Magnetic microparticle trapping and mechanical excitation using domain walls in magnetic microstructures

By

Daniel Mauricio Montana Fernandez

Submitted to the Department of Materials Science and Engineering in partial fulfillment of the requirements for the degree of

Bachelor of Science

At the

Massachusetts Institute of Technology

June 2011

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ABSTRACT

We examined the feasibility of using the resonant frequency of magnetic bead-domain wall (DW) couples in a host fluid to measure particle size. Nickel-Iron (Permalloy) rings, made using electron beam lithography, served as the tracks for nucleating and moving DWs, and Invitrogen Dynabeads M-270 magnetic beads were used for the experiment. Tween-20 surfactant in solution and SiO2 capping layers for the structures were used to overcome substrate-bead interaction and maintain bead mobility.

The resonant frequency of 40 bead-DW couples was measured and found to lie in a range between 18.3 and 42.7 Hz with a median of 31.1 Hz. In addition, sets of resonance experiments were performed to examine the dependence of the resonant frequency on driving amplitude, DW type, and position on the permalloy (Py) ring. The resonant frequency populations of beads bound to head-head and tail-tail DWs overlapped, but each DW type seemed to be centered around a different frequency.

Examining different positions on a ring showed that a large contribution to the spread in resonant frequencies may come from DW pinning due to structural defects or remanent surface-bead interaction. Finally, the resonant frequency is independent of the driving amplitude, a finding which supports the linear spring model for DW-bead interaction.

We conclude that resonance measurements made with optical methods reliably distinguish particles of different hydrodynamic radius. This work has also helped identify and address some of the obstacles to improve the reliability of these resonance measurements as indicators of particle size. By demonstrating this detection capability, we can proceed with the development of spin-valve-based resonance devices suitable for clinical applications.

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I. INTRODUCTION

A. Motivation

Despite significant advances in biosensors in recent decades, there is no general sensing platform that can be applied to detect any of the hundreds of biomolecules of interest in diverse clinical samples with high sensitivity. Commercially available detection methods like ELISAs, protein microarrays, and quantum dot systems detect biomarkers using fluorescent or colorimetric signals, and so they are limited by autofluorescence of the sample and the optical absorption of the matrix of the biological samples. [1] Furthermore, these methods have low sensitivity. Ten thousand or more binding events are needed for fluorescence-based detection to have a useful signal-to-noise (SNR) ratio.[2] Although current detection methods can successfully detect high concentrations of biomarkers, they are limited in their reliability and sensitivity by their operating principle.

In response to the shortcomings of fluorescence-based detection methods, researchers have developed new platforms like nanowires, microcantilevers, electrochemical sensors, and carbon nanotubes that take advantage of charge-based interaction between the protein of interest and the sensor for detection. Although some of these methods have shown high sensitivity in laboratory settings, they are unsuitable for clinical application. Because detection is charge-based, these sensors require that samples be presented in precisely controlled salt solutions or pure water, and they have been shown to be unreliable in conditions of varying pH and ionic strength, as would be present in a physiological environment.[1]

A more promising technology under development is magnetic biosensors based on Giant Magnetoresistance (GMR). Magnetic transduction strategies are advantageous for biodetection because even the most complex biological matrices lack a significant magnetic background signal, and so they do not interfere with detection, unlike with charge- or fluorescence-based strategies. GMR sensors detect biomarkers using a sandwich assay. Capture antibodies are covalently immobilized on the sensor surface. After the target antibody binds, the rest of the solution is washed away and magnetic particles coated with the complementary antibody are introduced: the target is sandwiched between two antibodies, one bound to the sensor and another to a magnetic nanoparticle. The stray magnetic field from the nanoparticle is then detected as a change in the electrical resistance across the sensor multilayer. GMR biodetectors must be very sensitive in order to detect the stray field from nanoparticles, and modern devices can detect the magnetic moment of as few as 14 Fe₃O₄ particles of 16-nm radius.[2]

Despite the inherent advantages of GMR biosensors, this technology has several shortcomings. For example, their high sensitivity poses problems due to nonspecific binding in the assay: only 14 events of nonspecific binding on a single sensor are enough to yield a false positive result for the biomarker of interest. In addition, GMR devices still fall short of the performance required for accurate accounting of binding events. The uncertainty in this method comes from the facts that the resistance signal recorded for an individual nanoparticle is a function of particle position along the length and width of the sensor, and its height above the sensor surface. For example, the signal from a single bead is constant with respect to transverse position only between the halfway points from the center to each edge of the detector. In addition, the detector records particles 200 nm above the detector as having over 50% of the signal of those only 20 nm from the detector.[2]
The strong dependence of the recorded signal with particle position poses several limitations for this device. First, it is difficult to quantify the number of binding events because of the spatial dependence of the signal, so estimates of biomarker concentration will be inaccurate. More importantly, the spatial dependence of the signal is very difficult to avoid: even if the biologically active region were restricted to the region of the sensor where signal from a particle is constant, a thorough second wash is needed to avoid false positives from particles suspended in solution above the device and those nonspecifically bound to the surface.

We propose a novel magnetic method for high-sensitivity detection of biomarkers. Unlike modern GMR biosensors, this device does not aim to detect the small magnetic moment of nanoparticle tags, but rather detect a shift in the resonance frequency of an oscillating magnetic microparticle when it binds to second, non-magnetic bead in a sandwich assay.

