

# Determination of energy barrier distributions of magnetic nanoparticles by temperature dependent magnetorelaxometry

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## Abstract

We present a new method for the characterization of magnetic nanoparticles based on the analysis of the dependence of the Néel relaxation signal on the sample temperature. In contrast to the established characterization methods, the new method directly delivers the energy barrier distribution of the magnetic system (in the case of ferrofluid particles or their aggregates). A water based ferrofluid consisting of magnetic nanoparticles with an iron oxide core and a shell of carboxydextran has been magnetically fractionated and immobilized and the fractions have been investigated in a temperature range from 77 to 350 K. The influence of the fractionation process on the distribution of the energy barriers of the particle system has been studied qualitatively.

## 1. Introduction

Magnetic properties of ferrofluids are strongly influenced by the distribution density of energy barriers  $E$  in these many particle systems. In the simplest case when the interparticle interaction can be neglected, this energy barrier distribution can be calculated from the distributions of the anisotropy constants  $K$  and the volumes  $V$  of the single particles, because  $E$  can be approximately calculated as the product of  $K$  and  $V$  (in this model  $K$  describes the effective anisotropy constant of these single domain particles resulting in a general case from shape, crystallographic and/or surface anisotropies). However, the measurement of these parameters using common methods such as AFM and TEM and their determination by the analysis of magnetization curves are very elaborate and need additional assumptions or *a priori* knowledge of the particle size distribution. In contrast to these methods the evaluation of the temperature dependence of the Néel relaxation signal provides direct access to the distribution of the energy barriers  $E$  as one of the most important parameters of this system [1–4].

The investigation of strongly diluted ferrofluids, where interaction between particles can be neglected (provided that the particles are not aggregated), enables the determination of magnetic parameters of the single particles.

In this paper we report on the investigation of the temperature dependent magnetization relaxation of a biologically compliant ferrofluid such as has already been applied in novel binding specific diagnostic techniques called magnetorelaxometry (MRX), *in vitro* [5] as well as *in vivo* [6].

## 2. Theory

In our experimental investigations we make use of the main result of [2]: the magnetization relaxation of a system with the energy barrier distribution  $\rho(E)$  (after this system has been magnetized in a *weak* external field during a finite time  $t_{\text{mag}}$ ) can be described as

$$M(\tau) = \int dE \rho(E) \delta m(E) [1 - e^{-\Gamma(E)\tau_{\text{mag}}}] e^{-\Gamma(E)\tau} \quad (1)$$

where  $\delta m(E)$  is the change of the system magnetization after the jump over the energy barrier  $E$ ,  $\Gamma(E) = \exp(-E/kT)$  and the reduced time  $\tau$  is defined via the ‘attempt frequency’  $\gamma_0$  ( $\sim 10^9$  Hz) as  $\tau = t\gamma_0$ .

To recover the distribution of system energy barriers  $\rho(E)$  from the magnetization relaxation measurements (which provide the dependence  $M(t)$  in (1)) we should, strictly speaking, solve the integral equation (IE) (1). Such a solution is an ill-conditioned problem (see any textbook on IEs) which poses strong limitations on the quality of the solution.

However, in our specific case we do not need to solve IE (1) explicitly due to the very ‘pleasant’ behaviour of the integrand  $f(E, \tau) = [1 - \exp(-\Gamma(E)\tau_{\text{mag}})] \exp(-\Gamma(E)\tau)$ .

