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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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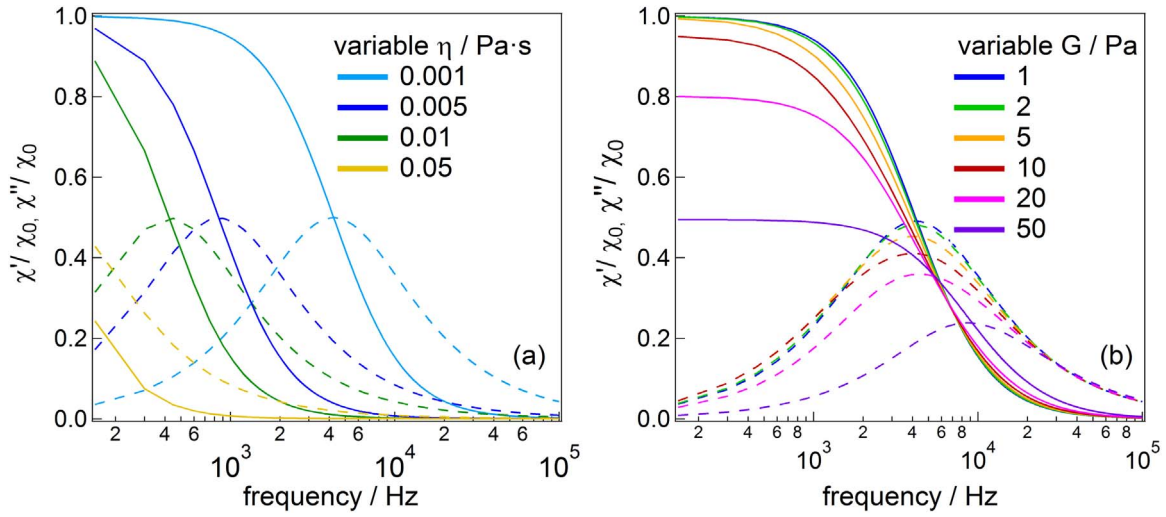

Fig. 1. Simulated ac susceptibility spectra (real part:solid lines, imaginary part:dashed lines) based on Raikher model: (a) G=0.1 Pa, η varying between 10^{-3} Pa ·s and $5{\cdot}10^{-2}$ Pa ·s (b) η=10^{-3} Pa·s, G varying between 1 Pa and 50 Pa.

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

the Debye model $\left(\xi_{ac} = \frac{\mu_0 m H_{ac}}{k_B T} << 1\right)$ with amplitude of the applied sinusoidal magnetic field H_{ac} is given by

$$\chi(\omega) = \frac{\chi_0}{1 - i\omega\tau_{eff}} \tag{12}$$

with the static susceptibility χ_0

$$\chi_0 = \frac{nm^2}{3k_B T}. \tag{13}$$

Here n is the number concentration of MNPs. For thermally blocked magnetic moments, the effective relaxation time is given by the Brownian one which - for a Newtonian fluid – is given by Eq. (1) which reads for spherical nanoparticles

$$\tau_B = \frac{4\pi\eta_0 r_h^3}{k_B T} = A\eta_0 \tag{14}$$

with hydrodynamic radius r_h and $A = \frac{4\pi r_h^3}{k_B T}$.

The frequency-dependent viscosity for the Voigt-Kelvin model is given by

$$\eta(\omega) = \eta_0 - \frac{G}{i\omega} \tag{15}$$

with viscosity η_0 and shear modulus G. Replacing η_0 in (14) by (15) and inserting it in (12), one obtains

$$\chi(\omega) = \frac{\chi_0}{1 - i\omega A(\eta_0 - G/(i\omega))} = \frac{\chi_0}{(1 + AG) - i\omega A\eta_0}. \tag{16}$$

Note that this phenomenological approach is basically the same that Roeben et al. [4] applied for the analysis of their ac susceptibility spectra measured on non-Newtonian aqueous TEG and PEG solutions. Comparing the complex shear modulus obtained from fitting the measured spectra with their modified Debye model and from macro-rheological measurements, good agreement was found.

The spectra simulated with Eq. (11) for the same parameters as in Fig. 1 are depicted in Fig. 2. The scaling or the real and imaginary part spectra with η_0 and G is qualitatively similar to that in Fig. 1.

The plausibility of this modified Debye model can be verified with two additional models: The DiMarzio-Bishop model [8] and an adaption of the model by Tschöpe et al. [5].

