# MSc projects offered in Laboratory for Soft and Complex Matter Studies, (http://folk.ntnu.no/fossumj/lab/) Department of Physics, NTNU:

## Abstract:


**Help us to discover an amazing nano-material formed by the nature itself – CLAY**

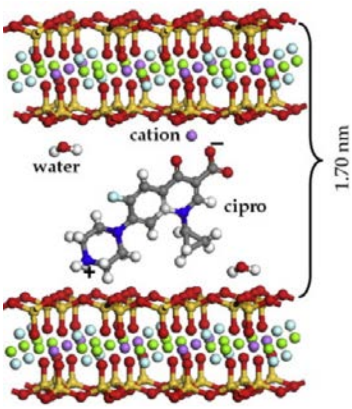
Here are few reasons why to study CLAY and use it in the real-world applications:

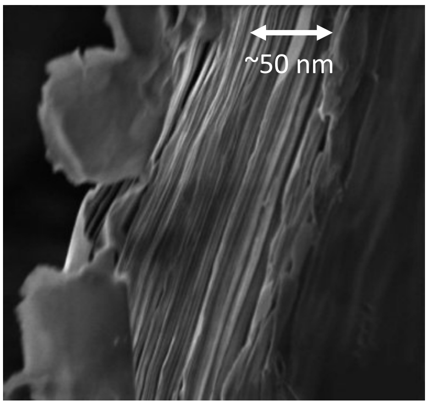
- CLAY can form various lamellar nano-structures, by electrically, magnetically or gravitationally guided self-assembly of the clay particles
- CLAY is a perfect material for greenhouse gas absorption, due to its high surface area and high absorbance for many molecules
- CLAY form lamellar nano-structures that can easily be combined with other 2D nano-materials, such as GRAPHENE, GRAPHENE OXIDE, in existing applications in electronics, such as in supercapacitors, batteries or smart sensors, thus targeting new electronic applications
- CLAY structures makes a feasible material for drug transport and controlled delivery
- CLAY is ecological and easy-to-handle

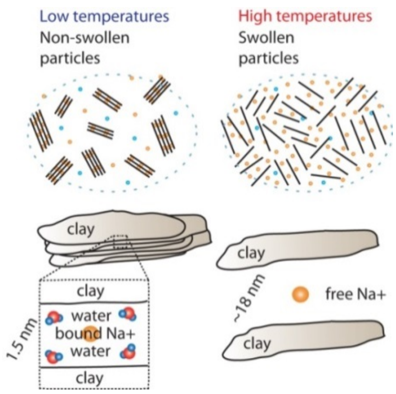
Do you want to explore the nano-world of clay and clayey materials?
Please check the projects offered and more detail specification of clay properties


## Contact persons:


Prof. Jon Otto Fossum (jon.fossum@ntnu.no)
Prof. Steinar Raaen (steinar.raaen@ntnu.no)
Adj. Prof. Paul Dommersnes (paul.dommersnes@ntnu.no)
(Paul Dommersnes is Senior Scientist at Giamag Technologies AS)
Adj. Prof. Kenneth D. Knudsen (kenneth.knudsen@ife.no)
(Kenneth Knudsen is Senior Scientist at IFE-Kjeller)
Postdoc Barbara Pacakova (barbara.pacakova@ntnu.no)

## Background and project in more detail:

Recent research highlights from the Laboratory include 5 articles by Nature Publishing Group[1,2,3,4,5]


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

The nano-lamellar structure of clay platelets with their well-defined internal crystallographic structure is illustrated in Figure 2 a. The nano-lamellar property of clay open up possibilities for clay based meta-materials and stacked hetero-structures such as exemplified in Figure 2 b which displays a stacked clay-ontop-of graphene-device, in this case studied by means of conductive AFM.

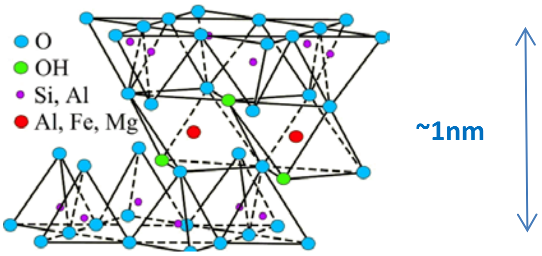



Figure 2 a)*: Sketch of single quasi two-dimensional nano-lamellar clay structure-. The lateral dimensions can be controlled (10 nm – 1 cm). The top and down clay surfaces are negatively charged, and the magnitude of this charge can also be controlled, which opens up for novel ways for designing clay based structures by guided self-assembly and for inclusion in complex materials such as illustrated below.*

