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Time-Domain Measurement Of Ultrafast Magnetization Dynamics In Magnetic Nanoparticles

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Time-Domain Measurement of Ultrafast Magnetization Dynamics in Magnetic Nanoparticles

by

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Abstract

Ultrafast time-domain measurements are made on collections of Fe₃O₄ magnetic nanoparticles using an inductive measurement technique. The 10nm particles are placed directly on a coplanar waveguide (CPW) situated in an adjustable external magnetic bias field. A fast-rising step current in the CPW quickly changes the orientation of the local magnetic field causing the magnetization to align in the new field configuration. This rapidly changing magnetization induces a voltage in the CPW that is detected by a sampling oscilloscope. Magnetization dynamics predicted by the Landau-Lifshitz (LL) equation including magnetic precession and phenomenological damping are observed. The time-domain data are fitted to damped sinusoidal solutions of the LL equation. Frequency analysis is done using a Fast Fourier transform on the time-domain data. Two prominent frequency peaks are observed centering around 1.3 GHz and 3.5 GHz. The frequency data are then fitted to the general Kittel equation for ferromagnetic resonance. The demagnetization factors are found to be those of very nearly spherical objects, rather than the collective shape of the overall sample. Fitted $g$-factors for samples are found to be in excellent agreement with previously published values. Low frequency damping generally decreases with increasing bias field, a result in qualitative agreement with published pulsed inductive detection on magnetic films. High frequency damping reaches a minimum at sample-dependent field values.
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Chapter 1

Introduction to Magnetic Nanoparticles

Nano-manufacturing techniques have made it possible to fabricate magnetic nanoparticles with excellent control over their shape and size. Spherical magnetic nanoparticles typically range in size from a few nanometers to sub-micron dimensions [1]. These magnetic particles can be put into a colloidal suspension of oil or water to create magnetic liquids, called ferrofluids. When coated with a hydrophobic surfactant, agglomeration, or clumping, of the particles can be avoided making ferrofluids ideal for many applications. Whether suspended in fluids or prepared in a solid form, magnetic nanoparticles have an ever-growing variety of uses a few of which include cancer research [2], [3], medical in vivo imaging [4], drug delivery [5], and magnetic sensors [6].

In practically all of these applications the particles are excited by, or interact with electromagnetic waves. Being magnetic, their dynamical behavior in the presence of time-varying magnetic fields from these waves is of interest. Many studies have been done on the frequency response of such particles, including ferromagnetic resonance (FMR) experiments, which detect the frequencies and complex modes of oscillations the particles undergo in the presence of electromagnetic waves [7]-[12]. Work has also been done in theoretical computational models of their frequency response [13]. While there has been plenty of frequency-domain work on these particles, experiments measuring
their time-domain behavior is much less prevalent. This is likely due to the smallness of the particles and the fact that most of the interesting dynamics occur in the sub-nanosecond regime. Accurately measuring this small of a magnetic field over such a time scale may be possible by means of an inductive technique, the current state of which was put forth by [14], to be described later.

The nanoparticles used in this work are composed of Fe₃O₄ (magnetite) and have a 10nm diameter with a 1nm nonmagnetic coating. This shell is a hydrophobic coating that prevents agglomeration when the particles are in aqueous solution. A drawing of such a particle is shown in Fig. 1.1 where the particle radius and shell thickness are to scale. The ferrofluid that contains the nanoparticles has a particle concentration of 2% by volume [15]. To study the nanoparticles, the ferrofluid is evaporated on glass slides leaving the particles behind to be peeled off with tape.

Figure 1.1. Cut-away drawing of a coated particle with shell thickness one-fifth of the particle radius.
For a particle of 10nm diameter, a 1nm shell results in an overall physical diameter of 12nm and reduces the overall magnetic volume of the particle to ~58%. Spherical objects such as these also leave empty space between them when assembled, which is quantified by a packing fraction. These facts, along with water molecules trapped during the drying process, reduce the overall magnetic content of the sample. This has to be accounted for in the results analysis.

The intent of this work is to study the ultrafast time-domain response of magnetic nanoparticles to a step change in their local magnetic field. As will be described in Chapter 2, it is expected that this response will result in exponentially damped precession of the magnetization. In particular, the following problems will be addressed:

1) To determine if collections of magnetic nanoparticles undergo the precession dynamics predicted by the Landau-Lifshitz (LL) theory and if these time-domain dynamics can be measured by a magnetic inductive technique to be described.

2) To fit the time domain data to a damped sinusoidal solution of the LL equation.

3) To calculate the frequency-domain response by employing a Fast Fourier Transform to the time-domain data.

4) To understand the progression of the frequency as a function of applied magnetic bias field.

5) To estimate the phenomenological damping parameter $\lambda$ of the magnetite particles as a function of applied field and the spectroscopic splitting factor $g$, of the particles.
Chapter 2

Review of Magnetism

Before discussing the experiment, a brief review of some basic but pertinent topics in magnetics is in order.

2.1 Magnetic dipole moments

Broadly speaking, magnetic dipole moments can be put into two classifications; those arising from electron orbital motion and those from electron spin. Both of these vector quantities are summed to give the total magnetic moment. The following discussion is for an ideal system of an orbiting electron with spin, without consideration of the coupling between the two types of moments, moments due to nuclei, nor other considerations stemming from complex interaction of multiple particles.

2.2 Orbital moments

According to Ampere’s Law, an electric current is accompanied by a magnetic field that curls around the instantaneous displacement vector of the current path according to the right-hand rule. A circular current path flowing in a plane thus gives rise to a magnetic moment [16]

\[ \mathbf{m} = I\mathbf{A} \]

(1)

where \( I \) is the current and \( \mathbf{A} \) is the vector area which is normal to the plane of the current loop and whose magnitude is numerically equal to the area of the loop. The
magnetic moment carries units of $Am^2$. This magnetic dipole moment experiences a torque when placed in an external magnetic field, $\vec{B}$, given by [17]

$$\vec{\tau} = \vec{m} \times \vec{B}$$

(2)

The magnitude of this torque is thus given by $mB\sin(\theta)$.

![Figure 2.1. The magnetic dipole moment, $\vec{m}$, associated with the electric current, $I$, at an angle $\theta$, in an external $\vec{B}$ field.](image)

Consider a single electron circulating in an atomic orbital, with speed $v$. The time required for one full revolution is given by $t = 2\pi r/v$. The electrical current in this simple model is then $I = -q/t = -qv/2\pi r$ where $-q$ is the charge of the electron.

Substituting this expression for $I$ into the equation for the magnetic moment yields

$$\vec{m} = -\frac{1}{2} q \vec{\tau} \times \vec{v}$$. Classical mechanics dictates that the angular momentum of a particle of mass $m$, traveling at speed $v$, orbiting a point at a distance $r$, has an angular momentum given by $\vec{L} = m\vec{r} \times \vec{v}$. It can be seen from this form that the magnetic
moment can be expressed as a function of the orbital angular momentum of the single electron [16] \( \mathbf{\alpha} = -\frac{q}{2m} \mathbf{l} \). The constant of proportionality in this equation, typically represented by \( \gamma \), is known as the gyromagnetic ratio of this system and carries units of Hz/T:

\[
\mathbf{\alpha} = \gamma \mathbf{l} ~ \tag{3}
\]

It is the ratio of the magnetic moment to the angular momentum and is different for different systems. The gyromagnetic ratio is negative for an orbiting electron owing to its negative charge, thus the magnetic moment \( \mathbf{\alpha} \) and the angular momentum, \( \mathbf{l} \) point in opposite directions. A unit in magnetism that can be related to \( \gamma \) is called the Bohr magneton [17, Ch. 3, p. 64]

\[
\mu_B = \frac{q \hbar}{2m_e} = \gamma \hbar ~ \tag{4}
\]

where \( m_e \) is the electron mass and \( \hbar \) is the reduced Planck constant. The \( g \)-factor of a magnetic material is defined as the ratio of the magnitude of the magnetic moment in units of \( \mu_B \) to the magnitude of the angular momentum in terms of \( \hbar \) [17, Ch. 3, p. 65]:

\[
\left| \mathbf{m} \right| / \mu_B = \left| \mathbf{l} \right| / \hbar = g ~ \tag{5}
\]

By substituting the above expressions into this equation it can be seen that \( g = 1 \) for orbital magnetic moments. This is not the case for spin-induced moments or composite magnetic solids in general. With corrections stemming from the theory of quantum electrodynamics [18], the \( g \)-factor for an electron’s spin moment is somewhat larger than 2, \( g \simeq 2.0023 \). The preceding equations can be combined to obtain a rather useful form of the gyromagnetic ratio
\[ \gamma = \frac{g\mu_B}{\hbar} \]  

In most materials the magnetic moments are absent due to compensation by paired electrons. In some of the so-called transition metals this is not the case [19]. The magnetization, \( \mathbf{M} \), of a spherical magnetic nanoparticle is the ratio of volume density of the moments and the volume: \( \mathbf{M} = I\mathbf{A}/V \) and thus has units of amperes per meter [20]. It is the dynamics of the magnetization that will be measured and characterized in the present experiment.

2.3 Spin moments

Electrons also have angular momentum, and hence magnetic moments, due to their quantum spin. Spin is an intrinsic quantum mechanical quantity with no real classical analogue. Unlike classical angular momentum, the quantum counterpart does not involve physical rotation and cannot change its magnitude. The spin angular momentum of the electron measured along any axis is quantized and is given by [19] \( \mathbf{s} = \pm \frac{1}{2}\hbar \). It turns out that magnetic moments associated with spin are not half, but approximately one Bohr magneton [17, Ch. 3, p. 65]. The magnetic moment along a given axis in this case is given by \( \mathbf{m} = \frac{q}{m_e} \mathbf{s} \). Given that \( \mathbf{s} \) is the angular momentum, Eq. (3) gives the gyromagnetic ratio for spin moments as \( \gamma \approx \frac{q}{m_e} \approx 28 \frac{\text{GHz}}{T} \) where the approximation \( g = 2 \) has been employed.

