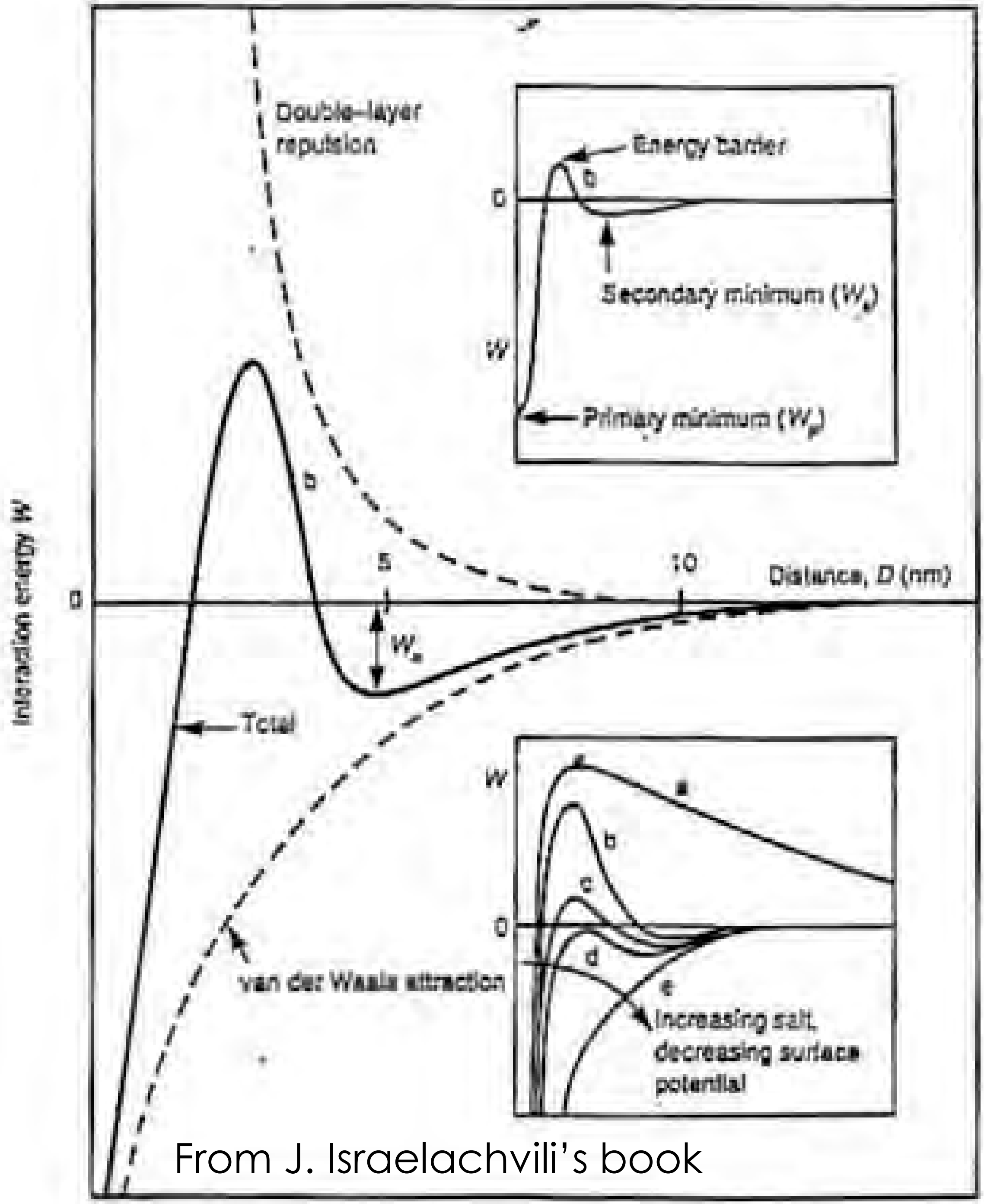
DLVO Theory:
vdW
+ Screened Electrostatic Rep.



From J. Israelachvili's book

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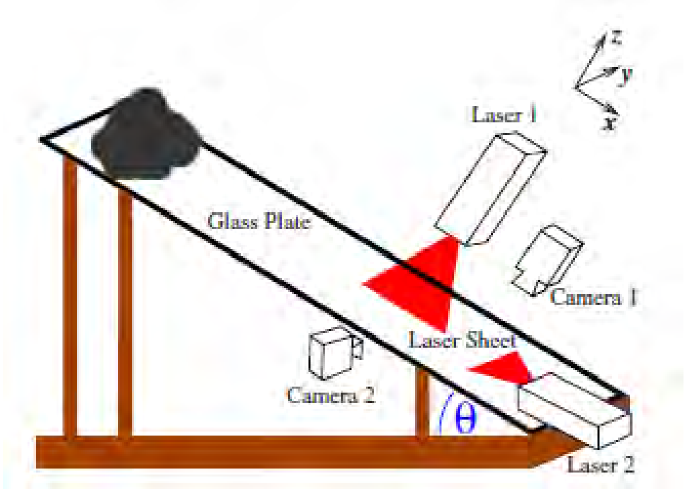
Norwegian University of
Science and Technology

TOOLS

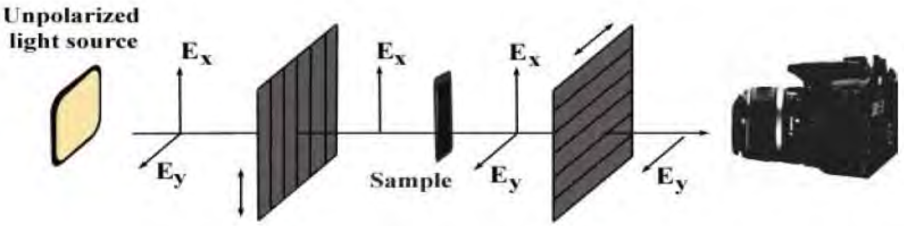
Macroscopic tools:

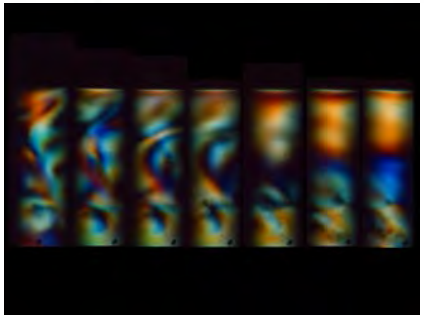
Tilted plane experiments on clays:



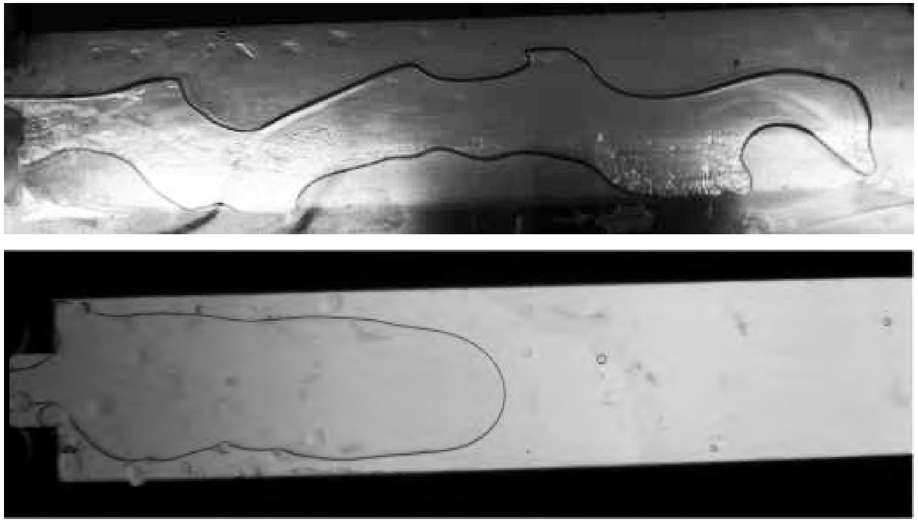
Rheometry:

Birefingence studies of clay nematics:

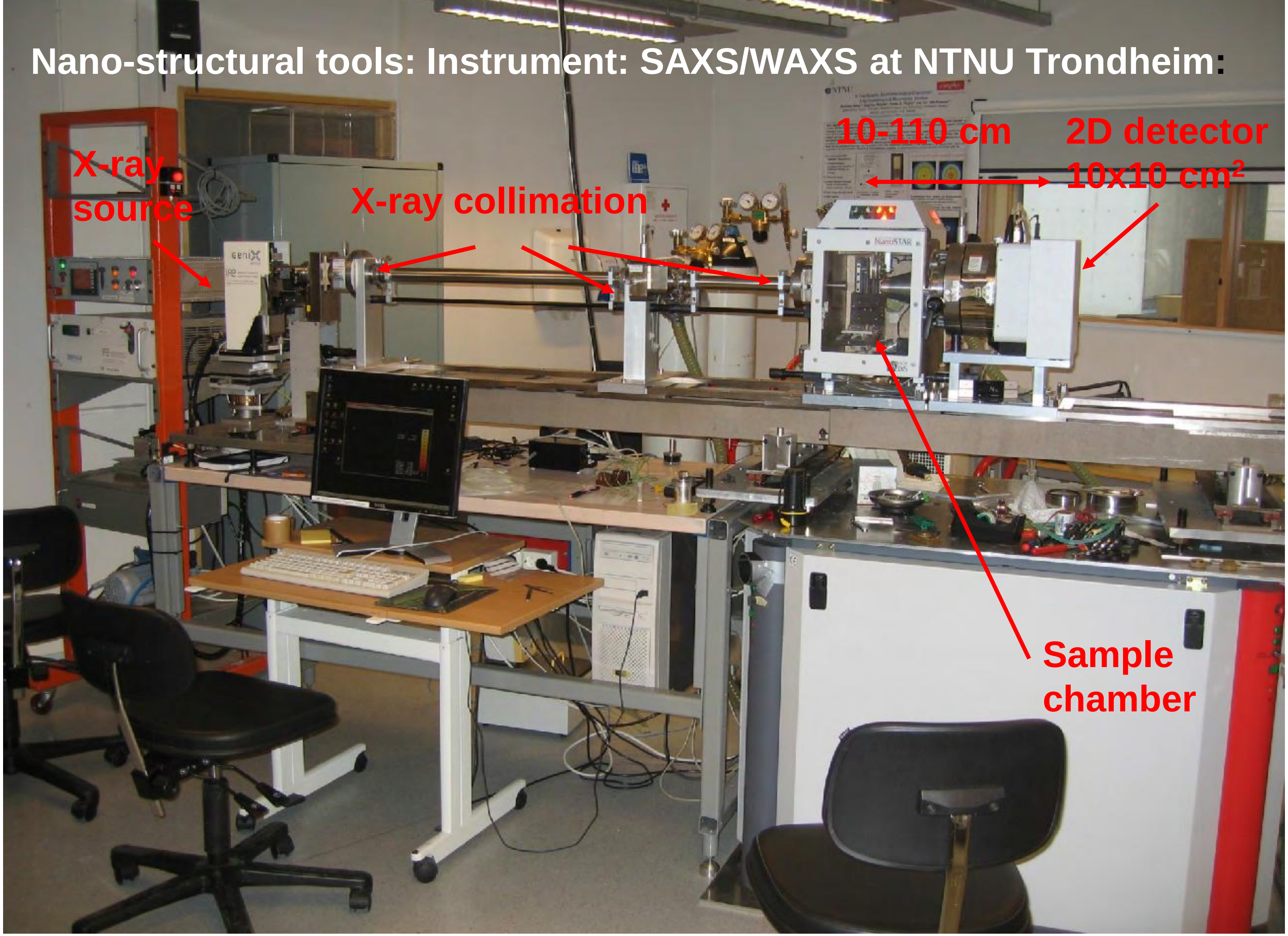




Observations of fingering and fracturing in clay gels:



Nano-structural tools: Instrument: SAXS/WAXS at NTNU Trondheim:



Nano-structural tools: X-ray synchrotrons facilities/neutron facilities:

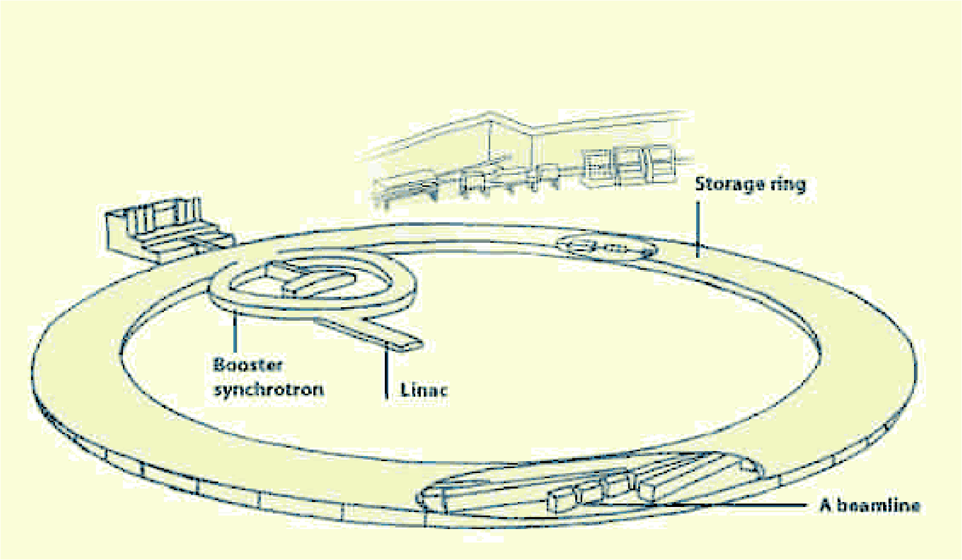
ESRF – Grenoble, France
Maxlab – Lund, Sweden
LNLS – Campinas, Brasil
PLS – Pohang, S-Korea
(In the past: BNL; APS – USA)
+++++++++++