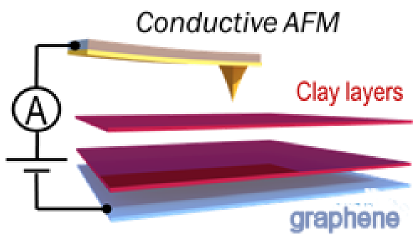



Figure 2 b): *Clay nano-platelets can be integrated with other lamellar materials such as graphene or graphene oxide, to form meta-materials and hetero-structures. The sketch illustrates a graphene-clay prototype electronic device assembled at Univ. Manchester (Prof. Nobel Laurate Sir Konstantin Novoselov) in collaboration with the present NTNU group.*

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[1] *Transition from glass- to gel-like states in clay at a liquid interface*, A. Gholamipour-Shirazi, M. S. Carvalho, M. Huila, K. Araki, P. Dommersnes & J. O. Fossum SCIENTIFIC REPORTS BY NATURE 6, 37239 (2016)

[2] *Intercalation and Retention of Carbon Dioxide in a Smectite Clay promoted by Interlayer Cation*, L. Michels, J. O. Fossum, Z. Rozynek, H. Hemmen, K. Rustenberg, P. A. Sobas, G. N. Kalantzopoulos, K. D. Knudsen, M. Janek, T. S. Plivelic & G. J. da Silva, SCIENTIFIC REPORTS BY NATURE 5, 8775 (2015)

[3] *Electroformation of Janus and patchy capsules,* Z. Rozynek, A. Mikkelsen, P. Dommersnes & J. O. Fossum, NATURE COMMUNICATIONS 5, 3945 (2014)

[4] *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)

[5] *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)

A large variety of molecules may adsorb onto clay surfaces by means of different mechanisms which means that clay surfaces can be used to capture molecules, and also that clay surfaces can be functionalized at will. Two examples are sketched in Figure 3, for the case of CO2 capture and retention by clay nano-layered particles, and for the case of drug molecule capture and delivery by clay nano-layered particles. The mechanisms for molecular capture are believed to be different in the two cases: It is believed that the CO2 molecules are captured by charge compensating cations in the structure and that the clay surfaces themselves are not primarily active in this capture mechanisms- The clays contribute with a large effective surface area, effectively more than 1000 square kilometers surface area contained in 1 cubic meter. On the other hand, for the case of the drug molecules it has been suggested that they are trapped by the clay surfaces themselves by partly replacing the charge compensating cations. Our group has demonstrated that clays can capture nearly as much CO2 as any material considered for CO2 capture[2], and we are currently investigating how clays can capture even more CO2 per unit volume.

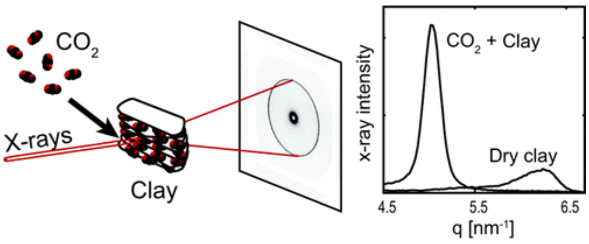


Figure 3 a*): From Refs. 2 and 6: Intercalated charge compensating cations in between the lamella of a stacked nano-layered clay particle may capture and retain CO2 molecules. This results in an expansion of the structure that can be measured by means of standard X-ray scattering methods.*

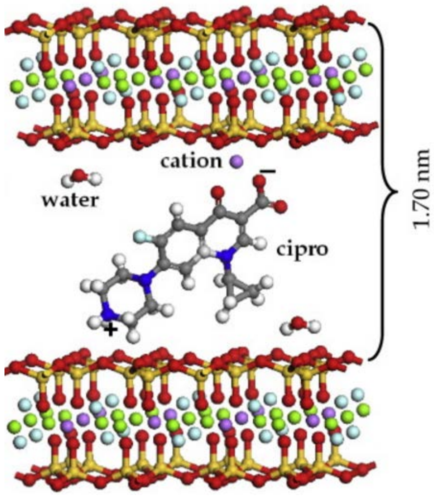


Figure 3 b): *From Ref. 7: Sketch of a possible configuration of Lithium Fluorohectorite clay with intercalated and captured Ciproflaxicin drug molecules, that can be released in a controlled manner*.

