Polarization Analyzed Small Angle Neutron Scattering of Ferrite Nanoparticles

Kathryn Hasz
Physics and Astronomy
Oberlin College

Honors Thesis
March 31, 2014
Executive Summary

Magnetic nanoparticles are particles that are magnetic and much smaller than the width of a human hair. Like a collection of compass needles, the particles respond to magnets and can interact and influence the direction and arrangement of nearby particles. Magnetic nanoparticles have many potential uses in data storage and biomedical targeted drug delivery, to name a few possibilities. These uses depend on the interactions between particles, making the study of those interactions a question of interest.

However, the very small size of the particles makes them undetectable by human eye or even through an optical microscope. In this thesis, we discuss one way to investigate these particles: polarization analyzed small angle neutron scattering (PASANS). We use this technique to look at two samples—one of iron oxide and one of cobalt iron oxide. The data reveal that the iron oxide nanoparticles have a magnetic core that aligns with an applied magnetic field and a magnetic shell that tips away from an applied magnetic field, while the cobalt iron oxide nanoparticles tip away from an applied magnetic field. We have also developed a model to explain this shell and tipping based on minimizing the energy present in the system.
To those who kept me here when I wanted to give up.
Acknowledgments

I would not have been able to complete this thesis without the help of many people. A simple thank you is insufficient, but it will have to do for now.

First, I am deeply grateful to my advisor, Yumi Ijiri. She welcomed me into her lab when I was a little freshman who knew next-to-nothing and has guided me through the entire research process. Her patience, support, and high expectations have helped me through the past four years and made me grow as a physicist, a thinker, and a person.

My fellow labmates, past and present, have also been a joy to work with. In particular, Chetan Poudel has been just a desk away as we wrote our theses and procrastinated on writing our theses.

Our collaborators at NIST and Carnegie Mellon have been incredibly helpful. They have answered numerous questions, synthesized the samples, and laid the groundwork necessary for the work I have done.

The National Science Foundation has provided support and funding for this work through grants DMR-0944772 and DMR-1104489.

I also must thank the rest of the physics faculty and staff. They have taught me so much physics, such as many ways to approximate with Taylor expansions and simple harmonic oscillators. They have also cared about my classmates and me as people and made sure we took care of ourselves.

My classmates have made my time as a physics major so much better. From late nights finishing problem sets to random Mandarin dinners, David, Jocienne, Ben, Che, Liz, Zach, Noah, Mattie, Sujoy, Elizabeth, Dagmawi, and Kara have become my physics family.

My friends outside the department also deserve a big thank you. They have made sure I don’t spend too much time in Wright. I love all the wonderful times I have spent with them doing things that have nothing to do with physics.

As always, my family has provided love and support as I wrote this thesis and completed my time at Oberlin.

And you, whoever you happen to be, thank you for reading my thesis. I hope you find it understandable and informative.
CONTENTS

4 Experimental Procedures
  4.1 Nanoparticle Synthesis and Preparation ........................................... 24
  4.2 Characterization .............................................................................. 26
  4.3 SANS .......................................................................................... 27
  4.4 PASANS ....................................................................................... 29
    4.4.1 Supermirror ........................................................................... 29
    4.4.2 Flipper .................................................................................. 30
    4.4.3 Magnetic Guide Fields ............................................................. 30
    4.4.4 $^3$He Polarizer ...................................................................... 31
    4.4.5 Polarization Correction ........................................................... 31

5 Results and Discussion
  5.1 Previous Work .............................................................................. 35
  5.2 Results of this Thesis ................................................................. 40
    5.2.1 Iron Oxide .............................................................................. 40
    5.2.2 Cobalt Iron Oxide ................................................................. 44

6 Summary and Future Work
  6.1 Summary ...................................................................................... 51
  6.2 Ongoing and Future Work ........................................................... 52

A Mathematic Code for Energy Based Model ........................................ 54

B Analysis of SAXS data using NIST SANS macro techniques ............. 59
  B.1 SAXS Geometry ........................................................................... 59
  B.2 USANS Geometry ......................................................................... 60
  B.3 Resolution Function ....................................................................... 62
  B.4 Procedure ..................................................................................... 63
  B.5 Verification ................................................................................... 64

Bibliography ......................................................................................... 67
List of Figures

1.1 Model of core-shell particle ...................................... 5
2.1 Spin alignment for different types of magnets ......................... 8
2.2 Hysteresis loop .................................................. 9
2.3 Hysteresis loop for superparamagnetic materials ..................... 10
3.1 Schematic of scattering process ..................................... 15
3.2 Form factor for simple sphere (red) and shell (blue) .................. 17
3.3 Structure factor for an FCC lattice ................................ 19
3.4 Traditional SANS experiment schematic ............................... 21
3.5 Example of PASANS data ........................................... 23
4.1 Nanoparticle crystal preparation ..................................... 25
4.2 Hysteresis loops of cobalt iron oxide ............................... 26
4.3 TEM image of the iron oxide nanoparticles ........................... 27
4.4 Diagram of the SANS beamline .................................... 28
4.5 Schematic of PASANS scattering ..................................... 29
4.6 $^3$He cell ......................................................... 32
5.1 Iron oxide structural and magnetic intensities vs Q .................. 36
5.2 Spinel structure ................................................... 37
5.3 Interstitial site tilt angles .......................................... 38
5.4 Energy landscapes for iron oxide nanoparticles ...................... 39
5.5 Iron oxide structural and magnetic intensity evolution vs Q .......... 40
5.6 Iron oxide $M_{PARL}^2$ vs Q under various temperature and magnetic field conditions ........................................ 41
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.7</td>
<td>Iron oxide $M^2_{\text{PERP}}$ vs Q evolution with changing magnetic field</td>
<td>41</td>
</tr>
<tr>
<td>5.8</td>
<td>Iron oxide $M^2_{\text{PERP}}$ vs Q long range correlations</td>
<td>42</td>
</tr>
<tr>
<td>5.9</td>
<td>Iron oxide $M^2_{\text{PERP}}$ vs Q initial upturn</td>
<td>43</td>
</tr>
<tr>
<td>5.10</td>
<td>Iron oxide $M^2_{\text{PARL}}$ vs Q initial upturn</td>
<td>43</td>
</tr>
<tr>
<td>5.11</td>
<td>Iron oxide energy landscape at 100 K</td>
<td>44</td>
</tr>
<tr>
<td>5.12</td>
<td>Iron oxide energy vs shell thickness at 100 K</td>
<td>45</td>
</tr>
<tr>
<td>5.13</td>
<td>Cobalt iron oxide structural and magnetic intensities vs Q</td>
<td>46</td>
</tr>
<tr>
<td>5.14</td>
<td>Cobalt iron oxide $M^2_{\text{PERP}}$</td>
<td>47</td>
</tr>
<tr>
<td>5.15</td>
<td>Comparison of 200 K and 10 K energy minima</td>
<td>49</td>
</tr>
<tr>
<td>5.16</td>
<td>Cobalt iron oxide energy landscape</td>
<td>49</td>
</tr>
<tr>
<td>5.17</td>
<td>Effects of anisotropy enhancement</td>
<td>50</td>
</tr>
<tr>
<td>B.1</td>
<td>Schematic of SAXS setup</td>
<td>61</td>
</tr>
<tr>
<td>B.2</td>
<td>Schematic of USANS scattering</td>
<td>61</td>
</tr>
<tr>
<td>B.3</td>
<td>Curve fits for various resolution functions</td>
<td>63</td>
</tr>
<tr>
<td>B.4</td>
<td>SANS macros and Nanosolver fit particle sizes</td>
<td>65</td>
</tr>
<tr>
<td>B.5</td>
<td>SANS macros and Nanosolver fits</td>
<td>66</td>
</tr>
</tbody>
</table>
1

Introduction and Motivation

Magnetic nanoparticles are particles that exhibit magnetic properties and range in size from about 5-500 nm in diameter. The small size scale leads to behavior that can differ dramatically from that of bulk macroscopic quantities of chemically identical materials. Depending on the synthesis methods, the particles can either consist entirely of one material or have a core of one material and a chemically unique shell.

1.1 Uses of Magnetic Nanoparticles

Magnetic nanoparticles have established uses in a range of fields and potential uses in many more. Commonly discussed applications include data storage, ferrofluids, and biomedical devices.

In computer hard drives, the particles can be used to store data by encoding information in the direction of the net magnetic moment. Binary code can be represented by assigning one direction of net magnetization to be a 1 and the opposite direction to be a 0. This method allows for compact data storage by reducing the size of a bit. However, the size cannot be reduced to an arbitrarily small volume because thermal fluctuations can overcome the energy associated with a particular configuration, making the information no longer reliably encoded (1).

Magnetic nanoparticles are also used to make ferrofluids. These ferrofluids are colloidal suspensions of particles often around 10 nm in diameter that are coated with a surfactant to make them soluble in a variety of solvents. The particles are often magnetite (Fe₃O₄) or similar ferrites. These ferrofluids are used to form a seal around
1.2 Methods of Investigating Magnetic Nanoparticles

moving parts, with a magnet holding the ferrofluid in place. Since the ferrofluid is a liquid, the amount of friction is nearly negligible, and the seal is long-lasting. For these ferrofluids to be effective, the particles have to remain stable in solution. This stability relies on the interplay between the magnetization of the particles and applied field and the properties of the solvent (2), (3).

In addition, the biomedical uses of magnetic nanoparticles are being studied. One such use involves coating the particles with some protein, antibody, or drug that is biologically relevant. Once in the body, these coated particles can be directed with an external magnetic field. This direction can lead to targeted drug delivery or localized separation of undesirable molecules that attach to the particles (4). Another biomedical use is the reduction of tumors through hyperthermia. If a tumor is injected with nanoparticles and then a rapidly changing magnetic field is applied, the nanoparticles lose energy as heat. This lost energy will in turn heat the surrounding tissue and cause its death, allowing for localized reduction in tumors. This technology is still in early stages, but it is being prototyped (4). For either of these biomedical applications, safety is an important concern. The particles must be stable and uniform and their magnetic interactions must be well-regulated before these technologies can be implemented safely (4).

Taken in total, all of these applications rely on well-characterized magnetic particles with tight control on fundamental properties, such as the net magnetic moment, coercivity, magnetic structure, and size distribution. These uses also depend on the manner in which individual nanoparticles interact with each other in relevant temperatures, applied magnetic fields, and geometries. For hard drives, particle-particle interactions that can flip the magnetic moments need to be avoided as these would render the hard drive useless. In ferrofluids, the interplay between the nanoparticles in an applied magnetic field lead to the desired viscosity changes but can also promote instability. The interactions in biomedicine are unclear, but particle clustering is often present.

1.2 Methods of Investigating Magnetic Nanoparticles

Given the promising uses of magnetic nanoparticles, many approaches have been taken to understand these materials in more detail.
1.2 Methods of Investigating Magnetic Nanoparticles

1.2.1 Traditional Magnetometry Methods

Established over fifty years ago, standard magnetometers such as superconducting quantum interference device (SQUID) magnetometers are commonly used to measure the net moment of a sample. However, they usually reveal information about the sample as a whole and do not detect local variations. Advances have been made in reducing the necessary sample size through a μSQUID, a modification of a SQUID that is sensitive to much smaller magnetic variations. In the μSQUID technique, the SQUID loop itself becomes the magnetic signal input coil which results in spatial resolution of less than a micrometer. While the μSQUID modification does allow for more localized magnetic measurements, sufficiently small particles can still be difficult to measure. Magnetometry cannot provide insight into structural order either.

1.2.2 Spectroscopy Methods

Another longstanding approach has been to use Mössbauer spectroscopy. This approach relies on the absorption and emission of gamma radiation by nuclei in a sample. This technique can also provide insight into the composition of the sample due to changes in the local environment. It can measure differences in energy levels due to a magnetic field. While this technique can reveal some information about particle size and composition, it requires a source that is a gamma emitter and does not reveal much information about the longer range structure of the system. In the case of iron, Mössbauer is sensitive to $^{57}$Fe but not the more common isotopes, so the sample must be doped or we must rely on the naturally occurring (typically small) amount of isotope.

1.2.3 Microscopy Methods

Electron microscopy has traditionally been used to characterize particles at small scales. In transmission, it is a standard technique to directly observe the size and ordering of particles by imaging a thin layer of sample with electrons. However, observing magnetic behavior using microscopy techniques is more difficult. Some advances have been made by using spin-polarized electrons to sense the magnetic moments, a method known as spin-polarized scanning tunneling microscopy. If a beam of polarized electrons is sent through a magnetic sample, the current detected fluctuates depending on the relative magnetic arrangements.
Atomic force microscopy (AFM) is another method that can detect the size of particles on the nanoscale, this time as a result of a delicate cantilever moving across the sample surface. While traditional AFM is not sensitive to magnetization, modifications allow AFM to be sensitive to spins. In magnetic force microscopy (MFM), a non-magnetic probe tip is coated with a ferromagnetic or antiferromagnetic material, and the tip becomes sensitive to certain magnetic moments in the sample to very high resolution (9). For magnetic resonance force microscopy, a magnetic cantilever is brought close to a sample that has been excited through NMR methods and experiences a magnetic force (10). That force is detected using a very small mechanical oscillator. The technique has been able to measure single spins (11). These microscopy methods can probe structural and some magnetic properties of samples. However, they are often destructive and only study small portions of the sample.

