# Relaxation behaviour of spherical and cylindrical magnetic nanoparticles in liquid media

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# Summary

Magnetic nanoparticles are very promising for various applications in medicine. In this research the relaxation behaviour of superparamagnetic particles is investigated. Magnetic relaxation is defined as the return or adjustment to equilibrium after a change of the external magnetic field. Superparamagnetic nanoparticles have the same high magnetic response as ferromagnets, but exhibit no hysteresis. This makes them particularly suited for relaxation experiments. The relaxation behaviour is influenced by both characteristics of the particles and their environment. This is used in clinical applications, which include in vitro sensing and immunoassays.

Physical models describing the relaxation behaviour of both spherical and cylindrical particles are made. Cylindrical particles are thought to be beneficial due to their shape anisotropy. Simulations show indeed that cylindrical particles are allowed to have larger volume at the superparamagnetic limit, indicating a higher magnetic response due to the increased amount of magnetic material. However, surface effects counteract this effect. Quantification of these surface effects was outside the scope of this research, but measurements of the magnetization curves of spherical and cylindrical particles showed that the surface effects are larger than the shape anisotropy effects in the superparamagnetic regime.

The relaxation behaviour was measured with two different setups i.e. a superconducting quantum interference device (SQUID) magnetometer measuring the relaxation as a function of time and a differential transformer measuring the susceptibility as a function of frequency. The SQUID magnetometer setup was designed and built in our own lab, partly during this assignment. It uses a static magnetic field to align the magnetic particles. After the field is switched off, the particles will return to a random orientation. The corresponding decrease of magnetic moment as a function of time is measured with the SQUID. The setup using the differential transformer was already developed at Utrecht University, where the measurements took place as well. This setup uses an oscillating magnetic field to align the particles. At low frequencies, the particles are able to align to the magnetic field before it changes direction. As the frequency increases, full alignment is not possible anymore. This transition point corresponds to the relaxation time.

Multiple samples were used to verify the simulation model with the experiments. Unfortunately, none of the samples was able to confirm or reject the simulation models. The relaxation time of samples containing iron oxide particles was outside the measurement regime for both setups. Samples containing spherical nickel particles showed sedimentation and clustering. At last, the cylindrical nickel particles could not be compared to the simulation model, since they turned out to be ferromagnetic instead of superparamagnetic.

# Samenvatting

De toepasbaarheid van magnetische nanodeeltjes in de geneeskunde is veelbelovend. In dit onderzoek zal het relaxatie gedrag van superparamagnetische nanodeeltjes worden onderzocht. Magnetische relaxatie is gedefinieerd als het terugkeren naar of het vinden van een nieuwe evenwichtspositie na een verandering in het externe magneetveld. Superparamagnetische nanodeeltjes hebben eenzelfde hoge magnetische respons als ferromagneten, maar vertonen geen hysterese. Hierdoor zijn ze uitermate geschikt voor relaxatie metingen. Het relaxatiegedrag wordt beïnvloed door zowel de eigenschappen van de deeltjes als de eigenschappen van de omgeving van het deeltje. Dit wordt gebruikt voor klinische toepassingen, onder andere in vitro sensing en immunoassays.

Natuurkundige modellen die het relaxatie gedrag van zowel sferische als cilindrische deeltjes beschrijven zijn ontwikkeld. Van cilindrische deeltjes wordt gedacht dat zij geschikter zijn door hun vorm-anisotropie. Simulaties hebben inderdaad aangetoond dat cilindrische deeltjes een groter volume kunnen beslaan in de superparamagnetische limiet. Dit houdt in dat zij meer magnetisch materiaal mogen bevatten, waardoor zij een grotere magnetische respons hebben. Echter, oppervlakte effecten werken dit effect tegen. Kwantificatie van de oppervlakte effecten was helaas buiten het kader van dit onderzoek, maar metingen aan de magnetisatie krommen van sferische en cilindrische deeltjes heeft aangetoond dat in het superparamagnetisch regime de oppervlakte effecten groter zijn dan de vorm-anisotropie effecten.

Het relaxatie gedrag is met twee verschillende opstellingen gemeten i.e. een supergeleidend kwantum interferentie apparaat (SQUID) magnetometer die de relaxatie als functie van de tijd meet en een differentiële transformator die de susceptibiliteit meet als functie van de frequentie. De SQUID opstelling is ontworpen en gebouwd in ons eigen laboratorium, gedeeltelijk als onderdeel van deze opdracht. De opstelling maakt gebruik van een DC magneetveld om de deeltjes te richten. Nadat het magneetveld is uitgezet keren de deeltjes terug naar een willekeurige oriëntatie. De afname in het magnetisch moment dat hiermee gepaard gaat wordt gemeten met de SQUID. De opstelling met de differentiële transformator was eerder al ontwikkeld aan de Universiteit Utrecht, waar ook de metingen hebben plaats gevonden. Deze opstelling gebruikt een AC magneetveld om de deeltjes te richten. Op lage frequenties van dit veld zijn de deeltjes in staat zich naar het magneetveld te richten voordat deze van richting verandert. Wanneer de frequentie toeneemt, is er een punt waarop dit niet meer mogelijk is. Dit overgangspunt typeert de relaxatie tijd.

Er is gebruik gemaakt van meerdere samples om het simulatie model te kunnen verifiëren. Helaas kon geen van deze samples de juistheid van het model bevestigen danwel weerleggen. De relaxatietijd van het sample met ijzeroxide deeltjes lag buiten het meetbereik van beide opstellingen. De samples met sferische nikkel deeltjes hadden last van sedimentatie en clustering. Tot slot waren de cilindrische nikkel deeltjes ferromagnetisch in plaats van superparamagnetisch, waardoor ze niet konden worden beschreven met het gemaakte model.

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# Chapter 1

# Introduction

The first use of radioactive substances in medicine was over 100 years ago in cancer treatment. Nowadays, nuclear medicine also comprises diagnostic purposes. Radioactive materials are used to enhance contrast in MRI and CT and as tracers in PET and SPECT [1]. The main disadvantage of radioactive materials is the ionizing radiation emitted. Ionizing radiation has negative long-term effects on the health of patients and staff and it comes with extra regulations and a complex logistics procedure. The result is not all hospitals having access to radioactive materials.

Magnetic materials might prove to be a good alternative. Magnetic materials do not transmit ionizing radiation and recently much research is done on magnetic materials for similar applications and more [2]. An overview of applications up to now is depicted in figure 1.1.

The applications of the research described in this report can be found in in vitro sensing and immunoassays, which cannot be accomplished with radioactive materials. The focus of this research is on magnetic relaxation behaviour of superparamagnetic nanoparticles. Relaxation is defined as the return or adjustment to equilibrium after a change of the environment, in this case an external magnetic field. The relaxation behaviour is determined by the characteristics of the particles and their environment, for example the material, size, shape, temperature and medium. Measurement of the relaxation behaviour reveals changes in one of these parameters. Relaxation measurements can therefore be used to identify the viscosity of body fluids or to monitor magnetic particles as they travel through areas with different fluids viscosities. Another application of relaxation measurement involves biomarkers, attached to the particles, that bind with specific substances. The particle size increases when the substance is bonded to the biomarker, which leads to a change of the relaxation behaviour. This indicates the presence of the specific substance.

In this research a model is developed that describes the relaxation behaviour of various particles, so optimum particle dimensions can be found. Special attention is paid to the shape of the particles. Cylindrical superparamagnetic particles are expected to be beneficial over spherical particles due to their shape anisotropy [4]. Therefore, these particles are described in separate models.

The simulation models are used to find the requirements for an experimental setup that can accurately measure the relaxation behaviour. A prototype of a magnetometer based on a superconducting quantum interference device (SQUID) is already available, but needs to be improved before it can be used for relaxation measurements. This setup uses a DC magnetic field to align the magnetic nanoparticles. After the magnetic field is turned off, the decay of the magnetic moment is measured as a function of time with the



Figure 1.1: Applications for magnetic nanoparticles [3].

SQUID, a device that very accurately measures gradients in magnetic fields.

Another setup able to measure relaxation behaviour is already available at Utrecht University. This setup applies an AC magnetic field to the particles. The change of the magnetization of the sample as a reaction to the magnetic field, the susceptibility, is measured with a differential transformer. The frequency of the magnetic field is varied to find the specific frequency at which the particles cannot align their magnetic moment with the magnetic field anymore in the given time frame of the AC magnetic field. This frequency corresponds to the relaxation time of the particles.

Experiments with both setups are conducted to verify the simulation model. Different samples where shape, size and medium are varied were used to test the simulation model and to investigate the capability of relaxation experiments to distinguish these differences.

In this report we will focus on three research questions. Firstly, the physical behaviour of the particles is investigated and described in a simulation model. Here we have to include different sizes, materials and media to find the optimal particle dimensions. Special attention will be paid to the difference between spherical and cylindrical particles, for which separate models will be developed. Secondly, the present prototype setup of a SQUID magnetometer needs to be improved before relaxation measurements can be done. Finally, experiments with two different setups will be conducted to verify the models. Our goal is to make a thorough analysis of the characteristics of the particles, such that we can identify which attributes of both the samples and the setup have to be improved in order to apply these relaxation measurements in the clinic.

# Chapter 2

# Superparamagnetic nanoparticles

### 2.1 Introduction

The particles used in this study are superparamagnetic. Superparamagnetic particles are made from ferro- or ferrimagnetic material. The size of these magnetic particles is decreased sufficiently, which gives rise to some special characteristics. The particles consist of one magnetic domain and show no hysteresis. These characteristics are exploited in the relaxation experiments. Applying a magnetic field aligns the particles, which results in a high net magnetic moment. The absence of hysteresis ensures a fast decay of the net magnetic moment at removement of the magnetic field.

This chapter gives an insight in superparamagnetism and relaxation behaviour. First, the characteristics of superparamagnetism are explained. Then the magnetic moment of a nanoparticle and its direction due to anisotropy are discussed. After that, it is explained how the alignment of magnetic particles changes with changing magnetic fields.

## 2.2 Superparamagnetism

#### 2.2.1 Magnetic domains

Every physical system aims to minimize its energy. In terms of orientation of spins in a particle, there is the interplay between the exchange energy and the demagnetization energy [5]. Minimal exchange energy is reached when the spins are aligned parallel to each other. However, parallel spins give rise to a magnetic field, called the demagnetization field, and every new spin has to fight against this field in order to be aligned parallel to the others. So the exchange energy wants a uniformly magnetized particle, while the demagnetization energy prefers a net magnetization of zero. For very small particles, the demagnetization field is still small and the gain from exchange energy is large enough to align the spins. At certain dimensions of the particle, the demagnetization of the particle will split into multiple domains of uniformly magnetized spins, see figure 2.1. These domains are separated by domain walls i.e. transition areas in which the orientation of the spins turns gradually.

The size and energy of a domain wall are not only determined by the exchange energy,



Figure 2.1: A single domain particle has a net magnetic moment, while the net magnetic moment of the multidomain particle is cancelled by the orientation of the different domains.

but also by the anisotropy energy, which favours the magnetization to be in the direction of certain axis, called the easy axis. In the case of cylindrical particles, this is in the direction of the long axis of the cylinder. The ideal thickness of the domain wall can be determined by minimizing the exchange and the anisotropy energy. Very small particles consist of a single domain i.e. there are no domain walls. Single domain particles are characterized by demagnetization energies that are smaller than the domain wall energy.

#### 2.2.2 Hysteresis

The direction of the magnetization of a single domain particle depends on the externally applied magnetic field and on internal forces. In absence of an external magnetic field, the particle has two equivalent equilibrium positions along two opposite directions of the anisotropy axis. The preferred directions, also called easy axis, represent energy minima which are the result of a number of anisotropies. To switch from one position to the other, an energy barrier has to be overcome, see figure 2.2.

Particles with multiple domains have no net magnetic moment in the absence of a magnetic field. However, the magnetic moments of the domains will align when a magnetic field is applied. The magnetic moment of the particle is then along the anisotropy axis which has the smallest angle to the magnetic field, resulting in a net magnetic field can rotate the magnetic moment of the domains away from their easy axis, towards the direction of the magnetic field. Once the magnetic domains are oriented in a direction, it costs energy to turn them back again, since the anisotropy energy has to be overcome. Therefore, the magnetic moment will not return to zero when the magnetic field is switched off again. This is called hysteresis. A magnetic field in the opposite direction is needed to overcome the energy barrier and change the direction of the magnetic moment. The magnetic moment is mainly reversed by the movement of domain walls. Only a weak magnetic field is necessary to move the domain walls and so reverse the magnetization [6]. Particles of this kind are called ferromagnetic and are in the multidomain regime in figure 2.3.

When the particle gets smaller, the number of domains decrease and finally only one domain equal to the size of the particle remains. With decreasing particle size it is harder to switch the magnetization by just the movement of domain walls. Therefore, the coercivity increases, which means a higher magnetic field is needed to reduce the magnetization of the particle to zero after it has been driven to saturation. The coercivity increases until it reaches its maximum when the size of the particle is reduced to a single domain, see also figure 2.3.



Figure 2.2: Energy as a function of the angle of rotation in a particle. a) When there is no external magnetic field, the particle has two equilibrium positions due to the anisotropy of the particle. b) Switching on a magnetic field, these energies change. c) When the magnetic field gets sufficiently large, one of the equilibrium states disappears and the magnetic moment is forced to be in the direction of the remaining minimum [5].

In the single domain state the particle still exhibits hysteretic behaviour, since it has to overcome a relatively high anisotropy barrier to reverse its magnetic moment. However, the energy barrier decreases with decreasing particle size. So there is a critical limit at which the energy barrier gets smaller than the thermal energy, resulting in a constantly changing direction of magnetization [6]. The hysteretic behaviour is now lost and the total magnetic moment of the system of particles will be zero, since the chance of the particle to be in either favourable state is equal.

However, when a small external magnetic field is applied, the magnetization of the particles will be along the anisotropy axis which has the smallest angle to the magnetic field, resulting in a net magnetic moment of the system along the direction of the magnetic field. This behaviour is very similar to paramagnetism, only the role of the single atoms is now played by the single domain particles. Since the magnetic moment of a single domain ferromagnetic particle is much bigger than that of a single atom in a paramagnet, the net magnetic moment is often about  $10^4 - 10^6$  times as big as in paramagnetism, see also figure 2.4. Consequently, this behaviour is called superparamagnetism [7, 8, 9, 10].

## 2.3 Magnetic moment

The magnetization of an ensemble of particles depends on the magnetic moment of the individual particles. In this section, first the magnetic moment of one atom or molecule is discussed. After which this is used to determine the magnetic moment of an anoparticle. Finally, this can be used to determine the magnetic moment of an ensemble of particles. The magnetic moment of an ensemble of particles is the quantity that decays in a relaxation process and therefore the quantity to be measured. The magnetic moment of an ensemble of particles determines the strength of the signal in the measurements.

#### 2.3.1 Magnetic moment of atoms

The magnetic moment of an atom is described by

$$\mu_H = g J \mu_B, \tag{2.1}$$



Figure 2.3: Coercivity as a function of particle size. Particles in the multidomain range are ferromagnetic and show hysteresis. The hysteresis increases with decreasing particle size until it reaches its maximum at the critical size of a single domain particle,  $d_c$ . The single domain particles in the shaded area are still ferromagnetic, while the particles smaller then  $d_s$  show no hysteresis and are superparamagnetic [6].



Figure 2.4: Magnetization curves for different types of magnetism. Unlike ferromagnetism, superparamagnetism does not show hysteresis and compared to paramagnetism, superparamagnetism shows much higher magnetization at saturation.

where J represents the quantum number representing the total angular momentum,  $\mu_B$  the Bohr magneton and g the spectroscopic splitting factor given by

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)},$$
(2.2)

where S represents the spin angular momentum, L the orbital angular momentum and J is given by J = L + S. So the quantum numbers J, S and L are needed to calculate the magnetic moment of an atom. These quantum numbers can be derived from the electronic structure of the material. However, these quantum numbers are only valid for isolated atoms and can therefore not be used to describe the magnetic moment of a solid. Though, under certain simplifying assumptions, the magnetic moment of some materials can be calculated. Such an assumption is that the contribution of the orbital momentum is zero, i.e. J=S. This assumption is valid for many materials and arises from the force of the electric field acting on the orbits. All atoms in the area contribute to the electric field, which therefore depends on the crystal configuration. These forces result in a rather strong coupling of the orbits to the lattice. On the other hand, the spins are coupled weakly to the lattice. Hence, when a magnetic field is applied to the material, the spins can rotate in the direction of the magnetic field, while the orbits are bound to their positions by the strong orbit-lattice coupling. Therefore, the orbital moments do not contribute to the resultant magnetic moment and the assumption J = S is valid.

The quantum numbers needed to calculate the magnetic moment can be derived from the electronic structure of the material. The electronic structure of nickel is  $3d^84s^2$ . The quantum numbers S, L and J can be determined from this structure, which leads to S = 1and L = 3. Considering the nickel atom is part of solid nickel, the total angular momentum is zero and the magnetic moment of the nickel atom becomes  $\mu_H = 2\mu_B$ .

Magnetite (Fe<sub>3</sub>O<sub>4</sub>) consists of three iron ions, two Fe<sup>3+</sup> ions and one Fe<sup>2+</sup> ion. The electronic structure of Fe<sup>3+</sup> is 3d<sup>5</sup>, which gives S = 5/2 and L = 0. The magnetic moment of a Fe<sup>3+</sup> atom is then  $\mu_H = 5\mu_B$ . The electronic structure of Fe<sup>2+</sup> is 3d<sup>6</sup>, which gives S = 2 and L = 2. Considering the Fe<sup>2+</sup> is in a solid so the orbital angular momentum is zero, the magnetic moment of a Fe<sup>2+</sup> atom is  $\mu_H = 4\mu_B$ . For a ferromagnetic material the magnetic moment can be determined by adding the magnetic moments of the atoms of the molecule. However, magnetite is not ferromagnetic but ferrimagnetic. The two Fe<sup>3+</sup> atoms are anti-ferromagnetically ordered, cancelling each other's magnetic moments. The Fe<sup>2+</sup> atoms are ferromagnetically ordered, so the net magnetic moment is due to these atoms. The resultant magnetic moment is then  $\mu_H = 4.1\mu_B$  [5].

#### 2.3.2 Magnetic moment of a superparamagnetic nanoparticle

Since superparamagnetic nanoparticles consist of one single domain, the magnetic moments of the individual atoms are aligned. Therefore, the magnetic moment of a nanoparticle can be determined by adding the magnetic moments of the individual atoms and is given by

$$\mu_{NP} = \mu_H \frac{N_A V}{M_V},\tag{2.3}$$

where  $N_A$  represents Avogadro's constant, V the volume of a nanoparticle and  $M_V$  the molar volume of the material. The combination  $\mu_H \frac{N_A}{M_V}$  is also referred to as saturation magnetization,  $M_s$ , since it is the maximum magnetization reached when all the dipoles are aligned.

However, at the surface of the particle the lattice symmetry is broken, which prevents the particle to reach the maximum magnetization. Since nanoparticles have a relatively high surface to bulk ratio, the surface effects significantly alter the particles final magnetic moment. Therefore, the saturation magnetization of nanoparticles is less than that of the bulk and depends on the surface to bulk ratio [11].

#### 2.3.3 Magnetic moment of an ensemble of particles

For a paramagnetic material with atoms having a small permanent magnetic moment, the magnetic moment of the material is described by

$$M = N_p g J \mu_B B_J(x), \tag{2.4}$$

where  $N_p$  represents the number of atoms, J the quantum number representing the total angular momentum,  $\mu_B$  the Bohr magneton, g the spectroscopic splitting factor and  $B_J$ the Brillouin function, given by

$$B_J(x) = \frac{2J+1}{2J} \coth\left(\frac{2J+1}{2J}x\right) - \frac{1}{2J} \coth\left(\frac{x}{2J}\right).$$
(2.5)

The quantity x can be described by

$$x = \frac{\mu_0 \mu_H H}{k_B T},\tag{2.6}$$

where  $\mu_H$  represents the maximum magnetic moment of each atom given by  $\mu_H = gJ\mu_B$ , H the magnetic field,  $k_B$  the Boltzmann constant and T the temperature. In quantum mechanics the magnetic moment is restricted to a couple of directions i.e. the space is quantized. The number of possible directions depends on the quantum number J. In the classical approach space is not quantized and the magnetic moment can be in any direction and J approaches infinity. In this limit, the Brillouin function reduces to the Langevin function [8]

$$B_{J\to\infty}(x) = L(x) = \coth(x) - \frac{1}{x}.$$
 (2.7)

The magnetic moment of an ensemble of superparamagnetic particles, with magnetic moment  $\mu_{NP}$  and dispersed in a carrier liquid, can be approached in the same way as that of a paramagnetic material. Only the magnetic moment of the atom should be replaced by the magnetic moment of the particle. The magnetic moment of the nanoparticles can be directed in any orientation, since the particles are dispersed in a carrier liquid. Hence, the number of possible directions for the magnetic moment is infinite and the Brillouin function can be replaced by the Langevin function.

$$M = M_s N_p \Big( \coth \frac{\mu_0 \mu_{NP} H}{k_B T} - \frac{k_B T}{\mu_0 \mu_{NP} H} \Big), \tag{2.8}$$

where  $M_s$  represents the saturation magnetization and  $\mu_{NP}$  the magnetic moment of a nanoparticle. The magnetization as a function of the applied magnetic field is depicted in figure 2.5.

