Experimental report

13/02/2017

Proposal: 5-53-267 **Council:** 10/2016

Title: Spin correlation in clusters of magnetic nanoparticles

Research area: Physics

This proposal is a new proposal

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Samples: Fe2O3/Fe3O4 in H20 (sample3)
Fe2O3/Fe3O4 in H20
Fe2O3/Fe3O4 in H20 (sample2)
Fe2O3/Fe3O4 in H20 (sample4)
Bacteria Magnetospirillum gryphiswaldense + Fe3O4- nanoparticles in H2O

Instrument	Requested days	Allocated days	From	To
D33	7	3	30/01/2017	02/02/2017

Abstract:

By use of spin-resolved POLARIS experiments it is planned to analyze the spin coupling between magnetic nanoparticles in 5 different types of particle clusters. With particle sizes in the range of 8 - 40 nm these particles can be regarded in all cases as single-domain particles and are aggregated to small clusters. The cluster size (~ 30 nm to a few µm) and type of arrangement (e.g. close packed clusters or linear chains) varies between the samples. Within the clusters the individual particle moments (single-domains) are strongly interacting due to dipole-dipole interactions/stray fields.
It is expected that within the 5 samples the spin coupling due to dipolar interactions significantly varies, which can be verified by the proposed POLARIS experiments. The results would be of high interest regarding a wide range of potential biomedical applications of these nanoparticle clusters, such as hyperthermia, magnetic drug targeting or magnetic biosensing.

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In this study the structural and magnetic properties of two systems of iron oxide nanoparticles were analyzed by polarized neutron scattering. The first sample were so-called nanoflower particles and the second sample magnetotactic bacteria, both dispersed in water.

Polarized SANS experiments were conducted at the instrument D33 at the Institut Laue Langevin (ILL), Grenoble. Employing a longitudinal neutron-spin analysis (POLARIS)[1] all four partial neutron intensities $I^{++}(\vec{q})$, $I^{--}(\vec{q})$, $I^{+-}(\vec{q})$ and $I^{-+}(\vec{q})$ of the colloidal dispersion were measured in presence of an externally applied, homogeneous magnetic field $\vec{H}$. The field was applied perpendicular to the neutron beam ($\vec{H} \perp \vec{k}$) with applied field amplitudes between $\mu_0 H_{min} = 2\,\mathrm{mT}$ (minimal field) and $\mu_0 H_{max} = 1\,\mathrm{T}$ (maximal field). The mean wavelength of the neutrons was $\lambda = 0.6\,\mathrm{nm}$, with a wavelength spread of $\Delta\lambda/\lambda = 10\%$. The detector distances for the nanoflowers were 6 m as well as 10.3 m, and for the magnetotactic bacteria 6 m as well as 13.4 m.

Due to the large incoherent scattering background the data analysis will be focused on the (spin leakage corrected) non spin flip intensities $I^{++}(\vec{q})$ and $I^{--}(\vec{q})$. Defining x as the direction of the neutron beam and z of the applied magnetic field it can be written[1]

$$\begin{aligned} I^{\pm\pm}(\vec{q}) \propto & |\tilde{N}|^2 + b_H^2 |\tilde{M}_z|^2 \sin^4\Theta \\ & + b_H^2 |\tilde{M}_y|^2 \sin^2\Theta\cos^2\Theta \\ & - b_H^2 (\tilde{M}_y \tilde{M}_z^* + \tilde{M}_z \tilde{M}_y^*) \sin^3\Theta\cos\Theta \\ & \mp b_H (\tilde{N}\tilde{M}_z^* + \tilde{N}^*\tilde{M}_z) \sin^2\Theta \\ & \pm b_H (\tilde{N}\tilde{M}_y^* + \tilde{N}^*\tilde{M}_y) \sin\Theta\cos\Theta, \end{aligned} \tag{1}$$

with Θ being the angle between the scattering vector $\vec{q}$ and the magnetic field $\vec{H}$. Here, $\tilde{N}(\vec{q})$ and $\tilde{M}_{y,z}(\vec{q})$ are the Fourier transforms of the nuclear scattering length density and of the magnetization in y, z direction, respectively. The constant $b_H = 2.7 \cdot 10^{-15}\,\mathrm{m}/\mu_B$, with μ_B being the Bohr magneton.

For the data analysis we use the same approach for the Indirect Fourier transform (IFT) as in[2].

I. NANOFLOWERS

Fig. 1 shows a TEM image of the nanoparticles, which display spherical shape but with an irregular, rough surface. By measuring the size D_p of 200 nanoflowers a mean value of $\langle D_p \rangle = 39\,\mathrm{nm}$ was determined.

High resolution TEM indicates that the particles itself are composed of several core particles which are fused together. Due to their characteristic shape these particles are commonly referred to as *nanoflowers*. Of high interest was to investigate if these particles are magnetically single-domain particles (atomic magnetic spins preferentially aligned in one direction) despite their nanocrystalline substructure.

