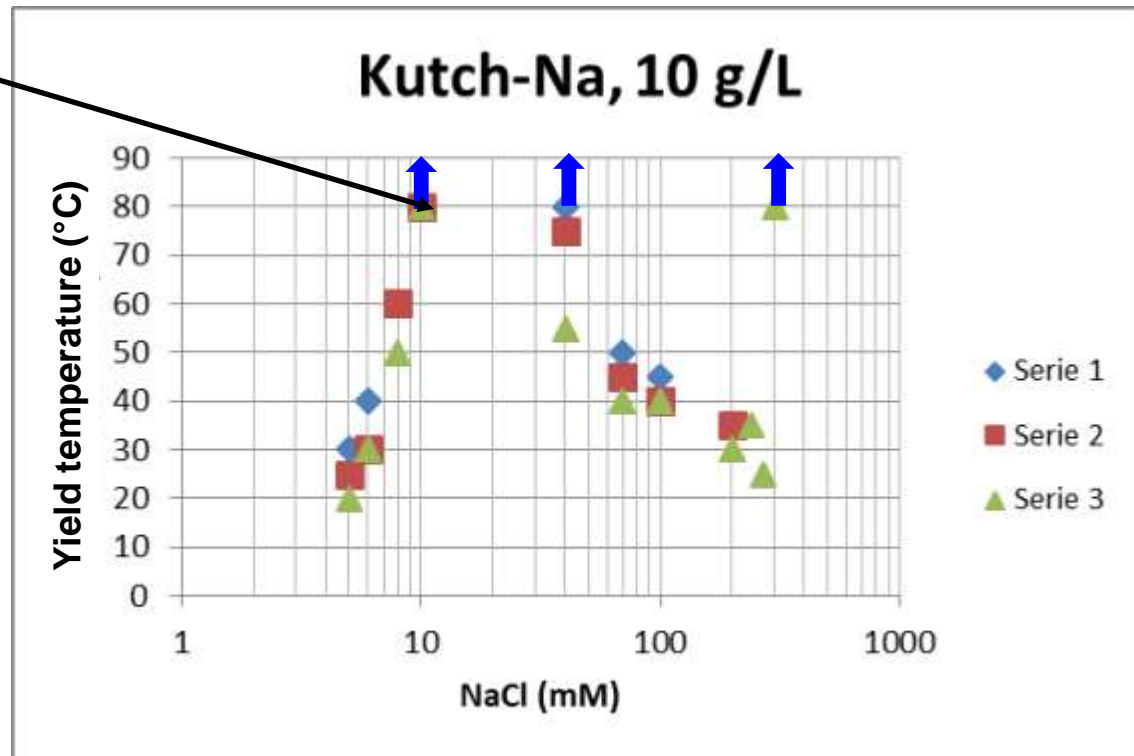


Yield temperatures of attractive gel Ionic strength influence

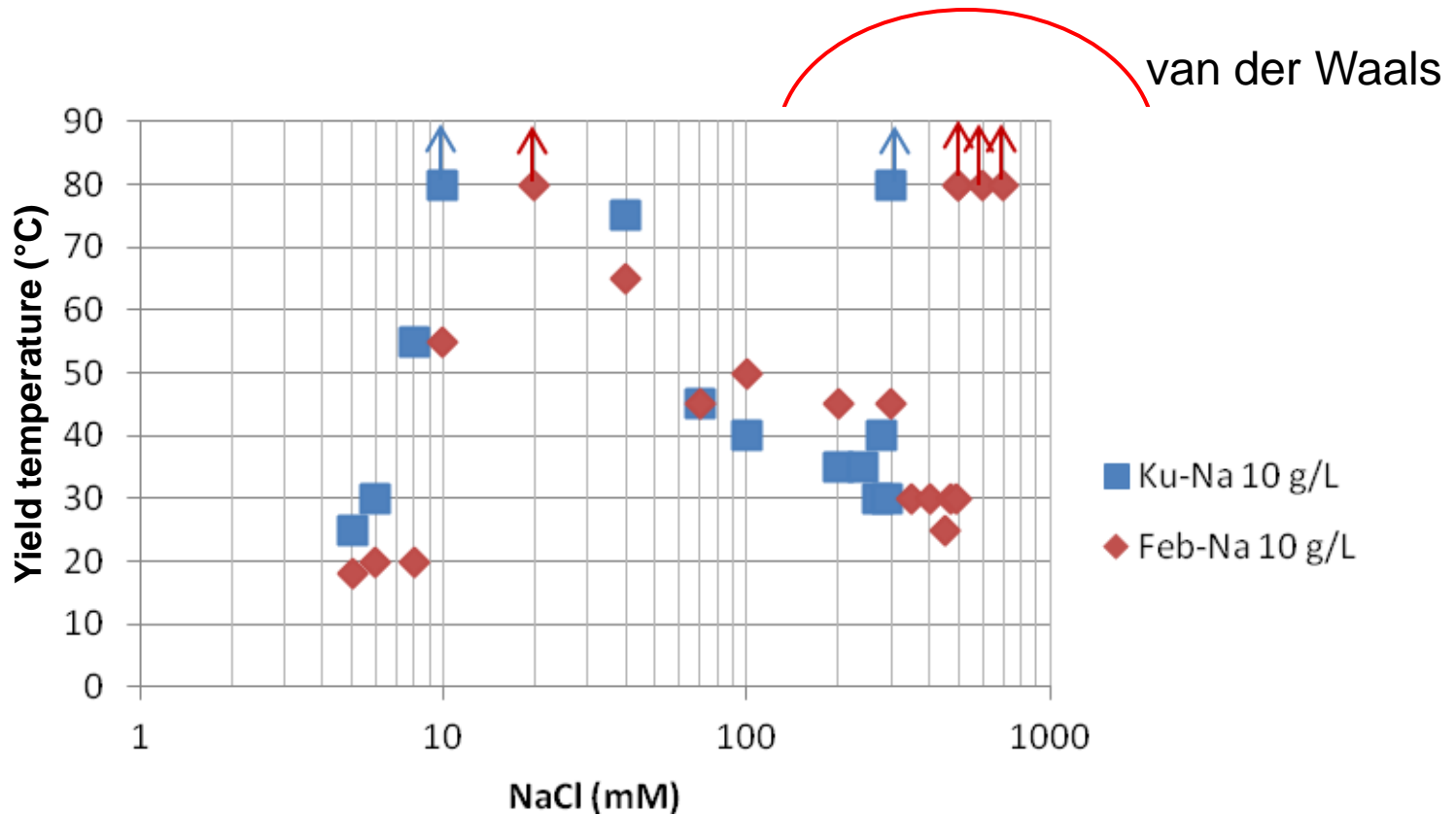
First sign of deformation upon heating → transition temperature

Transition not observed

The ionic strength have a direct impact on the strength of the inter-particle bonds, in accordance with the spillover effect.

