Interacting Magnetic Nanosystems

An Experimental Study Of Superspin Glasses

MIKAEL SVANTE ANDERSSON
Abstract

This thesis presents experimental results on strongly interacting γ-Fe₂O₃ magnetic nanoparticles and their collective properties. The main findings are that very dense randomly packed (≈60%) γ-Fe₂O₃ nanoparticles form a replica of a spin glass. The magnetic properties of the nanoparticle system are in most regards the same as those of an atomic spin glass. The system is therefore proposed as a model superspin glass. In superspin glasses the interacting building blocks that form the collective state are single domain nanoparticles, superspins with a magnetic moment of about 10000 μₜ, which can be compared to the atomic magnetic moment in spin glasses of approximately 1 μₜ. It was found that the relaxation time of the individual nanoparticles impacts the collective properties and governs the superspin dimensionality. Several dense compacts, each prepared with nanoparticles of a specific size, with diameters 6, 8, 9 and 11.5 nm, were studied. All the studied compacts were found to form a superspin glass state. Non-interacting reference samples, consisting of the same particles but coated with a silica shell, were synthesized to determine the single particle magnetic properties. It was also found that the effects of the nanoparticle size distribution, which lead to a variation of the magnetic properties, can be mitigated by having strong enough interparticle interactions. The majority of the work was carried out using SQUID magnetometry.

Keywords: spin glass, SQUID magnetometry, maghemite, magnetism, nanoparticles

Mikael Svante Andersson, Department of Engineering Sciences, Solid State Physics, Box 534, Uppsala University, SE-751 21 Uppsala, Sweden.

© Mikael Svante Andersson 2017

ISSN 1651-6214
ISBN 978-91-554-9893-1
urn:nbn:se:uu:diva-319717 (http://urn.kb.se/resolve?urn=urn:nbn:se:uu:diva-319717)
Dedicated to the ones that came before and gave us what we have today.

Allt har jag sett, både fröjd och misär,
det har tillsammans fört mig hit
Nu står jag här, och jag är den jag är
och jag vill inte ändra en bit

Allt jag har sett, Sånger ur Sten 1994
Big Fish
Mikael Svante Andersson born in Uppsala in 1988 earned his Master’s Degree in Materials Engineering from Uppsala University in spring 2013. The same spring he joined the division of Solid State Physics at Uppsala University. His research is focused on magnetic materials and especially interacting magnetic nanoparticles.
This thesis is based on my research on strongly interacting magnetic nanoparticle systems during 2013-2017. This research was supervised by Dr. Roland Mathieu, Prof. Per Nordblad and Prof. Peter Svedlindh at the department of Engineering Sciences, Division of Solid State Physics at Uppsala University in Sweden and Dr. Jose A. De Toro at the department of Physics at University Castilla-La Mancha in Spain. The thesis is based on work published in peer-review journals and some unpublished work. Published work which do not contribute to the discussion of interacting magnetic nanosystems is only mentioned as “Other publications” in the list of publications. In Sweden there are two common ways to write a thesis; a monograph or a comprehensive summary with the publications attached, this thesis is written as a comprehensive summary. The thesis is divided into the following chapters: **Introduction**, in which an short introduction to the field of magnetism, with a focus on spin glasses, is given. The introduction also covers the relevant parts of the field of supermagnetism to set the stage for the rest of the thesis. **Experiments**, in which the measurement protocols and equipment are described as well as the synthesis of the samples used in the studies covered in this thesis. **Results and discussion**, in which the main results are presented and discussed. **Concluding remarks and outlook**, in which the results are summarized and concluding remarks are made, as well as a short discussion of the future in interacting nanosystems. **Summary in Swedish** includes a short summary of the thesis written in Swedish. The papers which this thesis is based upon are attached at the end (the papers are omitted in the digital version).
# CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Preface</td>
<td>vii</td>
</tr>
<tr>
<td>Contents</td>
<td>ix</td>
</tr>
<tr>
<td>List of Publications</td>
<td>xi</td>
</tr>
<tr>
<td>1 Introduction</td>
<td>1</td>
</tr>
<tr>
<td>1.1 Magnetism</td>
<td>1</td>
</tr>
<tr>
<td>1.2 Spin glasses</td>
<td>3</td>
</tr>
<tr>
<td>1.3 Superspin glasses</td>
<td>5</td>
</tr>
<tr>
<td>2 Experiments</td>
<td>7</td>
</tr>
<tr>
<td>2.1 Sample Fabrication</td>
<td>7</td>
</tr>
<tr>
<td>2.2 Magnetic Measurements</td>
<td>7</td>
</tr>
<tr>
<td>2.3 Magnetic measurement protocols</td>
<td>8</td>
</tr>
<tr>
<td>2.3.1 DC magnetization as a function of temperature</td>
<td>8</td>
</tr>
<tr>
<td>2.3.2 DC-Memory</td>
<td>8</td>
</tr>
<tr>
<td>2.3.3 Low field isothermal remanent magnetization as a function of temperature</td>
<td>9</td>
</tr>
<tr>
<td>2.3.4 Relaxation measurements</td>
<td>10</td>
</tr>
<tr>
<td>2.3.5 Magnetization as a function of applied magnetic field</td>
<td>12</td>
</tr>
<tr>
<td>2.3.6 $\delta M(H)$</td>
<td>12</td>
</tr>
<tr>
<td>2.3.7 Magnetic AC-susceptibility as a function of temperature</td>
<td>13</td>
</tr>
<tr>
<td>3 Results and discussion</td>
<td>15</td>
</tr>
<tr>
<td>3.1 Non-interacting magnetic nanoparticles</td>
<td>16</td>
</tr>
<tr>
<td>3.1.1 Surface spin disorder and its impact on single particle magnetic properties</td>
<td>16</td>
</tr>
<tr>
<td>3.1.2 Intraparticle interactions and their impact on $\delta M$</td>
<td>20</td>
</tr>
<tr>
<td>3.2 A dense ensemble of magnetic nanoparticles with spin glass like properties</td>
<td>23</td>
</tr>
<tr>
<td>3.3 Size dependence of particle interactions and superspin glass properties</td>
<td>28</td>
</tr>
<tr>
<td>3.3.1 Interparticle interactions</td>
<td>28</td>
</tr>
<tr>
<td>3.3.2 Size dependence of superspin glass properties</td>
<td>30</td>
</tr>
<tr>
<td>3.4 Superspin glass properties in a system consisting of mixed particles</td>
<td>33</td>
</tr>
<tr>
<td>3.5 Demagnetization effects for high concentrations of magnetic nanoparticles</td>
<td>36</td>
</tr>
<tr>
<td>3.6 Effects of the individual particle relaxation time on the superspin glass state</td>
<td>42</td>
</tr>
<tr>
<td>4 Concluding remarks and outlook</td>
<td>47</td>
</tr>
<tr>
<td>Contents</td>
<td>Page</td>
</tr>
<tr>
<td>-------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>4.1 Concluding remarks</td>
<td>47</td>
</tr>
<tr>
<td>4.2 Outlook</td>
<td>47</td>
</tr>
<tr>
<td>5 Summary in Swedish</td>
<td>49</td>
</tr>
<tr>
<td>Acknowledgments</td>
<td>53</td>
</tr>
<tr>
<td>References</td>
<td>55</td>
</tr>
</tbody>
</table>
LIST OF PUBLICATIONS

Publication discussed in this thesis

I Ageing dynamics of a superspin glass
  M. S. Andersson, J. A. De Toro, S. S. Lee, R. Mathieu and P. Nordblad
  EPL (Europhysics Letters) 108, 17004 (2014)

II Size-dependent surface effects in maghemite nanoparticles and its impact on interparticle interactions in dense assemblies
  M. S. Andersson, R. Mathieu, S. S. Lee, P. S. Normile, G. Singh, P. Nordblad and J. A. De Toro
  Nanotechnology 26, 475703 (2015)

III Particle size-dependent superspin glass behavior in random compacts of monodisperse maghemite nanoparticles
  M. S. Andersson, R. Mathieu, P. S. Normile, S. S. Lee, G. Singh, P. Nordblad and J. A. De Toro
  Materials Research Express 3, 045015 (2016)

IV Effects of the individual particle relaxation time on superspin glass dynamics
  M. S. Andersson, J. A. De Toro, S. S. Lee, P. S. Normile, G. Singh, P. Nordblad and R. Mathieu
  Physical Review B 93, 054407 (2016)

V Magnetic properties of nanoparticle compacts with controlled broadening of the particle size distributions
  M. S. Andersson, R. Mathieu, P. S. Normile, S. S. Lee, G. Singh, P. Nordblad and J. A. De Toro
  In manuscript
VI Demagnetization effects in dense nanoparticle assemblies
P. S. Normile, M. S. Andersson, R. Mathieu, S. S. Lee, G. Singh and J. A. De Toro

VII Spin disorder in nanoparticles: A cautionary tale on the use of Henkel and δM plots to assess interparticle interactions
In manuscript

Contributions to papers

I Planned the experiment and performed the measurements. Analyzed the data and had an active roll in the discussion of the results. Wrote most of the paper.

II Planned and performed some of the magnetic measurements. Analyzed the data for the magnetic measurements and had an active roll in the discussion of the results. Wrote most of the paper.

III Planned and performed the magnetic measurements. Analyzed the data for the magnetic measurements and had an active roll in the discussion of the results. Wrote the paper.

IV Planned and performed the magnetic measurements. Analyzed the data for the magnetic measurements and had an active roll in the discussion of the results. Wrote the paper.

V Performed the magnetic measurements. Analyzed the data for the magnetic measurements and had an active roll in the discussion of the results. Wrote the paper.

VI Took part in the data analysis of the magnetic measurements and had an active roll in the discussion of the results. Took part in the writing of the paper.

VII Took part in the data analysis of the magnetic measurements and had an active roll in the discussion of the results. Took part in the writing of the paper.
Reprints were made with permission from the respective publisher.