This description of the magnetic moment of an ensemble of particles would only fit an ensemble with identical particles i.e. no variation in the size of the particles is allowed. In real particle systems there is always a distribution in particle sizes. Often a lognormal



Figure 2.5: Magnetization curve for spherical particles of  $Fe_3O_4$  with a diameter of 100 nm. Both the exact Langevin function and the linear approximation model are shown. The Langevin function is only valid for spherical particles, whereas the linear approximation can also be made for particles with other geometries.

distribution function is used to describe the size distribution of both the magnetic cores and the hydrodynamic particle size of superparamagnetic nanoparticles. The probability density function is [7, 12, 13]

$$f(d) = \frac{1}{\sqrt{2\pi\sigma}d} e^{-\frac{\ln^2 d/\mu}{2\sigma^2}},$$
(2.9)

where d represents the diameter and  $\sigma$  and  $\mu$  represent respectively the standard deviation and the mean diameter of the natural logarithm of d.

$$\mu = \ln\left(\frac{m^2}{\sqrt{v+m^2}}\right)$$

$$\sigma = \sqrt{\ln\left(\frac{v}{m^2}+1\right)}$$
(2.10)

where m is the mean diameter of the particles and v the variance.

The magnetic moment can now be described as

$$M(H) = M_s N_p \int_0^\infty f(d_h, \mu_h, \sigma_h) \int_0^\infty V(d_c) f(d_c, \mu_c, \sigma_c) L(d_c, H) dd_c dd_h.$$
 (2.11)

The indices c and h refer to the core and the hydrodynamic diameter respectively.

#### Cylindrical particles

In the derivation of the Langevin function it is assumed the particles have a spherical shape. Therefore, the Langevin function cannot be applied to describe the magnetization curve of cylindrical particles. For particles of all shapes the magnetization can be approximated by a linear function [14]

$$\mathbf{M} = \chi_{in} \mathbf{H}_{in}, \tag{2.12}$$

where  $\chi_{in}$  represents the initial susceptibility of the material and  $H_{in}$  the internal field in the particle. The internal field depends on both the applied field, H, and the demagnetization field of the particle,  $H_d$ , as  $H_{in} = H + H_d$ . Above a certain magnetic field the particle becomes saturated and the magnetization will be  $M = M_s$ , see also figure 2.5. The demagnetization field depends on the shape of the particle and can be described for symmetrical particles as

$$\mathbf{H}_{\mathbf{d}} = -N\mathbf{M},\tag{2.13}$$

where N is the demagnetization factor, depending on the shape of the particle. It is described as [15, 16]

$$N_{ij}(\mathbf{r}) = \frac{1}{8\pi^3} \int d^3 \mathbf{k} \frac{D(\mathbf{k})}{k^2} k_i k_j e^{i(\mathbf{k}\cdot\mathbf{r})},\tag{2.14}$$

where k represents the frequency in the space domain,  $D(\mathbf{k})$  the Fourier transform of the shape function, often called the shape amplitude or shape transform. For a cylinder the shape amplitude is given by

$$D(\mathbf{k}) = \frac{4\pi R}{k_{\perp} k_z} J_1(k_{\perp} R) \sin(\frac{hk_z}{2}), \qquad (2.15)$$

where  $k_{\perp} = \sqrt{k_x^2 + k_y^2}$  and  $J_1$  represents the Bessel function of the first kind. The magnetization can be described as

$$\mathbf{M} = \frac{\chi_{in}}{1 + N\chi_{in}} \mathbf{H}.$$
(2.16)

Taking the distribution of particle sizes into account, the magnetic moment of an ensemble of particles is now described as

$$M(H) = M_s N_p \int_0^\infty f(d_h, \mu_h, \sigma_h) \int_0^\infty V(d_c) f(d_c, \mu_c, \sigma_c) \frac{\chi_{in}}{1 + N\chi_{in}} H dd_c dd_h.$$
 (2.17)

The indices c and h refer to the core and the hydrodynamic diameter respectively.

## 2.4 Anisotropy energy

The direction of the magnetic moment of a nanoparticle depends on the energy of the system. The direction with the lowest energy is the direction of the magnetization. There are several contributions to the energy of the system, which makes the magnetization dependent on the orientation. The most important contributions are

- Magnetocrystalline anisotropy
- Surface anisotropy
- Shape anisotropy



Figure 2.6: Coordinate system as used in this report. This coordinate system assumes particles which are grown in the [001] direction.

The magnetocrystalline anisotropy is the only anisotropy that is fully caused by the intrinsic material properties. The other contributions to the anisotropy are induced by the design of the particle. The total energy of the system can be written as

$$\varepsilon = KV\sin^2\theta,\tag{2.18}$$

where K represents the anisotropy constant, which contains all anisotropies mentioned, V the volume of the particle and  $\theta$  the angle between the z-axis and the magnetization, see figure 2.6.

#### 2.4.1 Magnetocrystalline anisotropy

The coupling between the orbits and the lattice is very strong in a crystal, as explained in section 2.3.1. The orientation of the orbits is strongly fixed to the lattice. Likewise, the spins are coupled to the orbits, although this coupling is much weaker than the orbitlattice coupling. So, when a magnetic field tends to rotate the spin, it has to rotate the orbit as well. However, the orbit is strongly fixed to the lattice and will keep the spin in its original position. The spin can only be rotated when the magnetic field has more energy than the spin-orbit coupling. We recall from section 2.3.1 that the strength of the orbitlattice coupling depends on the crystal configuration. Therefore, the energy needed to overcome the spin-orbit coupling is spatially variable and is called the magnetocrystalline anisotropy energy [8].

For a cubic lattice, the anisotropy can be described as [8, 17]

$$E_{crys} = K_0 + K_1(\alpha_1^2 \alpha_2^2 + \alpha_1^2 \alpha_3^2 + \alpha_2^2 \alpha_3^2) + K_2 \alpha_1^2 \alpha_2^2 \alpha_3^2$$
(2.19)

where  $K_0$ ,  $K_1$  and  $K_2$  represent material constants and  $\alpha_1$ ,  $\alpha_2$  and  $\alpha_3$  represent the fractions of the unit vector of magnetization on the axis of the crystal lattice. For particles

$K_1$	+	+	+	_	_	_
$K_2$	$+\infty$ to	$-9K_{1}/4$	$9K_1$	$-\infty$ to	$9 K_1 /4$	$9 K_1 $
	$-9K_{1}/4$	to $9K_1$	to - $\infty$	$9 K_1 /4$	to $9 K_1 $	to $+\infty$
Easy	$\langle 100 \rangle$	$\langle 100 \rangle$	$\langle 111 \rangle$	$\langle 111 \rangle$	$\langle 110 \rangle$	$\langle 110 \rangle$
Medium	$\langle 110 \rangle$	$\langle 111 \rangle$	$\langle 100 \rangle$	$\langle 110 \rangle$	$\langle 111 \rangle$	$\langle 100 \rangle$
Hard	$\langle 111 \rangle$	$\langle 110 \rangle$	$\langle 110 \rangle$	$\langle 100 \rangle$	$\langle 100 \rangle$	$\langle 111 \rangle$

Table 2.1: Easy, medium and hard magnetization directions for a cubic lattice [8].



Figure 2.7: Coordinate system for particles grown in the [110] direction.

grown in the [001] direction, the  $\alpha_1$ ,  $\alpha_2$  and  $\alpha_3$  axis coincide with the x, y and z axis respectively. These can also be expressed in the angles  $\theta$  and  $\phi$  defined in figure 2.6, as

$$\begin{aligned}
\alpha_1 &= \cos\phi\sin\theta \\
\alpha_2 &= \sin\phi\sin\theta \\
\alpha_3 &= \cos\theta
\end{aligned}$$
(2.20)

The magnetocrystalline energy density for a cubic crystal lattice then becomes

$$E_{crys} = K_0 + K_1 (\sin^2 \phi \cos^2 \phi \sin^2 \theta + \cos^2 \theta) \sin^2 \theta + K_2 (\sin^2 \phi \cos^2 \phi \sin^2 \theta \cos^2 \theta) \sin^2 \theta.$$
(2.21)

The favoured magnetization direction depends on the sign and the magnitude of the constants  $K_1$  and  $K_2$ , see table 2.1.

#### Application to our home-made wires

The nickel wires used in this research are grown in the [110] direction. The x,y and z axis do not coincide with  $\alpha_1$ ,  $\alpha_2$  and  $\alpha_3$  anymore, so another expression needs to be used for

the description of  $\alpha$  in the angles  $\phi$  and  $\theta$ , see also figure 2.7.

$$\alpha_1 = \cos(\pi - \theta)$$

$$\alpha_2 = \sin\theta \sin(\phi - \pi/4)$$

$$\alpha_3 = \sin\theta \cos(\phi - \pi/4)$$
(2.22)

The magnetocrystalline anisotropy energy density for cylindrical particles grown in the [110] direction becomes

$$E_{crys,Ni} = K_0 + K_1 \left( \sin^2 \left( \phi - \pi/4 \right) \cos^2 \left( \phi - \pi/4 \right) \sin^2 \left( \theta \right) + \cos^2 \left( \pi - \theta \right) \right) \sin^2 \left( \theta \right) + K_2 \left( \sin^2 \left( \phi - \pi/4 \right) \cos^2 \left( \phi - \pi/4 \right) \sin^2 \left( \theta \right) \cos^2 \left( \pi - \theta \right) \right) \sin^2 \left( \theta \right).$$
(2.23)

#### 2.4.2 Surface anisotropy

The magnetocrystalline symmetry is broken at the surface of the particle. The breaking of the lattice symmetry is associated with several chemical and physical effects leading to a site-specific surface energy [18].

For large particles, the amount of surface atoms is very small compared to the amount of bulk atoms. Therefore, the surface effects will be negligible compared to the magnetocrystalline anisotropy. However, the fraction of atoms located at the surface increases with decreasing particles size. So for small particles, the surface atoms will contribute significantly to the total anisotropy. For nanoparticles, the surface anisotropy is often one order of magnitude larger than the magnetocrystalline anisotropy energy [7, 19].

There are two models that describe the surface anisotropy, the transverse anisotropy model (TSA) and the Neel surface anisotropy model (NSA). The TSA model is simple, but not always valid. The NSA model is more complicated, but also more accurate [20, 19, 21]. In the scope of this research, the transverse anisotropy model is sufficient en will therefore be used.

The transverse surface anisotropy model assumes that the surface particles are magnetized perpendicular to the surface. The energy of the surface can be described as [20, 22]

$$\varepsilon_{surface} = \int_{S} K_s \left( \mathbf{m} \cdot \mathbf{n} \right)^2 dS, \qquad (2.24)$$

where **m** represents the unit vector of magnetization, **n** the normal vector,  $K_s$  the surface anisotropy constant and S the surface.

#### Spherical particle

For spherical particles, the energy contribution from the surface will be uniform. Therefore, it will not influence the anisotropy, although there is an absolute contribution to the total energy. The contribution to the energy per area is

$$E_{surface,area} = \int_{S} K_s \left(\cos^2\phi \sin^2\theta + \sin^2\phi \sin^2\theta + \cos^2\theta\right)^2 dS = \int_{S} K_s dS = 4\pi R^2 K_s.$$
(2.25)

The total energy will be [7, 23]

$$\varepsilon_{surface} = K_s S = \frac{3}{R} K_s \frac{4}{3} \pi R^3 = \frac{3}{R} K_s V, \qquad (2.26)$$

where  $K_s$  represents the surface anisotropy constant, S the surface area and V the volume of the spherical particle. The energy density can now be written as

$$E_{surface} = \frac{3}{R} K_s. \tag{2.27}$$

#### Cylinderical particle

For cylindrical particles, the surface anisotropy will contain contributions from the top and bottom and from the rest of the tube. Looking at equation 2.24, a cylindrical particle has two different normal vectors, one for the top and bottom and one in the radial direction. For the top and bottom, equation 2.24 becomes

$$E_{surface,area} = K_s (\cos \theta)^2 = K_s \cos^2 \theta.$$
(2.28)

For the rest of the tube this becomes

$$E_{surface,area} = K_s \left(\cos^2 \phi \sin^2 \theta + \sin^2 \phi \sin^2 \theta\right)^2 = K_s \sin^2 \theta.$$
(2.29)

The total energy of the surface then becomes

$$\varepsilon_{surface} = 2\pi RhK_s \sin^2 \theta + 2\pi R^2 K_s \cos^2 \theta. \tag{2.30}$$

The energy density now becomes

$$E_{surface} = \frac{2}{R} K_s \sin^2 \theta - \frac{2}{h} K_s \sin^2 \theta + \frac{2}{h} K_s.$$

$$(2.31)$$

#### 2.4.3 Shape anisotropy

The demagnetization field is the magnetic field inside the particle, that is caused by the microscopic magnetic moments of the individual atoms [5]. Next to an atom with a magnetic moment, the demagnetization field is directed opposite to the magnetic moment. This makes it hard to add another atom with its magnetic moment parallel to the first one. Above the atom, the demagnetization field is directed parallel to the magnetic moment, which makes it easier to add another atom with its magnetic moment parallel to the first one. So, it is more difficult to align atoms with magnetic moments next to each other, than to align them above one another. This makes the magnetic moment dependent on the shape of a particle.

The energy needed to overcome the demagnetization field is called the demagnetization energy. For a particle with a given geometry, the direction in which the demagnetization energy has its minimum is the easy direction of magnetization.

#### Spherical particle

For spherical particles the demagnetization energy density can be described as

$$E_{shape} = \frac{2\pi}{9V} \mu_0 M_s^2 R^3, \tag{2.32}$$

where  $\mu_0$  represents the permeability of free space,  $M_s$  the saturation magnetization and R the radius of the particle. This energy is constant, since a spherical particle is symmetric. Therefore, there is no preferred direction for the magnetic moment for a spherical particle.

#### Cylindrical particle

The demagnetization energy density of a cylindrical particle is more complicated to calculate. A general description for the demagnetization energy is written as [15]

$$E_{shape} = \frac{\mu_0 M_s^2}{16\pi^3} \int d^3 \mathbf{k} \frac{|D(\mathbf{k})|^2}{k^2} (\hat{\mathbf{m}} \cdot \mathbf{k})^2, \qquad (2.33)$$

where D(k) represents the shape amplitude given by equation 2.15. This gives for the demagnetization energy of a cylinder

$$E_{shape} = \frac{\mu_0 M_s^2 R^2}{\pi} \int d^3 \mathbf{k} \frac{J_1 (k_\perp R)^2}{(k_\perp^2 + k_z^2) k_\perp^2 k_z^2} \sin^2(\frac{hk_z}{2}) (\mathbf{\hat{m}} \cdot \mathbf{k})^2$$
(2.34)

After some manipulation this becomes

$$E_{shape} = \frac{\mu_0 M_s^2 R^3}{6} \Big[ 4(3m_z^2 - 1) + 6\pi p m_z^2 - 3\pi \sqrt{1 + p^2} (3m_z^2 - 1)_2 F_1(-\frac{1}{2}, \frac{3}{2}; 2; \frac{1}{1 + p^2}) \Big],$$
(2.35)

where p represents the ratio between the height and the diameter of the cylinder and  ${}_2F_1(-\frac{1}{2},\frac{3}{2};2;\frac{1}{1+p^2})$  represents a hypergeometric function. In our case h >> R, which reduces the hypergeometric function to  ${}_2F_1(-\frac{1}{2},\frac{3}{2};2;\frac{1}{1+p^2}) \approx 1$ . With  $m_z = \cos\theta$ , the demagnetization energy density reduces to

$$E_{shape} = \frac{4\mu_0 M_s^2 R^3}{3V} - \frac{\mu_0 M_s^2 R^3}{6V} \Big[ 12 + 6\pi p - 9\pi \sqrt{1+p^2} \Big] \sin^2 \theta, \qquad (2.36)$$

#### 2.4.4 Direction of the magnetic moment

The total energy of the system can be determined by adding the contributions from the different anisotropy energies. For spherical particles the total anisotropy energy density can be described as

$$E_{spherical} = K_0 + K_1 (\sin^2 \phi \cos^2 \phi \sin^2 \theta + \cos^2 \theta) \sin^2 \theta + K_2 (\sin^2 \phi \cos^2 \phi \sin^2 \theta \cos^2 \theta) \sin^2 \theta + \frac{2\pi}{9} \mu_0 M_s^2 R^3 + \frac{3}{R} K_s.$$
(2.37)

whereas the total anisotropy energy density for cylindrical particles is described as

$$E_{cylinder} = K_0 + K_1 (\sin^2 \phi \cos^2 \phi \sin^2 \theta + \cos^2 \theta) \sin^2 \theta + K_2 (\sin^2 \phi \cos^2 \phi \sin^2 \theta \cos^2 \theta) \sin^2 \theta + \frac{4}{3V} \mu_0 M_s^2 R^3 - \frac{\mu_0 M_s^2 R^3}{6V} (12 + 6\pi p - 9\pi \sqrt{1 + p^2}) \sin^2 \theta - \frac{2}{R} K_s \sin^2 \theta - \frac{2}{h} K_s + \frac{2}{h} K_s \sin^2 \theta.$$
(2.38)

The particle is magnetized in the direction that requires the smallest amount of energy. The total energy densities for a spherical and a cylindrical particle are shown in figure 2.8. The minima in the plot correspond with the direction of the magnetic moment. For the spherical particle this is at angles  $\theta = 54.7^{\circ}$  and  $\phi = 54.7^{\circ}$ , which corresponds with the



Figure 2.8: Total energy density for both spherical and cylindrical particles of nickel as a function of the angles  $\theta$  and  $\phi$ . The minima of these plots represent the direction of the magnetic moment. Both spherical and cylindrical particles have a diameter of 100 nm, the cylindrical particle is 2  $\mu$ m long.

[111] direction of the lattice. The energy minima of a cylindrical particle are at  $\theta = 0$  and  $\theta = \pi$ , which corresponds with the long axis of the cylinder.

For a spherical particle the only anisotropy energy that varies in space is the magnetocrystalline energy, the surface and shape energy are constant. This means the magnetocrystalline anisotropy determines the direction of the magnetic moment. This is in accordance with an energy minimum at  $\theta = 54.7^{\circ}$  and  $\phi = 54.7^{\circ}$ .

For a cylindrical particle with diameter of 100 nm and a height of 2  $\mu$ m the shape anisotropy is the dominant energy, see figure 2.9. Reducing the diameter of the cylinder will increase the contribution of the surface anisotropy. At diameters of about 10.0 nm, the contribution from the surface and the shape will be in the same order of magnitude and therefore cancel each other out. This leads to a dominating role for the otherwise relatively small magnetocrystalline anisotropy. When the diameter decreases even more, the contribution from the surface anisotropy will dominate, which leads to the magnetic moment pointing in the radial direction, see figure 2.10.

## 2.5 Relaxation mechanisms

The response of the magnetization to a change in the magnetic field strength or direction is called magnetic relaxation [24]. Magnetic relaxation can be described by two processes. First, the orientation of the magnetization with respect to the crystal axis can be changed and second, the whole particle can rotate in order to align its magnetic moment with the external magnetic field. The first process is called Néel relaxation and the second is called Brownian relaxation [25]. The relaxation time indicates the time at which the magnetization signal is decayed with a factor 1/e, with *e* Euler's number.



Figure 2.9: Different anisotropy energy contributions for spherical and cylindrical particles of nickel as a function of angle  $\theta$  for  $\phi = 0$ . The sphere has a diameter of 30 nm and the diameter of the cylinder is 100 nm and the height is 2  $\mu$ m.