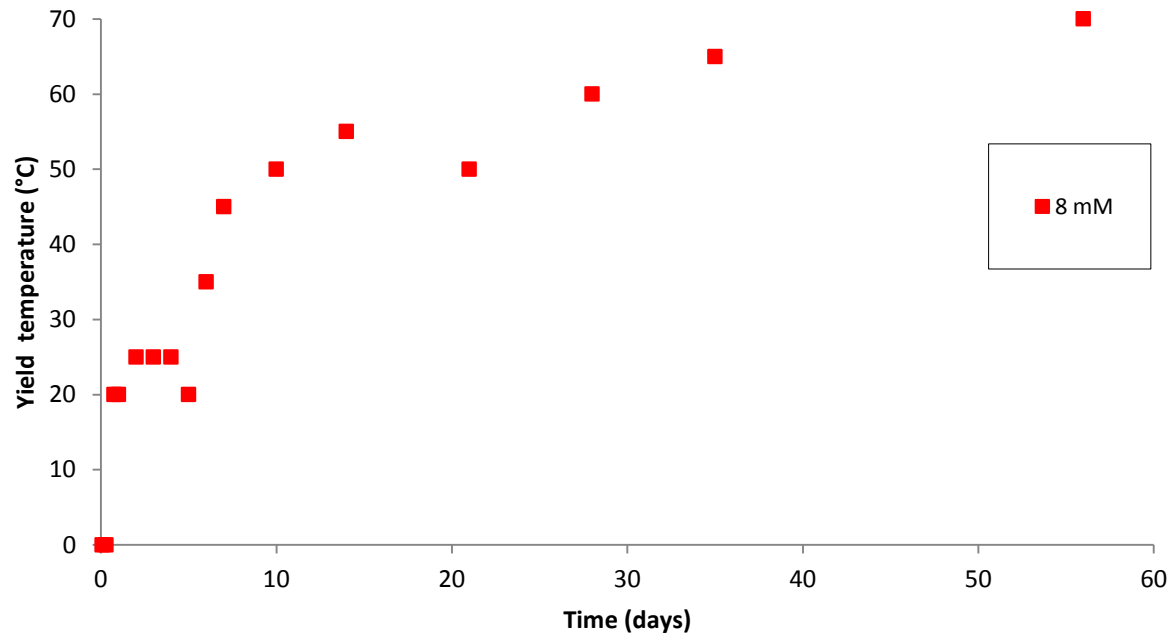


Ku-Na and FEBEX-Na

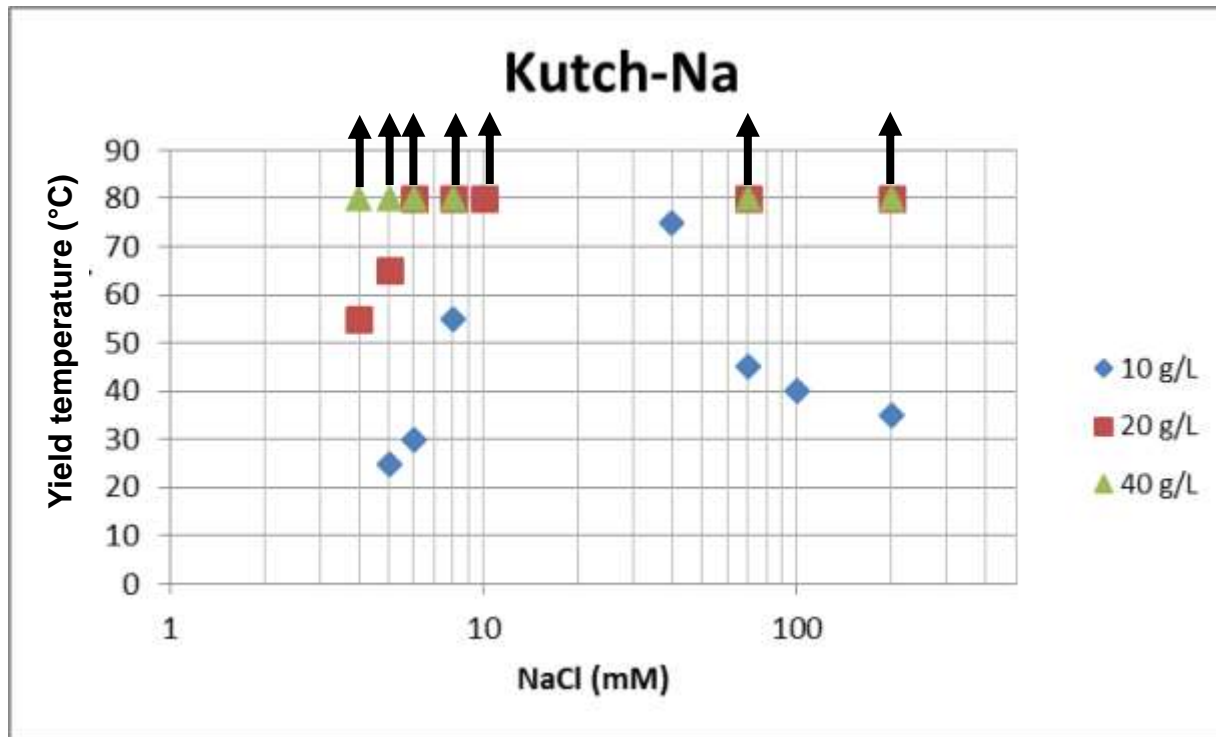


Effect of ageing

FEBEX-Na, 10g/l



Influence of clay concentration



Higher clay concentration gives stronger structure
Gelatin gels show similar behaviour Eldridge & Ferry (1954)
Typical for **percolation gels**

Bond percolation: Bethe lattice

Each “particle” can connect to z other particles, probability g .