**Disclaimer** This thesis is based on my licenciate thesis "PROPERTIES OF A MODEL SUPERSPIN GLASS SYSTEM: An experimental study of densely packed $\gamma$-Fe$_2$O$_3$ nanoparticles", which was written as a half-time report during my Ph.D studies. Some of the papers treated in this thesis have also been discussed in the licenciate thesis and some passages in this thesis are based on passages in the licenciate thesis.
Other publications


IX  Irreversible structure change of the as prepared FeMnP$_{1-x}$Si$_x$-structure on the initial cooling through the curie temperature V. Högl, J. Cedervall, M. S. Andersson, T. Sarkar, P. Nordblad and M. Sahlberg Journal of Magnetism and Magnetic Materials 374, 455-458 (2015)


XI  Sample cell for in-field X-ray diffraction experiments V. Högl, J. Ångström, M. S. Andersson, O. Balmes, P. Nordblad and M. Sahlberg Results in Physics 5, 53-54 (2015)


XIV Hydrogenation-Induced Structure and Property Changes in the Rare-Earth Metal Gallide NdGa: Evolution of a \([GaH]^2–\) Polyanion Containing Peierls-like Ga-H Chains
Inorganic Chemistry 55, 345-352 (2016)

XV Hydrogenation induced structure and property changes in GdGa

XVI Magnetic structure of the magnetocaloric compound AlFe$_2$B$_2$

XVII Thermally induced magnetic relaxation in square artificial spin ice
M.S. Andersson, S.D. Pappas, H. Stopfel, E. Östman, A. Stein, P. Nordblad, R. Mathieu, B. Hjörvarsson and V. Kapaklis
Scientific Reports 6, 37097 (2016)

XVIII Tailoring Magnetic Behavior in the Tb-Au-Si Quasicrystal Approximant System
G. Gebresenbut, M. S. Andersson, P. Nordblad, M. Sahlberg and C. P. Gómez
Inorganic chemistry 55, 2001-2008 (2016)

XIX Superspin dimensionality of a mono-dispersed and densely packed magnetic nanoparticle system
M. S. Andersson, J. A. De Toro, S. S. Lee, R. Mathieu and P. Nordblad
CHAPTER 1

INTRODUCTION

1.1 Magnetism

Magnetism is all around us in our everyday lives [1], being the functional mechanism in applications ranging from generation of electricity, high density data storage devices, and advanced medical equipment such as an MRI scanner, to simply keeping a paper on the fridge. The magnetic order inside the materials used for these applications can differ substantially, e.g. in a power transformer a soft ferromagnetic iron-silicon alloy is used. In this material the magnetic moment of the iron atoms order in a parallel fashion (ferromagnetism). In the read heads (spin valves) of current magnetic hard disk drives, a combination of many magnetic layers are used, and commonly at least one of them is an antiferromagnet. In antiferromagnets the magnetic moments order in an anti-parallel fashion, thereby canceling each other and yielding a net magnetic moment of zero. A third possibility is to have an anti-parallel configuration, but with magnetic moments of different magnitudes, yielding a net moment, this is known as ferrimagnetism, see Fig. 1.1. At high temperatures the interaction energy responsible for the order becomes weak in comparison to the thermal energy and the order breaks down yielding randomly fluctuating magnetic moments, this is known as paramagnetism. In macroscopic ferromagnets the material will be divided into magnetic regions, known as magnetic domains. An illustration of domain formation is shown in Fig. 1.2, where the direction of the magnetic moments and the size of the domains yield a net magnetization of zero. The driving force behind domain formation, namely the dipolar (magnetostatic) field, strives to demagnetize the material. At the boundary between two domains there exists a domain wall across which the magnetic

Figure 1.1: Different magnetic states. Typically ferrimagnets include different magnetic cations.
moments reorientate themselves from one domain orientation to the next, which implies non-parallel spin configurations increasing the exchange energy. In case of a very small particle (sub micron) it will not be energetically favorable to form a domain wall and there will only be one domain, this is known as a single domain particle. Since there is only one domain the magnetic moment of the particle can be described as one giant moment, commonly called a superspin. For a single domain particle with uniaxial anisotropy there will be two energy minima separated by an energy barrier, the two minima correspond to opposite directions, at low temperature the superspin will lie along one of these two directions. If the temperature is increased the thermal energy causes the superspin to switch direction between the two minima at a certain rate governed by a relaxation time, $\tau^*$, given by the Arrhenius law, eqn. 1.1 [2, 3]. In eqn. 1.1 $\tau_0$ is the relaxation time at high temperature ($k_B T \gg KV$) and typically of the order of $10^{-10}$ s, $K$ is the effective anisotropy constant, $V$ the volume of the particle, $k_B$ the Boltzmann constant and $T$ the temperature. As seen from the equation, the relaxation time will be very long at low temperatures and approach $\tau_0$ as temperature is increased.

$$\tau^* = \tau_0 e^{KV/k_B T}$$

At low temperatures the thermal energy will be much smaller than $KV$ and the superspin will be locked on experimental timescales and appear frozen in place. At high temperatures the thermal energy will be much larger than $KV$ and the superspin will relax with a very short relaxation time and on experimental timescales the moment will appear to be continuously fluctuating. Between these two extremes there will be a temperature for which the relaxation time will be equal to the experimental observation time, this temperature called the blocking temperature, $T_b$, is the temperature for which particle goes from being blocked (low T) to getting unblocked (high T) [3]. Above its blocking temperature, an ensemble of superspins behaves similarly to a paramagnet, since the system is able to follow any applied magnetic field within the experimental observation time. The magnetization above $T_b$ will decrease with increasing temperature, due to thermal excitations of the superspin, which is also similar to the behavior of a paramagnet. Because of the similarities to paramagnetism this behavior is called superparamagnetism. A few differences between a superparamagnet and an ordinary paramagnet are: the size of the magnetic moment (atomic $\sim 1 \, \mu_B$, superspin $\sim 10^3 - 10^8 \, \mu_B$), the temperature dependence of its relaxation time, and the
magnetic field required to saturate the system. When working with superparamagnets it is important to remember the impact of the observation time, since for short observation times the system could appear frozen while at longer observation times the system is changing, this means that the blocking temperature is different for different measurement techniques. The use of nanoparticles as building blocks can be taken at least one step further by creating systems were the particles interact magnetically and form new materials such as superferromagnets and superantiferromagnets [4, 5]. The particles can interact via magnetic dipolar interactions, via Ruderman-Kittel-Kasuya-Yosida (RKKY) [6–8] interactions if the particles are in a metallic matrix or through exchange interactions if the particles are in contact. Like in atomic magnetic materials these new supermagnetic materials can exhibit a transition from their respective supermagnetic state to a superparamagnetic state as temperature is increased due to the thermal energy overcoming the interaction energy. In this thesis much of the focus is put on a magnetic super state known as a superspin glass. To understand what a superspin glass is, one first has to look into what a spin glass is, which is covered in the next section.

1.2 Spin glasses

The first paper using the name spin glass was published in 1970 on the topic of Mn doping in a matrix of Cu by P. W. Anderson [9] inspired by a suggestion from B. R. Coles. During the coming decades the research on spin glasses (now the official name) continued with progress both in the theoretical and experimental domains [10–18]. But what is actually a spin glass? A good starting point is what P. W. Anderson wrote in 1970: “Below a rather broad transition region at ≈ 1-100 K (proportional to concentration) is a magnetically “ordered” state in which there is no visible regularity...” [9]. The key concept contained in this sentence is a magnetic state with no apparent order that forms below a transition temperature. From this it can be understood that the system behaves like a collectively ordered state.

A magnetic material which exhibits both frustration and disorder in its spin system may be a spin glass. An example of a material that is a spin glass is a dilute Cu(Mn) alloy where small amounts of Mn atoms are randomly distributed (disordered) in a Cu matrix. Since the interaction mechanism in Cu(Mn) is RKKY, for which the distance between the interacting species determines the sign (ferro- or antiferromagnetic) and strength of the interaction, it is possible to have competing

Figure 1.3: An example of frustration and competing interactions. The + indicates ferromagnetic interactions while - indicates antiferromagnetic interactions.
interactions due to disorder that lead to magnetic frustration, see Fig 1.3. Magnetic frustration means that not all interactions can be satisfied simultaneously; in spin glasses this gives rise to a broad range of relaxation times, which starts from atomic timescales ($10^{-12}$ s) and extends to experimental time scales (seconds) at low temperatures and diverges at the transition temperature, $T_g$, to remain infinite at lower temperatures, see Fig. 1.4. This is much broader than what any Ph.D student (or their supervisor) could ever hope to measure.

As indicated by P. W. Anderson the systems order below a temperature known as the glass transition temperature, $T_g$. At this temperature the correlation length, $\xi$, diverges and the system undergoes a second order transition from a paramagnetic to a spin glass state. The correlation length describes the maximum length scale for which a magnetic moment affects other moments. This means that moments further away will be unaffected by a change. This divergence of the correlation length can be probed using static and dynamic scaling. In this

---

**Figure 1.4:** Distribution of relaxation times, $\tau(s)$, for an atomic spin glass at different temperatures.
thesis the focus has been on dynamic scaling. At the freezing temperature, $T_f$, the observation time, $\tau_{\text{obs}} \sim 1/\omega = 1/2\pi f$ will be equal to the longest relaxation time, $\tau$. Combining $\xi \propto |(T_f(f) - T_g)/T_g|^{-\nu}$ and $\tau \propto \xi^z$ gives a power law $\tau = \tau^* |(T_f(f) - T_g)/T_g|^{-z\nu}$ describing the critical slowing down of $\tau$ [19]. $\nu$ and $z$ are critical exponents and $\tau^*$ is the individual relaxation time of the interacting building blocks at this temperature, which for atomic spin glasses will be the temperature independent atomic relaxation time. $T_f$ can be experimentally determined using AC-magnetometry and thus the longest relaxation time can be determined. By fitting $T_f$ and the corresponding $\tau$ to this power law, $T_g$, $z\nu$ and $\tau^*$ can be determined.

Because of the frustration occurring in spin glasses the system is constantly evolving and has some unique non-equilibrium properties such as aging, memory and rejuvenation below $T_g$ [13, 16, 17, 20]. Aging in magnetic systems implies that the time spent before a field change is made impacts the development of the magnetization after the field change is made. This is in contrast to most magnetic materials where the time spent before the change is irrelevant. Two other unique non-equilibrium properties are memory and rejuvenation, which imply that the system will remember an age attained at any given temperature below $T_g$ and that aging at one temperature will not affect the age at any other lower temperature.

To date spin glasses lack any direct application, but their physics is still a rich field which fascinates both experimental and theoretical physicists alike, since the field of spin glasses pose important fundamental science questions that allow an increased understanding of magnetism [21]. There are however areas outside of magnetism in which spin glass research has come to use, e.g. modeling of processes in our brains [22].

1.3 Superspin glasses

The basic idea of a superspin glass is to make a spin glass like phase built up of interacting superspins instead of atomic magnetic moments. A way to do this is by making a random ensemble of magnetic particles, which have competing interactions due to the random position of the particles relative to each other. In case of dipolar interaction this can easily be understood, since if one particle is placed like in Fig. 1.5 a) the interaction will be ferromagnetic, while if the particles are placed like in Fig. 1.5 b) the interaction will be antiferromagnetic. Early studies on aging in magnetic nanoparticle systems...
1.3 Superspin glasses

were mostly done on concentrated frozen ferrofluids [23, 24], were the interparticle interaction mechanism is of dipolar origin. However these studies were made on particles with a rather large size distribution. The samples with higher concentration showed collective behavior, but due to the broad size distribution they did not exhibit critical dynamics. In Ref. [25] studies on ferrofluids with much narrower size distributions were made. One of the studied systems exhibited critical slowing down suggesting a spin glass like phase transition. The study also included a dilute reference sample which had a blocking temperature of roughly half of that of the concentrated sample. Hiroi et al. [26] used silica and oleic acid coated particles to be able to accurately determine the interparticle distance, however the size distribution of the particles was broader than that of some previous studies. De Toro et al. built on this idea and made a dense disc of $\gamma$-Fe$_2$O$_3$ uncoated particles as well as dense discs of silica coated $\gamma$-Fe$_2$O$_3$ particles to be able to study the impact of concentration on the magnetic properties [27, 28]. Both the uncoated sample and the coated samples were originally from the same particle synthesis batch, which had a very narrow size distribution. The work in this thesis is an expansion of that work.
CHAPTER 2

EXPERIMENTS

2.1 Sample Fabrication

In this thesis samples of densely packed $\gamma$-Fe$_2$O$_3$ nanoparticles have been investigated. Bulk $\gamma$-Fe$_2$O$_3$ is an oxide ferromagnet below $\sim 860$ K [29]. In this section the particle synthesis and the following pressing of the particles into dense discs are described. One of the pressed discs is shown in figure 2.1, it has a diameter of 6 mm and a thickness of 2 mm. The particles are synthesized through thermal decomposition of iron pentacarbonyl followed by an oxidation step at elevated temperature using trimethylamine N-oxide, the process is described in detail in reference [30]. A part of the synthesized particles were coated with a thick silica shell [27] yielding two types of particles, uncoated $\gamma$-Fe$_2$O$_3$ particles (“bare”), where the remaining oleic-acid had been washed away using aceton, and silica coated $\gamma$-Fe$_2$O$_3$ particles (coated) to be used as references for weakly interacting particles. Using a hydraulic press compact discs were made, from the bare particles and from the coated particles. The pressure used was approximately 0.7 GPa [27]. Through the synthesis described above several particle sizes were made for both bare and coated particles, which were also pressed into discs. The filling factor was determined using Archimedes’ method in combination with wide-angle X-ray scattering [27]. The filling factor is around that of random close packing (64%).