The aim of this work is to demonstrate that resonance measurements made with optical methods can reliably distinguish particles of different hydrodynamic radius and identify some of the obstacles that must be overcome in order to improve the reliability of these resonance measurements as indicators of binding events. By demonstrating this detection capability, we can proceed with the development of spin-valve-based resonance devices suitable for clinical applications.
B. Background

i. Magnetic Domains and Domain Walls

In ferromagnetic materials, the exchange interaction between unpaired electrons in adjacent atoms favors parallel spins. As a result, the magnetization direction of neighboring atoms is aligned at short distances. However, not all macroscopic pieces of ferromagnetic material have a net magnetization in the absence of a field, which seems to contradict the fact that exchange interaction favors a single magnetic domain in a given sample with a unique magnetization direction.

A single-domain specimen minimizes its exchange energy because all the magnetic moments in the material are aligned, but there is an energetic cost attached: there is magnetostatic energy in the field produced around the specimen, as shown in Fig. 1(a). Below a certain characteristic size for a given material, the single-domain state is the lowest-energy configuration. However, the breakup of the magnetization into smaller regions (domains) that provide flux closure can reduce the magnetostatic energy at the cost of forming domains—as shown in Fig. 1 (b)-(e). Above a critical size, the energy involved in the formation of domain walls (DWs) is less than that of the field around a single-domain specimen, so the lowest-energy configuration is a multi-domain state.

![Different domain configurations for a ferromagnetic material. (A) is a single-domain state, and (B)-(E) show the reduction of magnetic flux outside the specimen as domains in different directions are nucleated. Figure adapted from O’Handley [3].](image)

The change of magnetization direction at a domain wall is not abrupt: the magnetization direction rotates slightly from one atom to the next, changing direction over a few tens of nanometers. In thin permalloy (Py) rings like the ones used in this research, vortex domain walls arise. This particular type of wall has a significant fringing field, which is strong enough to draw magnetic particles in suspension towards the DW.
ii. Micromagnetic Wires

Thin-film nanowires are quasi one-dimensional structures, as the length is orders of magnitude larger than either the thickness or the width. By imposing geometrical constraints in this type of structure, we can control where and what type of domain walls nucleate as well as control these walls. With the help of micromagnetic simulations, micromagnetic wires can be engineered for a desired magnetic configuration. For example, structures can be engineered to act as logic circuits, as shown by Allwood et al. [4]

![Micromagnetic Wires Image]

Fig. 2: Magnetic nanowire structures. a) shows a focused ion beam image of a nanowire magnetic logic circuit (adapted from Allwood et al. [4]). By imposing geometric constraints on the wires, we can control where domain walls will nucleate and what type of wall they will be. (b) shows a micromagnetic simulation of a transverse DW, and (c) shows a vortex DW.

iii. Superparamagnetism and Magnetic microbeads

There exist different kinds of magnetic ordering and response in materials. In addition to ferromagnetism, this research relies heavily in superparamagnetism. Paramagnetic materials have a linear response to an applied magnetic field, with the magnetization proportional to the applied field until the saturation magnetization is reached. Unlike ferromagnetic materials, paramagnetic materials show no hysteresis in their magnetization curves and have no net magnetization in the absence of a magnetic field.

![Magnetization-Applied Field Image]

Fig. 3: Magnetization-Applied Field (M-H) curves for different kinds of magnetic materials. Notice that ferromagnetic materials have a remanent magnetization when the field is switched off and their M-H curve is hysteretic. On the other hand, superparamagnetic materials have zero magnetic moment in the absence of a field and their magnetization increases linearly until it reaches its saturation value.
Superparamagnetism is paramagnetic-like behavior in nanoparticles of ferromagnetic materials. For a ferromagnetic particle, the relaxation time of the magnetization is approximated by

$$\tau \sim \tau_0 \exp(-k_U V/kT)$$

where $\tau_0$ is inversely proportional to the attempt frequency ($\tau_0$ is typically $10^{-9}$ sec), $k_U$ is the anisotropy energy coefficient, $V$ is the volume of the particle, $k$ is Boltzmann’s constant, and $T$ is the temperature of the particle. From this expression, we can conclude that for a given anisotropy energy, there exists a critical size below which the magnetization is volatile, i.e., $kT$ is comparable to the anisotropy energy, $k_U V$. For the anisotropy energies of ferromagnetic materials, this critical size is typically of the order of 1 nm.

Although the bulk material is ferromagnetic, ferromagnetic nanoparticles have so little material that each is in a single-domain state: each particle can be thought of as a magnetic dipole. Above a certain temperature, the thermal energy becomes comparable to the magnetic anisotropy energy of the nanoparticle and as a result, the magnetic moment of the particle does not remain fixed, but rather is randomly oriented. This random orientation results in a zero net moment when no external magnetic field is applied, but this single-domain situation also means that the particle’s magnetization can easily align with an external magnetic field.

Instead of using nanoparticles, we use superparamagnetic microbeads. The microbeads used in this research consist of a polymer matrix in which superparamagnetic particles are encased. The reason for this composite structure is straightforward: the composite structure allows this micron-sized bead to be superparamagnetic. Because the magnetic material lies in single-domain nanoparticles, the microparticle magnetizes just as a superparamagnetic particle would: there are no domain walls to move around, and therefore no hysteresis. In effect, the particle can be thought of as an individual dipole.

