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BELBaR

EURATOM

Clay Colloids in Aqueous Systems

3-4 February 2016, Berlin, Germany

Venue: Seminaris CampusHotel Berlin

Flow of clays

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Trondheim, Norway


NORWAY
Nordkapp
Vardø
Hammerfest
Norwegian Sea
Kirkenes
Alta
Tromsø
Kautokeino
Lofoten Islands
Narvik
Å
Arctic Circle
Bodø
Mo i Rana
NTNU
SWEDEN
FINLAND
0 400 km
0 200 miles
Trondheim
Bottenhavet
Ålesund
Åndalsnes
Central Norway
Jotunheimen National Park
Helsinki
Lillehammer
Finse
Geilo
ATLANTIC OCEAN
Bergen
Oslo
Stockholm
Tallinn
Fredrikstad
Stavanger
ESTONIA
Risør
Baltic Sea
Kristiansand


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

NTNU

Department of Physics

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

Soft condensed matter are complex materials which are easily deformable by external stresses, electric or magnetic fields, or by thermal fluctuations.

Examples:
Foods, cosmetics, personal care products, household products, plastics at vatious stages of processing, salves, paints, crude oils, clays…………., i.e. complex materials built from nano-, micro- particles/structures.

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

Our main motivation for studying <u>clays</u> is that clays may be viewed as good representative model systems for soft condensed matter and complex materials, with ”near” applications.

Questions to ask:

How does nano-scale physics (fex. clay nanostructures) translate into macroscopic (fex. clay flow) behaviors?
What is universal? What is specific?

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We are curiosity driven:

«HEY, SÀM, THE BIG ROUND YELLOW THING CAME UP AGAIN»

Clay avalanches

Norwegian Geotechnical Institute

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 m3 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**

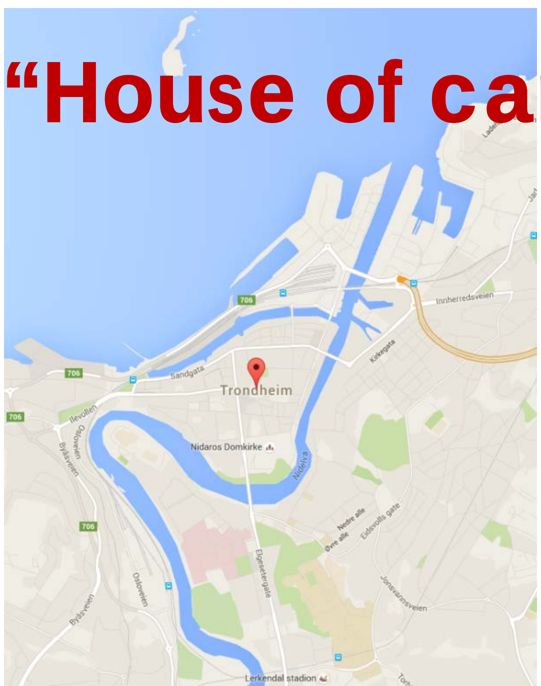
NGI

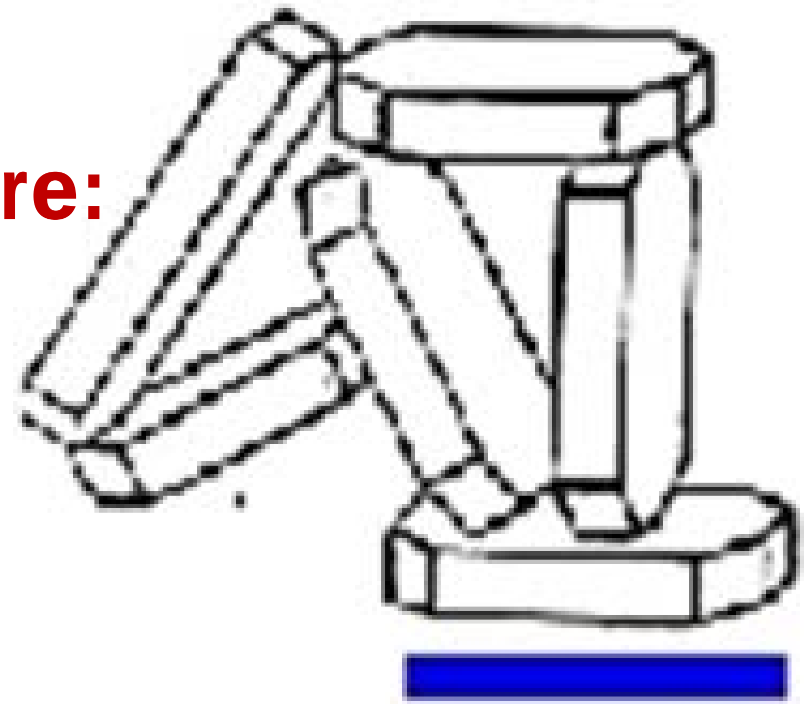
Natural clays are found as sediments.

The <u>natural quick clays</u> were sedimented at the en of the last ice age, for example at river mouths in saline water.

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

"House of card" structure:





~1 μm


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

Simple analog landslide experiments

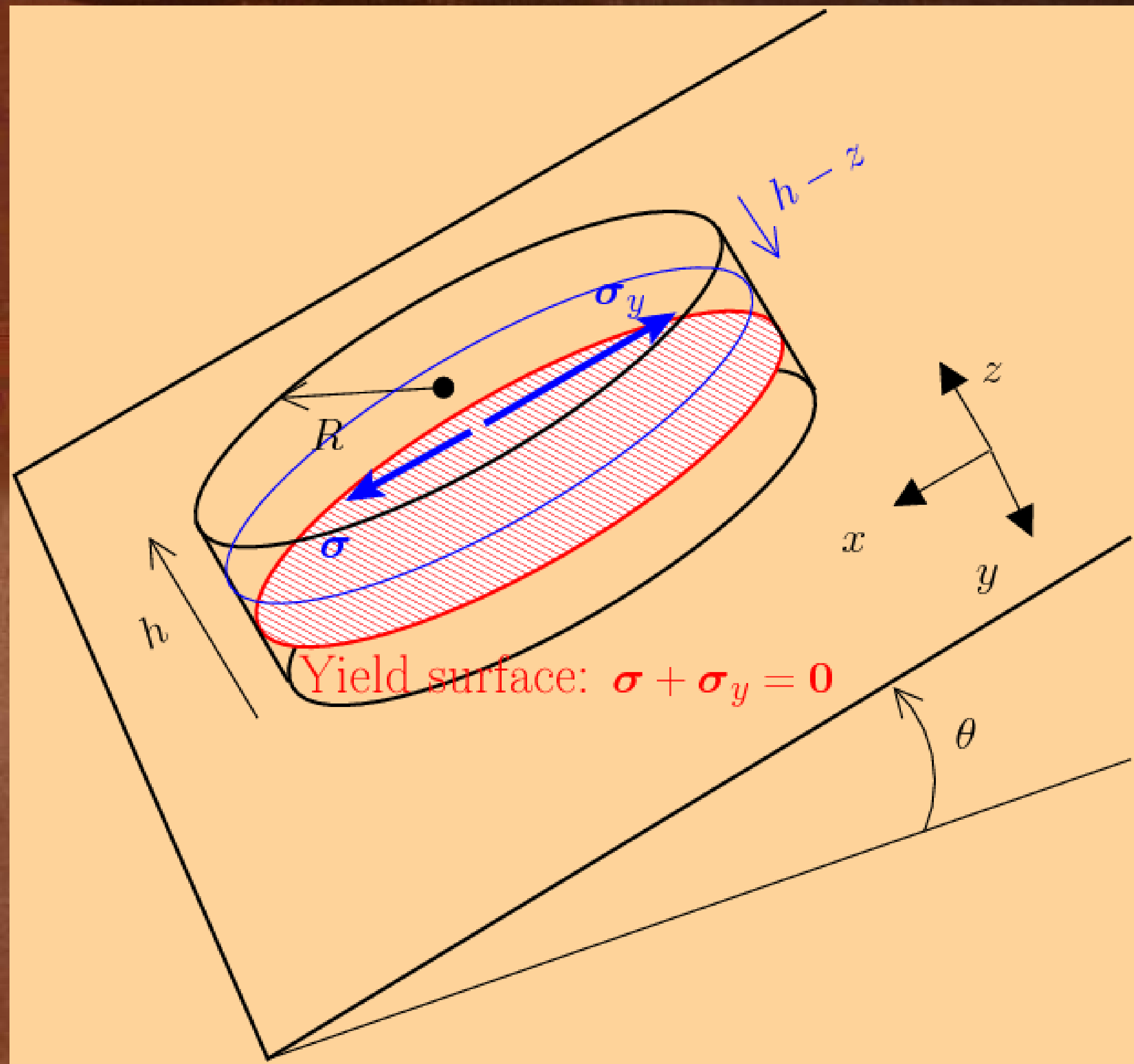
Quickclay and Landslides of Clayey Soils,
A.Khaldoun, P.Moller, A. Fall, G.Wegdam,B. De Leeuw, Y. Meheust, J.O. Fossum, D. Bonn,
Géosciences Rennes 1, University of Amsterdam, ENS-Paris, NTNU-Trondheim
Physical Review Letters 103, 188301 (2009)

Shear stress imposed by gravity:

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

(null at the free surface)

All material below the yield surface is expected to flow

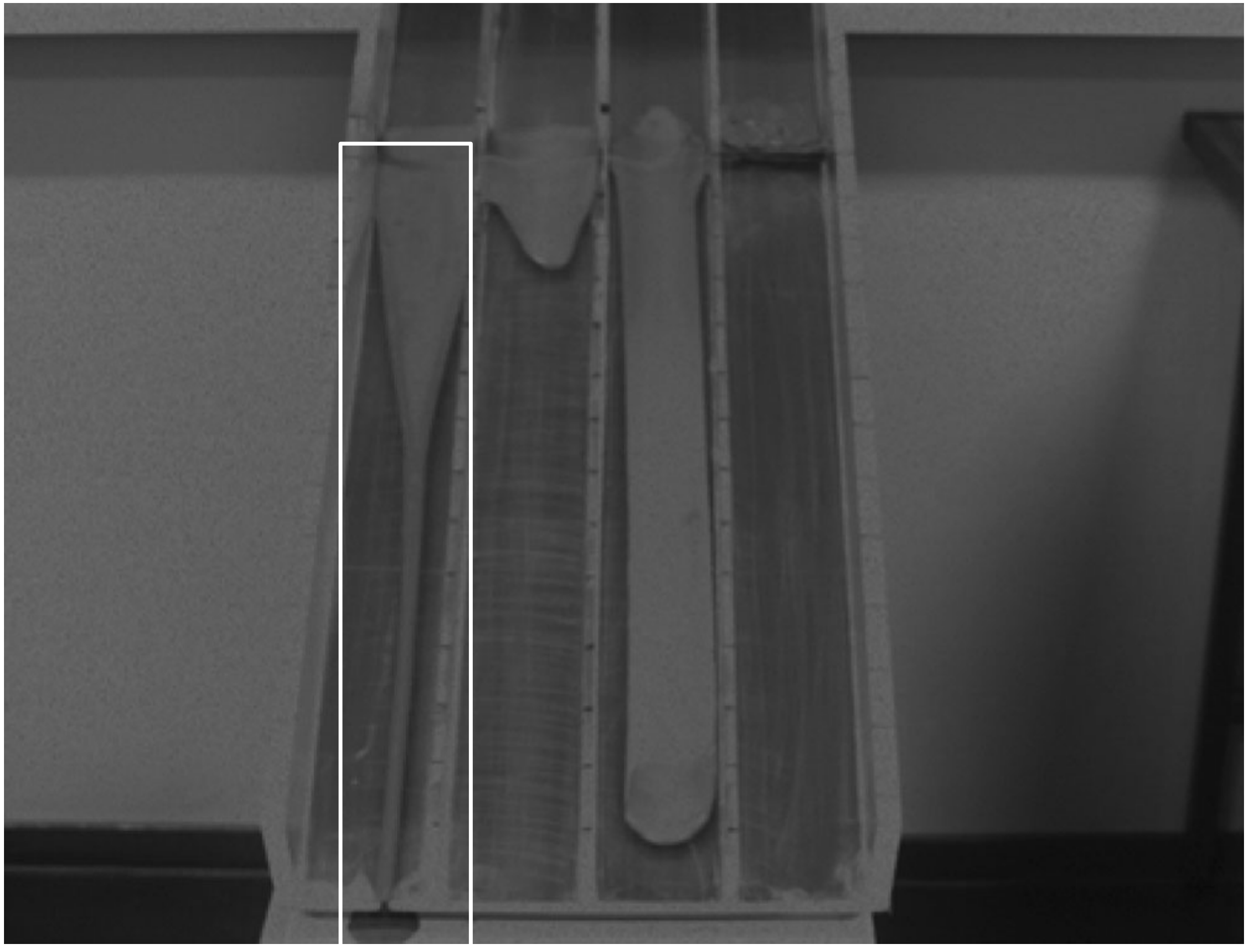


Our samples:

The marine clay from the Trondheim area is a quick clay consisting of:
70% non-swelling clays [kaolinite 1:1, illite 2:1, chlorite 2:1]
1% swelling clays [vermiculite, montmorillonite]
The rest is primary minerals (quartz, …)

Our samples were made from the natural clay, with controlled amount of water.
The samples at rest are colloidal gels with a **Yield stress!**

Analog laboratory landslide experiments

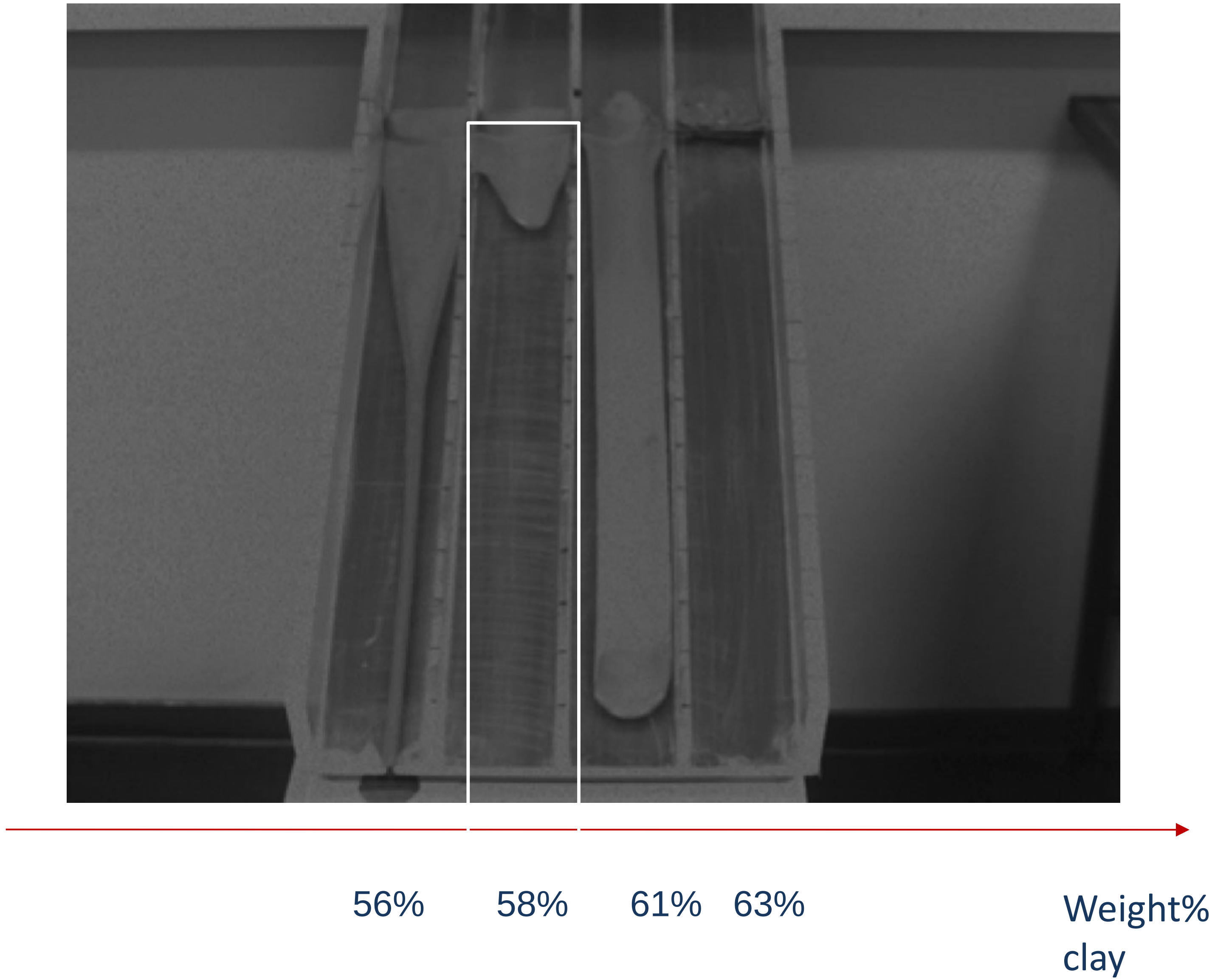


56% 58% 61% 63%

Weight% clay

Quasi-newtonian flow

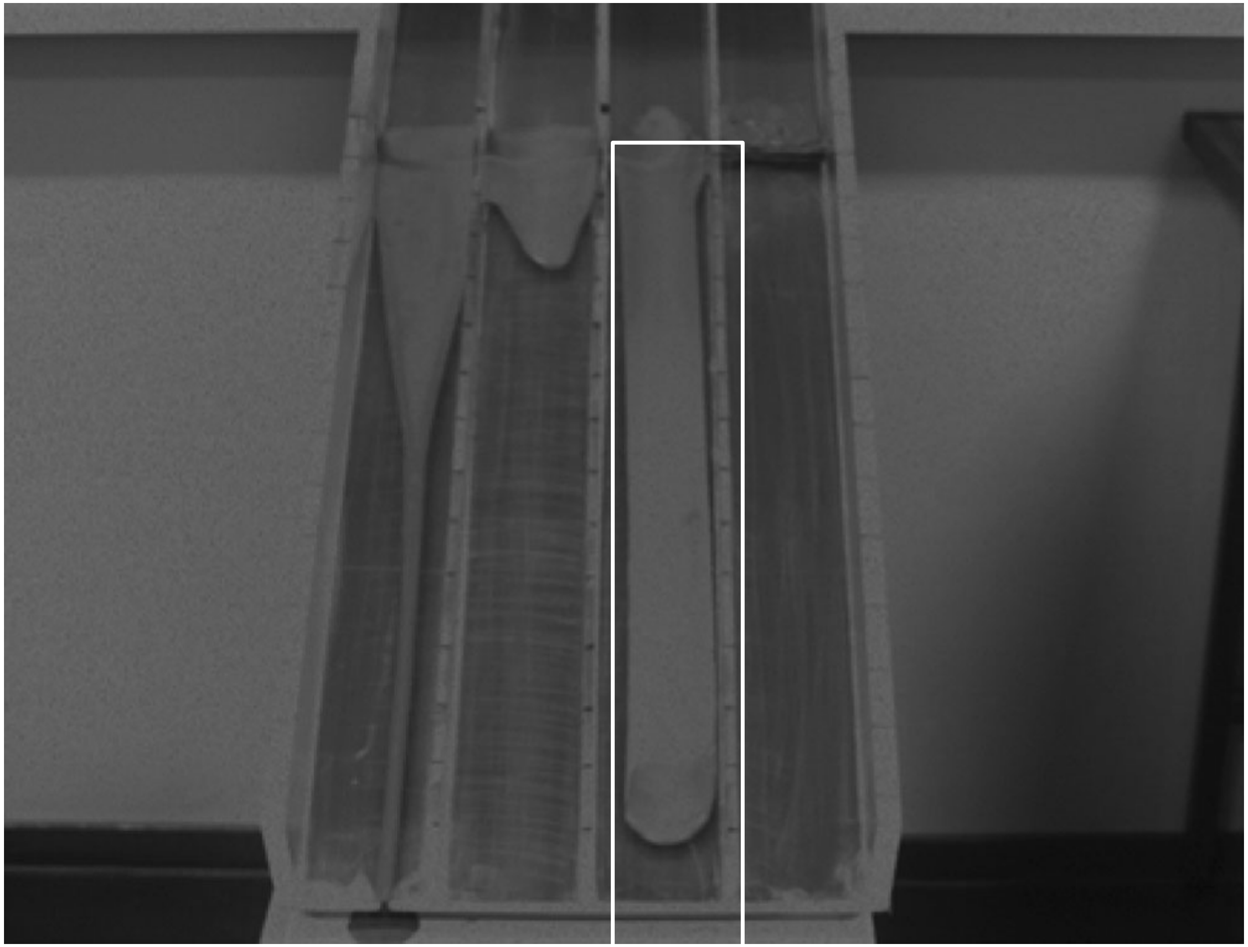
Analog laboratory landslide experiments (3)



Yield stress fluid flow

Analog laboratory landslide experiments

NTNU



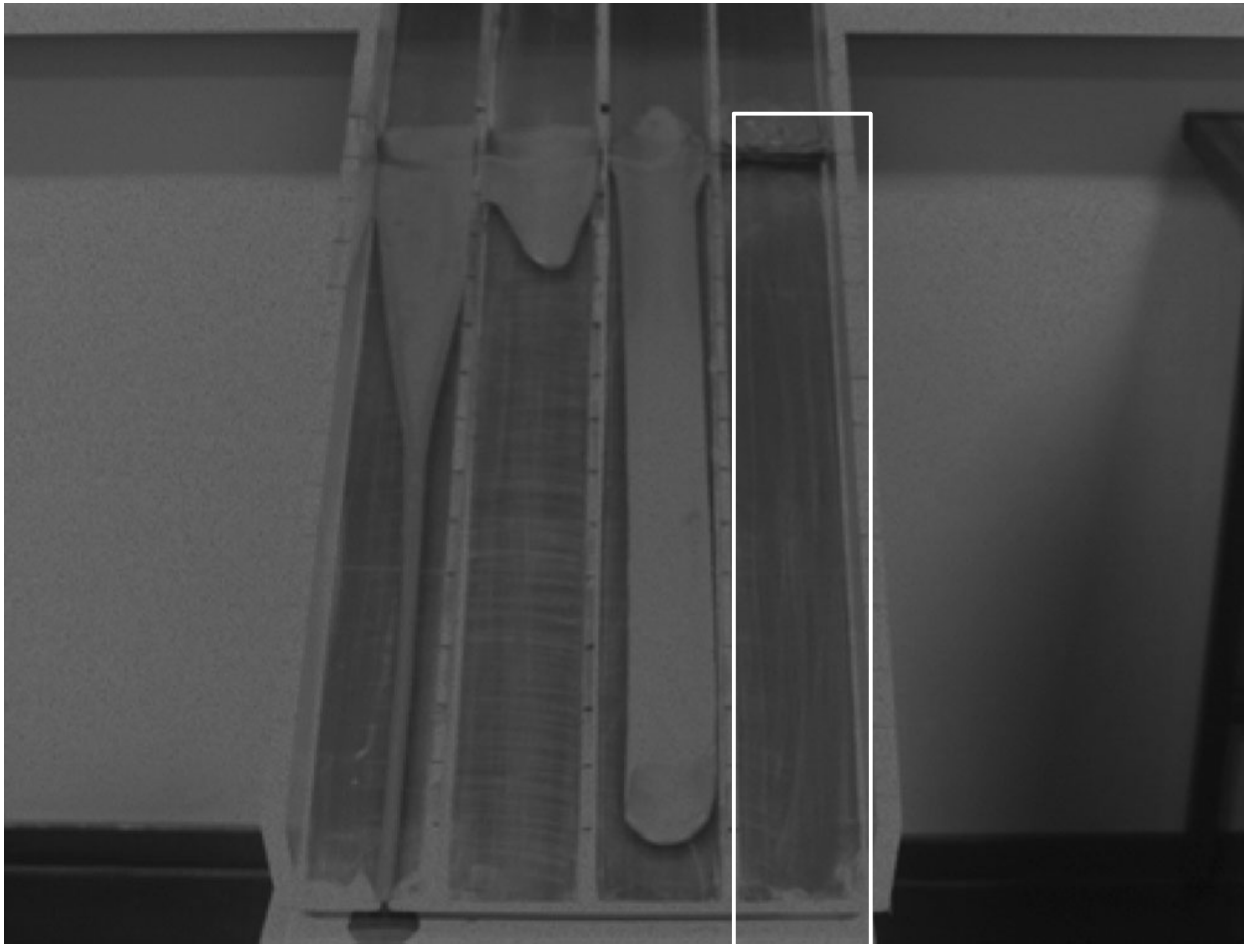
56%   58%   61%   63%

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

(steric hindrance of particle alignment ?)

Laboratory land slide experiments:

Model includes:

Slide length and velocity

Runoff length as a function of yield stress

Initial settling of the heap on the horizontal plane

Critical yield stress that separates two regimes:

Depending on a heap's initial aspect ratio, which is controlled by its yield stress, the flow regime will be controlled either by friction at the base of the heap, or by inner cohesion.

In addition: Preparation of a synthetic quick clay

- Composition: illite + bentonite + salt
- Protocol: 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) on quick clay avalanches:

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→ A material containing more water is not necessarily more unstable

→ For a limited range of water contents, the slide occurs 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

What can trigger a slide under natural conditions?

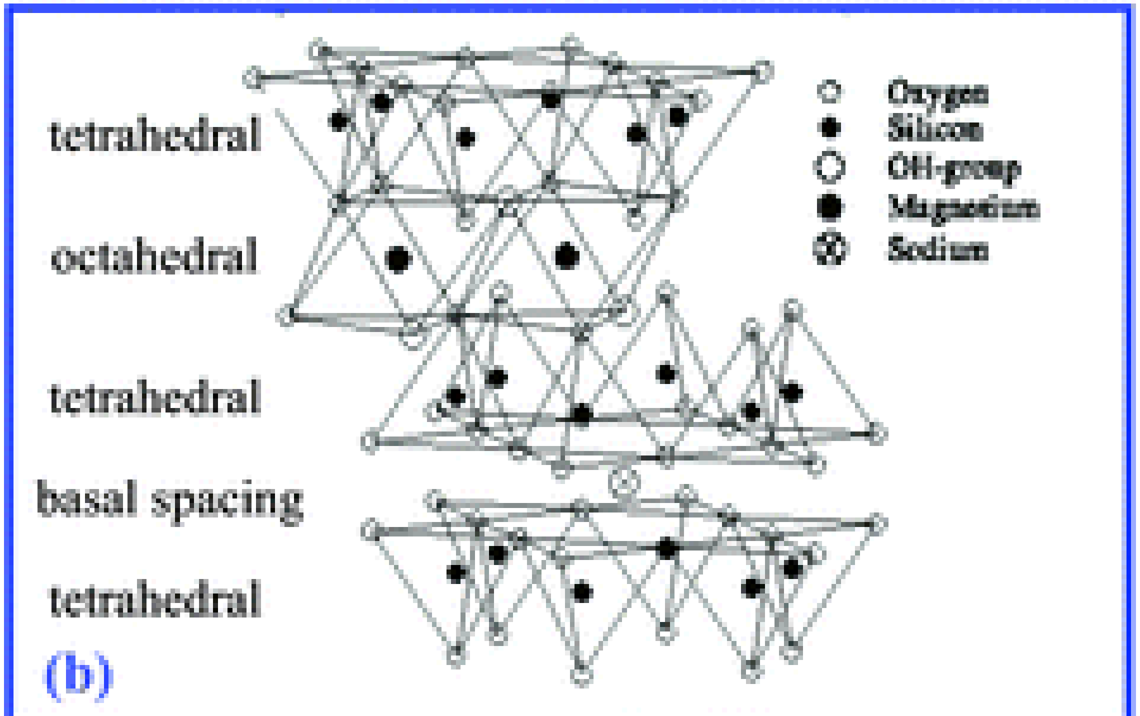
- Mechanical perturbation: Fex. an earthquake
  The Rissa landslide was triggered by excavation work
- Other triggering factor: Rain prior to the mechanical pertubation:
  A 1% concentration change can be enough!

Phys.Rev.Lett. 103, 188301 (2009)

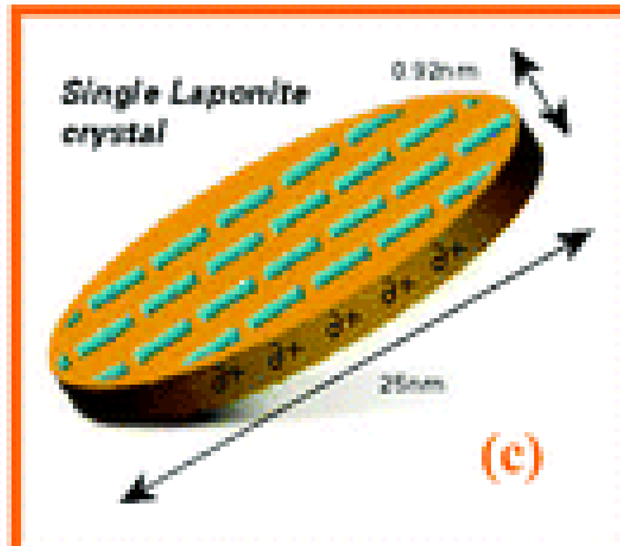
Appropriate question: Did we really study the "native" quick clay?