2.2 Magnetic Measurements

Magnetic measurements were preformed using a commercial Superconducting Quantum Interference Device (SQUID) mag-
2.3 Magnetic measurement protocols

2.3.1 DC magnetization as a function of temperature

Three types of measurements were performed: zero-field cooling (ZFC), field cooling (FC) and theremoremanent magnetization (TRM) measurements. The $M_{ZFC}(T)$ measurement is made in the following way, the sample is cooled from high temperature down to a low temperature in zero magnetic field. At this temperature a magnetic field is applied and the magnetization is measured upon reheating. In the $M_{FC}(T)$ measurement the sample is cooled and measured in a field. For $M_{FC}(T)$ measurements there are two types, field cool cooling (FCC) and field cool heating (FCH) where the difference is that the magnetization is measured on cooling or on reheating. In $M_{TRM}(T)$ the sample is cooled in a field from high temperature down to a low temperature. At this temperature the field is switched off and the magnetization measured on reheating in zero field. In Fig. 2.3 a schematic drawing of how ZFC, FC and TRM magnetization curves could look like for a sample of interacting magnetic nanoparticles.

2.3.2 DC-Memory

For spin glasses it is common to measure the so called memory effect which was proposed as a protocol in [32], demonstrated in AC susceptibility measurements in [16] and in DC magnetization measurements in [33]. The purpose is to reveal the existence or non-existence of non-equilibrium dynamics of the sample. For DC memory experiments a reference $M_{ZFC}(T)$ curve is measured as described above, and then a memory curve is measured. This is similar to a normal $M_{ZFC}(T)$ measurement, but with the exception that during the cooling from above the glass transition temperature, $T_g$, in zero field the cooling is halted at a specific temperature $T_h<T_g$ and the tem-
Experiments

Figure 2.4: A ZFC memory experiment for a Cu(Mn) spin glass. The stop during cooling was made at $T/T_g \approx 0.7$.

Temperature is kept constant for a halting time $t_h$. It is important to stress that during the entire cooling, including the stop, the applied magnetic field is zero. Once the halting time $t_h$ has passed the cooling is resumed down to the lowest temperature. At the lowest temperature the field is switched on and the magnetization recorded on reheating as a function of temperature as in an ordinary $M_{ZFC}(T)$ measurement. Around $T_h$ there will be a decrease in magnetization compared to the reference curve as the system remembers the aging which occurred during the cooling.

There is also the possibility of doing a TRM memory experiment [33]. The sample is cooled in an applied field, including a stop at $T_h$ as in the ZFC memory experiment. At the lowest temperature the field is switched off and the magnetization is recorded as a function of temperature during the heating of the sample. Around $T_h$ there will be a bump in the magnetization curve. For TRM memory a $M_{TRM}(T)$ curve without a stop is used as a reference. An example of how a ZFC memory curve for a spin glass looks like is seen in figure 2.4.

2.3.3 Low field isothermal remanent magnetization as a function of temperature

Another experimental protocol used to study the properties of spin glasses is the so called isothermal remanent magnetization $IRM(T)$ [34]. The measurement is described in detail in references [18, 33]. The sample is cooled in zero field from $T>T_g$, the cooling is halted at a temperature $T_h<T_g$ and the sample is subjected to an applied magnetic field, typically 80-800 A/m
2.3.4 Relaxation measurements

Relaxation measurements can be performed in three different ways, $M_{ZFC}(t)$, $M_{FC}(t)$ and $M_{TRM}(t)$. For $M_{ZFC}(t)$ the sample is cooled from a temperature ($T_{ref}$) above $T_g$ (paramagnetic region or superparamagnetic region for superspin glasses) to a temperature $T_M$ (below $T_g$) in zero field. At $T_M$ the sample is held at constant temperature for a specific time $t_w$ ($t_w$ can be zero). After $t_w$ has passed a field is applied and the magnetization is measured as a function of time, a schematic description of the protocol is shown in figure 2.6. For $M_{TRM}(t)$ the procedure is almost the same, the sample is cooled in a constant non-zero field and at $T_M$ the field is switched off and the magnetization is recorded as a function of time. When plotting the

Figure 2.5: IRM for two spin glasses: Ising (blue) is Fe$_{0.5}$Mn$_{0.5}$TiO$_3$ and Heisenberg (red) is Cu(Mn). The $T_h/T_g \approx 0.6$ for the Ising sample and 0.7 for the Heisenberg sample.
data $t_M$ is used as the zero reference time. For $M_{FC}(t)$ the sample is cooled in an applied field to $T_M$ and the magnetization measured as a function of time (there is no field change after $t_w$ for FC relaxation) [20]. In a typical measurement $t_w$ is between 0 and $10^5$ s for ZFC and TRM relaxation. For normal magnetic materials which do not exhibit any waiting time dependence (aging), the difference in $t_w$ will not affect the magnetization curves, but for spin glasses and superspin glasses which exhibit aging the curves will differ depending on which $t_w$ was used. An example of a relaxation measurement ($M_{ZFC}(t)$) for an atomic spin glass is shown in figure 2.7. The relaxation rate $S(t)=dM/d\log_{10}(t)$ can be used to show changes in $M(t)$ more clearly.

Figure 2.7: Experimental relaxation curves for a Ag(Mn) spin glass sample after different waiting times. $H=8$ A/m, $T_g=33.5$ K.
2.3.5 Magnetization as a function of applied magnetic field

The measurement is performed by cooling the material from above $T_g$ down to the measurement temperature either in zero magnetic field or in a field. The magnetization is then measured as a function of applied magnetic field at constant temperature. Magnetization as a function of magnetic field curves, $M(H)$, are usually symmetric, however some materials exhibit the exchange bias effect where the $M(H)$ curve is shifted [36], see Fig. 2.8.

2.3.6 $\delta M(H)$

$\delta M(H)$ plots is a common tool for evaluating the interparticle interaction type and strength in magnetic nanoparticle systems [37–39]. The method relies upon two remanence measurements $IRM(H)$ and $DCD(H)$ (described below). $\delta M(H) = M_{DCD}(H) - [M_{rs} - 2M_{IRM}(H)]$, where $M_{rs}$ is the saturation remanence and here defined as the highest value of $M_{IRM}(H)$. In case of non-interacting particles the $\delta M$ curve is expected to be zero; any deviation from this is normally interpreted as being caused by the presence of interparticle interactions.

High field Isothermal remanent magnetization as a function of applied magnetic field, $IRM(H)$

The sample is cooled in zero field from a temperature above $T_g$ down to the measurement temperature. At the measurement temperature a relatively small field is applied and then removed. After the applied field is zero again remanent magnetization is measured. A new field is applied, this field is slightly larger than the previously applied field. The field is once again removed and the new remanence is measured. The measurement continues this way until the highest field (typically saturating) has been applied and the remanence corresponding to this field has been measured. This measurement will be referred to as $IRM(H)$ and should not be confused with the previously mentioned $IRM(T)$.

DC Demagnetization, $DCD(H)$

The sample is cooled from above $T_g$ down to the measurement temperature and then saturated with a large negative magnetic field. The field is removed and the remanence is measured. After this a small positive field is applied and then removed and the remanence is again measured. This step is repeated with increasingly larger fields being applied before removing
the field and measuring the remanence until the largest field has been applied and the corresponding remanence has been measured. The measurement is referred to as DCD(H).

2.3.7 Magnetic AC-susceptibility as a function of temperature

Since DC magnetization measurements generally probe the response of the system on time scales of seconds or more and spin glasses have dynamics on time scales from picoseconds to geological timescales, it is therefore convenient to use AC measurements to extend the time scales that can be probed. In such measurements, an AC-excitation field is used to measure the in-phase, $\chi'$, and the out-of-phase, $\chi''$, components of the AC-susceptibility. AC-susceptibility measurements generally covers timescales from $10^2$ to $10^{-6}$ s ($\tau_M=1/2\pi f$, where $\tau_M$ is the observation/measurement time and $f$ is the frequency of the AC magnetic field). In the commercial SQUID MPMS AC measurements cover the time window of $10^1$ to $10^{-4}$ s. By using several frequencies it is possible to examine the critical slowing down which happens around the glass transition temperature $T_g$. 
CHAPTER 3

RESULTS AND DISCUSSION

This chapter is organized as follows:

• Section 3.1 deals with the behavior of non-interacting magnetic nanoparticles and their properties.

• Section 3.2 presents data comparing a dense interacting nanoparticle ensemble, made from one of the particle sizes presented in the first part, to an atomic spin glass.

• Section 3.3 presents data on how such a dense ensemble behaves if the particle size is changed.

• Section 3.4 deals with what happens if there is a mixture of particle sizes. Data for a controlled mixture series of dense ensembles made from 9 and 11 nm particles is presented.

• Section 3.5 deals with demagnetization effects in concentrated magnetic nanoparticle systems and when these effects should be taken into account.

• Section 3.6 deals with superspin dimensionality and the impact of the relaxation time of the individual building blocks on the collective properties of the interacting nanoparticles.
3.1 Non-interacting magnetic nanoparticles

3.1.1 Surface spin disorder and its impact on single particle magnetic properties

When studying collective properties it is important to understand as much as possible about the building blocks used to form the collective. As described in the experimental sections the building blocks studied here are maghemite nanoparticles of a few different sizes which can be controlled by synthesis parameters [30]. During the synthesis, while still in dispersion, the particles were coated with a thick silica shell so that the minimum distance between the magnetic particles could be controlled. Fig. 3.1 shows TEM images of the particles before and after silica coating. The size distribution for the 8 nm particles is also presented. This distribution is very narrow and is representative for all sizes.