We chose to use microbeads instead of nanoparticles because microbeads are commercially available, widely used in research, and a relatively mature technology. Microbeads produced by companies like Invitrogen have a narrow size distribution and high uniformity, which are highly desirable characteristics for our experiment since we rely on the assumption that beads from a given stock solution have uniform geometry. In addition, microbeads have a large surface area and are easy to functionalize, so the transition from single-bead resonance experiments to bead-binding resonance experiments (a requirement for our intended application) is straightforward.

![Image of microbeads](attachment:image.png)

Fig. 4: 2.8 um radius M-280 Dynabeads produced by Dynal Biotech. These superparamagnetic beads are similar to the M-270 beads used in this research. Figure adapted from Graham et al. [5]
C. Model for bead-domain wall interaction

In the vicinity of a DW, there exists a highly localized stray field, $\vec{B}(r)$, with a large gradient. This field is present in a region of the order of the DW size (about 100 nm) and superparamagnetic particles in its vicinity are strongly drawn to the domain wall. The magnetic binding energy of the bead and DW, $U$, is given by

$$U = -\vec{M} \cdot \vec{B}$$

where $\vec{M}$ is the magnetization of the bead and $\vec{B}$ is the magnetic field. For a superparamagnetic bead, the magnetization is proportional to the external field, so we have

$$U = -\left( \frac{X}{\mu_0} \vec{B} \right) \cdot \vec{B} = -\frac{X}{\mu_0} |\vec{B}|^2$$

This quadratic form for the binding energy can be approximated to first order by a linear spring, whose energy is given by

$$U = \frac{1}{2} k (\Delta x)^2$$

where $k$ is the spring constant and $\Delta x$ is the displacement from the equilibrium position.

If we approximate the bead-DW interaction in a host fluid as a linear spring, the bead will experience a linear restoring force,

$$F_{\text{elast}} = -k (x_{\text{bead}} - x_{\text{DW}})$$

where $x_{\text{bead}}$ is the position of the bead and $x_{\text{DW}}$ is the position of the DW as shown in the figure below.
Fig. 6: A schematic of the model proposed. In this case, the position of the domain wall, \( X_{DW} \), is driven by an oscillating external field, \( H_{magnet} \). As the bead responds to the DW moving, it is subject to two forces, \( F_{drag} \), the drag force from the host fluid, and \( F_{elastic} \), which is the restoring force between the wall and the bead.

In addition to the binding force, a drag force from the surrounding fluid will also act on the bead, but its exact form depends on the fluid flow around the bead. We calculate the Reynolds number (Re), approximating the solution's density (\( \rho \)) and viscosity (\( \mu \)) as those of water

\[
Re = \frac{\rho V L}{\mu}
\]

Because we have \( Re \ll 1 \), we expect Stokes drag, which means that the drag force will be proportional to the velocity of the particle

\[
F_{drag} = -\eta \frac{dX_{bead}}{dt}
\]

where \( \eta = 6 \pi \mu r \), where \( \mu \) is the viscosity of the fluid and \( r \) is the hydrodynamic radius of the bead. Therefore, the net force on the bead is

\[
F_{net} = F_{drag} + F_{elastic}
\]

\[
F_{net} = -\eta \frac{dX_{bead}}{dt} - k(X_{bead} - X_{DW}) = m a_{bead}
\]

At low Re, the inertial term is much smaller than the viscous term, so we expect a highly overdamped response. Hence, we ignore the inertial term, \( m a_{bead} \) and write

\[
0 = -\eta \frac{dX_{bead}}{dt} - k(X_{bead} - X_{DW})
\]

Let \( X_{DW}(t) = A \times \text{Exp}[i\omega t] \), with \( A \) real. We write \( x_{bead} \) in a similar fashion

\[
x_{bead}(t) = B \times \text{Exp}[i\omega t]
\]
where B is a complex number that contains the phase shift between \( x_{\text{bead}} \) and \( x_{\text{DW}} \). We write
\[
\eta \frac{d x_{\text{bead}}}{d t} + k x_{\text{bead}} = k x_{\text{DW}}
\]

\[(k + i \omega \eta) B \ast \text{Exp}[i \omega t] = k A \ast \text{Exp}[i \omega t]\]

The amplitude of the response, B, is given by
\[
B = \frac{k A}{k + i \omega \eta}
\]

and the normalized amplitude is
\[
C = \frac{B}{A} = \frac{1}{1 + i \omega \frac{\eta}{k}} = \frac{1}{1 + i \left( \frac{\omega}{\omega_0} \right)} = \frac{1 - i \left( \frac{\omega}{\omega_0} \right)}{1 + \left( \frac{\omega}{\omega_0} \right)^2}
\]

where \( \omega_0 = \frac{k}{\eta} \). We define \( C = C' + i C'' \), such that
\[
C' = \frac{1}{1 + \left( \frac{\omega}{\omega_0} \right)^2} \quad \text{and} \quad C'' = -\frac{\left( \frac{\omega}{\omega_0} \right)}{1 + \left( \frac{\omega}{\omega_0} \right)^2}
\]

We examine the imaginary part of C, which has the form of a Lorentzian distribution
\[
C'' = -\frac{\left( \frac{\omega}{\omega_0} \right)}{1 + \left( \frac{\omega}{\omega_0} \right)^2}
\]

and look for an extremum. Let
\[
\omega_{\text{norm}} = \frac{\omega}{\omega_0}
\]

\[
\frac{d}{d \omega_{\text{norm}}} \left( \frac{\omega_{\text{norm}}}{1 + \omega_{\text{norm}}^2} \right) = \frac{1 + \omega_{\text{norm}}^2 - 2 \omega_{\text{norm}}^2}{(1 + \omega_{\text{norm}}^2)^2}
\]
\[
\frac{d}{d\omega_{\text{norm}}} \left( \frac{\omega_{\text{norm}}}{1 + \omega_{\text{norm}}^2} \right) = 0 \text{ when } 1 - \omega_{\text{norm}}^2 = 0
\]

the extremum of \( C'' \) will be found at \( \omega = \omega_0 = \frac{k}{\eta} \), as is shown on the plot of \( |C'| \) below. Since \( \eta = 6\pi\mu r \), the resonance maximum, \( \omega_0 \), is therefore inversely proportional to the bead radius, \( r \), and directly proportional to the bead-DW binding energy, which is encoded in \( k \).

