

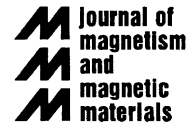


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Brownian relaxation of magnetic colloids

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Abstract

Ferrofluids based on nanoscaled cobalt ferrites, stabilized either sterically or electrostatically, are prepared by controlled precipitation and subsequent surface modification. The translational and rotational dynamics are studied by means of photon correlation spectroscopy and frequency-dependent AC magnetic susceptibility measurements, respectively. From these data, the distribution of hydrodynamic diameters is determined. The agreement in the resulting diameters in the case of sterical stabilization indicates the absence of agglomerates, whereas the disagreement in the case of electrostatical stabilization points to weak agglomerates. The proportionality of the magnetic relaxation times to the viscosity of the dispersion medium (different glycerol/water mixtures) is evidence for Brownian-type relaxation behavior.

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1. Introduction

Experimental studies of ferrofluids in alternating magnetic fields have been published by Maiorov [1]. Fannin later developed a special measuring technique [2] and demonstrated how vital the susceptibility measurements are for an understanding of the dynamic behavior of these colloidal suspension. Fannin estimated the particles' hydrodynamic radius on the basis of the Debye theory and found a simple method to detect agglomerates in ferrofluids [3]. In the present contribution, we study CoFe₂O₄-based fluids, because CoFe₂O₄ is a magnetically hard material (anisotropy constant $K \approx 200 \text{ kJ m}^{-3}$); by a systematic variation of the viscosity of the carrier liquid we will, by measuring the frequency-dependent complex magnetic susceptibility, confirm the Brownian-type of the relaxation.

Another aim of this contribution is to compare the hydrodynamic diameter derived from the AC-susceptibility data (which is associated with particle rotation) and that derived from dynamic light scattering data (which is associated with particle translation).

2. Theory

The characteristic Brownian relaxation time is determined by the rotational mobility of the colloidal magnetic particles [4] and given by

$$\tau_B = \frac{3V_{\text{hyd}}}{k_B T} \eta = \frac{\pi D_{\text{hyd}}^3}{2k_B T} \eta. \quad (1)$$

Here η is the dynamic viscosity of the suspending medium, V_{hyd} and D_{hyd} denote the hydrodynamic particle volume and diameter, respectively.

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The relaxation time τ_B is experimentally accessible from the complex magnetic susceptibility (as a function of the frequency f) of the ferrofluid which for a monodisperse system of noninteracting and rigid dipoles immersed in a liquid carrier turns out to be of Debye form

$$\chi(f) = \frac{\chi_0}{1 - i2\pi f\tau_B}, \quad (2)$$

with the static susceptibility:

$$\chi_0 = \frac{N}{V} \frac{m^2}{3\mu_0 k_B T}, \quad (3)$$

N/V denotes the number density of the (spherical) particles, and m , the giant magnetic moment of one (single domain) particle, is connected to the spontaneous magnetization of the particle's material by

$$m = M_s \frac{\pi}{6} D_{\text{mag}}^3, \quad (4)$$

where D_{mag} is the diameter of the magnetic core of the particle, i.e. we assume a core/shell structure of the particle with

$$D_{\text{hyd}} = D_{\text{mag}} + 2\delta \quad (5)$$

with the shell thickness δ . In the case of sterically stabilized ferrofluids δ can be interpreted as the length of the surfactant molecules plus the thickness of a possibly present nonmagnetic surface layer on the crystalline, magnetic particle material. For electrostatic stabilization one has to consider the rigid Helmholtz double layer.

In reality, the ferrofluid system is polydisperse and therefore the complex magnetic susceptibility is now given by a superposition of Debye terms, each with its specific relaxation time:

$$\chi(f) = \frac{1}{3V\mu_0 k_B T} \sum_{i=1}^N \frac{m_i^2}{1 - i2\pi f\tau_{B,i}}. \quad (6)$$

Using the relation defined above and replacing the discrete sum in Eq. (6) by an integral weighted with a diameter distribution $P(D_{\text{hyd}})$ we may write the reduced susceptibility as

$$\frac{\chi(f)}{\chi_0} = \frac{1}{\langle (D_{\text{hyd}} - 2\delta)^6 \rangle} \times \int_{2\delta}^{\infty} \frac{(D_{\text{hyd}} - 2\delta)^6}{1 - i2\pi f \frac{\pi\eta}{2k_B T} D_{\text{hyd}}^3} P(D_{\text{hyd}}) dD_{\text{hyd}}. \quad (7)$$