DiMarzio and Bishop derived an equation for the dielectric permittivity of a Voigt-Kelvin element. Transferring their equation to the magnetic case, one obtains for the complex susceptibility

$$\frac{\chi(\omega) - \chi_\infty}{\chi_0 - \chi_\infty} = \left(1 - \frac{i\omega\eta_0\left(\frac{K_0(\chi_0 + 2)}{(\chi_0 + 2)(K_0 - 1) + (\chi_\infty + 2)}\right)\frac{4\pi r_h^3}{k_B T}}{1 + \left(\frac{K_0(\chi_0 + 2)}{(\chi_0 + 2)(K_0 - 1) + (\chi_\infty + 2)}\right)\frac{4\pi r_h^3}{k_B T}G}\right)^{-1} \tag{17}$$

$$K_0 = \left(1 + \frac{4\pi r_h^3}{k_B T}\right)^{-1}. \tag{18}$$

Eq. (17) can be significantly simplified since for a diluted suspension of magnetic nanoparticles $\chi_\infty, \chi_0 << 2$. This provides

$$\frac{\chi(\omega) - \chi_\infty}{\chi_0 - \chi_\infty} = \left(\frac{1 + \frac{4\pi r_h^3}{k_B T}G - i\omega\eta_0\frac{4\pi r_h^3}{k_B T}}{1 + \frac{4\pi r_h^3}{k_B T}G}\right)^{-1} = \frac{1 + \frac{4\pi r_h^3}{k_B T}G}{1 + \frac{4\pi r_h^3}{k_B T}G - i\omega\eta_0\frac{4\pi r_h^3}{k_B T}}$$
$$= \frac{1 + AG}{(1 + AG) - i\omega A\eta_0}. \tag{19}$$

Assuming that χ_∞=0, one obtains the same expression for the complex susceptibility as for the modified Debye model (Eq. (16)) except that now χ_0 is replaced with $\chi_0(1 + AG)$.

Adapting the model described in [5], the expression of the complex susceptibility of spherical magnetic nanoparticles in an oscillating magnetic field with $\xi >> 1$ reads

$$\chi(\omega) = \chi_0\frac{\gamma}{1 - i\omega\gamma\tau_v} \tag{20}$$

with $\tau_v = \frac{\zeta\eta_0}{\mu_0 mH} = \frac{2\tau_B}{\xi}$ and $\gamma = \left(1 + \frac{\kappa}{\mu_0 mH}\right)^{-1}$. Thus, Eq. (20) results in

$$\chi(\omega) = \chi_0\frac{1}{\left(1 + \frac{2AG}{\xi}\right) - i\omega\frac{2A\eta_0}{\xi}} = \chi_0\frac{1}{\left(1 + \frac{8\pi G r_h^3}{\xi k_B T}\right) - i\omega\frac{2\tau_B}{\xi}}. \tag{21}$$

This equation differs from (16) only by the fact that G and η_0 are now divided by $\xi/2$ each. The fact that τ_B in (16) is replaced by $2\tau_B/\xi$ is identical to the asymptotic limit of the transverse relaxation time of a Brownian nanoparticle [9].

The spectra of real and imaginary parts of the ac susceptibility simulated for T=296 K, d_h=46 nm, G=0 Pa, and η=1 mPa ·s simulated with the different models are depicted in Fig. 3. Apparently, there are no differences between the models by DiMarzio and Bishop (Eq. (19)), the model by Tschöpe (M_s=4·10^5 A/m and B=4 mT, corresponds to ξ=2) (Eq. (21)) and the modified Debye model (Eq. (16)) and the spectra accord with the standard Debye model (see Fig. 3(a)). The numerical Raikher model cannot be calculated for G=0 Pa. The spectra in Fig. 3(b) calculated with the same parameters like for Fig. 3(a) but