Figure 7: Linear-Log plot of the out-of-phase amplitude of oscillation against \( \omega/\omega_0 \). In particular, notice a maximum at \( \omega = \omega_0 \).
We also examine the behavior of $C'$, the real component of $C$, in Fig. 8.

![Linear-Log plot of the in-phase amplitude of oscillation against $\omega/\omega_0$.](image)

In summary, if the binding energy is well-approximated by a linear spring, with $E_{\text{binding}} = 1/2 k (x_{\text{bead}} - x_{\text{DW}})^2$ so that the binding force is $F_{\text{magnetic}} = -k (x_{\text{bead}} - x_{\text{DW}})$ and the drag acting on the bead is Stokes drag, $C''$ will have a maximum at $\omega_0 = k/\eta$. If we can excite this magneto-mechanical resonance, we can measure the resonance peak to be at a frequency inversely proportional to $\eta$ and therefore inversely proportional to $r$, the radius of the particle.

In other words, driven oscillation of this system will yield a resonant frequency that is independent of the amplitude of the driving displacement and inversely proportional to particle size: a way to distinguish particle sizes in solution.
II. Design of Apparatus

A. Goal of Experiment

To examine the predictions of the model presented above, the experiment must allow precise control over the position of a DW to which a superparamagnetic (SPM) bead is attracted. We use permalloy rings as the structures on which the DWs are nucleated. To examine the oscillatory response of the bead to the driven position of the DW, we use an optical approach. We focus a 530-nm laser beam onto the bead and compare the reflected beam to the voltage that drives the electromagnet moving the DWs.

B. Sample fabrication

All the magnetic ring structures were prepared using standard electron beam lithography and lift-off procedure. PMMA positive resist was spin-coated and baked on Si (100) wafers. A Raith 150 scanning electron beam (10 keV) was used to pattern the resist. Resist patterns were developed for 90 s in 3:1:IPA:MIBK solution. A 40-nm layer of permalloy, the magnetic material, was DC sputter deposited in ~10^-7-10^-8 Torr and a 70-nm capping layer of SiO₂ was added without exposure to atmosphere. Lift-off was done in 135 °C NMP with periodic 30-second sonication intervals for ~10 min. The rings used for resonance experiments had 14.2 μm radius and 800-nm width. These dimensions and the quality of patterned structures were characterized with scanning electron microscopy.

C. Imaging, tracking, and domain wall control

i. Particle imaging and tracking

In order to image the magnetic beads as they move on the ring and measure their response to the driven DW, we use a custom-built system with a wide-field microscope and laser imaging combined. The optical path of the light from the microscope and the laser beam are tuned so that when the surface of the rings is in focus, the laser spot is also focused. This configuration allows very positioning of the oscillating bead into the laser spot using a computer-
controlled stage without having to change focus heights for laser measurement. In fact, our system is capable of sub-micron resolution in bead position.

Fig. 10: Microscope images of (a) magnetic bead on domain wall in the middle ring on the top row and (b) laser spot positioned over the particle. These images were captured by a digital camera attached to the wide-field microscope in our custom-built system.

ii. Domain wall control

The first requirement for the proposed experiment is precise DW control. To this end, a quadrupole magnet which allows controlled DW motion was built. This magnet has a 2mm x 2mm region of homogeneous field (to within 5%) that is also constant several millimeters above and below the plane of the pole pieces. Because the uniform region is much larger than the arrays of rings, we know that the magnetic control of each DW in each ring is identical.

Fig. 11: Quadrupole projection magnet built by graduate student Elizabeth Rapoport. It is capable of generating homogenous in-plane rotating fields at -40 Oe A^-1 up to -500 Oe. (Photo credit: Elizabeth Rapoport)

Manipulation of the DWs is achieved by superimposing two magnetic fields. For this experiment, the fields produced by the magnet are controlled though a LabView program. The bias field, \( H_b \), is the larger of the two and is a constant field produced by a constant voltage signal directly from the LabView program, which can set the direction and magnitude of \( H_b \). The oscillating field, \( H_s \), comes from a sinusoidal voltage produced by a DS 345 Function Generator and is perpendicular to \( H_b \). The frequency and magnitude of the signal from the function generator is set by the LabView program, resulting in a controlled sinusoidal displacement of the DWs in each ring in the array.
The control loop begins with a computer running LabView code for bead-manipulation experiments. The computer sets the direction and magnitude of the bias voltage to the magnet as well as the frequency and amplitude of the sinusoid created by the function generator. The function generator, in turn, emits a synchronization signal to a lock-in amplifier (explained below) and to the LabView control. The output of the function generator, a sinusoidal driving voltage, is the input for Ch. 2 of the amplifier connected to the driving magnet. The bias voltage is the input to Ch. 1 of the same amplifier.

