DYNAMICS OF PARAMAGNETIC SPINS: A STUDY OF SPIN DEFECTS USING MAGNETIC RESONANCE FORCE MICROSCOPY

DISSERTATION

Presented in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy in the Graduate School of The Ohio State University

By
Jeremy David Cardellino, M.S, B.S.
Graduate Program in Physics

The Ohio State University
2015

Dissertation Committee:
Prof. P. Christopher Hammel, Advisor
Prof. Ezekiel Johnston-Halperin
Prof. David Stroud
Prof. Richard Furnstahl
Abstract

Magnetic Resonance Force Microscopy (MRFM) [1–11] is a challenging yet incredibly sensitive tool for characterizing and imaging magnetic materials down to the nanoscale. It combines the technology of scanned probe microscopy [12] with the powerful spectral techniques of magnetic resonance [13, 14]. The MRFM can measure very small spin ensembles, down to a single electron spin [2], and the measurements are performed at thermal equilibrium. Instead of perturbing the polarization away from equilibrium, the ‘spin noise’ or statistical spin fluctuations are used to generate a force signal [9, 15]. Here I show MRFM measurements on a nanoscale ‘spin wire’, which is a narrow, high spin density region implanted in a diamond substrate [1]. The spin wire measurements reveal an interesting interplay between the transport and lifetime of spins confined within the nanoscale diamond wire which are relevant for the development of nanoscale spintronics. Additionally, I show measurements which resolve the hyperfine spectrum of the defects in the spin wire by measuring less than 100 net spins.
I dedicate this to my wife Jen. You have made many sacrifices for me and our family. Thank you for having faith in me and for supporting me as I pursued my Ph.D.
ACKNOWLEDGMENTS

I can’t imagine having done this research without the help of many people, and I would like to thank them for their support. First and foremost, I would like to acknowledge my wife, Jen. She has helped me in so many ways to achieve a Ph.D. in physics. I will never forget her love, dedication, and even the occasional suggestion for my experiment. Jen has followed me on this path for the last several years, and I know it hasn’t been easy for her, but I am very grateful. She is a wonderful wife, and a loving mother. My son, Logan, has motivated me to succeed, because I want to teach him that it is important to work hard and achieve your goals. I also want him to have every opportunity he can in life, of course, so I must work hard to provide that for him. He’s not quite three years old, but he is my little buddy, and I’m very proud to watch him grow and learn.

Next, I would like to thank the rest of my family for their support. My Mom has always encouraged me to learn from a very young age and I believe she was the source of my initial interests in math and science. My aunts Terri, Patty, and Lori have given me great advice over the years, and Terri in particular has inspired me to pursue my interests in science. My Nana helped my mom raise me when I was young, and her cooking is delicious. I would also like to thank my brother Noah, my sister Abbie, and my step father John, who have always been there for me.

When I married Jen, I suddenly gained many more great people into my family. Kathy and Joe have been a huge source of support to my wife and I over the years. I feel very lucky to have them in my life, because they understand how important family is and how to be there for each other. I also want thank Joey, Jessie, and David for their support, and for just being family.
Chris Hammel, my advisor, gave me the initial opportunity to do research in his lab before I had even started taking classes at OSU. He continued to find funding for me throughout the majority of my time here so that I could focus on my research. Not only did Chris give me advice in experimental physics, but also in regards to professional development and maintaining a proper work-life balance. Chris has always emphasized communication skills and he gave me opportunities to travel to conferences where I could present my research. If you accomplish great things in research, but you can’t effectively convey that accomplishment to others, what good is it? Lastly, I want to thank Chris for helping me develop confidence in my work as I learned to do my research autonomously. To do that, he gave me the advice I needed to figure things out on my own, efficiently manage my own progress, and deal with issues related to coworkers.

I would like to acknowledge colleagues who I have worked with on various projects over the years. One of the most important colleagues, especially early in my work, was Michael Herman. Michael was basically my mentor for a year and a half on the MRFM experiment, when I first came to OSU. He showed me how to run most of the experiment and gave me an introduction to the basic concepts of MRFM and spin dynamics. Michael was also the lead person for the sample preparation and data collection in the spin transport experiment [1]. Nic Scozzaro also worked with me on the spin wire experiment, as well as the NV powder pattern modeling, LAO/STO measurements, MRFM in general, noise analysis in force and frequency detection schemes, and many other related projects and tasks. Nic is the lead researcher on the membrane MRFM project, which I collaborated with him on.

For the last two years, I have worked closely with Erick Blomberg, a post-doc in Professor Hammel’s group. In particular, I want to recognize his work on gluing magnetic particles to cantilevers, using the focused ion beam (FIB) to mill the cantilever particles, and imaging the cantilevers with optical microscopes and the scanning electron microscope (SEM). For those aspects of the project, Erick did the majority of the work while I took the lead on other aspects. Erick also worked with me on many of the tasks and operations for running the experiment in general. Next, I would like to thank Brendan McCullian, who is still at the beginning stages of his Ph.D. work, and who has been helping me run the
I wish him the best of luck as he continues to run the MRFM experiment after I have left. I want to specifically acknowledge Brendan for his work on collecting calibration data for the Attocube positioning system, research on superconducting microwave coils, cantilever fabrication, and magnetometry measurements. Brendan and Erick also put in many late nights with me (7 a.m. is pretty late!) as we worked in alternating shifts around the clock when the experiment was at 4 K.

I would like to thank Andy Berger, Richelle Teeling-Smith, Rohan Adur, Vidya Bhalamudi, and Chris Wolfe for their experimental advice, assistance, and friendship. Andy also played a role in writing and editing the paper for the spin transport experiment [1]. I had the opportunity to work with Richelle on the modeling for the NV diamond spectra in the single molecule DNA experiment that she was the lead on. I want to thank Kin Chung Fong and Palash Banerjee for their help and collaboration on projects. They provided valuable advice on the experiment via emails, phone calls, and in-person visits to the lab. I would also like to thank anyone else in Professor Hammel’s group that I may have missed. I am also grateful for many friends, specifically, Mike Prikockis, Adam Ahmed, Matthew Brehove, and Chi Zhang.

There are many people in the physics department that have supported me throughout my work. Denis Pelekov has almost been a second advisor for me, especially early on in my Ph.D. research. He is very busy, but he always found some time to come by the lab and help sort out some issue we were having. Very early in my research, he also taught me some valuable concepts regarding spin dynamics and resonance. He is a great resource for this type of work because he has a lot of experience in microscopy, low-temperature experiments, and spin physics. Camelia Selcu has also been helpful for training on specific user instruments and general experimental knowledge. Professor Jonathan Pelz gave me academic advice, especially in my first year or two at OSU. Kristina Dunlap is the graduate program coordinator in the OSU physics department, and she has helped me many times by either giving me advice or helping me with administrative issues like enrollment, reservations, and payments, among many other things. She has definitely earned the distinguished staff awards she has received over the years.
The physics computing facility (PCF) staff has helped me with numerous computer issues, specifically Terry Bradley, Brian Keller, Bryan Dunlap, and Matt Barber. Another important support group at OSU is the physics machine shop staff which helped me fabricate custom designed parts for multiple experiments. These people include Jonathan Shover, Josh Gueth, Pete Gosser, and Michael Graham. I would also like to thank Phil Davids and Mark Reed from facilities operations, and Kent Ludwig and Mark Studer from the electromechanical shop.

Lastly, I would like to thank anyone I may have forgotten. There are so many people that have helped me over the years, in so many ways, that it would be nearly impossible to mention them all. Thank you.
VITA

February 6, 1982 ......................... Born–State College, PA

May, 2010 ................................. B.S. Physics, Penn State University

December, 2012 ........................... M.S. Physics, The Ohio State University

January, 2013 .............................. Graduate Research Assistant, The Ohio State University

Publications


Fields of Study

Major Field: Physics
<table>
<thead>
<tr>
<th>Table of Contents</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abstract</td>
<td>ii</td>
</tr>
<tr>
<td>Dedication</td>
<td>iii</td>
</tr>
<tr>
<td>Acknowledgments</td>
<td>iv</td>
</tr>
<tr>
<td>Vita</td>
<td>viii</td>
</tr>
<tr>
<td>List of Figures</td>
<td>xi</td>
</tr>
<tr>
<td>List of Tables</td>
<td>xiii</td>
</tr>
</tbody>
</table>

**Chapters**

1 **Introduction**                                                      | 1    |
| 1.1 Background                                                      | 1    |
| 1.2 Organization                                                    | 4    |

2 **Basic Principles**                                                  | 7    |
| 2.1 Introduction                                                     | 7    |
| 2.2 Spin                                                             | 7    |
| 2.3 Thermal and Statistical Spin Polarization                       | 10   |
| 2.4 Spin Resonance                                                   | 14   |
| 2.5 Adiabatic Inversion of Spins in the Rotating Frame               | 15   |
| 2.6 Spin Relaxation                                                  | 19   |
| 2.7 Spin Diffusion                                                   | 21   |
| 2.8 Power Spectral Density                                           | 23   |

3 **The MRFM Experimental Setup**                                       | 25   |
| 3.1 Overview of the Setup                                            | 25   |
| 3.2 Ultrasoft Cantilevers as High Sensitivity Force Detectors         | 27   |
| 3.3 Micron-Sized Magnetic Particle Tip                               | 41   |
| 3.4 Magnetic Resonance Bowl                                          | 48   |
| 3.5 Resonance Coil for Providing Microwaves                          | 51   |
| 3.6 Laser Interferometry for Displacement Detection                  | 54   |
| 3.7 Low Temperature Cryostat                                         | 60   |
| 3.8 Instrumentation                                                  | 64   |

4 **The MRFM Signal and Noise**                                         | 70   |
| 4.1 Introduction                                                     | 70   |
# List of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1 MRFM Images of the Tobacco Mosaic Virus</td>
<td>5</td>
</tr>
<tr>
<td>2.1 Zeeman Energy Level Diagram</td>
<td>9</td>
</tr>
<tr>
<td>2.2 Binomial Distribution for Net Spin Polarization</td>
<td>12</td>
</tr>
<tr>
<td>2.3 Thermal and Statistical Polarizations</td>
<td>13</td>
</tr>
<tr>
<td>2.4 Plot of EPR Spectrum for E' Defects in Silica</td>
<td>16</td>
</tr>
<tr>
<td>2.5 Adiabatic Theorem Diagram</td>
<td>17</td>
</tr>
<tr>
<td>2.6 Rotating Frame Diagram</td>
<td>20</td>
</tr>
<tr>
<td>2.7 Flip-Flop Mechanism</td>
<td>22</td>
</tr>
<tr>
<td>3.1 Image of Myself Working on the Probe</td>
<td>26</td>
</tr>
<tr>
<td>3.2 Diagram of the MRFM Setup</td>
<td>27</td>
</tr>
<tr>
<td>3.3 Ultra-Soft Cantilevers</td>
<td>29</td>
</tr>
<tr>
<td>3.4 Plot of Thermally-Limited Cantilever Frequency Noise</td>
<td>35</td>
</tr>
<tr>
<td>3.5 Mean Square Cantilever Displacement Vs Temperature</td>
<td>36</td>
</tr>
<tr>
<td>3.6 Cantilever Ring-Down Measurement</td>
<td>37</td>
</tr>
<tr>
<td>3.7 Image of Cantilever Bending</td>
<td>39</td>
</tr>
<tr>
<td>3.8 Gluing a Particle onto a Cantilever</td>
<td>42</td>
</tr>
<tr>
<td>3.9 Scanning Electron Micrographs of an Ion-Milled Magnetic Particle</td>
<td>43</td>
</tr>
<tr>
<td>3.10 Cantilever Magnetometry Setup</td>
<td>45</td>
</tr>
<tr>
<td>3.11 Image of Room-temperature Ultrasoft Magnetometer</td>
<td>46</td>
</tr>
<tr>
<td>3.12 Cantilever Magnetometry Data</td>
<td>47</td>
</tr>
<tr>
<td>3.13 Magnetic Particle, Field, and Resonance Bowl Diagram</td>
<td>50</td>
</tr>
<tr>
<td>3.14 Microwave Resonance Coil Image and Diagram</td>
<td>52</td>
</tr>
<tr>
<td>3.15 Reflected Power Versus Frequency for the Microwave Coil</td>
<td>53</td>
</tr>
<tr>
<td>3.16 Laser Interferometry Diagram</td>
<td>55</td>
</tr>
<tr>
<td>3.17 Plot of Cantilever Visibility via Laser Sweep</td>
<td>57</td>
</tr>
<tr>
<td>3.18 Plot of Cantilever Visibility via Fringing Drive</td>
<td>58</td>
</tr>
<tr>
<td>3.19 Experiment Dewar Diagram</td>
<td>67</td>
</tr>
<tr>
<td>3.20 Cryogenic Thermometer</td>
<td>68</td>
</tr>
<tr>
<td>3.21 Instruments Setup Diagram</td>
<td>69</td>
</tr>
<tr>
<td>Section</td>
<td>Title</td>
</tr>
<tr>
<td>---------</td>
<td>------------------------------------------------------------------------</td>
</tr>
<tr>
<td>4.1</td>
<td>iOSCAR Timing Diagram and Signal From One Spin</td>
</tr>
<tr>
<td>4.2</td>
<td>Long Time Record for Signal from Two Hundred Spins</td>
</tr>
<tr>
<td>4.3</td>
<td>Method of Construction of Spin Signal PSD</td>
</tr>
<tr>
<td>5.1</td>
<td>Defects in Diamond Diagram</td>
</tr>
<tr>
<td>5.2</td>
<td>Energy Level Diagram for the P1 Center</td>
</tr>
<tr>
<td>5.3</td>
<td>Energy Level Diagram for the NV Center</td>
</tr>
<tr>
<td>5.4</td>
<td>ODMR Spectrum for NV Centers in Diamond</td>
</tr>
<tr>
<td>5.5</td>
<td>SRIM Simulations for Nitrogen Implantation</td>
</tr>
<tr>
<td>5.6</td>
<td>Setup and Measurements for MRFM Spin Wire Scan</td>
</tr>
<tr>
<td>5.7</td>
<td>Simulation for Spin Wire Diffusion</td>
</tr>
<tr>
<td>5.8</td>
<td>Comparison of piOSCAR and iOSCAR Protocols</td>
</tr>
<tr>
<td>5.9</td>
<td>Setup and Data for the Spin Wire Hyperfine Measurements</td>
</tr>
<tr>
<td>6.1</td>
<td>LAO/STO Interface Structure Diagram</td>
</tr>
<tr>
<td>6.2</td>
<td>Angular Dependence of LAO/STO EPR Measurements</td>
</tr>
<tr>
<td>6.3</td>
<td>NV DNA Setup Diagram</td>
</tr>
<tr>
<td>6.4</td>
<td>ODMR Data for Single Molecule DNA with NV Center</td>
</tr>
<tr>
<td>7.1</td>
<td>Graphene Vacancy Spin Defect Center</td>
</tr>
<tr>
<td>A.1</td>
<td>Slow Warm-up Diagram</td>
</tr>
</tbody>
</table>


List of Tables

<table>
<thead>
<tr>
<th>Table</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>Properties of Cryogenic Gases</td>
<td>62</td>
</tr>
<tr>
<td>3.2</td>
<td>Instrument List</td>
<td>65</td>
</tr>
</tbody>
</table>
Chapter 1
INTRODUCTION

1.1 Background

To begin with, I would like to give a quick background describing the history and development of magnetic resonance [13, 14] and magnetic resonance force microscopy (MRFM) [1–11]. I will also introduce spins, describe what they are, and give some motivation for why they are currently the focus of so much research.

Magnetic resonance is a powerful spectroscopic tool which is primarily used in medicine and material research. Much of the technology related to magnetic resonance was developed during the Second World War. For example, microwave frequencies were developed for radar detection during the war, and these are necessary to excite spins for magnetic resonance. Magnetic resonance was first observed by Isidor Rabi in 1938 [16], and then further advanced in the mid-1940s. In 1944, Rabi was awarded the Nobel Prize in Physics for this work. Felix Bloch and Edward Purcell expanded on Rabi’s technique and shared the Nobel Prize in Physics in 1952 [17–20]. Today, magnetic resonance is a rich and diverse field which spans a wide array of techniques and applications [21, 22].

In general, there are two types of magnetic resonance. Nuclear magnetic resonance (NMR) is performed on the spins of atomic nuclei, while electron spin resonance (ESR) is a magnetic resonance technique for measuring electron spin. In both cases, when the spins are subject to a strong external magnetic field, the energy of each spin is split into multiple (at least two) levels. These levels correspond to the orientation of the spins with respect to the direction of the applied magnetic field. Resonance occurs when electromagnetic radiation is
supplied which has an energy that is equal to the difference in the spins' energy levels. The electromagnetic radiation is absorbed by the spins as they transition between the levels and this absorption can be detected to give the NMR or ESR signal.

A widely-used application of NMR is magnetic resonance imaging (MRI) for medical diagnosis and study. MRI scans part of a patient’s body (often the head) by applying a strong magnetic field with a gradient and then uses radio waves to excite hydrogen nuclei (protons) of water molecules within the living tissue. MRI was invented in 1971 by Paul Lauterbur [23], and as recently as 2003, Lauterbur shared the Nobel Prize in Medicine with Sir Peter Mansfield for their development of the MRI. Aside from its medical applications, NMR is also used in chemistry to measure the structure of molecules and compounds. This is achieved by comparing well-known nuclear signals to those in which the nuclei are surrounded by a different chemical environment or have different chemical bonds which leads to a shift in the standard NMR signal. In fact, NMR is commonly used as evidence for confirming the synthesis of new materials.

ESR is very analogous to NMR, except that it utilizes the spin of free radicals (a defect that has an unpaired electron) found in certain solids and liquids. ESR is widely-used in science (particularly biology, chemistry, and physics) to study the structure of materials by probing the orbitals of the measured defects via its interactions (associated energy) with the surrounding crystal. In addition to unpaired electrons which are paramagnetic, ESR can be used to study ferromagnetic materials in which the spins in a material spontaneously align due to quantum mechanical interactions. These are called ferromagnetic resonance (FMR) studies. Historically, ferromagnets have provided a powerful tool for discovering electromagnetic principles, and today ferromagnets are integrated into many aspects of current technology, particularly for storage applications. Right now there is also a lot of research done with ferromagnetic materials because their strong magnetic interactions provide useful avenues for studying spin physics.

So magnetic resonance measures spins, but what are spins? I describe the nature of spins in greater detail in Chapter 2, but here I will just give a basic description. Spin is a very small amount of angular momentum of subatomic particles, such as electrons or nuclei.
This spin is also inextricably related to the magnetic properties of the particle. Also, the spin of a particle can only take on certain discrete values. The basic formalism for describing spin was developed in the mid-1920’s by Wolfgang Pauli, primarily using Erwin Schrodinger and Werner Heisenberg’s recently developed theory of quantum mechanics. Much of the motivation for this development came from trying to understand the fundamental nature of atomic structure, in particular, the electron orbital of the atom, in which spin plays an important role. Pauli is famous for his exclusion principle which states that no two electrons of an atom can be in the same quantum state. This means that if they reside in the same orbital, they must have different spin quantum numbers, \( m_s \).

Currently, spin is a huge area of research in condensed matter physics [24]. One of the main reasons for this is that spin is a very promising avenue for advancing information technology. Starting with the invention of the transistor in 1947, computing technology has increased at an exponential rate. About 50 years ago Gordon Moore, who is the co-founder of Intel, made a prediction that the number of transistors on an integrated circuit would roughly double every 2 years [25]. This is commonly referred to as Moore’s law, and for the last 50 years, the technological growth has closely followed this trend. This has primarily been achieved by shrinking the size of electronic components on integrated circuits so that more of them can fit on a single processor chip. However, the size of these components is approaching the nanoscale where quantum mechanical effects begin to dominate, and it is becoming increasingly difficult to shrink these components further. There is also a huge problem with these components overheating as electrical leakage current is passed through the densely packed components.

Spin-based technology (also known as spintronics) shows promise for overcoming many of the challenges that conventional electronics is facing [24, 26]. Since spin is a quantum mechanical property of sub-atomic particles, it is inherently suited for operating at the nanoscale or even smaller. Ultimately, the hope is that spin can be used as a quantum binary digit (qubit) for information storage and processing. The main challenges people are working on with spintronics deal with initializing the spins to encode information, transporting the spin information, manipulating the spins to alter the information or achieve
if some computation process, and reading the spin information at a later time.

If information is encoded onto the spin, with the desire to read it out later with high fidelity, then that information must stay intact over some period of time. This is related to what is called the lifetime of a spin, which is something I studied extensively in my experiments and will discuss further in Chapters 2, 4, and 5. In regards to the overheating problem mentioned earlier, spintronics offers some promising solutions because it is possible to transport information encoded on spins without transporting charge (i.e. without an electrical current). In fact, much of my research was focused on studying this type of spin transport by directly measuring spins as they diffused within a fabricated diamond spin-wire.

To fully utilize spin in information technology applications, we must first understand it better, so that we can better control it. That is why tools that can probe the properties of spin materials at the nanoscale are important in today’s research, and magnetic resonance force microscopy (MRFM) is a very powerful tool in this regard. MRFM combines the spectroscopic principles of conventional magnetic resonance \cite{13, 14} with the sensitive detection capabilities of scanned force probes \cite{12} (such as AFM, MFM, and STM \cite{27–30}). This results in a remarkably sensitive probe that is capable of measuring the dynamics of a single electron spin \cite{2}, and which also has imaging capabilities. An example of this, Figure 1.1 shows a scanned MRFM image of tobacco mosaic virus particles taken by researchers at IBM \cite{11}. In MRFM research, the challenge now is to continue advancing the capabilities of the MRFM as a tool, and to use it to uncover interesting spin phenomena in novel materials for the advancement of spin-based technology.

1.2 Organization

This dissertation is organized in the following manner. First, I introduce the basic physics of spins in Chapter 2, including their dynamics and magnetic resonance techniques for measuring them. In Chapter 3 I describe the main components of the MRFM experimental probe: ultra-soft cantilever, micron-sized magnetic tip, magnetic resonance bowl, resonance
Figure 1.1: MRFM images of tobacco mosaic virus particles. a) Scanned electron micrograph of the tip of a MRFM cantilever which has tobacco mosaic virus particles on it. The image is 1.9 µm X 2.5 µm. b) Zoom-in on a small group of the virus particles seen in a). The size of the image is 390 nm X 390 nm. c) A scanned MRFM image corresponding to the image in b). These images were taken from the work of Degen et al. [11].

Chapter 4 describes exactly how the MRFM signal is acquired. This covers the detection protocols for the MRFM signal and also noise analysis of the experiment. The noise in the experiment is an important topic, of course, because it is at the heart of what makes this experiment so challenging. Next, in Chapter 5, I present the main results of the spin wire experiment in which I studied spin transport and spin dynamics in a confined nanoscale system [1]. Chapter 6 covers a few topics of supplementary work that are related to or compliment my primary MRFM research. These topics include measurements and research on the lanthanum aluminate and strontium titanate interface (LAO/STO), work on the development of electron-nuclear double
resonance (ENDOR) for MRFM, a project using membranes for MRFM to achieve direct
detection (i.e. does not require microwave excitation), and nitrogen-vacancy EPR powder
pattern simulations for understanding optically detected magnetic resonance (ODMR) on
nanodiamonds attached to single strands of DNA. Chapter 7 has conclusions and ideas for
future directions in MRFM, including spin measurements on vacancy defects in graphene.
Chapter 2
Basic Principles

2.1 Introduction

In the last chapter, I briefly described that spin is a small amount of angular momentum which is also related to magnetism. In this chapter, I will provide a detailed description of spins, including what they are, their dynamics, some methods for measuring them, and how they can be manipulated. I will also look at the net behavior of an ensemble of spins, like the average net polarity and the amount of fluctuations about that average. This will provide the fundamental understanding for MRFM concepts I describe in later chapters. Also, in chapter 5, I will provide further modeling of spins and go through simulations for spin flip-flop dynamics. I performed these simulations to better understand the results of the spin wire measurements that I present in that chapter.

2.2 Spin

Spin is a very small, quantized, intrinsic amount of angular momentum found in elementary particles (or composite particles called hadrons). Spin is measured in units of $\hbar$ which is the fundamental quantum of angular momentum and has a value of $1.055 \times 10^{-34} \text{ J} \cdot \text{s}$. In addition to having angular momentum, a particle’s spin $\vec{S}$ is typically accompanied by a small magnetic moment $\vec{\mu}$. For a free electron, this relationship is given by:

$$\vec{\mu} = \gamma_e \vec{S} = \frac{-g_e \mu_B}{\hbar} \vec{S}$$

(2.1)
Here, $\gamma_e$ is the gyromagnetic ratio of a free electron where $\gamma_e/2\pi = 28.025$ GHz/T, $g_e = 2.0023$ is the dimensionless g-factor, and $\mu_B = 9.274 \times 10^{-24}$ J/T is the Bohr magneton. Note that the negative sign in equation 2.1 comes from the fact that $\gamma_e$ is actually negative, which means that $\vec{\mu}$ and $\vec{S}$ point in opposite directions, and this does result in observable effects in some experiments.

A classical analogy for spin would be a rotating sphere such as a basketball or the earth, both of which have angular momentum. If the sphere is charged up, its rotation will create a magnetic field. Similarly an electron has charge, spin, and an associated magnetic moment. However, the problem with this analogy is that it breaks down in many ways very quickly at the nanoscale where quantum mechanical effects dominate. For example, we can easily stop a spinning basketball in which case its angular momentum becomes zero, but this isn’t true for an electron. The electron has intrinsic spin that cannot be removed (unless the electron itself is annihilated in some way).

With a concentration on my own research, I will focus on paramagnetic spins, such as a free electron or an electron that is only weakly interacting with neighboring spins. Free electrons and many singly-bound electrons are spin-1/2 systems, and in the presence of a strong applied magnetic field, it will always have exactly two stationary states. If you measure the spin, you will observe that it is either aligned or anti-aligned to the field direction (this is commonly referred to as ‘spin-up’ and ‘spin-down’). The spin also has components in the directions orthogonal (perpendicular) to the applied field, however, the magnitude of these can not be simultaneously known due to the uncertainty principle of quantum mechanics. For the purposes of this work, we won’t have to worry about the orthogonal components. In the presence of the applied field $B$, the associated energy of the spin system can be described by the Zeeman Hamiltonian:

$$\mathcal{H} = -\vec{\mu} \cdot \vec{B}$$  \hspace{1cm} (2.2)$$

and the eigenvalue solutions for the spin are $+\hbar/2$ and $-\hbar/2$ (up and down), with respective energy values:

$$E_{\pm} = m_s g_e \mu_B B$$  \hspace{1cm} (2.3)$$
where \( m_s = \pm 1/2 \) (up and down). Note that if the spin is down (i.e. \( m_s = -1/2 \)), this means that \( \mu \) is up (which is aligned to \( \vec{B} \)) which corresponds to the ground state energy of the system.

These are the eigensolutions for the spin, which are stationary in the sense that if the spin starts in one of those states, it will persist in that state, assuming there are no perturbations. On the other hand, what happens if the spin starts in some other state? For example, what if it is in a superposition of up and down? Having found the eigensolutions to the Hamiltonian above, one can solve the time-dependent Schrödinger equation:

\[
\frac{i\hbar}{\partial t} |\Psi(t)\rangle = \hat{H} |\Psi(t)\rangle
\]

where the spin state is represented by a time-dependent wave function \(|\Psi(t)\rangle\) and the Hamiltonian is written as an operator \(\hat{H}\). The solutions to this result in a time-dependent phase \(\phi\) in the wave function which corresponds to a precession of the spin about the field axis. The angular rate \(\omega\) at which the spin precesses about the field turns out to be proportional to the Zeeman energy splitting \((\Delta E = E_+ - E_-)\) of the two spin eigenstates.
given by equation 2.3:

\[ \omega = \frac{\Delta E}{\hbar} = \frac{g_e \mu_B B}{\hbar} = \gamma B \]  

(2.5)

A classical analogy to the spin’s precession would be a top that spins on a table, but also slowly precesses (wobbles in a small circle). The top revolves about its axis of rotation, but the rotation axis itself also slowly rotates (which is the precession). The Earth is another example of something that rotates and precesses. Because of the precession, the north star, Polaris, will not always point north. In fact, it is interesting to note that in about 13,000 years, Polaris will be about 47° off of the celestial north pole, which means it will actually be closer to the celestial equator. At that time, Vega, which is the second brightest star in the northern sky and is relatively close to Earth (about 25 light-years away), will be considered our north star. Also, at this time the month of June will be in the middle of winter (in terms of weather) for someone living in the Earth’s northern hemisphere, and Christmas will be celebrated during the summer.

