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# STRUCTURE OF MAGNETITE FERROFLUIDS INVESTIGATED BY SANS WITH POLARIZED NEUTRONS

M. Kammel, A. Hoell and A. Wiedenmann  
Hahn-Meitner-Institut, Glienicker Strasse 100, D-14109 Berlin, Germany

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## 1. Introduction

Colloidal solutions of nanoscaled magnetic particles (“Ferrofluids”) are stabilized against coagulation either by electrostatic repulsion or by coating the core with organic chain molecules acting as surfactants [1]. New bio-compatible ferrofluids [2,3] containing the same cores of magnetite,  $\text{Fe}_3\text{O}_4$ , but with different composition of the shell in mixed  $\text{H}_2\text{O}/\text{D}_2\text{O}$  solutions have been prepared. In order to evaluate the unknown structure and the size distribution of the core-shell particles as well as the magnetic structure of the magnetite cores we currently perform a Small Angle Neutron Scattering (SANS) study using polarised neutrons (SANSPOL) [4–6]. This technique takes advantage from the strong modification of the contrasts for the two polarisation states.

## 2. Experimental

Nanosized magnetite particles were prepared by co-precipitation of ferric salt mixtures with concentrated ammoniumhydroxide. The magnetite cores are electrostatically stabilized (denoted as ELEC) which can be coated by different surface active organic molecules. The first example, denoted as LM, coating consists on a bilayer of dodecanoic acid (inner layer) and  $\text{C}_{12}$  ethoxylated alcohol with 9 mol/mol ethoxy groups. The ferrofluid (DEX) has a dextrans shell, whose chains are tangled by subsequent heat treatment. The volume fraction of magnetite is about 1 vol% in all 3 samples. For SANS contrast requirements the content of D with respect to H in the carrier liquid is larger than 90%.

SANS measurements have been performed at the instrument V4 installed at the BERII reactor of HMI, Berlin using polarized neutrons with a wavelength  $\lambda = 0.6$  nm, covering a range of momentum transfer  $Q$  between 0.04 and  $4 \text{ nm}^{-1}$ . A horizontal magnetic field (1.1 T) was applied at the sample position, oriented perpendicular to the incoming neutrons. Polarized neutrons are provided by a transmission polarizing super-mirror cavity. The polarization direction is reversed using a spin flipper in front of the sample [6].

## 3. Results

Elastic scattering of neutrons with wavelength  $\lambda$  at an angle  $2\Theta$  leads to the momentum transfer of magnitude  $Q = 4\pi\sin(\Theta)/\lambda$  and hence to the phase shift of  $\exp(i\mathbf{Q}\mathbf{r})$ . The form factors for nuclear ( $F_N$ )

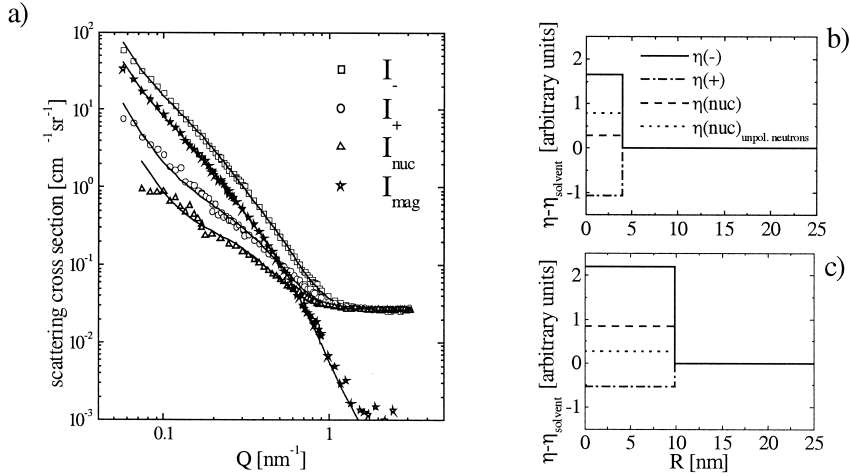


Figure 1. Scattering cross sections a) and corresponding scattering length density profiles of small b) and large c) spherical particles b) of electrostatically stabilized sample ELEC.