The oscillating voltage and the bias voltage leave the amplifier on separate paths. The oscillating voltage goes through a load resistor and is split into three branches, one of which returns to the computer as the driving voltage for $H_s$, another which is connected to an oscilloscope for viewing, and the last is connected to the magnet. The bias voltage is split into two branches, one of which is connected to the same oscilloscope for viewing, and second is connected to the magnet. Both channels of the amplifier reach the magnet, where the voltages from each source induce magnetization of the core and produce $H_s$ and $H_b$.

The detection loop begins with a laser source emitting a beam focused onto the oscillating particle. The reflected beam shines onto a photodetector, which converts the signal into a voltage and passes it to a pre-amplifier. The pre-amplifier processes this raw signal, sending its output to the computer (for display) and to a lock-in amplifier that is synchronized to the function generator. The lock-in amplifier then separates the in-phase and out-of-phase signal, sends each to a multimeter for display, and on to the computer for recording. The in-phase and out-of-phase components at each driving frequency are recorded in a data file for each frequency sweep.
III. Experiments

A. Particle Mobility

In the first attempts to manipulate particles, particle mobility decreased significantly over the first few minutes after pipetting the particle solution onto a Si substrate, and similar behavior was observed on Py. Within 15 minutes of placing the solution in contact with the substrate, particles had sedimented and were immobile on substrate even when large field gradients were applied using AlNiCo permanent magnets. A detailed study of surface treatments and detergent concentrations was undertaken to minimize surface-particle interaction.

I examined four sputtered coatings, Pt, SiO₂, Py, and Ta. The solutions examined had five volume concentrations of Tween-20, 0.1%, 0.05%, 0.025%, 0.01% and 0%, and all were 1:100 dilutions of as-received Dynabeads M-270 particle solution, which contains 2.8-micron particles coated with carboxylic acid. Particle solutions were placed in a polydimethyl siloxane (PDMS) well on the substrate and were sealed with a cover slip. Twenty minutes later, the samples were imaged with a LECO LM 247 AT Microhardness Tester microscope at 10x magnification and a field gradient was applied using a permanent magnet (another image was captured at this point). Ten minutes later, another image was captured before the magnet was removed to observe dissociation of particle clusters.

i. Experimental Procedure

After the solution was introduced to the well, particles continuously sedimented out of suspension and settled on the substrate. By the 20-minute mark, particles were densely dotted on the substrate, but thermal vibration was readily visible in every SiO₂, Pt, and Ta sample with detergent present.

![Image of sedimented particles](image-url)

**Fig. 14:** 1-um Dynabeads sedimented out of suspension 20 minutes after the solution is placed on a SiO₂ substrate. The three clear shapes in the left side of the image are chips of PDMS.

20 minutes after the solution was placed in the well, an AlNiCo magnet was placed next to the sample, creating a large field gradient. When the magnet was introduced, particles flowed through the solution towards the magnet immediately. Some particles remained immobile, attached to the substrate and in most cases, these immobile particles attracted a few mobile
particles flowing by, forming a tail of particles magnetically bound to one or a few particles firmly attached to the substrate by secondary bonds as shown in Fig. 15.

Fig. 15: Sedimented Dynabeads moving under the influence of a magnetic field from a permanent magnet placed close to the bottom of the image. Notice that mobile beads show on the image as streaks, whereas particles attached to the surface remain stationary and magnetically collect a tail of mobile particles.

Ten minutes after introducing the magnet, all particles which were free to move had either flown out of the field of view or attached to the tail of one of the surface-bound particles as seen in Fig. 16. The effectiveness of each substrate-detergent combination in promoting mobility was measured by the number of attachment sites per unit area.

Fig. 16: Ten minutes after introducing the magnet, the particles that remain in the field of view are those attached to the surface and their magnetically-drawn tails.
ii. Summary of particle mobility studies

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Tween-20 concentration (volume%) in PBS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.1</td>
</tr>
<tr>
<td>SiO₂</td>
<td>Intermediate mobility</td>
</tr>
<tr>
<td>Pt</td>
<td>Intermediate mobility</td>
</tr>
<tr>
<td>Ta</td>
<td>Low mobility</td>
</tr>
<tr>
<td>Py</td>
<td>No mobility</td>
</tr>
</tbody>
</table>

Table 1: Qualitative comparison of the particle mobility of each substrate/solution combination. The qualifiers low, intermediate, medium, high, and highest are used to compare the same substrate across a range of detergent concentrations. No mobility indicates that samples showed no change when a magnet was introduced.

1. Effect of Tween-20 on particle mobility

Without the aid of surfactant, all surface coatings performed equally poorly: in fact, no surface coating maintained particle mobility without Tween. However, the addition of even a small volume of surfactant dramatically improved particle mobility. As shown below, a small volume of Tween enabled particles to move in response to a large gradient in magnetic field, while the particles were immobile in the absence of Tween when the magnet was applied.

![No detergent on SiO₂](image1.png) ![0.01% Tween on SiO₂](image2.png)

Fig. 17: Comparison of particle mobility in the presence of a magnetic field with no Tween and a low (0.01% volume) surfactant concentration. The sharp difference in mobility indicates that the use of surfactant is key to conduct our experiments.
Although the presence of Tween in solution was necessary for particle mobility, the number of attachment sites did not decrease monotonically with increasing detergent concentration. Instead, in all substrates where particles moved, an intermediate detergent concentration was found to be more effective than either extreme concentration.