1.2.4 Scattering Methods

Scattering methods are ideal to probe the whole structure of a sample. Small angle X-ray scattering (SAXS) and small angle neutron scattering (SANS) are both scattering techniques that can probe the longer range structure and order of particles and are sensitive to the nanoscale. They are non-destructive methods, so the same sample can be investigated under many conditions and at separate times. These techniques are particularly useful in investigating interactions between particles (12).

The use of neutrons as a scattering source differentiates SANS from SAXS. Since neutrons have no charge, they are able to interact with the nucleus instead of the electron cloud and effectively image elements with lower atomic numbers. The structure can be detected, much like in X-ray scattering. The intrinsic magnetic moment of the neutron makes neutron scattering sensitive to magnetic properties of the sample. SANS has been used to investigate magnetic interactions in samples with nanometer-sized grains and found that the magnetic behavior differs greatly for grain sizes above and below the domain wall width (13). It has also studied weak magnetic interactions in magnetic glassy samples and found a high volume of fine-grained particles with a weakly magnetic interface (14). However, while there is magnetic information in SANS data, it can be difficult to deconvolute the magnetic signature from the nuclear scattering.

In recent years, there have been new developments employing polarized neutrons to further probe these magnetic signatures (15),(16),(17),(18),(19). Polarization analyzed
1.2 Methods of Investigating Magnetic Nanoparticles

Figure 1.1: Model of core-shell particle

Previous work revealed particles with a magnetic core (pink) aligned with an applied magnetic field and a magnetic shell (green) aligned perpendicular to the applied magnetic field \(^{20}\).

Small angle neutron scattering (PASANS) is a specific type of SANS that allows for complete separation of magnetic and nuclear scattering contributions with greater ease. In this case, polarization and spin flipping devices are used to investigate the scattering for an allowed spin state of the neutron both before and after scattering off the sample. This process allows for separation of the magnetic and structural elements of the neutron scattering. Like magnetometry, it can be used to find a net magnetic moment, but PASANS is sensitive to local order and can reveal magnetic domain interplay within a sample or even a single nanoparticle as well as net properties of a sample.

Past work from this lab in collaboration with Dr. Julie Borchers and Dr. Kathryn Krycka at NIST and the lab of Dr. Sara Majetich at Carnegie Mellon University has revealed that 9 nm iron oxide particles have a magnetic shell under high applied magnetic fields and temperatures (see Fig. 1.1 \(^{20}\)). This shell disappears at a remanent magnetic field, showing it is solely magnetic in nature. However, the evolution of this shell and its behavior at intermediate magnetic fields and temperatures are not yet well understood. Dr. Krycka has proposed a model to account for the shell formation based on competing energy terms, but its viability at intermediate temperature and field conditions needs further testing \(^{21}\).
1.3 Thesis Organization

Given the questions that remain about the magnetic structure within nanoparticles, the rest of this thesis is organized as follows: chapter 2 will give a brief overview of magnetism and the relevant properties of the magnetic nanoparticles, while chapter 3 will review scattering theory. Chapter 4 outlines the process of PASANS. Chapter 5 presents results of PASANS investigations of iron oxide and cobalt iron oxide nanoparticles. It also presents a model for the cause of the nanoparticle behavior based on the interplay of the various energies and the structure. Chapter 6 summarizes the results and presents future work.
2

Background on Magnetic Nanoparticles

2.1 Overview of Magnetism

There are four types of magnetism that appear in bulk materials that are relevant to our discussion: paramagnetism, ferromagnetism, antiferromagnetism, and ferrimagnetism. These types all involve the spins $S$ or magnetic moments $\mu_s$ of electrons, defined as $\mu_s = -\frac{eS}{2m}$. Paramagnetism is the alignment of spins in a material due to an applied magnetic field with no interaction between the spins. In general, it is a weak effect and disappears when the applied field is removed. Ferromagnetism is the type of magnetism with which most people are most familiar in which spins interact via some exchange mechanism. It produces an ordered alignment of spins resulting in a permanent magnetic moment in the absence of an applied magnetic field, such as in a refrigerator magnet. Iron, cobalt, nickel, and gadolinium exhibit natural ferromagnetism, and most permanent magnets contain at least one of these elements. Antiferromagnetism is another natural ordering of spins, yet in antiferromagnetic materials, the spins arrange themselves in opposing directions so that there is no net magnetic moment. Ferrimagnetism is like a combination of ferromagnetism and antiferromagnetism. The spins align so that some point in opposition to others, but they do not fully cancel as in antiferromagnetism. This lack of cancellation leaves a net magnetic moment similar to that in ferromagnetism. These net magnetic moments form domains of aligned particles (see Fig. 2.1). These regions can grow, shrink, or rotate depending on applied
Ferromagnets have a net moment due to an alignment of all spins. Antiferromagnetism has no net moment due to an ordering of spins where the individual moments cancel. Ferrimagnetism has the same opposite alignment of antiferromagnetism, yet a net moment remains due to weaker spins in one direction than the other. 

magnetic fields and other parameters.

The different arrangements of spins all involve energy costs and gains. In equilibrium, the spins prefer to be in certain magnetic environments and minimize the energy costs between the magnetic field or nearby spins to be in the most favorable environment possible.

We are most concerned with ferro- and ferrimagnetic systems. Such systems are often described in terms of their hysteresis loop. The hysteresis loop is a visual representation of how easy or difficult it is to get the moment direction to flip depending on the applied magnetic field (see Fig. 2.2). A greater width to the loop means a greater coercivity $H_C$, and more difficulty flipping the direction of magnetization. These loops also show the saturation magnetization $M_S$, which is the maximum moment normalized to mass or volume, and the remanent magnetization $M_R$, which is the strength of magnetization left when an applied field is removed.

### 2.2 Magnetism in Nanoparticles

The magnetism exhibited in nanoparticles can differ from that found in bulk ferro- or ferrimagnetic materials. Bulk materials often form multiple domains of different magnetization direction to minimize the magnetostatic energy and close flux lines external to the sample (22). The small scale of nanoparticles can lead to new phenomena that need to be considered.
2.2 Magnetism in Nanoparticles

Figure 2.2: Hysteresis loop

Schematic hysteresis loop of magnetization vs applied magnetic field illustrating the saturation magnetization, \( M_S \), the remanent magnetization, \( M_R \), and the intrinsic coercivity, \( H_{Ci} \). Taken from (23)

Magnetic nanoparticles are often small enough that they are monodomain, that is the moments within a nanoparticle coherently point in one direction. The size constraint for monodomain particles is traditionally written as (24)

\[
d_{cr} = \pi S \sqrt{\frac{J}{K \cdot a}},
\]

where \( d_{cr} \) is the maximum diameter to be monodomain, \( S \) is the spin per atom, \( J \) is the exchange constant, \( K \) is the uniaxial anisotropy energy constant to align in a particular crystallographic direction, and \( a \) is the lattice constant.

In monodomain particles, the individual magnetic moments of electrons collectively behave like a single magnetic moment for the particle. When the coercivity of the particles decreases to zero, they are considered superparamagnetic (25). The associated hysteresis loop has no width (see Fig. 2.3). Once particles are superparamagnetic, they change magnetic moment by a rotation of the entire particle as opposed to growing magnetic domains. Because of this behavior, the energy of thermal fluctuations, \( k_B T \), can overcome the stabilizing anisotropy energy, \( KV \), to flip a particle’s direction at approximately the Larmor precession frequency, leading to a time scale of \( \tau_0 \sim 10^{-9} \) s (25). The Arrhenius Law gives the time it takes a moment to equilibrate at a given
2.2 Magnetism in Nanoparticles

Since superparamagnetic materials have no coercivity, the associated hysteresis loop has no width.

\[ \tau = \tau_0 e^{KV/kT}. \]  

(2.2)

When \( \tau \) is smaller than the time it takes to measure the system in some state, no hysteresis is seen and the particles are superparamagnetic. However, when \( \tau \) is greater than the time of a measurement, \( \tau_m \), the particles cannot reach equilibrium and the particles only become superparamagnetic at sufficiently high temperatures. This temperature is called the blocking temperature and is

\[ T_B = KV ln(\frac{\tau_m}{\tau_0}). \]  

(2.3)

Superparamagnetism occurs for materials that are ferro- or ferrimagnetic in bulk. In the non-interacting limit, each particle acts like an individual spin in a paramagnet. When this non-interacting limit has not been reached, these interacting particles are sometimes considered superferromagnetic. The magnetic nanoparticles act like new building blocks for the system. They can have defined moments and organize into
defined crystal structures. The interparticle interactions must be considered when working with particles in these region. For data storage uses, the lack of coercivity in superparamagnetic materials is problematic because the information stored is lost if spins spontaneously flip. However, superparamagnetic properties are desired for biomedicine and ferrofluids to have high response and no lag.

In addition, it is well-established that complex magnetic structure in nanoparticles can exist below the traditional size criterion for monodomain particles (20). These additional magnetic structures can complicate the necessary considerations when studying magnetic nanoparticles.

2.3 Energy Considerations for Nanoparticles

The energy interplay within a system is the main factor that will determine the behavior of interacting nanoparticles. In this system, there are four competing energies that need to be considered: Zeeman, anisotropy, exchange, and dipole. Minimizing the overall energy from these four contributions leads to a predicted nanoparticle configuration that can be tested against the experimental neutron scattering data.

2.3.1 Zeeman

The Zeeman energy term depends on the alignment of a magnetic moment with an applied magnetic field. If the magnetic moment is not aligned parallel with the applied magnetic field, the magnetic field exerts a torque on the moment. The energy associated with this torque is (22)

\[ U_{\text{Zeeman}} = -\vec{m} \cdot \vec{H}, \]  

(2.4)

where \( \vec{m} \) is the magnetic moment and \( \vec{H} \) is the applied magnetic field. The negative sign shows that the energy is at a minimum when \( \vec{m} \) and \( \vec{H} \) are aligned.

In the case of monodomain nanoparticles, \( \vec{m} \) corresponds to the net moment of the whole particle. For more complicated systems, it can be the result of a combination of domain alignments.

2.3.2 Anisotropy

The magnetocrystalline anisotropy energy comes from a preferred alignment of magnetic moments with the axes of the crystal structure arrangement of atoms within the
nanoparticle. This energy term will vary for different crystal structures and symmetries. Most materials have one or more axes along which alignment is easier and the material saturates faster, thus labeling these the easy axes. The anisotropy energy is usually represented as an energy density and depends on the angle between the moment and the easy axis in the specific material. A material with an anisotropy constant of higher magnitude will have a more defined easy axis. The anisotropy energy density for a uniaxial crystal is

\[ E_{\text{anisotropy}} = K_v \sin^2(\theta), \]  

(2.5)

where \( K_v \) is the anisotropy constant. The expression is more complicated and includes additional constants for cubic and hexagonal crystal structures. The anisotropy energy is minimized when the magnetic moments point along the easy axis. Harder magnets tend to have higher anisotropy constants than softer magnets, resulting in higher coercivity.

### 2.3.3 Exchange

The exchange energy comes from the energy cost of having the spins that cause magnetic moments aligned in unpreferred directions. The misalignment of spins that would naturally prefer to point in a particular direction creates an energy that can be written as

\[ U_{\text{exchange}} = J_{ij}(r) \sum S_i \cdot S_j, \]  

(2.6)

where \( J_{ij} \) is the exchange constant and \( S_i \) and \( S_j \) are the spins. \( J_{ij} \) can be positive or negative. This exchange energy can come about at interfaces between two types of materials or from antialigned magnetic moments within a ordered arrangement, such as a ferrimagnet.

### 2.3.4 Dipole

The dipole energy comes from the interactions between magnetic moments of neighboring particles. A dipole moment within a particle can exist, but it is minimal compared to the exchange energy within a particle. Energy is minimized when two neighboring
2.3 Energy Considerations for Nanoparticles

particles are aligned with their moments parallel to each other. The dipole energy term is \( U_{\text{dipole}} \) and is given by:

\[
U_{\text{dipole}} = \mu_0 \left( \vec{m}_i \cdot \vec{m}_j - 3(\vec{m}_i \cdot \hat{r}_{ij})(\vec{m}_j \cdot \hat{r}_{ij}) \right) / \left( 4\pi |\vec{r}_{ij}|^3 \right),
\]

where \( \vec{m}_i \) and \( \vec{m}_j \) are the moments of the two particles of interest and \( \vec{r}_{ij} \) is the vector between them. For fixed particles, the dipole interaction is minimized when particles have net spins which are antialigned. However, \( \vec{r}_{ij} \) can vary if the particles are free to choose a lowest energy configuration, leading the moments to not always align, particularly in consideration of other energy terms as described above.
3

Background on Neutron Scattering

As described in the introduction, neutron scattering and small angle neutron scattering in particular are powerful techniques to probe the structure of magnetic nanoparticles. In this chapter, the basic theory of the scattering process is reviewed with special attention to the effects of a periodic potential such as a crystal lattice. The scattering spin selection rules for small angle neutron scattering (SANS) are described along with the more complete analysis possible for polarization analyzed small angle neutron scattering (PASANS).

