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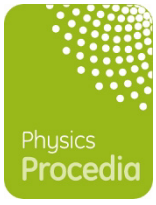

Dynamics of $CoFe_2O_4$ Single-Core Nanoparticles in Viscoelastic Media

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Abstract

The dynamics of single-core $CoFe_2O_4$ nanoparticles in viscoelastic media was studied utilizing ac susceptibility and fluxgate magnetorelaxometry measurements. As viscoelastic medium aqueous gelatin suspensions with gelatin contents between 2.5 wt% and 10 wt% were used. Specifically, the gelation kinetics after cooling the sample from the sol state (313 K) to 296 K was investigated. It is shown that the measurement results can be analyzed with the Voigt-Kelvin model thus providing information on local dynamic viscosity and shear modulus.

Keywords: Magnetic nanoparticles, dynamics, viscoelastic media, ac susceptibility, magnetorelaxometry

1 Introduction

The dynamics of magnetic nanoparticles (MNPs) has been subject of numerous theoretical (for comprehensive overview article see (Coffey, Cregg, & Kalmikov, 1993), (Raikher & Shliomis, 1994)) and experimental studies. If the MNPs are suspended in a Newtonian fluid, such as DI water, the response to a magnetic field pulse, a sinusoidal or rotating magnetic field can take place via the Brownian and the Néel mechanism. In the former case, the whole particle including a shell rotates. The Brownian time constant is given by

$$\tau_B = \frac{3\eta V_h}{k_B T}$$

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with the dynamic viscosity η, the hydrodynamic particle volume V_h and the thermal energy k_BT. In the Néel mechanism, the magnetic moment changes its direction within the particle. The corresponding Néel time constant is given by

$$\tau_N = \tau_0 \exp\left(\frac{KV_c}{k_BT}\right)$$

where τ_0 is a time constant which is typically assumed between 10^{-9} s and 10^{-11} s, K is the anisotropy constant and V_c the core volume. Both mechanisms are present in a fluid and the one with the shorter relaxation time dominates resulting in an effective time constant

$$\tau_{eff} = \frac{\tau_N \tau_B}{\tau_N + \tau_B}.$$

If the MNPs are immobilized, e.g., by freeze-drying them in a mannite matrix, only the Néel relaxation can take place.

The investigation of the dynamic properties of MNPs has been utilized for their characterization via the dependency of the Brownian time constant on hydrodynamic size and of the Néel time constant on anisotropy constant and core size (Eberbeck, Wiekhorst, Steinhoff, & Trahms, 2006), (Ludwig, Heim, & Schilling, 2009), (Adolphi, et al., 2010), (Ahrentorp, et al., 2015). On the other hand, it has been successfully applied for the realization of homogeneous bioassays. Here magnetically blocked MNPs are needed which are characterized by $\tau_N >> \tau_B$. Thus, the specific binding of biological targets such as proteins cause an increase of the hydrodynamic size and consequently of the Brownian time constant.

Recently, several groups reported on investigations of the dynamics of MNPs in non-Newtonian fluids (Roeben, Roeder, Teusch, Effertz, Schmidt, & Deiters, 2014) and viscoelastic matrices (Tschöpe, Birster, Trapp, Bender, & Birringer, 2014). For example, Tschöpe et al. (Tschöpe, Birster, Trapp, Bender, & Birringer, 2014) presented magneto-optical investigations of the dynamics of Ni nanorods in aqueous gelatin solutions in oscillating magnetic fields. They showed that the measured dynamics can be well described by the Voigt-Kelvin model describing a viscous and an elastic term in parallel.

In this paper, we present ac susceptibility (ACS) and fluxgate magnetorelaxometry (MRX) measurements on magnetically blocked single-core $CoFe_2O_4$ nanoparticles in aqueous gelatin solutions – representing a well-established model system for a viscoelastic medium – during the gelation process. While for Ni nanorods with lengths of more than 250 nm and magnetic field amplitudes of the order of 10 mT thermal agitation is negligible compared to the magnetic energy, thermal effects must be taken into account for the 15 nm core diameter $CoFe_2O_4$ nanoparticles studied here. The measured ACS spectra are analyzed in terms of a theoretical model by Raikher et al. (Raikher, Rusakov, Coffey, & Kalmykov, 2001), for the analysis of the MRX data the moment superposition model (MSM) is modified by inserting the asymptotic expressions for the effective time constant as derived by Raikher et al. (Raikher, Rusakov, Coffey, & Kalmykov, 2001).