This function varies very fast with  $E$  for the given  $\tau_{\text{mag}}$ , having a sharp maximum at  $E^{\text{max}} \approx kT \log(\tau_{\text{mag}})$  with the width  $\Delta E \sim kT$ . For the values of  $E$  outside this interval  $f(E, \tau)$  is exponentially small. This enables us to rewrite IE (1) for systems where the distribution  $\rho(E)$  varies slowly compared with  $kT$  (it is almost always the case) as

$$M(t) = kT\rho(E^{\text{max}})\delta m(E^{\text{max}}) \log(1 + t_{\text{mag}}/t). \quad (2)$$

Hence, the relaxation amplitude  $M_0$  in the expression  $M(t) = M_0 \log(1 + t_{\text{mag}}/t)$  (see below) is simply proportional to the height of the energy barrier distribution  $\rho(E^{\text{max}})$  at the known energy  $E^{\text{max}} \approx kT \log(\tau_{\text{mag}})$ :

$$M_0 = kT\rho(E^{\text{max}})\delta m(E^{\text{max}}). \quad (3)$$

This means that by measuring the magnetization relaxation for the given temperature  $T$  and magnetization time  $\tau_{\text{mag}}$  and fitting the obtained dependence by the  $\log(1 + t_{\text{mag}}/t)$  curve we can directly obtain the height of the energy barrier distribution  $\rho(E)$  multiplied by the corresponding magnetization change  $\delta m(E)$ . This product is the most important characteristics of any magnetic system when we are interested in its equilibrium and non-equilibrium thermodynamical properties.

### 3. Experimental details

#### 3.1. Measurement set-up

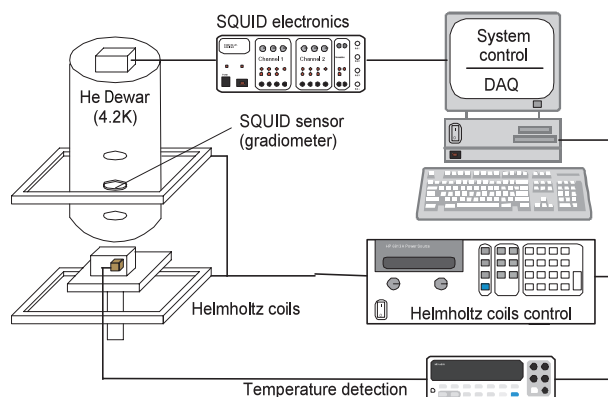
The measurement set-up for the temperature dependent determination of the magnetic relaxation (TMRX) of immobilized magnetic nanoparticles consists of a second order SQUID gradiometer to measure the magnetic relaxation signal and Helmholtz coils to magnetize the sample [4, 5]. The set-up has been improved by adding a platinum thermometer, Pt100, to determine the temperature dependent relaxation signal of MNP over a range from 77 to 350 K (figures 1 and 2).

To reliably extract the necessary information from our measurements, we have used the result (2) that the time decay of the sample magnetization  $M(t)$  due to the Néel relaxation can be described by

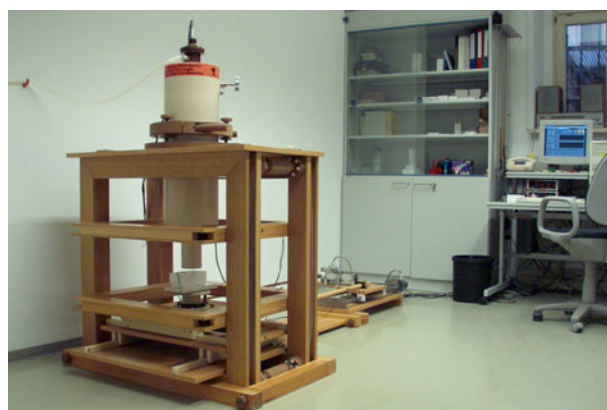
$$M(t) = M_0 \ln(1 + t_{\text{mag}}/t), \quad (4)$$

where  $M_0$  is the magnetization at  $t/t_{\text{mag}} = 1/(e - 1)$ . Accordingly, the measured field can be fitted by