2.4 Magnetic precession

The equations in the preceding section for the torque on a magnetic dipole can be combined to reveal the equation of motion for the magnetization, \( \mathbf{M} \) (volume density
of the moments), in an external magnetic field. Newton’s Law for rotational motion equates torque to the time derivative of angular momentum

$$ \vec{\tau} = \frac{d\vec{L}}{dt} \tag{7} $$

Differentiating the relation $\vec{m} = \gamma \vec{L}$ with respect to time gives

$$ \frac{d\vec{m}}{dt} = \gamma \frac{d\vec{L}}{dt} \tag{8} $$

Thus according to Eq. (7), the right hand side of Eq. (8) is a scaled torque. Substituting the torque relation $\vec{\tau} = \vec{m} \times \vec{B}$ into Eq. (8) and dividing by the volume to obtain the magnetization yields

$$ \frac{d\vec{M}}{dt} = \gamma \vec{M} \times \vec{B} = \gamma \mu_0 \vec{M} \times \vec{H} \tag{9} $$

where the constitutive relationship $\vec{B} = \mu_0 \vec{H}$ has been employed. Equation (9) says that the instantaneous rate of change of the magnetization vector in an external magnetic field points along the direction perpendicular to the plane defined by both vectors. The resultant motion is thus a circle in the counterclockwise direction when viewed from above. This direction is opposite to the typical cross product direction, owing to the negative value of $\gamma$ for electrons. Note that Eq. (9) is for a single spin, or a collection of spins acting in concert. This is referred to as the macrospin approximation, and allows one to use the value $\mu_0$ for the permeability, which corresponds to the immediate external environment to a single crystal, not to the local magnetic environment of its internal atomic moments, which would require $\mu_r \mu_0 = \mu$. Figure 2.2 shows the directional relationship.
2.5 Landau-Lifshitz theory

In the foregoing discussion it was shown that the magnetization vector of a collection of moments precesses about the external magnetic field. This motion is indefinite as long as there is no way for the system to dissipate energy. In reality, the moments will lose energy to the surrounding medium and eventually come to rest aligned with the external field. The equation of motion (in this case the orientation) of the magnetization vector in an external magnetic field is given by the Landau-Lifshitz equation [17, Ch. 9, p. 316]

$$\frac{d\overrightarrow{m}}{dt} = -\frac{\gamma}{1 + \alpha^2} \mu_0 \overrightarrow{m} \times [\overrightarrow{H} + \alpha (\overrightarrow{m} \times \overrightarrow{H})]$$

(10)

where $\gamma$ is the gyromagnetic ratio, $\mu_0$ is the magnetic permeability of free space, $\alpha$ is the dimensionless damping factor, $\overrightarrow{H}$ is the external effective magnetic field vector, and $\overrightarrow{m}$
is the magnetization unit vector $\vec{M}/M_s$ where $M_s$ is the magnitude of the saturation magnetization. Saturation magnetization is the inherent magnetic field of magnetic materials, given in units of $A/m$. As will be investigated in this experiment the saturation magnetization of magnetic nanoparticles is not as simple a matter as it is for bulk materials and is a discussion of continuing debate [21], [22]. The time derivative of the magnetization vector as described by the Landau-Lifshitz equation is the resultant sum of the two (scaled) vectors shown in Fig. 1 in red and blue.

![Image of magnetization vectors](image)

Figure 2.3. Landau-Lifshitz theory of damped motion of the magnetization, $\vec{m}$ in an effective external magnetic field, $\vec{H}$ (vectors not to scale). The resultant motion is traced out by the spiral. Both actual vector quantities are scaled by a factor of $\frac{\gamma \mu_0}{1+\alpha^2}$ not depicted here for clarity.

The $-m \times H$ term gives rise to the previously discussed circular motion of the magnetization known as Larmor precession. The second term $-a m \times m \times H$, points inward toward the effective $H$ field and is scaled by the dimensionless damping
parameter, $\alpha$. The larger this constant, the faster the precession is damped, resulting in alignment of the magnetization and the external magnetic field. The resultant trajectory of the magnetization vector is thus a decaying spiral. This time-varying magnetic field will induce an electric field in accordance with Faraday’s Law. The voltage from this electric field is proportional to the damped magnetic precession. The details of the measurement are covered in Chapter 3.

The origin of the phenomenological damping has been the subject of some debate [23]-[25]. The current models of the damping mechanism can be broken down into two broad categories: spatial and temporal. In the spatial treatment, the energy loss can be modeled using scattering theory [24]. The concept of a breathing Fermi surface is introduced wherein the precessing magnetization causes spin-orbit interactions which change the energy of electron states near the Fermi surface. This causes some states to go above the Fermi level of the material while some fall below it [23]. This creates electron-hole pairs near the Fermi level, which are dissipated via lattice scattering. The damping is a function of temperature, however it is not monotonic in nature. There is a material-dependent minimum at a given temperature and an increase at low and high temperatures. In [23] these two phenomena are referred to as resistivity-like and conduction-like damping, owing to their similarity with resistance and conductance at extreme temperatures. The Fermi surface accounts for the conductivity-like damping (low temperature) but not the high temperature resistivity-like term. It is shown in [23] that a torque-correlation model can include both the breathing Fermi surface as well as the resistivity-like damping mechanism.
The temporal aspect of damping is outlined in [25] and is shown to be the result of time retardation. The model described is considered outside of a thermal bath, that is to say the component of temporal damping does not dissipate energy to the same reservoir as thermal damping. This model was done computationally and compares the damping parameter and the so-called correlation time, which is a measure of how long the magnetic moment is aware of its past trajectory. Thus the retarded damping at time \( t \) is caused by previous orientations of the magnetization vector at an earlier time \( t' \) [25].

2.6 Superparamagnetism

When magnetic particles have a radius below \( R \sim 10 \) nm they are single-domain and exhibit a property called superparamagnetism [17, Ch. 8, p. 267]. Its name is adapted from the concept of paramagnetism. Paramagnetic metals develop a magnetic moment only in the present of an external field. It is similar to the electric dipoles in dielectrics, which become polarized in the presence of an electric field but do not retain the polarization field once the external field is removed. Superparamagnetism (SP) has a similar effect as paramagnetism but is caused by a different mechanism. The magnetization is thermally randomized and hence does not remain after the external field is removed. Néel postulated the spin moment flipped directions according to a relaxation function [26]

\[
\tau = \tau_0 e^{K_u V / k_B T}
\]  

(11)

where \( K_u V \) is an energy term due to anisotropy, \( k_B \) is Boltzmann’s constant, \( T \) is absolute temperature, and \( \tau_0 \) is the attempt time. The exponent of the quantity \( e^{K_u / k_B T} \) is the ratio of the energy required to flip the magnetization and the average
thermal energy of the system. It quantifies if the particle has the thermal energy to overcome the potential energy barrier keeping the magnetization aligned in the crystal and allows it to flip directions. The quantity $\tau_0^{-1}$ is called the attempt frequency and is on the order of 1GHz. It is a measure of how often the particle “tries” to change orientation. Note whether a particle is in the SP regime is a function of temperature as well as time. If a measurement is made quickly enough for a given particle, it will not have had time to flip and will be normally magnetic. Below the blocking temperature $T_B$, the particle is again normally magnetic. The relaxation times for various particle radii and temperatures range from fractions of a second to billions of years [17, Ch. 8, p. 296]. A more general form of Eq. (11) is given in Section 7.5.

When a SP sample is placed in an external bias field parallel to the easy direction of magnetization, as they are in this work, the magnetization becomes a function of $H$ and is approximated by Langevin function [27]

$$M(H) \approx n m \left[ \coth \left( \frac{\mu_0 H m}{k_B T} \right) - \frac{k_B T}{\mu_0 H m} \right]$$  \hspace{1cm} (12)

where $n$ is the number density of particles in the sample and $m$ is the magnetic moment of a particle. The number density in this case includes the packing fraction of the particles as well as the ~1nm hydrophobic coating on each particle. Equation (12) is plotted in Fig. 2.4 with initially expected values from the experiment. This dependency on $H$ means the magnetization is less random and spends more time aligned with the field. This is due to the bias field making it less probable that the magnetization will have the energy to overcome the energy barrier that keeps it aligned along an easy direction. The particles used in this experiment are SP in their ferrofluid state according
to the manufacturer [15], however it has been shown that large groups of strongly interacting particles can affect this outcome as the macroscopic structure can take on the behavior of a bulk material, which is in general not fully SP [28]. As the particles in this work are out of the fluid suspension and in direct contact with many neighbors a so-called mixed-state of ferrimagnetism and superparamagnetism may be possible [28]-[31].

![Langevin Function](image)

**Figure 2.4.** Plot of the Langevin function. The x-axis denotes an external magnetization in A/m. The y-axis is the normalized saturation magnetization. A unity value denotes the SP particle is saturated and the magnetization $M_0$ takes on the value of $M_s$ found in the corresponding bulk material.

2.7 Demagnetization and the Kittel Equation for Ferromagnetic Resonance

To describe the magnetic field inside a uniformly magnetized body, the constitutive relationship $\mathbf{B} = \mu_0 \mathbf{H}$ is extended to include the magnetization [17, Ch. 2, p. 35], $\mathbf{M}$

$$\mathbf{B} = \mu(\mathbf{H} + \mathbf{M}) \quad (13)$$
In this magnetized body $\vec{B}$, $\vec{H}$, and $\vec{M}$ have different directional dependencies that obey certain boundary conditions. Figure 2.5 shows the relationships of the three quantities whose components sum at each point in the magnet according to Eq. (13).

