Regarding the Néel relaxation time constant in magnetorelaxometry

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Magnetorelaxometry (MRX) is an established measurement technique frequently employed in biomedical applications for imaging magnetic nanoparticles (MNP). In this letter we employ a first principles model to investigate the effects of different MNP sample properties on the Néel relaxation time constant \( \tau_N \) in magnetorelaxometry. Using this model we determined that dipolar interactions start to have an impact on the MRX signal from Fe concentrations of 100 mmol/l, and result in a smaller \( \tau_N \). Additionally, the micromagnetic damping constant, closely related to \( \tau_N \), was found to be between 0.0005 and 0.002 by comparison to an MRX measurement of iron oxide particles. This is significantly lower compared to the bulk value of 0.07 for this material.

Magnetorelaxometry (MRX) is an established measurement technique for the quantitative imaging of magnetic nanoparticles (MNP) \(^1\)–\(^5\) which can be used in biomedical applications such as disease detection \(^6\), drug targeting \(^7\) and thermal ablation \(^8\). Furthermore, binding processes of MNP-based biochemical reactions can be analyzed \(^9\)–\(^11\) and it is actively utilized to investigate the physical properties of MNP suspensions in biomedical applications \(^12\)–\(^15\).

An MRX measurement starts with the application of a magnetizing field of typically 1 mT to a superparamagnetic MNP sample. After a certain time (typically 1 second) this field is switched off and the sample relaxes again towards its demagnetized state \(^16\).

\[
m = \int_V m_0 \exp \left( -\frac{t}{\tau_N(V)} \right) P(V) dV \quad (1)
\]

Equation 1 describes how the magnetization \( m \) of a sample of MNP with size distribution \( P(V) \) relaxes from \( m_0 \) towards 0 with a characteristic time constant \( \tau_N \), called the Néel relaxation constant \(^17\). Note that the magnetization decays exponentially when all particles have the same volume. Otherwise the signature is characterized by the size distribution of the particles. The Néel relaxation constant is given by eq. 2:

\[
\tau_N = \tau_0 \exp \left( \frac{KV}{k_BT} \right) \quad (2)
\]

with \( \tau_0 \) having values between \( 10^{-8} \) and \( 10^{-12} \) s \(^16\), \( K \) the uniaxial anisotropy constant, \( V \) the magnetic core volume of the particle, \( k_B \) the Boltzmann constant and \( T \) the temperature. During the relaxation time of typically 0.5 s, the magnetization can be measured at a certain distance from the sample under study with sensitive magnetometers such as SQUIDs or Fluxgates.

To obtain quantitative information from these measurements a comparison with a reference sample of known MNP concentration measured under equal conditions is needed \(^16\). This reference sample must have the same physical properties because these have a large impact on the MRX curve. When assuming that dipolar interactions between the MNP are negligible, the concentration of the sample can be obtained by the ratio of the two MRX measurement amplitudes (reference and investigation), as this scales linearly with the concentration.

There exist different theoretical models that describe the relation between the physical properties of the MNP and the MRX signal. Examples of such models are the moment superposition model (MSM) \(^13\),\(^18\) and the cluster moment superposition model (cluster-MSM) \(^13\),\(^16\). However, these models are high-level and do not take into account possible dipolar interactions between the MNP.

In this letter we employ a first principles numerical model to simulate the MRX signal starting from MNP material parameters and their size distribution. Using this model we investigate the Fe concentration above which dipolar interactions affect the MRX curve. As reference samples in some cases \(^3\),\(^13\),\(^19\),\(^20\) contain MNP amounts which differ to a great extent with respect to the sample, it might be possible that the comparison between the reference and sample MRX curves is no longer valid. Furthermore, it has been shown that MNP samples tend to form aggregates during aging of the reference sample \(^13\), which locally results in even higher Fe concentrations.

Another topic of debate is the value of the material parameter, \( \alpha \), the Gilbert damping constant, which is not accurately known for MNP but determines the value of \( \tau_0 \) in eq. 2. There are indications \(^21\)–\(^23\) that this value can be significantly lower in nanoscale magnets than in the bulk material. Therefore we compare our numerical model to an actual MRX experiment to determine \( \alpha \).