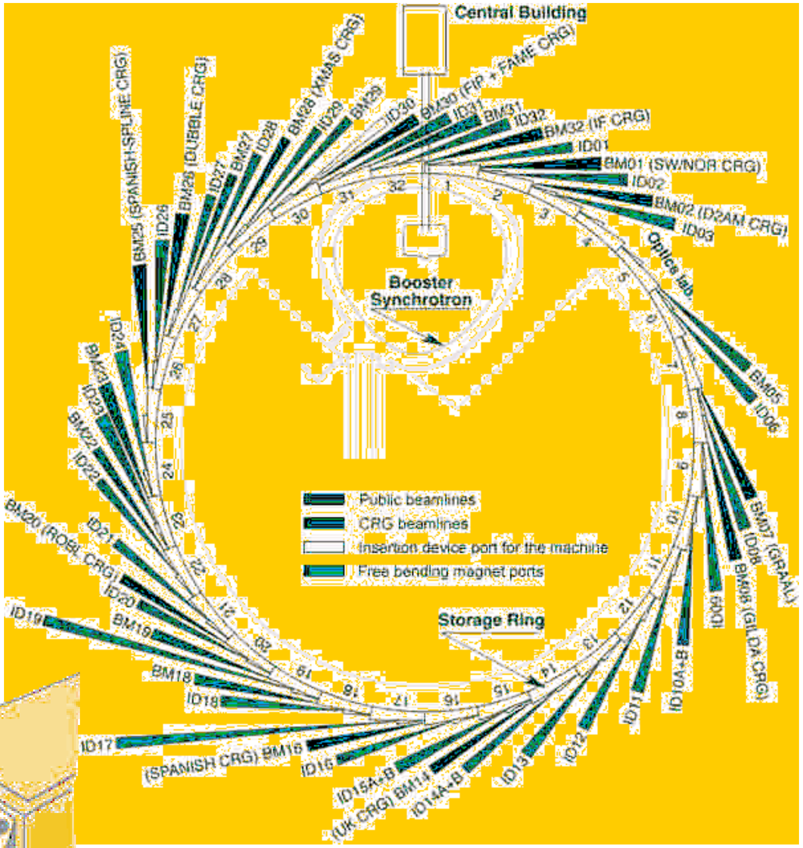
Neutron scattering at IFE – Kjeller, Norway

Jeep II reactor:

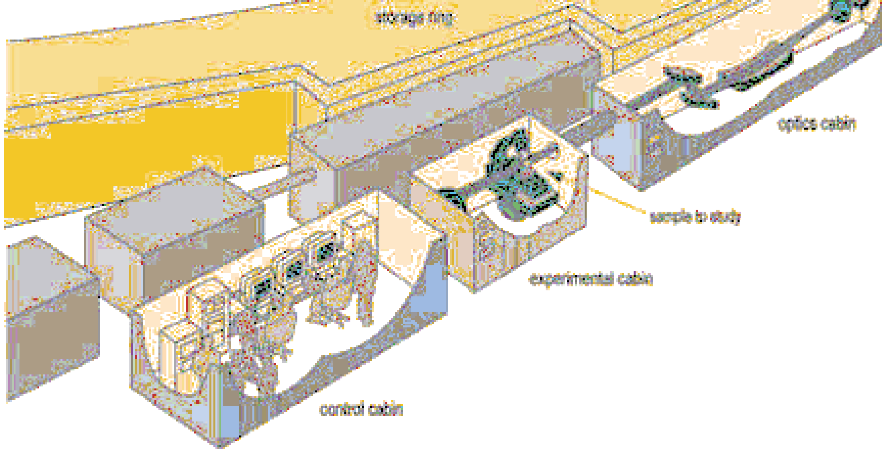
SANS at IFE:

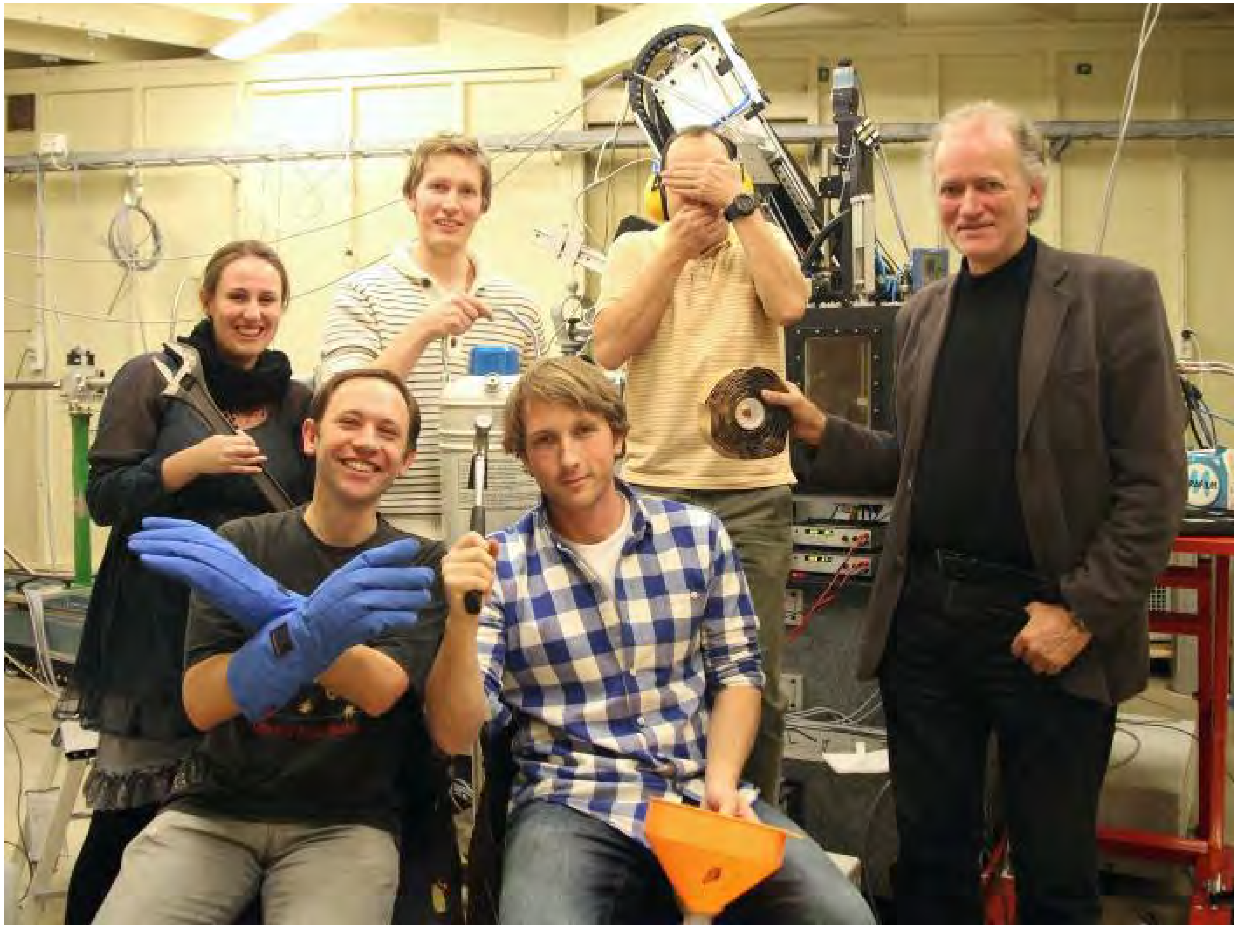
X-ray synchrotron sources:





Beamline:





Elisabeth Erlend Davi

Tomás Henrik Jon Otto

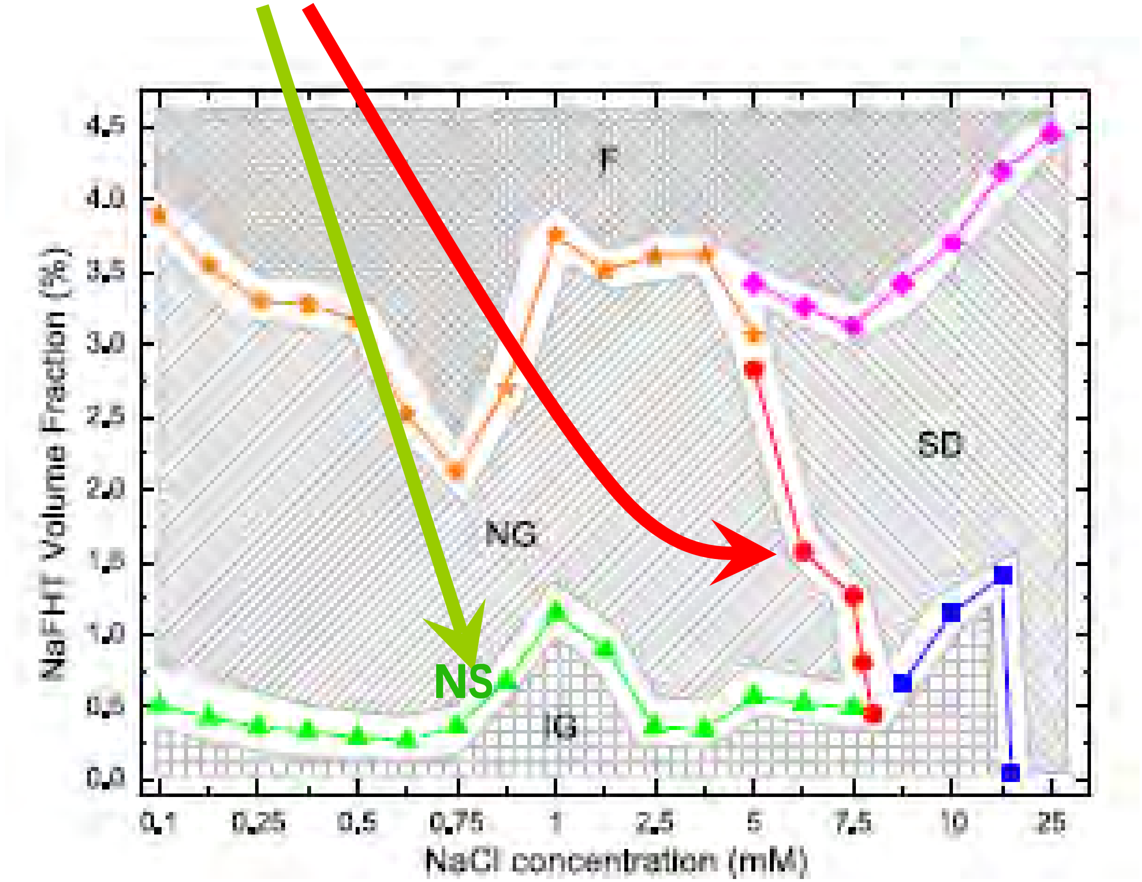
Karin

Leander

Zbigniew

From SAXS experiments at ESRF: ”True phase diagram”:

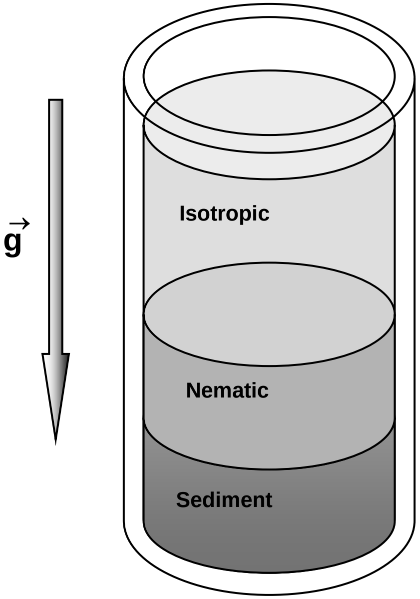
Transitions of interest



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

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)**

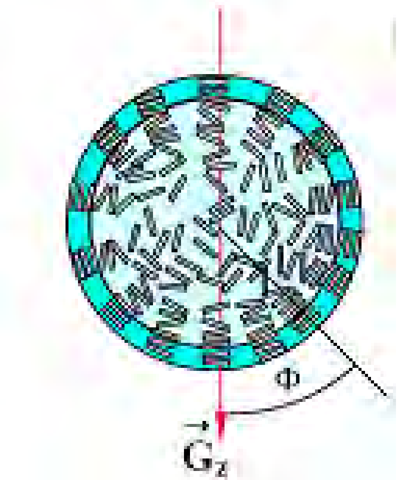
Response to magnetic field: Magnetic field guided self-organization:



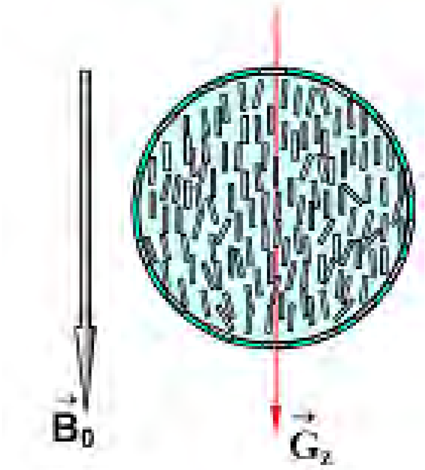
Glass wall anchoring confirmed by spatially resolved MR measurements of anisotropic self-diffusion coefficient of water in the nematic phase.