Figure 2.10: Energy density for cylindrical particles of nickel as a function of the angles  $\theta$  and  $\phi$ . The magnetic moment is in the direction of the energy minimum. As the size of the particle changes, the contributions from the different anisotropy energies change and the location of the energy minimum changes. The diameters are 8.0 nm and 10.0 nm respectively for figures (a) and (b). The height of the cylinder is constant at 2  $\mu$ m.

#### 2.5.1 Néel relaxation

As described in section 2.2, the magnetization direction of a single domain particle can switch between the two equilibrium positions when the energy barrier is overcome. The mean time between two flips is called the Néel relaxation time,  $\tau_N$ , and is described by

$$\tau_N = \tau_0 e^{\frac{\Delta \varepsilon}{k_B T}} \tag{2.39}$$

where  $\tau_0$  represents a material constant, usually with a value between  $10^{-9}$  and  $10^{-11}$  s,  $k_B$  the Boltzmann constant, T the temperature and the energy barrier  $\Delta \varepsilon$  depends on the effective anisotropy constant  $K_{eff}$  and the volume of the particle V. It is very hard to accurately calculate the Néel relaxation time, because there are uncertainties in  $\tau_0$  and  $K_{eff}$  [26]. Small variations in the effective anisotropy constants have major influence on the calculated Néel relaxation time.

#### **Energy** barrier

The magnetization direction can change from one crystal axis to another when an energy barrier is overcome. The energy needed to switch the magnetization depends on the material, the size and the shape of the particle. For example, the energy increases when the particle size increases. Also, the symmetry of the crystal is easily broken at the surface of the particle, which changes the energy [27].

The height of the energy barrier can be evaluated by computing the difference between the energy at the saddle point and at the minimum of the effective energy of the system [19, 28, 29]. Given the complex character of the effective energy with three competing anisotropies, multiple energy barriers can exist. The relevant energy barrier for switching corresponds to the lowest energy path between global minima, see figure 2.8.

#### Spherical particle

In the description of the energy density for spherical particles the magnetocrystalline energy is the only contribution that depends on the orientation of the particle. The energy density of these spherical particles is described in equation 2.37. The minimum of this energy density is at  $(\theta = n\pi \pm 0.30\pi; \phi = \pi/4 + n\frac{\pi}{2})$ . The energy density is then

$$E_{sphere}(\theta = 0.30\pi; \phi = \pi/4) = K_0 + \frac{1}{3}K_1 + \frac{1}{27}K_2$$
(2.40)

There are two saddle points with a comparable energy, at  $(\theta = n\pi \pm 0.30\pi; \phi = \pi/2 + n\frac{\pi}{2})$  and  $(\theta = \pi/2 + n\pi; \phi = \pi/4 + n\frac{\pi}{2})$ . The latter saddle point has a slightly lower energy.

$$E_{sphere}(\theta = \pi/2; \phi = \pi/4) = K_0 + \frac{1}{4}K_1$$
(2.41)

For particles with negative magnetocrystalline anisotropy constants, the energy barrier that has to be overcome in order to switch the magnetization direction is

$$K_{eff,sphere} = E_{sphere}(\theta = \pi/2; \phi = \pi/4) - E_{sphere}(\theta = 0.30\pi; \phi = \pi/4)$$
  
=  $-\frac{1}{12}K_1 - \frac{1}{27}K_2.$  (2.42)

The energy needed to overcome this barrier is

$$\Delta \varepsilon_{sphere} = K_{eff,sphere} V. \tag{2.43}$$

#### Cylindrical particle

The energy density of a cylindrical particle can be described by the contributions from the different anisotropies, as was given in equation 2.38. For particles with radii larger than the minimum for magnetization along the direction of the cylinder, as mentioned in section 2.4.4, the minima for this energy density are at  $\theta = 0 + n\pi$  for all  $\phi$ . The energy density is then

$$E_{cylinder}(\theta = 0) = K_0 + \frac{4}{3V}\mu_0 M_s^2 R^3 - \frac{2}{h}K_s.$$
(2.44)

The saddle points are at  $\theta = \pi/2 + n\pi$  with  $\phi = \pi/4 + n\pi$ . The energy densities of the saddle points are then

$$E_{cylinder}(\theta = \pi/2; \phi = \pi/4) = K_0 + \frac{1}{4}K_1 + \frac{4}{3V}\mu_0 M_s^2 R^3 - \frac{\mu_0 M_s^2 R^3}{6V}(12 + 6\pi p - 9\pi\sqrt{1+p^2}) - \frac{2}{R}K_s.$$
(2.45)

The energy barrier can now be described by the effective anisotropy constant as

$$K_{eff,cylinder} = E_{cylinder}(\theta = \pi/2; \phi = \pi/4) - E_{cylinder}(\theta = 0)$$
  
=  $\frac{1}{4}K_1 - \frac{\mu_0 M_s^2 R^3}{6V}(12 + 6\pi p - 9\pi\sqrt{1 + p^2}) - \frac{2}{R}K_s + \frac{2}{h}K_s.$  (2.46)

The energy needed to overcome this barrier is

$$\Delta \varepsilon_{cylinder} = K_{eff,cylinder} V. \tag{2.47}$$

Figure 2.11 shows the Néel relaxation time of a particle with constant volume as a function of the aspect ratio of the cylinder. The Néel relaxation time decreases exponentially with increasing aspect ratio, due to the increase of surface anisotropy energy.

#### 2.5.2 Brownian relaxation

The Brownian relaxation time is the mean time between two flips of the entire particle and depends on the size and shape of the particle. For spherical particles the Brownian relaxation time is described by

$$\tau_{B,sp} = \frac{3\tilde{V}\eta}{k_B T},\tag{2.48}$$

where  $\tilde{V}$  is the hydrodynamic volume of the particle, i.e. the volume including the surfactant layer,  $\eta$  is the viscosity of the carrier liquid,  $k_B$  is the Boltzmann constant and T is the temperature.

For cylindrical particles Tirado et al [30, 31] suggested the following approximation

$$\tau_{B,cy} = \frac{\pi \eta \tilde{h}^3}{6k_B T} \Big( \ln \tilde{p} + \delta_\perp \Big)^{-1}, \tag{2.49}$$

where  $\tilde{p}$  represents the ratio between the hydrodynamic height and diameter of the cylinder  $\tilde{p} = \tilde{h}/2\tilde{R}$  and  $\delta_{\perp}$  is a correction for the end-effect of the cylinder. The end-effect correction also depends on the ratio  $\tilde{p}$  and is expressed in a power expansion in  $\tilde{p}^{-1}$  [32]:

$$\delta_{\perp}(\tilde{p}) = a_0(\tilde{p}) + a_1(\tilde{p})\tilde{p}^{-1} + a_2(\tilde{p})\tilde{p}^{-2}.$$
(2.50)



Figure 2.11: Relaxation times of a cylindrical particle as a function of the aspect ratio. The volume is kept constant at  $4.2 \cdot 10^{-24}$  m<sup>3</sup>. The Néel relaxation time exponentially decreases with increasing aspect ratio, while the Brownian relaxation time increases slightly with increasing aspect ratio.

The coefficients  $a_i$  depend on the ratio  $\tilde{p}$  and there has been some discussion on their exact values. Broersma [33] did some experiments and the numerical values of Tirado [31] had the best match for ratios between  $3 < \tilde{p} < 30$ . Equation 2.49 now becomes

$$\tau_{B,cy} = \frac{\pi \eta \tilde{h}^3}{6k_B T} \Big( \ln \tilde{p} - 0.662 + 0.917 \tilde{p}^{-1} - 0.050 \tilde{p}^{-2} \Big)^{-1}.$$
(2.51)

Figure 2.11 shows the Brownian relaxation time of a particle with constant volume as a function of the aspect ratio of the cylinder. The Brownian relaxation time increases with increasing aspect ratio due to the increased length of the particle.

#### 2.5.3 Effective relaxation time

Which relaxation mechanism dominates the magnetic behaviour of the colloidal suspension depends strongly on the size of the particles. For small particles, this is Néel relaxation and for larger particles this is Brownian relaxation, see figure 2.12. In the transition regime between Néel and Brownian relaxation both mechanisms will be present. The effective relaxation time can then be described as

$$\tau_{eff} = \left(\frac{1}{\tau_N} + \frac{1}{\tau_B}\right)^{-1}.$$
(2.52)

## 2.6 Superparamagnetic limit

Nanoparticles are superparamagnetic when their size is sufficiently small that remanence and coercivity go to zero i.e. there is no hysteresis in superparamagnetic particles. The superparamagnetic limit indicates the diameter at which the particle loses its hysteresis and becomes superparamagnetic and is described by  $d_s$ , see also figure 2.3.



Figure 2.12: Relaxation times of a spherical particle of nickel in water as a function of its radius. The particle has no non-magnetic shell, so the hydrodynamic radius is equal to the radius of the magnetic core. For small particles the Néel relaxation dominates, while in larger particles the Brownian relaxation time determines the behaviour of the particles.

Superparamagnetic particles behave according to the Néel equation described in equation 2.39. The threshold for the superparamagnetic limit can be determined by substituting a critical relaxation time,  $\tau_s$ , in this equation. For laboratory experiments the critical relaxation time can be taken as  $\tau_s = 100$  s [34]. The superparamagnetic limit for spherical particles is now described by [35]

$$d_s(T) = \left(\frac{6}{\pi}k_B T \left(\frac{12}{K_1} + \frac{27}{K_2}\right) \ln(\tau_s/\tau_0)\right)^{1/3}$$
(2.53)

where  $K_1$  and  $K_2$  represent magnetocrystalline anisotropy constants. Particles with a diameter smaller than  $d_s$  exhibit superparamagnetic behaviour.

Spherical magnetite particles are superparamagnetic below a diameter of 55 nm. For nickel particles this is below 71 nm. This is in agreement with values found in literature [6, 35, 36, 37].

Determining the superparamagnetic limit for cylindrical particles is a little more complicated, since now the effective anisotropy constant depends on the size of the particle as well. Next to that, the volume of the particle does not depend solely on the diameter, but also on its height. The superparamagnetic limit is given by,

$$k_B T \ln(\frac{\tau_s}{\tau_0}) = \left(\frac{1}{4} K 1 - \frac{\mu_0 M_s^2}{12\pi p} \left(12 + 6\pi p - \sqrt{1 - p^2}\right) - \frac{2K_s}{(V/2\pi p)^{1/3}} + \frac{2K_s}{2p(V/2\pi p)^{1/3}}\right) V. \quad (2.54)$$

Figure 2.13 shows the superparamagnetic limit for cylindrical nickel particles as a function of their volume and aspect ratio. It can be seen that increasing the aspect ratio allows the use of particles with larger volumes. This was also found by Sun et al [38].

From the model it follows that the volume of a cylindrical particle with low aspect ratios should be smaller than the volume of a spherical particle. This is very illogical, since the same model also states that the higher aspect ratios have lower energy barriers and are therefore allowed to have larger volumes. In the determination of the shape and surface anisotropy for the cylindrical particles some approximations and simplifications



Figure 2.13: The superparamagnetic limit for cylindrical nickel particles as a function of volume and aspect ratio. Particles with volumes smaller than the blue line exhibit superparamagnetic behaviour. Increase of the aspect ratio allows the use of particles with larger volumes.

are made. Probably, these approximations and simplifications have caused inaccuracies in the energy barrier of the cylindrical particle and therewith in the superparamagnetic limit.

# Chapter 3

# Relaxation experiments with a SQUID magnetometer

## 3.1 Introduction

The relaxation behaviour of magnetic nanoparticles is characterized by a time constant, which is influenced by both the environment of the particle and the properties of the particle itself. Investigating the relaxation time can give information about for example the size, the shape and the material of the particles and the carrier medium.

A physical system shows relaxation behaviour when returning or adjusting to equilibrium after a change of the environment. There are two ways to study the relaxation behaviour of magnetic nanoparticles. One is to change the external magnetic field and look at how the system adjusts to the new situation. Another way is to induce a temporary change of the external magnetic field and see how the system returns to the original situation. In the following experiment the latter is done. Measuring after the external magnetic field is removed cancels the effect of the magnetic field changing over time, for example by coil heating. Another advantage is that sensitive measurement devices cannot be influenced by the magnetic field.

In this research, the magnetic moment of samples of superparamagnetic nanoparticles is measured over time. These nanoparticles are dispersed in a carrier liquid, so both Néel and Brownian relaxation processes can occur. The environment is disrupted by the application of a DC magnetic field. This magnetic field aligns the magnetic moments of the individual nanoparticles. After the magnetic field is switched off, the nanoparticles will relax to their original random orientation. This relaxation process is monitored by our setup.

The setup is based on a superconducting quantum interference device (SQUID). This is a very sensitive device that measures magnetic field gradients. With noise levels up to three orders of magnitude lower than fluxgate magnetometers, SQUIDs are considered the most promising device for applications in which high sensitivity is required [39].

After the magnetic pulse is given, there is no limitation on the duration of the measurement. This makes the setup suited for measurements of very long relaxation times.

# 3.2 Model describing the relaxation behaviour of superparamagnetic particles

The relaxation experiment starts with the application of a magnetic field. This magnetic field brings extra energy to the system and therefore changes the energy barrier the particle has to overcome in order to switch the direction of its magnetic moment. This was illustrated earlier in figure 2.2. The energy due to the magnetic field is given by [8]

$$\varepsilon_{magneticfield} = -\mu_0 V(\mathbf{M_s} \cdot \mathbf{H}), \tag{3.1}$$

where H represents the applied magnetic field. The total energy of the system can now be described as

$$\varepsilon = K_{eff}V\sin^2\theta - \mu_0 V(\mathbf{M_s} \cdot \mathbf{H}) = K_{eff}V\sin^2\theta - \mu_0 M_s V H (\cos\theta\cos\theta_H + \sin\theta\sin\theta_H\cos\phi - \phi_H),$$
(3.2)

where  $\theta_H$  and  $\phi_H$  represent the angles between the easy axis and the applied magnetic field [40].

For small magnetic fields, the contribution from the magnetic field is only a small perturbation on the anisotropy energy. The minimum of the energy occurs close to the easy axis that is located closest to the magnetic field direction.

The particles will align their magnetic moments in this energy minimum. The state of alignment of the particle over time can be described as  $1 - e^{-\frac{t_{mag}}{\tau}}$ , where  $t_{mag}$  represents the duration of the magnetic field pulse and  $\tau$  the relaxation time.

The magnetic moment of an ensemble of superparamagnetic particles was already described in section 2.3.3. Under influence of the magnetic field it is described as

$$M(t_{mag}, H) = M_s N_p \int_0^\infty f(d_h, \mu_h, \sigma_h) \int_0^\infty f(d_c, \mu_c, \sigma_c) V(d_c) \frac{\chi_{in}}{1 + N\chi_{in}} H$$
$$\left[1 - e^{-\frac{t_{mag}}{\tau_{eff}(K, d_c, d_h, H)}}\right] dd_c dd_h,$$
(3.3)

and for the spherical particles as

$$M(t_{mag}, H) = M_s N_p \int_0^\infty f(d_h, \mu_h, \sigma_h) \int_0^\infty f(d_c, \mu_c, \sigma_c) V(d_c) L(d_c, H) \\ \left[ 1 - e^{-\frac{t_{mag}}{\tau_{eff}(K, d_c, d_h, H)}} \right] dd_c dd_h.$$
(3.4)

These equations describe the situation of the magnetic moment when the sample is magnetized. This is the actual start position of the measurements. Since the particles are superparamagnetic, they will relax from the aligned state into a random oriented state under influence of thermal energy, as explained in chapter 2. The magnetic field is turned off, so it does not influence the energy barriers anymore. The nanoparticles can show Brownian and/or Néel relaxation depending on their size. This relaxation process is described as

$$M(t, t_{mag}, H) = M_s N_p \int_0^\infty f(d_h, \mu_h, \sigma_h) \int_0^\infty f(d_c, \mu_c, \sigma_c) V(d_c) \frac{\chi_{in}}{1 + N\chi_{in}} H \\ \left[ 1 - e^{-\frac{t_{mag}}{\tau_{eff}(K, d_c, d_h, H)}} \right] e^{-\frac{t}{\tau_{eff}(K, d_c, d_h)}} dd_c dd_h.$$
(3.5)



Figure 3.1: Schematic drawing of the setup. The sample is magnetized with a Helmholtz coil. After the magnetic field is switched off, the detection coil will detect the magnetic moment of the sample. The detection coil is coupled to the SQUID, which is able to accurately quantify the change of the magnetic moment. The data acquisition card (DAQ) is used to transport the SQUID data into the computer. The DAQ is also used to control the SQUID electronics and the Helmholtz coil.

or more accurately for the spherical particles as

$$M(t, t_{mag}, H) = M_s N_p \int_0^\infty f(d_h, \mu_h, \sigma_h) \int_0^\infty f(d_c, \mu_c, \sigma_c) V(d_c) L(d_c, H) \\ \left[1 - e^{-\frac{t_{mag}}{\tau_{eff}(K, d_c, d_h, H)}}\right] e^{-\frac{t}{\tau_{eff}(K, d_c, d_h)}} dd_c dd_h.$$
(3.6)

## 3.3 Method

In this experiment the sample material is magnetized by a DC magnetic field for a certain amount of time. The magnetic field aligns the superparamagnetic particles in the sample. Then the magnetic field is turned off and the superparamagnetic particles will relax under the influence of thermal energy. The magnetization of the particles will be measured after the magnetic field is switched off, so the relaxation behaviour is visible.

The setup is shown in figure 3.1. The sample is magnetized by an external applied magnetic field for a time,  $t_{mag}$ . The magnetic field is created by means of a Helmholtz coil. The Helmholtz coil produces a homogeneous magnetic field in the centre of the coil. The size of the magnetic moment of the sample depends on the strength and the duration of the magnetic field. A stronger magnetic field will lower the energy barrier towards the easy magnetization axis, which results in a higher net magnetic moment. A longer magnetic field pulse gives the particles more opportunity to switch their magnetic moment. Increasing the pulse duration is only effective at pulse lengths in the order of the relaxation time or shorter.



Figure 3.2: The input circuit of the SQUID. The detection coil measures the flux coming from the sample. This induces a current in the input circuit. This current induces a magnetic flux in the second coil in the input circuit, which is coupled to the SQUID. The detection coil is much larger than the SQUID and is therefore able to detect more flux.

The magnetization as a function of the time is measured with the use of a superconducting quantum interference device (SQUID). This is a very sensitive magnetometer that is used to measure extremely small magnetic field gradients. The actual SQUID is a superconducting loop of wire with two Josephson junctions. The SQUID needs to be cooled with liquid helium and is therefore placed in a cryostat. The loop of the SQUID should be kept small in order to keep the inductance as low as possible and therewith the SQUID sensitivity high. Therefore, the SQUID loop is not used to directly sense the field. This is done by a detection coil that is coupled to the SQUID via the input circuit, see figure 3.2. The detection coil is an axial gradiometer and it is placed at the bottom of the cryostat. The sample is placed outside the cryostat against its underside, so it is as close as possible to the detection coil. The sample and the detection coil are located in the middle of the Helmholtz coil, so the field they experience is homogeneous. The SQUID is connected to the SQUID electronics, which are located outside the cryostat. The SQUID electronics are connected to the computer using a data acquisition card. Labview is used to collect the data from the data acquisition card. The SQUID and the magnetic field are also controlled by the combination of Labview and the data acquisition card.

The setup is located in a magnetically shielded room. The magnetic signals obtained in this measurement are very small and their detection is easily disturbed by magnetic noise from the environment. The magnetically shielded room should discard this noise.

## **3.4** Hardware specifications

#### 3.4.1 Helmholtz coil

A Helmholtz coil consists of two identical circular magnetic coils. The distance between the two coils is equal to their radius. This geometry is chosen in order to produce a homogenous magnetic field between the two coils. The magnetic fields produced by the individual coils can be determined by the Biot-Savart law and added in order to get the magnetic field of the Helmholtz coil. The result is shown in figure 3.3.


Figure 3.3: The magnetic field inside the Helmholtz coil as a function of the height. The green stars indicate the location of the windings of the detection coil. The red plus sign indicates the location of the sample.

The Helmholtz coil has a radius of 200 mm and both the upper and the lower coil have 150 windings. The Helmholtz coil is tested to give a magnetic field of 674  $\mu T/A$ . The current can be adjusted to change the strength of the magnetic field.

