ESRF	**Experiment title:** **Flow induced orientation of small magnets in external magnetic fields**	**Experiment number:** SC 3496
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Report:

The aim of experiment SC-3496 was to investigate the interplay between flow-induced and magnetic field-induced (particle-particle) interactions in microfluidic devices. The experiments were performed on iron oxide nanoparticle solutions. The iron oxide nanoparticles differ in size and shape (spheres/cubes between 6-12nm radius). As microfluidic setup, a microchannel made of UV-curable polymer (NOA81, Nordland Optical Adhesives) with a width of 500 µm and a height of 100 µm was used. This microchannel featured a tapering which narrows down hyperbolically to 50 µm. To scan the orientation and self-assembly of nanocubes the channel was mapped in an array of 7 points along the tapered microchannel with each 3 points across its width. The sample flow rates and the magnetic field strengths were varied between 0-1000 µl/h and 0-1 T respectively. We found that in the investigated concentration range (up to 27 wt% in toluene) only cubic nanoparticles over 6-7 nm radius in size, which were stabilized with a perfect cystalline oleic acid layer, self-assemle to superlattices (with dimensions up to hundreds of nm) in external magnetic fields. This self-assemly of superlattices also requires a concentration of ≥10 wt%. Without flow these superlattices could be described as long chains, 2D-sheets and 3D cuboids. Under these conditions, each of these superstructures posesses a simple cubic (sc) lattice that built up from nanocubes.

The self-assembly of the nanocubes to superstructures and their orientational behavior changed upon the application of flow. Under laminar flow conditions a self-assembled structure was hard to produce without a magnetic field. If at all, the nanocubes preferred a face-center cubic assembly (fcc) in contrast to the sc lattice of the superstructure without flow. Under flow the ordering was best in the center of the device's tapering, where the highest shear and elongation forces exist. For a 10 wt% solution and a flow rate of 100 µl/h a pure ABCABC stacking was observed at this point. While no magnetic field is applied, the scattering patterns only showed the initial particles, mainly nanocubes, before and after the tapering.

By applying a strong external magnetic field, the formation of ordered superstructures with fcc arrangement could be stimulated. We found self-assembly of the nanocubes, even under conditions where no ordering was obtained at pure low flow conditions (without magnetic field). These superstructures are formed before and after the tapering, but at longer distances they disassembled. We conclude that the superstructure formation effect is enhanced in magnetic fields, probably due to dipolar coulpling.

The preliminary results obtained for laminar flow conditions and in presence of an external magnet field are shown exemplarily in fig. 1. At longer distances, away from the tapering center, no ordered superstructures have not been found. Shortly before and after the tapering the scans across the width of the channel revealed fcc twinning with similar ratios. Directly in the center of the tapering, a pure fcc phase (ABCABC stacking) was observed. This fact is attributed to the high shear rate at this position. The order of the formed superstructures disappeared with decreasing shear forces on the sample at longer channel distances. It seemed that the superstructures are disassembeled into nanocubes again.

Further measurements yielded that higher flow rates hinder the formation of structures even if the magnetic field is applied. In this case single nanocubes dominate the sample.

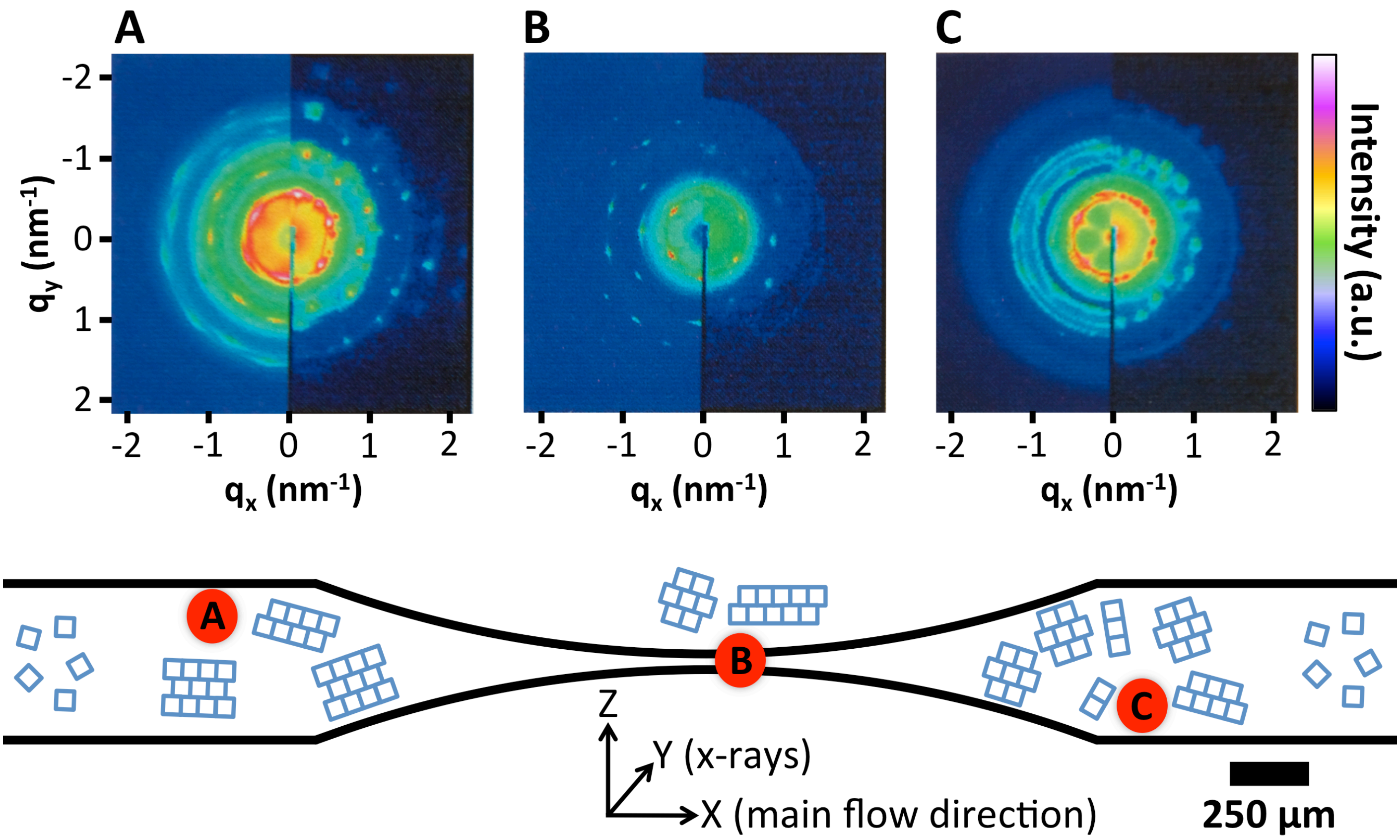

Fig. 1: Top: Experimental (right half) and theoretical (left half) SAXS patterns of an iron oxide suspension (10 wt%). The flow rate was set to 100 µl/h. The external field strength was 0.4 T (parallel to the x-ray beam). The red dots show the measurment positions in the microfluidic channel (spot size not to scale). The theoretical intensities are based on a mixture of fcc and lamellar ordered superstructures. The superstructures are built up of self-assembled nanocubes. The reflex at q = ca. 1.45 nm^{-1} steems from the lamellar assembled oleic acid layers between the assembeld nanoparticles. Bottom: Illustration of the dependence between formation and orientation of the self-assembled superstructures at the positions within the microchannel.

The results lead to following preliminary picture: The starting solutions mainly consist of single nanocubes, which can self-assembe under certain conditions. Without magnetic field, the ordering was reached around the tapering, indicating that a critical strain must be reached for well ordered (fcc) superstructures. In presence of external magnetic field, the kind of lattice structure is mainly influenced by the flow conditions. This effect is most pronounced around the tapering where we observed: sc for no flow, fcc at low/intermediate flow and no order at very high flow.

The interplay between flow characteristics and magnetism is not easy to understand in detail. The external magnetic field interacts with the internal magnetic field of the nanocubes and superstructures, leading to a better preordering of the building units (nanocubes) of the superstructures. In a simple description, all superstructueres consist of dipolar chains in a suited spatial orientation. Under a critical value of shear and elongation force, the (dipolar) coupling between the chains seems not to be strong enough which leads to the disassembly of the chains/superstructures.

The evaluation is still in progress. Therefore, we can not rule out other ordering mechanisms.