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

$S_2 \sim -0.3$



$S_2 \sim +0,5$



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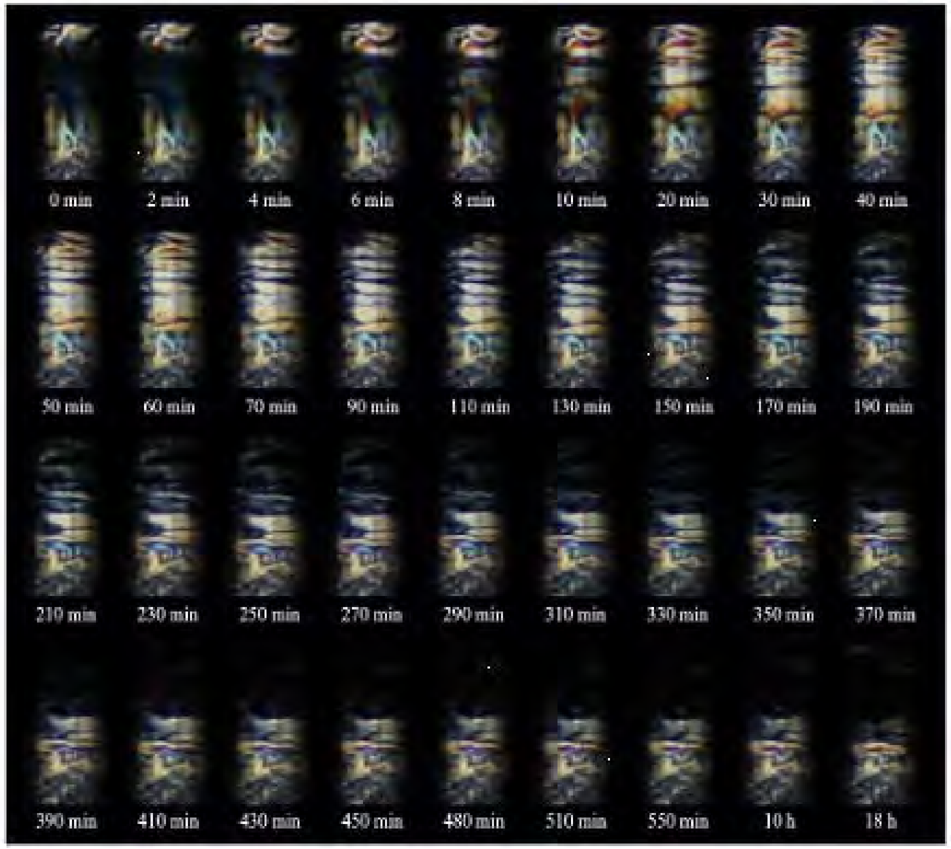
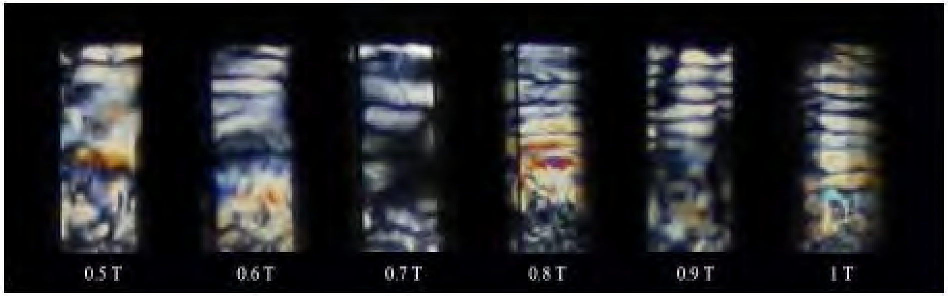
Science and Technology

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)**

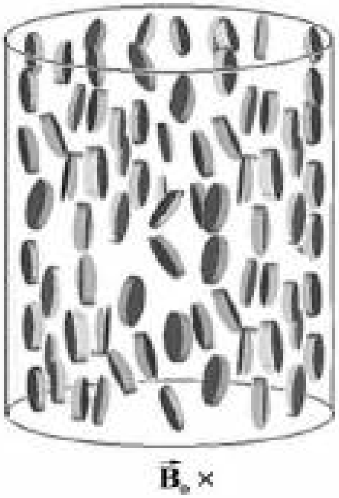
Freedericksz configuration in nematic liquid crystals:

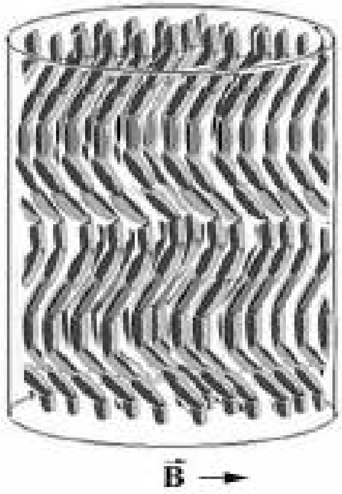
Transient competiton between wall anchoring and magnetic field alignment

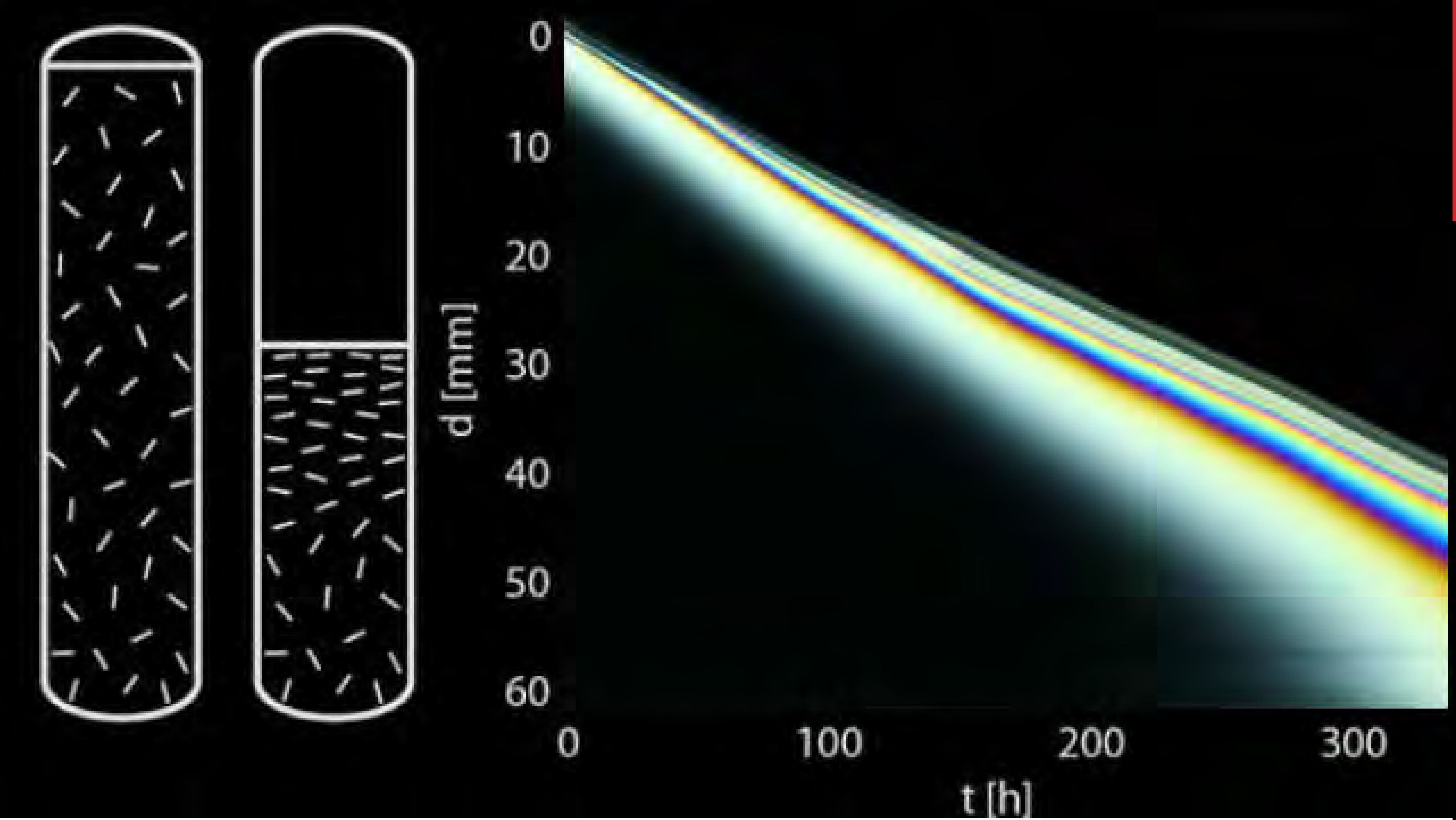




The Frederiks transition in an aqueous clay dispersion,
H. Hemmen, E.L. Hansen, N.I. Ringdal and J.O. Fossum,
Revista Cubana de Fisica, vol. 29-1E, 59-61 (2012)







Orientational order in a glass of charged platelets with a concentration gradient, Elisabeth Lindbo Hansen, Sara Jabbari-Farouji, Henrik Mauroy, Tomás S. Plivelic, Daniel Bonn and Jon Otto Fossum, ***Soft Matter*, 9, 9999-10004 (2013)**

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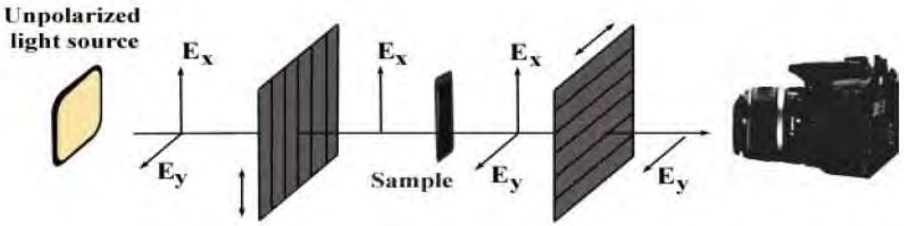
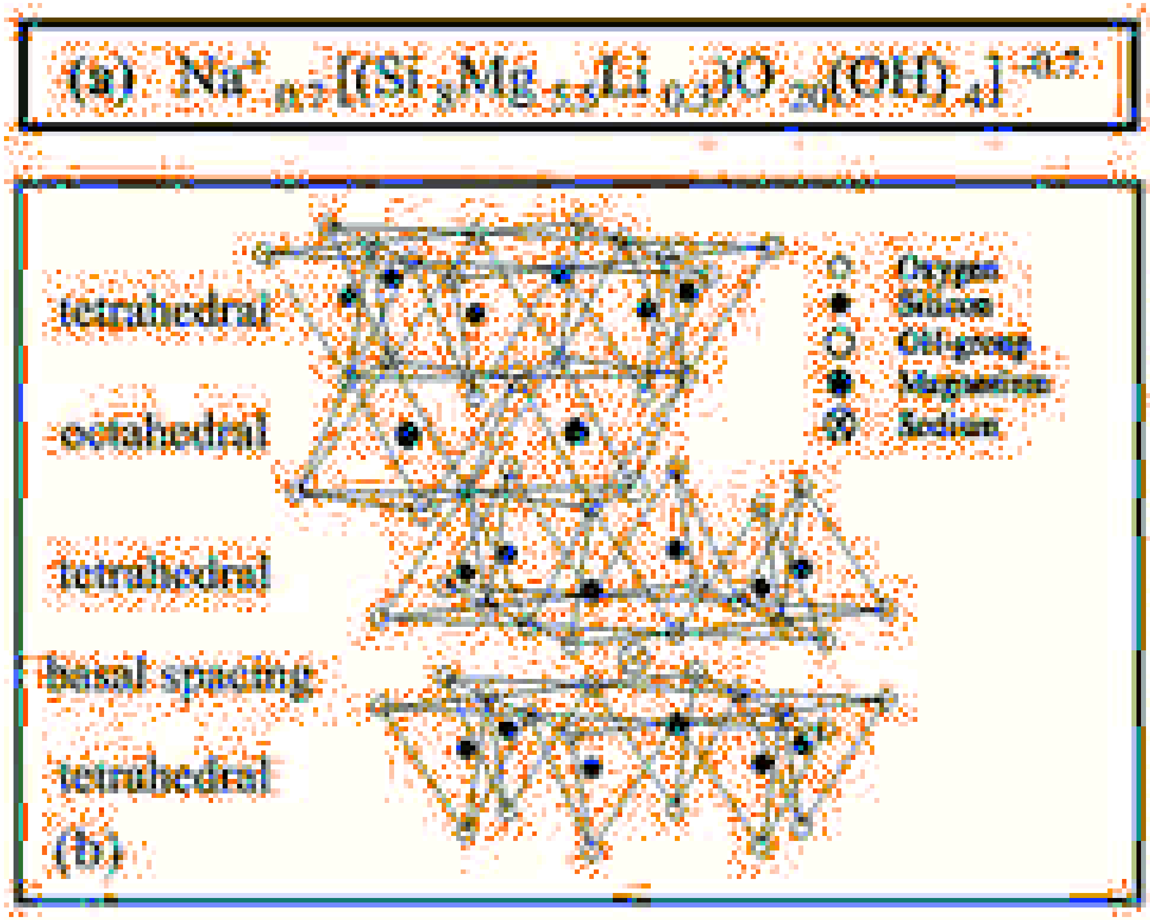
Norwegian University of
Science and Technology



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]

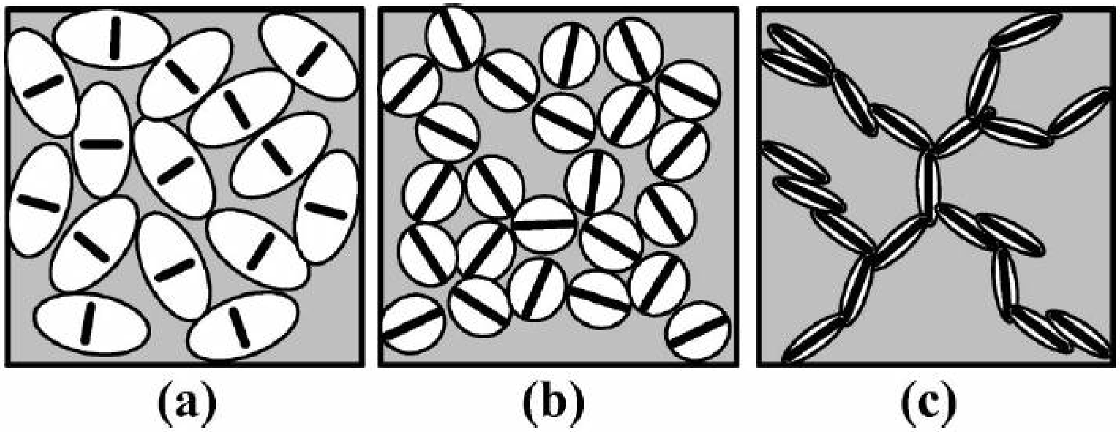
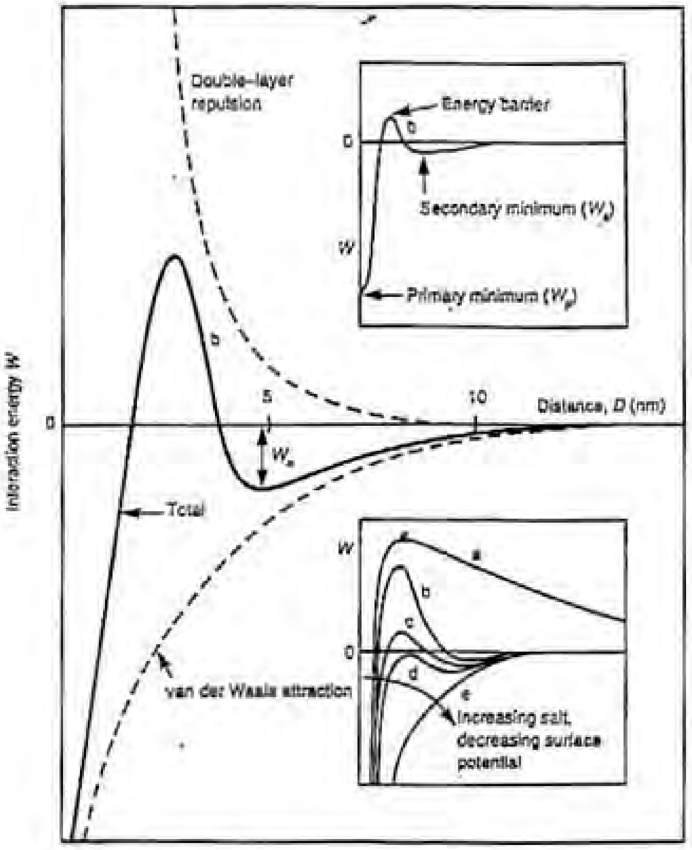


