The physics of clay minerals: From the nano-scale to the geo-scale, and everything in between

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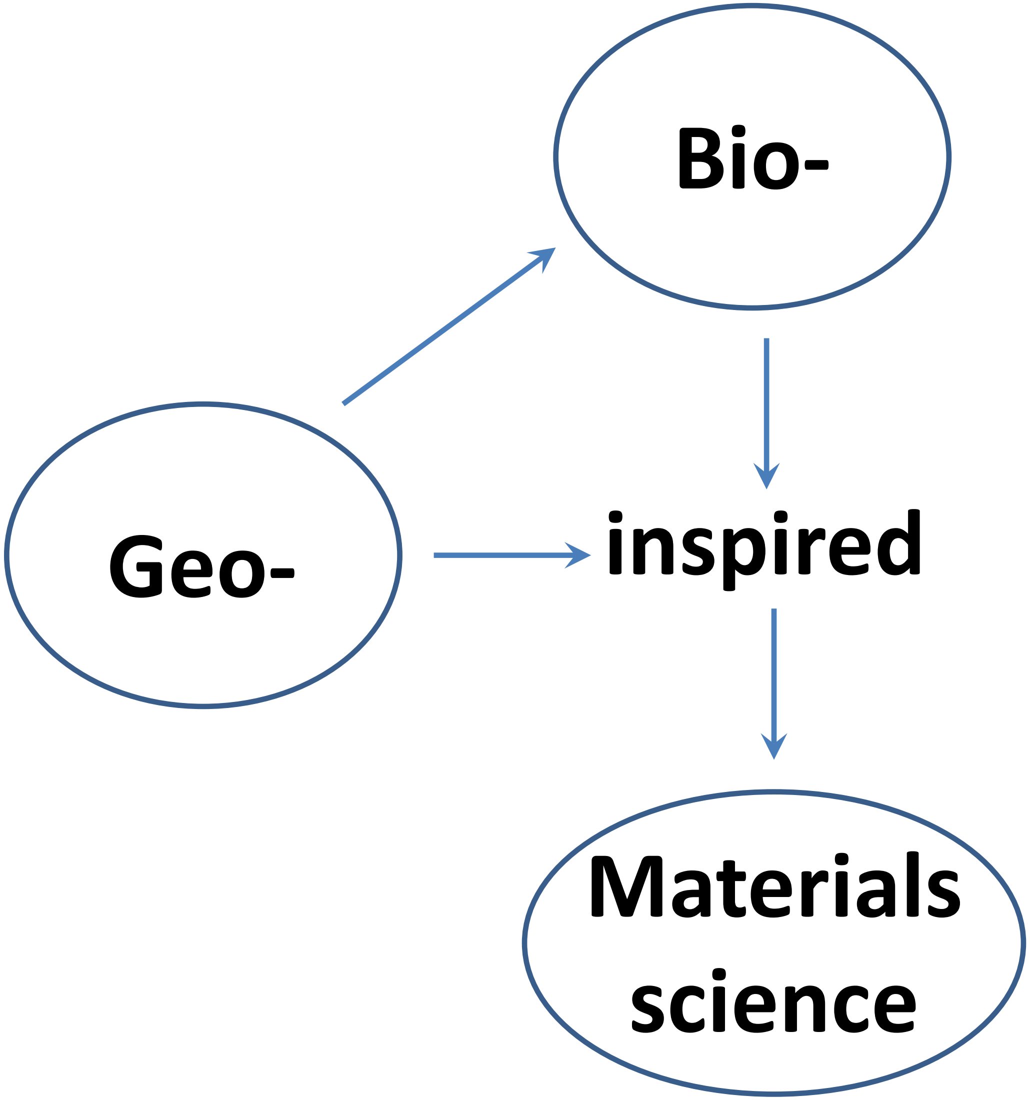
NORWAY

Laboratory for Soft and Complex Matter Studies at NTNU, Trondheim, Norway:



Bio-

Geo-

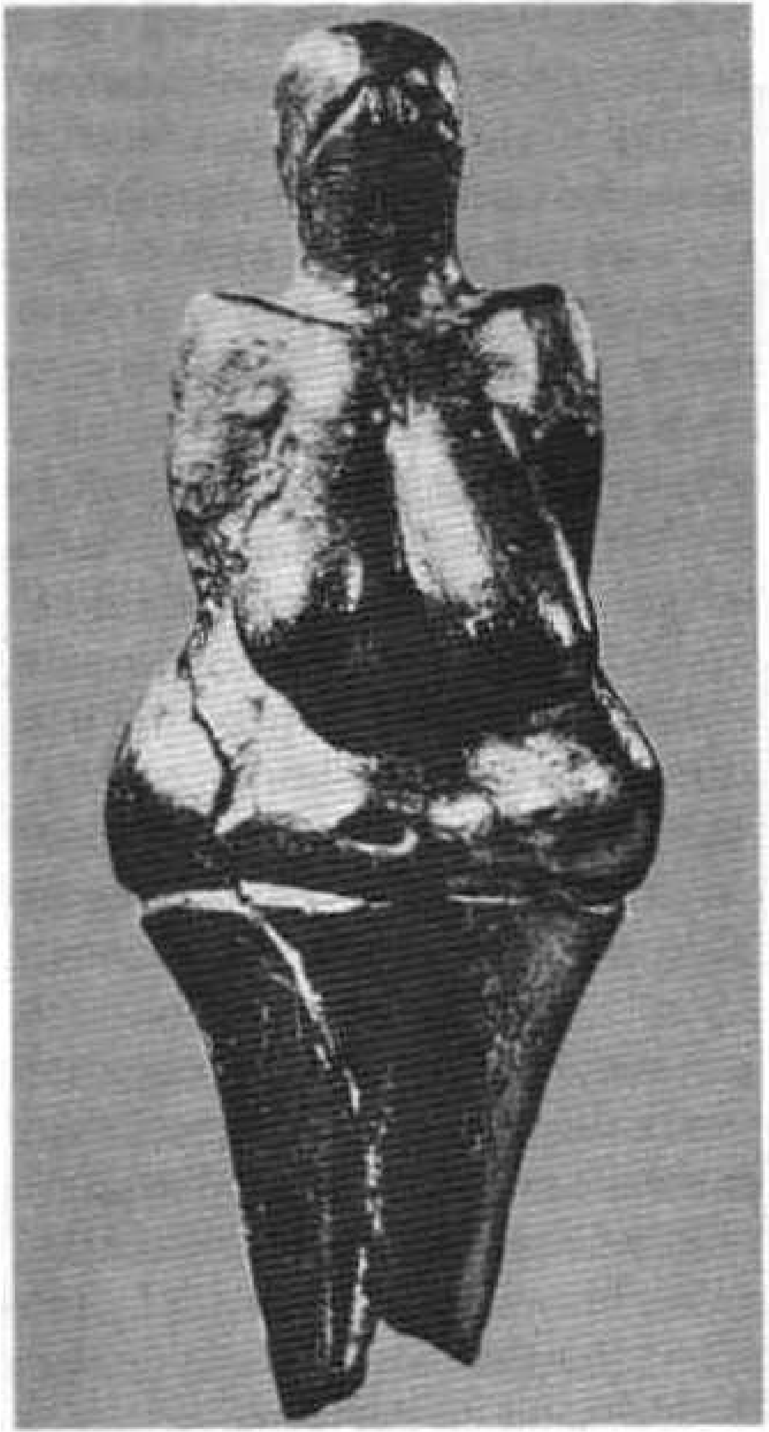
inspired

Materials science

Question:

What is the first that comes to your mind when I say the word: Clay?

MUD?



Clays in ART

The oldest surviving piece of art:

The oldest sample known of baked clay:

Figurine: "Venus of Vestonice"

Found in 1920 in the Czech Republic.

Approximate age: 23000 B.C.
(Dated from mammoth bone ash in the clay)

Clay avalanches

Clay avalanche: Rissa Norway 1978

Observation: Extreme mechanical instability of certain clayey soils, under given humidity conditions

Example: the Rissa landslide (1978, near Trondheim, Norway)

- Triggered by the excavation of 1000 m^3 prior to building a barn
- Duration: 6 min
- 7 to 8 millions m^3 of soil were displaced
- 40 persons were taken, 1 died
- 7 farms were rammed
- 33 ha of lands were touched
- A linear length of 80 m of coast ended up in the fjord
- The slope was very moderate

The natural quick clays were sedimented at the end of the last ice age, commonly at river mouths in salty water.

The specificity of the natural quick clays is that the salt has been washed away by water over time, which has weakened the cohesion of the material.

“House of card” structure?

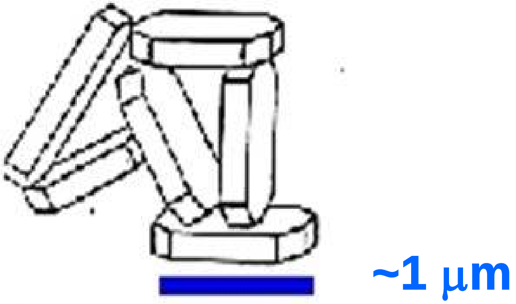
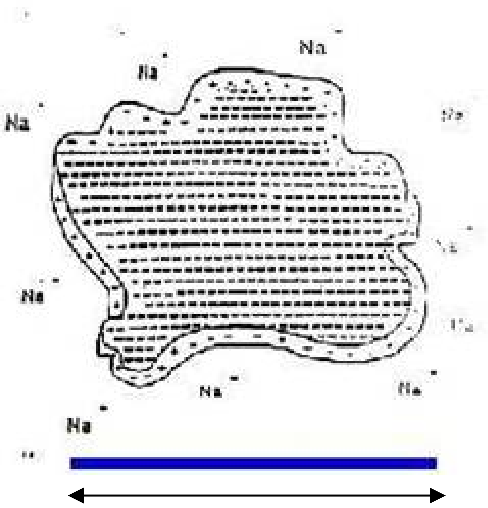


Figure 1 *The left panel above is from a natural clay deposit, and it illustrates on a macroscopic scale that clays are anisotropic materials. The right panel is an electron microscope image of vermiculite clay demonstrating its lamellar structure on the nano-scale, reminiscent of graphene, which is one of the main characteristics of clay minerals.*

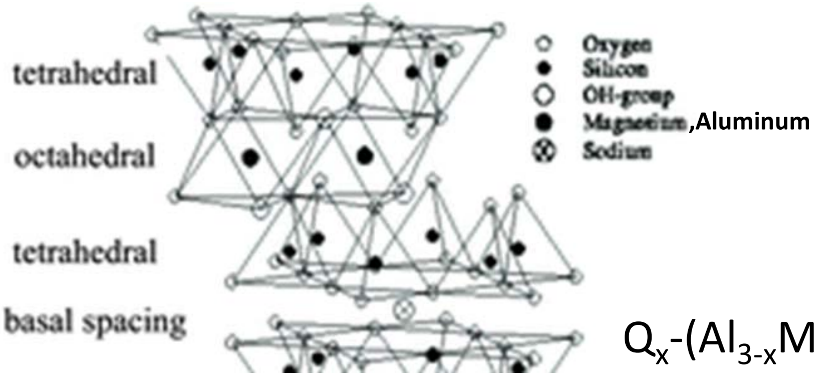
Clays are nano-/micro-particles:

Two basic forms at nano-/micro-scale:

1 nm thick ”nanocards” (Bentonite/Laponite)

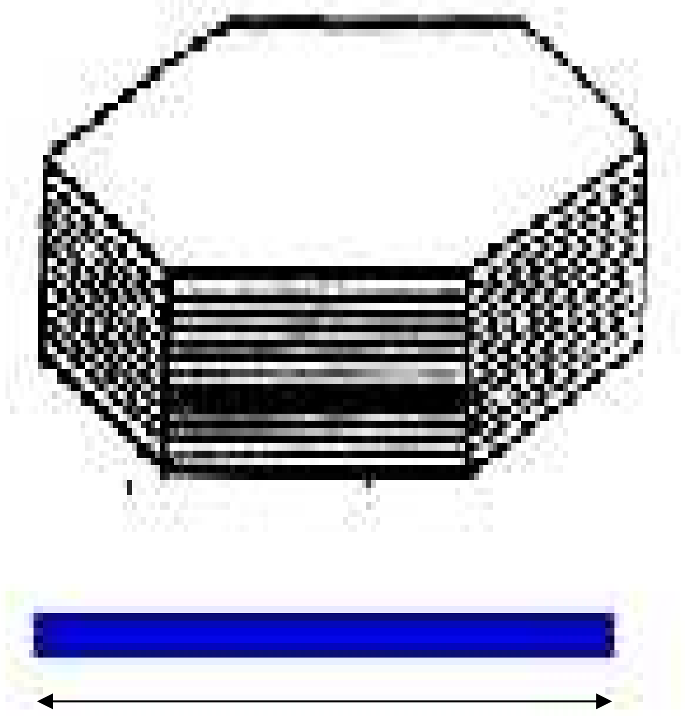


~ µm



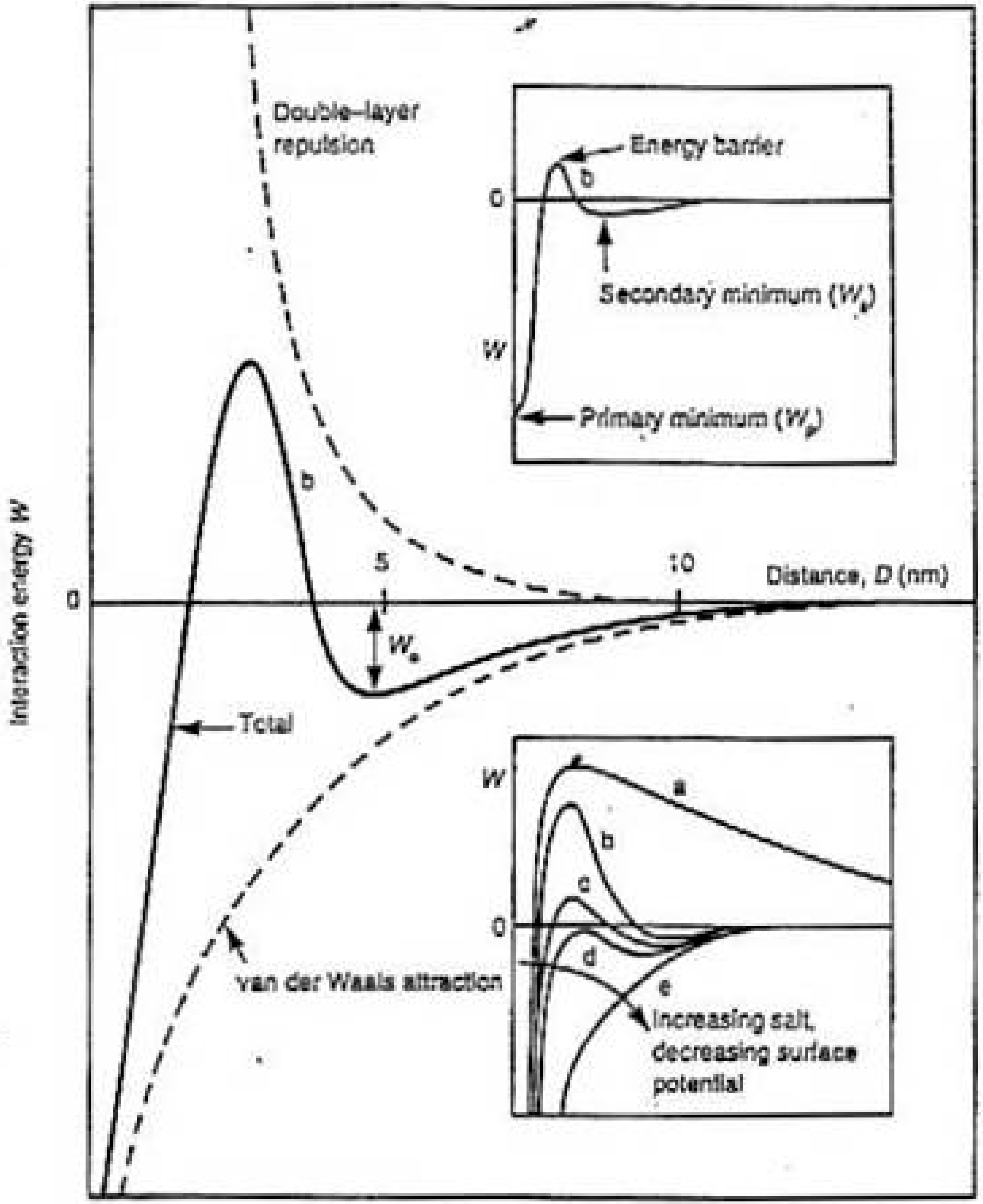
Q_x-$(Al_{3-x}Mg_x)Si_4O_{10}(OH)_2$

100 nm thick nanolayered particles ”decks of nanocards” (Kaolinite)



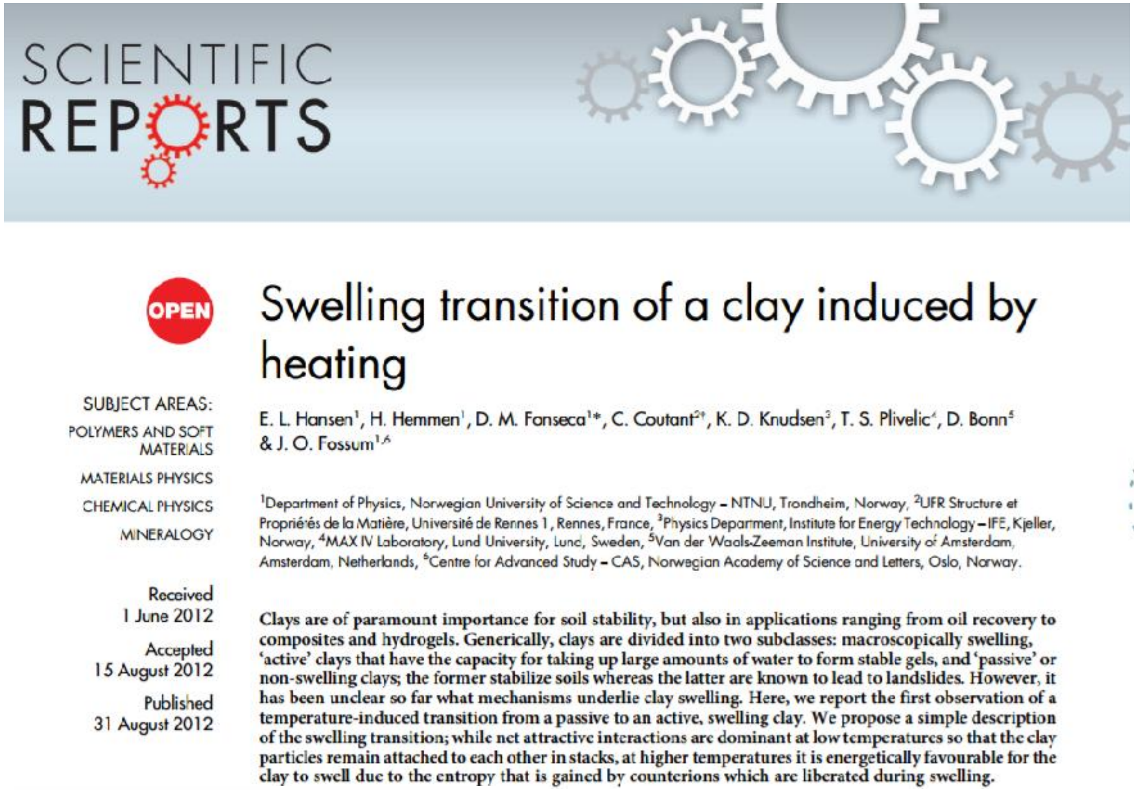
~ µm

DLVO Theory:
vdW
+ Screened Electrostatic Rep.



