Brownian relaxation of magnetic colloids

B. Fischer\textsuperscript{a,}\textsuperscript{*}, B. Huke\textsuperscript{b}, M. Lücke\textsuperscript{b}, R. Hempelmann\textsuperscript{a}

\textsuperscript{a}Physical Chemistry, Saarland University, 66123 Saarbrücken, Germany
\textsuperscript{b}Theoretical Physics, Saarland University, 66123 Saarbrücken, Germany

Available online 28 November 2004

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 electrostatic 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.

© 2004 Elsevier B.V. All rights reserved.

PACS: 76.60.Es; 75.50.Tt; 75.50.Mm; 82.70.Dd

Keywords: Relaxation effects; Fine-particle systems; Magnetic liquids; Colloids

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 CoFe\textsubscript{2}O\textsubscript{4}-based fluids, because CoFe\textsubscript{2}O\textsubscript{4} 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 $\eta$ is the dynamic viscosity of the suspending medium, $V_{\text{hyd}}$ and $D_{\text{hyd}}$ denote the hydrodynamic volume and diameter, respectively.
The relaxation time $\tau_{B}$ 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

$$\chi(f) = \frac{\chi_0}{1 - i2\pi f \tau_{B}},$$

(2)

with the static susceptibility:

$$\chi_0 = \frac{N m^2}{3 \mu_0 k_B T};$$

(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

$$m = M_s \frac{\pi}{6} D_{mag}^3,$$

(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

$$D_{hyd} = D_{mag} + 2\delta$$

(5)

with the shell thickness $\delta$. In the case of sterically stabilized ferrofluids $\delta$ 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 electrostatical 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:

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

(6)

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

$$\chi(f) = \frac{1}{\chi_0} \int_{D_{hyd} = \delta}^{\infty} \int_{2\delta}^{\infty} \frac{(D_{hyd} - 2\delta)^6}{1 - i2\pi f \frac{2\pi \sigma}{2\delta} D_{hyd}} P(D_{hyd}) \, dD_{hyd}.$$ 

(7)

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

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

(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 $\sigma$ and the nonmagnetic layer depth $\delta$ as fit parameters. It turns out, however, that the value of $\delta$ 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 $\delta$ always fixed.

3. Experimental

The CoFe$_2$O$_4$ 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 tetrathylenammonium hydroxide (N(CH$_3$)$_4$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 C$_{21}$H$_{39}$NO$_3$ as a surfactant. The mixture of CoFe$_2$O$_4$ 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$_2$O$_4$ 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$_2$O$_4$ powder. We achieve for the crystalline particle diameter of the FF$_{el}$ $D_{0,cryst} = 8.8$ nm and $\sigma = 1.45$ and of the FF$_{st}$ $D_{0,cryst} = 8.4$ 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$_{st}$ with decane. FF$_{el}$ has a hydrodynamic diameter $D_{0,hyd} = 13.4$ nm with $\sigma = 1.65$ and FF$_{st}$ $D_{0,hyd} = 11.2$ 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.
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 ($\chi'/\chi_0$) and ($\chi''/\chi_0$), respectively versus $f$ (kHz) for this fluid is shown together with the fit result. We achieve an hydrodynamic diameter $D_{\text{hyd}}$ of 8.5 nm and a width $\sigma$ of 1.45, assuming $\delta = 0$ nm.

### 4.3. Sterically stabilized ferrofluid

In Fig. 3B $\chi'/\chi_0$ and $\chi''/\chi_0$ for FFste are displayed and compared to the corresponding fit with $\delta$ fixed at 0 nm. The fit procedure was repeated with the surfactant thicknesses $\delta$ 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 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 $\delta$ 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 $\delta$ 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.

References