2.3 Thermal and Statistical Spin Polarization

Consider a large ensemble of \( N \) spins at thermal equilibrium. At finite temperature \( T \), there will be a distribution of up and down spins (\( m_s = \pm 1/2 \)), and we can calculate what fraction of \( N \) is in each state (or equivalently the probability, \( p \) of finding a given spin in that state) according to Maxwell-Boltzmann statistics [31]:

\[ p_i = \frac{1}{Z} \exp \left( \frac{-E_i}{k_B T} \right) \]  

(2.6)

Here, \( k_B = 1.381 \times 10^{-23} \text{ J/K} \) is the Boltzmann constant, and \( Z \) is the partition function given by:

\[ Z = \sum_i \exp \left( \frac{-E_i}{k_B T} \right) \]  

(2.7)

where \( i \) corresponds to the two states up and down (which I will denote as \( \uparrow \) and \( \downarrow \)). I will also define the number of up and down spins as \( N_{\uparrow} \) and \( N_{\downarrow} \), respectively. For the electron spin system described above, we can substitute \( E_{\pm} \) from equation 2.3, and we find that the fraction of up spins is \( p_{\uparrow} \approx 49.99\% \) and the fraction of down spins is \( p_{\downarrow} \approx 50.01\% \).
for a magnetic field of 785 gauss at room temperature \((T = 296 \text{ K})\). The 785 gauss value for the field comes from my MRFM experiment. That is the field that corresponds to the microwave frequency \(\omega\) that I use (equation 2.5).

In many spin-detection experiments, the net polarization \(N_{\text{net}} = N_\downarrow - N_\uparrow\) is proportional to the measured signal, so it is useful to write this in a simplified form:

\[
N_{\text{net}} = N(p_\downarrow - p_\uparrow) = N \left( \frac{e^\Lambda - e^{-\Lambda}}{e^\Lambda + e^{-\Lambda}} \right) = N \tanh(\Lambda)
\]  

(2.8)

where \(\Lambda = \frac{\mu_B B}{k_B T}\). Note that \(\mu_B/k_B = 0.672 \text{ K/T}\), which is convenient for quick calculations. Thus in the example, for \(T = 296 \text{ K}\) we have \(N_{\text{net}} = (1.78 \times 10^{-4}) N\). In that case, \(\Lambda\) itself is equal to \(1.78 \times 10^{-4}\), since \(\tanh(x) \approx x\) for \(x \ll 1\). So the net polarization at room temperature is just a small fraction of \(N\), but for lower temperatures, the system becomes more polarized of course (1.26\% of \(N\), for 785 gauss and 4.2 Kelvin), but this is still quite small in many cases. This Boltzmann polarization (or thermal polarization) will simply be linear in \(N\), and the slope will depend on the strength of the applied field and the temperature the experiment is performed at. However, this only considers the average polarization in time (i.e. this is really \(\langle N_{\text{net}} \rangle\)). What about the fluctuations about this average? How large are they compared to the average and how does this depend on the temperature of the experiment or the size of the spin ensemble?

As I will discuss further in sections 2.6 and 2.7, spins in a given material will spontaneously flip due to interactions with their surrounding environment which lead to fluctuations in \(N_{\text{net}}\). These can be interactions with the crystal lattice of the spin material, other nearby spins, incident photons, itinerant electrons in metallic systems, etc. Whatever the interaction(s), the spins will flip at some characteristic time scale, but at any point in time, each spin will have some probability, \(p_\downarrow\) (given by equation 2.6) of being down.

Then, the probability of finding some number, \(N_\downarrow\) of spins in the down state is described by the probability mass function (pmf, in statistics) of a binomial distribution. Of course the average or expected value for this is still \(N_\downarrow = p_\downarrow N\), as given above, but we can now start looking at the probability distribution about that average. Figure 2.2 shows an example of this binomial distribution for \(N = 100\) and \(p_\downarrow = 0.5063\). This value of \(p_\downarrow\) corresponds to
the 1.26% polarization at a temperature of 4 K in a field of 785 gauss discussed above.

Figure 2.2: Plot of the binomial distribution showing the probability of finding a given number of net spins \( N_{\text{net}} = N_\downarrow - N_\uparrow \) when \( N = 100 \) and the probability for each spin to be in the down state is \( p_\downarrow = 0.5063 \). This value of \( p_\downarrow \) corresponds to a temperature of 4 K and a field of 785 gauss.

The variance of the binomial distribution pmf is given by \( Np(1 - p) \) and thus we can express the fluctuations of \( N_{\text{net}} \) as the standard deviation \( \sigma_{N_{\text{net}}} \) given by:

\[
\sigma_{N_{\text{net}}} = 2 \sqrt{Np_\uparrow p_\downarrow} \tag{2.9}
\]

where the factor of 2 comes from the relationship \( N_{\text{net}} = N_\downarrow - N_\uparrow = N_\downarrow - (N - N_\downarrow) = 2N_\downarrow - N \).
Figure 2.3: Plot of the thermal and statistical polarizations for a paramagnetic electron spin ensemble at 4 K in a magnetic field of 785 G. The plot shows the net polarization, $N_{\text{net}}$ versus the total number of spins $N$ for both the thermal polarization (blue) given by equation 2.8 and the statistical polarization (green) given by equation 2.9. The thermal polarization is the average value while the statistical polarization is the fluctuation (standard deviation) about the average, shown clearly in figure 2.2.

Equation 2.9 characterizes what is called the statistical polarization of the spin ensemble, which is the typical instantaneous polarization due to spin fluctuations (also called ‘spin noise’).

The importance of this result is that the fluctuations of the net polarization is proportional to the square root of the number of spins (also note that $2\sqrt{Np_\uparrow p_\downarrow} \approx \sqrt{N}$, for
\( p_\uparrow \approx p_\downarrow \), and thus, in some situations when \( N \) is small, the statistical polarization is actually larger than the thermal polarization (see figure 2.3). This is almost always the case when running the MRFM experiment, and so the spin signal I measure is the statistical fluctuation of the spins at thermal equilibrium, which is unlike most magnetic resonance experiments.

### 2.4 Spin Resonance

In general, spin resonance (magnetic resonance) is performed by supplying electromagnetic radiation to a spin system that corresponds to a difference of the spins’ energy levels. In figure 2.1 for example, the energy would equal \( g_e \mu_B B \) (I will label this field as \( B_0 \) sometimes to differentiate it from other magnetic fields). Typically the electromagnetic radiation is supplied in the form of an alternating magnetic field denoted \( B_1 \), conventionally, which has a frequency, \( \omega \) that matches the Larmor precession of the spins:

\[
\omega = \gamma B_0
\]  

(2.10)

and thus has the correct energy according to equation 2.5. Equation 2.10 is known as the resonance condition of the spin [13, 14]. To maximize the magnetic resonance effect, \( B_1 \) is usually applied perpendicular to \( B_0 \), because only the perpendicular component can excite transitions in the spins’ state.

Since all of my measurements focus on electron spin resonance (ESR) or, more specifically, electron paramagnetic resonance (EPR), I will focus the discussion accordingly, although nuclear magnetic resonance is analogous in many ways. Conventionally, EPR measurements have been performed by supplying a \( B_1 \) with a fixed frequency, and then slowly varying the magnitude of \( B_0 \). This allows for a sweep through the resonance condition yielding an EPR spectrum. Most EPR spectrometers today use a resonance cavity to create the \( B_1 \) field, and the dimensions of the cavity result in standing wave modes that have fixed frequency \( \omega \). Figure 2.4 shows an example of an EPR spectrum for a silica sample containing E’ spin defects. To collect this data, I used a Bruker EPR spectrometer with a
fixed frequency of about 9.7 GHz (this is known as an X-band spectrometer), and this is why the spectrum occurs around 3,462 gauss (according to the resonance condition). Some measurements sweep the frequency of the $B_1$ field and hold the magnitude of $B_0$ constant, although this is usually more difficult in practice.

When spins are brought onto resonance, spins in a lower energy state absorb a photon with energy $\hbar \omega$ and are excited up to the higher energy state that is directly adjacent. The spin can then relax back to its original state through a number of non-radiative processes which I will discuss more in section 2.6. At the same time, spins in a higher energy state can absorb a photon, relax down to a lower adjacent energy state, and emit two photons. This is known as stimulated emission. Although both of these processes are occurring on resonance, there are more spins in the lower energy state than in the higher, so the net effect is an absorption of electromagnetic radiation, which is what the EPR spectrometer measures. Apart from the electron resonance I have described here, there are many other types of electron spin resonance. For example, ferromagnetic systems can have many modes of resonance which involve the excitation of an ensemble of ferromagnetically interacting spins as a whole. It is also possible to excite resonance optically with certain materials that have optically addressable spin properties. Overall, magnetic resonance is a very rich and extensive field, and I have only covered the simplest example which is necessary as a basis for understanding the magnetic resonance concepts related to my measurements. Building on this basic understanding of magnetic resonance, in the next section, I will go over the adiabatic inversion technique which is crucial to my MRFM experiment.

2.5 Adiabatic Inversion of Spins in the Rotating Frame

In many magnetic resonance studies and applications, it is often desirable to invert spin populations. For example, if the net polarization of a spin ensemble is aligned to a static magnetic field at equilibrium, you may wish to invert the polarization (to anti-aligned) and then measure how long it takes the spins to re-align back to the original equilibrium state. This is known as an inversion-recovery experiment. A number of inversion techniques have
Figure 2.4: Plot of electron paramagnetic resonance spectrum for E’ defects in silica. This data was collected by myself using a Bruker EPR spectrometer. The spectrum shows the asymmetric peak of E’ centers which has a characteristic ‘shoulder’ on the left side of the peak. The asymmetric shape is known as a powder pattern which I discuss in detail in section 6.3. For reference, the inset shows a similar spectrum of E’ defect in silica which was collected by Raffi Budakian et al. [32].

been developed to accomplish this, and in this section I will go over the adiabatic inversion technique since it is pivotal to my MRFM experiment.

Adiabatic inversion (also called adiabatic fast passage or adiabatic rapid passage) is a common means of inverting spins in magnetic resonance experiments. This inversion is best understood through the rotating reference frame that corresponds to the spins’ precession, and I will describe this rotating frame in further detail shortly. Adiabatic inversions can have many advantages over other inversion techniques. For example, π-pulses are a common magnetic resonance inversion method, however, their efficiency is very susceptible to variation in the alternating field $B_1$.

An adiabatic inversion relies on what is known as the adiabatic theorem which is a general theorem that applies to many systems (not just spin). For our purposes however,
in the context of a spin system subject to a Zeeman Hamiltonian, this theorem states that if the direction of the magnetic field $\vec{B}$ is varied slowly enough (compared to the spin precession rate $\omega = \gamma B$) and if the spin starts in an eigenstate of the system (up or down, in our case), then the spin will simply follow the slowly varying field and remain in that eigenstate. Figure 2.5 demonstrates this concept. A proof of the adiabatic theorem for this spin system can readily be found [13,33], which provides further understanding of why the spin $\vec{S}$ follows the field $\vec{B}$ in this situation.

![Diagram illustrating the adiabatic theorem for a spin in a slowly-varying magnetic field $\vec{B}$. The magnetic field $\vec{B}$ is rotating in the $z$-$y$ plane at a rate $\omega_r$. If $\omega_r \ll \omega$ where $\omega = \gamma B$ is the Larmor precession rate of $\vec{S}$, then $\vec{S}$ will follow $\vec{B}$ in a small-angled cone (in green), and the size of the cone angle depends on the relative sizes of $\omega$ and $\omega_r$.]

Figure 2.5: Diagram illustrating the adiabatic theorem for a spin in a slowly-varying magnetic field $\vec{B}$. The magnetic field $\vec{B}$ is rotating in the $z$-$y$ plane at a rate $\omega_r$. If $\omega_r \ll \omega$ where $\omega = \gamma B$ is the Larmor precession rate of $\vec{S}$, then $\vec{S}$ will follow $\vec{B}$ in a small-angled cone (in green), and the size of the cone angle depends on the relative sizes of $\omega$ and $\omega_r$.

With this theorem in mind, we can now consider how an adiabatic inversion is carried out in magnetic resonance. In the previous section, I described the basics of magnetic resonance of a paramagnetic spin. The applied field $B_0$ quantizes the spin to be either parallel or anti-parallel to itself, and the perpendicular alternating field $B_1$ provides a perturbation. The
\(B_1\) field is often broken up into two counter rotating fields:

\[
\begin{align*}
\vec{B}_R(t) &= B_1(\cos \omega t \hat{x} + \sin \omega t \hat{y}) \\
\vec{B}_L(t) &= B_1(\cos \omega t \hat{x} - \sin \omega t \hat{y})
\end{align*}
\] (2.11)

As the spin precesses, its axis will rotate in the direction of one of these components. It can also be shown that the other component, which rotates in the other direction, can be neglected in understanding the behavior of the spin.

In order to analyze this more generally, we will evaluate situations in which the precession frequency of the spin and the frequency of \(\vec{B}_1\) are not necessarily identical. Therefore, I will denote the spin’s precession frequency as \(\omega_0\) and the frequency of \(\vec{B}_1\) as \(\omega\). Next, we will consider the torque \(\vec{\tau}\) on a magnetic moment \(\vec{\mu}\) due to an applied field \(\vec{B}\):

\[
\vec{\tau} = \vec{\mu} \times \vec{B}
\] (2.12)

Thus we can write the equation of motion for the spin which has an associated moment (given by equation 2.1) as:

\[
\frac{d\vec{\mu}}{dt} = \vec{\mu} \times \gamma \left( \vec{B}_0 + \vec{B}_1(t) \right)
\] (2.13)

Next, what is typically done to simplify this analysis is a transformation into a frame that rotates about \(\vec{B}_0\) (the z-axis) at the same frequency as \(\vec{B}_1\). This will remove the time dependence of equation 2.13. I will also chose the x-axis of this rotating frame to coincide with the direction in which \(\vec{B}_1\) points. I will denote the axes in the laboratory frame as \(x, y,\) and \(z\) and the axes of the rotating frame as \(x', y',\) and \(z'\), but note that \(z = z'\) by choice. Then in the rotating frame, equation 2.13 becomes:

\[
\frac{d\vec{\mu}}{dt} = \vec{\mu} \times \gamma \vec{B}_{\text{eff}}
\] (2.14)

where we have introduced the effective field \(\vec{B}_{\text{eff}}\) which is defined as:

\[
\vec{B}_{\text{eff}} = \left( B_0 - \frac{\omega}{\gamma} \right) \hat{z} + B_1 \hat{x}'
\] (2.15)

where the term \(\frac{\omega}{\gamma} \hat{z}'\) comes from the transformation from the lab frame into the rotating frame. Figure 2.6 shows a diagram of the rotating frame with all of these field components.
The spin aligns (or anti-aligns) to the effective field in the rotating frame and precesses about it in a small-angled cone.

Now if the magnitude of $\vec{B}_0$ or $\omega$ were to change, then the magnitude and direction of $\vec{B}_{\text{eff}}$ would also change, and as long as this happens slowly (relative to $\omega_0 = \gamma B_0$) the spin would follow $B_{\text{eff}}$ according to the adiabatic theorem discussed above. Thus by slowly tuning either the frequency of $B_1$ or the magnitude of $B_0$, the direction of the spin can be rotated. When $\omega = \omega_0$ (which is the resonance condition), the spin will have been rotated to point perpendicular to $B_0$. Continuing past the resonance condition, the spin ends up pointing in the negative $z'$ direction. This is an adiabatic inversion.

It is important to note that since the spin remains aligned (or anti-aligned) to the effective field in the rotating frame throughout the inversion process, it’s state can be considered unchanged with respect to that effective field. For example, if the spin were initially anti-aligned to the effective field and then it spontaneously flipped due to some relaxation mechanism, it would then remain aligned to the effective field until it relaxed again or some other perturbation occurred. So for discussions in later chapters where I talk about spins flipping from ‘up’ to ‘down’, I’m not referring to the slow adiabatic inversion of the spins. I am instead discussing instantaneous flips with respect to the effective field the spins follow during adiabatic inversion.

### 2.6 Spin Relaxation

Up to this point I have mentioned that spins can relax via a variety of mechanisms which causes them to flip their orientation. The term ‘relaxation’ originates historically from experiments in which an ensemble of spins are excited above their equilibrium polarization, and then ‘relax’ back to equilibrium through natural processes. Spin relaxation, however, also happens when the ensemble is steady at equilibrium, and it includes instances in which the spins lose energy and drop down to a lower state or absorb energy and move up into an excited state, by some mechanism. In general, there are two main types of spin relaxation: spin-lattice and spin-spin.
Figure 2.6: Diagram illustrating the rotating frame. Relative to the lab frame, this frame rotates at a frequency $\omega$ about the $z$-axis, which is the axis $B_0$ points along. $\omega$ is the frequency of the alternating field $B_1$, and so $B_1$ is stationary along the $x'$-axis. There is also a fictitious field $\frac{\omega}{\gamma} \hat{z}'$ which is a consequence of the transformation of frames. The sum of these three fields is represented by $B_{\text{eff}}$, and the spin precesses about this total field in the rotating frame.

Spin-lattice relaxation is a relaxation of the longitudinal component of the spin (the component parallel to the applied field direction). Typically this happens when the spins exchange energy with their surrounding environment, such as the crystal lattice they are coupled to. One common method for observing spin-lattice relaxation is to rotate the spins $90^\circ$ and then watch the net polarization (magnetization) recover back to thermal equilibrium. Spin-lattice relaxation is characterized by the spin-lattice relaxation time $T_1$ which is the time scale of the exponential recovery.

Spin-spin relaxation is a relaxation of the transverse components of the spins’ state with respect to each other. This is typically described by a dephasing of the transverse phase of the spins. This has been observed conventionally by rotating the spins $90^\circ$ and then watching the exponential decay in the transverse magnetization. The signal is usually detected through an induction coil which is positioned to pick up the oscillating magnetization as
it precesses in the transverse plane. Spin-spin relaxation is characterized by the spin-spin relaxation time $T_2$ which is the time scale of the exponential decay.

Since the MRFM experiments I performed only measure the longitudinal component of the spin, I will focus mainly on spin-lattice relaxation mechanisms, and I will quickly review two of these that are common in many materials: the direct process and the Raman process [3,34]. There are other well-known relaxation mechanisms that I won’t cover here including: the Orbach process, a three-phonon process, collision processes, local mode process, etc.

In the direct process, the spin’s energy changes when it emits (or absorbs) a single phonon into (or from) the lattice. One necessary requirement for this, however, is that the energy splitting of the spin’s states must correspond to a frequency below the Debye cutoff ($E_\uparrow - E_\downarrow \leq \hbar \omega_D$). This gives the direct process a signature by which you can identify it. If you vary the temperature of the lattice, you will see a sudden change in $T_1$ as the Debye temperature transitions past this condition [34].

The Raman process is a two-phonon process. A spin in the excited state can absorb a phonon, and then emit a second phonon of higher energy which relaxes the spin into the ground state. The condition for this to happen, of course, is that the difference in the phonon frequencies must correspond to the energy splitting of the spin ($E_\uparrow - E_\downarrow = \hbar \omega_1 - \hbar \omega_2$). It may seem confusing that the excited spin can absorb a phonon, when it is already in the highest energy spin state that we have defined thus far. However, this is treated as a temporary, virtual transition of the spin into an intermediate level, and must be followed by the emission of the second phonon. Here I have described the Raman process for transitioning an excited spin into the ground state, but the opposite transition is also possible by a similar Raman process.

2.7 Spin Diffusion

Spin diffusion is a type of spin transport, and spin transport is a high-interest research topic because it is an important element for many spin-based devices. Many times when people discuss spin diffusion they are describing a metallic system in which the spins diffuse
via itinerant electrons that are free to move within the metallic material. Here I will review a different form of spin diffusion that occurs in insulating paramagnetic materials. This diffusion drives the observed spin lifetime behavior for the measurements I present in Chapter 5.

Figure 2.7: Diagram illustrating the flip-flop mechanism. Two neighboring spins with opposite orientation flip-flop. Initially the spin on the right is up and the right one is down, but after the flip-flop the left one is down and the right one is up. The dashed lines emanating from the spins are contours of the spins’ magnetic fields which illustrate the dipolar coupling between them.

This well-known type of spin diffusion relies on what is called the dipolar flip-flop mechanism [20]. A flip-flop is the simultaneous flip of two neighboring spins that have opposite orientation. It is their dipolar coupling that leads to the exchange of their spin states. For two spins, labeled 1 and 2, the dipolar Hamiltonian is conventionally written as [20]:

$$\hat{H}_D = \frac{\mu_0 h^2 \gamma_1 \gamma_2}{4\pi} \left( \hat{A} + \hat{B} + \hat{C} + \hat{D} + \hat{E} + \hat{F} \right)$$

(2.16)

where $\gamma_1$ and $\gamma_2$ are the gyromagnetic ratio of spin 1 and spin 2, respectively, and $\hat{A}$ through $\hat{F}$ represent six separate components of the dipolar interaction. I will not go through all
six of these; however, the $\hat{B}$ term is responsible for the flip-flop mechanism:

$$\hat{B} = -\frac{1}{4} \left( \hat{S}_1^+ \hat{S}_2^- + \hat{S}_2^+ \hat{S}_1^- \right) (1 - 3 \cos^2 \theta) \quad (2.17)$$

where $\hat{S}_i^+$ and $\hat{S}_i^-$ are conventional raising and lowering operators for spin $i$, which increase or decrease the spin’s state, respectively. The angle $\theta$ is the polar angle between the spins with respect to the applied field. Figure 2.7 illustrates a flip-flop transition for two neighboring spins.

Successive flip-flop events between an ensemble of spins can result in the transport of spin information throughout the ensemble. You can imagine this as a domino effect, however, it happens diffusively, in a random walk fashion. This random walk diffusive behavior is a well-understood phenomena, and can be modeled as a continuum in the limit that the ensemble is very large. In chapter 5, however, I will show that this model breaks down when the spin ensemble is small, and that a discrete model can be used to characterize the system.

### 2.8 Power Spectral Density

Everything in this chapter up until this point has covered some essential spin physics which is necessary for understanding some of the later material I will present. However, I will now introduce a mathematical tool known as the power spectral density (PSD) of a quantity, which is necessary for understanding some of the later analysis. The PSD is particularly useful at describing the average fluctuations of a signal $x(t)$ (some time-varying quantity) within the frequency domain (hence spectral).

In signal analysis and statistics, the term ‘power’ often refers to the square of a quantity (i.e. $x^2$) [35], not an actual physical power (i.e. physical energy per unit time). Many signals are measured as a voltage, and power is proportional to voltage squared, however, even when the signal is not a voltage, but just some arbitrary signal, its square value is often referred to as a power in a statistical sense. Similarly, the total energy of a signal is
usually defined by integrating up this square value over all time:

$$E = \int_{0}^{\infty} |x(t)|^2 dt$$  \hspace{1cm} (2.18)

Notice that this makes sense in terms of units, since energy is power multiplied by time. Sometimes it is useful to look at the energy of a signal within a narrow time interval. For example, transient signals are often analyzed this way. Sometimes signals are fairly constant in terms of power and it is more useful to look at the average value. We can define the average power of the signal by dividing out the time from the total energy:

$$P = \lim_{T \to \infty} \frac{1}{T} \int_{0}^{T} |x(t)|^2 dt$$  \hspace{1cm} (2.19)

which is equivalent to the average square value $\langle |x(t)|^2 \rangle$. Finally, we may want to look at how the power of our signal is distributed across different frequencies. This typically invokes Fourier analysis, but for many signals, the ordinary Fourier transform does not exist, and so a truncated Fourier transform $\tilde{x}_T(f)$ can be defined as:

$$\tilde{x}_T(f) = \sqrt{\frac{1}{T}} \int_{0}^{T} x(t)e^{-2\pi if t} dt$$  \hspace{1cm} (2.20)

Then, we can use this to define the average power as it is distributed across the frequency domain, which is the PSD. I will denote the PSD of the signal $x$ as $S_x$ which is:

$$S_x(f) = \lim_{T \to \infty} \langle |\tilde{x}_T(f)|^2 \rangle$$  \hspace{1cm} (2.21)

here $\langle \ldots \rangle$ indicates expectation value or average over time. In section 2.3 I described the statistical fluctuations of the spins which is what I measure as the spin signal in the MRFM experiment. These fluctuations are measured by analyzing the PSD of the cantilever frequency signal, and I will explain this in greater detail in chapters 3 and 4.

Another useful concept to keep in mind, is that the total energy of the signal (given by equation 2.18) can be calculated equivalently in the time or frequency domain. This is known as Parseval’s theorem:

$$\int_{-\infty}^{\infty} |x(t)|^2 dt = \int_{-\infty}^{\infty} |\tilde{x}(f)|^2 df$$  \hspace{1cm} (2.22)
Chapter 3

The MRFM Experimental Setup

3.1 Overview of the Setup

In this chapter, I will go through the experimental setup I used for taking MRFM measurements. This MRFM probe is custom-made and has many sensitive components which require delicate handling as well as strict cleanliness protocols in order to maintain the probe’s operation. These technical challenges are one of the most difficult aspects of the MRFM experiment. Figure 3.1 is an image of myself working on the probe. Directly in front of me is the head of the probe which is suspended by three springs to reductive vibrational noise. The probe head contains all of the critical components of the probe. The four main components of the MRFM experiment include a custom-made ultra-soft silicon cantilever with a magnetic tip, a resonance coil for providing microwaves, a laser interferometer for detecting the displacement of the cantilever, and a sample with (usually paramagnetic) spins. Figure 3.2 illustrates the geometry of the MRFM setup. For scanned experiments (including imaging) it is necessary to move the sample relative to the spin-detecting cantilever, and for this I use two piezo-based positioners (for both coarse and fine positioning). Although it is not necessary in general, the temperature of the MRFM experiments I performed was approximately 4.2 K, where thermal noise is small, and this is achieved with a low-temperature cryostat filled with liquid helium. In the following sections, I will go through these components in detail to emphasize their purpose and how they function in the MRFM experiment.
Figure 3.1: Image of myself working on the probe. In the lower left, the head of the probe which contains all of the sensitive components of the experiment is suspended by a set of 3 springs. This is often referred to as the hanging probe. This is clamped into a stainless steel block which holds it so that I can work on it. Clearly visible is a thick copper braid that thermally sinks the hanging probe to the rest of the probe body. Also visible is a large silver-colored spring-like cable going down to the hanging probe. This is the microwave cable that delivers power to the microwave coil, and its spring-like shape is for minimizing mechanical coupling and thus vibrational noise. Not seen in the image is the vacuum can that seals up the hanging probe during the experiment. In this image, I am tightening a screw that holds the microwave coil in place. Behind me are two instrument racks that hold most of the instruments needed to run the experiment.
3.2 Ultrasoft Cantilevers as High Sensitivity Force Detectors

We use IBM-style ultra-soft cantilevers [8] as force detectors for the MRFM experiment. These are single-crystal silicon cantilevers that are 90 \( \mu m \) long, about 2 \( \mu m \) wide, and 100
nm thick. Near the end of the cantilever is an octagon-like pad region which is used for laser interferometry and has a width of about 8 µm, and below this is a thicker mass-loaded region that is about 4 µm wide which serves to suppress the cantilever’s higher order modes of oscillation. Figure 3.3 shows an image of the ultrasoft cantilevers which are attached to a silicon chip. In the experiment, the cantilever is driven into oscillations through mechanical pulses applied using a piezoelectric transducer.

