Master thesis

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Tuning the Self-Organization of Iron Oxide Nanoparticles in Solution

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Abstract

The magnetic relaxation behaviour of magnetic nanoparticles in dispersions is the subject of extensive investigations for a range of medical applications, including magnetic particle imaging (MPI), hyperthermia and biosensing. The magnetic relaxation behaviour of magnetic nanoparticles can be divided into Néel and Brown relaxation. This thesis examines the distinction between Néel relaxation and Brownian relaxation in a wide temperature range for iron oxide nanoparticles of sizes between 10 nm and 20 nm, which are dispersed in two different solvents, i.e. water or toluene.

For nanoparticles dispersed in water, a blocking of the Brownian relaxation was observed in the frozen state using zero field cooled (ZFC)/field cooled (FC) measurements. Furthermore, disruption of the nanoparticle arrangement due to crystallisation effects during supercooled freezing was observed with ZFC/FC measurements, ACsusceptibility measurements and small angle X-ray scattering (SAXS).

For nanoparticles dispersed in toluene, a similar blocking of the Brownian relaxation is observed in the frozen state with ZFC/FC measurements. For nanoparticles with a diameter of approximately 10 nm, partial Brownian relaxation is observed even in the frozen state. This phenomenon is likely due to the formation of a thin film of molten toluene around the nanoparticles, which arises from surface interactions between the nanoparticles and the toluene. A further finding of this thesis is the observation of a "Brownian relaxation peak" during the ZFC/FC curve, which exhibits a similar behaviour to the "Néel relaxation peak" that is typically observed in ZFC/FC curves of magnetic nanoparticles.

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1. Introduction

Since P. Feynman's famous lectures "There's Plenty of Room at the Bottom" in 1959 nanoscale technology has been of great scientific interest. Specifically magnetic nanoparticles are in the focus of intense research because of a multitude of already existing and potential applications. Such as a variety of application in ferrofluids [1]–[3], uses in electrochemical sensing [4]–[6], utilisation in wastewater treatment [7] and a multitude of uses in biomedicine.

To enhance the efficacy of biomedical applications such as hyperthermia treatments, magnetic particle imaging, and biosensing [8]–[11] numerous studies have been conducted on magnetic nanoparticles. In the context of bioassays utilising magnetic markers, a distinction was observed between the Brownian relaxation of the bound and unbound markers [12], [13]. Furthermore, the use of the binding-induced modification of Brownian relaxation of magnetic nanoparticles for biological sensing was also investigated [14].

Brownian relaxation has been studied in many ways. Ota and Takemura investigated the superimposed Néel and Brownian relaxation to characterize these in isolation [15]. Lucchini and Canepa measured Brownian relaxation of magnetic nanoparticles dispersed in a variety of solvents [16]. Tu et al. studied the detection of Néel and Brownian relaxation using a mixed frequency method [17] and Dieckhoff et al. examined the field dependence of Néel and Brownian relaxation [18].

The objective of this thesis is to investigate the distinction between Néel relaxation and Brownian relaxation of nanoparticle dispersions, with a focus on the temperature dependence of the magnetic and structural properties. An understanding of the temperature dependence will facilitate a more in-depth comprehension of nanoparticle dispersions at room temperature which is relevant for medical applications. Moreover, since the Brownian relaxation is blocked when the solvent is frozen, this allows for a straightforward comparison of Néel relaxation in isolation and hence a comparison to the case of the combination of Néel and Brownian relaxation.

The magnetic properties of the nanoparticles were studied using zero-field-cooled (ZFC) /field-cooled (FC) measurements, which allows for the characterization of the magnetic properties over a wide temperature range. Hysteresis measurements and AC-susceptibility measurements were employed for supplementary analysis. Transmission electron microscopy (TEM) and small-angle X-ray scattering (SAXS) were utilized to investigate the structural properties. These techniques enable the characterization of the nanoparticles' size and polydispersity. Furthermore, SAXS measurements with applied magnetic field and during cooling and heating were conducted to investigate the structural effects of the magnetic fields and the relaxation processes.

This thesis is structured into 6 chapters:

Chapter 2 provides an overview of the theoretical knowledge required for this thesis. It begins with an introduction to magnetism and the types of magnetic orders, before moving on to examine the theory of magnetic nanoparticles, their interactions and relaxation processes. Finally, it concludes with a brief discussion of scattering theory. **Chapter 3** provides an overview of the samples, the measurement instruments and the measurement methods used in this thesis. First, the nanoparticle dispersions are introduced and the process of preparing them for measurements is explained. Then the measurement procedures are described and finally the measurement instruments are introduced.

In **chapter 4** the measurement results as well as our interpretation of these results are presented. This chapter is divided into three sections: nanoparticles dispersed in water, nanoparticles dispersed in toluene, and a comparison between these samples. These are further divided into subsections where the structural properties are analysed and subsections where the magnetic properties are studied.

Finally **chapter 5** gives a summary of the results of our thesis and **chapter 6** gives an outlook on how these results could be used and further investigated.

2. Theoretical Background

2.1. Magnetism

2.1.1. Basics of Magnetism

In classical electromagnetism a magnetic moment $\vec{\mu}$ arises when a current I flows in a loop dS around a area A:

$$\vec{\mu} = \int \vec{d\mu} = I \int \vec{dS} = I \cdot A \tag{2.1}$$

The magnetic moment $\vec{\mu}$ of an orbiting electron is associated with its angular momentum \vec{L} by the gyromagnetic constant γ :

$$\vec{\mu} = \gamma \vec{L} \tag{2.2}$$

The orbital magnetic moment caused by an electron orbiting an atom is given by

$$\vec{\mu_L} = -g_L \mu_B \frac{\vec{L}}{\hbar} \tag{2.3}$$

where $\hbar \approx 1.055 \cdot 10^{-34}$ is the reduced Planck's constant, $\mu_B \approx 9.274 \cdot 10^{-24} \text{Am}^2$ is the Bohr magneton and g_L is the electron orbital g-factor which is given by [19]:

$$g_L = 1 - \frac{m_e}{m_N} \tag{2.4}$$

where m_e is the electron mass and m_N the mass of the nucleus. The electron also possesses an intrinsic angular momentum S called the spin. This gives rise to the spin magnetic moment given by:

$$\vec{\mu_S} = -g_S \mu_B \frac{\vec{S}}{\hbar} \tag{2.5}$$

where $g_S \approx 2.002319$ is the spin g-factor. The spin of an electron can take the two quantum states $m_S = \pm \frac{1}{2}$ with an angular momentum along a given axis z of:

$$S_z = \hbar m_S \tag{2.6}$$

This means that the spin magnetic moment along z can take the values:

$$\mu_{S_z} = -g_S \mu_B m_S \tag{2.7}$$

Magnetic materials contain a large number of atoms, each possessing a magnetic moment. To describe macroscopic systems, the magnetization M is defined as the magnetic moment per unit volume. Together with the magnetic field strength \vec{H} the magnetization \vec{M} gives the magnetic flux density \vec{B} by:

$$\vec{B} = \mu_0 (\vec{H} + \vec{M})$$
 (2.8)

Where $\mu_0 = 4\pi \cdot 10^{-7}$ Hm⁻¹ is the vacuum permeability. The relationship between M and H can be described via the susceptibility χ in the linear response approximation:

$$\vec{M} = \chi \vec{H} \tag{2.9}$$

Any magnetic moment $\vec{\mu}$ inside a magnetic field \vec{B} will have a potential energy E_{Zeeman} given by:

$$E_{Zeeman} = -\vec{\mu} \cdot B \tag{2.10}$$

2.1.2. Magnetic Susceptibility

2.1.2.1. Diamagnetism

Diamagnetism is a quantum mechanical phenomenon that generates a weak magnetic moment in a material, which acts to oppose an external magnetic field ($\chi < 0$). Diamagnetism is present in all materials, though it is often overshadowed by the stronger magnetic effects discussed below.

2.1.2.2. Paramagnetism

Paramagnetism is a phenomenon where two effects compete. Firstly, the magnetic moments in a material align with an external magnetic field. Secondly, the alignment is destroyed by thermal fluctuations. The magnetic moments arise from the presence of unpaired electrons whose spins and orbital motion generate a total magnetic moment for each atom. The alignment of these magnetic moments enhances the materials overall magnetization ($\chi > 0$).

2.1.3. Magnetic interactions

2.1.3.1. Magnetic dipolar interaction

A fundamental property of magnetic dipoles is that they generate a magnetic field and respond to external magnetic fields. Consequently, magnetic dipoles interact with one another. The energy of the interaction between two dipoles, $\vec{\mu_1}$ and $\vec{\mu_2}$, with a relative position to each other given by \vec{r} , can be expressed as follows [20]:

$$E_{dd} = \frac{\mu_0}{4\pi} \left(\frac{\vec{\mu_1} \cdot \vec{\mu_2}}{r^3} - \frac{3(\vec{\mu_1} \cdot \vec{r})(\vec{\mu_2} \cdot \vec{r}))}{r^5} \right)$$
(2.11)

For the interaction of spins of neighbouring atoms, the values can be estimated as $|\vec{\mu_1}| = |\vec{\mu_2}| \approx \mu_B$ and $\vec{r} \approx 0.1$ nm. If the spins are aligned this results in an energy

 $|E_{dd}| \approx 0.1$ meV. This energy corresponds to a temperature of about 1 K. This indicates that the magnetic dipole interaction is insufficient to align spins at regular temperatures. However for interacting nanoparticle moments this contribution can become significant as shown below.

2.1.3.2. Exchange interactions

The exchange interactions between electrons arise from two fundamental principles: Coulomb interactions and the Pauli exclusion principle. According to the Heisenberg uncertainty principle, electrons bound to an atom can reduce their kinetic energy by decreasing their localisation, causing them to spread out to neighbouring atoms. However, the Pauli exclusion principle prevents two electrons from occupying the same state. As a result, the wave function of two electrons in neighbouring atoms must be either spatially antisymmetric and spin symmetric or spatially symmetric and spin antisymmetric. The Coulomb interactions in the surrounding atoms determine whether a symmetric or antisymmetric spatial distribution is energetically favorable, leading to either antisymmetric or symmetric spin ordering, respectively. Exchange interactions can be categorized into different types:

Direct exchange interaction

Direct exchange interaction originates from the direct Coulomb interaction between electrons on neighbouring atoms or ions. This interaction does not require any intermediary, but needs sufficient direct overlap between neighbouring magnetic orbitals. **Indirect exchange interactions**

Indirect exchange Interactions are mediated through an intermediary such as conduction electrons or anions in the lattice. Types of indirect exchange interactions include: **Superexchange:** Occurs when the exchange interaction is mediated through an intermediate non-magnetic ion situated between two non-neighbouring magnetic ions. **Double exchange:** Double exchange occurs between ions with different valence states. For electrons to delocalize using the vacancies in neighbouring ions, the spins of these ions must be aligned approximation.

of these ions must be aligned symmetrically. Since delocalization decreases energy, this causes an exchange interaction that aligns spins in the neighbouring ions parallely.