The most common and most used synthetic clay: Laponite (the only monodosperse colloidal clay)

(a) $Na^{+}_{0.7}[(Si_{8}Mg_{5.5}Li_{0.3})O_{20}(OH)_{4}]^{-0.7}$



(b)



(c)

Clay Minerals (1971) **9**, 231.

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THE RHEOLOGICAL PROPERTIES OF DISPERSIONS OF LAPONITE, A SYNTHETIC HECTORITE-LIKE CLAY, IN ELECTROLYTE SOLUTIONS

B. S. NEUMANN AND K. G. SANSOM

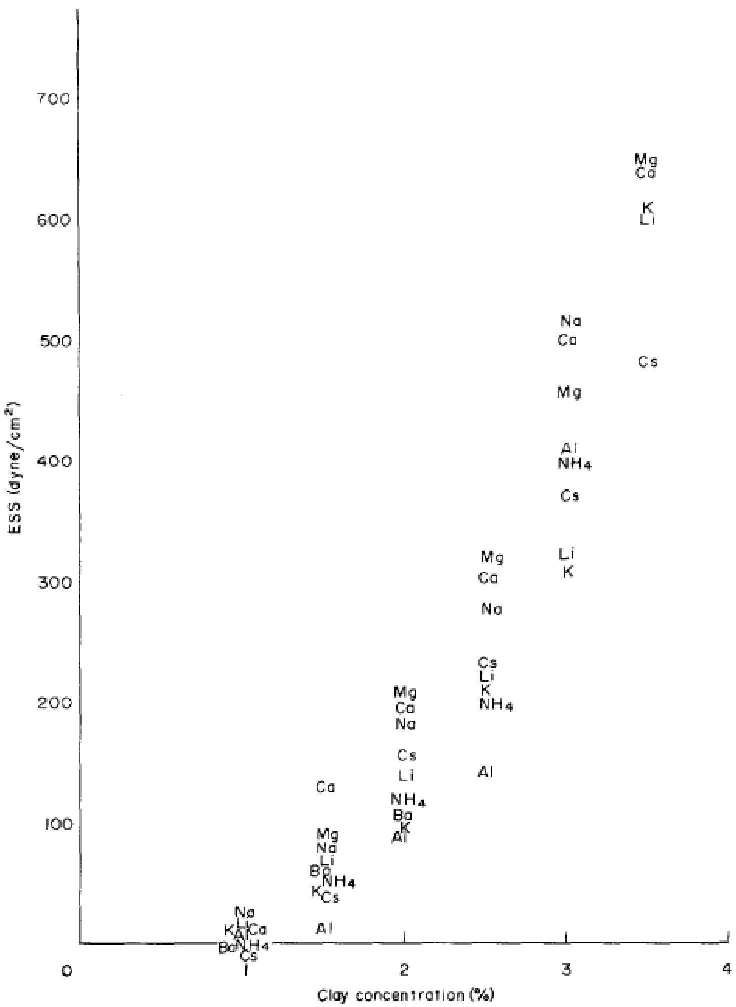


FIG. 5. Effect of clay concentration on yield value.

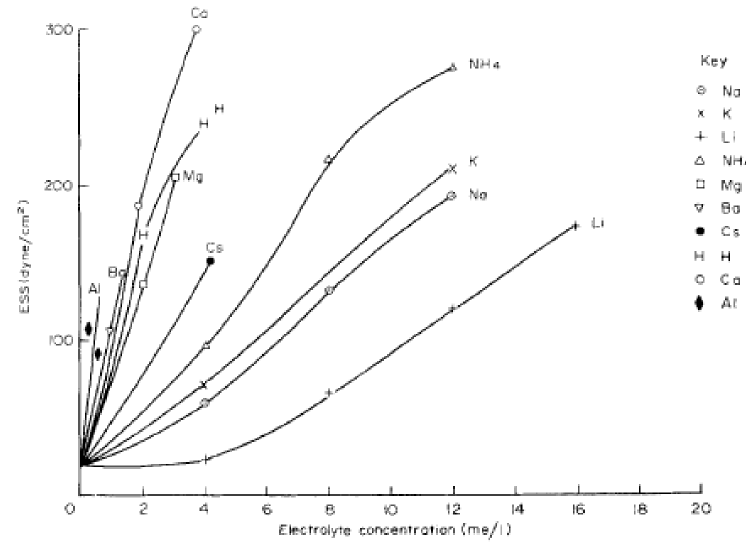


FIG. 2. Effect of electrolyte on Yield Value at 2% clay concentration.

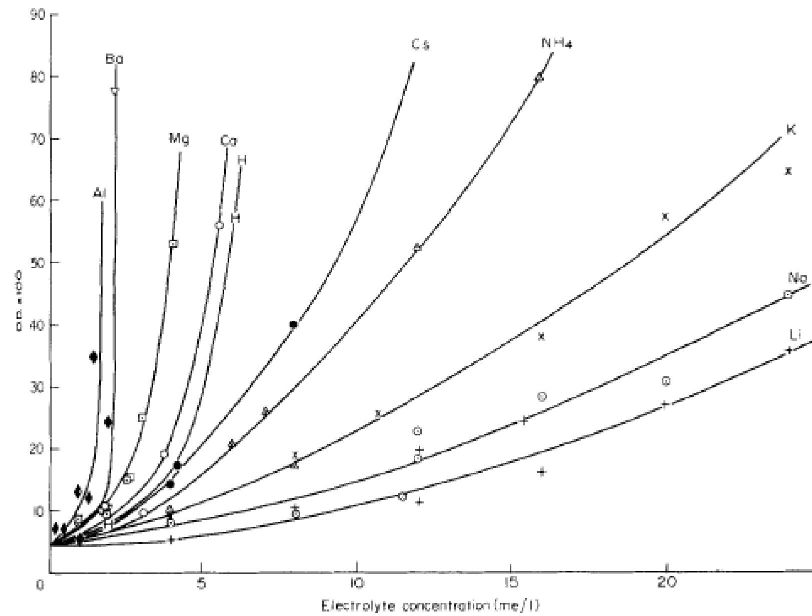
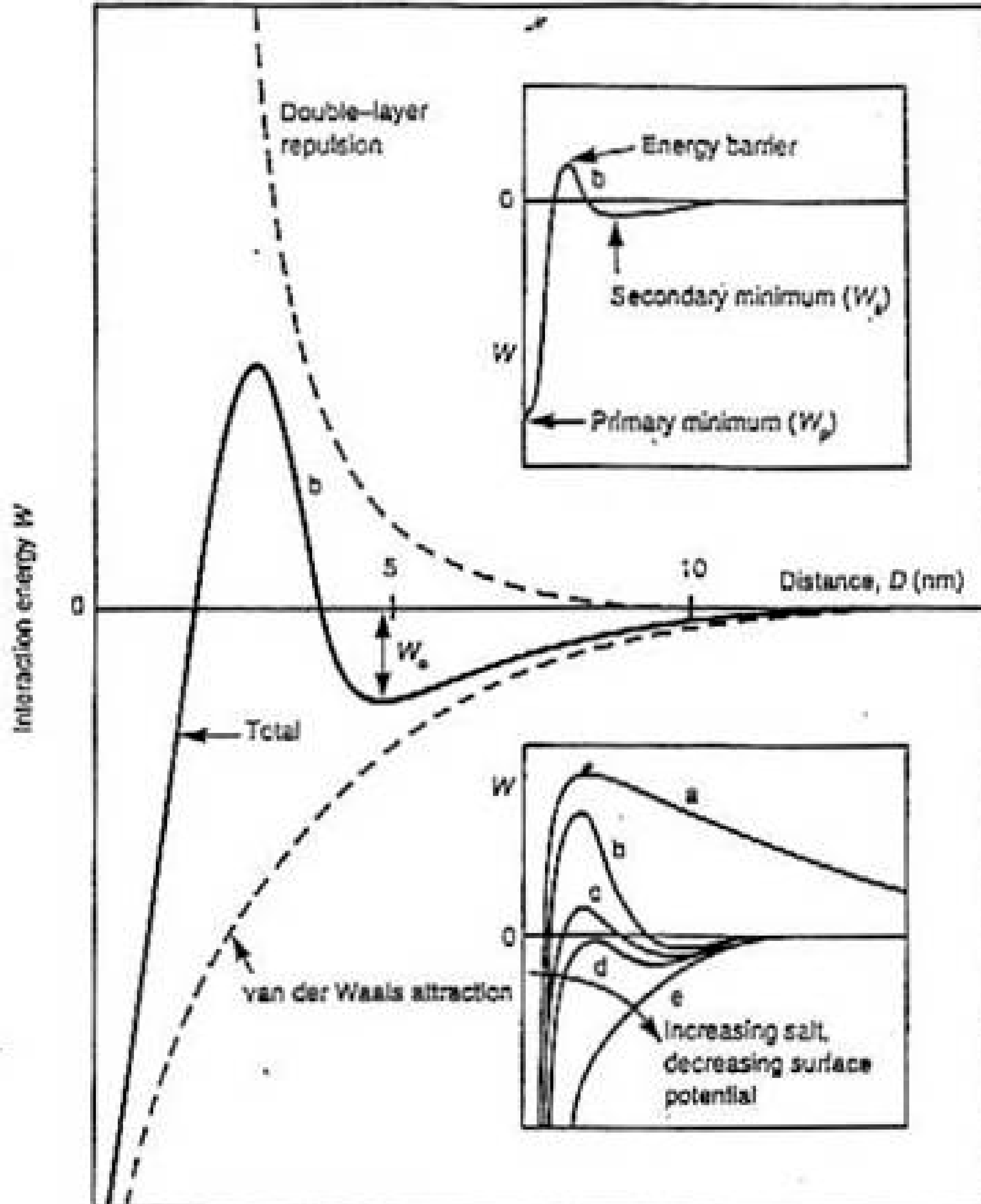


FIG. 3. Effect of electrolyte on optical density at 2% clay concentration.

DLVO Theory:
vdW
+ Screened Electrostatic Rep.



J. Israelachvili

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]

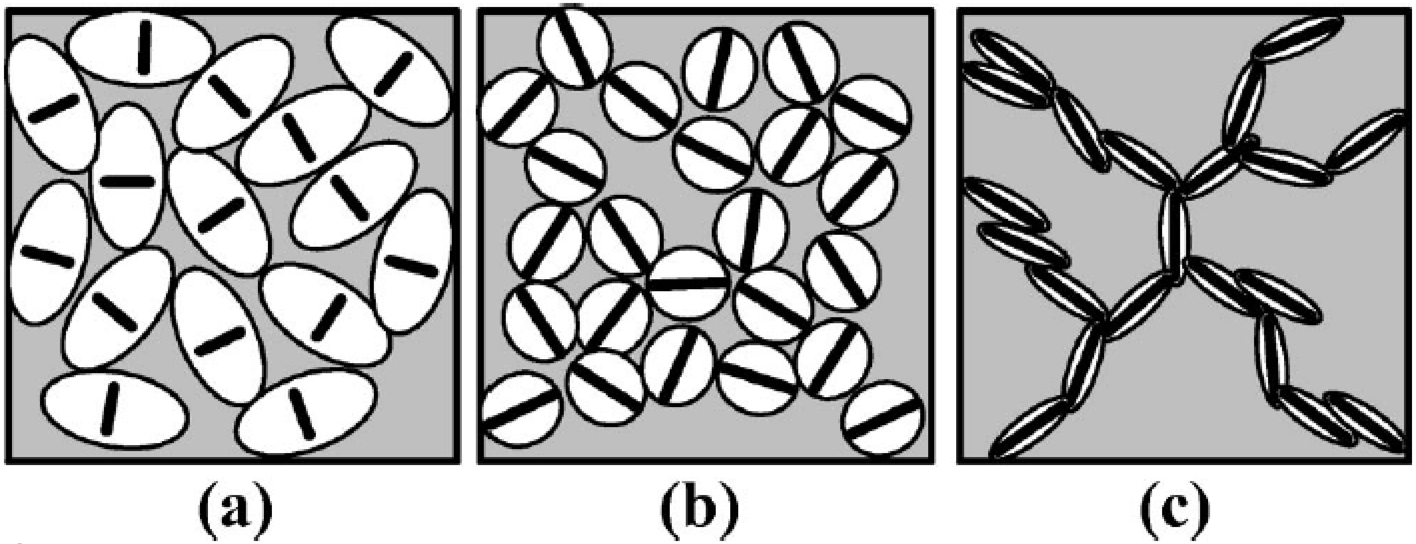


FIG. 1.
Schematic figures representing repulsive ''Wigner'' colloidal glass (a), attractive glass (b), and gel (c). Each thick line represents a Laponite disk, while a white ellipsoid represents the range of electrostatic repulsions:

(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.

Langmuir **1998**, *14*, 4718−4723

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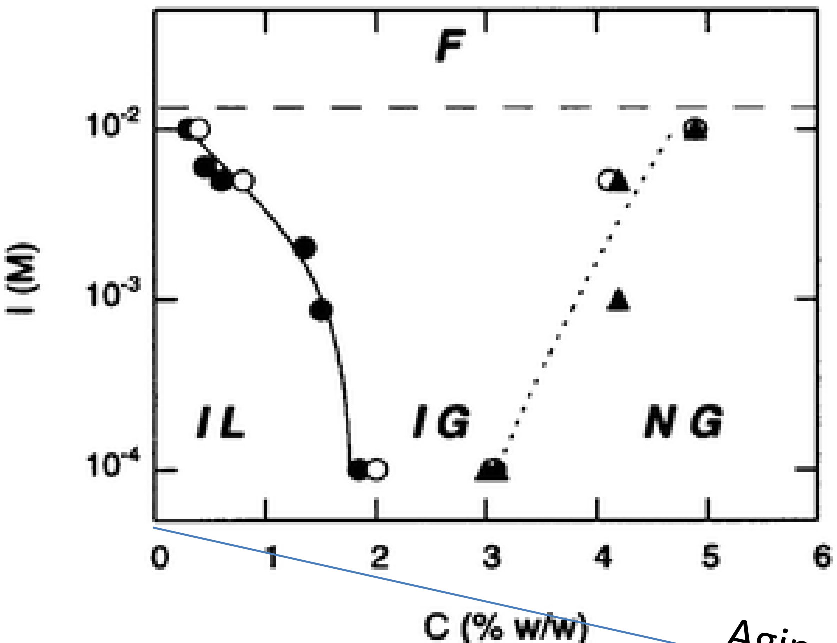
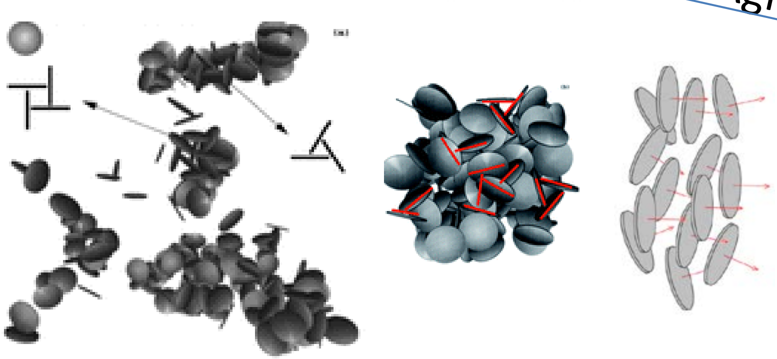
On Viscoelastic, Birefringent, and Swelling Properties of Laponite Clay Suspensions: Revisited Phase Diagram

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





Aging time

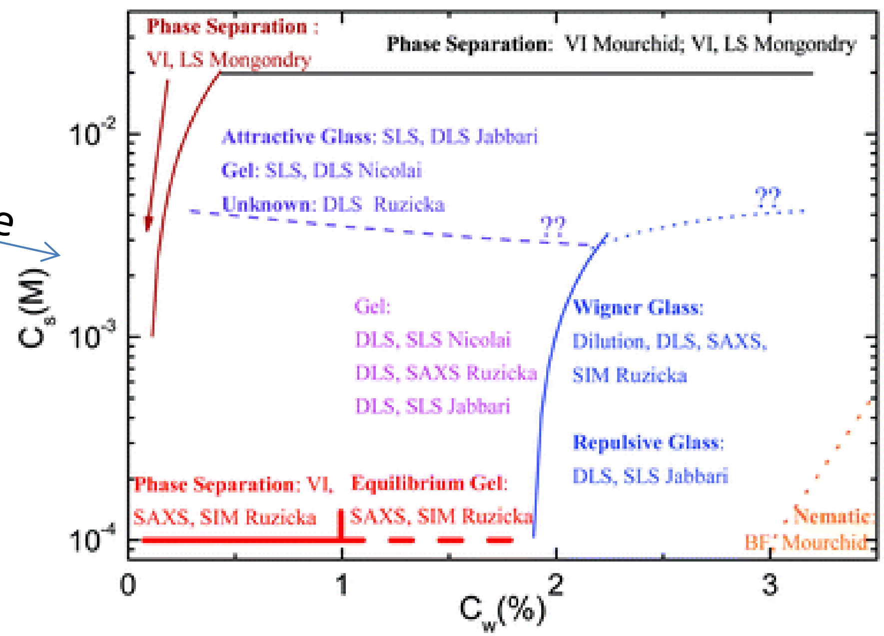
Soft Matter

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

www.rsc.org/softmatter

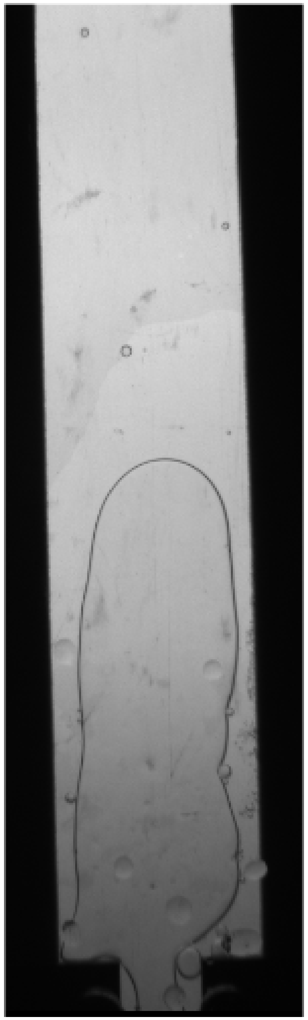
A fresh look at the Laponite phase diagram

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

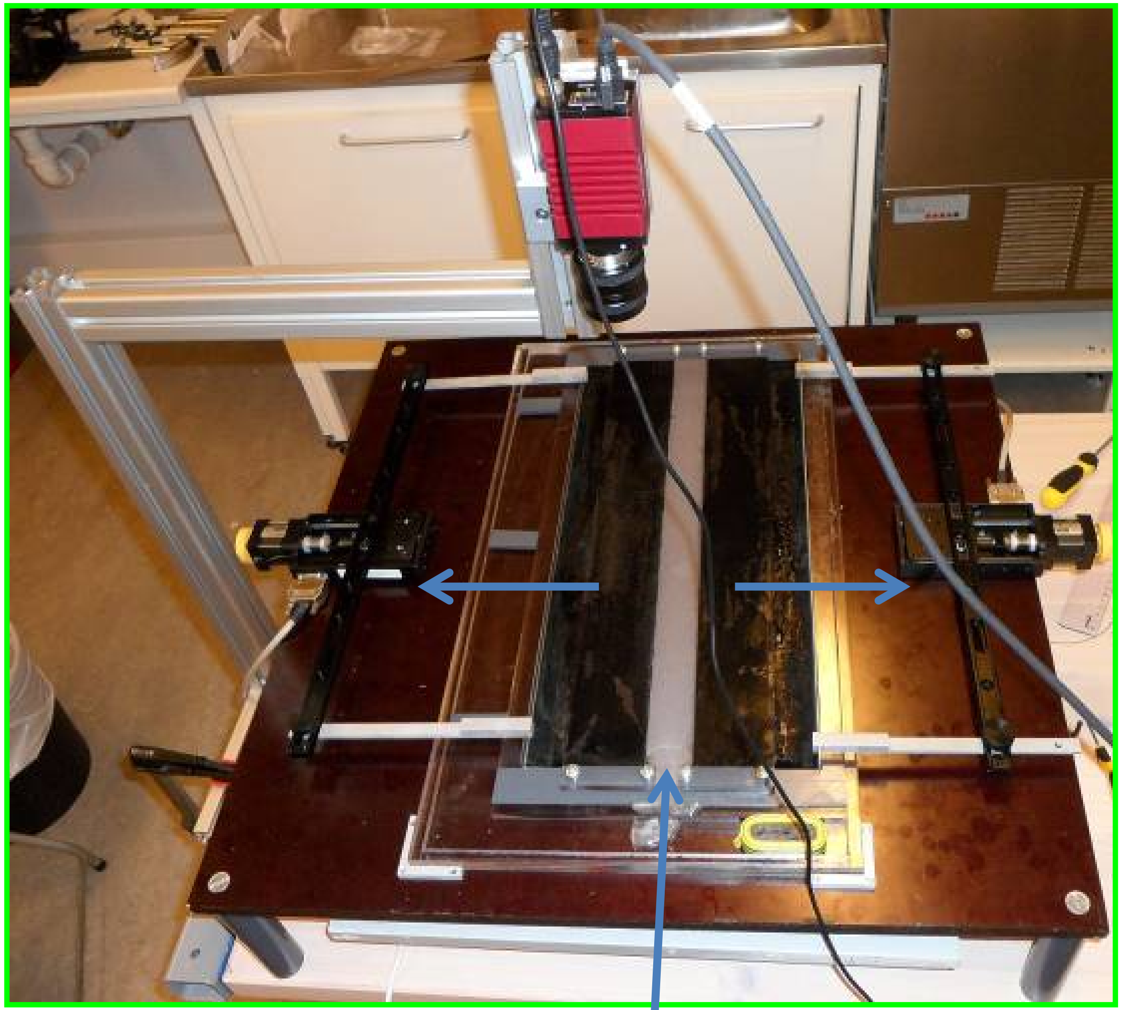


Ongoing experiments ESPCI-ParisTech/NTNU:
Fingering to fracturing transition at sol-gel transitions: Transparent clay gel

3 wt%, 2.5 hours, 2 mm/s



3 wt%,17 hours, 2 mm/s



Air inlet

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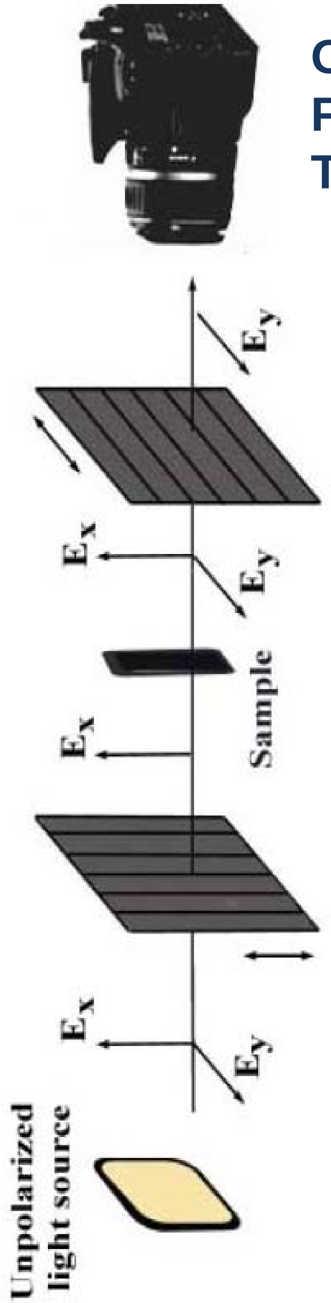
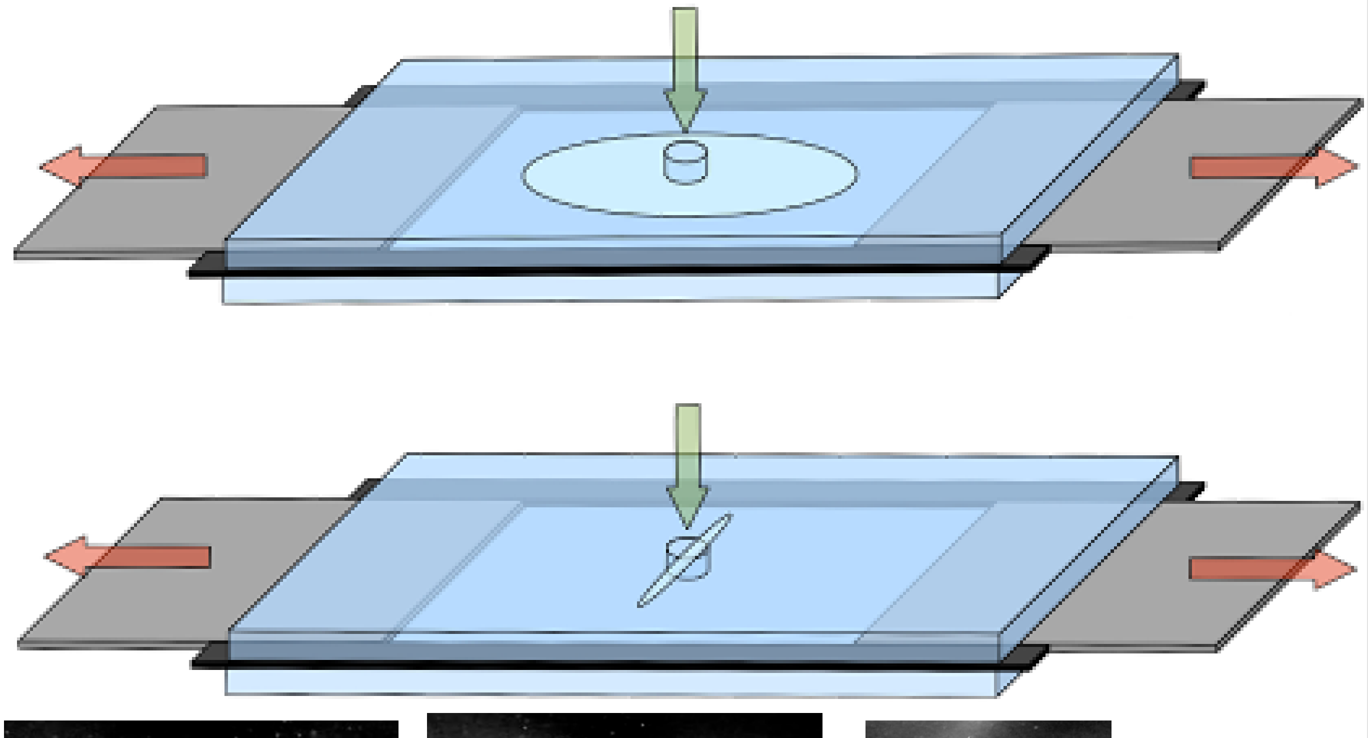
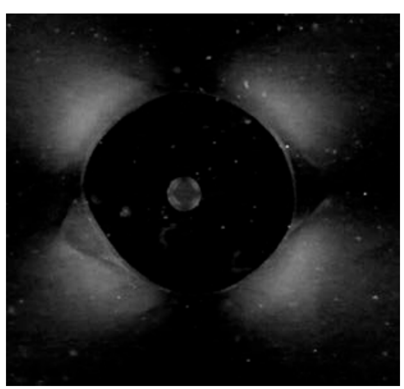
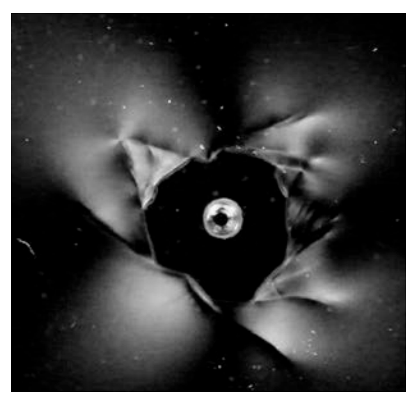
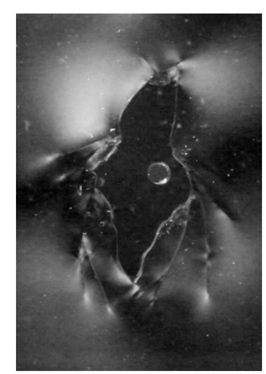
Ongoing experiments ESPCI-ParisTech/NTNU:
Fingering to fracturing transition at sol-gel transitions:
Transparent Laponite clay gel







