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Dynamics of magnetic nanoparticles in viscoelastic media

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ABSTRACT

We compare different models for the description of the complex susceptibility of magnetic nanoparticles in an aqueous gelatin solution representing a model system for a Voigt-Kelvin scheme. The analysis of susceptibility spectra with the numerical model by Raikher et al. [7] is compared with the analysis applying a phenomenological, modified Debye model. The fit of the models to the measured data allows one to extract the viscoelastic parameter dynamic viscosity η and shear modulus *G*. The experimental data were recorded on single-core thermally blocked $CoFe_2O_4$ nanoparticles in an aqueous solution with 2.5 wt% gelatin. Whereas the dynamic viscosities obtained by fitting the model – extended by distributions of hydrodynamic diameters and viscosities – agree very well, the derived values for the shear modulus show the same temporal behavior during the gelation process, but vary approximately by a factor of two. To verify the values for viscosity and shear modulus obtained from nanorheology, macrorheological measurements are in progress.

1. Introduction

The dynamic of magnetic nanoparticles (MNPs) are determined by two distinct mechanisms: the Brownian rotation and the Néel relaxation. In the former one, the whole nanoparticle including shell rotates with a characteristic relaxation time τ_B which – for a Newtonian fluid - is given by

$$\tau_B = \frac{3\eta V_h}{k_B T}. \quad (1)$$

Here η is the dynamic viscosity of the fluid, V_h the hydrodynamic volume of the particle, k_B the Boltzmann constant and T the thermodynamic temperature. Thus, measurements of the Brownian relaxation time reflect information on the matrix. In the latter mechanism, the magnetic moment flips between easy axes by thermal agitation. For MNPs with uniaxial anisotropy, the Néel relaxation time is often approximated by

$$\tau_N = \tau_0 \exp\left(\frac{KV_c}{k_B T}\right) \quad (2)$$

with τ_0 being a characteristic time between 10^{-9} s and 10^{-11} s, the anisotropy constant K, and the core volume V_c. Thus, measurements of the Néel relaxation time do not provide any information on the matrix. If the MNPs are suspended in a liquid, both mechanisms are possible and the one with the shorter relaxation time dominates resulting in an effective relaxation time

$$\tau_{eff} = \frac{\tau_N \tau_B}{\tau_N + \tau_B}. \quad (3)$$

The use of the Brownian relaxation time of thermally blocked MNPs for rheological studies on a nano- or micro-scale has already been proposed by Bacri et al. [1]. Whereas the MNP dynamics are well understood in media like Newtonian fluids, e.g. DI water, or if they are immobilized, e.g. by freeze drying [2,3], only recently theoretical and experimental studies on the MNP dynamics in non-Newtonian fluids or viscoelastic matrices were published. The understanding of the MNP dynamics in non-Newtonian and viscoelastic matrices is of particular importance for many biomedical and technical applications, e.g. in ferrogels.

Roeben et al. [4] performed measurements of the ac susceptibility (ACS) on aqueous solutions of ethylene glycol, triethylene glycol (TEG) and poly-(ethylene glycol) (PEG) using $CoFe_2O_4$ nanoparticles as nanoprobes, analyzed the susceptibility spectra with modified Debye models and compared the rheological parameters with those obtained from macrorheology. Tschöpe et al. [5] performed optical measurements of the dynamics of Ni nanorods in oscillating magnetic fields in aqueous gelatin solutions, resembling a model for a Voigt-Kelvin system, and in a worm-like micellar solution, acting as a Maxwell model system, as matrices. Recently, Remmer et al. [6] presented ACS measurements on aqueous gelatin solutions with gelatin contents ranging from 2.5 to 10 wt% using $CoFe_2O_4$ nanoparticles as probes. The measured imaginary parts of the complex susceptibility were analyzed with a numerical model by Raikher et al. [7] to extract the

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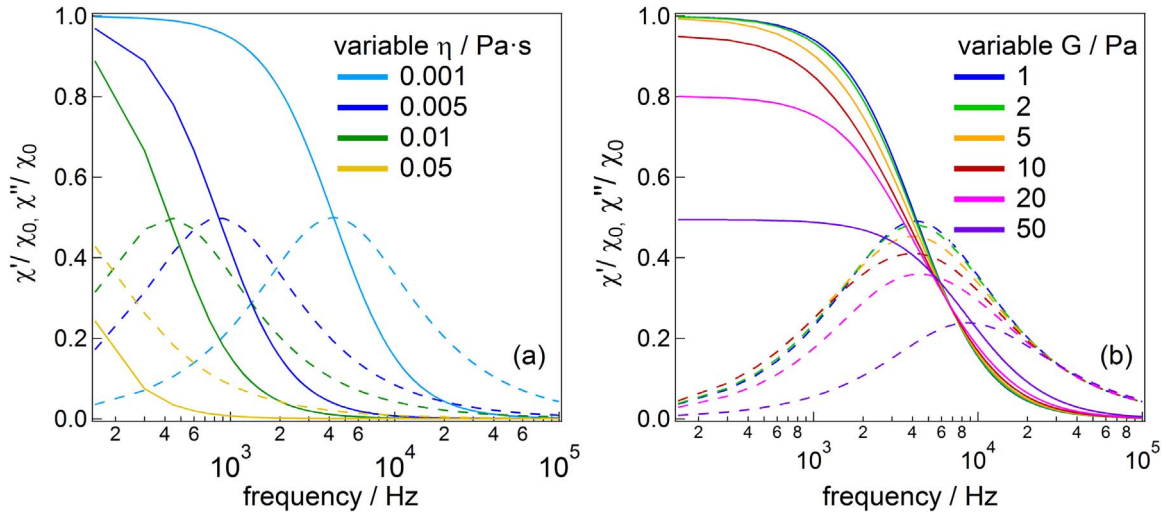

Fig. 1. Simulated ac susceptibility spectra (real part:solid lines, imaginary part:dashed lines) based on Raikher model: (a) G=0.1 Pa, η varying between 10^{-3} Pa ·s and $5{\cdot}10^{-2}$ Pa ·s (b) η=10^{-3} Pa·s, G varying between 1 Pa and 50 Pa.

dynamic viscosity and the shear modulus as a function of gelation time.