RKKY interaction: The RKKY (Ruderman-Kittel-Kasuya-Yosida) interaction is present when localized magnetic moments spin-polarize conduction electrons. These spin-polarized conduction electrons then couple to a neighbouring localized magnetic moment at a distance r away. Assuming a spherical Fermi surface of radius k_F , this coupling is given by [20]:

$$J_{RKKY}(r) \propto \frac{\cos(2k_F r)}{r^3} \tag{2.12}$$

In this expression, J(r) represents the exchange interaction strength as a function of distance r, and k_F is the Fermi wave vector. The oscillatory nature of the cosine term reflects the fact that the interaction can cause either parallel or antiparallel alignment depending on the distance between the localized moments.

2.1.4. Magnetic order

2.1.4.1. Ferromagnetism

In a ferromagnet, exchange interactions favor spin states that are aligned in parallel, leading to spontaneous local magnetization even in the absence of an external field. In materials of considerable size the formation of magnetic domains can be energetically favorable. In these magnetic domains the spins are aligned parallely to reduce the exchange interaction energy, but the spins in other domains may be aligned differently. This means there must be domain walls between the domains where the exchange interaction energy is not minimised. Magnetic domains can be energetically favorable despite this because they can minimise other energies like the demagnetisation energy. With the application of an external field domains that are aligned with the field grow. If the field is sufficiently strong, this process will continue until the entire material has become a single magnetic domain. In the case of smaller fields, domain growth is reversible. However a strong external field can result in the domain wall crossing a crystal defect. In this case the domain remains pinned at the defect until a sufficiently large field in the opposite direction is applied. This phenomenon results in ferromagnets retaining their remanent magnetization following exposure to a strong external field.

2.1.4.2. Antiferromagnetism

Antiferromagnetism is a phenomenon whereby the exchange interaction favours an antiparallel alignment of the magnetic moments of neighbouring atoms. This typically divides the material into two sublattices with magnetic moments aligned in opposite directions, resulting in the cancellation of the magnetic moments and a net magnetization of zero at zero applied magnetic field.

The response of an antiferromagnet to an external field is dependent on the alignment of the field relative to the magnetic moments within the sublattices. If the field is perpendicular to the magnetic moments of both sublattices, the moments will tilt, resulting in a net magnetization. Conversely, if the field is parallel to one sublattice and antiparallel to the other, the changes in the magnetization of the two sublattices will cancel each other out, maintaining a net magnetization of zero. However, if the field is sufficiently strong, it can overcome the exchange interaction, causing the antiparallel sublattice to flip.

2.1.4.3. Ferrimagnetism

Ferrimagnetism occurs when the magnetic moments in a material align like antiferromagnets, but the magnetic moments in the different sublattices are not equal, resulting in a net magnetization. Ferrimagnets exhibit many similarities to ferromagnets, including spontaneous magnetization and domain formation. However, ferrimagnets often show more complex temperature dependencies, as the magnetic moments in the different sublattices can have significantly different responses to temperature changes.

2.1.4.4. Spin glass

A spin glass is a non-magnetic material that is sparsely populated with a dilute, random distribution of magnetic atoms. The magnetic moments of these magnetic atoms are only able to interact via long-ranged interactions, such as the RKKY interaction. As demonstrated in eq. 2.12, this interaction oscillates in sign depending on the distance between the magnetic moments. This results in a system that is frustrated, with no well-defined ground state, but a multitude of alternative possible ground states.

2.1.5. Magnetic anisotropy

Magnetic anisotropy refers to the phenomenon whereby the magnetization of a material can have a different energy cost depending on the direction. In this case, the axis with the lowest energy cost is referred to as the easy axis, and the axis with the highest energy cost is referred to as the hard axis. Magnetic anisotropy can be caused by a number of factors. For example, magnetocrystalline anisotropy is caused by the symmetry of the crystal lattice, which induces a preferred magnetization direction. For ferromagnetic materials, the magnetic anisotropy energy caused by this effect can be approximated as [21]:

$$E_a = KV\sin^2(\theta) \tag{2.13}$$

where K is the anisotropy constant and θ is the angle between the magnetization and the anisotropy (i.e. easy) axis.

Magnetic anisotropy can also be caused by shape and surface effects. These are especially important for small-scale systems, such as nanoparticles, which are the subject of this thesis. Shape anisotropy is caused by the demagnetization field induced by the magnetic moments inside the material. The demagnetization energy of this field can be written as:

$$E_{d} = -\frac{\mu_{0}}{2} \int \vec{M} \vec{H_{dm}} dV$$
 (2.14)

where \vec{M} is the magnetization and $\vec{H_{dm}} = -\vec{N}\vec{M}$ is the demagnetization field induced by the magnetic moments inside the material with \vec{N} being the demagnetization tensor.

The effective surface anisotropy for a spherical particle can be described by [21]:

$$K_{eff} = K_V + \frac{6}{d}K_S \tag{2.15}$$

where d is the diameter of the particle, K_S describes the surface anisotropy and K_V is the volume anisotropy consisting of multiple contributions like magnetocrystalline anisotropy and shape anisotropy.

2.2. Magnetic Nanoparticles

Magnetic nanoparticles are solid state particles, typically ranging from a few nanometers to several hundred nanometers in size, that exhibit magnetic properties. These nanoparticles can be composed of various magnetic materials, which in this thesis is iron oxide, and often possess unique magnetic behaviors due to their size and composition. The following sections will briefly introduce some key aspects of magnetic nanoparticles.

2.2.1. Superparamagnetism

This thesis will study only spherical nanoparticles with a size between 10 and 20 nm, made from ferromagnetic and ferrimagnetic materials. For nanoparticles smaller than the critical singe-domain radius [20] it is energetically favourable to only form one magnetic domain. If, in addition, the spins in a single domain particle reverse their magnetization via coherent rotation, the magnetic moment of the entire nanoparticle can be described as one single large magnetic moment, usually referred to as superspin. For an ellipsoidal particle the energy of such a system is described by the Stoner-Wolfarth model [22]:

$$E = KV\sin^{2}(\theta) - \frac{1}{2}\mu_{0}M_{S}^{2}(N_{\perp} - N_{\parallel})\sin^{2}(\Psi) - \mu_{0}HM_{S}V\cos(\alpha - \theta)$$
(2.16)

where K is the magnetocrystalline anisotropic constants θ is the angle between magnetocrystalline anisotropy axis and the superspin moment, α is the angle between magnetocrystalline anisotropic axis and the external field H, V is the volume, M_S is the saturation magnetization, N_{\perp} and $N \parallel$ are the demagnetization factors perpendicular and parallel to the symmetry axis of the ellipsoid and Ψ is the angle between shape symmetry axis and the superspin moment.

In a simplified case for a spherical particle $(N_{\perp} = N_{\parallel})$ without an external field (H=0) this equation simplifies to:

$$E = KV\sin^2(\theta) \tag{2.17}$$

This equation has two minima at $\theta = 0^{\circ}$ and $\theta = 180^{\circ}$ representing two superspin states. Between these two states there is an energy barrier $\Delta E = KV$, which must be overcome for the superspin to flip. An ensemble of non-interacting single-domain nanoparticles with an energy barrier ΔE that is below or similar to the thermal energy k_bT is called superparamagnetic.

2.2.2. Blocking temperature

The process by which the superspins within a nanoparticle flip in order to return to an energetically favourable ground state is referred to as Néel relaxation. The characteristic relaxation time τ_{SPM} for Néel relaxation of a superparamagnetic particle due to thermal activation over an energy barrier $\Delta E = KV$ can be described by the Arrhenius law:

$$\tau_{SPM} = \tau_0 \exp\left(\frac{KV}{k_B T}\right) \tag{2.18}$$

Hereby $k_B \approx 1,381 \cdot 10^{-23} \frac{J}{K}$ is the Boltzmann constant, T is the temperature and τ_0 is the elementary spin flip time, which is usually assumed to be in the order of 10^{-12} s to 10^{-9} s. It is important to note that this prefactor is not a constant and depends on both the field and temperature [22].

This relaxation time can change greatly depending on the temperature. For example, a particle with $\tau_0 \approx 10^{-9}$ and $\frac{KV}{k_B} = 315$ K can have relaxation times between 10^{+18} s and 10^{-9} s in the temperature rang of 5 K to 300 K.

This implies that at high temperatures, the superspins flip almost instantaneously, while at lower temperatures, they hardly flip at all. Consequently, it is practical to differentiate between temperatures at which the superspins are "blocked" and those at which they fluctuate freely. The blocking temperature T_B is defined as the temperature at which the relaxation time τ matches the measurement time τ_m Using eq. 2.18 for a superparamagnet with $\tau = \tau_{SPM}$, this yields:

$$T_B = \frac{KV}{k_B \ln \frac{\tau_m}{\tau_0}} \tag{2.19}$$

It is important to note that this equation uses the assumption $\Delta E = KV$. However, for more complex particles or with an external field a more general $\Delta E(H)$ needs to be considered [22].

For an ideal superparamagnet, the blocking temperature can be determined experimentally as the peak of the zero-field-cooled curve that will be discussed in section 3.2. However, this method is not effective for systems with a complex history-dependent relaxation behavior.

2.2.3. Brownian relaxation

In addition to Néel relaxation, whereby the superspins of mechanically fixed nanoparticles flip, nanoparticles in dispersion can also relax as a result of Brownian relaxation, in which the nanoparticles can move while their superspins remain stationary relative to the nanoparticle. In the absence of an external field the characteristic relaxation time τ_B for Brownian relaxation of a nanoparticle dispersed in a solvent is determined by [23]:

$$\tau_B = \frac{3\eta V_H}{k_B T} \tag{2.20}$$

where η is the viscosity coefficient of the solvent and V_H is the hydrodynamic volume of the nanoparticle. The hydrodynamic volume is the volume of the nanoparticle including its coating which usually larger than the magnetic volume of the nanoparticle which only includes the parts of the nanoparticle which are magnetic. Because Néel relaxation and Brownian relaxation can take place in parallel the effective relaxation time τ_{eff} is given by [23]:

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_N} + \frac{1}{\tau_B} \tag{2.21}$$

where τ_N is the Néel relaxation time.