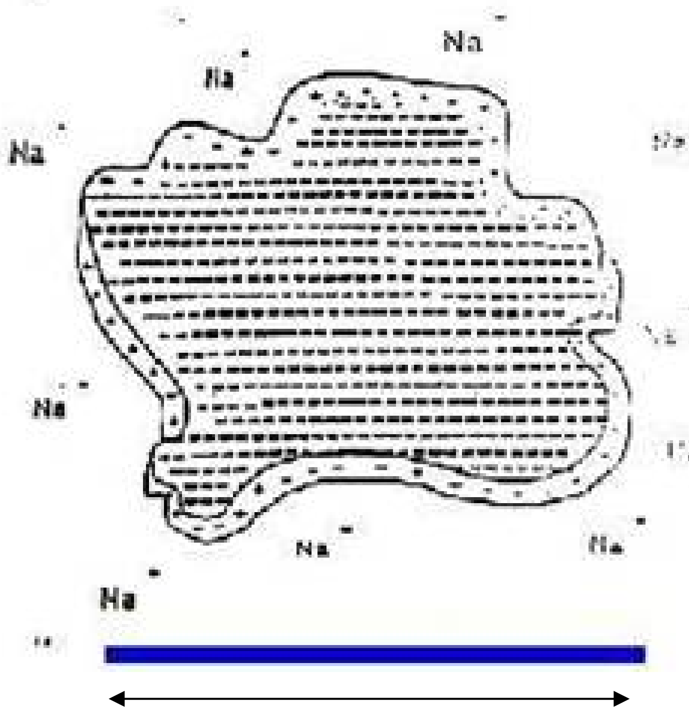




Clays are nano-/micro-particles:

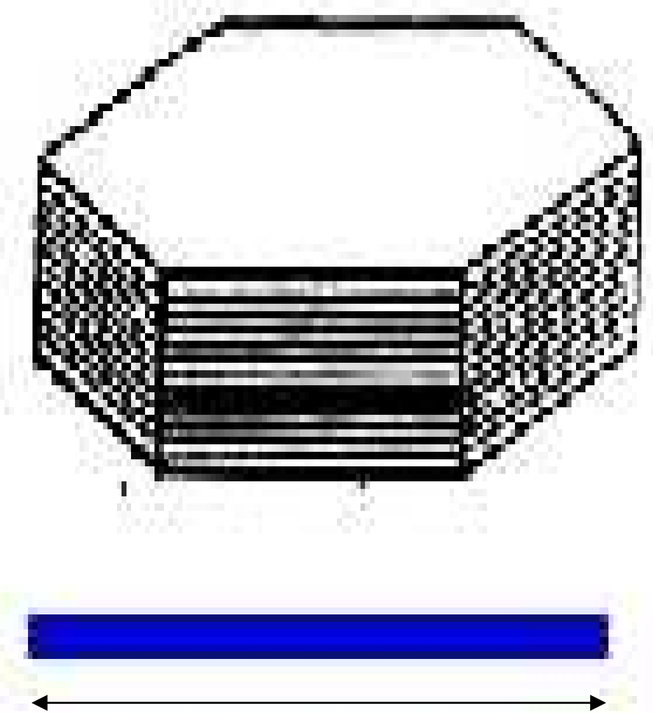
Two basic forms at nano-/micro-scale:

1 nm thick "nanocards"
(«Osmotic Bentonite»/Laponite)



~ µm

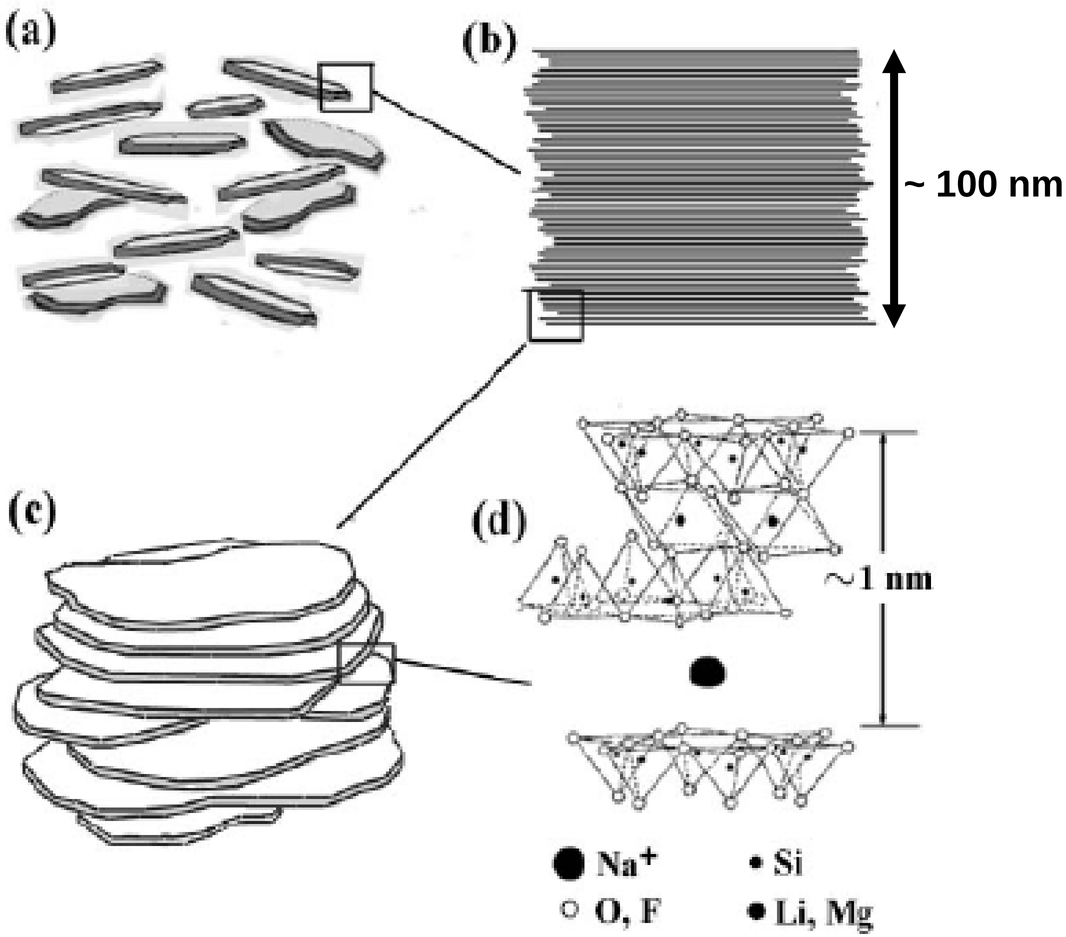
~100 nm thick nanolayered particles
"decks of nanocards"
(Kaolinite/ «Crystaline bentinite»)



~ µm

Our clay experimental model system:

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



Sources of fluorohectorite:

Corning Inc.
x ≈ 0.6 ± 0.05
Lateral ~ 0.5-10 μm
(incl. 20% known impurities)

Inorg. Chem.
Univ. Bayreuth, Germany
Prof. Josef Breu
x = (0.2 <->0.6) ± 0.005
Lateral > 100 μm
(pure)

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)**

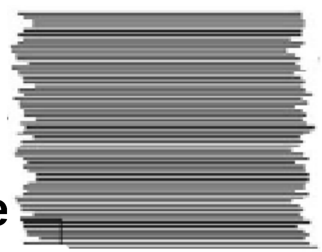
Pure Water

Clay (Fluorohectorite)
powder
About 3 % in weight

NaCl

About 10^{-3} M

Basic clay particle



~100nm

~μm

Liquid

Isotropic gel or glass?

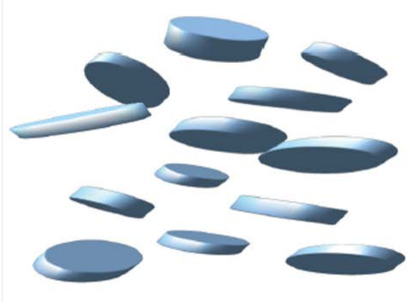
Nematic like gel or glass?

Sediment

4 ”Phases” in same Sample Tube

Self-assembly is essential in materials science:

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.



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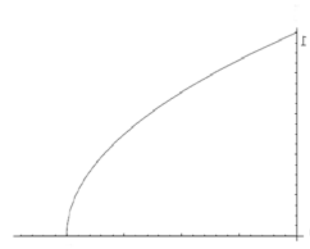
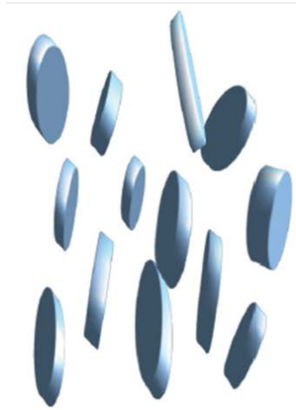
Liquid Crystalline Phases Characterization

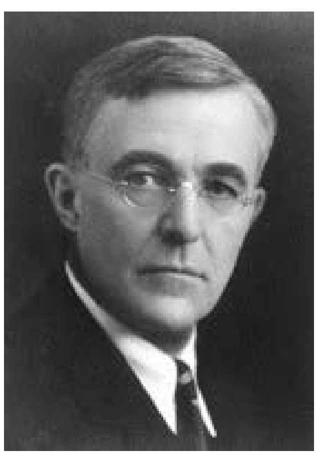
Order Parameter = O.P.
= Angular distribution function
$= S_2 = \frac{1}{2}\langle 3\cos^2\theta - 1\rangle$

Isotropic
Phase (O.P. = 0)



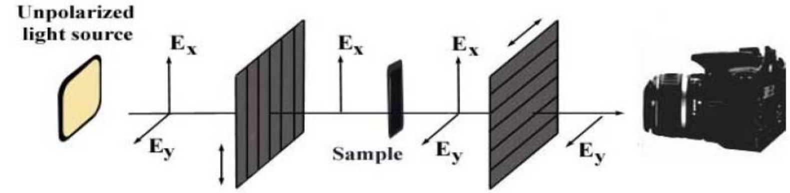
Nematic
Phase (O.P. ≠ 0)



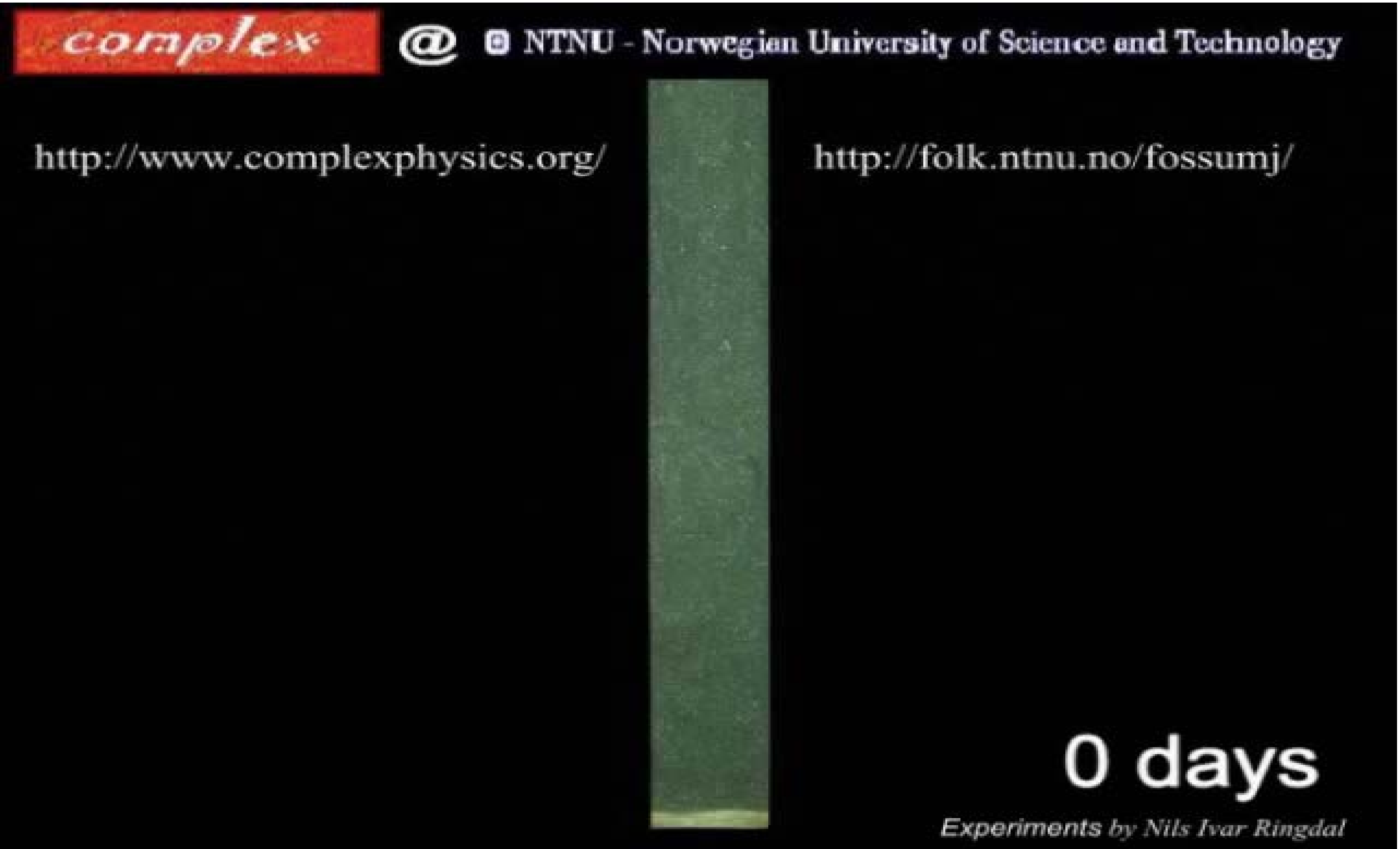


Irving Langmuir (Nobel Prize in Chemistry 1932): 1st experimental work in 1938 on liquid crystal structures in a clay suspension.

J. Chem Phys. 6, 873 (1938)



Self-organization by sedimentation clay particles in H_2O:



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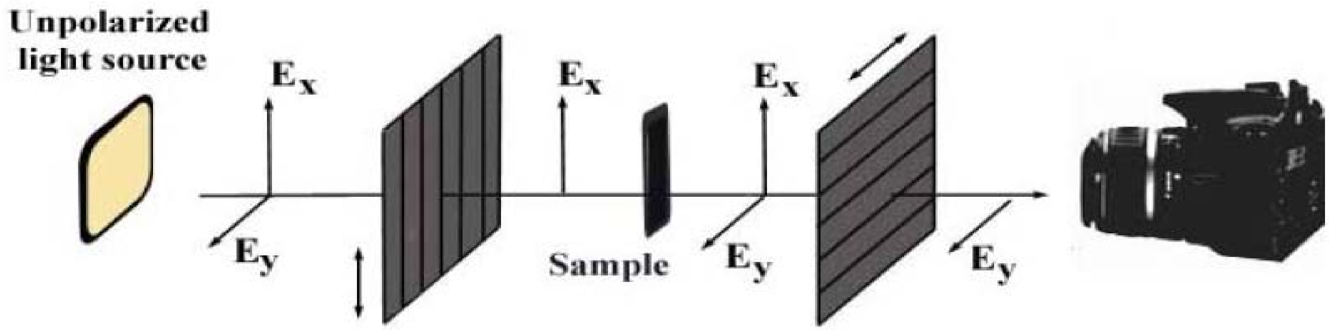

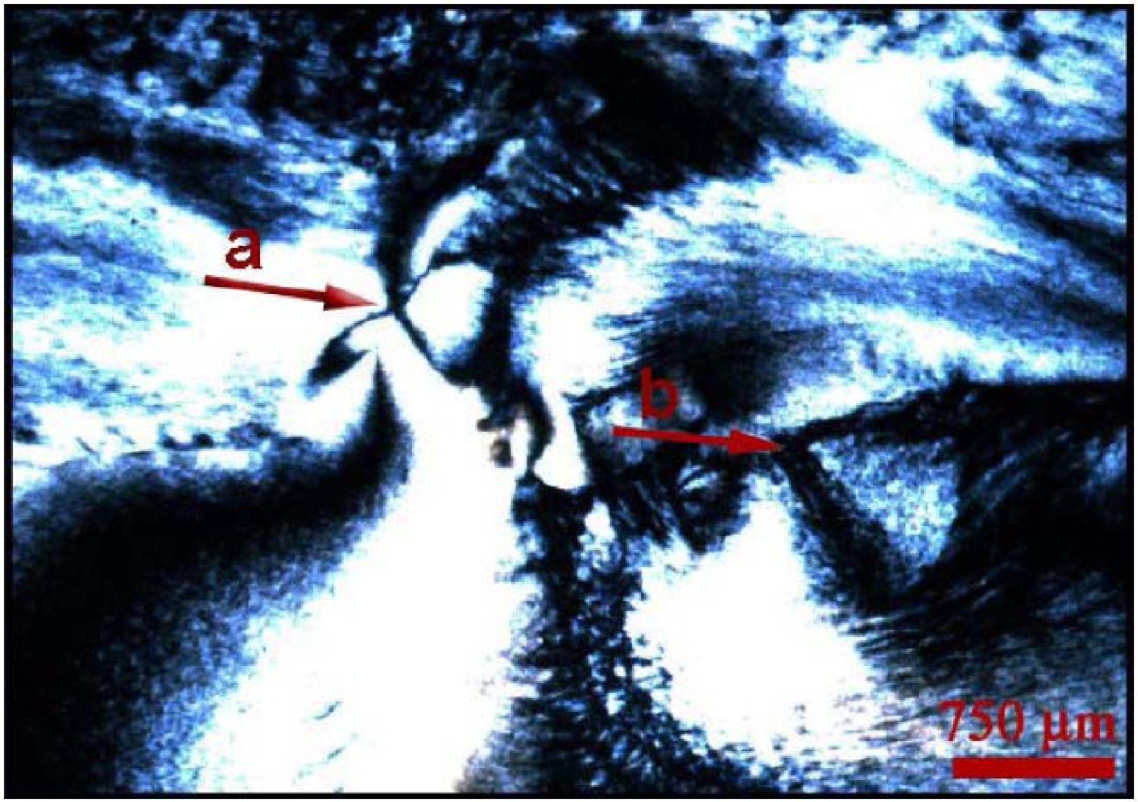

a and **b**
are ”typical” nematic defect signatures: Disclinations ("discontinuity" in the "inclination" of the director)

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)**

Increasing NaCl salt:

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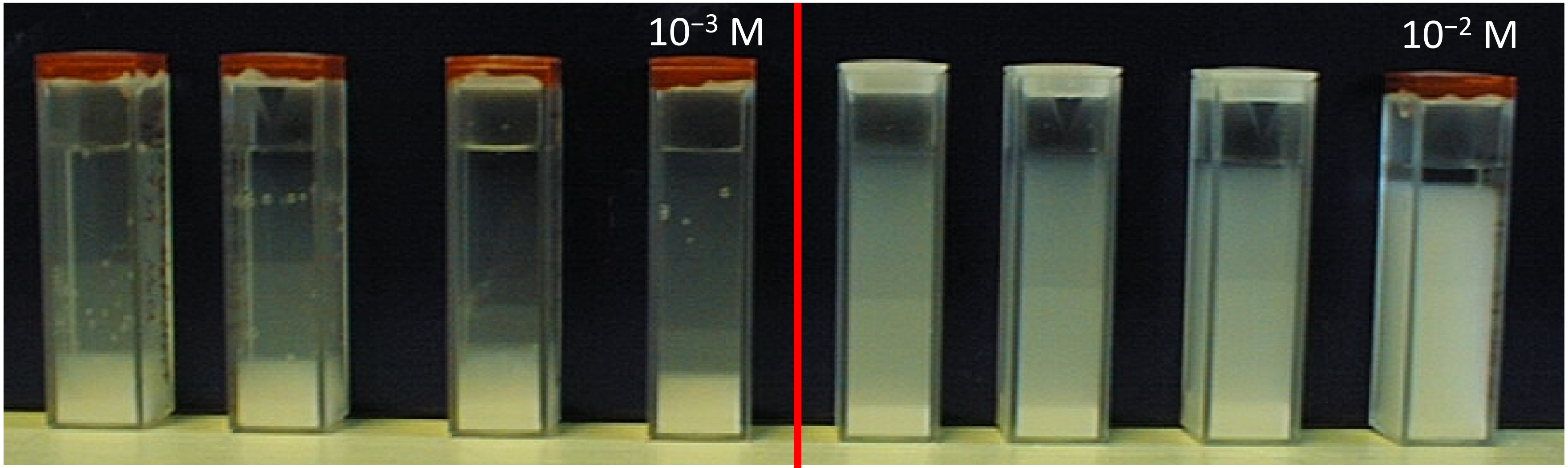


"Repulsive nematic"
"Wigner glass"

Particles push each other out towards container walls,
→ nematic
at high enough concentration
→ «large» domains

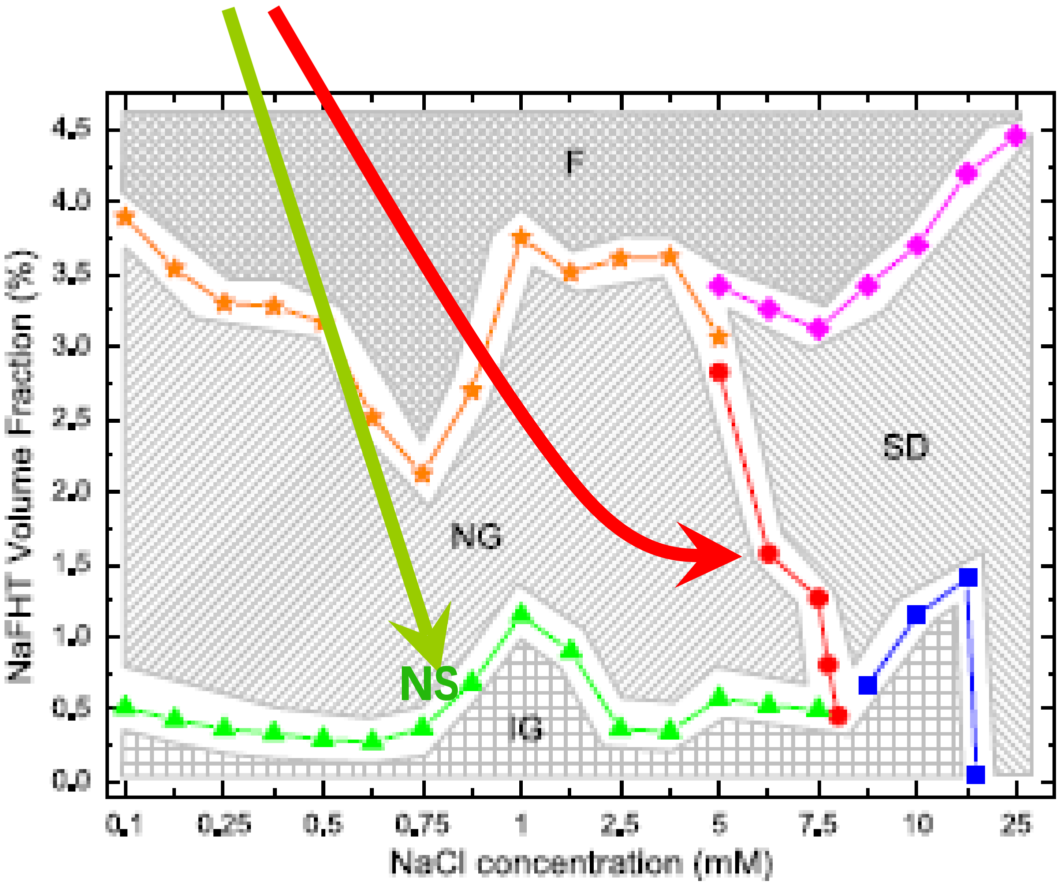
"Attractive nematic"
"Gel"

Particles "catch each other" in DLVO local minima
→ «small» domains

The phase diagram of polydisperse Na-Fluorohectorite–water suspensions: A synchrotron SAXS study.

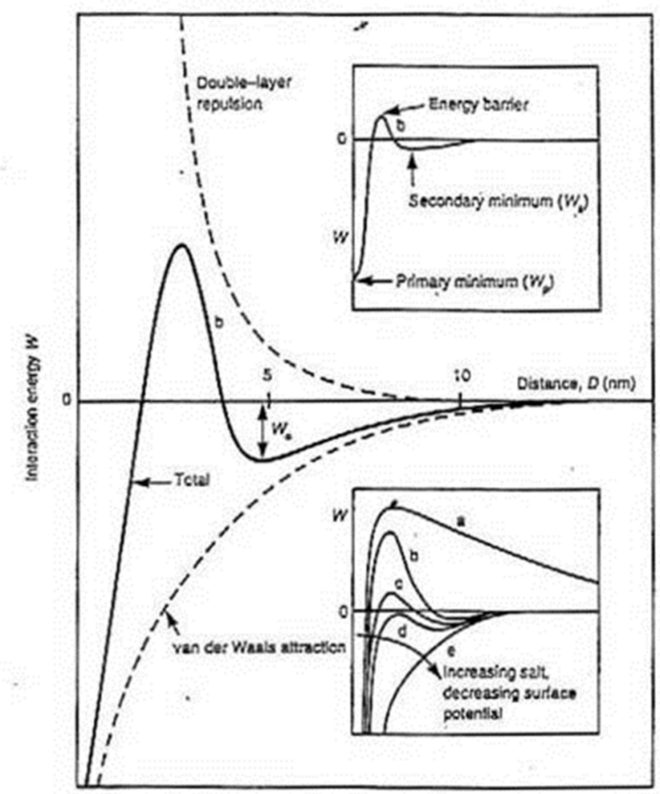
D. M. Fonseca, Y. Meheust, J. O. Fossum, K. D. Knudsen, and K. P. S. Parmar, **Phys.Rev. E 79, 021402 (2009)**

Transitions of interest



Obtained by combining:

- Eccentricity of SAXS scattering
- Angle of tilt of SAXS scattering
- X-ray transmission



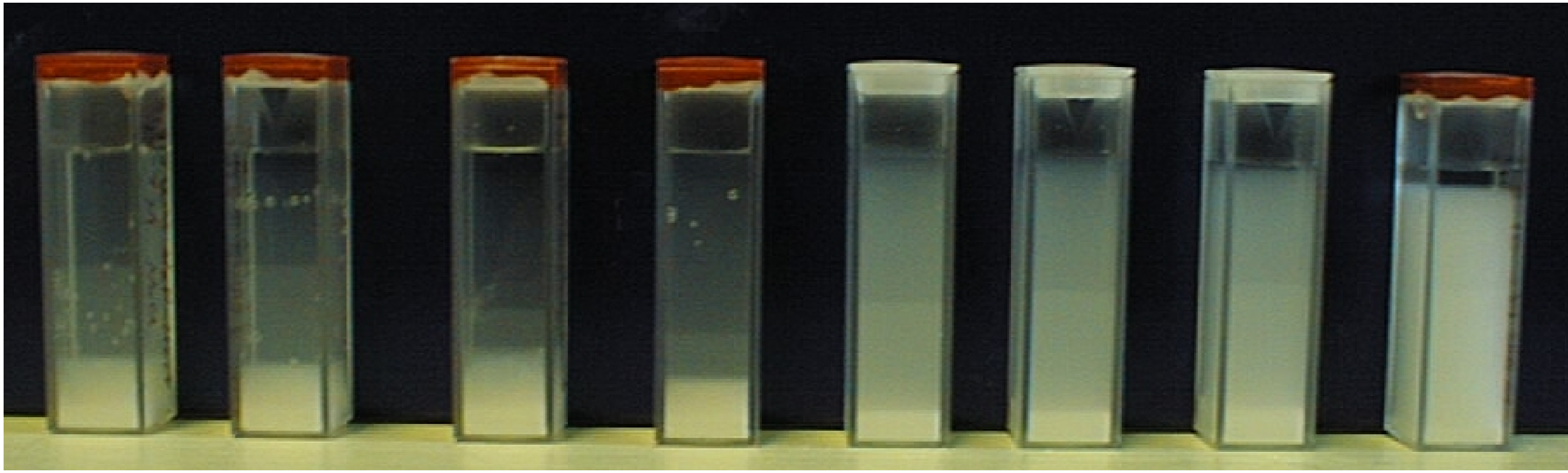
DLVO theory: vdW + Screened electrostatic rep.
(i.e The clay particles are effectively soft)

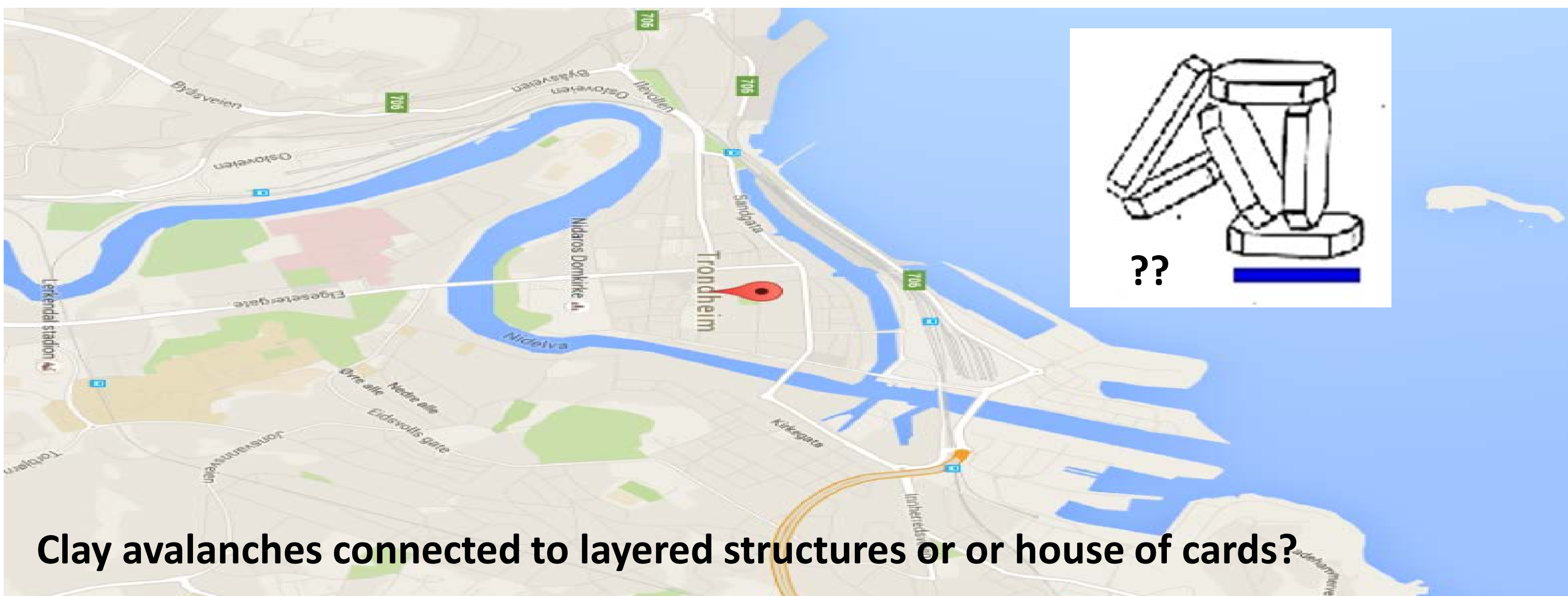
Clay avalanches

Norwegian Geotechnical Institute

Clay avalanche: Rissa Norway 1978

Increasing salt:



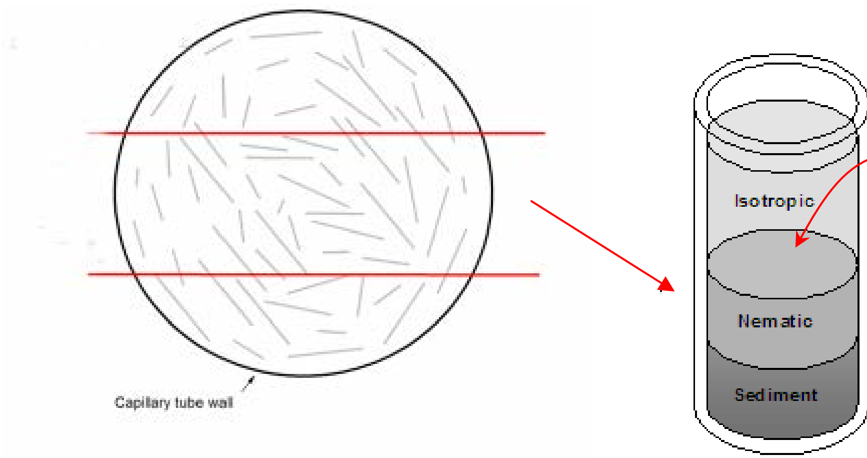


Clay avalanches connected to layered structures or or house of cards?