The ultrasoft cantilever (and its magnetic tip) is absolutely the most essential component of the MRFM experiment. It is also one of the most fragile components which necessitates the procedures that increase the technical difficulty of the experiment. See appendix A for more of the practices and procedures for storing and handling ultrasoft cantilevers. The main advantage of the ultrasoft cantilever is its very low spring constant, \( k \approx 100 \mu N/m \) in combination with its frequency, \( \omega_0 \approx 10^4 \) and relatively high quality factor \( Q \approx 10^4 \). I will soon explain how this allows for the detection of forces from very small spin ensembles.

The magnetic tip of the cantilever is actually a small micron-sized particle which is glued on. I will discuss the magnetic particle in more detail in the next section, but for now, I will just say that this tip produces an inhomogeneous field \( \bar{B} \) which couples to the spins in the sample. Consider the force on the magnetic tip of the cantilever from a single spin located at position \( \bar{r} \):

\[
\vec{F}(\bar{r}) = \bar{\nabla} \left( \vec{\mu}(\bar{r}) \cdot \vec{B}(\bar{r}) \right)
\]

To a good approximation, the spins measured in the experiment are parallel or anti-parallel to the applied field \( \vec{B} \) so the dot product is trivial. Also, the cantilever can only respond to forces in the direction that it bends (to first order), which I will denote as the \( x \)-direction in the geometry of the experiment. So equation 3.1 simplifies to:

\[
\vec{F} = \mu_B \vec{\nabla}_x |\vec{B}| = \mu_B \frac{\partial |\vec{B}|}{\partial x} \hat{x}
\]

where I have dropped the \( (\bar{r}) \) notation for simplicity, and I have set \( \mu = \mu_B \) since \( g_e \approx 2 \). The \( x \) component of the gradient of the magnitude of the magnetic field is \( \frac{\partial |\vec{B}|}{\partial x} \) and I will simply label this \( G \), for gradient. Typically in the MRFM experiment, \( G \approx 1 \text{ G/nm} \) (10^5...
Figure 3.3: Image of ultra-soft cantilevers provided by collaborators in Switzerland [36]. More details on these cantilevers are provided at the end of this section. a) A zoomed-out view of the chip that holds 6 cantilevers. b) A zoom-in of the 6 cantilevers on the end of the chip. The lengths of the cantilevers in microns are etched into the chip. The 90 \( \mu \text{m} \) cantilever on the far right is the only one that is suitable for the MRFM experiment due to the geometry of the setup. c) A zoom-in of a 90 \( \mu \text{m} \) cantilever. The interferometry pad, mass-loaded region, and narrow tip are all clearly visible.

\[ F \sim 1 \text{aN} \]

\( \mu_B = 9.274 \times 10^{-24} \text{ J/T} \), we have a force for a single spin \( F \sim 1 \text{ aN} \). So can an ultrasoft with the \( k \) and \( Q \) that I listed earlier measure this small of a force? To answer that, we need to look at the noise in the experiment, which I will go through shortly.
Cantilevers are typically modeled as harmonic oscillators. The displacement of the cantilever responds linearly to applied forces, just like a spring, and this is characterized by the spring constant $k$ of the cantilever, and is known as Hooke’s law:

$$F = -kx$$  \hspace{1cm} (3.3)

Here, the minus sign simply keeps track of the fact that the restoring force $F$ is in the opposite direction of the displacement $x$. Then, according to Newton’s second law this becomes:

$$m\ddot{x} = -kx$$ \hspace{1cm} (3.4)

To find solutions for $x(t)$ that satisfy this, the following ansatz is typically chosen:

$$x(t) = x_{pk} \sin(\omega t)$$ \hspace{1cm} (3.5)

where $x_{pk}$ is the peak amplitude of the cantilever oscillation (which is typically $\sim 100$ nm) and $\omega$ is the cantilever’s angular frequency. Plugging equation 3.5 into 3.4 we have:

$$-m\omega^2 x_{pk} \sin(\omega t) = -kx_{pk} \sin(\omega t)$$ \hspace{1cm} (3.6)

which gives us the frequency of the cantilever in terms of its mass and spring constant:

$$\omega_0 = \sqrt{\frac{k}{m}}$$ \hspace{1cm} (3.7)

I should note here that this mass $m$ is not the entire mass of the cantilever, but just the effective mass [27, 37] which is approximately $33/140$ of the mass of the cantilever plus all of the mass-loaded region, which is near the tip of the cantilever.

Like most real systems, in addition to the restoring force ($kx$), the cantilever has a damping force and is also driven by an external force. Therefore we expand equation 3.4 to give us the damped, driven, harmonic oscillator equation:

$$m\ddot{x} + c\dot{x} + kx = F$$ \hspace{1cm} (3.8)

Here, $c$ is the viscous damping coefficient, and $F$ is the driving force. Note that the damping
term goes like the first derivative of $x$, which means it is in quadrature, or 90 degrees out of phase. So if we plug in equation 3.5 we have:

$$-m\omega^2 x_{pk} \sin(\omega t) + c\omega x_{pk} \cos(\omega t) + k x_{pk} \sin(\omega t) = F_s \sin(\omega t) + F_c \cos(\omega t)$$  \hspace{1cm} (3.9)$$

where I have expanded the driving force to first order into in-phase and quadrature components $F_s$ and $F_c$, respectively. In the experiment, the cantilever is driven to steady state oscillations using a piezoelectric drive which would be the largest component of the $F_c$ term for optimal drive efficiency. Algebraically, this can be seen as counteracting the damping term. When MRFM measurements are taken, the spins are modulated in phase with the cantilever oscillation, and therefore contribute to the $F_s$ term. I will discuss the force from the spins in greater detail later, but for now we can see that this can be grouped with the spring constant term $k x_{pk} \sin(\omega t)$, which means the modulation of the spins effectively changes the compliance of the cantilever:

$$k' = k + \delta k$$

$$\delta k = \frac{F_s}{x_{pk}}$$  \hspace{1cm} (3.10)$$

This, in turn, modifies the frequency of the cantilever, which can be seen by taking the derivative of equation 3.7 with respect to $k$:

$$\frac{d\omega}{dk} = \frac{1}{2} \sqrt{\frac{m}{k}} \frac{1}{m} = \frac{1}{2} \frac{1}{k} \frac{1}{\sqrt{k}} \frac{1}{m} = \frac{1}{2} \frac{\omega}{k}$$  \hspace{1cm} (3.11)$$

which we can re-write as:

$$\frac{d\omega}{\omega} = \frac{1}{2} \frac{dk}{k}$$  \hspace{1cm} (3.12)$$

This means that we can detect the forces from modulated spins by measuring the frequency shift of the cantilever, and indeed this is the basis for the force detection in the MRFM experiments I performed. Earlier I showed that the force from a single spin is $\sim 1$ aN. Then with regards to equations 3.10 and 3.12, this corresponds to an effective shift in the spring constant of $\delta k \sim 10^{-11}$ N/m, which approximately corresponds to $\delta \omega \sim 1$ mHz for $\omega \sim 10$ kHz. Now let’s return to the question of whether or not it is possible to detect forces on
the order of 1 aN by looking at the primary sources of noise in the experiment.

First I will describe the thermal noise of the cantilever, because at a given temperature (like 4.2 K where the experiment is typically performed) there is no getting around this thermal noise. In fact one of the goals for each experiment is to ensure that you are working in a regime in which thermal noise is the limiting factor, because that means you have optimized everything you can in terms of noise sources. To determine this thermal noise, let’s return to equation 3.9. It is much easier to rewrite this in terms of the undamped resonant frequency of the cantilever \( \omega_0 \) (equation 3.7) and the quality factor \( Q = \frac{k}{\omega_0} \):

\[
\ddot{x} + i\omega_0 \frac{Q}{\omega_0} \dot{x} + \omega_0^2 x = \frac{\omega_0^2}{k} F
\] (3.13)

The quality factor \( Q \) is a dimensionless quantity that characterizes the efficiency of a resonator (the cantilever in this case). Later in this section, I will discuss the quality factor more, but for now I will just give a simple definition for it. \( Q \) is the ratio of the energy stored in the resonator to the energy dissipated each cycle (which is why it is inversly proportional to the damping, \( c \)). For high values of \( Q \), this is also approximately the same as the ratio of the resonant frequency \( \omega_0 \) to the bandwidth \( \Delta \omega \) (which is the full width at half max of the resonance peak in the frequency domain):

\[
Q = 2\pi \times \frac{\text{total energy stored}}{\text{energy dissipated per cycle}} \approx \frac{\omega_0}{\Delta \omega}
\] (3.14)

The piezoelectric drive system is designed to provide self-excitation of the cantilever at its current frequency. This means if the cantilever’s frequency suddenly changes, the piezoelectric drive also changes to match the new frequency. Driving the cantilever this way results in a steady state oscillation such that the energy dissipated each cycle is supplied by the drive force \( F(t) \) (in accordance with it’s quality factor).

We can convert equation 3.13 from a differential equation to an algebraic one by taking the Fourier transform of it. I will denote the Fourier transform operation as \( \mathcal{F} \). This yields:

\[
-\omega^2 \tilde{x} + i\omega_0 \frac{Q}{\omega_0} \tilde{x} + \omega_0^2 \tilde{x} = \frac{\omega_0^2}{k} \tilde{F}
\] (3.15)
Note that taking the Fourier transform also allows us to work towards an expression for the PSD (see section 2.8) of the cantilever signal which describes the fluctuations (or noise in this case). Here, \( F(x) = \tilde{x} \) and \( F(F) = \tilde{F} \) and \( i = \sqrt{-1} \). We have also used \( F(\dot{x}) = i\omega \tilde{x} \) via integration by parts. Next, solving equation 3.15 for \( \tilde{x} \) we have:

\[
\tilde{x} = \frac{Qf_0^2\tilde{F}}{kQ(f_0^2 - f^2) + ikf_0f}
\]  

(3.16)

Here I have replaced the angular frequencies \( \omega_0 = 2\pi f_0 \) and \( \omega = 2\pi f \). Next, to find the PSD, we want to look at the mod squared of this by multiplying both sides by its complex conjugate. We also need to take the limit of this as \( T \) goes to infinity. Remember that \( T \) is contained within the definition of the transform. This gives us:

\[
\lim_{T \to \infty} \frac{1}{T}|\tilde{x}|^2 = \lim_{T \to \infty} \frac{1}{T} \frac{Q^2f_0^4|\tilde{F}|^2}{k^2Q^2(f_0^2 - f^2)^2 + k^2f_0^2f^2}
\]  

(3.17)

Now the right hand side of this contains the PSD of the force, so we can replace that. For this, note that the time averaging of \( \tilde{F} \) was handled when we took the Fourier transform over all time. Similarly, the left hand side of equation 3.17 is the PSD of the cantilever displacement, and if we integrate this over all \( f \), it can be re-written as \( \langle |x(t)|^2 \rangle \) according to Parsevel’s theorem (see equations 2.19 and 2.22). This yields:

\[
\langle |x(t)|^2 \rangle = S_F \int_0^\infty \frac{Q^2f_0^4}{k^2Q^2(f_0^2 - f^2)^2 + k^2f_0^2f^2}df
\]  

(3.18)

Here the \( S_F \) was pulled out of the integral because thermal force noise is a constant with respect to frequency (this is known as ‘white’ noise). Now if we evaluate the integral we find:

\[
\langle |x(t)|^2 \rangle = S_F \frac{2\pi f_0Q}{4k^2}
\]  

(3.19)

To make the right hand side more useful, we can use Hooke’s law and the equipartition theorem

\[
\frac{1}{2}k\langle x(t)^2 \rangle = \frac{1}{2}k_BT
\]  

(3.20)
as a substitution to find the thermal force PSD:

$$S_F = \frac{4k k_B T}{\omega_0 Q}$$

(3.21)

Typical measured values for the cantilever are: $k \sim 100 \, \mu N/m$, $Q \sim 30000$, and $\omega_0 \sim 2\pi \times 3000 \, \text{Hz}$. Plugging these into equation 3.21 we have $\sqrt{S_F} \sim 3.5 \, \text{aN/}\sqrt{\text{Hz}}$, which means that in unity bandwidth the cantilever sensitivity is thermally limited to about 3.5 attoNewtons, which is on the order of a force from a single spin in the experiment.

Figure 3.4 shows an example of the measured thermal force noise of the cantilever at 4.2 K. The plot shows $\sqrt{S_F}$ as a function of frequency. This is actually measured by looking at the frequency dependence of the fluctuations in the cantilever’s frequency, and then converting these frequency fluctuations to force fluctuations according to equations 3.10 and 3.12. This can be confusing, so I will try to clarify this further. Imagine we had a time record of the cantilever’s frequency. This record would fluctuate nominally about the mean cantilever frequency and we can imagine the frequency at which these fluctuations occur (similar to a Fourier transform of that record). To be clear, there are two uses of the word frequency here. We are looking at the spectrum of frequencies at which the cantilever frequency is fluctuating.

This thermal force noise causes the cantilever’s displacement to fluctuate enough that it can clearly be seen in the cantilever signal, on an oscilloscope for example. By measuring these fluctuations $\langle x(t)^2 \rangle$ at different temperatures $T$, you can determine a value for the spring constant $k$ via equation 3.20. Figure 3.5 shows measurements I took of the cantilever’s mean square displacement versus temperature to determine a value of $k = 114 \, \mu N/m$.

The next major source of noise to consider in the MRFM experiment is the detection noise. Here I mean detection in the sense of using the laser interferometer to detect the position of the cantilever. I will discuss this detection noise more in section 3.6, when I describe the laser interferometer, but for now I will just say that typically one can adjust parameters in the experiment such that the detection noise is less than the thermal noise limit.

The last source of noise that I will quickly mention is non-contact friction of the can-
Figure 3.4: Thermally-limited cantilever frequency noise. The cantilever’s frequency, which is converted to force, is fluctuating at a spectrum of frequencies. This spectrum is the horizontal axis of the figure. This measurement was taken at 4.2 K, and the thermal noise at this temperature is around $4 \text{ aN/} \sqrt{\text{Hz}}$, which is in agreement with equation 3.21 for this cantilever. The noise spike near 4 Hz is likely due to some vibration noise in the cantilever or spurious coupling of the cantilever drive to something else in the probe. These noise spikes are easily avoided by setting the signal frequency in the iOSCAR detection protocol, which I will describe further in chapter 4. After about 40 Hz, the noise floor starts to steadily rise to $10 \text{ aN/} \sqrt{\text{Hz}}$ and beyond. This is due to shot noise of the laser interferometry, which can be adjusted by changing the laser’s power and RF mixing.

tilever with the sample surface. This is primarily due to electrostatic charge that can build up on the cantilever, and usually goes like $1/f$. To minimize this noise, I used deionizers manufactured by NRD. Specifically I used the Nuclecel P-2063 and 2U500 models which are radioactive sources that have 31.5 mCi and 0.5 mCi of activity, respectively. The radioactive source is polonium-210 which has a half-life of 138 days, so it must be replaced every 6 months to a year to remain effective. The alpha decay of the polonium is responsible for
Figure 3.5: Plot of mean square cantilever displacement versus temperature. The mean square displacement of the cantilever is shown for three different temperatures: 4.2 K, 77.4 K, and 294 K. These correspond to three stable temperature situations: liquid helium, liquid nitrogen, and room temperature, respectively. In this case, the mean square displacement is the same as the variance since the mean displacement is zero. The measurements were taken in the absence of an applied drive to the cantilever. Instead, thermal energy is responsible for driving the cantilever. There are 40 measurement points for each of these temperatures, and each variance measurement point corresponds to the variance of 5 seconds of cantilever signal. The large data points are the average of the 40 measurements for each temperature, and so correspond to the variance of 200 seconds of cantilever signal. The black line is a power law fit of the form: $\sigma^2(T) = aT^b + c$ with fit constants: $a = 1.21 \times 10^{-19}$ m\(^2\)/K, $b = 1.05$, and $c = -4.92 \times 10^{-19}$ m\(^2\). As seen by the value of $b$, the fit is nearly linear, in agreement with equation 3.20, and the value of $a$ corresponds to a cantilever spring constant of $k = 114$ µN/m.

how the deionizers operate. The expelled helium nuclei scatter off of many air molecules within a vicinity of about 1 cm from the source. These air molecules become ionized as a result and the cantilever, or any other charged object in that region, attracts ions with a charge opposite of itself, and repels ions of the same charge. This results in neutralization
of the charge.

If a cantilever has not been properly deionized, it will have an extremely large interaction with the sample surface. I have observed the frequency of charged cantilevers increasing by a factor of 3 or more as they approach the sample, as well as huge fluctuations (10s or even 100s of Hz) when the cantilever is fixed at some typical operating distance above the sample. When this happens, the experiment has to be restarted, which typically results in a loss of about 1 to 2 weeks in the time frame of the experiment.

Figure 3.6: Plot of cantilever ring-down measurement. The plot shows the average envelope of the cantilever oscillation signal and the exponential fit for 20 iterations of a 5 second ring-down. The fit is of the form of equation 3.22, and the fit parameters are: $x_0 \approx 0$ nm, $x_{pk} = 52.4$ nm, and the measured Q-factor is approximately 30,400. The measured frequency of the cantilever is 3.71 kHz, and the exponential time constant for the decay is $\tau = 2.606$ seconds. The deviation of the data from the exponential fit (most notably in the first 0.2 seconds or so) is likely due to the non-linear response of the cantilever displacement signal which is worse for large displacements. This non-linear behavior is discussed in detail in section 3.6.
Since having a large cantilever quality factor $Q$ is important for reducing the noise and thus detecting a signal, it is necessary to choose a cantilever initially that has a high $Q$, and take precautions to ensure the $Q$ remains high. In conjunction with the thermal force noise I just covered (equation 3.21), I discuss the signal to noise ratio (SNR) of the spin signal later in section 4.4. The main conclusion of this with regards to $Q$ is that the amount of time needed to acquire a given signal is proportional to $Q^{-2}$. Therefore if the $Q$ drops by a factor of 4, for example, it would take 16 times longer to get an equivalent signal as before. Thus, good cantilevers can become essentially useless if their $Q$ drops significantly, and this seems to happen slowly over time, and can happen suddenly if they are exposed to some kind of contamination. I’ve observed that even occasional exposure to atmosphere for limited amounts of time can ruin good cantilevers.

The $Q$ factor of the cantilever is usually measured via a ring-down method. This is done by driving the cantilever with the piezoelectric self-excitation system to a relatively large amplitude ($\sim 150$ nm peak-to-peak), and then turning off the drive and recording the exponential decay of the cantilever signal. The exponential behavior of the decay can be understood through the definition of $Q$ (equation 3.14), which states that each cantilever cycle results in a loss of a fraction of the stored energy. So $Q$ is found by fitting to this exponential decay:

$$x(t) = x_0 + x_{pk} \exp\left(\frac{\pi t f_0}{Q}\right)$$  \hspace{1cm} (3.22)

When the ring-down is done, the cantilever must first decay to a displacement value which is much less than the maximum displacement so that the conversion between the readout voltage and the displacement approach a linear regime. Therefore, in equation 3.22, the value of $x_{pk}$ is usually much less than the maximum amplitude. I explain this in more detail when I talk about the interferometer used to detect the cantilever displacement in section 3.6. Figure 3.6 shows a plot of this type of ring-down measurement for a cantilever with a $Q \approx 30,400$ which was measured at $T = 4.2$ K.

One of the problems I faced in working with ultra-soft cantilevers, is that they sometimes bend significantly in vacuum. If the bend is significant enough, it can render the cantilever
Figure 3.7: Micrographs of a cantilever bending in vacuum due to contamination. This is an IMB cantilever [8], not one from our collaborators in Switzerland.  

a) Micrograph of a side view of an ultra-soft cantilever in atmosphere taken with an optical microscope. The straight blue line below the cantilever was added to the image for reference, and is approximately 100 \( \mu m \) long.  
b) Micrograph of the same cantilever in vacuum, which is bending about a point mid-way down the cantilever. This image was taken with a scanning electron microscope (SEM). Again, the straight blue line was added for reference, and is approximately 100 \( \mu m \) long. The end of the cantilever is bent away from the straight blue line by approximately 13 \( \mu m \) as shown by the black double-arrow.  
c) Zoom-in of the middle of the cantilever image in panel (b). The image’s colors have been inverted, and the brightness and contrast have been adjusted to enhance the visibility of the contamination in the center of the cantilever, which is located at the inflection point of the cantilever’s bend.

useless, because it makes aligning the laser to it impossible. You may start off having excellent visibility under atmospheric conditions, but then they immediately lose some or all visibility when you pump the system down to vacuum. Figure 3.7 shows an example of a cantilever straight in atmosphere, but bending in vacuum. You can also see some sort of contamination around the middle of the cantilever at exactly the point where the bending is the greatest. It seems that most ultra-soft cantilevers are susceptible to this issue, because
after some time, most develop moderate to severe bending issues.

Although I never fully determined the cause of this bending behavior, I believe it is likely due to one of two possibilities. Either the surface of the silicon is oxidizing [36, 38] or there is adsorption of organic polymers (or surfactants) on the surface [38]. The oxide or surfactant is likely to be reacting with the water vapor in the air either hydrophobically or hydrophilically, and this creates more surface tension on one side of the cantilever which results in bending. Since the image in figure 3.7 shows visible contamination near the middle of the cantilever, I believed that surfactants were the likely cause.

With this in mind, I baked two cantilevers in a vacuum furnace at 250° C for 2 hours, in an attempt to blast off any contamination. However, one of these cantilevers broke in the process, and the remaining cantilever still showed significant bending after baking. Although these results are not very conclusive, this seems to suggest that the bending is not due to organic surfactants, but rather oxidation.

Ultimately, after many months of struggling with this, the bending issue was solved (or avoided altogether actually) by acquiring a newer set of cantilevers from collaborators Martino Poggio and Christian Degen in Switzerland [36]. The cantilevers shown in figure 3.3 are Swiss cantilevers. So far, these cantilevers do not seem to be prone to bending, and thus maintain high visibility, typically between 60% to 85% while pumping down from atmosphere to vacuum. The Swiss cantilevers also have relatively high $Q$, typically a few tens of thousands, they have a very small spring constant $k$ typically just below 100 $\mu$N/m, and they have a similar resonant frequency $f_0 \approx 3,700$ Hz. This makes them ideal for the MRFM experiment, and an improvement over the original IBM cantilevers. The original IBM cantilevers were used for this experiment since its initial run (over a decade ago), and I attribute the bending issue to the fact that they are so old and have thus developed some sort of contamination, although whether this is from oxidation or adsorbed organic polymers, I'm not sure.

40
3.3 Micron-Sized Magnetic Particle Tip

At the tip of the ultrasoft cantilever, a small (∼ 1 micron) magnetic particle of SmCo$_5$ is glued on. The field from this particle, along with any externally applied field, and the oscillating field from the microwave coil define the resonant spin detection volume of the MRFM measurement. I will discuss the spin detection volume and the bowl-shaped magnetic resonance surface that sweeps out the volume in the next section.

The magnetic particles are prepared by taking a piece of samarium cobalt (∼1 cm) and grinding it with a file. The particles are then glued onto the tip of the cantilever viewed under an optical microscope using glass needles. Figure 3.8 illustrates part of this process, and the full procedure for this is given in Appendix A. After gluing them onto the cantilever, the particles are ion milled using a focused ion beam (FIB). Figure 3.9 shows an example of a particle milled with the FIB into a particular shape that should increase the magnetic gradient of the particle, which is important for having a strong MRFM signal (see equation 3.2).

For several years now, we have used SmCo$_5$ magnets from Dexter Magnetics to make the particles for our cantilevers. A former graduate student, Michael Herman, prepared many cantilevers with particles from different magnets and found that the SmCo$_5$ magnets from Dexter produce particles with high saturation magnetization, $M_s \approx 7 \times 10^5 \frac{1}{\text{Tm}^3}$. One particularly successful cantilever had a particle with a magnetic moment, $m = 3.60 \times 10^{-12} \text{ J/T}$. I will refer to this cantilever as cantilever 11 for short (which is cantilever 11-34-11-90-R, for reference). The moment and saturation magnetization of cantilever 11 correspond to a particle of radius $R \approx 1 \mu$m:

$$M_s = \frac{m}{V} = \frac{m}{\frac{4}{3} \pi R^3} \quad (3.23)$$

Choosing the right size particle is an important step when making a new cantilever for MRFM. After milling them with the FIB, if the particle is too small, the experiment won’t work because the magnetic moment and spin detection volume will also be too small (or non-existent). If the particle is too large, the magnetic gradient within the spin detection
volume will be too small, which in turn reduces the MRFM signal. Over the years, we have found that the particles need to be about 1 or 2 microns in diameter to optimize the MRFM signal. Also, when the particles are about 2 microns in size or less, it is likely that they will be single domain ferromagnetic particles [39]. However, if the SmCo$_5$ particle is too small ($\lesssim 300$ nm) the particle loses it’s coercivity and essentially becomes paramagnetic [39] which would be unusable for doing MRFM.

Another consideration for selecting a good magnetic particle for the experiment is the particle’s anisotropy. High anisotropy fields are important for reducing magnetic field fluc-
Figure 3.9: Micrographs of an ion-milled magnetic particle taken with an SEM. The micron-sized magnetic particle is glued onto the tip of an ultra-soft cantilever. a) Micrograph of the particle before any milling has occurred. b) Micrograph of the particle after the bottom has been milled with a focused ion beam (FIB). c) Micrograph of the particle after the front has been cut twice: once vertically, and once at an angle that removed the top right corner as seen from this side view.

tuations from the particle (which arise from thermal fluctuations within the particle). These field fluctuations can artificially reduce the lifetime of the spins being measured via MRFM,
and therefore SmCo\textsubscript{5} particles with higher anisotropy energy are desirable for the MRFM experiment. Most of the particle’s anisotropy is magnetocrystalline (as opposed to shape anisotropy). The anisotropy field of cantilever 11 was about 2.6 T.

After gluing them onto the cantilever, I used cantilever magnetometry to measure the magnetic moment and the anisotropy field of the SmCo particles [5]. This cantilever magnetometry is a measure of the cantilever’s frequency and equilibrium position as a function of an externally applied field which is colinear to the axis of the cantilever and nominally the axis of the magnetic moment. The applied field produces a torque on the magnetic moment of the particle which acts as an additional restoring force. This effectively increases the spring constant of the cantilever which in turn increases the cantilever’s frequency. One slight complication to this picture arises from the fact that the magnetic moment of the particle will cant by a small angle $\theta$ away from its equilibrium direction (relative to the particle) during the cantilever oscillation. This is due to a competition between the anisotropy and Zeeman energies of the magnetic particle. Appendix B.1 walks through the derivation of the cantilever frequency shift signal for the magnetometry experiment. Figure 3.10 shows the magnetometry setup. The effective length of the cantilever (which is illustrated in red) is defined as the distance between the end of the cantilever and the location to which it always points back to throughout the oscillation. For the fundamental flexural mode of oscillation (which is all we need to consider for this) the effective length is about 72.5% of the length of the cantilever (65.2 microns for a 90 micron cantilever) [40].