2 Model

The Voigt-Kelvin model represents a viscous and an elastic term in parallel. According to Raikher et al. (Raikher, Rusakov, Coffey, & Kalmykov, 2001), the equation of motion reads

$$I\ddot{\vartheta} + \zeta\dot{\vartheta} + K\vartheta = y(t).$$

Here ϑ is the angle between magnetic moment and applied magnetic field, I the moment of inertia of the particle, ζ the rotational friction coefficient, K the linear elastic restoring parameter and $y(t)$ the stochastic driving torque due to thermal energy. Note that the magnetic torque is assumed to be negligibly small. The dynamic susceptibility was shown to be given by

$$\chi_\alpha(\omega) = \chi_{0,\alpha}\left(1 + i\omega\int_0^\infty d\tau e^{i\omega\tau} G_\alpha(\tau)\right) \tag{1}$$

with

$$\chi_{0,\parallel} = \frac{nm^2}{k_B T}\exp\left(-\frac{k_B T}{K}\right)\left[\cosh\left(\frac{k_B T}{K}\right) - 1\right] \text{ and } \chi_{0,\perp} = \frac{nm^2}{k_B T}\exp\left(-\frac{k_B T}{K}\right)\sinh\left(\frac{k_B T}{K}\right)$$

as well as

$$G_\parallel(\tau) = \frac{\left(\cosh\left(\frac{k_B T}{K}\exp\left(-\frac{t}{\tau_K}\right)\right) - 1\right)\exp(i\omega t)}{\cosh\left(\frac{k_B T}{K}\right) - 1} \text{ and } G_\perp(\tau) = \frac{\sinh\left(\frac{k_B T}{K}\exp\left(-\frac{t}{\tau_K}\right)\right)\exp(i\omega t)}{\sinh\left(\frac{k_B T}{K}\right)}.$$

The time constant $\tau_K = \zeta/K$. The total susceptibility calculates to $\chi_{tot}(\omega) = \frac{1}{3}\left(\chi_\parallel + 2\chi_\perp\right)$.

It was shown in (Raikher, Rusakov, Coffey, & Kalmykov, 2001) that analytical expressions could only be obtained for the limiting cases of high ($K >> k_B T$) or low ($k_B T >> K$) rigidity. For monitoring the temporal evolution of the shear modulus in the intermediate range ($k_B T \approx K$) we therefore evaluated eq. (1) numerically.

While the viscosity η which is related to the rotational friction coefficient via $\zeta = 6\eta V_h$ causes a shift of the maximum of the imaginary part, the shear modulus G which is related to the elastic restoring parameter via $K = 6GV_h$ affects both the amplitude and the position of the maximum in the imaginary part. In order to fit the experimentally measured imaginary parts of the ACS, lognormal distributions of the hydrodynamic diameter (assuming spherical MNPs) and of the local dynamic viscosity had to be included. In the analysis it is assumed that the hydrodynamic size distribution does not change during gelation. Thus, an increase of G as well as an increase of the standard deviation of the distribution of local dynamic viscosities σ_η cause a decrease of the amplitude of χ.

Currently, there is no model describing the response of MNPs in a viscoelastic medium to a magnetic field pulse. However, in the paper by Raikher et al. (Raikher, Rusakov, Coffey, & Kalmykov, 2001) an expression for the asymptotic time constant is provided. In the low-rigidity regime $k_B T >> K$, the effective time constant is given by

$$\tau_{eff} = \tau_B\left(1 + \frac{K}{k_B T}\right).$$

For spherical particles, $K = G\pi d_h^3$ so that the expression modifies to

$$\tau_{eff} = \frac{\pi\eta d_h^3}{2k_B T}\left(1 + \frac{G\pi d_h^3}{k_B T}\right).$$

To simulate MRX curves, the so-called magnetic moment superposition model (Eberbeck, Wiekhorst, Steinhoff, & Trahms, 2006), (Ludwig, Heim, & Schilling, 2009) was accordingly modified including distributions of the hydrodynamic particle diameter and local dynamic viscosities – as used for the analysis of the ACS spectra:

$$B(t) = C\int f(\eta)\int f(d_h)\left[1 - \exp\left(-\frac{t_{mag}}{\tau_{eff}}\right)\right]\exp\left(-\frac{t}{\tau_{eff}}\right)dd_h d\eta.$$

The term C is a geometric prefactor multiplied with the Langevin function and the mean magnetic moment of the MNPs.