In this case $z=3$.

Number of particles in generation n is a quantity of interest

$$N_n \sim [g \times (z - 1)]^n$$

•

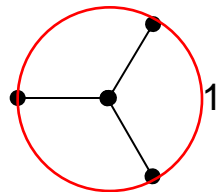
Bethe lattice 1st generation

Each “particle” can connect to z other particles, probability g .
In this case $z=3$.

Number of particles in generation n is a quantity of interest

$$N_n \sim [g \times (z - 1)]^n$$

$$N_1 = 3$$



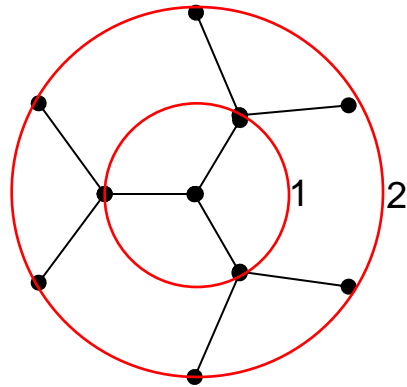
Bethe lattice 2nd generation

Each “particle” can connect to z other particles, probability g .
In this case $z=3$.

Number of particles in generation n is a quantity of interest

$$N_n \sim [g \times (z - 1)]^n$$

$$N_2 = 6$$



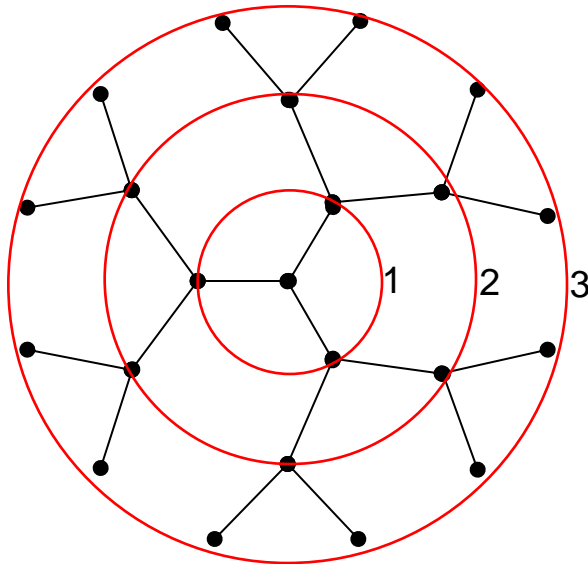
Bethe lattice 3rd generation

Each “particle” can connect to z other particles, probability g .
In this case $z=3$.

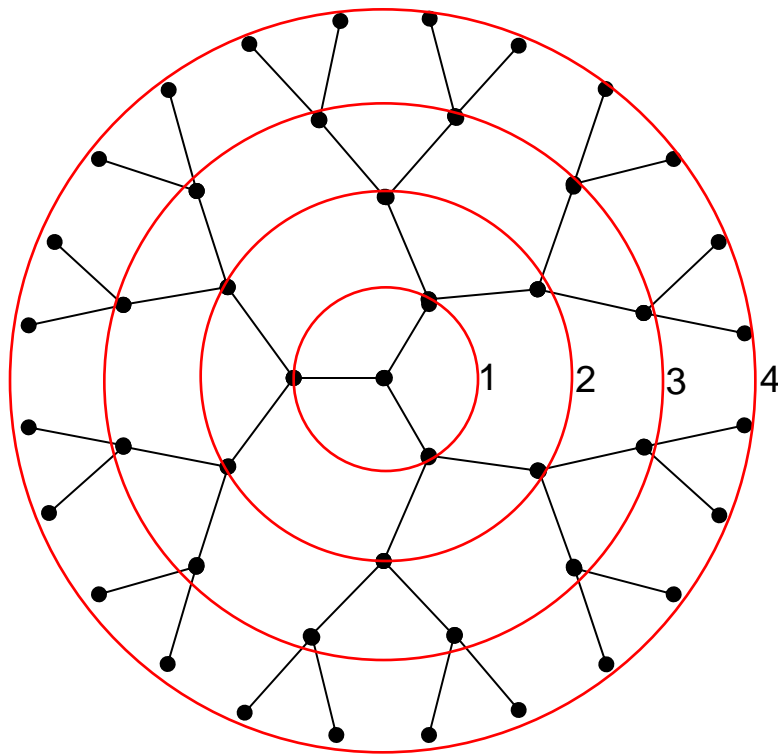
Number of particles in generation n is a quantity of interest