The MRX simulations are performed with the in-house developed simulation tool Vinamax \link{vinamax}{vinamax}. Vina-
\[
\frac{dm}{dt} = -\frac{\mu_0 \gamma_0}{1 + \alpha^2} (m \times H_{\text{eff}} + \alpha m \times m \times H_{\text{eff}})
\]  

(3)

In this equation, \( m \) denotes the magnetization vector normalized with respect to the saturation magnetization, \( \mu_0 = 4\pi \times 10^{-7} \) Tm/A, \( \gamma_0 \) is the gyromagnetic ratio \((1.7595 \times 10^{11} \text{ rad/Ts})\) and \( \alpha \) is the dimensionless Gilbert damping constant. \( H_{\text{eff}} \) denotes the effective field working on each nanoparticle, taking into account the demagnetizing, thermal, and anisotropy field. This software allows to simulate the micromagnetic behavior of large MNP ensembles on the long timescales (seconds) customary in experiments, while still being accurate on the ps timescale of the magnetic dynamics. It was specifically developed to increase our understanding of the collective behavior of magnetic nanoparticles, and could help to increase the performance of several biomedical applications.

Our aim is to investigate the influence of the dipolar interactions between MNPs in MRX experiments. Therefore we first perform a simulation in which these interactions are not taken into account, representing a sample with an infinitely diluted concentration. Figure 1 shows a simulated MRX signal of an ensemble of 30000 magnetite nanoparticles having identical diameters of 11 nm, a saturation magnetization of 400000 A/m and an uniaxial anisotropy constant of 14400 J/m\(^3\).

Insets a) to d) in Fig. 1 show a reduced MNP ensemble of 3 particles to explain their magnetic states at the different stages in the MRX simulation. The magnetization of the MNP is represented by a red arrow and the MNP have a random uniaxial anisotropy axis that is fixed in time (black line).

As dipolar interactions equally affect the magnetizing as the demagnetizing phase of an MRX experiment, we only simulate the demagnetizing phase for practical purposes. To be able to accurately determine the relaxation constant \( \tau \), we initialize the MNP in a fully magnetized state along the \( z \)-axis. The normalized net magnetic moment along the \( z \)-axis of the particles is represented by \( < m_z > \) and equals 1 in this stage (Fig. 1 a)).

In the next stage (Fig. 1 b)) the MNP relax (with the thermal field still switched off) towards one of their energetic groundstates, i.e. their magnetization parallel with their uniaxial anisotropy axis in the positive \( z \) direction, due to the initialization along the \( z \)-axis. The theoretical prediction of \( < m_z > \) when having randomly orientated anisotropy axes is \( \int_0^{\pi/2} \sin(x) \cos(x) \, dx = 0.5 \).

In the subsequent stage (Fig. 1 c)) the thermal field is switched on corresponding to a temperature of 300 K and the magnetization slightly vibrates around the anisotropy axis. Due to these thermal fluctuations the magnetization can switch between the two anisotropy directions at random intervals. Consequently, \( < m_z > \) decays towards zero at a rate given by the Néel relaxation constant \( \tau_N \) (eqs. 1 and 2) as shown in Fig. 1 d)). By fitting an exponential curve to the simulated MRX curve, \( \tau_N \) can be determined which equals 60 ns for this simulation.

This relaxation constant is employed to investigate the impact of dipolar interactions on the MRX curve. Due to the prohibitive computational cost of evaluating the dipolar interactions, we prefer simulations in which the relaxation constant is of the order of nano- to microseconds. To this end we used the MNP ensemble of the previous simulation as this ensemble had a relaxation constant of 60 ns (without dipolar interactions). The damping constant \( \alpha \) equals 0.01 in this simulation (note that the dipolar interaction is independent of the value of \( \alpha \), which we verified numerically). We repeated the MRX simulation for increasing MNP concentrations, taking into account the dipolar interactions by evaluating the dipolar field working on each particle every 10 ps. The MNP in the experiments are fixed in space at uniformly distributed positions. As MNP in biomedical applications are typically iron oxides, the MNP amount is represented by a black line and the MNP magnetization by a red arrow.

a) The magnetizations lay along the \( z \)-axis. b) The magnetizations relax towards their respective anisotropy axis in the positive \( z \)-direction. c) The thermal field is switched on and the magnetizations randomly move slightly around the anisotropy axes. d) The thermal field randomly switches the magnetization towards the opposite anisotropy direction, and the total magnetization relaxes exponentially towards 0.

FIG. 1. Simulation of an MRX experiment (red line) resulting from an ensemble of 30000 particles with an initial magnetization along the \( z \)-axis. Insets a) to d) show an ensemble of 3 magnetic nanoparticles in the different stages of the MRX signal. The uniaxial anisotropy axis is represented by a black line and the MNP magnetization by a red arrow.