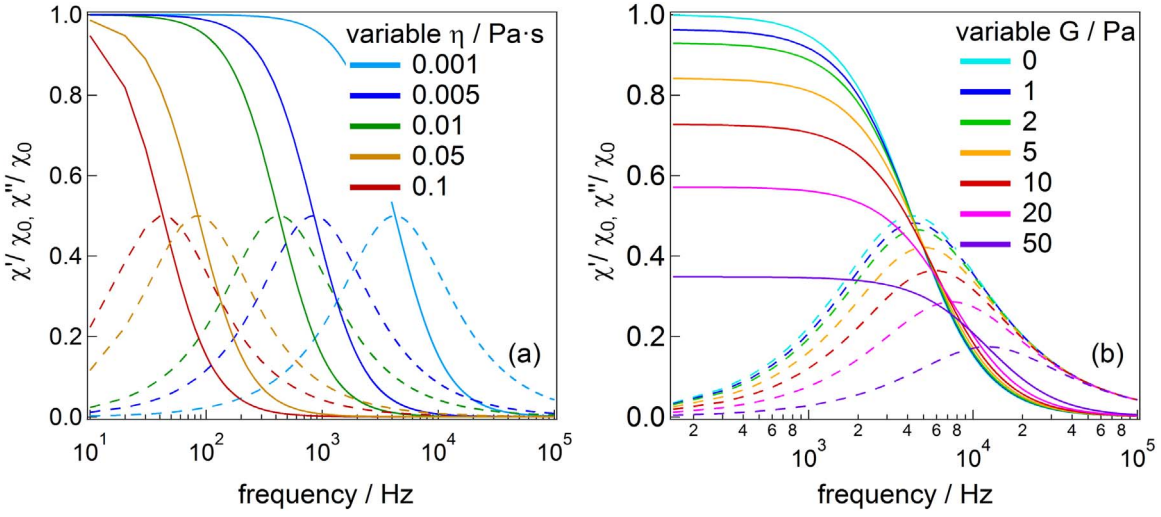

Fig. 2. Simulated ac susceptibility spectra (real part:solid lines, imaginary part:dashed lines) based on modified Debye model: a) G=0 Pa, η varying between 10^{-3} and $1\cdot10^{-1}$ Pa·s b) η=10^{-3} Pa·s, G varying between 0 and 50 Pa.

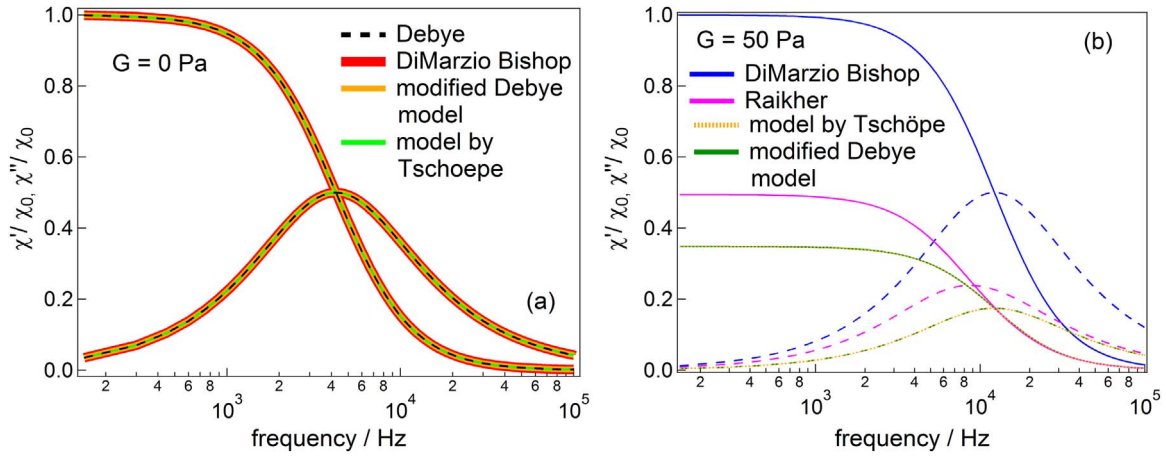

Fig. 3. Comparison of ac susceptibility spectra based on the models Debye, DiMarzio Bishop, modified Debye model, model by Tschöpe for (a) G=0 Pa and additional with Raikher's model for (b) G=50 Pa.

G=50 Pa show differences between the models. The DiMarzio Bishop model does not cause a change in susceptibility amplitude (as expected from comparing Eqs. (16) and (19)). The adaption of the model by Tschöpe et al. and the modified Debye model show the same behavior, but a higher shift of the imaginary part to higher frequencies and a bigger change in the susceptibility amplitude than the spectrum based on the Raikher model. If the susceptibility spectra calculated for the DiMarzio Bishop model were normalized to $\chi_0(1 + AG)$, they would coincide with those calculated with the modified Debye model.

3. Comparison with experiment

To compare the Raikher model and the modified Debye model with experimental data, the results acquired on an aqueous solution with 2.5 wt% gelatin content were used. As magnetic nanoprobes, $CoFe_2O_4$ single-core nanoparticles with a PAA shell and a mean core diameter of 15.0 ± 0.2 nm determined by TEM were utilized. The hydrodynamic diameter with 18.0 ± 0.4 nm was determined by ac susceptibility measurements at room temperature and in DI water solution [10]. As a consequence of the large anisotropy constant of $CoFe_2O_4$ (about 10^5 J/m^3), the particles are thermally blocked at room temperature. The sample volume amounts to 150 µL with 0.038 wt% MNPs.