From J. Israelachvili

Temperature effects:



SCIENTIFIC REPORTS

OPEN

Swelling transition of a clay induced by heating

SUBJECT AREAS:
POLYMERS AND SOFT MATERIALS
MATERIALS PHYSICS
CHEMICAL PHYSICS
MINERALOGY

E. L. Hansen[1], H. Hemmen[1], D. M. Fonseca[1*], C. Coutant[2†], K. D. Knudsen[3], T. S. Plivelic[4], D. Bonn[5] & J. O. Fossum[1,6]

[1]Department of Physics, Norwegian University of Science and Technology – NTNU, Trondheim, Norway, [2]UFR Structure et Propriétés de la Matière, Université de Rennes 1, Rennes, France, [3]Physics Deparment, Institute for Energy Technology – IFE, Kjeller, Norway, [4]MAX IV Laboratory, Lund University, Lund, Sweden, [5]Van der Waals-Zeeman Institute, University of Amsterdam, Amsterdam, Netherlands, [6]Centre for Advanced Study – CAS, Norwegian Academy of Science and Letters, Oslo, Norway.

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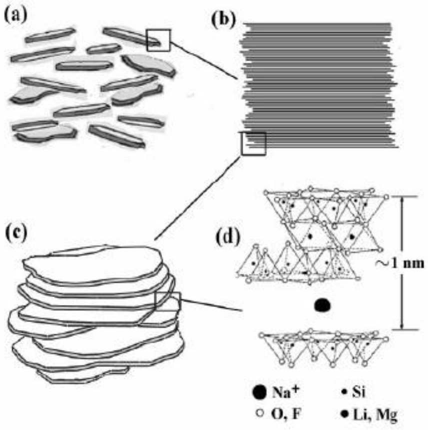
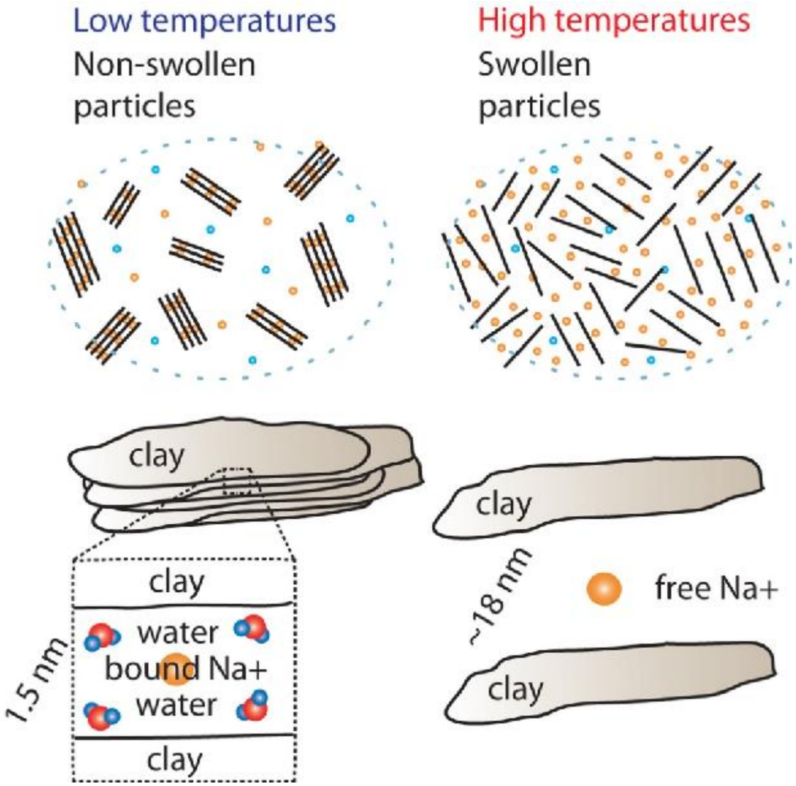
Clays are of paramount importance for soil stability, but also in applications ranging from oil recovery to composites and hydrogels. Generically, clays are divided into two subclasses: macroscopically swelling, 'active' clays that have the capacity for taking up large amounts of water to form stable gels, and 'passive' or non-swelling clays; the former stabilize soils whereas the latter are known to lead to landslides. However, it has been unclear so far what mechanisms underlie clay swelling. Here, we report the first observation of a temperature-induced transition from a passive to an active, swelling clay. We propose a simple description of the swelling transition; while net attractive interactions are dominant at low temperatures so that the clay particles remain attached to each other in stacks, at higher temperatures it is energetically favourable for the clay to swell due to the entropy that is gained by counterions which are liberated during swelling.



WAXS + SAXS + Rheometry



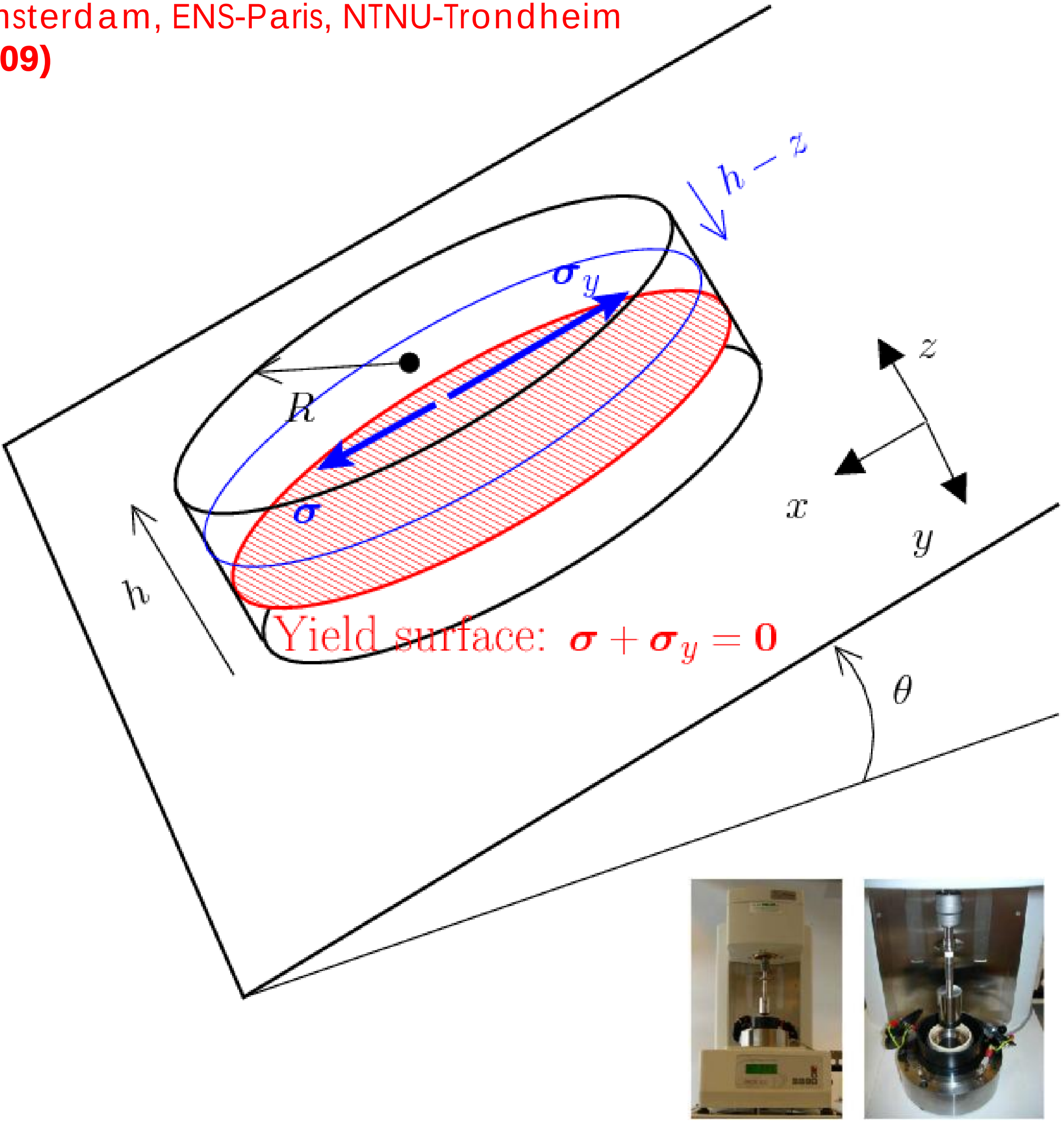
Simple analog landslide experiments

Quickclay and Landslides of Clayey Soils,
A.Khaldoun, P.Moller, A. Fall, G.Wegdam,B. De Leeuw, Y. Meheust, J.O. Fossum, D. Bonn,
Géosciences Rennes 1, University of Amsterdam, ENS-Paris, NTNU-Trondheim
Physical Review Letters 103, 188301 (2009)

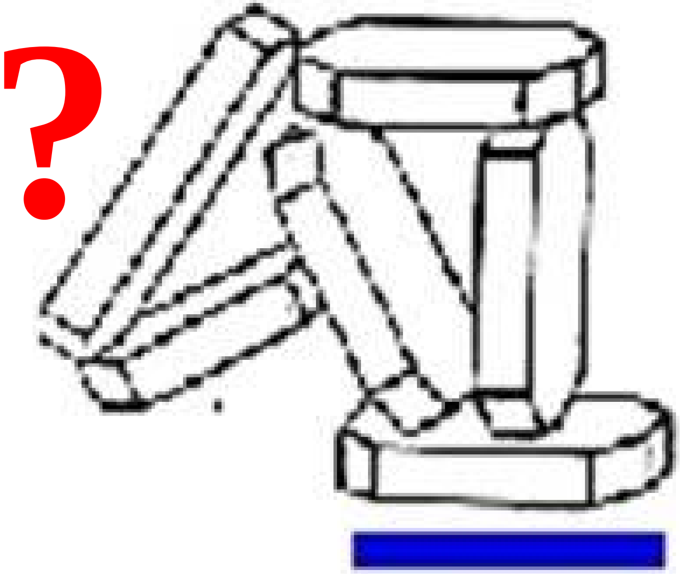
$$\sigma(z) = \rho\, g\, (h - z)\, \sin\theta$$

(null at the free surface)

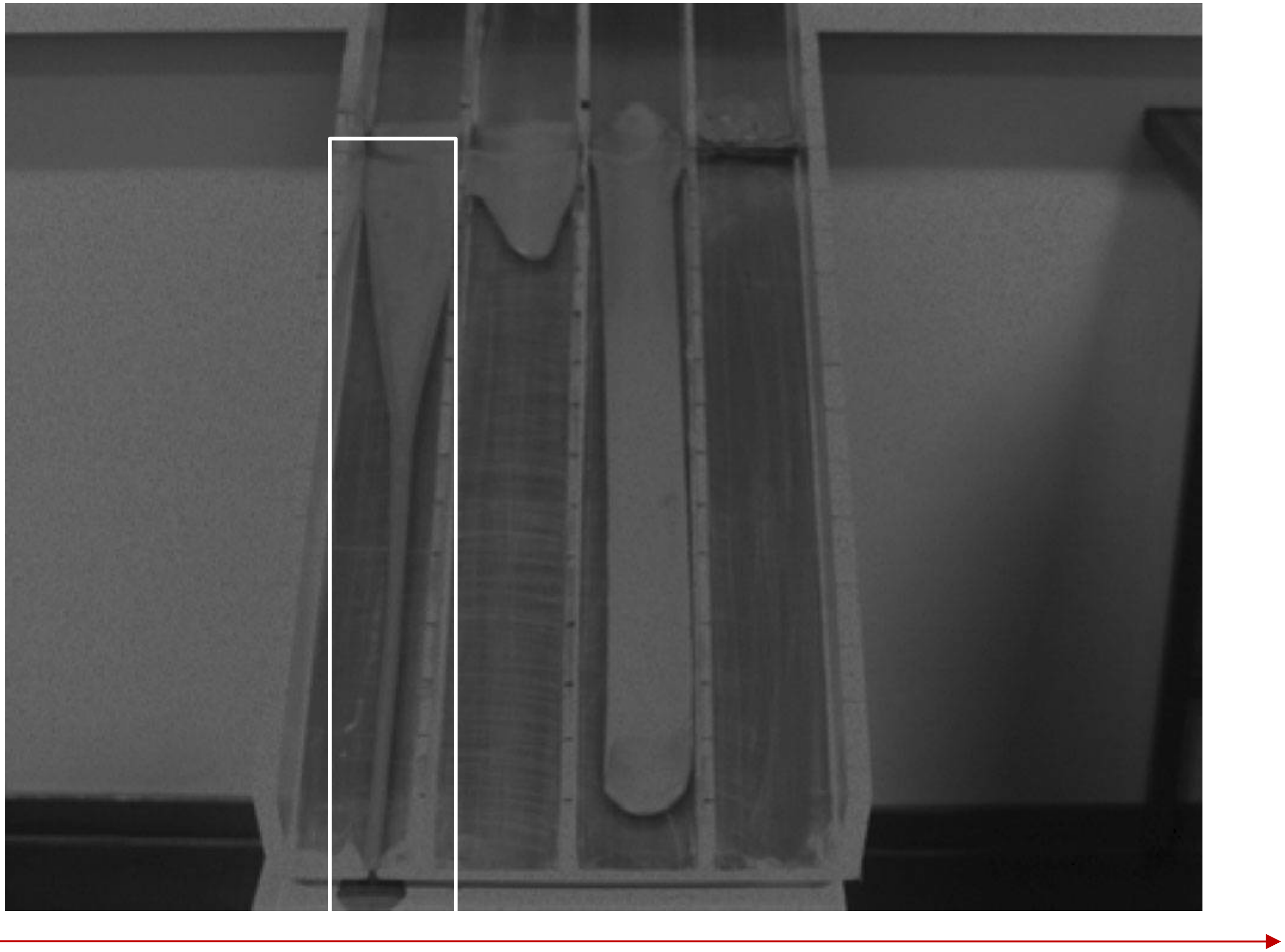
All material above the yield surface is expected to flow



?



Analog laboratory landslide experiments

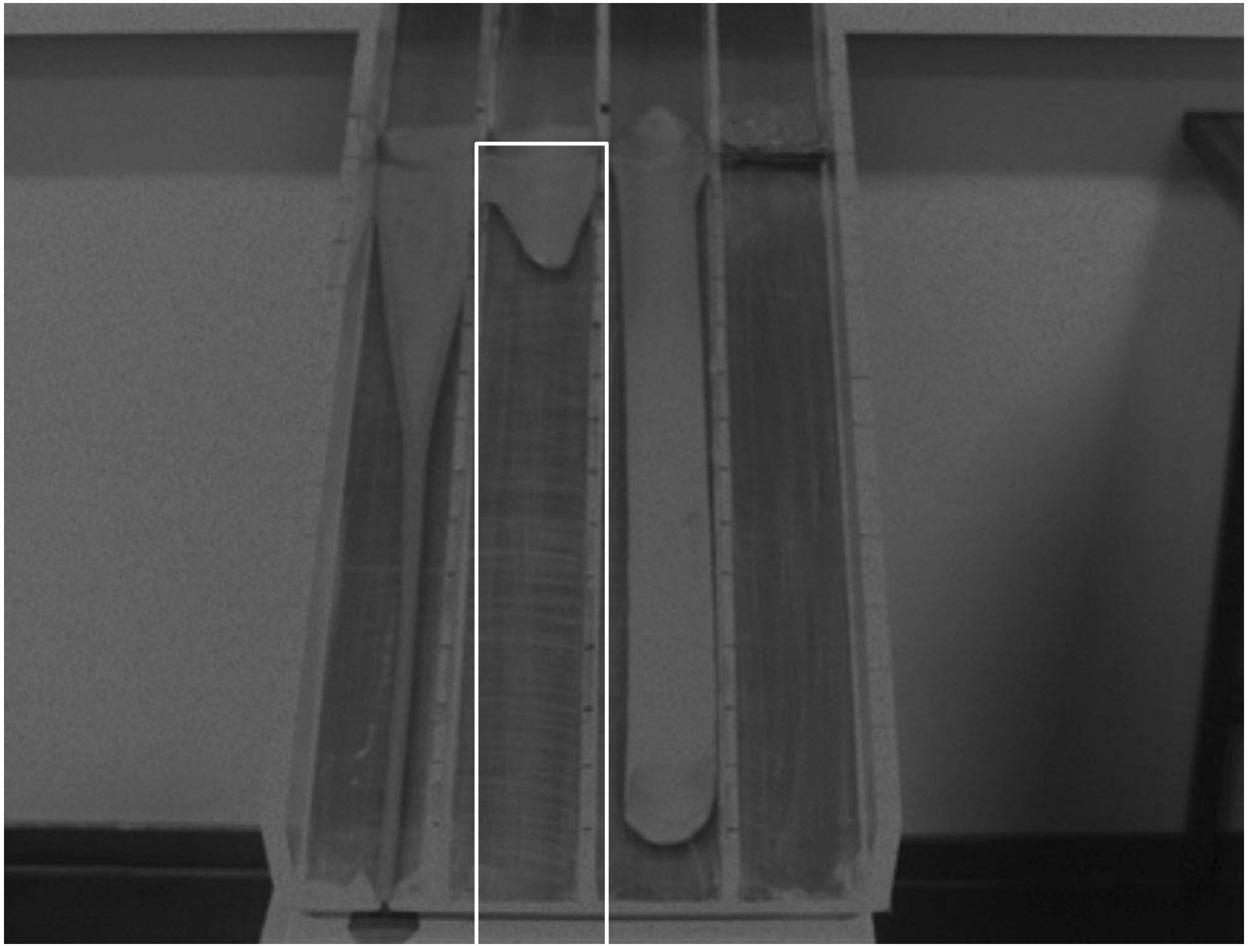


56% 58% 61% 63%

Weight% clay

Quasi-newtonian flow

Analog laboratory landslide experiments (3)