3 Experimental

In this paper we use $CoFe_2O_4$ single-core nanoparticles with a hydrate shell. Details on the nanoparticle synthesis can be found in (Roeben, Roeder, Teusch, Effertz, Schmidt, & Deiters, 2014), (Sun, et al., 2004), (Dai, et al., 2010). The mean core diameter of 15 ± 0.18 nm was determined from TEM. Due to their large magnetocrystalline anisotropy the particles are magnetically blocked (Torres, et al., 2010), (Cullity & Graham, 2011). The particles were characterized by ac susceptibility measurements of aqueous suspensions (Ludwig, Guillaume, Schilling, Frickel, & Schmidt, 2010) and the mean hydrodynamic diameter of these particles was determined to 18 ± 0.4 nm.

As viscoelastic model system, aqueous gelatin solutions were utilized. Gelatin from porcine skin (mean mass = 23 kDa with broad polydispersity) was mixed with DI water. Details of the gelatin sol fabrication are described in (Tschöpe, Birster, Trapp, Bender, & Birringer, 2014). Samples with 2.5 wt%, 5 wt%, 7.5 wt%, and 10 wt% gelatin were prepared.

To start in the sol, i.e., viscous state, the samples were heated to 313 K and hold at this temperature for 60 min. The first ACS measurement was performed at a sample temperature of 313 K, i.e., before cool-down. The viscosity values at 313 K were independently determined using an Anton Paar SVM 3000 Stabinger viscosimeter. Knowing the dynamic viscosity at 313 K, the ACS spectra measured at 313 K were fitted with the Debye model extended by inserting a lognormal distribution of hydrodynamic diameters. For the 2.5 wt% sample a mean hydrodynamic diameter of 36 nm was determined, for the 7.5 wt% sample a value of 47 nm was found. These values are significantly larger than the value obtained for an aqueous suspension at room temperature indicating that an adsorbant gelatin layer has formed around the nanoparticles. After cooling the samples to 296 K within 30 min, ACS spectra were repetitively recorded, thus monitoring the gelation process which is accompanied by changes of dynamic viscosity and shear modulus.

To measure the complex ac susceptibility, the MNP sample is exposed to a sinusoidal magnetic field and a frequency sweep is performed. Here we utilize our temperature adjustable fluxgate-based setup which was originally designed for investigations of the MNP response to a rotating magnetic field. Real and imaginary parts of the ac susceptibility are calculated from the differential fluxgate signal for a field amplitude of 200 µT in the frequency range between 2 Hz and 9 kHz. Details on the experimental setup can be found in (Dieckhoff, Schilling, & Ludwig, 2011).

In a magnetorelaxometry (MRX) measurement, a magnetizing field – typically 2 mT amplitude and 2 s duration – aligns the MNP's magnetic moments. After abruptly switching off the magnetizing field, the decay of the sample's magnetic moments is measured as a function of time. Here we utilized our gradiometric fluxgate MRX system (Ludwig, Mäuselein, Heim, & Schilling, 2005). Since the fluxgate MRX system does not allow a sample heating, the samples were externally heated and thermalized. After cooling the sample to 296 K, repetitive MRX measurements were performed.

4 Results

Figure 1 (a) shows the imaginary part χ'' of the ac susceptibility vs. frequency for the sample with 2.5 wt% gelatin. With increasing gelation time the maximum position of the imaginary part shifts monotonously to lower frequencies, the spectra become wider and the amplitudes decrease. The χ'' spectra of the sample with 5 wt% gelatin also shows the same trend regarding amplitude and width. In contrast, the maximum of the imaginary part first shifts to smaller frequencies, but at long gelation times a shift to higher frequencies takes place (see Fig.1 (b)). The measurement curves of the sample with 7.5 wt% and 10 wt% gelatin are not shown since the peaks of the imaginary part of ACS shift very rapidly towards lower frequencies and before reaching 296 K they are out of the measurement window, i.e., below 1 Hz.

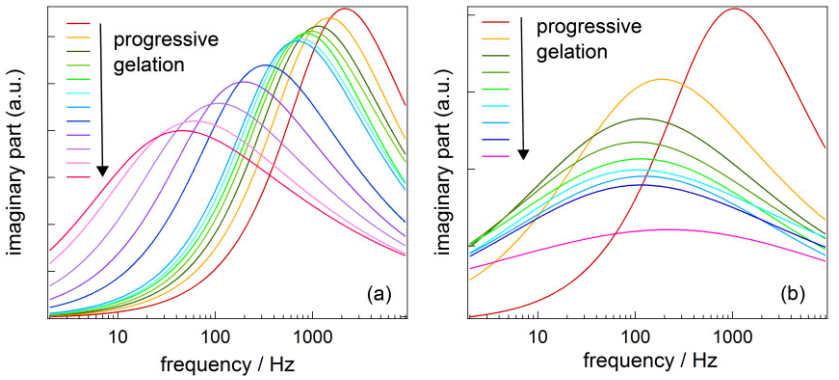

Fig. 1: Imaginary part of ACS spectra for the sample with (a) 2.5 wt% and (b) 5 wt% gelatin.