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).

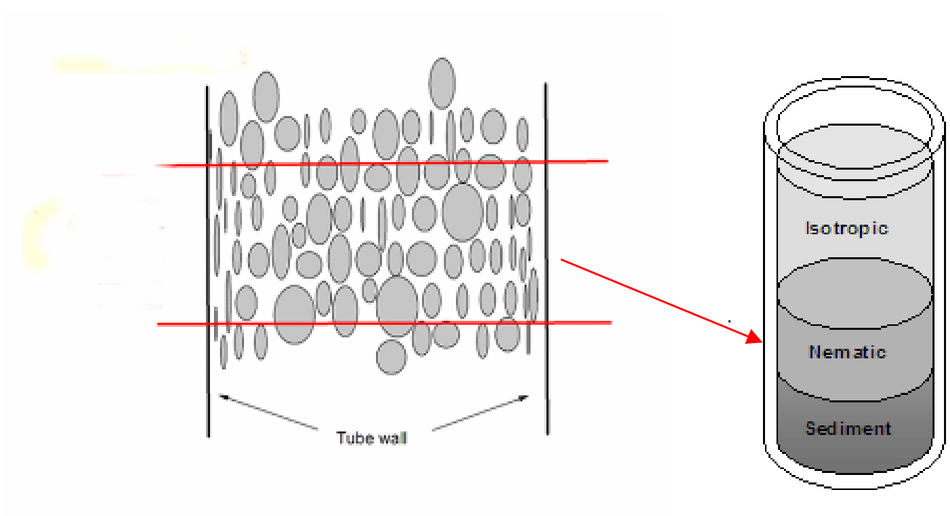
When the snowpack is stressed by rapid changes (e.g. wind-drifted snow, new snow, or rain) this stress can cause the weak layer to fracture.

Cartoon of nematic phase of clay platelets seen from above:



Wall anchoring

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

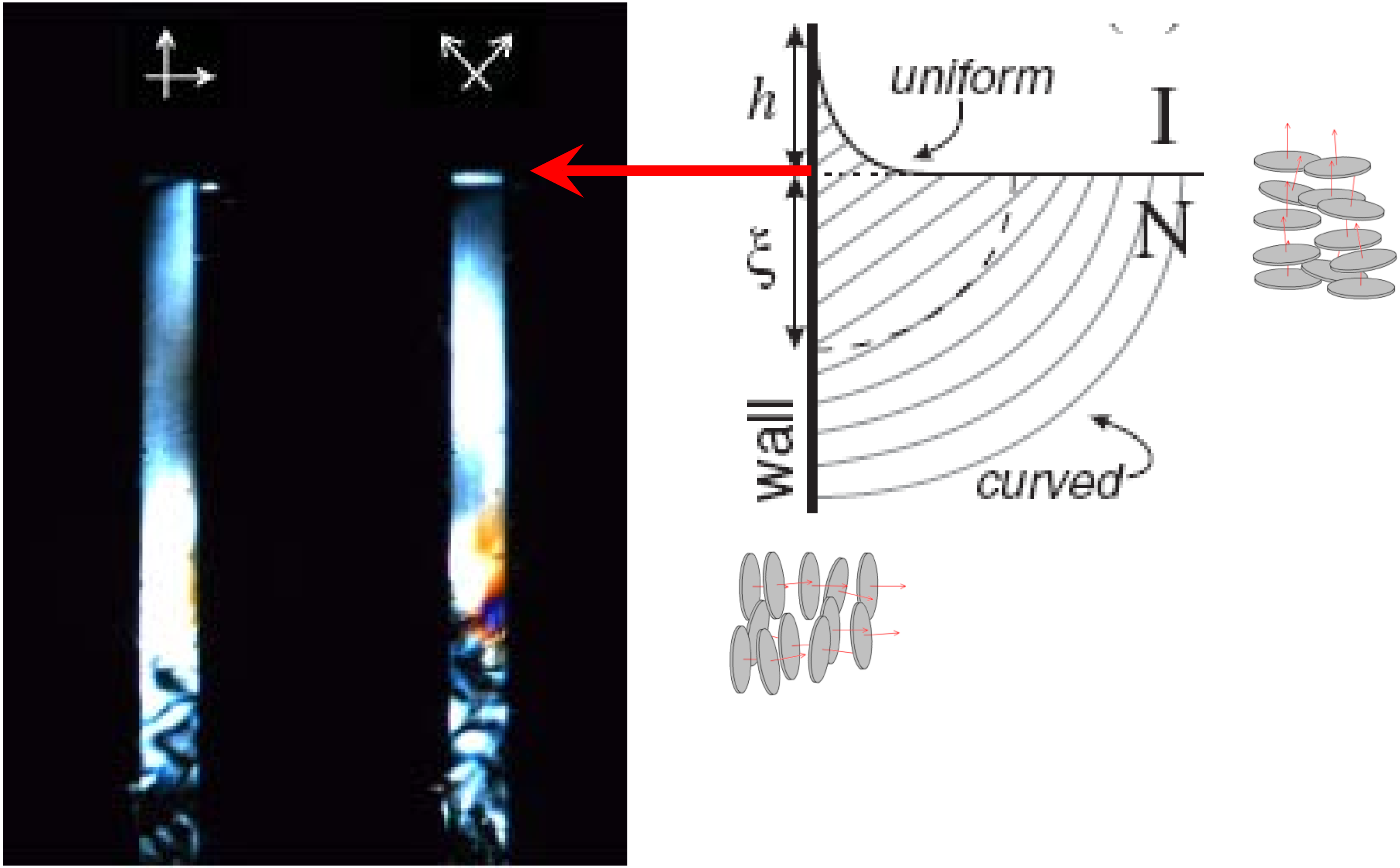


Order Parameter = O.P.

= Angular distribution function

$= S_2 = ½\langle 3\cos^2\theta - 1\rangle$

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)**

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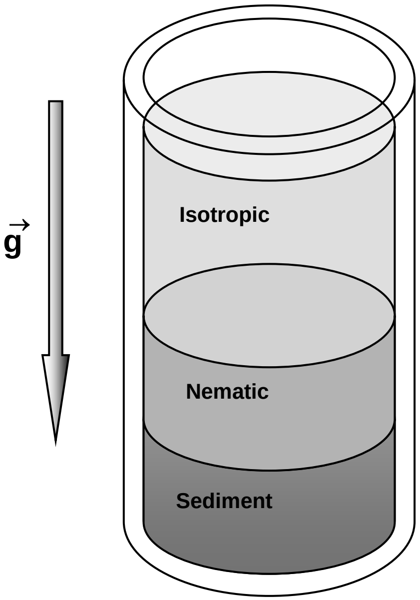
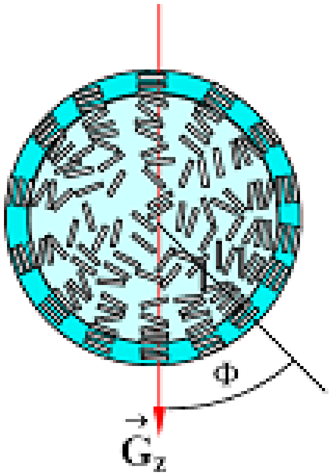
Response to magnetic field: Magnetic field guided self-organization:



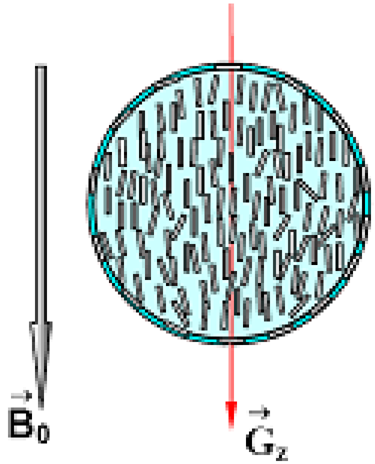
Glass wall anchoring confirmed by spatially resolved MRI measurements of anisotropic self-diffusion coefficient of water in the nematic phase.

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

$S_2 \sim -0.3$



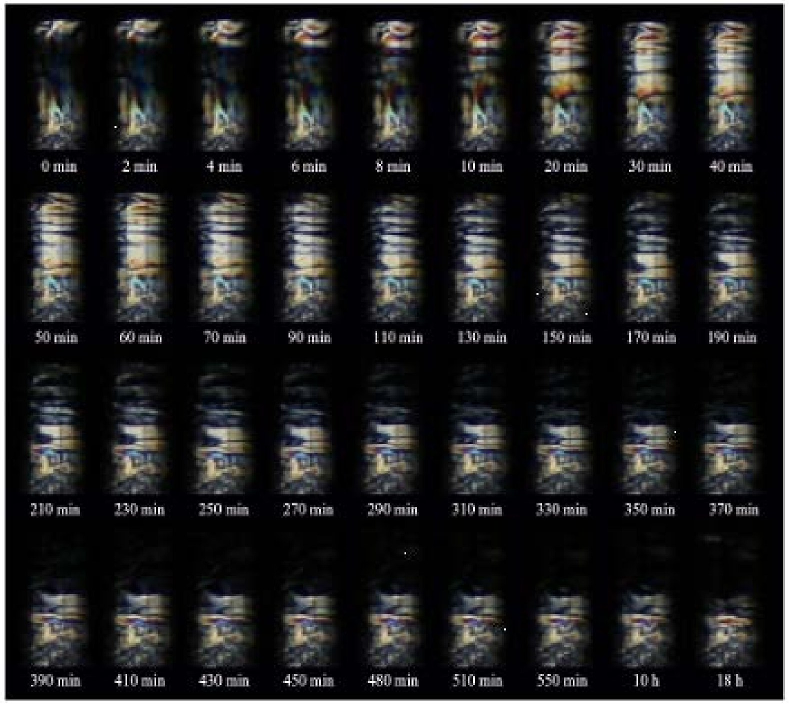
$S_2 \sim +0{,}5$



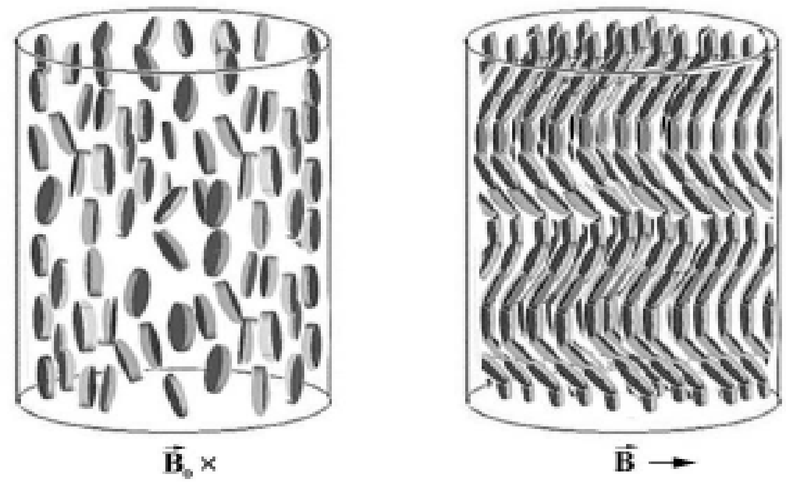
Anisotropic water diffusion in nematic self assemblies of clay nano-platelets suspended in water. E. N. de Azevedo, M. Engelsberg, J. O. Fossum and R. E. de Souza, **Langmuir 23, 5100 (2007)**

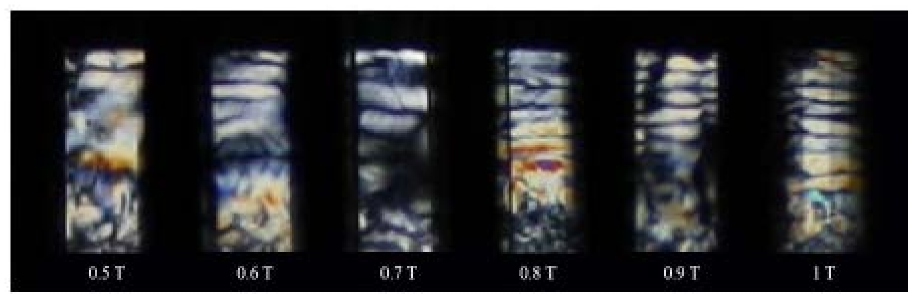
NTNU

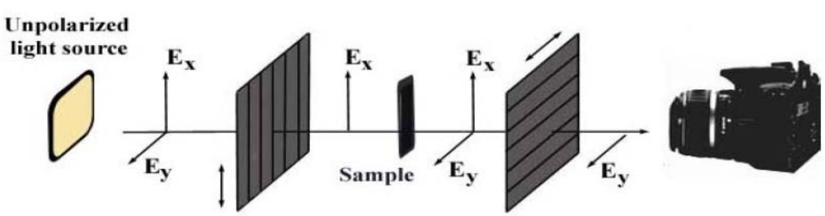
Color control of clay nematics between crossed polarizers



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)

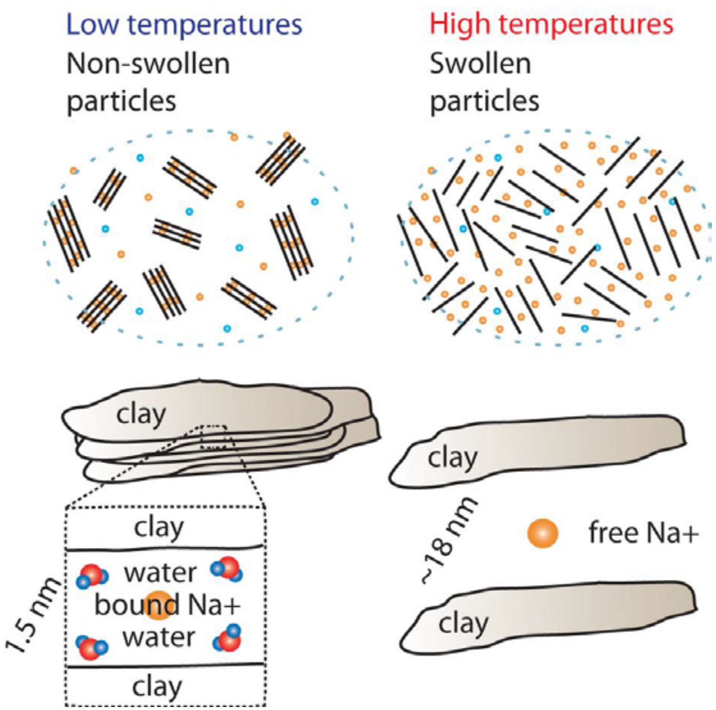


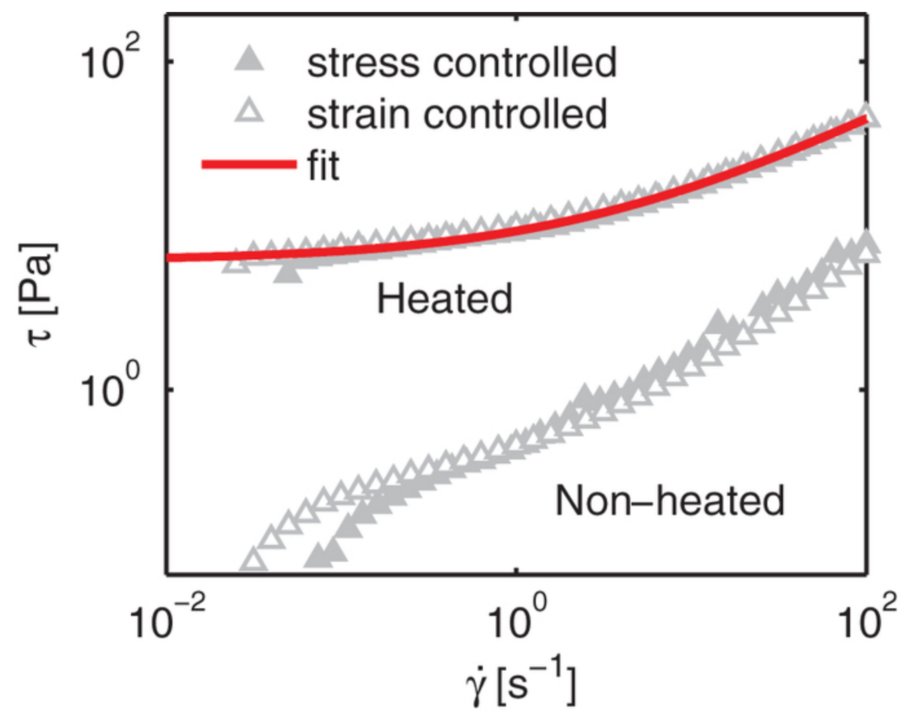




Swelling transition of a clay induced by heating, E. L. Hansen, H. Hemmen, D. M. Fonseca, C. Coutant, K. D. Knudsen, T. S. Plivelic, D. Bonn & J. O. Fossum, Scientific Reports by Nature 2, 618 (2012):

Crystalline → Osmotic $\xrightarrow{\text{Reversible only through drying}}$ Crystalline





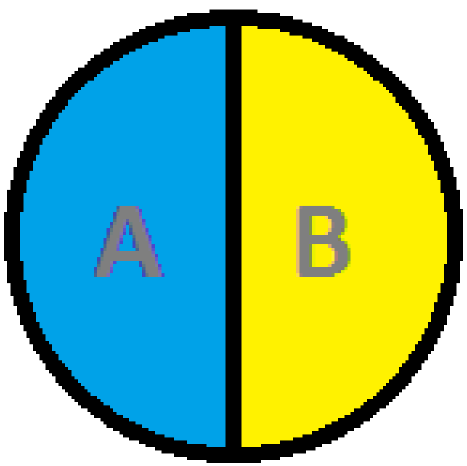
Measured by synchrotron X-ray scatttering

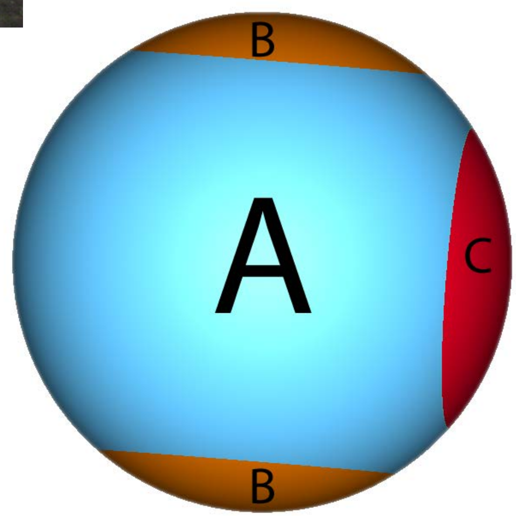
Measured by rheometry

Current trends in soft matter physics: Active matter; Patchy particles

In ancient Roman religion and myth, Janus is the god of beginnings and transitions, thence also of gates, doors, passages, endings and time.

Usually depicted with **two faces**, looking to the future and to the past





Janus particles

Patchy particles: Colloids with a valence

Applications Janus or patchy units: Self-assembly into (ordered) structures «Colloids with valence»

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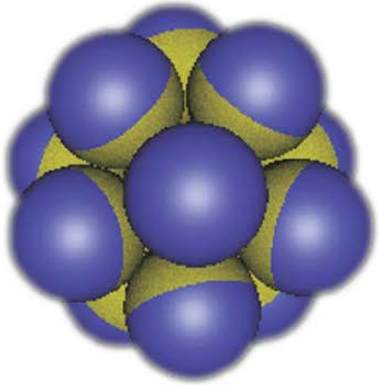
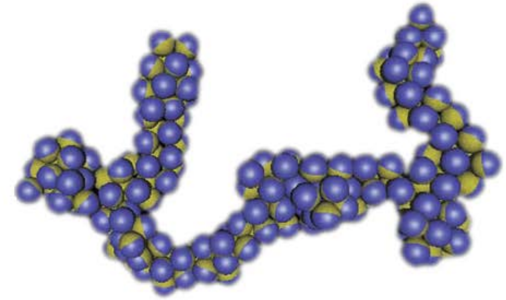
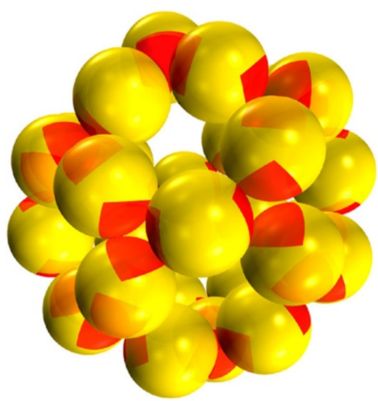
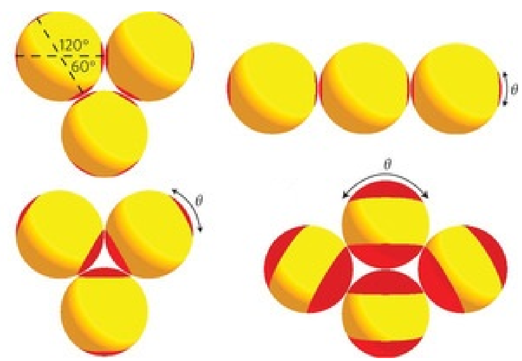
Janus



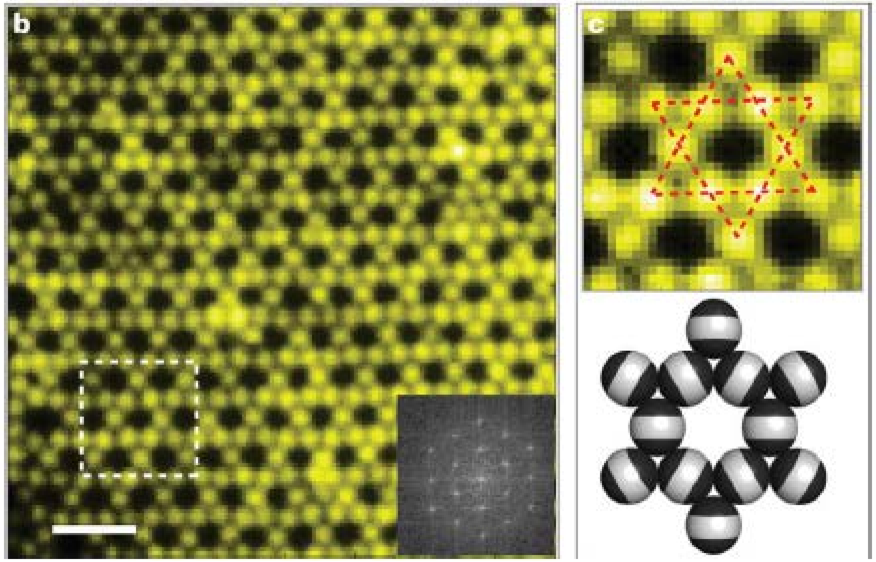


Patchy



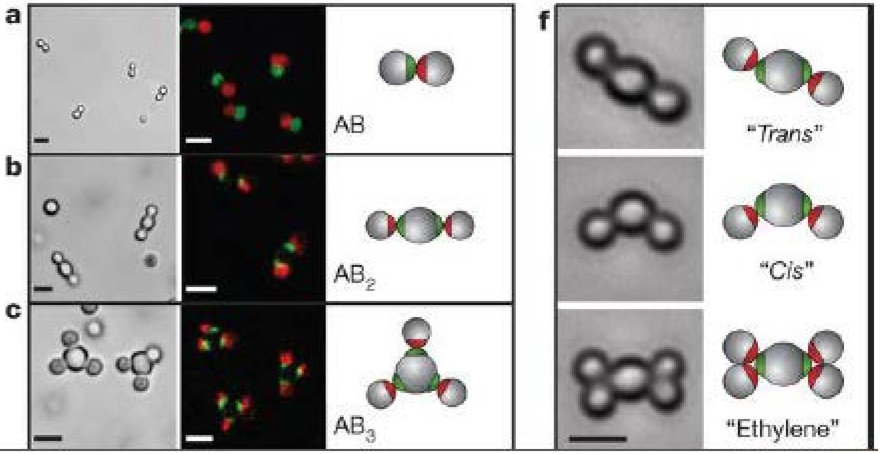


S. Granick & S. Jiang & Q. Chen, **“Janus particles”**, Physics Today, **68** (2009)
F. Romano & F. Sciortino, **“Patterning symmetry in the rational design of colloidal crystals”,** Nature Commun. **3**, 975 (2012)



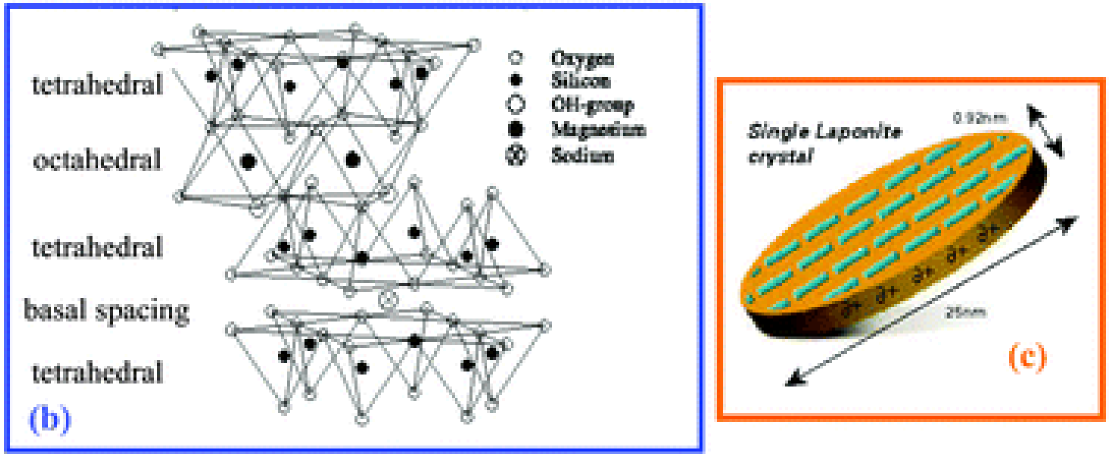
Patchy colloidal “molecules”
David Pine Group, Nature 2013

“Kagome lattice”
Q. Chen, S. C. Bae & S. Granick, Nature 2012



Self-assembly into (ordered) structures

(a) $Na^{+}_{0.7}[(Si_{8}Mg_{5.5}Li_{0.3})O_{20}(OH)_{4}]^{-0.7}$



Laponite
(synthetic clay particles)

Figure 2: Behaviour of the patchy-particle model for Laponite discs.