The silica shell of the particles keeps the core distances large enough so that dipolar interactions can be neglected. Fig. 3.2 a) shows magnetization as a function of temperature using the ZFC and FC protocols for several sizes of non-interacting magnetic nanoparticles. The particles will hence forth be referred to as REFx; x=6a, 6b, 8, 9a, 9b and 11, a and b represent particles of similar particle size, i.e. the maghemite cores in REF6a have a diameter of 6.2 nm and those in REF6b a diameter of 6.3 nm, while the cores in both REF9a and REF9b have a diameter of 9.0 nm. These duplicates come from different synthesis batches. Three observations that can be directly made from the data are that: (i) the temperature for the maximum in the ZFC curve increases with increasing particle size, (ii) $M_{ZFC}(T)$ and $M_{FC}(T)$ merge above the maximum in $M_{ZFC}(T)$, and (iii) the curves show the expected behavior of non-interacting magnetic particles, with a superparamagnetic tail ($\sim 1/T$) at higher temperatures and a slow/blocked regime at lower temperatures as well as the maximum in $M_{ZFC}(T)$ indicating the crossing from a superparamagnetic to a blocked state (here the maximum is used to define the blocking temperature, $T_b$). Examining the development of $T_b$ as a function of volume of the magnetic particles it can be seen that the smallest particles (6.2 and 6.3 nm) deviate from the trend set by the larger particles by having a lower $T_b$ than that suggested by the trend line in Fig. 3.2 b). For non-interacting magnetic nanoparticles the parameter which determines $T_b$ is the energy barrier $E_b = KV$, where $K$ is the anisotropy energy constant and $V$ is the volume of the particle. If $K$ is volume independent $T_b$ is linearly proportional to $V$. $T_b$ increases linearly for all particles of size 8 nm and larger. It is not always the case that all of the contributions
Figure 3.1: Transmission electron microscope images of uncoated (left side) and corresponding silica coated particles (right side). The particles on the same row originates from the same synthesis batch, i.e. the left side particles were taken out before the silica coating step. The scale bars correspond to 20 nm in all images, (a)-(h).
3.1.1 Surface spin disorder and its impact on single particle magnetic properties

Figure 3.2: a) $M_{ZFC}(T)$ and $M_{FC}(T)$ for non-interacting magnetic particles of selected sizes. b) Blocking temperature $T_b$ as a function of volume. The inset shows $K$ as a function of the inverse diameter.

to $K$ are volume independent, since $K$ is a sum of many different anisotropies e.g. crystalline, shape and exchange. The inset of Fig. 3.2 shows that $K$ is not volume independent, but increases linearly with decreasing diameter for the larger particles. REF6a and 6b have much lower anisotropy and do not follow the trend set by the other REF samples. The linear increase of $K$ with $1/d$ for the larger particles indicates that the extra anisotropy could be related to the surface of the particles. To examine this further, magnetization as a function of magnetic field measurements at different temperatures were made. An estimate of the magnetic diameter of the particle, assuming that the particle consists of pure $\gamma$-Fe$_2$O$_3$ can be determined
Results and discussion

from a fit of the high temperature data (300 K) to:

\[ M = M_s(T) \times L(\mu \mu_0 H/k_B T) - SH, \]

(3.1)

where \( L(x) = 1/tanh(x) + 1/x \) is the Langevin function, \( H \) is the magnetic field, \( \mu \) the particle moment, \( \mu_0 \) the permeability of vacuum, \( M_s(T) \) the saturation magnetization for bulk \( \gamma \)-Fe\(_2\)O\(_3\) at temperature \( T \) and \( S \) is a linear magnetic susceptibility term used to account for the silica shell separating the particles [40]. This diameter can be compared to the TEM diameter and if they differ it indicates that there is a part of the magnetic volume which does not couple to the rest of the particle and thereby decreases the total magnetic moment of the particle. When comparing the magnetic diameter and the TEM diameter there is a smaller difference for the 6.2 and 6.3 nm particles while the difference is larger for the 8 nm and larger sizes, see Table 3.1. This suggests spin disorder within the larger particles. At the surface of the particle the coordination number is not the same as for the bulk atoms and therefore they behave differently, possibly giving rise to a magnetically disordered layer.

The results of the low temperature (5 K) magnetization as a function of magnetic field measurements show that the 8 nm and larger particles exhibit exchange bias, while the 6.2 and 6.3 nm particles do not exhibit exchange bias, see paper II for more information. Exchange bias is commonly associated with two interacting layers, as in a layered structure or a core/shell particle [36]. The exchange bias and the results from the Langevin fits both indicate that there is a surface spin disordered layer in the 8 nm and larger particles, see Fig. 3.3. If such a layer exists it could give rise to exchange bias as well as an increase of the anisotropy and thereby an increase in \( T_b \).

Further investigations were carried out by performing an in-field Mössbauer spectroscopy study of the 6.2 nm sample as well as the 8 nm sample, which showed that a substantial amount of spins do not align with the field in the 8 nm sample even in as large fields as 6400 kA/m (80 kOe), while most of the spins align in the 6.2 nm sample. The question then arises, why would there not be a magnetically disordered layer for the smallest particles? X-ray diffraction (XRD) was used to estimate the crystalline size of the particles by extracting the Full Width at Half Maximum (FWHM) corresponding to a specific peak in the diffractogram. Using the FWHM the Scherrer size [41] of the respective particles could be determined and it was found that the Scherrer sizes are smaller than the TEM diameter for the 8 nm and larger particles while it is slightly larger for the 6.2 and 6.3 nm particles. That the Scherrer diameter is
larger than the TEM diameter is not unexpected, since for XRD it is the volume weighted diameter which is relevant, which leads to a shift of the mean diameter to larger values due to that more weight is put on larger particles. Only the crystalline parts of the particle contributes to the Scherrer size and the results can therefore be interpreted as if the surface of the larger particles is less structurally ordered leading to magnetic disorder. Two comments should be made in regard to this; firstly there is no direct proof that the disorder appears at the surface and not in the bulk even though this is a reasonable assumption, and secondly that to this date no satisfying explanation has been found to why the smallest particles should be more structurally ordered.

<table>
<thead>
<tr>
<th>Sample</th>
<th>6a</th>
<th>6b</th>
<th>8</th>
<th>9a</th>
<th>9b</th>
<th>11</th>
</tr>
</thead>
<tbody>
<tr>
<td>d (nm)</td>
<td>6.2</td>
<td>6.3</td>
<td>8.0</td>
<td>9.0</td>
<td>9.0</td>
<td>11.5</td>
</tr>
<tr>
<td>d_{mag} (nm)</td>
<td>5.7</td>
<td>5.7</td>
<td>7.2</td>
<td>8.1</td>
<td>8.3</td>
<td>10.7</td>
</tr>
</tbody>
</table>

A common way to evaluate interactions between grains or particles is by using the so called $\delta M$-plot, which is a remanence based technique used in areas ranging from paleomagnetism [42] to nanomagnetism [43].

**Figure 3.4:** IRM, DCD and $\delta M$ curves as a function of magnetic field for a) non-interacting (silica shell coated) 6 nm particles, b) non-interacting (silica shell coated) 8 nm particles and c) strongly interacting “bare” 8 nm particles. The bare and silica coated 8 nm particle are from the same synthesis, except that the bare particles were taken out before the silica coating step and the oleic acid coating was removed by repeated rinsing in acetone. The measurements were made at 5 K.
Results and discussion

Figure 3.5: $\delta M$ depth as a function of concentration. The 0 nm and 17 nm indicate the shell thickness of the particle coating. The shell thickness from left to right is 62, 45, 17, 3, 2, OA and 0 nm, were OA stand for oleic acid coated.

$\delta M(H) = M_{DCD}(H) - [M_{rs} - 2M_{IRM}(H)]$, where $M_{rs}$ is the saturation remanence taken as the highest value of $M_{IRM}(H)$. When evaluating the silica coated particles with the $\delta M$ method an unexpected result was obtained. The non-interacting particles showed a $\delta M$ dip which is indicative of interparticle interactions [44], however the smallest coated particles of REF6a and 6b (6.2 and 6.3 nm) showed no dip, see Fig. 3.4. To further study this, a series of samples with varying silica shell thickness (0, 2, 3, 17, 45 and 62 nm, the series also included particles coated only with oleic acid), were made for the 8 nm particles. The shell thicknesses correspond to a magnetic particle packing fraction ($p$) of about 60% to 0.01%, with the 17 nm shell thickness corresponding to a packing fraction of about 0.5% and the oleic acid coated particles corresponding to a packing fraction of about 50%. Comparing the $\delta M$ curves for the dense compact without any shell ($p\approx60\%$) and the 17 nm silica coated particles ($p\approx0.5\%$) a difference in the shape and depth of the curves can be seen in Fig. 3.4 b) and c).

The depth of $\delta M$ as a function of concentration is shown in Fig. 3.5 and reveals that for the low concentration regime, 0.01% to 0.5% (62 to 17 nm shell thickness), the depth is constant and non-zero. In the high concentration regime, 20% to 60% (3 nm to 0 nm shell thickness), the depth increases rapidly with increasing concentration. The later behavior is expected since the dipolar interaction increases with increasing concentration and the $\delta M$ depth should therefore also increase. If dipolar interactions were important in the low concentration
regime it could be expected that there would be a change in $\delta M$. This, together with the fact that only the REF6a and 6b samples which do not show significant surface spin disorder show $\delta M = 0$, suggest that it is not the extremely weak dipolar interaction between particles which is relevant, but rather the interactions between the disordered surface and the magnetically ordered core of the nanoparticles. To make certain that there are no particles which have aggregated during the coating step, an extensive TEM study was made, where thousands of particles were examined without finding any coated particle for which there was more than one particle within the silica shell.

Summary

In this section several sizes of $\gamma$-Fe$_2$O$_3$ magnetic nanoparticles, with very narrow size distributions, have been presented. Dipolar interactions between the particles could be avoided by coating the particles with a thick silica shell, so that the properties of the individual particles could be studied without having to take into account effects from interparticle interactions. From magnetic and Mössbauer spectroscopy measurements it was found that all particles (particle batches) with a mean size larger than 8 nm have a magnetically disordered surface layer, which seems to stem from crystalline disorder at the surface as indicated by XRD measurements. The surface spin disorder gives rise to exchange bias, via interaction between the ordered core and the disordered surface spins. It was found that the smallest particles (particle batches), 6.2 and 6.3 nm, have a higher degree of crystalline order and show negligible exchange bias. It was also found that intraparticle interactions between the surface spins and the core give rise to a dip in the so-called $\delta M$ plots, even though the particles are non-interacting showing that the $\delta M(H)$ method is not only sensitive to interparticle interactions but also to intraparticle interactions. This adds complexity to the interpretation of $\delta M(H)$ studies. This section is based on papers II and VII and includes figures from these papers.
3.2 A dense ensemble of magnetic nanoparticles with spin glass like properties

As described in the Introduction chapter a spin glass exhibits the unique characteristics: aging, memory and rejuvenation [17, 20]. In order to be able to call an ensemble of strongly interacting nanoparticles a superspin glass (a nanoparticle replica of a spin glass) a requirement is that all these collective characteristics are present in the ensemble. Furthermore it is expected that a superspin glass, like atomic spin glasses, should exhibit a second order phase transition from a (super)paramagnetic to a (super)spin glass phase and exhibit critical slowing down.

Using the 8 nm $\gamma$-Fe$_2$O$_3$ particles described in section 3.1, but without the silica shell (i.e. bare particles), a dense disc was made by pressing the particles together. The disc had a packing fraction of about Random Close Packing (64%) and it will thus be referred to as RCP8. The particles were synthesized during the same synthesis as the silica coated reference system, but were taken out before the silica coating step and washed repeatedly to remove the oleic acid coating. The end result is a bare maghemite nanoparticle powder which was used to make the dense disc by pressing the powder (about 0.7 GPa). The disc is shown in Fig. 2.1 and it is the same sample as used in Refs. [27], [28] and [45]. A small piece of the disc was mounted into a custom built SQUID, which is described in the Experiment.
3.2 A dense ensemble of magnetic nanoparticles with spin glass like properties

iments. Some initial characterization was made to determine that the sample showed linear response. This was made by measuring several M_{ZFC}(T), M_{FC}(T) and M_{TRM}(T) curves for different magnetic fields strengths, H=2.4, 24 and 240 A/m. In Fig. 3.6 the M_{ZFC}(T) data is presented as M/H vs. T and as seen in the figure all of the M_{ZFC}(T)/H curves overlap, indicating that the sample is in the linear response regime.