To obtain information about the viscosity η and the shear modulus G, the Voigt-Kelvin model described in Sect. 2 was applied. Since it can be assumed that the gelatin solution is still liquid for the first curve measured at 296 K (typically 30 min after starting the cool-down process) because the gel formation did not yet start the shear modulus can be assumed to be negligibly small. The viscosity η and the corresponding standard deviation σ_η can thus directly be determined. The decrease of the amplitude of the maximum in χ'' of the subsequently measured spectra is caused by an increase of σ_η and G. The obtained data from the fits of the measured curves are depicted in figure 2. In spite of the qualitatively different variation of the ACS spectra with gelation time, the extracted viscoelastic parameters show qualitatively similar trends.

According to Normand et al. (Normand, Muller, Ravey, & Parker, 2000) there are four phases in the gelation kinetics. We attribute the time interval up to 300 min to phase 2 which is characterized by the gel formation and a rapid increase of G and η. The time up to about 4000 min may be attributed to phase 3 which according to Normand et al. is related to the extension of existing cross-links in the network rather than the formation of new ones. The rise of G at longer times was also observed by the authors applying a stress-controlled rheometer technique.

Figure 3 (a) shows the MRX curves for the sample with 2.5 wt% gelatin measured after reaching 296 K. The curves are normalized to the flux density signal before the magnetizing field is switched off. The signal decay monotonously slows down with increasing gelation time caused by an increase

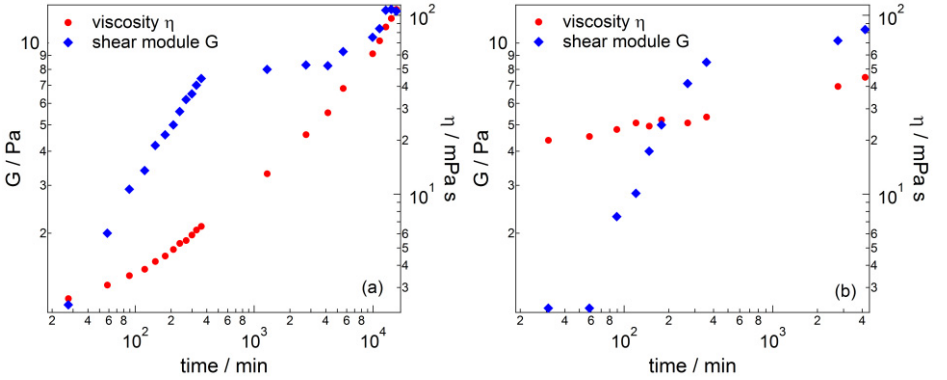

Fig. 2: Viscosity η and shear modulus G as function of gelation time for the samples with (a) 2.5 wt% and (b) 5 wt% gelatin.

of the effective relaxation time. Fig. 3(b) depicts the simulated MRX curves calculated with the parameter obtained from the fits at the ACS spectra measured at similar times after reaching 296 K. The simulated and measured data agree fairly well. The curves of the sample with 5 wt% gelatin are qualitatively similar to the MRX curves for the sample with 2.5 wt% gelatin.

The behavior of the sample with 7.5 wt% and 10 wt% gelatin is more complex. Figure 4 shows the measured, not normalized MRX curves of the sample with 7.5 wt% gelatin. The behavior is no longer systematic and even a crossing of curves is observed. The MRX curves of the sample with 10 wt% gelatin measured after reaching 296 K show only marginal differences and they are barely distinguishable from the curve recorded on a freeze-dried reference sample where relaxation can only take place via the Néel mechanism. These findings are caused by the fact that the effective Brownian time constant becomes or is larger than the Néel time constant of the utilized $CoFe_2O_4$ nanoparticles.