3.1 Basic Theory

A single scattering event can be described in terms of an incident wavevector \( \vec{k}_i \) interacting with a sample that changes it in some manner to emerge as a final wavevector \( \vec{k}_f \) (see Fig. 3.1). The scattering vector \( \vec{Q} \) is the difference such that \[ \vec{Q} = \vec{k}_f - \vec{k}_i. \] (3.1)

In elastic scattering, \( |\vec{k}_i| = |\vec{k}_f| \) and \( \vec{Q} \) is a result of a directional change only.\(^1\)

Basic trigonometry leads to the magnitude of \( \vec{Q} \):
\[ Q = \frac{4\pi \sin \theta}{\lambda}, \] (3.2)

\(^1\)For inelastic scattering, this condition does not hold. However, inelastic scattering is rarer and is often overshadowed in intensity by elastic scattering. This thesis limits itself to elastic scattering.
3.1 Basic Theory

The scattering vector, $\vec{Q}$, is the difference between the incident wave vector $\vec{k}_i$ and the final wave vector $\vec{k}_f$.

where $2\theta$ is the angle between $\vec{k}_f$ and $\vec{k}_i$ and $\lambda$ is the wavelength of the scattering wave given by $\lambda = \frac{2\pi}{|\vec{k}|}$. This relation is similar to Bragg’s law \[(3.2)\]

\[2d \sin(\theta) = n\lambda,\]  

where $d$ is the distance between planes of scattering centers and $n$ is an integer indicating the index or order. Note that for $n = 1,$

\[d = \frac{2\pi}{Q}.\]  

Since the nanoparticle length scale of 5-500 nm (50-5000 Å) is of interest, the corresponding scattering vectors of interest are between 0.001-0.2 Å\(^{-1}\). Scattering can be measured in regards to $\theta$ or $\vec{Q}$, but $\vec{Q}$ is more general due to the dependence of $\theta$ on $\lambda$. In addition, the 3D nature of the scattering may be of importance, thus the scattering vector $\vec{Q}$ is more convenient than a series of angles $\theta, \phi,$ and $\psi$. This thesis will work exclusively in $\vec{Q}$, measured in Å\(^{-1}\).

Instead of a single scattering event, we must consider the result of many such events as expected for a beam of X-rays or neutrons incident on a real sample. As explained in \[(22)\], this amplitude of scattered waves by a collection of atoms can be considered as a combination of the scattering off of individual atomic sites $R_A$ such that

\[F(\vec{Q}) = \sum f_A(\vec{Q})e^{i\vec{Q} \cdot R_A},\]  

where $f_A(\vec{Q})$ is the atomic form factor described in more detail later in this section and the sum encompasses all the atoms in the sample. The intensity of scattering relates to the square of the amplitude through

\[I(\vec{Q}) \propto |F(\vec{Q})|^2.\]  

15
The specifics of the scattering amplitude are affected by both the makeup of the
scattering atoms and the arrangement of them. For nanoparticles, \( F(\vec{Q}) \) is most
conveniently broken down into a form factor \( f(\vec{Q}) \) that is determined by the shape and
composition of the particles and an overall structure factor \( S(\vec{Q}) \) that appears if the
particles have an orderly arrangement. The form factor and structure factor combine
to give a scattering amplitude of\(^1\)

\[
F(\vec{Q}) = f(\vec{Q})S(\vec{Q}). \tag{3.7}
\]

The form factor due to the particle shape and composition is defined as

\[
f(\vec{Q}) \propto \int n(\vec{r}) e^{i\vec{Q} \cdot \vec{r}} d\vec{r}, \tag{3.8}
\]

where \( n(\vec{r}) \) is the scattering density and the integral is over the particle volume.

The structure factor from the arrangement of nanoparticles located at points \( \vec{r}_j \)
within the sample can then be defined as

\[
S(\vec{Q}) = \sum_j f(\vec{Q}) e^{-i\vec{Q} \cdot \vec{r}_j}. \tag{3.9}
\]

In this way, the expected scattering amplitude can be generalized for any type
of particle and arrangement. There are a number of types of common particles and
lattice constructions for which the form and structure factors have been derived. These
range from very simple systems, such as hard sphere particles in a simple cubic lattice,
to much more expansive systems, such as polymers that form monoclinic cells. The
relevant form and structure factors for spherical particles in a face centered cubic crystal
are presented below.

For the case of spheres in solution, we can isolate just the spherical form factor and
simplify it using the approximation (26)

\[
\langle e^{iQr} \rangle = \frac{\sin(Qr)}{Qr}. \tag{3.10}
\]

This substitution simplifies the form factor given in eq. 3.8 to

\[
f(Q) = \frac{1}{V_p} \int_0^R \frac{\sin(Qr)}{Qr} dr = \frac{3}{(QR)^3} \left[ \sin(QR) - QR \cos(QR) \right], \tag{3.11}
\]

\(^1\)There are cases when the form factor and structure factor cannot be isolated. Analysis in those
cases must include a convolution of the form and structure factor instead of two separable components.
3.1 Basic Theory

Figure 3.2: Form factor for simple sphere (red) and shell (blue)

The theoretical intensity vs Q for spherical particle 12 nm in diameter with no structure factor (red) and a 1 nm thick shell 12 nm in diameter with no structure factor (blue) (27).

where $R$ is the radius of the particle. Therefore simple sphere scattering with no other structural features yields

$$I(\vec{Q}) \propto |f(\vec{Q})|^2,$$

(3.12)

which is plotted in Fig. 3.2. If the scattering source is a shell rather than a solid sphere, the scattering pattern is modified as seen in Fig. 3.2.

In the opposite extreme of a crystallized face centered cubic (FCC) lattice of point-like scattering sources, the form factor reduces to a common number while the structure factor greatly simplifies due to the ordered arrangement (28). When a sample is crystalline in structure, it acts as a periodic potential that creates interference conditions on the scattered waves. This potential and the resulting scattering intensity can be derived following (22). To reflect the crystal order, the potential must remain invariant under translation by a lattice vector $\vec{R}$ such that

$$V(\vec{r} + \vec{R}) = V(\vec{r}).$$

(3.13)

The translation vector $\vec{R}$ is a linear combination of primitive lattice translation vectors $\vec{u}_j$ that reflect the symmetry of the structure such that

$$\vec{R} = n_1 \vec{u}_1 + n_2 \vec{u}_2 + n_3 \vec{u}_3,$$

(3.14)
where \( n_1, n_2 \) and \( n_3 \) are a set of integers. Associated with the translation vector are reciprocal lattice vectors \( \vec{g}_i \) such that

\[
\vec{g}_i \cdot \vec{u}_j = 2\pi \delta_{i,j}.
\]  

(3.15)

A linear combination of these reciprocal lattice vectors form a general reciprocal lattice vector \( \vec{G} \) such that

\[
\vec{G} = h\vec{g}_1 + k\vec{g}_2 + l\vec{g}_3.
\]  

(3.16)

The coefficients \( h, k, \) and \( l \) are integers that are referred to as the Miller indices of a plane of a crystal.

The periodic potential can now be expressed as

\[
V(\vec{r}) = \sum_G V_G e^{i\vec{G} \cdot \vec{r}},
\]  

with \( V_G \) being a set of Fourier coefficients and the scattering amplitude becomes

\[
F(\vec{G}) = \sum_R \sum_j f_j(\vec{G}) e^{i\vec{G} \cdot (\vec{R} + \vec{r})}.
\]  

(3.18)

If the scattering vector \( \vec{Q} \) is an integer multiple of \( \vec{G} \), then the scattering waves will constructively interfere to produce a measurable intensity. If that condition is not satisfied, then the scattering waves in sum will not add in phase and the intensity will be much weaker.

In the FCC unit cell, there are atoms at 000, 0\( \frac{1}{2} \)\( \frac{1}{2} \), \( \frac{1}{2} 0 \frac{1}{2} \), and \( \frac{1}{2} \frac{1}{2} 0 \). From eq. 3.9 and these atomic positions,

\[
S = f(1 + e^{-i\pi(k+l)} + e^{-i\pi(h+l)} + e^{-i\pi(h+k)}).
\]  

(3.19)

The associated intensity pattern is plotted in Fig. 3.3. In terms of Miller indices \( hkl \), an FCC lattice must satisfy the conditions that \( h, k, \) and \( l \) must all be odd or all be even for any given plane (29).

These model functions and many others are available through SANS macros available on the NIST website for data analysis using the Igor Pro software package (27),(30).
3.2 Special Features of Small Angle Neutron Scattering

3.2.1 Conventional SANS

The basic principles described in Section 3.1 apply regardless of the type of probe used. As mentioned in the introduction, neutrons are particularly useful since the neutrons have an intrinsic magnetic moment and the nuclear density variations associated with atoms are quite random, especially in comparison to X-rays which scale with electron density. Both of these factors alter the contrast in $n(\vec{r})$ from eq. 3.8.

However, neutron scattering is much less common than X-ray scattering due to logistical issues. While many colleges and universities own X-ray diffractometers, no analogous compact source exists for neutrons. Neutron beamlines are much more complicated and require a nuclear reactor or spallation source to produce sufficient flux of incident neutrons. Therefore nearly all neutron scattering experiments are done at government-associated facilities. There are three principal neutron scattering facilities in the United States: the NIST Center for Neutron Research in Maryland, LANSCE/Lujan Neutron Scattering Center in New Mexico, and HFIR/SNS at Oak Ridge National Lab in Tennessee. These facilities offer scattering options in a variety of geometries which differ in the range of $\vec{Q}$ probed and the possible sensitivity to energy changes (i.e. inelastic scattering). This thesis focuses on work done using small angle neutron scattering (SANS) where the Q-range is approximately 0.001-1
3.2 Special Features of Small Angle Neutron Scattering

Å$^{-1}$, corresponding to distances from about 5-1000 nm [30]. While this range is above the atomic length scale, it matches to the corresponding distances of proteins, macromolecules, porous materials, and nanoparticles [12]. The neutron’s intrinsic magnetic moment means that the resulting scattering has both structural and magnetic properties. However, the two are convoluted as described below.

Instead of just being proportional to $|F(\vec{Q})|^2$, the scattered intensity $I$ is now related to the scattering amplitudes for both nuclear $N(\vec{Q})$ and magnetic $M(\vec{Q})$ features. This intensity can be written as the spatial Fourier transform of the nuclear and magnetic scattering length density $\rho_{N,M}$ through

$$N, M(\vec{Q}) = \sum_K \rho_{N,M}(K)e^{i\vec{Q}\cdot\vec{R}_K}, \quad (3.20)$$

where $\vec{R}_K$ is the position of the $K$th scatterer in the sample. Nuclear and magnetic scattering are intertwined and must be separated if we want to analyze the magnetic structure. This separation is possible with traditional SANS under certain conditions. For instance, if the nuclear scattering is isotropic with $\vec{Q}$, the scattering geometry of a magnetically saturated state allows for subtraction of the nuclear scattering. Magnetic scattering will only occur with the magnetic moments that are perpendicular to $\vec{Q}$ due to a directional factor in the selection rules that vanishes when the magnetization $\vec{M}$ and $\vec{Q}$ are parallel [31]. Therefore the direction of applied field will contain only nuclear scattering for a fully saturated sample (see Fig. 3.4). Additionally, a reference non-magnetic sample can be used to subtract from the scattering of a desired magnetic sample.

With such approaches, SANS techniques have been used to investigate nanoscale correlation lengths, densities, concentrations, and magnetic fluctuations. They have allowed for probing of weak interactions of magnetic particles embedded within a non-magnetic matrix [14]. They can investigate exchange interactions across grain boundaries in nano-grain materials [13]. Some insight into magnetic correlation length scales within nanoparticle systems can also be found [32]. However, complications arise if magnetic saturation cannot be reached or an appropriate reference sample cannot be found. These problems can limit the ability to fully separate magnetic and nuclear scattering.
3.2 Special Features of Small Angle Neutron Scattering

3.2.2 PASANS

While conventional SANS has been quite important in probing magnetic nanostructures, polarization analyzed small angle neutron scattering (PASANS) has the potential to be much more powerful. It allows for complete separation of the structural and magnetic scattering contributions and even further division of the magnetic contributions into those parallel and perpendicular to the applied magnetic field. It can also be applied in cases when the sample does not reach magnetic saturation, making it a valuable tool for samples that will not saturate under easily achievable laboratory conditions and systems that adapt a more complicated spin structure.

