

Laboratory for Soft and Complex Matter Studies at NTNU:

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

Active full-time researchers in our NTNU lab. 2012-13:

- Prof. Jon Otto Fossum
- Post.doc Zbigniew Rozynek
- Ph.D. student Henrik Hemmen
- Ph.D. student Elisabeth Lindbo Hansen
- Ph.D student NN to begin spring 2012
- Research Technician Ole Tore Buset, (helps us in all exp. activities)
- Masterstudents

Regular visiting scientists in our NTNU lab. 2012-13:

- Adjunct Prof. Kenneth D. Knudsen, is full-time Senior Researcher at IFE

Main supervisor for project number 1.d):

- Prof. Arne Mikkelsen

Principal contact for all projects given below:

Prof. Jon Otto Fossum, email: jon.fossum@ntnu.no, tel. 91139194, Realfagbygget NTNU. You may also contact the other people listed, of course.

In many of the experiments that we describe below, it may be necessary to perform synchrotron X-ray investigations either in France, Brazil, South-Korea, or Sweden, or neutron scattering at IFE, Kjeller.

Some of the activities below are new, while some are ongoing, and in the latter cases, the master student projects are continuations of these ongoing activities.

The projects below have "a common denominator" and a common basic question: *What kind of relations are there between physics and structures on the nano-scale, and macroscopic and "global behaviors" on the human scale?* It is in this context that we for example study self-organization of nano-particles: Think of how to make "something smart" from nano-particles, "something" which is so large that you can hold it in your hand. Such an object contains about 10^{20} nano-particles (Avogadro's number). Even if you use as little as 1 millisecond in order to move a nano-particle into its planned place in a pre-designed structure, one particle by one particle, it will take about 300 million years to organize the 10^{20} particles the way you want. This means that self-organization of nano-particles is the only practical way to do this, and that basic studies of self-organization of particles is a "hot topic" in science.

See also the following popular science presentations and other news from the lab:

- University of Amsterdam, Netherlands: News and Agenda: [Clay soil landslides cause greater damage after minor rainfall](#), November 11 2009
- European Space Agency (ESA) 2009 [Meet the teams 2009: Complex](#)
- Norwegian Space Centre, November 11th 2009: [Spinnville studentmuligheter](#)
- Forskning.no April 13th 2009: [Leire i fritt fall](#)
- European Space Agency (ESA), January 12th 2009: [Four student teams selected to fly their theses!](#)
- Norwegian Space Centre, January 13th 2009: [Norwegian students become weightless](#)
- Forskning.no April 6th 2007: [Nanoleire demper støt](#)
- Research Council of Norway NANOMAT news April 2007: [Norske leireforskere i teten](#)
- Research Council of Norway NANOMAT Newsletter May 2007: [Fra komplekse fenomener i leire til nanoteknologi](#)

We need more master-students, and we offer the following projects 2012-13.

Note that we may hire students for up to a 1 month summer-job (each) during the summer of 2012, as a “jump-start” to a project of the fall semester 2012.

The projects that we offer are outlined in the following pages. They are all experimental physics projects.

List of contents:

1. Nano-science:

Self-organization from nano-particle assemblies:

1. a) Liquid crystalline phases and self-organization
1. b) Electric field droplet manipulation
1. c) Medical drugdelivery by means of clay nanolayered particles
1. d) Optical studies of field induced order-disorder transitions

2. Geophysics Petroleum related physics, environmental physics, related to nano-science:

Studies of fluid transport in nano-structures:

2. a) Fluid-transport in nanoporous materials
2. b) Studies of fluid CO₂ in porous media and near surfaces

Pattern-formation in, and stability of, soft materials:

2. c) Fingering to fracturing transition in gels
2. d) Avalanches in clays

Project descriptions (supervisors in parenthesis):

1.a) Liquid crystalline phases and self-organization

(E. Lindbo Hansen, K.D. Knudsen-IFE, Z. Rozynek, J.O. Fossum)

Liquid crystalline phases of disc-shaped nanoparticles in water: the ordering effects of walls and phase boundaries.