To investigate if the ensemble shows aging, M_{ZFC}(t) relaxation measurements were made, the protocol is described in Experiments. The H field (H=40 A/m) was chosen so that the ensemble was in the linear response regime. The measurements were made at different temperatures (T=50, 80 and 110 K) and at different waiting times before switching on the field (t_w = 0, 300, 1000, 3000 and 10000 s). The results are presented

![Figure 3.7](image)

**Figure 3.7:** (a) M_{ZFC}(t) at 110 K after different waiting times as indicated in the figure; H=40 A/m (b) Corresponding relaxation rate S curves, S=dM_{ZFC}(t)/dlog_{10}(t). (c) ZFC relaxation at 50 and 80 K after different waiting times. (d) Corresponding relaxation rate curves.
Results and discussion

Figure 3.8: Relaxation($M_{ZFC}(t)$) and relaxation rate ($S(t)$) of an atomic spin glass.

in Fig. 3.7a) and c). In Fig. 3.7b) and d) the relaxation rate, $S = dM/d\log_{10}(t)$, is also presented. The first observation that can be made is that there is a waiting time dependence of the $M_{ZFC}(t)$ and $S(t)$ curves, which means that the ensemble exhibits aging. A second observation is that the curves qualitatively look similar to the atomic spin glass relaxation curves presented in Fig. 3.8. Looking at the $S(t)$ curves it can be seen that there is a maximum around $t = t_w$, this feature is also seen in atomic spin glasses. From the presented data it can be concluded that the studied dense ensemble of magnetic nanoparticles not only exhibits aging but also in a qualitatively similar way to an atomic spin glass.

To study memory and rejuvenation effects associated with the aging phenomenon of spin glasses, so-called DC memory experiments were performed. The experimental protocol is described in detail in the Experiments. As in the relaxation measurements a field which fulfills the requirement of being small enough to keep the sample in the linear response regime was used ($H = 40$ A/m). A halting time $t_h = 10^4$ s was used as well as three different halting temperatures $T_h = 50, 80$ and $110$ K.

Figure 3.9: $M_{ZFC}(T)$ and $M_{FC}(T)$ magnetization as a function of temperature. Three of the $M_{ZFC}(T)$ curves include a stop at one temperature; 50, 80 or 110 K for $10^4$ s during cooling, $M_{Mem}(T)$. The last $M_{ZFC}(T)$ does not include any stop and is used a reference, $M_{Ref}(T)$. The inset shows the difference between the memory curves and the reference; $\Delta M = M_{Mem}(T) - M_{Ref}(T)$. 
3.2 A dense ensemble of magnetic nanoparticles with spin glass like properties

From the data presented in Fig. 3.9 a difference is observed between the reference curve and the memory curves, where the memory curves exhibit a dip in magnetization around the respective halting temperatures. This difference is easily seen in the difference plot, $\Delta M = M_{\text{Mem}}(T) - M_{\text{Ref}}(T)$, shown as an inset in Fig. 3.9. The dip in magnetization at the halting temperature is the so called memory effect, which is caused by the system remembering the aging that occurred during the stop. The lack of difference between the memory and reference curves at temperatures further away from the halting temperature is the so called rejuvenation, which means that at these temperatures the effective age is the same for the memory and reference curve, this is due to that the age of the system is tied to a specific temperature. This means that the system can be aged at one temperature while all other temperatures remain unaffected, however there is a small region of temperature in which the age at a nearby temperature is affected, which is the reason behind the width of the memory dips [20].

To investigate if the ensemble obeys critical slowing down and undergoes a phase transition from a superparamagnetic to a superspin glass phase, a dynamical scaling analysis was performed using AC magnetic susceptibility data recorded us-

![Figure 3.10](image.png)

**Figure 3.10:** The $\chi''$ data for the frequencies indicated in the legend. $\ast$ indicates the freezing temperature $T_f$ chosen for each frequency. The inset shows the best fit to the power law describing critical slowing down.
Results and discussion

ing a field of 320 A/m and AC frequencies between 0.17 to 510 Hz. From the out-phase-component a freezing temperature, $T_f$, was determined for each frequency as shown in Fig. 3.10. By fitting the freezing temperatures to $\tau = \tau^* [(T_f(f) - T_g)/T_g]^{-2\nu}$, with $\tau \sim 1/\omega = 1/2\pi f$, $T_g$, $2\nu$ as well $\tau^*$ where determined, were $T_g$ is the superspin glass transition temperature, $2\nu$ the dynamical critical exponent and $\tau^*$ the individual relaxation time of the interacting building blocks at this temperature. The fit is presented in the inset of Fig. 3.10 and yielded $T_g = 140$ K, $2\nu = 9$ and $\tau^* = 10^{-10}$ s. This implies that the systems exhibits critical slowing down and thereby a second order phase transition.

Summary

In this section it was shown that dense compacts of magnetic nanoparticles exhibit the properties associated with a spin glass phase, non-equilibrium dynamical effects such as aging, memory and rejuvenation, as well as a second order phase transition from a superparamagnetic phase to a superspin glass phase and the system can therefore be considered a model superspin glass. This section is based on papers I, II and III and includes some figures from these papers.
3.3 Size dependence of particle interactions and superspin glass properties

3.3.1 Interparticle interactions

To study how the particle size affects the superspin glass behavior, several samples of maghemite nanoparticles of different sizes were made as described in section 2.1. Each sample also had a corresponding reference sample, where the particles were coated with a thick silica shell, see section 3.1. The dense discs made from bare particles will be referred to as RCPx and the silica coated reference samples will be referred to as REFx; \(x=6a, 6b, 8, 9a, 9b\) or 11), a and b represent duplicates of the same size but come from different synthesis batches. Not all measurements were made on disc shaped samples, since some of the discs broke into large pieces which were used for magnetometry. With increasing size of the particles it can be expected that the transition temperature will increase due to increased dipolar interaction. Fig. 3.1 shows the particles used to make dense discs as well as their silica coated references, note that the TEM picture is taken on unwashed particles so the TEM images on the left side are on oleic acid coated particles. This is to avoid aggregation and facilitate the determination of the size distribution. As mentioned in section 3.1, the size distribution of all particle sizes is very narrow, an example of a size distribution is shown for the 8 nm particles as an inset in Fig. 3.1 (c).

The data for the non-interacting silica coated particles was presented and discussed in section 3.1. There the magnetization as a function of temperature data for these non-interacting particles was presented in a small temperature range to better resolve the features of the data. Here the same data is presented in Fig. 3.12 (a) on a larger temperature scale, 0 to 400 K. The magnetization as a function of temperature for the dense compacts is presented in Fig. 3.12 (b). The temperature corresponding to the maximum magnetization in the ZFC curves, \(T_{max}\), for the RCPx samples is several times larger than the blocking temperature, \(T_b\), for the corresponding non-interacting REFx samples, e.g. \(T_{max}/T_b\) is about a factor 12 for RCP6a/REF6a and about 4 for RCP8/REF8. A model for estimating \(T_{max}\) from the dipolar interaction energy was proposed by Mørup et al. [46]. Using a point dipole approximation it can be expected that \(T_{max}\) increases with increasing size of the particles, since dipolar interaction energy \(E_{dd} \propto \mu^2/L^3\), where \(\mu = M_s V \propto M_s d^3\) is the magnetic moment, \(L\) is the distance between the dipoles and \(M_s\) is the saturation magnetization of the particle. For dense ensemble \(L = d\), since the distance will
Results and discussion

Figure 3.12: Magnetization as a function of temperature using the ZFC and FC protocol for (a) the non-interacting reference sample and (b) the dense compacts made from the corresponding size of particles as the reference samples. The data in panel (a) is the same data as presented in Fig. 3.2 but on a different temperature scale.

be equal to the diameter of the particle, see Fig. 3.11. This results in a net growth of $T_{\text{max}}$ proportional to $d^3$, (assuming $M_s$ is size independent). Using the estimation ($T_{\text{dd}} = E_{\text{dd}}/k_B$) for all samples and plotting the measured values of $T_{\text{max}}$ as a function of $T_{\text{dd}}$, a linear trend is found for all RCPx samples of 8 nm and larger sizes, see inset of Fig 3.12. The compacts made from the smallest particles (RCP6a and 6b) deviate from the trend by having a higher than expected $T_{\text{max}}$. The question then arises as to why the smallest particles would have a larger $T_{\text{max}}$ than suggested by the trend. Is it possible that there is another interaction mechanism at play between the particles that for some reason is absent for the larger particles? Due to the particles being in contact it could be possible for superexchange to take place. Normal exchange interaction can be ruled out since the particles are oxides. Superexchange has
been reported as an interaction mechanism between magnetic oxide particles which are in contact [47, 48]. RCP6a and 6b differ in two ways from the rest of the series, they are the smallest particles and they lack significant surface spin disorder. Since the surface is important for transferring the interaction in case of superexchange it is possible that the surface disorder disrupts or weakens the interaction. It is also possible that the smallest particles are the only particles that are small enough, since it could be expected that superexchange becomes more important as the surface to volume ratio grows. This is because the surface is the part of the particle which transfers the superexchange interaction, which affects the whole particle volume.

### 3.3.2 Size dependence of superspin glass properties

Since the RCP8 sample was found to be a model superspin glass it can be expected that also other dense samples of strongly interacting magnetic nanoparticles should be superspin glasses. To verify this an AC-susceptibility study was made which included all RCPx samples. Using a frequency of 10 Hz a wide temperature scan was made. The data is presented in Fig. 3.13 with panel (a) corresponding to the in-phase and panel (b) corresponding to the out-of-phase data. The in-phase data looks similar to the \( M_{ZFC}(T) \) data with the temperature corresponding to the maximum susceptibility increasing with increasing particle size. The out-of-phase data shows a sharp onset for all samples when cooling from high to low temperature. Below the onset there is a pronounced “bump”, which was later identified to originate from demagnetization effects, this is discussed further in section 3.5. Comparing the sharpness of the onset of dissipation on a relative temperature scale it was found that the onset is equally sharp for all samples, see Fig. 3.14, indicating that all the samples could exhibit a superspin glass phase transition. As in section 3.2 several frequencies between 0.17 and 510 Hz were measured and from each of them a freezing temperature was extracted. These freezing temperatures were fitted to 

\[
\tau = \tau^* \left( \frac{T_f(f) - T_g}{T_g} \right)^{-z\nu},
\]

see section 3.2 for further details. The extracted \( T_g \), \( z\nu \) and \( \tau^* \) values are presented in Table 3.2. Due to the relatively small frequency window used the error bars on the \( z\nu \), \( T_g \) as well as the \( \tau^* \) values are rather large. With this in mind \( z\nu \) seems to be around 8 and \( \tau^* \) around \( 10^{-10} \) s. Overall the fits are good and indicate that all samples exhibit a transition from a superparamagnetic state to a superspin glass state upon cooling. It is also seen that there is no real difference in the studied superspin glass properties for RCP6 and
Results and discussion

Table 3.2: Particle size (TEM) and parameters from critical slowing down analyses for all RCPx samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>RCP6a</th>
<th>RCP6b</th>
<th>RCP8</th>
<th>RCP9a</th>
<th>RCP9b</th>
<th>RCP11</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEM (nm)</td>
<td>6.2</td>
<td>6.3</td>
<td>8.0</td>
<td>9.0</td>
<td>9.0</td>
<td>11.5</td>
</tr>
<tr>
<td>$T_g$ (K)</td>
<td>153</td>
<td>145</td>
<td>140</td>
<td>200</td>
<td>190</td>
<td>338</td>
</tr>
<tr>
<td>$z^\nu$</td>
<td>7</td>
<td>10</td>
<td>9</td>
<td>7</td>
<td>9</td>
<td>8</td>
</tr>
<tr>
<td>$\tau^*$ (s)</td>
<td>$4 \times 10^{-11}$</td>
<td>$2 \times 10^{-11}$</td>
<td>$7 \times 10^{-11}$</td>
<td>$7 \times 10^{-10}$</td>
<td>$6 \times 10^{-11}$</td>
<td>$1 \times 10^{-12}$</td>
</tr>
</tbody>
</table>

the rest of the samples, indicating that the properties are not dependent on interaction type, only on the strength. It should be noted that it is required that competing interactions occur to form a superspin glass phase, i.e. that the interaction has to be random in sign (ferromagnetic/antiferromagnetic).