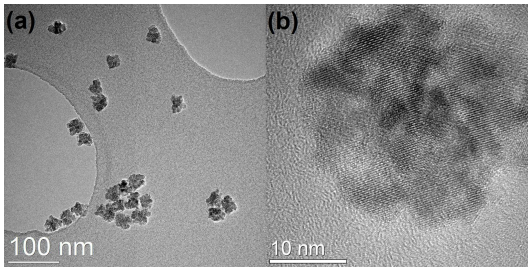

FIG. 1: (a) TEM image of the nanoflowers. (b) High resolution TEM of one nanoflower.

Fig. 2a shows the 2D scattering pattern of the non spin flip intensity $I^{++}(\vec{q})$ and the difference between $I^{++}(\vec{q})$ and $I^{--}(\vec{q})$, measured at $\mu_0 H = 2\,\mathrm{mT}$ with a detector distance of 10.3 m. Integration of $I^{++}(\vec{q})$ in the sector parallel to $\vec{H}$ ($\Theta = 0° \pm 10°$) enabled to determine the purely nuclear 1D scattering intensity $I_{nuc}(q)$ of the nanoflowers, plotted in Fig.2b. Comparison with the SAXS intensity $I(q)$ (measured with a Kratky system with slit focus, SAXSess by Anton Paar) shows that in the low q part both intensities are basically identical. Accordingly, an IFT of $I_{nuc}(q)$ and $I(q)$ results in comparable pair distance distribution functions $P(r)$, with one main peak at $r \approx 16\,\mathrm{nm}$ (Fig. 2d). Assuming spherical shape this indicates an average particle size of $\approx 31\,\mathrm{nm}$. This is slightly below the mean size determined by TEM which can be attributed to the irregular shape of the nanoflowers (reduced density in surface region). That for both SAXS and SANS values $P(r) > 0$ are observed in the range $31\,\mathrm{nm} < r < 63\,\mathrm{nm}$, indicates an agglomeration of some of the nanoflowers.

To gain information about the spatial magnetization configuration within the nanoflowers the nuclear magnetic cross term $I_{cross}(q) \propto (\tilde{N}\tilde{M}_z^* + \tilde{N}^*\tilde{M}_z)$ was determined at $\mu_0 H = 2\,\mathrm{mT}$ and 1 T. For this purpose $I^{++}(\vec{q}) - I^{--}(\vec{q})$ was integrated in the sectors perpendicular to $\vec{H}$ (Fig.2a, $\Theta = 90° \pm 10°$). For dilute systems of magnetic nanoparticles $I_{cross}(q) \propto F_N(q) F_M(q)$, with $F_N(q)$ and $F_M(q)$ being the nuclear and magnetic form factor, respectively[3]. In case of homogeneously magnetized particles $F_M(q) = F_N(q)$, and hence $I_{cross}(q)$ should equal the purely nuclear scattering intensity.

As can be seen in Fig.2b, the functional form of $I_{cross}(q)$ detected for $\mu_0 H = 2\,\mathrm{mT}$ and 1 T is comparable to the nuclear scattering intensities. As a result the pair distance distribution functions $P(r)$ determined by an IFT of the cross sections $I_{cross}(q)$ are quite similar to the purely nuclear $P(r)$'s (Fig. 2d). Just the maximum of the primary (main) peak is in both cases shifted by about 1 nm to lower values.

