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High-quality structure parameter for magnetic liquids obtained by small-angle scattering of polarized neutrons

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The preparation of magnetic liquids with the aid of different aluminium alkyl chains leads to narrow size distributions. A structural investigation of different ferrofluid samples was performed with small-angle neutron scattering of polarized neutrons (SANSPOL). The use of polarized neutrons extends the known method for composition exploration in nanometre-scale magnetic systems. For these new possibilities special data-analysis procedures are indispensable. We use a new simultaneous fitting procedure for the spin-up, spin-down and nuclear–magnetic interference term to obtain the structure parameter information. The advantage of this method is the reduction of parameter correlations for the independent model parameters. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: magnetic liquids; structure parameters

SANSPOL THEORY

Experiments using small-angle neutron scattering of polarized neutrons (SANSPOL) profit from the spin dependence of all scattering amplitudes. This information can be used to enhance the quality of the data analysis. If an external magnetic field **H** generates a preference direction we denote this as the z-axis. The neutron-spin eigenvectors in this basis are $(\hbar/2,\ 0) := |+\rangle$ and $(0,\ \hbar/2) := |-\rangle$. For a polarized incoming beam let P define the degree of neutron polarization and ε the spin-flipper efficiency. If the polarization of the scattered neutrons is not analysed then one can distinguish between I^{on} and I^{off} scattering by switching a spin flipper in front of the sample on and off. In the case of a diluted ferrofluid we assume that the magnetic part is generated by superparamagnetic spherical particles with volume V_{p} and a saturation magnetization $\mathrm{M_s}$ in a nonmagnetic matrix. In this case (see Refs 1 and 2) I^{on} evaluates to

$$I^{\mathrm{on}} = \int \mathrm{d}RN(R)\left\{F_{\mathrm{n}}^2 + \frac{2F_{\mathrm{m}}^2 L_\beta}{\beta}\right.$$

$$\left. + \left[F_{\mathrm{m}}^2 - \frac{3F_{\mathrm{m}}^2 L_\beta}{\beta} + 2P(2\varepsilon - 1)F_{\mathrm{n}}F_{\mathrm{m}}L_\beta\right]\sin^2\Psi\right\} \quad (1)$$

I^{off} is obtained from Eqn (1) for $\varepsilon = 0$. $L_\beta = \coth(\beta) - 1/\beta$ is the classical Langevin function with $\beta = \mu_0 V_{\mathrm{p}}\mathbf{H}\,\mathbf{M}_{\mathrm{s}}/k_{\mathrm{B}}T$ and Ψ the angle between the magnetic field and the **Q** vector. Magnetic field **H** or temperature T variation can change β and thereby the fraction of isotropic and anisotropic scattering.[2] For $I^{\mathrm{on-off}}$ one obtains

$$I^{\mathrm{on}} - I^{\mathrm{off}} = 4P\varepsilon \int \mathrm{d}N(R)L_\beta(H,\ R^3)F_{\mathrm{n}}F_{\mathrm{m}}\ \sin^2\Psi \quad (2)$$

CONTRAST VARIATION AND SIMULTANEOUS FITS

In many cases the nuclear and magnetic scattering amplitudes F_{n} and F_{m} can be written as:

$$F_{\mathrm{n}} = \sum_{i=1}^{N}(\eta_{\mathrm{n}}^i - \eta_{\mathrm{n}}^\infty)f_{\mathrm{n}}^i(Q,\ R) \quad (3)$$

and

$$F_{\mathrm{m}} = \sum_{j=1}^{N}(\eta_{\mathrm{m}}^j - \eta_{\mathrm{m}}^\infty)f_{\mathrm{m}}^j(Q,\ R) \quad (4)$$