Figure 3.13: The in-phase (a) and out-of-phase (b) component of the magnetic AC susceptibility ($f=10$ Hz) for the RCPx samples.

Summary

In this section the effects of the interaction strength was studied using a series of compacts comprising different sizes of
3.3.2 Size dependence of superspin glass properties

Figure 3.14: Normalized out-of-phase component of the AC-susceptibility \( \chi'' \) as a function of normalized temperature. The temperature is normalized to the temperature \( T_{\text{norm}} \), which is defined as the temperature corresponding to the maximum slope for \( \chi''(T) \). \( \chi'' \) is normalized by the maximum value just below the onset.

particles, each compact having its own particle size. As the particle size is increased the dipolar field which each particle is subjected to increases and with this the transition temperature of the compacts increases. The compacts made from the smallest particles (RCP6a and 6b) have a higher than expected transition temperature. In section 3.1 data for the corresponding 6 nm particles were presented and it was shown that they deviate from the rest of the particles by having a lower than expected \( T_b \) (lower anisotropy) and lack of significant exchange bias, indicating the absence of a shell of disordered spins at the surface of the particles occurring for the larger particles. In this section it was suggested that the reason for the higher transition temperature in the RCP6 samples is that the dominating interaction mechanism is not dipolar but of superexchange origin. It was also suggested that it is the lack of surface spin disorder which allows superexchange to develop between the smallest particles. Further it was shown that all RCP samples exhibit superspin glass behavior as well as a second order transition from a superparamagnetic to a superspin glass phase. This section is based on papers II and III and includes figures from these papers.
3.4 Superspin glass properties in a system consisting of mixed particles

Up to this point only monodisperse systems have been considered to diminish the effects of the size distribution. However, many investigations on magnetic nanoparticles are made on systems with a wide particle size distribution. To evaluate the effects of the size distribution two batches of monodisperse $\gamma$-Fe$_2$O$_3$ particles were synthesized, 9 and 11.5 nm in diameter, see Fig. 3.16 (a), (b) and (d). After synthesis the two batches were mixed into different concentrations of small (9 nm) and large (11.5 nm) particles (Fig. 3.15), ranging from 100% small and 0% large particles to 0% small and 100% large particles. The volume ratio between the small and large particles is a factor two. The samples were named MIXx, x=0, 10, 20, 30, 50, 65, 85 or 100, where x denotes the weight concentration of large particles in percent. A high resolution SEM image of one of the samples (MIX65) is shown in Fig. 3.16 (c). In the image no size aggregation is seen and the sample appears well mixed. Using SEM images of samples from the rest of the series the same conclusion was made for the entire series. In Fig. 3.17 the AC susceptibility data for all MIXx samples are presented ($H_{AC}=80$ A/m and $f=10$ Hz). It should first be commented that only one smooth curve and not a superposition of curves from the two sizes is seen for $\chi'(T)$, see Fig. 3.17 (a). Further it can be seen that $T_{max}$ increases linearly with increasing concentration of large particles indicating that it is the average dipolar strength which determines $T_{max}$, see inset of Fig. 3.17 (a). As in Fig. 3.13 a sharp onset is seen in $\chi''(T)$ upon cooling from a high temperature for all MIXx samples. An anomalous feature is seen below the onset, which, as mentioned in section 3.3, is

Figure 3.15: Schematic image showing mixing of the particles and the final sample.

Figure 3.16: (a) TEM image the 9 nm particles used to make the MIX0 sample. (b) TEM image the 11.5 nm particles used to make the MIX100 sample. (c) SEM image of the MIX65 sample. (d) size distributions determined from TEM images for the 9 and 11.5 nm particle batches.
3.4 Superspin glass properties in a system consisting of mixed particles

Figure 3.17: (a) Normalized in-phase AC susceptibility as a function of temperature and (b) corresponding normalized out-of-phase curves. All curves have been normalized to the maximum value of the in-phase component, $T_{\text{max}}$. The inset in (a) shows $T_{\text{max}}$ determined from the data presented in (a) as a function of concentration of 11.5 particles, i.e. 0% corresponds to MIX0.

related to demagnetization effects (see section 3.5).

To study the non-equilibrium properties of the samples DC memory experiments were performed and it was found that all samples show spin glass like memory dips suggesting that the samples enters a superspin glass state. Since the size distribution of e.g. MIX50 is large and of bimodal type the question arises if these polydispersed compacts could undergo a superspin glass phase transition. To answer this question critical slowing down analysis was performed by extracting freezing temperatures from the out-of-phase component for several frequencies and fitting these temperatures to a power law,

Table 3.3: Parameters from critical slowing down analysis for all MIXx compacts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_g$ (K)</th>
<th>$zv$</th>
<th>$\tau^*$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MIX0</td>
<td>180</td>
<td>10</td>
<td>$1 \times 10^{-11}$</td>
</tr>
<tr>
<td>MIX10</td>
<td>185</td>
<td>10</td>
<td>$5 \times 10^{-11}$</td>
</tr>
<tr>
<td>MIX20</td>
<td>200</td>
<td>9</td>
<td>$1 \times 10^{-10}$</td>
</tr>
<tr>
<td>MIX30</td>
<td>205</td>
<td>9</td>
<td>$1 \times 10^{-10}$</td>
</tr>
<tr>
<td>MIX50</td>
<td>215</td>
<td>11</td>
<td>$1 \times 10^{-11}$</td>
</tr>
<tr>
<td>MIX65</td>
<td>245</td>
<td>10</td>
<td>$1 \times 10^{-11}$</td>
</tr>
<tr>
<td>MIX85</td>
<td>265</td>
<td>10</td>
<td>$5 \times 10^{-12}$</td>
</tr>
<tr>
<td>MIX100</td>
<td>275</td>
<td>9</td>
<td>$1 \times 10^{-11}$</td>
</tr>
</tbody>
</table>
\[ \tau = \tau^* \left( \frac{T_f(f) - T_g}{T_g} \right)^{-z\nu}. \] These analyses indicated that all MIXx samples enter a superspin glass phase, which may seem surprising considering the bimodal size distribution, where the relaxation times of the large and small particles are very different [24]. However, taking into account the very large interaction strengths involved, the relaxation time of the small and large particles are much shorter than the observation time at \( T_{\text{max}} \), since \( T_{\text{max}} \) is several times larger than \( T_b \) for both particle sizes. The determined values for \( T_g, z\nu \) and \( \tau^* \) are presented in table 3.3.

**Summary**

The results presented in this section on binary compacts suggest that it is the average and not the strongest dipolar interaction strength, which determines the cusp temperature in magnetization as a function of temperature measurements. The results also suggest that the dipolar interparticle interactions are strong enough to force the system into a homogenous collective magnetic state instead of two separate states corresponding to each of the two sizes. This section is based on paper V and includes figures from this paper.
3.5 Demagnetization effects for high concentrations of magnetic nanoparticles

Demagnetizing fields are present in all fields of magnetism and are very important in some of them. The internal magnetic field, $H_{int}$, is the field that affects the sample. The internal field is related to the applied magnetic field, $H_{applied}$, through the relation, $H_{int} = H_{applied} - NM$, where $N$ is the demagnetization factor and $M$ is the magnetization. Many magnetic nanoparticle studies discuss one aspect of demagnetization effects, i.e. shape anisotropy, which often gives rise to an easy axis of magnetization for single domain particles. When measuring on assemblies of magnetic particles the sample will have a geometric shape. This shape is often determined by the shape of the sample holder, as in the case of a packed nanoparticle powder or a frozen ferrofluid in a cup [1]. If the volume magnetization (susceptibility) of the sample is large enough demagnetization effects become important. An estimate of the total demagnetization factor in a specific direction of the sample can be made using:

$$N_{tot,\alpha} = N_{p,\alpha} + p(N_{s,\alpha} - N_{p,\alpha}), \quad (3.2)$$

where $N_{p,\alpha}$ is the particle demagnetization factor in the $\alpha$ direction (x, y or z) and $p$ is the packing fraction (concentration) of the magnetic particles. $N_{s,\alpha}$ is the demagnetization factor from the sample shape in the $\alpha$ direction which can be estimated from the sample geometry [1]. Assuming spherical particles this is simplified to:

$$N_{tot,\alpha} = \frac{1}{3} + p(N_{s,\alpha} - \frac{1}{3}). \quad (3.3)$$

It is worth noting that unless $p = 0$ there will always be a demagnetizing factor in every direction independent of the shape of the sample, e.g. for a sample shaped like a thin film ($N_{s,x}=N_{s,y} = 0$ and $N_{s,z}=1$) $N_{tot,\alpha} \neq 0$ due to the contribution from the individual particles to the total demagnetization factor. The z direction is perpendicular to the plane of the film. For a sample with $p = 0.5$ the result would be, $N_{tot,x}=N_{tot,y} = \frac{1}{6}$ and $N_{tot,z} = \frac{4}{6}$. As seen from eqn. 3.3 this effect decreases with decreasing concentration (particle packing fraction). As a rule of thumb demagnetization effects for concentrated particle systems ($p \approx 50\%$) with thin disc geometry starts to be important when the susceptibility exceeds 0.05 (SI) (assuming 5% error is acceptable). The difference in this case between the internal susceptibility, $\chi_{int}$, and the external (measured) susceptibility, $\chi_{ext}$, for the x,y direction is about 1%
Results and discussion

Figure 3.18: DC and AC susceptibility data as a function of temperature measured in the parallel (∥) and perpendicular (⊥) direction of a dense disc (5 mm in diameter and 2 mm thick). a) and d) DC susceptibility as a function of temperature. b) and e) AC in-phase susceptibility as a function of temperature. c) and f) AC out-of-phase susceptibility as a function of temperature. The measurements used $H_{DC} = 400$ A/m, $H_{AC} = 80$ A/m and $f = 10$ Hz. Left side panels presents the data without demagnetization correction. The right side panels presents the data after demagnetization correction.

while in the z direction the difference is about 3.5%. This can be compared to the case if the susceptibility is about 0.5 (SI) which, for the same geometry and concentration, gives a difference of 8.5% and 33% for the x,y and z directions, respectively.