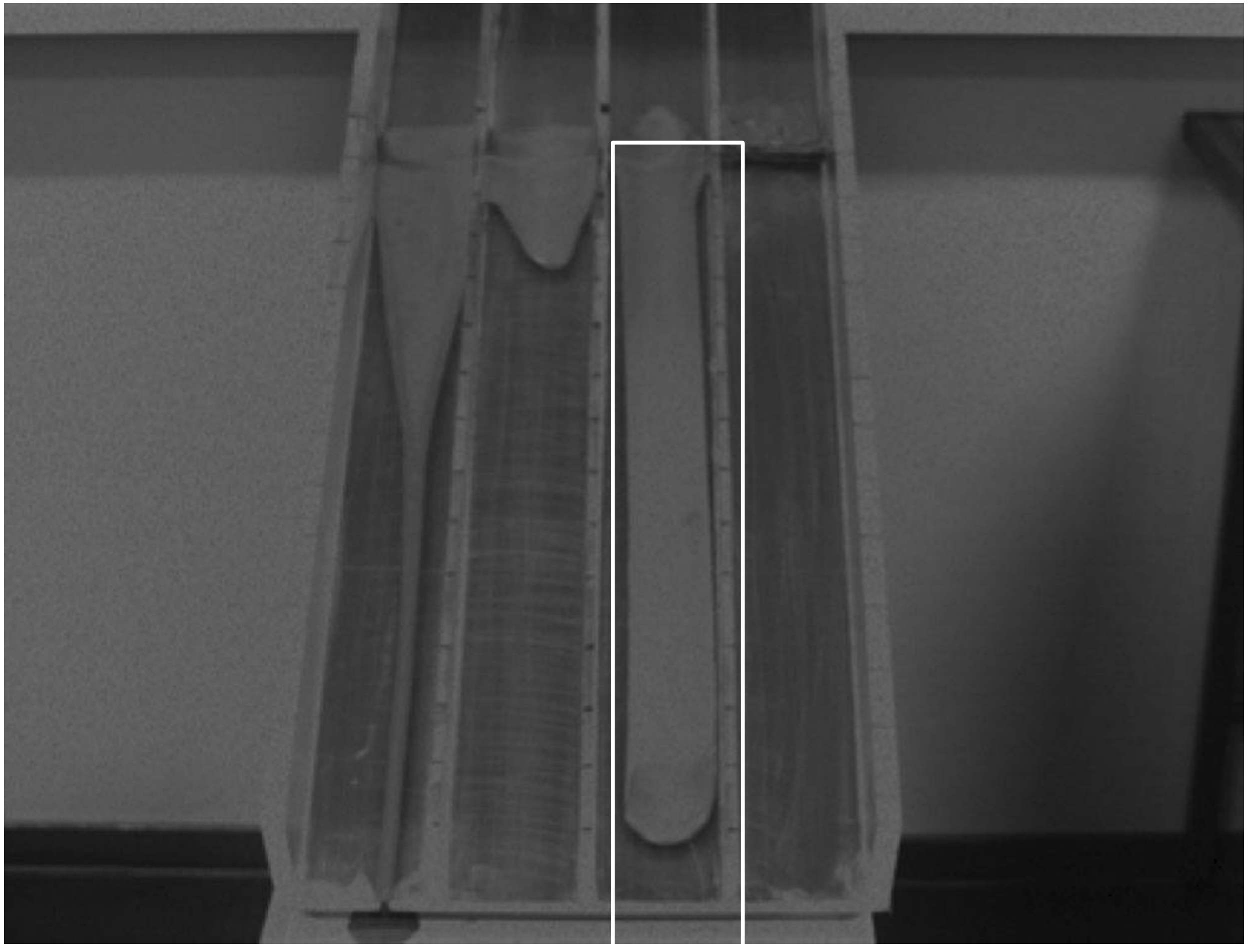


56% 58% 61% 63%

Weight%
clay

Yield stress fluid flow

Analog laboratory landslide experiments



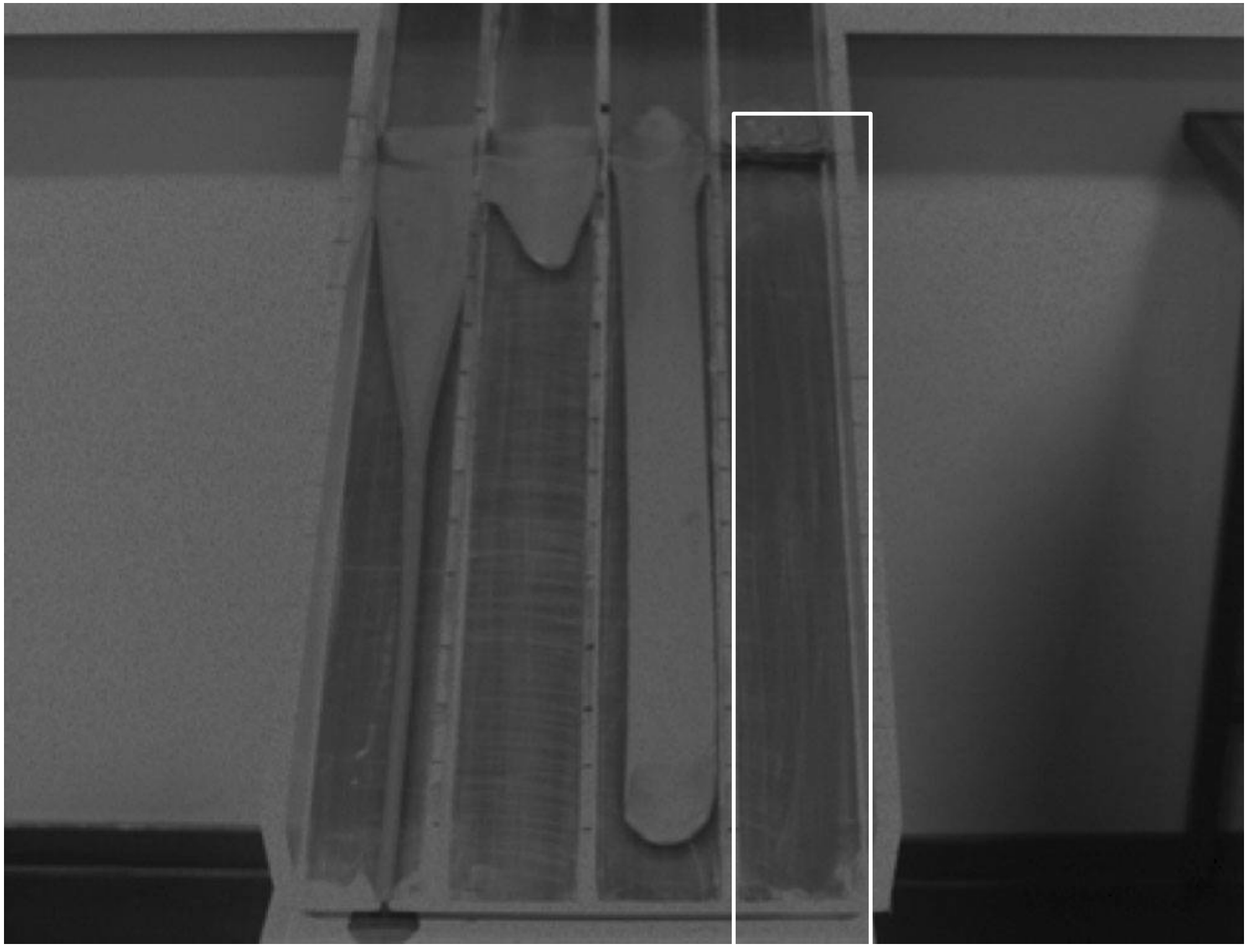
56% 58% 61% 63%

Weight% clay

Landslide regime = flow on a **thin lubrication layer**

⇒ This is why the Rissa farm buildings remained upright

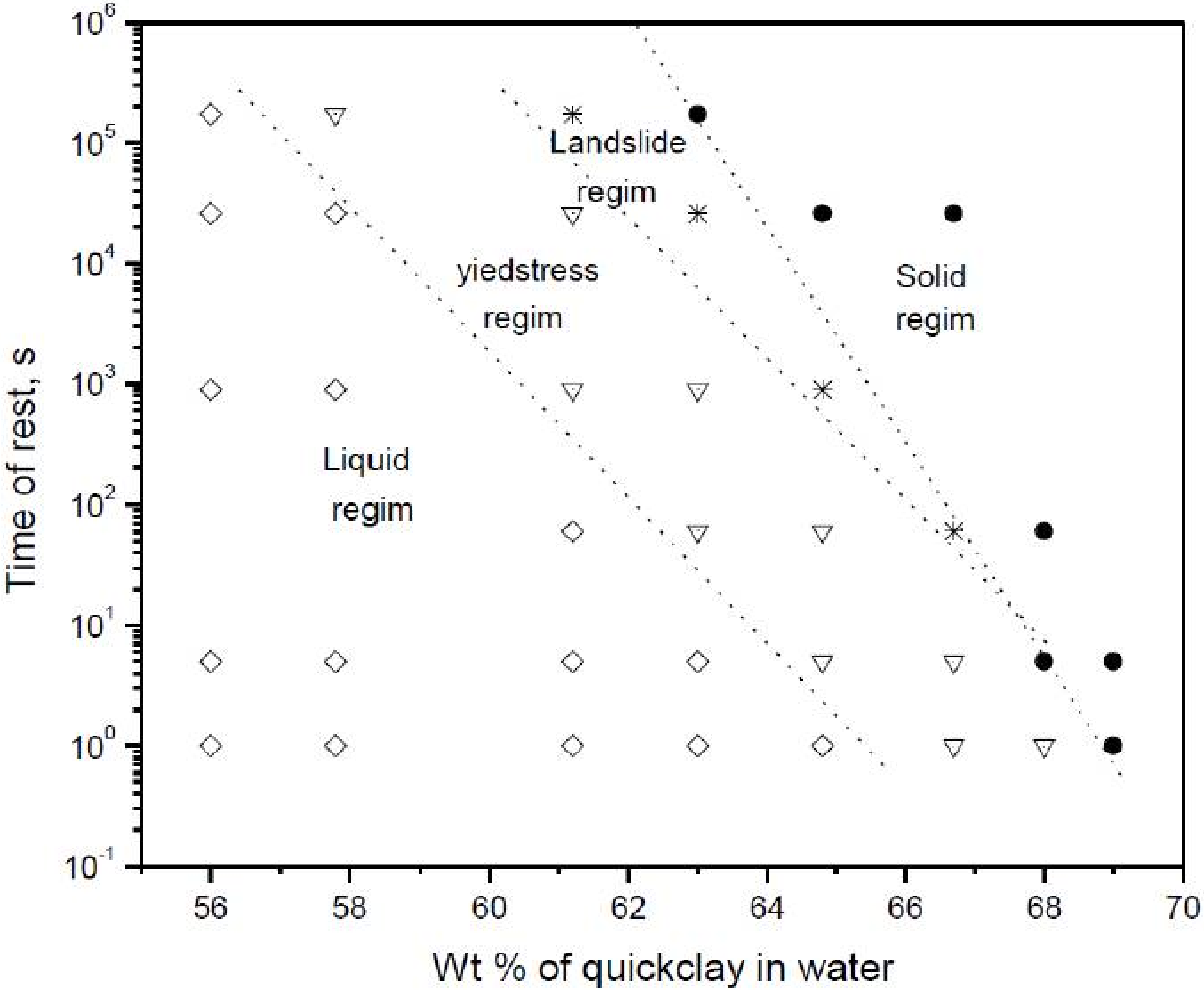
Analog laboratory landslide experiments



56% 58% 61% 63%

Weight%
clay

No flow:
steric hindrance of particle alignment?



Similar to that observed in earlier study on bentonite/montmorillonite muds (Coussot, P., N. Roussel, S. Jarny, and H. Chanson: Continous or catastrophic solid-liquid transition in jammed systems, Phys. Fluids, 17, 011,704 (2005))

In addition: Preparation of a synthetic quick clay

Composition: illite + bentonite + salt

Illite is washed to remove any salt
3% of washed bentonite (swelling clay)
Controlled addition of salt and measure of the elastic modulus as a function of the salt concentration

Our conclusions (so far) regarding quick clay materials science and avalanches:

→ A material containing more water is not necessarily more unstable

→ For a limited range of water contents, the slide can occur on a very thin lubrication layer (lubrication layer/threadmill effect)

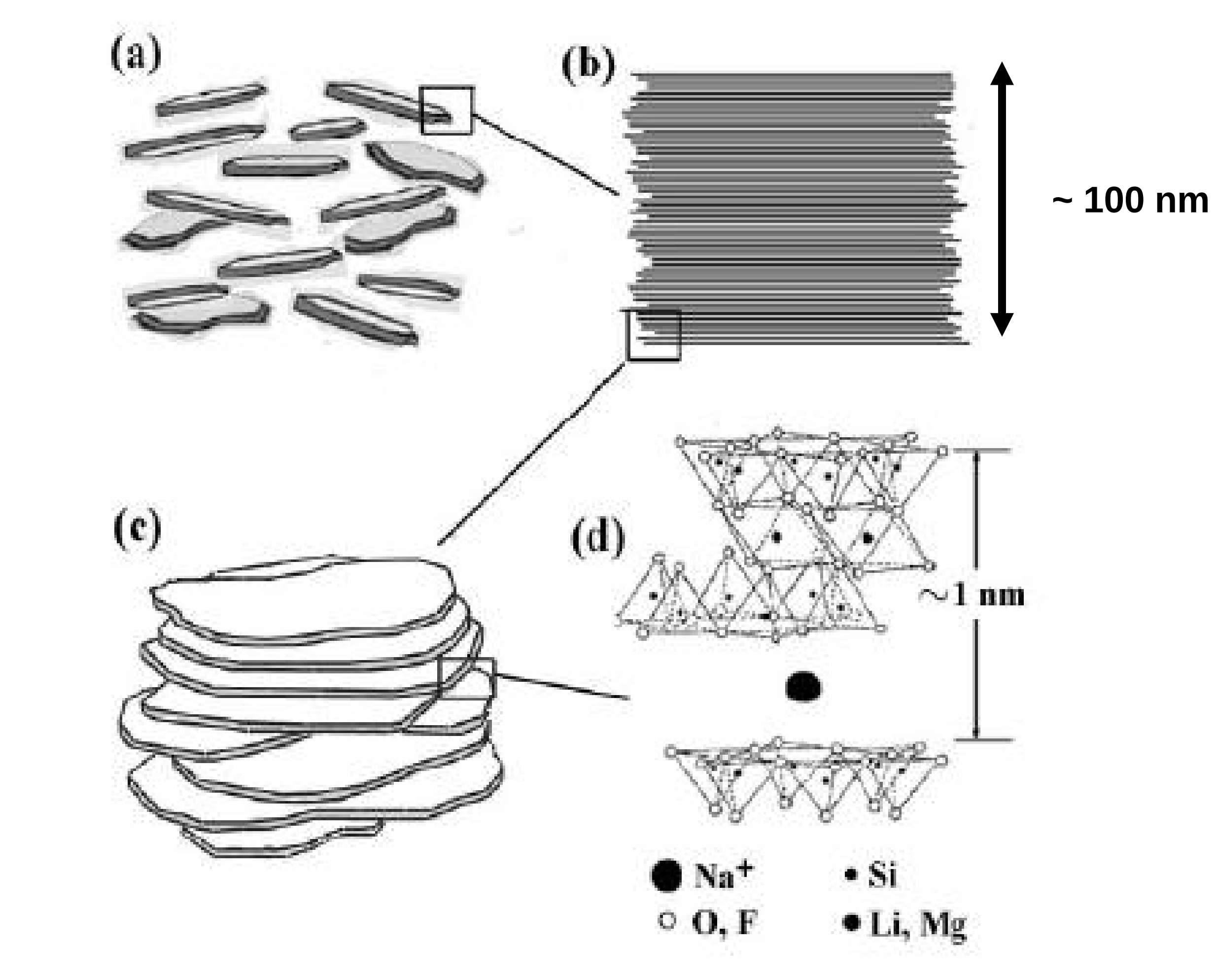
→This occurs when the material's yield stress is larger than a critical value that can be related to a simple theoretical model including the volume of the sample

→ It is possible to prepare in the laboratory a synthetic material that has the same mechanical properties as the natural quick clay: A small amount of swelling (smectite) clay is essential for the behavior observed

Appropriate question: Did we really study the “native” quick clay?

Our clay experimental model system:

Q-fluorohectorite synthetic clay: Q_x-$(Mg_{3-x}Li_x)Si_4O_{10}F_2$,
Q is the exchangeable cation (Q = Na^+, Li^+, Ni^{2+}, Fe^{3+}, etc)



One of our experiments:

Orientational order in gravity dispersed clay colloids: A synchrotron x-ray scattering study of Na-fluorohectorite suspensions.
E. DiMasi, J.O. Fossum, T. Gog, and C. Venkataraman. **Phys.Rev. E 64, 061704 (2001)**

Clay (Fluorohectorite)
powder
About 3 % in weight

Pure Water

NaCl

About 10^{-3} M

Basic clay particle

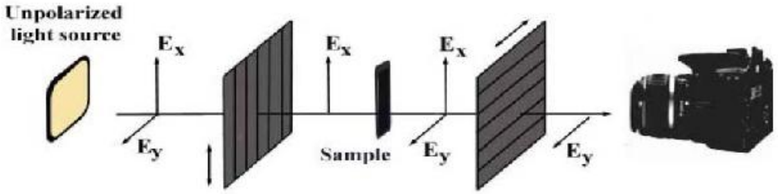
4 "Phases" in same Sample Tube

Liquid

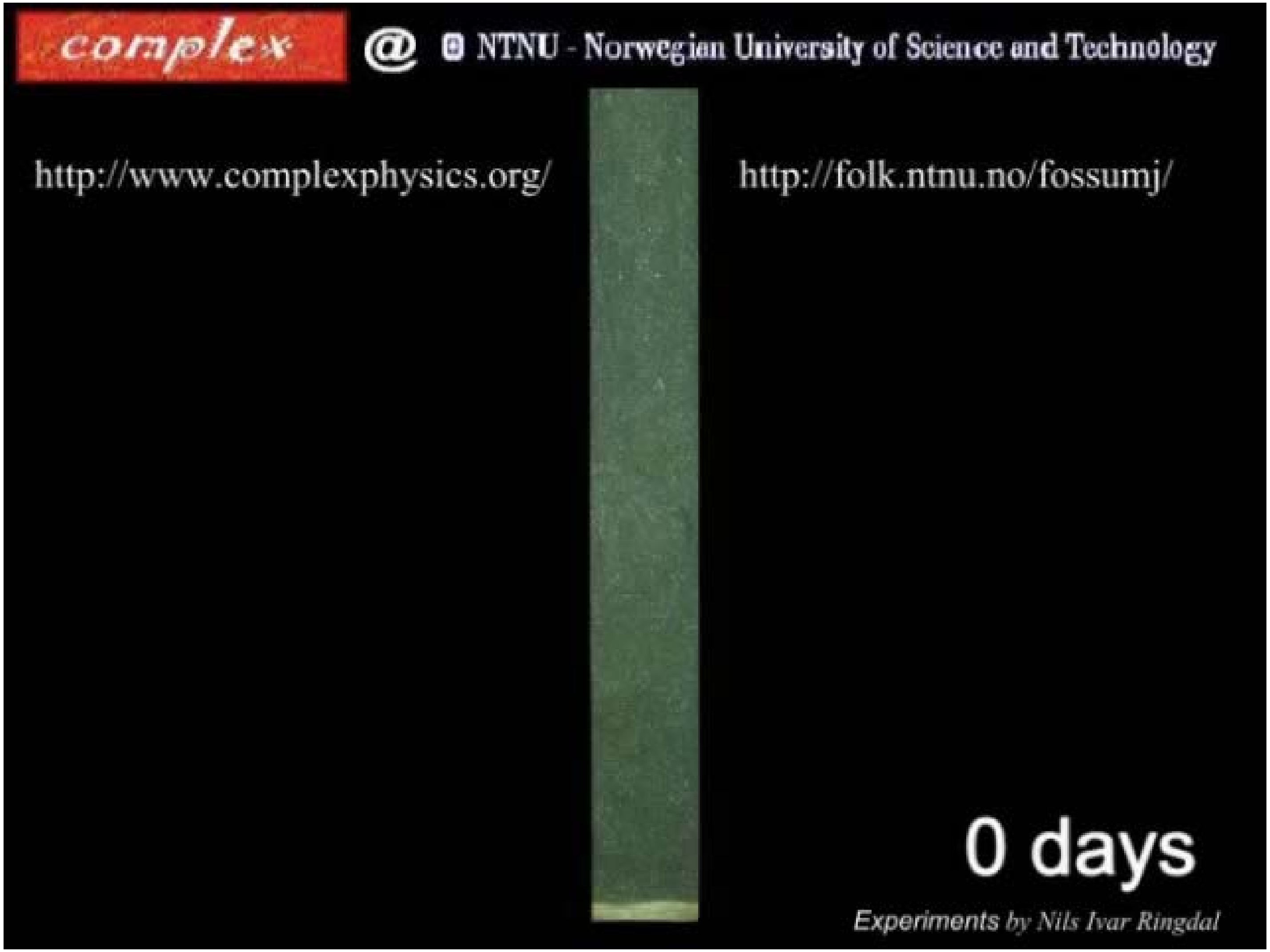
Isotropic gel or glass?