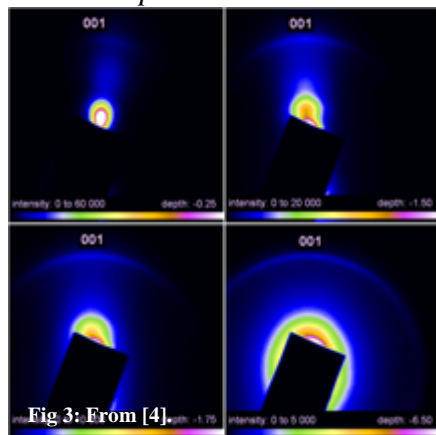
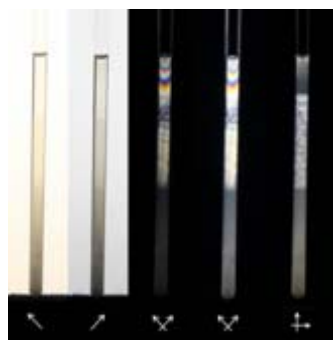


Fig 3: From [4].

This project focuses on the liquid crystalline order that develops in initially isotropic aqueous suspensions of disc-shaped sodium-fluorohectorite clay nanoparticles in the gravitational field [1,2]. The master student who chooses this project will use optical birefringence techniques and x-ray diffraction, likely also at synchrotron sources in either France, Brazil, Sweden or South-Korea, to study how anisometric nanoparticles suspended in water spontaneously order. Neutron experiments at IFE, Kjeller may also be performed. The main aim of the proposed project is to further investigate the effects of

container walls and suspension-air interfaces on the nematic order of nanosized clay platelets suspended in water. As illustrated in the uppermost to the left, X-rays scattered off anisotropic samples will show anisotropic scattering patterns. It is also possible to



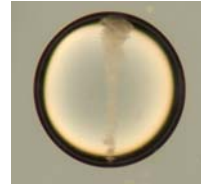
extract quantitative measures of the degree of order from such diffractograms, by calculating values for the so-called nematic order parameter S_2 [3]. Another way to investigate nematically ordered samples, is to observe the samples between crossed linear polarizers. Isotropic samples will allow no light to emerge from between a crossed polarizer setup, and the field of view of a camera observing the setup will thus be dark. Nematically ordered, anisotropic samples on the other hand will change the polarization state of the incoming light so that some light will be transmitted from a

crossed polarizer setup. A camera can record the amount of light transmitted, and this can be related to the degree of ordering in the sample. As a master student on this project, you will become familiar with investigations of ordering through both such birefringence observations, and through in-house and likely also synchrotron based x-ray scattering experiments, the latter of which is a technique that is widely employed within a large range of scientific disciplines, going from biology and medicine to physics and materials science.

References:

- [1] 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).
- [2] Phase diagram of polydisperse Na-fluorohectorite-water suspensions: A synchrotron small angle x-ray scattering study, D. M. Fonseca, Y. Méheust, J. O. Fossum, K. D. Knudsen and K. P. S. Parmar, Phys. Rev. E 79, 021402 (2009).
- [3] Inferring orientation distributions in anisotropic powders of nano-layered crystallites from a single two-dimensional WAXS image, Y. Méheust, K. D. Knudsen and J. O. Fossum, J. Appl. Cryst. 39, 661 (2006).
- [4] Colloidal Dispersion of Clay Nanoplatelets: Optical birefringence and x-ray scattering studies of nematic phases, E. L. Hansen, Master's thesis, NTNU (2008).