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Here, we assume the η_n^i and η_m^j as piecewise constant nuclear and magnetic scattering-length densities (SLDs) and introduce f_n^i or f_m^i as the ith partial amplitude from N regions. All magnetic contrast is based on the z-components of the magnetization $\mathbf{M}$ perpendicular to $\mathbf{Q}$. Therefore, F_m is related to the absolute value of the saturation magnetization $|M_j|$ for the different phases j. It is known that the number of independent parameters which can be derived from a single small-angle neutron scattering (SANS) curve is limited. The maximum number depends on the Q-range and Q-value spacing. One way out is a contrast variation with a simultaneous fit procedure. The basic principle is sketched in Fig. 1 and the inset of Fig. 2. Fig. 1 shows the typical situation in a ferrofluid. Spherical magnetic particles with a nonmagnetic stabilization layer and free nonmagnetic particles are placed in a solvent (see Kammel *et al.*[3] for details). Different H : D ratios in the solvent lead to different nuclear SLD (e.g. η_n^∞ (D) and η_n^∞ (H : D) in the inset of Fig. 2. Additionally Eqn (1) shows that by changing the value of L_β one can produce different scattering patterns from only one sample by changing the external field $\mathbf{H}$ or temperature T. This is the magnetic contrast-variation method. Finally, I^{on-off}, I^{nuc} and I^{mag} can be extracted from the I^{on} and I^{off} measurements. This leads to five different (but not independent) scattering curves for one configuration. From a simultaneous fit of all curves with parameter constraints one can avoid the parameter-correlation limit to obtain stringent model-parameter values.

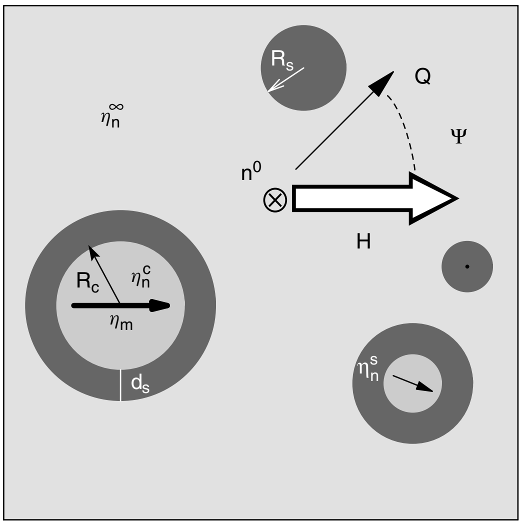

Figure 1. A core–shell cobalt ferrofluid with free surfactant material in a solvent. Here R_c is the mean radius of the magnetic cobalt core (with nuclear SLD η_n^c and magnetic SLD η_m), d_s the thickness of the nonmagnetic stabilization layer and R_s the mean nonmagnetic micelle radius. We assume that the nuclear SLDs η_n^s of the shell and the micelles are identical. η_n^∞ denotes the SLD of the solvent, which was changed during contrast variation.

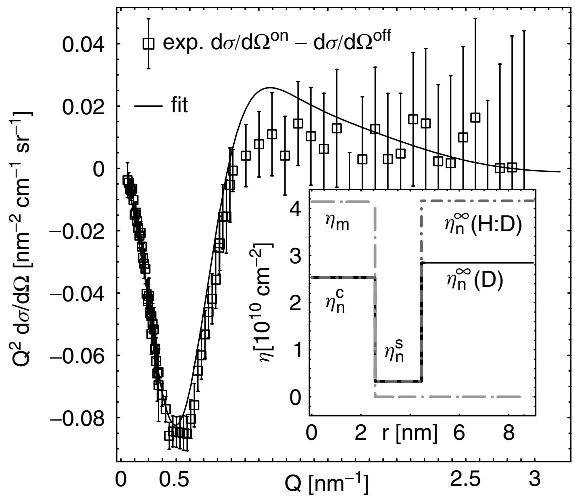

Figure 2. Experimental $Q^2(I^{on} - I^{off})$ data and a least-squares fit curve. The inset shows the SLD in different solvents.