A simple theoretical argument that only takes into account the dipolar interaction due to the nearest neighbours shows that the concentration from which on the dipolar interaction starts to affect the relaxation time is
independent of the size of the particles: the size of the dipolar field of a nearest neighbour on a particle scales as \( V/r^3 \) with \( V \) the volume of the particle and \( r \) the distance to its nearest neighbour. When considering larger particles at a fixed concentration, the distance \( r \) between the particles scales as \( \sqrt{V} \) so that the dipolar field is independent of the volume of the particles \( V \). Nonetheless, we have performed additional simulations of MNP with diameters 12.59, 13.86 and 14.94 nm, corresponding to a MNP volume of 1.5, 2 and 2.5 times the volume of the MNP in Fig. 2. The relaxation constants \( \tau_N \) without dipolar effects for these particles are 173, 524 and 1522 ns respectively. These values are then used to obtain a relative relaxation constant for simulations at different Fe concentrations, as shown in the inset of Fig. 2. These results imply that, although comparable, the effect of dipolar interactions is not exactly the same for different MNP sizes and appears to become more important for larger particles, which means that the nearest neighbour approximation of our theoretical argument was too crude. We therefore emphasize that during experiments caution should be taken when using samples with an Fe concentration above 100 mmol/l in experiments (where typically MNP with diameters in the 16 to 22 nm range are used\[^1\] ).

A second topic of interest when discussing \( \tau_N \) is the inverse of the attempt frequency: \( \tau_0 \) (eq. 2). Brown\[^2\] determined that in the high barrier limit, and in the absence of an external field \( \tau_0 \) is given analytically by eq. 4 with \( H_K = 2K/M_s \).

\[
\tau_0 = \frac{1 + \alpha^2}{\alpha \gamma} \sqrt{\frac{2\pi k_B T}{H_K^2 M_s V}}
\] (4)

In this equation every quantity except \( \alpha \) is known for MNP. Thus we are able to determine \( \alpha \) by comparing to an MRX experiment. Typically, \( \tau_0 \) is described as a time constant that can take values between \( 10^{-8} \) and \( 10^{-12} \) s\[^2\]. This large range is inconvenient, and an estimate of \( \alpha \) together with eq. 4 could lead to a more accurate estimate of \( \tau_0 \). For iron oxide MNP there is no accurate data available for \( \alpha \). There is however a typical value of 0.07 determined for the bulk material\[^3\]. For thin films there is a clear trend visible in which \( \alpha \) decreases with decreasing dimensions\[^2\], also seen in other materials\[^23,24\] , and in Ref.\[^22\] an upper limit for \( \alpha \) in iron oxide thin films of 0.0365 is found. We argue that in MNP this value is expected to be significantly smaller, because of the nanoscale dimensions in every direction.

We compare our numerical model to an MRX experiment performed at the Physikalisch-Technische Bundesanstalt in Berlin\[^5\] to determine the Gilbert damping constant \( \alpha \). The MNP under investigation are large single magnetite core SHP-20 particles (Ocean Nanotech, USA) coated by oleic acid combined with an amphiphilic polymer. The size distribution was obtained by TEM\[^1\] and showed a lognormal distribution with a mean diameter of 19 nm and a standard deviation of 0.11 nm. The saturation magnetization was determined to be 250000 A/m and \( K = 14500 \) J/m\(^3\). The MNP are freeze dried so only Néel relaxation occurs allowing to simulate the MRX signal using our numerical model. The Fe concentration is 4.85 mmol/l, which is sufficiently low to neglect dipolar interactions (see Fig. 2). The magnetizing field was applied for 1 second and had an amplitude of 1600 A/m. In contrast to the numerical method described earlier in this letter (Fig. 1), we now consider an experiment in which the particles are not fully magnetized. Consequently, the magnetizing stage of the experiment also has to be simulated. After this stage, the MRX signal is generated as the sample is allowed to relax for 0.4 seconds.

Figure 3 shows the result of MRX simulations for a range of different \( \alpha \) values. The smooth full blue line shows the measurement data from the MRX experiment. The green line shows a simulation of the experiment for \( \alpha = 0.07 \), for which we observe a large discrepancy between the simulated and measured MRX curve. The gray region shows the simulation results for \( \alpha \) ranging from 0.0005 to 0.002, in close correspondence to the MRX measurement data. Therefore we suggest \( \alpha = 0.001 \) for these type of particles, which is indeed significantly lower...
The physical principles of magnetism


E. Flynn and H. Bryant, Physics in medicine and biology 50, 1273 (2005).