In PASANS, the incoming neutron beam is polarized, and the neutron spin state is analyzed both before and after scattering. This analysis allows for separation between non-spin flip (NSF) and spin flip (SF) scattering events where the neutron spin is $++, --$ or $++, --$ respectively with the first $+$ or $-$ indicating the incident spin state and the second the scattered state. In geometries with the neutron polarization either perpendicular or parallel to $\vec{Q}$, NSF scattering comes from the nuclei in the sample and whatever magnetic moments are parallel to the neutron’s incident spin. SF scattering comes from magnetic moments perpendicular to the neutron’s spin. Moon, et al formalizes the generalized mathematics of this spin selection. If the spin direction is perpendicular to the beam direction, these generalized equations for...
3.2 Special Features of Small Angle Neutron Scattering

the resulting intensity can be written as (19)

\[
I^{++,-,-}(\vec{Q}) = N(\vec{Q})N^*(\vec{Q}) + M_x(\vec{Q})M_y^*(\vec{Q}) \sin^4(\theta) + M_y(\vec{Q})M_x^*(\vec{Q}) \cos^2(\theta) \sin^2(\theta)
\]

\[
- [M_x(\vec{Q})M_y^*(\vec{Q}) + M_y^*(\vec{Q})M_x(\vec{Q})] \sin^3(\theta) \cos(\theta)
\]

\[
\pm [N(\vec{Q})M_x^*(\vec{Q}) + N^*(\vec{Q})M_x(\vec{Q})] \sin^2(\theta) \pm [N(\vec{Q})M_y^*(\vec{Q})]
\]

\[
+ N^*(\vec{Q})M_y(\vec{Q})] \sin(\theta) \cos(\theta),
\] (3.21)

\[
I^{+-,+-}(\vec{Q}) = M_x(\vec{Q})M_y^*(\vec{Q}) + M_y(\vec{Q})M_x^*(\vec{Q}) \cos^3(\theta) + M_x(\vec{Q})M_y^*(\vec{Q}) \sin^2(\theta) \cos^2(\theta)
\]

\[
- [M_x(\vec{Q})M_y^*(\vec{Q}) + M_y^*(\vec{Q})M_x(\vec{Q})] \sin(\theta) \cos^3(\theta)
\]

\[
\pm i[M_x(\vec{Q})M_z^*(\vec{Q}) - M_z^*(\vec{Q})M_x(\vec{Q})] \sin(\theta) \cos(\theta) \mp i[M_y(\vec{Q})M_z^*(\vec{Q})]
\]

\[
- M_y^*(\vec{Q})M_z(\vec{Q})] \cos^2(\theta),
\] (3.22)

where \(N, M_x, M_y, \) and \(M_z\) are the spatial Fourier transforms of the structural and magnetic scattering and \(\theta\) is the angle between the X axis and the projection of \(\vec{Q}\) on the XY plane.

For certain angles, these spin selection rules greatly simplify. In the case where the incoming beam is along Z, the applied field along X, and the detector within the XY plane (see Fig. 3.4), they become (35)

\[
I^{++,-,-}(\vec{Q}) = N(\vec{Q})N^*(\vec{Q}) + M_x(\vec{Q})M_y^*(\vec{Q}) \sin^4(\theta) + M_y(\vec{Q})M_x^*(\vec{Q}) \cos^2(\theta) \sin^2(\theta)
\]

\[
- [M_x(\vec{Q})M_y^*(\vec{Q}) + M_y^*(\vec{Q})M_x(\vec{Q})] \sin^3(\theta) \cos(\theta)
\]

\[
\pm [N(\vec{Q})M_x^*(\vec{Q}) + N^*(\vec{Q})M_x(\vec{Q})] \sin^2(\theta) \pm [N(\vec{Q})M_y^*(\vec{Q})]
\]

\[
+ N^*(\vec{Q})M_y(\vec{Q})] \sin(\theta) \cos(\theta),
\] (3.21)

\[
I^{+-,+-}(\vec{Q}) = M_x(\vec{Q})M_y^*(\vec{Q}) + M_y(\vec{Q})M_x^*(\vec{Q}) \cos^3(\theta) + M_x(\vec{Q})M_y^*(\vec{Q}) \sin^2(\theta) \cos^2(\theta)
\]

\[
- [M_x(\vec{Q})M_y^*(\vec{Q}) + M_y^*(\vec{Q})M_x(\vec{Q})] \sin(\theta) \cos^3(\theta)
\]

\[
\pm i[M_x(\vec{Q})M_z^*(\vec{Q}) - M_z^*(\vec{Q})M_x(\vec{Q})] \sin(\theta) \cos(\theta) \mp i[M_y(\vec{Q})M_z^*(\vec{Q})]
\]

\[
- M_y^*(\vec{Q})M_z(\vec{Q})] \cos^2(\theta),
\] (3.22)

For the iron oxide and cobalt iron oxide nanoparticles of interest for this thesis, the \(N^2\) and interference terms dominate in the NSF scattering cross sections, forming a clear ring as seen in Fig. 3.5 for iron oxide. The distortion in the ring shape in
Figure 3.5: Example of PASANS data

After polarization correction, the data consist of four cross sections. Those of iron oxide at 1.2 T and 200 K are shown. The spin-flip cross sections (+− and −+) are the same. Taken from (36).

The horizontal and vertical directions of the ++ and −− cross sections indicate the magnetic component. The SF cross sections are solely magnetic scattering and thus less intense.
Experimental Procedures

This chapter outlines the synthesis and preparation of two nanoparticle samples, one of iron oxide and the other of cobalt iron oxide. It explains the experimental process of small angle neutron scattering (SANS) and the specifics of polarization analyzed small angle neutron scattering (PASANS). The polarization correction procedure is also described.

4.1 Nanoparticle Synthesis and Preparation

The particles studied in this work were synthesized by Dr. Ryan Booth, one of our collaborators at Carnegie Mellon University (23). The particles were made by decomposing a metal precursor, iron acetylacetonate, in the presence of 1,2-hexadecanediol, oleic acid, and oleyamine based on the procedure outlined in Sun, et al (37). This method produced monodisperse iron oxide (Fe$_3$O$_4$) nanoparticles that are 9 ± 1 nm in diameter. The cobalt iron oxide (CoFe$_2$O$_4$) particles were made using the same procedure, except cobalt acetylacetonate was partially substituted for iron acetylacetonate in a 1:2 ratio. The monodisperse cobalt iron oxide particles produced were 11 ± 1 nm in diameter. Both types of particles had a thin oleic acid coating and remained suspended in a solution of toluene.

While suspended particles are useful for some characterization techniques, ordered arrangements are more desired for the controlled study of magnetic interactions. Through slow, controlled destabilization of the nanoparticle solution, our collaborators have demonstrated the growth of close-packed crystals that have long range order (32). This
4.1 Nanoparticle Synthesis and Preparation

The nanoparticles are layered with propanol and ethanol for a slow growth into an ordered lattice. Figure taken from (23).

Figure 4.1: Nanoparticle crystal preparation

The nanoparticles are layered with propanol and ethanol for a slow growth into an ordered lattice. Figure taken from (23).

growth was done by layering 2-propanol on top of a diluted toluene solution of nanoparticles with a layer of ethanol placed on top of the 2-propanol (see Fig. 4.1). The ethanol diffused through the 2-propanol over the course of several weeks and destabilized the nanoparticles. It is essential that this destabilization was slow. If the destabilization happened too quickly, the particles could not find their minimum energy configuration and subsequent destabilized particles would pin them into a glassy order. The slow destabilization produced a polycrystalline powder of nanoparticles with typical crystalline size of over 1 µm.
4.2 Characterization

Hysteresis loops show the dramatic change in magnetic coercivity depending on temperature. Courtesy of Dr. Ryan Booth.

Figure 4.2: Hysteresis loops of cobalt iron oxide

The bulk magnetic properties of the samples were probed using a Quantum Design Superconducting Quantum Interference Device (SQUID) magnetometer. Dr. Booth took hysteresis measurements for both samples with temperatures ranging from 10 to 300 K and fields from -50 to 50 kOe. For the iron oxide particles that were superparamagnetic over the whole temperature range, the important parameter was the saturation magnetization. The mass saturation magnetization for the iron oxide particles was measured to be 85 emu/g at 300 K compared to 92 emu/g in bulk, indicating the high quality of the sample (38). For the cobalt iron oxide sample, the coercivity was of most interest and dramatically increased with lower temperatures (see Fig. 4.2).

Transmission electron microscopy (TEM) was done to characterize the size of the nanoparticles (see Fig. 4.3). After careful calibration, Dr. Booth calculated the size and distribution of the particles using the ImageJ software package (39). The iron oxide particles were $8.3 \pm 1.3$ nm in diameter, and the cobalt iron oxide particles were $11 \pm 1$ nm.
4.3 SANS

Neutron scattering experiments were performed on beamlines NG3 and NG7 at the National Institute of Standards and Technology’s Center for Neutron Research in Gaithersburg, Maryland. A nuclear source produced neutrons with a range of wavelengths that could be selected for use in experiments.

The SANS beamline geometry gave access to a Q range of $0.015 \text{ nm}^{-1}$ to $6.0 \text{ nm}^{-1}$. As shown in Fig. 4.4, it was a 30 m beamline from velocity selector to maximum detector distance with the sample in the middle. It had a pinhole collimator and allowed samples up to 25 mm in diameter.

A mechanical velocity selector was implemented to select the wavelength of incoming neutrons. It consisted of a set of rotating disks made of a highly absorbing material with regular slots machined into the circumference. Choosing the rotational speed and pitch of the device allowed neutrons of a certain velocity to pass, which defined their wavelength. Varying the speed allowed for a selection of wavelengths between 5.0 and 20.0 Å. Varying the pitch allowed for a selection of wavelength spreads between 10% and 30%. Wavelength spread was defined as $\Delta \lambda/\lambda$ at full-width, half-max.

Figure 4.3: TEM image of the iron oxide nanoparticles

The image shows the 8.3 nm particles to be well ordered. Taken from (23).
4.3 SANS

Figure 4.4: Diagram of the SANS beamline
The neutrons travel from the velocity selector and scatter off the sample. The movable 2D detector registers the scattering. Taken from (30).

Measurements at temperatures below ambient temperature were taken by attaching a cryostat and mounting the sample on a copper slab in thermal contact with the sample. The cryostat was a closed-cycle refrigerator that could reach temperatures as cold as 5 K (30).

A Titan electromagnet with a 65 W power supply generated the magnetic field applied to the sample. This field could be as high as 15.5 kOe (30).

A position sensitive detector array collected the 2-D scattering patterns (30). It measured 640 mm x 640 mm with a resolution of 5.08 mm x 5.08 mm. The distance from the sample to the detector could be varied from 1.3 m to 13.1 m continuously to change the available Q range. There was a mixture of $^3$He and CF$_4$ gas at about 243 kPa in the detector. $^3$He efficiently absorbs thermal neutrons following the reaction (23)

$$^1n + ^3He \rightarrow ^1H + ^3H + 765keV.$$ (4.1)

The 765 keV produced by the absorbed neutron process ionized the surrounding CF$_4$ gas. A high voltage anode attracted the ions and generated a signal. Small variances in sensitivity could be corrected for by scattering off of a highly isotropic sample such as water or Teflon for which the $\vec{Q}$ dependence is known.
4.4 PASANS

In using polarization analyzed small angle neutron scattering (PASANS), we took the technique of SANS and added components to polarize the neutron beam and analyze that polarization. These components are described in this section and illustrated in Fig. 4.5.

4.4.1 Supermirror

A supermirror was used to polarize the incoming neutron beam (41). The supermirror consisted of a multilayer structure of alternating magnetic and non-magnetic layers with the ferromagnetic layers causing polarization-dependent scattering. Initially, the incoming beam had an equal number of spin up and spin down neutrons. The supermirror was optimized to maximize the number of neutrons reflected in one state while minimizing the number reflected in the other state.

Like an optical thin film interference structure, there was a maximum angle between the plane of the mirror and the neutron’s incident wave vector that produced total internal reflection. Since neutrons had a range of incident wave vectors, a supermirror that polarized a wide variety of incident angles would increase total polarized flux. Alternating layers of the supermirror were built so that the reflected polarization state from the magnetic layers constructively interfered due to the path length differences. Neutrons of the opposite polarization were not reflected. If all the incident neutrons

Figure 4.5: Schematic of PASANS scattering

Neutrons are polarized by the supermirror. Their spin state can be flipped 180° by the flipper. After scattering, one spin state is selectively absorbed by the $^3$He cell before detection. Taken from (20).
had the same incident angle and wavelength, the system could be thought of as a simple optical thin film and the alternating layers would be of the same thickness. However, a range of angles and wavelengths needed to be polarized with this supermirror, so a monotonically decreasing layer thickness was used (42).

In our experiments, an Fe/Si supermirror polarized a well collimated incident beam of 5 Å⁻¹ neutrons with a 15% spread to a polarization efficiency of 0.94, where the polarization efficiency was the normalized absolute value of the difference between the two spin states (23).

4.4.2 Flipper

While the supermirror polarized the neutron beam, another device was used to flip the polarization direction to the opposite state. While a slowly varying, finite magnetic field preserved the polarization state of the neutrons, a precise magnetic field pulse could be used to flip the polarization state by 180° (i.e. spin up to spin down). In this case, the neutrons precessed around the orthogonal axis by π radians and ended up antiparallel to the original state when they returned to the guide field direction (19). This precession could be achieved in multiple ways (43). An rf flipper and an aluminum coil flipper have both been used in these experiments. Through careful consideration of the applied magnetic field and neutron velocity, a flipper was used to switch between the up (+) and down (−) states with an efficiency of 0.95 (36).