Nematic like gel or glass?

Sediment



Self-organization by sedimentation clay particles in H_2O:



complex @ NTNU - Norwegian University of Science and Technology

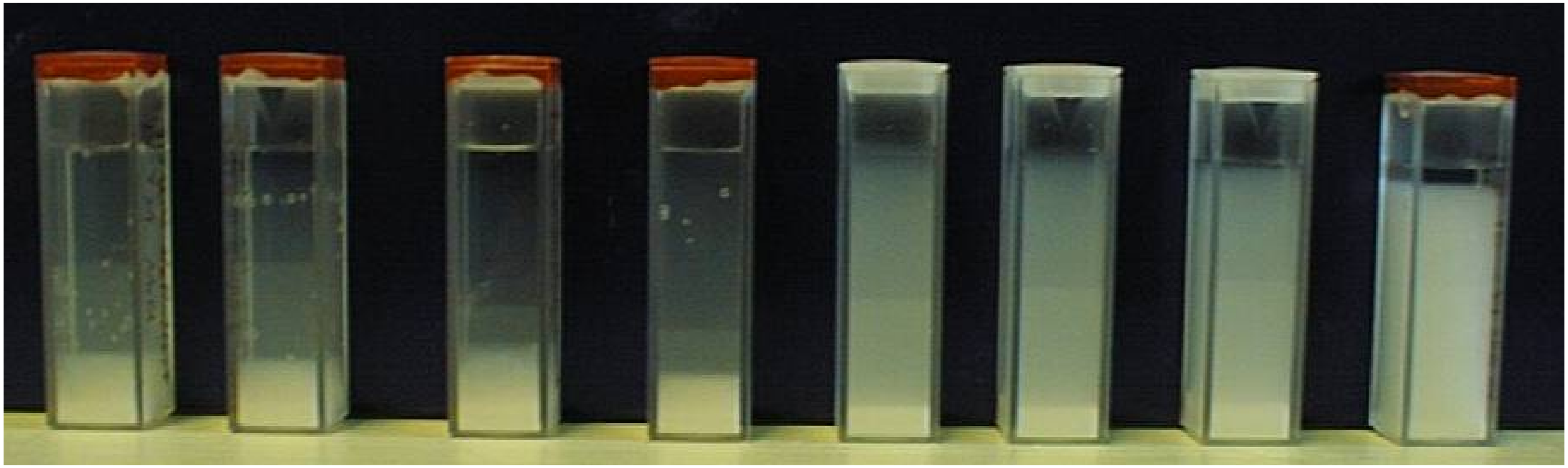
http://www.complexphysics.org/

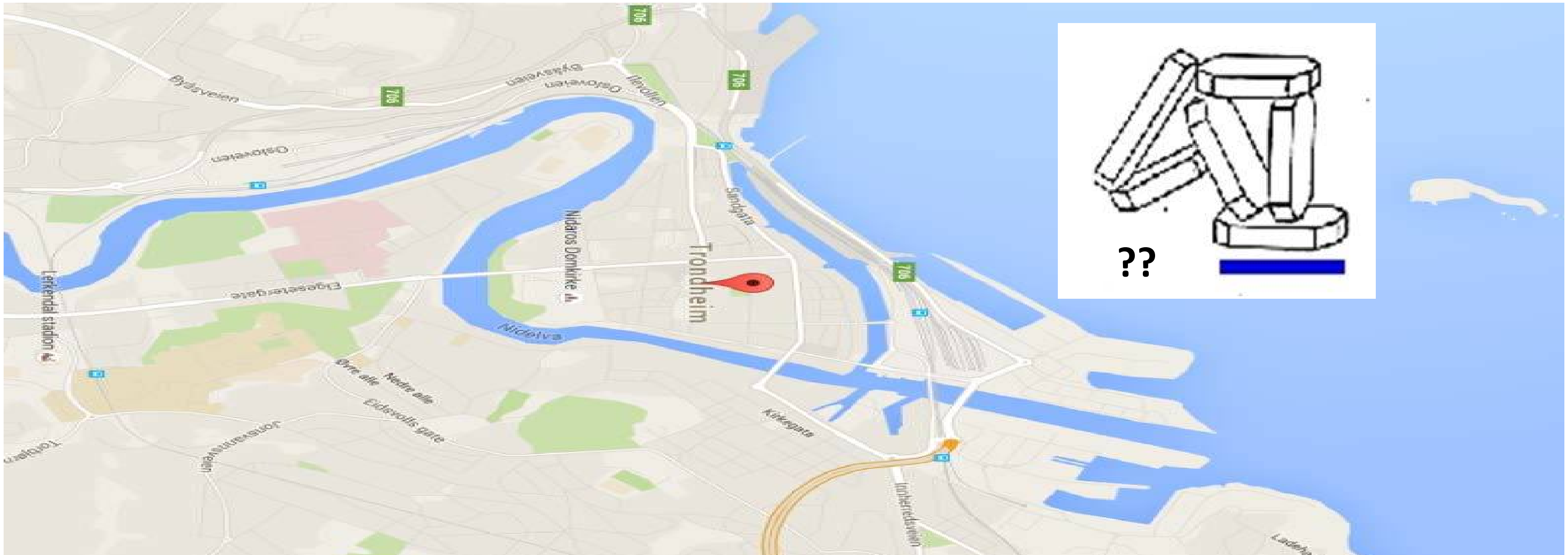
http://folk.ntnu.no/fossumj/

0 days

Experiments by Nils Ivar Ringdal

Increasing salt:





Clay avalanches connected to layered structures or or lubrication layer of house of cards?

Snow avalanches and weak layers:
All snow exists as layers. Some layers are relatively more cohesive (stronger layers) and others are relatively less cohesive (weaker layers).

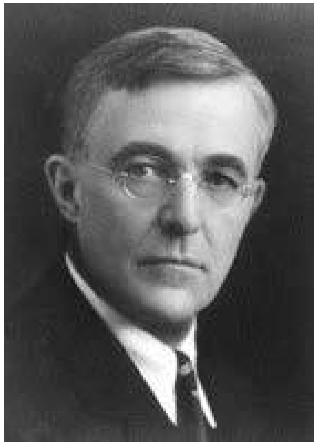
When the snowpack is stressed by rapid changes (e.g. wind-drifted snow, new snow, or rain) this stress can cause the weak layer to fracture.

Liquid Crystalline Phases Characterization

Order Parameter = O.P.
= Angular distribution function
= $S_2 = ½\langle 3\cos^2\theta - 1\rangle$

Isotropic
Phase (O.P. = 0)

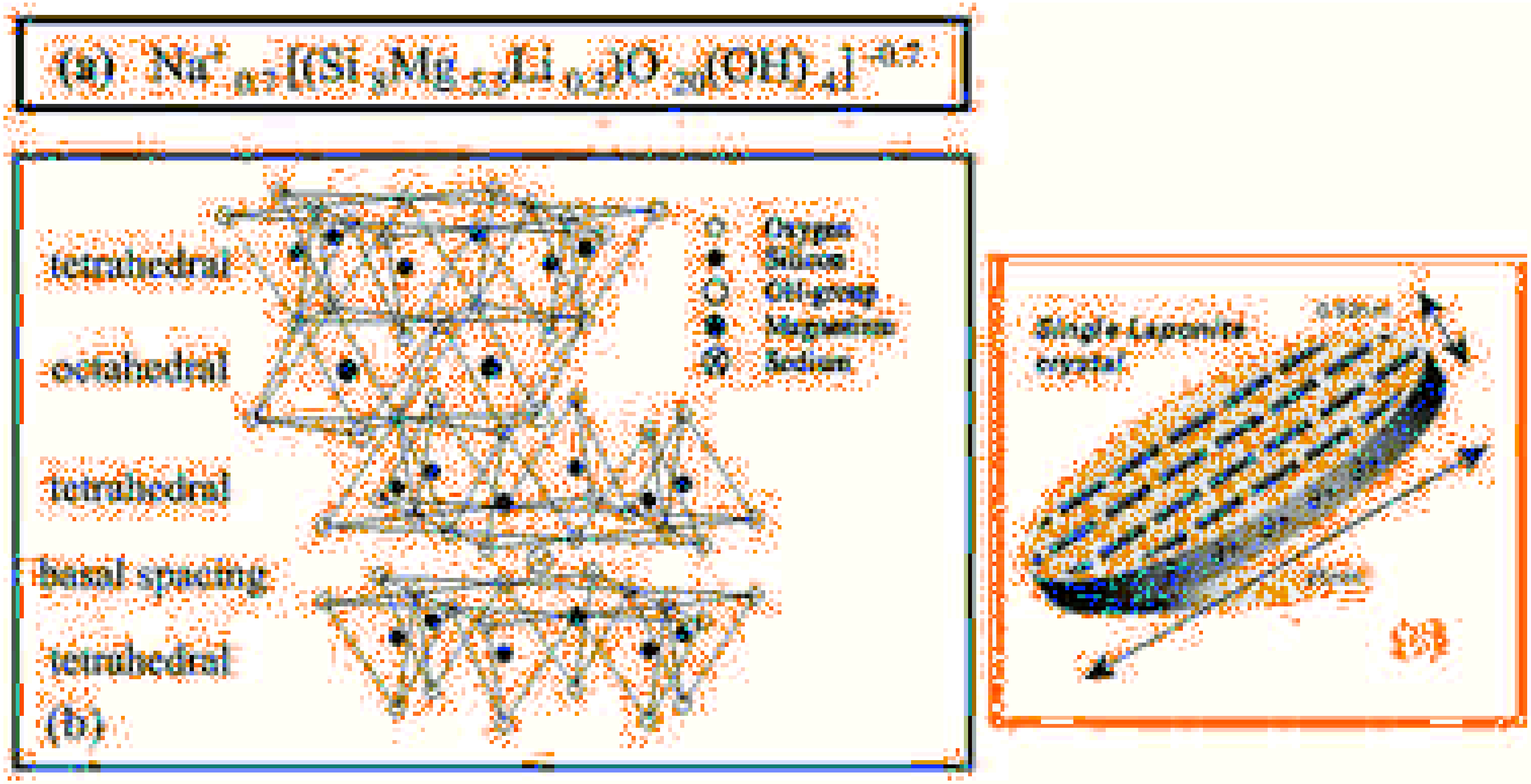
Nematic
Phase (O.P. ≠ 0)



Irving Langmuir (Nobel Prize in Chemistry 1932): 1st experimental work in 1938 on liquid crystal structures in a clay suspension.

J. Chem Phys. 6, 873 (1938)

The most common and most used synthetic clay: Laponite



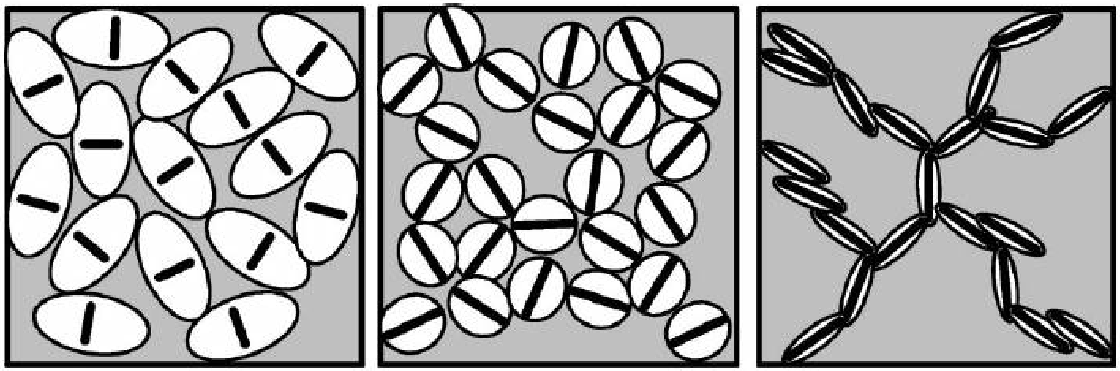
Colloidal gels: **Clay goes patchy**,
W. K. Kegel & H. N. W. Lekkerkerker,
Nature Materials 10, 5–6 (2011)

Observation of empty liquids and **equilibrium gels in a colloidal clay**,
B. Ruzicka, E. Zaccarelli, L. Zulian, R. Angelini, M. Sztucki, A. Moussaïd,
T. Narayanan and F. Sciortino, **Nature Materials 10, 56-60 (2011)**

PHYSICAL REVIEW E **69**, 031404 (2004)

Nonergodic states of charged colloidal suspensions: Repulsive and attractive glasses and gels

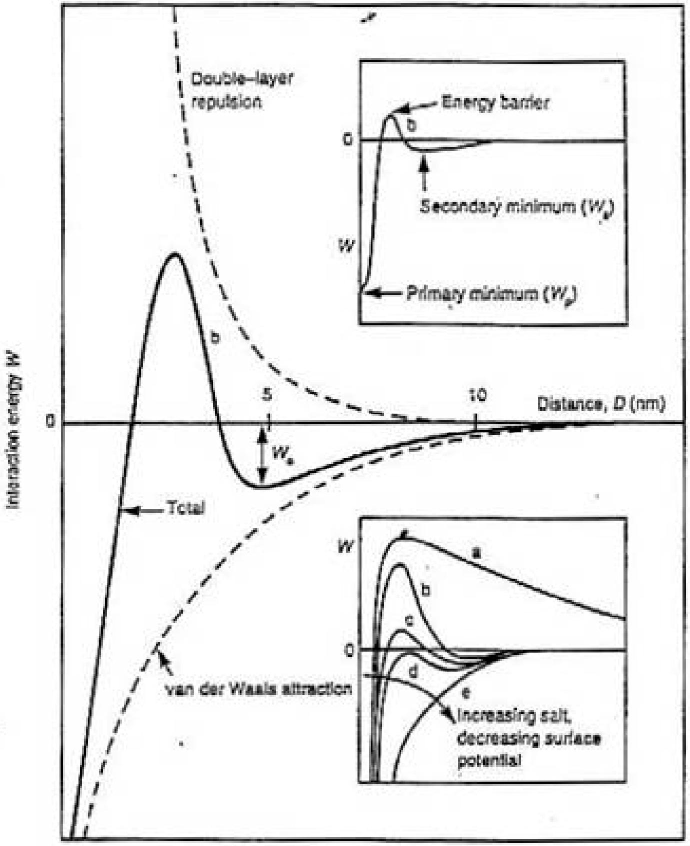
Hajime Tanaka,[1] Jacques Meunier,[2] and Daniel Bonn[2,3]



(a) (b) (c)

FIG. 1.
Schematic figures representing repulsive ‘‘Wigner’’ colloidal glass (a), attractive glass (b), and gel (c). Each thick line represents a Laponite disk, while a white ellipsoid represents the range of electrostatic repulsions: (a), long-range electrostatic repulsions dominate. (b), attractive interactions affect the spatial distribution but repulsive interactions still
play the predominant role in the slow dynamics of the system. (c), attractive interactions play a dominant role; a percolated network forms, which gives the system its elasticity and higher yield stress.

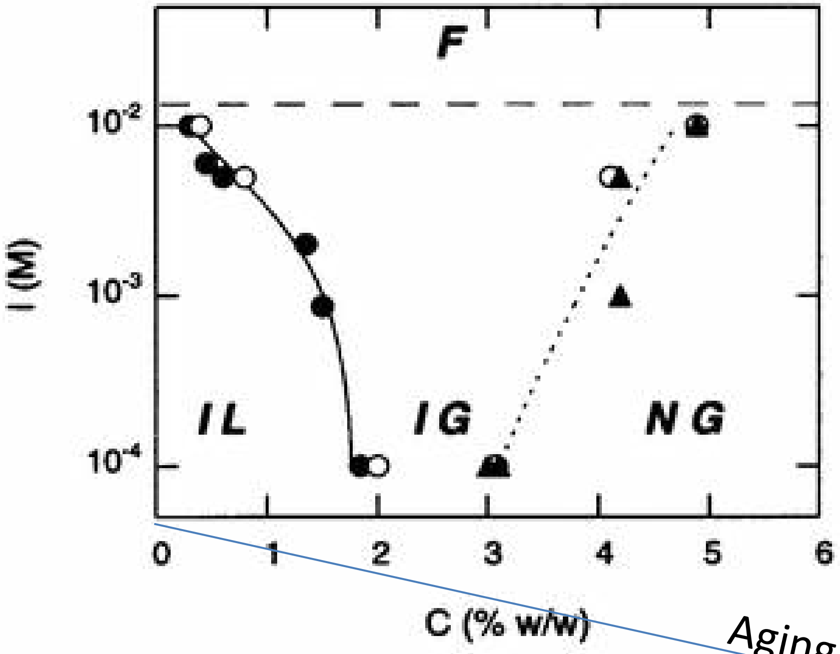
DLVO Theory:
vdW + Screened Electrostatic Rep.