2. Particle mobility on different substrates

The samples with the fewest attachment sites for each substrate were compared, and this showed that Pt outperformed other substrates at their best conditions. Ta and SiO₂ were of similar efficacy, and no particle mobility was observed on Py with any concentration of surfactant studied.

![image](image-url)

Fig. 18: Comparison for the best-performing Tween-20 concentrations on each coating. The best combination overall was 0.025% Tween with Pt, while no detergent concentration enabled mobility on Py.
3. Dissociation of particle clusters

The formation of clusters of microbeads was observed in a few occasions in the absence of a magnetic field and whenever particles moved under a large field gradient. One important question to answer is whether chemical interaction between the particles is of comparable strength to the magnetic forces to which the beads are subjected, as this experiment relies heavily upon minimal particle-particle and particle-surface interaction. To examine the relative strength of chemical and magnetic particle interaction, the behavior of clusters formed under a high field gradient was observed. The clusters began to dissociate as soon as the field was removed, so we can conclude that dominant particle-particle interaction in the solutions used is magnetic, not chemical.

![Image a) Dissociation of particle clusters upon removal of external field.](image-a) ![Image b) Dissociation of particle clusters upon removal of external field.](image-b)

Fig. 19: Dissociation of particle clusters upon removal of external field. In a) we see particles (on an SiO2 substrate in 0.025% Tween solution) ten minutes after a magnetic field was applied. Notice the formation of clusters around attachment sites. The image in b), where the clusters are spread out was captured immediately after the field was removed. The dissolution of clusters upon removal of the field suggests that the dominant particle-particle interaction is magnetic, not chemical.

iii. Conclusions for experiment design

From this analysis, the best conditions for particle mobility were a Pt surface coating and 0.025% Tween. Although a few nm of Pt were an effective surface coating, SiO2 was ultimately used because it allowed us to locate ring structures visually using a microscope. Initial resonance experiments showed that some particles remain on the surface after cleaning, so an increased concentration of Tween was used. This raised concentration kept the particles in solution mobile while helping re-suspend particles that remained on the surface from previous experiments.
B. Background of Resonance Measurements

i. Experimental protocol

For these experiments, two dilutions of as-received Dynabeads M-270 beads were used. Starting with a stock solution with \( \sim 9 \times 10^9 \) beads/ul, 1:6000 and 1:3000 dilutions were prepared. Stock solution of these superparamagnetic (SPM) beads was mixed with 1% Tween-20 in phosphate buffer saline (PBS) and stock PBS to reach the desired dilution of particles as well as a 0.1% concentration of Tween-20 to maintain particle mobility.

Wells of poly-dimethyl siloxane (PDMS) were cut from a thin sheet made using Dow Corning's Sylgard 184 Silicone Elastomer Kit. These wells were placed around the patterned arrays of rings and adhered to the SiO\(_2\) capping layer through secondary bonding such that the well-wafer interface was airtight. Particle solution was added using a micropipette, and a glass cover slip was placed over the filled well and pressed to create a seal with the PDMS well.

![Figure 20: Preparation of beads on magnetic ring structures for the measurement of resonant frequencies. (a) Sample before bead deposition. (b) Sample overlain with PDMS well. (c) Deposition of bead suspension into PDMS well. (d) Sample with bead suspension covered with glass cover slip. (Figure adapted from presentation given by Elizabeth Rapoport at 2011 APS Conference)](image)

Once the sample is prepared, it is positioned on a horizontal Plexiglas sheet at the height of the magnet poles. Using a DC source, a bias magnetic field is turned on to initiate DWs in the Py rings and once particles settle over the DWs, a smaller in-plane field perpendicular to the bias field is introduced. This second field, drawn from a function generator, is sinusoidal and it drives the oscillation in the position of the DWs.

Once the particles are oscillating, the laser spot is placed over a particle and aligned such that the entire amplitude of oscillation lies within the laser spot. Once the particle is aligned, an image of the array is captured and the frequency sweep is initiated. The frequency sweep begins at 1 Hz and increases logarithmically up to 1 kHz in 101 steps, measuring five curves for each frequency.

ii. Explanation of the measurements

As mentioned earlier, we use an oscillating magnetic field perpendicular to the bias field to sinusoidally move the DW to which the bead of interest is drawn. We need to examine the motion of the bead against the magnetic field that drives the DW in order to calculate the in-phase and out-of-phase components of the response. The motion of the bead is recorded by measuring the reflected intensity of a laser beam focused on the ring surface as the bead oscillates inside the laser spot. The oscillation of the DW is monitored by recording \( H_S \), the field driving the motion. In this experiment, we record the sinusoidal voltage input to the magnet, as it is proportional to \( H_S \) by a known factor.

The reflectivity signal and \( H_S \) (from the magnet voltage input) are passed to a lock-in amplifier that is also synchronized to the function generator which produces the voltage sinusoid
that produces $H_S$. The lock-in amplifier analyzes the reflectivity signal against $H_S$ and extracts the in-phase and out-of-phase components of the bead’s motion relative to the driving field.

![Diagram of optical resonance measurements](image)

Fig. 21: Schematic of the principle involved in optical resonance measurements. The DW to which the bead is drawn is driven by a known external field $H_S$. As the particle oscillates inside the laser spot, the reflectivity signal measured by the photodetector also varies. A lock-in amplifier compares the reflectivity signal to the driving field and extracts the in-phase and out-of-phase components of the amplitude for each frequency in the sweep.