4.4.3 Magnetic Guide Fields

A magnetic guide field defined a direction $\hat{p}$ about which the neutrons precessed at the Larmor frequency. While the neutrons initially had projections half parallel and half antiparallel to $\hat{p}$, the supermirror and flipper polarized the beam so there was only one direction remaining. This polarization was maintained as long as there was a non-zero magnetic guide field. The neutrons adiabatically followed the direction of the guide field since the field varied slowly compared to the Larmor precession frequency of the neutrons. These guide fields came from stacks of ferrite magnets at various locations along the beamline (23). With slow enough variance, the polarization direction could be rotated for convenience of measurements.
4.4 PASANS

4.4.4 $^3\text{He}$ Polarizer

While a supermirror worked well for selectively choosing the spin state of the incoming neutrons, it had a limited range of angles over which it was effective. Using one to select a spin state after scattering would have severely constrained the Q-range and made many measurements impossible or extremely time consuming. However, the efficiency of $^3\text{He}$ as a neutron absorber made it a much more effective state selector for the scattered neutrons. The large absorption cross section for neutrons anti-parallel to the $^3\text{He}$ polarization and small absorption cross section parallel to it allowed for this efficiency. While polarized $^3\text{He}$ could selectively absorb one neutron spin state quite well, its use had been limited because of experimental difficulties (44).

More recently, a method of using cells of $^3\text{He}$ gas as a neutron analyzer had become available (44),(45),(46). The gas was contained in a cylindrical cell made of boron free glass at high pressure, around 975 Torr (see Fig. 4.6) (44). Conventional glass could not be used because boron absorbs neutrons. The gas was polarized using a method known as spin-exchange optical pumping (47). This method involved adding a small amount of rubidium and nitrogen to the $^3\text{He}$ cell and raising the Rb vapor pressure by heating the cell to a temperature between 80°C and 130°C. Both the electron and nuclear spins of the Rb were polarized through optical pumping with 794.7 nm circularly polarized light (48). Through the hyperfine interaction, collisions of the Rb atoms and the $^3\text{He}$ atoms polarized the $^3\text{He}$ nuclei. The ambient nitrogen absorbed radiated light during Rb relaxation.

The direction of the $^3\text{He}$ polarization state could be flipped by applying a pulsed field at the Larmor precession frequency. NMR was done in situ to measure the polarization. The absolute transmission measurements of both polarization states allowed for calibration. A solenoid producing a field of about 50 G protected the cell from stray magnetic fields that would depolarize it.

4.4.5 Polarization Correction

While the $^3\text{He}$ cell made an excellent state selector, its polarization decayed exponentially. The relaxation time, $\Gamma$, varied from 150-300 hours depending on stray field gradients. Data on the nanoparticles were typically collected for 12 hours per temperature and magnetic field condition. For accurate analysis, the time dependence of
the polarization had to be explicitly included. The following polarization correction procedure summarizes that presented in (36).

The $^3\text{He}$ polarization followed

$$P_{\text{He}} = P_0 e^{-t/\Gamma},$$  \hspace{1cm} (4.2)

where $t$ was the elapsed time and $P_0$ was the initial polarization of about 0.7. The overall time-dependent majority/minority spin transmission was

$$T = T_e e^{-(1\pm P_{\text{He}})l},$$  \hspace{1cm} (4.3)

where $T_e$ was the empty cell transmission of 0.86-0.87 and $l$ was the opacity of 2-3. The opacity took into account the neutrons of the majority transmitted spin that were absorbed. The decay rate was found through a fit of NMR absorption measurements taken throughout the experiment, with the transmission values providing a magnitude check.

Since the polarizing elements (the supermirror, flipper, and $^3\text{He}$ cell) were not perfect, the beam could end up incompletely polarized due to spin leakage. We defined $N_+^+$ as the percentage of $+, -$ neutrons transmitted by the supermirror and flipper.
and $T^\pm$ as the percentage through the $^3$He cell, so the true spin-dependent scattering cross-sections, $I_t$, related to the experimentally measured intensities, $I_m$, through

\[
\begin{bmatrix}
N^+_+ & N^+_T & N^-_+ & N^-_- \\
N^+_T & N^-_+ & N^-_T & N^-_+ \\
N^+_+ & N^+_T & N^-_+ & N^-_- \\
N^+_+ & N^+_T & N^-_+ & N^-_- \\
\end{bmatrix}
\begin{bmatrix}
I^+_+ \\
I^-_+ \\
I^+_+ \\
I^-_+ \\
\end{bmatrix}
= \begin{bmatrix}
I_{m,++} \\
I_{m,-+} \\
I_{m,-} \\
I_{m,-} \\
\end{bmatrix}
\tag{4.4}
\]

The superscript referred to the recorded majority spin direction at the detector, while the subscript referred to the majority spin direction of the polarizing element. The true scattering cross sections, $I_t$, were found based off of the measured intensities, $I_m$ and the spin leakage terms, $N$ and $T$. However, the polarization of the supermirror, $P_{SM}$, and flipper efficiency, $P_F$, still needed to be calculated. There was also the possibility of partial beam depolarization, $\chi_D$, due to stray magnetic fields, but that small effect was accounted for with an effective supermirror polarization of $P'_{SM} = (1 - \chi_D)P_{SM}$.

Using these polarizations,

\[
N^+_+ = \left(1 + \frac{P_F'_{SM}}{2}\right),
\tag{4.5}
\]

\[
N^-_+ = \left(1 - \frac{P_F'_{SM}}{2}\right),
\tag{4.6}
\]

\[
N^+_+ = \left(1 - P_F P'_{SM}\right),
\tag{4.7}
\]

\[
N^-_+ = \left(1 + P_F P'_{SM}\right),
\tag{4.8}
\]

where + is understood to be the state selected for by the supermirror, i.e. neutrons following the polarizer should be predominantly +.

The polarizations were calculated based off of transmission measurements with no sample in place. We expected no spin flip scattering without a sample and the (++) cross section to equal the (--) cross section. Combining these assumptions and the above equations led to

\[
P'_{SM} = \frac{(T^+_+ + T^-_+) - (T^+_+ + T^-_+)(I_{m,++} \mid I_{m,-+})}{(T^+_+ - T^-_+)(I_{m,++} \mid I_{m,-+}) - (T^+_+ + T^-_+)}
\tag{4.9}
\]
and

\[ P_F = \frac{1}{P'_{SM}} \frac{(T^- + T^+) - (T^- + T^+)(I^-_{m,-} + I^+_{m,+})}{(T^+ - T^-)(I^+_{m,+} - I^-_{m,-})}, \]  

(4.10)

This polarization correction process was done with the 2D form of the scattering files to prevent loss of spatial information.

Following these corrections, the data were now in 2-D cross sections: \( I^{++} \), \( I^{--} \), \( I^{+-} \), and \( I^{-+} \) for a variety of temperature and field conditions. Because these cross sections represent the true cross sections, we have dropped the explicit designation between true and measured. All subsequent intensities are implied to be true. These cross sections were analyzed to extract and separate \( N^2 \), \( M^2_{PARL} \), and \( M^2_{PERP} \), which are the Fourier transforms of the nuclear scattering, magnetic scattering parallel to the applied field, and magnetic scattering perpendicular to the applied field respectively.

These separations were done by taking \( \pm 10^\circ \) sector averages at certain \( \theta \) angles, where \( \theta \) is the angle between the applied magnetic field and the scattering vector \( \vec{Q} \). We took advantage of the geometry of our setup and used certain \( \theta \)s that greatly simplified the analysis. This simplification relies on the selection rules first developed by Moon, Riste, and Koehler (34) and were used in (20),(19):

\[ N^2(Q) = I^{++}_{\theta=0^\circ} + I^{--}_{\theta=0^\circ}, \]  

(4.11)

\[ M^2_{PARL}(Q) = \frac{(I^{++}_{\theta=90^\circ} - I^{++}_{\theta=0^\circ})^2}{8N^2}, \]  

(4.12)

\[ M^2_{PARL} = (I^{++}_{\theta=90^\circ} + I^{--}_{\theta=90^\circ}) - (I^{++}_{\theta=0^\circ} + I^{--}_{\theta=0^\circ}), \]  

(4.13)

\[ M^2_{PERP} = \frac{1}{6}(I^{++}_{\theta=0^\circ,90^\circ} + I^{--}_{\theta=0^\circ,90^\circ}), \]  

(4.14)

which are rearrangements of eqs. 3.23 - 3.26. The two relevant ways to find \( M^2_{PARL} \) represent different versions of the Fourier transform amplitude. Equation 4.12 gave the proportion of magnetization convoluted with the structural scattering due to the inclusion of a phase coherent cross term in eq. 3.24. Equation 4.13 gave the total magnetization not assuming coherence with the structural component. While the second gave a more complete picture, it involved the subtraction of two different sector cuts. Any systematic errors or inhomogeneity in polarization could distort the results of this subtraction and therefore the expected uncertainty was greater for this calculation.
5

Results and Discussion

This chapter describes the results of our latest PASANS experiments to probe the magnetic correlations between nanoparticles, spin canting within an individual particle, and the overall magnetic structure both within a particle and within the nanoparticle array. We first review key features of prior work on iron oxide nanoparticles and then discuss new results and analysis in this system as well as in the cobalt iron oxide system.

5.1 Previous Work

As mentioned in the introduction, earlier work done by past Oberlin students and collaborators discovered evidence for magnetic structure within chemically homogeneous iron oxide nanoparticles. Explicitly, PASANS revealed a magnetic core aligned with the applied field and a shell with a component perpendicular to the applied field \( \overline{M_{PARL}} \), which showed a Bragg peak that aligned with the structural Bragg peak (see Fig. 5.1a). The presence of a perpendicular shell manifested itself in a dip in \( M_{PERF} \) (see Fig. 5.1b). This dip fit to a model of a shell, not a sphere. Fitting to a sphere model gave an unphysical sphere size of at least 12 nm. Because this dip occurred at high applied magnetic fields but disappeared under remanent magnetic fields, we knew this shell was solely magnetic in nature. If there had been a structural difference, such as the shell being \( \text{Fe}_2\text{O}_3 \) and the core being \( \text{Fe}_3\text{O}_4 \), the dip would not have completely disappeared by changing the field and temperature conditions. The shell was originally thought to have a moment direction fully perpendicular to the core moment direction. However, further analysis
5.1 Previous Work

**Figure 5.1:** Iron oxide structural and magnetic intensities vs Q

Data were taken at 12 kOe and 200 K. The Bragg scattering peak for the $M_{2,PARL}^2$ data and the $N^2$ data match in location but differ in intensity. The $M_{2,PERP}^2$ data show a clear dip corresponding to the shell. Taken from (20).

showed that the shell was not fully perpendicular but instead canted at an angle away from the core direction which varies by experimental condition.

Our NIST collaborator Dr. Krycka developed an energy-based model to explain the formation of the shell (21). Four energies were considered: Zeeman, anisotropy, exchange, and dipole. The energies were calculated by approximating each of the 9 nm spherical nanoparticle as consisting of small cubes of side length $f.u. = 0.42$ nm each corresponding to one formula unit of Fe$_3$O$_4$. Each of these formula units had an inverse spinel structure with three interstitial sites filled with iron ions (see Fig. 5.2). The tetrahedral site of the spinel was filled with a magnetic moment of 5 $\mu_B$ and the two octahedral sites were filled with magnetic moments 4 $\mu_B$ and 5 $\mu_B$ (see Fig. 5.3). In bulk iron oxide with no applied magnetic field, the tetrahedral site is usually aligned nearly antiparallel to the octahedral sites via exchange interactions to give a
5.1 Previous Work

The spinel structure is illustrated here. The shaded oxygen atom is shared in both subcells. Taken from [49].

net magnetization of 4.1 $\mu_B$ per formula unit [58]. However, for the nanoparticle, we allowed an individual site to cant to change the magnetic moment of the formula unit and thus the particle. The 9 nm nanoparticle spheres were then close-packed into an FCC array with lattice length 13.6 nm. In the case of this nanoparticle array, the general equations for the energies presented in Chapter 2 can be specified as follows [21]. The Zeeman energy density is

$$E_{\text{Zeeman}} = - \sum_{i \text{ within NP}} \vec{m}_i \cdot \vec{H}, $$

where $m_i$ is the moment of a formula unit and $\vec{H}$ is the applied magnetic field. The anisotropy energy density is

$$E_{\text{anisotropy}} = - \left[ \cos^2(\theta - T_d) \frac{R^3}{R^3} - (R - t)^3 + \cos^2(\theta) \frac{(R - t)^3}{R^3} \right] \kappa, \quad (5.2)$$

where $R=4.5$ nm is the nanoparticle radius, $\theta$ is the canting angle, $T_d$ is the tilt angle of the tetrahedral site, $t$ is the shell thickness, and $\kappa$ is set to 4 time the bulk crystalline anisotropy constant $K_V$ for iron oxide (0.13 ev per nanoparticle). The exchange energy density is

$$E_{\text{exchange}} = \frac{-J_{\text{exch}}}{f.u.} \beta (1 - \cos(T_d)) \sum_{i=1}^{R/\delta(t)} \omega \frac{4\pi}{3} \frac{(R - i\delta(t))^3 - (R - (i - 1)\delta(t))^3}{f.u. \delta(t)}, \quad (5.3)$$

where $\delta(t)$ discretizes the nanoparticle into annular rings 0.05 nm thick and $\omega = \frac{R}{3(R - i\delta(t))}$ if $i\delta(t) \leq 3$ nm and $\omega = 1$ if $i\delta(t) \geq 3$ nm to correct for the decreasing number of nearest neighbor formula units at the edge of the nanoparticle. $J_{\text{exch}}$ is a fit parameter and was consistent with PASANS results for a range of 1.80-1.95 meV/formula unit.
The tetrahedral $T_d$ and octahedral $O_h$ tilt angles change the net moment of a formula unit. They determine the canting angle $\theta$.

