



Small-angle scattering investigations of cobalt-ferrofluids using polarised neutrons

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Abstract

Combining contrast variation using polarised neutrons and various H/D mixtures of solvents allowed different structural units in Co-ferrofluids to be identified by small-angle scattering. In diluted liquids, the magnetic core behaves as a non-interacting single-domain. The core is encapsulated by a shell of surfactant molecules which was found to be impenetrable for the solvent. In more concentrated samples aggregation appears in an external magnetic field which is described by a densely random packing of hard spheres.

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Keywords: Magnetic colloids; Polarised neutrons; Small angle neutron scattering

1. Introduction and experimental

Small-angle neutron scattering (SANS) studies are presented on ferrofluids with single-domain magnetic particles where we face the problem that weak magnetic scattering signals have to be analysed besides strong contributions from other sources or vice versa. For polarised neutrons where the neutron spins are aligned antiparallel (+) or parallel (−) to the magnetic field vector \mathbf{H} the scattering cross-sections depend on the polarisation P of the incident neutrons $I^+(Q)$ and $I^-(Q)$, respectively [1,2]. The scattering intensity (denoted here as SANSPOL) has been derived in Refs. [3,4], using the formalism presented in Ref. [5]. When the magnetic moments and neutron polarisation are fully aligned along the external field [3], the SANSPOL intensities perpendicular to the applied field are given for the two states by $I^{(\pm)}(\mathbf{Q} \perp \mathbf{H}) = [F_N \pm F_M]^2 S(Q)$. The difference $I^-(Q, \alpha) - I^+(Q, \alpha) \propto F_N F_M S(Q)$ represents a magnetic-nuclear cross term, which is linear in the amplitudes allowing the magnetic contrast with respect to the nuclear contrast to be determined. The arithmetic mean of both corresponds to the cross-section

for unpolarised neutrons, i.e. $[I^{(-)}(\mathbf{Q} \perp \mathbf{H}) + I^{(+)}(\mathbf{Q} \perp \mathbf{H})]/2 = [I^{\text{unpol}}(\mathbf{Q} \perp \mathbf{H}) = [F_N^2 + F_M^2]S(Q)$. The scattering cross-section parallel to \mathbf{H} is independent of the polarisation state resulting from pure nuclear contrast and given by $I(\mathbf{Q} // \mathbf{H}) = F_N^2 S(Q)$.

Samples of Co-ferrofluids have been prepared by Berlin Heart AG. In a first series on very diluted samples size distributions, composition: and magnetic moment: of the composite particles were evaluated. Solutions of Co-(C₂₁-H₃₉-N-O₃) (MF56) have been diluted to about 0.5 vol% Co in mixtures of protonated and deuterated toluene. The set-up of inter-particle correlation $S(Q)$ under the influence of magnetic field was studied in a second series of higher concentrated systems with nominal Co-concentrations as about 1 vol% (D1) and 5 vol% (D5) (MF 239). SANSPOL measurements [3,6] have been performed at the instrument V4 installed at the BERII reactor of HMI, Berlin. Samples were placed in a horizontal magnetic field of strength up to 1.1 T applied perpendicular to the incoming neutrons.

2. Results and discussion

SANSPOL intensities $I^\pm(\mathbf{Q} \perp \mathbf{H})$ for the very diluted samples (0.5%) are compared for the different solvents