FIRST EXPERIMENTS WITH COBALT FERROFLUID: EVIDENCE OF FREE SURFACTANCE MATERIAL

New potential medical applications[4] for ferrofluids demand a small size distribution of magnetic particles and well-known structural properties. A novel size-selective preparation route leads to air-stable colloidal cobalt nanoparticles via the thermolysis of $Co_2(CO)_8$ in the presence of aluminium alkyls.[5] By varying the aluminium alkyl chain lengths and the cobalt-to-aluminium ratio the particle size may be adjusted between 3 and 15 nm. After thermolysis of the $Co_2(CO)_8$, synthetic air is slowly bubbled through a capillary into a suspension of cobalt(0) particles (10 nm) in toluene over 6–10 h. The resulting cobalt powder appears to be completely stable at room temperature. Air-stable magnetic fluids in toluene and toluene-d_8 were prepared using korantin as surfactant. We performed SANSPOL measurements on three cobalt ferrofluid samples of the same preparation with different H : D ratios. The concurrent least-squares parameter estimators differ strongly from the results for the single curve fit. For example, the set of parameters from magnetic particles can be estimated separately by an Q^2I^{on-off} fit as shown in Fig. 2. However, the values obtained cannot satisfactorily explain the on and off scattering curves as demonstrated by the dashed lines in Fig. 3. Obviously, an additional nonmagnetic constituent has to be taken into account. Fig. 3 shows the results of a simultaneous least-squares fit for the $\log(I^{on})$, $\log(I^{nuc})$ and $\log(I^{off})$ and likewise in Fig. 2 for the Q^2I^{on-off} curves. All data are fitted with different analytical gamma particle-size distributions for the core–shell particles and micelles. If $N(R, \sigma)$ is the probability density function then the mean radius $\overline{R}$ is defined as $\overline{R} = \int N(R, \sigma)R \, dR$, were σ is the variance of the distribution. For the smaller nonmagnetic particles a mean radius of $R_s = 1.1$ nm, a variance of

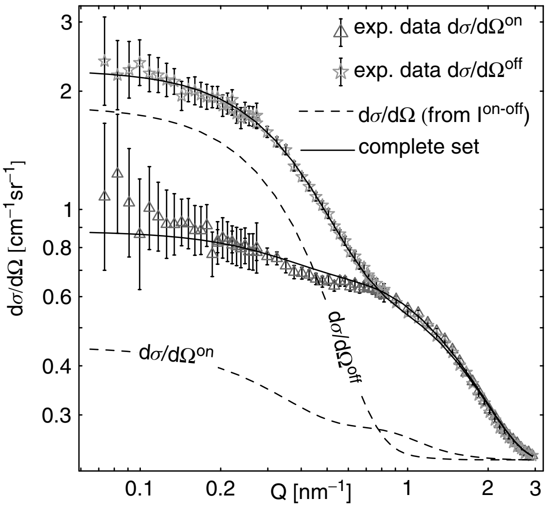

Figure 3. The magnetic particles' properties calculated from the cross-term $Q^2I^{\text{on-off}}$ cannot explain the full on and off curves (dashed lines). Including nonmagnetic contributions from micelles gives a perfect agreement in a simultaneous fit.

$\sigma_s = 0.2$ nm, and an SLD for oleoylsarkosine is obtained. The bigger magnetic particles are the core–shell particles with a mean radius of $R_c = 2.9$ nm and a variance of $\sigma_c = 0.8$ nm. The thickness of 1.9 nm for the nonmagnetic layer and an $\eta_n^s = 0.5 \times 10^{10}$ cm^{-2} for the shell indicates that this layer also consists of oleoylsarkosine. The magnetic scattering length of the cobalt core is fixed to $\eta_m^c = 4.1 \times 10^{10}$ cm^{-2}, the bulk value of cobalt. The confidence interval for all estimated parameter values was less than 5%. In a constrained fitting routine, nuclear and magnetic scattering intensities, together with the nuclear–magnetic interference term and the intensities of polarized neutrons, are used simultaneously, which allows the complete structure to be determined without correlations between the parameters.