$$B(t) = B_{\text{offset}} + B_0 \ln(1 + t/t_{\text{mag}}) \quad (5)$$



**Figure 1.** The scheme for the TMRX measurement set-up.

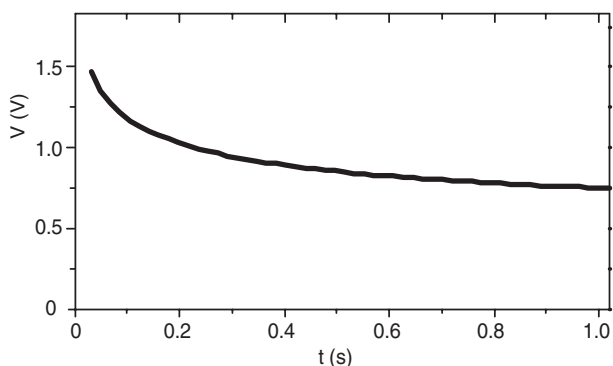


**Figure 2.** A photograph of the TMRX magnetization system containing the cryostat and the SQUID sensor. The system control, data acquisition and magnetization current source had to be placed at an appropriate distance beneath the SQUID sensor to avoid disturbances due to its extremely high sensitivity. (This figure is in colour only in the electronic version)

where the offset term is arbitrary, since SQUIDs do not supply absolute values.

After switching off the magnetizing field and a delay time of 20 ms the SQUID gradiometer measures a time dependent signal  $B(t)$  caused by the sample magnetization. For our measurements a 1 kHz antialiasing filter and a sampling rate of 2 kHz were applied. A typical relaxation signal is shown in figure 3. It was obtained by the investigation of a sample of freeze-dried ferrofluid, so only the Néel relaxation was observed. The sample containing  $0.1 \mu\text{mol Fe}$  was located 20 mm underneath the SQUID sensor and was magnetized with a field  $B_0 = 1$  mT during the time interval  $t_{\text{mag}} = 1$  s. To suppress the influence of power line frequencies, 50 and 100 Hz filters were used.

Because of the unshielded operation in a disturbed environment the MRX signal is strongly affected by signals from interference sources such as power lines (50 Hz and its harmonics) and computer monitors, as well as random events such as switching, cars being driven near the building and equipment use in other laboratories in the same building, especially laser systems. These disturbances produce different artefacts in the measured signal  $B(t)$  such as steps, peaks and shifts. For this reason a diagnostic program for detecting signal steps and a signal drift was implemented. It compares



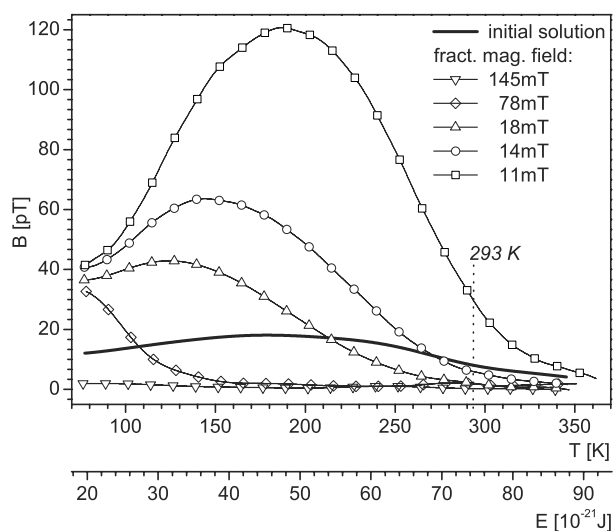
**Figure 3.** A fit of a typical relaxation signal measured using an axial SQUID gradiometer for sample magnetization with a field of 1 mT for 1 s, deadtime 20 ms, data acquisition  $B(t)$  for 1 s with a sampling rate of 2 kHz. Magnetic flux density to voltage conversion:  $650 \text{ pT V}^{-1}$ .

the low pass filtered (40 Hz) MRX signal and the MRX fit of the filtered signal. The standard deviation of the difference between these two signals must not exceed a defined value. Another diagnostic program detects particular peaks in the signal curves. Only relaxation signals which fulfil all defined conditions were used to determine the fit parameter  $B_0$ . Subsequently, the measured data were smoothed using an FFT filtering procedure.

