International Journal on Magnetic Particle Imaging
Vol 9, No 1, Suppl 1, Article ID 2303084, 4 Pages

Infinite Science Publishing

Proceedings Article

Pulsed rotational drift spectroscopy sequences for magnetorelaxometry

M. A. Rückert[a,*] · P. Vogel[a] · V. C. Behr[a]

[a]Department of Experimental Physics 5 (Biophysics), University of Würzburg, 97074, Würzburg, Germany
*Corresponding author, email: Martin.Rueckert@physik.uni-wuerzburg.de

Abstract

Rotational Drift Spectroscopy (RDS) is a novel spectroscopic method for magnetic nanoparticles. It is based on measuring the rotational drift of magnetic nanoparticle ensembles in a rotating magnetic field, which is below the magnetic field strength necessary for rotating the magnetic nanoparticles synchronously. Magnetorelaxometry (MRX) measures the decaying magnetization after applying a magnetic pulse, allowing to determine the zero-field relaxation time of magnetic particle systems. It is used, e.g., for general particle characterization or bioassay applications. The following work presents pulsed RDS sequences for measuring the zero-field relaxation behavior of magnetic particles. Measuring the zero-field relaxation using an RDS setup provides the advantage of allowing the combination of additional measurement sequences for more specific particle characterizations. The pulse sequence can be tailored to the necessary relaxation time range of the particle system, allowing to cover a wide range of different relaxation times.

I. Introduction

Magnetic particles show rotational drift in rotating magnetic fields, which are too weak to rotate them synchronously. The resulting drift frequency of the magnetic particles strongly depends on the rotational friction or the amplitude and frequency of the rotating magnetic field. This phenomenon was used in [1] for constructing a single bacteria detector by optically measuring the rotating frequency of a single functionalized magnetic microparticle. Rotating Drift Spectroscopy [2, 3] aims at inductively measuring the rotational drift of magnetic nanoparticle ensembles in liquid suspension. This requires orienting all magnetic moments in one direction before the measurements starts, otherwise all magnetic moments are oriented randomly, resulting in zero net magnetization with respect to any asynchronous frequency components. The start phase of an RDS measurement therefore is very similar to MRX [4], which measures the decaying magnetization after an initial pulse. While MRX measures the magnetization directly, this is not easily possible in RDS, where the rotating magnetic field of up to tens of millitesla is present during the measurement and incompatible with highly sensitive magnetic field sensors. Measuring the signal inductively makes it directly proportional to the derivative $dM(t)/dt$ of the magnetization $M(t)$. For a particle diameter range between, 20 to 200 nm the decay rate and hence the $dM(t)/dt$ term differs by three orders of magnitudes for Brownian relaxation, which scales proportional to the hydrodynamic particle volume [4]. This makes inductive measurement of the magnetization decay impractical.

In RDS as performed in [2], the rotating field is started after a delay. The start of the rotating magnetic field leads to a rotating magnetization, which induces a signal proportional to the magnetization, which remains after the delay time. This generated signal can have a much higher $dM(t)/dt$ value compared to the $dM(t)/dt$ in the zero-field relaxation process, depending on strength and frequency of the applied rotating magnetic field. There-

10.18416/ijmpi.2023.2303084

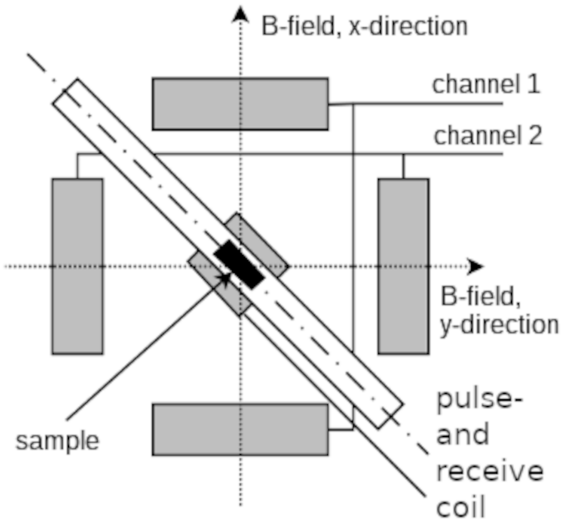

Figure 1: Schema of the used setup. Two orthogonal coil pairs generate short rotating magnetic field pulses with about 15 mT at 53.3 kHz. The pulse- and receive coil are diagonally oriented in the center. The samples were 5 mm glass tubes filled with 40 µL suspension.