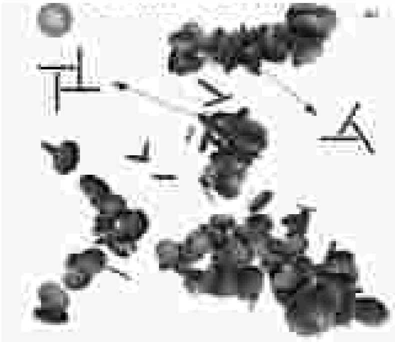
Langmuir **1998**, *14*, 4718–4723

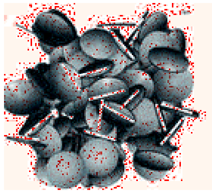
On Viscoelastic, Birefringent, and Swelling Properties of Laponite Clay Suspensions: Revisited Phase Diagram

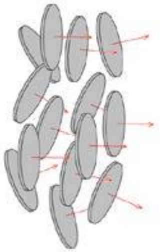
A. Mourchid,* E. Lécolier, H. Van Damme, and P. Levitz*



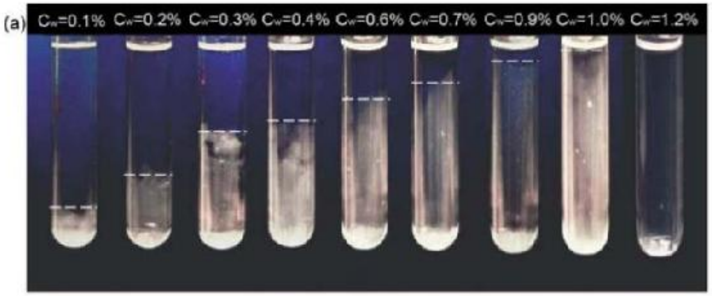
Aging time







One sample for each point



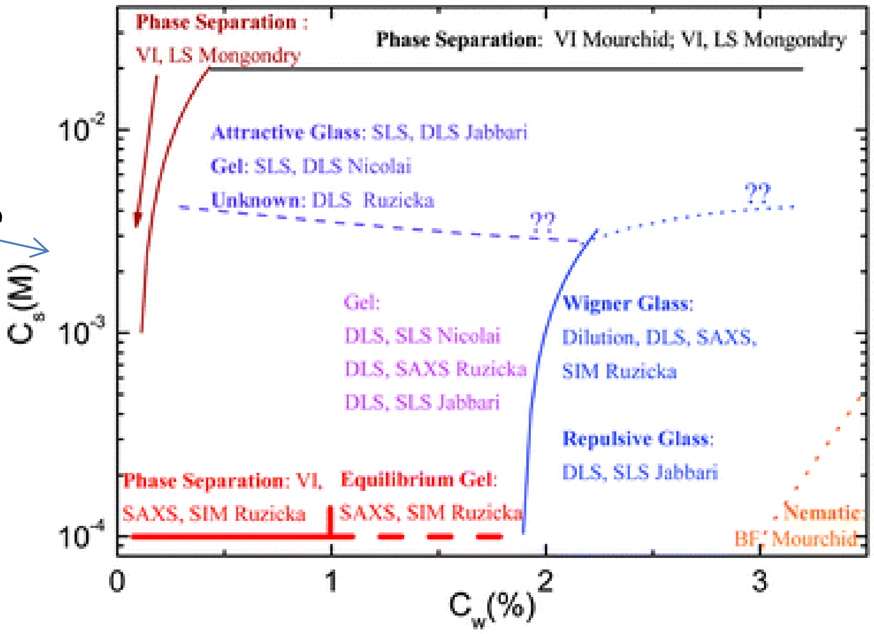
Soft Matter

Cite this: *Soft Matter*, 2011, **7**, 1268

www.rsc.org/softmatter

A fresh look at the Laponite phase diagram

Barbara Ruzicka*[a] and Emanuela Zaccarelli*[b]



Soft Matter

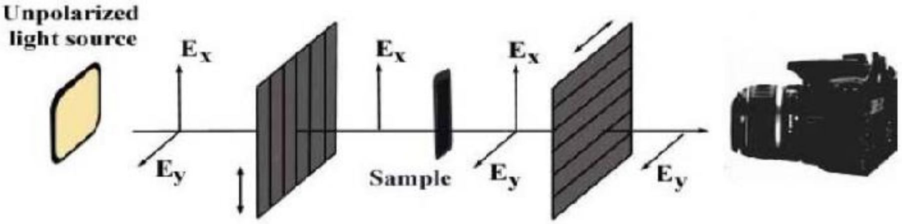
RSC Publishing

PAPER

Orientational order in a glass of charged platelets with a concentration gradient

Cite this: *Soft Matter*, 2013, **9**, 9999

Elisabeth Lindbo Hansen,*[a] Sara Jabbari-Farouji,[b] Henrik Mauroy,[c] Tomás S. Plivelic,[d] Daniel Bonn[e] and Jon Otto Fossum[a]



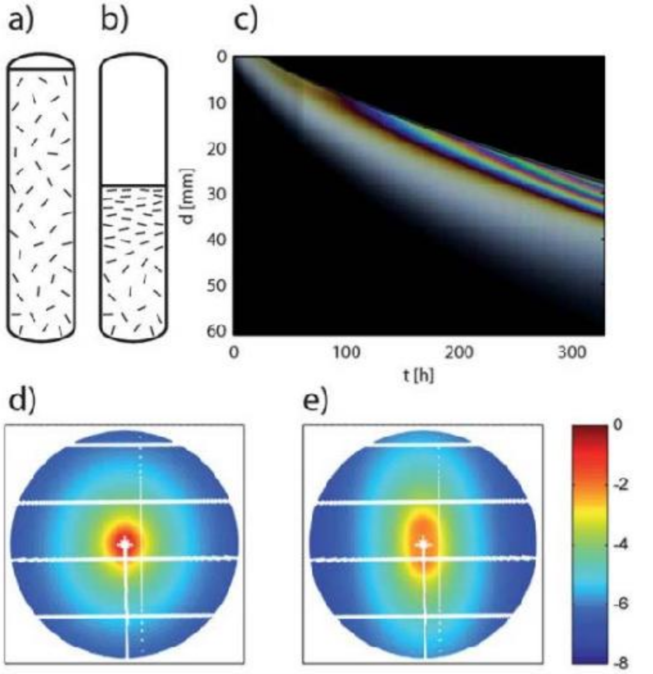
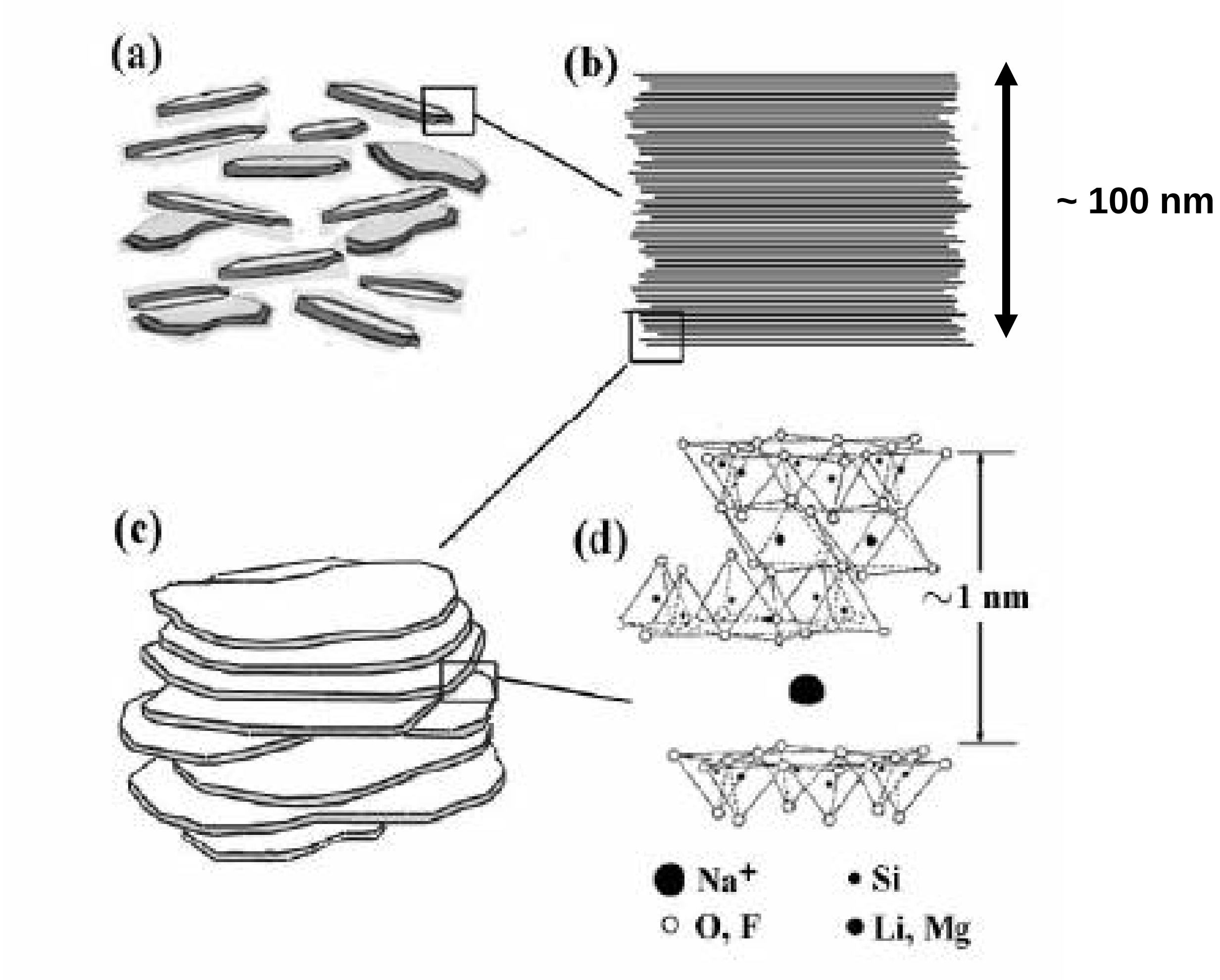


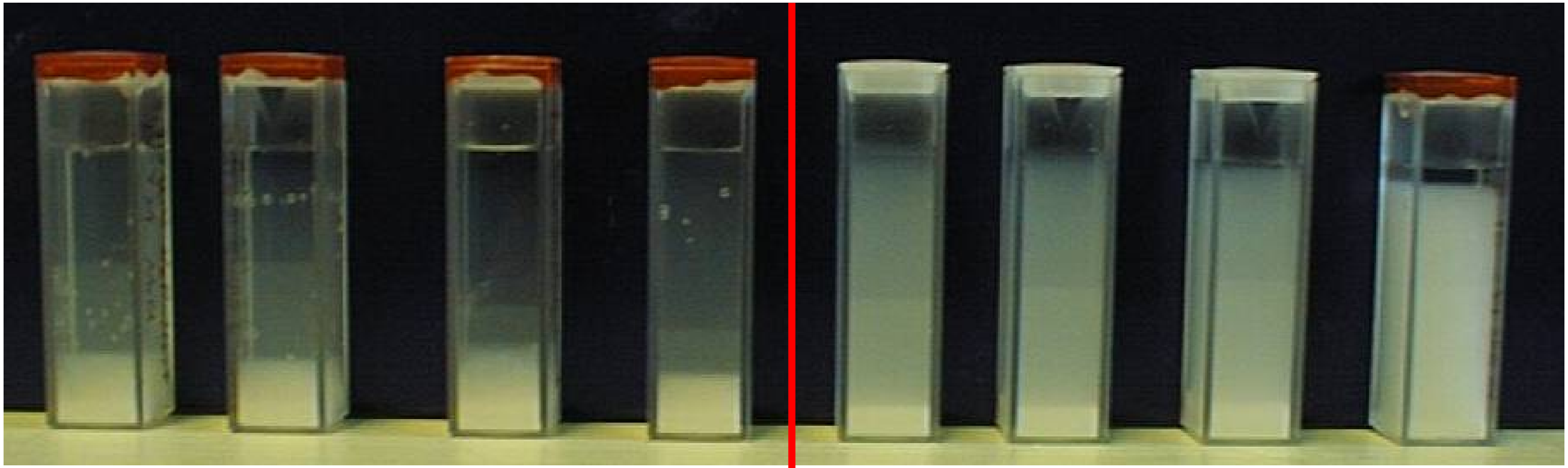
Fig. 2 a) Schematic of the structure of an isotropic Laponite glass and (b) of a Laponite glass with evaporation-induced orientational order. (c) A spatio-temporal plot of developing birefringence in an evaporating $C_w = 3.0$ wt% LRD sample, showing the central part of a capillary imaged at successive waiting times. Crossed linear polarizers were oriented at 45 deg with the vertical capillary axis. The thickness of the sample was $l = 2.65$ nm, so that 4th order magenta, appearing at the interface near the end of this time series, implies a $\Delta n = 8.3 \times 10^{-4}$. (d) SAXS pattern collected from the sample imaged in (c) at a distance of 10 mm from the interface, at the end of the time series, and (e) just below the interface.

Our clay experimental model system:

Q-fluorohectorite synthetic clay: Q_x-$(Mg_{3-x}Li_x)Si_4O_{10}F_2$,
Q is the exchangeable cation (Q = Na^+, Li^+, Ni^{2+}, Fe^{3+}, etc)



Increasing salt:



”Repulsive nematic”
”Wigner glass”

Particles push each other out towards container walls,

➡ nematic

at high enough concentration

➡ «large» domains

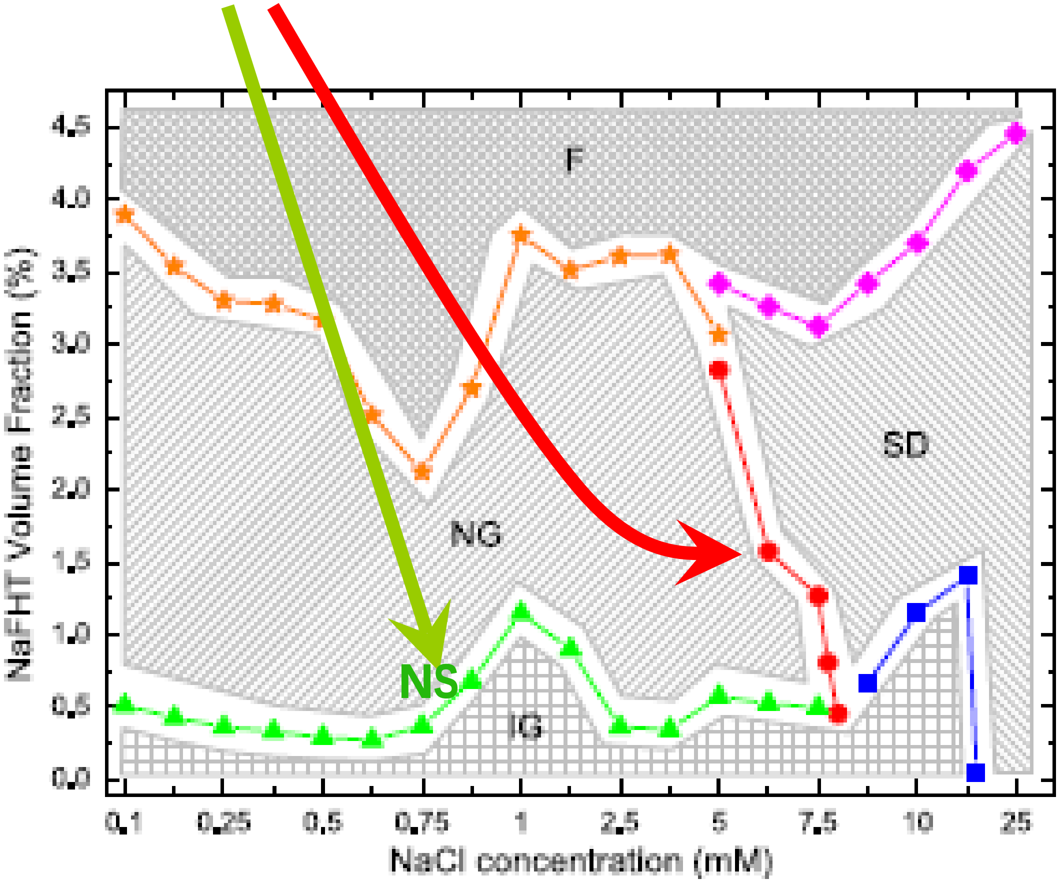
”Attractive nematic”
”Gel”

Particles ”catch each other” in DLVO local minima

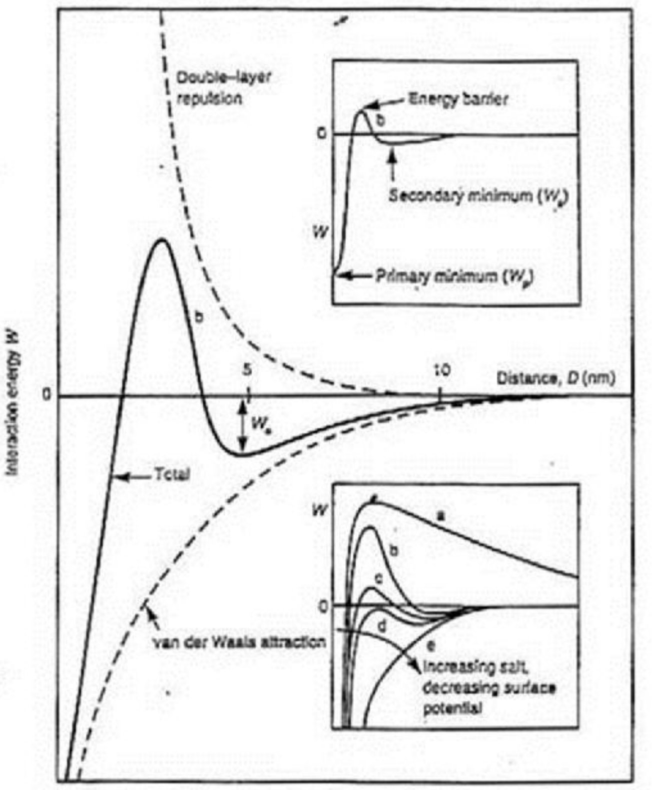
➡ «small» domains

The phase diagram of polydisperse Na-Fluorohectorite–water suspensions: A synchrotron SAXS study, D. M. Fonseca, Y. Meheust, J. O. Fossum, K. D. Knudsen, and K. P. S. Parmar,
Phys.Rev. E 79, 021402 (2009)

Transitions of interest



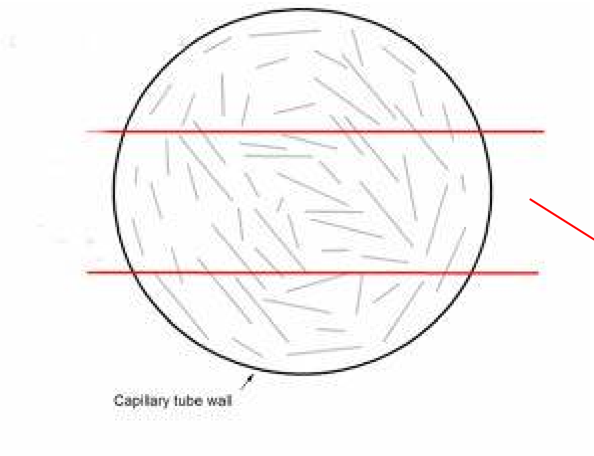
Obtained by combining:
- Eccentricity of SAXS scattering
- Angle of tilt of SAXS scattering
- X-ray transmission

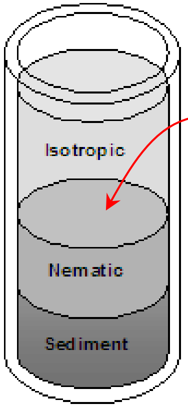


Order Parameter = O.P.
= Angular distribution function
= $S_2 = ½\langle 3\cos^2\theta - 1\rangle$

DLVO theory: vdW + Screened electrostatic rep.
(i.e The clay particles are effectively soft)

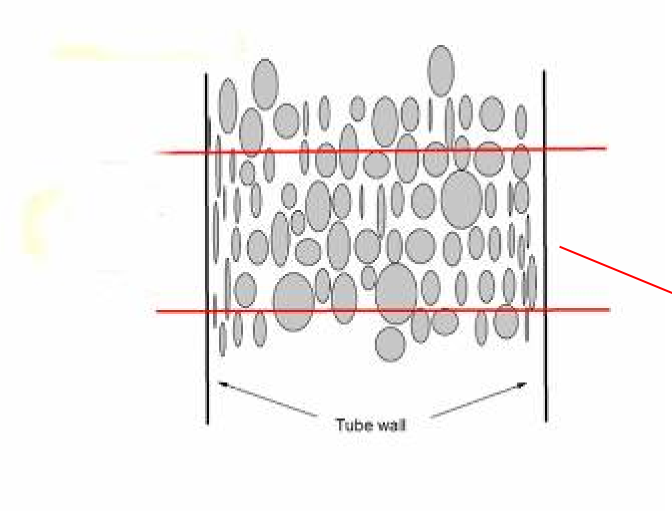
Cartoon of nematic phase of clay platelets seen from above:

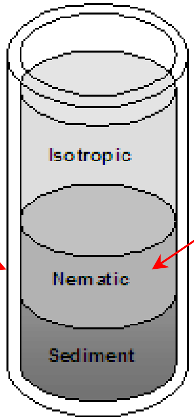




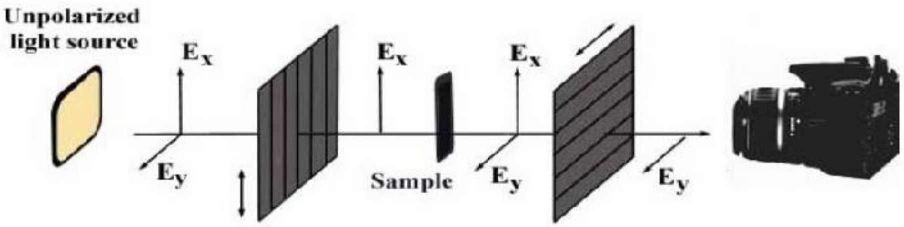
Wall anchoring

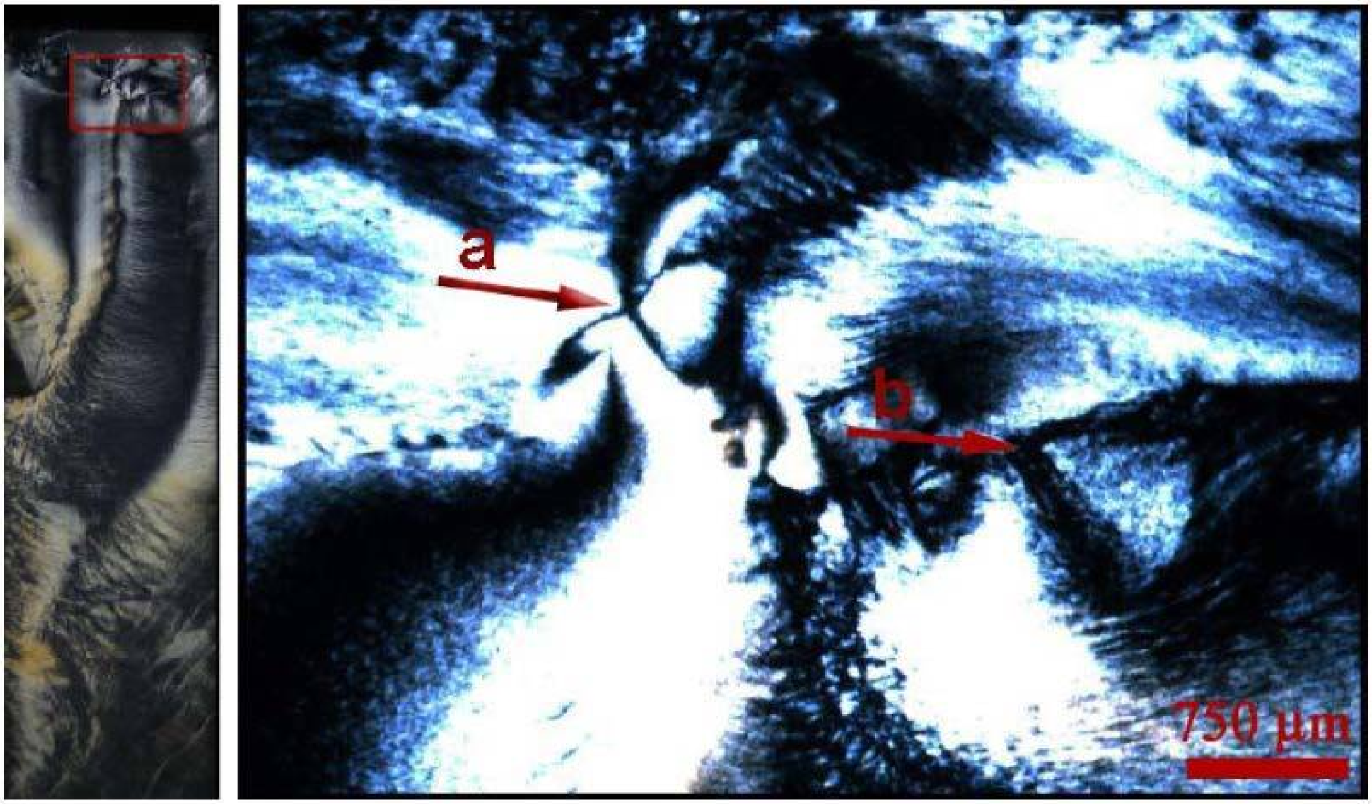
Cartoon of nematic phase of clay platelets, side-view:





Order Parameter = O.P.
= Angular distribution function
= $S_2 = ½\langle 3\cos^2\theta - 1 \rangle$





a and **b**
are ”typical”
nematic defect
signatures:
Disclinations
("discontinuity" in
the "inclination"
of the director)

Nematic textures in colloidal dispersions of Na-fluorohectorite synthetic clay. N.I. Ringdal, D.M. Fonseca, E.L. Hansen, H. Hemmen, and J.O. Fossum. **Phys.Rev. E 81, 041702 (2010)**

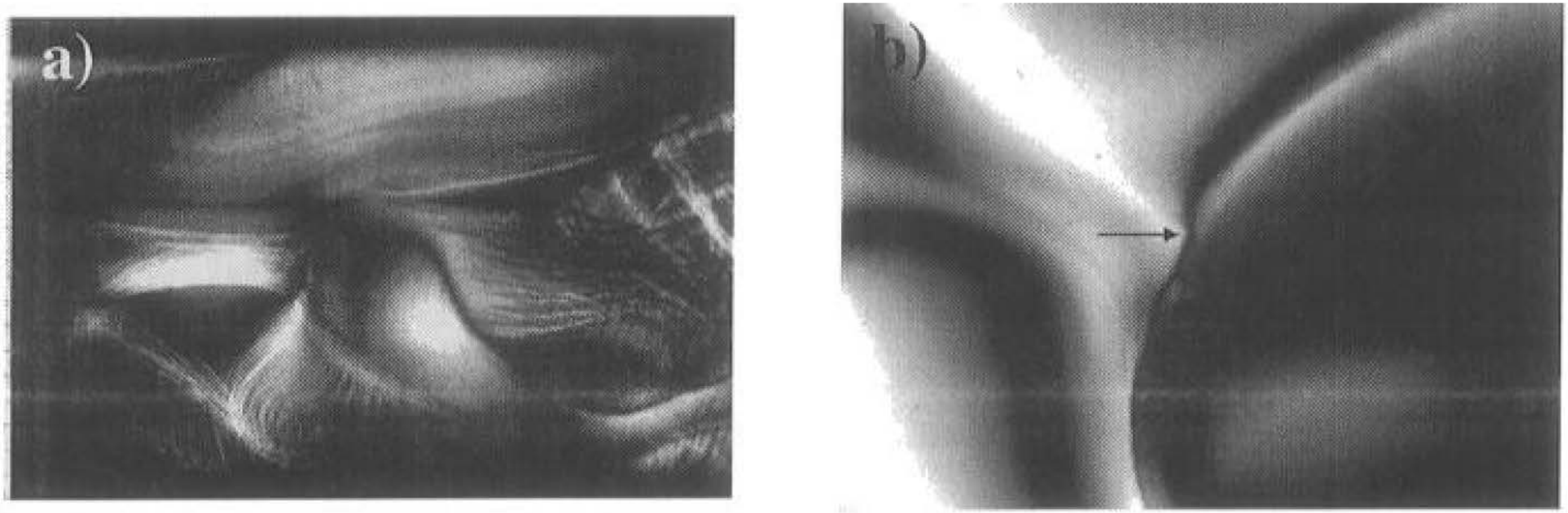
J. Phys. Chem. **1996,** *100,* 11139−11143 **11139**

Observation of Nematic Liquid-Crystal Textures in Aqueous Gels of Smectite Clays

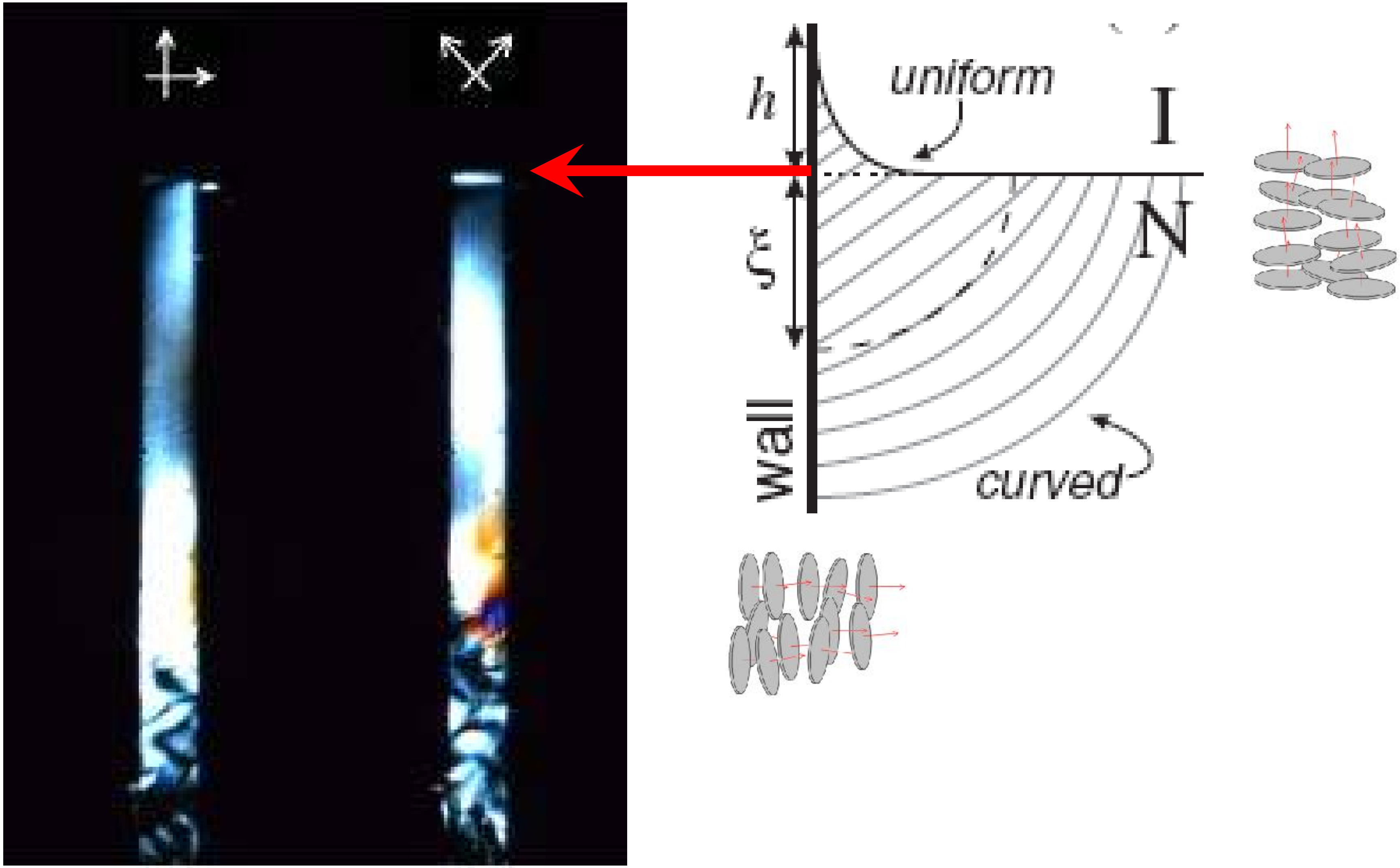
Jean-Christophe P. Gabriel,[*,†] **Clément Sanchez,**[‡] **and Patrick Davidson**[†,§]

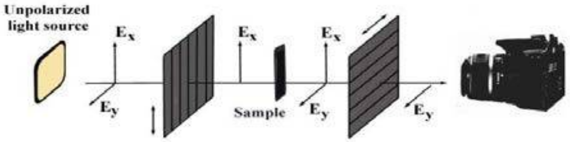
Materials Research Laboratory, University of California, Santa Barbara, California 93106, and Laboratoire de Chimie de la Matière Condensée (CNRS), Université Pierre et Marie Curie, 75252 Paris, France

Received: April 11, 1996[⊗]



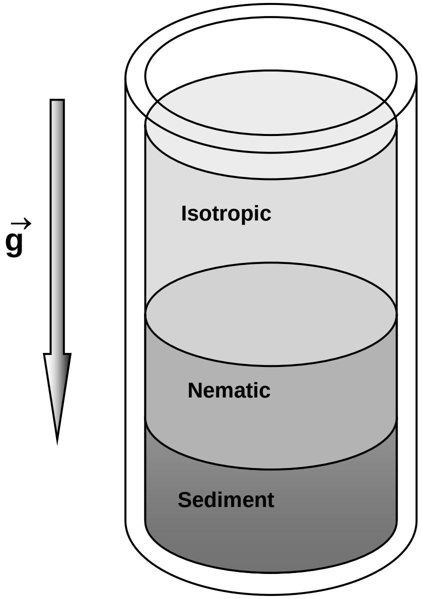
Anchoring to Nematic-Isotropic Interface:





The Isotropic-Nematic Interface in Suspensions of Na-Fluorohectorite Synthetic Clay. H. Hemmen, N. I. Ringdal, E. N. De Azevedo, M. Engelsberg, E. L. Hansen, Y. Meheust, J. O. Fossum and K. D. Knudsen. **Langmuir 25, 12507–12515 (2009)**

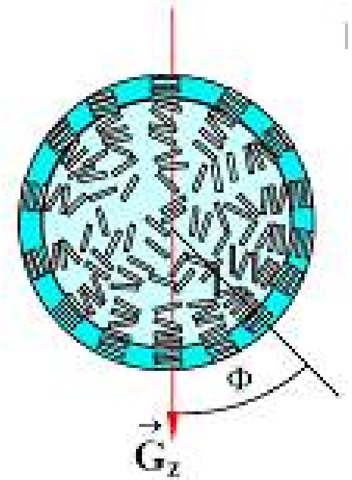
Response to magnetic field: Magnetic field guided self-organization:



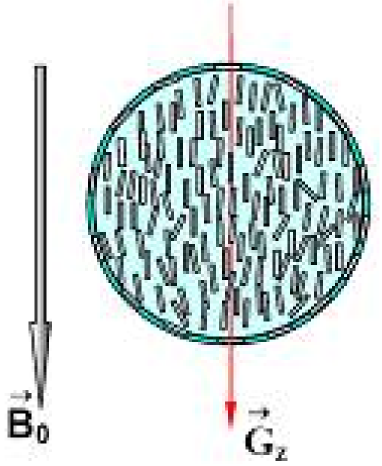
Glass wall anchoring confirmed by spatially resolved MRI measurements of anisotropic self-diffusion coefficient of water in the nematic phase.

Magnetic field induced ordering, due to diamagnetic anisotropy of the platelets at fields <u>above about 1 Tesla</u>.

S_2 ~ -0.3



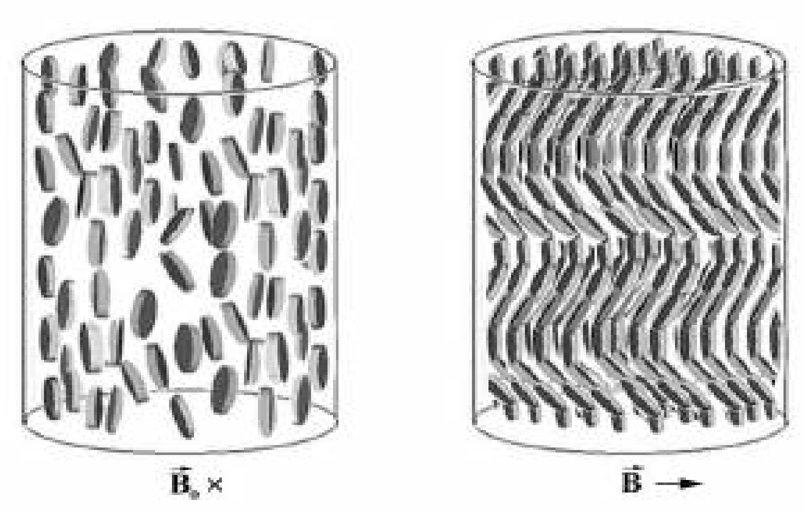
S_2 ~ +0,5

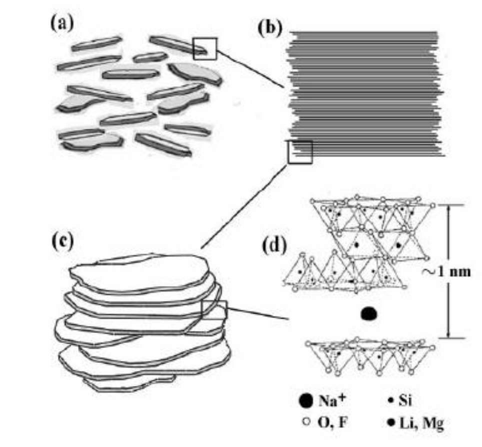


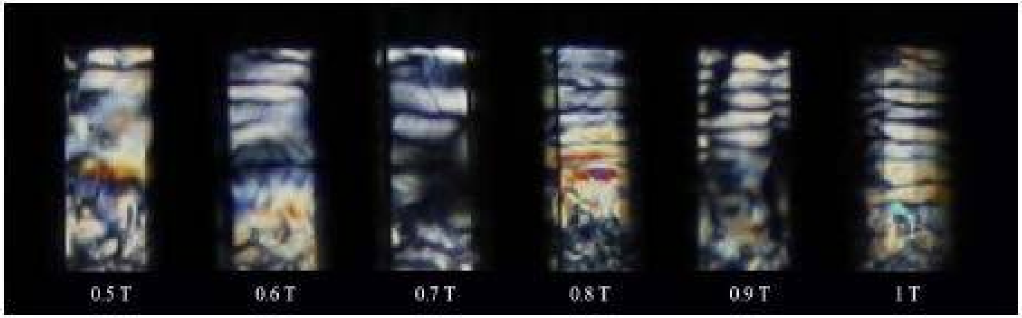
Anisotropic water diffusion in nematic self assemblies of clay nano-platelets suspended in water. E. N. de Azevedo, M. Engelsberg, J. O. Fossum and R. E. de Souza, **Langmuir 23, 5100 (2007)**

Color control of clay nematics between crossed polarizers

The Frederiks transition in an aqueous clay dispersion, H. Hemmen, E.L. Hansen, N.I. Ringdal and J.O. Fossum,
Revista Cubana de Fisica, vol. 29-1E, 59-61 (2012)

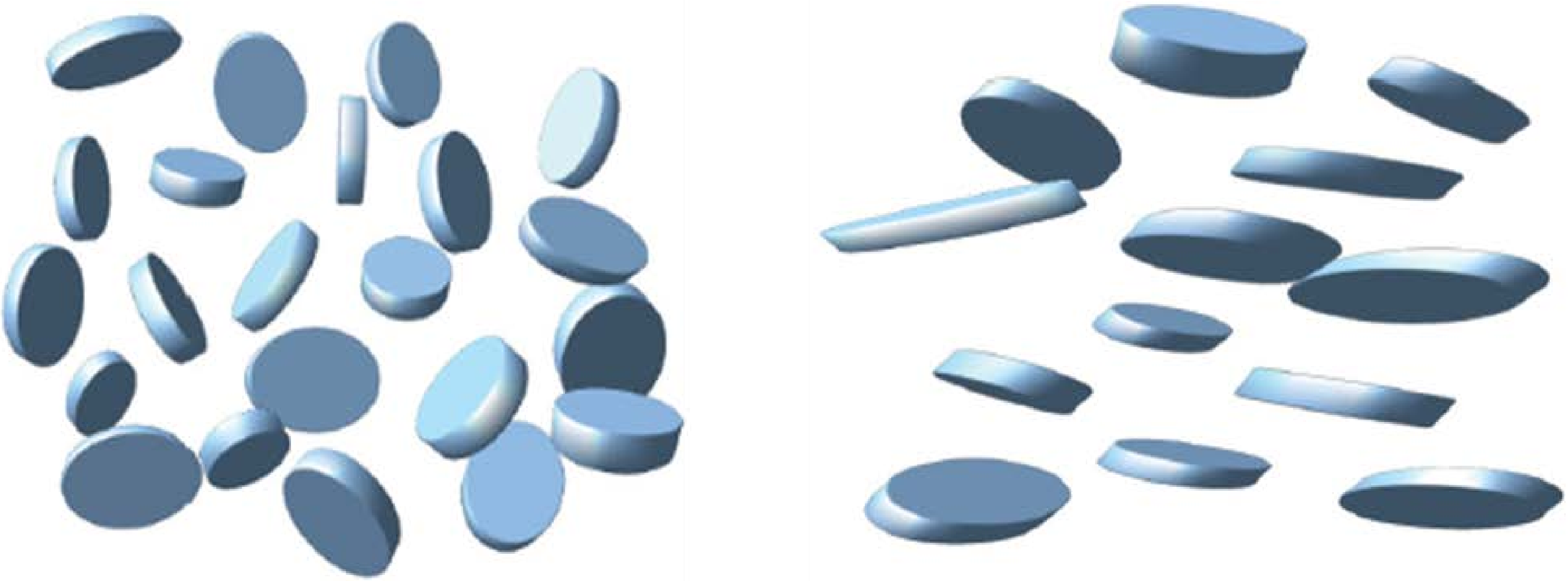






Self-assembly:

Making a macroscopic sample (i.e. about 10^{20} nanoparticles) by physically picking up and moving nanoparticles into place, one by one, would take about 300 million years, even if the time for moving individual particles could be made as short as 1 millisecond.