### 3.4.2 Gradiometer

The detection coil used in this research is an axial gradiometer. An axial gradiometer consists of two equal magnetometers placed in series and separated by the baseline. The coils are wound in opposite direction, so the induced currents cancel each other and only the gradient of the magnetic field will contribute to the current [41]. The gradiometer used in this research consists of two times three windings, see also figure 3.4. The diameter of the windings is 20 mm and the baseline is 40 mm. The lower windings are separated by a distance of 0.5 mm, while the upper windings are separated by 6 mm.

### 3.4.3 SQUID

In this research a dcSQUID with superconducting switch from the company Supracon (Jena, Germany) was used. The SQUID was delivered in a compact package combining SQUID sensor model 'CE2blue' and superconducting switch model 'SW1'. The integrated



Figure 3.4: Gradiometer used as detection coil. The gradiometer has two times three windings. The windings of the upper coil and have a bigger spacing than the windings of the lower coil.

superconducting switch makes it possible to turn off the SQUID when the large external magnetic field is applied. This protects the SQUID from potential large magnetic fields. The electronic scheme is depicted in figure 3.5.

# 3.5 Measurement procedure for the relaxation measurements

The particles used in this research exhibit sedimentation i.e. they sink under influence of gravity to the bottom of the sample tube, where a thick layer is formed. This significantly changes the relaxation behaviour, since the effective volume of the particles has increased and the ability to rotate is lost. Therefore, this sediment should be dispersed again. For samples dispersed in water this can be done by placing the sample in an ultrasonic bath for about 5 minutes. For particles dispersed in glycerol it is more effective to place the sample in the microwave for a 10-20 seconds. This has to be done shortly before the measurement starts, so there is not enough time for the particles to sediment again. For water based samples this process is repeated before every single measurement with a decreased sonication time of 20 seconds.

When the sample is dispersed the actual measurement can start. The sequence starts with the superconducting switch turning off the SQUID, after which the magnetic field is switched on. Before the magnetic field is switched off again, the SQUID reset is enabled. The magnetic field is switched off, after which the SQUID is switched on and finally the SQUID reset is disabled. This sequence is shown in figure 3.6.

The SQUID needs to be reset to allow transient fields, induced in conductive elements of the measurement system by the magnetic field, to decay sufficiently to enable operation of the SQUID in its most sensitive range [42]. The reset of the SQUID causes a 'dead time' of 200 ms at the start of the measurement. Samples with small relaxation times that fall within this 'dead time' can therefore not be measured with this setup.

### 3.5.1 Pulse length

The duration of the different components in the sequence can be varied. Changing the duration of the magnetic pulse influences the degree of alignment that is reached at the start of the measurement. A maximal alignment of the particles is preferred, since this



Figure 3.5: Scheme of the chip at which the SQUID is provided by the manufacturer. The open dots indicate connecting points on the chip.



Figure 3.6: Relaxation behaviour of the sample (above) and the sequence used (below). The dead time between the end of the magnetic pulse and the start of the measurement is indicated by the red lines in the upper graph.

will result in the highest magnetic moment. However, applying a magnetic field for a long period of time increases the chance of particles clustering, as will be explained further in chapter 6. Next to that, the Helmholtz coil will warm up, which causes deviations from the applied magnetic field. It is therefore desirable to apply the magnetic field no longer than necessary

For particles relaxing by Néel behaviour, the duration of the magnetic pulse needed for maximal alignment can easily be calculated by the method explained in section 3.2.

For particles showing Brownian behaviour it is much harder to calculate the exact duration of the pulse for maximal alignment, since it is not exactly known how the Brownian relaxation time depends on a magnetic field. However, the particles should align faster than they would relax, since the magnetic field brings extra energy into the system. Maintaining the magnetic pulse for 5 relaxation times without magnetic field, would yield a magnetization of at least 99% of its magnetization at infinite magnetic pulse duration. However, the particles have a log-normal size distribution, which indicates that there are large particles present, which give a relatively large signal and have relatively long relaxation times. So in order to compensate for this, a magnetic pulse is applied to the sample for 10 times the relaxation time of the average particle size. The resulting start position of the magnetization for the relaxation measurement is now approximately equal to the value of a pulse of infinite duration.

### 3.5.2 Reference measurements

Next to the measurements with samples containing superparamagnetic particles, measurements without samples are done. These measurements will give information about the background effects. The magnetically shielded room should eliminate all sources of noise from the environment. However, the magnetically shielded room is not perfect and there might be small magnetic noise sources present in the shielded room. Also, the setup can magnetise itself, therewith influencing the measurement. Therefore, the magnetic relaxation of the background is measured. This is done multiple times, after which the average of the reference measurements is taken. This averaged reference signal is subtracted from the actual measurements containing a sample. This procedure ensures us the measured signal originates from the sample. A typical reference measurement is shown in figure 3.7

# 3.6 Model describing the detection of the magnetic moment by the SQUID setup

The behaviour of the magnetic moment of an ensemble of particles was described in section 3.2. The current section takes the magnetic moment as an input value and simulates the effect of the setup described in section 3.3 on this signal. The actual output of the setup is simulated, so the simulations can easily be compared to the measurements.

### **3.6.1** Detection of magnetic moment

The magnetic moment of the sample creates flux lines which induce a current in the detection coil. The amount of flux that is detected by the detection coil depends i.a. on the magnetic moment of the sample and on the distance between the sample and the detection coil and is described in this section.



Figure 3.7: Measurement of the relaxation behaviour of the background. This reference signal is subtracted from the actual measurements.



Figure 3.8: Setup of the sample with the detection coil. The sample is represented as a magnetic dipole.

The sample is described as a loop of wire with radius a, current I and magnetic moment m. These are related to each other by  $\mathbf{m} = I\mathbf{S}$ , with S the area enclosed by the loop [43]. The vector potential of this system in point p in space can be calculated by

$$\mathbf{A}(\mathbf{r}) = \frac{\mu_0}{4\pi} \int \frac{\mathbf{I}}{s} dl = \frac{\mu_0}{4\pi} I \oint \frac{1}{s} d\mathbf{l}, \tag{3.7}$$

where s is the distance between the edge of the sample and point p, described by

$$\frac{1}{s} = \frac{1}{\sqrt{r^2 + a^2 - 2ar\cos\theta'}} = \frac{1}{r} \sum_{n=0}^{\infty} \left(\frac{a}{r}\right)^n P_n(\cos(\theta'))$$
(3.8)

where  $P_n(x)$  represents the Legendre polynomial and  $r = \sqrt{d^2 + b^2}$ , with *b* the radius of the detection coil and *d* the distance between the sample and the detection coil, see also figure 3.8. This turns the vector potential into a multipole expansion. When the sample is very small compared to the detection coil, the vector potential can be approximated by only the contribution of the dipole term. However, in our case the radius of the sample is in the same order of magnitude as the detection coil. Therefore, more terms of the expansion should be considered. These terms are elaborated in appendix B. The magnetic vector potential is then

$$\mathbf{A}(\mathbf{r}) = \frac{\mu_0 I}{32r^5} \left(1 - \sin 2\phi\right) \left(3a^3b^2 - 30\frac{a^5b^2}{r^2} + 35\frac{3a^5b^4}{64r^4} \left(1 - \sin 2\phi\right)\right) \hat{\theta} + \frac{\mu_0}{4\pi} \left(\frac{1}{r^2} - \frac{3a^2}{2r^4} + \frac{15a^4}{8r^6}\right) \mathbf{m} \times \hat{\mathbf{r}}$$
(3.9)

The flux through the detection coil can be determined using this vector potential,

$$\Phi = \int \mathbf{A} \cdot d\mathbf{l},\tag{3.10}$$

which for the circular loop of the detection coil can be written as

$$\Phi = \int_0^{2\pi} A_\theta b d\phi. \tag{3.11}$$

The flux through the detection coil then becomes

$$\Phi = \mu_0 b^2 m_z \left(\frac{1}{2r^3} - \frac{3a^2}{4r^5} + \frac{15a^4}{16r^7}\right) + \frac{3\pi\mu_0 I a^3 b^3}{16r^5} \left(1 - \frac{5a^2}{2r^2} + \frac{105a^2 b^2}{128r^4}\right).$$
(3.12)

The detection coil used in the experiment is a gradiometer with two times three windings, see also figure 3.4. The sample is located beneath the gradiometer, so all windings have a different distance to the sample and therefore experience a different flux. This is illustrated in figure 3.9

### 3.6.2 Flux transmission

The magnetic relaxation process causes a change in the magnetic moment of the sample over time and therefore also a change in the amount of flux detected by the detection coil. According to Lenz's law a changing magnetic field induces an electromagnetic force which gives rise to a current in the detection coil with its magnetic field opposite to the original



Figure 3.9: Flux through a loop as a function of the distance from the source. The source is 100ng of nickel particles. The green stars indicate the location of the windings of the detection coil.

change in magnetic flux. The detection coil is part of the input circuit shown in figure 3.2. The induced current in the input circuit can be described as

$$I(t) = \frac{\Phi_p(t)}{L_{total}} \tag{3.13}$$

where  $\Phi_p$  represents the flux in the detection coil, I the current induced in the input circuit and  $L_{total}$  the total self-inductance of the loop, given by  $L_{total} = L_{grad} + L_{in} + L_{shunt} + L_{wire}$ . The individual self-inductances depend on the geometry of the coils. The flux in the detection coil can be described as

$$\Phi_p(t) = \Phi_1(t) + \Phi_2(t) + \Phi_3(t) - \Phi_4(t) - \Phi_5(t) - \Phi_6(t), \qquad (3.14)$$

where  $\Phi_i$  represents the flux through the  $i^{th}$  turn of the gradiometer. The input coil induces a magnetic field which gives a flux through the SQUID. This flux can be described by

$$\Phi_{SQUID}(t) = I(t)M_{SQUID,in},\tag{3.15}$$

where  $M_{SQUID,in}$  represents the mutual inductance between the SQUID and the input coil.

So the flux in the SQUID is related to the flux in the detection coil by

$$\Phi_{SQUID} = \frac{M_{in}}{L_{total}} \Phi_p = 0.00623 \Phi_p. \tag{3.16}$$

The flux-to-voltage responsivity of the SQUID was measured to be 1.6 V/ $\Phi_0$ . The final output voltage of the SQUID is then given by

$$V_{SQUID} = 1.6 \frac{\Phi_{SQUID}}{\Phi_0}.$$
(3.17)

### 3.7 Verifications, specifications and limitations

### 3.7.1 Calibration of the setup

The SQUID setup is calibrated by measuring the SQUID voltage of a test coil at different distances from the detection coil. The setup shown in figure 3.1 is used, although the sample is replaced by a single loop of wire carrying a sinusoidal current, I. A resistance of  $1k\Omega$  is placed parallel to the loop. The magnetic moment can be described by

$$\mathbf{m} = I\mathbf{S},\tag{3.18}$$

where S is the area of the loop. The flux through the detection coil can be determined as described in section 3.6.1. The resultant output voltage of the SQUID can be determined as described in section 3.6.2. Figure 3.10 shows a comparison between the simulation and the measurements. The distance between the underside of the cryostat and the detection coil is not exactly known. It is expected to be approximately 10 mm. However, this length does not make a fit with the measurements, see figure 3.10a. For the simulation of figure 3.10b it is taken as 22.5 mm. This is a little high, but it could still be possible. Another unknown is the exact value of the self-inductance of the shunt coil that is placed in the input loop in the electronics. This could also cause a deviation of the simulation.



Figure 3.10: The green and red stars indicate the measured SQUID voltage at different distances from the detection coil. The blue line represents the simulation of the SQUID output voltage as a function of distance. The distance between the underside of the cryostat and the detection coil is taken as 10 mm in figure (a) and 22.5 mm in figure (b).

### 3.7.2 Noise levels

The noise of the system can be determined from the power spectral density of the measured voltage noise

$$S_{\Phi} = \frac{S_V}{V_{\Phi}^2},\tag{3.19}$$

where  $S_{\Phi}$  is the noise of the SQUID system,  $S_V$  is the power spectral density of the voltage noise and  $V_{\Phi}$  is the flux-to-voltage responsivity given by  $V_{\Phi} = \partial V / \partial \Phi_0$ .

The voltage noise was obtained by measuring the SQUID output when no sample was present and no magnetic pulse was applied. The power spectral density was computed from this signal, see figure 3.11. The flux-to-voltage responsivity was measured to be 1.6 V/ $\Phi_0$  for this SQUID system. The corresponding noise of the system is  $34 \ \mu \Phi_0 / \sqrt{Hz}$ . This is about ten times as high as the SQUID noise given in the documentation of the SQUID, which is  $3 \ \mu \Phi_0 / \sqrt{Hz}$ . However, other sources like the cryostat also contribute to the noise in the system.

The signal to noise ratio can be determined by

$$SNR = \frac{P_{signal}}{P_{noise}},\tag{3.20}$$

where  $P_{signal}$  represents the power of the signal and  $P_{noise}$  the power of the noise. The signal to noise ratio depends on the sample. Here, the signal to noise ratio is calculated for a simulation of 16 ng nickel particles dispersed in glycerol. The power depends strongly on the time interval taken, since the signal shows an exponential decay. The power is calculated in the time interval 0.2-2 s, which starts at the end of the 'dead time' and lasts until most of the signal has decayed. The signal to noise ratio is then 104.



Figure 3.11: Frequency spectra of the noise of the SQUID system. The measurement is performed three times. The resulting noise of the system is  $34 \ \mu \Phi_0 / \sqrt{Hz}$ .

### 3.7.3 Flux jumps

Sometimes, large steps arise in the measurements, see figure 3.12. These steps are caused by flux jumps in the SQUID. The SQUID is actually a single loop of wire that only allows an integer number of flux quanta through its loop [44]. A non-integer number of flux quanta is compensated by extra current through the loop. This induced current is periodic with the number of flux quanta. The number of flux through the SQUID loop is 'locked' by a feedback coil. This coil applies extra flux to the SQUID loop to compensate for a changing external flux. This way the SQUID loop always experiences the same amount of flux. The current in the feedback coil is then a measure of the change in the external magnetic field. Sometimes, the electronics of the feedback coil cannot keep up with a rapidly changing external magnetic field. The amount of flux locked in the SQUID loop then changes with an integer amount of flux quanta. This is called a flux jump.

Some flux jumps are so severe that they drive the SQUID system to its limit. The SQUID system is then unable to record magnetic field changes until it is reset. This is seen at the second flux jump in figure 3.12. The output voltage jumps to -10 V, which is the limit of the SQUID system. Further changes in the magnetic field are not recorded anymore. Sometimes the cause of the flux jump was easily traced to noise sources like automatic awnings or amplifiers switching on and off. Other times the cause of flux jumps was unknown.

### 3.7.4 Anisotropy field

For small deviations of the magnetic moment away from the easy axis, the crystal anisotropy acts like a magnetic field trying to keep the magnetic moment in the direction of the easy axis. This magnetic field is also called anisotropy field and it is denoted as  $H_K$  [8]. For applied magnetic fields larger than the anisotropy field the easy axis will disappear and the magnetic moment will be in the direction of the applied magnetic field.

The model described in section 3.2 assumes the easy axis determines the magnetization direction and the applied magnetic field is only a small perturbation on the anisotropy energy. Therefore, the model is only valid for situations in which the condition  $H \ll H_K$ 



Figure 3.12: Flux jumps during measurements with the SQUID system. The first flux jump is relatively small and can be corrected for in software. The second flux jump is so severe that it drives the SQUID to its limit. The SQUID does not record any changes in magnetic field anymore and needs to be reset.

is satisfied. Under this condition, the direction of the magnetic moment is located in the easy axis that is closest to the direction of the magnetic field.

The anisotropy field of a spherical particle with easy axis in the < 111 > direction is described as [8]

$$H_K = \frac{-4(3K_1 + K_2)}{9\mu_0 M_s}.$$
(3.21)

The anisotropy field of a cylindrical particle with easy axis in the longitudinal direction is described as

$$H_K = \frac{2K_1}{\mu_0 M_s} - \frac{M_s R^3}{3V} \left(12 + 6\pi p - 9\pi \sqrt{1+p^2}\right) - \frac{4K_s}{\mu_0 M_s R} + \frac{rK_s}{\mu_0 M_s h}.$$
(3.22)

# Chapter 4

# Susceptibility experiments

## 4.1 Introduction

In the previous chapter the relaxation process of superparamagnetic particles returning to a random orientation after alignment due to a magnetic field was studied. In this chapter an experiment is described in which the relaxation process of alignment to the magnetic field is studied.

In the following experiment a superparamagnetic sample is exposed to an AC magnetic field. Since the magnetic field continuously changes direction, the superparamagnetic sample has limited time to align to the magnetic field. Depending on the frequency at which the magnetic field changes, the superparamagnetic particles are either able to adjust in the given time or not. The degree of magnetization as a result of an applied magnetic field is called susceptibility and that quantity is measured in this experiment. Making a frequency sweep, there is a transition point above which the particles cannot keep up anymore with the varying magnetic field. The susceptibility reduces from a finite value at low frequencies to zero at high frequencies. The frequency at which this transition occurs is called the characteristic frequency and it corresponds to the relaxation time.

In this setup the changing magnetic moment of the superparamagnetic sample is measured with a differential transformer. These coils are not superconducting, so in contrast to the SQUID setup no cryogenic infrastructure is needed here. However, the coils are less sensitive than the SQUID, so more sample material in needed.

In contrast to the SQUID setup, this setup does not have a 'dead time' before the measurement starts. Therefore, this setup is very convenient for detection of short relaxation times.

# 4.2 Model susceptibility measurements

Magnetic susceptibility is the reaction of a material to an applied magnetic field. It is a dimensionless quantity and can be described as

$$\chi = \frac{\partial M}{\partial H} \tag{4.1}$$

with  $\chi$  the magnetic susceptibility, M the magnetization and H the external magnetic field. For small magnetic field strengths the magnetization is often very accurately linear to the magnetic field, which can be seen in figure 2.5. This reduces the above relation to

 $\chi_0 = \frac{M}{H}$ . Two types of susceptibilities can be distinguished. The first one is the susceptibility that describes the behaviour of a specific particle, which depends on its shape. This susceptibility is denoted by  $\chi$ . The other susceptibility is a material constant,  $\chi_{in}$  and cannot be used to describe the behaviour of a finite amount of that material. The magnetization curve of spherical particles is described according to the Langevin function as described in section 2.3.3. The steady state value of the susceptibility in the low-field limit can now be described by a Taylor expansion of equation 2.8 around H=0:

$$\chi_{0,sp} = \frac{\mu_0 \mu_{NP} M_s}{3k_B T}.$$
(4.2)

The susceptibility as described above depends on the shape of the particle. Using the linear approximation model as described in equation 2.16 an expression for the initial susceptibility, which is a material constant and does not depend on shape, can be derived

$$\chi_{in} = \frac{\chi_{0,sp}}{1 - \frac{1}{3}\chi_{0,sp}},\tag{4.3}$$

where N = 1/3 for spherical particles.

For cylindrical particles with a high aspect ratio, p > 10, the demagnetization factor vanishes,  $N \approx 0$ . The steady state susceptibility of cylindrical particles can thus be described as

$$\chi_{0,cy} = \chi_{in} = \frac{\chi_{0,sp}}{1 - \frac{1}{3}\chi_{0,sp}} = \frac{3\mu_0\mu_{NP}M_s}{3k_BT - \mu_0\mu_{NP}M_s}.$$
(4.4)

When the magnetic field changes, the magnetization of the particles follows this change with a time lack. The rate of change in the low-field limit depends on the difference between the steady state magnetization and the current magnetization and is described as

$$\frac{dM}{dt} = -\omega_{char} \left( M - \chi_0 H \right),\tag{4.5}$$

where  $\omega_{char}$  is the characteristic frequency at which the rate changes. This frequency corresponds with the Néel or Brownian relaxation time as described in section 2.5. When an alternating magnetic field is applied, the magnetization follows the harmonic change of the field

$$i\omega\tilde{M} = -\omega_{char} \left(\tilde{M} - \chi_0 \tilde{H}\right),\tag{4.6}$$

where  $\omega$  represents the frequency of the AC magnetic field and  $\tilde{H} = H_0 e^{i\omega t}$ . The magnetization can now be described as

$$\tilde{M} = \left(\frac{\omega_{char}}{\omega_{char} + i\omega}\right) \chi_0 \tilde{H}.$$
(4.7)

The magnetic susceptibility can now be described as

$$\chi(\omega) = \frac{d\tilde{M}}{d\tilde{H}} = \left(\frac{\omega_{char}}{\omega_{char} + i\omega}\right)\chi_0,\tag{4.8}$$

which consist of a real, in-phase and an imaginary, out-of-phase part.

$$\chi(\omega) = \chi'(\omega) - i\chi''(\omega) \tag{4.9}$$



Figure 4.1: Susceptibility in the low magnetic field limit. The susceptibility is indicated by the blue line, which overlaps with the green line that represents the real (in-phase) susceptibility.

$$\chi'(\omega) = \left(\frac{\omega_{char}^2}{\omega_{char}^2 + \omega^2}\right)\chi_0 \tag{4.10a}$$

$$\chi''(\omega) = \left(\frac{\omega\omega_{char}}{\omega_{char}^2 + \omega^2}\right)\chi_0 \tag{4.10b}$$

In figure 4.1 the susceptibility as a function of the frequency of the magnetic field is shown. In the low frequency limit, when  $\omega \ll \omega_{char}$ , the real (in-phase) susceptibility reaches the value of  $\chi_0$ . At higher frequencies,  $\omega \gg \omega_{char}$ , the orientations of the magnetic dipole moments cannot keep up with the rate of change of the magnetic field and the susceptibility goes to zero. The characteristic frequency of the particle is given by the intersection of the real and imaginary susceptibility, which occurs at the maximum of the imaginary component.

