DUBBLE	**Experiment title: The transition from a columnar to a smectic liquid crystal phase in suspensions of polydisperse colloidal platelets**	**Experiment number**: **26-02-111**
Beamline: BM-26B	**Date(s) of experiment**: From: 06-03-2002 To: 09-03-2002	**Date of report**: 30 - 09 - 2002
Shifts: 9	**Local contact(s)**: Igor Dolbnya, DUBBLE, NWO/ESRF	

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In our experiments, we have used sterically stabilised gibbsite (γ-$Al(OH)_3$) platelets in organic solvent. Dispersions of this kind of particles are known to display both the isotropic (I) to nematic (N) and the nematic to columnar (C) phase transition, due to their anisotropy (diameter = 200 ± 30 nm, thickness = 13 ± 4 nm). A sample was brought at a volume fraction of about 40% (in the N-C biphasic regime), after which two glass capillaries (0.3 x 3 x 50 mm^3) were filled with the sample. In the solution, non-adsorbing polymer (PDMS, molecular weight M_w = 423 kg/mol, concentration 0.2 g/l) was present, promoting the formation of oriented single-domains. After 1 week, N-C phase separation was complete. At this point, the capillaries were subjected to SAXS experiments at DUBBLE, using an X-ray beam with a photon energy of 10 keV. Scattering patterns were obtained using a gas-filled detector at a distance of 8 metres from the sample. By placing the beam stop at the corner of the detector, access to a q range of about 0.025 to 0.8 nm^{-1} was achieved.

Figure 1 shows two examples of typical scattering patterns of the nematic phase. In fig. 1A the scattering presumably originates from two domains with different orientation.
We were also able to measure scattering patterns from single-domain regions (fig. 1B). The features in the scattering at higher q values (typically 0.3 to 0.6 nm^{-1}) originate from the shortest interparticle distances d, in the direction normal to the platelets. The pronounced directionality (especially in fig. 1B) reflects a high degree of orientational order in the irradiated part of the sample. A second-order maximum of the structure factor can be also seen in fig. 1B.

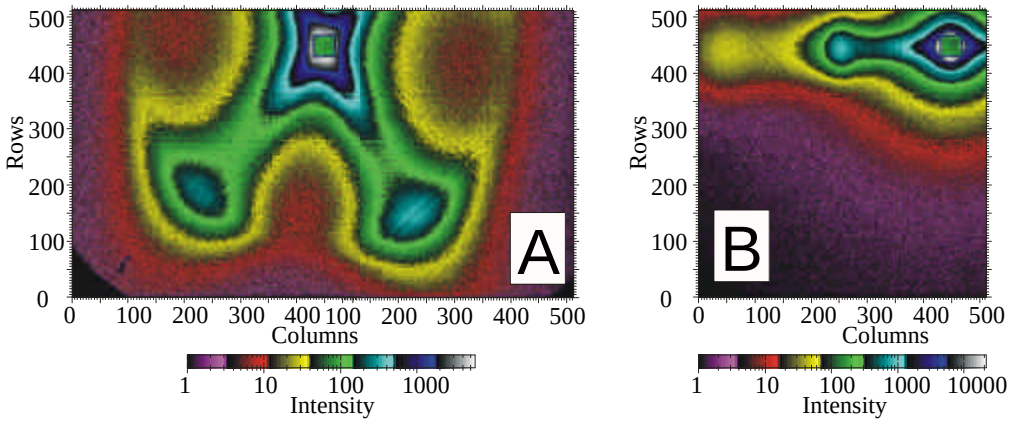

Figure 1 - Scattering patterns of the nematic phase, at two different locations in the sample. In the first case (A) the X-ray beam illuminates two differently oriented domains; in the second (B) only one. (A) was obtained by joining two scattering patterns with different detector positions (shifted horizontally).

By scanning the samples vertically, we have observed a pronounced effect of gravitational compression on the interparticle separation d in the (presumed) columnar liquid crystalline phase, as depicted in fig. 2. By moving downwards through the sample (fig. 2A through 2D), the position of the maximum q_{max} in the scattered intensity shifts to higher q values. This shift reflects a decrease of the interparticle separation distance due to an increasing osmotic pressure. In figure 3 we show the dependence of d on the height in the sample y (with the y axis pointing downwards),

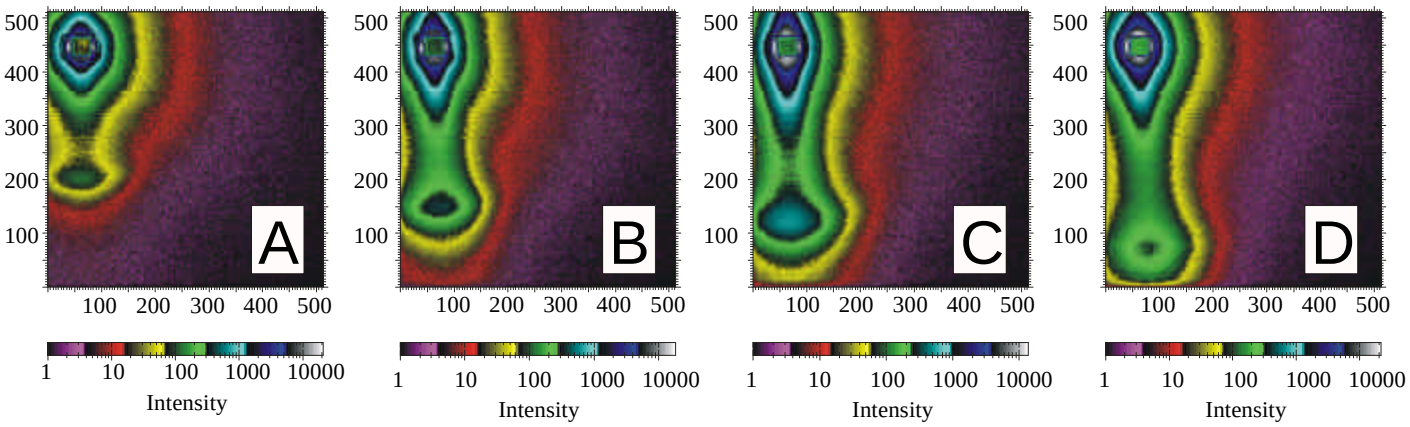

Figure 2 - Scattering patterns obtained in the columnar phase at different height. The positions y in the sample are: y = 51.5 mm (A), 54 mm (B), 56 mm (C) and 60 mm (D).

where d is calculated from the scattering data as $d = 2\pi/q_{max}$. Note that in this sample the orientational correlation (vertical columns of horizontally-oriented platelets) persists over an extraordinary long distance of nearly 1 centimetre. The height dependant interparticle distance $d(y)$ can be analysed using a simple osmotic pressure model. The gravitational force experienced by the colloidal platelets should be compensated by the gradient of their osmotic pressure Π. Starting from mechanical equilibrium and using a Taylor expansion, it can be shown that

$$\frac{\partial \Pi}{\partial n}\frac{\partial n}{\partial y} = gnm^*, \tag{1}$$

where n is the number density of platelets, m^* is their excess mass (relative to the mass of the equivalent volume of solvent) and g is gravitational acceleration. We assume that the osmotic pressure can be written as

$$\Pi(y) = \frac{kT}{A\,(d(y) - d_0)}, \tag{2}$$

where kT is the thermal energy, A is area per particle and d_0 is the minimum distance between the plates (at infinite pressure). Moreover, we assume that A is virtually independent of the height y. This assumptions can be shown to lead to the following relation between the platelets separation distances d_1 and d_2 at two different heights y_1 and y_2

$$\ln\left(\frac{d_2 - d_0}{d_1 - d_0}\right) + \frac{(d_2 - d_1)d_0}{(d_1 - d_0)(d_2 - d_0)} = \frac{y_1 - y_2}{x}, \tag{3}$$

where $\xi = kT / gm^*$ is the gravitational length. The solid line in figure 3 presents a fit of Eq. 3 through the data points $d(y)$ as obtained from the SAXS experiment. The best fit is obtained with d_0 = 9.2 nm and ξ = 3 mm, which are within a reasonable range for our system.

In conclusion, we have been able to identify oriented single domains in the nematic phase. Furthermore, we observed gravitational compression in the more highly ordered phase. The height dependence can be fitted quite reasonably using a simple osmotic pressure model. Yet, from the scattering data we could not explicitly determine whether this denser phase was smectic or columnar.

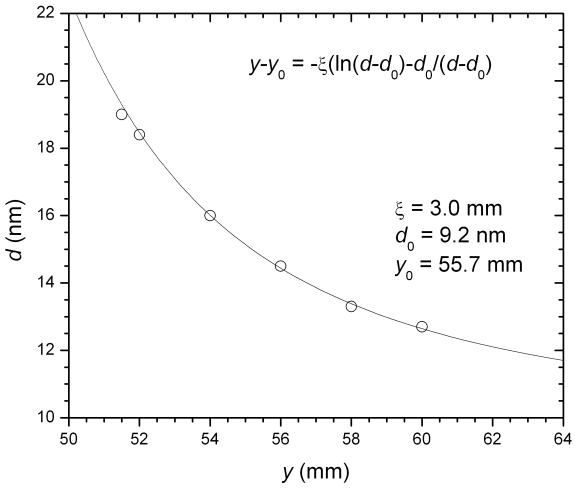

Figure 3 - Interparticle separation distance d as a function of vertical position y in the sample, as determined experimentally (**?**) and by fitting Eq. 3 to the data points.