![Figure 2.5. $\vec{B}$, $\vec{H}$, and $\vec{M}$ for the interior and exterior of a uniformly magnetized body. The vector sum of $\vec{H}$ and $\vec{M}$ at every point are given by $\vec{B}$. Note that $\vec{H}$ points opposite to the other two within the body but is parallel to $\vec{B}$ outside. This is the source of demagnetization within the magnet.](image)

The direction of the $H$ field within the magnetized body is due to the phenomenon of *demagnetization*, and is hence called the demagnetizing field, $\vec{H}_d$. Since this field is due to the magnetization, it is expressed as a scaled $M$ field [32]

$$H_{di} = -N_i M_i$$  \hspace{1cm} (14)

where $N_i$ is the so-called demagnetizing factor along the $i^{th}$ axis. Since this applies to 3-dimensional vectors, Eq. (14) is usually expressed in terms of a demagnetizing tensor [32]
\[
\vec{H}_d = -\begin{bmatrix} N_x & 0 & 0 \\ 0 & N_y & 0 \\ 0 & 0 & N_z \end{bmatrix} M.
\]

(15)

The tensor is assumed to be diagonal; meaning the magnetization along one axis cannot cause demagnetization along another axis. Another requirement of the tensor is that its trace is unity [32],

\[ N_x + N_y + N_z = 1. \]

(16)

The exact shape of the demagnetizing field depends on the shape of the magnet and is quite complicated for most arbitrary shapes. A few ideal shapes, however, can be solved analytically and are well known.

When a magnetic bias field is applied along an axis, the magnetization will precess about it according to Eq. (10). For convenience, let us assume the bias field is along the z-axis. In this case the magnetic precession is given by

\[ \vec{M} \approx M_s \hat{a}_z + \vec{m}(t) \]

(17)

where \( M_s \) is the saturation magnetization and \( \vec{m}(t) \) is the part of the magnetization that rotates in time according to Eq. (10). This component, which in this case rotates in the x-y plane, is assumed to be small compared to \( M_s \). This yields the field components [32]

\[ H_x^1 = H_x - N_x M_x ; H_y^1 = -N_y M_y ; H_z^1 = H_z - N_z M_z. \]

(18)

This can be shown to lead to the general Kittel equation for the resonant frequency [32]

\[ \omega_0^2 = \mu_0^2 y^2 \left[ H_0' + (N_x - N_z)M(H) \right] \left[ H_0' + (N_y - N_z)M(H) \right] \]

(19)

where \( H_0' \) includes all anisotropic fields and the relationship \( M_z \rightarrow M(H) \) has been employed to reflect the superparamagnetic nature of the particular experiment.
In the case of perfect spheres [17, Ch. 9, p. 314], $\mathcal{N}_x = \mathcal{N}_y = \mathcal{N}_z = \frac{1}{3}$. For these demagnetizing factors, the Kittel equation reduces to a linear relationship

$$\omega_0 = \mu_0 \gamma H'_0$$

(20)

Note that for *perfect* spheres the precession frequency is due only to the contribution of $H'_0$, which is the total field exterior to the sphere, and not influenced by the magnetization. For thin films with an in-plane bias field [17, Ch. 9, p. 314], $\mathcal{N}_x = 1$, which according to Eq. (16) leaves the other two equal to zero and the resonance equation as $\omega_0 = \mu_0 \gamma \sqrt{H'_0(H'_0 + M_s)}$. 


Chapter 3

Inductive Technique Overview

This experiment will measure the time-domain response of a collection of magnetic nanoparticles as they precess in a magnetic field. This field is the vector sum of an external bias field, a dynamic field from a step current, and the magnetic fields from the surrounding particles in the sample. It is carried out by an inductive technique, the current state of which was developed by [14]. In what follows, a broad, descriptive overview of the inductive technique is given. In Chapter 4 the specifics of the equipment are given and in Chapter 5 each step of the experiment is covered in full detail.

3.1 Inductive technique

The inductive measurement technique is a method to directly measure the time-domain rotation of magnetization for a collection of magnetic moments as they undergo the damped precession described by the Landau-Lifshitz equation, depicted in Fig. 2.3. The technique is relatively inexpensive to implement and is best suited for magnetic samples with flat geometries.

Time-changing magnetic fields are accompanied by electric fields that are defined by Faraday’s Law of induction.
\[
- \frac{\partial \vec{B}}{\partial t} = \nabla \times \vec{E}
\]  

The magnetic moments, and the associated magnetic flux, \( \vec{B} \), of the nanoparticles have a non-zero time derivative when they precess, inducing an electric field. It is the voltage due to this induced electric field that is measured by the inductive technique. The voltage is induced onto a coplanar waveguide (CPW) and measured by a high-bandwidth sampling oscilloscope. A CPW consists of a center conductor trace flanked on both sides by ground planes. The descriptor “coplanar” derives from the fact that the trace and ground planes are on the same plane of the dielectric substrate.

Figure 3.1. Model of a coplanar waveguide (CPW). The signal trace is located in the center of the two ground planes. Axes conventions shown on left.

The flat magnetic sample is placed directly on top of the copper signal trace of the waveguide. Depending on the sample size, it may bridge the signal trace and ground planes. A natural oxidation layer on the copper as well as a nonconductive layer on the nanoparticles prevents this from shorting the signal trace to ground. An external magnetic bias field is oriented along the \( x \)-axis (see Fig. 3.1 for axes conventions). A
signal generator using a remote pulse head (RPH) supplies a -5V step to the signal trace, with a fall time of ~80ps. The characteristic current of this voltage step has an associated magnetic field according to Ampere’s Law. At the upper surface of the CPW, the y-directed transverse magnetic field from the current combines with the x-directed longitudinal bias field to create a resultant magnetic field that is in the x-y plane at a small angle away from the x-axis, as shown in Fig. 3.2.

Figure 3.2. Resultant vector of the pulse and bias fields. The resultant vector (red) is in the x-y plane at an angle away from the initial x orientation of the magnetization. The angle away from the x-axis is exaggerated for clarity.

The bias fields in Fig. 3.2 include any fields intrinsic to the sample itself. The magnetization of the sample then undergoes the damped precession depicted in Fig. 2.3 as it aligns in the new field configuration. The magnetization of the sample is oriented along the new field long enough for all magnetic precession to decay to zero. The red arrow in Fig. 3.3 shows the path traced out by the magnetization. The geometry of this technique is such that for thin films, where $\mathcal{N}_x = 1$, oscillations in the y-direction are
detected; the projection of the red arrow onto the signal trace is what is detected by the oscilloscope [14]. It is not immediately apparent for particles, whose demagnetizing factors along the coordinate axes are different than those of a continuous film, if a $z$-component of precession is present or how it would change the results. The equation for the measured voltage of a film is given in the next section. The voltage signal for this technique may be understood by considering the theorem of reciprocity. Here this means that if a unit current in a conductor creates a specific magnetic field that threads the conductor, then if an identical magnetic field is made to thread that conductor, it must generate a unit current [33]. Thus the inductive technique works similarly to magnetic read heads. The changing magnetic fields represent a magnetic storage medium moving relative to the read head, which is represented by the signal trace of the waveguide [14], [33]. The dynamical fields induce voltages that are thus representative of the fields.

Figure 3.3. Induction in the CPW. A magnetization vector (blue) precesses about the $x$-axis traces a path (red) which threads the signal trace of the CPW.
Due to the small angle of precession, the induced signal is in the mV range, making it difficult to distinguish from the 5V step signal. To mitigate this problem and obtain useable data, subtractive analysis is employed. To achieve this, the sampling oscilloscope must first measure the voltage step signal without any magnetic precession. This waveform is extracted from the oscilloscope along with the waveform containing precession and the two are point-wise subtracted, leaving only the precession component. One obvious way to accomplish this would be to take the measurement of the step signal before placing the magnetic sample onto the waveguide. Though simple, this method would not work. Since placing magnetic material on the traces alters the inductance and capacitance of the waveguide in unpredictable ways, step signal measurements cannot be done on the waveguide alone with the sample added later. The change in the characteristics of the waveguide would make the signals from each stage of the measurement fundamentally different. The subtraction method would then be comparing signals sent down two effectively different waveguides, corrupting the comparison. To get the correct waveform, the magnetic sample is placed on the waveguide and the external magnetic field is configured to a $y$-directed saturation field. The saturation field strongly aligns the magnetization along $y$, effectively pinning it along that direction, ensuring no magnetic precession takes place in the presence of the $y$-directed step field. That is, the step field does not change the direction of the total field hence no magnetic excitations are produced. The subtractive comparison step removes all components of the signal
common to both scenarios, leaving only the induced voltage signal from the magnetic precession.

3.2 Expected Signal

According to [34] the voltage signal induced onto a CPW for a thin film can be derived from the Landau-Lifshitz (LL) equation given in Eq. (9). Silva et al. derived a similar equation [14] in SI units and their approach will be given here. The LL equation can be expressed in terms of the torque equation:

\[ \frac{d\mathbf{M}}{dt} = -\gamma|\mathbf{T}| - \frac{\lambda}{\mu_0 M_s} (\mathbf{M} \times \mathbf{T}) \]  \hspace{1cm} (22)

In spherical coordinates this torque is given by

\[ \mathbf{T} = \frac{1}{\sin(\theta)} \frac{\partial U}{\partial \phi} \hat{\theta} - \frac{\partial U}{\partial \theta} \hat{\phi} \]  \hspace{1cm} (23)

where \( U(\phi, \theta) \) is the free energy density of the system. Smith showed that under the approximations of a soft ferromagnet \( M_s \gg H_k \), and underdamped oscillator \( \lambda \ll \gamma 4\pi M_s \) are made, LL can be reduced to [34]

\[ \frac{\partial^2 \phi}{\partial t^2} + \lambda \frac{\partial \phi}{\partial t} + \mu_0 \gamma^2 U \frac{\partial U}{\partial \phi} = 0 \]  \hspace{1cm} (24)

In this experiment a step field is applied as in [14]. For a small displacement angle \( \phi \), the energy term in Eq. (24), \( \frac{\partial U}{\partial \phi} \), can be expanded in a Taylor series and the approximation becomes [14]

\[ \frac{\partial^2 \phi}{\partial t^2} + \lambda \frac{\partial \phi}{\partial t} + \mu_0 \gamma^2 \left( \frac{\partial U}{\partial \phi} \right)_0 \left[ \phi - \phi_0 u(t) \right] = 0 \]  \hspace{1cm} (25)
where \( u(t) \) is the Heaviside step function. Initially the magnetization has not rotated and so the initial conditions are \( \phi = \phi' = 0 \). Applying a Laplace transform yields

\[
s^2 \Phi + \lambda s \Phi + \omega_0^2 \Phi = \frac{\omega_0^2 \phi_0}{s}
\]

(26)

where the substitution \( \omega_0^2 = \mu_0 \gamma^2 \left( \frac{\partial^2 u}{\partial \phi^2} \right)_0 \) is made. Solving for \( \Phi \),

\[
\Phi \approx \phi_0 \left[ \frac{1}{s} - \frac{s + \lambda/2}{(s + \lambda/2)^2 + \omega_p^2} - \left( \frac{\lambda}{2 \omega_p} \right) \frac{\omega_p}{(s + \lambda/2)^2 + \omega_p^2} \right]
\]

(27)

where \( \omega_p^2 = \omega_0^2 - (\lambda/2)^2 \). Solving with the inverse Laplace transform gives [11]

\[
\phi(t) = \phi_0 \left[ 1 - e^{-t/\tau} \left( \cos(\omega_p t) - \left( \frac{1}{\tau \omega_p} \right) \sin(\omega_p t) \right) \right] u(t)
\]

(28)

where \( \tau = 2/\lambda \).