and magnetic ( $F_M$ ) scattering for a particle of species  $j$  embedded in a homogeneous matrix are given by  $F_j = \int_{V_{pj}} d\mathbf{r} \Delta\eta_j \exp(i\mathbf{Q}\cdot\mathbf{r}_j) = \Delta\eta_j V_{pj} f(QR)$ , where  $V_{pj}$  is the volume of the particle and  $f(QR)$  depends only on its shape. The contrast  $\Delta\eta$  is the difference between the scattering length densities of particle and matrix,  $\Delta\eta = \eta_p - \eta_{\text{matrix}}$ . For nuclear scattering  $\eta_N = \sum c_i b_i / \Omega_i$  where  $b_i$  is the nuclear scattering length,  $c_i$  the atomic concentration and  $\Omega_i$  the atomic volume of constituent  $i$ . Similarly a magnetic scattering amplitude is defined by  $\eta_M = (0.27 \times 10^{-12} \text{ cm}) \sum c_i \mathbf{M}_i^\perp / \Omega_i$ , where  $\mathbf{M}_i^\perp$  (in Bohr magnetons) is the projection of the moment on a plane perpendicular to the scattering vector  $\mathbf{Q}$ .

For SANSPOLE [4,5,7,8] where the neutron spins are aligned antiparallel (denoted by +) or parallel (-) to a preferred orientation  $\mathbf{z} // \mathbf{H}$  (where  $\mathbf{H}$  is the magnetic field vector) the cross sections for the case of a dilute system of non-interacting particles depend on the polarization state according to

$$I^+(Q, \alpha) = F_N^2 + \{F_M^2 - 2P F_N F_M \sin^2 \alpha\}$$

$$I^-(Q, \alpha) = F_N^2 + \{F_M^2 + 2P F_N F_M \sin^2 \alpha\} \quad (1a)$$

$\alpha$  is the azimuth angle between  $\mathbf{H}$  and  $\mathbf{Q}$

The arithmetic mean of the intensities  $[I^+(Q, \alpha) + I^-(Q, \alpha)]/2$  corresponds to the intensity of a non-polarized beam

$$[I^+(Q, \alpha) + I^-(Q, \alpha)]/2 = I(Q, \alpha)_{\text{non-polarized}} = F_N^2 + F_M^2 \sin^2 \alpha. \quad (1b)$$

Thus, from Eq. 1b we obtain the magnitude of the nuclear and magnetic contributions and Eq. 1a allows to determine the absolute value of the magnetic contrast with respect to the nuclear contrast, i.e. magnetization and compositions of particles and matrix.

The SANSPOLE intensities perpendicular to the applied field  $I^\pm(\mathbf{Q} \perp \mathbf{H})$  as obtained by an adjustment of the 2-d pattern to the  $\sin^2 \alpha$  dependence given in Eq. (1) are compared to nuclear and magnetic contributions as derived from (eq. 1b) for the different samples in Figs. 1a–3a. In DEX and LM samples  $I^-(\mathbf{Q} \perp \mathbf{H})$  is lower than  $I^+(\mathbf{Q} \perp \mathbf{H})$  at high values of  $Q$  and exhibit a crossover around  $Q = 0.2 \text{ nm}^{-1}$  below which  $I^-(\mathbf{Q} \perp \mathbf{H}) < I^+(\mathbf{Q} \perp \mathbf{H})$ . For the ELEC no such crossover occurs and  $I^-(\mathbf{Q} \perp \mathbf{H}) > I^+(\mathbf{Q} \perp \mathbf{H})$ . In all samples the scattering curves of  $I(\text{mag})$  and  $I(\text{nuc})$  revealed some shoulder at low  $Q$  which is a strong indication of the presence of two distinct sizes of the particles.