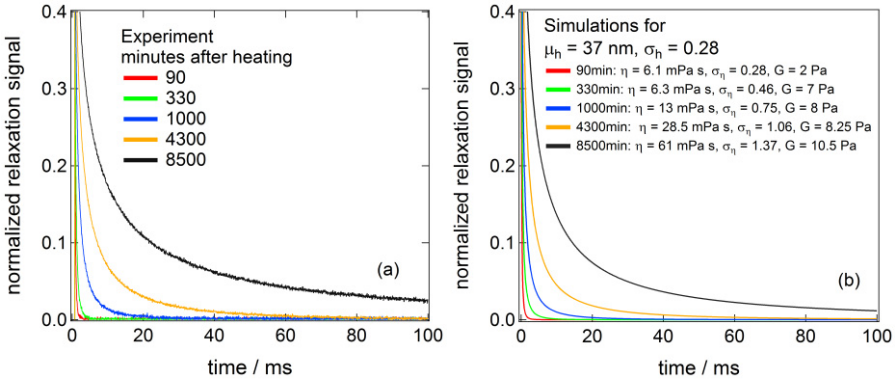

Fig. 3: Normalized MRX curves measured (a) and simulated (b) on the sample with 2.5 wt% gelatin.

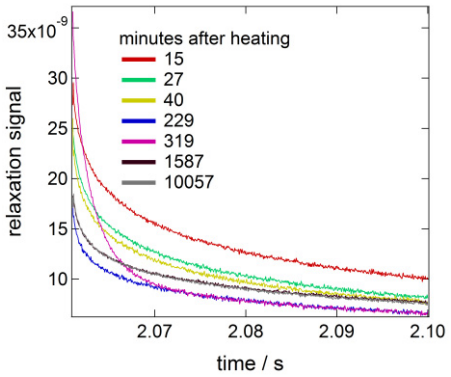

Fig. 4: MRX curves measured on the sample with 7.5 wt% gelatin.

5 Conclusions

We performed ACS and MRX measurements to investigate the dynamics of magnetically blocked $CoFe_2O_4$ nanoparticles in aqueous gelatin solution acting as model system for a viscoelastic medium. The utilized ACS setup allowing measurements in the frequency range 2 Hz – 9 kHz was found to be suited for the analysis of samples with gelatin contents up to 5 wt%. For samples with higher gelatin contents, the maximum in the imaginary part of the ACS shifts very rapidly to frequencies below 1 Hz.

The measured ACS spectra were analyzed by comparison with numerical solutions for the Langevin rotational dynamics of dipolar spheres in a viscoelastic matrix as derived by Raikher et al. (Raikher, Rusakov, Coffey, & Kalmykov, 2001) for the Voigt-Kelvin model. It was demonstrated that the dynamics are much more complex than in a Newtonian fluid. The position of the maximum in χ'' is influenced by viscosity η and shear modulus G, whereas its amplitude is determined by G and the standard deviation of the distribution of dynamic viscosities σ_η. For the analysis it was assumed that distribution of hydrodynamic size of nanoparticles does not change with gelation time. With this assumption and having position, amplitude and width of the maximum in the imaginary part as experimental parameters, a reliable estimation of the viscoelastic parameters from ACS spectra is possible. Unfortunately, the determination of the static susceptibility via the real part χ' was not possible since it was outside the measurement window for most measurements.

For the measurement of relaxation processes with larger time constants one usually performs magnetorelaxometry measurements in the time domain. Unfortunately, there is currently no theoretical model for the step response of MNPs in a viscoelastic medium. To circumvent this problem, the moment superposition model was modified by implementing the asymptotic relaxation time derived by Raikher et al. (Raikher, Rusakov, Coffey, & Kalmykov, 2001). It was shown that the calculated MRX curves using the viscoelastic parameters obtained from ACS measurements agree fairly well with the measured curves. Since only the time constant in the applied model contains information on η (including its distribution parameter σ_η) and G, an independent estimation of these parameters from a single MRX curve is not possible.

The $CoFe_2O_4$ single-core nanoparticles utilized as probes for nanorheological investigations were found to be well suited for these measurements due to their small size. However, measurements on the higher viscous samples, 7.5 wt% and 10 wt% gelatin, show that they are not completely magnetically blocked. For matrices with higher rigidity, the Néel relaxation is the dominant process. In this case, it is not possible to get information about the ambient matrix.

In summary, dynamic magnetic measurements, such as ac susceptibility and magnetorelaxometry, performed on suited, magnetically blocked nanoparticles in combination with proper physical models are a powerful tool for the nanorheological characterization of non-Newtonian fluids and viscoelastic media.

Acknowledgements

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