Thus it is seen that the position function of the magnetization is an exponentially damped sinusoid under a step change in magnetic field, as found by Silva et al. In their work they further simplify Eq. (28) to the form

\[
\phi(t) = \beta_0 \sin(\omega_p t + \phi) e^{-t/\tau}
\]

(29)

where \( \phi(t) \) is the in-plane angle of magnetization and \( \beta_0, \tau = 2/\lambda \), and \( \phi \) are fitted parameters. In this work a sinusoidal function is assumed to govern the motion (e.g. time derivative of Eq. (29)) of the magnetization of the particles, therefore a similar function will govern the magnetic flux from this motion. The exact equation used for the present model is given in Chapter 7.

Ampere’s law can be used to show the magnetic field due to a step voltage, \( V \), sent down a trace of width \( w \) and impedance \( Z_0 \) is given by
\[ H = \frac{V}{2Z_0 w}. \]  

(30)

As will be discussed in Chapter 4, the step voltage is 5V, which yields only a 50A/m magnitude of the step field. In most cases, this is 2 orders of magnitude below the bias field strength, meaning the final resting orientation angle of the magnetization is negligible, as well as the step field’s contribution to the net magnetic field.

As for the expected magnitude of the inductive signal from a film, it can be shown that the voltage for a magnetic film on a coplanar waveguide with length \( l \), width \( w \), and impedance \( Z_0 \) excited by a step pulse is given by [14]

\[
V_p = \left( \frac{\mu_0 l \delta f(z,w)}{4} \right) \left( \frac{Z_0}{Z_0 + \frac{1}{2} R_{DC}} \right) \frac{d\overline{M_y}}{dt}
\]  

(31)

where \( V_p \) is the step voltage, \( R_{DC} \) is the resistance of the center trace, \( f(z,w) \) is a spatial loss function due to a nonzero spacing of the film from the waveguide, and \( \overline{M_y} \) is the average magnetization along the y direction. According to Silva et al. the magnetization is assumed uniform across the length and thickness of the sample in Eq. (31) as well as primarily in-plane magnetic precession due to the demagnetization tensor of films.

Unfortunately, for a collection of discrete particles the above assumptions cannot be made. There are many voids between the particles due to the coating and packing fraction, which likely has arbitrary spatial variations. The magnetization profile is further complicated by the superparamagnetic nature of the particles and interparticle interactions. The demagnetization factor for a continuous magnetic medium like a film cannot be assumed to apply to a collection of particles either. Being
single crystal magnetic particles however, the measured inductive voltages are still expected to evolve as exponentially damped sinusoids proportional to the time derivative of the magnetization, albeit with magnitudes that are difficult to predict \textit{ab initio}.
Chapter 4

Equipment Overview

In what follows, descriptions and images of the equipment used in the experiment are given.

4.1 Signal Generator

The step signal used in this experiment is generated from a Remote Pulse Head (RPH), which is excited by a repetitive pulse generator (PG). Both units are manufactured by Picosecond Pulse Labs, Inc. The step voltage signal goes from 0V to -5V, with a 10%-90% fall time of 12ps. Due to additional cabling required to perform the experiment, the fall time is increased to ~80ps, which is sufficient for the present purposes.

![Remote Pulse Head (RPH)](image)

Figure 4.1. Remote Pulse Head (RPH). This is used to generate the step voltage in the CPW.
4.2 Sampling Oscilloscope

The sampling oscilloscope is an Agilent Infiniium DCA-J 86100C Digital Communications Analyzer. It has a 50Ω input impedance and a 50GHz bandwidth. The device runs Windows XP and can save data files from temporary memory on an internal hard drive or external USB thumb drive. The sampling rate can be customized as well as the number of averages per data point. Taking many samples of the signal reduces the signal to noise ratio (SNR) of the reading and the average of each point is reported by the analyzer as a single reading. The sampling rate is adjusted simply by setting the total number of data points to be collected over the specified time window. This experiment uses 255 averaged readings, 2700 data points, and a time window of 4ns.

Figure 4.2. Sampling oscilloscope capture of the negative step signal from the RPH.
4.3 Coplanar Waveguide

The magnetic nanoparticle samples are placed onto a 50Ω coplanar waveguide (CPW) during the experiment. The CPW is required to produce the rapid change in the local magnetic field of the sample as well as pick up the voltage induced by the magnetic precession and relay it to the sampling oscilloscope. The CPW has a center conductor width of 1mm and uses standard SMA connectors. The coaxial cables used in this work have a 26.5GHz bandwidth and are manufactured by Insulated Cable Incorporated [35].

![Image of 50Ω Coplanar Waveguide (CPW). The nanoparticle samples are placed on the center trace during the experiment.](image)

Figure 4.3. 50Ω Coplanar Waveguide (CPW). The nanoparticle samples are placed on the center trace during the experiment.

4.4 Electromagnets

The external bias field in the experiment comes from four electromagnets. The magnets are arranged in pairs that are diagonally positioned relative to one another. Bars of soft iron connect the cores of each pair at the bottom and the windings are electrically connected in such a way that flux enters one pole piece and exits the pole
piece diagonally across from it. That is, with the exception of stray leakage, all of the flux is guided across the air gap centered on the CPW.

Figure 4.4. Bias field electromagnets. The electromagnets comprise four solenoids through which DC current is passed.

Guiding the flux toward the waveguide is important, as is ensuring it is properly focused. To achieve this, special pole pieces were machined with wide flat tips. The flux passes out of these tips and is largely confined to a thin plane above the waveguide. This geometry makes the most out of the available flux and helps minimize any component of the field that would be normal to the surface of the CPW. Figure 4.5 shows the layout of the CPW along the shape of the pole pieces.
The narrow face of the pole pieces concentrates the magnetic flux near the surface of the waveguide.

The experiment requires that the field be in the $x$-$y$ plane only, and that it be directed along $y$ while acquiring the zeroing waveform, and then along $x$ for the precession waveforms. To achieve this, the magnitude of the current in the magnets is controlled electronically and is identical for both pairs, and only the current direction through one of the pairs is changed.

![Electromagnet flux](image)

Figure 4.6 Electromagnet flux. Red and black arrows show the direction of magnetic flux from each pole piece. The black arrows are in a constant direction and the red arrows change direction to rotate the net field (blue arrow) by 90°.
A precise value of the external bias field is important to properly interpret the results of the experiment. The magnets’ field was measured using a magnetometer, the results of which are shown in Fig. 4.7.

![Magnetic Bias Field H_b](image)

**Figure 4.7.** Magnetic field intensity of the electromagnets.

### 4.5 Magnet Power Supplies

The power supplies used to supply current to each pair of magnets are Bipolar Operational Power Supplies (BOP) from Kepco, Inc. They are programmable and can operate in current or voltage control mode. Since the current is controlled with knobs and the output an analog needle, a better method of controlling the precise current is required. The method used in this work is to connect a digital voltage source in parallel to both of the programming ports on each BOP. A 1:1 relationship is then established between input voltage and output current of the power supply. Stepping through
precise voltages is possible on the digital voltage supply, which is otherwise less precise on each analog control of the BOP. This method also ensures the current magnitudes are identical since one voltage supply controls both current sources simultaneously.

4.6 Magnetometer

To accurately measure the magnetic bias field, a digital magnetometer is clamped with a retort stand and positioned at the center of the poles of the electromagnets. The supply current is then stepped through the values to be used in the experiment and the value recorded. The measurement is carried out five times and the mean taken as the actual value. The setup is shown in Fig. 4.7.

Figure 4.7 Magnetometer positioning. The magnetometer wand clamped to the retort stand for positioning (left). The position of the sensor inside the wand is shown by the green dot (right).
Chapter 5

Experiment

5.1 Experiment Block Diagram

Below is a block diagram of the experimental setup. Electromagnets A1 and B1 are flux coupled to A2 and B2, respectively, beneath the CPW. This causes the flux lines to cross the nanoparticle sample located at the mutual center of the pole pieces. The direction of the current in one of the magnets will determine if the resultant bias field is $x$- or $y$-directed. Precise details are provided in Chapter 4.

![Block diagram of experimental setup. Not pictured is the digital voltage source to precisely control the current amplitude and polarity for both electromagnet power supplies.](image)
The pulse generator (PG) sends a signal to the Remote Pulse Head (RPH) that triggers the 5ns, -5V step signal. This is sent down the coplanar waveguide (CPW) and carries with it a $y$-directed magnetic field per Ampere’s Law. The center conductor of the CPW is 1mm wide.