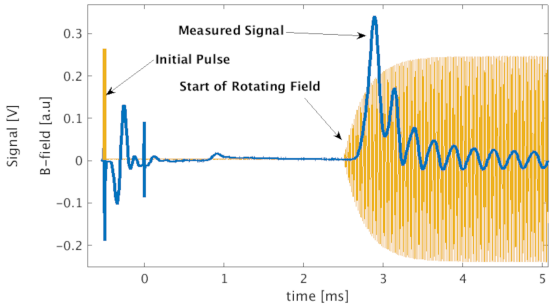

Figure 2: Example of a typical RDS sequence. It starts with a short magnetic pulse (here 20 µs duration and 200 mT field strength) and the rotating magnetic field starts with a certain delay. The signal is generated by rotating the magnetization. The first peak of this signal can be used to measure the zero-field relaxation time, which requires at least two measurements with different delay times.

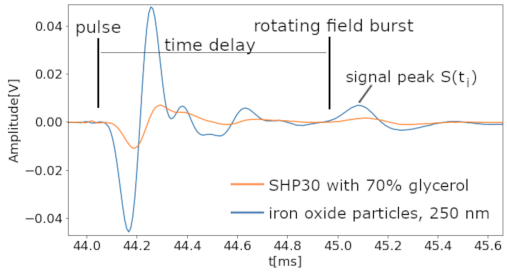

Figure 3: Snippet of two signals for two different particle systems. Marked are the end of the 60 mT pulse and the start of the 10 periods of the rotating field burst. The pulse generates a signal heavily distorted by the chebychev low-pass filter (corner frequency: 10 kHz). The main part of the signal starts after the rotating field burst, which generally will be an exponentially decaying sine curve. The signal peak is used for estimating the zero-field decay time by comparing it for at least two measurements with different delay times.

fore, the necessary signal strength can be forced by the rotating magnetic field. This allows to measure the zero-field relaxation for a wide range of particle types and has the advantage of further combining the measurement with RDS sequences. The following work evaluates this measurement method with some basic RDS pulse sequences.

II. Material and methods

The schema of the setup is shown in Fig. 1. The coil system can accept 5 mm glass tubes. The receive coil inside the coil system is realized as a gradiometer. The pulse coil is wound coaxially to the reciever coil and decoupled with an external air coil transformer. The x-, y- and pulse coils were driven with three AE Techron 7000 amplifiers (Indiana, USA).

The applied sequence is similar to the sequence used in [2], which is shown in Fig. 2. An initial pulse generates magnetization. The rotating field starts after a time delay. The rotating magnetic field rotates the magnetization, which generates the signal. In the example of Fig. 2, an echo sequence was applied, leading to a signal echo train. The presence of an alternating magnetic field (rotating or linearly oscillating) typically also causes an accelerated magnetization decay, as is the case in the example in Fig 2.

In order to measure just the zero-field relaxation, the sequence can be simplified. The sequence used for the following measurements consisted of the repetition of the following pattern shown in Fig. 3: a short pulse followed by a short burst of 10 periods of a rotating magnetic field with 53.3 kHz after a given delay time, reaching a peak value of 15 mT at the end of 10 periods. The pulse duration was 10 µs (half-sine shaped) and its peak value around 60 mT. Fig. 3 shows a snippet of a signal generated by this sequence.

The full measurement sequence consisted of 50 repetitions with a time delay increasing in steps of 50 µs between each following repetition. The expected ratio $S(t_{n+1})/S(t_n)$ of two signal peaks $S(t_n)$ and $S(t_{n+1})$ between two consecutive repetitions n and n+1 is $S(t_{n+1})/S(t_n) = \exp(-\Delta t / \tau)$, with Δt being the difference of the time delays applied for $S(t_n)$ and $S(t_{n+1})$ (here: Δt=50 µs) and τ being the zero field relaxation time constant of the given particle system. τ can therefore be

10.18416/ijmpi.2023.2303084

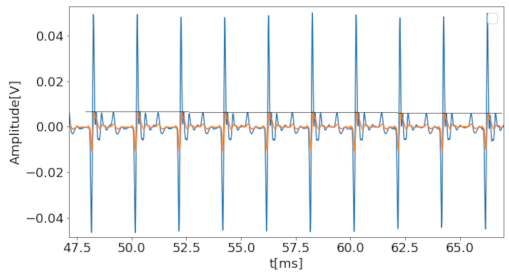

Figure 4: Signal train for two different particles (same as Fig. 3). Blue: plain iron oxide particles with 250 nm diameter (micromod, Rostock, Germany); Orange: SHP30 (Ocean NanoTech, San Diego, USA) with 70% glycerol added to the original suspension. Black line: linear fit of the signal maxima for the iron oxide particles.