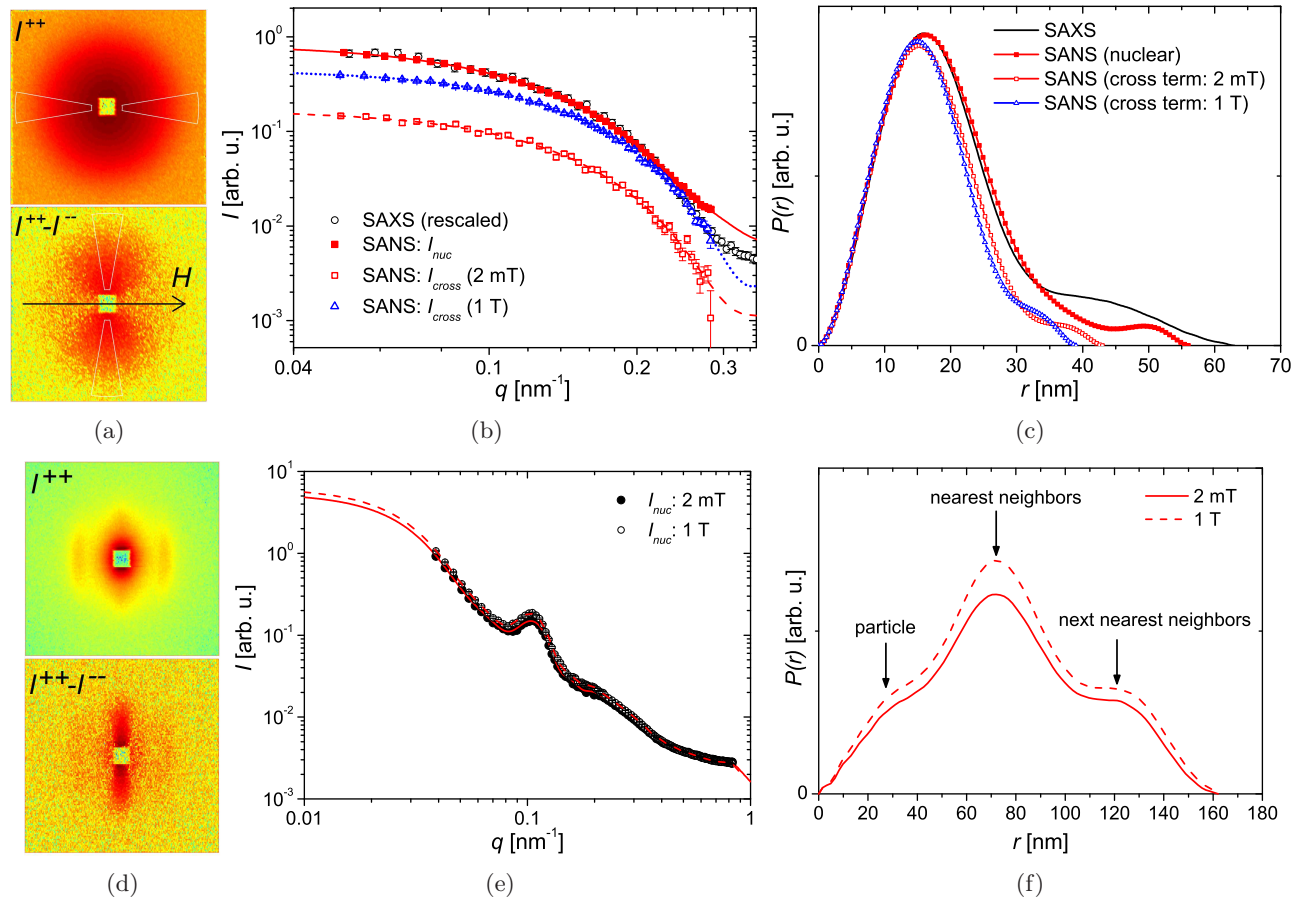

FIG. 2: Nanoflowers: (a) 2D scattering patterns of $I^{++}(\vec{q})$ (top) and of $I^{++}(\vec{q}) - I^{--}(\vec{q})$ (bottom), detected for $\mu_0 H = 2\,\mathrm{mT}$. (b) 1D SAXS scattering intensity $I(q)$, nuclear scattering intensity $I_{nuc}(q)$ (parallel sector of $I^{++}(q)$) and the nuclear magnetic cross terms $I_{cross}(q)$ (vertical sectors of $I^{++}(\vec{q}) - I^{--}(\vec{q})$). The straight, dashed and dotted lines are the reconstructed curves for the corresponding SANS pair distance distribution functions. (c) Rescaled pair distance distribution functions $P(r)$ determined by an IFT of $I(q)$ (SAXS), $I_{nuc}(q)$ and $I_{cross}(q)$. Bacteria: (d) 2D scattering patterns of $I^{++}(\vec{q})$ (top) and of $I^{++}(\vec{q}) - I^{--}(\vec{q})$ (bottom), detected for $\mu_0 H = 2\,\mathrm{mT}$. (e) Nuclear SANS intensities determined for $\mu_0 H = 2\,\mathrm{mT}$ and 1 T and reconstructed curves for the corresponding $P(r)$'s. (f) Pair distance distribution functions $P(r)$ determined by an IFT of $I_{nuc}(q)$.

Thus, we can conclude that magnetic moments inside the nanoflowers are preferentially aligned along a certain direction, meaning, at first approximation the nanoflowers can be regarded as single-domain particles. The slightly reduced magnetic core volume can be probably attributed to uncorrelated surface spins, as also observed in other studies of magnetic nanoparticles[3].

II. MAGNETOTACTIC BACTERIA

A good overview about the synthesis and main structural properties of the bacteria can be found in[4]. Briefly, within such bacteria iron oxide nanoparticles with sizes of about 40-50 nm are arranged to chain-like structures of 10-20 particles. In the present study we wanted to investigate their alignment inside the colloidally dispersed bacteria in external magnetic fields.

In Fig. 2e the purely nuclear scattering intensities $I_{nuc}(q)$ are shown and in Fig. 2f the extracted pair distance distribution functions $P(r)$ for $\mu_0 H = 2\,\mathrm{mT}$ and 1 T. The $P(r)$'s nicely show the chain-like arrangement of the nanoparticles and comparison between both $P(r)$'s shows that already at 2 mT the bacteria seem to be completely aligned in field direction.

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