5.2 Nanoparticle Sample Preparation

The nanoparticles used in this experiment are 10nm diameter with a 1nm nonmagnetic, hydrophobic coating. The samples of nanoparticles are prepared by depositing 20$\mu$L of Ferrotec EMG 707 water-based ferrofluid onto glass slides with a pipette. The glass slides are pretreated with a very thin layer of hydrophobic coating which prevents the dried ferrofluid from sticking and causing the sample to be damaged or destroyed in the peeling process. To ensure the coating on the glass did not affect the samples in a measureable way, samples dried on non-treated glass were also tested with the same experimental results to those peeled from treated glass. The only difference in the two cases is that total sample transfer is possible with the treated glass. Only results from samples taken from treated glass are presented here.

To align the easy directions of the particles the liquid samples are placed in a 2.5kA/m field during the drying process. Half of the samples are not dried in a magnetic field to compare the effect of field versus non-field drying. Assuming the Brownian motion (e.g. physical rotation) of the particles ceases once dried, and that the field strength is enough sufficiently align the superparamagnetic moments, the crystal axes of the particles should remain fixed allowing the sample to retain a collective easy direction. This does not mean that the magnetization will always lie along this direction,
owing to the superparamagnetic state of the particles, but that once a spin aligns with the x-directed field it will not be at an angle to the easy axis.

The samples were prepared in two distinct geometries: circular disks of diameter ~1cm and thin strips of width ~1mm. This was done to compare the results and determine if any effects arise from having portions of the sample extend over the ground planes of the CPW and to see if any edge effects arise due to sharp, parallel edges. These two geometries are shown in place on the CPW in Fig. 5.2.

![Sample geometries](image)

Figure 5.2. Sample geometries. The two nanoparticle sample geometries considered in the experiment. The 1cm circular sample (top) and the 1mm wide strip (bottom).
5.3 Field application and Data Capture

In the experiment, the bias field is stepped through 24 values ranging from 0kA/m (0 A) to 45.6kA/m (2.3A). At each point the 255 averaged samples are taken of all 2700 data points and then the field is increased. Due to a ~0.5kA/m remanent field of the pole pieces after a typical run of the experiment, each zero bias field reading is taken with the CPW on the bench, far away from the electromagnets.

![Figure 5.3. The CPW positioned in the electromagnet. A circular nanoparticle sample can be seen in place. (Coaxial cables not pictured.)](image)

5.4 Signal Processing

The recorded data are processed and analyzed on a computer. The data files are exported from the oscilloscope and entered into a comprehensive MATLAB routine written specifically for the experiment. The first step of the algorithm performs the temporal alignment of each of the 24 precession signals with the transverse (zeroing)
waveform. This is required because over the length of the experiment the sampled waveforms arrive at slightly different times than the initial transverse waveform. This step is crucial to properly analyze the data; a simple point-wise subtraction of the raw data leads to a corrupted waveform, as shown in Fig. 5.4.

![Signal Comparison](image)

Figure 5.4. Signal comparison. Processed versus unprocessed precession data. Note the initial ~0.25V spike of the unprocessed (raw) signal due to a small temporal drift in the trigger signal. Another smaller spike is visible around t=1ns.

The source of the error in the raw data is due to temporal drift in the trigger signal from the pulse generator. Due to the rapid fall time of the negative step signal, a small drift in the arrival of the trigger can result in a relatively large voltage spike at the transition as seen in Fig. 5.4. Measuring the time for the step function to fall from 10% to 90% of the full -5V yields a fall time of

\[ t_f \approx 80\text{ps}. \]

If the signal is approximated to be linear in this region the slope is readily found to be
\[ \frac{dV}{dt} = -5 \times 10^{10} \frac{V}{s}. \]

Thus a trigger drift of only 5ps will lead to a 0.25V spike near the transition. This spike is seen in Fig. 5.4, resulting from the temporal drift shown in Fig. 5.5.

![Signal Coincidence Comparison](image)

Figure 5.5. Signal coincidence comparison. Temporal drift for raw data waveforms of the zeroing and precession signals. There is a maximum of \(~250\text{mV}\) difference around 0.16ns, giving rise to the spike of the same magnitude in Fig. 5-4. The correlation algorithm time shifts the precession signals to minimize the error for the region where \(V \geq 2.5V\).

To make the correct time shift to minimize this error the signals must be linearly interpolated over a small time window containing the transition from \(V = 0V\) to \(V \approx -2.5V\). The window of comparison must not go too far beyond \(-2.5V\) as this is near the point that significant magnetic precession begins and the signals are inherently different. The effective sampling frequency of this experiment is \(6.75 \times 10^{11} s^{-1}\). The interpolation algorithm divides each sampling interval into 1000 equal parts yielding an effective temporal discretization of
\[ t_{\text{eff}} \approx 1.48 \times 10^{-15} \text{s} \]

The two signals are point-wise subtracted and the absolute value of the differences are summed and stored in a temporary variable. The precession waveform is then time shifted by approximately 1.48fs and the procedure repeats. This process is iterated until the time shift with the smallest residual error is found. Depending on the direction of the temporal drift, the signals will need to be shifted to the left or right. To simplify the code, all raw precession signals are pre-shifted by a fixed number of samples to ensure time shifting is only required in one direction. Values of \( t_{\text{eff}} \) as small as \( 0.5 \times 10^{-15} \text{s} \) were tried with identical results, so the above value was used in the interest of computational efficiency. Once the time shift values are obtained for a given data set, they are stored permanently in the code significantly reducing the future execution time of the algorithm.

Once each optimal time shift value is found, each interpolated waveform is shifted and the difference between the transverse and precession waveforms is calculated. The resulting vectors are then “resampled” back to the original size. That is, every 1000\(^{\text{th}}\) data point is pulled out and mapped to a new vector, which is the corrected waveform. Keeping all of the data points from the interpolation makes the vectors too large for MATLAB to handle and introduces an artificially high sampling rate. It also causes errors in the subsequent stages of the signal-processing algorithm.

Once all waveforms are subtracted from the zeroing waveform, a Fast Fourier Transform (FFT) is performed on each one. One key point of interest in the experiment is to understand how the frequency of magnetic precession changes as a function of
applied bias field. Calculating an FFT over the range of all bias field values allows this
data to be fit to the general ferromagnetic resonance model in Eq. (19) using nonlinear
least-squares regression. The result is critical to understanding whether the particles
are acting collectively as a coherent structure (e.g. a film) or as individual spherical
particles. It also allows one to estimate a sample-wide demagnetization due to the
surrounding particles and the spectroscopic splitting factor $g$, discussed in Chapter 2.
Apart from the resonance behavior, another nonlinear least-squares regression model
fits the observed time-domain signals to damped sinusoids predicted by the Landau-
Lifshitz equation as a function of the applied field. Knowing how the damping behaves
in the time domain is another key point of interest of the experiment and the inductive
technique has the advantage of measuring this directly. Details of these fitting models
are covered in Chapter 7.
Chapter 6

Measurement Results

6.1 Time-Domain Induction Signals

Data collected from the sampling oscilloscope that has been corrected by the algorithm discussed in Chapter 5 is presented in this chapter. Data is presented for samples that were both dried in a magnetic field and dried in the absence of a field. This is done to examine the effect of field drying on the precession behavior. Data is also presented for circular shaped samples as well as samples cut into approximately 1mm wide strips and placed along the center conductor of the CPW. This was done to determine qualitatively if any unexplained effects are due to the geometry and what effects, if any, occur when portions of the magnetic sample are located above the ground planes of the CPW. Both geometries are shown in Fig. 5.2 (field drying does not alter the physical appearance of the samples). Time-domain data from each of these 4 cases is presented first, followed by FFT plots for the circular field-dried case. The spectrum for this case is typical of other geometries and is representative of their results. Plots of the frequency progression as a function of bias field for all cases is presented in Chapter 7. Finally, the measurement made on the vibrating sample magnetometer is presented. The analysis of these results is covered in Chapter 7.
6.2 Field-Dried Samples

Samples dried in a longitudinal bias field, parallel to the direction of the bias field in the experiment are presented in this section.

Figure 6.1. Time-domain plots for field-dried circular sample.

Figure 6.1 shows measured inductive signals for a field-dried circular sample. Damped sinusoidal waveforms for the sample magnetization are apparent. Figure 6.2 shows inductive signals for a field-dried strip sample.

Figure 6.2. Time-domain plots for field-dried strip sample.
6.3 Non-Field-Dried Samples

Signals from samples dried in the absence of any magnetic field are presented here.

Figure 6.3. Time-domain plots for non-field-dried circular sample.

Figure 6.4. Time-domain plots for non-field-dried strip sample.

6.4 Frequency-Domain Results

In what follows, FFT data are presented for circular field-dried samples. FFTs from all geometries have a similar profile, which features two distinct peaks. Owing to
their similar profiles, only a few actual FFT plots are presented. Chapter 7 contains the results for all geometries of plotted data points of the progression of frequencies as a function of bias field along with the fitted model of frequency progression.

Figure 6.5. FFT of circular field-dried sample at $H_b=0\text{kA/m}$. Two notable resonances are marked.

Figure 6.6. FFT of the circular field-dried sample at $H_b = 33.5\text{kA/m}$.
The results of Figs. 6.5 and 6.6 are typical for all sample preparations. With the exception of the exact values all samples contain two peaks centered approximately on 1.3 GHz and 3.5 GHz. As shown in Chapter 7, these values vary somewhat differently as the field is increased but are a feature of all samples tested. Figure 6.7 shows the difference between the initial and final values of $H_b$ for the circular field-dried sample.

![Graph showing FFT comparison](image)

Figure 6.7. FFT comparison of the circular field-dried sample. Curves represent the FFT at the beginning and end values of the applied bias field. The low frequency mode decreases in amplitude while the higher mode increases slightly.

6.5 Vibrating Sample Magnetometer Results

Given the superparamagnetic nature of the nanoparticles, the magnetization as a function of the applied field. Knowledge of the magnetization is critical to fit the data and interpret the results. A sample was put into the vibrating sampling magnetometer (VSM) to measure the sample moment, which given the volume of the sample, diameter of the particles, and the concentration of ferrofluid yields the magnetization. The VSM
steps through an external magnetic field and vibrates the sample at 30 Hz through a pair of pick up coils and measures the magnetic moment. The results are shown in Fig. 6.8.