However, this assumes that Néel relaxation and Brownian relaxation are equivalent. A crucial distinction between them lies in their effects: Néel relaxation solely influences the orientation of superspins, whereas Brownian relaxation can also affect the orientation of the anisotropy axis as well as the arrangement of nanoparticles. Conversely Brownian relaxation cannot influence the angle of the superspin to the anisotropy axis.

2.2.4. Interactions of magnetic nanoparticles in dispersion

The interactions between magnetic nanoparticles (MNPs) in dispersion are complex, due to the combined effects of magnetic forces, thermal motion, and the medium's properties. These interactions significantly influence the stability, aggregation, and overall behavior of MNPs in various applications.

2.2.4.1. Dipolar interactions between magnetic nanoparticles

In section 2.1.3.1 it was shown that the energy of dipole-dipole interactions is negligible for magnetic moments of electrons. However eq. 2.11 shows that this energy falls of with r^3 , but increases with μ^2 . Moreover as long as a ferromagnetic nanoparticle is small enough to only form one magnetic domain the magnetic moment μ of its superspin increases proportional to their volume. Thus the energy of the dipole interaction of two neighbouring nanoparticles is proportional to $\frac{\mu^2}{r^3} \propto \frac{V^2}{r^3} \propto \frac{r^6}{r^3} = r^3$. This simple approximation implies that neighbouring magnetic nanoparticles with a diameter of 10 nm interact 10^6 times stronger via dipole-dipole interaction than electrons of neighbouring atoms.

2.2.4.2. Van der Waals force

The van der Waals force is a weak, short-range interaction caused by electromagnetic fluctuations from the random motion of positive and negative charges in an atom, molecule, or bulk material. While it can be both attractive and repulsive, for nanoparticles dispersed in a solution, it typically acts as an attractive force, leading to the aggregation of particles in the solution.

However, nanoparticles can be coated with ligands to tune the effects of the van der Waals force. This approach can be employed to guide the self-assembly of nanoparticles and to prevent their aggregation.

2.2.4.3. Other forces

Numerous other forces act upon nanoparticles in a solution, including steric repulsion, electrostatic forces, capillary effects, and convection forces. However, these will not be discussed in further detail here.

2.2.5. Superspin glass

This thesis investigates the behavior of nanoparticles suspended in a solution at low temperatures, where the solvent undergoes freezing. Under these conditions, the nanoparticles will act as sparsely distributed superspins in a non-magnetic material. These superspins interact primarily through dipole-dipole interactions, resulting in a frustrated system. The physics of such dipolarly interacting superspins at random positions is identical to the physics of atomic spin glass systems described in section 2.1.4.4. Therefore they are referred to as superspin glasses.

The characteristic relaxation time τ_{SSP} of such a superspin glass system can be described by a critical power law [22]:

$$\tau_{SSG} = \tau^* \left(\frac{T - T_G}{T_G}\right)^{-z\nu} \tag{2.22}$$

where τ^* is the relaxation time of an individual particle moments, T_G is the static spin glass temperature and $z\nu$ is the dynamic critical exponent.

2.3. Scattering and diffraction

The term scattering is used to describe the general physical process whereby radiation is redirected out of the original direction of propagation due to interaction with another object. This thesis will only consider scattering using photons in the X-ray regime.

2.3.1. Scattering theory

Assuming that an X-ray source sends X-rays with a wavelength of λ to a sample that is a large distance \vec{L} away, then the X-rays arriving at the sample can be approximated as a plane wave:

$$A_{i}(t) = A_{0}e^{i(\vec{k}_{i}(\vec{L}+\vec{r}))-\omega t)}$$
(2.23)

where A_0 is the amplitude of the incoming wave, $\vec{k_i}$ is the wave vector with $|\vec{k_i}| = \frac{2\pi}{\lambda}$ that indicates the propagation direction of the incoming wave, \vec{r} is the position vector that indicated the specific location within the sample, t is the time and $\omega = c \cdot |\vec{k}|$ is the angular frequency of the wave with c being the speed of light.

After scattering the outgoing wave is described by [24]:

$$A_f(t) = A_i(t)\rho(\vec{r}) \frac{e^{i\vec{k_f}(\vec{L'}-\vec{r})}}{|\vec{L'}-\vec{r}|}$$
(2.24)

where $\rho(\vec{r})$ is the complex scattering density of the sample that the incoming wave scatters from, \vec{L}' is the distance from the sample to the detector and $\vec{k_f}$ is the wave vector of the outgoing wave. For the case of elastic scattering one has $|\vec{k_f}| = |\vec{k_i}|$. With the assumption that $|\vec{L}|, |\vec{L}'| \gg |\vec{r}|, \vec{L} \parallel \vec{k_i}$ and $\vec{L}' \parallel \vec{k_f}$ eq. 2.23 and eq 2.24 can be combined to:

$$A_{f}(t) = \underbrace{\frac{A_{0}}{\vec{L'}} e^{i(\vec{k_{i}}\vec{L} + \vec{k_{f}}\vec{L'})}}_{A_{0}^{*}} e^{-i\omega t} \rho(\vec{r}) e^{i(\vec{k_{f}} - \vec{k_{i}})\vec{r}}$$
(2.25)

Integrating this over the whole sample yields:

$$A_{f,total}(t) = \int_{V} A_{f}(t) d^{3}r$$

$$= A_{0}^{*} e^{-i\omega t} \int_{V} \rho(\vec{r}) e^{i(\vec{k_{f}} - \vec{k_{i}})\vec{r}} d^{3}r$$

$$\propto \mathcal{F}(\rho(\vec{r}))(\vec{k_{f}} - \vec{k_{i}})$$

$$(2.26)$$

Consequently, the process of scattering corresponds to the Fourier transform of the scattering density of the sample. This means that the intensity $I(\vec{k_f} - \vec{k_i}) = |\mathcal{F}(\rho(\vec{r}))|^2$ is the reciprocal representation of the scattering density.

For simplicity $\vec{q} = \vec{k_f} - \vec{k_i}$ is often defined. For elastic scattering it is related to the angle 2θ between $\vec{k_i}$ and $\vec{k_f}$ by:

$$\left|\vec{q}\right| = \frac{4\pi\sin(\theta)}{\lambda} \tag{2.27}$$

2.3.2. Small angle X-ray scattering (SAXS)

SAXS is a scattering method where the scattered x-rays are measured at a small angles. The small angles represent small \vec{q} values. Because the scattered x-rays reflect the reciprocal arrangements inside the sample these small \vec{q} values represent large sizes in comparison to the wavelength of the x-rays. For the scale of roughly 10 nm studied in this thesis it corresponds to angles $0.1^{\circ} < 2\theta < 10^{\circ}$.

In this thesis nanoparticles in dispersion are studied. Hence both their shape and their arrangement is of interest. The measured scattered intensity is a convolution of the form factor $F(\vec{q})$ that describes the size and shape of the nanoparticles and a structure factor $S(\vec{q})$ that describes the positions of the nanoparticles relative to each other. Using:

$$\mathcal{F}(A \otimes B) = \mathcal{F}(A) \cdot \mathcal{F}(B) \tag{2.28}$$

these two factors can be separated to yield:

$$I(\vec{q}) = |F(\vec{q}) \cdot S(\vec{q})|^2$$
(2.29)

In this thesis, the majority of SAXS measurements are radially averaged and then fitted assuming a spherical form factor, without considering a structure factor. In these instances, the model consists of [25]:

$$I(|\vec{q}|) = \frac{scale}{V} \left| V(\Delta SLD) \frac{\sin\left(|\vec{q}|R\right) - |\vec{q}|R\cos\left(|\vec{q}|R\right)}{(|\vec{q}|R)^3} \right|^2 + background$$
(2.30)

Here *scale* represents the volume fraction, V represents the scattering volume of the nanoparticles, R is the radius of the nanoparticles and ΔSLD is the difference between the scattering length density of the solvent and the nanoparticles. The scattering length density being a measure of the scattering power of a material.

In this thesis only the structure factor of the hard sphere model [26] is considered. This structure factor is calculated using the Percus-Yevick closure relationship [27] for a potential U(R) given by:

$$U(r) = \begin{cases} \infty & , \text{if: } r < 2R \\ 0 & , \text{if: } r \ge 2R \end{cases}$$
(2.31)

For the fitting a Taylor series is used for numerical stability.

3. Experimental Methods and Instruments

3.1. Samples

3.1.1. Iron Oxide Nanoparticle Dispersions

The nanoparticles used in this study are spherical iron oxide nanoparticles from the company OceanNanoTech, with a size in the order of 10–20 nm. The nanoparticles are dispersed in toluene or in water as solvents. The water-based nanoparticles are coated with organic ligands, while the toluene-based nanoparticles are coated with oleic acid and hydrocarbon chains. The main composition of the particles is ferromagnetic maghemite (γFe_2O_3) with some amounts of magnetite (Fe_3O_4). In [28] the same nanoparticles are used and their composition was measured to consist of roughly 90% maghemite and 10% magnetite.

3.1.2. Sample preparation

Magnetometry and AC-susceptibility measurements: For the magnetometry and AC-susceptibility measurements, the magnetic nanoparticle dispersions with a concentration of 5 mg/ml were initially squeezed between two plastic stamps, as shown in fig. 3.1a. These were sealed with silicon grease and Scotch tape to prevent solvent leakage. However, this method posed challenges with the toluene-based samples, as the toluene would diffuse into the plastic. Consequently, the sample holders were replaced with glass sample holders for subsequent experiments. These were made from glass capillaries with two distinct inner diameters, forming a thermometer-like shape as illustrated in fig. 3.1b. The nanoparticles were injected using a syringe, and the glass capillary was then sealed. The capillaries were melted 6 cm above the nanoparticle dispersion volume to prevent thermal annealing of the nanoparticles. Due to the thin inner diameter of the upper part of the capillaries, capillary forces prevent significant amounts of nanoparticles from leaking into the upper part of the capillaries. These sample holders were inserted into a colorless plastic straw to attach them to the device rod, as shown in fig. 3.1c **SAXS measurement:** For SAXS measurement, the nanoparticles are filled into glass capillaries. These are fabricated with thin-walled glass tubes from (Hilgenberg GmbH) with an outside diameter of 2.1 mm and a wall thickness of 0.05 mm. The capillaries are melted of from one side and cut on the other. After filling these with nanoparticle dispersions they are closed using a silicon ball using a silicon gun. The particle mass concentration in the order of 5 mg/ml was used for the nanoparticles dispersed in water and a concentration of 8.3 mg/ml was used for the nanoparticles dispersed in toluene. The capillaries are inserted vertically into the sample holder as shown in fig. 3.1d.