From

Observation of empty liquids and equilibrium gels in a colloidal clay

Barbara Ruzicka, Emanuela Zaccarelli, Laura Zulian, Roberta Angelini, Michael Sztucki, Abdellatif Moussaïd, Theyencheri Narayanan & Francesco Sciortino

Nature Materials **10**, 56–60 (2011) | doi:10.1038/nmat2921

Received 30 April 2010 | Accepted 09 November 2010 | Published online 12 December 2010

Example of «natural patchy nano-particles»

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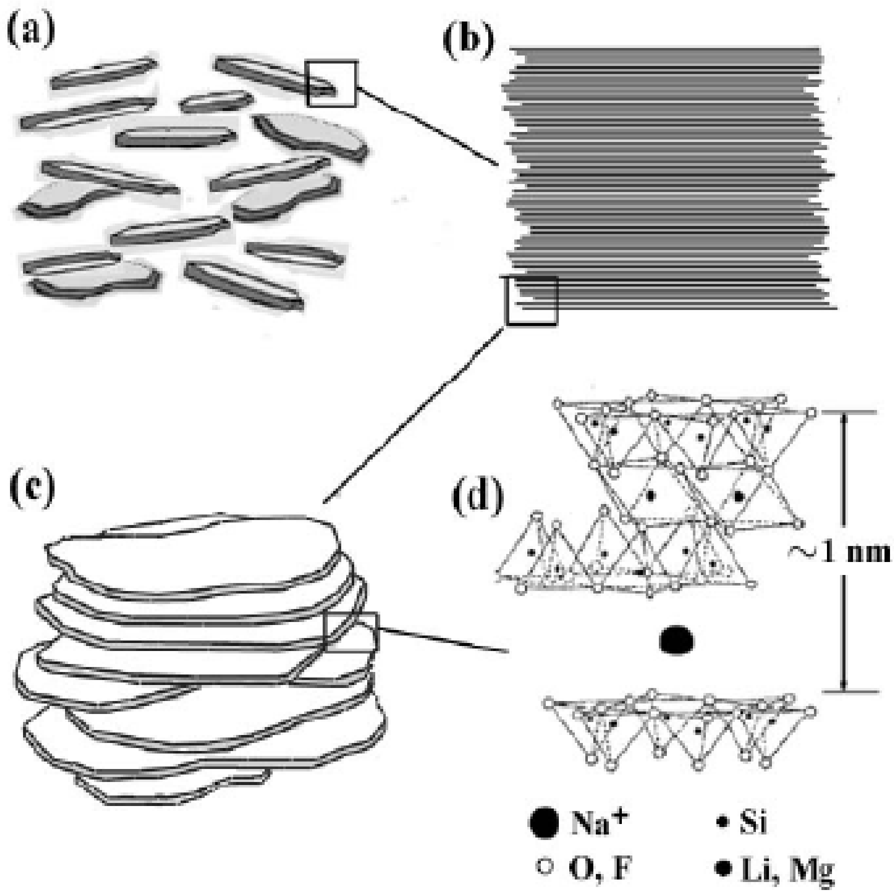
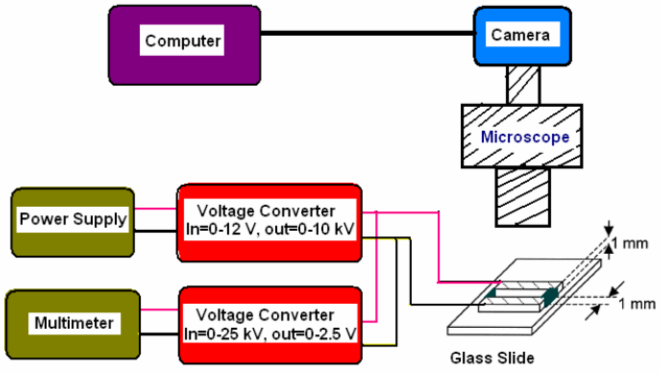
Q-fluorohectorite: Q_x-$(Mg_{3-x}Li_x)Si_4O_{10}F_2$,
Q is the exchangeable cation (Q = Na^+, Ni^{2+}, Fe^{3+}, etc)

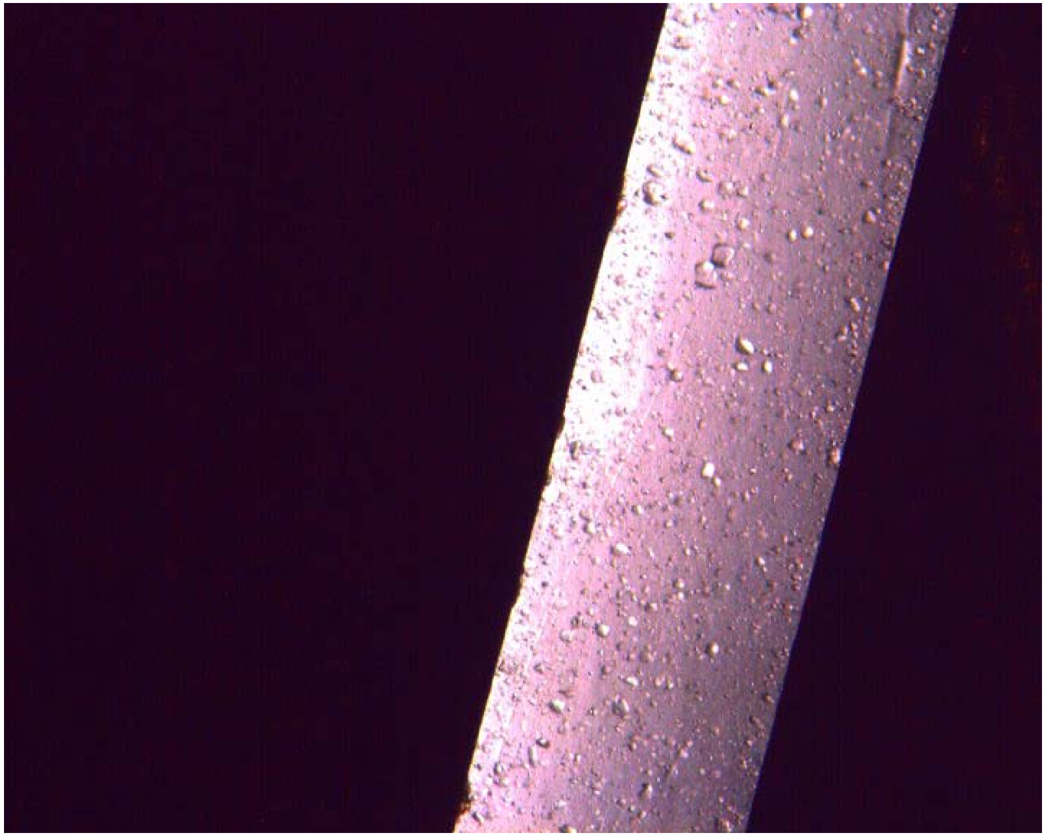


Clay particles suspended in oil:

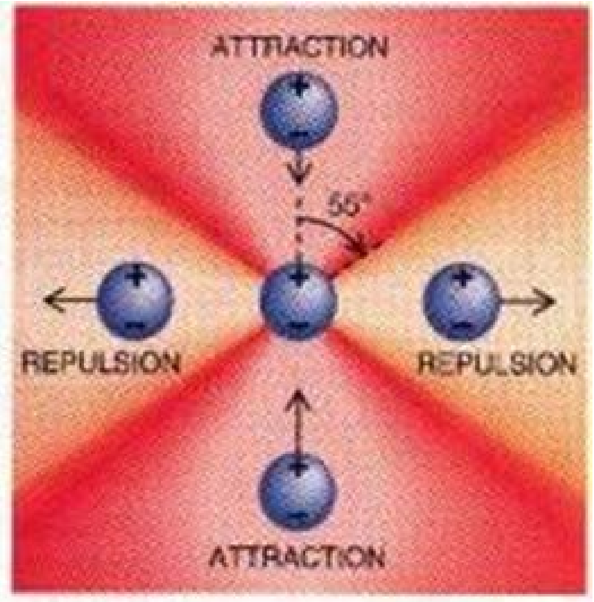


Video microscopy (real time):

-~500 V -



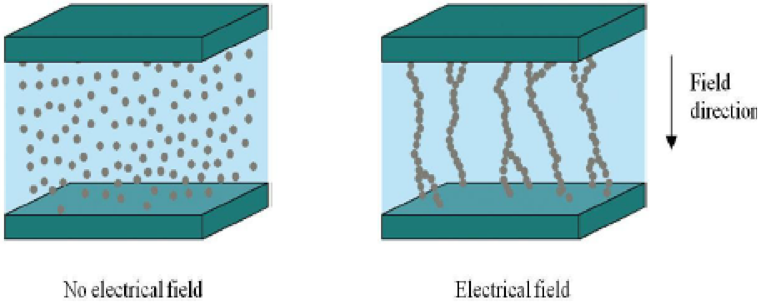
- 1 mm -



Electrorheology: Smart Materials

Electro-rheological fluids

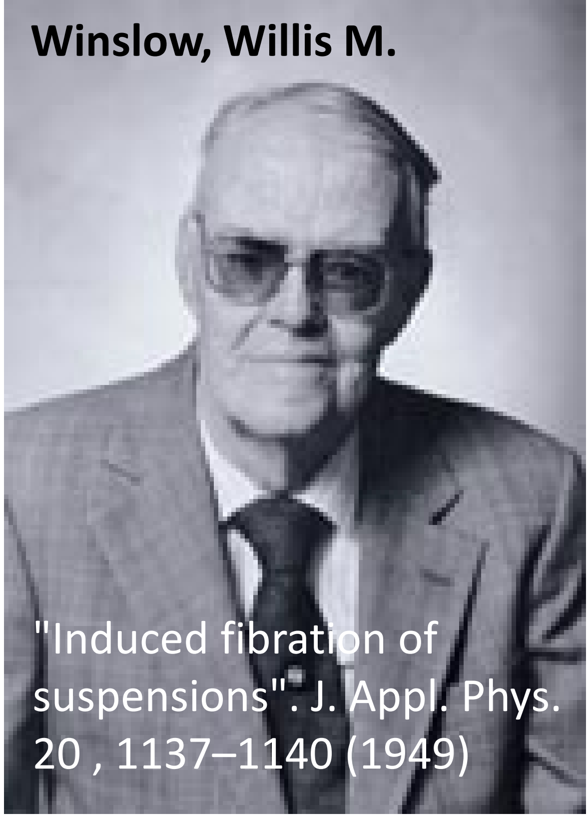
<u>Winslow effect:</u>



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

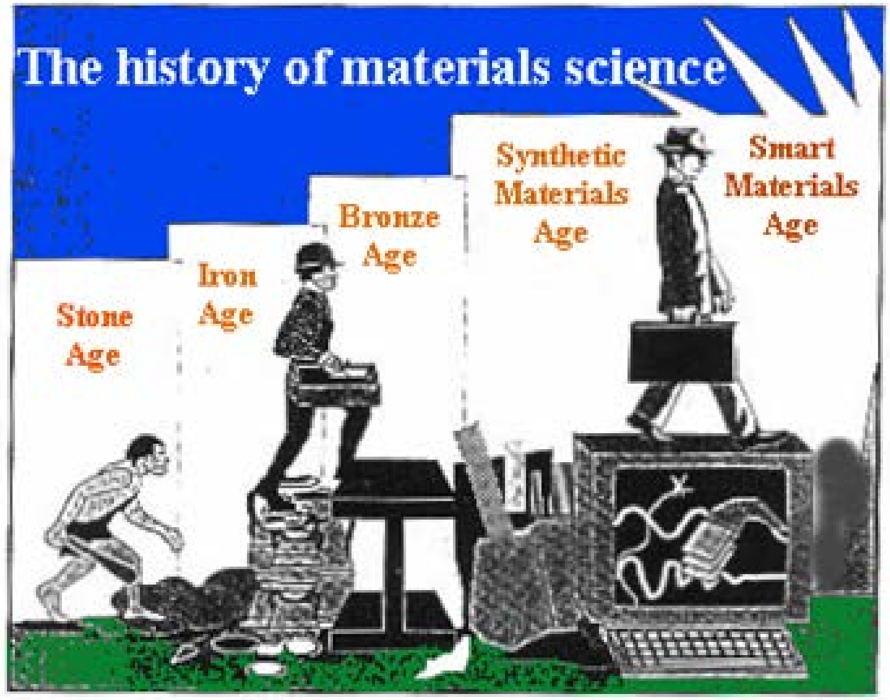
- Electric fields induce dipole attraction and chain formation
- Rapid and reversible: valves, clutches, breaks, flexible electronics, microfluidics
  http://en.wikipedia.org/wiki/Electrorheological_fluid

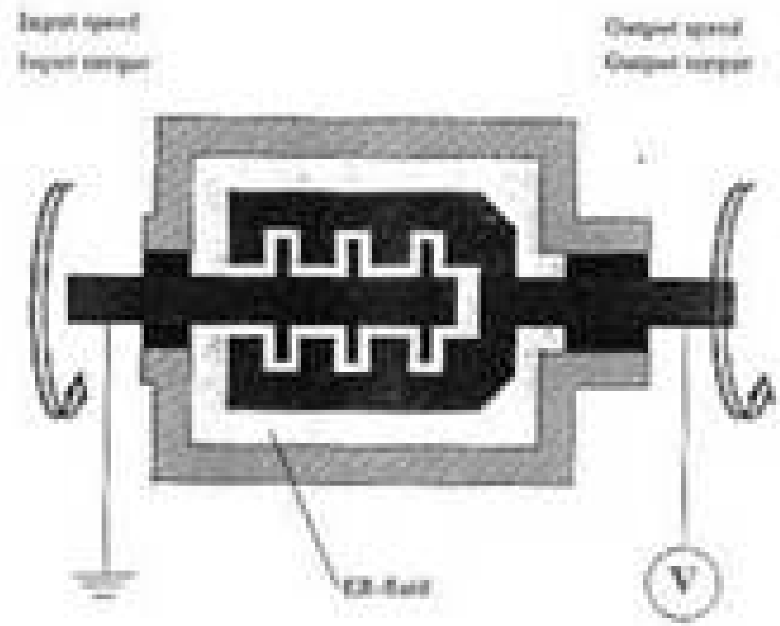
Large yield stress -> 200 kPa or more 100 times viscosity increase (up to 100000 times according to wiki)



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

NTNU

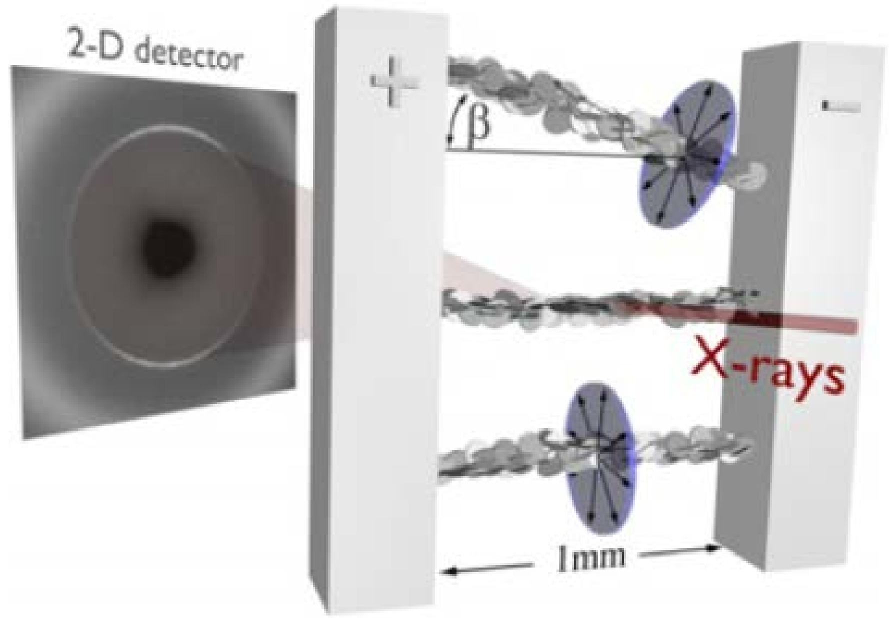

The history of materials science
Stone Age
Iron Age
Bronze Age
Synthetic Materials Age
Smart Materials Age


Input speed
Input torque
Output speed
Output torque
ER-fluid
V

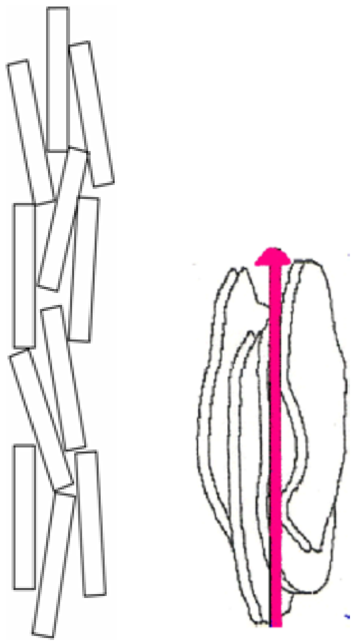
Swiss Norwegian Beam Line SNBL at ESRF Grenoble:

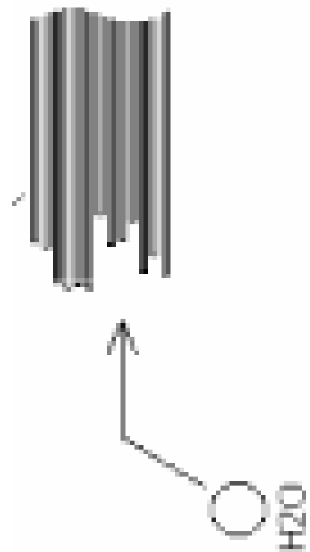
ESRF = European Synchrotron Radiation Facility

WAXS:



Experiments at SNBL/ESRF:



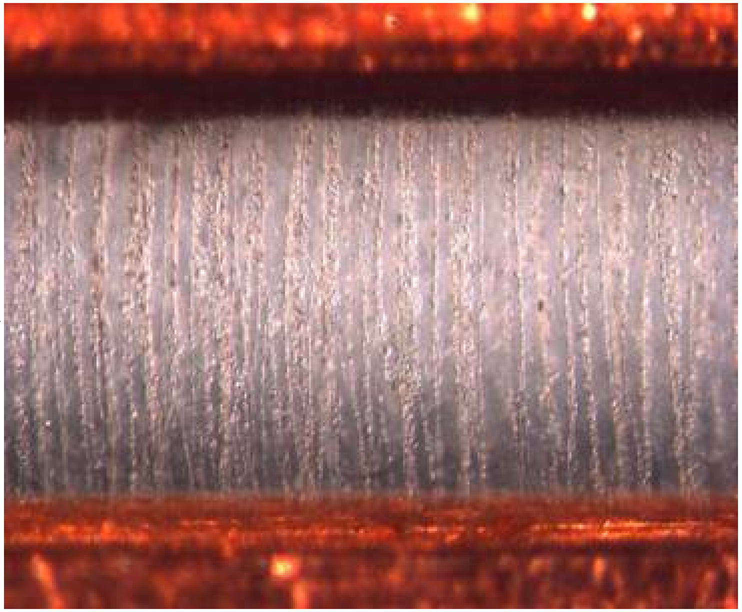


Cu

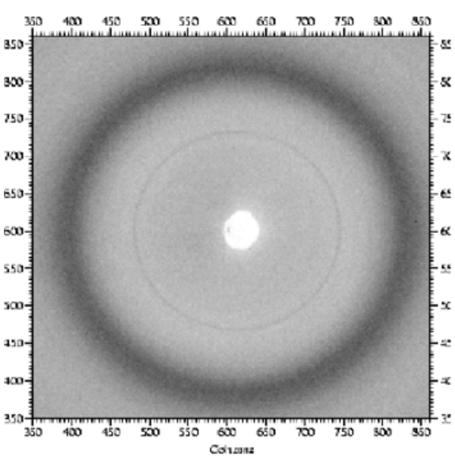
1mm

0.5 kV

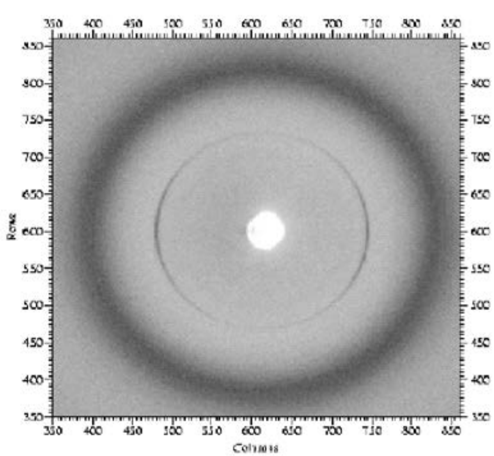
Cu

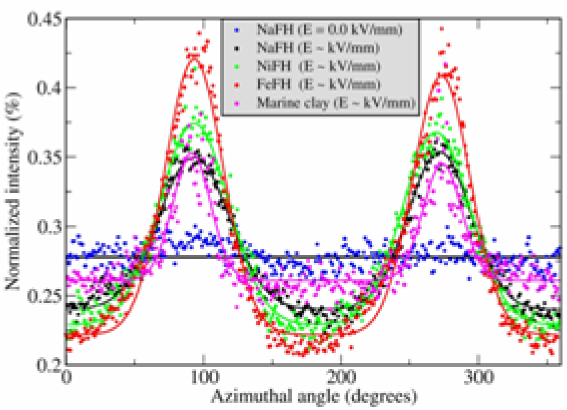


Before: 0 V/mm

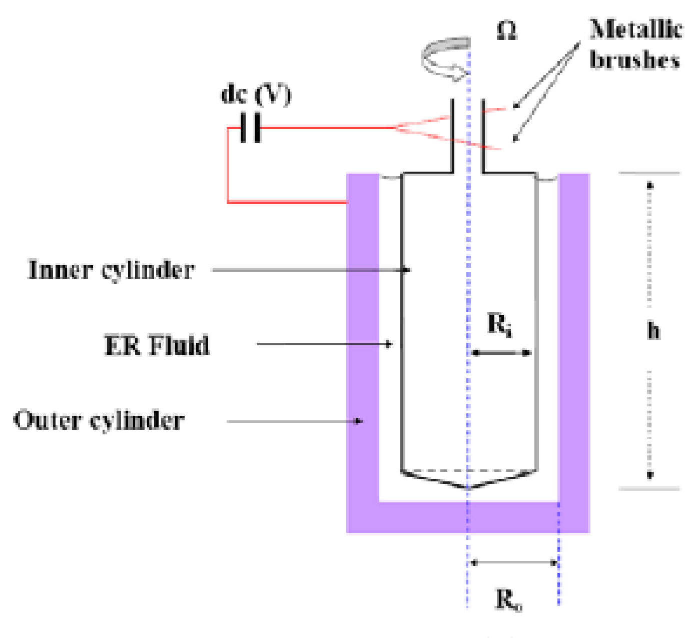


After: 500 V/mm





Our Physica MCR 300 Rheometer inl electrorheol. cell:



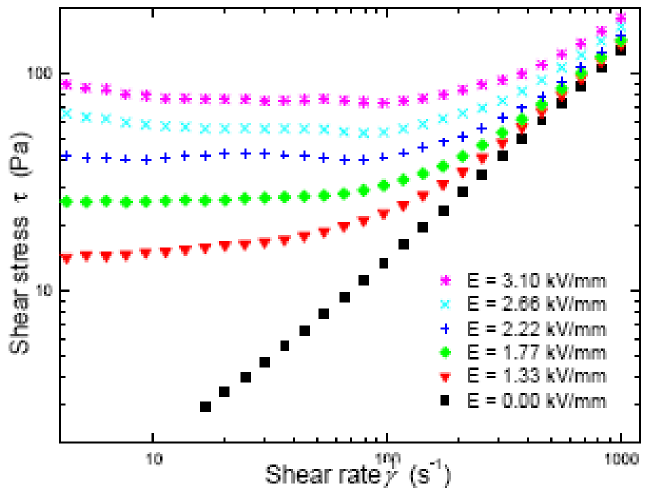
Langmuir 24, 1814 (2008)

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

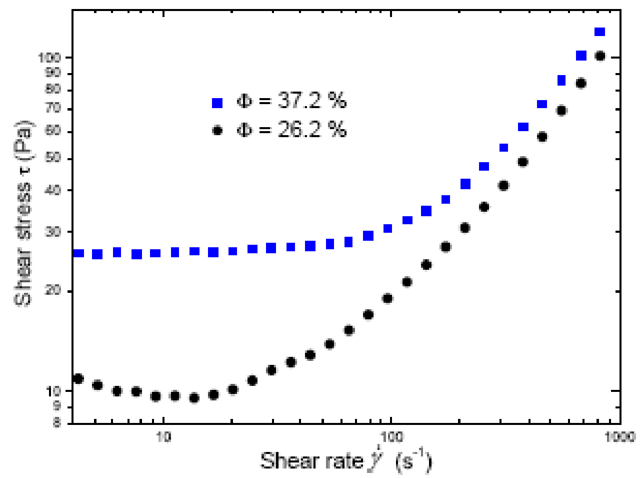
J. Rheol. 55, 2011 (2010)

Flow-curves for fluorohectorite in silicone oil:

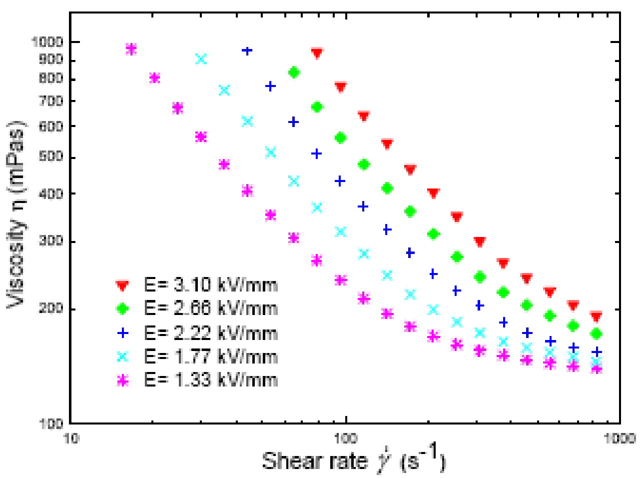
Dynamic yield stress:
Yield stress for a completely broken down (i.e., subjected to continuous shearing) ER fluid.
CSR Tests: **Steady-State Shearing.**
Typically measured by extrapolating the shear stress versus shear rate curve back to the shear stress intercept at zero shear rate.