To take these measurements, I designed and built a magnetometer whose primary components are an interferometry system with optical fiber and lens, a mechanical clamp for holding the cantilever (with both coarse and fine 3D positioning), and a piezoelectric transducer for driving the cantilever into large oscillations ($\sim 100$ nm). Figure 3.11 shows images of the home-built magnetometer. The magnet I used for this measurement was capable of sweeping from about -7000 G to 7000 G (parallel and anti-parallel to the particle’s moment). In the parallel geometry (positive field values), the applied field exerts a torque of the magnetic particle which helps keep the cantilever aligned and maintains good visibility during the measurement. For negative field values however, the cantilever starts to bend
Figure 3.10: Diagram for cantilever magnetometry. The frequency of the cantilever increases in the presence of an externally applied field $B$ due to the torque on the moment $m$ which effectively increases the spring constant of the cantilever. The effective length of the cantilever is shown in red. The zoom-in of the cantilever tip illustrates that the direction of the particle’s magnetic moment is not static (with respect to the particle) during the cantilever oscillation. Instead, the moment cants away from the equilibrium direction by an angle $\theta$ due to a competition between the Zeeman energy and the particle’s anisotropy.

out of alignment with the laser, and as the field magnitude increases, this eventually results in a complete loss of the interferometer visibility and makes it difficult or impossible to collect data in that range.

Figure 3.12 shows an example of cantilever magnetometry data that I collected with the custom-built magnetometer. For reference, this data was collected on cantilever 826-90-R, which was the 4th Swiss cantilever. I will refer to this as cantilever 4s for short. The data shows a measured moment of $m = 1.79 \times 10^{-12}$ $J/T$ and an anisotropy field of $B_k =$
Figure 3.11: Images of the room-temperature ultrasoft magnetometer. Left: Image of the magnetometer sitting in a rectangular stand. Top right: Image of the magnetometer held in a U-shaped holder. The vacuum can has been removed and the inside of the probe is exposed for working. Bottom right: Image of the end of the probe (which is also visible in the top right panel). The cantilever is placed at the end of the diving board shaped piece and the fiber can be seen going into the bullet-like assembly which has a lens on its end.

4,200 G. These values are much lower than those of cantilever 11 \((m = 3.60 \times 10^{-12} \text{ J/T} \text{ and } B_k = 26,000 \text{ G})\). Comparing these values, it is likely that the magnetic particle on
Figure 3.12: Cantilever magnetometry data. The cantilever’s frequency is plotted as a function of the applied magnetic field. As the field increases, there is a larger torque on the magnetic particle glued onto the tip of the cantilever which acts as a restoring force on the cantilever, thus increasing its frequency. This allows for determination of the magnetic moment $m$ and anisotropy field $B_k$ of the particle, according to equation B.7. Here, the properties of this magnetic particle were found to be $m = 1.79 \times 10^{-12}$ J/T and $B_k = 4200$ G.

cantilever 4s was much smaller than the particle on cantilever 11, and it is not obvious if 4s would have worked well for collecting MRFM data. Unfortunately, before I could attempt to collect MRFM data with cantilever 4s, it broke during an alignment procedure in the probe. Even when tedious precautions are taken, the successful creation of a good working cantilever for MRFM is quite low due to the many delicate procedures involved in preparing the cantilevers, and a lot of time can be wasted throughout this process.

Having measured the magnetic moment of the cantilever particle, we can model the magnetic field (and the gradient) of the particle. The particle’s magnetic field and gradient are an essential component of the MRFM experiment. In the next section, I will go over the
field from the magnetic particle and show how this defines what is known as the resonance bowl, in accordance with the resonance condition. This bowl determines which spins are detected in the experiment.

3.4 Magnetic Resonance Bowl

The resonance bowl is defined as the region of the sample which has a total magnetic field magnitude $B_0$ that corresponds to the resonance condition for the measured spins (also see equation 2.10):

$$\omega = \gamma B_0$$

(3.24)

In the experiment, the frequency $\omega$ is set by the microwave frequency of the coil, which I discuss in the next section. For my measurements, this frequency was $\omega/2\pi = 2.2$ GHz.

Now, if we assume for our calculations that the magnetic particle is approximately spherical, we have for the magnetic field:

$$\vec{B}_{\text{probe}}(\vec{r}) = \frac{\mu_0 m}{4\pi r^3} (3\hat{r}(\hat{m} \cdot \hat{r}) - \hat{m}) = \frac{\mu_0 m}{4\pi r^3} \left(2\cos(\theta)\hat{r} + \sin(\theta)\hat{\theta}\right)$$

(3.25)

Here, I have taken the magnetic moment of the cantilever to point along the cantilever axis in the +$\hat{z}$ direction. Therefore in spherical coordinates, $\hat{m} = \hat{z} = \cos(\theta)\hat{r} - \sin(\theta)\hat{\theta}$. If there is zero applied field, then the total field is given by that from the magnetic particle tip (equation 3.25). Setting these fields equal gives the condition for the resonance bowl in the MRFM experiment:

$$f = \frac{\mu_0 m}{4\pi r^3} |3(\hat{z} \cdot \hat{r})\hat{r} - \hat{z}|$$

(3.26)

If we write this in spherical coordinates, evaluate the magnitude, and solve for $r$ we have:

$$r = \alpha^{-1/3} (3\cos^2(\theta) + 1)^{1/6}$$

(3.27)

Here I have simplified the notation by introducing:

$$\alpha = \frac{4\pi f}{\gamma \mu_0 m}$$

(3.28)
where $\alpha$ has units of inverse volume and $\alpha^{-1/3} \approx 1$ micron for typical parameters in the experiment. Figure 3.13 shows a model of a typical resonance bowl (in red) from a magnetic particle that has a radius $r_p$ of 1.5 microns where the tip-sample separation $d_{t-s}$ is 300 nm. The resonance bowl is a contour of constant field magnitude, which is about 785 G for a frequency of 2.2 GHz. The angle at which the bowl and sample surface intersect is important for some of our calculations and I will denote this as $\theta_i$, which can be found by finding the real solutions of:

$$\alpha^2 (r_p + d_{t-s})^6 = 3\cos^8(\theta_i) + \cos^6(\theta_i)$$  \hspace{1cm} (3.29)

To find the area of the bowl $A$, we can consider the general integral over the surface $S$:

$$A = \int \int_S dA$$  \hspace{1cm} (3.30)

and by noting the symmetry in $\phi$ (about the $z$-axis) we can simply calculate the arc length of the curve of the bowl $L$ from $\theta = \theta_i$ to $\pi$:

$$A = \int_L dl \int_0^{2\pi} r\sin(\theta) d\phi \hspace{1cm} $$

$$= \int_{\theta_i}^{\pi} \sqrt{r^2 + \left( \frac{dr}{d\theta} \right)^2} d\theta \int_0^{2\pi} r\sin(\theta) d\phi$$

$$= \int_{\theta_i}^{\pi} \int_0^{2\pi} (\alpha v)^{-2/3} \sin(\theta) \left( v^2 + w^2 \right)^{1/2} d\phi d\theta \hspace{1cm} (3.31)$$

where $v = 3\cos^2(\theta) + 1$ and $w = \cos(\theta)\sin(\theta)$. For typical parameters in the experiment, the surface area of the bowl that is within the sample is usually several square microns.

In addition to the surface area of the resonance bowl, what is more useful is knowing the volume that the bowl sweeps out in the sample as the cantilever oscillates back and forth. This is the detection volume of the experiment and defines what spins are coupling to the cantilever. Following equation 3.30 we can find this volume by calculating:

$$V = \int \int_S (\vec{x}_e \cdot \hat{n}) dA$$  \hspace{1cm} (3.32)

where $\vec{x}_e = x_{pk} \hat{x}$ is the extrusion vector that is defined by the motion of the cantilever that has a peak-to-peak oscillation amplitude of $x_{pk}$ and $\hat{n}$ is the unit normal vector at any point
Figure 3.13: Model of the magnetic particle, dipolar field, and resonance bowl. The particle is modeled as a sphere in the center with a diameter of 1.5 µm, and a total magnetic moment of \( m = 1.24 \times 10^{-12} \text{ J/T} \) (corresponding to \( M_s \approx 7 \times 10^5 \frac{1}{\text{m³}} \)). The cantilever is not shown. The blue and black lines are a model of the dipolar magnetic field lines due to the magnetic particle only (no external field). The sample is shown as a semi-transparent, grey-green rectangle below the particle, and the separation between the tip of the particle and the sample surface is 300 nm. The magnetic resonance bowl is shown in red. The magnitude of the field is approximately 785 G on the bowl. This corresponds to an electron spin resonance frequency of 2.2 GHz which would match the microwave frequency of the coil (which is also not shown).
on the surface of the bowl. We can calculate \( \hat{n} \) by solving equation 3.27 for \( \alpha \) and taking its gradient:

\[
\hat{n} = \frac{v \hat{r} + w \hat{\theta}}{\sqrt{v^2 + w^2}} \tag{3.33}
\]

where \( \hat{n} \) has a nice form when written in terms of \( v \) and \( w \) which are defined the same as above. Taking the dot product of the integrand gives:

\[
\hat{n} \cdot \vec{x} = \frac{x_{pk} \cos(\phi)}{\sqrt{v^2 + w^2}} (v \sin(\theta) + w \cos(\theta)) \tag{3.34}
\]

and finally combining equations 3.30, 3.31, 3.32, and 3.34 we have an expression for the volume that is swept out by the resonance bowl:

\[
V = \int_{\theta_i}^{\pi} 4 x_e (\alpha v)^{-2/3} \sin(\theta)(v \sin(\theta) + w \cos(\theta)) \, d\theta \tag{3.35}
\]

where the factor of 4 comes from taking the absolute value of the \( \phi \) integral separately so as to avoid adding up ‘negative volume’ inside the integration. Plugging in some typical experimental parameters for the tip-sample separation, resonance frequency, and magnetic moment, the spin detection volume is typically a little less than 1 cubic micron.

### 3.5 Resonance Coil for Providing Microwaves

To provide the oscillating resonant field \( B_1 \) which needs to oscillate at GHz frequencies, I used a microwave coil. The coil was constructed with niobium wire that is 25 \( \mu \)m thick and wound \( 2 \frac{1}{2} \) times into a coil with a diameter of about 200 \( \mu \)m. The inductance of the coil is approximately 2 nH. Figure 3.14 shows an image of the coil.

Before the niobium wire can be wound into a coil, it must first be annealed so that it becomes ductile enough for winding. The wire was annealed in a vacuum chamber by applying about 30 V across the wire for several minutes. During this time the current through the wire causes it to heat up and glow white hot, thus annealing the wire. After annealing and winding, the coil is wirebonded to a patterned sapphire chip (see figure 3.14).

The sapphire has three patterned regions of niobium on it, all of which have a thickness of only 0.4 nm. The first region, is the entire back side of the chip which is used as a
Figure 3.14: Image and diagram of microwave coil. Left: Image of microwave resonance coil. The diameter of the coil is approximately 200 µm, and it has about two and a half windings. Right: Diagram of microwave coil and niobium patterning on sapphire substrate. The coil is wirebonded to the microstripline region on the top of the substrate and also to the grounding plane on the back. The launch end is connected to an SMA launch which goes to the microwave source. There is a capacitive gap between the microstripline region and the launch end region.

ground plane and the coil is wirebonded to this. The second region called the launch end, is 3 mm by 425 µm and is connected to an SMA launcher which connects to the microwave source. The third region is the microstripline which is 1 mm by 3.1 mm and the other end of the coil is wirebonded to this. In between regions 2 and 3 is a 200 µm gap that has a capacitance of about 220 pF. This capacitance was adjusted to achieve impedance matching of the microwave resonator and source.

At 4.2 K, the niobium wire becomes superconducting, and so the impedance matching is only achieved below the niobium critical temperature ($T_c = 9.3$ K). The resonance coil operates at approximately 2.2 GHz, and has a relatively narrow bandwidth of about 8.5 MHz. Then, from equation 3.14, the quality factor of the coil is approximately 260. The resonance of the coil is measured by sweeping the frequency of the sourced microwave power and measuring the reflected power from the circuit. Figure 3.15 shows an example of this
For this scan, the microwave source supplied 1 mW of power down to the coil. Irregardless of the amount of power sourced (as long as the coil remains in the normal state), about 75% (or 6 dB) of the power is lost when the frequency is off resonance due to power absorption throughout the transmission line and resonator circuit. In this particular case, this amounts to about 750 µW, as can be seen in the plot. Another 75% drop (6 dB loss) occurs when the microwave coil comes on resonance around 2.19 GHz. This is the power absorbed by the microwave coil as it generates the $B_1$ field necessary to drive the spins to resonance. In this case this is approximately 180 µW of power. The full width at half max of the dip is about 8.5 MHz.

The sourced power is 1 mW, and there is a 6 dB loss within the total microwave circuit that happens when the coil is both on and off resonance. Thus the baseline reflected power in figure 3.15 is about 250 µW. When the resonance frequency of the coil is matched (at about 2.19 GHz) there is another 6 dB drop in the reflected power, as power is absorbed by the coil to generate the oscillating $B_1$ field that drives the resonance of the measured spins.
The microwave coil is very fragile, but has many benefits over other microwave sources. Although the frequency range is not wide-band, the power absorbed within the narrow band of the coil is very efficient. This allows for relatively strong $B_1$ fields to be generated, on the order of a few gauss, for a relatively low microwave power source. This results in lower heat dissipation in the probe, which is important for the thermal noise of the spin system and other cryogenic aspects of the experiment. Another benefit is that the coil circuit is free-standing in the sense that it is not patterned onto the sample you are measuring. This allows it to be used over and over again for multiple experiments with different samples.

One of the drawbacks to this is that you must take care not to destroy the coil by smashing the sample into it during the experiment. Since the probe is cooled from room temperature down to about 4.2 K, the thermal expansion of the probe system puts the coil at risk for collision. Because of this, the coil has been slightly damaged over the years, and I have had to reshape it with a glass needle. The quality factor of the coil has diminished over the years, and this is likely due to slight damage sustained throughout the experiments.

### 3.6 Laser Interferometry for Displacement Detection

To detect the displacement of the cantilever as it oscillates, the experiment uses laser interferometry. The wavelength of the laser light is 1551 nm. The interferometry setup is shown in Figure 3.16. The incident light is reflected back in two places: the interface at the end of the fiber and the cantilever pad. Figure 3.21 shows how the interferometry setup is integrated into the rest of the experiment. The setup consists of a distributed feedback (DFB) laser, optical fiber, coupler, lens, and the cantilever. For more information on the laser, see section 3.8.

The laser light travels down the fiber toward the cantilever, and when it reaches the end of the fiber, about 40% of the light reflects off of that interface and the rest of the light transmits through. The transmitted light is focused by a small lens onto the cantilever pad. To ensure the optimal performance of the interferometer, the end of the fiber and the lens are both glued into a metal sleeve with a separation equal to the focal length of the lens.
Figure 3.16: Laser interferometry diagram. The laser sends incident light through the coupler and then down to the experiment. At the end of the fiber, some light is reflected back and the rest is transmitted through. The transmitted light is then focused onto the cantilever’s pad, reflected into the lens, and then back into the fiber. The two reflected light waves superpose and this light is incident onto a photodiode detector. The detector gives an interferometry voltage signal that is proportional to the power of the reflected light.

The light then reflects off of the pad, back through the lens and into the fiber. The sum of the two reflected light waves give the interference signal which is measured by a photodiode detector. The photodiode converts the power of the interference signal (this is typically hundreds of nanowatts) into a voltage which is measured by the DAQ and then sent to the experiment computer.

Because the wavelength of the laser light used for the interferometry is known, it is straightforward to convert the oscillating voltage signal from the photodiode into displace-
ments of the cantilever which are on the order of nanometers. To do this, we can first consider the superposition of the two backwards traveling electromagnetic light waves with frequency $\omega$ that produce the interferometry signal. For simplicity, I will be working with the electric field components of the propagating light waves ($E_1$ and $E_2$), but the magnetic field components can be treated analogously:

$$E_1 = E_{10} \sin(\omega t)$$

$$E_2 = E_{20} \sin(\omega t + \delta)$$

In general, the two waves have an arbitrary phase difference given by $\delta$, and different amplitudes $E_{10}$ and $E_{20}$. Now since we are interested in detecting the displacement of the cantilever, it is more convenient to write $E_1$ and $E_2$ in the position domain, rather than the time domain:

$$E_1 = E_{10} \sin \left( \frac{2\pi x}{\lambda} \right)$$

$$E_2 = E_{20} \sin \left( \frac{2\pi x}{\lambda} + \delta \right)$$

(3.37)

where $\lambda$ is the wavelength of the laser light (about 1550 nm for the experiment). We can write the sum of the two electromagnetic waves, $E_\Sigma$ as:

$$E_\Sigma = E_1 + E_2 = E_{\Sigma 0} \sin \left( \frac{2\pi x}{\lambda} + \phi \right)$$

(3.38)

where $E_{\Sigma 0}$ is given by:

$$E_{\Sigma 0} = \sqrt{E_{10}^2 + E_{20}^2 + 2E_{10}E_{20} \cos \delta}$$

(3.39)

and where the phase $\phi$ is given by:

$$\tan \phi = \frac{E_{20} \sin \delta}{E_{10} + E_{20} \cos \delta}$$

(3.40)

For the interferometry measurement, the value of $\phi$ is not important. This is because the voltage signal, $V_{\text{sig}}$ measured by the photodiode is directly proportional to the power of
Figure 3.17: Cantilever visibility collected using laser temperature sweep. As the temperature of the laser is swept, the wavelength of the laser light changes slightly causing the interferometry signal to oscillate between constructive and destructive fringes. The measured visibility is over 73%. The DC voltage signal drops off linearly as the laser temperature is swept because responsivity of the photodiode detector is not constant with respect to the wavelength of the detected light.

The incident light and this goes as $E_{20}^2$:

$$V_{\text{sig}} = G R K E_{\Sigma 0}^2 = G R K \left( E_{10}^2 + E_{20}^2 + 2E_{10}E_{20} \cos \delta \right)$$

(3.41)

where $G$ is the dimensionless photodiode gain setting that is used to amplify the signal so as to avoid significant detector noise, $R$ is the responsivity of the photodiode which has units of volts per mW, and $K = (\mu_0 c)^{-1}$. Here, $\mu_0$ is the permeability of free space and $c$ is
Figure 3.18: Cantilever visibility collected using by driving the cantilever into oscillations large enough to make the interferometry signal fringe. As the cantilever oscillates, the signal sweeps past constructive and destructive fringes. Using these maximum and minimum voltages, the measured visibility is around 74%, which is in close agreement with the other measurement (see figure 3.17). The manually calculated visibility shown (i.e. 0.447) is left over from a previous measurement, and is therefore not related to the plotted data. The bottom plot shows the FFT of the cantilever signal with a cantilever resonance frequency around 3.7 kHz.

the speed of light, such that $KE_{\Sigma 0}^2$ has units of power. Since $E_{\Sigma 0}^2$ depends on the relative phase $\delta$, we can rewrite $\delta$ in terms of more meaningful variables:

$$\delta = 2\pi \left( \frac{2d}{\lambda} \right)$$

(3.42)

where $2d$ is the path length of the light that travels from the end of the optical fiber, reflects off the cantilever pad, and back into the fiber when the cantilever is a distance $d$ away from the fiber. The maximum voltage occurs when $d$ is equal to $\frac{\lambda}{4}$ and the minimum voltage occurs when $d$ is equal to $\frac{\lambda}{4}(2n + 1)$, where $n$ is an integer. This corresponds to $\delta$ equals 0
and π, respectively, which gives us:

\[ V_{\text{sig}} = V_{\text{max}} = E_{10}^2 + E_{20}^2 + 2E_{10}E_{20} \quad \text{for} \quad d = \frac{u\lambda}{2} \]  
\[ V_{\text{sig}} = V_{\text{min}} = E_{10}^2 + E_{20}^2 - 2E_{10}E_{20} \quad \text{for} \quad d = \frac{\lambda}{4}(2n + 1) \]  

(3.43)

I will define the fringing voltage to be the total difference between the maximum and minimum voltage:

\[ V_{\text{fringe}} = V_{\text{max}} - V_{\text{min}} = 4E_{10}E_{20} \]  

(3.44)

In the experiment, the value of \( d \) is tuned to what is called the ‘working point’ such that the interfering waves are in quadrature (i.e. \( \delta = \pi/2 \)). This tuning can be done by changing the distance between the end of the fiber and the cantilever, however this is difficult to do in practice. Instead, what is typically done is changing the laser’s temperature by an amount on the order of 1 degree of Celsius, which in turn changes the value of \( \lambda \) by a small amount which effectively modifies \( \delta \). Since the voltage signal goes like \( \cos \delta \), when the interferometry setup is tuned to the working point, small changes in \( \delta \) due to cantilever displacement result in a linear response of the signal \( V \). This can be seen by taking a series expansion of \( \cos \delta \) about the point \( \delta = \pi/2 \):

\[ \cos \delta \approx 0 + (\pi/2 - \delta) + \ldots \]  

(3.45)

Now consider the small change in voltage \( \Delta V \) resulting when \( d \) changes by a small amount \( \Delta x \) about the point \( \delta = \pi/2 \) (i.e. \( d = \lambda/8 \)):

\[ V_{\text{sig}} = V_1 = E_{10}^2 + E_{20}^2 \quad \text{when} \quad d = \lambda/8 \]  
\[ V_{\text{sig}} = V_2 = E_{10}^2 + E_{20}^2 - 4E_{10}E_{20} \left( \frac{2\pi\Delta x}{\lambda} \right) \quad \text{when} \quad d = \lambda/8 + \Delta x \]  

(3.46)

\[ \Delta V = V_1 - V_2 = V_{\text{fringe}} \frac{2\pi\Delta x}{\lambda} \]  

(3.47)

Therefore we have a means of converting our voltage signal into small displacements of the cantilever (\( \sim 100 \) nm) when the interferometry is tuned to the working point and given that we know the fringing voltage and laser wavelength:

\[ \frac{\Delta x}{\lambda} = \frac{1}{2\pi V_{\text{fringe}}} \Delta V \]  

(3.48)

59
It is important to remember that this conversion is only valid for small displacements of the cantilever such that the linear expansion remains valid. For example, if the cantilever is driven to 100%, 90%, 75%, 50%, and 25% of the fringing voltage, our conversion (equation 3.48) gives the estimated displacement of the cantilever to be 247 nm, 222 nm, 185 nm, 123 nm, and 61.7 nm however, the actual displacement of the cantilever would be 388 nm, 276 nm, 209 nm, 129 nm, and 62.3 nm respectively. This is an error of 36%, 20%, 12%, 5%, and 1% respectively. Therefore to avoid this error it is good practice to drive the cantilever to an amplitude which is well below the fringing voltage, if possible.

In the experiment, the voltage signal from the photodiode is amplified by a gain such that it is much larger than any detection noise. Here, detection noise is the noise due to fluctuating voltages in any of the detection equipment (photodiode, pre-amp, DAQ, etc.). Since the voltage signal is amplified by an arbitrary gain, the magnitude of the fringing voltage does not have any inherent significance. Instead, what is usually used to characterize the alignment and optimization of the interferometer is the visibility, which is defined as [41,42]:

\[ V = \frac{V_{\text{max}} - V_{\text{min}}}{V_{\text{max}} + V_{\text{min}}} \]  

(3.49)

The visibility, \( V \) is typically reported as a percent because it is zero when the fringing voltage is zero \( (V_{\text{max}} = V_{\text{min}}) \), and it is unity when \( V_{\text{min}} \) is zero (the two interfering light waves perfectly cancel).

### 3.7 Low Temperature Cryostat

To take MRFM measurements at low temperatures, the probe was built to work within a low temperature cryostat (see figure 3.19). The inside of the cryostat is divided into three regions: the neck, belly, and tail. The neck is at the top of the dewar, it has an inside diameter of 7.12 inches, and uses a baffle system to further subdivide the region into smaller pockets where cold gas is trapped which acts as a thermal barrier. The belly is the largest region of the dewar’s interior, and it acts as a reservoir holding about 45 liters of cryogenic liquid. The system was designed to use liquid nitrogen (LN2, at \( T = 77.4 \) K) and liquid
helium (LHe, at $T = 4.2$ K) for cooling down to and maintaining low temperatures. The tail is at the base of the dewar, it also has an inside diameter of 7.12 inches, and this is where the superconducting external magnet and the end of the probe (called the ‘can’) sit. The external magnet has a superconducting critical temperature $T_c \sim 9$ K, and so it only works when the dewar is filled with LHe. The magnet is designed to fit within the cryostat, and the probe is designed to fit within the magnet.

Liquid helium and nitrogen are very effective at keeping the experiment cold. When the belly of the dewar is nearly full of liquid helium, it will keep the experiment operational for about 2 days and 8 hours. After that point, the liquid helium level drops below the superconducting external magnet, and it is not longer safe to use the magnet. The MRFM experiment, however, can operate in zero applied field, and so you can continue collecting some data for another 12 hours or so. After that point, the system will start to warm up. If the dewar is instead filled with liquid nitrogen, the probe will stay around 77 K for about 4 days and 19 hours before it begins to warm up.

Each liter of liquid helium requires about 2.6 kJ of energy to vaporize, and then another 113 kJ to bring the helium gas from 4.2 K to room temperature. So the total energy that can be extracted from the system per liter of helium is about 116 kJ. You can see from this that almost all of the cooling power of the liquid helium comes from the cold helium gas, and not the boiling of the liquid. This is because the latent heat of vaporization is very low for helium, and this is why the baffle system that was mentioned above is so important. Ideally, under a perfectly designed system, the helium gas that leaves the exhaust would be at room temperature and would have absorbed all that energy from the experiment as it left. Similarly, each liter of liquid nitrogen requires 161 kJ to vaporize, and 182 kJ to bring the cold gas to room temperature. So for the liquid nitrogen, the cooling power comes almost equally from these two processes. Table 3.1 summarizes many important cryogenic properties for helium, nitrogen, oxygen, and water. Notice the large expansion ratios. This is the ratio of the volume of liquid to the volume of gas at room temperature and atmospheric pressure. Each cryogenic liquid expands to fill a volume nearly 1,000 times larger when it evaporates to a gas. This is important to be aware of because spilling cryogenic liquid
(especially in a small, poorly ventilated area) can quickly result in asphyxiation as the resulting gas displaces normal atmosphere.

<table>
<thead>
<tr>
<th></th>
<th>Helium (He)</th>
<th>Nitrogen (N₂)</th>
<th>Oxygen (O₂)</th>
<th>Water (H₂O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molar mass (g/mol)</td>
<td>4</td>
<td>28</td>
<td>32</td>
<td>18</td>
</tr>
<tr>
<td>Liquid density (g/ml)</td>
<td>0.125</td>
<td>0.807</td>
<td>1.141</td>
<td>1</td>
</tr>
<tr>
<td>Latent heat of vapor. (J/g)</td>
<td>21</td>
<td>199</td>
<td>214</td>
<td>2257</td>
</tr>
<tr>
<td>Latent heat of fusion (J/g)</td>
<td>–</td>
<td>25.7</td>
<td>13.9</td>
<td>335</td>
</tr>
<tr>
<td>Specific heat, liquid (J/g·K)</td>
<td>–</td>
<td>1.94</td>
<td>1.73</td>
<td>4.2</td>
</tr>
<tr>
<td>Specific heat, gas (J/g·K)</td>
<td>3.13</td>
<td>1.04</td>
<td>0.91</td>
<td>1.85</td>
</tr>
<tr>
<td>Expansion ratio</td>
<td>1:757</td>
<td>1:696</td>
<td>1:861</td>
<td>1:1700</td>
</tr>
</tbody>
</table>

Table 3.1: List of cryogenic properties for helium, nitrogen, oxygen, and water. The table doesn’t have a latent heat of fusion for helium because it remains liquid down to absolute zero under atmospheric pressure due to the zero point energy in the liquid phase. Also, the specific heat of liquid helium between 4.2 K and absolute zero varies by many orders of magnitude and is not necessary consideration in the MRFM experiment, so that is also left blank.

Cryogenic systems can be very dangerous, and anyone who operates one should be aware of several safety issues. Always wear specially designed cryogenic safety gloves when handling anything that is cold in a cryogenic procedure. From personal experience, I know that it is very easy to get a third degree burn by accidentally touching something that is extremely cold and getting stuck to it. Appendix A.1 gives procedures for cooling down to, maintaining, and warming up from LN2 and LHe temperatures. Because the probe is also under vacuum during normal operation, there are even more safety concerns to be aware of. In general, it is important to be mindful of the state of the probe at any point (the temperature and pressure inside the probe), and also be aware of any potentially harmful (to either yourself or the probe) situations that could arise related to these extreme pressures and temperatures.