$$N_n \sim [g \times (z - 1)]^n$$

$$N_3 = 12$$



Bethe lattice 4th generation



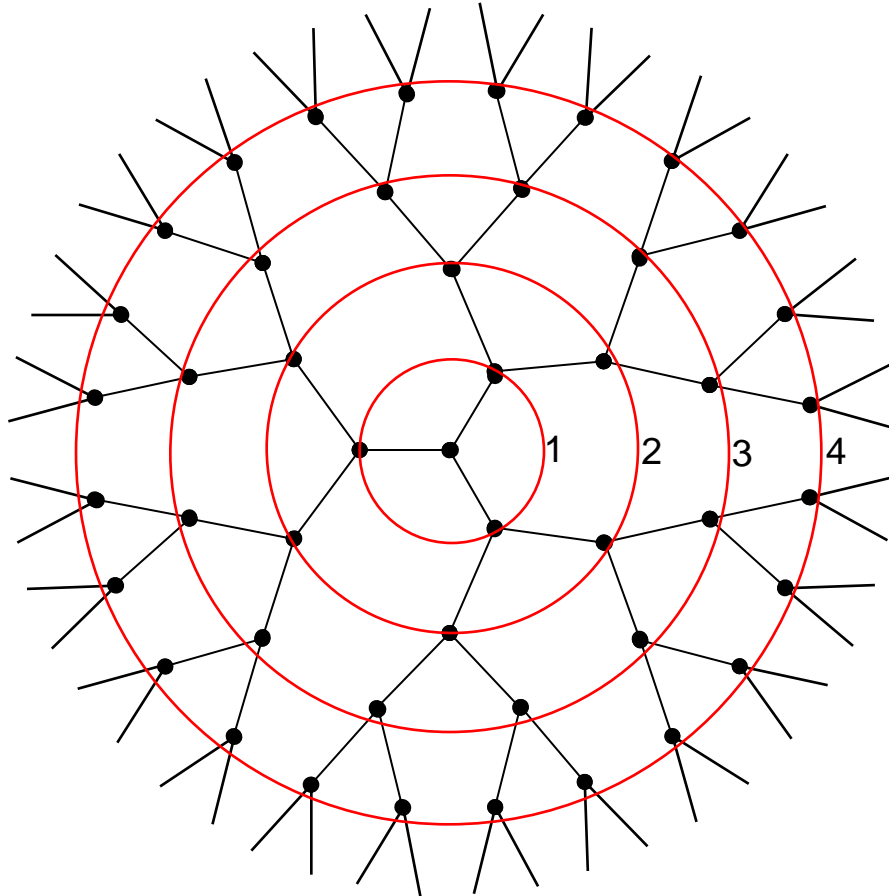
Each “particle” can connect to z other particles, probability g .
In this case $z=3$.

