ESRF/SNBL REPORT

Proposal Code 01-02-877

The effect of polar walls and sample geometry on the self-organization of synthetic clay particles in water: WAXS studies.

Responsible for proposal/experiment: Jon Otto Fossum
Participants at the experiment: Fossum Jon Otto, Lindbo Hansen Elisabeth (main author of report), Hemmen Henrik, Rolseth Erlend Granbo, Knudsen Kenneth Dahl

This experiment (proposal code 01-02-877) was conducted at SNBL during 6 shifts from the 03th to the 05th of February, 2010. The samples studied were dispersions of the synthetic, platelet-shaped clay Na-fluorohectorite (NaFh), kept in either round 2 mm in diameter capillaries, or in flat 2 mm thick sample cells (rectangular cells). We have previously shown that dispersions of NaFh in water, due to the anisometric shape of the clay particles and their polydispersity in size, phase separate under the influence of gravity into several strata, of which some may be characterized as possessing liquid crystalline nematic order [1,2]. The aim of the current experiment was to study the effects that container geometry, walls and interfaces have on the ordering in the liquid crystalline state. Previous studies have shown that NaFh particles align with their platelet normals pointing towards the walls of polar glass sample containers [3] and towards phase interfaces [4]. In order to study the role of the polar, hydrophilic nature of the sample containers upon wall anchoring and order, some of the flat sample cells of the current experiment were treated with a silanization solution that rendered the walls hydrophobic.

At SNBL, the experiment was performed at a wavelength of 0.80 Å with a sample-to-detector distance of 343 mm and a beam spot of about 250 x 175 μm at the sample. User-supplied motors for x- and y-translations allowed for data collection along the symmetry axis of the capillaries and in fine-stepped vertical and horizontal scans (matrix scan) across the flat sample cells. At the end of the experiment, we also studied powder samples of NaFh and Li-fluorohectorite (LiFh), to address questions on sample purity and differences in water intercalation depending on the type of intercalated cation (Na or Li).

A typical 2D diffractogram recorded in a given point for one of the capillary samples, is depicted in Figure 1. In the figure one can observe a faint 001 peak close to the beam stop and an anisotropic ring corresponding to the 110,020 peaks before the diffuse scattering from water. Analysis of the vertical and matrix scans showed clear differences between hydrophilic and hydrophobic walls, for instance, the nematic phase occupies a larger volume fraction of the sample in silanized containers. In order to study the wall effects observed in the differences in azimuthal asymmetry of the 110,020 ring, we fitted a Maier-Saupe distribution to this ring according to the procedure outlined in [5]. The fitting procedure allows for the calculation of a nematic order parameter S2 for each recorded diffractogram. This parameter characterizes the degree of orientational ordering of the NaFh particles present in the scattering volume. The order parameter, as calculated from the 110,020 scattering, reaches values as high as around 0.8. Figure 2 shows the order parameter mappings obtained for flat non-silanized (left) and silanized (right) sample cells.

The capillaries samples employed in the experiment undergone some degree of evaporation as evidenced by the scattering patterns; hence, they cannot be directly compared with samples in rectangular cells. But their study prove fruitful since it allowed us to re-think future experiments using capillaries and also because the collected data was used to complement another experiment on the effects of increasing particle concentration, namely experiment 01-02-874. Indeed, results from the current experiment and from experiment 01-02-874 can be found in our report from the latter, entitled *Guided self-assembly of synthetic clay particles in saline water: order induced by particles aligning to the water-air surface. WAXS studies.*

Furthermore, integration of the scattered x-rays revealed that the silanized rectangular cell had less scatterers than the non-treated cells, this observation together with the above result regarding the nematic phase occupying a larger volume in hydrophibic cells leads to the conclusion that the nematic phase formed inside treated walls presents a lower density of scatterers in the scattering volume. In addition, the integrations revealed that the rectangular cell with hydrophobic walls presented more particles in homogeneous alignment, i.e. the platelet normals pointing away from the walls, in the nematic sol phase. This observation suggests that without the hydrophilic walls the particles align towards the phase interface, which can be seen for the nematic sol phase owing to its shortness and is in agreement with previous studies [4]. However, the same is not true throughout the nematic gel phase contained in hydrophobic walls and further studies are needed of its bulk. Since the current experiment showed different scattering behaviour for the different wall types in the different phases at lower angles of scattering, a future experiment should include a more detailed inspection of the scattering at small angle.