The possibilities of molecular adsorption at clay surfaces of a large variety of molecules means that clay surfaces can be functionalized at will. This is essential for governing self-assembly of clay particles into structures with defined properties, and for assembly of complex materials where clay particles constitute one of the ingredients. These points are illustrated in the following: In aqueous suspension clay nano platelets may self-assemble into various structures, governed by clay particle concentration, by temperature, by their given clay nano-lamellar shape, as well as by the magnitude of the clay layer charge, which in turn is coupled to the ionic strength of the aqueous solution, as illustrated in Figure 4 a). In a complex material such as the three-phase system of water-oil-clay particles, the water-oil interface will additionally take part in the governing of the self-assembly, since the particles will be trapped by capillary forces and confined in a film at the liquid-liquid interface, as illustrated Figure 4 b).

Figure 4 b) illustrates one precursor way of making nanostructured capsules with designed mechanical strength and permeability from clay particles. The oil drop in this case can be completely encapsulated by a porous elastic membrane made out of clay particles, salt and water. Nano-structured capsules are of interest for use in areas such as for drug delivery, for food and cosmetic applications, for enhanced oil-recovery etc. In addition, in all

[6] *X-ray Studies of Carbon Dioxide Intercalation in Na-Fluorohectorite Clay at Near-Ambient Conditions*, H. Hemmen, E, G. Rolseth, D, M. Fonseca, E, L. Hansen, J. O. Fossum & T. S. Plivelic LANGMUIR 28, 1678-1682 (2012)
[7] *Smectite as ciprofloxacin delivery system: Intercalation and temperature-controlled release properties*, A. Rivera, L. Valdés, J. Jiménez, I. Pérez, A. Lam, E. Altshuler, L.C. de Ménorval, J.O. Fossum, E.L. Hansen, Z. Rozynek, APPLIED CLAY SCIENCE 124-125, 150-156 (2016)

these areas so-called Janus or patchy microfluidic drops or capsules with heterogeneous surface properties are of great interest. Figure 5 illustrates examples of electro-structuring of clay assemblies on microfluidics drop surfaces that we have developed in our group recently:

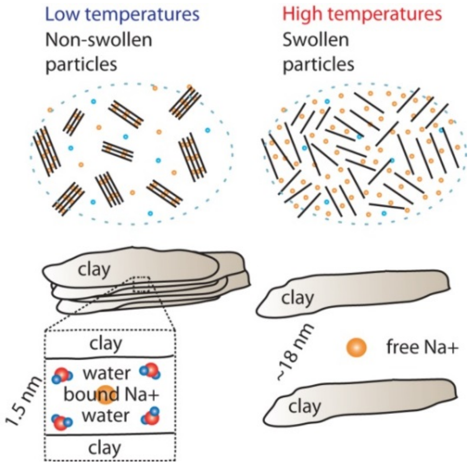


Figure 4 a): *From Ref. 5: Self-assembly of clay nano-platelets is governed by parameters such as clay particle concentration, ionic strength and temperature. This also illustrates that clay nano-lamella can be exfoliated into single lamella just like graphene. The clay platelets in this case are 1 nm thick, and their lateral dimension is about 1 micron.*

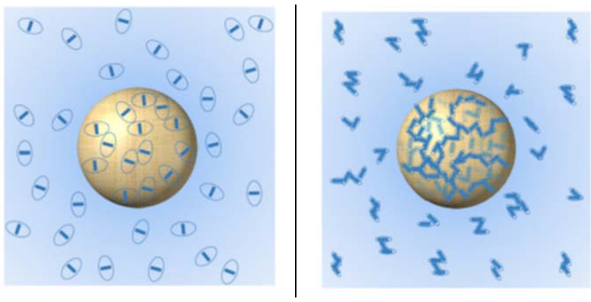

Figure 4 b): *From Ref. 1: Schematic (not to scale) representation of clay particle structure on an oil drop in water, without salt (left), and with salt (right), respectively. For the system without salt, a repulsive "Wigner" colloidal glass is formed at the interface. For the system with salt, a particle network is formed at the interface, leading to a gel state. In the schematic representation, each thick line represents a Laponite clay nano-disk, while the ellipsoids around them represent the range of electrostatic repulsions.*

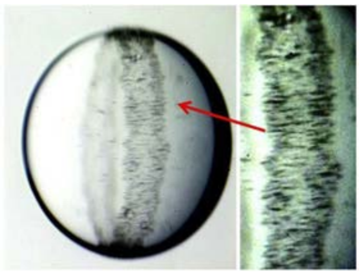

Figure 5 a): *From Ref. 4:* Microfluidic o*il droplet with clay particles assembled into a ribbon like structure droplet surface by externally driven electro-hydrodynamic flow.*