Number of particles in generation n is a quantity of interest

$$N_n \sim [g \times (z - 1)]^n$$

$$N_4 = 24$$

Bethe lattice 5th generation



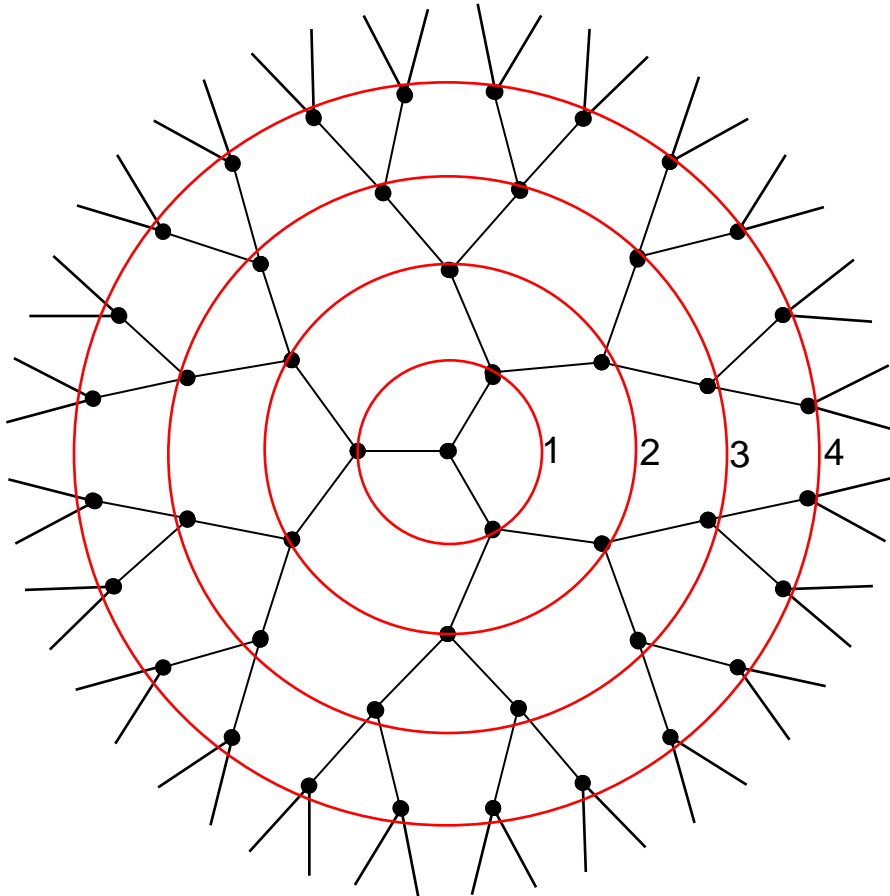
Each “particle” can connect to z other particles, probability g .
In this case $z=3$.

Number of particles in generation n is a quantity of interest

$$N_n \sim [g \times (z - 1)]^n$$

$$N_5 = 48$$

Percolation limit – infinite cluster



Existence of a critical bond probability g_c

$$N_n \sim [g \times (z - 1)]^n$$

if $g < g_c = \frac{1}{z - 1}$ then

$$N_n \rightarrow 0 \text{ as } n \rightarrow \infty$$

if $g > g_c = \frac{1}{z - 1}$ then

$$N_n \rightarrow \infty \text{ as } n \rightarrow \infty$$

Infinite cluster is equivalent to a space-filling connected structure, i.e. a gel