FIG. 1.
Schematic figures representing repulsive ‘‘Wigner’’ colloidal glass (a), attractive glass (b), and gel (c). Each thick line represents a Laponite disk, while a white ellipsoid represents the range of electrostatic repulsions: (a), long-range electrostatic repulsions dominate. (b), attractive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

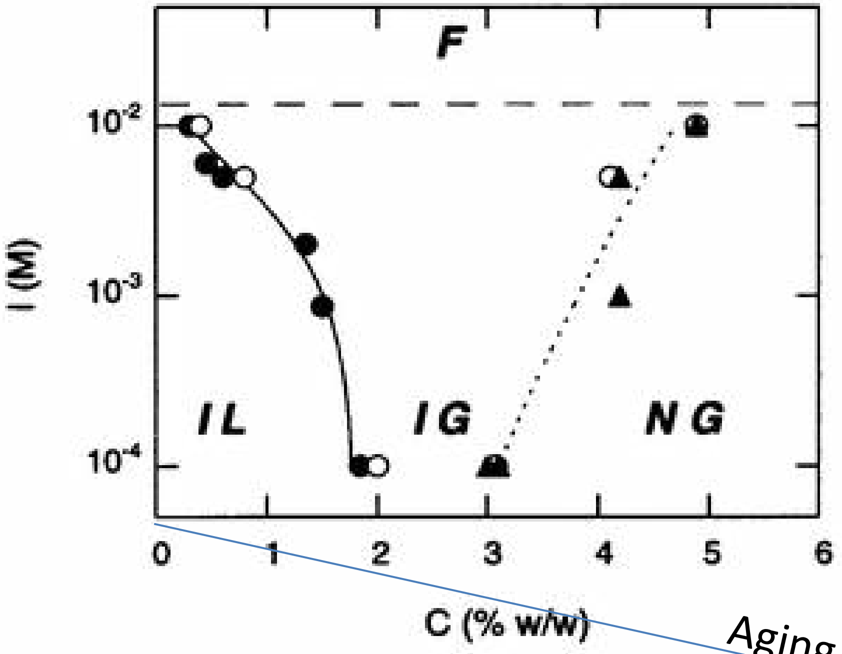
DLVO Theory:
vdW + Screened Electrostatic Rep.

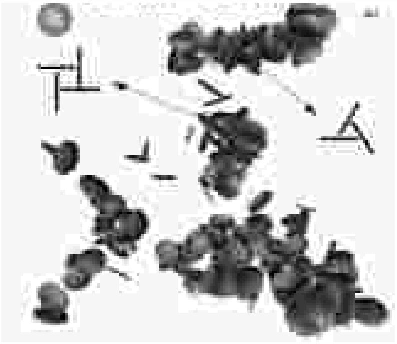


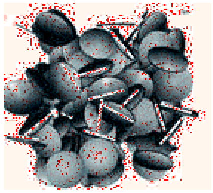
Langmuir **1998,** *14,* 4718–4723

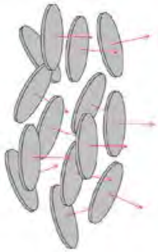
On Viscoelastic, Birefringent, and Swelling Properties of Laponite Clay Suspensions: Revisited Phase Diagram

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

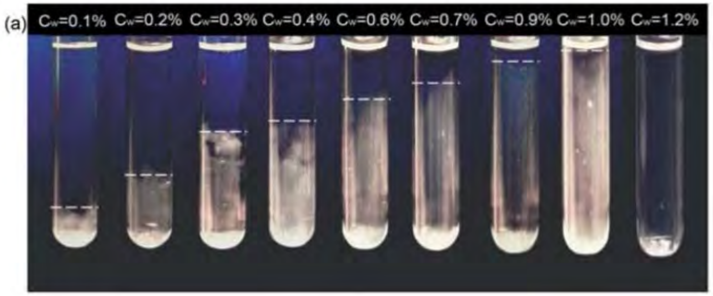








One sample for each point



Soft Matter

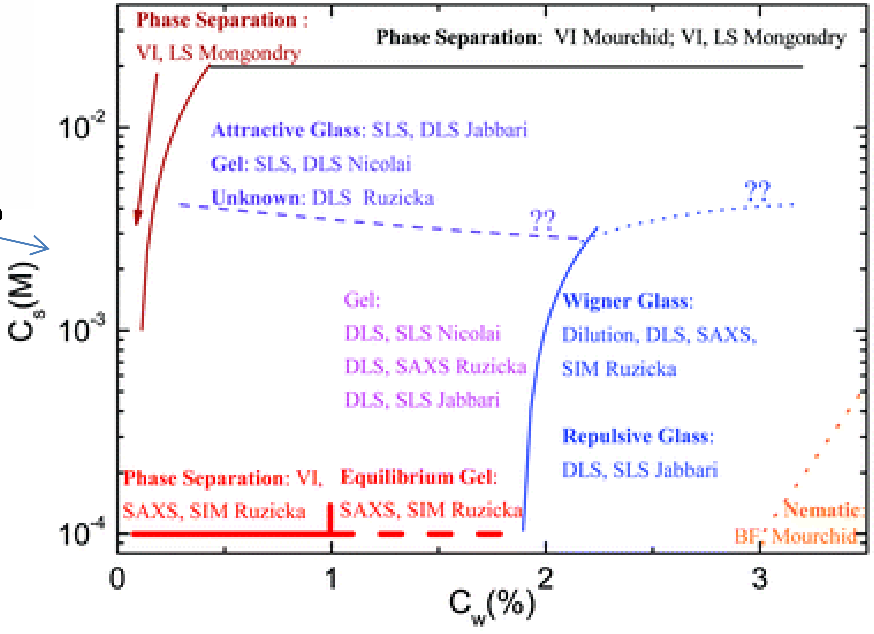
Cite this: *Soft Matter*, 2011, **7**, 1268

www.rsc.org/softmatter

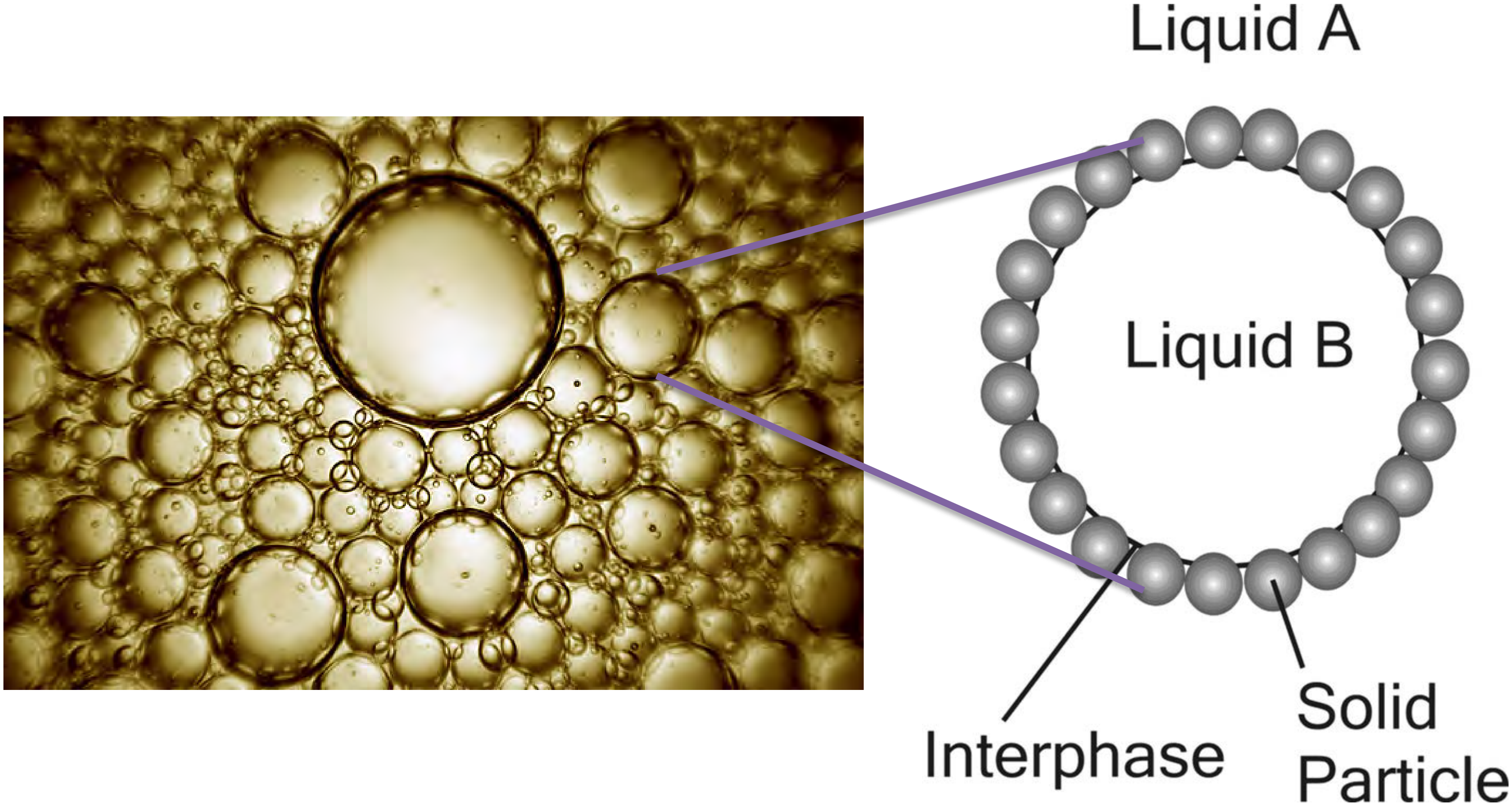
A fresh look at the Laponite phase diagram

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

Aging time



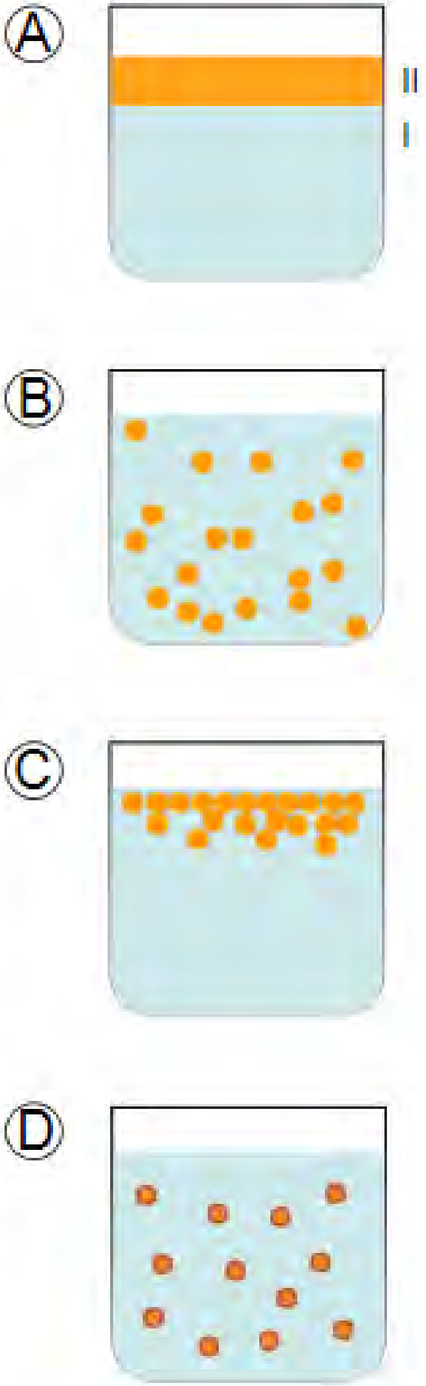
Clay particles as emulsion stabilizers: Pickering («physical») emulsions



Emulsions (= Systems of MANY drops) are important in many every day and industrial contexts such as:

- in **foods**,
- in the **paint, dyeing and tanning industries**,
- in the manufacture of **synthetic rubber and plastics**,
- in the preparation of **cosmetics** such as shampoos,
- in salves and **pharmaceutical products** for drug delivery,
- in the **petroleum industry** for certain drilling muds, for enhanced oil recovery, in oil refining and oil separation (de-emulsification) and oil&gas transport.