The dipole energy between the eighteen nearest neighbor nanoparticles of the FCC array yields

$$E_{\text{dipole}} = \sum_i \sum_{j \neq i} \mu_0 (\vec{m}_i \cdot \vec{m}_j - 3(\vec{m}_i \cdot \hat{r}_{ij})(\vec{m}_j \cdot \hat{r}_{ij})) \frac{4\pi |\vec{r}_{ij}|^3}{|\vec{r}_{ij}|^3},$$

(5.4)

where $m_i$ and $m_j$ are the moments of the $i$th and $j$th nanoparticles and $\vec{r}_{ij}$ is the vector between them.

The energies were combined, and a minimum was found by allowing the shell thickness and angle of the magnetic moment of the shell relative to the applied field to vary.

The tilt angle and shell thickness needed to minimize energy varied with temperature. The magnetic moment, $m$, had a temperature dependence incorporated through a temperature parameter, $\beta$, which was the reduction of net moment due to thermal fluctuations (21). Analysis as described in Krycka, et al (21), showed energy minima with a shell of about 1 nm in 200 K and 300 K data and no discernable shell for 10 K data, which were consistent with PASANS results (see Fig. 5.4).

While this model successfully characterized behavior at the temperature extremes of 10 K and 300 K and applied field extremes of 12 kOe and a remanent field, it had not been tested against a range of intermediate temperature and field conditions. The enhancement of anisotropy contributions by letting $\kappa = 4K_V$ also merited further investigation.
5.1 Previous Work

Figure 5.4: Energy landscapes for iron oxide nanoparticles
Landscapes are plotted as a function of shell thickness and canting angle at 1.2 T and
a. 320 K, b. 300 K, c. 200 K, d. 160 K, e. 10 K, and f. 10 K with the exchange
constant increased by a factor of 2. Pink stars show global minima and white space
high energy. Figure reproduced from [21].
5.2 Results of this Thesis

Figure 5.5: Iron oxide structural and magnetic intensity evolution vs Q

The structural ($N^2$) and magnetic ($M^2_{PARL}$ via eq. 4.12) data both show the Bragg diffraction peak around 0.08 Å$^{-1}$. The greater magnetic alignment in phase with the structure with high fields is seen through the increasing peak height. All data were taken at 100 K.

5.2 Results of this Thesis

Work described in this section now focuses on probing some of those intermediate stages and trying to understand the evolution of this behavior in the iron oxide nanoparticles. We further test the model by applying it to a second system of cobalt iron oxide nanoparticles.

5.2.1 Iron Oxide

Initially, we investigated $N^2$ and $M^2_{PARL}$ via eq. 4.12. The $N^2$ profile shows the same Bragg diffraction peak as the $N^2$ profile from previous data, confirming the integrity of the sample. The $M^2_{PARL}$ profiles show the magnetic Bragg diffraction peak. This peak is most pronounced at high fields and low temperatures (see Figs. 5.5, 5.6). These relative peak intensities relate to the alignment of the magnetic moments within a sample to the applied magnetic field. However, we divide by $N^2$ in eq. 4.12, so only the component of magnetic scattering in phase with the nuclear scattering will be extracted. This expression is justified at high magnetic fields and temperatures, but it may not reveal the entire picture at intermediate fields and temperatures.

While we already had evidence of a magnetic shell, the evolution of said shell is still
5.2 Results of this Thesis

**Figure 5.6:** Iron oxide $M^2_{PARL}$ vs Q under various temperature and magnetic field conditions

The $M^2_{PARL}$ scattering component extracted through eq. 4.12 varies depending on temperature and field. Stronger magnetic fields and lower temperatures lead to greater intensity.

**Figure 5.7:** Iron oxide $M^2_{PERP}$ vs Q evolution with changing magnetic field

The dip in the perpendicular scattering corresponding to the magnetic shell increases with greater applied magnetic field. All data were taken at 100 K.
5.2 Results of this Thesis

As the temperature changes, the initial upturn corresponding to long-range correlations changes. All data were taken at an applied field of 100 Oe.

under investigation. We now aim to understand how the shell evolves under different temperatures and applied magnetic fields. We have extracted $M^2_{PERP}$ under a variety of temperature and field conditions to look for trends (see Figs. 5.7, 5.8). We also took data at lower Q to probe for longer range correlations and see an upturn in $M^2_{PERP}$ at lower Q (see Fig. 5.9). The intensity for low Q scattering is much reduced, thus making the associated data much noisier. This upturn occurs even in high applied fields and shows that the array is not fully aligned. The low Q upturn suggests some longer range interaction on the order of tens of nanoparticles. Such an interaction must be considered as another part of the magnetic structure of this array.

Consistent with $M^2_{PERP}$, $M^2_{PARL}$ extracted the other way via 4.13 has shown a clear upturn at low Q that varies with environmental conditions (see Fig. 5.10). Since the nuclear scattering does not show this upturn, it must be solely magnetic in nature. It corresponds to the longer range interactions between particles. There is a greater low Q intensity for weaker applied magnetic fields. However, as these correlations grow longer, such as with greater magnetic alignment, they tend toward $\vec{Q} = 0$ and an infinite correlation length [50]. We were not sensitive to scattering at such low values, so we instead see a decrease in the upturn as the magnetic field strength grows.

The behavior at a moderate temperature of 100 K is not as clear. While there is
Figure 5.9: Iron oxide $M^2_{PERP}$ vs Q initial upturn
The initial upturn varies with applied field and temperature. The upturn at low Q suggests longer range ordering that must be considered as part of the magnetic structure.

Figure 5.10: Iron oxide $M^2_{PARL}$ vs Q initial upturn
The upturn at low Q in $M^2_{PARL}$ via eq. 4.13 suggests longer range correlations between nanoparticles.
5.2 Results of this Thesis

Figure 5.11: Iron oxide energy landscape at 100 K
The energy in the system is minimized when the shell thickness goes to zero.

a clear dip in the 200 K, 12 kOe condition seen in Fig. 5.1 PASANS does not show a strong dip in the $M_{PERP}^2$ data at 100 K. The dip that seems more prominent from data collected on one beamline (Fig. 5.7) is not nearly as prominent in data collected later on another beamline (Fig. 5.10). However, there are no strong features present to fully rule out a dip. By extending this energy-based model to the 100 K case, we have been able to support our hypothesis that a magnetic shell does not form under these conditions. The Mathematic code based off of that from Krycka, et al. (21) and used to do the modeling described in this section is presented in Appendix A. In the 100 K, 12 kOe condition, the energy minimum occurs when the shell thickness goes to zero (see Fig. 5.11). However, this minimum is not very sensitive to changes in the anisotropy constant. The value for bulk iron oxide, the enhancement by a factor of 4 used in Krycka, et al. (21), and an enhancement by a factor of 8 all yield an energy minimum when there is no shell (see Fig. 5.12).

5.2.2 Cobalt Iron Oxide

To investigate whether analogous magnetic structures are present in other systems and to test the more general applicability of the energy model developed for iron oxide, we have here investigated the system of cobalt iron oxide particles. These particles are also an inverse spinel structure and have a magnetic moment of 3.3 $\mu_B$ in bulk at
5.2 Results of this Thesis

Figure 5.12: Iron oxide energy vs shell thickness at 100 K

The energy is minimized when the shell thickness goes to zero. This minimum occurs if the anisotropy is equal to the bulk value for iron oxide (purple), enhanced by 4 (blue), and enhanced by 8 (brown).

room temperature in comparison to 4.0 $\mu_B$ in bulk at room temperature for iron oxide (22). They are $11 \pm 1$ nm in diameter and ferrimagnetic. It is expected that these particles have a crystalline anisotropy approximately 18 times greater than the iron oxide particles, 180 kJ/m$^{-3}$ at room temperature vs -13 kJ/m$^{-3}$ respectively in bulk (35). Field cooled PASANS scattering data have been taken at 10 K and 200 K under an applied field of 14 kOe.

As the PASANS results in Fig. 5.13 show, the structural peak remains at the 0.07 Å$^{-1}$ position with the same intensity for all the conditions and fits nicely to a model of an FCC lattice with 10 ± 1 nm particles and a nearest neighbor distance of 15 nm, agreeing with TEM imaging.

$M^2_{PARL}$ reveals more information about the magnetic structure of the particles. The parallel magnetic scattering coherent with the structural scattering (eq 4.12) produces a prominent peak around 0.07 Å$^{-1}$, following the shape of the structural scattering. The magnitude of the peak is slightly higher for the 200 K than 10 K, but both are sizable.

Unlike the iron oxide particles, the cobalt iron oxide $M^2_{PERP}$ display no characteristic dip, even at high fields and moderate temperatures (see Fig. 5.14). This lack of a
5.2 Results of this Thesis

Figure 5.13: Cobalt iron oxide structural and magnetic intensities vs Q
Structural (black and gray, scaled down by 1/40 for convenience) and parallel magnetic (green and purple) scattering for cobalt iron oxide at both 200 K and 10 K. Structural scattering is the same for both cases. Data were taken at 14 kOe.

A dip signifies that there is no magnetic shell to contrast with a magnetic core. However, the perpendicular signal fits quite nicely to a modeled simple sphere of 10.5 ± 0.4 nm, which agrees with the TEM results. Both conditions fit to the same particle size, differing only in intensity, thus providing strong evidence that the entire particle tips in an applied magnetic field instead of generating a core and a shell.

To understand what drives the canting, we have extended the energy based model developed for the iron oxide particles to the cobalt iron oxide particles using the Mathematica code in Appendix [A].

We include the same four energy contributions as in the iron oxide model—Zeeman, anisotropy, exchange, and dipole—and the energy contributions corresponding to a single magnetic particle. However, the increased anisotropy in the cobalt iron oxide particles compared to the iron oxide particles leads to distinct changes. The first order anisotropy constant is about 18 times greater in magnitude than for iron oxide and the opposite sign. Since the anisotropy constant has a positive sign instead of a negative sign, the magnetic moments of the particles are most favored to align along the [100] directions. However, the cubic symmetry of the crystal means that the moment can still be no farther than 45° from aligning with a favorable direction. The difference in both net magnetic moment and component magnetic moments also merits consideration. A
5.2 Results of this Thesis

Figure 5.14: Cobalt iron oxide $M^2_{PERP}$
Perpendicular scattering for cobalt iron oxide showed no dip but rather the scattering pattern associated with single spheres. The solid line fits corresponded to the modeled scattering pattern for a simple sphere. Data were taken at 14 kOe.

Co ion with a magnetic moment $3 \mu_B$ replaces one of the Fe ions in an octahedral site. The oxygen atoms mediate the alignment of the three moments within a formula unit to give a net moment of $3.3 \mu_B$ in bulk room temperature cobalt iron oxide vs $4.0 \mu_B$ for bulk iron oxide \(^{(22)}\).

The differences in cobalt iron oxide cause it to match well with a model of coherent octahedral and tetrahedral canting. In this coherent cant, only the Zeeman and anisotropy terms need to be considered. The exchange and dipole terms are not affected if the particle cant coherently. Therefore the canting angle comes from the balance between the Zeeman cost of canting away from the applied magnetic field and the anisotropy savings of canting toward the easy axis. These two terms give an energy savings per formula unit of

$$E = mH(1 - \cos(\theta)) - K(\cos(45^\circ - \theta) - \cos(\theta)).$$

(5.5)

The temperature dependence of the anisotropy constant was included by letting $K = 1.96 \times 10^6 e^{-1.90 \times 10^{-5} T^2} J/m^3 \quad (51)$, and the magnetic moment per formula unit was scaled linearly from $3.94 \mu_B$ at 0 K to $3.3 \mu_B$ at 300 K.
5.2 Results of this Thesis

Analogous to the case for iron oxide, the canting angles come from the parallel and perpendicular components of the moment, which can be expressed through the tilt angles of the octahedral sites and the tetrahedral site. Depending on the tilt of the sites,

\[ m_{\text{part}} \propto 8\mu_B \cos(O_h) - 5\mu_B \cos(T_d), \]  
(5.6)

\[ m_{\text{perp}} \propto |8\mu_B \sin(O_h) - 5\mu_B \sin(T_d)|, \]  
(5.7)

\[ \theta = \tan^{-1}\left(\frac{m_{\text{perp}}}{m_{\text{part}}}\right), \]  
(5.8)

where \( O_h \) is the tilt angle of the octahedral site and \( T_d \) is the tilt angle of the tetrahedral site. Because the canting is coherent for cobalt iron oxide, \( O_h = T_d = \theta \). Based on the PASANS data, \( \theta = 24 \pm 2^\circ \) for 200 K, 1.4 kOe and \( \theta = 33 \pm 2^\circ \) for 10 K, 1.4 kOe.