### 4.3 Method

The system is based on a differential transformer [45]. An alternating current is applied to the primary coils of the transformers, inducing an alternating voltage in the secondary coils whose amplitude depends on the mutual inductance between the coils. The sample with magnetic material is placed in one of the two transformers. The change in signal due to the placement of the sample is proportional to the susceptibility of the sample. Since the transformers are identical and exposed to the same noise sources, subtraction of the signal from the empty transformer will remove the noise from the sample signal. This measurement is performed for a spectrum of frequencies of the AC current and the real and imaginary part of the susceptibility are plotted against the frequency. The frequency



Figure 4.2: Electronic scheme of the setup used for the susceptibility experiments. The setup is based on a differential transformer. An AC current is applied to two identical transformers of which one contains the sample material. The difference between the induced voltages in the secondary coils of the identical transformers is a measure of the susceptibility of the sample material [45].

at which the real and imaginary susceptibilities intersect, indicates the characteristic relaxation frequency of the sample material, see figure 4.1.

A schematic overview of the setup is shown in figure 4.2. A function generator is used to apply the AC current to the primary coils of the transformers. The transformers are placed in series, so they experience the same current. The induced voltages in the secondary coils of the transformers are subtracted from each other by a differential preamplifier. A second function generator is used to cancel this signal through a so-called nullification procedure. A minimal signal is now provided to the lock-in amplifier.

The setup is placed in a mu-metal box to shield it from low-frequency magnetic interference. The box is thermostatized by the circulation of cooling liquid in copper tubes surrounding the box. The mu-metal box is placed inside a Faraday cage of aluminum plates to further shield it from electrical interference.

## 4.4 Hardware specifications

### 4.4.1 Magnetic field strength

The strength of the magnetic field inside the transformer coils is determined by the AC current applied to the primary coils. However, the voltage in the secondary coils cannot



Figure 4.3: Schematic drawing of the transformer with the sample. The transformer consists of multiple layers of copper wire wound around a PVC cylinder. The six inner layers constitute the primary coil and the outer 86 layers the secondary coil [45].

exceed 1 V, since this is the maximum value the preamplifier can measure. The amplitude of the applied AC current is automatically reduced when the output voltage is exceeding this limit, for example due to a highly magnetic sample. Therefore, the AC current applied to the primary coils cannot exceed 12.9 mA, which corresponds to a maximum magnetic field of 730 A/m.

### 4.4.2 Transformers

The transformers are made of copper wire wound in multiple layers around a PVC tube [45]. The PVC tube has an external diameter of 12.6 mm and a height of 140 mm. The six inner layers constitute the primary coil, and the 86 outer layers constitute the secondary coil. The transformers have a total of 92 layers with 636 turns per layer. In theory, the transformers should have identical mutual inductances, however, there is a difference of 0.2 %. This difference is decreased to 0.05 % by adding 80 turns to the transformer with the lowest mutual inductance and it can be further improved by the placement of a small piece of ferrite near the transformer.

### 4.4.3 Sample tube

The sample tube is made of glass and has an external radius of 4.0 mm and an internal radius of 3.0 mm. The sample tube is longer than the transformer coils, it sticks out about 10 mm at both the top and bottom of the transformer. This is advantageous for samples that show sedimentation. The sediment that is formed at the bottom of the sample tube is now outside the transformer coils and therefore does not influence the output voltage of the secondary coil. However, for an accurate measurement the concentration of sample material in the area between the coils should remain the same during the measurement, so there is a limit to the degree of sedimentation that is allowed.



Figure 4.4: Schematic drawing of the measurement procedure of the susceptibility experiments [45].

# 4.5 Measurement procedure for the susceptibility measurements

The different steps of the measurement procedure are schematically depicted in figure 4.4. To start, the sample is placed in one of the transformers, so the output signal from the lockin amplifier corresponds to the difference between the sample and the reference secondary coils. Now the nullification procedure starts, at which the output of the second function generator is varied until the output of the lock-in amplifier is minimized. This output of the lock-in amplifier is called the remnant signal and is measured in step 3, together with the voltage of the secondary reference coil,  $V_{ref}(\omega)$ . Afterwards, the sample is removed in step 4. Since the removal of the sample can affect the total impedance of the primary coils, the AC current supplied by the first function generator is varied until the signal  $V_{ref}(\omega)$  measured by the secondary reference coil is again the same as in the presence of the sample. This is done to make sure the magnetic field in the transformers is the same as it was when the sample was inside. The output of the lock-in amplifier is measured again in step 6.

The signal due to the sample is the difference between the lock-in amplifier output voltage at step 6 and step 3,  $\Delta V(\omega)$ . This measurement is repeated a couple of times after which the average is taken. This is then repeated for various frequencies of the applied magnetic field. Since a large number of measurements is performed, the procedure can take up to 10 hours.

# 4.6 Derivation of the susceptibility from the measured voltage

The susceptibility of the sample material can be obtained from the increased output voltage due to the presence of the sample. The AC current in the primary coil of the transformer

induces a voltage in the secondary coil that is described as

$$V_{ref} = -i\omega M I(\omega), \tag{4.11}$$

where  $V_{ref}$  represents the voltage in the secondary coil,  $\omega$  the frequency of the AC current, M the mutual inductance between the primary and the secondary coil, I the AC current applied to the primary coil and  $i = \sqrt{-1}$ . When the sample is placed inside the transformer coils, the induced voltage changes to

$$V_{sample} = -i\omega M (1 + \chi(\omega)) F I(\omega), \qquad (4.12)$$

where  $\chi(\omega)$  represents the susceptibility of the sample and F the fill-factor, which expresses to what extent the space inside the coils is filled with the sample. The measured quantity  $\Delta V$  can now be related to the susceptibility of the sample via

$$\Delta V = V_{sample} - V_{ref} = V_{ref}(\omega)\chi(\omega)F.$$
(4.13)

# 4.7 Specifications and limitations

### 4.7.1 Sensitivity

The system is able to measure susceptibilities that correspond to relaxation frequencies in the range of 0.01-1000 Hz. Above the upper limit of 1000 Hz the impedance spectra of the transformers exhibit resonances, which makes the relation between the applied current and the magnetic field nonlinear and unsuited for susceptibility measurements. Besides, the effect of the sample decreases at increasing frequency due to absorption of the alternating magnetic field by the copper wires and capacitive losses between neighboring wires.

The system reaches its highest sensitivity in the range of 1-100 Hz, as can be seen in figure 4.5 where the background signal is depicted. The background signal increases with decreasing frequency due to the presence of 1/f noise. After the sensitive area between 1-100 Hz, the background signal increases again at higher frequencies due to heating of the transformer coils. Susceptibilities down to  $10^{-5}$  can be measured in the most sensitive area.

### 4.7.2 Low-field limit

The model described in section 4.2 is only valid when small magnetic fields are applied. The low magnetic field approximation is made twice in this model.

First, the susceptibility is assumed to be constant, see equations 4.2 and 4.4. This corresponds with a linear magnetization curve, which is only valid for low magnetic fields, as was shown in section 2.3.2.

Second, the relaxation process is studied when the applied magnetic field is still present. However, the contribution of the magnetic field to the energy of the particles is neglected. This assumption is only valid when the energy that the particles gain due to the magnetic field is negligible compared to the dominating energy, which is the thermal energy in this case. Therefore, only small magnetic fields that satisfy the condition  $\mu_0\mu_{NP}H \ll k_BT$  are allowed.



Figure 4.5: Background signal measured with an empty coil. At low frequencies the background signal is increased by 1/f noise. The increase of background signal at higher frequencies is due to the heating of the coils. The most sensitive measurements are performed between 1-100 Hz [45].

# Chapter 5

# **Results and analyses**

# 5.1 Introduction

The systems described in chapter 3 and 4 are used to investigate the relaxation behaviour of superparamagnetic nanoparticles. The first section of this chapter describes the samples that are used in these measurements.

The SQUID setup gives a measure of the change of the magnetic moment of the sample over time. The speed with which this signal decays corresponds to the relaxation time of the particles. It can be seen how the relaxation time changes during the relaxation process, due to the size distribution of the particles.

The susceptibility setup measures the change in susceptibility of the sample for a range of frequencies of the applied magnetic field. At low frequencies the magnetic moment of the particles changes according to the direction of the magnetic field. As the magnetic field changes direction faster, there is a point at which the particles cannot keep up anymore. The frequency at which this happens, corresponds to the relaxation time of the particles.

The measurement results are compared to the model to check whether the model accurately describes the relaxation behaviour of the particles.

## 5.2 Sample material

The samples are investigated before their use in the measurement systems. The relaxation measurements with the SQUID system and the susceptibility measurements are performed with the same samples.

The characteristics of the samples determine the outcome of the measurements. The material of the nanoparticles determines the magnetization of the particles. For example, nickel has a stronger magnetic effect than magnetite. Therefore, nickel will have a stronger signal, which is easier to detect.

The shape of the particle also influences its behaviour. The shape and surface anisotropy have large influences on the Néel relaxation time of the cylindrical particles. Also, the increased surface area of cylindrical particles with respect to spherical ones leads to longer relaxation times. In these experiments both spherical and cylindrical particles are investigated.

The choice of the medium is an important parameter in the determination of the Brownian relaxation time. The viscosity of the medium can be varied to obtain a relaxation time in a desirable regime. The medium can also be used to stabilize the particles. Viscosity influences the speed with which the particles sink to the bottom, sedimentation. Also, the presence of certain ions in the medium influences the stability of the sample.

The size of the particle has large influence on the relaxation time of the particle. Larger particles show longer relaxation times. It is therefore important to know the actual size of the particles and the distribution of the size. An often used technique to determine the size and the size distribution of a sample is Dynamic Light Scattering (DLS). DLS is a method that relates Brownian motion to the size of the particle by illuminating the particles with a laser and analyzing the intensity fluctuations in the scattered light [46]. These fluctuations indicate the size of the particle present in the sample. The Zetasizer Nano system from Malvern Instruments (Malvern, United Kingdom) is used to characterize the samples.

Another way to characterize the sample material is by performing a VSM measurement. VSM stands for Vibration Sample Magnetometer. The VSM can be used to measure the magnetization curve. The magnetization curve shows whether the sample is superparamagnetic or not. A superparamagnetic sample shows no hysteresis. Next to that, the magnetization curve gives us a measure of the saturation magnetization. As discussed in section 2.3.2, the surface effects of nanoparticles significantly influence the magnetic moment, making the value of the bulk saturation magnetization invalid.

### 5.2.1 Spherical iron oxide particles

Spherical iron oxide particles are made by adaption of the organic synthesis methods of Lattuada et al [47] and Sun et al [48]. The iron oxide particles are made of magnetite (Fe<sub>3</sub>O<sub>4</sub>), have a diameter of 5 nm and are in a stable solution. Water is used as a solvent and citric acid and polyethylene glycol amine (PEG-NH<sub>2</sub>) are used as dispersant. The particles are coated with oleic acid. PEG molecules with a molecular weight of 10000 g/mol are attached to the citric acid. The coating hinders the formation of aggregates. The particles show no signs of sedimentation and do not form large aggregates.

### DLS measurements on spherical iron oxide particles

Figure 5.1 shows DLS measurements of the iron oxide samples. The DLS only measures the hydrodynamic size of the particles. The iron oxide particles contain a layer of citric acid, so these measurements cannot be used to check whether the magnetic cores are 5 nm. The measurements show a hydrodynamic diameter of 30 nm with a standard deviation of the natural logarithm of the diameter of 0.25.

### VSM measurements on spherical iron oxide particles

The magnetization curve of the iron oxide particles is obtained with a Vibrating Sample Magnetometer (VSM). The magnetization curve is shown in figure 5.2 and it is used to determine the saturation magnetization of the sample. The saturation magnetization has decreased significantly due to the relatively large surface of the nanoparticle. The bulk saturation magnetization is  $3.8 \cdot 10^5$  A/m, while the VSM measurements show a saturation magnetization of  $2.3 \cdot 10^3$  A/m, which is only 0.6% of the bulk value.

The magnetization curves show hysteretic behaviour, which is remarkable since superparamagnetic particles do not exhibit any hysteresis. However, the particles were not dispersed in liquid in this measurement. Therefore, Brownian relaxation is not possible and the particles show only Néel relaxation. As was seen in section 2.5 the Néel relaxation time increases exponentially with increasing particles size. It is very likely that there is a small number of larger particles present in the sample. These particles cannot align with



Figure 5.1: Dynamic Light Scattering (DLS) measurements performed on the spherical iron oxide particles dispersed in water. Figure (a) shows the measurement series performed on the iron oxide samples. Figure (b) shows the average of the measurement compared to a simulation of the particles size. It follows from this simulation that the hydrodynamic diameter is 30 nm and the natural logarithm of its standard deviation  $\sigma = 0.25$ .

the magnetic field in the time scale of the VSM, which results in the hysteretic behaviour.

### 5.2.2 Spherical nickel particles

Spherical particles are commonly used for research purposes and therefore lots of variations are commercially available. In this research two samples of spherical nickel particles of respectively 20 nm (9225SJ) and 60 nm (9221XH) diameter of Sky Spring Nanomaterials Inc. (Houston, USA) are used. These nickel particles are supplied as a powder, so the particles must be dispersed before use.

The viscosity of the carrier liquid influences the Brownian relaxation time. Water is a common medium to disperse the particles in. However, the size of the particles would indicate very short relaxation times in water. The sample would be totally relaxed before the 'dead time' of the SQUID setup has elapsed. Therefore, these particles are also dispersed in glycerol. Glycerol has a high viscosity, which will slow down the Brownian relaxation behaviour significantly. An additional advantage of the high viscosity of glycerol is that it hinders sedimentation of the particles.

For the particles dispersed in water a dispersant has been added to the medium in order to stabilize the solution. The water contains 1mM carboxy methyl cellulose (CMC).

The spherical nickel particles are not coated. However, it is possible that the carboxy groups bind to the nickel and coat the particle. Unfortunately, it is hard to verify whether this happens or not.

The specifications of the different spherical nickel samples are depicted in table 5.1. The numbering of the samples will be used throughout the rest of this report.

#### DLS measurements on spherical nickel particles

Figure 5.3 shows Dynamic Light Scattering (DLS) measurements of the spherical nickel particles. The diameter is often assumed to be lognormally distributed [50] and the per-



Figure 5.2: VSM measurements performed on the spherical iron oxide particles dispersed in water. Figure (a) shows the magnetization curve and figure (b) is an enlargement of this. The particles show a saturation magnetization of  $2.3 \cdot 10^3$  A/m, which is much smaller than the bulk value of  $3.8 \cdot 10^5$  A/m.

	Dia-	Medium	Disper-	Concen-
	meter		sant	tration
	(nm) [49]			(mg/ml)
Sample 1	20	water	1% CMC	0.1
Sample 2	20	glycerol	-	0.2
Sample 3	60	water	1% CMC	0.1
Sample 4	60	glycerol	-	0.2

Table 5.1: Specifications of the spherical nickel samples.



Figure 5.3: Dynamic Light Scattering (DLS) measurements performed on the spherical nickel particles dispersed in glycerol. The actual size is much bigger than the size indicated by the supplier. The nickel particles that are supposed to have a diameter of 20 nm and 60 nm, show the best fit at average diameters of 40 nm and 57 nm respectively.

formed DLS measurements confirm this. The plotted lognormal distribution functions give an average diameter of respectively 40 nm and 57 nm for the 9225SJ and the 9221XH particles. Especially for the 9225SJ particles this deviates significantly from the specifications given by the supplier.

The 9221XH particles show a slight decrease of particle size in time, as can be seen in figure 5.3. The second measurement series is taken 20 minutes after the first one and shows a smaller diameter. This could be due to sedimentation of the larger particles in the sample. The sedimentation effect in the 60 nm particles is also seen when the sample is stored i.e. after a few days of storage a dark layer of particles has formed at the bottom of the sample.

#### VSM measurements on spherical nickel particles

Magnetization curves of the samples were obtained with a VSM. The magnetization curves are shown in figure 5.5 and are used to determine the saturation magnetization of the sample. The magnetization of the 9225SJ particles saturates at a magnetic field of  $3.4 \cdot 10^5$  A/m and for the 9221XH particles at  $3.9 \cdot 10^5$  A/m. This corresponds to 70% and 80% of the bulk saturation magnetization respectively.

The magnetization curves show hysteretic behaviour, which is remarkable since superparamagnetic particles do not exhibit any hysteresis. However, in section 2.6 the superparamagnetic limit for spherical particles of nickel was calculated to be 71 nm. Looking at the size distribution measured with the DLS, there are particles present that are larger than the superparamagnetic limit and therefore exhibit hysteretic behaviour.

### 5.2.3 Cylindrical nickel particles

Cylindrical particles are not commercially available, so the cylindrical particles were home made by our research group. The cylindrical particles are made of nickel and have a



Figure 5.4: Dynamic Light Scattering (DLS) measurements converted to relative percentage of the amount of particles in the sample. The size distributions fit a lognormal distribution with average diameters of 40 nm and 57 nm and standard deviation of  $\sigma = 0.25$ and  $\sigma = 0.23$ . The 9225SJ particles deviate significantly from the specifications given by the supplier.



Figure 5.5: Magnetization curves of the 9225SJ and 9221XH spherical nickel particles and the home-made nickel wires by VSM measurements. The particles show a saturation magnetization that is smaller than the bulk value due to surface effects. The bulk saturation magnetization is  $4.9 \cdot 10^5$  A/m, while the 9225SJ particles show a saturation value of  $3.4 \cdot 10^5$  A/m, the 9221XH particles  $3.9 \cdot 10^5$  A/m and the cylindrical particles  $3.2 \cdot 10^5$  A/m. Figure (b) is an enlargement of figure (a) and shows hysteretic behaviour.



Figure 5.6: SEM image of the cylindrical nickel particles. The particles are 2.5  $\mu m$  long and have a diameter of 150 nm.

diameter of 150 nm and a height of 2.5  $\mu \mathrm{m}.\,$  Figure 5.6 shows a SEM image of the particles.

The magnetic nickel wires are made through electrodeposition of nickel in the pores of a membrane. The size of the pores determines the diameter of the wire. The length of the wires depends on the duration of the reaction and the electrodeposition potential [51]. The wires grow in a favoured crystal direction, which depends on the electrodeposition potential and the pore diameter. The wires grown for this research have a diameter of 150 nm, a length of 2.5  $\mu$ m and have the [110] crystal direction along the long axis of the wire.

The wires are coated with a gold layer of 35-50 nm. The coating reduces the effect of the particles sticking together and forming large clusters. Besides, the coating makes the particles biocompatible.

The particles are not very stable, they easily sink to the bottom of the sample tube. To slow down this sedimentation process, the particles are dispersed in glycerol.

### VSM measurements on cylindrical nickel particles

The magnetization curve for the nickel wires is shown in figure 5.5. The cylindrical particles clearly exhibit hysteretic behaviour, which indicates that the particles are ferromagnetic. Considering the much larger volume of the cylindrical particles compared to the spherical ones, it is not very surprising that the superparamagnetic regime is left. Although an increased aspect ratio allows larger volumes within the superparamagnetic regime, the increase in volume of the cylindrical particles is too large to be compensated by the increased aspect ratio.