For example, if you are running the experiment at approximately 4.2 K and your vacuum pump suddenly shuts off (during a power outage, for example) or if there is a leak in your vacuum system, the atmospheric gases (primarily nitrogen and oxygen) that enter
the system can immediately freeze to the cold metal surfaces inside the probe. This in turn maintains a relatively low pressure inside the vacuum space (because the incoming gas freezes) which in turn continues to pull more atmospheric gas into that space. This is known as cryopumping. Cryopumping can lead to an even more serious situation if the condensing gas that enters the probe freezes onto a narrow constriction that becomes more and more narrow as more gas continues to freeze. This constriction can eventually seal itself up with a block of ice. The ice in this case could be a mixture of solid nitrogen, oxygen, and water. Later, when the system eventually warms up, and some of the nitrogen and oxygen return to the gaseous state, the pressure within the probe can become dangerously high, effectively forming a bomb. If the pressure rises high enough, eventually either the metal walls of the probe or the ice block can break and explode outwards.

One solution for this that I have implemented for the probe is to have an electronic solenoid valve with independent control on the inlet of the vacuum pump system. Connected to the solenoid valve is a supply of dry nitrogen gas. If the power to the building goes out and the pump shuts off, the valve will also turn off, which allows dry nitrogen gas into the system and this averts most of the cryopumping risk if the system is only at LN2 temperatures. This also keeps the system clean since nitrogen gas is inert and generally considered safe to keep the system in. If the system is at LHe temperatures, then the safest thing to usually do during a power failure is to slowly warm the system while monitoring the pressure and also consider venting the vacuum space depending on the condition of the probe and the specific situation. It is also good to keep in mind the various temperatures that nitrogen, oxygen, and argon boil and freeze at, since these are the elements that air is primarily composed of (see figure 3.20).

Another potential catastrophe can arise when cooling from LN2 temperatures to LHe temperatures. To transition from liquid nitrogen to liquid helium, the liquid nitrogen must first be removed by pushing it out via pressurizing the system with nitrogen gas. If the liquid nitrogen is not all pushed out, the liquid helium will freeze the nitrogen into solid nitrogen ice. During the experiment, this can be very bad for several reasons. First, since liquid helium is currently very expensive (roughly $1,600 for a 100 liter dewar), it is very
wasteful to use liquid helium to convert liquid nitrogen to solid nitrogen. Secondly, after you have solid nitrogen in your experiment dewar, you have no choice but to warm back up to room temperature to ensure you reset the system back to normal, and this can waste several days (especially if you have to open up the probe and re-align the laser, cantilever, sample, and coil). Thirdly, you can damage the probe if you freeze nitrogen. Fortunately, liquid nitrogen contracts when it freezes, like most liquids, however, there is a chance that you will put strain on the probe by essentially clamping it on two ends and then undergoing thermal expansion. For these reasons, it is very important to make sure you push out all of the liquid helium.

3.8 Instrumentation

In addition to the MRFM probe which contains all of the crucial, sensitive components necessary for the experiment, there are many external instruments required for the interferometry system, cantilever piezo drive system, data collections, etc. Figure 3.21 shows these instruments and how they are connected to the MRFM probe. Also, table 3.2 lists these instruments along with their manufacturer and model number information for the specific instruments I used to run the experiment. I will go through some of these in more detail to provide relevant information about them with regards to the MRFM experiment.

Laser

For this experiment, I used a distributed feedback (DFB) laser diode from Agere Systems Inc to take the interferometry measurements. The laser had a wavelength of 1551 nm and a typical continuous wave output power of about 10 mW. In contrast to common Fabry-Perot (FP) lasers which rely on a pair of mirrors to form the optical cavity and provide the feedback, the DFB laser uses a diffraction grating which acts as an optical filter and results in a much narrower linewidth. The DFB laser also has higher stability compared to FP lasers, which can fluctuate as they hop between different modes. Having a laser with a single, stable wavelength is necessary for the laser interferometry displacement detection in
the MRFM experiment.

<table>
<thead>
<tr>
<th>Instrument Name</th>
<th>Manufacturer</th>
<th>Model Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laser</td>
<td>Agere Systems Inc.</td>
<td>D2526G33</td>
</tr>
<tr>
<td>Current source</td>
<td>ILX Lightwave</td>
<td>LDX-3620</td>
</tr>
<tr>
<td>Laser temp. controller</td>
<td>Newport</td>
<td>3040</td>
</tr>
<tr>
<td>RF source</td>
<td>Wavetek</td>
<td>3000</td>
</tr>
<tr>
<td>Photodiode</td>
<td>New Focus Inc.</td>
<td>2011</td>
</tr>
<tr>
<td>90/10 Coupler</td>
<td>Newport</td>
<td>F-CPL-L22351-P</td>
</tr>
<tr>
<td>Microwave generator</td>
<td>Agilent</td>
<td>E4422B</td>
</tr>
<tr>
<td>Attocube controller</td>
<td>Attocube Systems</td>
<td>ANC 150</td>
</tr>
<tr>
<td>High voltage amplifiers</td>
<td>Trek</td>
<td>601C</td>
</tr>
<tr>
<td>Temperature controller</td>
<td>LakeShore</td>
<td>331</td>
</tr>
<tr>
<td>Pre-amp</td>
<td>Stanford Research Systems</td>
<td>SR560</td>
</tr>
<tr>
<td>Comparator</td>
<td>Home Built</td>
<td>Op Amp LM339N</td>
</tr>
<tr>
<td>Pulser</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3.2: List of Instruments used for the MRFM experiment. The instrument names in the first column correspond to the names in figure 3.21.

**Laser Current Source**

I used a LDX-3620 laser current source to provide the laser diode with 25 mA (typically) of low-noise current. This model is manufactured by ILX Lightwave, which is a Newport company. The current source is connected to the laser diode via a standard RS-232 serial cable, however, the pin configuration for different laser current sources is not standard. For example, the LDC 201 ULN manufactured by Thorlabs Inc. also uses an RS-232 serial port, but the pin configuration is completely different. One needs to be careful when switching between different current sources (when debugging for example) because you can easily damage the DFB laser diode, and they are expensive to replace.

**Laser Temperature Controller**

The laser’s temperature is maintained at a fixed value using a Newport Model 3040 temperature controller. The controller uses a feedback loop by measuring the laser diode’s
temperature with a thermistor, and then sending current to a thermoelectric cooling (TEC) element which relies on the Peltier effect to create a heat flux between two different materials. The temperature controller typically sends less than 1 amp of current to the laser diode’s internal TEC circuit to maintain a set temperature. It also sends a current of about 100 $\mu$A to the thermistor to read the temperature.

**RF Source**

The Wavetek radio frequency (RF) source provides $\sim$ 1 volt of AC at MHz frequencies to mix into the power supply to the laser diode to help stabilize the output of the laser. I have used frequencies anywhere between 7 and 210 MHz for this experiment. In part, it can depend on the individual laser you are using, but the general principle is to find the RF that helps stabilize the laser the most and minimize excess noise. One thing to keep in mind is that the voltage amplitude of the RF source can vary greatly as you sweep the RF frequency due to the nature of the mixing circuit. Therefore, it is useful to monitor the RF output when sweeping frequency so that you don’t accidentally send too much voltage to the laser and potentially damage it.
Figure 3.19: Diagram for the experiment dewar provided by Precision Cryogenic Systems Inc. The inside of the dewar is divided into three regions: neck, belly, and tail. The belly is the largest region in the middle which holds 45 liters of cryogenic liquid as a reservoir for keeping the system cold.
Cryogenic Thermometer

Figure 3.20: Cryogenic thermometer diagram. The thermometer shows the boiling and freezing points for nitrogen, oxygen, and argon as well as a few other important temperatures, and the temperatures are on a linear scale. As shown, the thermometer is currently reading about 77 K. The inset shows the composition of air which is primarily the same three elements along with some other trace gases.
Figure 3.21: Instrument diagram for the MRFM experiment. An image of the probe head is shown against a light blue background in the top right, and next to this, in the top left is a diagram which illustrates its key components. Below this are the primary instruments for the MRFM experiment. The red paths illustrate the laser light.
Chapter 4
THE MRFM SIGNAL AND NOISE

4.1 Introduction

In this chapter, I will introduce the basic concept of how the MRFM signal is acquired and then subsequently walk through the details of this as well as the noise that is typically encountered. In the MRFM experiments, I used frequency detection to measure forces from spins in the sample that are on resonance within the nanoscale detection volume. To do this, the cantilever is driven at it’s resonant frequency (which is on the order of a few kHz) and as it interacts with spins in the sample this frequency shifts slightly (by an amount on the order of mHz), and this frequency shift signal is analyzed to give us the spin signal we are after. Specifically, most of the MRFM experiments I performed during my graduate research were done using the interrupted oscillating cantilever-driven adiabatic reversals (iOSCAR) measurement protocol or a similar variation to that. This is a measurement scheme in which you resonantly invert spins synchronously with the cantilever’s oscillation (as well as periodically interrupting such an inversion) which results in a periodic shift of the cantilever’s frequency. By demodulating this periodic frequency record and using some statistical analysis, we acquire the frequency detected MRFM spin signal. The signal is actually force fluctuations that arise from spins that randomly flip due to thermal energy in the lattice. Even though it is random, the magnitude and characteristic time scale of the fluctuations contain information regarding the size of the spin ensemble and the spin dynamics, respectively. Next, I will walk through these concepts in detail to show exactly how this measurement is done and what it tells us about the spins in the sample.
4.2 The MRFM Signal

Since the experiment measures a small number of spins which are at thermal equilibrium, the time-averaged net force of these spin on the cantilever is zero (and thus the average frequency shift is zero). However, the variance of this net force is not zero.

\[ \langle F_{\text{net}} \rangle = 0 \]  \hspace{1cm} (4.1)

\[ \sigma^2_{F_{\text{net}}} \neq 0 \]  \hspace{1cm} (4.2)

Note that I dropped the subscript ‘net’ for the force in equation 4.2 to avoid confusion, but it is \( \sigma^2_{F_{\text{net}}} \). So the measurement relies on detecting the fluctuations of the net magnetization from the measured spins about their equilibrium value, and not the net magnetization itself. This is sometimes referred to as ‘spin noise’, and the average deviation about the mean at any time is the statistical polarization of the spin ensemble which was discussed in section 2.3. This can be somewhat confusing in the sense that noise is typically something you try to minimize in an experiment, but the ‘spin noise’ is actually the signal we are trying to measure. Later I will discuss experimental noise that we do try to reduce. Using the spin noise as a signal in the MRFM experiment is also nice because it allows us to measure the spins non-perturbatively (at thermal equilibrium) and measure their intrinsic dynamics without ever polarizing the spins.

In section 3.2 I showed how forces that are in phase with the cantilever oscillation (or \( \pi \) out of phase) contribute to the an effective spring constant, whereas forces that are in quadrature (\( \pi/2 \) phase shift) modify the damping of the cantilever. The force detection protocol I used for my MRFM measurements modulates the spin orientation synchronously and in phase with the cantilever, which effectively modifies the cantilever spring constant. This effective shift in the spring constant results in a shift in the cantilever frequency, as I showed in section 3.2 (see equations 3.9 and 3.10).

The modulation of the spins’ orientation is achieved through adiabatic inversions (see section 2.5). As the cantilever oscillates back and forth, so does the resonance bowl within
the sample. A given spin within the detection volume that is swept out by the bowl, will
adiabatically invert as the bowl sweeps past it, as long as the microwave coil provides the
oscillating $B_1$ field necessary for the inversion. This results in an oscillating force on the
cantilever at the cantilever’s frequency which in turn shifts the frequency of the cantilever.
Combining equations 3.2, 3.10, and 3.12 we have the frequency shift from each spin:

$$\delta f = \pm \frac{2f_0 G_{\mu_B}}{\pi k x_{pk}}$$  \hspace{1cm} (4.3)

Here there is a factor of $4/\pi$ which comes from the fundamental Fourier component of the
spin’s square wave inversion. Since this frequency shift applies to all the spins within the
spin detection volume, the net magnetization of those spins (either up or down) results in
either a net increase or decrease in the cantilever’s frequency (lock or anti-lock cases).

Figure 4.1 shows the timing diagram for the iOSCAR protocol, along with an example
signal from a randomly flipping spin. Figure 4.2 shows a similar timing diagram which
highlights a larger time record (1 s instead of 40 ms) and the case of 200 spins. The
adiabatic inversions follow the cantilever oscillations, but when the RF power is turned off
for half of a cantilever cycle, the phase of this modulation is shifted by $\pi$. This results in
flipping the sign of the associated cantilever frequency shift. The net magnetization of the
randomly flipping spins (the spin noise) changes the magnitude and sign of the frequency
shift which is modulated by the interrupts. By demodulating this signal at half the interrupt
frequency, the spin noise signal can be recovered.

In practice, the noise in the experiment (primarily thermal noise of the cantilever, see
equation 3.21), does not make it possible to directly recover the spin signal by deconvolving
with the interrupt modulation. Instead, a statistical approach is used which involves a
construction of the power spectral density of the spin noise signal by analyzing the variance
in different bandwidths of the signal. In general, the variance of a signal $x$ is given by:

$$\sigma^2 = \langle x^2 \rangle - \langle x \rangle^2$$  \hspace{1cm} (4.4)

However, since the average force from the spins is zero (equations 4.1) the variance is simply
the average square value:

$$\sigma^2 = \langle x^2 \rangle, \text{ for } \langle x \rangle = 0 \quad (4.5)$$

In section 2.8 I described the total energy of a signal, in a statistical sense (see equation 2.18) which is essentially the total integrated variance in this case. However, the spin noise signal is the sum of many individual spin signals, each of which can be described by a Poisson process. This means the spin noise signal is wide-sense stationary in time, meaning that the variance and mean of the signal does not change over large time periods. Therefore, the total energy of the signal is nothing more than the average energy per unit time multiplied by the total time, but if we divide out the total time, this is just the expected variance or average power.

Following the progression presented in section 2.8, we will look at how this power (variance) is distributed across different frequencies (i.e. the power spectral density) for the spin noise signal. This analysis will allow us to obtain the characteristic time scales of the spins’ dynamics. In addition to the definition I gave for the power spectral density (PSD) in section 2.8 (see equation 2.21), there is an equivalent definition of the PSD given by the Fourier transform of the signal’s autocorrelation function:

$$S(f) = \int_{-\infty}^{\infty} r_{xx}(\tau)e^{-2\pi i f \tau} d\tau \quad (4.6)$$

where the autocorrelation function of the signal is defined as:

$$r_{xx}(\tau) = \langle x(t)x^*(t-\tau) \rangle \quad (4.7)$$

This second definition of the PSD is a result of the Wiener-Khinchin Theorem, and it can provide a useful or intuitive way of understanding the spin signal. For example, the autocorrelation function evokes the concept of a correlation time, which for the spin signal is the intrinsic lifetime of the spins being measured. In other words, the correlation time of a spin describes the average time the spin remains in its current state. The autocorrelation function of a Poisson process (or sum of many Poisson processes) is a decaying exponential (the correlation time is the decay constant). Further, the Fourier transform of a decaying
exponential is a Lorentzian, and this correlation time is also the half-width at half-max of this Lorentzian which is the spin signal PSD.

Although the autocorrelation function provides a means of obtaining the PSD, it is difficult to execute this in practice. Instead, the PSD of the spin signal is obtained by measuring the variance of the signal within different frequency bandwidths. This is done by passing the demodulated signal through a bank of low-pass filters and then calculating the variance as a function of low-pass filter frequency. Together, the demodulation and low-pass filtering of the signal act as a lock-in detection technique. I will now show exactly how the PSD is obtained using the array of low-pass filters, and why this makes sense intuitively.

In section 2.8 I showed that the total energy of the signal can be obtained in either the time domain or frequency domain, and this is known as Parseval’s theorem. Starting with this expression

\[
\int_{-\infty}^{\infty} |x(t)|^2 \, dt = \int_{-\infty}^{\infty} |\hat{x}(f)|^2 \, df
\]

if we then normalize by the total time of the signal, \( T \), which we allow to go to infinity, and then take the expectation value (time average) of both sides, we have

\[
\langle \frac{1}{T} \int_{-\infty}^{\infty} |x(t)|^2 \, dt \rangle = \langle \frac{1}{T} \int_{-\infty}^{\infty} |\hat{x}(f)|^2 \, df \rangle
\]

(4.9)

On the left hand side, the quantity inside the \( \langle \ldots \rangle \) is simply the average square value \( \langle |x(t)|^2 \rangle \), and the expectation or time average of that is simply itself. On the right hand side, we can take the constant \( \frac{1}{T} \) and the time average inside the integral:

\[
\langle |x(t)|^2 \rangle = \int_{-\infty}^{\infty} \frac{1}{T} \langle |\hat{x}(f)|^2 \rangle \, df
\]

(4.10)

The integrand of the right hand side is now the PSD by definition, and thus we have:

\[
\langle |x(t)|^2 \rangle = \int_{0}^{\infty} S(f) \, df
\]

(4.11)

Note that I have written the integral to start from zero since negative frequencies are not meaningful in this case. This expression says that the variance of the signal can be obtained by integrating the power spectral density over all frequencies. This makes sense intuitively.
since power here means variance (see equation 2.19, for example), and thus the PSD is the spectral distribution of the variance per unit frequency and integrating it up over all frequencies gives the total variance.

This concept provides a means of constructing the PSD. Imagine you took a signal and computed it’s variance. This would give you the total integrated area of the signal’s PSD, but that doesn’t give you the PSD itself. However, if you filtered the signal with a low pass filter with a cut-off frequency of $\omega_{lp}$, and then computed the variance, you would have the integrated area of part of the PSD. This is equivalent to:

$$\langle |x(t)|^2_{\text{filtered}} \rangle = \int_0^{\omega_{lp}} S(f) \, df \quad (4.12)$$

Specifically, this integrated area would be the area in the frequency domain that occupies frequencies below $\omega_{lp}$. If you did this for many low-pass filters, you would construct the integral of the PSD. Taking the derivative of this integral with respect to frequency $\omega_{lp}$ would produce the PSD. This concept is illustrated in figure 4.3.

This is exactly what is done in the experiment to obtain the MRFM signal (the spin signal’s PSD). Having obtained the spin signal’s PSD, the total number of spins can be calculated because the area under the PSD is the total signal variance which is proportional to the number of spins (see equations 2.9 and 4.3):

$$\sigma_f^2 = (\delta f)^2 N = \left( \frac{2f_0G\mu_B}{\pi kx_{pk}} \right)^2 N \quad (4.13)$$

where $\sigma_f^2$ is the total integrated PSD (total variance) of the cantilever frequency shift signal which has units of Hz$^2$. The spin signal PSD also gives us the correlation time or lifetime of the spin ensemble. This is the inverse of the width of the Lorentzian, which follows from the autocorrelation analysis I discussed earlier. Now that I have described the MRFM spin signal, we should think about how we can determine some level of confidence in this signal and what the proper treatment of noise analysis is for the signal given that it is obtained through a statistical method.
4.3 Fisher-p Values

As I described in the last section, the MRFM spin signal is acquired using statistical analysis by looking at the variance of the demodulated frequency fluctuations of the cantilever throughout different frequency bandwidths, and also in the presence of large noise (the single shot noise is larger than the signal). Due to the nature of this signal collection, it is useful to estimate the likelihood or confidence of the acquired signal. To achieve this, I used Fisher-p values. For the MRFM experiment, the p-value estimates the probability that the signal you think you have measured is actually due to random noise or coincidence. This p-value confidence technique was first developed by Dan Rugar [10,43] and then subsequently used by collaborators at OSU, such as K. C. Fong [3].

Imagine you found a coin that you believed was fair, however, you soon realized that if you flip it on Tuesdays, it always lands on heads. As weeks go by you flip it more, and only on Tuesdays it comes up heads each time (and only when you use that coin), and you are convinced that this coin isn’t fair, but is somehow special. Then on a Tuesday, you show a friend the coin and flip it 6 times in front of him and he observes that it lands on heads each time. However, your friend is skeptical and he says, “Although that is unlikely to happen, it is still possible for a fair coin to do that”. Then you flip the coin 50 more times (56 total) and each result is heads. You calculate that the odds of this happening for a fair coin are about 1 in 72 quadrillion, and your friend says, “OK, maybe this coin isn’t fair”.

In the example above, the initial result of just 6 flips wasn’t as convincing as the final results of 56 total flips, because the statistical significance of 56 flips is much greater. This concept can be quantified by what is known as the Fisher p-value, which is the probability of getting a particular result assuming what is called the ‘null hypothesis’. Here, the null hypothesis would be that the coin actually is fair, and that the results are simply a random coincidence. In the case of just 6 flips \( p = 1.7 \times 10^{-2} \) (i.e. 1 in 64) and in the case of 56 flips, \( p = 1.4 \times 10^{-17} \) (i.e. 1 in 72 quadrillion). Typically a threshold value of about \( 1 \times 10^{-2} \) is used as an indicator, and if the p-value is equal to or less than that value, the results suggests that the null hypothesis is not true.
Similarly, in the MRFM experiment, I obtain Fisher \( p \)-values for the spin measurements. In this case, the null hypothesis is that there are no spins being measured, and what I’m actually measuring is just noise. However, since the spin signal comes from demodulating the cantilever frequency signal with respect to the iOSCAR interrupts, the noise would have to be modulated at the same frequency and phase as the interrupt modulations. Also, the fisher-\( p \) value for the experiment is more complicated than the simple coin flipping example above. I won’t go into detail regarding this calculation, but I will say that it involves what is known as an f-distribution, which handles the noise in variance measurements like the MRFM signal.

### 4.4 Noise in the MRFM Experiment

Previously in section 3.2 I described the largest sources of noise in the MRFM experiment, which are: thermal noise (Brownian motion of the cantilever), shot noise in our interferometry which arises from discrete photons hitting the photodiode, and the well-known 1/f noise which is ubiquitous and is due to many sources (vibration in the system and non-contact friction between the cantilever and sample surface are some important ones).

At finite temperature, thermal noise is inherent within the force detector (cantilever) and in the MRFM spin force detection experiment it is desirable to push your noise floor as close to this thermal limit as possible (i.e. nothing else is limiting the sensitivity of your measurement). By modeling the cantilever as a harmonic oscillator, the amount of thermal noise can be calculated via the equipartition theorem. This results in a ‘white’ (frequency independent) thermal noise floor which is \( \sim 10 \text{ aN/rtHz} \) for this experiment.

The iOSCAR protocol uses lock-in detection to reduce experimental noise, and measure the spins. The lock-in amplifier uses for its reference signals both in-phase and quadrature sinusoids (i.e. \( \sin(\omega_{\text{int}}t/2) \) and \( \cos(\omega_{\text{int}}t/2) \)) to find the in-phase and quadrature components of the cantilever frequency as a function of time with respect to the interrupts. The out-of-phase channel of the lock-in amplifier is sometimes also referred to as the quadrature channel. I will denote these in-phase and out-of phase components as \( x \) and \( y \) respectively.
The in-phase channel contains the net force of the spins acting on the cantilever as a function of time, but we are interested in the variance of this force (as mentioned above), so we are concerned with the variance of the in-phase and quadrature channels:

\[ \sigma_x^2 \equiv \langle x^2 \rangle - \langle x \rangle^2 \]  \hspace{1cm} (4.14)

\[ \sigma_y^2 \equiv \langle y^2 \rangle - \langle y \rangle^2 \]  \hspace{1cm} (4.15)

Note that according to equation 4.15, the average frequency shift of the cantilever is zero and the fluctuations about zero are symmetric such that the second term in equations 4.14 and 4.15 are each zero and thus the in-phase and quadrature variances are just the mean square values (i.e. the standard deviation is the RMS in this case). The in-phase and quadrature channel both contain experimental noise (discussed above), however only the in-phase channel contains a non-zero contribution from the resonant spins (the spin noise \( \sigma_F^2 \)), and subtracting the quadrature variance from the in-phase variance gives us \( \sigma_F^2 \):

\[ \sigma_x^2 = \sigma_F^2 + \sigma_{\text{noise}}^2 \]  \hspace{1cm} (4.16)

\[ \sigma_y^2 = \sigma_{\text{noise}}^2 \]  \hspace{1cm} (4.17)

\[ \sigma_F^2 = \sigma_x^2 - \sigma_y^2 \]  \hspace{1cm} (4.18)

Equation 4.16 is a result of what is known as the variance sum law which states that the variance of the sum (or difference) of two uncorrelated variables is simply the sum of their variances. In this case, the independent variables are the demodulated net force of the spins and the experimental noise that exists at the modulation frequency (i.e. the frequency \( \omega_{\text{int}}/2 \)). Now, since we are measuring the statistical variance of the net force due to the spins and this relies on time-averaging to build up a strong signal (increase SNR), we need to distinguish between the measured variance in the experiment and the true variance of the spin system. A measured variance is commonly denoted as \( s^2 \), and for the in-phase and
quadrature channels this is defined as:

\[ s_x^2 = \frac{1}{n} \sum_{i=1}^{n} x_i^2 \]  \hspace{1cm} (4.19)

\[ s_y^2 = \frac{1}{n} \sum_{i=1}^{n} y_i^2 \]  \hspace{1cm} (4.20)

where \( n \) is the number of measurements. Again, this contains the average of the squares, but not the square of the averages for the same reason as was mentioned above. Also, the measured values are just a subset of all the values and therefore in the limit \( n \to \infty \), the measured variance would become the true variance \( s^2 \to \sigma^2 \). We can also write the measured variance equivalent for equations 4.16 - 4.18:

\[ s_x^2 = s_F^2 + s_{\text{noise}}^2 \]  \hspace{1cm} (4.21)

\[ s_y^2 = s_{\text{noise}}^2 \]  \hspace{1cm} (4.22)

\[ s_F^2 = s_x^2 - s_y^2 \]  \hspace{1cm} (4.23)

Having made the distinction between a measured variance and a true variance, we can define the typical error or uncertainty (statistically, the standard deviation) in the measured variance with respect to the true variance. This standard deviation is given by [44](page 22):

\[ \sigma_{s^2} = s^2 \sqrt{\frac{2}{n-1}} \]  \hspace{1cm} (4.24)

Having this definition, we can now calculate \( \sigma_{s_F^2} \), which is the error in our measurement of the variance of the net force. Considering equations 4.23 and 4.24, and again using the
variance sum law we can write:

\[
\sigma_{s^2_F}^2 = \sigma_{s_x^2}^2 + \sigma_{s_y^2}^2
= (s_x^4 + s_y^4) \left( \frac{2}{n-1} \right)
= \left( (s_F^2 + s_{\text{noise}}^2)^2 + s_{\text{noise}}^4 \right) \left( \frac{2}{n-1} \right)
= (s_F^4 + 2s_F^2s_{\text{noise}}^2 + 2s_{\text{noise}}^4) \left( \frac{2}{n-1} \right)
= s_F^4 \left( 1 + 2s_{\text{noise}}^2/s_F^2 + 2s_{\text{noise}}^4/s_F^4 \right) \left( \frac{2}{n-1} \right)
\approx \frac{4s_{\text{noise}}^4}{n}
\]

The last line is an approximation which is valid in the limit that \( n \gg 1 \) and \( s_{\text{noise}} \gg s_F \) which are both true in our experiment. We can also express the standard deviation of our noise in terms of the single-shot bandwidth of the measurement \( \Delta S \) and the force power spectral density \( S_F \) (note that I’m using uppercase ‘S’ to denote a power spectral density and a lower case ‘s’ to denote measured standard deviation, following convention):

\[
\sigma_{s^2_F} = \frac{2s_{\text{noise}}^2}{\sqrt{n}} = \frac{2S_F \Delta \nu}{\sqrt{n}}
\]

