Experimental report

21/11/2016

Proposal: **5-53-264** **Council:** 4/2016

Title: Structure of hybrid ferrofluidic dispersions by polarized SANS

Research area: Physics

This proposal is a continuation of 5-53-261

Main proposer: **Dominika ZAKUTNA**

Experimental team: Dominika ZAKUTNA
Maria Katharina HENTSCHEL
Dominique DRESEN

Local contacts: Dirk HONECKER

Samples: Ni nanorods
Fe2O3 nanospindles
CoFe2O4 nanospheres
Fe2O3 nanospheres

Instrument	Requested days	Allocated days	From	To
D33	4	4	09/06/2016	13/06/2016

Abstract:

With the aim to enhance the magnetic, optical, and dynamic properties, conventional ferrofluids (consisting of spherical magnetic nanoparticles - maghemite and cobalt ferrite) are doped with anisometric nanoparticles (hematite nanospindles and nickel nanorods) resulting in so-called hybrid ferrofluids. The main objective of this proposal is the detailed study of the structural and magnetic morphology of arrangements of spherical magnetic particles around elongated nanoparticles in hybrid ferrofluidic dispersions using polarized SANS (SANSPOL). Furthermore, we intend to investigate the reorientation behaviour of the aggregate system with respect to the elongated particle scaffold as function of the external magnetic field. These information on the microstructure evolution will give important information in order to explain the macroscopic behavior of hybrid ferrofluidic dispersions.

Polarised SANS measurements on hybrid ferrofluidic dispersions

With the aim to enhance the magnetic, optical, and dynamic properties, conventional ferrofluids (consisting of spherical NPs) are doped with anisometric NPs resulting in so-called hybrid ferrofluids. The change of the macroscopic behavior induced by an external magnetic field can be explained by the evolution of an anisotropically oriented, magnetic phase due to aggregate formation around elongated NPs. The main aim of our work is to study the *in-situ* structure formation including the orientational behavior of anisotropic structures as function of the applied magnetic field in order to elucidate the correlation of superstructure formation and ferrofluidic properties.

The polarised SANS measurements were carried out at room temperature and ambient atmosphere, using 6 Å neutron wavelength and a horizontal magnetic field of $\leq$ 1.2 T. In a previous experiments [1] we have observed that spherical NPs ($CoFe_2O_4$) transferred into polar solvents contrast match in D_2O.
Therefore we first performed contrast variation studies of spherical NPs. Such will allow to stealth nuclear coherent scattering. The measurements were done on four pure systems (cobalt ferrite with three various particle diameter and hematite spindles) dispersed in various solvents (D_2O, d_6-acetone, d_6-DMSO). In *Fig. 1a-c*, the nuclear coherent SANS contrast variation studies of spherical nanoparticles (cobalt ferrite with particle diameter of 15.8(1) nm) are presented in absolute scale. It can be seen that there is a contrast matching of spherical nanoparticles with D_2O while in d_6-acetone and d_6-dimethylsulfoxide a form factor oscillation from NPs core at ~0.04 Å^{-1} is clearly visible. On the other hand, the elongated magnetic nanoparticles (hematite spindles) have good contrast in D_2O (*Fig. 1d*). This finding can be used to disentangle the scattering contributions of the individual constituents.