The saturation magnetization of the cylindrical particles is  $3.2 \cdot 10^5$  A/m, only 65% of the bulk saturation magnetization of nickel. This is substantially lower than the saturation magnetization of the spherical particles. Another research group [52, 53, 54] made

cylindrical nickel particles with a diameter fo 350 nm and lengths of multiple micrometers, which had a saturation magnetization of 82% of the bulk value. So the saturation magnetization increases with increased volume. This was also seen in our spherical particles, although they achieved similar saturation magnetizations at substantially less volume. The cylindrical particles have a relatively larger surface area than the spherical ones, therefore the surface effects influence relatively more atoms in cylindrically shaped particles than in spherically shaped ones. This reduces the saturation magnetization of the cylindrical particles below the value of the smaller spherical particles.

## 5.3 SQUID relaxation results

All samples described in section 5.2 are investigated with the SQUID setup described in chapter 3. The SQUID setup measures the change in magnetic moment as a function of time. The relaxation times of the particles can be derived from this.

The samples dispersed in water are placed in a water bath sonicator for 20 s right before every measurement in order to disperse the particles. This ensures an equal degree of dispersion in every measurement. The samples dispersed in glycerol are heated when placed in the sonicator, so the effect of the sonication bath is larger. The glycerol samples are not redispersed before every single measurement. The heating of the sample and the cooling down afterwards could influence the measurements.

The SQUID only detects gradients of a magnetic field, an absolute value of the magnetic field cannot be given. Every measurement has an offset, which fluctuates between different measurements. In order to easily compare the different measurements, the offset is changed so that the signal is zero at the end of the measurement. If the output voltage would represent absolute magnetic fields, the magnetic field would also be zero after the particles have relaxed.

The relaxation time is determined from the measurement signal by

$$\tau = -\frac{t}{\ln(\frac{V_{sq}}{V_{sq}(t=0)})},\tag{5.1}$$

where t represents the time,  $V_{sq}$  the output voltage of the SQUID and  $V_{sq}(t = 0)$  the initial output voltage of the SQUID.

The measurements are compared to simulations of the measurement made with the models in section 3.2 and 3.6. Parameters for the simulation are chosen as to best represent the sample and the setup. For example, the DLS measurements in section 5.2.2 showed that the diameter of the 9225SJ particles is 40 nm instead of 20 nm according to the supplier. Therefore, the measured diameter of 40 nm is used. The same applies to the saturation magnetization. Parameters of the simulation are shown in table 5.5.

### 5.3.1 Spherical iron oxide particles

The specifications of the sample and the settings of the SQUID setup are shown in table 5.2. The particles were expected to have a Brownian relaxation time of  $1.3 \cdot 10^{-5}$  s and a Néel relaxation time of  $1.0 \cdot 10^{-9}$  s. The particles should be completely relaxed by Néel relaxation before the 'dead time' of the SQUID setup has passed. The relaxation measurement is shown in figure 5.7 and shows a very small relaxation behaviour at the beginning of the measurement. However, the signal is very small and probably caused by the environment instead of the sample.



Figure 5.7: Relaxation measurements and simulations of spherical iron oxide particles with a diameter of 5 nm dispersed in water. Figure (a) shows the output voltage from the SQUID, which is a measure of the change of the magnetization of the sample and figure (b) shows the outcome of the simulation model.

Core dia-	Hydrody-	Medium	Dispersant	Concen-	Magnetic field	Pulse
meter	namic dia-			tration	strength	dura-
(nm)	meter $(nm)$			(mg/ml)	(A/m)	tion $(s)$
5	30	water	citric acid	3.4	800	5
			$PEG-NH_2$			

Table 5.2: Specifications of the sample and settings of the SQUID setup for the relaxation measurement on spherical iron oxide particles, section 5.3.1.

### 5.3.2 Spherical nickel particles

The relaxation behaviour of spherical nickel particles is measured with the SQUID setup. The settings of the setup are shown in table 5.4. The measurements and the simulations of the measurements for all samples described in section 5.2.2 are shown in figure 5.8, 5.9, 5.10 and 5.11. Figures (a) and (c) give the output voltage of the SQUID, which is a measure of the magnetic moment of the particle. Figures (b) and (d) give the corresponding relaxation times.

The measurements show much longer relaxation times than expected from the simulations. The simulation predicts all particles dispersed in water to be completely relaxed before the 'dead time' of the SQUID has passed. However, the actual measurements show relaxation behaviour over a much longer time. The particles dispersed in glycerol are not

H	$\eta$	$M_s$	$d_{core}$	$d_{hydrod.}$	$\sigma$	$t_{mag}$	Concentra-
(A/m)	$(Pa \ s)$	(A/m)	(nm)	(nm)		(s)	tion $(mg/ml)$
800	$1.25 \cdot 10^{-3}$	$3.8 \cdot 10^{5}$	5	30	0.25	$\infty$	3.4

Table 5.3: Parameters of the simulation of the relaxation behaviour of spherical iron oxide particles, section 5.3.1.

	Sample	Magnetic field strength (A/m)	Pulse duration (s)
Measurement A	1	118	5
Measurement B	2	118	5
Measurement C	3	118	5
Measurement D	4	118	5
Measurement E	4	380	300

Table 5.4: Settings SQUID relaxation measurement on spherical nickel particles in water, section 5.3.2.

	Sample	H	$\eta$	$M_s$	d	$\sigma$	$t_{mag}$	Concentra-
		(A/m)	$(Pa \ s)$	(A/m)	(nm)		(s)	tion $(\mu g/ml)$
Measurement A	1	118	$1.25 \cdot 10^{-3}$	$3.4\cdot 10^5$	40	0.25	$\infty$	0.1
Measurement B	2	118	1.42	$3.4\cdot 10^5$	40	0.25	$\infty$	0.1
Measurement C	3	118	$1.25\cdot 10^{-3}$	$3.9\cdot 10^5$	57	0.23	$\infty$	0.2
Measurement D	4	118	1.42	$3.9\cdot 10^5$	57	0.23	$\infty$	0.2

Table 5.5: Parameters of the simulation of the relaxation behaviour of spherical nickel particles, section 5.3.2.

	Expected diameter (nm)	Simulated Brownian relaxation	Simulated Néel relaxation	Measured maximum relaxation	Corresponding diameter (nm)
		time $(s)$	time $(s)$	time $(s)$	
Measurement A	40	$3.03 \cdot 10^{-5}$	$5.58\cdot 10^6$	10	$2.8\cdot 10^3$
Measurement B	40	$3.43 \cdot 10^{-2}$	$5.58\cdot 10^6$	14	$3.0\cdot 10^2$
Measurement C	57	$8.78\cdot10^{-5}$	$3.67\cdot 10^{36}$	8.5	$2.6\cdot 10^3$
Measurement D	57	$9.92 \cdot 10^{-2}$	$3.67\cdot 10^{36}$	14	$3.0\cdot 10^2$
Measurement E	57	$9.92\cdot 10^{-2}$	$3.67\cdot 10^{36}$	14	$1.4\cdot 10^3$

Table 5.6: Parameters of the simulation of the relaxation behaviour of spherical nickel particles, section 5.3.2.

even relaxed after one hour, see figure 5.11e and 5.11f.

These long relaxation times indicate the presence of very large particles, see table 5.6. The particles used here were much smaller according to the supplier. However, the small particles can stick together and form large clusters. More about clustering can be found in chapter 6.

Larger particles would have a larger relaxation time according to the simulations. Measurements A & C and B & D are similar except for the size of the particles. Therefore, an increase in relaxation times should be seen at the larger particles. Looking at the measurements results, there is no significant difference in relaxation time between the small and the large particles. This is another indication that the actual size of the particles is different than expected.

The simulations indicate Brownian behaviour based on the size of the particles. The measurements do not give relaxation times corresponding to the simulated Brownian or Néel relaxation times. However, comparing the water and the glycerol experiments it is clear that the use of glycerol as a medium increases the relaxation times. The medium only influences the Brownian relaxation time and not the Néel relaxation time. Therefore, the particles relax by Brownian relaxation.

Due to the size distribution of the particles, there are more relaxation times present in the samples. This causes the increase in relaxation time in figures (b) and (d). The small particles relax very fast, after which only larger particles remain. These larger particles have longer relaxation times, which causes the relaxation time to increase in time.

The relaxation times corresponding to the measurements, figures (b), show a broadening of the graph at the end of the measurement. Since the SQUID signal decays, the noise gets relatively larger at later times in the measurement, which causes the broadening of the graph. Next to that, the natural logarithm (which is used to determine the corresponding relaxation time, equation 5.1) gets more sensitive around zero, which also causes a broadening of the line.

The relaxation times in figures (d) go towards zero at the end of the measurement. This is a result of the offset given to every measurement to let it end at zero volt. A relaxation time of zero seconds means that all particles in the sample are relaxed. Measurements A and C are practically relaxed at the end of the measurement. It is therefore logical that the relaxation times go to zero, because there are no larger particles present in the sample. Samples in measurements B, D and E are not fully relaxed when the measurement is ended. The signal is made zero at the end of the measurement, indicating that the relaxation process has stopped there. This is actually not the case, larger particles can still be present. So an incorrect offset is chosen here, resulting in an incorrect initial value of the measurement signal,  $V_{sq}(t = 0)$  in equation 5.1. Figure 5.12 shows that a small offset still gives reasonable values of the relaxation time just after the start of the measurement, but that it severely changes the result at larger times.

So it is important to choose a good offset for the measurements. Therefore, the measurements should last until all particles are relaxed. However, this was not always possible for the samples with long relaxation times, due to the high chance of flux jumps occurring. Besides, the samples show sedimentation, which makes it hard to interpret data gathered over a longer time.

The corresponding relaxation times of the simulations do not go to zero at the end of the measurement, since the simulations are based on lognormal size distributions. This means that there is still a very small chance on an infinitely large particle, which would correspond to an infinite relaxation time.



Figure 5.8: Measurements A. Relaxation measurements and simulations of spherical nickel particles with a diameter of 20 nm dispersed in water.



Figure 5.9: Measurements B. Relaxation measurements and simulations of spherical nickel particles with a diameter of 20 nm dispersed in glycerol.



Figure 5.10: Measurements C. Relaxation measurements and simulations of spherical nickel particles with a diameter of 60 nm dispersed in water.



Figure 5.11: Measurements D in (a), (b), (c) and (d). Measurement C in (e) and (f). Relaxation measurements and simulations of spherical nickel particles with a diameter of 60 nm dispersed in glycerol.



Figure 5.12: Simulations of spherical nickel particles with a diameter of 60 nm dispersed in glycerol with and without an offset to the SQUID output voltage. The offset is 0.1 V. A small offset in the output voltage has huge consequences in the corresponding relaxation times. However, in the beginning of the relaxation process, the offset simulation is still a good approximation of the actual value.

### 5.3.3 Cylindrical nickel particles

The magnetization curve of the cylindrical nickel particles depicted in section 5.2.3 shows hysteresis. The particles are therefore not superparamagnetic, but ferromagnetic. Therefore, the relaxation behaviour of these particles cannot be described by the model developed in section 3.2.

The relaxation behaviour of the sample is measured anyway. The settings of the setup are shown in table 5.7. A long magnetic field pulse is given to align the particles. If the particles were to show Brownian behaviour, their relaxation time would be  $1.8 \cdot 10^3$  s (without coating). Using the Brownian relaxation time as an indication for the duration of the magnetic pulse gives the particles enough time to align to the field. If the particles do not align by Brownian motion, they will align by an energetically more favourable process, which will be faster.

From the magnetization curve it is not possible to determine whether the cylindrical particles still consist of a single domain or not. The particles show hysteresis, but it is not clear at which position in figure 2.3 they are. If the particles still consist of a single domain, they will align to the magnetic field by Brownian relaxation. If the particles have entered the multidomain zone, the particles can also align to the field by domain flipping or domain wall movement.

The measurement results of the SQUID relaxation measurements are depicted in figure 5.13. There is relaxation behaviour visible, which is strange since ferromagnetic particles have a large coercive field. However, when the magnetic field used to magnetize the particles is small, the magnetization of multidomain particles could still be in the reversible regime, see figure 5.14. In this regime the particles align through domain flipping, which is easily reversed when the external magnetic field is removed [55]. The magnetic fields used in this measurement are very small, so it is likely that if the particles have multiple domains, they are still in that regime and therefore show a relaxation effect. If the particles consist of a single domain, it is still be possible that they return to a random
Size	Medium	Magnetic field	Pulse
		strength $(A/m)$	duration $(s)$
$150 \text{ nm x } 2.5 \mu \text{m}$	glycerol	240	3600

Table 5.7: Specifications of the sample and settings of the SQUID setup for the relaxation measurement on cylindrical nickel particles, section 5.3.3.



Figure 5.13: Relaxation measurements and simulations of cylindrical nickel particles with a diameter of 150 nm and a height of  $2.5\mu$ m dispersed in glycerol. Figure (a) shows the output voltage from the SQUID, which is a measure of the change of the magnetization of the sample. Figure (b) shows the relaxation times corresponding to the measurement in figure (a).

orientation after alignment to a magnetic field. Only, the chance of this happening is smaller and therefore the time it will take for this to happen will increase. The corresponding relaxation times for this measurement are very high, so this could be possible.

#### 5.4 Susceptibility results

The susceptibility behaviour of the iron oxide and the spherical nickel particles was measured. Unfortunately, it was not possible to measure the cylindrical nickel particles and the spherical particles dispersed in water. An accurate measurement requires several hours, because individual measurements at different frequencies are done multiple times. These samples were not consistent and gave fluctuating measurement values when the measurement was repeated. Therefore, no accurate frequency spectrum could be made.

Before the actual susceptibility measurements on the iron oxide and the spherical nickel particles dispersed in glycerol were done, the dependence of the susceptibility of the samples on the magnetic field is studied. This is done to ensure the low-field limit described in section 4.7.2 was satisfied.

All measurements are performed with the settings in table 5.8.



Figure 5.14: The magnetization process for a ferromagnetic particle with multiple domains. At low magnetic fields the magnetization process is reversible [55].

	Magnetic field	Frequency	Measurement time	Iterations
	strength $(A/m)$	range $(Hz)$	per frequency $(s)$	per frequency
Amplitude	7-700	10	10	10
Frequency	700	0.1 - 100	10	10

Table 5.8: Settings susceptibility measurements. 'Amplitude' refers to the measurements of the magnetic field amplitude spectrum and 'Frequency' refers to the measurements of the frequency spectrum.



Figure 5.15: The magnetization process for a ferromagnetic particle with multiple domains. At low magnetic fields the magnetization process is reversible [55].

## 5.4.1 Susceptibility measurements on spherical iron oxide particles

The dependence of the susceptibility of the spherical iron oxide particles on the magnetic field is depicted in figure 5.15a. The susceptibility shows no dependence on the magnetic field amplitude. This ensures that the low-field limit is satisfied.

The frequency spectrum of the susceptibility is depicted in figure 5.15b. The spherical iron oxide particle is expected to have a Néel relaxation time of  $1.0 \cdot 10^{-9}$  s and a Brownian relaxation time of 0.0145 s, which means all particles will relax by Néel relation. The relaxation time of  $1.0 \cdot 10^{-9}$  s corresponds with a frequency of  $1.6 \cdot 10^8$  Hz. Unfortunately, this frequency lies outside the available spectrum. A frequency independent behaviour of the susceptibility is then expected in the available range. This is exactly what is shown in figure 5.15.

#### 5.4.2 Susceptibility spectra for spherical nickel particles

Since the setup requires stable solutions, only the spherical particles dispersed in glycerol could be measured. Both the smaller (9225SJ) and larger (9221XH) nickel spheres are investigated.

The magnetic field amplitude dependency of both types of particles shows the low-field limit is satisfied, see figures 5.16a and 5.16c.

The smaller nickel particles (9225SJ) are expected to have a relaxation time of  $3.43 \cdot 10^{-2}$ , which corresponds to a characteristic frequency of 4.64 Hz. However, in figure 5.16b there is no decrease of the real component and no maximum for the imaginary component seen. Therefore, the characteristic frequency does not lie in the measured frequency range.

The larger nickel particles (9221XH) are expected to have a relaxation time of  $9.92 \cdot 10^{-2}$ , which corresponds to a characteristic frequency of 1.60 Hz. Figure 5.16c shows an increase of the imaginary susceptibility at low frequencies. This could be an indication of the characteristic frequency being there. However, the real component of the susceptibility does not show any dependence of the frequency. When the characteristic frequency is passed, the real component should decrease from a finite value before to zero after the

	Magnetic field	Frequency	Measurement time	Iterations
	strength $(A/m)$	(Hz)	per frequency $(s)$	per frequency
Sample 1	700	1	10	3
Sample 3	700	1	10	3
Sample 4	700	0.1	10	3
Nickel wires	700	0.1	10	3

Table 5.9: Settings time depending susceptibility measurements.

characteristic frequency. The measurement should be repeated in order to conclude anything from it. When the measurement is repeated, lower frequencies should be included. The imaginary component should have a maximum at the characteristic frequency. In this measurement it is not possible to say whether the increase in susceptibility at 0.1 Hz decreases at lower frequencies.

#### 5.5 Time dependency of the measurements

As described in section 5.4, the spherical nickel particles dispersed in water and the cylindrical nickel particles gave fluctuating measurement results and therefore no accurate frequency spectrum could be measured. This raised the question whether the samples were stable enough. The samples are redispersed by the sonication bath treatment before every measurement, but it is not known how long the samples stay dispersed.

In the first part of this section, the susceptibility setup is used to measure the susceptibility over time. This is an indication of the stability of the sample.

In the second part of this section, the SQUID setup is used to measure the impact of the instability on the relaxation times.

#### 5.5.1 Time dependant susceptibility measurements

In this section the susceptibility is measured as a function of time. A decrease of the susceptibility over time indicates sedimentation i.e. the particles sink to the bottom of the sample tube due to gravity. Sedimentation leads to a thick layer of particles at the bottom of the sample tube. It is much harder for these particles to move or rotate, since they are stuck to the other particles at the bottom. The susceptibility setup is designed so that this sediment is outside the measurement coil. Therefore, these particles are not contributing to the measurement, which leads to a decrease of the susceptibility signal.

Figure 5.17 shows the time dependence of the susceptibility for samples 1, 3 and 4 as described in table 5.1 and the cylindrical particles, the settings are displayed in table 5.9. The spherical particles show a decrease of the susceptibility over time, which indicates that sedimentation takes place.

The cylindrical nickel particles do not show a decrease in susceptibility, so sedimentation does not seem to be the main cause of the inability to accurately measure the frequency spectrum. However, the susceptibility fluctuates enormously between various measurements, therefore weak signal strength is more likely to be the problem.

The sedimentation rate of the particles is an indication of the size of the particles. Larger particles sink faster than smaller particles. The sedimentation rate for spherical



Figure 5.16: Susceptibility spectra of spherical nickel particles dispersed in glycerol. Measurements on sample 2 are shown in figures (a) and (b) and the results for sample 4 are shown in figures (c) and (d). Figures (a) and (c) give the dependence on the amplitude of the magnetic field. Herewith the low-field limit can be checked, which is satisfied for both samples. Figures (b) and (d) give the frequency spectrum of the particles.



Figure 5.17: Susceptibility as a function of time. Figure (a) gives results of the spherical nickel particles dispersed in water. The results for the larger spherical nickel particles are shown in figures (b) and (c), for particles dispersed in water and glycerol respectively. Figures (a), (b) and (c) all show a decrease of the susceptibility over time, which indicates sedimentation. Figures (d) and (e) show measurements on the cylindrical nickel particles of amplitude and phase respectively. Both the phase and the amplitude of the susceptibility for the cylindrical nickel particles fluctuate enormously. Therefore, no accurate measurement of the frequency spectrum could be made.

	Sedimentation	Sedimentation	Corresponding
	rate $(cm/hour)$	rate $(m/s)$	particle size $(\mu m)$
Sample 1	10	$2.7 \cdot 10^{-5}$	2.8
Sample 3	5.0	$1.4 \cdot 10^{-5}$	2.0
Sample 4	0.67	$1.9 \cdot 10^{-6}$	25

Table 5.10: Sedimentation rates of the time dependant susceptibility measurements and the corresponding particles sizes.