The distribution function P is assumed to be of lognormal form:

$$P(D) = \frac{1}{\sqrt{2\pi} \ln \sigma D} \exp\left[-\frac{\ln^2(D/D_0)}{2 \ln^2 \sigma}\right]. \quad (8)$$

Eqs. (7) and (8) are used to fit both the real and imaginary part of the experimental susceptibility data

simultaneously, with the median D_0 , the geometrical distribution width σ and the nonmagnetic layer depth δ as fit parameters. It turns out, however, that the value of δ has almost no influence on the quality of the fit, although its choice influences the results of the other parameters. Therefore we had to keep δ always fixed.

3. Experimental

The CoFe_2O_4 is synthesized by a co-precipitation reaction that occurs upon mixing CoCl_2 and FeCl_3 solutions with a surplus of NaOH . To disperse the nanoparticles in water and also in glycerol (electrostatically stabilized ferrofluid, FF_{el}) we have used tetramethylammonium hydroxide ($\text{N}(\text{CH}_3)_4\text{OH}$). Details of the preparation are described by Massart et al. [5]. For the sterical stabilization of the ferrofluid (FF_{st}) in decane we have used N -oleoyl-sarcosine $\text{C}_{21}\text{H}_{39}\text{NO}_3$ as a surfactant. The mixture of CoFe_2O_4 particles and N -oleoyl-sarcosine in water is heated to 80°C for 1 h. After adding a small amount of hydrochloric acid, the precipitate agglomerates. The supernatant liquid can be decanted. After washing the coated particles several times with water to remove the salts, a colloidal dispersion of CoFe_2O_4 is achieved by adding decane to the wet slurry.

For the AC susceptibility measurements we use an impedance analyzer. The magnetic fluid is inserted in a coil and the changes in its inductance is detected. The photon correlation spectroscopy is performed using an ALV apparatus for static and dynamic light scattering.

4. Results

4.1. Characterization

The characterization of the particle size was done by XRD with dry CoFe_2O_4 powder. We achieve for the crystalline particle diameter of the FF_{el} $D_{0,\text{cryst}} = 8.8$ nm and $\sigma = 1.45$ and of the FF_{ste} $D_{0,\text{cryst}} = 8.4$ nm and $\sigma = 1.29$. The hydrodynamic diameter was measured by dynamic light scattering with a 1:1000 diluted dispersion of the fluid FF_{el} with water and FF_{ste} with decane. FF_{el} has a hydrodynamic diameter $D_{0,\text{hyd}} = 13.4$ nm with $\sigma = 1.65$ and FF_{ste} $D_{0,\text{hyd}} = 11.2$ nm with $\sigma = 1.51$.

4.2. Charge stabilized ferrofluid

We have systematically varied the viscosity of the suspension medium by mixing water with glycerol. The viscosity of the fluid we measured using a cone-plate rotating viscosimeter. The frequency-dependent, complex magnetic susceptibility was measured at room temperature over the frequency range 100 Hz–1 MHz.

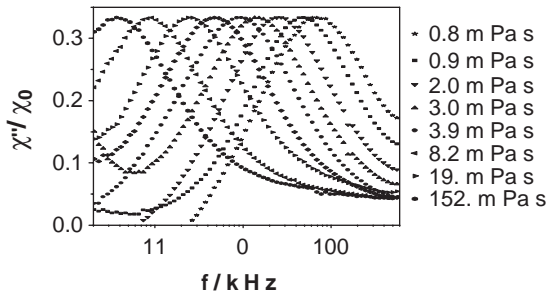


Fig. 1. Imaginary part of the susceptibility of CoFe_2O_4 in different ratio of glycerol/water.

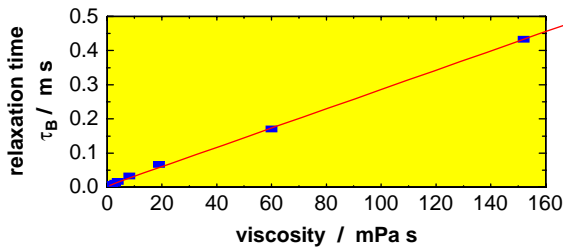


Fig. 2. Relaxation time vs. viscosity.