We can now write the signal to noise ratio (SNR) of our experiment. Remember that our signal is the measured variance of the force of the spins on our cantilever probe \( s_F^2 \), and the noise is the statistical error of that measured variance \( \sigma_{s^2_F} \) (which includes within it the experimental noise sources that were discussed above). Thus we have the ratio of these to give us our SNR:

\[
\text{SNR} = \frac{s_F^2}{\sigma_{s^2_F}} = \frac{\sqrt{n}N\mu_B^2G^2}{2S_F \Delta \nu}
\]
Figure 4.1: Timing diagram for the iOSCAR protocol and signal from one spin. a) Cantilever oscillation record for 40 ms, with a cantilever frequency of 2,500 Hz. The cantilever record has been normalized so that the maxima correspond to +1 and -1. b) RF power for the microwave coil. Here, +1 corresponds to on, and -1 corresponds to off. When the coil is on, the spins undergo adiabatic inversions synchronously with the cantilever oscillations. Every 10 cantilever cycles, the power to the coil is interrupted for half of a cantilever period (from one extrema to another). c) Adiabatic inversion sequence for a spin in the center of the detection volume. Each time the power to the coil is interrupted, the spin skips exactly one adiabatic inversion, compared to the case of continuous RF power. This switches the phase of the spins’ inversions with respect to the cantilever oscillation by an amount $\pi$, taking the spins from being locked to anti-locked, or vice versa. d) Frequency shifts due to the adiabatic modulation of the spins. When the phase of the spin modulation is changed from locked to anti-locked, the frequency shift of the cantilever changes signs. e) Single telegraph function which represents the random flipping (Poisson process) of one spin. In this example, the spin flips three times. This has the same effect as an RF power interrupt in the sense that it takes the spin from being locked to anti-locked, or vice versa, however the interrupts are controlled and periodic. Multiplying records c and e together would give the spin’s orientation during the time record. f) Combined frequency shift record of the cantilever due to the RF power interruptions and the random flipping of the single spin given by the example in e. By deconvolving with the known interrupt modulation of d, the spin record e can be recovered in theory. In practice, the noise of the experiment does not allow for this direct deconvolution recovery. The experimental noise is not shown here, but it far exceeds the intensity of the single spin frequency shift shown in e.
Figure 4.2: Timing diagram for a signal from 200 spins. This diagram is similar to figure 4.1 in the sense that the cantilever has a frequency of 2,500 Hz and there is an interrupt every 10 cantilever cycles. However, this figure shows a 1 second time record with 250 interrupts and illustrates a frequency shift record that corresponds to 200 spins (with no experimental noise). a) Frequency shift modulation signal due to the RF power interrupts. This corresponds to record d in figure 4.1. b) Telegraph function representing 1 spin with the same flipping probability as e in figure 4.1. This time the spin flips 15 times, and the probability to for an up flip is the same as a probability for a down flip. c) 200 telegraph functions summed together to represent the net magnetization of 200 spins as they flip due to thermal relaxation. The standard deviation of this is about 14.34, which is close to the expected deviation of $\sqrt{200} = 14.14$ according to equation 2.9 d) Combined frequency shift record of the cantilever due to the RF power interruptions and the random spin noise signal. This is the product of record a and c. In theory, this signal can be demodulated using a to give the spin signal in c. Again, this is not done in practice due to noise limitation in the experiment.
Figure 4.3: Construction of Spin Signal PSD using low-pass filters and variance calculation. Left: An ideal spin signal PSD is shown. The functional form of the PSD is a Lorentzian if the spin signal is Poisson-like. Integrating the PSD gives the variance of the spin signal, which is an arctan function in this case. Four low-pass filter are shown overlaying the PSD and variance curves. These correspond to the filtering of the signal shown to the right, and the large data points show the variance of the signals after being low-pass filtered, which fall onto the arctan plot. Right: The 200 spin signal from figure 4.2 is shown at the top in black. Below this (and shifted for clarity) are four examples of the same signal after it has been low-pass filtered. The low-pass filter cut-off frequency decreases in descending order of the plots. As the low-pass filter frequency decreases, so does the variance of the filtered signal. In the limit that only the DC component is allowed through, the variance goes to zero. This can be seen on the corresponding variance plot on the right with the matching colored data points.
Chapter 5
TRANSPORT AND DYNAMICS IN A DIAMOND SPIN WIRE

5.1 Motivation for the Experiment

Prior to 2010, measurements taken by Kin Chung Fong and Michael Herman showed that the lifetime of spins measured in MRFM experiments seemed to depend on the size of the detection volume. They observed that the lifetime would be longer in larger detection volumes. This did not make sense if the spin lifetime only depended on a spin-lattice relaxation mechanism ($T_1$), however, it did make sense if the spins were diffusing throughout the detection volume and across the volume boundaries.

Spin diffusion in paramagnetic samples has been extensively studied in the past via conventional magnetic resonance experiments [45] and it has also been suggested for explaining more modern results in MRFM [32]. In section 2.7 I discussed the origin of the flip-flop mechanism which is responsible for the paramagnetic spin diffusion. The work by Budakian et al. [32] focused on suppressing spin diffusion, to eliminate that mechanism as an affect on the spin lifetime. This was thought to be achieved via the strong gradient present in most MRFM experiments. What was needed however, was a clear understanding of how the spin diffusion could persist in the presence of a strong gradient, and how the diffusion and relaxation together affected the overall lifetime of the spins as a function of the MRFM spin detection volume.
5.2 Spin Defects in Diamond

Before going into the details of the experiment, I will provide some background on the two types of spin defects in diamond that I studied. The first defect is the P1 center, which is simply a single substitutional nitrogen atom in the diamond that is located at a lattice point where a carbon atom would normally be. P1 centers are the primary spin defect that I took measurements on. The second defect I will discuss is the NV center (nitrogen-vacancy center). In addition to a substitutional nitrogen atom, the NV center also has a vacancy directly adjacent to the nitrogen atom (a missing carbon atom at a nearest neighbor location to the nitrogen). Although I didn’t take many measurements of NV spins, I contributed modeling and analysis of NV centers measured via optically detected magnetic resonance (ODMR), which was taken by Richelle Teeling-Smith. In chapter 6, I go into the details of this modeling.

The P1 center spin is associated with an extra electron that is present due to the single nitrogen atom substitution in the diamond lattice, since neutral nitrogen has 7 electrons (compared to carbon’s 6). This extra electron occupies an unpaired dangling orbital along one of the four nearest-neighbor axes where a covalent bond would normally exist. There are also 2 paired electrons along that axis. In addition to the Zeeman energy term discussed in section 2.2, there is a nuclear Zeeman term arising from the nitrogen nucleus which is spin-1, and also a hyperfine term that is due to the interaction of the electron and nucleus. Therefore the Hamiltonian for the P1 system with these three largest energy terms is given by:

\[ H = g_e \mu_B \vec{S} \cdot \vec{B} + A \vec{S} \cdot \vec{I} - g_n \mu_n \vec{I} \cdot \vec{B} \]  \hspace{1cm} (5.1)

where \( A \) is the hyperfine tensor, and \( \vec{I}, g_n, \) and \( \mu_n \) are the nuclear spin, nuclear g-factor, and nuclear magneton, respectively. Figure 5.2 shows the energy level diagram for the P1 center.

The NV center in diamond has a slightly more complex electronic structure. The vacancy itself creates four dangling electron orbital where four covalent bonds should normally be, and when one of the vacancy’s neighbors is a substitutional nitrogen, this adds another
electron for a total of five (six electrons for the NV$^-$ defect). The electrons form a composite boson which is localized near the NV defect location, and is spin-1.

What is really interesting about the NV center is that it has optical properties which couple to the spin's state. If green light (532 nm) is incident onto the diamond, the NV spin can be excited from it's ground state to an excited state by absorbing a photon. This is true for the $m_s = 0$ state and also the $m_s = \pm 1$ states. The spin’s state is conserved during this process. After this, the spin can decay back down into the ground state by emitting a red photon (the PL spectrum is between 600 and 800 nm). Again, the spin state (value of $m_s$) is preserved during this process. However, for the $m_s = \pm 1$ spins, there is a probability for another decay path, which is not spin conserving. The $m_s = \pm 1$ spins can first decay non-radiatively to an intermediate state, and then to the ground state. When this happens, the $m_s = \pm 1$ spins change to $m_s = 0$. By continuously applying the 532 nm green laser light onto the diamond sample, it follows that all spins will eventually end up in the $m_s = 0$ state, and thus the spin population is polarized. This provides a unique and
powerful means for controlling the spin population in an experiment. Once all of the spins are in the $m_s = 0$ state, the PL intensity has saturated to a relatively maximum value since none of the spins have the non-radiative decay option. Figure 5.3 shows the energy level diagram for the NV center including the radiative and non-radiative decay paths.

Figure 5.3 also shows the zero-field splitting of the $m_s = 0$ and $m_s = \pm 1$ states, which is at 2.87 GHz. If the 532 nm green laser light is continuously applied and the microwave frequency is swept through the 2.87 GHz resonance, a drop in the PL intensity is observed as spins are excited from the $m_s = 0$ state to the $m_s = \pm 1$ states. This is known as optically detected magnetic resonance (ODMR), and figure 5.4 shows an example of this. This ODMR data spectrum was collected by Richelle Teeling-Smith.

5.3 Diamond Sample Preparation

Patterning and SRIM and implantation and annealing.
Figure 5.3: Energy level diagram for the NV center in diamond. The spin can be excited from the ground state to the excited state using green 532 nm light. Once excited, the spins can decay back down into the ground state by emitting a photon (600 to 800 nm wavelength), however, the $m_s = \pm 1$ spins have a probability of decaying non-radiatively into an intermediate state, and then into the ground state. This process leaves them in the $m_s = 0$ spin state. The zero-field splitting between the $m_s = 0$ spins and $m_s = \pm 1$ spins is 2.87 GHz, and applying microwaves at this frequency induces transitions between the states.

The diamond sample studied in this experiment had a background nitrogen concentration of 0.3 ppm ($5.27 \times 10^{16}$ cm$^{-3}$). In order to study how the lifetime of the spins depended on the volumes they were confined in, and to try and see if this was due to diffusion of the spins out of the measured volume, we fabricated a high-spin-density wire. To do this, the sample was first prepared using electron-beam patterning to form a mask. Next, the sample was exposed to nitrogen ion implantation at a variety of energies to create a uniform spin density. Finally, the sample was annealed to yield an approximately uniform channel (6 ppm or $1.05 \times 10^{18}$ cm$^{-3}$) with width, depth and length of 200 nm, 250 nm and 4 mm, respectively. The sample was purchased commercially from Element Six, grown via chemical vapor deposition, and the nitrogen ion implantation was performed by Leonard Kroko.

To simulate the implantation of the nitrogen ions into the diamond, I used SRIM software. SRIM is short for the stopping range for ions in matter. SRIM uses statistical algorithms and a quantum mechanical treatment of ions colliding into atoms to generate
Figure 5.4: Optically detected magnetic resonance (ODMR) spectrum for NV centers in diamond. The plot shows measured photoluminescence (PL) intensity of the optically active NV centers as a function of applied microwave frequency. When the NV spins resonance condition is matched (around 2.87 GHz), the NV center’s PL decreases as the spins relax through a non-radiative decay path. The blue curve is a Lorentzian fit of the NV resonance. This data was collected by Richelle Teeling-Smith.

random walk collisions of ions of a given energy into solid matter. I simulated implantation of 21 different energies (20, 30, 40, 50, 60, 80, 100, ... 260, 280, 300 keV) such that the superposition of the implantation density profile was relatively uniform within the first 400 nm of the diamond (see figure 5.5).

5.4 Spin Wire Measurements

The patterned structures in the diamond sample seemed ideal for studying spin diffusion. In particular, the patterned stripes (or spin wires, as we came to call them), were particularly useful for separating out the spins’ diffusion dynamics from the standard spin-lattice relaxation. I worked with Michael Herman to take measurements, and in fact he primarily ran the experiment while I assisted. The first set of data we collected was a series of MRFM measurements where the cantilever was scanned across a patterned stripe (spin wire) which
Figure 5.5: Stopping range for ions in matter (SRIM) simulations for nitrogen ion implantation into the diamond sample. The plot shows the ion implantation intensity, which is proportional to nitrogen density, as a function of implantation depth. A variety of energies were used between 20 and 300 keV. These are the alternating red and green implantation distributions. The superposition of all of these energies gives the total implantation profile, which is relatively uniform within the first 400 nm of the diamond sample surface.

was 4 µm long, 250 nm deep, and 200 nm wide. The scan was done by taking small steps (~ 12 nm at a time), and the magnetic resonance bowl (detection volume) was thereby scanned into the spin wire (see figure 5.6).

We scanned this detection volume into the spin wire (see figure 5.6a-e) and measured the force exerted on the cantilever by the selected spins using the iOSCAR frequency detection protocol, which I described in Chapter 4. From this measurement we could extract two quantities: the spin signal magnitude (figure 5.6f) and force correlation time $\tau_m$ (figure 5.6g). The correlation time $\tau_m$ describes the characteristic time it takes the net moment of the detected spins to decorrelate. This can arise from conventional spin relaxation processes, spurious mechanisms arising from the measurement protocol [3], or spin transport out of the detection volume through a random-walk diffusion processes via spin flip-flops, with each step taking an average time $T_{ff}$. We ruled out spurious effects, as discussed in detail
Figure 5.6: Setup and Measurements for MRFM Spin Wire Scan. a) The MRFM spin wire setup. The detection volume was positioned outside of a high density spin wire and then slowly scanned into the wire. b-e) Zoom-ins of the leading edge of the detection volume entering the spin wire.

in ref. [3], and conventional relaxation is much too slow to explain the measured correlation time. As I discuss below, the lifetime we observed is determined by spin transport out of the volume through the flip-flop mechanism I discussed in section 2.7.

As the detection volume begins to enter the wire, the spin signal grows with the overlap of the detected volume with the nanowire, eventually reaching a plateau when the volume completely enters the wire. The correlation time shows a complex behavior as the detection volume moves into the wire that can be understood within the framework of flip-flop-mediated spin transport: ensemble correlation is lost as spins diffuse into or out of the
detection volume. When the detection volume first enters (position = 0 nm in figure 5.6b),
the spins inside the volume interact with nearby outside neighbors, allowing the spins to
easily diffuse out of the detection volume which results in a relatively short correlation
time. With increasing overlap of the detection volume and the spin wire, spins must diffuse
further to exit the detection volume and change the overall magnetization of the ensemble,
thus increasing $\tau_m$. The correlation time peaks when $\sim 66\%$ of the detection volume has
entered the channel. This can be understood in detail from the force sensitivity profile of
the detection volume: spins in the middle of the volume are most sensitively detected (solid
red indicates highest sensitivity in figure 5.6a-e), while those on the edges are less sensitive.
As the detection volume approaches 100% overlap (at 150 nm), spins become able to diffuse
out either side of the most sensitive region, reducing the correlation time by a factor of $\sim 2$.
Scanning deeper into the channel results in no further change because the measurement
geometry becomes translationally invariant.

The relative impact of spin transport on lifetime depends on the relationship between the
diffusion length and the characteristic length of the measurement volume. Spin transport
affects spin lifetime in this case because two conditions are satisfied: there is an adjacent
spin reservoir (the remainder of the nanowire), and the diffusion length is larger than the
measurement volume, enabling spin transport into the reservoir. If, instead, the diffusion
length is smaller than the measurement volume, still in the presence of an adjacent reser-
voir, the lifetime is not affected by spin transport. We have observed this behavior in our
measurements of lifetime in the low-spin-density bulk outside the nanowire, in which the
diffusion length is significantly smaller than the measurement volume, and we find a much
larger $\tau_m$ of $\sim 1.5$ s. This is consistent with conventional electron paramagnetic resonance
(EPR) measurements of T1 for P1 centers in diamond [46], conducted in the regime where
the measurement volume is larger than the volume of the sample. In this case, spin trans-
port effects are not observed regardless of the spin diffusion length because flip-flops within
the measurement volume preserve the spin magnetization, thus the measured lifetime is $T_1$.
By systematically varying the size of the overlap of the detection volume with the spin wire,
the spin wire measurements of $\tau_m$ reveal the effects of spin transport on the lifetime of the
measured ensemble.

The average polarization gradient vanishes at thermal equilibrium, so the conventional model of diffusion driven by polarization gradient predicts that $\tau_m$ will be independent of detection volume position within our thermal equilibrium wire. Such a model neglects the dominant role spin fluctuations play in nanoscale ensembles. To fit the measured data in figure 5.6g I developed a Monte Carlo simulation that models the flip-flops between individual spins as a Markov process. I will discuss this in greater detail in section 5.5. From fits of this simulation to the data we can extract the flip-flop time, $T_{ff} = 0.21 \text{ ms}$, which is in good agreement with the theoretical flip-flop time, $T_{ff,th} = 0.13 \text{ ms}$. This corresponds to a diffusion constant of $D = 2a/T_{ff} = 4.8 \times 10^{29} \text{ cm}^2 \text{ s}^{-1}$, where $a = n^{-1/3} \approx 10 \text{ nm}$ is the average nearest-neighbor separation of spins with a density $n = 1 \times 10^{18} \text{ cm}^{-3}$ (6 ppm). Furthermore, I found a spin diffusion length of $L = \sqrt{DT_1} \approx 700 \text{ nm}$, which is significantly larger than the lateral dimensions of the wire (depth 250 nm, width 200 nm, length 4 mm). This spin diffusion length is competitive with those of metallic spin transport devices [47].

The above expression for $T_{ff,th}$ is strictly correct only in zero magnetic field gradient, but my experiments were performed in a field gradient ($G \approx 1.3 \times 10^5 \text{ T m}^{-1}$) that causes neighboring spins to experience a field difference $\Delta B$, thus making the Zeeman energy splittings unequal. This can suppress flip-flops because they no longer conserve energy [32, 48, 49]). Because the measured flip-flop time $T_{ff}$ agrees closely with the expected zero-gradient value $T_{ff,th}$, this implies an inhomogeneous line broadening of $\delta B \leq Ga/2 = 0.64 \text{ mT}$, which makes up this energy difference, allowing flip-flops to proceed. This broadening was confirmed by spectroscopic measurements, as described in section 5.6.

## 5.5 Simulations for Spin Wire Measurements

I developed Monte Carlo simulations to model the flip-flop spin dynamics of this spin wire experiment. These simulations support the explanation that the measured correlation time as a function of detection volume position (figure 5.6) is due to mutual spin flip-flops within the spin wire. In the simulation I model the spin wire, aligned along the x-direction, as a 1D
array of bins, of width $\Delta x$, each containing only a few net spins as shown schematically in figure 5.7a. The mutual spin flip diffusion along the wire is modeled by a sequence of time steps of size $\Delta t$. At each time step $n$ the probability of each spin to undergo a flip-flop with neighboring spins is evaluated. This results in a new spin configuration snapshot at time $n + \Delta t$ of the simulation. I assumed that spin flip is governed by random Poisson statistics with the average mutual spin flip-flop transition rate $W$. Once the spin configuration has been established, it is used to calculate the signal force for a given time step by multiplying it with the detection volume sensitivity profile of the iOSCAR protocol. The signal force is calculated for multiple positions of the detection volume relative to the wire, thus simulating cantilever motion along the length of the spin wire as was done in the experiment. After completing multiple time steps of calculation, the time record of the spin force acting on the cantilever is obtained for a given location of the sensitivity profile, as shown in figure 5.7c. The autocorrelation of this time record yields an exponential decay (see figure 5.7d) which is then fit to extract the correlation time $\tau_m$ of the spin ensemble.

In order to increase the computational efficiency of the simulation I represented a mutual flip-flop event between the spins in the neighboring bins as a transfer (or hop) of a single particle with the net effective moment $2\mu_B$. This approach is justified since, in the case of a mutual flip-flop event, one bin loses a net magnetic moment of $2\mu_B$, while the neighboring bin gains the same amount. Following this strategy, the simulation tracks only the up spins with the effective spin moment of $2\mu_B$ and ignores down spins with the effective spin moment of 0 thus reducing the number of spins that need to be tracked during the simulation by 50%

In order to simulate the spin dynamics at a given time step, I generated a Markov matrix that contains the probabilities that a given spin can transition from one particular spatial bin (represented by a column of the matrix) to another (rows of the matrix) over a time interval $\Delta t$. The probability of the transition is evaluated using the average flip-flop rate for neighboring spins given by $W = 3.8$ kHz, which is the expected rate we derived [1], thus giving the probability of a flip-flop event as $P = W\Delta t$. To eliminate the chance of an individual spin undergoing two or more flip-flops in a given time step, the condition $P \ll 1$ must be satisfied, therefore we set $\Delta t \ll T_{ff}$ where the average flip-flop time
Figure 5.7: Diagram illustrating the Monte Carlo simulation for the diffusion in the spin wire experiment. a) The force sensitivity profile (which represents the leading region of the spin detection volume) is shown in red. This is brought into the yellow spin wire region, and then the spins randomly diffuse within the wire which generates a fluctuating force time record. At $t = 350$ time steps there are relatively many spins within the detection profile corresponding to a large total force. b) At $t = 2,200$ time steps, there are relatively few spins within the detection profile, which results in a relatively small total force. c) The fluctuating force sensitivity record which is due to the flip-flopping spins in the wire. In the experiment, the average force is zero, but for the simulation, an offset was made to track half as many spins. Here the time record only shows about 2,500 steps, but in the final simulation about $10^7$ time steps were taken to generate the statistics needed to converge the results. d) The autocorrelation of the fluctuating force time record which gives the correlation time is shown in red. The initial decay for small lag values fits an exponential (in blue) very well, but then deviates for larger values. Increasing the number of time steps improves the fit.

$$T_{ff} = \frac{1}{W} = 0.26 \text{ ms}.$$ 

To incorporate the fact that the spin wire is not 1D, I assumed that flip-flops can
occur isotropically in any direction with only the x-component of the hop \( x = r \sin \theta \cos \phi \) contributing to spin transport along the wire. Here \( \theta \) and \( \phi \) are the components of a spherical coordinate system describing the direction of the hop, and \( r = 9.82 \) nm is the average spin-spin separation in the wire. Consequently, some flip-flops may occur in the same bin, which does not change the magnetic moment of the bin. I assumed that \( \theta \) and \( \phi \) are continuous variables since the lattice constant of diamond is 3.57 Å, and therefore there is a sufficient number of spin sites on a sphere of 9.82 nm radius to validate this assumption.

Taking into account all these considerations, the elements of the Markov matrix can assume the following three values: 1) the value of the element is \( p_1 = 0 \) if the spatial bin is too far away, at a distance \( > r \) from the origin of the hop. 2) The element is equal to \( p_2 = \frac{P}{N_b} \) where \( N_b = \frac{2r}{\Delta x} \) is the number of bins within a distance \( r \) from the origin of the hop. This is because the probability of a spin to land in a bin is proportional to the area of the surface of the sphere intersecting the bin. This area is constant for all bins within reach if the bin width \( \Delta x \) is chosen such that \( N_b \) is an integer (which I did to simplify the calculations). 3) The element is equal to \( p_3 = 1 - P + p_2 \), which reflects the probability of a spin to stay in the same bin due to either the lack of a hopping event or due to landing in the same bin after the hop (accounted for by the \( p_2 \) term). Thus the diagonal elements of the Markov matrix are all \( p_3 \).

During the simulation, the spin distribution in the bins for \( N_t \) time steps is calculated to generate the probe-sample interaction force time record for multiple positions of the sensitivity profile (resonance volume region) relative to the end of the spin wire. To extract the correlation time \( \tau_m \), the simulations calculates the autocorrelation of the force record and fits a decaying exponential \( f_{\text{fit}} \sim \exp - \frac{t}{\tau_m} \) as illustrated in figure 5.7c. The typical parameters for the simulation used to fit the data are: \( N_t \sim 10^7 \), flip-flop probability \( P \sim 0.02 \), and the spatial bin width \( \Delta x \sim 3 \) nm. The solid line in figure 5.6 represents the results of the Monte Carlo simulation, and shows excellent agreement with the experimental data.
5.6 Hyperfine Measurements

To measure the EPR spectrum of the spin wire, we implemented a modified iOSCAR protocol, which improves spatial resolution. Because of the hyperfine coupling for the P1 center, a high magnetic field gradient results in three spatially separated resonant slices. This can be revealed by probing a spatial discontinuity of spin density, so this enables spectral measurements on nanoscale spin ensembles. A conventional iOSCAR measurement utilizes the entire detection volume swept out by the cantilever oscillation, as this couples to the largest number of spins and creates the largest force signal. By interrupting the microwave power to the coil for less than half a cantilever period, we effectively truncate the detection volume (see figure 5.8). This enables us to maintain higher sensitivity while coupling to spins in a smaller spatial region. Utilizing this technique, which is called partially interrupted OSCAR (piOSCAR), we again scanned the detection volume into the spin wire. The improved resolution enabled us to resolve a staircase structure with three steps (see figure 5.9), corresponding to the three peaks of the P1 center’s hyperfine spectrum, as discussed in section 5.6.

The P1 center is hyperfine-coupled to the spin-1 nitrogen nucleus, and this results in a triplet of peaks in the EPR spectrum (figure 5.9), corresponding to the three nuclear spin states, $m_I = -1, 0, 1$. The hyperfine splitting for the diamond crystal orientation in this experiment relative to the external field is 3.3 mT [50]. In the magnetic field gradient of our probe magnet this splitting results in three spatially separated spin detection volumes. Each volume is defined by a surface of constant magnetic field that satisfies the resonance condition for a particular hyperfine transition (figure 5.9b). We observe a step-like increase in the spin signal as each volume enters the wire and the cantilever becomes coupled to an additional hyperfine transition (figure 5.9c). The spacing between steps ($s = 25$ nm) provides an accurate means of measuring the probe field gradient because the spacing is set by the ratio of the known hyperfine splitting (3.3 mT) to the gradient, which we find to be $1.3 \times 10^5$ T m$^{-1}$. This is consistent with our estimations of G obtained using a standard technique [7]. The staircase structure in figure 5.9c is a convolution of the implanted
Figure 5.8: Comparison of piOSCAR and iOSCAR resonance protocols. a) Timing diagram comparing the iOSCAR and piOSCAR spin manipulation protocols. In both protocols the microwave power is periodically interrupted to modulate the spins. The iOSCAR protocol utilizes the full volume swept out by the resonant slice as the cantilever oscillates, whereas the piOSCAR protocol modulates a definable subset of spins by means of partial interrupts. b) Schematic illustrating the spin detection volume of the iOSCAR (blue dashed lines) and piOSCAR (green dashed lines) protocols. Spins in the middle of the volume provide a stronger spin signal than those near the edge, as indicated by red shading. The piOSCAR protocol increases spatial resolution by controllably reducing the size of the measurement volume while optimizing spin sensitivity.