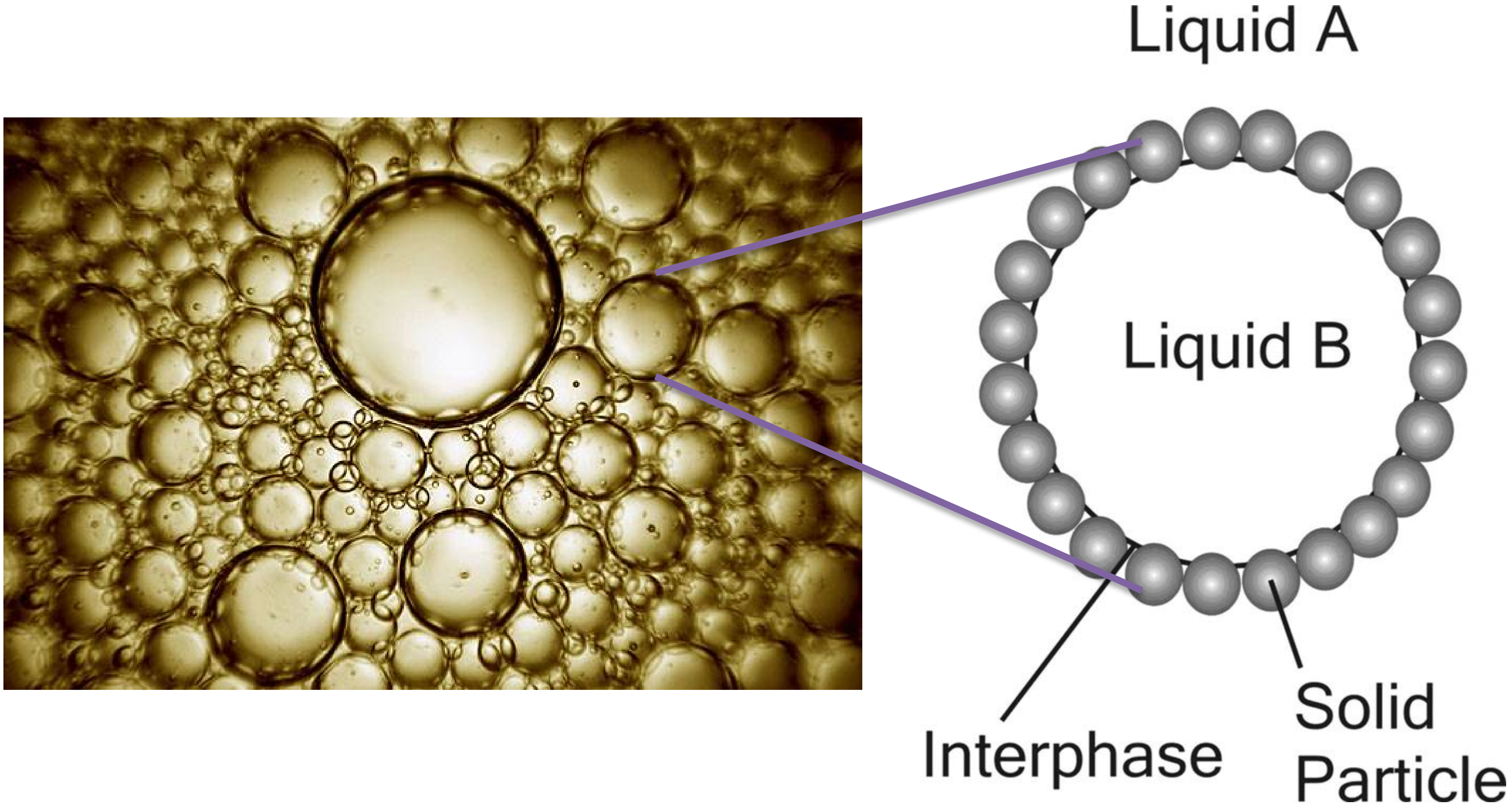
Human made design:
Top-down Self-assembly

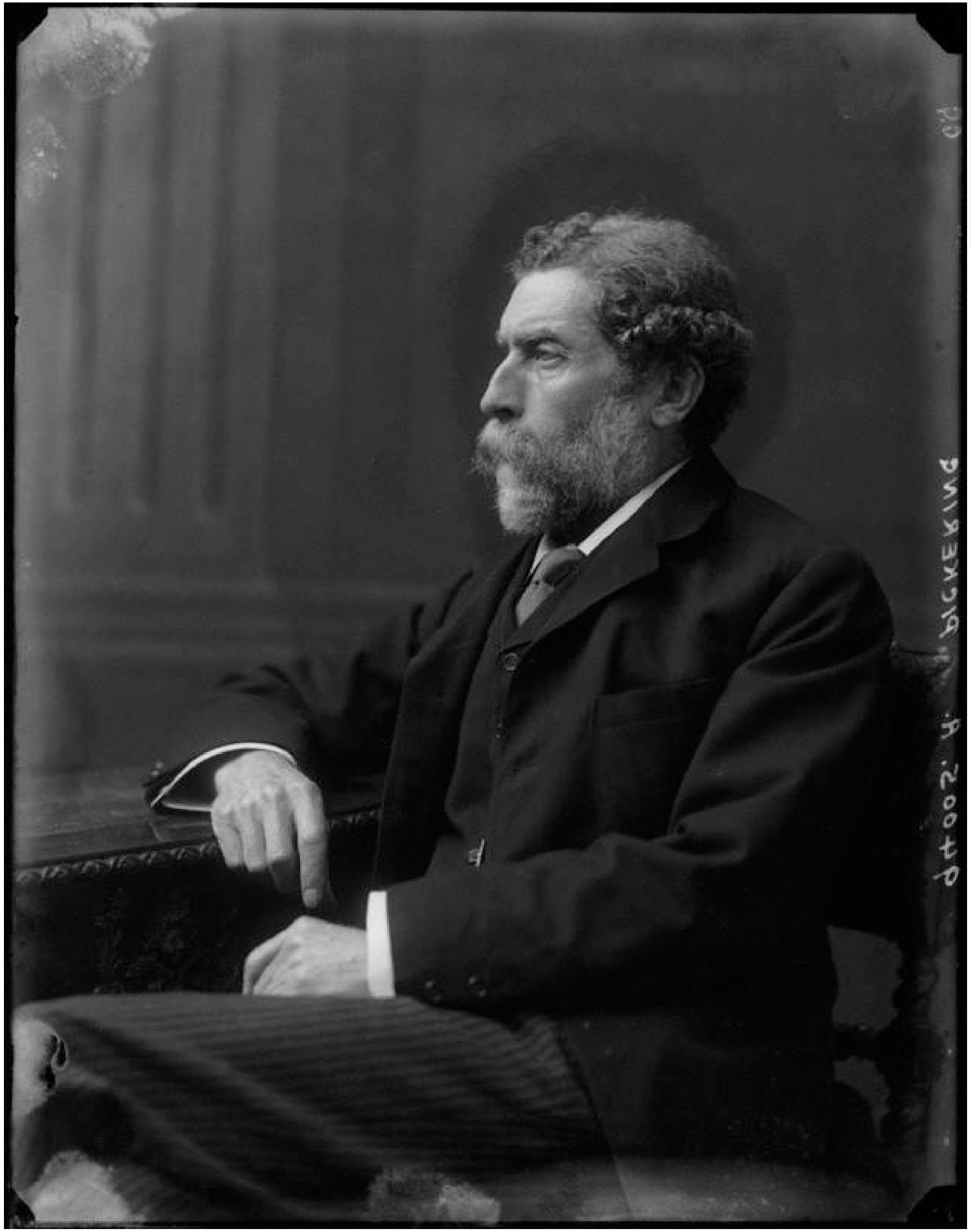
How nature works:
Bottom-up Self-assembly

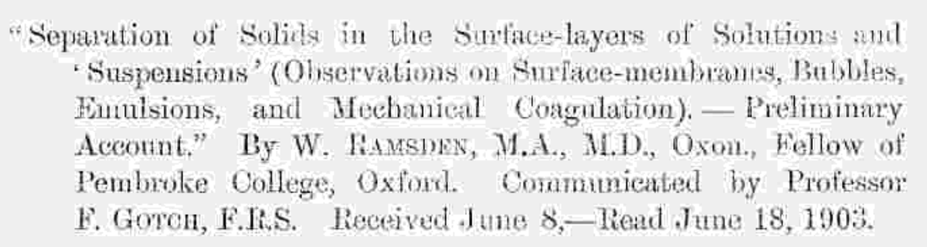
Scientific challenge of nanostructured self-assembly:
Combination of Top-down and Bottom-up:

Another pile of rocks

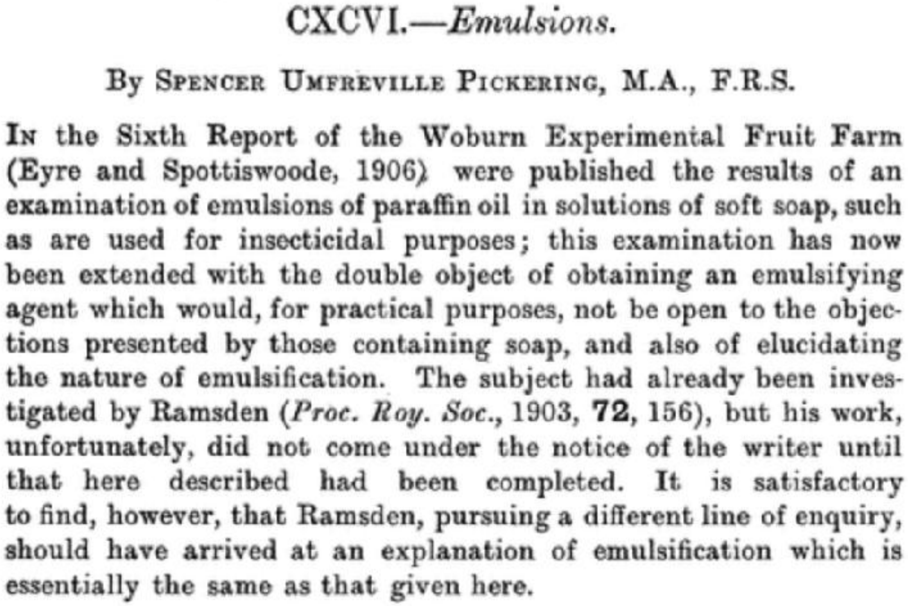
Clay particles as emulsion stabilizers: Pickering («physical») emulsions






"Separation of Solids in the Surface-layers of Solutions and 'Suspensions' (Observations on Surface-membranes, Bubbles, Emulsions, and Mechanical Coagulation). — Preliminary Account." By W. Ramsden, M.A., M.D., Oxon., Fellow of Pembroke College, Oxford. Communicated by Professor F. Gotch, F.R.S. Received June 8,—Read June 18, 1903.

J. Chem. Soc., Trans., 1907,**91**, 2001-2021

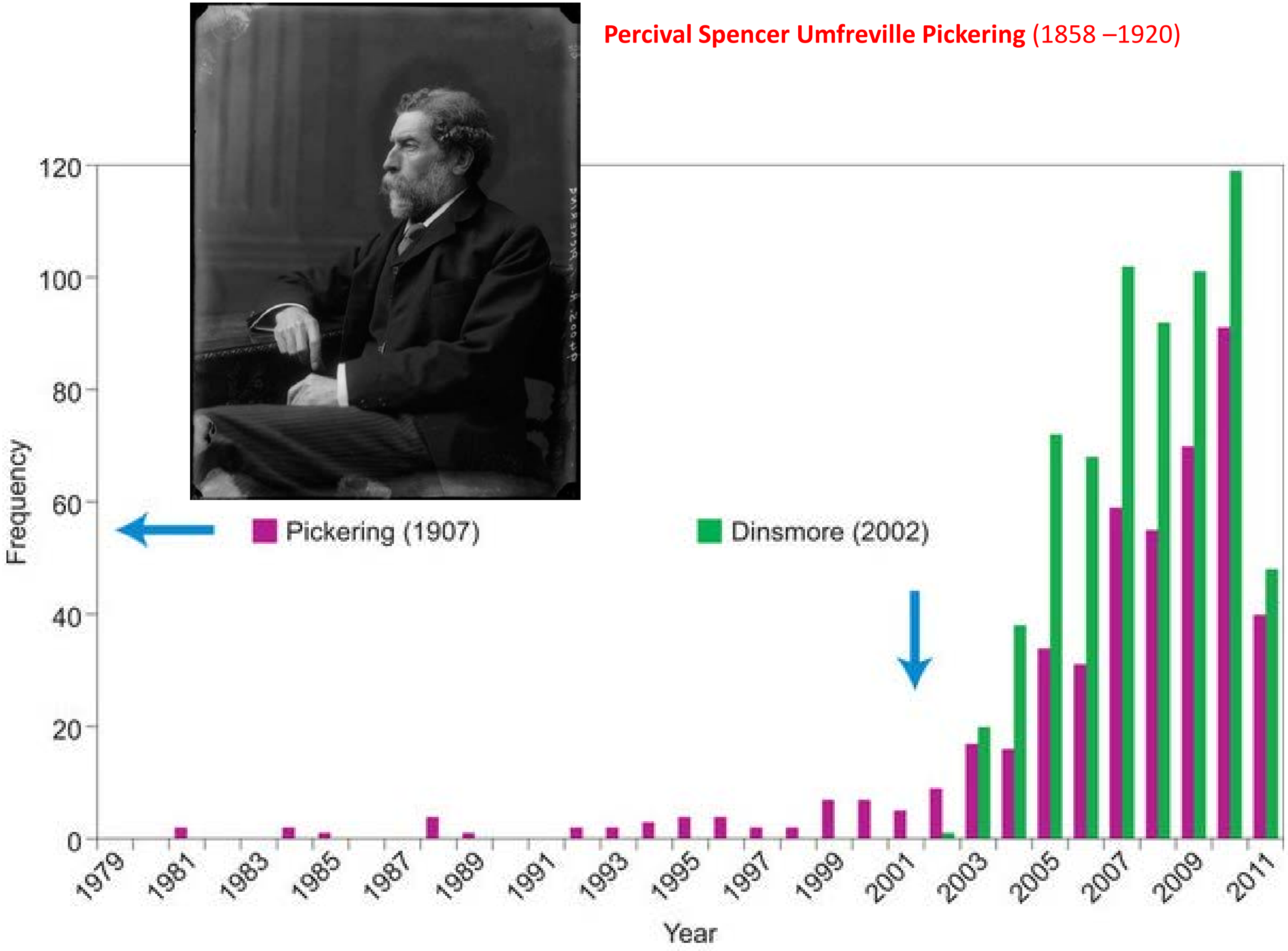

CXCVI.—*Emulsions.*

By Spencer Umfreville Pickering, M.A., F.R.S.

In the Sixth Report of the Woburn Experimental Fruit Farm (Eyre and Spottiswoode, 1906) were published the results of an examination of emulsions of paraffin oil in solutions of soft soap, such as are used for insecticidal purposes; this examination has now been extended with the double object of obtaining an emulsifying agent which would, for practical purposes, not be open to the objections presented by those containing soap, and also of elucidating the nature of emulsification. The subject had already been investigated by Ramsden (*Proc. Roy. Soc.*, 1903, **72**, 156), but his work, unfortunately, did not come under the notice of the writer until that here described had been completed. It is satisfactory to find, however, that Ramsden, pursuing a different line of enquiry, should have arrived at an explanation of emulsification which is essentially the same as that given here.

Percival Spencer Umfreville Pickering (1858 –1920)

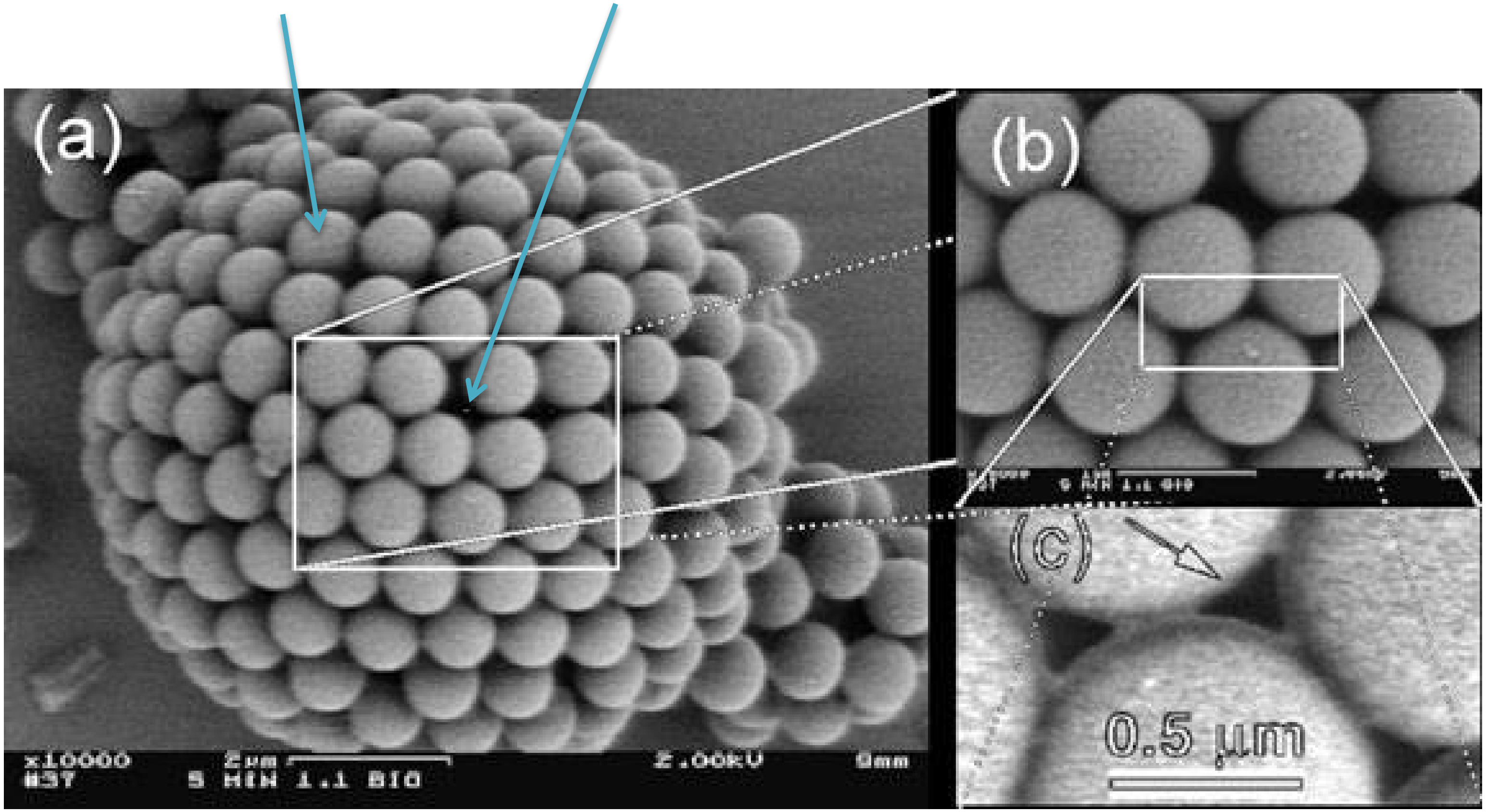
Percival Spencer Umfreville Pickering (1858 –1920)



Lost history versus good science, Qian Wang, & Chris Toumey,
Nature Chemistry 3, 832–833, doi:10.1038/nchem.1179 (2011)

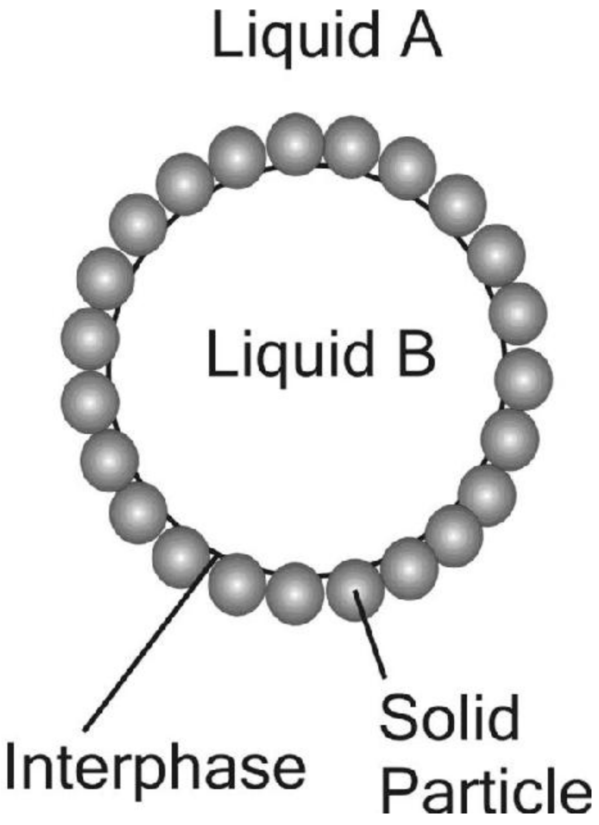
Colloidosomes

Composition and permeability



A.D. Dinsmore et. Al., Science, **298**, 1006 (2002); David Weitz group: Harvard Univ.