1.b) Electric field droplet manipulation (Z. Rozynek, R. Castberg-UiO, P. Dommersmes-Univ. Paris 7, J.O. Fossum)

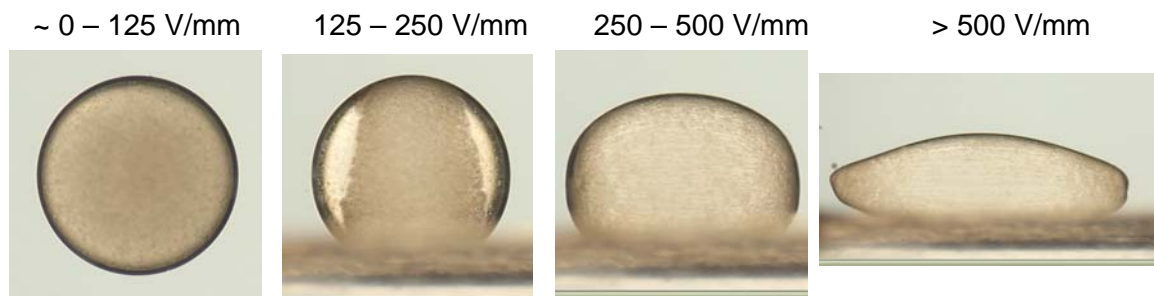


Goal: Understand physics behind clay particle structuring inside an oil-based droplet and manipulate the droplet deformation.

Deformation of droplets in electric fields is used in microfluidic applications, for example to induce droplet coalescence. When it comes to the electrorheological (ER) droplets, research has suggested many uses for "smart" droplets that can be controlled, including soft displays, lab-on-a-chip for accurate chemical reactions or biological processes such as drug delivery, or even boolean logic for simple microfluidic computing [1,2,3].

Our project on electric field droplet-with-clay manipulation has revealed interesting physical aspects and opened up new perspectives considering the future work. These include some of very concrete experimental tasks, such as:

- Determination of critical voltages for the processes of different structuring of clay.
- Filming 3D particle behaviour, noting behaviour of twister and chain formation and how they are formed.
- Determining a flow inside and outside drop with "inert" particles.
- Varying different viscosities while keeping system unchanged.
- Preparation of clay droplets with different clay concentration.
- Measuring an influence of water content.



Clay particles align in different manner depending on the field strength. "Twister-like" to "chain-like" at around 300 V/mm

References:

- [1] Xize Niu, Mengying Zhang, Jjinbo Wu, Weijia Wen and Ping Sheng, "Generation and manipulation of smart droplets", *Soft Matter*, 5:576-581 (2009)
- [2] A.R. Thiam, N. Bremond and J. Bibette, "Breaking of an Emulsion under an ac Electric Field", *Phys. Review Lett.* **102**:188304 (2009).
- [3] *Oil-oil droplet deformation under DC electric field as a method to investigate clay Electrorheology*, Master thesis NTNU Department of Physics (2010) – Kjetil Hersvik.

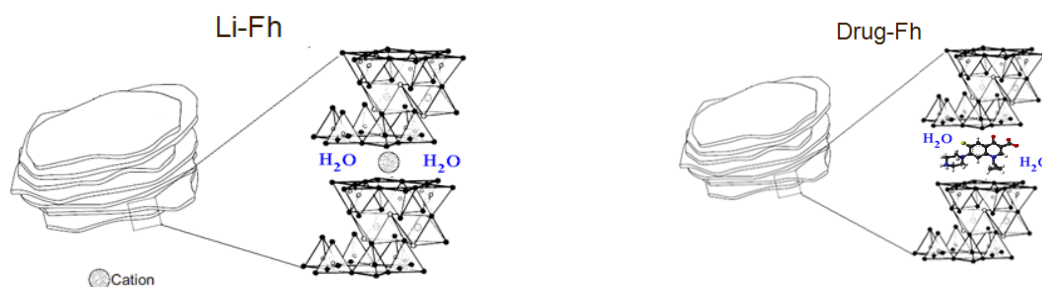
1.c) Medical drugdelivery by means of clay nanolayered particles. (Z. Rozynek, E. Lindbo Hansen, K.D. Knudsen-IFE, A. Rivera and E. Altshuler, Univ, Havana, Cuba, J.O. Fossum)

The field of Modified Drug Delivery Systems (MDDS) has a large impact in health applications, due to the possibility to control the release rate of the active principle, protect it against degradation, and also protect the gastrointestinal tract –among other advantages.