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in Fig. 1. Maxima occur only for $I^-(\mathbf{Q} \perp \mathbf{H})$ around $Q = 0.8 \text{ nm}^{-1}$ whereas $I^+(\mathbf{Q} \perp \mathbf{H})$ decreases continuously with increasing Q . This is characteristic for the scattering of a “composite” particle built up by a magnetised core of radius R' of Co atoms surrounded by a non-magnetic surface layer of radius $R = R' + dR$ with a constant thickness of the shell. The form factor is given by $F_{\text{shell}}(Q) = [(\Delta\eta_1 - \Delta\eta_2)f_{\text{sph}}(QR') + \Delta\eta_2 f_{\text{sph}}(QR)]V_p$, with $f_{\text{sph}}(x) = 3[\sin(x) - x \cos(x)]/x^3$. The scattering contrasts for the magnetic core $\Delta\eta_1^{\pm} = \eta_1^{\text{nuc}} \pm \eta_1^{\text{mag}} - \eta_{\text{solv}}$ depends on the polarisation while that for the non-magnetic shell $\Delta\eta_2 = \eta_2^{\text{nuc}} - \eta_{\text{solv}}$ is independent on P . The intensities were calculated according to $I^{(+,-)}(\mathbf{Q} \perp \mathbf{H}) = N_p \int F_{\text{shell}}^2(Q, R) N(R') dR S(Q)$ (N_p is the number density of particles), assuming a log-normal number distribution of the core radius $N(R')$. The parameters N_p , R' , dR and the width of the size distribution were constrained to be identical for both polarisation states and the contrasts $\Delta\eta_1^{\pm}$ and $\Delta\eta_2$ have been adjusted in a non-linear least square fitting routine. The solid lines in Fig. 1 represent the calculated intensities $I^{\pm}(\mathbf{Q} \perp \mathbf{H})$ with $S(Q) = 1$. The rather sharp distribution $N(R')$ (Fig. 1b) corresponds to a volume weighted average of the core radius of $\langle R' \rangle = 3.7 \text{ nm}$ and a constant thickness of the shell of $dR = 2.47 \text{ nm}$. The resulting scattering length density profiles are shown in Fig. 1c. The values of η_2 for the shell do not depend significantly on the solvent composition which indicates that the organic surfactant is nearly impenetrable for the solvent. The magnetic moment $m_0 = 1.7 \mu_B/\text{Co-atom}$ as derived from $\eta_1^{(+,-)}$ is very close to the bulk value. The variation of magnetic-nuclear cross term in the diluted ferrofluids as a function of the external magnetic field follows closely a Langevin-function as expected for superparamagnetic behaviour of non-interacting single domain Co-particles [4].

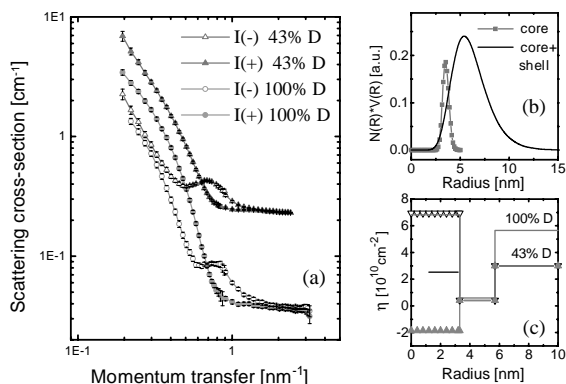


Fig. 1. SANSPOL of Co-ferrofluids (0.5%) in C_7D_8 - C_7H_8 with 100% D (circles) and 43% D (triangles) (a) Intensities $I^+(\mathbf{Q} \perp \mathbf{H})$ (full symbols) and $I^-(\mathbf{Q} \perp \mathbf{H})$ (open symbols). Solid lines: fit according to a shell model with size distribution of (b) and the scattering length densities of (c).

For the second series the azimuthally averaged intensities for unpolarised neutrons $\langle I(Q) \rangle$ plotted in Fig. 2 illustrate how the scattering behaviour changes as a function of Co-concentration and magnetic field. For random orientation $\langle I(Q)_{H=0} \rangle = [F_N^2 + 2/3 F_M^2] S(Q)$ is expected at $H = 0$ while for full alignment in strong magnetic fields $\langle I(Q) \rangle$ is given by $\langle I(Q)_{H_{\text{max}}} \rangle = [F_N^2 + 1/2 F_M^2] S(Q)$. For the sample D1, the scattering observed at zero field scales fully with that at $H = 1 \text{ T}$, i.e. there is no change of the particle arrangement in the external field. In the concentrated sample D5 a pronounced peak occurs at $Q_1 = 0.32 \text{ nm}^{-1}$ when the magnetic field is turned on indicating the set-up of correlation between the Co particles. This is fully confirmed by the SANSOL results shown in Fig. 3. In addition to the high Q features characteristic for the core-shell profile for both polarisation states a sharp peak occurs at $Q_1 = 0.32 \text{ nm}^{-1}$ in the concentrated case D5 only, i.e. the magnetic-nuclear cross term is clearly peaked resulting from the structure factor $S(Q)$. Compared to Fig. 1 an additional isotropic non-magnetic scattering contribution is superimposed to $I(+)$ and $I(-)$ at high Q . This is ascribed to a small amount (1–5%) of spherical particles with $R \approx 1.8 \text{ nm}$ which might result from excess surfactant molecules still present in the solutions. Taking into account this additional contribution, all curves $I^{\pm}(\mathbf{Q} \perp \mathbf{H})$, F_M^2 and F_N^2 could be adjusted simultaneously by the same core-shell model as described above with very similar values for the structural parameters. In the concentrated sample D5 the set-up of strong inter-particle-correlation between the Co-particles in an external magnetic field are clearly reflected by a structure factor $S(Q)$. All curves were well described by the same $S(Q)$ for which we used the hard sphere model of Percus–Yevick [7]. The resulting $S(Q)$ plotted in Fig. 3 corresponds to