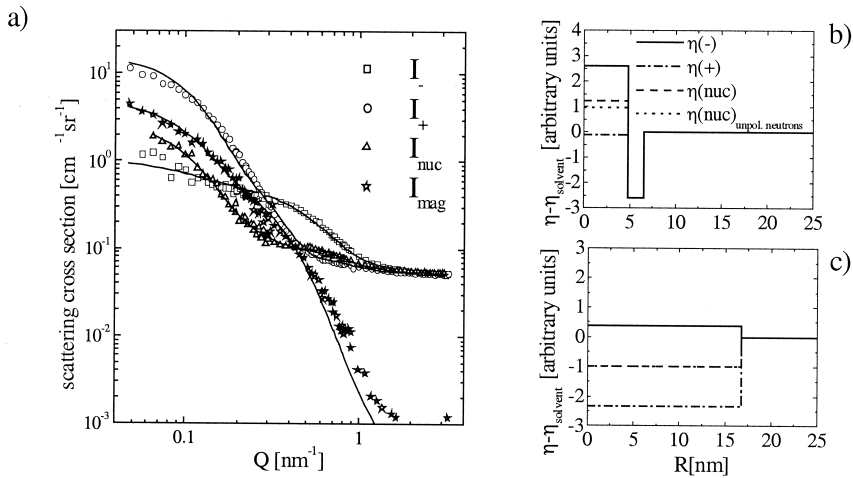


Figure 2. Scattering cross sections a) and corresponding scattering length density profiles of small composites b) and large c) spherical particles monolayer coated sample DEX.

The crossover phenomena observed in the polarized neutron data of DEX and LM is a characteristic feature of “composite” particle similar to that observed in Co-ferrofluids [5] which is expected to be built up by a magnetized core of  $Fe_3O_4$  atoms surrounded by a nonmagnetic surface layer. As the simplest description of such a “composite” we use a shell model consisting of a sphere with an inner core radius  $R'$  surrounded by a concentric shell of radius  $R$ . The form factor is given by

$$F_{shell}(Q) = [(\Delta\eta_1 - \Delta\eta_2)f_{sph}(QR') + \Delta\eta_2f_{sph}(Q(R))]V_p$$

with

$$f_{sph}(x) = 3[\sin(x) - x \cos(x)]/x^3. \tag{2}$$

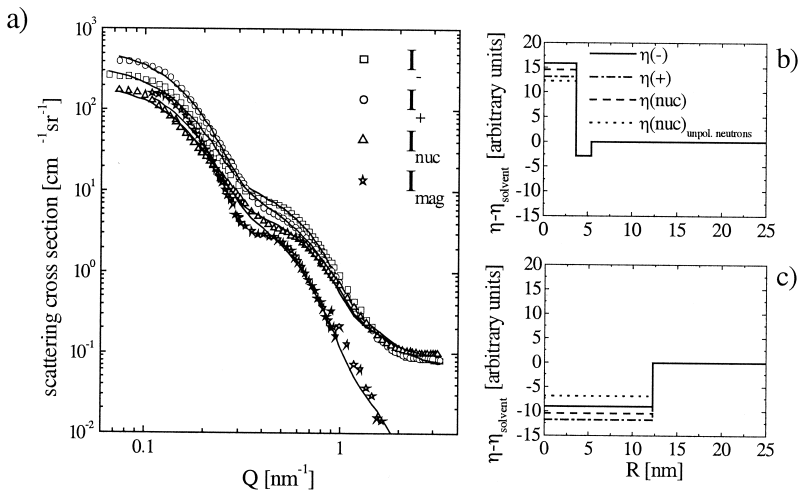


Figure 3. Scattering cross sections a) and corresponding scattering length density profiles of small composites b) and large c) spherical particles bi-layer coated sample LM.

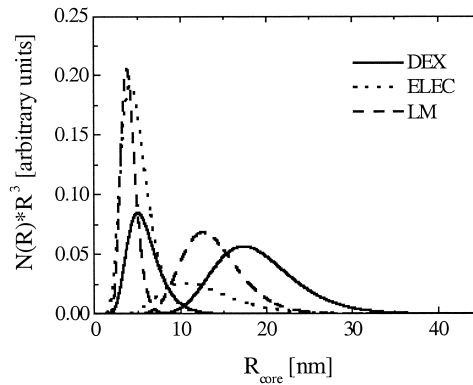


Figure 4. Volume weighted size distribution of ELEC (without shell), DEX (monolayer) and LM (bilayer).