(c) Glass tube inside the straw

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Figure 3.1.: Sample holders used for magnetization measurements (a, b, c) and for SAXS measurements (d).
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3.2. Magnetometry measurements

3.2.1. Zero Field Cooled (ZFC) & Field Cooled (FC) Curves

A ZFC measurement is initiated by cooling the sample from high temperatures to low temperatures in the absence of an external field. Subsequently, an external field is applied, and the magnetic moment is measured as the sample is heated. To measure the so-called memory effect, the previously mentioned ZFC procedure is slightly modified by halting the cooling process at a certain temperature for a certain amount



Figure 3.2.: Measurement procedures for ZFC, memory-effect ZFC and FC measurements

of time before resuming the standard procedure. The FC measurement is initiated by cooling the sample in an external field, and the magnetic moment is recorded during cooling down.

The cooling and heating speeds used in this thesis are typically 2 K per minute during measurements and 10 K per minute outside the measurements. These speeds have been, on occasion, to enable a more detailed examination of phase change phenomena.

3.2.2. Hysteresis curves

Hysteresis curves are obtained by measuring the magnetization of a material as a function of an applied magnetic field, while taking into account the material's magnetic history. In this thesis, most hysteresis measurements were conducted using the MPMS SQUID magnetometer. This involved first increasing the external field to 1 T, then measuring the magnetic response while decreasing it to 1 T, and then repeating the process while increasing the field back to 1 T. The magnetic history, i.e. which procedure has been applied prior to the hysteresis curve, is indicated at each measurement.

3.2.3. AC-Susceptibility

In this thesis, the so-called ACMS option of the PPMS device was used for AC-Susceptibility measurements. For AC-Susceptibility measurements an alternating field $H = H_0 \sin(\omega t)$ is applied. This induces an alternating magnetic response, which will show in general in-phase and out-of phase contributions:

$$M(t) = M_0 \sin(\omega t - \phi) = M' \sin(\omega t) + M'' \cos(\omega t)$$
(3.1)

From the coefficients one can obtain the complex susceptibility $\chi = \chi' - i\chi''$. The susceptibility was measured with an amplitude of $\mu_0 H_0 = 0.8$ mT while increasing the temperature for fixed frequencies $f = \frac{\omega}{2\pi}$.

3.3. Nanoparticle arrangement annealing (NPAA)

Nanoparticle Arrangement Annealing (NPAA) is a technique used to control and adjust the spatial arrangement of nanoparticles within a solvent matrix by applying specific external conditions during the freezing process [29]. This method is particularly useful for optimizing the properties of nanoparticle assemblies and enhancing magnetic properties, as well as for tailoring the nanostructures for specific applications, such as biomedical imaging and drug delivery. The method is named "Nanoparticle Arrangement Annealing" (NPAA) due to its similarity to annealing processes in metallurgy.

NPAA can be performed using various techniques and procedures, including the application of an external magnetic field, varying the freezing speed, or repeated freezing and melting cycles. In this study, NPAA is primarily conducted by applying an external magnetic field during the freezing process of the solvent containing the nanoparticles as illustrated in fig. 3.3. The field exerts a significant influence on the alignment and arrangement of magnetic nanoparticles. The primary objective is to achieve a controlled and uniform arrangement of the nanoparticles, thereby enhancing their collective magnetic properties. Additionally, NPAA using different freezing speeds and NPAA by repeated freezing and melting were also conducted.



Figure 3.3.: Schematics of the NPAA procedure using an external field during cooling.

3.4. Measurement Devices and Instruments

3.4.1. Transmission electron microscopy (TEM)

Transmission Electron Microscopy (TEM) is a powerful characterization technique used to investigate the detailed structure of nanoparticles at the atomic and molecular levels. TEM provides high-resolution images that can reveal the size, shape, and distribution of nanoparticles, as well as their crystallographic structure.

In this study, transmission electron microscopy (TEM) measurements were conducted using a JEOL JEM-F200 TEM from the Jülich Centre for Neutron Science (JCNS), Neutron Scattering and Soft Matter (JCNS-1) located at the Ernst Ruska-Centre for Microscopy and Spectroscopy with Electrons (ER-C), Forschungszentrum Jülich, Germany. A small drop of the nanoparticle dispersion is applied to a carbon film-coated copper grid with a 400-mesh aperture. The grid serves to support the nanoparticles during imaging. The grid is then allowed to dry on air for two days to remove any residual solvent, thus ensuring that the nanoparticles are securely attached to the grid surface. The TEM utilized in this study operates at an acceleration voltage of 200 kV, which provides sufficient energy to penetrate the samples and generate high-resolution images. The high-resolution images are captured digitally, allowing for detailed analysis of the nanoparticles' size, shape, and arrangement. The captured TEM images are analyzed using the ImageJ software [30] to characterize the size and shape of the nanoparticles.

3.4.2. Magnetometers

3.4.2.1. MPMS

In this thesis, the MPMS-XL SQUID Magnetometer from Quantum Design was used, which operates over a broad temperature range from 2 K to 400 K, generating a magnetic field up to 7 T. It uses a superconducting quantum interference device (SQUID) which provides high sensitivity for the detection of magnetic moments. The ZFC and FC measurements, as well as the hysteresis measurements, presented in this thesis were conducted using this device.

3.4.2.2. PPMS

The PPMS is a measurement device that allows a wide variety of measurements. It allows for applied fields in a range from -9 T to 9 T and a temperature range from 1.9 K to 400 K. In this thesis the PPMS was used with the ACMS option for AC-Susceptibility measurements.

3.4.3. Diffractometers

3.4.3.1. Ganesha

Ganesha (fig. 3.4) is the in-house small angle X-ray scattering (SAXS) instrument of the institute JCNS-1. It uses a Ga-Metaljet X-ray source by Bruker AXS and an EIGER 4M single photon counting detector. The specialized sample stage, visible in fig. 3.5, permitted SAXS measurements in air while cooling the temperature inoperando using liquid nitrogen and adjusting the field by mechanically moving small permanent magnets during operation.

SAXS measurements were conducted at room temperature in order to obtain a comprehensive overview of the particle size distribution and monodispersity. Subsequent measurements were performed while cooling and heating in the absence of an applied field. The aim was to study the impact of solvent freezing on the structure factor.



Figure 3.4.: Experimental setup of the instrument Ganesha.

Finally, SAXS measurements were conducted following a ZFC/FC procedure and by applying a constant magnetic field at room temperature, with the aim of investigating the influence of magnetic fields on the structure factor.

The data was analyzed in two stages. Initially, radial averaging was performed, and then the resulting data set was fit using the SasView software with a spherical form factor model and a hard sphere structure factor model. However, some data is discarded when radially averaging data from an experiment that is not radially symmetric; this is a relevant issue as the external field used in our measurements is not radially symmetric.



Figure 3.5.: Sample stage of instrument Ganesha.

4. Results and Discussion

4.1. FeOx nanoparticles dispersed in water

4.1.1. TEM

Figure 4.1 shows the transmission electron microscopy (TEM) images of iron oxide (FeOx) nanoparticles dispersed in water. Fig. 4.1a illustrates smaller nanoparticles with a diameter of 10 nm, while fig. 4.1c depicts larger nanoparticles with a diameter of 15 nm. In both images, the nanoparticles are visible as dark spots against a lighter background, a characteristic feature in TEM images where denser materials (FeOx) appear darker. The nanoparticles are generally spherical with a certain shape anisotropy and conform to the sizes that were specified from the company. To evaluate the particle size and distribution, the diameters of nanoparticles are measured manually. The size distribution is then assessed using a simple method, where a log-normal distribution function (eq. 4.1) is fitted to the resulting histogram.

$$f(D) = \frac{1}{D\sigma_D \sqrt{2\pi}} \exp\left(\frac{-\left(\ln\left(\frac{D}{D_0}\right)\right)^2}{2\sigma_D^2}\right)$$
(4.1)

 D_0 is the mean particle diameter and σ_D is the log-normal standard deviation. The average diameters are estimated to be 12.40(4) nm for the 10 nm particles and 15.38(7) nm for the 15 nm particles. The size distributions, determined by fitting a log-normal distribution to the histogram, are 12.4(8)% and 16.6(0)%, respectively.

	TE	EM	SAXS		
Sample size	$D_0 (\mathrm{nm})$	σ_D (%)	$D_0 (\mathrm{nm})$	σ_D (%)	χ^2
10 nm	12.40(4)	12.4(8)	13.22(3)	6.7(9)	29.839
15 nm	15.38(7)	16.6(0)	16.36(3)	8.5(2)	8.9962

Table 4.1.: Parameters of water based nanoparticles obtained from manual analysis of the TEM images and from fitted SAXS data with the spherical form factor. The diameter of the sphere is given in terms of D_0 . The respective log-normal size distribution is given as σ_D . The 94.6 $\cdot 10^{-3} \frac{1}{nm^2}$, 422 $\cdot 10^{-3} \frac{1}{nm^2}$ are the scattering length density of the core and the solvent, respectively.



Figure 4.1.: TEM images and histogramms of (a-b) 10 nm and (c-d) 15 nm FeOx nanoparticles in water

4.1.2. SAXS

The radially averaged data from the two-dimensional small-angle X-ray scattering (2D SAXS) patterns of nanoparticles dispersed in water are presented in fig. 4.2. This figure offers a comparative analysis of the scattering data for the 10 nm and 15 nm particles. The black dots represent the experimental data for the 10 nm particles, while the red dots represent the experimental data for the 15 nm particles. This comparison highlights the differences in scattering intensity between the two particle sizes. The data were fitted using the sphere model in the SasView software, which accurately reproduces the experimental results. The fits (lines) closely align with the experimental data (dots), indicating that the fitting model effectively represents the scattering behavior of both particle sizes. The log-log scale (indicated by the logarithmic axes) facilitates the visualization of the wide range of intensities and scattering vectors.



Figure 4.2.: SAXS data of 10 nm and 15 nm FeOx nanoparticles in water together with the fit (line) to the data (points) assuming a spherical form factor.

Figure 4.3 depicts the results of SAXS measurements conducted on 15 nm nanoparticles suspended in water with a concentration of 5 mg/ml, subjected to cooling and heating. During the cooling depicted in fig. 4.3a, a notable change in the nanoparticles' structure factor occurred once the temperature dropped below 246 K. This shift is likely reflective of a phase change or rearrangement of the nanoparticles, with the observed delay below 246 K suggesting a period of supercooling where the nanoparticles remained in a metastable state before transitioning further. Figure 4.3c illustrates that during the subsequent heating phase, the altered structure factor persisted until reaching 273 K, where it reverted to its original state. This temperature corresponds to a reversible phase change point, indicating that the nanoparticles undergo a transition between different structural configurations or aggregation states in response to temperature variations. These findings underscore the sensitivity of nanoparticles in aqueous suspension to temperature-induced phase transitions, thereby highlighting specific critical temperatures for phase change dynamics.