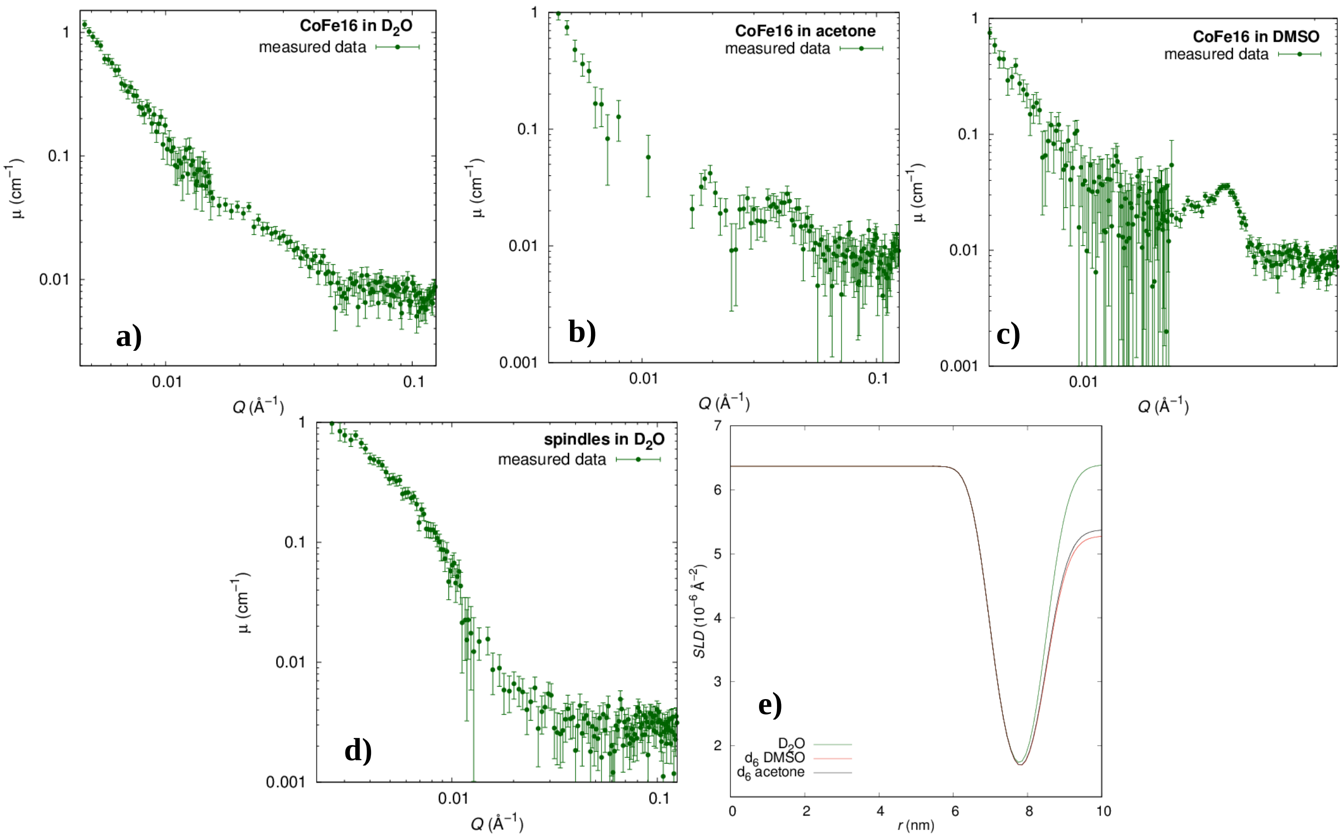

Fig. 1: Nuclear coherent scattering derived from horizontal, 20° sector averages obtained from the polarized neutron cross section *I*(-) + *I*(+) of cobalt ferrite nanoparticles in different solvents a) D_2O (SLD = $6.33\cdot10^{-6}$ Å^{-2}) b) d_6-acetone (SLD = $5.38\cdot10^{-6}$ Å^{-2}) c) d_6-dmso (SLD = $5.27\cdot10^{-6}$ Å^{-2}) and d) for pure hematite spindles in D_2O e) SLD profile of the spherical nanoparticles surrounded by polyacrylic acid (radius is fixed to value obtained from prior SAXS measurement).

By contrast matching of the spheroidal nanoparticles in hybrid ferrofluid dispersion it is possible to get information on the overall arrangement in the hybrid dispersion. At first sight the orientation behaviour of elongated nanoparticles (spindles) changes by doping with spherical nanoparticles. This can be seen in in the

2D SANS images *Fig. 2b-e* for 3 different concentration of spherical nanoparticles in D_2O. With increasing concentration of spherical nanoparticles the anisotropy is decreasing in an applied magnetic field of 1.2 T. The nuclear coherent scattering (obtained by 20° sector along field direction) of hybrid ferrofluidic dispersion in D_2O is presented in *Fig. 2a*. Compared to the pure system there is a visible increase of scattering intensity in the low q-regime which might be associated to the formation of bigger structures. This contrast variation studies (using D_2O and d_6-dmso) allows us to disentangle the scattering contributions of the individual constituents, and hence the arrangement in the hybrid ferrofluid dispersions. The in-depth data analysis is still ongoing and we have shown here some preliminary results.

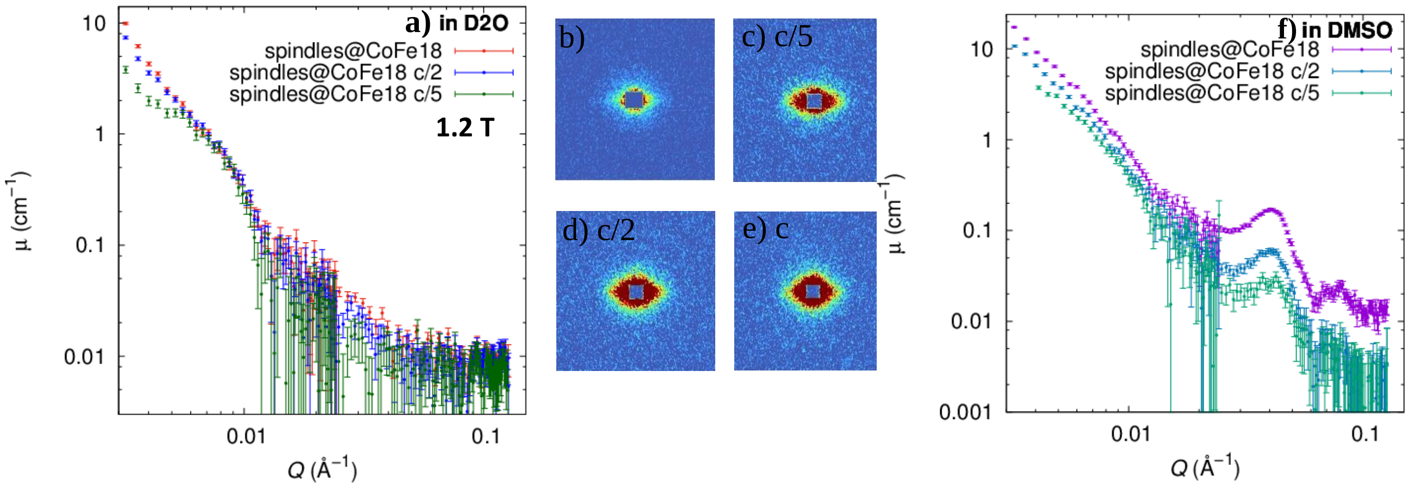

Fig. 2: a) Nuclear coherent SANS ($I(+) + I(-)$) obtained by 20° sector along field direction of hybrid ferrofluids (0.01 vol% of spindles with various concentration of spherical nanoparticles) in D_2O at room temperature. Corresponding 2D-SANS cross sections at long detector distance for b) spindles nanoparticles c-e) spindles doped with various concentration *c* of spherical nanoparticles at B = 1.2 T (same intensity color scale used). f) Nuclear coherent SANS of hybrid ferrofluids in DMSO (0.01 vol% of spindles with various concentration, *c*, of spherical nanoparticles) at room temperature.

References

[1] ILL experimental report No. 73769.