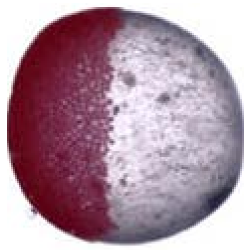

Figure 5 b): *From Ref. 3: Janus capsule produced in a two-step electro-process: Electro-hydrodynamics followed by electro-coalescence. One hemisphere of the capsule is made by a clay particle film (light grey), and the other hemisphere by plastic polystyrene particles (red).*

The present activities in Laboratory for Soft and Complex Matter Studies go beyond the state-of-the-art illustrated above and will apply excellence and innovation in hitherto unexplored scientific territory in three main areas of materials science. The Laboratory collaborates with several top international research groups, and of particular importance here is the firm connection that we have established with the activities of Prof. Josef Breu at Inorganic Chemistry/University of Bayreuth in Germany, who is responsible for the world leading activity on synthesis of large volumes of clays with precise tuning of layer size and charge. This means that our Laboraory has unique access to samples for studies and further development.

We offer MSc projects within the following four areas of research::

- Advanced molecular sorption in nano-fluidic systems, where the objective is to establish a “catalogue of reference” for active fundamental molecular interaction (sorption or desorption) mechanisms at nano-confined clay surfaces. Here we put particular emphasis on capture of $CO_2$, methane ($CH_4$) or drug molecules. In this context clays represent lamellar nano-fluidic systems in general and are very good model systems as such. At the same time clay are unique in the area of molecular capture due do their large effective surface area with more than 1000 square kilometers of effective surface area contained in 1 cubic meter, coupled to their tunable surface charge (order of magnitude 1 electron charge per square nm). “Hot” relevance here is for capturing and sequestration of green-house gases such as $CO_2$ or methane, for drug delivery by means of clays etc. Our group has already a considerable track record in studies of the nano-fluidics of $H_2O$ and $CO_2$, as well as in drug capture, and we wish to develop this further.
- Mass- or heat- transport in coupled nano-fluidic and micro-fluidic systems, where the objective is to model and tune properties of clay-derived self-assembled nanostructured complex materials. Fundamental phenomena to be addressed here are related to anomalous diffusion of molecules through designed microfluidic clay based systems coupled with nano-fluidic sorption mechanisms. In this context clays serve as designable model systems for coupled nano-fluidic and micro-fluidic flow. We will extend ongoing activities in our group by including clay based scaffolds fabricated using the non-invasive methods recently developed by us in Refs. 3,4 to produce hollow materials assembled from multiple capsules. In this case we will develop electromagnetic microfluidics. “Hot” areas of relevance are nuclear waste storage and pollution containment, physicochemical mechanisms of oil-recovery, materials properties related to plugging and safe abandonment of oil & gas wells, novel clay based artificial nacre-like complex materials, nano-clay-nano-cellulose composite materials, clay based composites with anisotropic heat or mass transport properties or anisotropic mechanical properties etc.
- Electromagnetic properties of layered materials beyond graphene, where the objective is to control and subsequently study the basic electronic physical properties of quasi-two dimensional hetero-structures made from clay lamella and other types of layered materials, such as graphene, graphene oxide, biofilms etc. This is a two-fold activity, where we (i) will manually assemble clays and other lamellar materials into stacked hetero-structures using for example the NorFab facilities at NTNU and UiO, and (ii) functionalize the surfaces of clay platelets and other nano-lamellar materials (graphene, graphene oxide, biofilms) in order to facilitate directed self-assembly into stacked hetero-structures for studies and design of electronic properties. Low-temperature properties of clay based nano-layered systems are relevant for applications including clays in room temperature electronic and optical components. This is related to and will go beyond recent research internationally by other groups, where it has been demonstrated that clays may act as supercapacitors, or be included as in lithium batteries for prevention of overheating, etc.
- Active Matter inspired by Living Systems, where the objective is to investigate and model experimentally and theoretically how dynamic activated colloidal (such as clay) particle assemblies can be used to mimic common structures found in nature, such as bird, fish or insect flocking, or even human or traffic crowding behaviors. Active matter (https://en.wikipedia.org/wiki/Active_matter) is currently itself a very active area in soft matter statistical physics, and we will initiate student projects looking at active processing of novel soft materials structures based on natural materials such as clay, zeolite, cellulose, graphite, etc.