ESRF/SNBL REPORT

Proposal Code 01-02-874

Guided self-assembly of synthetic clay particles in saline water: order induced by particles aligning to the water-air surface. WAXS studies.

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This experiment (proposal code 01-02-874) on nematic ordering in dispersions of Na-fluorohectorite induced by evaporation was conducted at SNBL during 9 shifts from the 25th to the 28th of November, 2009. The samples studied were dispersions of Na-fluorohectorite in saline water, that had undegone a slow concentration increase over the course of several weeks/months due to partial evaporation of the sample water. Na-fluorohectorite is a syntethic clay made up of plate-shaped, lamellar particles with lateral dimensions in the μm range and thicknesses varying from around 10 to 100 nm. An image of one of the studied samples is shown in Figure 1, where the sample was photographed between crossed polarizers before being brought to SNBL. Birefringence (bright areas) indicates that the sample is optically anisotropic. This anisotropy originates from the ordering of the highly anisometric clay particles, and the aim of the experiment at SNBL was to quantify the degree of order corresponding to the different birefringence colors by analyzing the anisotropy of the wide-angle x-ray scattering (WAXS) recorded from these samples at varying distances from the dispersion-air interface.

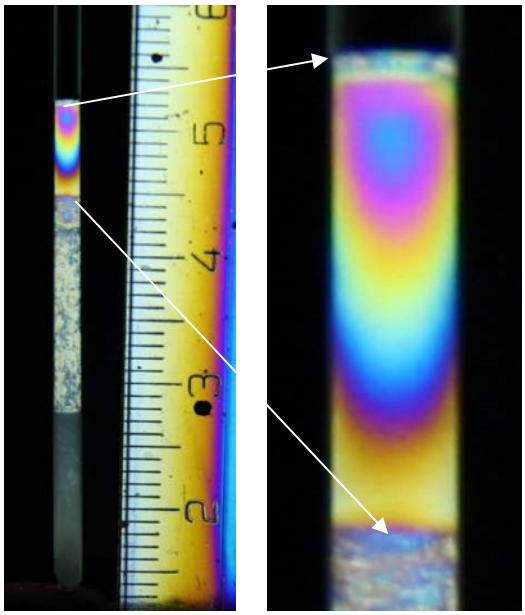

Figure 1: A sample of initially 3 wt % Na-fluorohectorite in saline solution of 1 mM NaCl after slow evaporation. The 2 mm in diameter capillary was photographed between polarizers crossed with their transmission axes oriented at 45 degrees with the symmetry axis of the capillary. The colors, going from the dispersion-air interface downwards, indicate a high degree of order that decays upon moving downwards in the sample. The aim of the experiment was to quantify this order as a function of distance from the interface by analyzing the anisotropy of the WAXS scattering from the sample. The colorful ordered domain at the top of the capillary was produced by a slow concentration increase due to water evaporation. The ordered domains below were already present before evaporation, and were produced by a gravity-induced concentration profile [1,2].

The experiment at SNBL was performed at a wavelength of 0.79 Å with a sample-to-detector distance of 349 mm and a beam spot of about 250 x 200 μm at the sample. User-supplied motors for x- and y-translations allowed for data collection along the symmetry axis of the

capillaries in fine vertical steps of 0.33 mm. A typical 2D diffractogram recorded close to the dispersion-air interface, is shown in figure 2. The most notable features are the anisotropy of the scattering and the missing 001 Bragg peak, which originates from the lamellar nature of Na-fluorohectorite particles [1]. The lack of 001 Bragg scattering indicates that the particles forming the colourful evaporation-induced phase of Figure 1 exist as single (or very few) clay sheets and not as lamellar stacks.

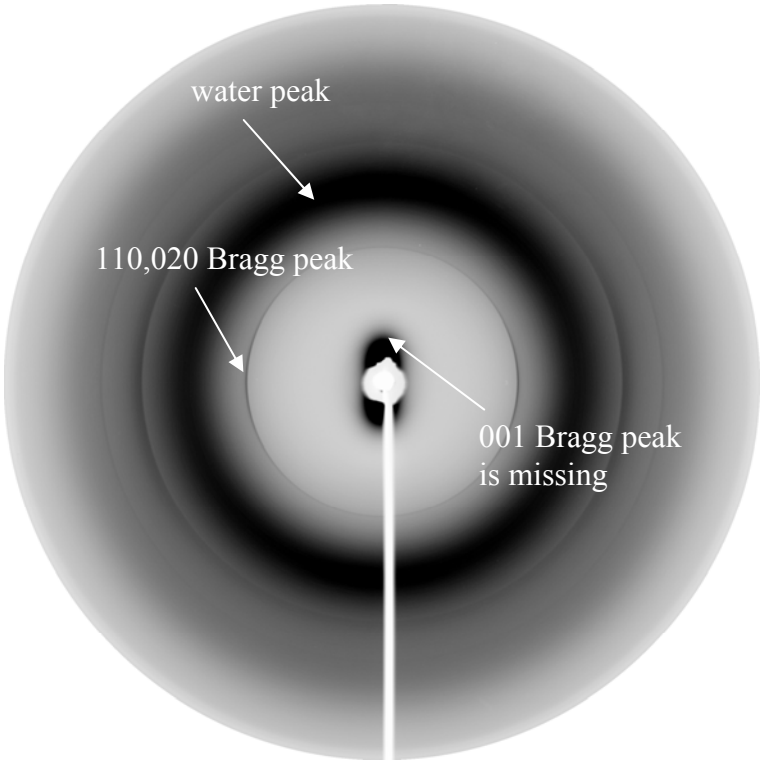

Figure 2: Raw 2D diffractogram recorded at SNBL 1 mm below the dispersion-air interface. The diffuse scattering from water indicated on the figure was subtracted before the Bragg ring indicated by its hkl indices on the diffractogram, was analyzed with regards to azimuthal anisotropy.