Clays have been incorporated for years to the list of drug hosts to produce Extended Release Systems.¹ The fact that clays are nano-layered materials of natural origin^{2,3} and have been shown to be non-toxic for skin application and oral administration^{4,5} make them an interesting material for health applications. A good example of a commercially available clay product in this category is SMECTA, which commonly is administrated to children with diharrea problems.⁶

We recently proposed that there is a vast and rather virgin field of applications for clays in health related problems, such as its use as hosts for the delivery of antibiotics, the possibility of temperature-dependent delivery of drugs, as well as cream formulations.

MDDS include Extended (or Prolonged) Release Dosage forms (ERDF), which are systems where the drug is made available during an extended period of time after administration as well as Site Specific Targeting Systems (SSTS), which are those that deliver the active substance at a diseased organ or tissue. Polymer matrices and membranes are typically used to produce MDDS, but in the last years some natural, porous and mesoporous⁷ materials have been explored, notably zeolites⁸ and clays¹.



Sketch of one possible mechanism of drug incorporation into a clay. Clay particle atomic structure of Li-fluorohectorite (Li-Fh) with Li⁺ cation occupying clay interlamellar gallery (left) and intercalated ciprofloxacin (right).

In this project the students will use in-house and synchrotron X-ray scattering methods, as well as various other techniques, for investigating the capture and release dynamics by clays for selected drugs.

References:

¹ C. Aguzzi, P. Cerezo, C. Viseras and C. Caramella, *Appl. Clay Sci.* 36 (2007) 22

² J.O. Fossum, *Physica A* 270 (1999) 270

³ *X-ray Studies of Carbon Dioxide Intercalation in Na-Fluorohectorite Clay at Near-Ambient Conditions*, Henrik Hemmen, Erlend G. Rolseth, Davi M. Fonseca, Elisabeth L. Hansen, Jon Otto Fossum and Tomás S. Plivelic, *Langmuir* 28, 1678-82 (2012), and references therein

⁴ T. Takahashi Y. Yamada, K. Kataoka, Y. Nagasaki, *J. Control. Release*, 107 (2005) 408

⁵ G. V. Joshi, R. R. Pawar, B. D. Kevadiya and H. C. Bajaj *Micropor. Mesopor. Mater.* 142 (2011) 542.

⁶ <http://www.bien-etre-beaute-forme.com/le-smecta-pour-lutter-contre-la-diarrhee/>

⁷ M. Vallet-Regi, F. Balas and D. Arcos, *Ang. Chemie (Int. Ed.)*, 46 (2007) 7548

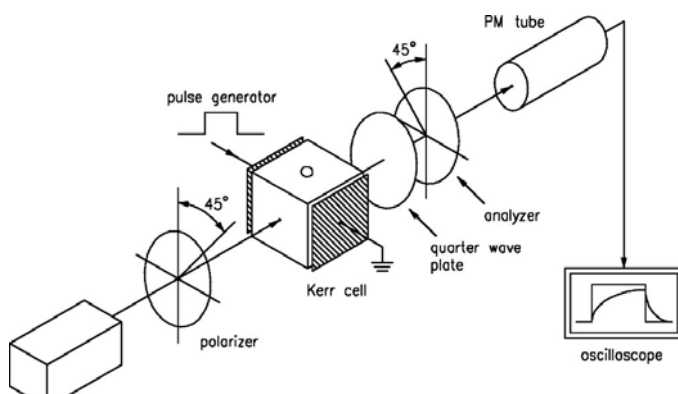
⁸ A. Rivera and T. Farías, *Micropor. Mesopor. Mater.* 80 (2005) 337

1.d) Optical studies of field induced order-disorder transitions: The effects of electric, magnetic and mechanical fields on anisotropic colloidal particles. (A. Mikkelsen, Z. Rozynek, J.O. Fossum)

This project focuses on the reponse of anisotropic, colloidal particles to external fields. The applied fields can be electric, magnetic or mechanical in nature and the response will be studied optically by birefringence observations with laser and white light, and likely also with x-rays and ellipsometry. Due to their anisotropy (non-spherical shapes, plus anisotropic electric and magnetic properties), nanoscaled platelets of synthetic clays suspended in water or oil will orient in response to applied fields, and such oriented systems will display a special kind of optical property known as birefringence. If such samples are placed between crossed polarizers, the light that reaches a camera observing the samples will be a direct result of the degree of anisotropy. Samples that are ordered will cause light to be transmitted towards the observer whereas isotropic samples will not affect the polarization of light, and the field of view for an observer will thus be dark.