Figure 4.3.: SAXS freeze-thaw measurement during (a-b) cooling and (c-d) heating of 15 nm FeOx nanoparticles in water. In (a, c) the SAXS measurements are plotted against the temperature. In (b, d) all the measurements for the different temperatures are shown stacked on top of each other.

Figure 4.4 illustrates that the SAXS measurement of the sample in its frozen state can be effectively fitted using the hard sphere model as a structure factor. This fitting suggests that the structure factor observed is predominantly influenced by the nanoparticles being pressed together due to the crystallization of water around them. In this context, magnetic interactions between nanoparticles appear to play a minor role compared to the physical forces exerted by the frozen water. This finding underscores that the crystallization process of water around nanoparticles significantly affects their spatial arrangement, as reflected in the SAXS data modeled by the hard sphere approach.

A SAXS experiment was conducted at a magnetic field of 0.21 T at room temperature, using a sample stage capable of higher fields shown in fig. A.4. The results indicate that the sample exhibited no significant structural changes. Radial averaging of the SAXS data (fig.4.5c) revealed no discernible differences, indicating that the overall structure remained unchanged. To ensure that no subtle changes were overlooked due to radial averaging, the azimuthal intensity (fig. 4.5d) was calculated for the q-range of 0.1 nm⁻¹ to 0.2 nm⁻¹. This analysis also demonstrates the absence of any notable features, apart from a minor peak that can be attributed to background contributions from the direct beam. An examination of the 2D SAXS patterns (fig.4.5a & 4.5b) serves to corroborate these findings, showing no unexpected features. The experiment concluded that the sample's structure is stable under the applied magnetic field, with only a small background peak observed in the azimuthal intensity analysis.



Figure 4.4.: SAXS freeze-thaw measurement of 15 nm FeOx nanoparticles in water at 244 K. The data fitted using a spherical form factor and a hard sphere structure factor.



Figure 4.5.: (a)- (b) 2D SAXS patterns for 10 and 15 nm nanoparticles in water under the magnetic field of 0.21 T. (c) Radial average of the 2D SAXS patterns with and without applying field. (e) Azimuthal profile from q=0.1 nm⁻¹ to q=0.2 nm⁻¹.

4.1.3. Magnetometry

The magnetic properties of the iron oxide (FeOx) nanoparticle dispersions in water were investigated primarily through ZFC and FC measurements. In addition, hysteresis, memory effect, and AC-Susceptibility measurements were carried out to further understand their magnetic behavior.

Hysteresis Measurements

Fig. 4.6 shows hysteresis loops for iron oxide (FeOx) nanoparticle dispersions in water, measured at two different temperatures (5 K and 300 K), and for two nanoparticle sizes (10 nm and 15 nm). At higher temperatures (300 K, red circles), both nanoparticle sizes exhibit superparamagnetism with negligible coercivity and remanence. This behavior fits the superparamagnetic model, where the spins of the nanoparticles do not interact with each other and respond to the magnetic field independently. However, at low temperatures (5 K, black squares), the hysteresis loop opens up. This opening is due to the blocking of Néel relaxation at low temperatures, which delays the reaction of the nanoparticle spins. Since the measurements were conducted over a finite timespan, this delay caused the hysteresis curve to open, an effect that should not be mistaken for ferromagnetic behavior. The measurement of 15 nm nanoparticles at 5 K reveals a linear increase in magnetic moment at high fields. This phenomenon can be explained by the superspins within the nanoparticles flipping to align with the field at low fields, while still aligning with the easy axis of the nanoparticles. As the field strength increases, the alignment with the external field becomes energetically more favourable than the alignment with the easy axis, leading to a further increase in magnetic moment.



Figure 4.6.: Hysteresis loops of iron oxide (FeOx) nanoparticle dispersions in water for (a) 10 nm and (b) 15 nm sizes, measured at 300 K (red circles) and 5 K (black squares).
The 300 K measurements were performed directly after installing the sample in the MPMS, while the 5 K measurements were done after cooling at 5 mT during a field-cooled (FC) measurement. The temperature dependence observed in the measurements confirms the superparamagnetic transition, where increased temperature reduces coercivity and remanence in both cases.

Memory measurements

A study of the magnetic history of the samples was done using memory effect measurements. These measurements indicate the behavior of the nanoparticles' magnetic moments over different temperatures.

The memory measurement was performed to determine whether a sample exhibits superspin glass behavior by analyzing the difference between a regular Zero-Field-Cooled (ZFC) measurements and an memory effect ZFC measurement. The results of memory effect measurements of 10 nm nanoparticles in water are shown in fig. 4.7. For the memory effect measurement, the sample was cooled to 110 K and held there for 3 hours, with the temperature selected to be slightly above the inflection point before the peak of the ZFC curve. The memory effect ZFC measurement was then compared to the reference ZFC measurement by subtracting the reference from the memory effect measurement. A peak was observed at the waiting temperature for 10 nm nanoparticles, characteristic of superspin glasses.



Figure 4.7.: Memory measurements for 10 nm nanoparticles dispersed in water.

AC-Susceptibility

Another method to determine whether a sample exhibits superspin glass behavior is by analyzing the peak temperature of AC-Susceptibility measurements at different frequencies. This method assumes that the peak temperature of the AC-Susceptibility corresponds to the temperature at which the relaxation time (τ) matches the applied frequency (f), according to the relation $\tau = \frac{1}{2\pi f}$. The data is then fitted using the characteristic relaxation times of nanoparticle ensembles to confirm the presence of superspin glass behavior [22].

Superspin glass
$$\tau = \tau_0^* \left(\frac{T - T_G}{T_G}\right)^{-z\nu}$$
(4.3)

This fit was performed for an AC-Susceptibility measurements of 10 nm nanoparticles in water, as shown in fig. 4.8. The peak temperature for 77 Hz was identified as an outlier and subsequently removed. Both eq. 4.2 and eq. 4.3 yield satisfactory fits to the data. However, the results of eq. 4.2 indicate that the energy barrier for a 10 nm nanoparticle is $\Delta E \approx 9.59 \cdot 10^{-20}$ J, which is considerably higher than expected for such a small particle. Additionally, the attempt time, τ_0 , is found to be unphysically



Figure 4.8.: (a) AC-Susceptibility of 10 nm nanoparticles is water. To convert the AC-Susceptibility into SI units the volume of the sample was estimated at 10 μm^3 (A.2). (b) The peak temperatures of the AC-Susceptibility in (a) where plotted against the relaxation time derived from their applied frequencies. These where fitted with the Arrhenius law for superparamagnetism (eq. 4.2) and a critical power law for superspin glass interaction (eq. 4.3). The peak temperature for 77 Hz was excluded as an outlier

small, with a value of $\tau_0 \approx 1.45 \cdot 10^{-19}$ s. In contrast, eq. 4.3 provides more realistic values. The individual spin flip time is $\tau_0^* \approx 8.9 \cdot 10^{-8}$ s, the spin glass temperature is $T_G \approx 173$ K, and the critical exponent is $z\nu \approx 4.1$. From this findings we can confirm that the sample displays superspin glass behavior.

ZFC/FC Curves

Figure 4.9a shows a typical ZFC/FC measurement for 10 nm iron oxide nanoparticles in water, measured between 10 K and 250 K at 5 mT. Since water is used as the solvent, it is frozen in this temperature range, suppressing Brownian relaxation. Consequently, the magnetic moment of the particles can only align via Néel relaxation. At low temperatures, the spins in the ZFC curve are not aligned, and the lowtemperature blocks Néel relaxation. As the temperature increases, the spins gradually become unblocked, and the magnetic moment increases. The ZFC curve peaks around 145 K, which corresponds to the blocking temperature where Néel relaxation matches the measurement speed of one measurement per minute. However, due to the non-superparamagnetic nature of the sample, these values do not match perfectly. Beyond the peak, the magnetic moment decreases following the Curie-Weiss law:

$$\chi \propto \frac{1}{T - T_C} \tag{4.4}$$

where T_C is the Curie temperature.

The FC curve follows the ZFC curve at higher temperatures but splits from it shortly before the ZFC peak. The proximity of the splitting to the peak indicates low polydispersity in the system. After splitting, the FC curve flattens while slightly increasing, indicating minimal interaction between the particles.



Figure 4.9.: ZFC/FC for 10 nm nanoparticles in water (a) between 10 K an 250 K and (b) between 10 K an 300 K.

Figure 4.9b extends the measurement of the same sample up to room temperature. The ZFC curve shows a sharp increase in magnetic moment from 276 K to 282 K, explained by the unfreezing of water, which allows for Brownian relaxation. This relaxation enables the particles to align themselves, increasing the magnetic moment since Néel relaxation cannot influence the alignment of the shape anisotropy of the nanoparticles to the field, as illustrated in fig. 4.10. This results in a splitting between the ZFC and FC curves.

The ZFC/FC curve between 10 K and 300 K from fig. 4.9b was repeated with an NPAA preparation. In this process, the sample was cooled from 300 K to 250 K at 1 T and then to 10 K at 0 T before being measured at 5 mT between 10 K and 300 K, as before. The NPAA process aligns the particles via Brownian relaxation. Once the water freezes and Brownian relaxation is suppressed, the external field is turned off. At this temperature, Néel relaxation is not yet suppressed, allowing the spins to lose their alignment.

Figure 4.11a shows the ZFC/FC measurement between 10 K and 300 K after NPAA and is compared to the previous measurement shown in fig. 4.9b. During the measurement, an increased magnetic moment is quickly observed, although the peak of the magnetic moment remains at the same temperature. During the unfreezing process, there is no shift in the magnetic moment, unlike in the normally prepared ZFC/FC curve. This aligns with the assumption that the shift is caused by nanoparticles aligning via Brownian relaxation. However, a small peak indicates a temporary increase in the magnetic moment during unfreezing. After unfreezing, the magnetic moment remains higher than in the normally prepared ZFC/FC curve, indicating that the alignment caused by the NPAA is stable for at least a few minutes.