The detection limit of the measurement system for a homogeneous distribution of MNP in a volume of 0.1 ml was found to be 0.3 nmol (17 ng) Fe for a distance of 20 mm between a sample and the SQUID sensor [6].

### 3.2. Sample preparation

A water based ferrofluid (DDM 128N, Meito Sangyo, Japan) consisting of magnetic nanoparticles with a core of iron oxide and a shell of carboxydextran was magnetically fractionated. The fractionation procedure comprises the stepwise reduction of an electromagnetic field applied to the ferrofluid from 1 T to zero. This was done using an electromagnet (Bruker B-10v) and magnetic separation columns (MACS Cell Separation Column LS, Miltenyi Biotec); for a detailed description of this procedure see [7]. In brief, the separation columns were fixed between the pole shoes of the electromagnet and rinsed with 2 ml of the buffer solution (phosphate buffered saline, pH = 7.4). Then, at the highest possible magnetic field (1 T), 500  $\mu\text{l}$  of the ferrofluid was added. The column was rinsed with the buffer solution until the eluate became clear (1 T fraction). Afterwards, the field was reduced to gather the next eluate. This procedure was repeated until the external field was reduced to zero. Subsequently, the column was removed from the magnet and the remaining nanoparticles were eluted with buffer solution and gathered ('out of magnet' fraction). The iron content of each fraction was determined by chemical analysis [8]. To prevent interparticle interaction, all samples were adjusted to contain only 0.25  $\mu\text{mol}$  Fe in 1.5 ml solution. As a result, the volume fraction  $\eta$  [9], i.e. the magnetic core volume in relation to the volume of the whole sample, is of the order of  $3 \times 10^{-6}$ . Indeed, interparticle interaction is negligible. The samples were lyophilized to immobilize the particles.



**Figure 4.** Magnetic relaxation signal versus temperature  $T$  and energy barrier  $E$ . Different curves indicate different fractionating magnetic fields.

## 4. Results and discussion

Figure 4 shows results obtained on a selection of the fractions of the ferrofluid DDM128N investigated, containing the same amount of magnetic material in each. The samples were magnetized and their relaxation was measured under the conditions described above. The energy scale in figure 4 was calculated using the time constant for Néel relaxation processes

$$t_{\text{Néel}} = t_0 e^{E/k_B T} \quad (6)$$

where  $t_0$  is usually quoted as  $10^{-9}$  s and  $t_{\text{Néel}}$  has been set equal to our measurement time of 1 s.

As the relaxation signal of the initial solution contains the full spectrum of all particles in the fluid, the corresponding  $B(T)$  curve is wide and its amplitude is relatively small. The high magnetic field fractions yielded no relaxation signal in the accessible temperature range (a signal would probably be detectable at lower temperatures). As the fractionating field decreases, the maximum of the relaxation signal shifts towards higher temperatures (higher energy barriers) corresponding to the relaxation of larger particles with higher energy barriers. Several investigations of the applied fractionation method have confirmed that the fractionation acts on the magnetic moment of the particles and yields an increase of the mean particle diameter with decreasing fractionation field. Measurements of hydrodynamic particle diameters have been performed by means of photon correlation spectroscopy (PCS) and magneto-optical relaxation (MORFF) measurements [10] as well as by atomic force microscopy (AFM) of the same type of ferrofluid [11]. The determination of magnetic core diameters of a fractionated ferrofluid has been discussed in [7]. Investigations have shown that the effective anisotropy of magnetite particles results mainly from their shape anisotropy [12], which is proportional to the square of the saturation magnetization  $M_S^2$ . Thus, the temperature dependence of the magnetic anisotropy in the temperature range investigated is relatively weak. Hence, we attribute the changes in our measured relaxation curves to an increase of the

mean particle size of the fractions with decreasing fractionating field (we do not take into account a possible influence of the distribution of the particle anisotropies).

