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Cobalt ferrite–silica core–shell colloids: a magnetic Yukawa system

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Colloidal core–shell particles consisting of a magnetic cobalt ferrite core surrounded by a silica shell are prepared via precipitation and a subsequent modified Stöber synthesis. The resulting particles with narrow size distribution interact due to weakly acidic surface groups at the silica shell via a screened Coulomb or Yukawa potential in addition to the magnetic dipole–dipole interaction of the magnetic cores.

The structural characterization of the particles is done by transmission electron microscopy and small-angle X-ray scattering (SAXS), and the potential parameters of the electrostatic monopole and magnetic dipole-dipole interactions are determined by laser Doppler electrophoresis and magnetogranulometry, respectively.

Owing to the interaction potential, the particles self-organize to a liquid-like ordered structure as determined by SAXS. The magnetic dipole–dipole interaction becomes evident from the anisotropic scattering pattern in the presence of an external magnetic field. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: core–shell nanoparticles; monopole potential; dipole–dipole interaction

INTRODUCTION

Charged colloids have, during the last few decades, been thoroughly studied owing to their relevance for both fundamental and applied research. The availability of highly defined, nearly monodisperse systems that can act as model systems for condensed matter on enlarged scales of length and time is interesting from a theoretical point of view. As a component in paints and coatings, they have daily practical applications.

Charged colloids are stabilized by a repulsive electrostatic interaction of equally charged particles or macroions. Owing to the presence of counterions, the effective interaction between two particles is a screened Coulomb or Yukawa interaction

$$V(r_{ij}) = \frac{1}{4\pi\varepsilon}\frac{z_i z_j e_0^2}{r_{ij}}\exp(-\kappa r_{ij}) \tag{1}$$

with the number of effective charges z, the Debye screening length κ^{-1}, the permittivity ε and the elementary charge e_0, as derived by Deryaguin, Landau, Verwey and Overbeek[1] (DLVO theory). Owing to the spherical symmetry of this potential, the resulting structures are also highly symmetric.

The magnetic interaction, however, described by

$$V(r_{ij}) = \frac{\mu_0}{4\pi}\left(\frac{\boldsymbol{\mu}_i\boldsymbol{\mu}_j}{r_{ij}^3} - 3\frac{\boldsymbol{r}_i\boldsymbol{\mu}_i \cdot \boldsymbol{r}_j\boldsymbol{\mu}_j}{r_{ij}^5}\right) \tag{2}$$

with the magnetic moments of the particles $\boldsymbol{\mu}_i$ and $\boldsymbol{\mu}_j$, the particle interdistance $\boldsymbol{r}_{ij}$ and the permeability μ_0, is of lower symmetry and should induce a structural distortion of the system, if the magnetic moments of the particles are oriented parallel to an external magnetic field. This should induce an additional attraction parallel to the field and an additional repulsion in the direction perpendicular to the magnetic field. This magnetic interaction is essential for colloidal suspensions of magnetic particles, known as ferrofluids. Conventional ferrofluids, however, exhibit quite broad particle size distributions. For this reason, a self-organization normally cannot be observed.[2] The combination of a defined colloidal system with both electrostatic and magnetic interactions as given by our core–shell particles can

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act as a model system for ferrofluids. Ferrofluids exhibit some interesting macroscopic properties, like magnetoviscosity.[3] The availability of a defined model system can provide some experimental evidence for the mesoscopic reasons for this effects.

PREPARATION AND CHARACTERIZATION

The preparation of the particles starts from the coprecipitation of cobalt and iron salts. The precipitate is suspended as aqueous cobalt ferrite fluid. The coating with silica is achieved by a subsequent Stöber synthesis,[4] i.e. a polycondensation of tetraethoxysilane. Details are published elsewhere.[5]

The core–shell structure becomes evident from the small-angle X-ray scattering (SAXS) of a highly dilute suspension (Fig. 1). In this case, the arrangement of the particles is random and the scattering pattern arises solely from intraparticular correlations and can be interpreted as a form factor. The solid line in Fig. 1 represents a least-squares fit assuming core shell particles with constant core-to-shell radius, whose overall radius follows a Schulz–Flory distribution.

$$c(r, r_0, Z) = \frac{r^Z}{Z!}\left(\frac{Z+1}{r_0}\right)^{Z+1} \mathrm{e}^{-(Z+1)r/r_0} \tag{3}$$

The corresponding scattering function (superposition of core–shell form factor and size distribution) can be calculated analytically and will be published elsewhere.