During the cooling process, no observable effect is seen at the freezing temperature. Nevertheless, at approximately 258 K, a pronounced decline in the magnetic moment is observed. This phenomenon is also discernible in the regularly prepared ZFC/FC curve, though it is sufficiently subtle that it may be misidentified as a measurement error. The underlying cause of this phenomenon is presumed to be supercooling of the



Figure 4.10.: Schematic diagram of the Brownian nanoparticle alignment during unfreezing.



Figure 4.11.: ZFC/FC curves for water freezing of (a) 10 nm nanoparticles with 1T and after NPAA and (b) 15 nm particles between 10 K an 300 K

water, which rapidly freezes at temperatures below 258 K. The crystallization of the water during the supercooling process may result in the application of forces on the nanoparticles, which could displace them from their original alignment and, consequently, reduce the magnetic moment. This would explain why the effect is stronger in a measurement with NPAA preparation, as it is assumed here that the NPAA caused a stronger alignment, which would in turn be more affected by the alignment being reduced due to crystallization forces. However, this temperature does not correspond with the temperature of 246 K at which a sudden change in the structure factor was observed and supercooling was attributed as the cause. However, the discrepancy in temperature can be attributed to differences in the freezing environment. While the SAXS measurements were conducted using a glass capillary where the sample was locally cooled in air, the magnetometry measurements were performed using a plastic stamp sample holder in the SQUID magnetometer, which provides a more uniform cooling in a vacuum environment.

Figure 4.11b depicts a ZFC/FC measurement of 15 nm FeOx nanoparticles in water, which was conducted between 10 K and 300 K at 5 mT. To enhance the visibility of the phase change effects, the heating/cooling speed was slowed down during the unfreezing/freezing process, from 2 K/min to 0.2 K/min. In this measurement, an increase in the peak temperature of the ZFC/FC curve to approximately 240 K can be observed. As the heating speed has not been modified at this stage of the measurement, it can be concluded that this effect is entirely attributable to the change to the 15 nm nanoparticles. The unfreezing shift of the magnetic moment is observed for the 10 nm nanoparticles. The shorter and lower temperature range of the shift is likely due to the slower heating speed, as evidenced by subsequent measurements of the same sample without an adjusted heating speed seen in fig. 4.12b which does not demonstrate this change in the temperature range of the shift in magnetic moment.

During cooling, a sharp decrease in magnetic moment at 257 K is noted, similar to the 10 nm nanoparticle measurement. In this case, the effect is significant even without NPAA preparation. The decreased cooling speed does not affect the temperature of the freezing effect, nor are intermediate points observed during the effect, supporting the hypothesis of sudden freezing by supercooling. After cooling below the blocking temperature, the magnetic moment decreases before flattening due to the blocking of Néel relaxation. This decrease indicates interaction between the nanoparticles [22]. Figure 4.12a shows ZFC measurements of 10 nm nanoparticles in water with different

Figure 4.12a shows ZFC measurements of 10 min hanoparticles in water with different fields between 1 mT and 0.5 T. The ZFC curve peaks broaden and shift to lower temperatures with increasing field, explained by the external field reducing the energy barrier preventing spin flips. This broadening is due to the easy axis of the nanoparticles not being aligned during freezing, causing differently aligned particles to be affected differently by the shift in blocking temperature. The shift in the magnetic moment during unfreezing increases with increased external magnetic field until 25 mT, after which it decreases. When normalized to the magnetic moment just before the shift, this behavior persists, with the greatest normalized shift at 5 mT. The reduction in the shift for large fields may be due to the field causing Brownian relaxation even in the frozen solvent. For low fields, the reduced shift can be explained by friction between particles and solvents, with the Curie-Weiss law suppressing Brownian relaxation stronger than suppressing the Néel relaxation.

Figure 4.12b shows ZFC measurements of 15 nm nanoparticles in water with different fields between 1 mT and 50 mT. As in the previous measurement, the ZFC curve peaks broaden and shift to lower temperatures. The effect of the external field on the shift in magnetic moment during unfreezing is observed, though the decrease of the shift at high fields is not well demonstrated, as only fields up to 50 mT were measured. The suppression of the shift at low fields is evident at 1 mT, where the shift is completely suppressed.



Figure 4.12.: Field series measurements for (a) 10 nm and (b) 15 nm nanoparticles in water.

4.1.4. Summary

In the previous section, FeOx nanoparticles dispersed in water have been studied. Structural characterization using TEM and SAXS revealed low polydispersity and no discernible structure based on magnetic interactions. When frozen, SAXS measurements of the nanoparticles are consistent with the hard sphere model, suggesting that crystallisation forces the nanoparticles to aggregate. The temperatures at which this structural change occurs indicate that the samples freeze by supercooling.

Magnetic characterisation indicates that the dispersed nanoparticles have superspin glass properties. ZFC/FC measurements show freezing and thawing behaviour consistent with the structural observations.

4.2. FeOx nanoparticles dispersed in toluene

4.2.1. TEM

Figure 4.13 shows TEM images of nanoparticles of different sizes dispersed in toluene. These nanoparticles show a relatively uniform spherical shape with a high degree of monodispersity, indicating a uniform size distribution. The 10 nm and 20 nm nanoparticles show a comparatively higher polydispersity and some irregularities in shape. The particle diameter was measured manually for 100 particles using ImageJ software as explained in the subsection 4.1.1. The mean particle diameter D and its standard deviation σ_D were obtained by fitting the corresponding histogram with a lognormal size distribution according to Eq. 4.1 are shown in table 4.2

	TEM		SAXS		
Sample size	$D_0 (\mathrm{nm})$	σ_D (%)	$D_0 (\mathrm{nm})$	σ_D (%)	χ^2
10 nm	11.36(5)	16.8(5)	11.74(4)	11.0(5)	14.769
15 nm	13.70(1)	10.4(9)	14.00(6)	06.9(0)	183.1
20 nm	20.44(8)	15.5(3)	21.40(8)	09.7(3)	64.837

Table 4.2.: Parameters of toluene based nanoparticles obtained from manual analysis of the TEM images and from fitted SAXS data with the spherical form factor. The diameter of the sphere is given in terms of D_0 . The respective log-normal size distribution is given as σ_D . The 79.6 $\cdot 10^{-3} \frac{1}{nm^2}$, 422 $\cdot 10^{-3} \frac{1}{nm^2}$ are the scattering length density of the core and the solvent, respectively.



Figure 4.13.: TEM images of nanoparticles of different sizes dispersed in toluene. (a) 10 nm (b) 15 nm, (c) & (d) 20 nm.

4.2.2. SAXS

Figure 4.14 shows the SAXS profiles of nanoparticles with different sizes dispersed in toluene. The black dots represent the experimental data for 10 nm particles, the red dots for 15 nm particles, and the blue dots for 20 nm particles. This comparison highlights the differences in scattering intensity between the three particle sizes. The data were fitted using the sphere model in the SasView software, with the fits (solid lines) closely aligning with the experimental data (dots). This indicates that the fitting model effectively represents the scattering behavior of the particles across the different sizes.



Figure 4.14.: SAXS profiles with the fit (solid line) to the data (points) assuming a spherical form factor of FeOx nanoparticles with 10, 15 and 20 nm dispersed in toluene.

Figure 4.15a presents a series of SAXS measurements of 20 nm nanoparticles in toluene at a concentration of 8.3 mg/ml, stacked one atop the other during cooling. These measurements were conducted in a manner analogous to the freeze-thaw measurements in water described in section 4.1.2, but with samples measured between 203 K and 163 K. A slight decrease in the low q region can be observed, though this effect is much smaller than the freezing effect seen in water.

Fig. 4.15b, the change in intensity at $q \approx 0.095$ during cooling and heating process is shown. The change in intensity during cooling is a gradual process that occurs over a temperature range of approximately 40 K, while the heating process is much more rapid, with a change in intensity occurring in approximately 5 K. The presence of a peak during the cooling process may explain the slowed change in intensity observed during this phase.



Figure 4.15.: (a) SAXS profiles during cooling and (b) the freeze-thaw measurement at $q \approx 0.095$ during cooling and heating of 20 nm nanoparticles in toluene between 163 K and 203 K

In fig. 4.16, a ZFC/FC measurement with an applied field of 4 mT was conducted. Instead of measuring the magnetic response, the structure was measured using SAXS. The change in the structure factor that this causes is gradual and difficult to discern. However, upon comparison of the sample at the start of the ZFC curve and the end of the FC curve, as shown in fig.4.16c, a clear distinction in the structure factor can be observed.



Figure 4.16.: SAXS profiles of nanoparticles with a diameter of approximately 20 nm in toluene during (a) ZFC and (b) FC measurement. (C) A comparison of SAXS profiles before and after ZFC and FC.

Additionally, a SAXS measurement with an applied external field of 0.21T was carried out at room temperature (fig. 4.17) using the the field setup shown in fig. A.4. Figure 4.17d presents a comparison of SAXS profiles with and without field. It can be observed that no difference is evident for the 10 nm and 20 nm nanoparticles. For the 15 nm nanoparticles, a slight difference can be observed. However, this difference is considerably smaller than that observed for the 20 nm nanoparticles, which were subjected to the ZFC/FC procedure with a much smaller field. This could suggest that Brownian motion disrupts the arrangement of the nanoparticles.

However, an alternative perspective is offered by the 2D images (fig. 4.17 (a-c)). For the 10 nm nanoparticles (fig.4.17a), no notable difference is apparent. In contrast, for the 15 nm nanoparticles in fig. 4.17b, a clear radial asymmetry can be observed at the low q range. This can be attributed to the formation of chain-like structures, as previously observed in [31]. Similarly, the 20 nm nanoparticles in fig. 4.17a exhibit this effect, albeit at a lower q range and obscured by the direct beam.

Figure 4.17e shows the azimuthal integration, which illustrates the angular distribution of photon intensity detected within the scattering vector range of 0.1 nm^{-1} to 0.2 nm^{-1} . For the 15 nm nanoparticles, two distinct peaks are discernible at angles of $-\pi/2$ and $\pi/2$, indicating a considerable degree of scattering at these angles. This indicates the presence of a structural regularity or orientation in the sample, which leads to higher intensity detection at these points. The 20 nm nanoparticles also exhibit peaks at $-\pi/2$ and $\pi/2$, although these peaks are less pronounced due to this asymmetry being concentrated within a lower q range, overlapping with the direct beam and thus reducing the intensity of the signal at higher q values. In contrast, the 10 nm nanoparticles exhibit no distinct peaks, with only a modest peak attributed to the direct beam. This absence of discernible features indicates that the 10 nm nanoparticles lack significant structural orientation or regularity within the measured range of q. This finding corroborates the observations made in the 2D image analysis. In summary, the azimuthal intensity distributions demonstrate that the larger nanoparticles (15 nm and 20 nm) exhibit more discernible structural features than the smaller 10 nm nanoparticles.