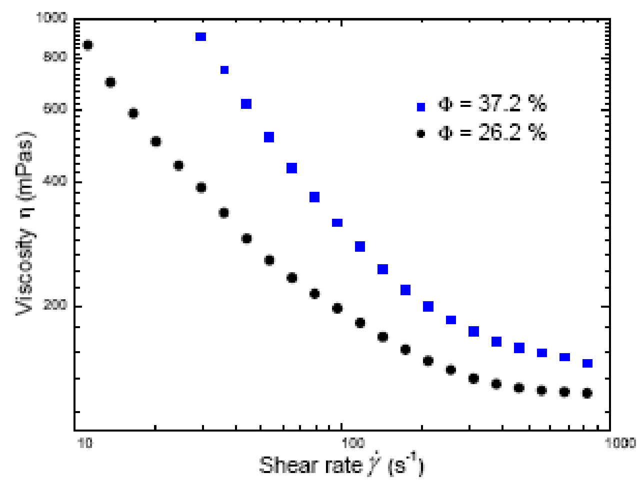
(a)



(a)



(b)



(b)

$$\tau = \eta \, d\gamma/dt$$

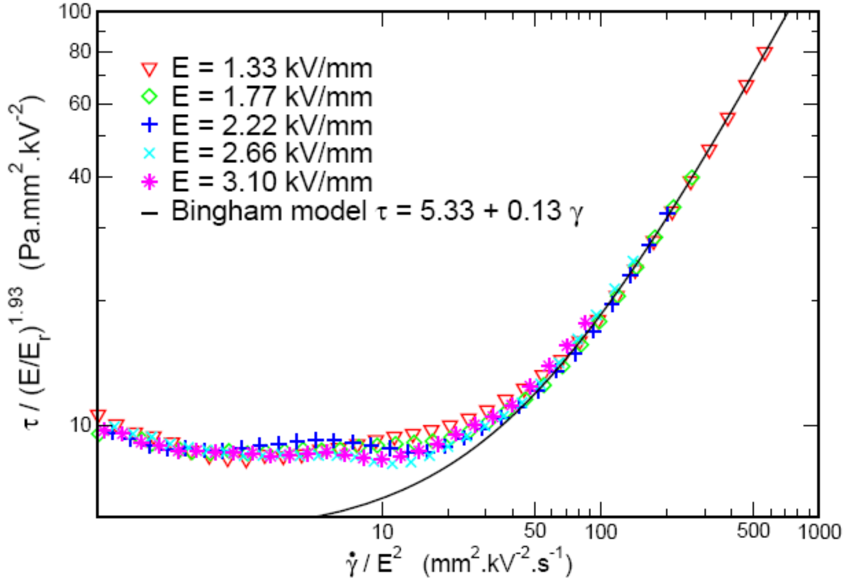
Scaling (data collapse) of flow curves:

•Dipole-dipole interaction is proportional to the square E^2 and to $(1/\text{distance})^2 = (1/\Phi)^{2/3}$

•Shear strength acting on a particle within an ER chain is proportional to the shear rate $d\gamma/dt$

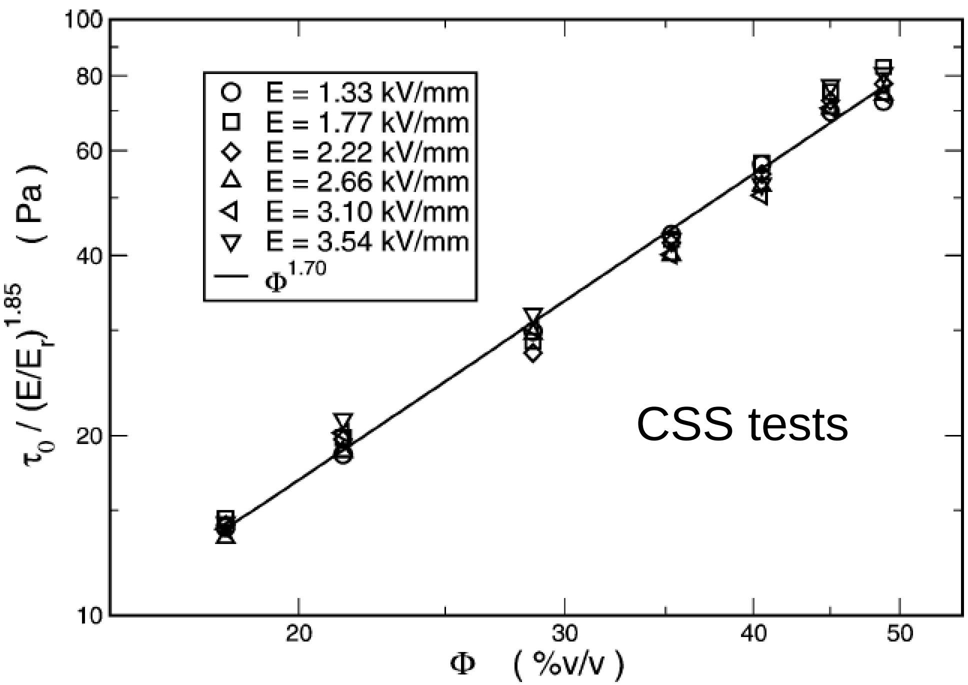
•Normalized shear representing relative impact of the shearing process on the cohesive ER structures, is $(d\gamma/dt)/(\Phi^{2/3}E^2)$

$$\tau(\Phi, E) = \Phi^{\beta} E^{\alpha} f\left(\frac{\dot{\gamma}}{\Phi^{2/3} E^2}\right)$$



Yield stress:

Theories predict: $$\tau \propto E^{\alpha}\,\Phi^{\beta}$$



Static yield stress:
Yield stress for an undisrupted ER fluid.

Log-log plot of the static yield stress, normalized by $E^{1.86}$, vs. the volume fraction at different strengths of the applied electric field. A power law $\beta \approx 1.70$ fits to the whole dataset..

ER Suspensions of Laponite in Oil *Langmuir, Vol. 24, No. 5, 2008* 1821

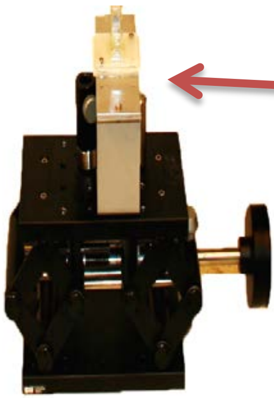
Table 1. Comparison of Static Yield Stress Values for Various ER Fluids Including That Addressed in the Present Paper, under an Applied Electric Field of About 1.0 kV/mm

ER fluids →	our sample	mica[18]	hematite[43]	saponite[44]	zeolite[45]	GER[46]
Φ →	1.9% (v/v)	15% (v/v)	15% (v/v)	0.11 g/mL	30% (v/v)	30% (v/v)
τ_0 (Pa) →	~20	~100	~85	~50	~3000	~15000

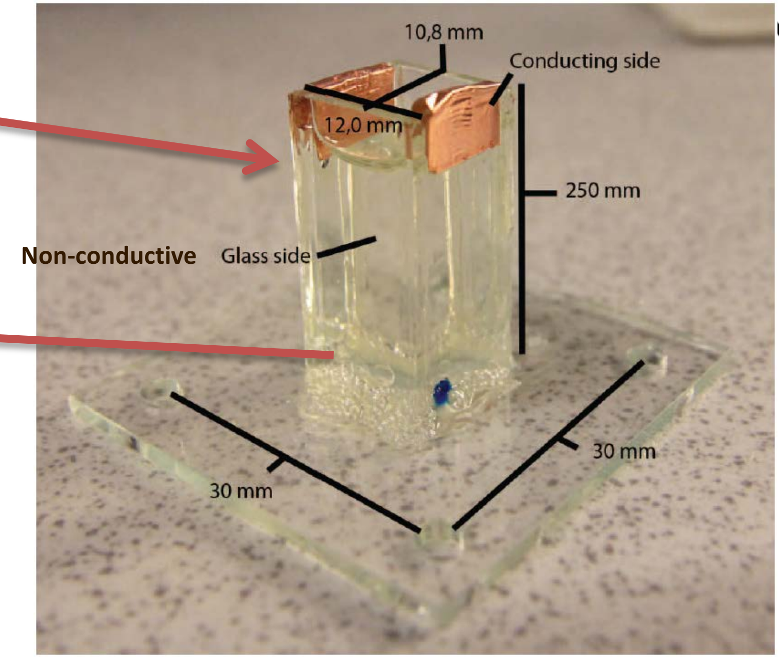
Sample cell

2x ITO transparent electrodes

2x glass walls

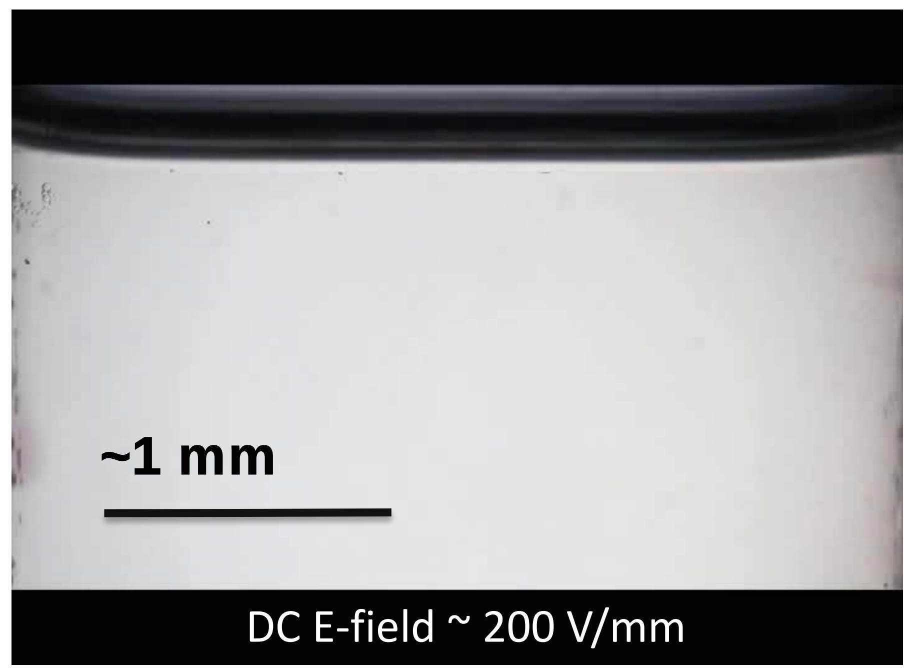


Translation stages



Clay in silicone oil dispersion
(~ 1 mm diameter drop)

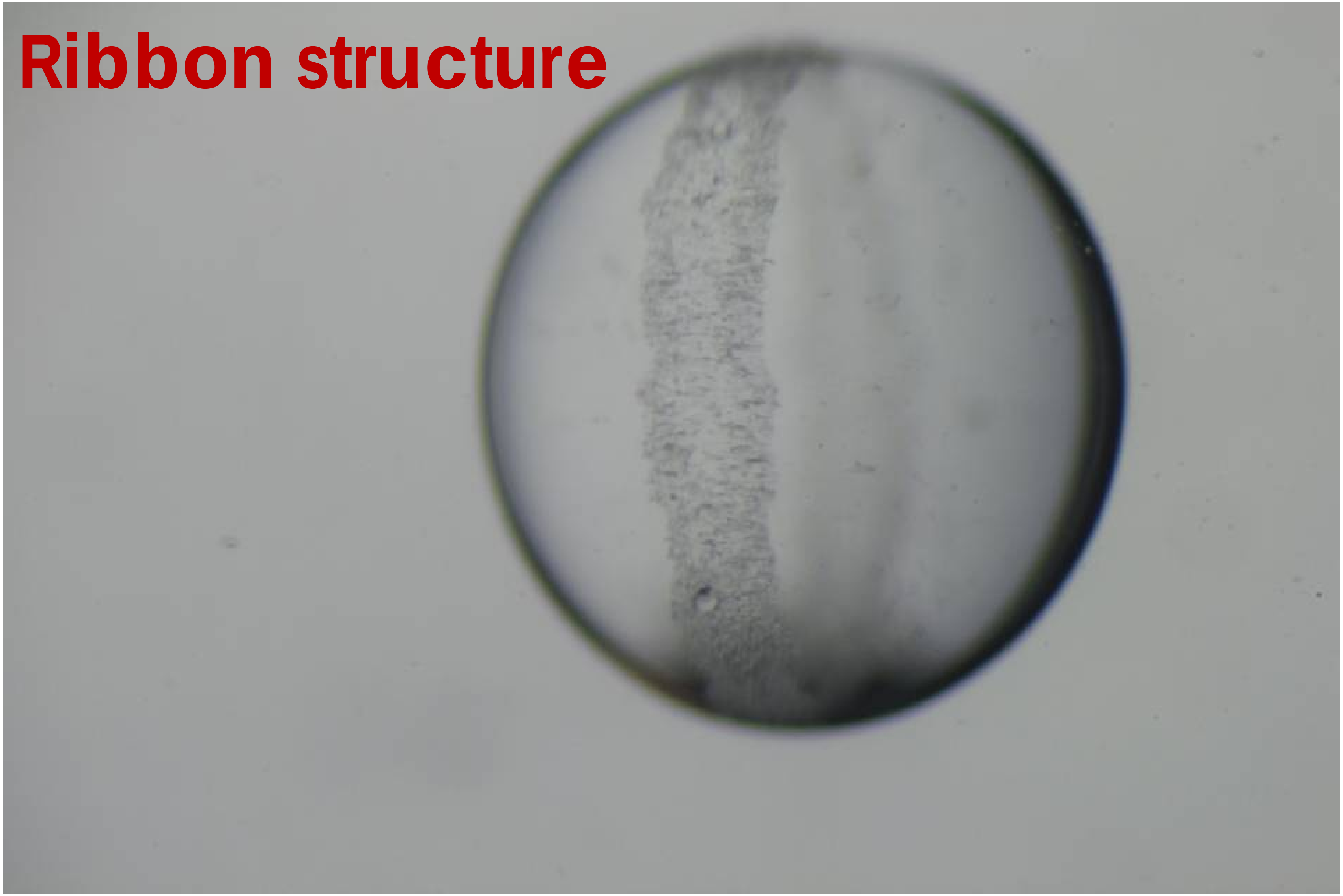
Castor oil
(continuous phase)



Speeded up x10

E-field induces flows of liquids

Ribbon structure



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Our Condition 1: Two leaky dielectric liquids

Our Condition 2: $\sigma_{drop} < \sigma_{surrounding}$

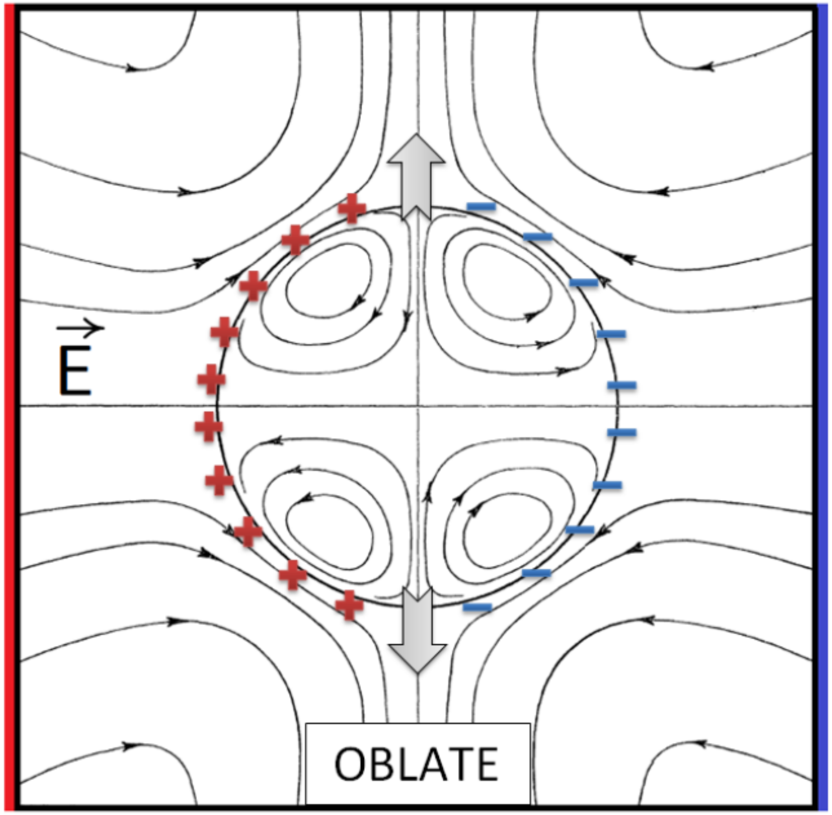
When DC E-field applied:

Free charge accumulation

Maxwell electric stress

Liquid circulation flows

Oblate deformation

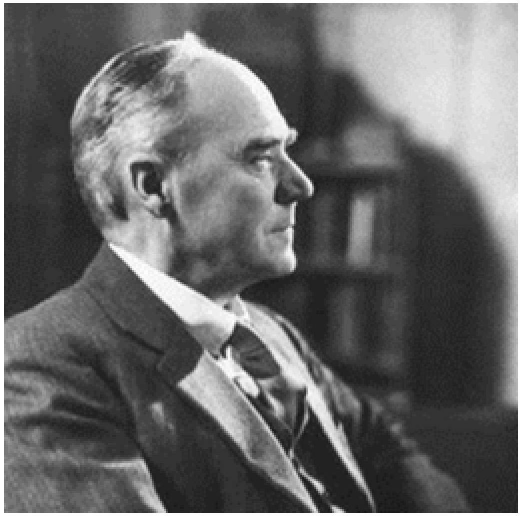


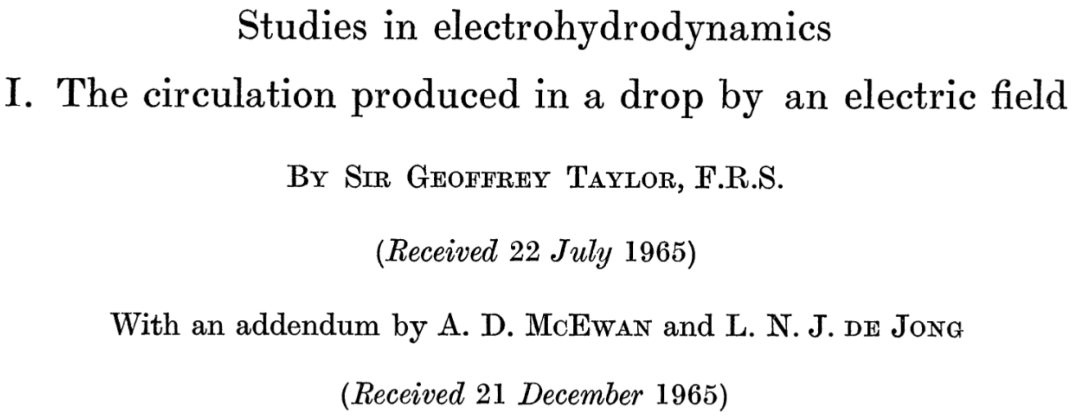
Adopted from [Taylor 1965]

Electro-hydrodynamic flow

Discard the notion that the suspending fluids can be treated as insulators:

- Conductors: water, mercury
- Dielectrics: benzene
- **"Leaky dielectrics":** castor oil, corn oil, mineral oils, etc





Studies in electrohydrodynamics

I. The circulation produced in a drop by an electric field

By Sir Geoffrey Taylor, F.R.S.

(*Received* 22 *July* 1965)

With an addendum by A. D. McEwan and L. N. J. de Jong

(*Received* 21 *December* 1965)

Proc. R. Soc. Lond. A 291,159-166 (1966)

Our Condition 1: Two leaky dielectric liquids

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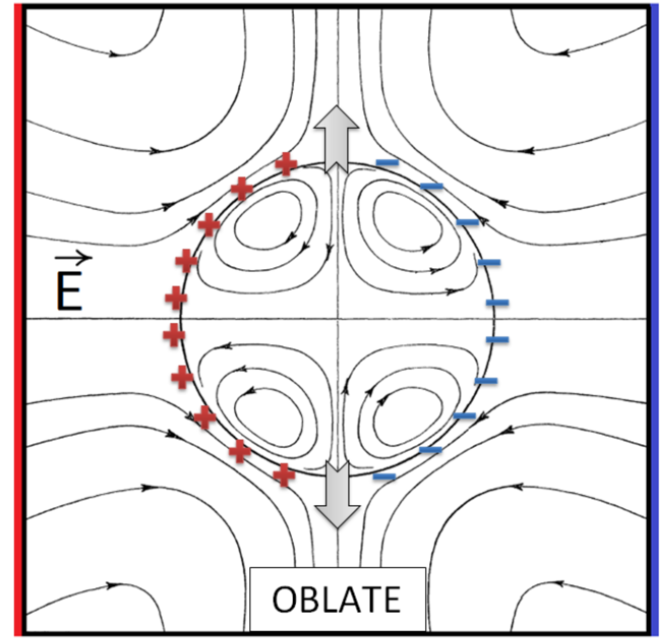
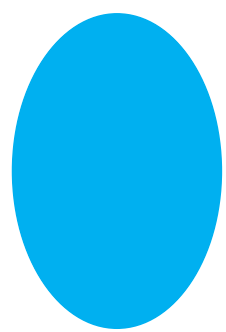
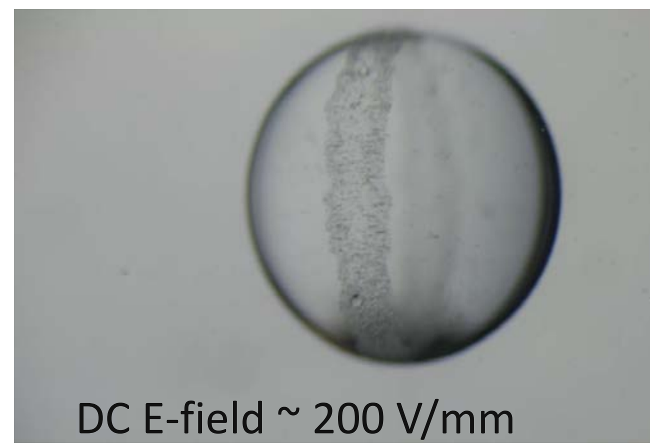


Adopted from [Taylor 1965]

Ribbon structure

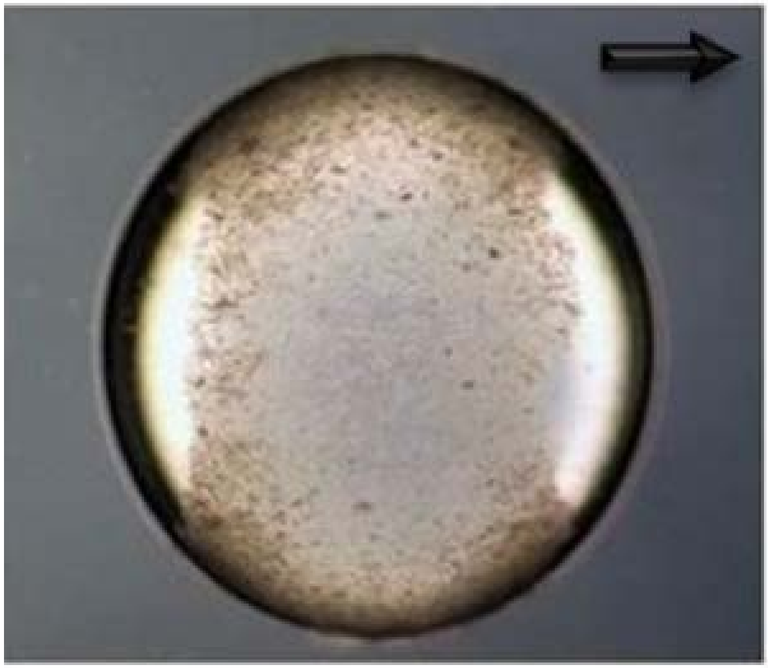


DC E-field ~ 200 V/mm



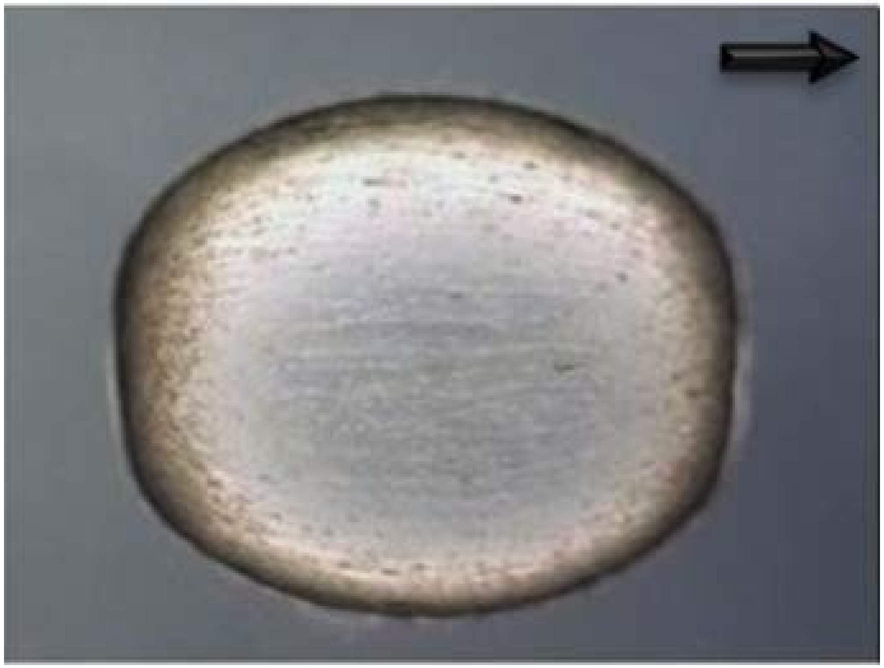
Electro-hydrodynamic Taylor flow

Oblate-to-Prolate transition



$E=200\ Vmm^{-1}$

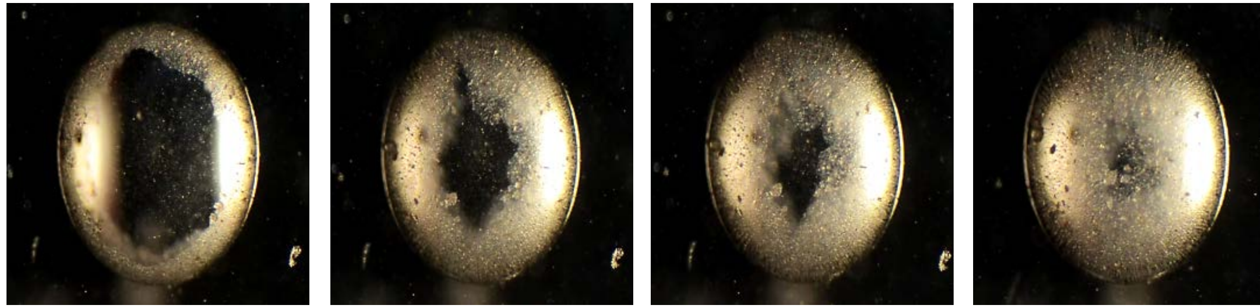
Electro-hydrodynamic flow



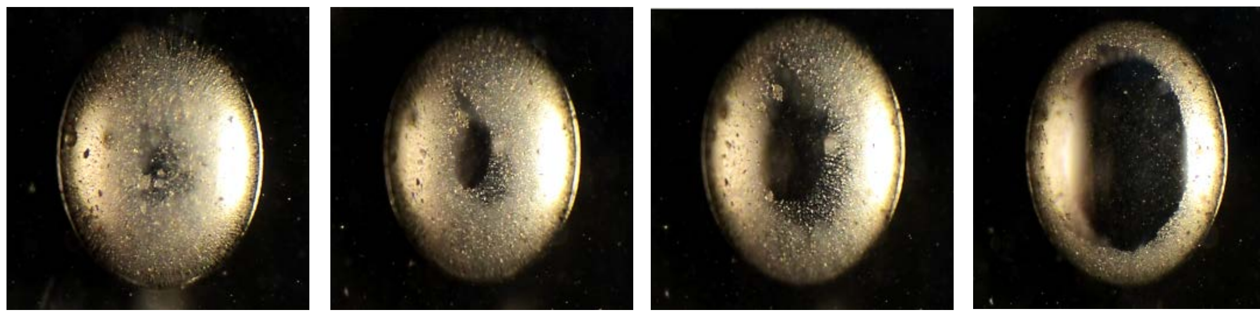
$E=500\ Vmm^{-1}$

Dipole-dipole interactions

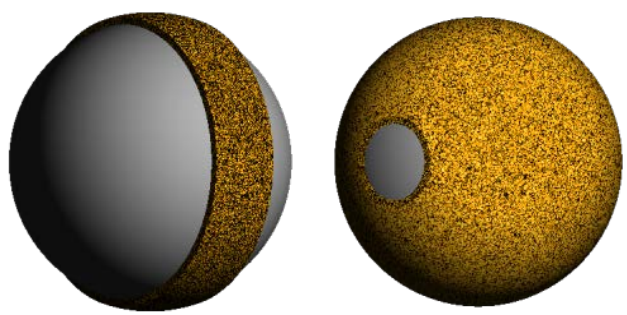
200 ⟶ 500 V/mm



200 ⟵ 500 V/mm



Electro-hydrodynamic flow



Dipole-dipole interactions

Active pupil-like colloidal shell (opening - closing)

Active pupil-like colloidal shell (opening - closing)

Active structuring of colloidal armour on liquid drops, P. Dommersnes, Z. Rozynek, A. Mikkelsen, R.Castberg, K. Kjerstad, K. Hersvik & J. O. Fossum, Nature Communications 4, 2066 (2013)