Supposing that we observe a relaxation of individual particles (no aggregates in the initial ferrofluid) we can estimate the particle size for various fractions. For Néel relaxation investigations of uniaxial single domain magnetite/maghemite particles, anisotropy values of  $K = (1-5) \times 10^4 \text{ J m}^{-3}$  [13, 14] are commonly used. Assuming for simplicity that each fraction consists of particles with a mean effective magnetic anisotropy constant  $K = 20 \text{ kJ m}^{-3}$  [15], for an accessible temperature range of 77–350 K we have estimated a particle core diameter 12–20 nm detectable by our measurement system. The relatively small particle size range over a wide range of temperature indicates the high sensitivity of our method with respect to the detection of changes in the energy barrier distribution of the particles.

## 5. Conclusions

It has been shown that by making measurements of the relaxing magnetization of magnetic nanoparticles for different sample temperatures, it is possible to determine directly the height of the energy barrier distribution  $\rho(E)$  multiplied by the corresponding magnetization change  $\delta m(E)$ . The influence of the change in the particle size distribution caused by the magnetic fractionation of a biologically compliant ferrofluid on the energy barrier distribution of the system has been studied qualitatively.

Assuming a known anisotropy distribution it is possible to reconstruct the distribution of magnetic particle volumes; or, vice versa, if the geometric particle size distribution is known from independent measurements (e.g., transmission electron microscopy), a reconstruction of the anisotropy constant distribution from our data would be possible.

Furthermore, we plan to investigate ferrofluids from a more quantitative point of view, using the TMRX method. Therefore, particle size distributions have to be determined by means of TEM measurements. Later, coercivity measurements of blocked nanoparticles (at very low temperatures) will enable us to determine the mean magnetic anisotropy.

Due to the extremely high sensitivity of SQUID systems we were able to investigate strongly diluted ferrofluids to avoid magnetic particle interactions. The TMRX method also allows to investigate effects caused by magnetic particle interactions by simply changing the volume fraction of magnetic particles in the fluid.

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## References

- [1] Chantrell R W, Hoon S R and Tanner B K 1983 *J. Magn. Magn. Mater.* **38** 133
- [2] Berkov D V and Kötz R 1996 *J. Phys.: Condens. Matter* **8** 1257
- [3] Berkov D V 1998 *J. Magn. Magn. Mater.* **186** 199
- [4] Weber P, Romanus E, Prass S, Groß C, Reinhard A, Weitschies W and Berkov D V 2002 *4th German Ferrofluid Workshop (Berlin, Germany, 2002)*
- [5] Lange J, Kötz R, Haller A, Trahms L, Semmler W and Weitschies W 2002 *J. Magn. Magn. Mater.* **252** 381
- [6] Romanus E, Hüchel M, Groß C, Prass S, Weitschies W, Bräuer R and Weber P 2002 *J. Magn. Magn. Mater.* **252** 387
- [7] Rheinländer T, Justiz J, Haller A, Kötz R, Weitschies W and Semmler W 1999 *IEEE Trans. Magn.* **35** 4055
- [8] Jäger E G, Schöne K and Werner G 1981 *Elektrolytgleichgewichte und Elektrochemie (Lehrwerk Chemie Arbeitsbuch 5)* (Berlin, Germany: Deutscher Verlag für Grundstoffchemie)
- [9] Berkov D V 1998 *J. Phys.: Condens. Matter* **10** L89
- [10] Romanus E, Groß C, Glöckl G, Weber P and Weitschies W 2002 *J. Magn. Magn. Mater.* **252** 384
- [11] Groß C, Büscher K, Romanus E, Helm C A and Weitschies W 2002 *Eur. Cells Mater.* **3/2** 163
- [12] Fannin P C, Kinsella L and Charles S W 1999 *J. Magn. Magn. Mater.* **201** 91
- [13] Fannin P C and Charles S W 1994 *J. Phys. D: Appl. Phys.* **27** 185
- [14] Fannin P C and Charles S W 1991 *J. Phys. D: Appl. Phys.* **24** 76
- [15] Kötz R, Weitschies W, Trahms L, Brewer W and Semmler W 1999 *J. Magn. Magn. Mater.* **194** 62