This paper focuses on the analysis of the complex susceptibility spectra of thermally blocked MNPs in aqueous gelatin solutions, representing a well-established Voigt-Kelvin model system. The analysis performed with the numerically elaborate model by Raikher et al. [7] is compared with that based on a much simpler model. The latter is based on the Debye model and the implementation of a complex viscosity in the Brownian relaxation time (Eq. (1)).

2. Models

A Voigt-Kelvin system is a viscoelastic matrix system with a viscous and an elastic term in parallel. The equation of motion of such a model system is [5,7]

$$I\ddot{\vartheta} + \zeta\dot{\vartheta} + K\vartheta = M(t) + y(t) \tag{4}$$

with the moment of inertia I, the rotational friction coefficient ζ, the linear elastic restoring parameter K, the magnetic torque $M(t)$, the stochastic driving torque $y(t)$, and the angle between magnetic moment and applied magnetic field ϑ. For a spherical particle the viscosity η is related to the rotational friction coefficient via $\zeta = 8\pi\eta r_h^3$ and the shear modulus to the elastic restoring parameter via $K = 8\pi G r_h^3$. Tschöpe et al. [5] analytically solved Eq. (1) by neglecting the inertia term and the influence of thermal fluctuations and for an oscillating magnetic field. This approach is justified since the magnetic moment of the utilized Ni nanorods amounts to about $4{\cdot}10^{-17}$ Am^2 which produces a dimensionless magnetic energy parameter $\xi = \mu_0 mH/(k_B T) >> 1$ for the applied static field of 9 mT/μ_0. Here m is the magnetic moment of a nanoparticle, μ_0 the vacuum permeability and H the applied magnetic field.

In contrast, Raikher et al. [7] derived a set of equations, which can only numerically be solved, in the limit of negligible inertia and magnetic torque terms:

$$\chi_\alpha(\omega) = \chi_{0,\alpha}\left(1 + i\omega\int_0^\infty d\tau e^{i\omega\tau}G_\alpha(\tau)\right) \tag{5}$$

with

$$\chi_{0,\parallel} = \frac{nm^2}{k_B T}\exp\left(-\frac{k_B T}{K}\right)\left[\cosh\left(\frac{k_B T}{K}\right) - 1\right] \tag{6}$$

and

$$\chi_{0,\perp} = \frac{nm^2}{k_B T}\exp\left(-\frac{k_B T}{K}\right)sinh\left(\frac{k_B T}{K}\right) \tag{7}$$

as well as

$$G_\parallel(t) = \frac{\left(\cosh\left(\frac{k_B T}{K}\exp\left(-\frac{t}{\tau_K}\right)\right) - 1\right)\exp(i\omega t)}{\cosh(\frac{k_B T}{K}) - 1} \tag{8}$$

and

$$G_\perp(t) = \frac{sinh\left(\frac{k_B T}{K}\exp\left(-\frac{t}{\tau_K}\right)\right)\exp(i\omega t)}{sinh(\frac{k_B T}{K})}. \tag{9}$$

The symbol α describes the orientations parallel (||) or perpendicular (⊥) to the excitation field. The time constant $\tau_K = \zeta/K$. The total susceptibility calculates to

$$\chi_{tot}(\omega) = \frac{1}{3}(\chi_\parallel(\omega) + 2\chi_\perp(\omega)). \tag{10}$$

Raikher et al. also provided analytical expressions for the limits of low- ($k_B T >> K$) and high-rigidity ($k_B T << K$). The expression for the dynamic susceptibility in the low-rigidity limit equates for negligible elasticity the standard Debye model

$$\chi(\omega) = \frac{\chi_0}{1 - i\omega\tau_B}, \tag{11}$$

however, the equation for the Brownian relaxation time $\tau_B = \frac{\zeta}{k_B T}$ given in [7] (therein denoted as Debye time τ_D) differs from the established expression in a purely viscous liquid by a factor of two. Therefore, we tentatively replaced $k_B T$ in Eq. (5) by $2k_B T$ in order to resemble the standard expressions for the dynamic susceptibility of a Newtonian fluid in the limit of negligible elasticity, i.e. $\tau_B = \frac{\zeta}{2k_B T}$.

Fig. 1 shows ac susceptibility spectra simulated with Raikher's model – including the aforementioned modification – for a temperature T=296 K and $CoFe_2O_4$ MNPs with a hydrodynamic diameter d_h=46 nm. In Fig. 1(a), the shear modulus was kept constant at G =0.1 Pa and the dynamic viscosity η was varied between 10^{-3} Pa·s and $5{\cdot}10^{-2}$ Pa ·s. For comparison, Fig. 1(b) shows the spectra for a constant η=10^{-3} Pa·s and varying G between 1 Pa and 50 Pa. As can be seen, an increasing viscosity provides a shift of the maximum in the imaginary part towards lower frequencies and an increasing G causes both a drop of amplitude of the complex susceptibility and for larger values a shift towards higher frequencies.

Thus, as an alternative analytical solution we apply the following approach, a modified Debye model. The complex susceptibility within