Spin density (approximately a step function), our force sensitivity profile and the EPR spectrum of spins in the sample. Deconvolution reveals the EPR spectrum shown in figure 5.9d. From the spectrum we find an average linewidth of 0.76 mT, which agrees with the expected linewidth of 0.65 mT and gives a measured flip-flop time $T_{ff}$ in agreement with the expected zero-gradient value $T_{ff,th}$ discussed above, and substantiates the proposed spin transport mechanism. We attribute the inhomogeneous broadening to crystal lattice damage or clustering caused by nitrogen ion implantation.
Figure 5.9: Setup, energy level diagram, data, and deconvolution for the spin wire hyperfine measurements. a) Energy level diagram showing the origin of the three separate magnetic resonance volumes for the experiment. At three distinct regions in the sample, the resonance condition is met for the three possible hyperfine conditions (nuclear spin values $m_I = -1, 0, +1$). The double arrows show the resonance condition given by the frequency $\omega_{rf}$. b) The three hyperfine spin detection regions (bowls) setup for measuring the spin wire. The relative size of the bowls and spin wire are to scale. c) Spin signal for the hyperfine measurement. As each hyperfine bowl enters the spin wire, there is an increase in the MRFM signal. This results in the step-like structure in the data. d) Deconvolution of the data with the single step-like profile of the spin wire density results in three hyperfine peaks. The center peak is expected to be larger, and is a well-known observation for P1 center spectra which is related to other spin defects present in the diamond.
Chapter 6
SUPPLEMENTARY WORK

6.1 Introduction

At least 75% of my time and effort during my graduate work was spent on the MRFM experiment that has been the focus of this dissertation thus far. However, over the course of this research, there were many related projects or experiments that either branched off of the MRFM project or were the focus of other individuals in which I was able to collaborate with. In this chapter, I will go through four of these topics which compliment the main MRFM experiment and also constitute a portion of my total research. The first of these is research and measurements of the lanthanum aluminate and strontium titanate interface (LAO/STO), which is a relatively novel material that exhibits both superconductivity and magnetism. Secondly, I will discuss studies and simulations of electron-nuclear double resonance (ENDOR) with MRFM. Although ENDOR MRFM proved to be much more complicated in diamond (and probably in many systems), I still believe it may be a useful and viable measurement technique in some materials. The third project I will discuss here is the use of thin membranes as force detectors in MRFM, which is the primary work of Nicolas Scozzaro, a colleague here at OSU. Lastly, I will discuss my contributions to Richelle Teeling-Smith’s optically detected magnetic resonance (ODMR) experiments on NV centers in diamond attached to double stranded DNA.
6.2 Lanthanum Aluminate and Strontium Titanate Interface (LAO/STO)

In the last few years, there has been an increase in the number of studies on the interface between lanthanum aluminate (LaAlO$_3$) and strontium titanate (SrTiO$_3$) [as many as 7 citations from my candidacy paper]. This attention is mostly due to the observation that LAO/STO exhibits both superconductivity and magnetism, two properties that are usually not found in the same material, and each of which is a huge area of research in condensed matter currently. Both LAO and STO are perovskites with chemical formula of the form ABO$_3$. Separately, they are non-magnetic insulators, but when a thin layer (at least 4 unit cells thick) of LAO is grown on a titanium-terminated STO substrate, a 2-D electron gas forms at the interface that is both conductive and magnetic.

The explanation for the emergence of these interface electrons has been a subject of debate for several years now. The most likely explanation is that the alternating negative and positive (001) planes in the LAO produce a polar gating effect that attracts 0.5 electrons per lateral unit cell down to the interface. Figure 6.1 shows the perovskite structure highlighting the (001) planes the help illustrate the polar gating effect. This polar gating hypothesis explains the observation of a critical thickness of 4 unit cells of LAO, because as more unit cells are placed, the resulting electric potential across the LAO increases until it surpasses the band gap (which is 5.6 V for LAO) which results in electrons moving to the interface. The polar gating hypothesis is often referred to as the polar catastrophe which refers to a hypothetical situation in which electrons do not redistribute to the interface regardless of how many LAO unit cells are added, and in that case the electric potential would diverge to infinity.

Although the conductivity and superconductivity (critical temperature $\approx 200$ mK [51]) of the interface has been the focus of much research, my interest has been in the magnetism of the LAO/STO interface. After all, the MRFM experiment is designed for sensitive measurements of the magnetic properties of materials. Many interesting experiments have already been done on the magnetism of the LAO/STO interface, but I was curious to see
if there was a unique opportunity to use the MRFM probe to discover something new and interesting about the magnetism at the LAO/STO interface.

To begin with, I took bulk measurements of LAO/STO as well as bare STO substrates using a Bruker EPR spectrometer. I varied the azimuthal angle of the sample between measurements and observed the angular dependence of well-known EPR peaks (see figure 6.2). These are well-known peaks that are associated with common impurities in the STO substrate, such as Fe$^{3+}$, Cr$^{3+}$, and Fe$^{3+}$V$_0$ (the last is iron ion next to an oxygen vacancy).

Unfortunately, the main result of these measurements was that the background impurities within the STO substrate as well as the noise limitations of the EPR spectrometer cavity were too large compared to the LAO/STO interface signal, if present at all. Even
after thinning down the substrate with a polisher, no clear interface signal could be observed with some degree of certainty, although there was a faint, broad signal that may be related to the interface. The fact that it is so broad in the EPR spectrum may indicate that the LAO/STO interface has many resonance conditions for the various so-called 2DEG puddles which are believed to be superparamagnetic.

In addition to the EPR measurements, I also worked on MFM, Low-temperature MFM, and Kerr magnetometry (MOKE) [55]. These measurements were done with Nicolas Scozzaro, and I will not show the results for all of them here, but I will say that none of the measurements led to any conclusive findings, however some of the low-temperature MFM measurements produced some interesting results (these were mostly done by Nicolas).

Another issue I ran into in pursuing the LAO/STO as a potential sample for MRFM measurements was that it was never obvious what would be the most appropriate measurement protocol. This is what initially motivated the EPR measurements. The hope was that the EPR measurements would reveal a resonance condition for the bulk LAO/STO interface which would inform future MRFM measurements. One issue with LAO/STO is that it is thought to have ferromagnetic or superparamagnetic behavior. This would make the iOSCAR measurement profile which I used in other MRFM experiments useless since that protocol relies on the ability to adiabatically invert spins at the cantilever frequency. This difficulty could easily be overcome by switching to a ferromagnetic measurement approach FMRFM [56–59], however, any MRFM experiment takes a lot of work, preparation, and cost (for liquid helium), and so it is better to have some idea of the material’s properties or resonance conditions before attempting the experiment. In conclusion, I think LAO/STO or other similar oxide samples could be measured using the MRFM, but it would likely be necessary to first learn a little more about the spin resonance of the material.

### 6.3 ODMR of NV Diamonds Attached to DNA

Since I spent a lot of time researching P1 centers in diamond with the MRFM, I was very interested in Richelle Teeling-Smith’s project which involved NV centers in diamond.
Richelle used optically detected magnetic resonance (ODMR) [60] to measure NV centers, because NV spins are optically addressable. In section 5.2, I went over the basic physics of the NV defect center and its optical resonance properties. What is really amazing in this experiment is that Richelle attached single NV nanodiamonds to tethered DNA strands that are suspended in aqueous solution. In fact, it is the biophysics of the DNA that she is ultimately interested in, and the NV diamonds are simply a powerful nanoscale label for the DNA biomolecule. Figure 6.3 illustrates a single NV nanodiamond attached to a strand of DNA in her experiment. The goal of Richelle’s project was to gain insight into the dynamics and functionality of the DNA structure by using the NV nanodiamond as a site-specific label (or probe).

The DNA is attached to the substrate (a glass slide) via some novel, non-trivial biochemistry. Since the NV nanodiamond is attached to the other end of the DNA, as the DNA moves and twists around, the nanodiamond explores all possible orientations equally. The resonance of the NV center depends on the orientation of the applied magnetic field relative to the symmetry axis of the NV center (the axis the nitrogen atom and vacancy lie on). If you measure a stationary, single-crystal diamond in a static field, you will observe 8 distinct peaks which correspond to the 2 possible transitions ($m_s = +1 \leftrightarrow m_s = 0$ and $m_s = -1 \leftrightarrow m_s = 0$) times the 4 possible crystal axes available to the NV. However, in the DNA experiment, these 8 distinct peaks are blurred out due to the motion of the DNA (and thus the nanodiamond) and this results in a powder pattern [13, 14, 61]. In other words, a single NV nanodiamond exploring all possible orientations equally in time, gives the same result as a large collection of NV nanodiamonds arranged in random orientations (a powder of nanodiamonds). Richelle took ODMR measurements of all three of these situations (single static nanodiamond, static powder of nanodiamonds, single nanodiamond attached to moving DNA), and her data shows a strong agreement between the latter two (see figure 6.4).

My contribution to this work, was to first understand what a NV diamond powder pattern should look like according to a simple Hamiltonian for the system. I developed a model using this Hamiltonian and simulated a powder pattern for the NV system. The
result of this was a resonance spectrum which was essentially a plateau, to first order, and which is rounded at the edges due to the convolution of the linewidth of the NV. After my initial modeling of this, I then worked with Nicolas Scozzaro who went on to developed a more complex model that accounted for some of the other features in the powder pattern, like the dip in the center, for example. The fits to the data in figure 6.4, are a result of the final modeling (which was done by Nicolas along with my contributions).

Powder patterns were first observed and understood in the 1940’s, and George Pake was able to measure the distance between the two hydrogen nuclei in water [61] by measuring and analyzing the powder pattern from gypsum hydrates (CaSO$_4$·2H$_2$O). He measured the separation of the hydrogen nuclei to be 1.58 Å, which is very close to modern measurements (1.61 Å). In an effort to understand powder patterns in general, I first simulated this well known Pake powder pattern which has two ‘horns’ near the center. The Pake powder pattern, with its distinctive features, is a more typical powder spectrum, and I mention it here to contrast the very flat NV powder pattern.
Figure 6.2: Angular dependence of LAO/STO EPR measurements. a) The well-known EPR peaks of STO arising from impurities: Fe$^{3+}$, Cr$^{3+}$, and Fe$^{3+}$V$_0$. b) Angular dependence of the well-known STO peaks. Here, 90 degrees corresponds to in the plane of the sample which is (100) crystal orientation (0 degrees, out of plane). The anisotropy of the Fe$^{3+}$V$_0$ defect arises from their axial symmetry in the presence of a tetragonal crystal field [52,53]. Similarly, the angular dependence of the Fe$^{3+}$ resonance line can be understood from it’s substitutional position of the Ti$^{4+}$ ion and interaction with neighboring oxygen atoms [54]. c) Angular dependence of the LAO/STO sample. The well-known STO peaks and the noise of the EPR cavity (large broad wave near 3000 G) make it difficult to detect any signals from the LAO/STO interface itself. There is some small noisy signal spread out near the last few Fe$^{3+}$ peaks, but it is hard to say anything conclusive about this.
Figure 6.3: Illustration of the NV diamond and DNA setup. The DNA is attached to a glass slide (gray substrate), and the NV nanodiamond is attached to the end of the DNA. The green laser light is focused onto the DNA and NV nanodiamond which. According to the resonance condition of the NV center, the nanodiamond will absorb the green laser light and then emit red light as it photoluminesces (hence the diamond’s pink color).
Figure 6.4: ODMR Data for Single Molecule DNA with NV Center. a) ODMR spectrum for a single stationary nanodiamond in a 50 G applied field. There are 8 distinct peaks which are expected from the product of 4 lattice axes and 2 EPR transitions. b) ODMR spectrum of a powder of nanodiamonds. Measurements were taken in three different applied fields, 0, 18, and 32 Gauss. c) ODMR spectrum of a single nanodiamond attached to a moving DNA molecule.
Chapter 7

CONCLUSIONS

7.1 Future Directions

Experimental physics can be quite competitive and therefore it is important to take advantage of the main strengths of the experimental tool you are using to achieve successful results. The extraordinary force sensitivity of the MRFM gives it a huge advantage over other experimental probes. With the ability to detect very small spin ensembles (down to a single electron spin [2]) the MRFM is ideally suited for investigating novel systems that are likely to have interesting physics and that containing a small number of spins.

One system that I have been interested in studying with the MRFM is paramagnetic spin defects in graphene. Since graphene is a 2-dimensional material and the typical density of these defects is on the order of ppm (parts per million, with respect to the density of carbon atoms in the lattice), the number of spins the MRFM could measure would be quite small, but this would also be a great opportunity for nanoscale detection of the local dynamics of these spin defects.

Graphene is currently one of the most widely studied materials in physics [62], because it possesses many remarkable properties including: efficient electrical and thermal conduction, optical transparency, and physical strength. In addition to these, graphene is a promising material for studying spin-based phenomena and developing spintronic devices[cite: Andre Geim, the rise of graphene]. Graphene has high spin transport [citation], however, not much is known about the mechanisms that limit the lifetime of the itinerant spins. It is likely that the dominant mechanism for this is due to the itinerant spins scattering off of
local spin defects and cross-relaxing in the process. Therefore any results that shed light on the lifetime of these local spin defects or the associated relaxation mechanisms would be interesting and useful for furthering graphene spin transport research.

There are at least two types of paramagnetic spin defects in graphene that have been closely studied: adatom defects and vacancies [63, 64]. The most common adatom defects are hydrogenated and fluorinated graphene. The main issue with adatom graphene defects is that they can be unstable in ambient conditions (which would require in situ measurements) and they can also cluster via diffusion on the surface. On the other hand, single carbon vacancies in graphene can potentially self-heal or diffuse together to form divacancies, however they seem to be more robust than adatom defects. The single carbon vacancy in graphene (see figure 7.1a) is a spin-1/2 paramagnetic defect that can occur naturally within the crystal with a very small density (typically $\sim 10$ ppm or less) and can be increased via ion irradiation up to about 1 part per thousand. Increasing the vacancy density beyond this leads to structural instability of the graphene [64].

The physical origins of the graphene vacancy’s spin one-half paramagnetism is very interesting, although still debated. Several experiments have been performed to sort out the proposed theories, and here I will give a quick summary of these models. With the removal of a single carbon atom, the symmetry of the two graphene sublattices is broken, and the $sp^2$ and $p_z$ orbitals that form graphene’s $\sigma$ and $\pi$ bonds (in-plane and out-of-plane, respectively) are left unsaturated. This results in a singly-occupied $\pi$ state localized near the vacancy with an energy close to the Dirac point [reference dual origin Geim references, middle of page 3, 1st column]. This $\pi$ state is the first source of the vacancy paramagnetism. However, this can be quenched by increasing the Fermi energy (via doping or gating for example) to the point where the $\pi$ state becomes doubly-occupied [63]. A second source of magnetism could be the resolution of the dangling $\sigma$ orbitals in the plane of the graphene. Since there are an odd number of these (three) there is likely to be some contribution that can not be saturated. It is possible that two of these bond, but then the third is left unpaired, or another possibility is that these orbitals hybridize in a way such that they electrically repel away from the graphene plane. However, if two move slightly away from
Figure 7.1: The graphene vacancy defect center. a) Illustration of a carbon vacancy spin defect in graphene. The dotted circle is highlighting the vacancy, where there would normally be a carbon atom. b) Top and side views of the graphene lattice near the vacancy defect which depict the frustration of the electron orbitals (in blue). ‘In’ and ‘out’ refer to the direction in which the orbitals protrude away from the plane of the graphene, and the question mark represents frustration.

The plane (in and out) to avoid overlap with each other, the third orbital is frustrated because it cannot avoid having significant overlap with one of the other two. Figure 7.1b
illustrates the frustration of the dangling electron orbitals as they interact repulsively.

7.2 Conclusions

In conclusion, I have shown measurements in chapter 5 that investigated the effects of flip-flop-mediated spin transport on the lifetime of nanoscale spin ensembles in an insulating diamond spin wire, in the complete absence of charge motion. This pure spin transport arises from the intrinsic spin dynamics of dipole-coupled P1 centers at thermal equilibrium, which were observed by measuring spin noise without imposing a polarization gradient. By spatially resolving the three electron spin populations (corresponding to the three spin states of the hyperfine-coupled nitrogen nucleus), the EPR spectrum of less than 100 net spins within the wire was obtained. This gave a linewidth that corroborates flip-flop-mediated spin diffusion as the mechanism responsible for the observed spin transport. The spectrum also enables accurate measurement of the applied magnetic field gradient. These measurements provide insight into the mechanisms of spin transport and lifetime relevant for the development of nanoscale spin device elements.

Regarding the LAO/STO interface, it is still not clear how an MRFM measurement of this material would proceed, but it seems that a better understanding of the type of magnetism and resonance conditions is necessary. It may be possible to measure the LAO/STO using an adiabatic inversion protocol like iOSCAR, however it is more likely that some kind of ferromagnetic MRFM protocol will be necessary.

7.3 Final Thoughts

Lastly, I want to consider the MRFM probe as a whole, and describe the difficulties and strengths of the experiment. Overall, high-sensitivity MRFM is a very challenging experiment in condensed matter physics. Unfortunately, the main component of the experiment, the ultra-soft cantilever, is very susceptible to being damaged or destroyed. While attempting to glue a magnetic particle, FIB the particle, load the cantilever into the system, and cooldown the experiment, there is a moderate chance of destroying or critically damaging
the cantilever, even when precautions are taken. These processes can take days or weeks, and at any point there is a risk that you will have to start over. Additionally, the particle you glue onto the cantilever may turn out to be non-magnetic (or not very magnetic), and you won’t know until you have spent almost a full day gluing that particle on and then baking the cantilever in an oven (this happened several times to me during my time on this project). Once you have glued a magnetic particle onto the cantilever, it can come off, either during the magnetometry or during the MRFM experiment (this happened several times). The gradient of the particle may not be strong enough to do the experiment. The Q-factor of the cantilever may not be high enough. There may be too much electrostatic charge on the cantilever to do the experiment. As was discussed in section 3.2, the cantilever may bend and result in all visibility being lost.

Other components of the experiment can easily break as well. The piezo tube connections, the Attocubes, the microwave coil, the vacuum system, and the laser are all fragile components and have broken at least once over the years that I have worked on this experiment. Each time one of these breaks, the experiment can be stalled for up to a month. The FIB that we use to mill the particle is also prone to going done for a week or so. This happened dozens of times to me over the years. The frustrating part of these technical challenges is that they are just that, technical. Solving these problems usually does not involve physics, but rather engineering. I think it is good to be challenged with experimental difficulties, but too much of that can take time away from uncovering new and interesting physics.

Despite all of these technical challenges, the MRFM probe has proven to be an extremely powerful tool for characterizing spin systems, and the payoff for having a successful experiment is often huge. That is why I am happy to have had the opportunity to work on this experiment. It was very rewarding to publish the results of the diamond spin wire experiment in a high-impact journal like Nature Nanotechnology, and I was really happy to present those results at the American Physical Society (APS) annual meeting and also give a long invited talk at the Industrial Diamond Association (IDA) annual meeting (both in 2014). The MRFM experiment has increased my patience and attention to detail. It
taught me to think outside of the box when faced with a difficult challenge, and remain
guarded against making naive assumptions. Aside from some of my experiences in the mil-
itary perhaps, this experiment has been the most challenging and unpleasant experience I
have faced thus far in my life, but I feel fortunate to have had that experience.
Bibliography


Appendix A

Experimental Procedures

A.1 Cryogenic Procedures

The following procedures outline the steps one should follow to successfully and safely cool the MRFM experiment to cryogenic temperatures. These procedures were developed over my time running the experiment based on my experience with the system, but should not be considered final. These procedures should constantly be revised as needed to maintain safe operation of the system. In addition to these procedures, I have outlined important information regarding general cryogenic principles and safety tips in section 3.7.

Initial Cooldown to LN2 Temperature

Cooling down to LN2 temperature is usually the first step for cooling the probe. This can certainly be one of the most dangerous steps, and can take several hours to fully cool down (see figure X as an example).

1. Acquire liquid nitrogen - Fill up a liquid nitrogen transfer dewar. It takes less than half a dewar to complete the transfer. When you fill up the transfer dewar, remember to open the valves in the correct order: first open the valve on the wall, then the inlet valve on the dewar, lastly open the exhaust valve on the dewar. When you finish filling up the transfer dewar, close the valves in the reverse order.

2. Insert transfer line - I recommend using the long (60 inch) transfer line for this, although you can probably use either one in principle.
3. **Connect line to dewar** - Connect the transfer line to the transfer dewar using the flexible transfer hose.

4. **Connect nitrogen gas** - Find the correct brass fitting and connect the nitrogen gas from the building supply to the liquid nitrogen transfer dewar using the clear plastic tubing. You need this to maintain a constant pressure of 15 psi throughout the transfer.

5. **Heat gun** - Have the heat gun ready to use in case the transfer line gets stuck or something else needs to be warmed up quickly.

6. **Safety gloves** - Have cryogenic safety gloves nearby and make sure to use them when handling anything cold.

7. **Open Temperature Log VI** - Open and test the Temperature Log VI to make sure it is working properly.

8. **Begin the transfer** - Open the transfer dewar valve one full turn, start the Temperature Log VI, and record the start time in the lab notebook.

9. **Monitor the transfer** - You need to monitor several things during the transfer to ensure it is going correctly. The following parameters can be a good indication of a successful transfer. The temperature of the probe should begin dropping within 5 minutes of starting the transfer, and continue to drop for several hours after the transfer is complete. The vacuum pressure of the probe will drop from $\sim 10^{-6}$ to $\sim 10^{-7}$ Torr due to cryopumping. Maintain about 15 psi of pressure in the transfer dewar during the transfer. The frequency of the cantilever and DC level will vary slowly. The flow rate of the cold nitrogen gas coming out of the exhaust should remain moderate and constant until the end of the transfer at which point it may start to plume (thick foggy air will come out).

10. **Stopping the transfer** - It should take roughly 1 hour to fill up the experiment dewar with liquid nitrogen. As soon as liquid nitrogen starts coming out of the exhaust, immediately close the transfer valve and record the time in the notebook. Let the
Temperature Log VI continue to record data over the next several hours until the temperature stabalizes.

11. **Disconnect transfer lines** - Approximately 20 minutes after the transfer has completed, the transfer line in the experiment should be warm enough to pull out safely.

12. **Plug the transfer hole** - Remember to plug the transfer line hole on the experiment so that air does not cryopump into the experiment dewar.

13. **Clean up** - Put away all the equipment for the transfer.

14. **Length of cooldown** - It will take about 5 to 6 hours for the temperature to drop to around 100 K, and about 9 to 10 hours for it to stabalize around 77 K (see figure X)

**Maintaining LN2 Temperature**

1. **Duration** - If the dewar is full, it should stay around 77 K for about 4.5 days.

2. **Power Outage** - Anytime the experiment is kept at low temperatures, it is important to be aware of power outages that would shut off the vacuum system and result in warm air entering the probe. This will result in cryopumping which I discuss in Section 3.7. If this happens, immediately start warming up the system, making sure to allow the system to vent any frozen air safely.

3. **Plan and monitor** - It is important to plan when you are going to warm up, refill, or cool the system. Always estimate when the liquid helium should run out (boil off entirely) and continue to monitor the pressure, temperature, cantilever frequency, etc. to ensure that the system is running optimally.
Refilling LN2

1. Acquire liquid nitrogen - Fill up the transfer dewar following the same steps outlined for the initial LN2 transfer above.

2. Connect flexible transfer hose - Connect the flexible transfer hose to the short transfer line (X inches long), before you insert the transfer line into the experiment dewar. This is safer because it avoids having liquid nitrogen shoot out of the transfer line and possibly onto yourself when you put it in.

3. Insert transfer line - After connecting it to the flexible hose, inset the short transfer line (X inches long) into the experiment. It is best to use the short one because the probe should already be at 77 K, and you don’t want to boil off liquid nitrogen you already have.

4. Follow steps 3 - 13 of initial LN2 transfer - The refill is very similar to the initial LN2 cooldown procedure, so follow steps 3 - 13 above, however, you don’t really need to run the Temperature Log VI and obviously it may not take as long (less than 1 hour) if there is a significant amount of LN2 in there already.

Pushing out LN2

1. Get collection dewar - You will need a small open-mouthed dewar for collecting the LN2 that is pushed out of the experiment dewar.

2. Nipple fitting on exhaust - Disconnect the exhaust on the experiment and replace it with the nipple fitting. Then attach the clear tubing of nitrogen gas from the building to the nipple fitting. Do not open the valve yet, but adjust the regulator for the nitrogen gas to a pressure of 15 psi.

3. Heat gun - Have the heat gun ready to use in case the transfer line gets stuck or something else needs to be warmed up quickly.
4. Safety gloves - Have cryogenic safety gloves nearby and make sure to use them when handling anything cold.

5. Open Temperature Log VI - Open the Temperature Log VI and make sure it is working, and update the save file name.

6. Read over initial cooldown with LHe - Typically after pushing out the liquid nitrogen, you immediately begin transferring LHe, and there is no time to read over that procedure since they are done consecutively. Therefore you should read over the procedure now before beginning the push-out, or at least be looking over it while you push out the LN2.

7. Insert 60 inch transfer line - Insert the long (60 inch) transfer line into the experiment dewar. It is absolutely critical that you use the long transfer line for pushing out the LN2. For more details on this, see Section 3.7.

8. Begin the push-out - To begin, open the valve on the wall for the nitrogen gas at 15 psi, and immediately start the Temperature Log VI. Also note the time in the lab notebook.

9. Visual confirmation - Once you have started the push-out, it is very important to visually confirm that LN2 is coming out of the flexible transfer hose and into the open-mouthed collection dewar. See Section 3.7 for more details on this.

10. Keep checking - Every 3 minutes, you need to check that LN2 is still coming out. Set a timer to go off every 3 minutes, because it is easy to get distracted. If you forget to check it and let it go too long, you can start warming up the system, which can waste a lot of LHe later.

11. Record the stop time - When the LN2 stops coming out, note the time in the log notebook.

12. Wait and then stop - After about 10 to 15 minutes have passed from when LN2 stopped coming out, or when the temperature of the probe increases by 1 Kelvin
(whichever happens first), stop the puch-out by closing the valve to the 15 psi nitrogen gas line and remove the transfer line. You may need the heat gun to remove the transfer line. Immediately begin transferring LHe.

**Measuring LHe in transfer dewar**

1. **Slowly open transfer dewar** - Slowly open the LHe transfer dewar to release the excess pressure.

2. **Insert a thin tube** - Slowly insert a long, thin, stainless steel tube into the liquid helium. There will be a plume of cold vapor coming out of the dewar as a result of inserting the room-temperature tube. Just be careful to do it slowly enough to not burn yourself. You want to have your thumb covering the top of the tube as you lower it into the dewar. Some people prefer to have a glove or some other equivalent material secured onto the end of the tube, but just using your thumb works fine as well.

3. **Feel the oscillations** - You will feel a fluctuating pressure of helium gas coming out the top of the tube due to liquid helium vaporizing in the dewar. This is a thermoacoustic effect known as Taconis oscillations.

4. **Mark the dewar bottom** - Keep lowering the tube until it hits the bottom of the dewar. Then use an alligator clip to mark this level on the tube.

5. **Mark the liquid surface** - Slowly raise the tube until you feel the frequency of the Taconis oscillations abruptly increase by a factor of 2 or 3. There will also be an increase in the amplitude of the oscillations at the same time. When this happens, the tube is at the liquid surface, and you should mark it with another alligator clip.

6. **Calculate the volume** - Take the tube out, close the transfer dewar, and convert the measured inches into volume using the table provided.
Initial cooldown with liquid helium

1. **Measure liquid helium** - Before you start, measure and record how many liters of liquid helium you have.

2. **Initial cooldown about 55 liters** - It takes about 55 liters to do an initial cooldown if you want to fill the experiment dewar all the way to the top of the belly (this corresponds to 29.9 inches on the liquid helium level monitor). About 40 liters of this is used to fill the dewar with liquid, and the remaining 15 liters is used to cool the system down from about 77 K to 4 K.

3. **First check the system** - It is important to check as many things as you can to ensure things are working before you cool down with liquid helium. For example, make sure the cantilever signal has good visibility, Q-factor, and an amount of noise that makes sense (should be thermally limited), and also confirm that the piezo tube and attocubes are working by approaching the sample. Make sure the piezo tube (or attocube external control voltage) has a range of motion which is significantly greater than a single attocube step.

4. **Reattach the exhaust** - Assuming you just pushed out the liquid nitrogen, make sure to take the nipple fitting back off and put the exhaust back on.

5. **Quick-connects** - Make sure you have the quick-connect components with the small O-ring for attaching the transfer line to the transfer dewar.

6. **Helium gas** - Make sure you have enough helium gas in the gas cylinder (when they are full, the gas cylinders have a pressure around 2,000 psi or about 14,000 kPa, and this goes linearly via the ideal gas law). Connect the helium gas to the transfer dewar using the brass fitting and the clear plastic tubing.