«Classical» («chemical») emulsions



Legend

- 🟦 Phase I
- 🟧 Phase II
- 🟪 Surfactant

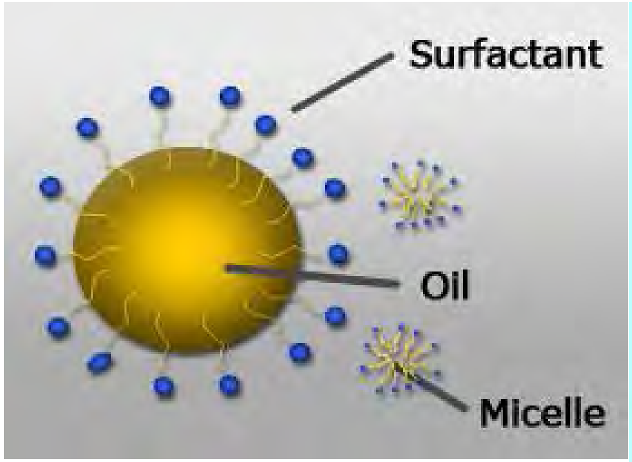
A. Two immiscible liquids, not emulsified

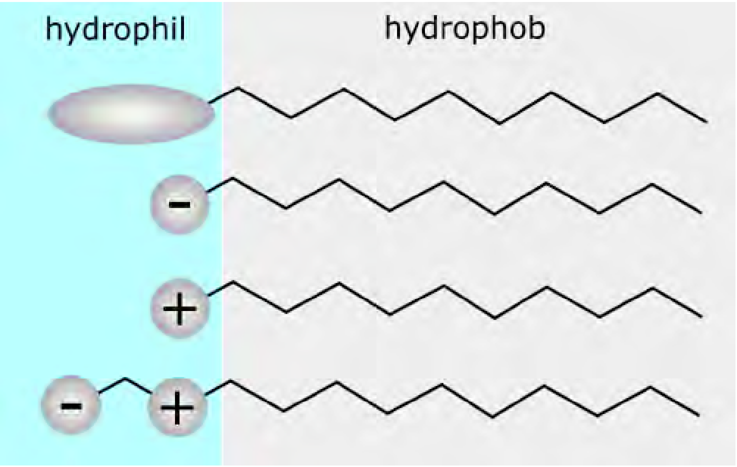
B. Emulsion of Phase II dispersed in Phase I

C. The unstable emulsion progressively separates

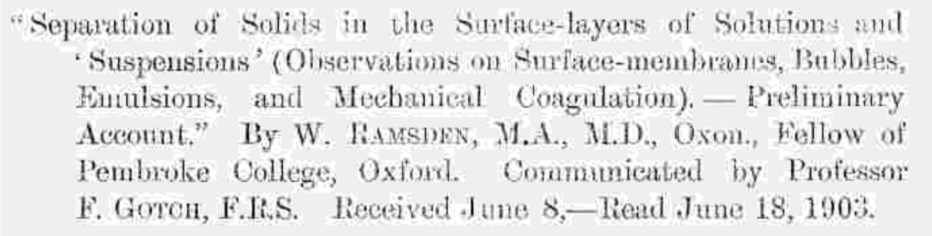
D. Surfactant positions itself on interface between Phases I and II, stabilizing emulsion

$E_{bind} > \sim k_B T$



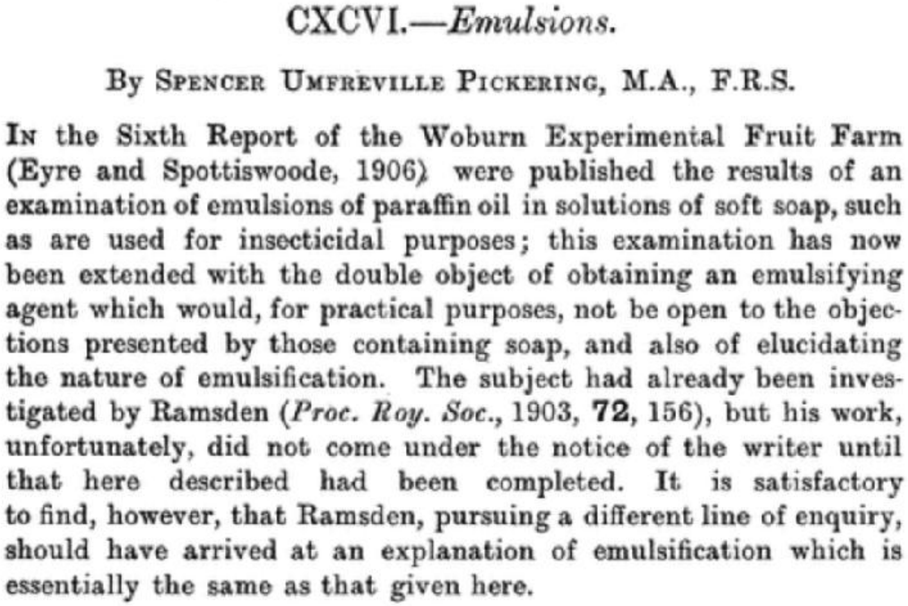


«Classical» («chemical») emulsions



"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



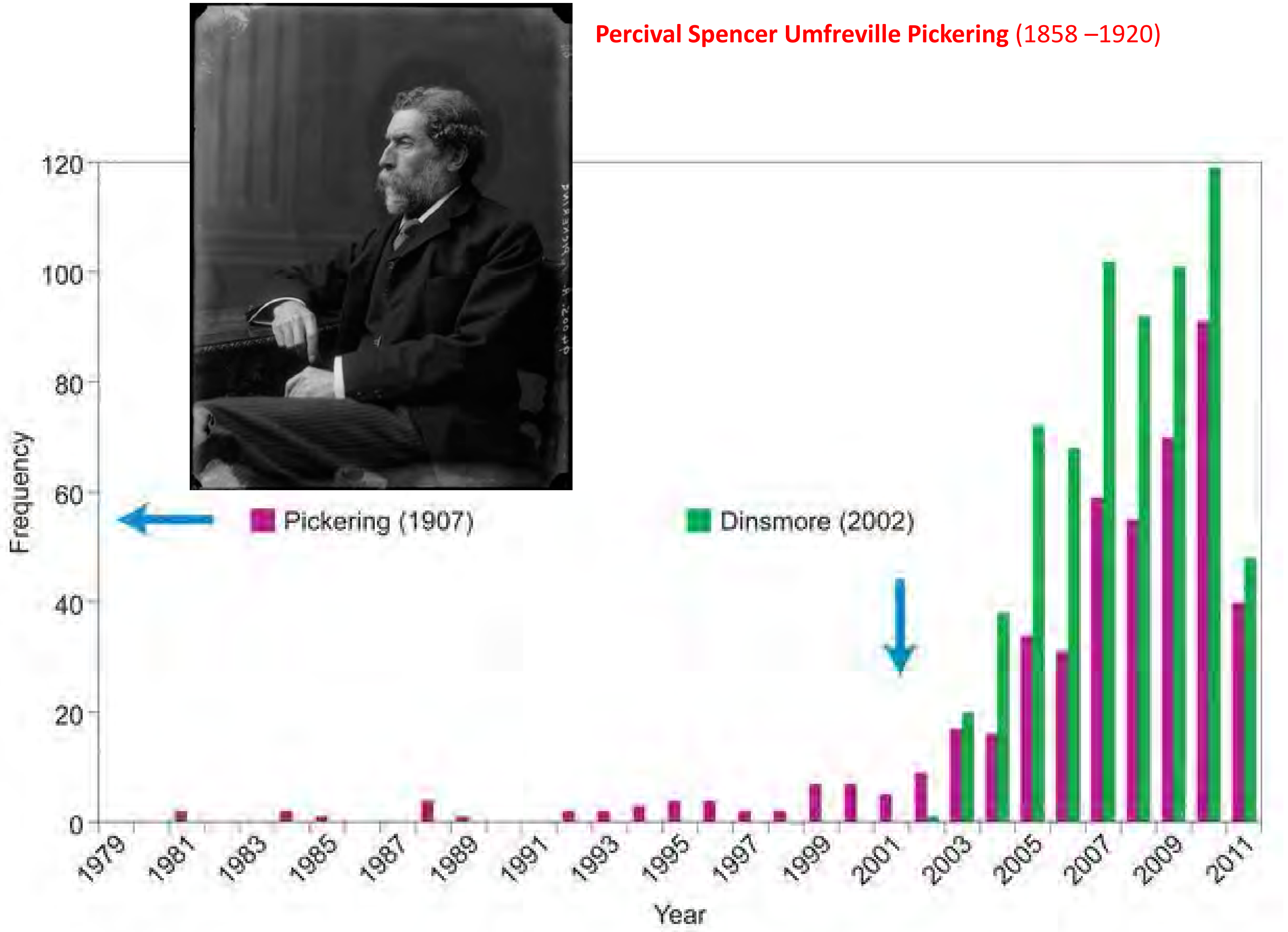
CXCVI.—*Emulsions.*

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)

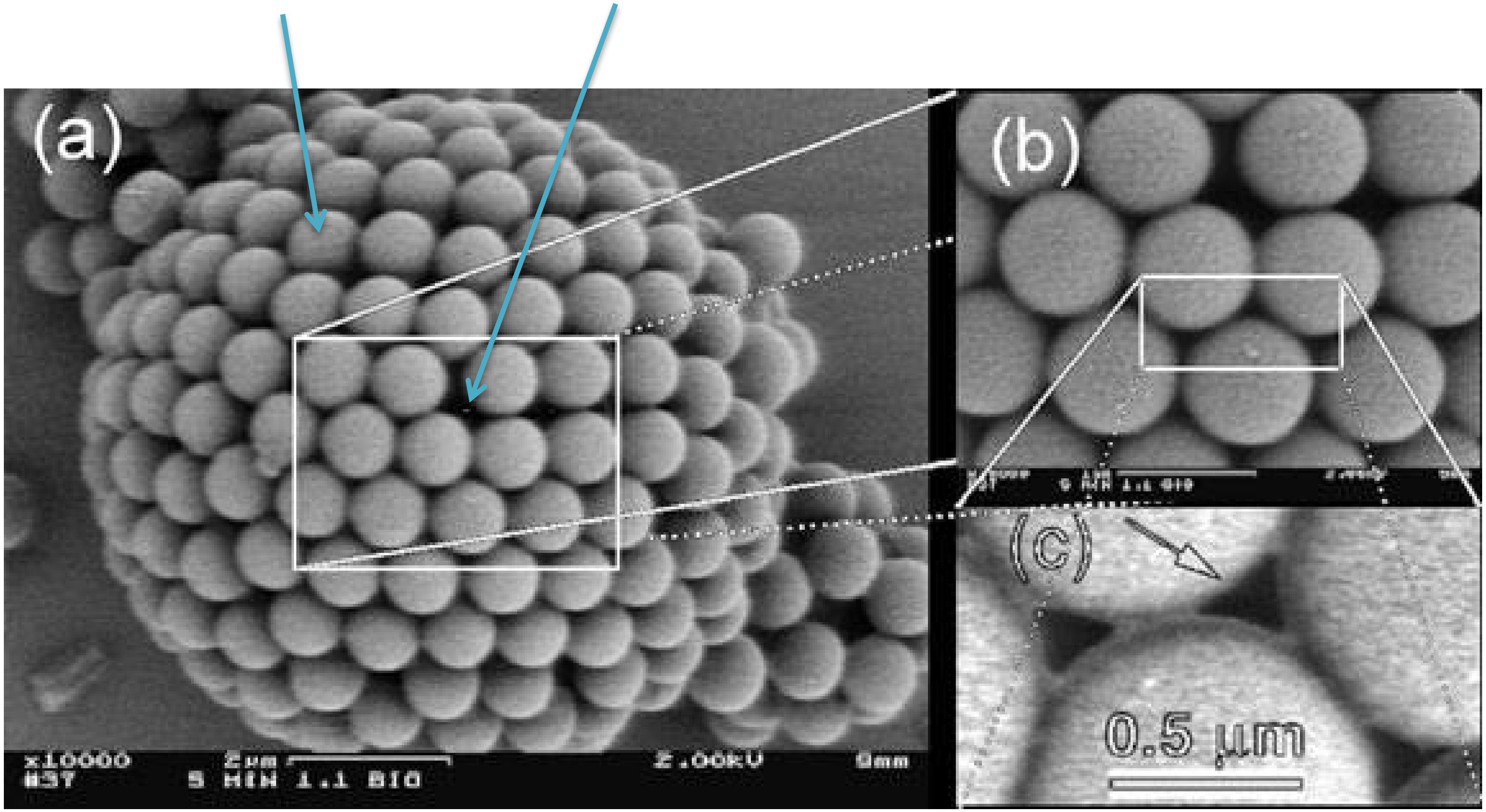
Percival Spencer Umfreville Pickering (1858 –1920)



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

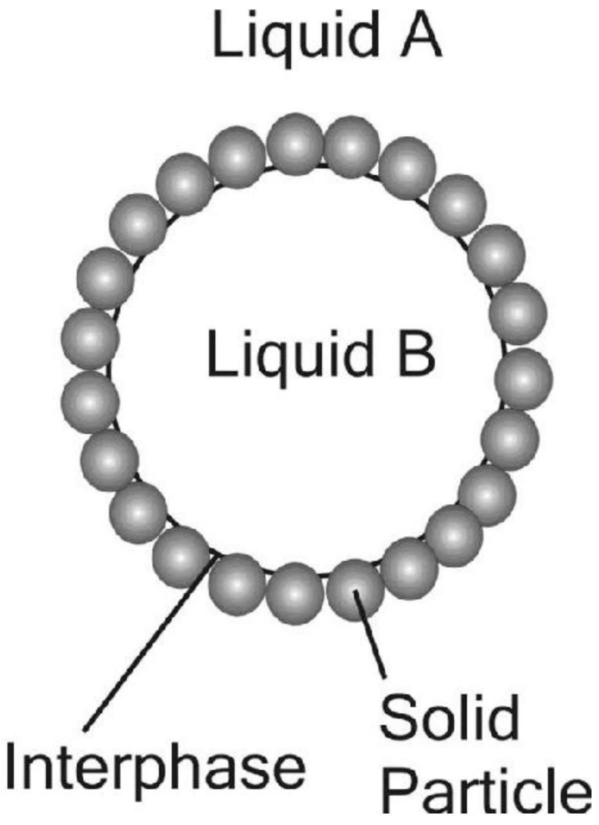
Colloidosomes

Composition and permeability



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

Capillary binding



Surface Energy: $E = \gamma A$

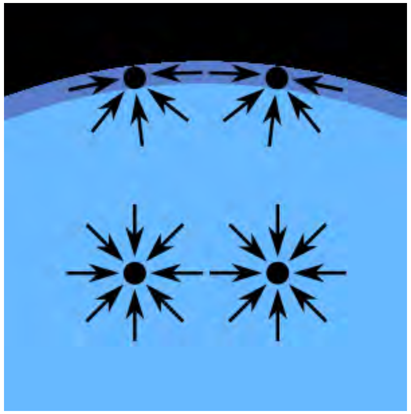
$A = \text{Surface area}$ $\gamma_{WA} = 0.0073\,\text{N/m}$