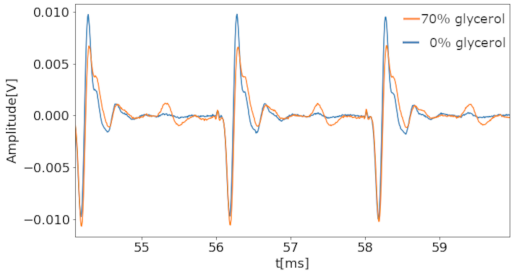

Figure 5: Signal comparison for the original suspension of SHP30 particles (blue) and with 70% glycerol added (orange).

calculated as

$$\tau = \frac{-\Delta t}{\log\left(\frac{S(t_{n+1})}{S(t_n)}\right)}. \quad (1)$$

III. Results and discussion

Fig 4. Shows two exemplary signals of a signal train. Without additional signal corrections, only a part of the signal bursts can be used, since the signal caused by the pulse is heavily distorted in the chebychev filter and interferes with the signal caused by the rotating magnetic field if the time delay is too short.

The zero-field decay time for the iron oxide particles in Fig. 4 is 2.4 ms +/-10% according to the linear fit. A linear fit is used as an approximation instead of an exponential fit since the maximum delay time difference used for the fit is 400 µs, which is significantly smaller than the expected relaxation time in the order of milliseconds.

The calculated Brownian relaxation time for particles in water with a hydrodynamic diameter of 250 nm at room temperature is 5.3 ms [4] and about a factor of two higher than measured. Since the relaxation time depends on the hydrodynamic diameter by the third power, a 25% deviation in the average diameter would already change the relaxation time by a factor of two. The used evaluation does not yet account for the interference between the pulse response and the signal shape generated by the rotating magnetic field, which are two linearly superposed wavelets. They could in principle be measured separately and used for a more precise evaluation. The corresponding error can be ignored if the delay time is sufficiently large. This is not exactly the case in the presented data and possibly the main reason for the difference between measurement and theoretical value.

Fig. 5 shows the signal difference for 30 nm particles with and without glycerol. The decay rate without glycerol is too fast for the used setup. The magnetite core diameter is 30 nm. Assuming 5 nm coating yields a hydrodynamic diameter of 40 nm, resulting in a theoretical relaxation time of 22 µs for water. In this case, the dM(t)/dt of the decay itself would yield sufficient signal. Using this signal directly is only possible after correcting for the distortion caused by the chebychev filter. The relaxation time with 70% glycerol content is expected to increase about a factor of 30 according to [5], which is about 0.6 ms. The data in Fig. 5 yields 0.9 ms +/- 30%. The mixing error in the glycerol content is estimated to be more than 10% and probably the main reason for the deviation between the calculated decay time and the measured decay time.

IV. Conclusions

The presented work shows how to measure the zero-field relaxation time with pulsed RDS sequences. This value is well defined and widely known in the literature. It avoids the magnetic field dependency of Néel relaxation and is useful for characterizing and comparing magnetic nanoparticle systems. In magnetorelaxometry the magnetic field of the magnetization decay is measured directly. The presented method allows increasing the signal-to-noise ratio for measuring the magnetization decay inductively, even if the relaxation time is in the order of seconds, resulting in a dM/dt that is otherwise too low for inductive sensing. This allows combining this measurement, e.g., with magnetic particle spectroscopy, which almost exclusively uses inductive sensing.

Acknowledgments

Research funding: This work was funded by the DFG (BE 5293/1-2, VO 2288/1-1).

Author's statement

Conflict of interest: Authors state no conflict of interest.

References

[1] McNaughton et. al, Single bacterial cell detection with nonlinear rotational frequency shifts of driven magnetic microspheres, Applied physics letters, 2007.

[2] Rückert et. al., Rotating Drift Spectroscopy for Magnetic Particle Ensembles, IEEE Proc. on IWMPI Berlin, 2014.

[3] Rückert et. al., Simulating the Signal Generation of Rotating Drift Spectroscopy, IEEE Proc. on IWMPI Berlin, 2014.

[4] Wiekhorst et. al., Magnetorelaxometry Assisting Biomedical Applications of Magnetic Nanoparticles, Pharm. Res., 2011.

[5] Gregory and Mach, Adaption of a High-Pressure Liquid Chromatography System for the Measurement of Viscosity, Chromatography, 2014.

10.18416/ijmpi.2023.2303084