The effective relaxation time, as derived from the frequency of the maximum of the imaginary part of the AC magnetic susceptibility, see Fig. 1, is proportional to the viscosity as displayed in Fig. 2, in accordance with Eq. (1).

In Fig. 3A the reduced magnetic susceptibility (χ'/χ_0) and (χ''/χ_0), respectively) versus f (kHz) for this fluid is shown together with the fit result. We achieve a hydrodynamic diameter $D_{0,\text{hyd}}$ of 8.5 nm and a width σ of 1.45, assuming $\delta = 0$ nm.

4.3. Sterically stabilized ferrofluid

In Fig. 3B χ'/χ_0 and χ''/χ_0 for FF_{ste} are displayed and compared to the corresponding fit with δ fixed at 0 nm. The fit procedure was repeated with the surfactant thicknesses δ fixed at 1 and 2 nm. The results are shown in Fig. 4B.

5. Discussion and conclusion

In the case of electrostatic stabilization the particle diameter measured by XRD of 8.4 nm plus a small surfactant length plus the Helmholtz double layer is in the order of the diameter determined by the fit of the AC-susceptibility (8.5 nm). This means that the rotation is accomplished by single individual particles. On the

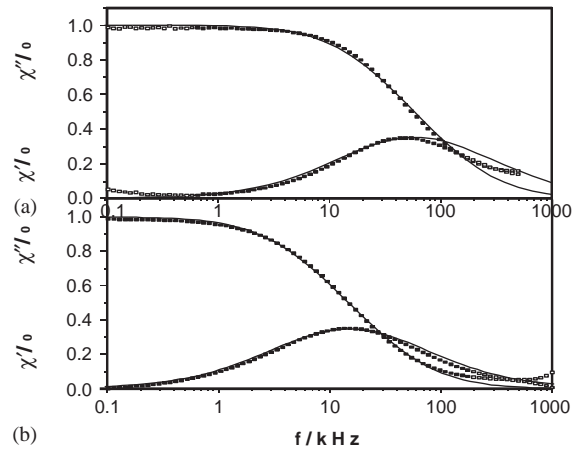


Fig. 3. Fit to the susceptibility data of CoFe_2O_4 in glycerol/water (A) and of CoFe_2O_4 in decane (B).

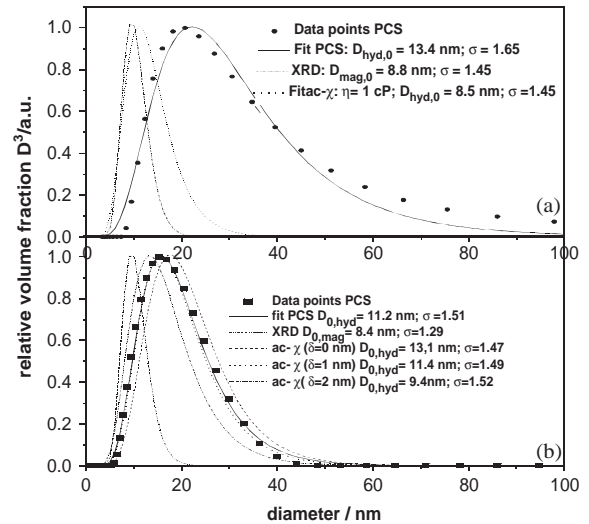


Fig. 4. Comparing the hydrodynamic diameter distribution of CoFe_2O_4 in glycerol/water (A) and CoFe_2O_4 in decane (B) by PCS, XRD and AC-susceptibility.

other hand, dynamic light scattering (which primarily measures diffusion) indicates small agglomerates of particles. The comparison of the diameters is shown in Fig. 4A.

In the case of sterical stabilization, if we assume a δ of 1 nm, we get an hydrodynamic diameter by the AC-susceptibility fit of 11.4 nm. It shows very good agreement to the diameter determined by DLS of 11.2 nm (Fig. 4B). It is nearly the crystalline particle size 8.4 nm plus 1 nm surfactant thickness. For δ is 0 and 2 nm we get similar values, see Fig. 4B. We conclude from these results that in this fluid both the translation

and the rotation is accomplished by individual single particles.

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