	Magnetic field	Pulse
	strength $(A/m)$	duration $(s)$
Sample 1	800	5
Sample 3	800	5

Table 5.11: Settings time dependant SQUID relaxation measurements.

particles is given by [56]

$$u = \frac{d^2(\rho_c - \rho_m)g}{18\eta},$$
(5.2)

where u represents the sedimentation rate, d the diameter of the particle,  $\rho_c$  the density of the particle,  $\rho_m$  the density of the medium, g the gravitational acceleration and  $\eta$  the viscosity of the medium. The sedimentation rate is derived from the initial slope of the susceptibility. The sample tube and the measuring coil have a length of 10 cm. The sedimentation rates and the corresponding particles sizes are shown in table 5.10. The sedimentation rates correspond to particles about 50 - 500 times larger than expected from the specifications of the supplier. Again, this indicates the formation of huge clusters of particles.

#### 5.5.2 Time dependant SQUID relaxation measurements

As explained in section 3.5, the particles in aqueous dispersion are redispersed by a sonication bath treatment. This happens right before every measurement. The following experiment compares measurements in which the measurement follows immediately on the sonication bath and measurements in which 300 s have passed between the sonication bath treatment and the measurement. This shows the stability of the samples just after they are redispersed. The SQUID measurements are performed in a much smaller time scale then the susceptibility measurements, minutes against hours. The effect of sedimentation as seen in the susceptibility experiments, could therefore be less significant. This experiment will show the effect of sedimentation on the SQUID experiments.

The settings of the experiment are shown in table 5.11 and the results in figure 5.18. The corresponding relaxation times show that the relaxation time is increased when there is a waiting period after the sonication bath treatment. So the particles have grown in the 300 s after the sonication bath. One way the particles could have grown is by the formation of clusters, as will be explained further in chapter 6. Another way is that the particles have sunk to the bottom and ended up on top of another particle. Together it is harder to relax and therefore the relaxation time increases.



Figure 5.18: Relaxation measurement of spherical nickel particles. Three measurements are performed in which the sample is immediately measured after the sonication bath treatment. Then three measurements are performed in which a waiting time of 300 s existed between the sonication bath treatment and the measurement. The waiting period increases the relaxation times.

### Chapter 6

# Clustering of superparamagnetic nanoparticles

#### 6.1 Introduction

In chapter 5 it was seen that the relaxation times of the spherical nickel particles measured with both the SQUID setup and the susceptibility setup were much larger than expected from the simulations. Larger relaxation times are most likely caused by larger particles. The measured relaxation times corresponded to particles with sizes in the micrometer regime, while measurements were started with nanometer sized particles. How is it possible that the size of the particle increases?

Magnetic nanoparticles in dispersion interact with each other. This interaction can lead to the aggregation or clustering of multiple nanoparticles. Since the relaxation times are very sensitive to the size of the particles, clustering will significantly change the relaxation behaviour. The interactions between the particles are ignored in the simulation model, so therefore the simulated relaxation times are too small.

The first section of this chapter explains which forces are involved in the formation of clusters. In the second section, this knowledge is used to design experiments that prove that the large relaxation times of the spherical nickel particles is caused by clustering.

#### 6.2 Interaction energies

The main interaction energies between magnetic nanoparticles are magnetic dipolar, Van der Waals and electrostatic interaction [57]. All of which depend crucially on the structural parameters of the particle. The magnetic dipolar and the Van der Waals interactions have an attractive character, while the electrostatic interaction is repulsive. Particles are likely to form aggregates when the minimum of the resultant interaction energy is lower than the thermal energy,  $k_BT$ .

#### 6.2.1 Magnetic dipole interaction

A magnetic particle is attracted to another magnetic particle with its magnetic moment in the opposite direction. This interaction energy is called dipole-dipole interaction energy and it can be described as [58]

$$E_m(r) = -\frac{\mu_0}{4\pi r^3} \big( 3(\mathbf{m}_1 \cdot \mathbf{e}_{1,2})(\mathbf{m}_2 \cdot \mathbf{e}_{1,2}) - \mathbf{m}_1 \cdot \mathbf{m}_2 \big), \tag{6.1}$$

where r represents the distance between the centers of the two particles, **m** the magnetic moment of the particle and **e** represents the unit vector parallel to the line joining the centers of the two particles. Depending on the orientation of the particles with respect to each other the dipole-dipole interaction energy can be either positive or negative. A minimum energy is reached when the particles are in a head-to-tail configuration.

In the absence of a magnetic field, all orientations of the particles will be present in the sample. When a magnetic field is applied, the particles will align their magnetic moment towards the field direction. The domination of this aligned configuration leads to a decrease of the dipole-dipole interaction energy, which increases the chance of clusters.

#### 6.2.2 Van der Waals interaction

The Van der Waals interaction energy describes the interaction between different atoms or molecules. The energies from the individual atoms or molecules can be added to give the resultant Van der Waals interaction energy of larger bodies, for example nanoparticles. Hamaker described the Van der Waals interaction energy between two spherical particles as [59]

$$E(R_1, R_2, s) = -\frac{AH}{12},$$
(6.2)

where A represents the Hamaker constant and H is given by

$$H(x,y) = \frac{y}{x^2 + xy + x} + \frac{y}{x^2 + xy + x + y} + 2\ln\left(\frac{x^2 + xy + x}{x^2 + xy + x + y}\right),\tag{6.3}$$

where x represents the ratio of the shortest distance s to the diameter of particle 1,  $x = \frac{s}{2R_1}$ and y represents the ratio of the radius of particle 2 and the radius of particle 1,  $y = \frac{R_2}{R_1}$ . The dimensions are depicted in figure 6.1. The Hamaker constant for two particles of different materials can be expressed as [60]

$$A_{12} = \frac{2A_{11}A_{22}}{A_{11} + A_{22}} \simeq \sqrt{A_{11}A_{22}} \tag{6.4}$$

The Hamaker constant for two particles of the same material in a medium is described as

$$A_{131} = A_{11} + A_{33} - 2A_{13} = \frac{(A_{11} - A_{33})^2}{A_{11} + A_{22}} \simeq (\sqrt{A_{11}} - \sqrt{A_{22}})^2, \tag{6.5}$$

and for two different materials in a medium it is

$$A_{132} = A_{12} + A_{33} - A_{13} - A_{23} \simeq (\sqrt{A_{11}} - \sqrt{A_{33}})(\sqrt{A_{22}} - \sqrt{A_{33}}).$$
(6.6)

The Van der Waals energy between two spheres of the same material in vacuum can now be described as

$$E_{spheres}(R_1, R_2, s) = -\frac{A_{11}}{6} \Big( \frac{2R_1R_2}{2(R_1 + R_2)s + s^2} + \frac{2R_1R_2}{4R_1R_2 + 2(R_1 + R_2)s + s^2} + \\ \ln\Big( \frac{2(R_1 + R_2)s + s^2}{4R_1R_2 + 2(R_1 + R_2)s + s^2} \Big) \Big).$$
(6.7)



Figure 6.1: Spherical particles with a shell.

When the particles contain a shell with thickness  $\delta$ , the interaction energy with the shell and the spheres should also be considered. The Van der Waals energy is then described as [61]

$$E_v(R_1, R_2, s, \delta_1, \delta_2) = E_V(core_1, core_2) + E_V(shell_1, shell_2) + E_V(core_1, shell_2) + E_V(core_2, shell_1).$$
(6.8)

Considering  $E_V(core_1, shell_2) = E_V(core_1, sphere_2) - E_V(core_1, core_2)$ , the interaction energy of the particles can now be described as

$$E_{V}(R_{1},\delta_{1},R_{2},\delta_{2},s) = -\frac{A_{11}}{6}H(\frac{s+\delta_{1}+\delta_{2}}{2(R_{1})},\frac{R_{2}}{R_{1}}) - \frac{A_{232}}{6}H(\frac{s}{2(R_{1}+\delta_{1})},\frac{R_{2}+\delta_{2}}{R_{1}+\delta_{1}}) \\ + \frac{A_{232}^{1/2}A_{22}^{1/2}}{6}H(\frac{s+\delta_{2}}{2(R_{1}+\delta_{1})},\frac{R_{2}}{R_{1}+\delta_{1}}) \\ + \frac{A_{232}^{1/2}A_{22}^{1/2}}{6}H(\frac{s+\delta_{1}}{2(R_{2}+\delta_{2})},\frac{R_{1}}{R_{2}+\delta_{2}}) - \frac{A_{22}}{6}H(\frac{s+\delta_{1}+\delta_{2}}{2(R_{1})},\frac{R_{2}}{R_{1}}) \\ - \frac{A_{11}^{1/2}A_{232}^{1/2}}{6}H(\frac{s+\delta_{1}}{2(R_{1})},\frac{R_{2}+\delta_{2}}{R_{1}}) + \frac{A_{12}}{6}H(\frac{s+\delta_{1}+\delta_{2}}{2(R_{1})},\frac{R_{2}}{R_{1}}) \\ - \frac{A_{11}^{1/2}A_{232}^{1/2}}{6}H(\frac{s+\delta_{2}}{2(R_{2})},\frac{R_{1}+\delta_{1}}{R_{2}}) + \frac{A_{12}}{6}H(\frac{s+\delta_{1}+\delta_{2}}{2(R_{2})},\frac{R_{1}}{R_{2}})$$

$$(6.9)$$

#### 6.2.3 Electrostatic interaction

Counteracting the attractive Van der Waals and dipole-dipole forces, ionic compounds can be added to the medium in order to induce a repulsive force between the nanoparticles. The golden shell around the nickel particles is electrophile, which means it has an electron deficiency and can easily absorb electrons [62]. The negatively charged ions of the



Figure 6.2: Electrophilic particles attract negatively charged ions from the medium, resulting in a double layer [63].

compound, called counter-ions, will be absorbed to the positively charged surface of the particle, resulting in a double layer, see also figure 6.2. The generation of the double layer will result in a coulombic repulsion between the particles. If this electrostatic repulsion is high enough, it will prevent particle aggregation. However, the double layer can easily be disrupted by thermal motion or by an increase of ionic strength of the medium, which compresses the thickness of the double layer. So these parameters have to be controlled very carefully in order to maintain a stable colloidal suspension [63].

The energy of the electrostatic repulsion of spherical equally charged particles can be described as [64, 65]

$$E_{el} = \frac{64\pi k_B^2 T^2 R\epsilon_0 \epsilon_r}{e^2 z^2} e^{\kappa s} \left( \frac{e^{\frac{z \epsilon \Psi}{2k_B T}} - 1}{e^{\frac{z \epsilon \Psi}{2k_B T}} + 1} \right)^2$$
(6.10)

where R represents the radius of the particle,  $\epsilon_0$  the permittivity of free space,  $\epsilon_r$  the permittivity of the medium, z the charge of the counter-ion, e the elementary charge, s the distance between the particles and  $\Psi_0$  the electrostatic potential at the surface. The thickness of the double layer is described by the Debye-Hückel length,  $1/\kappa$ ,

$$\kappa = \left(\frac{e^2}{\epsilon_0 \epsilon_r k_B T} \sum_n c_n z_n^2\right)^{1/2},\tag{6.11}$$

where c represents the number concentration of the ions of type n in the medium.

#### 6.2.4 Total interaction energy

The individual interaction energies are shown in figure 6.3, just as the total interaction energy. The total energy can be either positive or negative. Negative total interaction



Figure 6.3: Contributions to the interaction energy between two spherical particles. The contributions of the dipole-dipole interaction, the Van der Waals forces and the electrostatic repulsion are drawn, just as the total interaction energy of the two particles. Negative interaction energy corresponds to attraction between the particles, while positive interaction energy results in repulsion.

energy corresponds to attraction between the particles, while positive interaction energy results in repulsion. The electrostatic interaction energy strongly depends on the concentration of the ionic compound. The total energy as a function of the concentration is depicted in figure 6.4. Low concentrations of ionic compounds result in high energy barriers, which prevents particles to approach the primary energy minimum located at the edge of the particle. Particles with these interaction energies repulse each other, the suspension is stable. Increasing the concentration of the ionic compound gives rise to a secondary minimum. In this stage, the energy barrier is still too high to overcome and the particles cannot reach the energetically favourable primary minimum. Hence, the particles sit either in the secondary minimum or they remain dispersed in the medium. As the energy barrier drops below  $k_BT$ , the particles are able to reach the primary minimum and slow aggregation occurs. A critical coagulation concentration is reached when the energy barrier has dropped to zero. Here, the particle may either be in the primary or secondary minimum. The particles form clusters. Increasing the concentration even more leads to very rapid clustering.

#### 6.3 Clustering experiments

The last section explained how the clustering process works. In this section some measurements are performed to prove that clustering is the cause of the long relaxation times of the spherical nickel particles.



Figure 6.4: Total interaction energy for different concentrations of the ionic compound. The number concentrations are indicated by c and given in the legend of the graph.

#### 6.3.1 Pulse length variations in the SQUID setup

In section 6.2.1 it was explained that aligned particles are more likely to cluster than random oriented particles. In the SQUID setup, the duration of the magnetic field pulse can be used to control the degree of alignment and therefore also the degree of clustering. A higher degree of alignment will cause more clustering and therefore also larger relaxation times.

To induce a difference in alignment between two measurements, it is important that one of the magnetic field pulses is shorter than the relaxation time of the sample. In section 5.3.2 it was seen that the spherical nickel particles were not relaxed within 5 s. Therefore, a measurement with a magnetic field pulse of 5 s and a measurement with a pulse of 300 s are performed. The settings are shown in table 6.1.

The measurement results are shown in figure 6.5. It can be seen that the SQUID voltage amplitudes of the measurements with short magnetic field pulses are lower than the amplitudes of the measurements with longer magnetic field pulses. This confirms that the shorter magnetic field pulse did not fully align the particles yet.

From the corresponding relaxation time plots, it can be seen that the longer pulse lengths lead to longer relaxation times. The longer relaxation times indicate larger particles.

However, it is too soon to conclude that the longer relaxation times are definitely caused by clustering effects. In section 5.5.2 it was seen that waiting 300 s after the sonication bath treatment increases the relaxation times of the particles. It is therefore possible that the larger relaxation times are not caused by increased clustering due to the better alignment of the particles, but by the same effect that also caused the increase in section 5.5.2.

	Sample	Magnetic field	Pulse
		strength $(A/m)$	duration $(s)$
Measurement F	1	800	5
Measurement G	1	800	300
Measurement H	3	800	5
Measurement I	3	800	300

Table 6.1: Settings SQUID relaxation measurement with different pulse lengths.



Figure 6.5: SQUID measurements performed with magnetic field pulses of 5 s and 300 s on spherical nickel particles of 20 nm (figure (a) and (b)) and 60 nm (figure (c) and (d)).

	Sample	Magnetic field	Pulse
		strength $(A/m)$	duration $(s)$
Measurement J	1	350	30
Measurement K	1	1600	30
Measurement L	3	350	30
Measurement M	3	1600	30

Table 6.2: Settings SQUID relaxation measurement with different magnetic field strengths.

#### 6.3.2 Magnetic field strength variations in the SQUID setup

In section 6.2.1 it was explained that aligned particles are more likely to cluster than random oriented particles. In the previous section the duration of the magnetic field pulse was varied in order to induce different degrees of alignment.

In this section the strength of the magnetic field is used to induce different degrees of alignment. As can be seen in the magnetization curves in section 5.2, higher magnetic fields lead to a higher magnetization of the sample. Magnetization is a measure of the degree of alignment of the particles, so when the magnetization is increased this will also lead to more clustering.

In the following experiment the effect of different magnetic field strengths is compared. The settings are depicted in table 6.2 and the results in figure 6.6. The results do not show a clear distinction between the relaxation times from larger and smaller magnetic fields. It looks like measurement series M has higher relaxation times than measurement series L. However, the third measurement from the M series has relaxation times comparable to the ones from the L series. The relaxation times of measurement series J and K do not show any correlation. Therefore, these measurements do not prove that the relaxation times are prolonged due to clustering.

Figure 6.7 shows an enlargement of the VSM measurements of the samples performed in section 5.2.2. Due to the hysteretic behaviour, the magnetization of the sample hardly changes between 1600 and 350 A/m. This indicates that the degree of alignment is barely changed during this measurement.

A different degree of alignment between the samples should also have been visible in the begin amplitudes of the SQUID output voltage. Higher begin amplitudes indicate more magnetization and therefore more alignment. The measurements do not show different start amplitudes between the low and high magnetic field measurements. Therefore, these measurements cannot tell us something about the degree of clustering caused by a higher magnetic field.

#### 6.3.3 DLS measurements

DLS measurements give information about the particles size and its distribution directly. DLS measurements on the spherical nickel particles were already performed in section 5.2. These measurements did not show the presence of large clusters of particles that could explain the relaxation times found. However, the DLS measurement was probably falsely interpreted. To understand why this could happen, it is necessary to explain the working of the DLS in more detail.

Particles in a liquid medium move due to Brownian motion. Larger particles move slower than smaller particles, which makes it possible to determine the size of the particle by its velocity. DLS is based on this principle.

The sample is illuminated by the use of a laser. The particles in the sample scatter



Figure 6.6: SQUID measurements performed with magnetic field strengths of 1600 A/m and 350 A/m on spherical nickel particles of 20 nm (figure (a) and (b)) and 60 nm (figure (c) and (d)).



Figure 6.7: Magnetization curves from VSM measurement in the magnetic field range used in the SQUID measurements.

this light in all directions. A screen is placed near the sample to detect the scattered light. A speckle pattern is seen on the screen, bright spots representing particles and dark spots the absence of them.

A short period in time later, another screenshot is made. The particles have now moved due to Brownian motion, which slightly changes the speckle pattern. The velocity of the particle can be calculated from the movement of the spots on the screen and corresponds to the size of the particle.

The time interval between the screenshots should be chosen with care. If the time interval is too long the screenshots would not correlate with each other, since the particles move in random direction. If the time interval is too short, no movement of the particle is detected and therefore no size is calculated. These particles are not represented in the resulting particle size distribution.

In the DLS measurement performed in section 5.2, the time interval was too short to detect particles of micrometer sizes. The particles were dispersed in glycerol, because this highly viscous medium slows down the movement of the particles, which decreases the effect of sedimentation. However, it also hinders the detection of the particles with DLS, since micrometer sized particles move too slowly to be detected with the standard time interval of the DLS.

New DLS measurements were performed to see whether there are large clusters present in the samples. To ensure the time interval of the DLS is in the right range to detect micrometer sized particles, water is used as medium instead of the more viscous glycerol. Due to the use of water, the sample is more affected by sedimentation. This makes the measurement results fluctuating more.

Next to the size, the influence of a magnetic field is also investigated. Placing the sample in a magnetic field should increase the clustering. A sample with superparamagnetic nickel particles was measured with DLS. After the DLS measurement, the sample was placed in a magnetic field for 300 s, after which another DLS measurement was done. To rule out any time effects, an identical sample was measured with the same time between the measurements as the first one. This sample had not undergone magnetic field treatment.

The results of the experiment are shown in figure 6.8. Each measurement is performed three times. Due to the use of water as a medium, the samples are unstable and fluctuate between the different measurements. This makes it hard to compare the before and after measurements. Nor the magnetic field treatment nor the time that has passed has induced a significant change in particle size that could be detected.

However, all four measurements in figure 6.8 show the presence of large micrometer sized particles. Therefore, the long relaxation times in section 5.3.2 are caused by clustering of the nanoparticles in large micrometer sized particles.



Figure 6.8: Dynamic Light Scattering (DLS) measurements performed on two identical samples of spherical nickel particles dispersed in water. Sample A is has been placed in a magnetic field for 300 s and sample B did not undergo any treatment. Both samples are measured before and after the magnetic field treatment. The magnetic field treatment did not result in significantly larger clusters. However, all measurements show the presence of micrometers sized clusters.

# Chapter 7 Conclusions

Magnetic nanoparticles are recently introduced in medicine. There are many applications where patients can benefit of their use. The focus of this research was on relaxation behaviour of superparamagnetic nanoparticles for in vitro applications like sensing and immunoassays.