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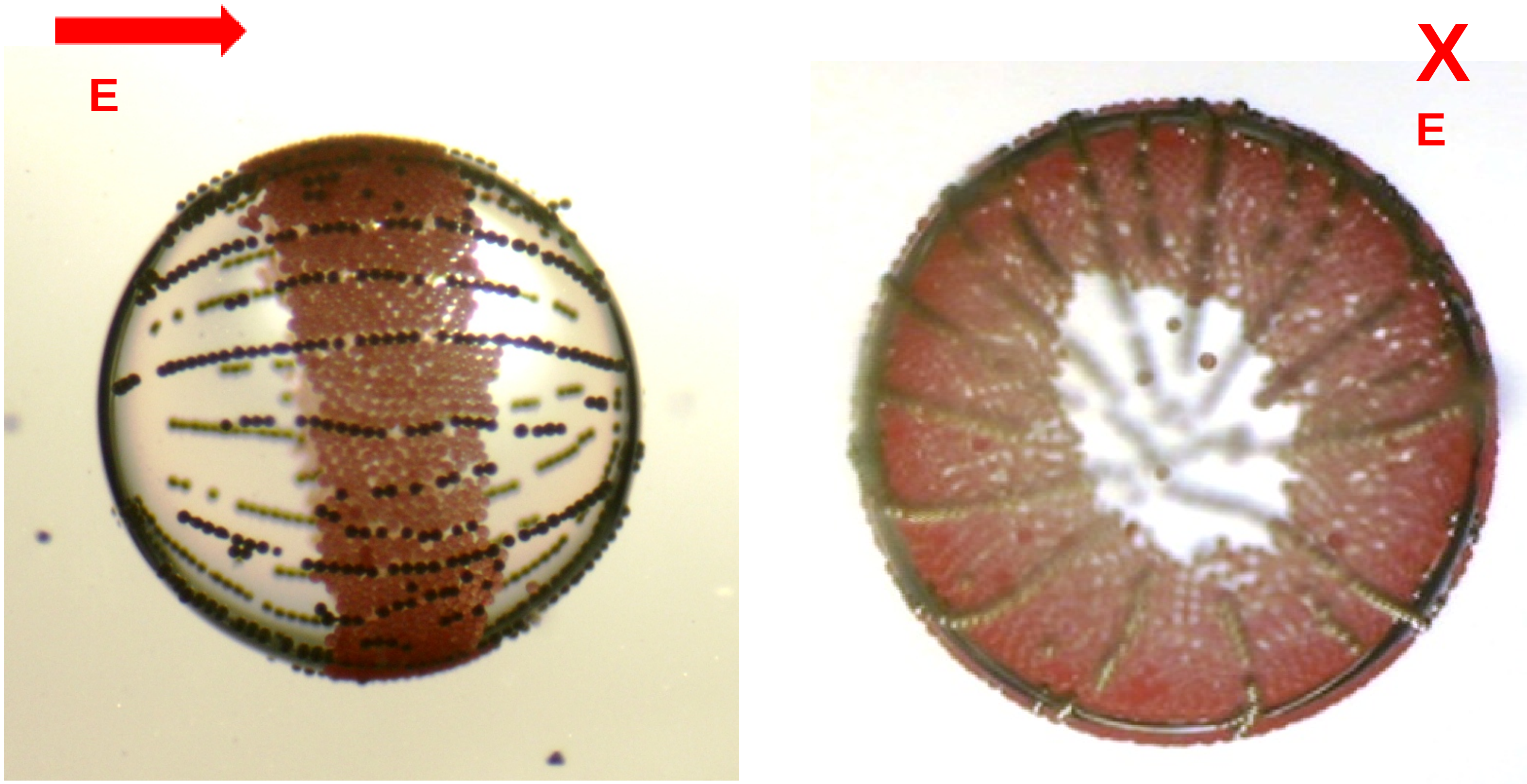
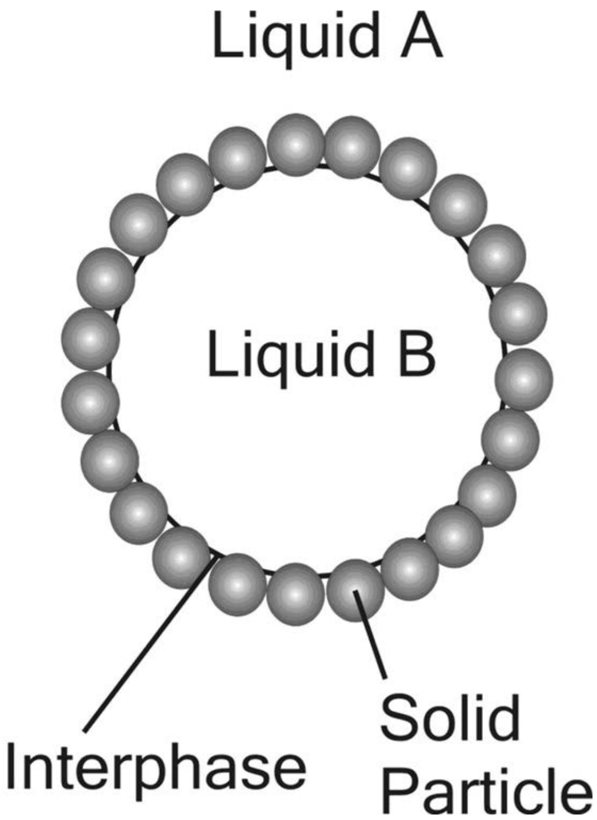


Electric field controlled particle structuring at droplet liquid-liquid interfaces

Capillary binding



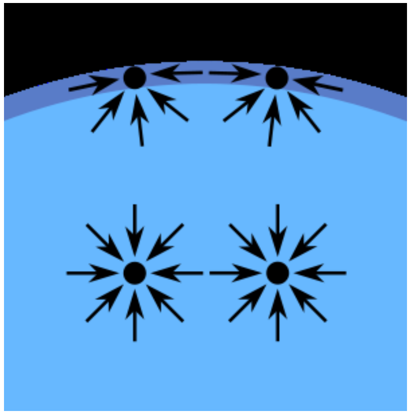
Surface Energy: $E = \gamma A$

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

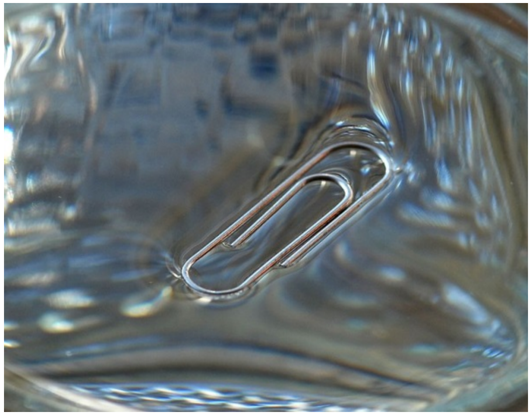
Capillary binding: A particle at the interface is trapped in a capillary barrier with a substantial energy cost of moving to either side of the liquid interface.

Origin of capillary binding:
Surface tension:

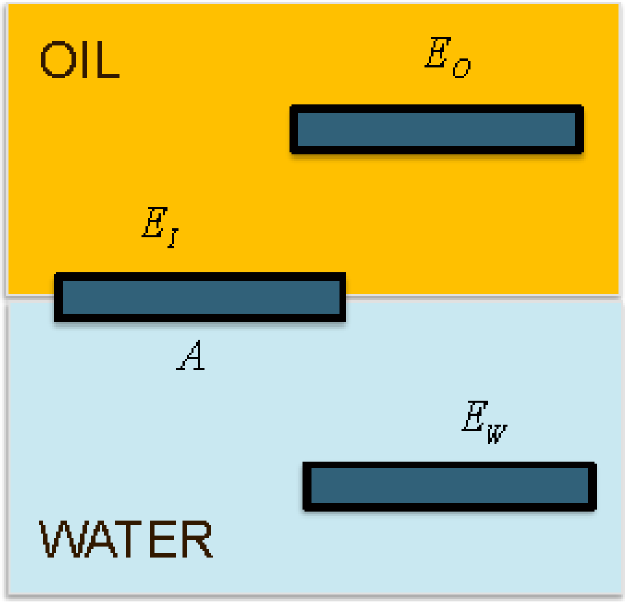
The forces on molecules of a liquid:



Surface tension preventing a paper clip from submerging



Capillary binding of a flat solid particle at a liquid interface



Particle surface energy :

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

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

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

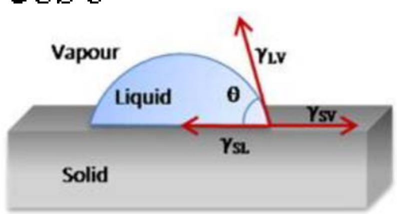
Energy gain :

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

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

Wetting angle Young's relation:

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



Energetically favorable to adsorb articles at the interface.

Typically:

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

Case 1: Partly covered drops ⇒ Coalescence
Case 2: Fully covered drops ⇒ No coalesence

Fully covered drops do not coalesce ⇒ Pickering emulsions: Experiments at NTNU Trondheim

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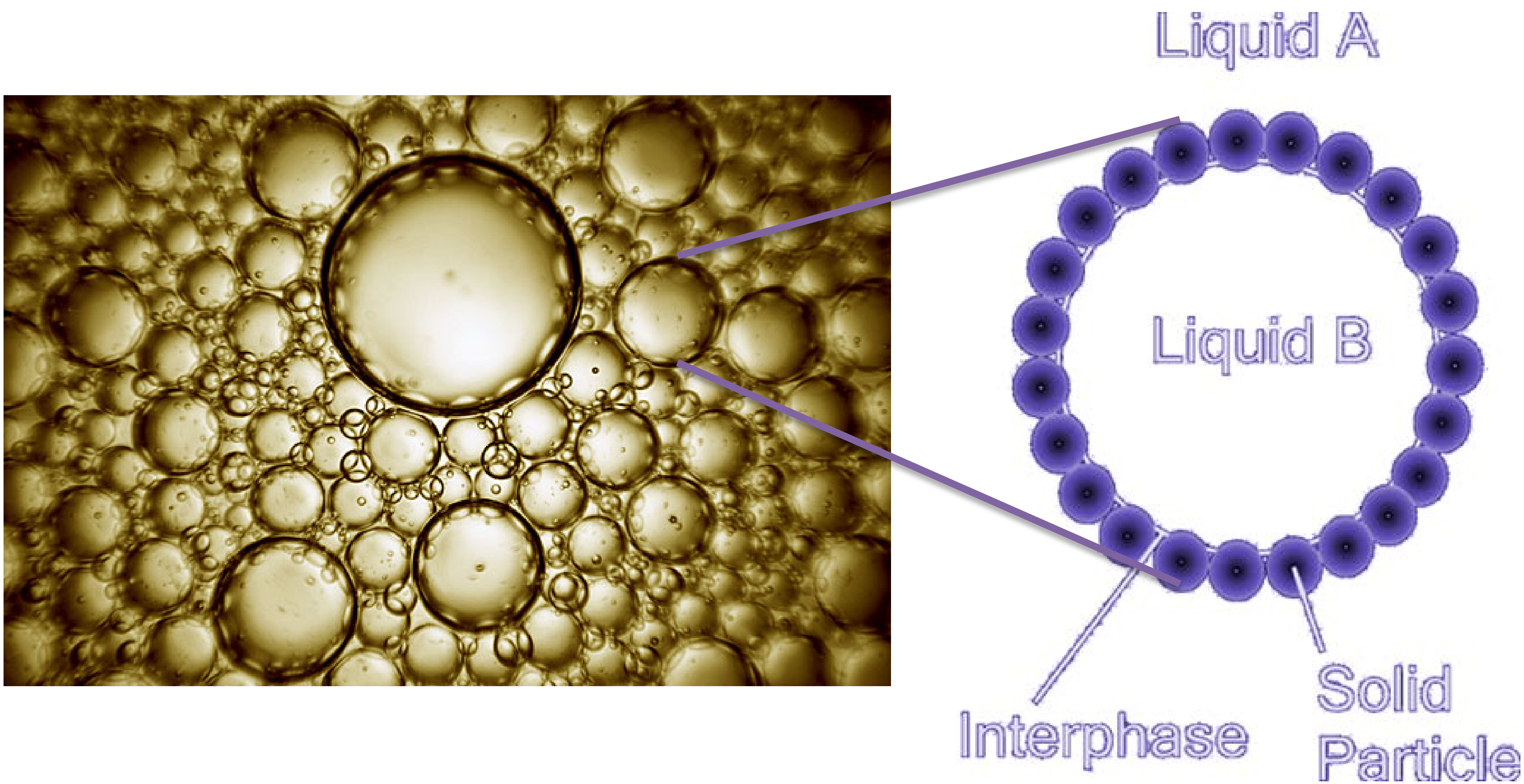
Colloidal particles as emulsion stabilizers: Pickering («physical») emulsions



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

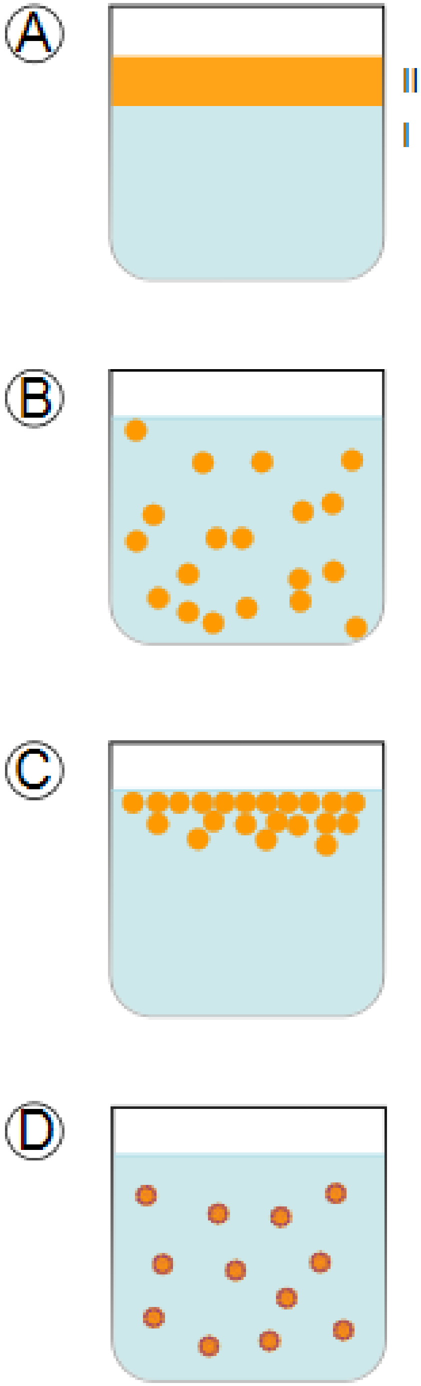
CXCVI.—*Emulsions.*

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)

«Classical» («chemical») emulsions



Legend

- Phase I
- Phase II
- Surfactant

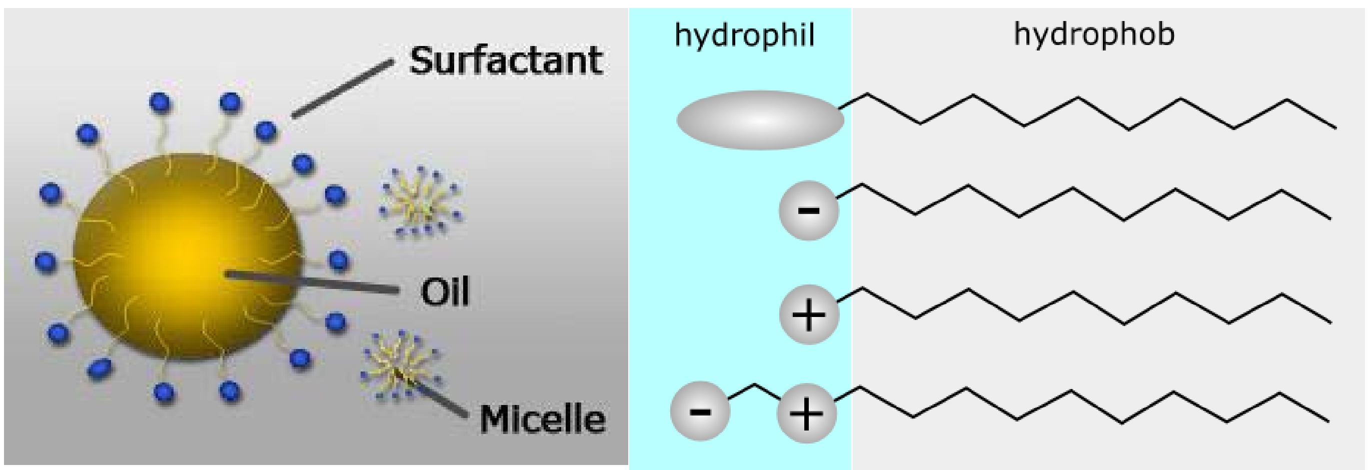
A. Two immiscible liquids, not emulsified

B. Emulsion of Phase II dispersed in Phase I

C. The unstable emulsion progressively separates

D. Surfactant positions itself on interface between Phases I and II, stabilizing emulsion

$E_{bind} >\sim k_B T$

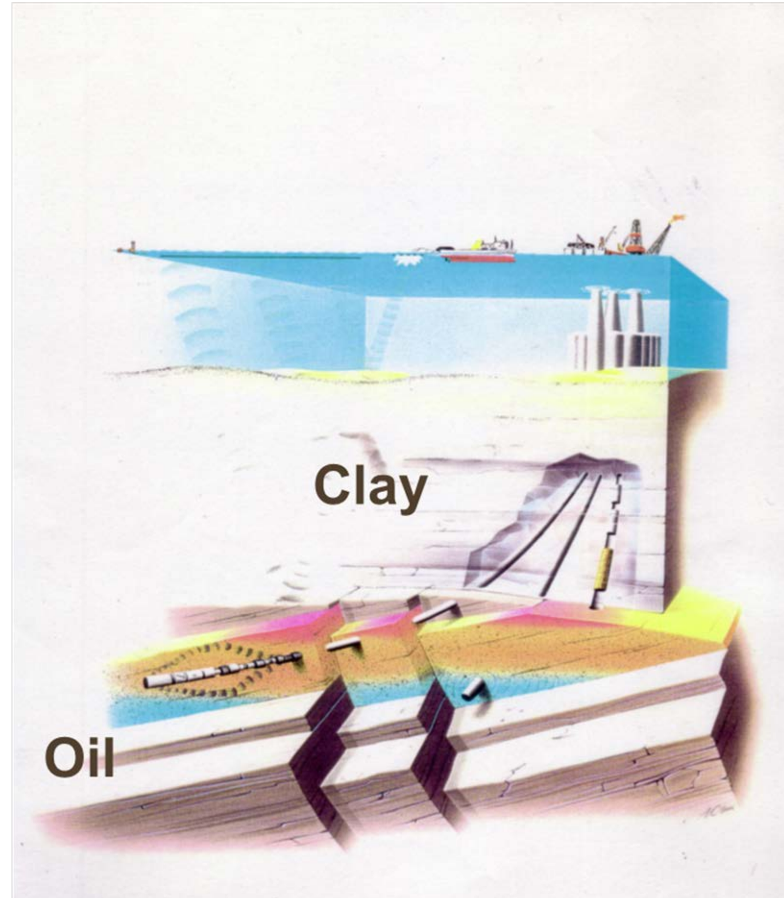


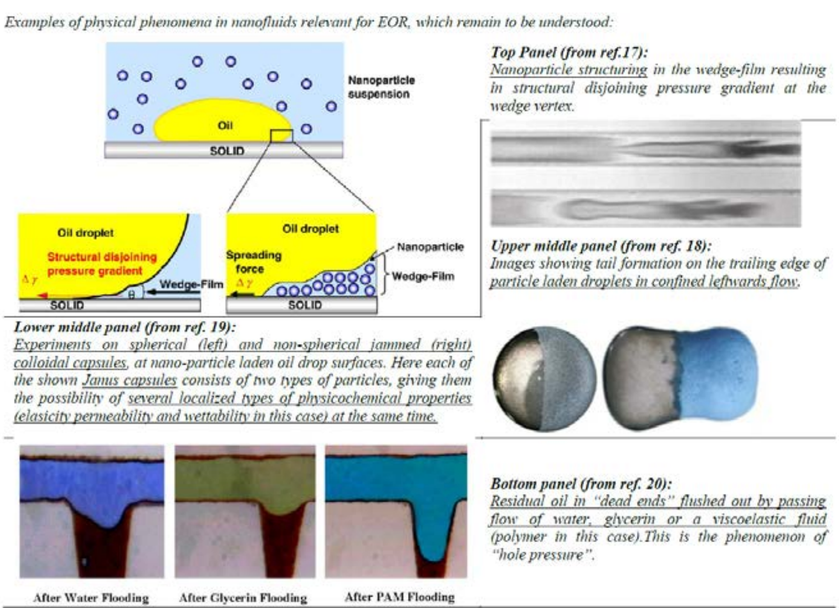
Classical» («chemical») emulsions

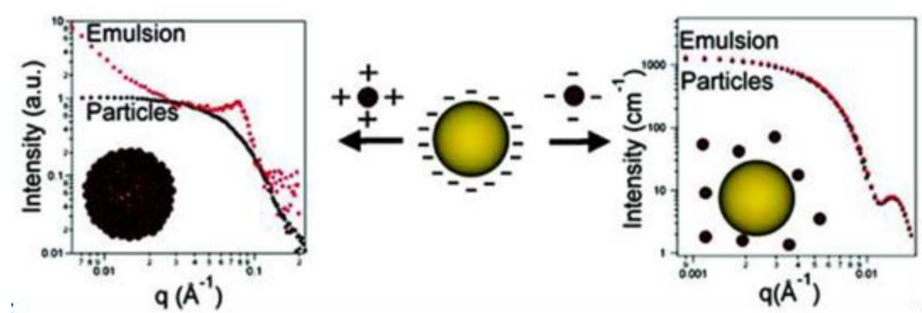
Experimental results indicate that some nanoparticles (silica, clay etc.) are good EOR agents => **Nanofluids**.

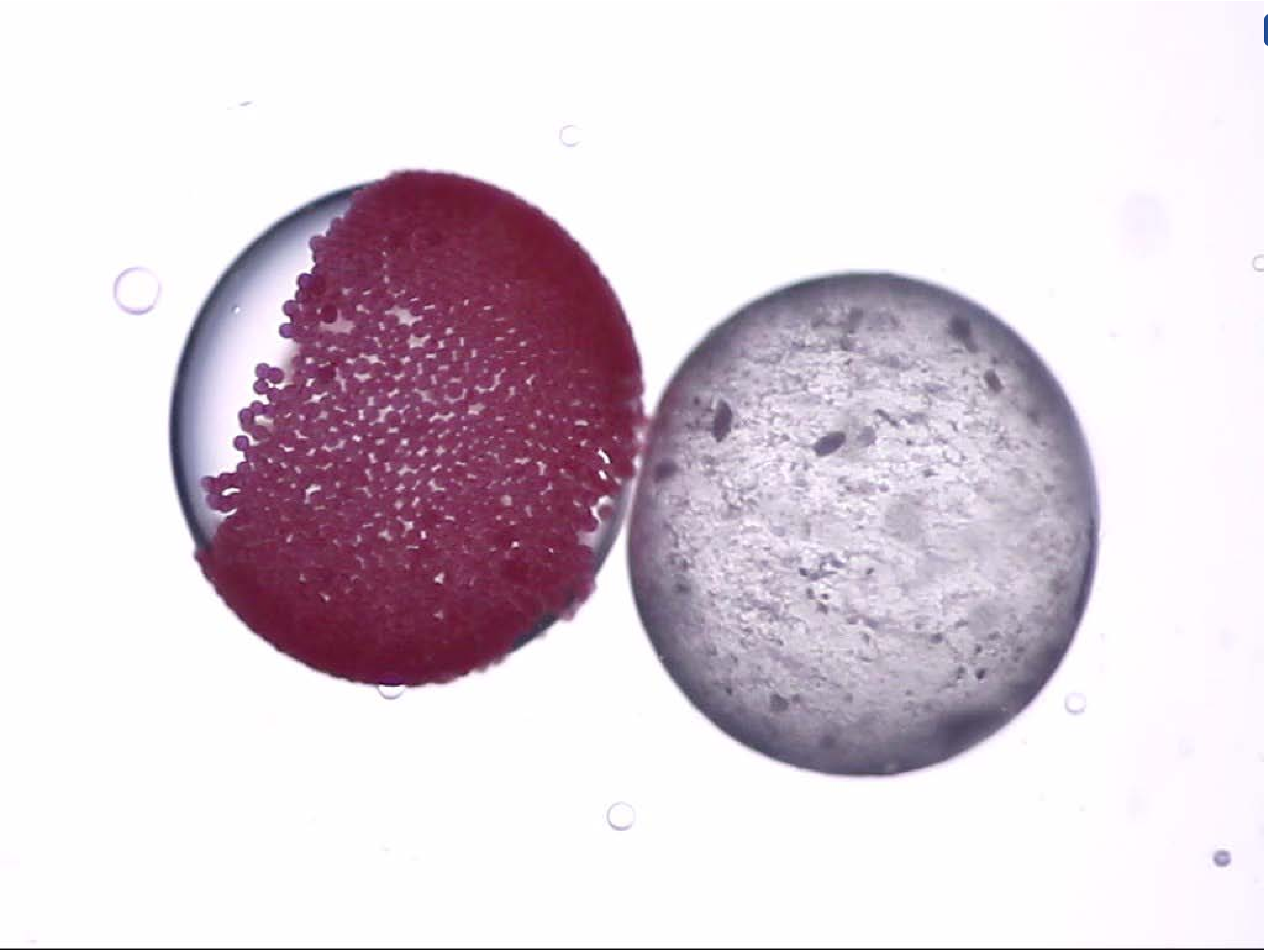
The mechanisms through which oil is enhanced using these nano agents are not well understood.

Important factors could include change of rock wettability, reduction of interfacial tension, reduction of oil viscosity, reduction of mobility ratio and permeability alterations.



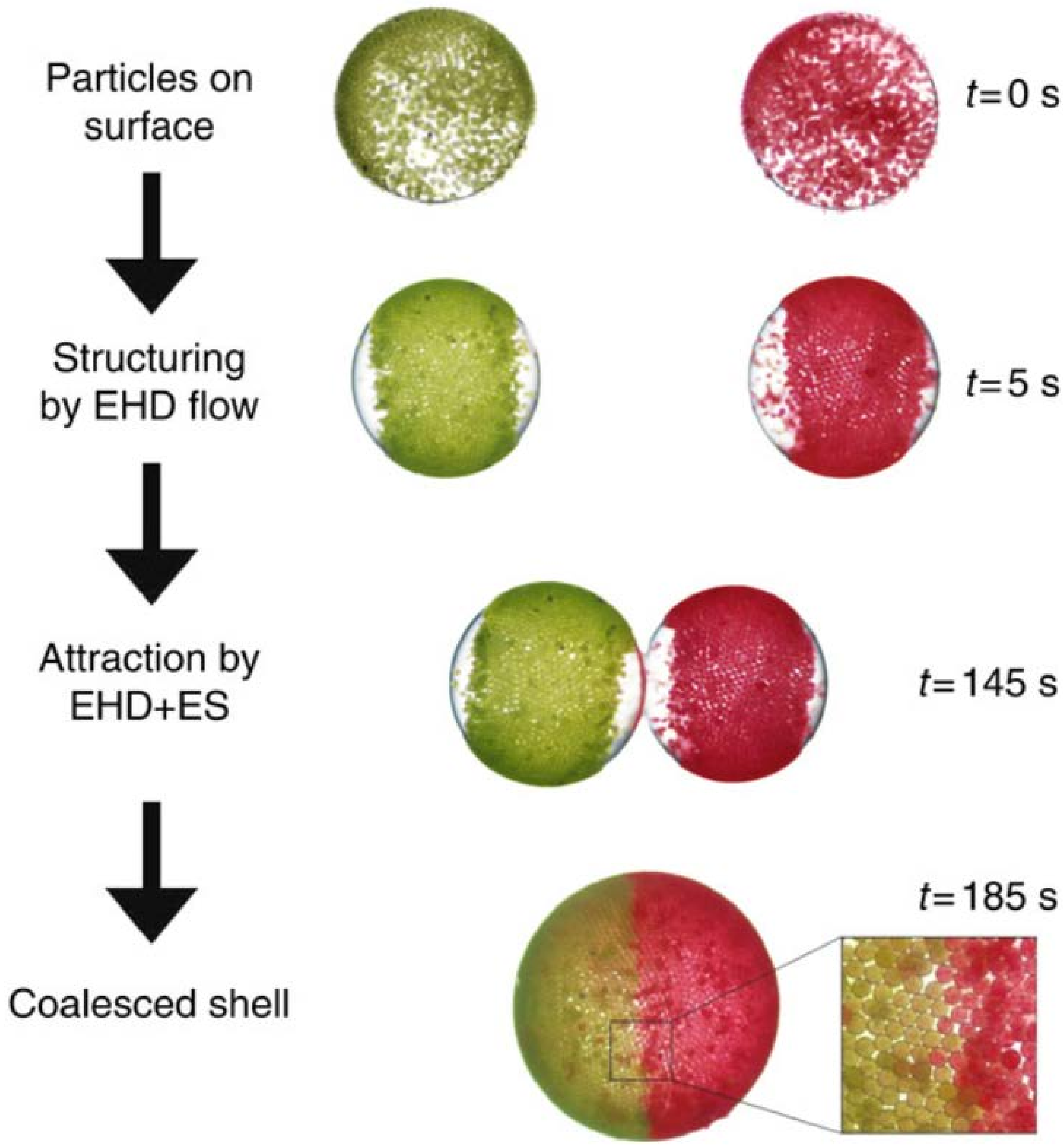






Janus shells with clay and PE particles, Experiments at NTNU Trondheim

Electroformation of Janus and patchy capsules, Z. Rozynek, A. Mikkelsen, P.Dommersnes & J. O. Fossum, Nature Communications 5, 3945 (2014)