The anisotropy of the 110,020 Bragg ring was analyzed by fitting the ring intensity versus azimuthal angle to a Maier-Saupe distribution, from which could be extracted an order parameter S2 according to a slighly modified version of the procedure described in [3]. The result for the sample depicted in Figure 1 is shown in Figure 3 (where data collected on the same sample at SNBL in February 2009 for experiment 01-02-877 are also included). It is seen that the calculated order parameter varies with distance from the dispersion-air interface in a manner which reproducibly follows the birefringence colors, as expected. Close to the dispersion-air interface the order parameter reaches quite high values of between 0.7 and 0.8, on a scale where 1 indicates perfect orientational order. Figure 4 depicts the order parameter found for another sample, where again the order reaches high values close to 0.8. These data, along with small-angle x-ray scattering (SAXS) data from DUBBLE, show that evaporation of initially isotropic phases of anisometric clay particles in water leads to high degrees of nematic order, where the local order as a function of distance from the dispersion-air interface follows closely a concentration profile that decays as one moves away from the interface.

[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] 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).

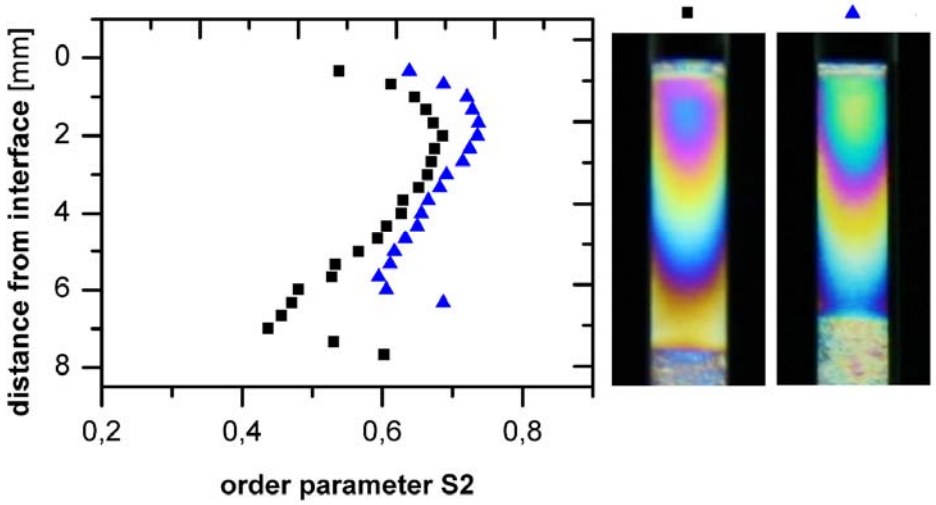

Figure 3: Calculated values for the nemtic order parameter (S2) as a function of distance from the interface for the sample depicted to the right at two different times. Black squares represent the sample as imaged at SNBL in Nov. 2009, blue upturned triangles the sample as imaged at SNBL in Feb. 2010. It is seen that the evaporation induced concentration increase between Nov. and Feb. experiments, has led to an overall increase in order.

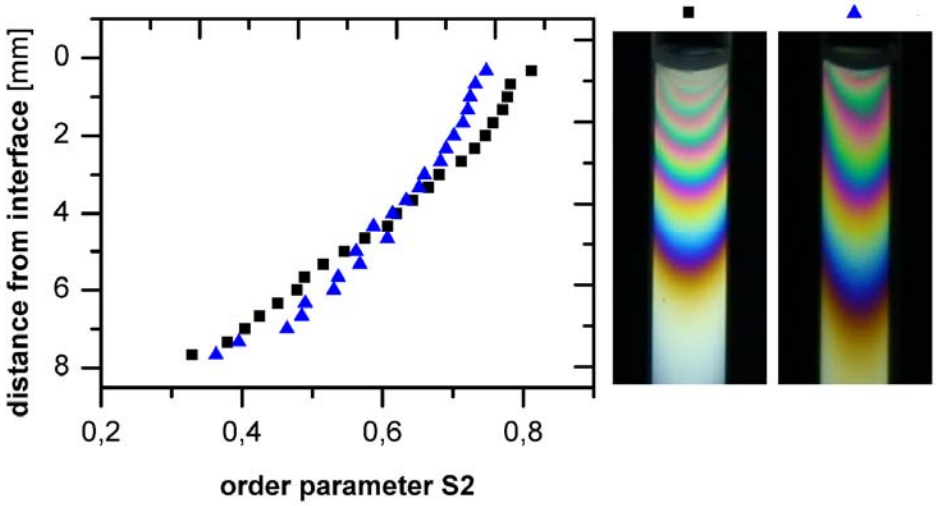

Figure 4: Calculated values for the nemtic order parameter (S2) as a function of distance from the interface for the sample depicted to the right at two different times. Black squares represent the sample as imaged at SNBL in Nov. 2009, blue upturned triangles the sample as imaged at SNBL in Feb. 2010. This sample was sealed after the Nov. experiment, so no further evaporation could occur. It is seen that between Nov. and Feb. experiments, there has been a relaxation in the steepness of the slope curve of S2 versus distance. This can be explained by considering that the reason for self-organized ordering of anisometric particles in dispersion is the local concentration of particles. The initial evaporation causes a concetration gradient, where the highest particle concentrations occur closes to the dispersion-air interface. After evaporation ceases, slow equilibration towards a uniform particle concentration can take place.