Figure 4.17.: (a) - (c) 2D SAXS patterns of nanoparticles in toluene with applied field of 0.21 T. (d) radially averaged SAXS data of 10, 15, and 20 nm particles in toluene with and without field. (e) Azimutal integration from $q = 0.1 \text{ nm}^{-1}$ to $q = 0.2 \text{ nm}^{-1}$.

4.2.3. Magnetometry

Hysteresis Measurements

Figure 4.18 show the Hysteresis curves at 5 K and 300 K were carried out on FeOx nanoparticles dispersed in toluene to investigate their magnetic properties. At 5 K, the measurements were taken after cooling the samples with a 5 mT field during a Field-Cooled (FC) procedure. As for the nanoparticles dispersed in water these hysteresis curves show negligible coercivity and remanence for the measurements at 300 K and the measurements at 5 K open up due to the blocking of the Néel relaxation. At high fields the magnetic moment increases linearly. The effect is particularly pronounced for the 10 nm nanoparticles, becomes somewhat weaker for the 15 nm nanoparticles, and is barely noticeable for the 20 nm nanoparticles. Since the potential energy that aligns the superspin with the easy axis is proportional to the volume of the nanoparticle, as seen in eq. 2.16, this trend aligns with the hypothesis that the field exerts a force on the superspin, turning it away from the easy axis.



Figure 4.18.: Hysteresis measurements at 5 K and 300 K for (a) 10, (b) 15 and (c) 20 nm nanoparticles dispersed in toluene.



Figure 4.19.: Memory measurements for (a) 10, (b) 15 and (c) 20 nm nanoparticles dispersed in toluene.

Memory measurements

Figure 4.19 shows the memory measurements for the FeOx nanoparticles with (a) 10, (b) 15 and (c) 20 nm. These show the difference between a normal ZFC curve and a ZFC curve where the cooling was paused at 85 K, 110 k and 210 K respectively. For the 15 nm and 20 nm nanoparticles a peak can be seen at these temperatures which indicate superspin glass behavior. For the 10 nm nanoparticles this effect does not occur indicating that the 10 nm nanoparticles are not a superspin glass system.

ZFC/FC and AC-Susceptibility measurements

The ZFC/FC curve of the 10 nm nanoparticles in toluene, as shown in fig. 4.20, reveals phenomena that were not observed in the water-based samples (fig. 4.9b). As with the water-based samples, a peak in the ZFC curve can be observed which marks the unblocking of the Néel relaxation. Immediately following the melting point of toluene, from 178 K to 190 K, an additional increase in magnetic moment can be observed, analogous to the observations made in the water-based samples. However, during the FC, another increase in magnetic moment is evident within this temperature range. Moreover, at 162 K, the ZFC curve exhibits a sudden bend, and from 136 K to 144 K, the magnetic moment of the ZFC rapidly increases.



Figure 4.20.: ZFC/FC curve for 10 nm nanoparticles in toluene.

This behavior is consistent with the observations made in the AC-Susceptibility measurement of 10 nm nanoparticles in toluene, as shown in fig. 4.21. A small downward shift in susceptibility is observed at 144 K, followed by a rapid decrease in susceptibility up to the melting temperature of 178 K. After the melting temperature, the susceptibility increases before decreasing following the expected pattern observed in an AC-susceptibility curve.



Figure 4.21.: AC-Susceptibility for 10 nm nanoparticles in toluene. For unit conversion the volume of the sample was estimated at 10 μ m.

The observed increase in magnetic moment from 136 K to 144 K in fig. 4.20 can be attributed to the influence of surface effects between the nanoparticles and the toluene. These effects result in a local reduction in the melting temperature of the toluene, creating a thin film of molten toluene around the nanoparticles. This allows for the rotation of the nanoparticles. Consequently it is possible to observe partial Brownian relaxation below the normal melting temperature of the toluene. Therefore, the Brownian relaxation can be divided into two distinct phases, as illustrated schematically in fig. 4.22a.



Figure 4.22.: (a) Schema of the interface melting process where the areas in which this phenomenon could occur in the ZFC curves is highlighted in (b) and (c).

For the nanoparticles in water this interface melting effect was not observed. However a slower measurement of the unfreezing of the 10 nm nanoparticles in water, as shown in fig. 4.22c, reveals that the shift in the magnetic moment during the unfreezing is, in fact, a two-step process. This could indicate that the interface between the solvent and the nanoparticles melts earlier for water-based nanoparticles as well, although the difference in the ordinary melting temperature and the interface melting temperature is relatively minor. This would explain why no similar second shift in magnetic moment was observed in the water-based nanoparticles prior to the melting point. However, the proximity of the temperatures and the delay caused by measuring during the heating process make it challenging to verify whether this two-step shift in magnetic moment is actually caused by such an interface melting phenomenon.

The field series measurement of 10 nm nanoparticles in toluene, as shown in fig. 4.23a, demonstrates a similar dependence on the external field as the water-based samples depicted in fig. 4.12. The shifts in the magnetic moment at 136 K exhibit a distinctive pattern of increasing with the external field up to 20 mT and subsequently decreasing. This aligns with the behavior observed in the water-based phase shift, thereby increasing the likelihood that this effect is a manifestation of a phase transition.

Figure 4.23b illustrates the field series for 15 nm nanoparticles in toluene. In this

instance, the phenomenon of magnetic moment shift at the interface melting does not occur. Moreover, the magnetic moment shift at the phase transition is observed only at external fields of 20 mT and above. Furthermore, two peaks can be observed in the ZFC curve. A peak is observed below the melting temperature, which is consistent with the Néel relaxation being blocked at low temperatures. Additionally, a peak is observed above the melting temperature. Moreover, as the peak above the melting temperature broadens sufficiently to reach the melting temperature, the shift in magnetic moment due to the phase shift begins to occur. Consequently, we hypothesize that this second peak is caused by the Brownian relaxation becoming unblocked in a manner analogous to how the first peak is caused by the unblocking of the Néel relaxation. These will be referred to below as "Néel-relaxation peak" and "Brownian-relaxation peak." If this conclusion is correct, it would explain why no shift in magnetic moment occurred at lower temperatures until the Brownian-relaxation peak reached the melting temperature. This is because these shifts are caused by Brownian-relaxation becoming unblocked, and thus it would become impossible if the Brownian-relaxation remains blocked after the phase transition.



Figure 4.23.: Field series measurements for (a) 10, (b) 15 and (c) 20 nm nanoparticles dispersed in toluene.

The field series shown in fig. 4.23c does not indicate any magnetic moment shift for the 20 nm nanoparticles in toluene. With low fields, only a single peak is visible, but as the field increases, this peak separates into two peaks. If the hypothesis of the Brownian-relaxation peak is correct, this implies that the Néel-relaxation peak broadens and shifts more in reaction to an increased external field. It should be noted, however, that this may be a property dependent on the sample and not a general rule.



Figure 4.24.: Toluene ZFC/FC with and without NPAA at 1 T from 300 K to 130 K.

To verify the conclusion that the absence of a magnetic moment shift is due to the Brownian relaxation being blocked, ZFC/FC measurements with NPAA preparation were conducted. The nanoparticles were cooled to 130 K with an external field of 1 T before proceeding with the standard ZFC/FC protocol. The resulting ZFC curves, shown in fig. 4.24, revealed a small shift in magnetic moment at 137 K, where the interface melting effect is expected, a larger shift at the melting temperature of 178 K, and a steady decline in the magnetic moment starting just below the Brownian-relaxation peak temperature.

This behavior can be understood by considering the alignment of nanoparticles during the freezing process. At the interface melting temperature, the nanoparticles begin to rotate, and because the measurement field of 5 mT is much smaller than the freezing field, this causes a decrease in magnetic moment. As this occurs well below the Brownian blocking temperature, the effect is small. At the melting temperature, nanoparticles become free to move, further reducing their alignment to the field. Once the blocking temperature is reached, Brownian motion fully disrupts the alignment of the nanoparticles. This disruption starts before the Brownian relaxation peak because the higher freezing field results in a lower blocking temperature. Additionally, the Brownian-relaxation peak may not correspond as closely to the Brownian blocking temperature as the Néel-relaxation peak does to the Néel blocking temperature. The ZFC/FC curves without NPAA show that the magnetic moment shift during field cooling occurs at the Brownian-relaxation peak rather than at the phase transition, indicating that the shift is linked to Brownian-relaxation becoming blocked, not directly to the freezing process. This might be due to Brownian motion disrupting nanoparticle alignment, and blocking this motion increases the magnetic moment if the nanoparticles have already aligned via Brownian-relaxation. This phenomenon did not occur in water-based samples, possibly due to supercooling and crystallization forces. The ZFC/FC curves of 15 nm nanoparticles split at a significantly higher temperature than the Brownian-relaxation peak, suggesting higher polydispersity or non-uniform friction between particles and the solvent.

The AC-Susceptibility measurement of 20 nm nanoparticles in toluene shows a rapid increase in susceptibility between 216 K and 286 K, corresponding to the temperature range where Brownian-relaxation becomes relevant in the ZFC curves. The detailed reason for the lack of a more gradual increase in AC-Susceptibility due to Brownian-relaxation remains unclear.



Figure 4.25.: AC-Susceptibility of 20 nm nanoparticles in toluene. For unit conversion, the volume of the sample was estimated at 10 μ m(A.2).

4.2.4. Summary

In the previous section, FeOx nanoparticles dispersed in toluene were studied.

Structural characterisation of the nanoparticles using TEM and SAXS shows low polydispersity with some shape irregularities in the 10 nm and 20 nm nanoparticles. SAXS measurements of the 15 nm and 20 nm nanoparticles show a change at low q when exposed to an external field, likely caused by the formation of chain-like structures.

Magnetic characterisation shows that the 15 nm and 20 nm nanoparticles have superspin glass properties. However, the 10 nm nanoparticles show only superparamagnetic properties.

A ZFC/FC measurement of the 10 nm nanoparticles showed several effects not observed in water based samples. One of these effects is a two-step process in the freezing-melting phase transition, where the toluene on the surface of the nanoparticles melts at a lower temperature due to surface effects, enabling partial Brownian relaxation due to particle rotation. ZFC measurements using the NPAA preparation allow this effect to be observed for the 15 nm and 20 nm nanoparticles as well.