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:

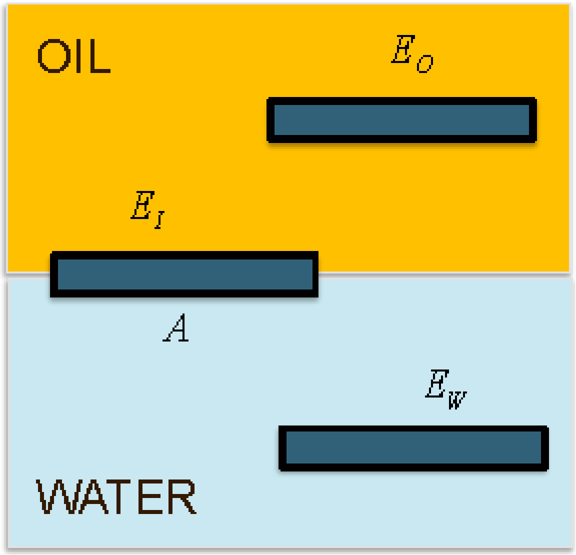
Surface tension:

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 :

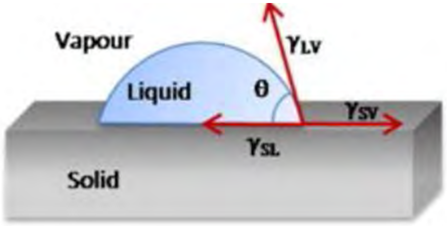
$$E_I - E_O = -A\gamma_{OW}(1+\cos\theta)$$

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

Wetting angle Young's relation:

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

Energetically favorable to adsorb particles at the interface.

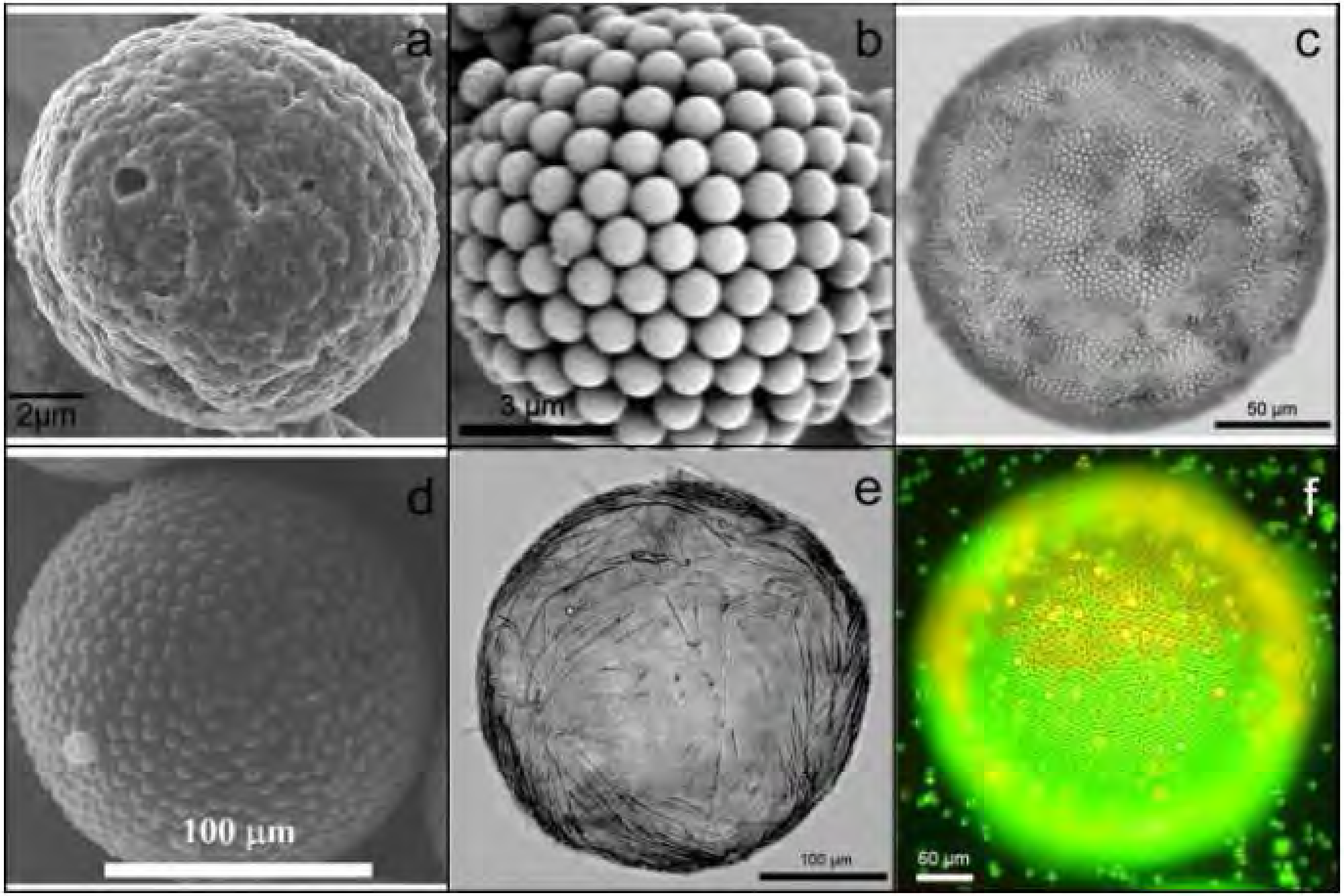


Typically:

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

Pickering (1907) : Emulsions

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



Dinsmore et.al.

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

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Article | OPEN

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

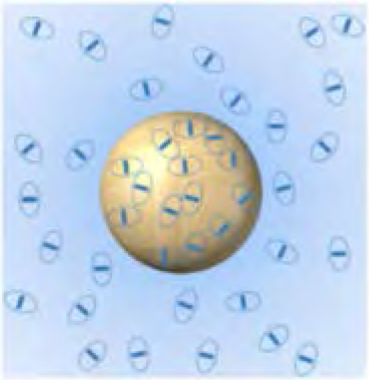
Received: 01 April 2016
Accepted: 18 October 2016
Published online: 24 November 2016

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

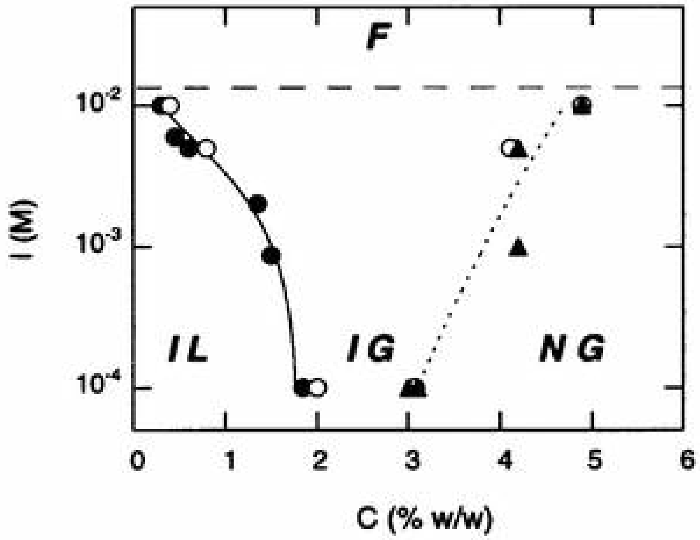
Authors | Authors and affiliations

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.



RELEVANCE OF CLAYS

Clay avalanches

Clay avalanche: Rissa Norway 1978

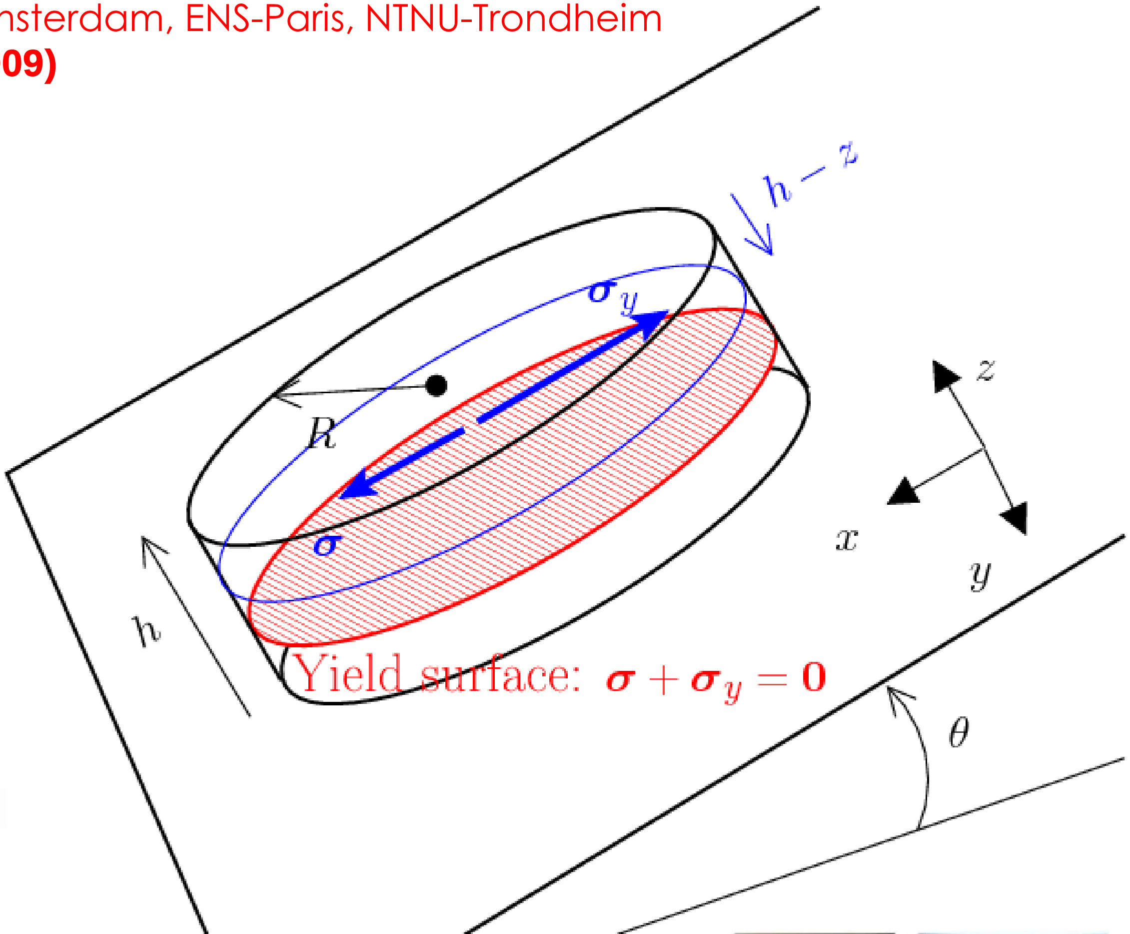
Simple analog landslide experiments

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)

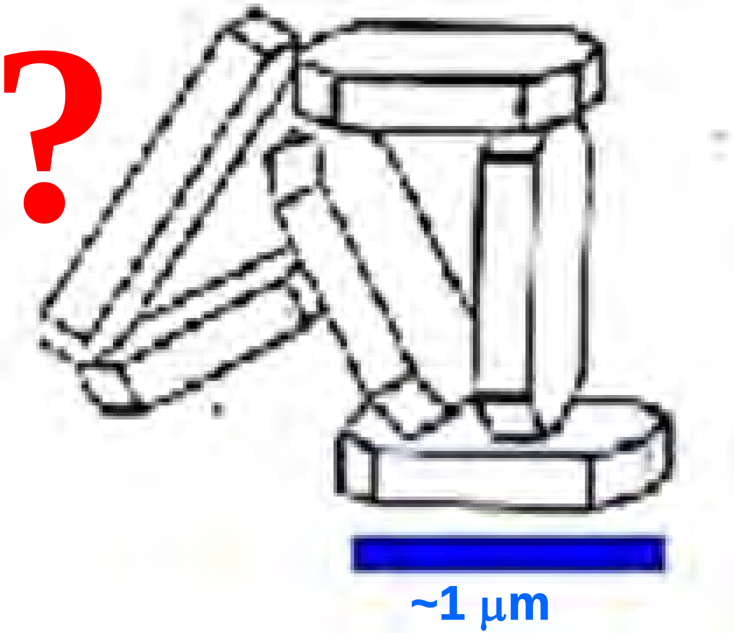
$$\sigma(z) = \rho\, g\, (h - z)\, \sin\theta$$

(null at the free surface)

All material above the yield surface is expected to flow



?