By modeling these energies as a function of a canted shell thickness and canting angle, we have found that the cobalt iron oxide particles had an energy minimum when there was no core, just a fully canted particle at a net canting angle of \( 27^\circ \pm 4^\circ \) for 200 K and \( 33^\circ \pm 4^\circ \) for 10 K (see Fig. 5.15). We have plotted the energy in eV as a function of shell thickness and tilt angle \( \theta \). The largest contributions come from the balance of the Zeeman energy and the anisotropy energy. This balance gives a valley area with a total minimum (see Fig. 5.16). Canting angles more than \( 4^\circ \) away from the minimum cause a noticeable energy increase. Shell thicknesses of less than 5 nm (i.e. a core of more than 1 nm in diameter) also cause a noticeable energy increase. The resulting minimization agrees with the results obtained from PASANS.

To understand the energy balance in more detail, we consider the separate energy terms. The Zeeman and anisotropy energies dominate the energy balance. However, anisotropy effects can be stronger or weaker in nanoparticles than in bulk. We have used the bulk value of anisotropy thus far. However, increasing the anisotropy by a factor of two increases \( \theta \) a noticeable amount (see Fig. 5.17). If the anisotropy is instead reduced to half of bulk, \( \theta \) decreases significantly (see Fig. 5.17). The pronounced effect of changing anisotropy merits more investigation into the actual anisotropy changes in the nanoparticles.

This system of cobalt iron oxide nanoparticles does not show evidence of a magnetic shell. This difference is likely due to the higher anisotropy contributions compared to
5.2 Results of this Thesis

Figure 5.15: Comparison of 200 K and 10 K energy minima
The energy minimum as a function of octahedral site tilt shifts from $27\pm4^\circ$ to $33\pm4^\circ$ as the temperature changes from 200 K (blue) to 10 K (purple). Curves are for a fully canted particle under an applied field of 1.4 kOe.

Figure 5.16: Cobalt iron oxide energy landscape
Energy landscape for the cobalt iron oxide nanoparticles for 200 K, 1.4 kOe conditions measured in eV.
The tilt angle associated with an energy minimum changes when the anisotropy is enhanced from bulk (blue) by a factor of 2 (purple) or 1/2 (brown). Shown for a fully canted particle at 10 K in an applied field of 14 kOe.

Figure 5.17: Effects of anisotropy enhancement

the iron oxide system. Instead, the particles exhibit a full cant at an angle that depends on temperature. PASANS results agree with the energy model.
Summary and Future Work

6.1 Summary

This thesis has outlined results obtained while investigating two nanoparticle systems—one of iron oxide and one of cobalt iron oxide. The particles have been investigated using PASANS techniques with supplemental analysis through TEM and SQUID magnetometry. This analysis has revealed a core-shell structure for the iron oxide particles with the shell disappearing at lower temperatures and lower applied magnetic fields. This shell is chemically identical to the core but has a net moment that is canted away from the direction of applied field. The cobalt iron oxide particles remain magnetically monodomain throughout the range of tested temperatures and applied magnetic fields. However, they are uniformly canted with a canting angle that varies with temperature.

To understand the results found by PASANS, we have developed an energy-based model consistent with the observed shell formation and canting. This model accounts for the competing contributions of Zeeman, anisotropy, exchange, and dipole energies to minimize the overall energy costs. This modeling found energy landscapes for both the iron oxide and cobalt iron oxide particles as a function of canting angle and shell thickness. In a 12 kOe applied magnetic field and temperatures above 200 K, the iron oxide particles had an energy minimum with a canted shell of about 1 nm \(21\). The shell clearly disappeared at low temperatures, consistent with PASANS results. At the intermediate temperature of 100 K, PASANS results were ambiguous, but the energy model was minimized when no shell forms. In an applied field of 14 kOe, the cobalt iron particles had a minimum with a full canting angle that varies with temperature. This
energy-based model provides quantitative agreement of magnetic structure to basic energy components.

6.2 Ongoing and Future Work

There is still much to be done with these ferrite nanoparticle systems. More temperatures and applied magnetic fields should be probed to test the robustness of this model, especially at intermediary values. While the model agrees with experimental results at extrema, the validity at intermediate fields merits further testing. The more general expressions developed in (19) will allow for more complete characterization of the evolution of correlations amongst the nanoparticles.

This model has been applied to two systems, iron oxide and cobalt iron oxide, that differ primarily in the anisotropy contribution. An enhancement or reduction of the anisotropy constant away from the bulk value greatly changed the energy model for cobalt iron oxide, but the iron oxide model at 100 K, 12 kOe was not highly affected. Because of these effects of changing anisotropy, we are interested in investigating other ferrite systems with different anisotropy levels. These other systems can probe possible trends and further test the validity of our approach. Our next target of interest is a manganese iron oxide with a bulk anisotropy of 2.5 kJ/m$^3$ (52), which is smaller than the bulk anisotropy of iron oxide or cobalt iron oxide. MnFe$_2$O$_4$ has been proposed for applications as an MRI contrast agent and a vehicle for targeted drug delivery (52). Through both PASANS techniques and this energy-based model, we hope to understand this manganese iron oxide system in its own rights and probe the importance of anisotropy in nanoparticle systems as a whole. We are in the process of creating and characterizing the sample using SQUID magnetometry and small angle X-ray scattering (SAXS) for an experiment scheduled for early May. To facilitate direct comparison to expected SANS data, we have developed a method of analyzing SAXS data using the same software as the SANS data (see Appendix [3]).

The PASANS process is still being improved as well. Magnetic screws that were found in the beamline have been removed to reduce any unnecessary magnetic contributions to the data. The lifetime of the $^3$He cells are being increased to allow for better polarization without having to change the cell as often. With the recent upgrade of the NG7 beamline at the NCNR, a better supermirror has been included to cut down on
some vertical asymmetry due to uneven polarization. One current challenge also comes from the geometry of the setup. The proximity of the electromagnet that generates the applied magnetic field to the $^3$He cell cannot be too close or else the cell loses polarization. This threat of polarization loss limits the maximum applied field to about 15 kOe. Ideally, we would like to take data at higher fields while maintaining good cell polarization. In addition, plans are underway for an *in-situ* polarization process that would remove the need for many of the cell decay concerns.

The work outlined here should continue to provide improved insights into the nature of magnetic nanoparticles and their structures. A better understanding of the behaviors of these representative systems of iron oxide and cobalt iron oxide may thus guide others in considering appropriate conditions for particles for data storage, advanced fluid seals, and biomedicine.
Appendix A

Mathematic Code for Energy Based Model

The following is the template code developed for the energy based modeling described in Chapter 5. It was written in Mathematica, a computational software program. Inputs were modified to reflect the specific sample and the temperature and field conditions to be modeled.
uBJ = 9.27 * 10^-2; (*muB in J/T*)
uB = 5.79 * 10^-4; (*muB in eV/T*)
H = 1.4; (*applied field in T*)
KvJ = 180 * 10^-3; (*anisotropy constant in J/m^3*)
Kv = 8.34 * 10^-5; (*anisotropy constant in eV/fu^3*)
T = 10; (*temperature in K*)
KviaT = 1.96 * 10^-6 * E^-(-1.90 * 10^-5 * T^-2); (*temperature dependent anisotropy constant in ergs/cm^3*)
KviaTJ = 1.96 * 10^-6 * E^-(-1.90 * 10^-5 * T^-2); (*temperature dependent anisotropy constant in J/m^3*)
fu = 0.42; (*formula unit in mm*)
Kv* = 1.26 * 10^-2; (*permeability of free space N/A^2*T*)
R = 5.5; (*radius in mm*)
Kv = 5.5 * 10^-3; (*radius in m*)
a = 15 * 10^-9; (*lattice constant of nanoparticle fcc lattice in m*)
Td = 0; (*tilt of tetrahedral site in degrees*)

\[ n = (4/3 \pi R n^3) / (2 \pi f^3) \] (*number of formula units in a nanoparticle*)

\[ \theta = 180 / \pi \cdot \text{ArcTan}(|\text{mperpJ} / \text{mparlJ}|); (*angle of tilt in degrees*) \]
\[ \text{mparlJ} = (-5 uBJ + \cos[\text{Td} / \pi / 180] + 5 uBJ + \cos[\text{Oh} + \pi / 180] + 3 uBJ + \cos[\text{Oh} + \pi / 180]) / (2 \pi \cdot f^3); (*magnetic moment aligned parallel to the applied field in J/T*) \]
\[ \text{mperpJ} = (-5 uBJ + \sin[\text{Td} / \pi / 180] + 5 uBJ + \sin[\text{Oh} + \pi / 180] + 3 uBJ + \sin[\text{Oh} + \pi / 180]) / (2 \pi \cdot f^3); (*magnetic moment aligned perpendicular to the applied field in J/T*) \]

\[ mJ = \sqrt{\text{mperpJ}^2 + \text{mparlJ}^2}; (*total magnetic moment in J*) \]

(*For Coherent Canting*)
\[ \text{energy} \text{ per \ formula \ unit \ based \ on \ canting \ angle}. \ \text{Oh}=Td=\theta \]
\[ \text{coherent} = 4 \cdot uBJ \cdot H \cdot (1 - \cos[\theta]); \]
\[ \text{Plot}[\text{coherent} \cdot 1.6 \cdot 10^{-19}, \{0, 0, 50\}]; (*energy \ per \ nanoparticle \ on \ canting \ angle \ and \ shell \ thickness*) \]
\[ \text{landscape} = -\text{coherent200} \cdot 4 / 3 \cdot \pi \cdot (\{R - t \cdot 10^{-9} \} - 3 - R^3) / (f^3); \]
\[ \text{Plot3D}[\text{landscape}, \{t, 0, 5.5\}, \{\text{Oh}, 0, 5.1\}]; (*multiplied \ by \ 1.6 \cdot 10^{-19} \ so \ the \ scale \ is \ in \ eV, \ plotted \ against \ thickness \ of \ canted \ shell \ (t) \ in \ nm \ and \ tilt \ of \ octahedral \ site \ (\text{Oh}) \ in \ degrees*) \]

(*Anisotropy energy per nanoparticle*)
\[ \text{Kv} = (4/12 \cdot \pi \cdot R n^3) \cdot \cos[\text{theta} - \text{Oh}]; \]
\[ \text{Plot3D}[\text{aj} \cdot 1.6 \cdot 10^{-19}, \{t, 0, 5.5\}, \{\text{Oh}, 0, 5.1\}]; (*multiplied \ by \ 1.6 \cdot 10^{-19} \ so \ the \ scale \ is \ in \ eV, \ plotted \ against \ thickness \ of \ canted \ shell \ (t) \ in \ nm \ and \ tilt \ of \ octahedral \ site \ (\text{Oh}) \ in \ degrees*) \]

\[ \text{aj} = 5 \cdot 10^{-19}, \{t, 0, 5.5\}, \{\text{Oh}, 0, 5.1\} \]
Exchange energy for one nanoparticle-exchange energy is $J*S_*L$

$J = 16*10^{-19}$; ($*$exchange constant in J, equal to 10 eV$*$)

$e = -J / \text{fum}*n$

$8 \text{ uBJ} + 5 \text{ uBJ} * \cos [ (\text{Oh} - \text{Td}) * \pi / 180 ] * (\text{Rm}^3 - (\text{Rm} - (t * 10^{-9}))^3) / (2 * \text{fum}^3) +$

$8 \text{ uBJ} + 5 \text{ uBJ} * \cos [ 0 * \pi / 180 ] * (((\text{Rm} - (t * 10^{-9}))^3) / (2 * \text{fum}^3) +$

$2 * \pi * (\text{Rm} - (t * 10^{-9})) / (\text{fum} * 2) + 3.3 \text{ uBJ} * \text{mJ}$; ($*$exchange energy in J$*$)

Plot3D [$e*1.6*10^{-19}, (t, 0, 5.5), (\text{Oh}, 0, 51)]$; ($*$multiplied by 1.6$*$

$10^{-19}$ so the scale is in eV, plotted against thickness of canted shell ($t$ in nm and tilt of octahedral site ($\text{Oh}$) in degrees$*$)
Dipole energy for one nanoparticle from the 18 nearest neighbors, all assumed to have equal magnetic moments.