The sample used for the measurements presented in this
section is a thin disc made by compacting monodisperse 8 nm particles. The thickness of the disc is 2 mm, the diameter is 5 mm and the packing fraction 59%. This corresponds to the sample demagnetization factors, $N_{s,x} = N_{s,y} = 0.146$ and $N_{s,z} = 0.708$ and after taking into account the demagnetization factors from the packed particles these translate to the total demagnetization factors $N_{tot,x} = N_{tot,y} = 0.223$ and $N_{tot,z} = 0.554$.

Demagnetization effects are more than simple scale factors and affect the shape of the magnetization as a function of temperature curves as shown in Fig. 3.18 (a) and (d), where it can be noted that there is a change in shape at high temperatures from a near linear to a $1/T$ shape [49]. At low temperatures there is a weak “bump” in the $M_{ZFC}(T)$ curve which disappears after demagnetization correction. It should also be noted that the maximum gets sharper after demagnetization correction, and that the larger the demagnetization factor is the broader the measured maximum becomes. The curves in Fig. 3.18 a) were corrected using:

$$\chi_{int} = \frac{\chi_{ext,\alpha}}{1 - N_{tot,\alpha}\chi_{ext,\alpha}},$$

where $\chi_{int}$ is the internal susceptibility, and $\chi_{ext,\alpha}$ is the external susceptibility measured in the direction $\alpha$ and $N_{tot,\alpha}$ is the demagnetization factor in the corresponding direction, which was determined using Eqn. 3.3.

In Fig. 3.18 b), c), e) and f) the in-phase and out-of-phase components for uncorrected and demagnetization corrected data are presented. The in-phase data b) and e) are very similar to the DC data in a) and d). However examining the out-of-phase component in c) and f) it can be seen that there is an even larger difference between the corrected and the uncorrected data, with the uncorrected data showing a broad large maximum at lower temperatures (see Section 3.3), which becomes a small shoulder after demagnetization corrections. The data in Fig. 3.18 b) and c) are corrected using Eqn. 3.5 and Eqn. 3.6, respectively.

$$\chi'_{int} = \frac{\chi'_{ext} - N_{tot,\alpha}[(\chi'_{ext})^2 + \chi''_{ext}]^2}{N_{tot,\alpha}[(\chi'_{ext})^2 + \chi''_{ext}]^2 - 2N_{tot,\alpha}\chi'_{ext} + 1},$$

$$\chi''_{int} = \frac{\chi''_{ext}}{N_{tot,\alpha}[(\chi'_{ext})^2 + \chi''_{ext}]^2 - 2N_{tot,\alpha}\chi'_{ext} + 1}.$$

Using the internal AC susceptibilities ($\chi'_{int}$ and $\chi''_{int}$) the external AC susceptibilities ($\chi'_{ext}$ and $\chi''_{ext}$) for different demagnetization factors can be calculated. These calculated values of
Results and discussion

Figure 3.19: a) and b) The effect of demagnetization on the in-phase susceptibility ($\chi'$), c) and d) and out-of-phase susceptibility ($\chi''$). $\chi'_{ext}$ and $\chi''_{ext}$ are normalized by the maximum of $\chi'_{ext}$ in b) and d). Panel a) and c) are the corresponding curves without normalization.

$\chi'_{ext}$ for $N_{tot}=0.1, 0.2, 0.3, 0.4, 0.5$ and 0.6 are presented in Fig. 3.19 a) and b) together with the $\chi'_{int}$ from which they were calculated. In the figure it can be seen that with increasing $N_{tot}$ the maximum gets broader. In Fig. 3.19 c) and d) the corresponding $\chi''_{ext}$ is presented with the $\chi''_{int}$ and it can be seen that the demagnetization introduces a maximum at low temperature that grows in magnitude relative to the onset of dissipation (at roughly 200 K). The temperature for this demagnetization induced maximum is also dependent on the demagnetization factor, with a lower temperature for the maximum at larger demagnetization factors.

From the presented data it can be concluded that demagnetization effects in the studied system are significant. The question is how do these effects affect the previously drawn conclusions. Overall the conclusions are unaffected by demagnetization effects, e.g. $T_{max}$ is not shifted after demagnetization
3.5 Demagnetization effects for high concentrations of magnetic nanoparticles

Figure 3.20: Out-of-phase component of the AC susceptibility ($\chi''$) as a function of temperature for demagnetization corrected as well as uncorrected measurements $\parallel$ and $\perp$ to the plane of the disc, which corresponds to a demagnetization factor of about 0.2 and 0.6 respectively. $\chi''$ is normalized by the maximum close to the onset of dissipation. The circle corresponds to a selection criterion of $T_f$ based on picking a $T_f$ corresponding to 1/6 of the value of $\chi''$ at the maximum.

Figure 3.21: The directions of the applied magnetic field on the disc.

corrections and Langevin analysis is made on the dilute reference system which means that demagnetization effects are negligible due to the low susceptibility. There is however one case which is worth having a closer look at. As shown in 3.19 c) and d) the onset of the out-of-phase component becomes broader and this could have an effect on the determination of the freezing temperature ($T_f$) used in the critical slowing down analysis. As can be seen in Fig. 3.20, if the criterion for determining $T_f$ is chosen close to the onset of dissipation, even for samples with a large demagnetization factor ($N_{tot}=0.6$), the effect of demagnetization on $T_f$ is small. If a criterion far away from the onset, e.g. the maximum of the out-of-phase component is used, the effects become significant.

Measuring in the hard direction on a thin disc-like sample (perpendicular to the disc plane, see Fig. 3.21) with a particle concentration of 50% is rather unusual, however samples like concentrated ferrofluids or a powder of particles in a measurement cup can have concentrations of particles well above 10% and high susceptibilities, leading to substantial demagnetization effects. In the supplementary material of paper VI there is a table showing in more detail the effects of demagnetiza-
tion factors for different packing fractions (concentrations) of magnetic particles.

Summary

From the data present in this section it can be concluded that demagnetization effects in magnetic nanoparticle systems can be substantial and should if possible be taken into account. The demagnetization can lead to effects like broadening and artificial maxima in AC-susceptibility as a function of temperature measurements. It is therefore important to be aware of this and be careful with interpretations if demagnetization effects are not taken into account. In some systems, e.g. dilute ferrofluids, demagnetization effects can be ignored due to the low magnetic susceptibility of the system. This section is based on paper VI and includes figures from this paper.
3.6 Effects of the individual particle relaxation time on the superspin glass state

In the study of different sizes, see section 3.3, it turned out that RCP6a (assembly of 6 nm particles) and RCP8 (assembly of 8 nm particles) had approximately the same \( T_g \) (140 K), but very different \( T_b \) (12.5 and 35 K). This means that at some temperatures the individual particles will have very different relaxation times, e.g. below 35 K the 8 nm particles will be blocked, while the 6 nm particles will be unblocked (on our experimental timescales). This is a major difference compared to atomic spin glasses where the building blocks have a constant relaxation time \( (10^{-12} \text{ s}) \) as compared to the temperature dependent relaxation time of nanoparticles. The relaxation behavior was measured for both samples using several waiting times \( (t_w = 0, 300 \text{ and } 3000 \text{ s}) \) and performing the measurements at several temperatures \( (T=50, 80 \text{ and } 110 \text{ K}) \). The data is presented in

**Figure 3.23**: Zero field cool magnetic relaxation, \( M_{ZFC}(t) \), for RCP6a and RCP8 at 110 K (a) and 50 and 80 K (b), for all temperatures using three different waiting times \( t_w = 0, 300 \text{ and } 3000 \text{ s} \). (c) and (d) show the corresponding relaxation rate, \( S(t) \), curves.
Results and discussion

Fig. 3.23, where it can be seen that both samples exhibit aging. Furthermore, the ratio $M_{RCP8}(t = 1\,s)/M_{RCP6a}(t = 1\,s)$ increases with increasing temperature from 0.75, 0.93 to 0.95 at 50, 80 and 110 K respectively, which indicates that the relaxation time of RCP8 approaches the relaxation time of RCP6a as the temperature is increased. From $\tau^* = \tau_0 e^{(KV/k_BT)}$ this is not strange, since $\tau^*$ of both sizes will approach the same minimum relaxation time, $\tau_0$, as temperature is increased, see Fig. 3.22. The individual relaxation time, $\tau^*$, will put a limit on how fast the sample can relax and if this limit is much slower for one sample it can be expected to relax slower and the magnetization should therefore be lower compared to the fast relaxing sample. Even though the particles of RCP6a will always have a shorter relaxation time at a finite temperature the relax-

Figure 3.24: The top panels show memory curves for RCP6a and RCP8 that were obtained after making a stop for 10 000 s during cooling at either 50, 80 or 110 K. A $M_{ZFC}(T)$ curve which did not include any stop during cooling is included as a reference curve. The bottom panels show the difference between the memory curves and the reference curve. The insets shows $\Delta M_{Relax} = M(t_w = 3000\,s) - M(t_w = 0)$ with $t = 100\,s$ as a function of temperature. $\Delta M_{Relax}$ is estimated using the data presented in Fig. 3.23.
3.6 Effects of the individual particle relaxation time on the superspin glass state

Figure 3.25: IRM(T) for two spin glasses; Ising (blue) and Heisenberg (red). The circles indicate the difference in behavior for Ising and Heisenberg spin glasses. The plotted data is the same as in figure 2.5.

tive difference will shrink with increasing temperature. In line with this the relaxation rate $S(t)$ is similar at 110 K, while it is larger for RCP6a at 50 and 80 K. Another comparison of the non-equilibrium dynamics were made by measuring the memory effect of the two samples, this is presented in Fig. 3.24. The measurements were made using a field of 40 A/m and the stop during cooling was 10 000 s at either 50, 80 or 110 K. For RCP6a the memory dips are deeper and sharper compared to RCP8 and the maximum depth is at 80 K, this is again in contrast to RCP8 for which the depth increases with increasing temperature. Comparing the $\Delta M_{\text{Relax}} = M(t_w = 3000 \text{ s}) - M(t_w = 0)$ at $t = 100 \text{ s}$, inset of Fig. 3.24, to the depth of the memory dips one can see that they match relatively well both in actual depth and relative difference of depth at different temperatures. A discrepancy between the $\Delta M_{\text{Relax}}$ and the depth of the memory dips is expected, since the memory is made using 10 000 s stop while $\Delta M_{\text{Relax}}$ is estimated using a difference of 3000 s. For the presented data it is clear that there is a difference in the temperature dependence of the relaxation function of the two samples, which here is attributed to the difference in energy barriers for the small and large particles.