As a master student on this project, you will be given the opportunity to study both isotropic suspensions and nematically ordered samples [1] of plateshaped clay nanoparticles by several experimental methods. Optical birefringence with laser and white light will be studied in both nematic samples, and in initially isotropic samples where short electric pulses [2] or flows will cause a temporary ordering that decays once the fields are switched off. The decay is caused by rotational Brownian diffusion, which promotes a random ordering of the nanoplatelets. You may also choose to study order-disorder transitions induced by flows via a static light scattering cell on an instrument known as a rheometer, and to perform dynamic light scattering experiments. The latter

will primarily be used to study diffusion and particle or aggregate sizes, whereas the static scattering gives information on structure and order. Both static and dynamic light scattering, as well as birefringence experiments, are classic techniques that are widely employed in studies of suspensions of nano- and microsized particles.



From [2]. Electric induced order studied by laser birefringence

References:

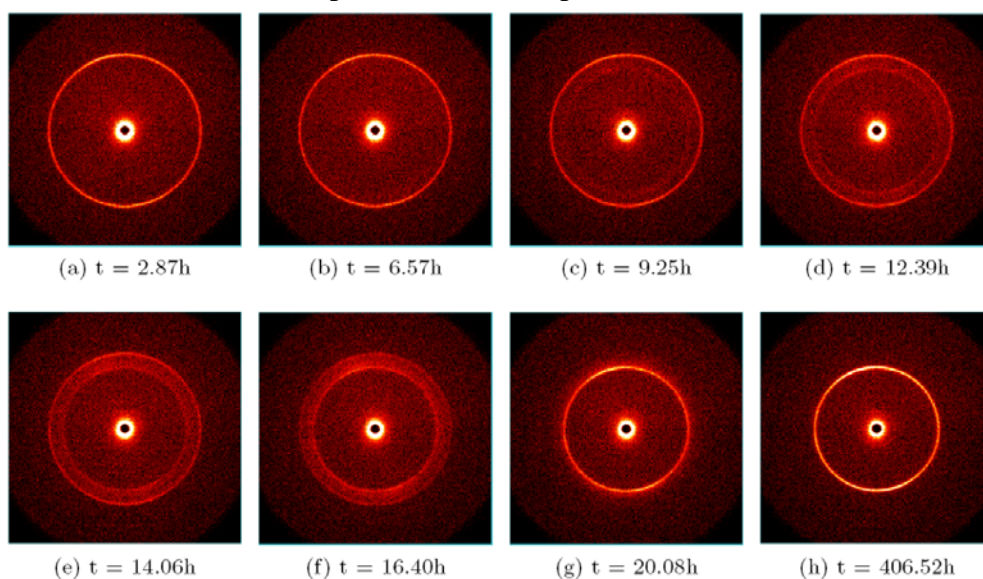
- [1] *Orientational order in gravity dispersed clay colloids: A synchrotron x-ray scattering study of Na fluorohectorite suspensions*, E. DiMasi, J. O. Fossum, T. Gog, and C. Venkataraman, Phys. Rev. E 64, 061704 (2001).
- [2] *Viscosity and transient electric birefringence study of clay colloidal aggregation*, A. Bakk, J. O. Fossum, G. J. da Silva, H. M. Adland, A. Mikkelsen, and A. Elgsaeter, Phys. Rev. E 65, 021407 (2002).

2.a) Fluid-transport in nanoporous materials (Z. Rozynek, J.O. Fossum)

This project is part of and a continuation of an international collaboration involving researchers in Brazil, in France and in South-Korea. The project deals with experimental studies of nanoporous media, and fluid transport/diffusion in such systems. This physics may have relevance for membrane technology, and for control of polluting agents in for example clay based soils. The latter application is relevant for sub-sea oil reservoirs, as well as for containment and storage of radioactive waste.