The ac susceptibility measurements were performed with a temperature adjustable fluxgate-based ac setup, originally designed for measurements of magnetic nanoparticles in rotating magnetic field [11]. The accessible frequency range is between 2 Hz and 9 kHz. A magnetic field amplitude of 200 µT was applied in order to be in the low-field limit ($\xi << 1$).

To study the gelation dynamics, the sample was heated up to 313 K for 60 min, so that the gelatin is in the sol state. Afterwards the sample was rapidly cooled down to 296 K and kept at this temperature. ACS measurements were carried out every 30 min, starting before cool-down. More details about material and measurements are described in [6].

The ac spectra show a shift of the peak position of the imaginary part χ′′ towards lower frequencies with increasing gelation time, a decrease of the amplitude and a broadening of the spectra (see Fig. 4). The real part of the measurements could not be analyzed because the static susceptibility was outside the measurement window.

The spectra of the imaginary part were fitted with the model by Raikher (Eq. (5)) and the modified Debye model (Eq. (16)). In both cases, lognormal distributions of hydrodynamic diameter and local dynamic viscosity had to be implemented to properly fit the experimental data. Fig. 5 shows the shear modulus and dynamic viscosity as a function of gelation time as obtained from the fitting procedure. The values for the dynamic viscosity are quite similar for both models.

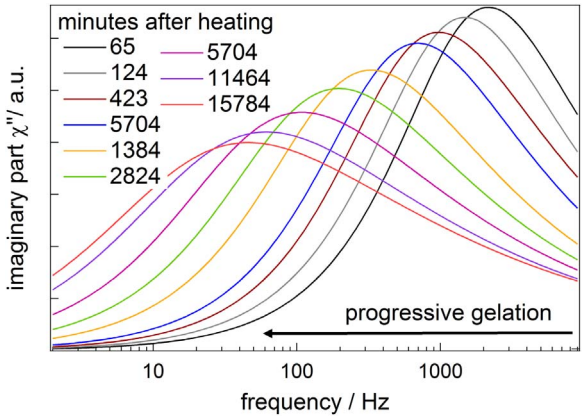

Fig. 4. The imaginary part of the ac susceptibility spectra measured on the 2.5 wt% gelatin solution.

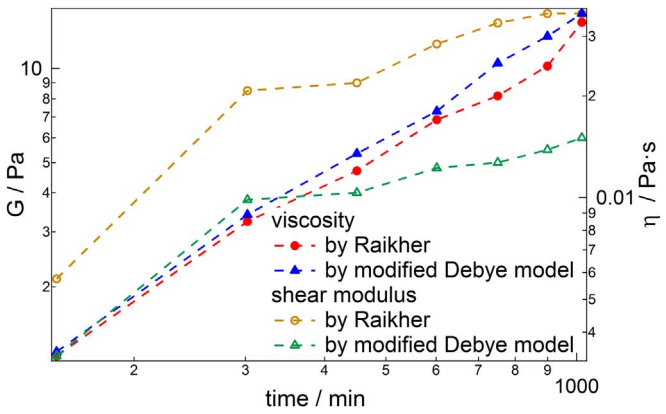

Fig. 5. Viscosity (closed symbols) and shear modulus (open symbols) determined by the models of Raikher and modified Debye model for a 2.5 wt% aqueous gelatin solution sample.

Qualitatively similar trends are observed for the shear modulus, but the values calculated by the Raikher model are approximately twice the shear modulus determined by the modified Debye model.

4. Conclusions

We compared two models based on a Voigt-Kelvin element to analyze ACS measurements of MNPs in aqueous gelatin solution. The modified Debye model and the model based on Raikher provide qualitatively the same behavior for varying viscosity η and shear

modulus G in simulations. With increasing viscosity the maximum in the imaginary part shifts towards lower frequencies. An increasing shear modulus causes both a drop of amplitude of the complex susceptibility and for larger values a shift towards higher frequencies.

The fitting of the measured data shows a good agreement for the viscosity. The values for the shear modulus differ approximately by a factor of two.

A decision which of the two models provides more accurate values for the shear modulus and dynamic viscosity requires a comparison with macrorheological measurements which are in progress. The modified Debye model is based on very simple assumptions whereas the Raikher model is based on solving the equation of motion of a Voigt-Kelvin element. On the other hand, a comparison of the modified Debye model with the DiMarzio-Bishop and the model by Tschöpe et al. justifies this simple approach. For comparison, the Raikher model – especially if extended by distributions of hydrodynamic particle diameter and viscosity – requires much larger computational effort. In addition, the equations in the Raikher paper suffer from some inconsistencies in the limit of vanishing elasticity.

Acknowledgements

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