Despite the model's simplicity, the fit reasonably describes the scattered intensity. The resulting parameters are the diameter $\sigma = 71.3 \pm 0.1$ nm, the core diameter $\sigma_c = 14.6 \pm 1$ nm, the polydispersity $p = \langle \sigma^2 \rangle / \langle \sigma \rangle^2 - 1 = 0.014$ and the core/shell ratio of scattering length densities $\rho_c/\rho_s = 5 \pm 1$. These parameters are in good agreement with the transmission electron micrographs.

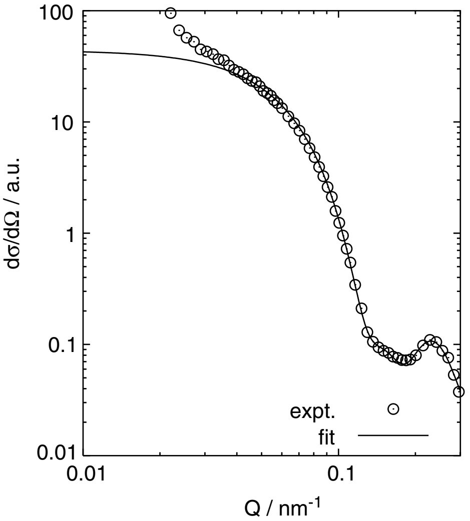

Figure 1. SAXS scattering of a dilute sample of the core–shell particles. The data fit corresponds to a total particle diameter of $\sigma = 71.3 \pm 0.1$ nm with a polydispersity of $p = 0.017 \pm 0.001$ and a core diameter of $\sigma_c = 14.6 \pm 1$ nm. The core–shell density ratio is $\rho_c/\rho_s = 5 \pm 1$.

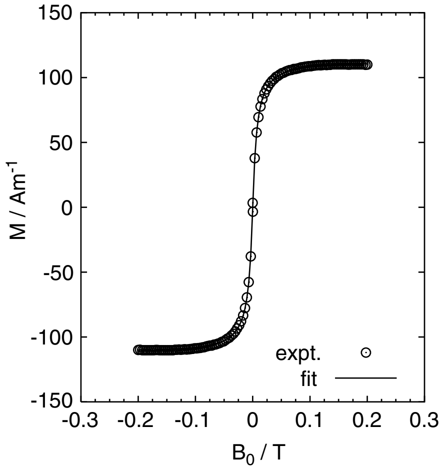

Figure 2. Magnetization of a sample with a volume fraction $\phi = 0.03$. The Langevin data fit leads to a magnetic particle diameter of $\sigma = 14.2 \pm 0.1$ nm and a polydispersity $p = 0.09$.

The magnetic characterization was done by a magnetization measurement of a fluid with an overall volume fraction (core plus shell) of $\phi = 0.03$ employing a vibrating-sample magnetometer (Fig. 2). The experimental data can be described accurately by an ensemble of noninteracting Flory–Schulz distributed spheres with a mean diameter $\langle \sigma_{c,m} \rangle = 14.2 \pm 0.1$ nm and a polydispersity $p = 0.09$, which coincides well in terms of the mean size with the small-angle scattering data. The stability of the colloidal dispersion as a function of the pH was determined by laser Doppler electrophoresis employing a Malvern 3000HS Zetasizer. The ζ-potential in dependence on the pH of the suspending medium is displayed in Fig. 3. The point of zero charge at pH = 4.5 indicates the weak acidity of surface groups. The number of charges, originating from the weakly acidic groups, which influence the electrophoretic mobility μ, i.e. the ratio of drift velocity to electric field, depends strongly on the local pH at the surface. The local pH again is influenced by the migration in an electric field, since the ionic cloud surrounding a macroion changes by hydrodynamic effects if a particle moves.

A much better description of the interaction is the effective number of charges z_{eff}, which determines the pair potential of two particles according to Eqn (1). The resulting forces give rise to interparticular correlations, as visible in the liquid-like structure factor displayed in Fig. 4. Employing the rescaled mean spherical approximation (RMSA), the Ornstein–Zernike equation can be solved analytically. The solid line in Fig. 4 represents a least-squares fit of the RMSA approach to the experimental structure factor, yielding $z_{\mathrm{eff}} = 200$ and a number density $\rho = 1.79 \times 10^{22}$ m^{-3}.