edge+face \rightarrow edge-face

Equilibrium $e + f \leftrightarrow e-f$

$$K = \frac{[e-f]}{[e][f]} = \exp(-(\Delta H - T\Delta S) / RT)$$

assume

$$[e] \propto [f] \propto c \times (1 - g)$$

c = clay concentration

$(1-g)$ = fraction non-reacted bonds

$$[e-f] \propto c \times g$$

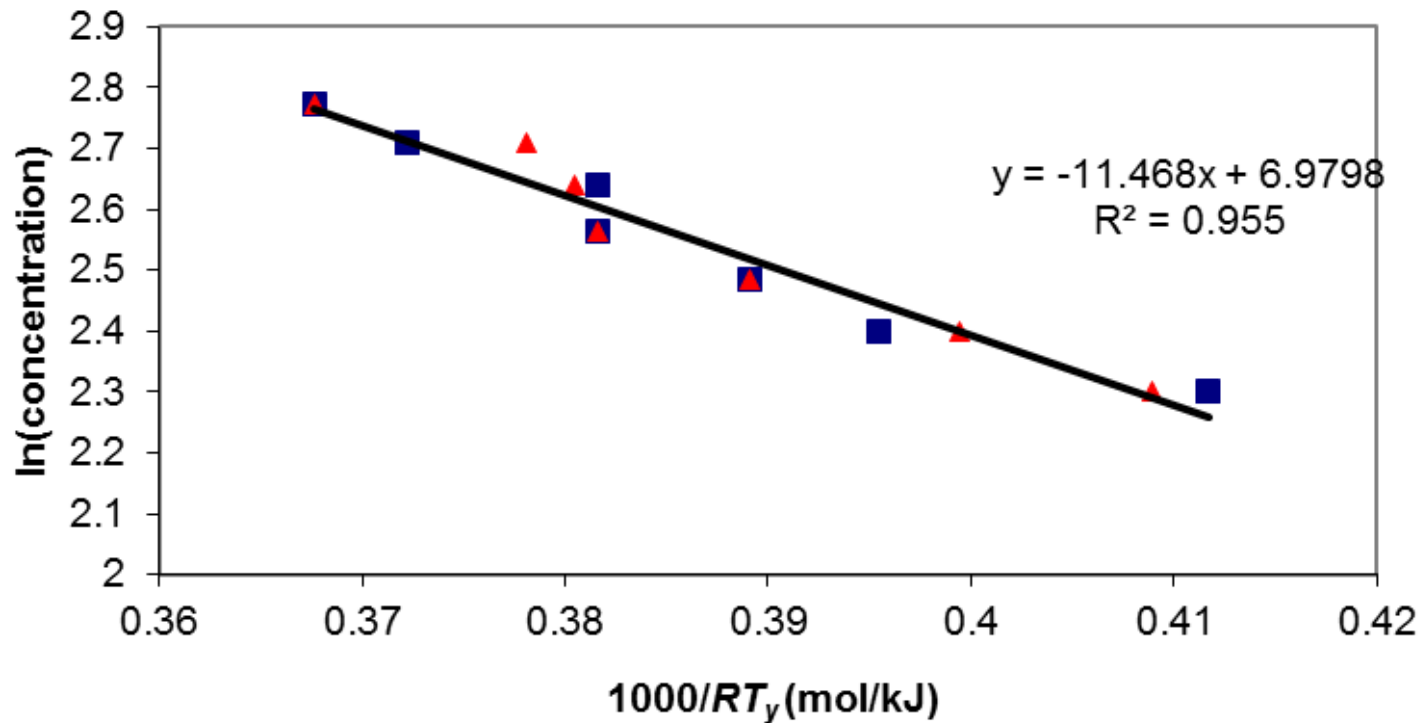
At transition temperature T^* , g = the critical value g_c

$$\frac{[e-f]}{[e][f]} \propto \frac{c \times g_c}{c^2 (1 - g_c)^2} \propto \exp(-(\Delta H - T^* \Delta S) / RT^*)$$

$$\ln c = \frac{\Delta H}{RT^*} + \text{const.}$$

plot $\ln c$ vs. $1000/RT^*$ and the slope should give ΔH in kJ/mol

Results for binding enthalpy Ku-Na at 5 mM



$$\Delta H = 11.5 \pm 0.7 \text{ kJ/mol or } 4.6 \pm 0.3 \text{ kT}$$

Conclusions & Outlook

- Gel formation is determined by ionic strength, with only minor pH dependence ($\text{pH} < 10$) (see, e.g., Goh et al. 2015)
- Edge – face electrostatic attraction cause gel formation
 - Primitive model or DLVO, for parallel layers is not relevant
 - Simulations with clay platelets carrying positive rim charge possible way forward
- Spillover effect corroborated from gel yield temperatures

Conclusions & Outlook

- Strength of attractive gel increases with clay content
 - Yield temperature increases
 - Yield stress increases
- Clay gels seem to behave in agreement with percolation theory
- Possible to estimate binding enthalpy for edge – face binding
 - Important input for realistic theory and modelling
 - Monte Carlo results for laponite similar order of magnitude
- Edge-face binding for non gelled structures (Angelini et al Nature Comm. 2014, Birgersson et al. TR-09-34 2009)
 - Sloped fractures

Acknowledgements

The research leading to these results has received funding from the European Atomic Energy Community's Seventh Framework Programme (FP7/2007-2011) under Grant Agreement no295487, the BELBaR project, and from the Swedish Nuclear Fuel and Waste Management Company (SKB).