



	Experiment title: Full 3D structure characterization of Liquid Crystal Phases in Dispersions of Polydisperse Colloids	Experiment number: 26-02-622
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Report:

Dispersions of board-like goethite ($\alpha\text{-FeOOH}$) particles display very rich phase behaviour [1-2], including nematic, smectic and columnar phases. The board-like particles have three distinct axes: the length-, width- and thickness-axis ($L > W > T$, respectively). For very specific particle dimensions, i.e. $L/W = W/T$, the particles can form a *biaxial* nematic (N_B) phase. In previous experiments performed at DUBBLE it was found [3] that a system of particles where L/W is slightly larger than W/T spontaneously formed a N_B phase. This was explained by the high (~25%) polydispersity, which stabilizes the N_B phase [4]. Goethite particles also have peculiar and interesting magnetic properties. They possess a permanent magnetic moment along their L -axis combined with an induced moment with an easy axis along the L -axis. Therefore the particles align their L -axis parallel to a weak magnetic field but reorient to align their T -axis parallel to a strong magnetic field. A weak magnetic field is often [3] used to align the nematic phase parallel and perpendicular to the x-ray beam to study the exact structure and to confirm biaxiality of the nematic phase.

During this experiment we studied the actual influence of the magnetic field on the N_B phase. Figure 1 shows SAXS patterns taken in a spontaneously formed N_B phase. The magnetic field was applied parallel to the direction of the x-ray beam. The pattern taken at 3 mT is anisotropic with reflections in perpendicular directions originating from the W - and T -dimensions of the particles, characteristic of N_B phase. Upon increasing the magnetic field strength, the SAXS pattern appears less anisotropic (40 mT). After increasing the magnetic field even further, to 80 and 120 mT respectively, the SAXS patterns lose all anisotropy and are now completely isotropic. Only one reflection is observed corresponding to correlations of both W and T . This indicates that the magnetic field has completely transformed the original N_B phase into a regular uniaxial phase (schematic drawings figure 1).

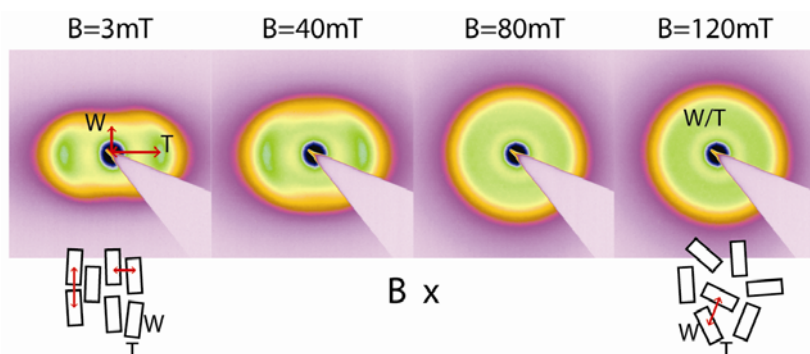


Figure 1. (top) SAXS patterns of a nematic goethite dispersion with their main L -axis oriented along the beam: an increasing magnetic field B along the beam gives a complete transformation from a biaxial to a uniaxial nematic phase; (bottom) schematic particle configurations and typical correlation distances (indicated by arrows).

These observations were confirmed by the SAXS patterns which were taken with the field directed *perpendicular* to the x-ray beam. The SAXS pattern taken at 10mT presented in figure 2a shows a reflection at $Q \approx 0.083 \text{ nm}^{-1}$, originating from the T dimension of the particles. Upon increasing the field, it was found that this reflection shifts to a smaller Q -value, corresponding to the W & T dimensions of the particles. This means that the particles can now freely rotate along their long axis, which is characteristic of the uniaxial nematic phase.

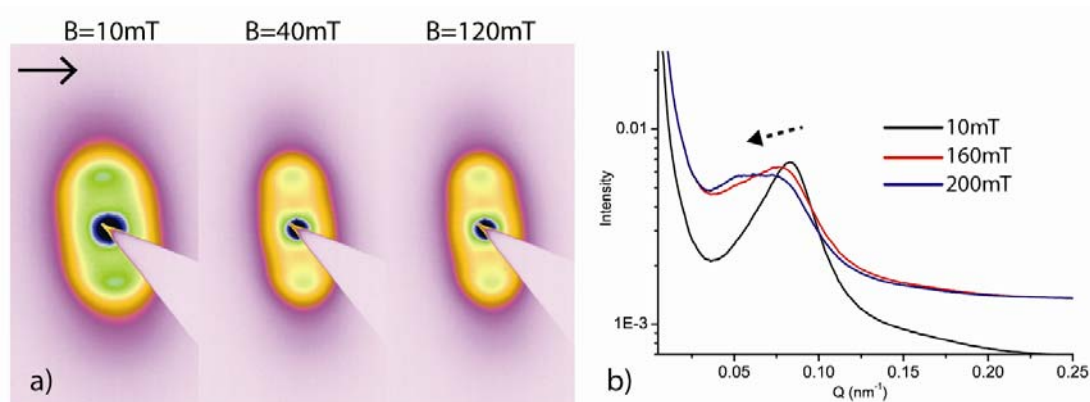


Figure 2. a) SAXS patterns of a nematic goethite dispersion with their L -axis oriented perpendicular to the beam. With increasing magnetic field the peak shifts from a Q -value corresponding to the correlation of the T -axis of the particles (N_B phase) to lower Q -values (b) originating from correlations from both the W & T -axis representative of the uniaxial nematic phase.

We suspect that the interaction of the permanent magnetic moment along the L -axis with the magnetic field substantially narrows the orientation distribution and releases more space for the particles to rotate freely along this axis, thereby increasing the orientational entropy which transforms the system into a uniaxial nematic. At the moment we are performing theoretical work to confirm this mechanism.

Recently, theoretical work predicted [5] that the addition of a depletant to a system of slightly elongated board-like particles can induce the formation of stable N_B phase. We therefore prepared several samples of goethite dispersions to which a depletant was added and we studied the biaxiality of the formed liquid crystal phases at DUBBLE. We found that the depletant induces the formation of the *smectic* phase. The systems only displayed an isotropic-smectic phase separation; the nematic phase was not observed. We again used a magnetic field to align the smectic phases to check if the particles within the smectic layers were biaxially ordered. We found indications that the formed smectic phases indeed are biaxial. However, due to the addition of depletant the systems were extremely dense and viscous and it was therefore impossible to properly reorient the smectic phase and thus to be conclusive about the biaxiality of the smectic phase.

Additionally, we also studied structure formation of gibbsite ($\gamma\text{-Al}(\text{OH})_3$) hexagonal platelets in dispersion confined in wedge-shaped cells. These platelets display an isotropic - nematic - columnar phase separation. In previous experiments at DUBBLE [6] we often found the presence of orientational fluctuations in the hexagonal columnar liquid crystal phase, e.g. decoupling of the average platelet orientation from the column axis as well as column undulations. We are currently processing the obtained data but preliminary results show that confinement suppresses these orientational fluctuations and hence induces the formation of well ordered columnar liquid crystals.

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