dipole energy is \(-u_0(m.m-3(m.r)(m.r))/(4\pi m^3)\)

d = (sixa * sixb + twelvea + twelvec + twelved) * (2 * \sum m^3)^2 * (Rm^3 - (Rm - t * 10^-9)^3 / (Rm^3) +
(sixa + sixb + twelvea + twelvec + twelved) * (2 * \sum m^3)^2 * (Rm - t * 10^-9)^3 / (Rm^3);

(total dipole energy weighted to account for shell and core magnetism in J)

sixa = 6 * u0 * (m.j)^2 * n / (4 * Pi * (a / 2)^3);

(shell contribution from m.m term for six nn that are distance a away)

sixb = -3 * u0 * (m.j)^2 * n / (4 * Pi * (a / 2)^3) *

(\cos[\theta - Pi / 180] * 2 + \cos[(90 - \theta) - Pi / 180] * 2 +
\cos[(135 - \theta) - Pi / 180] * 2 + \cos[(135 + \theta) + Pi / 180] * 2);

(shell contribution from m.r term for six nn that are distance a away)

twelvea = 12 * u0 * (m.j)^2 * n / (4 * Pi * (a / Sqrt[2])^3);

(shell contribution from m.m term for twelve nn that are distance a / Sqrt[2] away)

twelvec = -3 * u0 * (3.3 Ubj)^2 * n / (4 * Pi * (a / 2)^3) * (core contribution from m.m term for twelve nn that are distance a / Sqrt[2] away)

sixd = -3 * u0 * (3.3 Ubj)^2 * n / (4 * Pi * (a / 2)^3) * (core contribution from m.m term for twelve nn that are distance a / Sqrt[2] away)

sixd = -3 * u0 * (3.3 Ubj)^2 * n / (4 * Pi * (a / 2)^3) * (core contribution from m.m term for twelve nn that are distance a / Sqrt[2] away)

twelvec = 12 * u0 * (3.3 Ubj)^2 * n / (4 * Pi * (a / Sqrt[2])^3); (core contribution from m.m term for twelve nn that are distance a / Sqrt[2] away)

twelved = -3 * u0 * (3.3 Ubj)^2 * n / (4 * Pi * (a / Sqrt[2])^3) *

(\cos[(45 - 0) - Pi / 180] * 2 + \cos[(45 + 0) - Pi / 180] * 2 + \cos[(135 - 0) + Pi / 180] * 2 +
\cos[(135 + 0) + Pi / 180] * 2 + \cos[(180 - 0) + Pi / 180] * 2 + \cos[(180 + 0) + Pi / 180] * 2);

(shell contribution from m.r term for twelve nn that are distance a / Sqrt[2] away)

Plot3D[{d + 1.6 * 10^-19}, {t, 0, 5.5}, {Oh, 0, 51}]

(multiplied by 1.6 * 10^-19 so the scale is in eV, plotted against thickness of canted shell (t) in nm and tilt of octahedral site (Oh) in degrees)
Plot3D[(\(zJt + aJ + d + e\) \* \(1.6 \times 10^{19}\), \((t, 0, 5.5), (Oh, 0, 51)\)\]

(*total energy multiplied by \(1.6\times10^{19}\) so the scale is in eV, plotted against thickness of canted shell \(t\)
 in nm and tilt of octahedral site \(Oh\) in degrees*)

Plot[theta, \((Oh, 0, 51)\)] (*theta as a function of Oh tilt*)
Appendix B

Analysis of SAXS data using NIST SANS macro techniques

X-ray scattering techniques can provide helpful information as to the size and distribution of nanoparticles. However, comparisons between scattering techniques can be difficult due to differences in instrument hardware and software. In this section, we outline a method of analyzing small angle X-ray scattering (SAXS) data using the NIST macros developed for SANS analysis \( (27) \). X-ray data were taken using a Rigaku Ultima IV X-ray diffractometer at Oberlin College obtained through NSF grant DMR-0922588. These data are usually analyzed using the proprietary Rigaku program entitled Nanosolver \( (33) \). While this program is straightforward and convenient, it convolutes the instrument resolution with the scattering data and does not allow us to extract corrected data for further analysis in another program. Here we outline a technique to do so to assist in the analysis of more complex systems. This technique makes use of freely available macros that have been modified to allow for direct comparison between SAXS and SANS data. Through this direct comparison, the structural scattering can be isolated cleanly.

B.1 SAXS Geometry

Small angle X-ray scattering is a useful technique to characterize the size of molecules or particles in a sample that are in the tens to hundreds of nanometers size range. While it is not as useful at revealing crystallographic information as traditional X-ray diffraction,
it provides many insights for systems that may not have a strong crystallographic
component, such as a nanoparticle suspension or ferrofluid. It is able to distinguish
between two different size particles in a single solution and provide size distributions
of said particles.

SAXS can be adapted from a conventional X-ray diffraction setup (see figure B.1).
For the Rigaku Ultima IV X-ray Diffractometer (XRD) at Oberlin College, X-rays
are generated by colliding electrons with a copper target. The collisions create X-ray
radiation concentrated at the transition energies. The generated X-rays are converted
into a parallel wavefront using the parabolic mirror of Rigaku’s Cross Beam Optics
(CBO) system. While there are multiple wavelengths created in this process, filters in
the XRD limit the radiation to the K-α wavelength of $\lambda = 1.54$ Å. After generation,
the monochromatic X-rays are collimated and pass through several height limiting slits.
They then strike the sample and are scattered at various angles. The transmitted X-
rays travel through a vacuum path and are recorded by a scintillation counter detector.
An angular range of about $4^\circ$ is scanned in the SAXS configuration (53).

These data can be analyzed using the Nanosolver program (53). It has a built-in
resolution function for the diffractometer and can provide nanoparticle size and size
distribution for a variety of geometries allowed by the machine. The selection of a
scattering geometry automatically selects the appropriate input parameters such as
the sizes of the height limiting slits. The composition of the scattering particles and
the solvent must also be specified.

B.2 USANS Geometry

Ultra Small Angle Neutron Scattering (USANS) is a specific type of SANS that uses
a perfect crystal diffractometer (PCD) to get even higher resolution scattering results
(30). It uses a pyrolytic graphite premonochromator followed by a triple-bounce Si(220)
monochromator to further reduce the wavelength spread of the beam and a triple-
bounce Si (220) analyzer before the detector (see figure B.2). This geometry makes the
smearing of the data more dependent on the slit-like properties of the monochromator
and analyzer than the pinhole collimation used for the SANS experiments described in
the body of this thesis (54).
B.2 USANS Geometry

Figure B.1: Schematic of SAXS setup
The CBO unit creates a parallel beam and the slits select its size. The X-ray beam scatters off the sample and are detected after the receiving slit box. Figure taken from (53).

Figure B.2: Schematic of USANS scattering
A collimated neutron beam goes through a premonochromator and a monochromator before scattering off the sample labeled s. The scattered neutrons go through an analyzer before registering at the detector. Figure taken from (30).
USANS data can be analyzed using freely available macros that run in Igor Pro, a data analysis and graphics program (27). These macros assume a slit-smeared resolution and are able to model a variety of nanoparticle shapes and structures. The parameters for slit smearing come from the resolution function that is imported with the data. For USANS measurements at NIST, the function or parameters are collected and automatically associated with the data files. The scattering length densities of the scattering sources and the solvent must be specified as well.

B.3 Resolution Function

Because both SAXS and USANS data are slit-smeared, SAXS data can be analyzed using USANS macros if the correct resolution function can be found. For the USANS data, a resolution function is built into the data collected based on the geometries of the neutron beam configuration. No such resolution function is built into the SAXS data. Nanosolver generates such a function, but it is hidden within the black box of its inner workings and thus inaccessible for users. However, the resolution function used for USANS analysis is relatively straightforward. It relies solely on the vertical resolution of the instrument, \( \Delta q_v \), which is a constant value (27). In actual use, this resolution function consists of the final three columns of the six column data set. All the values in these three columns are set to \(-\Delta q_v\).

This resolution function allows for slit smearing through an adaptive trapezoidal integration (55) by

\[
I_s(Q) = \frac{1}{\Delta q_v} \int_0^{\Delta q_v} I[(q_v^2 + Q^2)^{1/2}]dq_v,
\]

where \( q_v \) is the vertical range, \( Q \) is the magnitude of the scattering vector, and \( I_s \) is the smeared intensity.

To apply this slit smearing to the SAXS data, one needs to find the appropriate \( \Delta q_v \). By investigating the geometry of the Rigaku Ultima IV X-ray diffractometer in SAXS configuration, we determined a vertical resolution corresponding to a 2\( \theta \) value of 6.1\( ^\circ \), or a Q-value of 0.43 Å\(^{-1} \) for \( K_\alpha = 1.54 \) Å. For a data set of 10 nm iron oxide nanoparticles synthesized to have a small size distribution, we produced good fits that replicate those found through Nanosolver. We confirmed the plausibility of this value of the resolution function by comparing results using extreme resolution functions for this...
The proper resolution function (red line) matches the SAXS data (black dots). Note the decrease in quality as the resolution function decreases.

same sample. If the resolution function is smaller than 0.43 Å⁻¹, there is an obvious decrease in the fit quality. This quality decrease is quite noticeable even at 0.2 Å⁻¹ (see figure B.3). If ∆q_v is much larger than 0.43 Å⁻¹, the quality of fit remains the same but the integration time increases to an unreasonable time. Therefore we know the chosen resolution function is at least within a factor of 2 and replicates the features of interest for this study.

B.4 Procedure

Data that are to be analyzed with the SANS macros need to be in a specific six-column format consisting of Q-value in Å⁻¹, intensity, standard deviation of intensity, and the three column resolution function. The output for SAXS data is a two column file consisting of 2θ values measured in degrees and intensity. The following procedure can be used to properly format the SAXS data.
First, the two column SAXS data are loaded into the SANS macro using the Plot option in 1-D Ops of the SANS Reduction Controls. Loading the data this way associates a standard deviation wave, labeled (file name)_s, with the data. The columns of 2θ (which will be labeled with a _q tag), intensity, and standard deviation now need to be copied to a program in which they can be further modified. One way to do so is to copy the values from a table of (file name)_q, (file name)_i, and (file name)_s to a program such as Microsoft Excel.

Now we can convert the 2θ values to Q values and add the resolution function. The conversion of

\[ Q = \frac{4\pi}{\lambda} \sin \left( \frac{2\theta \pi}{360^\circ} \right) \]  

(B.2)

should be used, where \( \lambda \) is the wavelength in angstroms. The resolution function is appended to the next three columns after the standard deviation column. It is three columns of the same length as the data with the value of -0.43 for each entry.

Once the data are in this proper six column format, they should be saved as a text file and loaded into Igor Pro through the Plot option in 1-D Ops of the SANS Reduction Controls. If the data are properly formatted, a pop-up window entitled USANS Slope Extrapolation should appear. This window shows that the loaded data are recognized as consistent with the USANS format. Click “Calculate” and “Accept Slope” to finish loading the data.

Now that the SAXS data have been correctly loaded, they can be analyzed using the same tools as SANS data, including curve fits smeared to the resolution of the SAXS setup.

The outlined procedure is effective and proves the feasibility of using SANS macros to analyze SAXS data. However, it is somewhat user-intensive. For a more streamlined method, one could write a macro to automate more of the process.

**B.5 Verification**

SAXS data concerning other samples of iron oxide particles were analyzed using both Nanosolver and the above method. These samples were commercially obtained iron oxide particles with an oleic acid coating suspended in toluene. They were from Sigma-Aldrich and had a greater spread in size distribution. The model for spheres with a Log-Normal size distribution was used to fit the data. The scattering length densities
B.5 Verification

Figure B.4: SANS macros and Nanosolver fit particle sizes

The SANS macros and Nanosolver particle sizes fit within error. The SANS macros method agrees with the Nanosolver method for both a single particle size sample and a mixture of two particle sizes.

for bulk iron oxide and toluene were specified as input parameters but the particle size and size distribution were allowed to vary to obtain the best fit. Both methods gave particle size distributions that agreed within error for multiple datasets (see Fig. [B.4]). They both fit datasets of a single mean particle size and mixtures with particles of multiple mean sizes. The fits between the two methods visually agree as well (see Fig. [B.5]). If the SANS macros input particle size and size distribution are constrained to match those obtained through Nanosolver fits, the resulting curves are very similar but slightly less precise at the very low Q values. The Nanosolver program does not account for deviations from ideal alignment in the diffractometer setup, which may cause the differences between the two approaches.

As a result of the developed modification, we can now probe more complicated particle systems such as the crystallites studied in this thesis and analyze the resulting SAXS data using the same tools available for SANS data. This process does require the use of Igor Pro, but the actual fitting process is easily customizable and can take advantage of the many developed modules for a range of particle shapes and distributions beyond the single particle model.
Figure B.5: SANS macros and Nanosolver fits

The SANS macros fit (red dotted line) agrees with the Nanosolver fit (yellow line). Both match the SAXS data. Both methods allow for fitting of a single particle size (left graph) and a mixture of particle sizes (right graph).
Bibliography