Figure 6.8. VSM magnetization curve. Results from the VSM are the sample moment. These results are scaled to give the magnetization.

The magnetization curve appears closed. Figure 6.9 is taken from Fig. 6.8 around the point of zero applied field. It is seen that the sample moment, while much smaller than the maximum value, is actually nonzero under this condition and the curve is slightly open.
Figure 6.9. VSM non-zero crossing. Measurement zoomed in reveals an open loop with non-zero crossing and finite remanence. Using linear interpolation, the top trace crosses at $M(H) \approx 26.32\text{kA/m}$ and the lower at $M(H) \approx -55\text{kA/m}$.

The nonzero crossing of the magnetization is responsible for magnetic precession when $H_b = 0$. The origin of this nonzero value is explained in the next chapter.
Chapter 7
Analysis and Discussion

7.1 Time-Domain Precession Fitting

Incoherent magnetic precession is not predicted by the Landau-Lifshitz (LL) equation, which is a model of an ideal, underdamped, single crystal. The multiple frequencies (modes) present here reflect the complex nature of the magnetization dynamics within the sample and often appear in thin film work when this inductive technique is employed [14], [36]-[39]. These double frequency peaks shown in Figs. 6.5–6.7 are characteristic of all recorded signals and the prominence of both requires both be accounted for in the time-domain fit of the data. These non-idealities significantly increase the difficulty of accurately fitting the data to a simple model such as LL. Nevertheless, the data, though multimodal, do lend themselves to being described as damped sinusoids to a reasonable degree of accuracy. As discussed in Chapter 3, Eq. (31) is used by [14] to describe the inductive voltage due to the magnetization. In this treatment, two such damped waves will be summed to account for the prominence of the two spectral peaks. The equation used to fit the time-domain data is thus

\[ V(t) = V_1 \sin(\omega_p t + \phi_1) e^{-t/\tau_1} + V_2 \sin(\omega_p t + \phi_2) e^{-t/\tau_2} \]  

(32)

where \( V_1 \) and \( V_2 \) are the voltage amplitudes which in this case absorb the inductive voltage amplitude prefactor discussed in Section 3.2, \( \omega_p \) and \( \omega_p \) are the low and high
precession resonance frequencies respectively, and the time constants $\tau_1$ and $\tau_2$ represent the damping by [14]

$$\lambda_i = \frac{2}{\tau_i}$$  \hspace{1cm} (33)

The magnitude, phase offset, and time constant for each wave will be fitted as one waveform to account for both spectral peaks. The use of sine functions in Eq. (32) is possible without the loss of generality due to the phase offset.

As for the two observed frequencies, theoretical models exist for describing higher precession modes within individual nanoparticles, however the frequencies are much higher than those reported here [13]. This is due to the standing-wave nature of these modes that are functions of the dimensions of the sample. There are however, two possible causes of the presently observed spectrum. The first is the core/shell morphology of nanoparticles (see, e.g. [23]). This well-known phenomenon arises due to the asymmetry of the composite atoms in a sufficiently small nanoparticle. Deep within a spherical particle the atoms (spins) are surrounded by neighbors on all sides per the crystalline structure of matter. On the outside of the particle, the atoms on the surface have neighbors on one side (the core of the particle) but not on the other side, where the coating resides. This change in atomic environment is important at the nanoscale, where a large fraction of the constituent particles are subject to it. On the macroscale, the volumetric fraction of atoms far outweighs those on the outer surface and these considerations are negligible. This abrupt change in the crystal environment leads to different properties, including those dealing with magnetism. It is possible that
the difference in anisotropy (and hence frequency) seen here is due to these two different “classes” of spins in a single particle. Presently, computer models are being considered to determine if this phenomenon can be modeled with a core/shell particle having different magnetic properties in each component.

The other possible cause of the sample response may be the multimodal precession measured by White et al. In that work spheres with diameters on the order of 1mm were put into a ferromagnetic (FMR) apparatus [39]. While not a time-domain inductive technique, the FMR results contained higher precession modes in magnetic spheres. Their theory models the magnetization dynamics of a sphere as 4 smaller magnetic dipoles situated within the sphere. Rather than considering classical dipolar interactions, they are modeled with shear and compression torques acting on one another since they are parts of a rigid solid body. The result is 4 possible modes of precession one of which is the classical Kittel expression given in Eq. (20) and others that are scaled versions of it. Their results and the model they develop to explain them, although done on much larger samples, are reported to be independent of sphere diameter to a first order approximation. The nanoparticles considered presently are spheres 5 orders of magnitude smaller than those of White et al. and are monodomain. It has been established however, that clusters resembling spheres can form within collections of nanoparticles and that these spherical clusters behave similarly to individual particles with larger diameters [40]. It may be that the modeled dipoles of White et al. representing quadrants of a single sphere are relatable to the actual dipoles (e.g. individual nanoparticles) comprising spherical clusters within the sample under
consideration here. That is, the higher order modes found here may be due to similar torque interactions of neighboring nanoparticles that comprise a solid body (clusters in the sample), rather than smaller parts of a single, monodomain nanoparticle. The primary concern of the present investigation however, is the time-domain magnetization dynamics, frequency change as a function of $H_b$, and estimation of the $g$-factor and damping parameter. As such, with the exception of a small digression in Section 7.3, the origin of the multiple resonances will not be considered further here, but these frequencies will be characterized and used to fit the data as required to address the goals of the present inquiry. As for the first (low) frequency mode (henceforth referred to as the “normal mode”), its value is close to the resonant frequency of magnetite nanoparticles as found in FMR experiments [41].

![Image](image_url)

Figure 7.1 Time domain fit for circular field-dried sample. The composite fit (center) is the sum of the two components (bottom).

The first time-domain fit is shown in Fig. 7.1. It is for the circular field-dried sample but the results are typical of other geometries. The composite fit of Fig. 7.1
(center plot) is seen to match the main features of the data signal. The initial negative swing of the signal is due to the sum of the negative-going frequency modes as shown in the bottom plot. This feature is seen in all collected data. There is a flat portion of the data around 0.8ns that is due to a beating of the frequency components. The fit plot decreases its amplitude there but does not fit as well as the surrounding peaks. A sparse overlay of the fit to the data is shown in Fig 7.2.

![Graph showing data and fit overlay]

**Figure 7.2.** Data and fitted plot of Fig. 7.1 overlaid. Every 10\textsuperscript{th} fit point is shown.

The beating around 0.8ns can be seen more clearly in Fig. 7.2. It is due in large part to small amplitude, higher precessional modes seen in the FFT spectra of Figs. 6.5 and 6.6 that are not in the fit model. It can also be seen particularly around 0.3ns that the fit does not overlay the data precisely. The relatively wide bandwidth in the FFT spectra shown in Figs. 6.5 – 6.7 is responsible for the approximate fit. The large frequency content around the two frequency peaks contributes significantly to the
shape of the wave and this is not modeled by the double sinusoid fit of Eq. (32).

Considering this, an exact match using only two frequencies is not possible. A comparison of several such fits is seen below.

Figure 7.3. Several fits to the circular field-dried sample shown in Fig. 7.2.

Comparing the low frequency component of the time-domain fits for several values of bias field shows an increase in precession frequency as predicted by the LL equation.

Figure 7.4. Several normal mode frequencies for the circular field-dried sample.
Figure 7.4 shows the normal mode frequency component shown for the same values of $H_b$ as Fig. 7.2. The higher precessional mode is shown below for the same field values. The damping features discussed later can be clearly seen.

![Graph showing different frequency components for varying $H_b$ values.]

Figure 7.5. Several higher mode fits for the circular field-dried sample.

Sparse plots for the fitted model similar to Fig. 7.2 are shown in Fig. 7.6 for the same value of bias field. The features discussed earlier concerning the flattening around 0.8ns and frequency mismatch around 0.3ns can be seen.
Figure 7.6. Strip field-dried time-domain fit.

Figure 7.7. Circular non field-dried time-domain fit.

Figure 7.8. Strip non field-dried time-domain fit.
7.2 Voltage Amplitudes

The amplitudes for both components of Eq. (32) are presented below for each sample geometry. No attempt is made to fit the amplitude profiles to a model owing to the complex nature of the samples, discussed in Chapter 3. Error bars represent the standard error.

![Circular Field-Dried Amplitudes](image1)

**Figure 7.9.** $V_1$ and $V_2$ for the field-dried circular case.

![Strip Field-Dried Amplitudes](image2)

**Figure 7.10.** $V_1$ and $V_2$ for the field-dried strip case.
The almost monotonic decrease in in $V_1$ and increase in $V_2$ is typical for all samples though not identical. It is clear that the amplitude of the higher frequency component is smaller for the field-dried strip case. The normal mode is comparable to the circular geometry. In the non-field-dried circular case in Fig. 7.11, the approximate monotonic

![Circular Non Field-Dried Amplitudes](image1)

**Figure 7.11.** $V_1$ and $V_2$ for the non field-dried circular case.

![Strip Non Field-Dried Amplitudes](image2)

**Figure 7.12.** $V_1$ and $V_2$ for the non-field-dried strip case.
decrease in $V_1$ and increase in $V_2$ is seen. This trend continues somewhat to a lesser extent for the non field-dried strip case.