### iii. Resonance curve Data

For each frequency in the sweep, the lock-in amplifier extracts the in-phase and out-of-phase component of the reflectivity relative to the driving field of the magnet. These data are recorded by the computer and are plotted as functions of frequency at the conclusion of the frequency sweep.
Fig. 22: Out-of-phase component of resonance curve for a 2.8-um Dynabead measured following the procedure outlined in the Experiment section. The peak of the curve was found using Origin software. For this bead, the peak is at 26.40 Hz.

Fig. 23: In-phase resonance component of resonance curve for a 2.8-um Dynabead measured following the procedure outlined in the Experiment section. The peak of the curve was found using Origin software. For this bead, the peak is at 26.40 Hz.
C. Experimental agreement with model

i. Curve fitting to data

To ascertain whether the measurements made agree with the theoretical predictions, out-of-phase measurements with little noise were fit with the Lorentzian distributions predicted by the model. This curve fitting shows close agreement between the experiment above 10 Hz and only some disparity below that frequency. Hence, the behavior of the experiment validates our model.

Fig. 24: Out-of-phase component of a resonance curve with a Lorentzian fit like the one predicted in the Model. The fit, which is centered around an angular frequency of 136 radians, closely agrees with the data above an angular frequency of 50 radians, or 7.95 Hz.

Fig. 25: In-phase component of a resonance curve with a fit like that predicted in the Model.
ii. Dependence of resonance maximum on drive amplitude

A single DW/bead couple was measured in the same physical location using four different driving voltages, spanning a five-fold range. The resonance maxima fell within the 4-Hz repeatability window described above, which suggests that the resonant peak is invariant with drive amplitudes and validates the linear model we have proposed.

---

<table>
<thead>
<tr>
<th>Drive Amplitude (V)</th>
<th>Angular Amplitude (radians)</th>
<th>Resonance Maximum (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.125</td>
<td>0.0890</td>
<td>32.7</td>
</tr>
<tr>
<td>0.1</td>
<td>0.0713</td>
<td>33.6</td>
</tr>
<tr>
<td>0.05</td>
<td>0.0357</td>
<td>36.3</td>
</tr>
<tr>
<td>0.025</td>
<td>0.0179</td>
<td>36.1</td>
</tr>
</tbody>
</table>

Fig. 26: Out-of-phase resonance curves for the same bead-DW pair with four different drive amplitudes. The resonance maxima differ by less than 4 Hz, which lies within the repeatability window imposed by optical misalignment explained in Variability in particle-beam alignment. In effect, these data suggest that the resonance maximum is independent of driving amplitude.

A single DW/bead couple was measured in the same physical location using four different driving voltages, spanning more than a four-fold range in angular displacement. This experiment was carried out some of with the first few resonance sweeps, before the bead alignment procedure was optimized. Nevertheless, the resonance maxima fell within the 4-Hz repeatability window described above. The close agreement among the highest four driving voltage suggests that the resonant peak is invariant with drive amplitudes and further supports the linear spring model we have proposed.

D. Distribution of Resonant Maxima

Fourty individual beads were examined with the frequency sweep outlined in the Experiment section. After each frequency sweep was carried out, the out-of-phase signal was plotted against frequency on a logarithmic scale and the peak of the curve was found using Origin software. The lowest measured peak was at 18.3 Hz and the highest was at 42.7 Hz, with a median value of 31.1 Hz.
Although forty individual beads were measured, many beads were measured more than once. In addition to the basic frequency experiment, experiments were carried out to (1) examine the dependence of resonant peak frequency with drive amplitude (2) examine the measurement of resonant peak frequency with position on a given ring. In total, 67 frequency sweep measurements were made.

E. Factors contributing to the spread in resonance maxima

Several factors widen the distribution in resonant frequency: bead-surface interaction, particle-beam alignment, and energetic differences between head-head and tail-tail domain walls.

i. Variability in particle-beam alignment

Variability in particle-beam alignment can result in shifts of the frequency of the resonance maximum. One particle-DW couple was measured in two occasions, with the beam brought out of and into alignment with the bead before the second measurement. With the bead-beam alignment optimized in both occasions, the resonance maxima for each run were just over 4 Hz apart. Even for the same particle-DW couple in the same physical location, experimental variability yielded a significant change in resonance frequency. In this case, the resonant peaks were measured as 27.5 and 31.7 Hz.
Fig. 28: Resonance curves for a single bead at the same point on a ring. The resonance measurement was made once, the laser spot moved away, and then the spot was re-positioned. The shift of the resonance peak shows that a robust procedure for alignment is necessary to replicate results.

The observed effect of beam-particle alignment on the repeatability of measurements led to the development of a robust procedure for alignment with improved repeatability as shown in Fig. 28. The procedure involved moving the particle into the beam along X (or Y) and maximizing the out-of-phase signal on the lock-in amplifier. The X (or Y, if that was chosen first) position was then fixed and the out-of-phase signal was maximized by moving along the second direction. The histogram of resonant frequencies presented earlier includes some spread due to alignment, as all it includes the data gathered. The earliest measurements were made before refining the alignment procedure, so the measured peaks may have been affected by alignment error.