The scattering contrasts with respect to the matrix are different for the magnetic core and non-magnetic shell and given by  $\Delta\eta_1(\pm) = \eta_1^{nuc} \pm \eta_1^{mag} - \eta_{matrix}$  and  $\Delta\eta_2 = \eta_2^{nuc} - \eta_{matrix}$ , respectively where only  $\Delta\eta_1(\pm)$  depends on the polarization. The intensities were calculated according to  $I(\mathbf{Q} \perp \mathbf{H}) = N_p \int F_{shell}^{(2)}(\mathbf{Q}, R) N(R') dR$ , ( $N_p$  is the number density of particles in the beam), assuming a log-normal number distribution of the core radius  $N(R')$  and a constant thickness of the shell, i.e.  $R = R' + dR$ . The parameters  $N_p$ ,  $R'$ ,  $dR$  and the width of the size distribution  $s$  were constrained to be identical for both polarization states and the contrasts  $\Delta\eta_1(\pm)$  and  $\Delta\eta_2$  have been adjusted in a non-linear least square fitting routine. The same model using identical parameters of  $R, dR$  and  $s$  were applied to  $I(mag)$  and  $I(nuc)$  data by simultaneously fitting the corresponding contrasts. The solid lines in Fig. 1–3 represent the calculated intensities  $I^\pm(\mathbf{Q} \perp \mathbf{H})$ ,  $I(nuc)$  and  $I(mag)$ . For all samples a second fraction of much larger particles has to be included in fit in order to adjust the low  $Q$  intensity. In ELEC where no crossover was observed two distinct lognormal distributions of spherical particles had to be assumed in the fits. It turned out that for all samples this simple model function lead to consistent parameters. The volume weighted size distributions are presented in Fig. 4. For the small particles a rather sharp distribution  $N(R')$  corresponding to a volume weighted average of the core radius of  $\langle R' \rangle = 3.7$  (LM), 4.8 nm (DEX) and 4.0 (ELEC) a constant thickness of the shell of  $dR = 1.7$  nm (LM) and 2.4 nm (DEX). For the second fraction the volume averaged radius is by a factor of 2.5–3.5 times larger than that of the core.

The scattering length densities resulting from simultaneous model fits of both polarization states as well as  $I_{nuc}$  and  $I_{mag}$  using the same model function are presented in Fig. 1–3 (b,c), normalized to absolute values with the known theoretical value for the magnetic scattering contrast of the core. From SANSPOLE it turned out that for the small particles the scattering length density of the core ( $\eta_1$ ) is clearly higher than  $\eta_{solvent}$  and higher than that of the shell ( $\eta_2$ ) for the samples DEX and LM. However, for the large particles  $\eta_1$  is found to be lower than  $\eta_{solvent}$  in LM and DEX but higher in ELEC. This is a strong indication that the large particles represents aggregates of magnetite units with an average radius 3.3 times higher than the core. However, the average nuclear density of this aggregates must be reduced in LM and DEX due to inclusion of some surfactant units which are absent in the aggregates in ELEC and hence  $\eta_1 \approx \eta_2$ . In any case this results indicate that steric or electrostatic screening is not fully efficient in these materials. The magnetic contrasts of both fractions are very similar in ELEC which indicates that also the aggregates present the ferrimagnetic ordering of magnetite.

#### **4. Summary**

Chemical or magnetization gradients have been evaluated in  $\text{Fe}_3\text{O}_4$ -ferrofluids by using SANSPOL. In the surfactant stabilized samples DEX and LM “composite particles” are formed by a magnetic core of average radius of  $\langle R' \rangle = 3.7\text{--}4.4$  nm and surrounded by a shell of thickness 1.7–1.8 nm of organic surfactants. In the electrostatic stabilized sample ELEC  $\langle R' \rangle$  of the spherical nanocrystals of magnetite is 4.0 nm. A second fraction of magnetite particles with an average radius  $\langle R \rangle = 2.4 R'$  were detected resulting from aggregation due to imperfect screening.

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