This first experiment using treated walls brought a number of interesting results; however it generated a number of questions and ideas for follow-up experiments. For instance, future experiments should compare similar samples, in terms of sample volume and lack of evaporation, in different geometries, i.e. rectangular cells compared to capillaries, including silanized capillaries. And the silanized capillary should be studied at different angles (around its axis of symmetry) at different heights. Also, the matrix scans provided further insight regarding wall effects on the nematic phase, however they were time consuming and should be avoided in the future; indeed, the results from the matrix scans of current experiment should be used in order to define the regions of interest in future studies. Moreover, rectangular cells should be built utilizing the 4 walls in order to answer questions regarding the alignment of the particles, for example a cell should be built presenting hydrophilic lateral walls but with hydrophobic walls in the beam path.

[1] Fossum, J O, et al. Observations of orientational ordering in aqueous suspensions of a nano-layered silicate. Energy, 30, pp. 873-883, (2004).

[2] D. M. Fonseca, Y. Méheust, J. O. Fossum, K. D. Knudsen and K. P. S. Parmar, Phase diagram of polydisperse Na-fluorohectorite-water suspensions: A synchrotron small angle x-ray scattering study, Phys. Rev. E 79, 021402 (2009).

[3] E. N. de Azevedo, M. Engelsberg, J. O. Fossum, and R. E. de Souza, Anisotropic Water Diffusion in Nematic Self-Assemblies of Clay Nanoplatelets Suspended in Water, Langmuir 23, 5100 (2007).

[4] H. Hemmen, N. I. Ringdal, E. N. De Azevedo, M. Engelsberg, E. L. Hansen, Y. Méheust, J. O. Fossum and K. D. Knudsen, The Isotropic-Nematic Interface in Suspensions of Na-Fluorohectorite Synthetic Clay, Langmuir 25(21), 12507 (2009).

[5] Y. Meheust, K.D. Knudsen and J.O. Fossum. Inferring orientation distributions in anisotropic powders of nano-layered crystallites from a single two-dimensional WAXS image, J.Appl.Cryst. 39, 661 (2006).

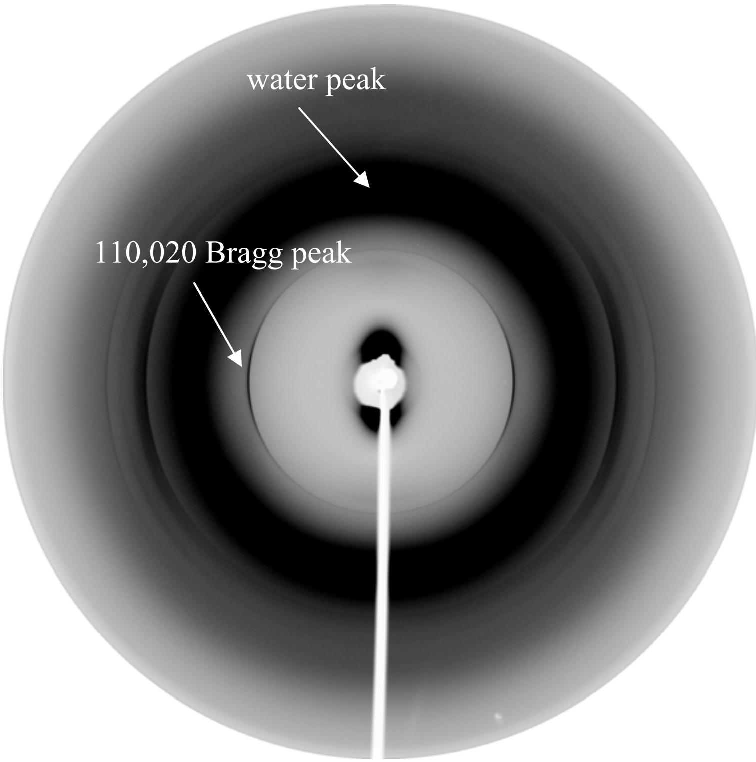

Figure 1: Raw 2D diffractogram recorded for a sample of NaFh dispersed in water. The diffuse scattering from water indicated on the figure was subtracted before the Bragg ring indicated by its hkl indices on the diffractogram, was analyzed with regards to azimuthal anisotropy.

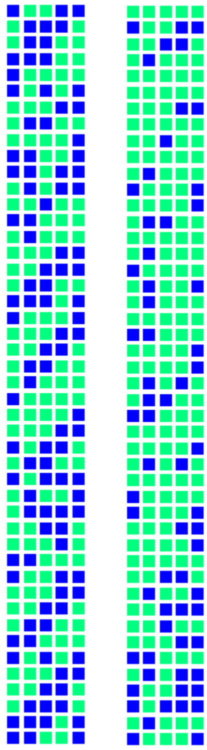

Figure 2. Matrix scans of rectangular cells. Green points: nematic order parameter 0.15<S2<0.8. Blue points: particle orientation does not allow S2 calculation.
Left: cell with hydrophilic walls.
Right: cell with hydrophobic walls.