Field series measurements of the 15 nm and 20 nm nanoparticles showed a Brownian relaxation peak with similar behaviour to the typical Néel relaxation peak observed in ZFC measurements, which is caused by Néel relaxation. At temperatures below the Brownian relaxation peak, no effects associated with Brownian relaxation were observed, and modification of the peak temperature by changing the size of the nanoparticles and the strength of the external field allows these effects to reappear. This leads to the conclusion that this peak is caused by Brownian relaxation, similar to how Néel relaxation causes the Néel relaxation peak.

4.3. Comparison water vs. toluene

4.3.1. Comparison of structural properties

TEM imaging and SAXS measurements indicate that both water-based and toluenebased nanoparticles fit their ordered sizes accurately and exhibit low polydispersity. At room temperature and without an external field, all nanoparticles display the expected structure factor of non-interacting particles, except for the 15 nm toluene-based nanoparticles, which shows a structure factor which may be caused by nanoparticle interactions or the direct beam contribution. During freezing and melting, water-based nanoparticles undergo fast and significant structural changes, fitting the hardsphere model in the frozen state due to rapid crystallization. In contrast, toluene-based nanoparticles exhibit slow and minor structural changes that do not fit the hardsphere model, indicating magnetic interactions. When an external field is applied at room temperature, water-based nanoparticles show little change, while 15 nm and 20 nm toluene-based nanoparticles show significant changes in the low q region, likely forming chains. Overall, the phase change in water has a more substantial impact on nanoparticle arrangement due to sudden crystallization, while toluene-based nanoparticles display more magnetic interactions, possibly influenced by their higher concentration (8.3 mg/ml) compared to water-based samples (5 mg/ml).

4.3.2. Comparison of magnetic properties

Both water-based and toluene-based nanoparticle samples exhibit similar behavior regarding Néel relaxation, resulting in comparable hysteresis curves, ZFC/FC curves, and AC-Susceptibility measurements in temperature regions where Brownian relaxation is blocked. This similarity is expected since Néel relaxation depends only on the spins inside the nanoparticles and is largely independent of the non-magnetic solvent. Memory measurements, except for the 10 nm nanoparticles in toluene, indicated superspin glass behavior across all samples. In water-based samples, Brownian relaxation is blocked for most of the studied temperature range, with unblocking observed only during the unfreezing process. Conversely, toluene-based samples, with a lower phase transition temperature, displayed a Brownian-relaxation peak and an interface melting effect not seen in water-based samples, which instead showed a two step process during unfreezing. The rapid freezing due to supercooling in water disrupted the nanoparticle alignment with the field, whereas toluene did not exhibit such effects. Instead, blocking Brownian relaxation in toluene, whether due to phase transition or low temperature, increased the magnetic moment. Additionally, several other phenomena were observed in toluene-based samples that weren't observed in water-based ones, suggesting these effects might be due to interactions between toluene and the nanoparticles or that these effects require unblocked Brownian relaxation.

5. Summary

In this thesis the magnetic and structural properties of iron oxide nanoparticles with various sizes dispersed in two types of solvents, i.e. water and toluene, were investigated. The structural properties were analyzed using SAXS and TEM techniques. The results of the SAXS measurements indicate that the crystallisation of water exerts a force upon the nanoparticles, causing them to aggregate. However, no discernible structural properties related to magnetic interactions were observed. In contrast, nanoparticles dispersed in toluene exhibited structural arrangements influenced by magnetic interactions. Notably, asymmetry was observed in SAXS images when measuring these nanoparticles under an applied magnetic field, indicating a distinct structural organization.

Magnetic properties were investigated through a series of hysteresis, AC-susceptibility, and ZFC/FC measurements. Memory ZFC measurements revealed that the dispersed nanoparticles, except for the 10 nm nanoparticles in toluene, exhibit characteristics of superspin glasses. Analysis of ZFC/FC measurements on the water-based samples indicates that the magnetic behaviors observed during the solvent freezing-melting phase transition are consistent with the structural findings.

Through ZFC measurements using NPAA protocols and field series measurements, it can be demonstrated that the freezing-melting phase transition observed in the toluene-based samples likely involves a two-step process. This process includes an initial interface melting, where the surface between the nanoparticles and toluene melts, enabling particle rotation, followed by conventional melting that allows nanoparticles to move freely within the solvent.

Another observed phenomenon is the Brownian relaxation peak, appearing as a distinct second peak in the ZFC curve, separate from the Néel relaxation peak. This peak exhibits behaviour similar to the Néel relaxation peak. Prior to its appearance, no effects associated with Brownian relaxation are detected. Modifying the Brownian relaxation time τ_B by varying the size of the nanoparticles and the strength of the external field moves the position of this peak. Furthermore, as this peak shifts to lower temperatures, effects related to Brownian relaxation start to appear again. This suggests that this peak results from Brownian relaxation, analogous to how Néel relaxation causes the typical Néel relaxation peak observed in ZFC measurements.

6. Outlook

Several phenomena observed in this thesis remain inadequately explained within the scope of this thesis. This is especially true for phenomena like the kink observed in the ZFC curve of 10 nm nanoparticles in toluene at 162 K, the sharp rise in AC-susceptibility between 216 K and 286 K for the 20 nm nanoparticles in toluene, and the increase in magnetic moment seen when Brownian relaxation becomes blocked during FC measurements of toluene-based samples. Further research on these effects could provide a more detailed understanding of the underlying mechanisms. Specifically, structural analysis has not provided sufficient depth to explain these phenomena fully. Utilising cryo-TEM could offer a more intuitive and conclusive understanding. Neutron scattering could concurrently investigate both structural and magnetic properties, offering insights into their interplay.

Insights gained from the Brownian relaxation peak could enable the study of Brownian relaxation phenomena using ZFC/FC methods, analogous to the analysis of Néel relaxation. It could also aid in distinguishing between Brownian and Néel relaxation peaks where they overlap. Detailed study of the Brownian relaxation peak is essential to determine its properties and their similarity to Néel relaxation peaks.

Understanding the underlying processes of the interface melting effect could provide fundamental insights into nanoparticle systems. It could also enhance NPAA processes for manipulating magnetic properties effectively in such systems. However, achieving this requires an understanding in which systems this phenomenon occurs and how to manipulate at which temperatures it takes place. Detailed studies investigating varying particle sizes, coatings, solvents with different viscosities, and their interactions with coating ligands are necessary. In addition to the insights into the interface melting effect such studies could also contribute significantly to a broader understanding of nanoparticle dispersions.

A. Appendix

A.1. Plots and images



Figure A.1.: AC-Susceptibility of 15 nm nanoparticles in toluene. For unit conversion, the volume of the sample was estimated at 10 μ m(A.2)



Figure A.2.: AC-Susceptibility of 15 nm nanoparticles in water. For unit conversion, the volume of the sample was estimated at 10 μ m(A.2)



Figure A.3.: ZFC/FC with and without NPAA for 10 nm nanoparticles in toluene. The black and red dots represent a regular ZFC/FC measurement between 10 K and 300 K. The blue and green dots represent a ZFC/FC measurement between 10K and 200K where a field of 1 T was applied during the initial cooling between 200 K and 130 K. The violet and brown dots represent a ZFC/FC measurement between 10K and 200K where a field of 1 T was applied during the initial cooling between 200 K and 160 K.



Figure A.4.: Sample stage of instrument Ganesha.

A.2. PPMS AC-Susceptibility unit conversion

The PPMS measurement device measures the AC-Susceptibility by measuring the slope dM of the magnetic response in emu. To convert this into an AC-Susceptibility of the SI unit system this needs to be divided by the amplitude dH of the applied external field in Oe and the volume V in cm³. Afterwards this needs to be multiplied by 4π to get the AC-Susceptibility in the SI unit system.

$$\chi_{AC}(SI) = 4\pi \frac{1}{V} \frac{dM}{dH}(CGS) \tag{A.1}$$

As the volume of the samples was not fixed accurately during sample preparation, this volume was estimated at 10 μm^3

B. List of acronyms

- ER-C Ernst Ruska-centre
- FC Field cooled
- FeOx Iron oxide
- JCNS Jülich centre for neutron science
- MNP Magnetic nanoparticles
- MPI Magnetic particle imaging
- MPMS Magnetic properties measurement system
- NPAA Nanoparticle arrangement annealing
- PPMS Physical property measurement system
- RKKY Ruderman-Kittel-Kasuya-Yosida
- SAXS Small angle X-ray scattering
- SLD Scattering length density
- SPM Superparamagnet
- SSG Superspin glass
- SQUID Superconducting quantum interference device
- TEM Transmission electron microscopy
- ZFC Zero field cooled

C. List of symbols

A	Area
V	Volume
V_H	Hvdrodvnamic volume
I	Current
m_e	Electron mass
m_N	Nuclear mass
S_z	Spin along a particular axis
μ_{S_z}	Spin magnetic moment along a particular axis
χ	Susceptibility
E	Energy
T	Temperature
T_B	Blocking temperature
T_G	Static spin glass temperature
T_C	Curie temperature
λ	Wavelength
ω	Angular frequency
f	Frequency
SLD	Scattering length density
R	Nanoparticle radius
D	Nanoparticle Diameter
D_0	Mean nanoparticle diameter
σ_D	Log-normal standard deviation of the nanoparticle diameter
$ au_{ m o}$	Elementary spin flip time
τ_0^*	Relaxation time of an individual nanoparticles magnetic moment
τ_m	Measurement time
τ_{SPM}	Characteristic Néel relaxation time of a superparamagnet
TSSP	Characteristic Néel relaxation time of a superspin glass
τ_{N}	Néel relaxation time
τ_{B}	Brownian relaxation time
$ au_{eff}$	Effective relaxation time
$o(\vec{r})$	Complex scattering density
$F(\vec{a})$	Form factor
$S(\vec{a})$	Structur factor
~ (4)	

- $\vec{\mu}$ Magnetic moment
- \vec{L} Angular momentum
- $\vec{\mu}$ Magn \vec{L} Angu \vec{S} Spin
- \vec{B} Magnetic flux density
- \vec{H} Magnetic field strength
- \vec{M} Magnetisation
- \vec{r} Position vector
- \vec{k} Wave vector
- \vec{q} Scattering vector
- γ Gyromagnetic constant
- μ_B Bohr magneton
- μ_0 Vacuum permeability
- g_L Electron orbital g-factor
- g_S Spin g-factor
- \hbar Reduced Planck's constant
- K Anisotropy constant
- k_B Boltzmann constant

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Statutory declaration

I declare that this thesis represents my own work and appropriate credit has been given where reference has been made to the work of others. This thesis has not been previously included in a thesis, or report submitted to this University or to any other institution for a degree, diploma or other qualifications.

Jülich, 13.07.2024

Maximilian Enneling

(Place, Date)

(Signature Maximilian Enneking)

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