7.3 Frequency-Domain Fitting

As mentioned in Chapter 2, the general Kittel equation given by Eq. (19) is used to fit the resonance frequency data. For the purpose of modeling, we rewrite Eq. (19) in a slightly different form

$$f_0 = \mu_0 \gamma \sqrt{[H'_0 + (N_x - N_z)M(H)][H'_0 + (N_y - N_z)M(H)]}$$  \hspace{1cm} (34)

where $\gamma$ is expressed in units of Hz/T, $N_i$ is the demagnetizing factor along the $i^{th}$ axis and $H'_0$ is the total field seen by a typical particle. It is expected that the particles will demagnetize themselves and this is expressed by the $N_i$ factors. What must also be taken into account given the composition of the samples is the demagnetization of the local field by the surrounding particles. That is, an interparticle demagnetization factor must be considered. The nature of such sample-wide demagnetization in complex clusters of nanoparticles is the subject of some research [40]. This demagnetizing term is included in $H'_0$ here but does not conform to a data fit if this is taken as a function of $M(H)$, as might be expected by Eq. (14). To make a fit the data possible, the sample-wide demagnetization must be taken as a function of the applied field, $H_b$. This effective bias field can be looked at as a scale factor for the applied field, $H_{b_{eff}} = KH_b$

or, putting it in a similar form of Eq. (14)

$$H_{b_{eff}} = H_b (1 - N)$$  \hspace{1cm} (35)
Equation (35) states that the partial cancellation of the bias field by the surrounding medium is a function of the applied field, not the dynamical magnetization of the sample. The sample magnetization (which is proportional to the particles’ moments) does however govern the demagnetization of the individual particles as expected from the Kittel equation. The nature of dipole-dipole interactions (DDI) on sample dynamics must also play a role in this as discussed in [40], and the effects of these interactions are the subject of much debate [28]-[31], [42], [43]. Even so, the dependence of $H_{b_{\text{eff}}}$ on $H_b$ rather than $M(H)$ is not presently understood.

One feature of DDI is the ability to raise the effective blocking temperature of dense collections of superparamagnetic particles [44]. That is, a non-zero remanent field is possible, which would give rise to magnetic precession even at zero applied field. In addition, magnetite nanoparticles as small as 7nm have been found to have nonzero remanence as exist in this so-called mixed state [45]. Magnetization curves from the VSM were found to be similar to those from [45] and are presented later. This nonzero field is also added to the expression of the effective field. The complete equation used to fit the frequency-domain data is thus

$$f_p = g \frac{\mu_0 \mu_B}{\hbar} \sqrt{[(KH_b + H_A) + (N_x - N_z)M(H)]} \sqrt{[(KH_b + H_A) + (N_y - N_z)M(H)]}.$$ \hspace{1cm} (36)

The value of $H_A$ is obtained from Eq. (20) by measuring the frequency when $H_p$=0. The fitted parameters are $g, K, N_x$, and $N_y$. $N_z$ is expressed as $N_z = 1 - (N_x + N_y)$ per Eq. (16).
The following plots are Fast Fourier transforms of all sample geometries as a function of magnetic bias field. Fits to the data are shown by a solid line. The normal mode is used in determining the $g$ factor but the high frequency mode also conforms to Eq. (36) with similar demagnetizing factors, indicating these precession dynamics are occurring on spheres as well, rather than a sample shape effect.

![Circular Field-Dried Sample FFT](image)

Figure 7.13. Normal mode FFT plot as a function of applied field for the circular field-dried case.
Figures 7.13 and 7.14 show the FFT data points for the circular field-dried geometry. The fit for the normal mode of Fig. 7.13 is used to calculate the $g$ factor from Eq. (36), found to be $g=2.10\pm 0.003$, which is within 1% error of a previously reported value of $g=2.1$ for room-temperature single-crystal magnetite particles [46]. The demagnetization factors are likewise found as $N_x=0.355\pm 0.003$, $N_y=0.309\pm 0.003$, and $N_z=0.335$ indicating behavior of nearly spherical particles. Recalling the discussion in Section 2.7, had the demagnetizing factors been less evenly distributed among the axes, a collective behavior of the particles to act as a unified structure (e.g. film) may have been at work. The results do not however, rule out the possibility of these modes as being caused by interparticle interactions within spherical clusters as discussed in Section 7.1, since they would exhibit similar behavior due to their shape. This can be
seen by examining the expression for the effective demagnetizing factor of a composite body made from isotropically packed spherical particles [17, Ch. 2, p. 39]:

\[ N_{eff} \approx \frac{1}{3} + \hat{\varepsilon} \left( N - \frac{1}{3} \right). \] (37)

In Eq. (37) \( \hat{\varepsilon} \) is the packing fraction of the particles and \( N \) is the demagnetizing factor of the larger shape. Thus if the particles are formed into spherical clusters, \( N \approx \frac{1}{3} \) and \( N_{eff} \approx \frac{1}{3} \) meaning the cluster as a whole will behave like a spherical particle. The inductive experiment alone however, is not enough to determine if this is indeed the cause of the higher mode.

The sample wide demagnetization (or perhaps more appropriately, bias field cancellation) given by the value of \( K \) in Eq. (36) is found to be \( K=0.097\pm0.013 \). The fact that only \( \sim10\% \) of the bias field is experienced by the particles is unexpected, and the dependence of \( K \) on \( H_b \) is presently not understood. \( H_A =38.5\text{kA/m} \) as determined by Eq. (20) for \( H_b = 0 \). In all measurements of \( H_A \), care was taken to ensure stray magnetic fields in the lab were not responsible for the precession. Measurements of the local field (e.g. Earth’s field etc.) in the lab were made and the experimental apparatus rotated with this field aligned along the \( y \)-direction. No amount of compensation of this type was found to alter the outcome significantly and the field was determined to come from within the sample itself as described by [45]. This is discussed in more detail in Section 7.5.

As for the higher frequency mode, the demagnetizing factors in the fit are found to be \( N_x =0.361\pm0.001 \), \( N_y =0.310\pm0.004 \), and \( N_z =0.328 \), again indicating spherical
behavior. The differences between the demagnetizing factors of the two fits are $N_{x_{\text{diff}}}=1.585\%$, $N_{y_{\text{diff}}}=0.410\%$, and $N_{z_{\text{diff}}}=2.06\%$. Figure 7.15 shows the data plotted against the fitted values to better compare the model with the data.

Figure 7.15. Frequency data for the circular field-dried sample plotted against the fitted Kittel equation. The $R^2$ values are given (inset).

Figure 7.16. Normal mode FFT plot as a function of applied field for the strip field-dried case.
The frequency-domain results for the strip geometry that was dried in a longitudinal bias field are shown in Figs. 7.16 and 7.17. The \( g \) factor from Eq. (36), is found to be \( g=2.095\pm0.004 \), which is within 0.25\% error of the previously reported value [46]. The demagnetizing factors for the normal mode fit in Fig 7.16 are \( \mathcal{N}_x=0.358\pm0.001 \), \( \mathcal{N}_y=0.306\pm0.001 \), and \( \mathcal{N}_z=0.335 \). For the higher mode they are \( \mathcal{N}_x=0.334 \), \( \mathcal{N}_y=0.334 \), and \( \mathcal{N}_z=0.332 \) where the standard error is less than that of the normal mode. The bias field cancellation factor is given by \( K=0.095\pm0.002 \). \( H_A =38.42\text{kA/m} \) as determined by Eq. (20) for \( H_b = 0 \). These results are similar to those seen in the circular case.
Figure 7.18. Frequency data for the strip field-dried sample plotted against the fitted Kittel equation. The $R^2$ values are given (inset).

Comparing the two field-dried geometries, the normal mode endpoint values are within 0.48% and 2.1% of each other for the low and high bias fields respectively. The same curve shapes are seen here and throughout indicating a small but finite dependence on the nonlinear magnetization. The high frequency low and high endpoints differ by 0.41% and 1.81% respectively. The two modes are compared in Figs 7.19 and 7.20.
Figure 7.19. Low frequency data comparison for field-dried circular and strip samples.

Figure 7.20. High frequency data comparison for field-dried circular and strip samples.
Comparing Figs. 7.19 and 7.20 it is clear that while the frequencies are similar in magnitude and tend to have similar curves for a given mode, the normal mode frequency for the circular sample is larger and the higher frequency mode for the strip is larger.

Analysis of the non field-dried samples is presented below.

![Circular Non Field-Dried Sample FFT](image)

**Figure 7.21.** Normal mode FFT plot as a function of applied field for the circular non field-dried case.

Figures 7.21 and 7.22 show the FFT data points for the circular non field-dried geometry. For this geometry the spectroscopic splitting factor is found to be $g=2.24\pm 0.014$, which is approximately 7% error of a previously reported value [46]. The normal mode demagnetization factors are found as $\mathcal{N}_x=0.367\pm 0.001$, $\mathcal{N}_y=0.298\pm 0.001$, and $\mathcal{N}_z=0.3338$ indicating behavior of nearly spherical particles. For the higher mode in Fig. 7.22 they are $\mathcal{N}_x=0.334$, $\mathcal{N}_y=0.334$, and $\mathcal{N}_z=0.333$. The bias field reduction is given by $K=0.1474\pm 0.0008$ and $H_A=38.2\text{kA/m}$.
Figure 7.22. Higher mode FFT plot as a function of applied field for the circular non field-dried case.

Figure 7.23 shows the frequency data plotted against the fitted Kittel equation to better see the linear relationship between the data and the model. With the exception of the last two points the normal mode data touches the line. The higher mode is linear within the error, which is clearly higher than the normal mode.

Figure 7.23. Frequency data for the circular non field-dried sample plotted against the fitted Kittel equation. The $R^2$ values are given (inset).
Figure 7.24. Normal mode FFT plot as a function of applied field for the strip non field-dried case.

Figure 7.25. Higher mode FFT plot as a function of applied field for the strip non field-dried case.
The frequency-domain results for the non field-dried strip geometry are shown in Figs. 7.24 and 7.25. The \( g \) factor is found to be \( g = 2.118 \pm 0.004 \), which is within 1% error of the previously reported value [46]. The demagnetizing factors for the normal mode fit in Fig 7.24 are \( \mathcal{N}_x = 0.351 \pm 0.001 \), \( \mathcal{N}_y = 0.313 \pm 0.001 \), and \( \mathcal{N}_z = 0.335 \). For the higher mode they are \( \mathcal{N}_x = 0.333 \), \( \mathcal{N}_y = 0.333 \), and \( \mathcal{N}_z = 0.332 \) where the standard error is less than that of the normal mode. The bias field cancellation factor is given by \( K = 0.079 \pm 0.004 \) and \( H_A = 38.8 \text{kA/m} \).