A simulation model that describes the relaxation behaviour of superparamagnetic nanoparticles was developed. Special attention was paid to the shape of the particles. Cylindrical particles are thought to be more suited in the superparamagnetic regime than spherical ones, because of their shape anisotropy. Comparison of the simulations for cylindrical and spherical particles confirmed that cylindrical particles can contain more volume at the superparamagnetic limit, since the Néel relaxation time decreases with increasing aspect ratio. The increase of magnetic material leads to a higher magnetic response, which means a better performance. However, the effect of the increased magnetic moment can be cancelled by surface effects, which affect cylindrical particles more due to their increased surface to bulk ratio. Theoretical quantification of this effect was outside the scope of this research, but VSM measurements of our home-made cylindrical nickel particles indicate that the increased volume of magnetic material cannot compensate for the loss due to surface effects. This indicates that the use of cylindrical particles in the superparamagnetic regime decreases the magnetic response. On the other hand, the increased surface to bulk ratio of the cylindrical particles results in more space to attach biomarkers to. Cylindrical particles also show higher Brownian relaxation time, since this increases with aspect ratio.

The simulation model describes the relaxation behaviour. Investigation of the relaxation behaviour is a possible method to determine viscosity or particle size changes in biological samples. Simulations show that relaxation times change significantly when the size of the particle changes. Simulations also show that relaxation times change with changing viscosity of the medium. However, the latter only occurs at Brownian relaxation behaviour. For applications of viscosity measurements, the magnetic nanoparticles should therefore be selected to have the proper size for Brownian relaxation.

The simulation model was tested with two different experimental setups i.e. a SQUID magnetometer measuring the relaxation as a function of time and a differential transformer measuring the susceptibility as a function of frequency. The simulation model for spherical particles was tested with iron oxide particles and with nickel particles. For the iron oxide particles, the simulation model predicted relaxation times that would fall outside of the measurement range of both setups. Indeed, no relaxation was seen in the available range.

The spherical nickel particles were dispersed in both water and glycerol. The SQUID setup showed relaxation times that were much larger than expected from the simulation model for all configurations. Moreover, relaxation times within the measurable range were expected in the susceptibility setup for glycerol, but no relaxation was observed. The water samples could not be measured with the differential transformer setup. Additional measurements with both setups showed that the measurements for spherical nickel particles changed over time. This instability is mainly caused by sedementation of the particles and possibly by clustering. The sedimentation rate of the particles indicates the presence of micrometer sized clusters of particles. DLS measurements confirmed the presence of micrometersized clusters, which are known for their larger relaxation times. Cluster formation prevented confirmation of the relation of the relaxation time on the particle size with experiments. Comparison of the water and glycerol samples showed a dependence of the relaxation time on the viscosity of the medium.

Unfortunately, the cylindrical nickel particles were ferromagnetic instead of superparamagnetic. Therefore, the simulation model for cylindrical particles could not be verified. Moreover, comparison of the spherical and the cylindrical model revealed an inconsistency between the models. The cylindrical model showed a decrease of Néel relaxation time with increasing aspect ratio, resulting in a larger volume for cylindrical particles at the superparamagnetic limit. Quantifying these results, the spherical particle was allowed to have more volume than the cylindrical particle at the superparamagnetic limit. This inconsistency is probably caused by approximations and simplifications in the surface and shape anisotropy.

It is possible to use the SQUID setup for relaxation measurements. The SQUID setup gives a measure of the decay of the magnetic moment over time. These results are easily quantified, which gives the relaxation time. A change in relaxation time due to the presence of different particle sizes is easily seen. The SQUID setup is able to detect small quantities of magnetic material. In this study 8 ng of nickel particles placed about 23 mm from the detection coil were easily detected.

It is also possible to use the susceptibility setup for relaxation measurements. The susceptibility is measured as a function of the frequency of an AC magnetic field. The relaxation time is easily identified as the point at which the real and imaginary susceptibility intersect. The setup can identify relaxation times between 0.2 ms and 16 s. However, there is a lot of sample material needed, which also has to be stable for several hours.

The best relaxation measurements are performed with spherical superparamagnetic nanoparticles, since they show a higher magnetic response than cylindrical ones. Particles should be as large as possible, since this significantly reduces the surface effects and results in higher saturation magnetization. The SQUID setup is most promising for relaxation measurements, since this setup is very sensitive and can detect small amounts of magnetic material. The SQUID measurement is also much faster than the susceptibility measurement. However, the SQUID setup should be improved, since the 'dead time' is too long to measure in low viscous media like blood. Fortunately, there is still room left to shorten the 'dead time'.

### Chapter 8

### Recommendations

Reliable in vitro diagnostics can only be done with stable particles. The spherical nickel particles showed sedimentation, which changes the characteristics of the sample over time. Since the sedimentation effects and the relaxation effects cannot be distinguished, the sedimentation should be decreased significantly, so the effect on the measurement is negligable.

The spherical nickel particles also show clustering. This is an often seen problem with magnetic nanoparticles. It would therefore be very useful if more research is done on this subject. This research should then come up with effective methods to prevent clustering of magnetic nanoparticles.

Improving the stability of the particles will also have positive effects on their description by the simulation model, since the simulation model does not include sedimentation and clustering effects. Moreover, the model needs improvement for the quantitative description. It was seen that the spherical and cylindrical model do not match quantitatively. This is probably due to approximations in the description of the surface and shape anisotropy. Further research on the surface and shape anisotropies can significantly improve the model. Besides, the findings can be used to quantify the influence of surface effects to the saturation magnetization of magnetic nanoparticles. This is very useful for the design of particles for various applications.

The main limitation of the SQUID setup is the 'dead time' before the start of the measurement. If the SQUID is ever used for relaxation measurements of superparamagnetic nanoparticles in low viscous media like blood or other body fluids, the 'dead time' should be well below 1 ms. Otherwise these superparamagnetic nanoparticles will be completely relaxed before the measurement starts. Also, the flux jumps that sometimes occur during measurements should be eliminated. Software can be written to correct for the flux jumps. However some flux jumps are so big that they drive the setup outside its limits. The measurement then needs to be repeated, which is very undesirable for the use in biological samples.

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## Appendix A

# List of symbols

Symbol	Description	Units
A	Magnetic vector potential	Vs/m
A	Hamakers constant	
a	Radius of sample	m
B	Magnetic field	Т
b	Radius of detection coil	m
c	Number concentration	$1/\mathrm{m}^3$
d	Diameter	m
$d_c$	Single domain limit	m
$d_s$	Superparamagnetic limit	m
E	Energy density	$\mathrm{J/m^3}$
$\Delta \varepsilon$	Energy barrier	J
ε	Energy	J
F	Fill factor	
g	Spectroscopic splitting factor	
g	Gravitational acceleration	$m/s^2$
h	Height	m
H	Magnetic field	A/m
$H_{in}$	Internal magnetic field	A/m
$H_d$	Demagnetization field	A/m
$H_K$	Anisotropy field	A/m
Ι	Current	А
J	Total angular momentum	
$k_B$	Boltzmann constant	J/K
K	Anisotropy constant	$\mathrm{J/m^3}$
L	Orbital angular momentum	
L	Inductance	Η
$\mathbf{M}$	Magnetization vector	A/m
m	Unit vector of magnetizaton	
m	Mean of diameter	m
M	Mutual inductance	Η
$M_s$	Saturation magnetization	A/m
$M_V$	Molair volume	$\mathrm{m}^{3}/\mathrm{mol}$
$\mathbf{n}$	Unit vector normal to a plane	
N	Demagnetization factor	

Symbol	Description	Units
N <sub>A</sub>	Avogadro's constant	1/mol
$N_p$	Number of atoms per unit volume	$1/m^3$
n	Normal vector	
p	Ratio between height and diameter of a cylinder	
$ ilde{p}$	Ratio between hydrodynamic height	
	and diameter of a cylinder	
R	Radius	m
S	Spin angular momentum	
T	Temperature	Κ
t	Time	s
$t_{mag}$	Magnetization time	s
u	Sedimentation rate	m/s
V	Voltage	V
V	Volume	$\mathrm{m}^3$
$ ilde{V}$	Hydrodynamic volume	$\mathrm{m}^3$
v	Variance of diameter	m
z	Charge	
$\delta_{\perp}$	Correction for end-effect in cylinder	
$\epsilon$	Permittivity	$s^4 A^2/(m^3 kg)$
$\eta$	Viscosity	Pa s
$\theta$	Angle between the z-axis and the magnetization	rad
$\mu$	Mean of natural logaritm of $d$	
$\mu_0$	Permeability of free space	$m kg/(s^2 A^2)$
$\mu_B$	Magnetic moment of an electron	$Am^2$
$\mu_H$	Magnetic moment of a atom or molecule	$Am^2$
$\mu_{NP}$	Magnetic moment of a nanoparticle	$\mathrm{Am}^2$
$\Phi$	Magnetic flux	Wb (Vs)
$\phi$	Angle between x-axis and component of	rad
	magnetization in the xy-plane	- / 2
ho	Density	kg/m <sup>3</sup>
$\sigma$	Standard deviation of natural logarithm of $d$	
$ au_0$	Attempt time	S
$ au_{eff}$	Effective relaxation time	S
$ au_N$	Neel relaxation time	S
$ au_B$	Brownian relaxation time	S
$\chi$	Susceptibility (of particle)	
$\chi_{in}$	Susceptibility (material constant)	3.7
Ψ	Electrostatic potential	V
ω	Frequency	Hz
$\omega_{char}$	Characteristic frequency	Hz

### Appendix B

### Multipole expansion

The vector potential of this system in point p in space can be calculated by [43]

$$\mathbf{A}(\mathbf{r}) = \frac{\mu_0}{4\pi} \int \frac{\mathbf{I}}{s} dl = \frac{\mu_0}{4\pi} I \oint \frac{1}{s} d\mathbf{l},\tag{B.1}$$

where I represents the current in the loop and s is the distance between the border of the sample and point p, described by

$$\frac{1}{s} = \frac{1}{\sqrt{r^2 + a^2 - 2ar\cos\theta'}} = \frac{1}{r} \sum_{n=0}^{\infty} \left(\frac{a}{r}\right)^n P_n(\cos(\theta')$$
(B.2)

where  $P_n(x)$  represents the Legendre polynomial and  $r = \sqrt{d^2 + b^2}$ , with b the radius of the pick-up coil, d the distance between the sample and the pick-up coil. This turns the vector potential into a multipole expansion

$$\mathbf{A}(\mathbf{r}) = \frac{\mu_0 I}{4\pi} \Big[ \frac{1}{r} \oint d\mathbf{l} + \frac{1}{r^2} \oint a \cos \theta' d\mathbf{l} + \frac{1}{r^3} \oint a^2 \Big( \frac{3}{2} \cos \theta' - \frac{1}{2} \Big) d\mathbf{l} + \dots \Big], \tag{B.3}$$

where the first term is called the monopole term, the second dipole, the third quadrupole and the fourth octupole. The monopole term vanishes and for small sample radii the dipole term dominates the equation and the quadrupole term can be ignored. However, in our case the radius of the sample and the pick-up coil are of the same order of magnitude. Therefore, the terms after the dipole term cannot be neclegted.

The multipole terms are worked out separately.

#### Dipole

The dipole term is described as

$$\mathbf{A}_{\mathbf{dip}}(\mathbf{r}) = \frac{\mu_0 I}{4\pi} \frac{1}{r^2} \oint a \cos \theta' d\mathbf{l} = \frac{\mu_0 I}{4\pi} \frac{1}{r^2} \oint \frac{\mathbf{a} \cdot \mathbf{r}}{||\mathbf{r}||} d\mathbf{l} = \frac{\mu_0 I}{4\pi} \frac{1}{r^2} \oint (\mathbf{a} \cdot \hat{\mathbf{r}}) d\mathbf{l}$$
  
$$= \frac{\mu_0 I}{4\pi} \frac{1}{r^2} \left( -\hat{\mathbf{r}} \times \int d\mathbf{S} \right) = \frac{\mu_0}{4\pi} \frac{\mathbf{m} \times \hat{\mathbf{r}}}{r^2},$$
(B.4)

#### Quadrupole

The quadrupole term is described as

$$\mathbf{A_{quadr}}(\mathbf{r}) = \frac{\mu_0 I}{4\pi} \frac{1}{r} \oint \frac{a^2}{r^2} \left(\frac{3}{2} \cos^2 \theta' - \frac{1}{2}\right) d\mathbf{l} = \frac{\mu_0 I}{4\pi} \frac{1}{r^3} \left[\frac{3}{2} \oint \left(\mathbf{\hat{r}} \cdot \mathbf{a}\right)^2 d\mathbf{l} - \oint \frac{1}{2} a^2 d\mathbf{l}\right]$$
(B.5)

The second term vanishes because the integral is just the vector displacement around a closed loop,  $\oint d\mathbf{l} = 0$ . The vector potential of the quadrupole becomes

$$\mathbf{A_{quadr}}(\mathbf{r}) = \frac{\mu_0 I}{4\pi} \frac{1}{r^3} \frac{3}{2} \int_0^{2\pi} \frac{a^3 b^2}{4r^2} \left(1 - \sin 2\phi\right) \sin^2 2\theta d\theta \hat{\theta} = \frac{3\mu_0 I a^3 b^2}{32r^5} \left(1 - \sin 2\phi\right) \hat{\theta}.$$
(B.6)

#### Octupole

The octupole term can be written as

$$\mathbf{A_{oct}}(\mathbf{r}) = \frac{\mu_0 I}{4\pi} \frac{1}{r} \oint \frac{a^3}{r^3} \frac{1}{2} \left( 5\cos^3\phi - 3\cos\phi \right) d\mathbf{l}$$
  
$$= \frac{\mu_0 I}{4\pi} \frac{1}{2r^4} \left[ 5 \oint (\mathbf{\hat{r}} \cdot \mathbf{a})^3 d\mathbf{l} - 3 \oint a^2 (\mathbf{\hat{r}} \cdot \mathbf{a}) d\mathbf{l} \right] = -\frac{\mu_0}{4\pi} \frac{3a^2}{2r^4} (\mathbf{m} \times \mathbf{\hat{r}})$$
(B.7)

with  $\mathbf{r} = b \cos \phi \hat{x} + b \sin \phi \hat{y} + d\hat{z}$  and  $\mathbf{a} = a \cos \theta \hat{x} + a \sin \theta \hat{y}$ . The first term  $(\mathbf{\hat{r}} \cdot \mathbf{a})^3$  can be described as

$$(\hat{\mathbf{r}} \cdot \mathbf{a})^3 = \frac{a^3 b^3}{8r^3} (\sin \phi - \cos \phi - \sin 2\phi \sin \phi + \cos 2\phi \cos \phi) \sin^3 2\theta.$$
(B.8)

Integrating gives

$$\int_{0}^{2\pi} a(\hat{\mathbf{r}} \cdot \mathbf{a})^{3} d\theta = \frac{A^{3}b^{3}}{8r^{3}} \left(\sin\phi - \cos\phi - \sin 2\phi\sin\phi + \cos 2\phi\cos\phi\right) \frac{1}{24} \left(\cos 6\theta - 9\cos 2\theta\right) \Big]_{0}^{2\pi} = 0.$$
(B.9)

So the first tern in equation B.7 vanishes, which reduces the vector potential of the octupole to

$$\mathbf{A_{oct}}(\mathbf{r}) = -3\frac{\mu_0 I}{4\pi} \frac{1}{2r^4} \oint a^2 (\mathbf{\hat{r}} \cdot \mathbf{a}) d\mathbf{l} = -\frac{\mu_0}{4\pi} \frac{3a^2}{2r^4} (\mathbf{m} \times \mathbf{\hat{r}})$$
(B.10)

#### Hexadecapole

The hexadecapole can be described as

$$\mathbf{A}_{\mathbf{hex}}(\mathbf{r}) = \frac{\mu_0 I}{4\pi} \frac{1}{r} \oint \frac{a^4}{r^4} \frac{1}{8} \left( 35 \cos^4 \phi - 30 \cos^2 \phi + 3 \right) d\mathbf{l}$$
  
$$= \frac{\mu_0 I}{4\pi} \frac{1}{8r^5} \left[ 35 \oint (\mathbf{\hat{r}} \cdot \mathbf{a})^4 d\mathbf{l} - 30a^2 \oint (\mathbf{\hat{r}} \cdot \mathbf{a})^2 d\mathbf{l} + 3a^4 \oint d\mathbf{l} \right].$$
(B.11)

Again, the third term vanishes. With

$$(\hat{\mathbf{r}} \cdot \mathbf{a})^2 = \frac{a^2 b^2}{4r^2} (1 - \sin 2\phi) \sin^2 2\theta \hat{\theta}$$
(B.12)

and

$$(\hat{\mathbf{r}} \cdot \mathbf{a})^4 = \frac{a^4 b^4}{16r^4} (1 - \sin 2\phi)^2 \sin^4 2\theta \hat{\theta}, \tag{B.13}$$

the vector potential can be rewritten as

$$\mathbf{A}_{\mathbf{hex}}(\mathbf{r}) = \frac{\mu_0 I}{32r^5} \Big[ 35 \frac{a^5 b^4}{16r^4} (1 - \sin 2\phi)^2 \frac{3}{4} - 30 \frac{a^5 b^2}{4r^2} (1 - \sin 2\phi) \Big] \hat{\theta}$$
(B.14)

#### Dotriacontapole

The dotriacontapole can be described as

$$\begin{aligned} \mathbf{A_{dot}}(\mathbf{r}) &= \frac{\mu_0 I}{4\pi} \frac{1}{r} \oint \frac{a^5}{r^5} \frac{1}{8} \left( 63\cos^5\phi - 70\cos^3\phi + 15\cos\phi \right) d\mathbf{l} \\ &= \frac{\mu_0 I}{4\pi} \frac{1}{8r^6} \Big[ 63 \oint a^5\cos^5\phi d\mathbf{l} - 70a^2 \oint a^3\cos^3\phi \mathbf{l} + 15a^4 \oint a\cos\phi d\mathbf{l} \Big] \quad (B.15) \\ &= \frac{\mu_0 I}{4\pi} \frac{1}{8r^6} \Big[ 63 \oint \left( \hat{\mathbf{r}} \cdot \mathbf{a} \right)^5 d\mathbf{l} - 70a^2 \oint \left( \hat{\mathbf{r}} \cdot \mathbf{a} \right)^3 \mathbf{l} + 15a^4 \oint \left( \hat{\mathbf{r}} \cdot \mathbf{a} \right) d\mathbf{l} \Big]. \end{aligned}$$

Again,  $\oint (\hat{\mathbf{r}} \cdot \mathbf{a})^3 d\mathbf{l} = 0$  and also

$$\oint (\hat{\mathbf{r}} \cdot \mathbf{a})^5 d\mathbf{l} = \oint \frac{a^6 b^5}{32r^5} (1 - \sin^2 2\phi)^2 (\sin \phi - \cos \phi) \sin^5 2\theta d\theta$$
  
=  $\frac{a^6 b^5}{32r^5} (1 - \sin^2 2\phi)^2 (\sin \phi - \cos \phi) \frac{1}{480} (-150\cos 2\theta + 25\cos 6\theta - 3\cos 10\theta) \Big]_0^{2\pi}$   
= 0. (B.16)

So what remains for the vector potential of the dotria contapole is

$$\mathbf{A_{dot}}(\mathbf{r}) = \frac{\mu_0}{4\pi} \frac{15a^4}{8r^6} \mathbf{m} \times \hat{\mathbf{r}}.$$
(B.17)

#### Total vector potential

The total vector potential of the first six multipole terms can be written as

$$\mathbf{A}(\mathbf{r}) = \frac{\mu_0}{4\pi} \frac{\mathbf{m} \times \hat{\mathbf{r}}}{r^2} + \frac{3\mu_0 I a^3 b^2}{32r^5} (1 - \sin 2\phi) \hat{\theta} - \frac{\mu_0}{4\pi} \frac{3a^2}{2r^4} (\mathbf{m} \times \hat{\mathbf{r}}) + \frac{\mu_0 I}{32r^5} \Big[ 35 \frac{a^5 b^4}{16r^4} (1 - \sin 2\phi)^2 \frac{3}{4} - 30 \frac{a^5 b^2}{4r^2} (1 - \sin 2\phi) \Big] \hat{\theta} + \frac{\mu_0}{4\pi} \frac{15a^4}{8r^6} \mathbf{m} \times \hat{\mathbf{r}} = \frac{\mu_0 I}{32r^5} (1 - \sin 2\phi) \Big( 3a^3 b^2 - 30 \frac{a^5 b^2}{r^2} + 35 \frac{3a^5 b^4}{64r^4} (1 - \sin 2\phi) \Big) \hat{\theta} + \frac{\mu_0}{4\pi} \Big( \frac{1}{r^2} - \frac{3a^2}{2r^4} + \frac{15a^4}{8r^6} \Big) \mathbf{m} \times \hat{\mathbf{r}}$$
(B.18)
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