7. **Turn on level monitor** - Turn on the liquid helium level monitor and make sure it is on update.
8. **Transfer line extension** - For the initial cooldown with LHe, you need to attach the extension rod for the part of the line that goes into the experiment dewar. This is so that the line goes all the way to the bottom and makes use of all the liquid helium’s cooling power, and not doing this will waste a lot of LHe.

9. **Heat gun** - Have the heat gun ready to use in case the transfer line gets stuck or something else needs to be warmed up quickly.

10. **Safety gloves** - Have cryogenic safety gloves nearby and make sure to use them when handling anything cold.

11. **Open Temperature Log VI** - Open the Temperature Log VI and make sure it is working, and update the save file name. Note the time in the lab notebook and run the program. The program is likely to already be running since you will have just finished pushing out the LN2.

12. **Insert transfer line** - With the help of a colleague, take the transfer line over to the experiment and carefully open the transfer dewar to release the pressure. Then slowly lower the line into the transfer dewer using a step ladder and connect it with the quick-connects. Close the emergency pressure relief valve to maintain pressure in the dewar. The other person will notice cold helium gas coming out the other end of the transfer line. Since this is an initial cooldown, you shouldn’t wait until the gas starts pluming out, just put it in the experiment dewar right away. Once the transfer line is in both dewars, check to see if there is a moderate current of cold helium gas coming out of the exhaust.

13. **Maintain 2 to 3 psi** - Make sure to keep a constant pressure of 2 to 3 psi in the transfer dewar.

14. **Temperature increases** - Initially, the temperature will start to climb for a few minutes, but it shouldn’t go much past 80 K.

15. **Monitor the system** - You need to keep an eye on at least 5 things during the transfer:
the temperature, the pressure in the transfer dewar, the flow coming out of the exhaust, the cantilever frequency, and the reading on the liquid helium level monitor.

16. **Temperature decreases** - After about 7 minutes or so the temperature should start to decrease.

17. **Liquid starts to collect** - After about 10 minutes or so, the liquid helium level monitor should register the first tenth of an inch.

18. **Maintain proper rate** - The liquid helium should collect within the transfer dewar at a rate of about 1 inch every 45 seconds or so. The liquid helium level monitor should increase steadily in single increments of tenths of an inch. If the level is fluctuating between 3 or more values at a time, this is a good indication you are transferring too quickly (which will waste LHe) and you need to decrease the pressure in the transfer dewar. The correct fill rate should correspond to a pressure between 2 and 3 psi.

19. **Stopping the transfer** - When the liquid helium level monitor reaches about 29.7 inches, you can close the valve supplying the helium gas to the transfer dewar and allow the remaining pressure to fill the last two tenths of an inch. During this time, remove the clear plastic tubing from the brass fitting. After the monitor reads 29.9 inches, vent the transfer dewar and remove the transfer line.

20. **Replace plug** - Replace the plug/cap on the experiment where the transfer line was inserted.

21. **Measure LHe left** - Measure and record how much liquid helium is left in the transfer dewar. It should have taken about 55 liters.

22. **Open the pressure relief valve** - Make sure to leave the transfer dewar in the correct state, which includes opening the emergency pressure relief valve. This is a safety concern which helps prevent turning the dewar into a bomb.

23. **Continue Temperature Log VI** - Let the Temperature Log VI continue to run for a couple hours or until the temperature stabilizes.
Maintaining liquid helium temperature

1. **Monitor the level** - Use the liquid helium level monitor to frequently measure and record the number of inches left in the experiment dewar and the time of the measurement.

2. **Typical rate** - The MRFM experiment will typically lose about 0.4 inches per hour (in the belly) which corresponds to just shy of 3 days cold, but only about 2 days and 8 hours until the level drops from 29.9 inches to 6.0 inches.

3. **Plan for refill** - Estimate the boil off rate and the expected time that the level will drop below 6.0 inches. Then plan when you will do the next LHe refill (if you are going to). This is also important for ensuring the liquid helium level doesn't drop below the the external magnet (around 6.0 inches) while there is current in the magnet. If this happens, the magnet will quench, which can be damaging to the magnet and which will also waste some liquid helium.

Warming up

1. **Safely pull sample away** - Before the probe begins to warm up, you need to pull the sample away from the cantilever and coil so that it doesn’t collide into them during the warm up due to thermal contraction/expansion. Use the attocube controller to move the attocubes a total of -5,000 steps in the x-direction and -13,000 steps in the z-direction. Do this by first moving in single steps a few times, and then 3 steps at a time a few times, 10 steps at a time a few times, and continue with 30, 100, and finally 1,000 steps at a time. Also, make sure to alternate the x-direction steps and the z-direction steps as you go. In other words, don’t take all the x-directions steps and then alll the z-direction steps.

2. **Two options for warming** - You can warm up slowly by just letting the experiment go, or you can warm up more quickly by flowing room-temperature nitrogen gas. If the probe is around 4 K when you do this, there is a concern that you will liquify
or solidify and nitrogen gas that you send down there, which could be problematic, however, the system usually heats up so quickly that this hasn’t been a problem in the past. To do this quicker option, use the nitrogen gas dewar fitting and attach it to the long, 60 inch transfer line. If you let the probe warm up slowly on its own, it takes at least 3 or 4 days before it is warm enough to pull out of the pit and open it up or work on.

#### A.2 Cleanliness Protocols

As was mentioned in Chapters 3 and 7, the cleanliness of the MRFM system is critical for maintaining a working cantilever that does not bend, has high Q-factor, and a small spring constant. Therefore, it is important to follow strict cleanliness guidelines when working with the system. I have developed the following protocols for keeping the MRFM experiment clean, which were strongly influenced by Michael Herman who previously worked on this experiment.
Strict Cleanliness Rules

The following is the strictest level of cleanliness that I adopted from Michael Herman. Following these rules is tedious, and can be time consuming, however it is the safe way to ensure the cleanliness of the system.

1. Only clean tools, clean parts, and clean gloved hands can touch the inside of the probe or other clean items.

2. All tools and parts should be sonicated according to the cleaning procedure and kept in a clean container to be considered clean for using on the probe. Also, they must be re-cleaned every 2 weeks at most to remain clean.

3. A gloved hand is only considered clean if the glove hasn’t touched anything dirty, it was put on recently, and was new from the box.

4. If a dirty tool or part touches a clean tool or part, both are then considered dirty.

5. Always use brand new TechniCloth non-woven wipers (9” X 9”) for placing clean parts and tools. Never put a clean tool on the work bench, and if you do, it is then considered dirty (even if you just cleaned the work bench).

6. Do not leave clean tools and parts out on the work bench for more time than is necessary. If they are left out unnecessarily, they are considered dirty.

7. Clean tools and parts can only be stored in designated clean environments. Some acceptable examples include the clean nitrogen flow box next to the experiment or the clean tool container which should be cleaned by thoroughly wiping it down with solvents. If tools and parts are stored elsewhere, then they are considered dirty.

8. Cover vacuum flanges, vacuum parts, open experiment cans, and other clean components with clean alluminum foil (2 layers thick) when appropriate.

9. If you don’t know if something is clean, you must assume it is dirty.
Moderate Cleanliness Rules

This set of rules is less strict than the previous set and the rules are written more generally. You can follow these rules to increase the efficiency of your work, however, you may compromise the cleanliness of the system. These rules are also good for compromising with co-workers who don’t agree to following the stricter set.

1. Wipe down clean tools with acetone if you don’t know when they were last cleaned. 

2. Clean tools should be sonicated every couple weeks (following the sonication procedure).

3. Tools which are not in use should be put away.

4. Wipe down tool container when replacing clean tools.

5. Don’t skimp on clean supplies (ie foil, gloves, kimwipes, etc). Use fresh ones.

6. Don’t skimp on clean supplies (ie foil, gloves, kimwipes, etc). Use fresh ones.

7. Change gloves if you touch anything which you believe is unclean.

Cleaning Procedure for Parts and Tools

1. Place the parts in a beaker and fill the beaker with the liquid corresponding to whatever step you are on (see the list below).

2. Place the beaker in the ultra-sonicator for 20 to 30 minutes for each cycle.

3. Make sure to turn on the heater (green LED switch), and then turn it off when you are done with all the sonication steps.

4. After all of the cycles are complete, dry the parts using Nitrogen gas while holding the parts with clean gloves.

5. Immediately place the cleaned parts in a clean storage container.
(a) Water with a single drop of Liquinox
(b) De-ionized water
(c) Acetone
(d) Ethanol
(e) Methanol
(f) De-ionized water

A.3 Alignment of Experimental Setup

Include in this the procedure for deionizing as well

A.4 Sample Installation and Removal

When switching the sample, it is safest if the cantilever has already been removed, however this is not necessary. If all you need to do is change samples and you already have the laser and cantilever aligned well, you can carefully removed the sample with relatively little risk to the cantilever. To remove the sample:

1. Use the attocubes to move the sample as far away from cantilever and coil as possible (negative z and negative x directions)
2. Loosen both screws a very small amount, but don’t remove either.
3. When you loosen the sample holder screws, you need to hold the copper sample holder firmly with two fingers to counter the torque you are applying with the hex driver.
4. Loosen the screw farthest from the coil all the way and remove it.
5. Carefully rotate the sample away from the coil and cantilever.
6. While holding the sample, remove the second screw all the way.
7. Carefully remove the sample.
8. To install the sample, you basically want to do the same steps in reverse. This can be harder however, because you need to line up the screw holes and make sure you don’t drop anything. Holding screws with clean tweezers can be very helpful.

A.5 Gluing Magnetic Particle to Cantilever

To glue magnetic particles onto the tip of the ultra-soft cantilevers, I used glass needles. To make these needles, I used a glass puller from Sutter Instruments Co., model number P-2000. First, you place a glass rod which is about 4 mm thick and approximately 13 cm long into the puller. The P-2000 executes programs with user-defined parameters for the heating and pulling of the glass rod. The program I used (number 60, for reference) is a two-step program that has the following parameters:

\[
\text{HEAT} = 900, \text{FIL} = 4, \text{VEL} = 55, \text{DEL}=132, \text{PUL} = 99 \\
\text{HEAT} = 900, \text{FIL} = 4, \text{VEL} = 50, \text{DEL}=127, \text{PUL} = 99 
\]

This program consistently produced glass needles with a tip sharpness \( \sim 1 \mu m \) which is important for gluing the particles. After making many needles, I would put on a pair of clean nitrile gloves and take a small piece of SmCo\(_5\) and file it. The shavings of the SmCo\(_5\) would stick to the magnet due to magnetic forces, but you could rub them off and make them stick to the gloves. The powder-like shavings would give the gloves a sooty look.

After getting a gloved finger covered in the magnetic powder, I would pick up a clean glass slide with my other hand and place it on top of another permanent magnet which was flat enough to support the slide. Note that it is very important to make sure that the slide is clean because any dust on it could accidentally be picked up later by the glass needle and glued onto the cantilever. This would result in a non-magnetic particle on the cantilever.

Next, I would grab the glass slide and flat magnet together in one hand and flip them upside down while holding them together. Then with my gloved hand that is covered in magnetic powder, I would slowly wave my finger just below the glass slide, careful not to touch the slide. The flat magnet on the other side of the glass slide pulls small magnetic particles off of the gloved finger and deposits them onto the clean glass slide. Doing it this
way ensures the particles are very magnetic, because they must overcome the attractive electrostatic forces that keep them on the gloved finger as well as the force of gravity (which is much smaller) since they are pulled up onto the glass slide. Next, carefully set the glass slide down face up. You may want to cover it with a beaker to prevent dust from settling on it until it is needed.

The glue I used for gluing particles onto cantilevers is G1 epoxy from Gatan Inc. The epoxy must first be prepared by mixing 10 parts resin (which is a clear liquid) with 1 part hardener (which is an amber-colored liquid). The 10:1 ratio is by weight, so I used a scale to prepare the epoxy. Mix the two liquids together thoroughly and then place a small drop onto the side of a different glass slide.

Next, clamp a good cantilever in the particle mounting jig. This jig has a strong magnet mounted behind the cantilever clamp which aligns the particle you glue onto the cantilever so that its magnetic moment is parallel to the cantilever axis. There is room on the jig to place the glass slide with the drop of epoxy below the cantilever. Take this jig setup over to the optical microscope and load a glass needle into the micro positioner. The micro positioner has knobs on it that allow you to make small, precise movements of the needle in all three dimensions. Next, you dip the glass needle into the drop of epoxy and then carefully deposit some epoxy onto the tip of the cantilever.

Remove the glass slide with the drop of epoxy and replace it with the glass slide that has the magnetic particles on it. Also replace the glass needle with a new glass needle. Next, you need to find a magnetic particle that if only a few microns in width by scanning the glass slide under the optical microscope. After finding a suitable particle, carefully pick it up with the end of the glass needle. Electrostatic forces should hold the particle to the glass needle. Bring the needle with the particle over to the tip of the cantilever and carefully deposit the particle onto the glue-covered tip. Finally, bake the cantilever in an oven for a few hours at 80°C.
Appendix B

Derivations

B.1 Cantilever Frequency Shift for Magnetometry Signal

For the cantilever magnetometry experiment, the magnetic moment \( m \) and anisotropy field \( B_k \) of the particle glued to the cantilever are determined by measuring the shift in cantilever frequency in an applied field (see section 3.3). To understand how the cantilever’s frequency changes as a function of applied field, we first need to calculate the angle the moment cants away from its equilibrium position, relative to the particle (see figure 3.10). The total energy of the magnetic moment is given by two opposing terms:

\[
E_m = K_u V \sin^2(\theta) - BM_s V \cos(\beta - \theta) \quad (B.1)
\]

The first term is the (magneto-crystalline and shape) anisotropy energy, where \( K_u \) is the uniaxial anisotropy constant. The second energy term is the Zeeman energy of the particle with the applied field. Taking the derivative of this with respect to \( \theta \) and setting the result equal to zero, gives the energy minimization:

\[
2K_u \sin(\theta)\cos(\theta) = BM_s \sin(\beta - \theta) \quad (B.2)
\]

If we then expand this to first order for small \( \theta \) and define the anisotropy field \( B_k = 2K_u/M_s \) we have:

\[
\theta = \left( \frac{B}{B_k + B} \right) \left( \frac{x}{L_e} \right) \quad (B.3)
\]

Next, if we write the torque of the magnetic field on the particle and substitute for \( \theta \)
using equation B.3 we have:

\[ \tau_m = |\vec{m} \times \vec{B}| \]

\[ = M_s VB \sin(\beta - \theta) \]  \hspace{1cm} (B.4)

\[ = M_s V \beta \left( \frac{B_k B}{B_k + B} \right) \]

and if we compare this to the torque associated with the spring force of the cantilever:

\[ \tau_s = |\vec{r} \times \vec{F}| \]

\[ = rF \sin(\phi) \] \hspace{1cm} (B.5)

\[ = L_e k x \sin(\phi) \]

\[ = L_e^2 k \beta \]

where \( \phi \) is defined as \( \pi/2 - \beta \) according to this geometry (see figure 3.10). Then, if we consider the torque on the particle from the magnetic field as giving rise to an additional spring constant \( \Delta k \) we have (combining equations B.4 and B.5):

\[ \Delta k = \frac{m}{L_e^2} \left( \frac{B_k B}{B_k + B} \right) \]  \hspace{1cm} (B.6)

Given that a small change in the cantilever’s spring constant results in a linear response of its frequency (see equation 3.12), we have the frequency response of the cantilever with a magnetic particle in the presence of an applied external field:

\[ f = f_0 \left( \frac{m B_k B}{2 k L_e^2 (B_k + B)} + 1 \right) \]  \hspace{1cm} (B.7)

### B.2 Partially Interrupted iOSCAR Protocol

For the spin wire experiment, we implemented a slightly modified version of the iOSCAR protocol which improves spatial resolution, which we call partially-interrupted oscillating cantilever-driven adiabatic reversals, or pi-OSCAR. The iOSCAR protocol involves periodically interrupting the microwave power for a half cantilever cycle, which causes the orientation of spins in the measurement volume to change by 180 degrees with respect to the cantilever motion. This in turn causes the sign of the force on the cantilever to be
periodically reversed, which can then be demodulated via a lock-in amplifier to obtain the spin signal. The use of a lock-in allows for increased spin sensitivity. The modification we implement in pi-OSCAR is to interrupt the microwave power for less than a half cantilever cycle, about the center of the cantilever’s motion. Since only the spins that are periodically interrupted contribute to the spin signal due to the lock-in detection, by decreasing the width of the interrupt it correspondingly decreases the measurement volume width. Using this modification, we get larger signals from the same measurement volume compared to iOSCAB, enabling us to probe down to smaller measurement volumes before we become limited by noise. The larger signal is due to the fact that the center of the spin detection volume has a larger force sensitivity per spin than the edges of the volume. The following derivation solves for the force sensitivity of the detection volume as a function of lateral position within the volume for the standard iOSCAB protocol measurement. From this iOSCAB sensitivity profile we can then show how implementing partial interrupts in pi-OSCAR results in greater spin sensitivity per unit volume for small detection volumes.

We treat the cantilever in our experiment as a simple, damped, driven harmonic oscillator with spring constant $k$, viscous damping coefficient $c$, effective mass $m$, and driving force $F(t)$. From Newton’s second law we have

$$ m\ddot{x} = F(t) - kx - cx $$ (B.8)

which can be rewritten in a more conventional form:

$$ \ddot{x} + 2\Gamma \omega_0 \dot{x} + \omega_0^2 x = \frac{F(t)}{m} $$ (B.9)

where the damping ratio is $\Gamma = \frac{c}{2\sqrt{mk}}$ and the undamped angular frequency is

$$ \omega_0 = 2\pi f = \sqrt{\frac{k}{m}} $$ (B.10)

Driving the cantilever results in a steady state oscillation such that the energy dissipated each cycle is supplied by $F(t)$ (in accordance with it’s quality factor). Thus the position of
the cantilever’s magnetic tip is given by

\[ x_c(t) = x_{pk} \sin(\omega_c t) \] (B.11)

where \( \omega_c = 2\pi f_c \) is the steady state cantilever frequency and \( x_{pk} \) is the cantilever peak oscillation amplitude. Now, as the cantilever oscillates, the resonance bowl sweeps past spins within the spin detection volume and causes them to adiabatically invert. This results in the spin’s magnetic moment \( \vec{m} \) to vary as a pulse wave in time:

\[ \vec{m}(t) = \mu_B f_{\text{pulse}}(t) \] (B.12)

here, \( \mu_B \) is a Bohr magneton and \( f_{\text{pulse}}(t) \) is a pulse wave modulation signal with a pulse period (width) \( T_{\text{pulse}} \) and unit amplitude:

\[ f_{\text{pulse}}(t) = \begin{cases} 1 & \text{for } T_c(\frac{1}{4} + m) - \frac{T_{\text{pulse}}}{2} < t < T_c(\frac{1}{4} + m) + \frac{T_{\text{pulse}}}{2} \\ -1 & \text{otherwise} \end{cases} \] (B.13)

where \( m = 0, 1, 2, 3... \) and \( T_c = \frac{1}{f_c} \) is the cantilever period. For a spin in the center of the detection volume this results in a 50% duty cycle pulse wave (i.e. a square wave with \( T_{\text{pulse}} = \frac{T_c}{2} \)) modulation of the spin’s moment \( \vec{m} \) with a period equal to that of the cantilever, and for spins not in the center, the pulse is greater or less than a 50% duty cycle (see fig. S1). Because it is the cantilever’s magnetic tip that cause the spins to invert, the pulse wave modulation is necessarily phase-locked and frequency-locked to the cantilever motion. This modulation of \( \vec{m} \) provides a small additional driving force on the cantilever

\[ F_{\text{spin}}(t) = |\nabla (\vec{m}(t) \cdot \vec{B})| = G\mu_B f_{\text{pulse}}(t) \],

where \( \vec{B} \) is the magnetic field from the cantilever tip and \( G \) is appropriate magnetic field gradient, which we take to be uniform within the shallow spin wire. Adding this additional force to eq. B.15 and plugging in the steady state solution from eq. B.11 yields:

\[ -x_{pk}\omega_c^2 \sin(\omega_c t) + 2\Gamma x_{pk}\omega_c \cos(\omega_c t) + \omega_0^2 x_{pk} \sin(\omega_c t) = \frac{F(t)}{m} + \frac{F_{\text{spin}}(t)}{m} \] (B.14)
but since $F_{\text{spin}}(t)$ is a pulse wave modulation that is frequency and phase locked to the oscillation of the cantilever, and because the cantilever itself shows sensitive response only near its resonant frequency (for high quality factor), we can keep only the Fourier series component of $F_{\text{spin}}(t)$ at the cantilever frequency $\omega_c$. This gives:

$$-x_{pk}\omega_c^2 \sin(\omega_c t) + 2\Gamma x_{pk} \omega_0 \omega_c \cos(\omega_c t) + \frac{k}{m} x_{pk} \sin(\omega_c t) = \frac{F(t)}{m} + \frac{G\mu_B}{m} b_1 \sin(\omega_c t) \quad (B.15)$$

where $b_1$ is the dimensionless amplitude of the Fourier component of interest (defined below).

Note that the 3rd term on the left hand side can be grouped with the 2nd term on the right hand side:

$$-x_{pk}\omega_c^2 \sin(\omega_c t) + 2\Gamma x_{pk} \omega_0 \omega_c \cos(\omega_c t) + \left[ k - \frac{G\mu_B b_1}{x_{pk}} \right] \frac{x_{pk}}{m} \sin(\omega_c t) = \frac{F(t)}{m} \quad (B.16)$$

This demonstrates that the modulation of the spin effectively results in a small shift $\delta k$ in the cantilever’s spring constant:

$$\delta k = \frac{G\mu_B b_1}{x_{pk}} \quad (B.17)$$

From the undamped angular frequency equation B.10, we can calculate small changes in the cantilever’s frequency $\delta f$ for small changes in the spring constant $\delta k$:

$$\frac{\delta f}{\delta k} = \frac{1}{4\pi m} \sqrt{\frac{m}{k}} = \frac{1}{2k} \left( \frac{1}{2\pi} \sqrt{\frac{k}{m}} \right) \quad (B.18)$$

and upon substitution back into eq B.10 this gives us a result which shows that small changes in the spring constant give a linear response to changes in the oscillator’s frequency:

$$\frac{\delta f}{f} = \frac{1}{2k} \frac{\delta k}{k} \quad (B.19)$$

Now we need to find the Fourier component $b_1$ for a given spin (not necessarily in the center
of the volume). First, we define the Fourier series of a given function $f(t)$ with period $T$:

$$f(t) = a_0 + \sum_{n=1}^{\infty} \left( a_n \cos \left( \frac{2\pi nt}{T} \right) + b_n \sin \left( \frac{2\pi nt}{T} \right) \right)$$  \hspace{1cm} (B.20)

and Fourier coefficients:

$$a_0 = \frac{1}{T} \int_{-T/2}^{T/2} f(t) dt$$  \hspace{1cm} (B.21)

$$a_n = \frac{2}{T} \int_{-T/2}^{T/2} f(t) \cos \left( \frac{2\pi nt}{T} \right) dt$$  \hspace{1cm} (B.22)

$$b_n = \frac{2}{T} \int_{-T/2}^{T/2} f(t) \sin \left( \frac{2\pi nt}{T} \right) dt$$  \hspace{1cm} (B.23)

where $f(t)$ in this case is the pulse modulation of the spin $f_{\text{pulse}}(t)$. By plugging eq. B.13 into eq. B.23 and calculating a straightforward integration we can solve for $b_1$ as a function of $T_{\text{pulse}}$:

$$b_1(T_{\text{pulse}}) = \frac{2}{T} \int_{-T/2}^{T/2} f(t) \sin \left( \frac{2\pi t}{T} \right) dt = \frac{4}{\pi} \sin \left( \frac{T_{\text{pulse}}}{T_c} \pi \right)$$  \hspace{1cm} (B.24)

Figure B2 shows $b_1$ as a function of $T_{\text{pulse}}$.

Having found $b_1(T_{\text{pulse}})$, we now need to relate the pulse wave of a given spin to its lateral location $x_s$ within the detection volume. Let $x_s = 0$ be the center of the detection volume (i.e. the location of the resonant slice when the cantilever is at its equilibrium position). From eq. B.11 the range of $x_s$ is: $-x_{pk} < x_s < x_{pk}$. We note that the time $t_{\text{flip}}$ at which the spin will flip as a function of its location $x_s$ can be found by equating $x_s = x_{pk} \sin(2\pi f_c t_{\text{flip}})$ which gives $t_{\text{flip}} = \frac{T}{2\pi} \arcsin \left( \frac{x_s}{x_{pk}} \right)$. However, the function $\arcsin(x)$ has a restricted range $-\frac{\pi}{2} < x < \frac{\pi}{2}$ as a consequence of satisfying the vertical line test for a well defined (one-to-one mapped) function. As a consequence of this we need to pick up the 'other' solution (sometimes referred to as the geometric reflection), and the spacing between these solutions gives the pulse width. Since the other solution is symmetric about $\frac{\pi}{2}$,
, where $\frac{\pi}{2}$ corresponds to one fourth of the cantilever period, we can write the pulse width as 

$$T_{\text{pulse}}(x_s) = 2\left(\frac{T_c}{4} - \frac{T_c}{2\pi} \arcsin\left(\frac{x_s}{x_{pk}}\right)\right) = T_c\left(\frac{1}{2} - \frac{1}{\pi} \arcsin\left(\frac{x_s}{x_{pk}}\right)\right).$$

Having solved for $T_{\text{pulse}}$ as a function of spin location $x_s$, we can now combine eqs. B.24 and B.25 to give $b_1(x_s)$:

$$b_1(x_s) = \frac{4}{\pi} \sin\left(\frac{\pi}{2} - \arcsin\left(\frac{x_s}{x_{pk}}\right)\right)$$

Since the $b_1$ coefficient of a detected spin is proportional to the frequency shift of the cantilever due to that spin (eqs. B.17 and B.19) we have:

$$\delta f(x_s) = \frac{2G\mu_Bf_c}{\pi x_{pk}} \sin\left(\frac{\pi}{2} - \arcsin\left(\frac{x_s}{x_{pk}}\right)\right)$$

We see that $b_1(0) = \frac{4}{\pi}$ for a spin in the center of the detection volume, which gives the frequency shift:

$$\delta f = \frac{2G\mu_Bf_c}{\pi k x_{pk}}$$

Although we use frequency detection in our measurements and therefore $\delta f$ is a useful quantity, it is often more useful to report the corresponding forces that are detected from the spins acting on the cantilever. Therefore, we can convert back to force via Hooke’s law $(F = \delta k \cdot x_{pk})$ where $x_{pk}$ is used to yield the peak force and $\delta k$ is given by eq. B.17 which gives the force sensitivity per spin of the detection volume as a function of lateral position (see fig. B3).

$$F(x_s) = G\mu_B \left[\frac{4}{\pi} \sin\left(\frac{\pi}{2} - \arcsin\left(\frac{x_s}{x_{pk}}\right)\right)\right] \sim 1 \text{aN}$$

Having found the force sensitivity of the iOSCAR protocol, we can consider the modification of this in pi-OSCAR. The partial interruptions in the pi-OSCAR protocol result in a truncated force sensitivity, since only spins that are interrupted contribute to force detec-
tion (see fig. B4). This provides an opportunity for increasing the force sensitivity of small detection volumes. Typically, in the iOSCAR protocol, smaller volumes are probed by decreasing the cantilever oscillation amplitude, and thus shrinking the entire force sensitivity profile. With pi-OSCAR, the cantilever oscillation amplitude is kept at a large fixed value, and the volume is decreased by applying partial interruptions to the microwave resonator, and thus truncating the sensitivity profile. This results in relatively large force sensitivity for small detection volumes. To compare iOSCAR and pi-OSCAR directly, measurements were taken using both protocols, where the width of the detection volume was varied in these two different ways (fig. B6). In the small detection volume regime, pi-OSCAR results in a \((\frac{4}{\pi} - 1) \rightarrow 27\%\) increase in the measured spin signal versus iOSCAR.