Most porous materials that surround us absorb water, either due to direct contact with liquid water, or from water vapor in the surrounding air that condenses in small pores. The water may often be modeled as capillary flow: The water wets the porous material and is “pulled in” (blotting paper effect). This gives a water front that progresses as the square root of the time. But if the material has pores with nanometer size (1 water molecule is about 0.2 nm), the observed dynamics is often different from this, and there is today no good understanding of this so-called anomalous water transport.

Small-Angle-X-ray-Scattering (SAXS) studies of water transport in a nanoporous clay material has been studied by us recently, and the project will continue such studies. The following pictures show examples of 2-dimensional SAXS diffractograms from our studies in our home-lab. at NTNU. Such diffractograms give direct information about the water content in different pore sizes in nanoporous materials.



We also want to extend our studies beyond clay based nanoporous systems, and include other nanoporous materials, such as zeolites or paper (the blotting paper effect studied by X-rays).

References:

- [1] Fluid imbibition in paper fibers: Precursor front, Eduardo N. de Azevedo, Lars R. Alme, M. Engelsberg, Jon Otto Fossum, and Paul Dommersnes, *Phys.Rev.E* 78, 066317 (2008)
- [2] *X-ray studies of interlayer water absorption and mesoporous water transport in a weakly hydrated clay*, H. Hemmen, L.R. Alme, J.O. Fossum and Y. Meheust, *Phys.Rev. E* 82, 036315 (2010)
- [3] *Erratum: X-ray studies of interlayer water absorption and mesoporous water transport in a weakly hydrated clay*, H. Hemmen, Y. Meheust, J.O. Fossum, *Phys.Rev. E* 83, 019901(E) (2011)

2.b) Studies of fluid CO₂ in porous media and near surfaces (At NTNU, IFE or UiO) (Z. Rozynek, K.D. Knudsen-IFE, K.J. Måløy-UiO, J.O. Fossum)

Our group has large grant from the Research Council of Norway, concerned with “Sorption and Migration of CO₂ in porous media. The project is a collaboration within the COMPLEX-network (www.complexphysics.org), and involves experimental studies as well as numerical studies focused on the behaviour of CO₂ in general porous materials, and near surfaces made out of clays. At NTNU the project involves synchrotron X-ray scattering techniques and rheometry, at IFE we use neutron scattering techniques, and at UiO we study the flow of CO₂ in model porous media.

The project is relevant both for capturing and storage of CO₂. In particular it is important to understand the interactions between clay particles, and CO₂ in the context of CO₂ storage in underground reservoirs, since the cap-rock in such systems contains large amounts of clays, i.e. the project will work on understanding CO₂ near and inside material from the nano scientific point of view, and then focus on how to upscale the nanophysics, to the macrophysics scale. We recently published an article concerned with this [1].

Our group has an extensive history behind us in such upscaling studies, involving water-clay systems, see for example:

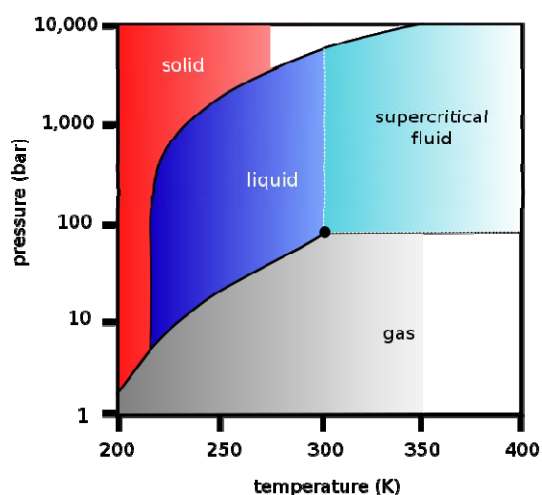
Quickclay and Landslides of Clayey Soils, Khaldoun, P.Moller, A. Fall, G.Wegdam, B. De Leeuw, Y. Meheust, J.O. Fossum, D. Bonn, Phys.Rev.Lett. 103, 188301 (2009)