Clays in ENERGY and Environement

Part geological formation
Drilling muds
Oil refining

Clays in SOFT NANOTECHNOLOGY

Clays are shear-thinning materials, like for example ketchup or toothpaste

Elastic behavior below treshold stress
Newtonian (or non-Newtonian) flow above treshold stress

Striped toothpaste:

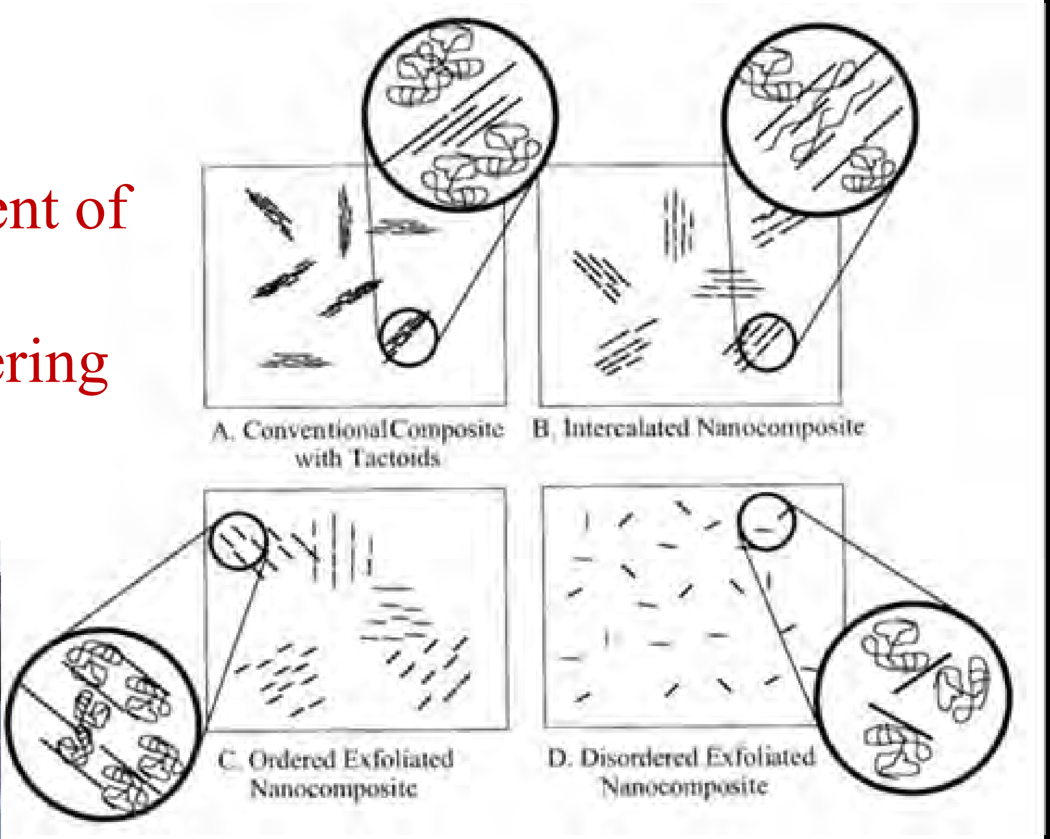
The colors do not mix because there are clay nanoplatelet particles mixed into each color? Is it true?

Clays in Advanced MATERIALS

Polymer Nanocomposite Materials:

Adding nanoparticle (clays) to polymer matrix:

Central issues:
- Dispersion
- Selfassembly, and alignement of clay platelet particles
- Liquid Crystalline like ordering

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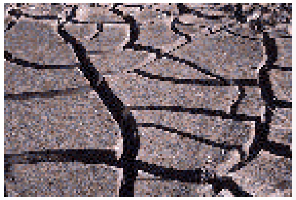
Clays in BIONANOTECHNOLOGY

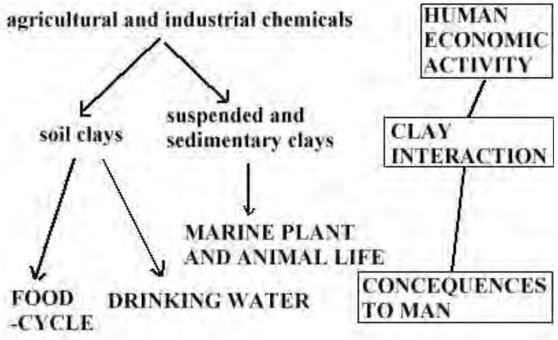
Parrots of the Amazones:

Parrots of the Amazon eat clay at riverbanks for breakfast in order to prevent stomach-ache from alkaloid poisons of the seeds in the fruits they eat for lunch.

Shows that clays may be interesting drug delivery systems

Other ”places” where clays are important:





agricultural and industrial chemicals

soil clays

suspended and sedimentary clays

MARINE PLANT AND ANIMAL LIFE

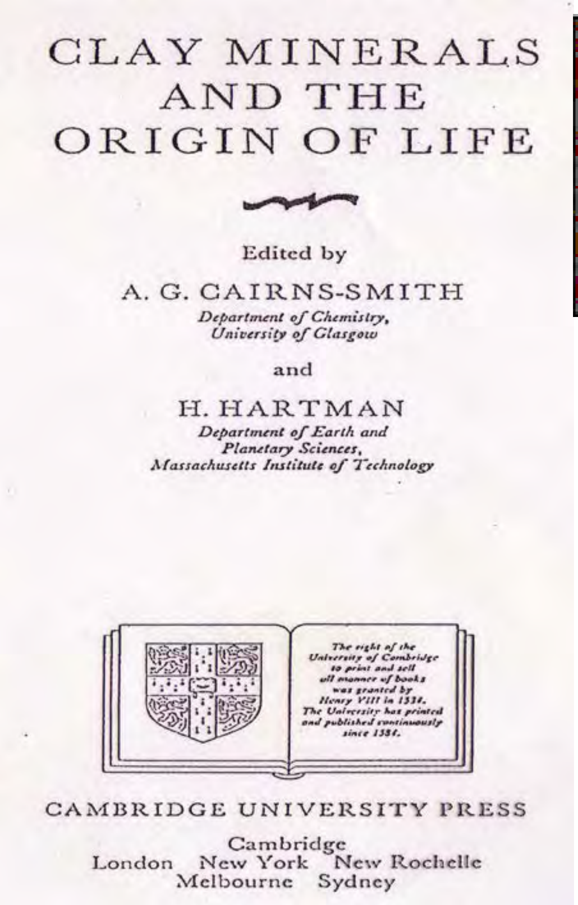
FOOD -CYCLE

DRINKING WATER

HUMAN ECONOMIC ACTIVITY

CLAY INTERACTION

CONCEQUENCES TO MAN



CLAY MINERALS
AND THE
ORIGIN OF LIFE

Edited by

A. G. CAIRNS-SMITH
Department of Chemistry, University of Glasgow

and

H. HARTMAN
Department of Earth and Planetary Sciences, Massachusetts Institute of Technology

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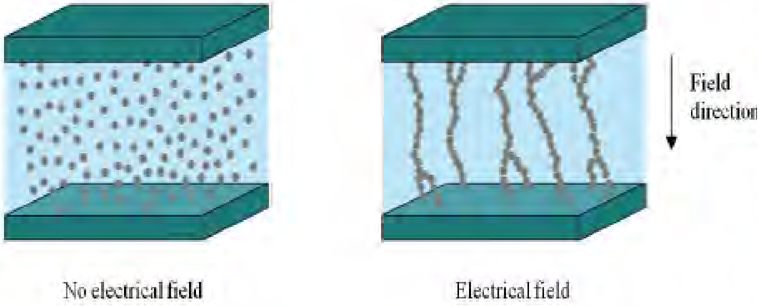
PHYSICS:

CLAYS IN OIL

NTNU – Trondheim
Norwegian University of
Science and Technology

Electro-rheological fluids

Winslow effect:

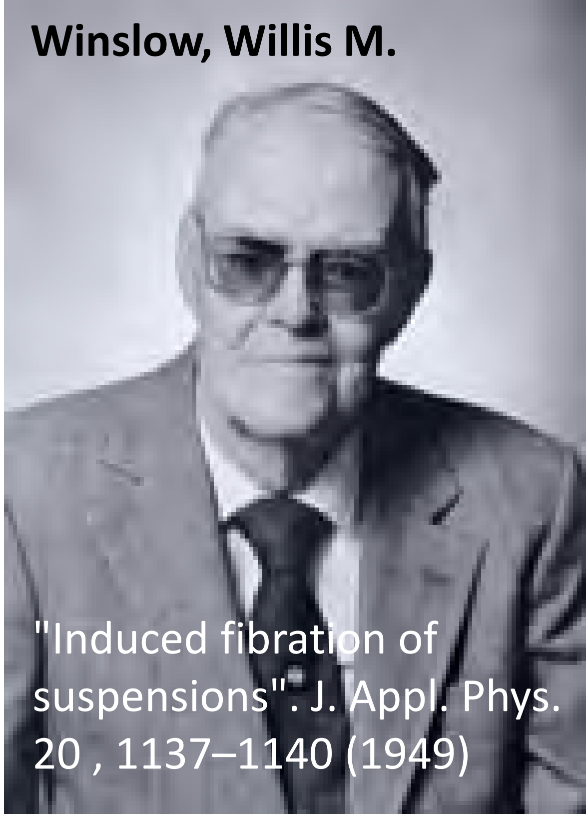


No electrical field

Electrical field

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

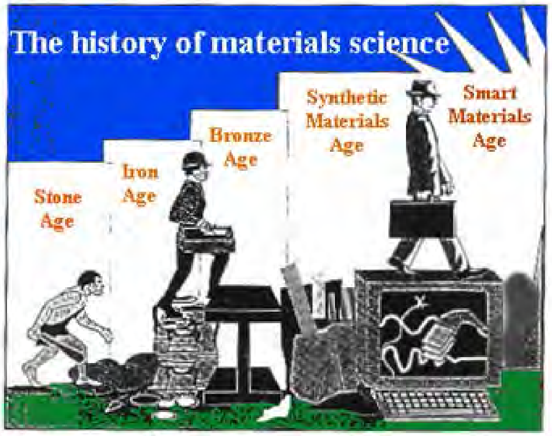
- Electric fields induce dipole attraction and chain formation
- Large yield stress -> 200 kPa or more 100 times viscosity increase (up to 100000 times according to wiki)

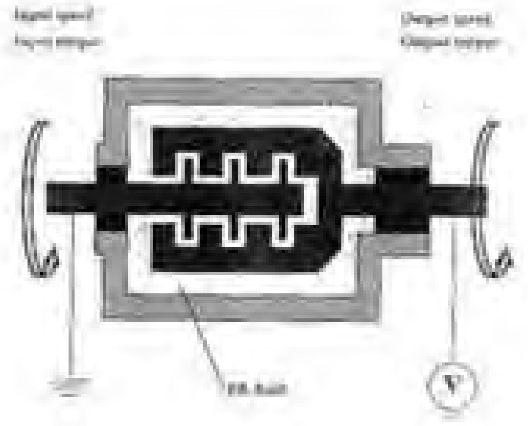


Winslow, Willis M.

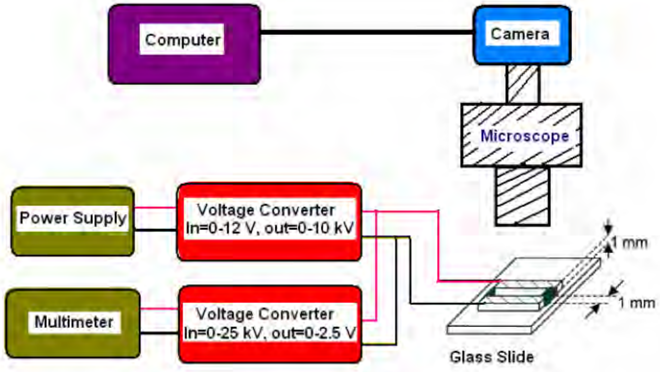
"Induced fibration of suspensions". J. Appl. Phys. 20 , 1137–1140 (1949)

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



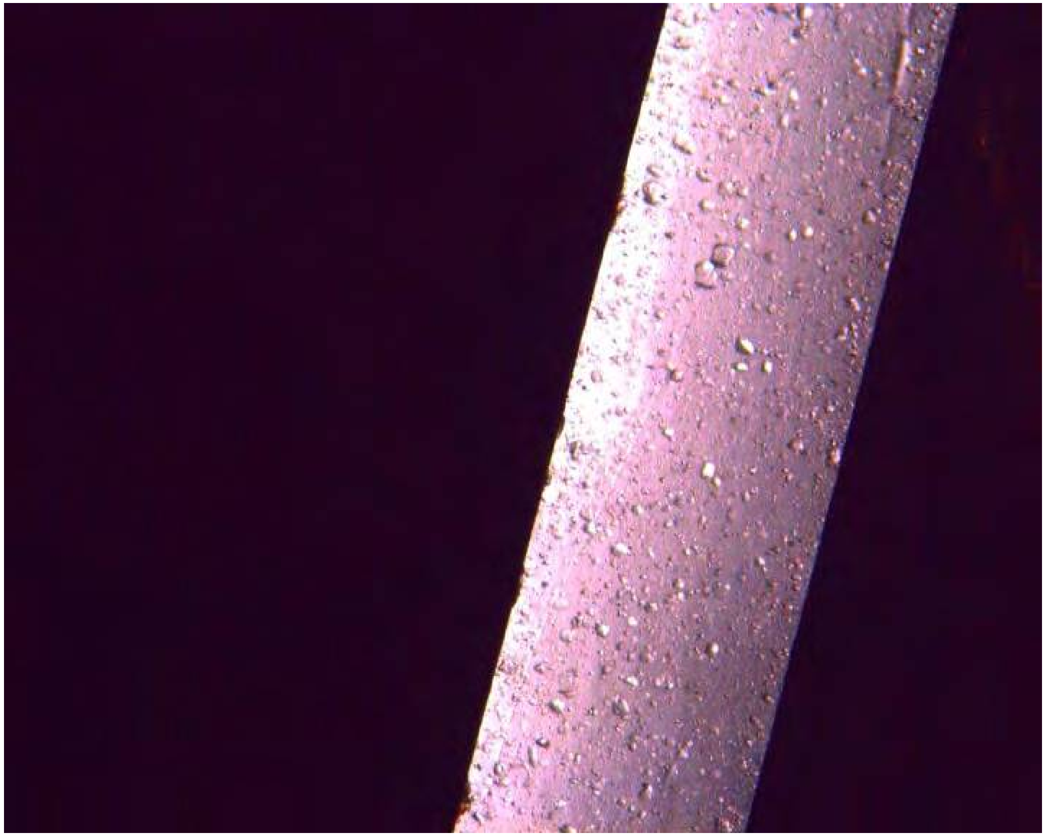


Clay particles suspended in oil:

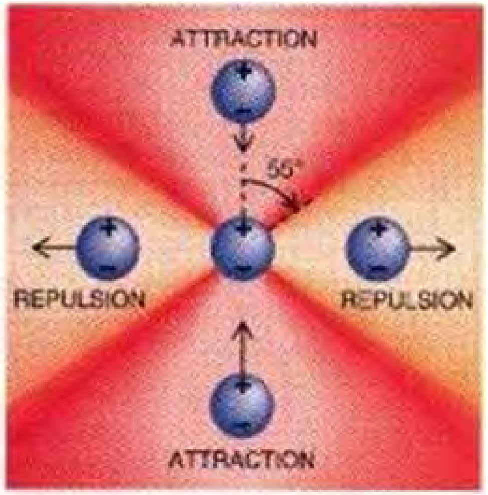


Video microscopy (real time):

~500 V



1 mm

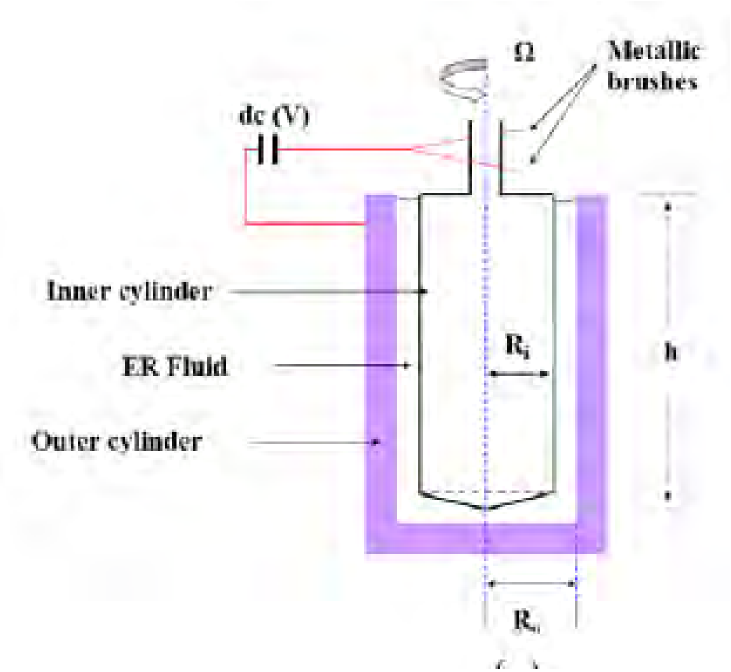


Electrorheology:

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)

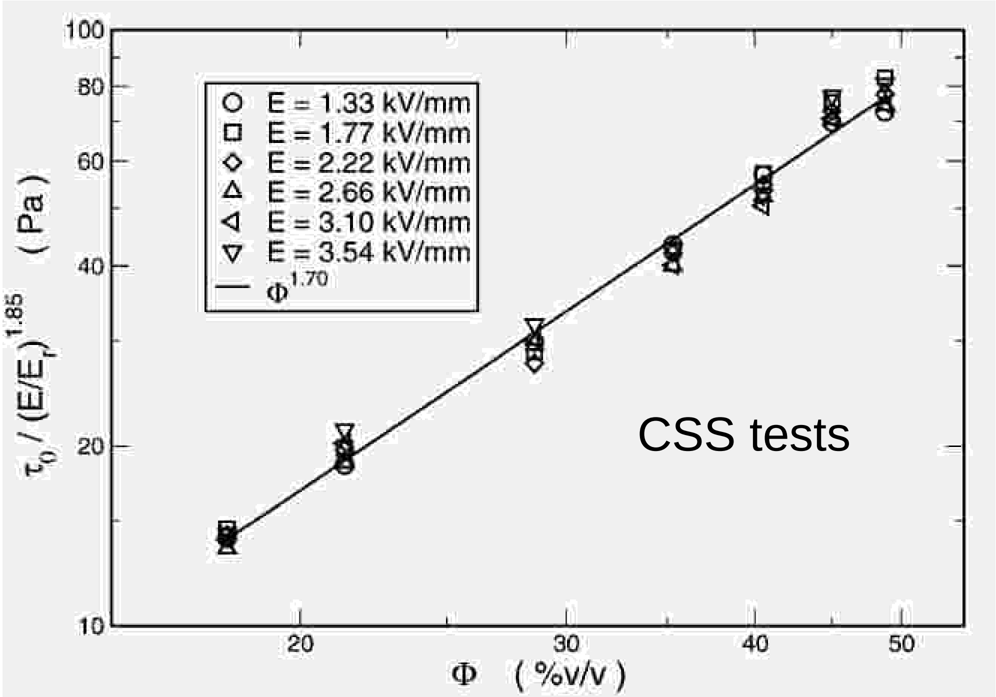
J. Phys.: Condens. Matter 22, 324104 (2010)

J. Rheol. 55, 2011 (2010)

Yield stress:

Theories predict:

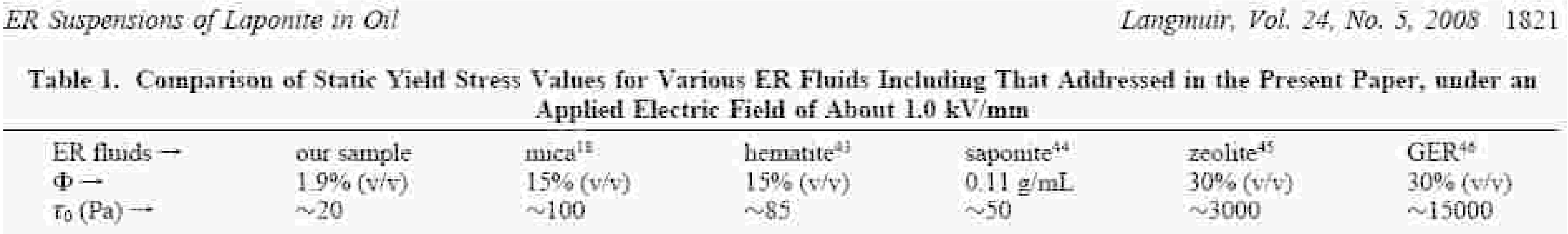
$$\tau \propto E^{\alpha}\,\Phi^{\beta}$$



CSS tests

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..

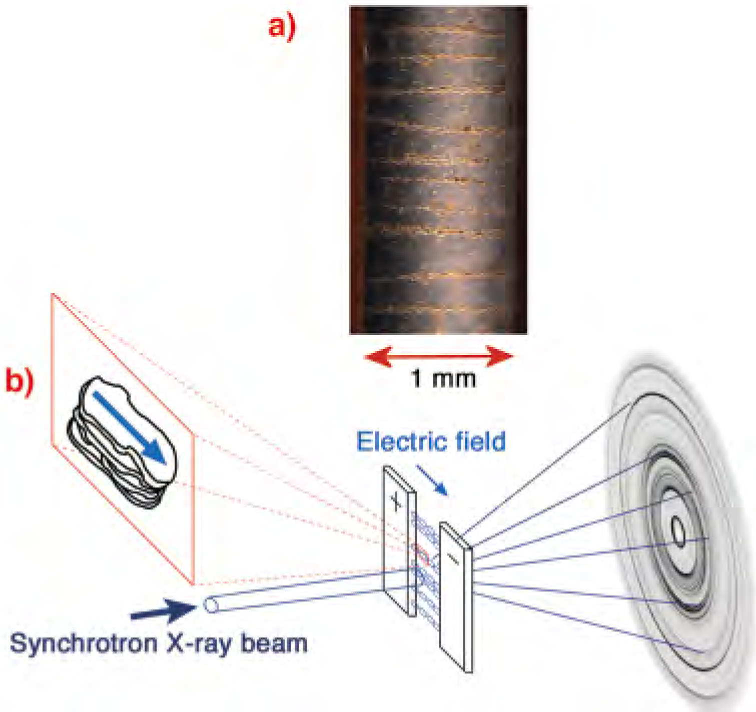


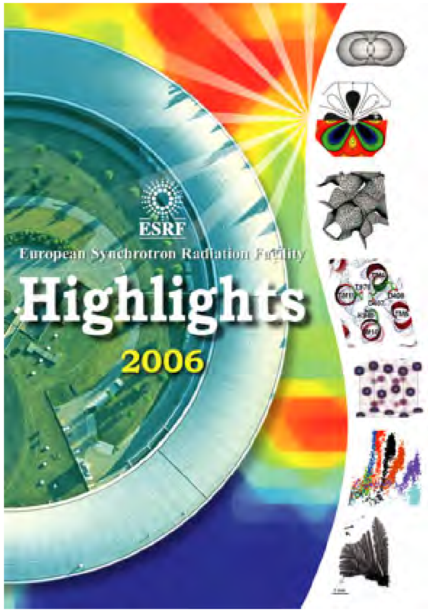
ER Suspensions of Laponite in Oil *Langmuir, Vol. 24, No. 5, 2008* 1821

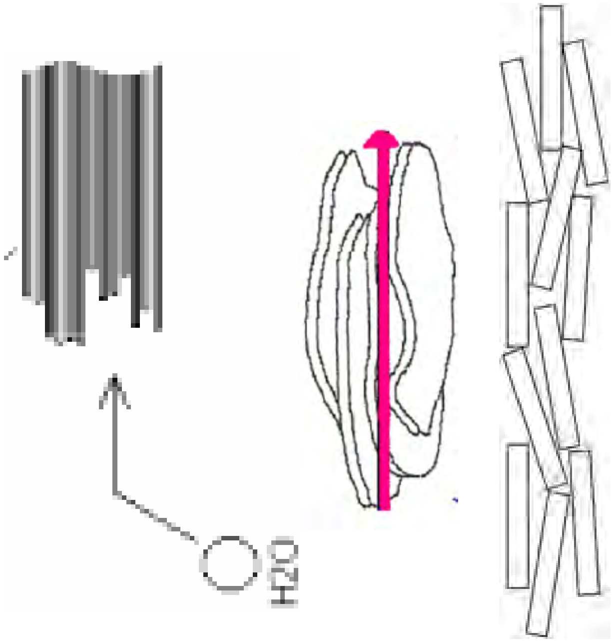
Table 1. Comparison of Static Yield Stress Values for Various ER Fluids Including That Addressed in the Present Paper, under an Applied Electric Field of About 1.0 kV/mm

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

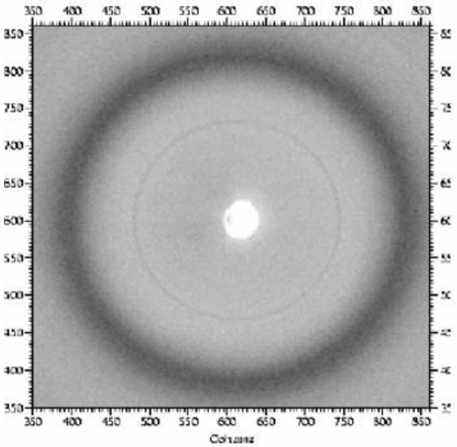
Experiments at ESRF, Grenoble:
In ESRF Scientific Highlights 2006



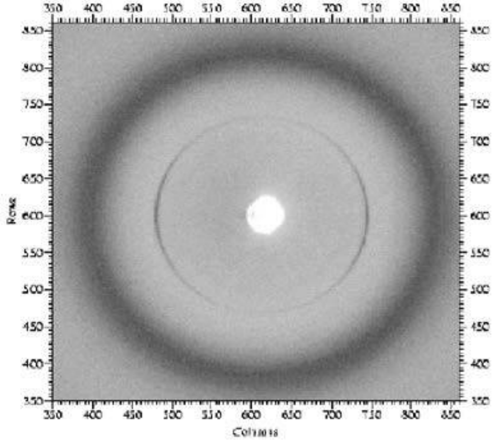


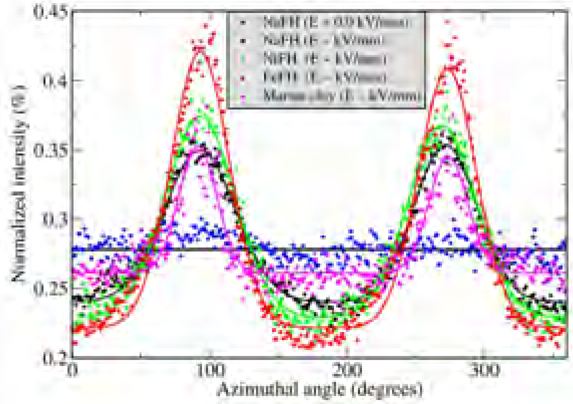


Before: 0 V/mm

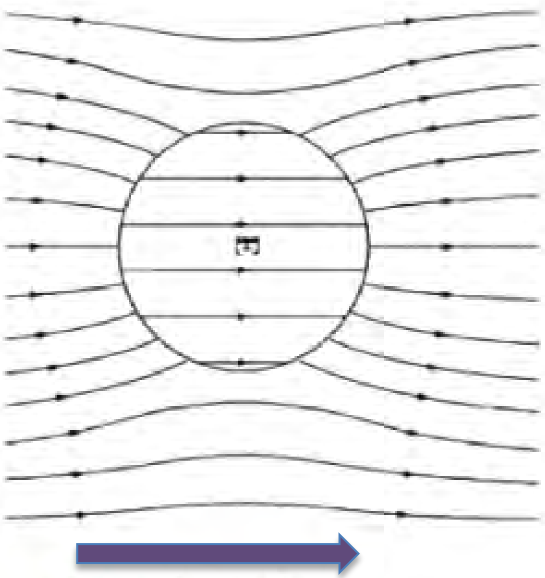


After: 500 V/mm

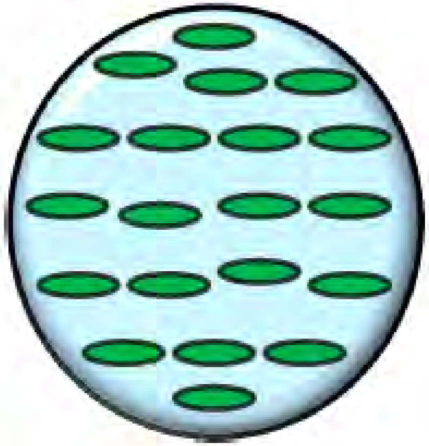




Angular distribution function
$= S_2 = \frac{1}{2}\langle 3\cos^2\theta - 1 \rangle$



Electric field



Chain formation inside a drop?

Electrorheological droplets for microfluidics
Electrorheological emulsions

Is it possible to make electrorheological drops?