For spin glasses the interacting units have a spin dimensionality which can be either Ising (1D), XY (2D) or Heisenberg (3D); this is a temperature independent (quantum mechanical) property. A way to distinguish between 1D and 3D spin systems is by the use of low field Isothermal Remanent Magnetization as a function of temperature (IRM(T)) measurements, as shown in Ref. [18]. The IRM(T) curve of an Ising system will be mostly flat and then have a drastic drop in magnetization at the temperature at which the stop was made, see Fig. 3.25. This is in sharp contrast to the Heisenberg case for which an increase in magnetization is seen before the magnetization drop, see Fig. 3.25. A detailed description of the protocol is given in Experiments. Using the IRM(T) protocol the two samples were analyzed by making stops at either 50, 60, 70, 80, 90, 100 or 110 K for 300 s during cooling. The field used during this stop was 40 A/m. A clear difference between the two samples is seen in Fig. 3.26, where RCP6a looks Heisenberg-like at all temperatures while RCP8 looks Ising-like at low temperatures, but Heisenberg-like at higher temperatures. Considering the difference between the energy barriers of the particles making up the two samples, one can understand that for the small particles (RCP6a) the energy barrier is small in comparison to the thermal energy, and the superspin is therefore not restricted to the easy axis of anisotropy at any of the studied temperatures. For the larger particles (RCP8) the energy barrier is much larger and the superspins align along the easy
Results and discussion

Figure 3.26: IRM(T) for several temperatures for a) RCP6a and b) RCP8. The IRM(T) curves are normalized to the value of the corresponding FC curve at the temperature of the stop during cooling, $T_h$. c) IRM(T) curves for $T_h = 50$, 80 and 110 K for both RCP6a and RCP8.

Axes of anisotropy at low temperatures, and thus behave in an Ising-like fashion. As the temperature is increased the super-spins start to fluctuate away from the easy axes becoming more Heisenberg-like.

Summary

This section has shown that the individual relaxation time of the particles affects many properties of the superspin glass, such as memory and superspin dimensionality. It should be mentioned that for both the studied samples the individual relaxation time at $T_g$ is much faster than the observation time used in the experiments. This section is based on paper IV and includes figures from this paper.
4.1 Concluding remarks

This thesis concerns extensive studies on strongly interacting $\gamma$-Fe$_2$O$_3$ magnetic nanoparticle systems. The studies include non-interacting reference systems to separate the single particle properties from the collective properties. The strongly interacting dense particle compacts are found to show collective properties very similar to those of atomic spin glasses. Due to the striking similarities to atomic spin glasses the system can be considered a model superspin glass. The different building blocks (atoms vs. nanoparticles) give rise to two major differences. Firstly, the relaxation time of the particle superspin is temperature dependent, whereas that of the atomic spin is not. This leads to a temperature dependence in the superspin dimensionality, since it is tied to the ratio between the anisotropy and the thermal energy. Secondly, nanoparticles exhibit a size distribution, which implies a variation of the properties of the building blocks. It was however concluded that with strong enough interparticle interactions it is possible to mitigate the effects of the size distribution.

4.2 Outlook

In the field of interacting nano objects there is still plenty to do. The systems that this thesis has dealt with have been disordered three-dimensional systems. The research on supermagnetism is not limited to this. One example is research made on interacting 2D nano islands, made using well developed nano
4.2 Outlook

fabrication techniques [50], trying to mimic the spin ice behavior seen in e.g. pyrochlores. These systems can show complicated dynamical properties, see paper XVII. For these kinds of systems there are myriads of possibilities to change the properties of the interacting entities and their relative position to each other [51].

A topic which has been touched upon in this thesis is to which extent the anisotropy plays an important role in determining $T_g$ and other superspin glass properties. Based on the results presented here it can be concluded that for some collective properties anisotropy definitely plays a role. A follow up study investigating how the properties of the system develop with increasing anisotropy could shed some more light on this. One could systematically vary the anisotropy and see how it affects the system. A way to do this is by cobalt doping the maghemite particles to increase the anisotropy without affecting the magnetization too much.
Denna avhandling behandlar magnetiska egenskaper hos ensembler av tätpackade $\gamma$-Fe$_2$O$_3$ magnetiska nanopartiklar (endomänpartiklar). Vid låga temperaturer kan dessa partiklar bilda en kollektiv fas med unika dynamiska egenskaper. Egenskaperna hos denna fas är slående lika de egenskaper som atomära spinglas uppvisar och den kollektiva fasen kallas därför ett superspinnglas. Anledningen till att epitetet super används i namnet är att det magnetiska momentet hos endomän partiklar ofta kallas ett superspinn på grund av sin stora storlek i förhållande till ett atomärt magnetiskt moment (spinn). Partiklarna som studerats i denna avhandling har ett magnetisk superspinn på ungefär 10000 $\mu_B$ medan atomära moment är av storleksordning 1 $\mu_B$. De $\gamma$-Fe$_2$O$_3$ nanopartiklar som används i denna avhandling tillverkades med en mycket snäv storleksfördelning. I slutet tillverkningsprocessen skildes en andel av partiklarna ut och återstående partiklar belades med ett tjockt lager kiseldioxid. Detta ledde till två pulver, ett med ”nakna” $\gamma$-Fe$_2$O$_3$ nanopartiklar och ett med kiseloxid belagd partiklar. Dessa pulver pressades var för sig till varsin kompakt puck som sedan kunde användas för egenskapsmätningar. Den magnetiska dipol-dipol växelverkan mellan superspinnen hos de nakna partiklarna är stark, medan växelverkan mellan de belagda partiklarna är försumbar eftersom de tjocka omagnetiska kiseloxidskalen separerar de magnetiska $\gamma$-Fe$_2$O$_3$ kärnorna från varandra. Genom att göra mätningar på pucken av kiseloxid beklädda partiklar kunde partiklarnas intrinsiska egenskaper bestämmas medan mätningar på pucken med nakna partiklar gav information kring de kollektiva egenskaperna som uppstår på grund av väx-
elverkan mellan partiklarna. Ett superspinnglas bildas genom att de obelagda nanopartiklarna under pressningen packas slumpvis och tätt (ca 60%) vilket ger upphov till en stark slumpvis magnetisk växelverkan mellan partiklarna. Det är denna slumpvisa växelverkan som är grunden till att ett spinnnglas liknande material bildas. När systemet kyls från hög temperatur uppvisar det en andra ordningens fasövergång vid en glasövergångstemperatur, $T_g$. Vid temperaturer under $T_g$ uppvisar systemet icke-jämviktsdynamik vilket tar sig utryck i fenomenen åldring, minne och återfödelse. Magnetisk åldring innebär att materialets egenskaper kontinuerligt förändras med tiden vid konstant temperatur i lågtemperaturfasen. Det innebär att tiden innan man utsätter (super)spinnglaset för en magnetisk fältförändring påverkar hur provet reagerar på fältförändringen. Magnetiskt minne i spinnglas sammanhang innebär att systemet kommer ihåg hur det har åldrats vid en temperatur, d.v.s. om man kyla systemet till en lägre temperatur och sedan återvänder till temperaturen som systemet åldrades vid kommer systemet ihåg att det har åldrats. Återfödelse innebär att åldringen vid en temperatur inte påverkar åldern vid en annan temperatur, systemet glömer bort att det har åldrats till dess att det återvänder till temperaturen där åldringen skedde. Att tätpackade monodispersiva $\gamma$-Fe$_2$O$_3$ magnetiska nanopartiklar uppvisar alla dessa spinnglas karaktäristika innebär att de kan användas som modellsystem för superspinnglas egenskaper och för att finna och undersöka egenskaper som särskiljer superspinnglas från atomära spinnglas. Som nämnts ovan är superspinnglas uppbygdda av magnetiska partiklar. Den individuella relaxationstiden hos dessa partiklar är beroende av temperaturen, vilket inte är fallet hos atomära magnetiska moment. En konsekvens av detta är att spinndimensionaliteten hos superspinnen utvecklas från ett Isinglikt (1D) till ett Heisenberglikt (3D) tillstånd med stigande temperatur. I nanopartikelsystem finns det alltid en storleks spridning mellan partiklarna vilket i sin tur ger upphov till en spridning i magnetiska egenskaper hos partiklarna. Genom att blandas två olika partikelsystem med en snäv storleksfördelning men med olika storlekar, kan nya bredare fördelningar skapas. Mätningar på kompaka prover med bredare storleksfördelning visade att även i dessa system sker det en fasövergång från en superparamagnetisk fas till en superspinnglas fas när systemet kyls till låg temperatur. Orsaken till att en skarp superspinnglas övergång förfarande existerar i dessa system med bred fördelning av partikelstorlekar är att dipol-dipol växelverkan är så stark att superspinnglastemperaturen är mycket högre än blockeringstemperaturen för de största partiklarna.
Studier av växelverkande magnetiska nanosystem har utöver sin grundvetenskapliga betydelse även en samhällsmässig betydelse, då bland annat koncentrerade magnetiska nanopartikelsystem har gjort sitt intåg i vår vardag genom tillämpningar inom exempelvis medicinsk diagnostik.
I would first and foremost like to thank my main supervisor Roland Mathieu for your scientific guidance as well as putting up with my countless questions (ignorance). I would also like to state that it is never boring to work with you. I would like to thank Per Nordblad for both the scientific and social part that you bring to my life everyday. I still do not know why you chose to hire me, I am however grateful that you did, since I have been blessed with the best job in the world for 4 years. I would also like to thank José De Toro for his supervision and his advice regarding science and life in general. I am happy that I got to share this trip with you. I would also like to thank my supervisor Peter Svedlindh for his scientific and moral support during the last five years (it is almost five years since I started my masters project at FTF). If not for you I would probably not have gotten the chance to make this journey, since it was you who suggested me to apply for the position during the Christmas table of 2012.

Big thanks to the magnetism group: Ankit, Daniel, Changgang, Erik, Klas, Matthias, Rimantas, Serkan, Sergey, Sofia, Tapati and Tian for help and discussion in and outside the field of magnetism, I would also like to thank you for being very nice and helpful persons. I would like to thank all of the people at FTF for providing a nice working environment with a lot of laughter.

From Spain I would like to that Peter Normile, the guy who really knows how to live life, I think I will never be as brave as you when it comes to making life decision. Thank you for four nice years of collaboration, social chatting and beer drinking. I would also like to thank the families of José, Peter and Pablo for accepting me with open arms during my stays in Ciudad Real, I had a really nice time during my stays and that is due to all of you being so friendly and nice people.

During the years I have had the chance to work with a lot
of talented people from all over the world. I would like to thank you all for your expertise and for the opportunity to learn from you. I would especially like to thank Johan Cedervall and Martin Sahlberg, my buddies from chemistry. Thank you for a lot of nice memories as well as for being generally awesome people. I would also like to thank my colleagues from across the courtyard Björgvin, Bjön- Erik, Erik, Henry, Spyridon and Vassilios.

    Shuyi thank you for being there for me both during the good as well as the bad days. I would like to thank you for helping me with the cover. Last but not least I would like to thank my family and my closest friends, thank you for existing and making my life easier and more meaningful in so many ways.

For financial support I would like to thank, K G Westmans stipendiestiftelse, Vetenskapsrådet (VR), and Göran Gustafsson stiftelse.

    “When you get up in the morning, you have two choices - either to be happy or to be unhappy. Just choose to be happy”

Norman Vincent Peale
1898-1993
REFERENCES


REFERENCES


A doctoral dissertation from the Faculty of Science and Technology, Uppsala University, is usually a summary of a number of papers. A few copies of the complete dissertation are kept at major Swedish research libraries, while the summary alone is distributed internationally through the series Digital Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology. (Prior to January, 2005, the series was published under the title “Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology”.)