Electrorheological properties of organically modified nanolayered laponite: Influence of intercalation, adsorption and wettability, Baoxiang Wang, Min Zhou, Zbigniew Rozynek and Jon Otto Fossum, J. Mater. Chem. 19, 1816 (2009)

Fluid imbibition in paper fibers: Precursor front, Eduardo N. de Azevedo, Lars R. Alme, M. Engelsberg, Jon Otto Fossum and Paul Dommersnes, Phys.Rev.E 78, 066317 (2008)

Electrorheological suspensions of laponite in oil: Rheometry studies, Kanak Parmar, Yves Méheust, Børge Schjelderupsen and Jon Otto Fossum, Langmuir 24, 1814 (2008)

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. d.M.Fonseca, Europhysics Letters, 74, 438 (2006)



In the context of master student projects, the work will involve performing one or some of the 1a), or 2a) above, simply replacing CO₂ for water. We have recently purchased the equipment needed for these studies, since liquid CO₂ only is achieved at above atmospheric pressures, see the CO₂ phase diagram to the left.

[1] *X-ray Studies of Carbon Dioxide Intercalation in Na-Fluorohectorite Clay at Near-Ambient Conditions*, Henrik Hemmen, Erlend G. Rolseth, Davi M. Fonseca, Elisabeth L. Hansen, Jon Otto Fossum and Tomás S. Plivelic, Langmuir 28, 1678-82 (2012)

2.c) Fingering to fracturing transition in gels (E. Bouchaud ESPCI - Paris, France, J. O. Fossum)

Viscoelastic materials respond to an external stress either as a solid or as a liquid, depending on the rate at which the external load is applied. This can be an interesting and innovative way to characterize a liquid to solid phase transition. With the scope that this study reveals useful to shed light on the still mysterious glass transition, we focus here on the vicinity of the well known, continuous sol-gel transition. Actually, the elastic modulus of mixtures made of a solvent and polyfunctional units (see Fig. 1 “monomers” which can link to more than two of their kind) increases from zero to a finite value when the concentration of the latter overpasses a critical value: this determines the so-called “sol-gel” transition.

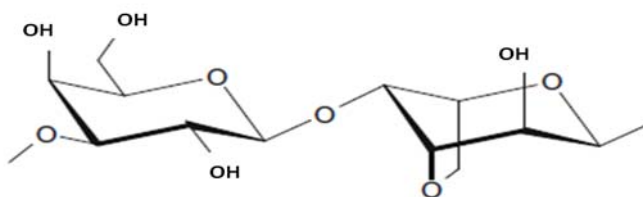


Figure 1: Repeating unit of an Agar gel.

During the thesis of Baudouin Saintyves, we have built up an experimental setup with which both a viscous liquid and a viscoelastic solid can be stressed (Fig. 2).

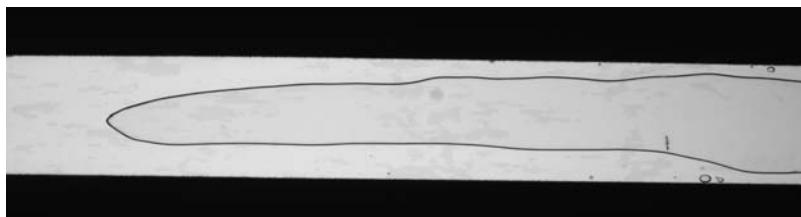


Figure 2: Crack propagating into a gel

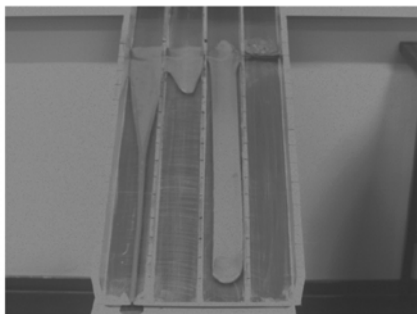
With applying a tensile stress to the system at various rates, we are now ready to explore the whole phase diagram, by varying the concentration, the temperature and the age of the system. Both the morphology and the dynamics of cracks will be studied in each case, and compared to the predictions of theoretical models. The same parameters will be observed at various magnifications in order to correlate the observed mechanical response to the small-scale structure of the material, determined using X-rays. In parallel, the rheology will be thoroughly studied, both to determine clearly the position of the sol-gel transition as a function of the parameters, and to measure in each case the viscosity, the shear modulus and the relaxation time (or the several relaxation times).