Fabrication of Janus **shell**

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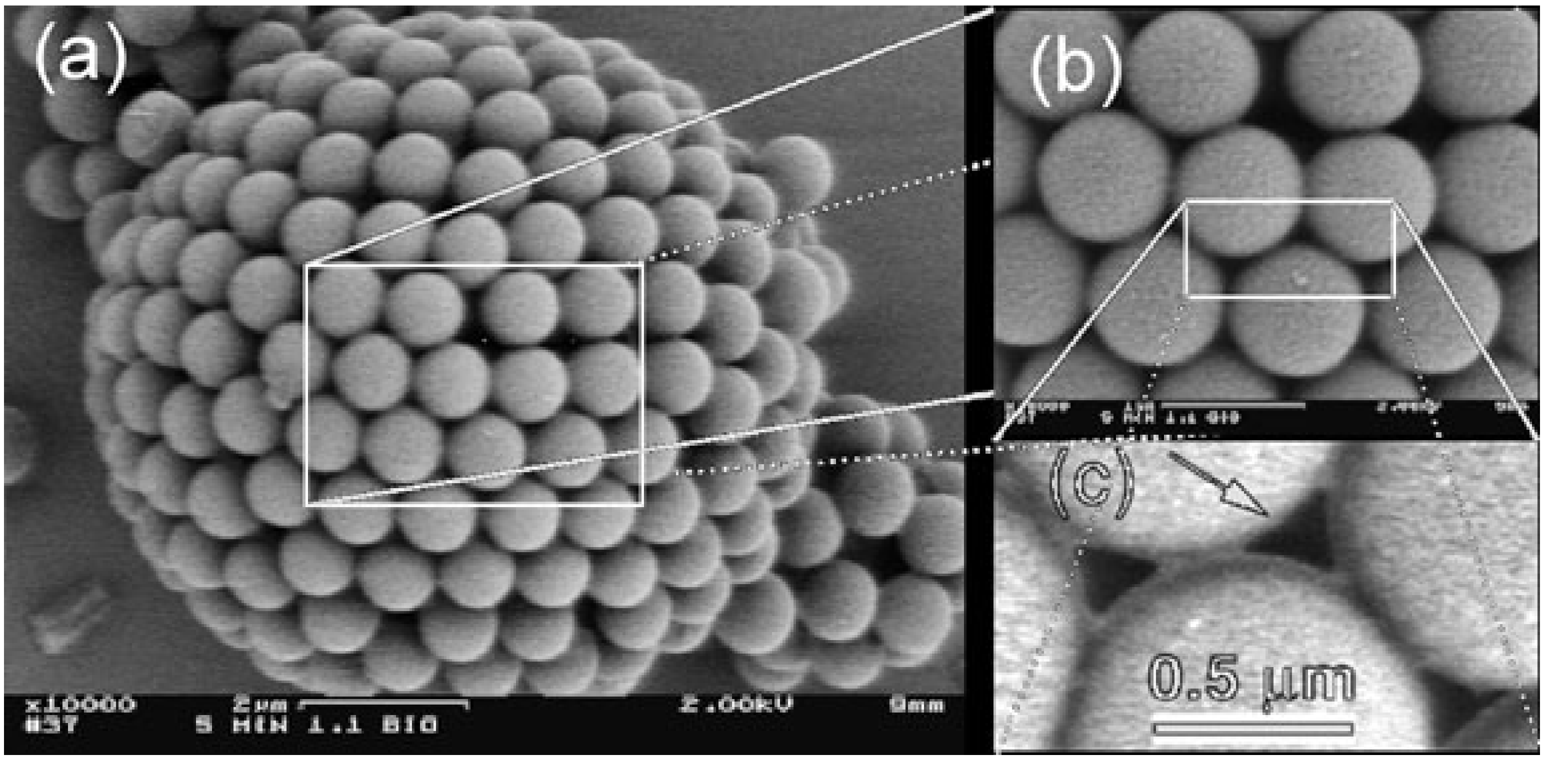
glass (500 nm) and blue PE (20 µm) particles

PS (1 µm) and clay mineral (~1 µm) particles

Arrested shells : Small particles:

Experiments at NTNU Trondheim

Colloidosomes



A.D. Dinsmore et. Al., Science, **298**, 1006 (2002)

Pickering (1907) : Emulsions

Dinsmore et al. Science (2002): ”Colloidosomes”

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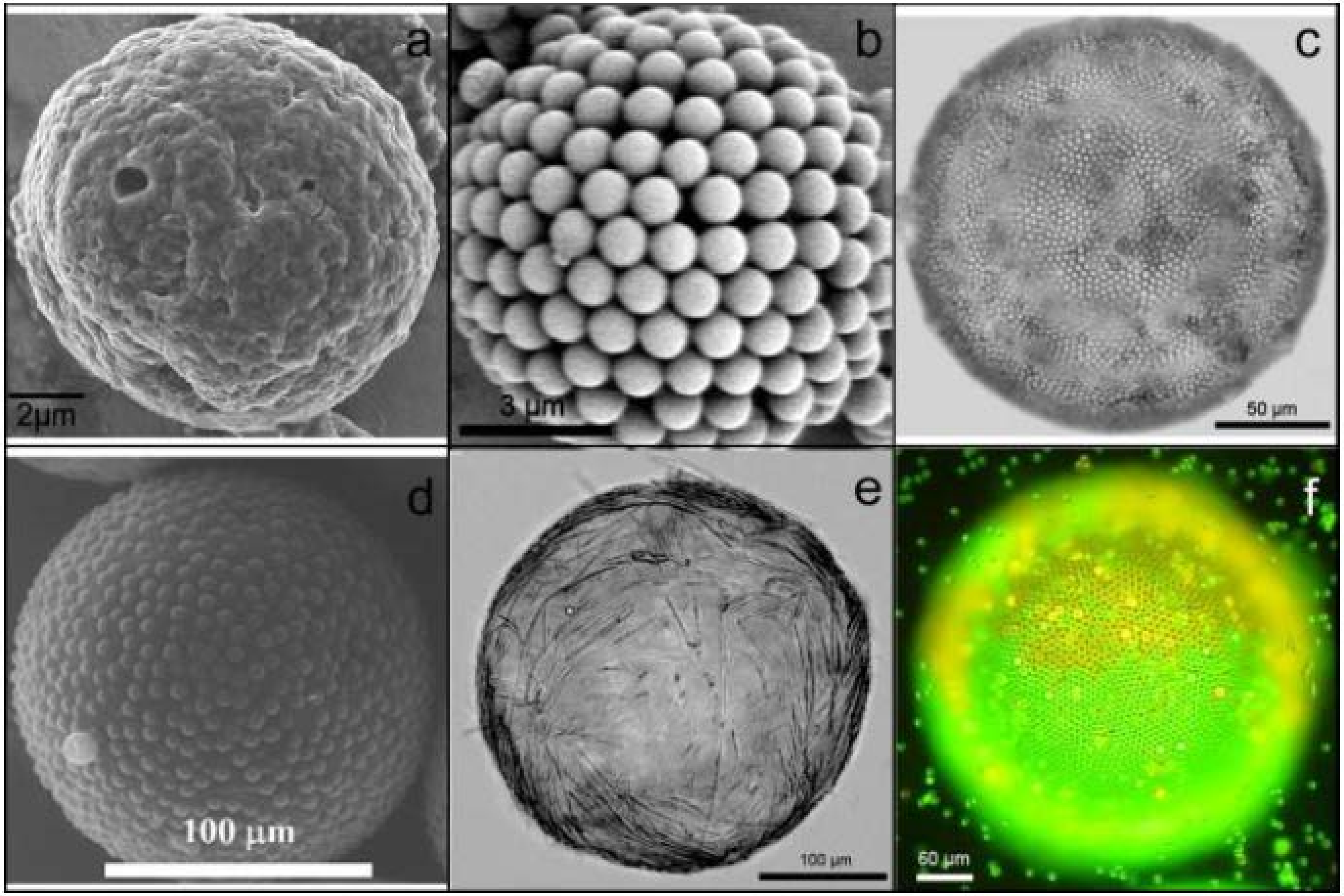

Dinsmore et.al.

Colloidal clay shells: Example

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Soft Matter

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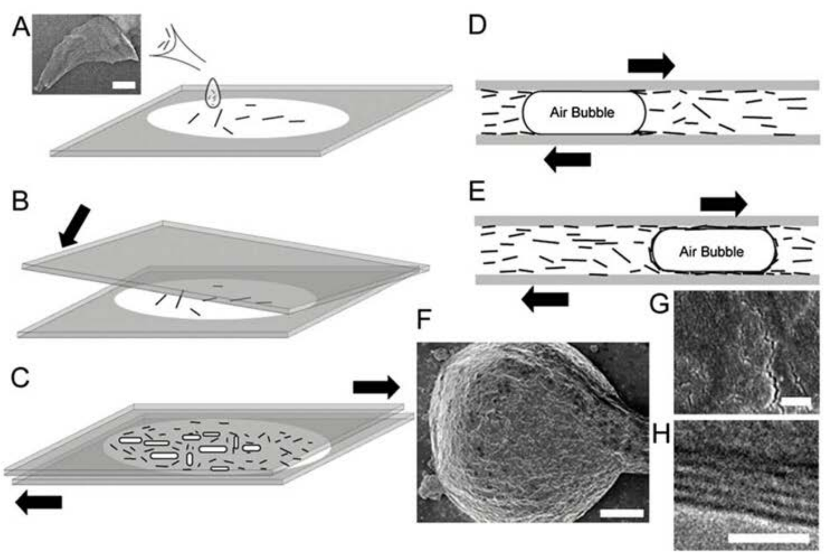
PAPER

Semi-permeable vesicles composed of natural clay†

Anand Bala Subramaniam,[*a] Jiandi Wan,[b] Arvind Gopinath[c] and Howard A. Stone[*b]

Received 21st November 2010, Accepted 3rd January 2011

DOI: 10.1039/c0sm01354d



Journal of Dispersion Science and Technology, 31:632–640, 2010

ISSN: 0193-2691 print/1532-2351 online
DOI: 10.1080/01932690903218062

Rheological Properties of Particle-Stabilized Emulsions

Sébastien Simon, Stefan Theiler, Agnethe Knudsen, Gisle Øye, and Johan Sjöblom

Ugelstad Laboratory, Department of Chemical Engineering, The Norwegian University of Science and Technology (NTNU), Trondheim, Norway

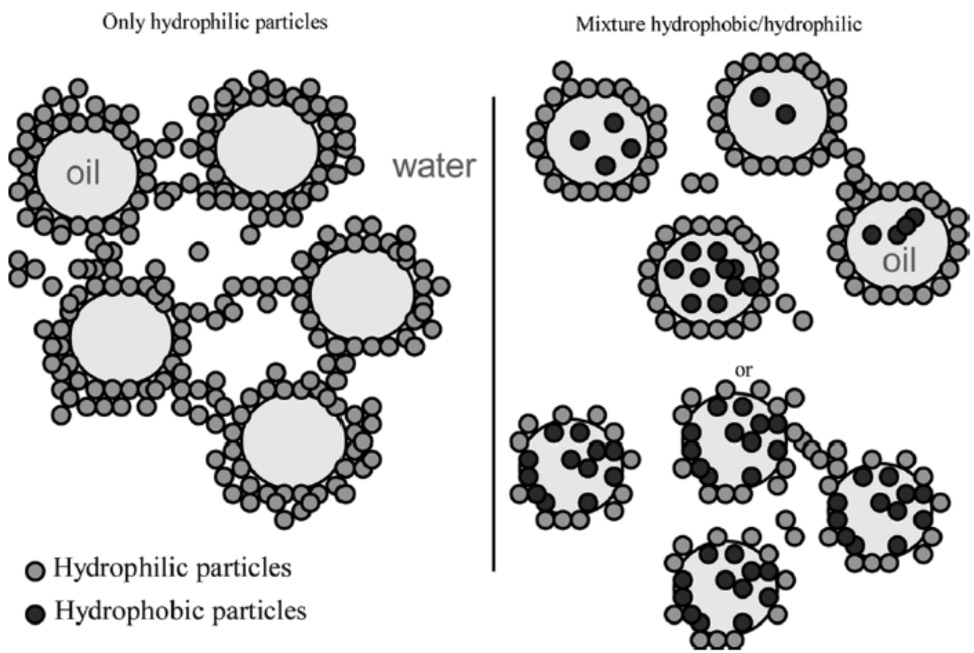


FIG. 12. Sketch of structure of o/w emulsions stabilized by only hydrophilic particles (left) and mixtures of hydrophilic and hydrophobic particles (right).

The infinite road:

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Permanent and safe storage of nuclear waste

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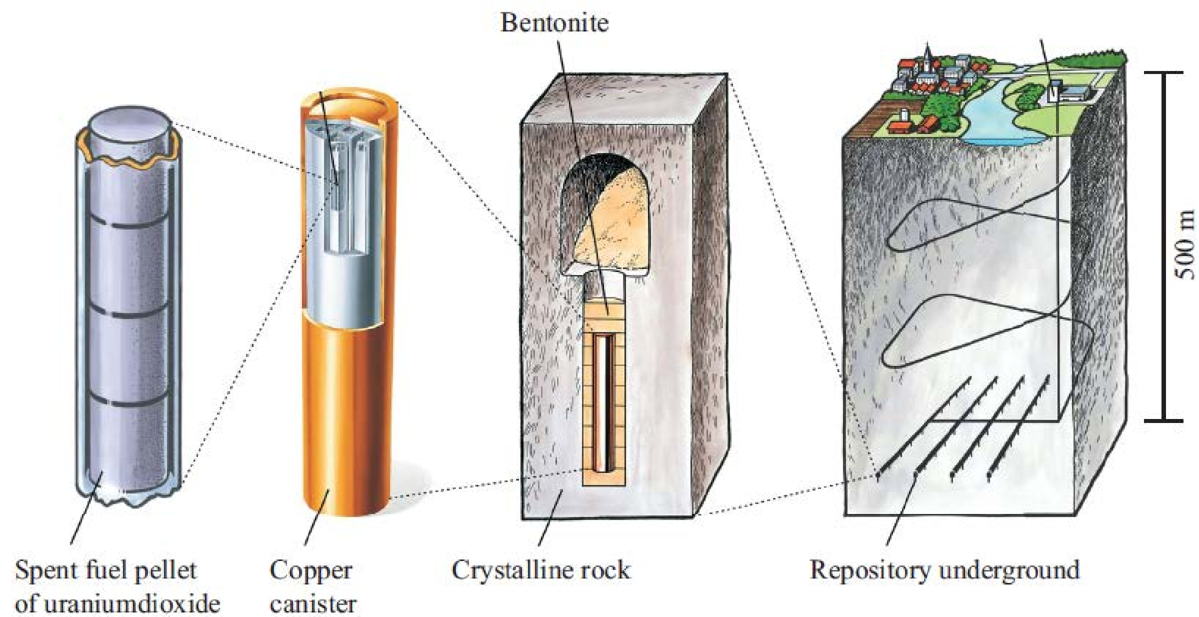
The Bentonite Barrier

Swelling properties, redox chemistry and mineral evolution

P. Daniel Svensson

LUND UNIVERSITY



DOCTORAL DISSERTATION
by due permission of the Faculty of Engineering, Lund University, Sweden.

To be defended in public at the Center for Chemistry and Chemical Engineering, Lecture Hall K:C, on March 9, 2015, at 13:15.

Faculty opponent

Prof. Jon Otto Fossum, Norwegian University of Science and Technology

Synthetic clays?

NTNU

Permanent plugging for safe abandonment of terminated oil & gas wells

IRIS (International Research Institute of Stavanger):

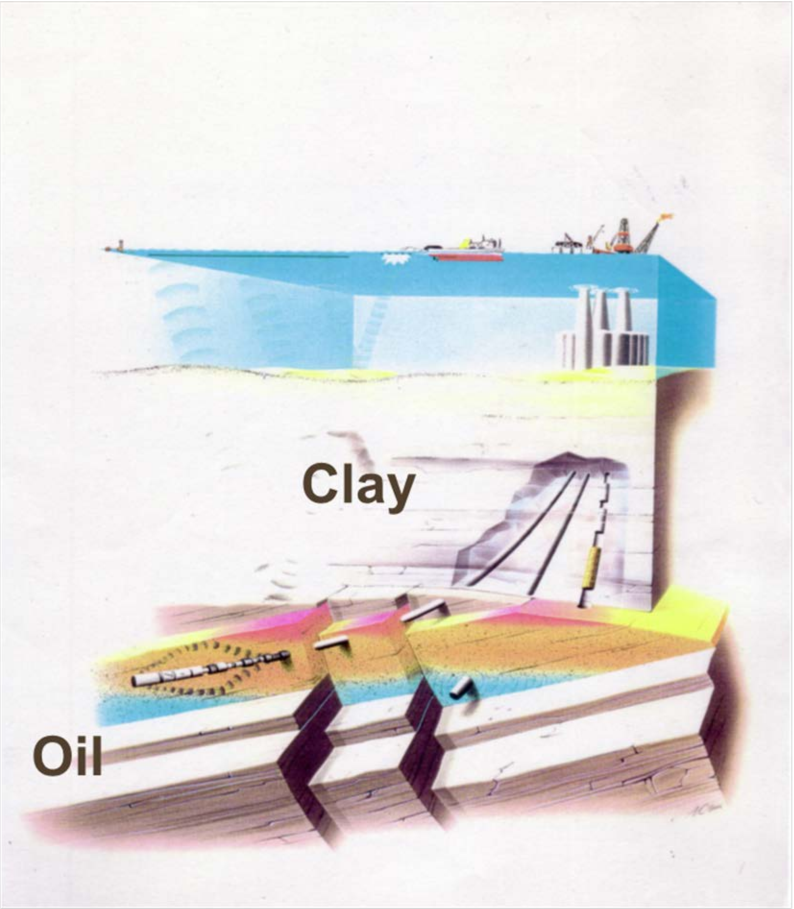
The average time for a P&A operationis 35 days

For Statoil only, the company has planned to permanently abandon approximately 1200 wells in the next 40 years

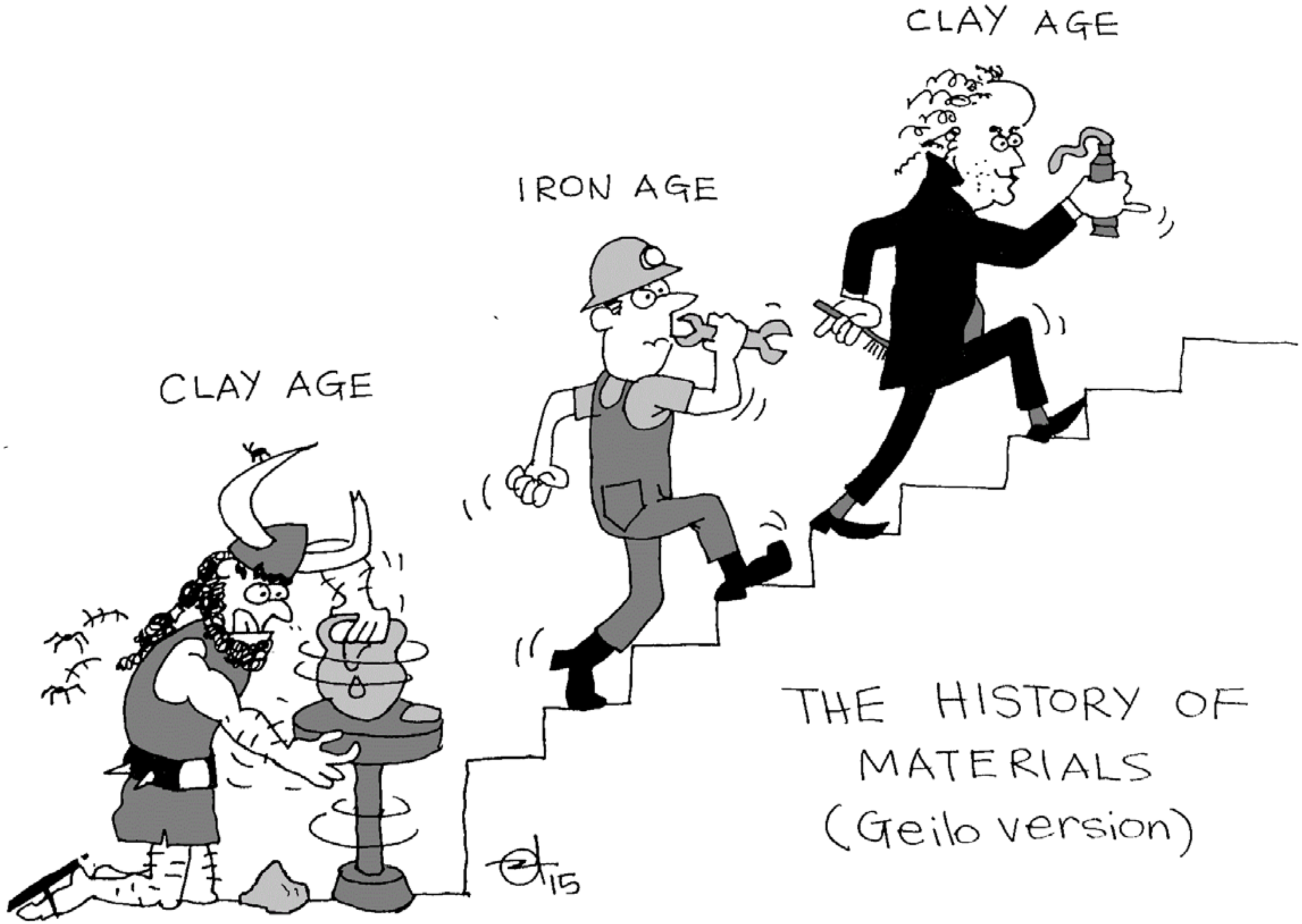
On the UK sector, a total number of 4600 wells are to be PP&Aed over the next 15 years.

Due to these large numbers, there is great interest in trying out new technologies and methods for P&A that can reduce the time and/or equipment costs.

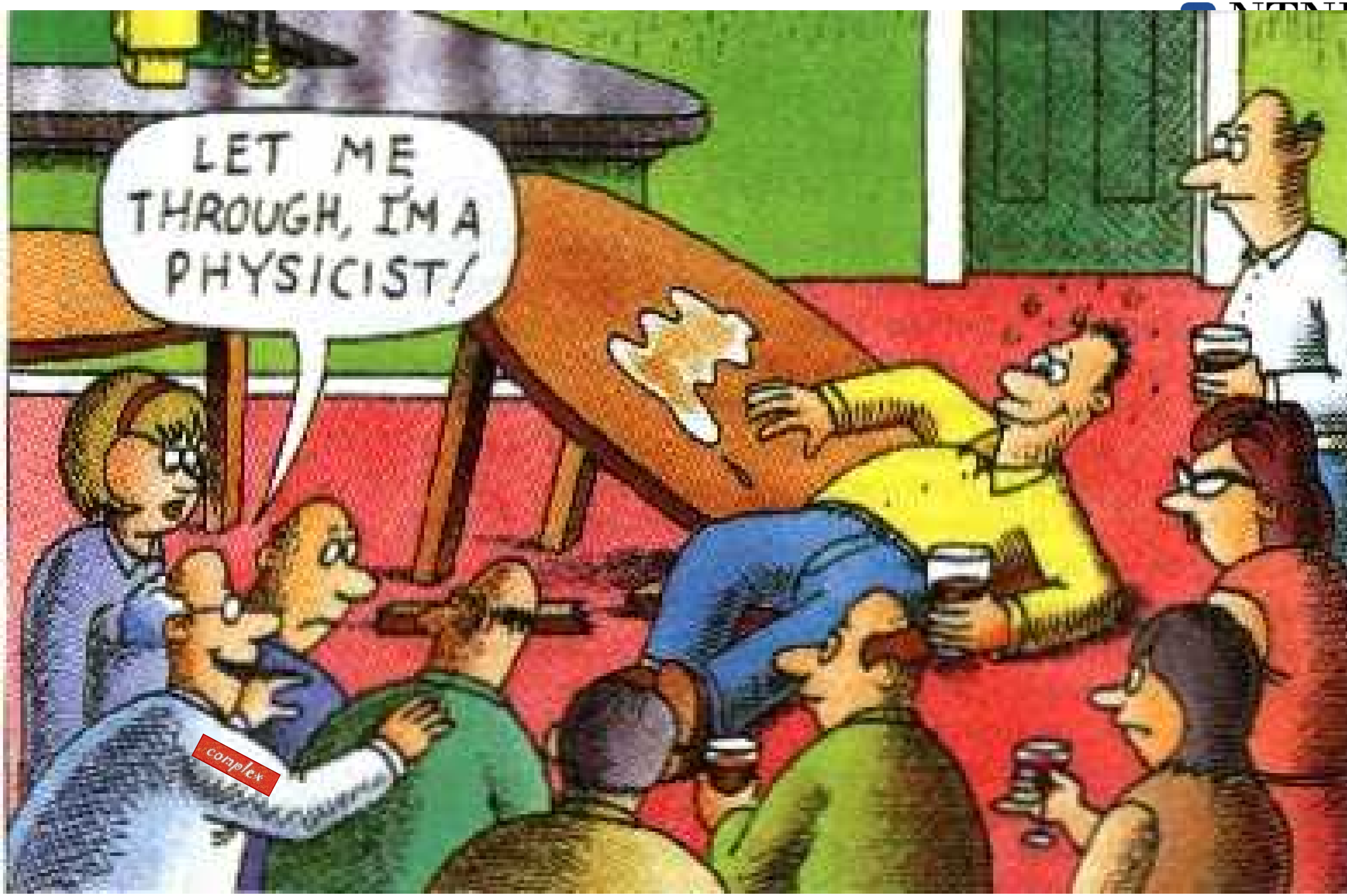
For the Norwegian continental shelf estimates suggest that with present day technology this may cost around **360 Billion NOK ≈ 30 Billion EUR.**

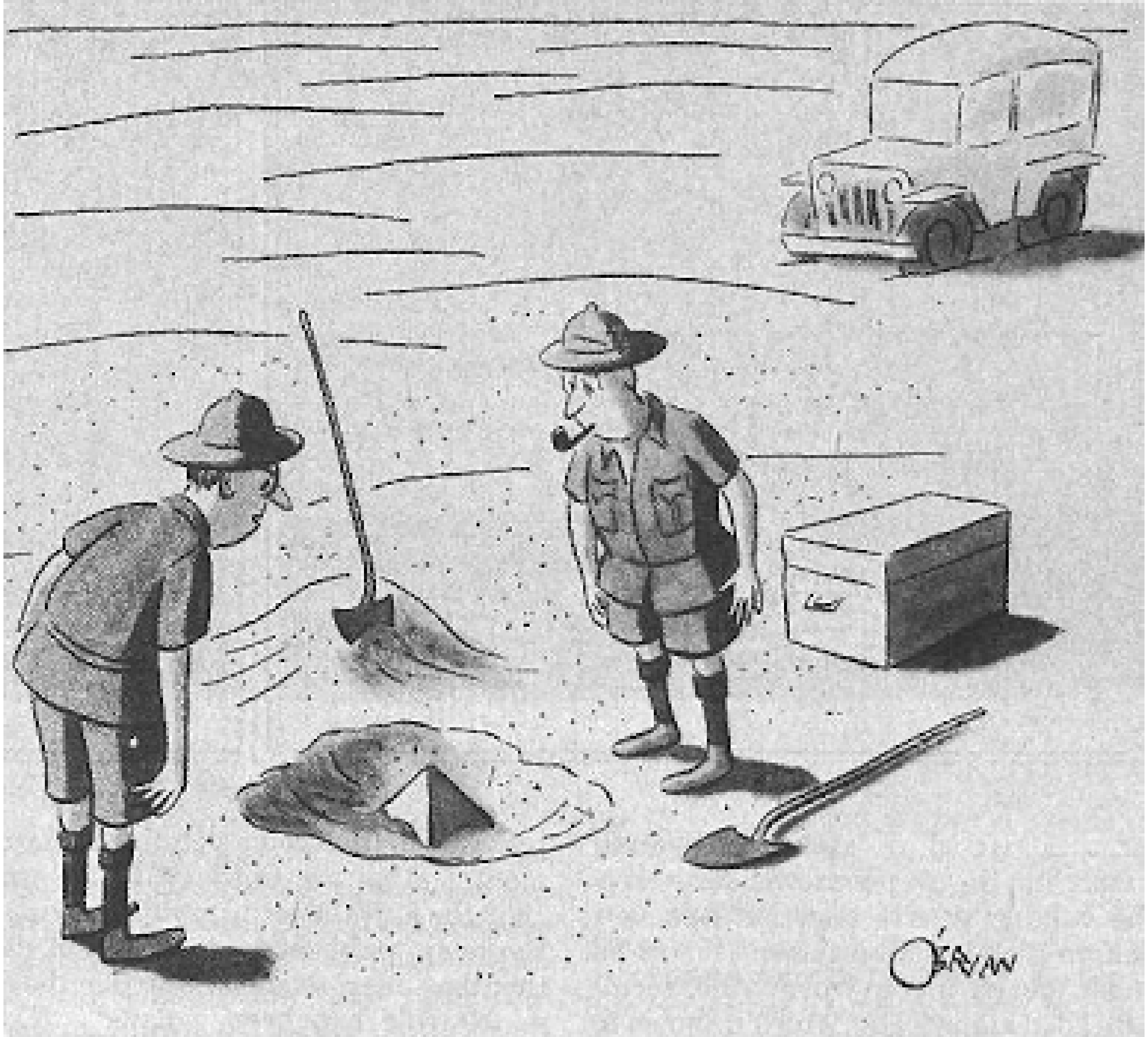


Key technological challenges: Design of material strength, cementation, adhesion properties and integration with other materials.



Drawn by Ernesto Altshuler


LET ME THROUGH, I'M A PHYSICIST!
complex



"This could be the discovery of the century. Depending, of course, on how far down it goes."

Thank you for your attention!

Clay baths will prolong your life: