Experimental report

09/02/2016

Proposal: **5-53-261** **Council:** 4/2015

Title: Polarised SANS measurements on hybrid ferrofluidic dispersions

Research area: Physics

This proposal is a new proposal

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Samples: Ni nanorods
Fe2O3 nanospindles
CoFe2O4 nanospheres

Instrument	Requested days	Allocated days	From	To
D33	2	2	07/12/2015	09/12/2015

Abstract:

Viscoelastic and magnetoviscous phenomena in ferrofluids are closely related to their internal microstructure. For sufficiently strong magnetic fields, chain-like aggregates may form in highly concentrated ferrofluids, which goes together with an increase of viscosity, the so-called magnetoviscous effect. In addition, shear-induced degradation of the field-induced structures is observed, which apparently is related to strong shear thinning behaviour.
A promising approach towards improved, shear-resistant magnetoviscous material is the integration of elongated magnetic nanoparticle into conventional ferrofluid (consisting of magnetic nanospheres). Polarised SANS of such hybrid ferrofluids will provide the necessary information to reveal the reorientation and ordering of field-induced structures.
The inter-particle correlations will be studied on a series of multi-component, hybrid ferrofluids with different concentration under the influence of an external magnetic field. The proposed experiment will give the opportunity to understand the connection between the microstructure mechanisms and magnetoviscous behavior of hybrid ferrofluidic dispersions.

Polarised SANS measurements on hybrid ferrofluidic dispersions

Magnetic fluids are functional materials with attractive, potential technological application [1]. For instance, conventional ferrofluids, *i.e.* dispersions of spheroidal magnetic nanoparticles stabilized in a carrier liquid, exhibit astonishing field-induced phenomena based on particle rearrangement and organization [2]. With increasing particle volume fraction, magnetic dipolar interactions leads to the formation of various nanoparticle arrangements (chains, hexagonal columns), which was confirmed by small-angle neutron scattering (SANS) techniques [3]. In a modest stabilizing magnetic field, these reversible structural changes give rise to an increase of viscosity. With the goal to enhance macroscopic (magnetic, dynamic) behavior, conventional ferrofluids consisting of spherical nanoparticles are doped with elongated magnetic nanoparticles, producing a so-called hybrid ferrofluidic dispersion. Our long term objective is to study the correlation of their microstructure with the macroscopic properties of hybrid ferrofluidic dispersions.

In order to perform a structure analysis of the base material for our hybrid ferrofluids, polarised SANS measurements were carried out on D33 at room temperature and ambient atmosphere, using 6 Å neutron wavelength and a horizontal magnetic field of $\leq$ 1.2 T. The measurements were performed on four pure systems (two cobalt ferrite nanospheres, maghemite nanospheres, and hematite spindles) dispersed in d_8-toluene and D_2O solvent, respectively. As an example, SANS results in absolute scale for toluene dispersion of cobalt ferrite with mean particle diameter of 11.4(1) nm and log-normal distribution size of σ_{log} = 5.4% (from SAXS measurements) at an applied field of 1.2 T are presented in *Fig. 1a-e*.

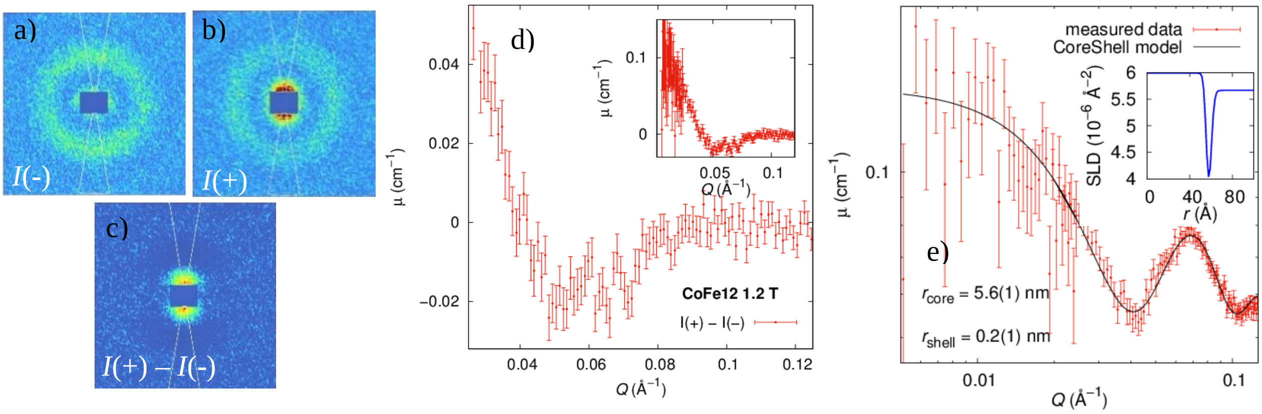

Fig. 1: Polarized 2D-SANS cross sections a) *I*(-) and b) *I*(+) of cobalt ferrite nanoparticles in d_8-toluene at *B* = 1.2 T. c) Variation of *I*(-) and *I*(+) with 20° sectors used for integration. d) Nuclear-magnetic cross term derived from the sector average of *I*(+) – *I*(-). e) Pure nuclear SANS of spherical cobalt ferrite nanoparticles with SLD profile as an inset.

It can be seen that by varying the incident beam polarization there is a clear variation between scattering cross sections *I*(+) and *I*(-) due to nuclear-magnetic interference (*Fig. 1c, d*). The pure nuclear form factor was determined by means of sectors with opening angle of ±10° along the applied field direction. The obtained pure nuclear

scattering cross-section presented in *Fig. 1e* has been refined according to a spherical core-shell form factor. With fixed lognormal size distribution, the radius of the inorganic particle core of r_{core} = 5.6(1) nm are in good agreement with the SAXS results. Additionally, an oleic acid ligand shell thickness of r_{shell} = 0.2(1) nm could be resolved. The corresponding scattering length density profile for the cobalt ferrite nanoparticle dispersion in d_8-toluene is presented as inset in *Fig. 1e.*
Since the elongated magnetic hematite nanoparticles (spindles) - which will be incorporated in the hybrid ferrofluid - are stabilized in water, all spherical magnetic nanoparticles (cobalt ferrite, maghemite) were transferred by ligand exchange synthesis from toluene solution into water. The phase transfer does not affect the particle size nor the size distribution, which was verified by SAXS. However for neutrons, one observes a magnetic contrast in maghemite and cobalt ferrite spherical nanoparticles in D_2O, but there exists hardly any visible nuclear scattering of nanoparticles which is caused by contrast matching of cobalt ferrite (SLD = $5.989 \cdot 10^{-6}$ Å^{-2}) and maghemite (SLD = $6.711 \cdot 10^{-6}$ Å^{-2}) nanoparticles with D_2O. In order to enhance the nuclear contrast for maghemite nanoparticles we have tried successfully a mixture of D_2O and H_2O (6:4) (*Fig. 3a-d*) and d_6-ethanol. Other possible polar solvents which can be used to further enhance the nuclear scattering contrast are d_4-acetic acid (SLD = $5.432 \cdot 10^{-6}$ Å^{-2}) and d_3-acetonitril (SLD = $4.899 \cdot 10^{-6}$ Å^{-2}). In contrast, Ni nanorods (SLD = $9.406 \cdot 10^{-6}$ Å^{-2}) [5] and hematite spindles (SLD = $7.258 \cdot 10^{-6}$ Å^{-2}) have a good contrast already in D_2O. In a follow-up experiment, we will investigate hybrid ferrofluid dispersions of spherical nanoparticles with different doping degrees of Ni nanorods and hematite spindles. The possibility for contrast variation study opens up the possibility to disentangle the scattering contributions of the individual constituents.

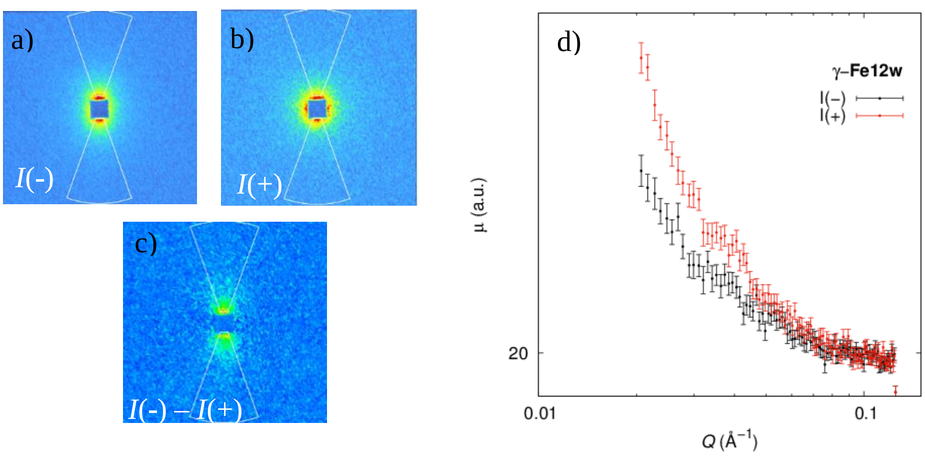

Fig. 3: Polarized 2D-SANS cross sections a) *I*(-) and b) *I*(+) of maghemite nanoparticles in mixture of D_2O:H_2O (6:4), at room temperature an applied magnetic field *B* = 1.2 T. c) Variation of *I*(-) and *I*(+) with 20° sectors used for integration. d) Corresponding radially averaged, polarised SANS cross section *I*(-) and *I*(+) at *B* = 1.2 T.

References

[1] S. Odenbach, 'Magnetoviscous Effects in Ferrofluids', Springer, Berlin, 2002.
[2] L. Pop, S. Odenbach, *J.Phys.: Condens. Matter* **18**, S2785 (2006).
[3] A. Wiedenmann *et al.*, *Phys. Rev. E* **68**, 031203 (2003).