![Figure 7.26. Frequency data for the strip non field-dried sample plotted against the fitted Kittel equation. The \( R^2 \) values are given (inset).](image)

A comparison between the strip and circular samples for each mode is shown in Figs. 7.27 and 7.28. The normal modes are close at low bias fields but diverge more as the bias field increases. They differ by 0.69% at \( H_b = 0 \text{kA/m} \) and by 3.77% at \( H_b = 45.6 \text{kA/m} \). The higher modes are clearly different by a nearly constant amount over the whole range of \( H_b \). This difference varies between 1.14% and 3.49%, corresponding to a frequency difference of between about 42MHz and 49MHz.
Figure 7.27. Low frequency data comparison for non field-dried circular and strip samples.

Figure 7.28. High frequency data comparison for non field-dried circular and strip samples.
7.4 Damping

The phenomenological damping predicted by the Landau-Lifshitz equation is generated from the time constants used in the damped sinusoidal solution given in Eq. (32). This is a measurement of the frequency of rotation that the magnetization vector undergoes as it aligns with the new field configuration depicted in Fig. 3.2. In other inductive work the values of damping parameters are reported in cgs units where the expression in Eq. (33) is redefined as

$$\lambda_{cgs} = \frac{\lambda}{4\pi} = \frac{2}{4\pi \tau}.$$  \hspace{1cm} (38)

This convention will be followed here for easier comparison to reported damping values from continuous magnetic media experiments.

Figure 7.29. Circular field-dried sample damping values.
As mentioned earlier the complex nature of the sample composition and multimodal precession precludes the damping from being fitted to a quantitative model, though some qualitative observations can be made from the data. The damping parameters of both modes for all samples in Figs. 7.29-7.32 are clearly bias field dependent. The normal mode undergoes a nearly monotonic decrease above $H_b \approx 6\text{kA/m}$ for all but the circular non field-dried sample beyond $H_b = 35\text{kA/m}$. The error in the damping estimation for this sample increases as $H_b$ grows but even considering this error the damping increases (a slight increase is also seen for the last two points of the circular field-dried sample but there is a more significant error in the data relative to the increase there). A monotonic decrease in damping as the bias field is increased is reminiscent of results by [34] and the $n=1$ mode of [14] for impulse (not step) induction experiments in Permalloy films. The damping seen in [14] for step...
excitations decreased sharply with increasing bias field but then remained relatively constant. In that case there were large excursion angles of the magnetization due to step fields with amplitudes comparable to the bias fields. In the present setup the step field is calculated to be 50A/m, roughly 3 orders of magnitude lower than the largest bias field. The magnetization does not end up at a significant angle away from the x-axis (as in impulse experiments, where it is zero). The small step field perturbs the magnetization, but it essentially precesses about the x-axis, which may explain why the damping follows (albeit qualitatively) that of impulse excitations in other inductive work. The shallow dip and subsequent peak of the normal mode before 6kA/m shown in Figs. 7.29-7.32 were not observed in the Permalloy experiments.

There is a different trend in the higher mode. The damping for field-dried samples reaches a minimum at $H_b = 9.76kA/m$ the circular sample and $H_b = 7.79kA/m$ for the strip. Both samples then see a monotonic increase for the higher mode damping. Thus for higher bias fields, the longer wavelength component of field dried samples persists longer in time and the high frequency component quickly disappears. Comparison of these two damping profiles to the non field-dried data in Figs. 7.31 and 7.32 indicates that field drying plays a role in the way the high frequency damping changes as a function of bias field.

For the damping profiles of the non field-dried samples in Figs. 7.31 and 7.32, the low and high frequency values are never equal. The high frequency for the strip sample starts out with the higher value but its value changes only by about 10% over the range of $H_b$. The high mode damping for samples not dried in a magnetic field
remains below 540MHz, a stark contrast to the high field behavior of field dried samples. Damping in these samples stays constant over a wider range of external bias fields. The field drying process should theoretically allow the magnetization to better align with the bias field. It seems this alignment may contribute to a sample energy profile, which preferentially extinguishes the higher mode at larger bias fields.

Figure 7.31. Circular non field-dried sample damping values.
Figure 7.32. Strip non field-dried sample damping values.

7.5 VSM Results Discussion

Figure 7.33. VSM results over experimental range.
The magnetization of a field-dried sample is shown in Fig. 7.33. The applied field range shown is that used in the experiment bias field. The non-zero crossing can be seen. As discussed in Section 2.6, Néel proposed the time the typical magnetization of a single crystal spends along a given direction is governed by the equation \( \tau = \tau_0 e^{K_u V / k_B T} \). Thus for small temperature, \( T \), the magnetization is “blocked” and behaves as a stable moment. For higher temperatures, a measurement made over a significant window of time will yield zero magnetization due to cancellation.

The foregoing discussion is for single particles or collections of non-interacting particles. It has been proposed that for collections of particles where dipole-dipole interactions (DDI) cannot be ignored, Néel’s equation must be modified to the form [47]

\[
\tau = \tau_0 e^{K V / k_B T_0}
\]

In Eq. (39) \( T_0 \) is called the interaction temperature parameter, a measure of the interaction strength. This has the effect of raising the effective blocking temperature, meaning the collection of interacting particles exist in a mixed state. In this case the sample behaves in a slightly ferrimagnetic manner, while remaining mostly superparamagnetic. It is assumed that this finite remanence, along with the findings in [45], is largely responsible for the precession at zero bias field discussed earlier. This phenomenon makes it particularly difficult to derive parameters of single nanoparticles, such as blocking temperature and anisotropy constants in experiments [48]. This is because large numbers of particles must be measured to ensure enough magnetic material to make a reasonably accurate measurement. This results in effective
parameters, rather than those of single particles. Similar difficulties are present in this work as well, though not a temperature-dependent study. While the $g$-factor estimation was generally successful, the multimodal precession complicates matters and a single solution to the LL equation is not possible. This also likely affected the nature of the damping, which is effective, and sample-wide, not that of an individual particle.

As for the final value of the VSM measurement shown in Fig. 6.8, the magnetization is 532kA/m. This is about 10.7% higher than the commonly reported value of 480kA/m [17, Ch. 11, p. 422]. The reason for this error has a few plausible explanations, all of which likely contribute to some degree. To obtain the magnetization, the sample moment must be divided by the volume of magnetite in the sample. This is calculated by using the reported 2% by volume from the manufacturer [15] and the 20$\mu$L volume of the sample. An error in either of these values will result in an incorrect volume. Given such a small volume, the error can be quite significant. The other possible contributing factor is the reported observed enhancement in magnetization in some nanoparticles [31]. As the foregoing discussion addresses, the result from such a phenomenon is an effective saturation magnetization of the sample that is modeled as the magnetization.
Chapter 8

Conclusion

Collections of coated nanoparticles dried from ferrofluid solutions were prepared in two geometries, circles and strips. Each type of geometry was further differentiated by drying them in an external field of 2.5kA/m for one case and in the absence of a magnetic field for the other. The objective of the experiment was to determine if these collections of particles displayed the time-domain magnetization dynamics predicted by the Landau-Lifshitz theory and further if these dynamics could be captured by an inductive technique typically employed in the study of thin magnetic films. The estimation of the $g$-factor and damping parameters were sought, as was the nature of the frequency progression as a function of magnetic bias field.

To implement the inductive technique, the samples were placed on a coplanar waveguide in an external adjustable magnetic bias field. A rapid step current in the waveguide generated a change to the local magnetic field giving rise to magnetization dynamics predicted by the Landau-Lifshitz theory. These magnetic dynamics in the vicinity of the waveguide induced a voltage measured by a sampling oscilloscope.

The data were corrected to account for temporal drift in the triggering circuit by a comprehensive MATLAB routine written for the experiment. This routine then fitted the data to models using nonlinear least squares regression methods. Two
exponentially damped sinusoids were required to describe the time-domain results in light of two prominent frequency components around 1.3GHz and 3.5GHz. Two possible origins of the second frequency were briefly discussed but the ultimate cause could not be conclusively deduced from the present experiment alone. The frequencies, derived from an FFT analysis were seen to progress with a change in bias field according to the general Kittle equation of ferromagnetic resonance. The demagnetizing factors derived from this equation were those of spheroids, not that of the overall planar shape of the sample. That is, though there were likely interparticle interactions, the measured magnetic precession was that of the individual particles. The spectroscopic splitting factors, or $g$-factors, derived from the normal precession mode were found in excellent agreement with previously published values. In most cases the agreement was within 1% error and at most 7% for the circular non field-dried geometry. The sample-wide demagnetization was predicted to exist but it was found to depend upon the applied field, not the field-dependent magnetization as expected. This type of dependence is not presently understood.

The damping factors were derived from the time constants of the exponentials in the fitted time-domain models. Due to the complexity of the sample interaction and the fact that the Landau-Lifshitz model describes the dynamics of single particles, the damping was reported and discussed qualitatively, but not fitted to a theoretical model. A decrease in normal mode damping with increasing external field was seen to behave similarly to that seen in pulsed inductive experiments on thin films.
The amplitudes of the inductive signals were reported and discussed however, as in the case of the damping, were not fitted to a predictive model due to the complexity of randomly assembled clusters of interacting superparamagnets. The normal mode amplitude was found to generally decrease with increasing bias field and the higher frequency mode was typically seen to increase.

The inductive technique was largely successful in measuring the time-domain dynamics of the samples and revealed the spherical nature of their constituents. The technique is not difficult to implement once understood, but the large number of particles required to inductively couple to the waveguide makes the analysis of the data challenging. Large numbers of closely spaced particles are typically used in the many applications of magnetic nanoparticles discussed in the introduction. Understanding the time-domain behavior of such agglomerations is useful in predicting the short time-scale performance of an application.
References