Capillary binding



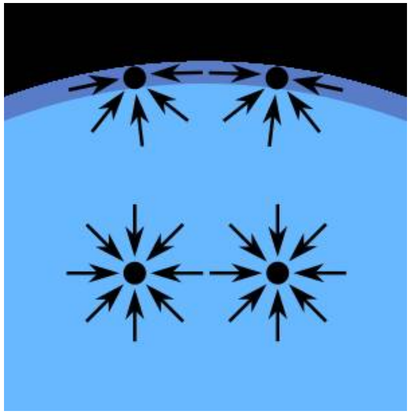
Surface Energy: $E = \gamma A$

$A = \text{Surface area}$ $\gamma_{WA} = 0.0073\,\text{N/m}$

Capillary binding: A particle at the interface is trapped in a capillary barrier with a substantial energy cost of moving to either side of the liquid interface.

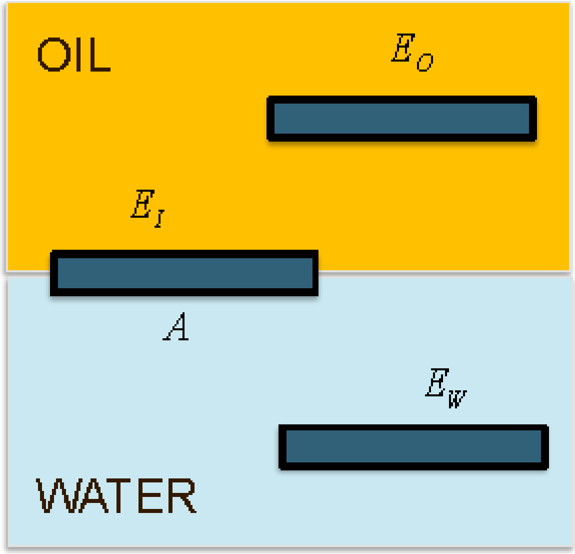
Origin of capillary binding:
Surface tension:

The forces on molecules of a liquid:



Surface tension preventing a paper clip from submerging

Capillary binding of a flat solid particle at a liquid interface



Particle surface energy :

$$E_O = 2A\gamma_{SO}$$

$$E_W = 2A\gamma_{SW}$$

$$E_I = A\gamma_{SO} + A\gamma_{SW} - A\gamma_{OW}$$

Energy gain :

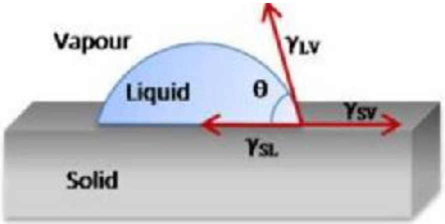
$$E_I - E_O = -A\gamma_{OW}(1+\cos\theta)$$

$$E_I - E_W = -A\gamma_{OW}(1-\cos\theta)$$

Wetting angle Young's relation:

$$\gamma_{SO} = \gamma_{SW} + \gamma_{OW}\cos\theta$$

Energetically favorable to adsorb particles at the interface.



Typically:

$A_p\gamma_{OW}$ ~ 10000 kT for microparticles

Oil drops in saline water with suspended Laponite clay particles: Pickering emulsion

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Transition from glass- to gel-like states in clay at a liquid interface

A. Gholamipour-Shirazi, M. S. Carvalho, M. F. G. Huila, K. Araki, P. Dommersnes & J. O. Fossum

Scientific Reports **6**,
Article number: 37239 (2016)
doi:10.1038/srep37239

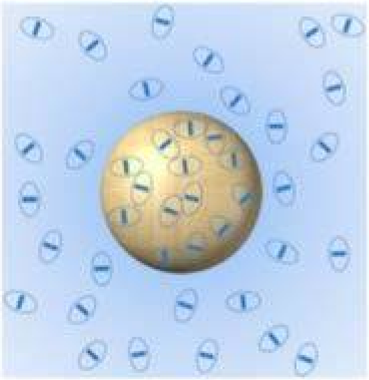
Received: 01 April 2016
Accepted: 18 October 2016
Published online: 24 November 2016

The European Physical Journal Special Topics
July 2016, Volume 225, Issue 4, pp 757–765

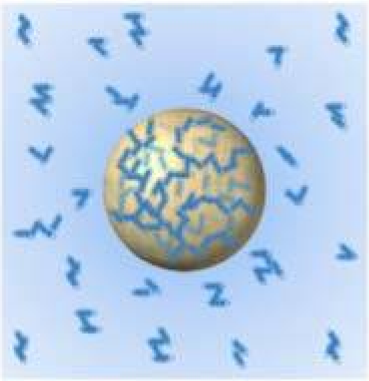
Controlled microfluidic emulsification of oil in a clay nanofluid: Role of salt for Pickering stabilization

Authors Authors and affiliations

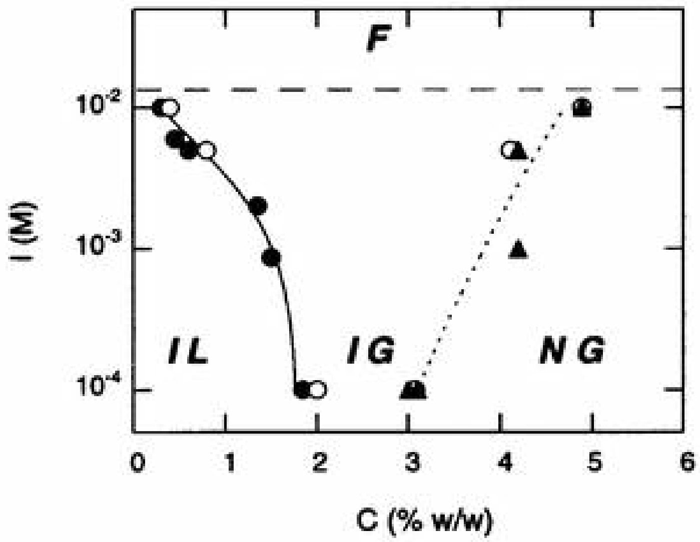
A. Gholamipour Shirazi, M.S. Carvalho, J.O. Fossum



No salt:
Pickering film
not observable by
Raman microscopy.
Observable surface tension.



With salt:
~ 4 μm Pickering film.
Increased surface tension.



Until now in this talk:

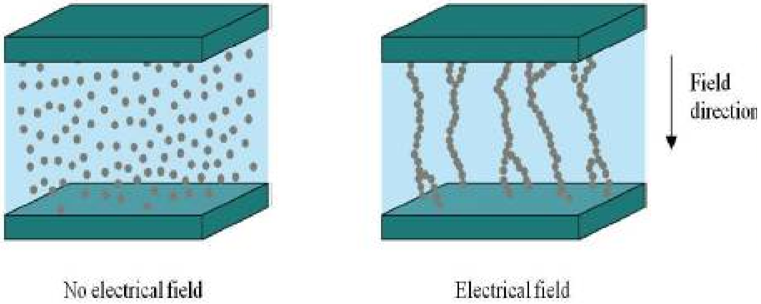
Self-assembly of clay particles suspended in saline water

(+ in one case with oil drops)

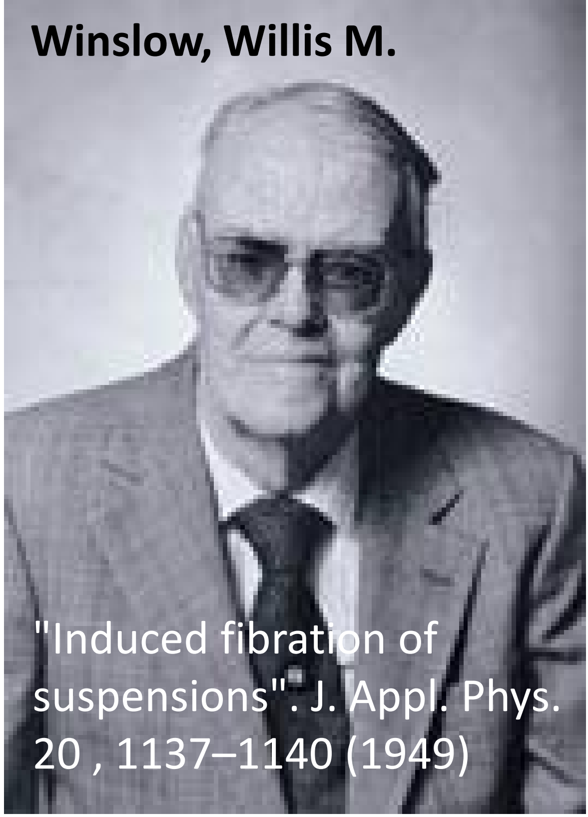
What about clay particles suspended in oil?

Electro-rheological fluids

Winslow effect:



Viscosity can increase by a factor 100 000 in response to an electric field!

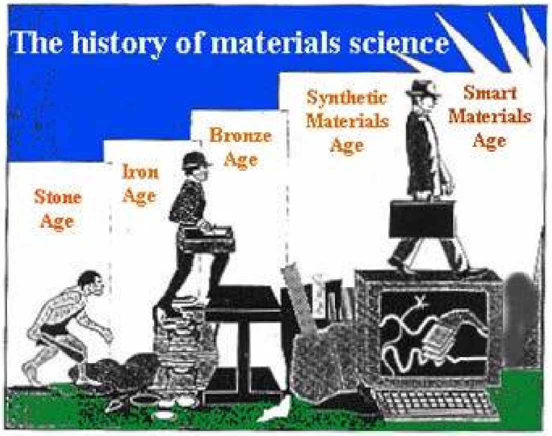


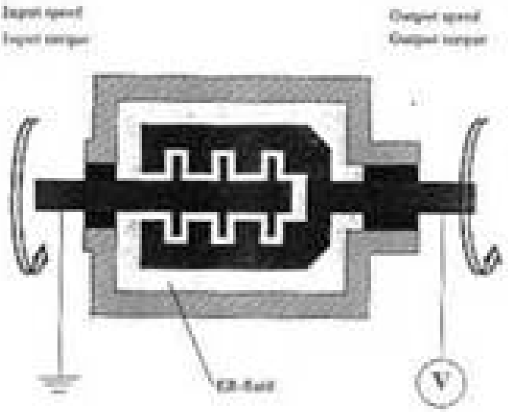
Winslow, Willis M.

"Induced fibration of suspensions". J. Appl. Phys. 20 , 1137–1140 (1949)

- Electric fields induce dipole attraction and chain formation
- Large yield stress -> 200 kPa or more 100 times viscosity increase (up to 100000 times according to wiki)

U.S. Patent 2,417,850: Winslow, W. M.: 'Method and means for translating electrical impulses into mechanical force', 25 March 1947

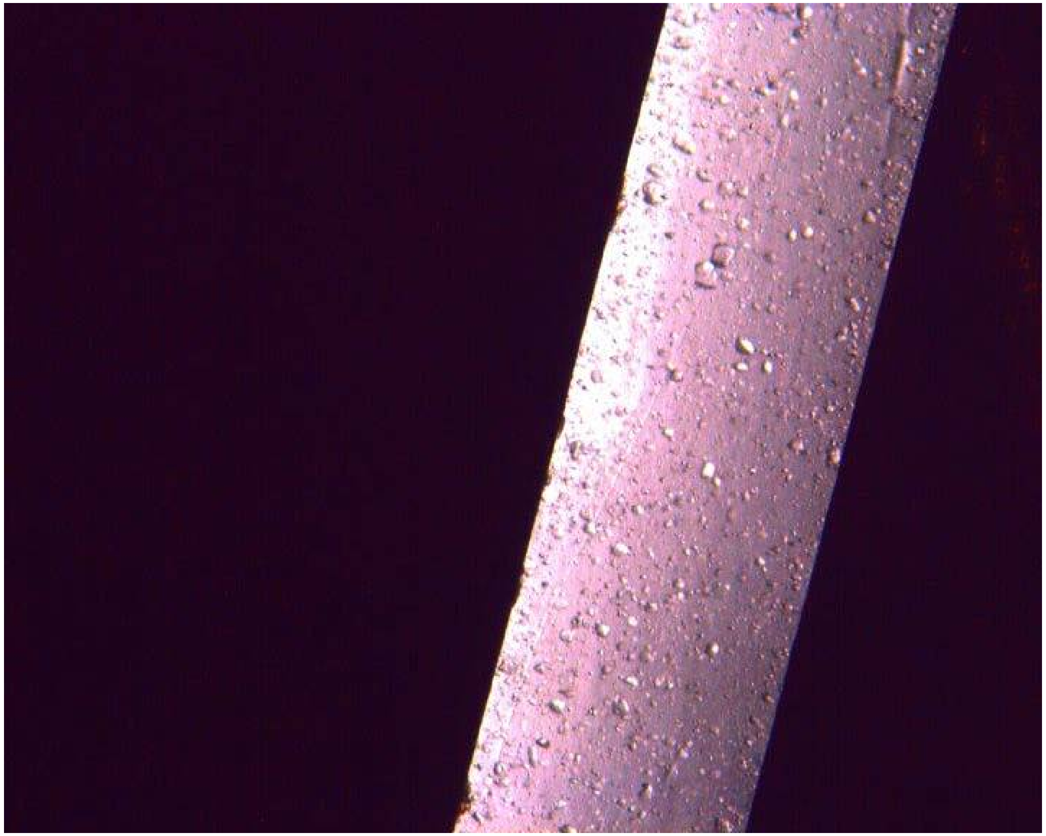




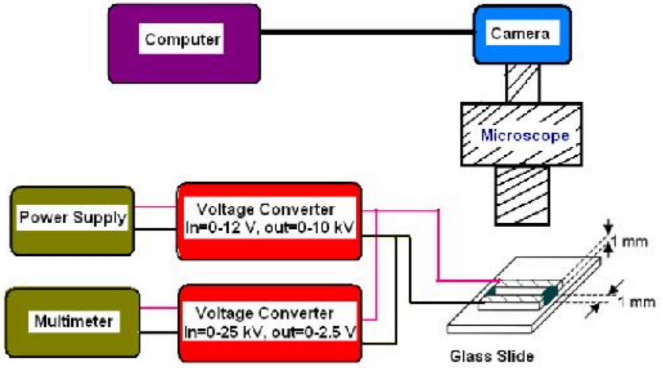
Clay particles suspended in oil:

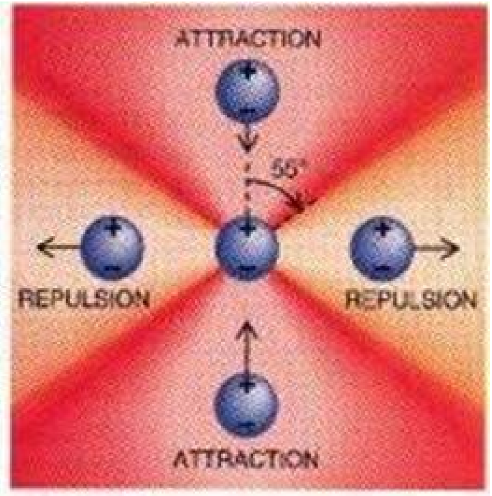
Video microscopy (real time):

~500 V



1 mm

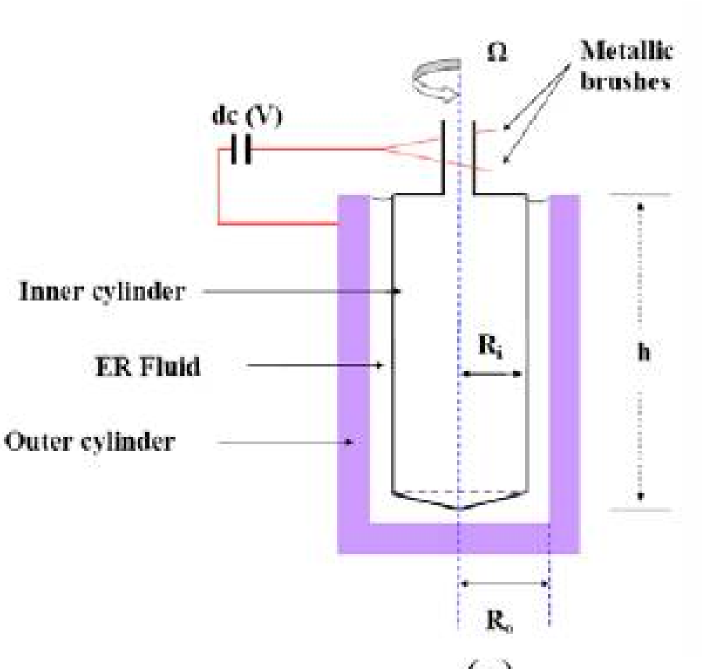




Electrorheology: Smart Materials

Intercalation-enhanced electric polarization and chain formation of nano-layered particles, J.O. Fossum, Y. Méheust, K.P.S. Parmar, K.D. Knudsen, K.J. Måløy and D. M. de Fonseca, Europhys. Lett., 74, 438-444 (2006)

Our Physica MCR 300 Rheometer inl electrorheol. cell:



Langmuir 24, 1814 (2008)

J. Phys.: Condens. Matter 22, 324104 (2010)

J. Rheol. 55, 2011 (2010)