This project is a collaboration with the group of Elisabeth Bouchaud at ESPCI in Paris, and will involve visits there.

2.d) Avalanches in clays (Yves Meheust-*Univ. Rennes1, France*, J. O. Fossum)

Different mechanisms for the onset and development of landslides have been reported. However, the extreme instability ('quickness') of clayey soils in particular remains poorly understood. Quickclay has caused many deadly landslides in Canada, Russia, Alaska, Norway and Sweden. The occurrence of quickclay landslides is usually attributed to variations in water content and/or external perturbation of the soil. As merely one example of the latter, the infamous Rissa slide (movies are available from the Norwegian geotechnical service) was caused by small excavation works at a nearby farm.

So far [1], our group has investigated this extreme sensitivity by studying the flow behaviour of quickclay with different water contents in a rheometer. The sample used was a quickclay collected from 10m depth at Tiller, Trondheim which is similar in

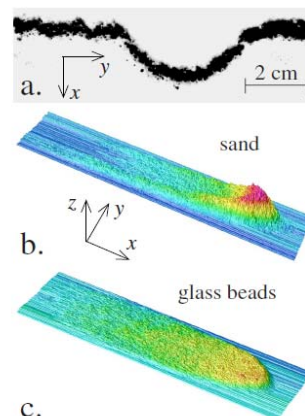
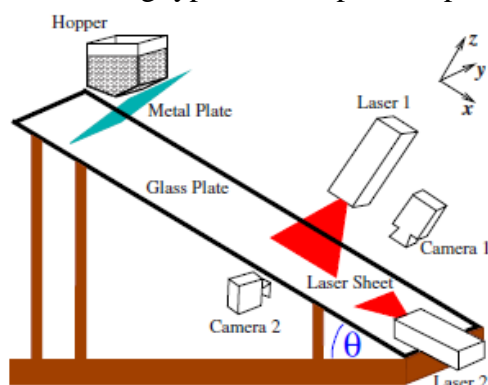


Laboratory landslides: Picture of the final stage of the slides: in the four lines from left to right the concentration of quickclay in water increases [1].

composition to quickclays that may be collected from other regions in the world. Our laboratory experiments (performed in Amsterdam) on the Tiller natural quickclay samples reveal a spectacular liquefaction of the material under flow that explains the instability.

Laboratory landslide experiments in addition show that, contrary to what is expected, higher water content does not lead to more unstable soils. For high clay content, the liquefaction occurs in a very thin layer of the material, the rest of the clay moving as a solid block; this explains the large distances over which quickclay landslides travel. We have reproduced the flow behaviour of the natural samples mixing different clays, water and salt, which has allowed us to assess the impact on the quickness of the different constituents of the clay.

In order to investigate such avalanches further, we want one master student to setup and use the following type of tilted plane experiment in our lab [2]:



Left: Tilted plane experiment for studies of avalanches [2]. Right: Avalanches in systems of sand and glass beads respectively studied using the experimental tilted plane setup to the left [2].

References:

- [1] *Quick Clay and Landslides of Clayey Soils*, A. Khaldoun, P.Moller, A. Fall, G. Wegdam, B. de Leuw, Y. Meheust, J.O. Fossum, D. Bonn, *Phys. Rev. Lett.* 103, 188301 (2009)
 [2] *Avalanche dynamics on a rough inclined plane*, T. Börzsönyi, T.C. Halsey, R. E. Ecke, *Phys. Rev. E* 78, 011306 (2008)