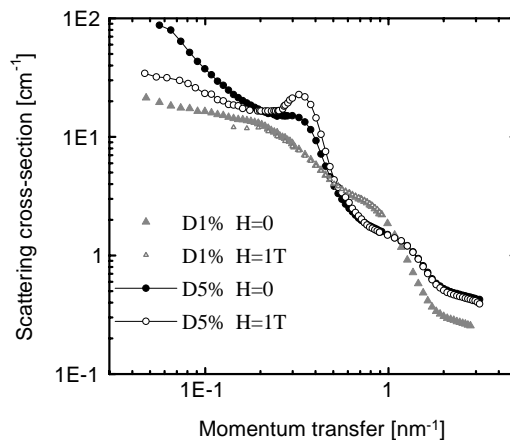


Fig. 2. Radial averaged SANS intensity of 1 vol% (triangles) and 5 vol% (circles) Co-ferrofluids in C_7D_8 at $H = 0$ (full symbols) and $H = 1.1 \text{ T}$ (open symbols).

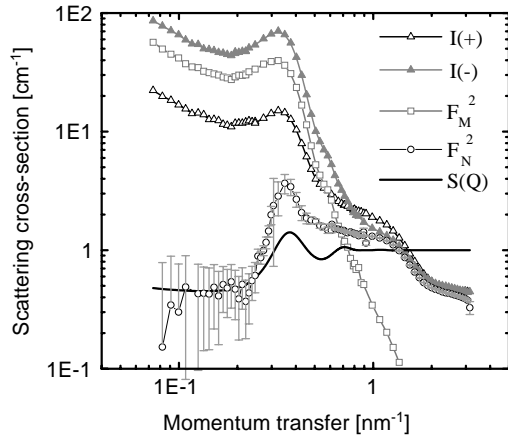


Fig. 3. SANS POL intensities $I^+(\mathbf{Q} \perp \mathbf{H})$ (solid triangles) and $I^-(\mathbf{Q} \perp \mathbf{H})$ (open triangles) of 5 vol% Co-ferrofluids in C_7D_8 and magnetic (squares) and nuclear (circles) contributions from non-polarised neutrons. The solid line represents the common structure factor $S(Q)$ used in the model fits.

volume fraction $\eta = 0.3$ of hard spheres with a radius $R_{hc} = 8.65$ nm. R_{hc} is by a factor of about 1.5 larger than the total radius $R' + dR$ of the particles which implies a rather dense packing of the particles under the influence of the magnetic field. It compares favourably with the total particle size as experienced from field induced magneto-viscous damping [8]. Dipole interaction between the particle moment should favour the formation of chains with the moment and chain directions along the magnetic field. Such a chain formation should give rise to stronger inter-particle correlation along H i.e. to an anisotropic structure factor $S(Q)$. Comparing the intensities along H and perpendicular to H did not show evidence for such anisotropic structure factor. $S(Q)$ seems to reflect the rather dense packing of the core-shell particles in the concentrated systems which is induced by an external magnetic field.

3. Summary

Combining contrast variation using different H/D mixtures of solvents with SANS POL allowed different structural units in Co-ferrofluids to be identified. Diluted liquids (< 1 vol%) consist on isolated “composite particles” formed by a superparamagnetic core of average radius of 3.7 nm and surrounded by a shell of organic surfactant. Within a thickness of 2.4 nm, the shell was found to be nearly impenetrable for the solvent. In higher concentrated samples (5 vol%) aggregation appears in an external magnetic field which is described by a densely random packing of hard spheres of radius which is by a factor of about 1.5 larger than the total particle radius.

Acknowledgements

Ferrofluid samples were kindly provided by Dr. G. Gansau, Berlin Heart AG, Germany. The work is partly supported by Priority program of the German Research Foundation (DFG project No. WI-1151).

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