EXPERIMENTS WITH MAGNETIC CONTRAST VARIATION

For samples prepared with an advanced technique (see Bönnemann *et al.*[6] and the brief description in the previous section), extensive SANSPOL experiments with chemical and magnetic contrast variations were performed. We will present here the results of the magnetic contrast variation technique to demonstrate the capability of this method to obtain stringent structure parameters for the ferrofluids investigated. As explained briefly in the 'SANSPOL theory' section, one can influence the magnetic scattering by an external magnetic field variation. Owing to the polydispersity of the nanoparticles this is not a linear correlation. If the ferrofluid can be treated as a system of diluted ideal superparamagnetic particles π then the cross-section for the $(\text{d}\sigma^{\text{on-off}}/\text{d}\Omega)$ scattering can be written as

$$\frac{\text{d}\sigma^{\text{on-off}}}{\partial\Omega} \propto \int_0^\infty N(R)L_\beta(H,\ R^3)|F_n(R)F_m(R)|\ \text{d}R \qquad (5)$$

where the magnetic contrast of a particle depends not only on the external field and the specific saturation magnetization of the material, but also on the particle volume. This considerably more complex model for the fitting functions has the great advantage that one can fit different $\text{d}\sigma^{\text{on-off}}/\text{d}\Omega$ (**H**) curves simultaneously with the constraint of identical amplitudes F_n, F_m and the same particle size distribution $\text{d}N(R)$ for all curves. In this case, only the Langevin function L_β can vary in a well-known way. This strongly reduces the possible parameter correlations and, therefore, increases the stringency of the fitting parameters obtained.

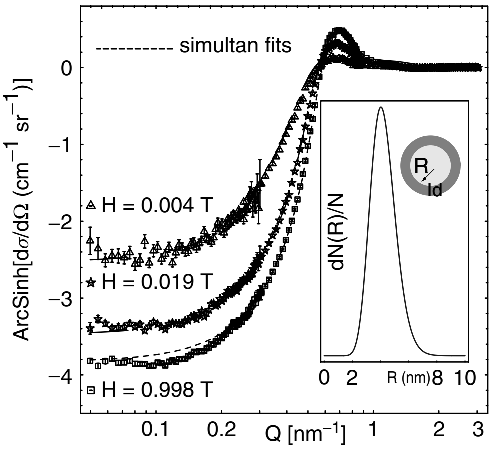

Figure 4. Experimental data and fitted scattering cross-sections in a cobalt ferrofluid. The dashed lines are the results of a simultaneous fit of the $I^{\text{on}} - I^{\text{off}}$ intensity for different external magnetic fields. The inset shows the magnetic particle-size distribution obtained.

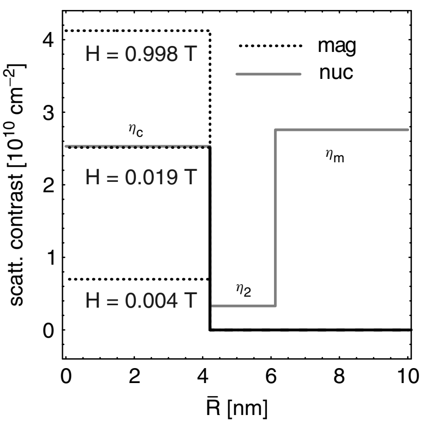

Figure 5. The nuclear and magnetic scattering contrasts for three different external magnetic fields for the cobalt core with a mean volume of 356.6 nm^3.

Table 1. Mean values and limits of the 95% confidence intervals for the constrained fitting procedure

	c_a (vol.%)	$\overline{R}$ (nm)	σ (nm)	d (nm)
Fit value	0.7	4.2	0.9	1.9
Error	±0.2	±0.1	±0.1	±0.1

The results of the experiment and the nonlinear constrained fit procedure are shown in Fig. 4. We found a very good agreement of the fits with both the experimental data and the assumption of free superparamagnetic particles. The inset in Fig. 4 shows that the observed particle size distribution is very narrow. This was the aim of the special synthesis techniques of these particles and was also found qualitatively by other methods, like transmission electron microscopy and nuclear magnetic resonance. Figure 5 shows the absolute value of the magnetic contrast for a particle with the mean volume $\int N(R) 4/3\pi R^3 \mathrm{d}R = 4/3\pi(\overline{R}^3 + 3\overline{R}\sigma^2 + 2\sigma^4/\overline{R})$ at different external magnetic fields. The nuclear scattering contrast is independent of the external field and determined by the chemical constitution of the magnetic particles and the shell only. From this experiment we were able to obtain the structure parameter for the magnetic particles. The results are shown in Table 1. Here, c_a is the volume fraction of the magnetic core of the ferrofluids.

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