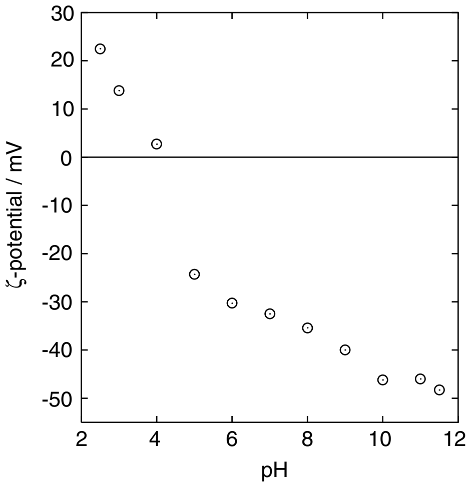

Figure 3. ζ-potential dependence on the pH.

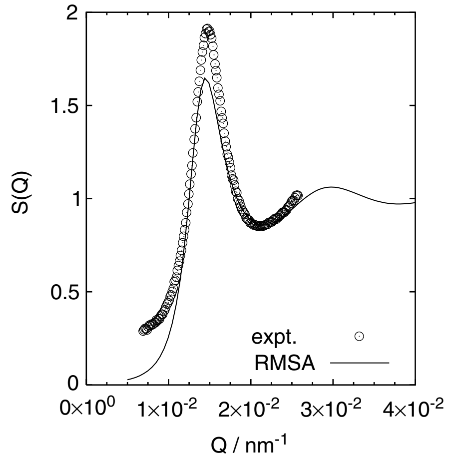

Figure 4. Structure factor $S(Q)$ of a highly dilute sample. The effective charge $z_{\text{eff}} = 200$ is obtained from the RMSA fit.

Fig. 5 displays the two-dimensional scattering pattern without and with horizontally applied magnetic field. On the right-hand side, the anisotropy induced by a field of $H = 1$ T is clearly visible, whereas at $H < 10^{-5}$ T on the left-hand side the pattern is radially symmetric. Despite the small magnetic contribution to the interaction potential, which even at the closest possible interdistance $r_{ij} = \sigma$ is as small as approximately 0.04 k_BT, a distortion of the liquid-like structure can be observed in external fields as low as 10 mT. A detailed description of the structural influence of an external field will be reported in a forthcoming publication.

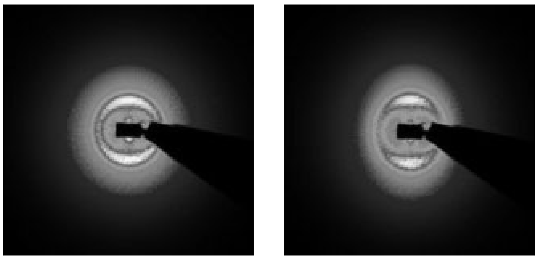

Figure 5. Scattered intensity without ($B_0 < 10^{-5}$ T) (left) and with horizontally applied magnetic field of $B_0 = 1$ T (right).

DISCUSSION

The cobalt ferrite–silica core–shell particles are a well-defined model system for ferrofluids. The narrow size distribution allows self-organization on length scales accessible by SAXS. The experiments show a good agreement between topological and magnetic size of the cores. The magnetic polydispersity of $p = 0.09$ is considerably small compared with conventional ferrofluids.

Even a small magnetic interaction, much less than the thermal energy k_BT, can induce structural changes in liquid-like ordered colloidal suspensions, interacting via extremely soft screened Coulomb potentials. This can only be explained by long-range indirect interactions resulting from collective phenomena, i.e. a coupling of magnetic moments. The cobalt ferrite–silica particles as a model system are well suited to determine a critical ratio of interaction to distance at which a magnetic coupling arises. This might be of interest to the understanding of ferromagnetism in atomic systems.

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REFERENCES

1. Overbeek JThG, Verwey EJ. Theory of the Stability of Lyophobic Colloids. In *Colloid Science*, Kruyt HR (ed.). *Advances in Colloid Interface Science*. Elsevier: Amsterdam, 1948; 17.
2. Pusey PN. In *Liquids, Freezing and the Glass Transition*, Levesque D, Hansen JP, Zinn-Justin J (eds). Elsevier: Amsterdam, 1991; 765–942.
3. Odenbach S. In *Magnetoviscous Effects in Ferrofluids*. Springer: Berlin, 2002.
4. Stöber W, Fink A, Bohn E. *J. Colloid Interface Sci.* 1968; **26**: 62.
5. Wagner J, Autenrieth T, Hempelmann R. *J. Magn. Magn. Mater.* 2002; **252**: 4.