Fig. 29: Resonance curves for a given DW-bead couple. The curve in red was measured first using the alignment procedure outlined above and the beam spot was then moved away. The bead was re-acquired using the same procedure and another resonance measurement made. The peak for the first curve was at 30.43 Hz, while that of the second was at 31.39 Hz, showing a significant improvement in repeatability.
ii. Location of domain wall-bead couple on Py rings

The largest contribution to the distribution of resonant frequencies comes from the physical location on the ring. For one domain-wall/bead couple, resonance measurements were done at four places on a given ring by rotating the sample so that the DW and the associated bead was positioned over different points on the ring. Local differences in surface conditions can lead to significant variability in the resonance peak frequency for a given particle-DW couple well beyond the 4-Hz range expected from beam-particle alignment. This measurement was done on a 3-nm particle on a 600 nm-wide ring:

![Out-of-phase resonance curves for a single DW-bead couple at different positions on the same ring.](image)

<table>
<thead>
<tr>
<th>Bead Position on ring</th>
<th>Resonance Maximum (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>North</td>
<td>14.32</td>
</tr>
<tr>
<td>East</td>
<td>17.95</td>
</tr>
<tr>
<td>South</td>
<td>38.57</td>
</tr>
<tr>
<td>West</td>
<td>22.08</td>
</tr>
</tbody>
</table>

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Although nothing in the design of the experiment or the physics involved suggests that the physical position on the ring should change the observed behavior, particle-surface interaction and DW pinning in the structure may cause this position-dependent behavior. The SiO$_2$ coating and addition of surfactant greatly increased particle mobility, some attachment sites remain on the surface under the best conditions for the experiment. In addition, defects in the ring structures can pin DWs and prevent them from moving freely when a magnetic field is applied. For DW-bead couples where the oscillation was not uniform, the photodetector signal showed discrete jumps in the position of the particle at some points; these jumps are indicative of DW pinning.
Fig. 31: Driving voltage and reflectivity signal for a DW-bead couple driven at 3 Hz. In comparison to the smooth driving voltage sinusoid, there is a discrete jump in the position of the bead at the times indicated by the blue circles. These jumps are indicative of DW pinning.

iii. Different domain wall types

Measurements of a pair of beads on a single ring show a consistent difference in resonance frequency between beads depending on the type of domain wall they are bound to. Specifically, two such pairs were studied. As Fig. 32 shows, particles on DWs closest to the arrow point of the bias field have a higher resonance maximum than particles away from the bias field. The difference in frequency between the two DW types was consistent (10 Hz) and larger than the measurement variability reported earlier. The ratio of the higher frequency to the lower one was also nearly constant: 1.32 for the first set and 1.39 for the second.
Fig. 32: Two sets of resonance maxima for two beads on the same ring. For each set in a) and b), there is a bead drawn to each of the DWs in a single ring. Both sets of data show similar ratios for the resonance maxima of one DW type to the other.

To further explore this change in resonance maxima, the full data set was divided in two sets depending on what type of domain wall the bead was attached to. Wall 1 is the set of beads furthest from the arrow point of the bias field; Wall 2 is the set of beads closest to the arrow point of the bias field. Beads for which the DW type was unclear (i.e., beads without an image) were left out of this histogram:
Fig. 33: Histogram of resonance maxima split into domain wall types. Although the data do not show two clear peaks, the distributions for each DW type are centered about different frequencies. There are fewer data points in this histogram than in Fig. N because the wall type could not be ascertained for every bead measured.

Although the distribution of data does not clearly show two peaks, it suggests that there is a difference in resonant maxima depending on DW type.
IV. Conclusion

We examined the feasibility of using the resonant frequency of magnetic bead-domain wall (DW) couples in a host fluid to measure particle size. The resonant frequency of 40 bead-DW couples was measured and found to lie in a range between 18.3 and 42.7 Hz with a median of 31.1 Hz. In addition, resonance experiments were performed to examine the dependence of the resonant frequency on driving amplitude, DW type, and position on the Py ring. The resonant frequency populations of beads bound to head-head and tail-tail DWs overlapped, but each DW type seemed to be centered on a different frequency.

We conclude that resonance measurements made with optical methods reliably distinguish particles of different hydrodynamic radius. Our experiments validated the linear spring model for DW-bead interaction, as curve fits to data showed close agreement. In addition, we showed that the resonant frequency is independent of the driving amplitude, which further supports the linear spring model for DW-bead interaction. In addition, this work has helped identify and address some of the obstacles to improve the reliability of these resonance measurements as indicators of particle size. Examination of different positions on a ring showed that a large contribution to the spread in resonant frequencies that come from DW pinning may be due to structural defects or remanent surface-bead interaction.

The next steps in the development of resonance biosensors is closer study of the factors that contribute to the spread in resonant frequencies, like DW type dependence, DW pinning, and bead-surface interaction. Improvements in lithographic patterning for our structures and surface engineering may significantly reduce the spread in resonance maxima, increasing the capability of this technique to resolve particle sizes. Beyond these experiments, the next experiments include examining the resonance spreads of particle populations of different radii and also the resonance spreads of single particles and particles covalently bound to nonmagnetic particles, as in a sandwich assay.

We hope the findings from these experiments will enable the optimization of fabrication methods and measurement protocols thus enabling the transition from optical to magnetoresistive methods for resonance measurements and serving as a stepping stone to the eventual development of spin-valve–based resonance biosensors.
V. Acknowledgements

I would like to thank Professor Geoffrey Beach for his mentorship and teaching in the two years I have worked in his research group. Without Professor Beach’s work designing and building the apparatus as well as writing most of the code to operate it, I and other students would have been unable to perform high-quality experiments.

I would also like to thank Elizabeth Rapoport for her work in designing and building the magnet that was crucial to this experiment and for her help in learning to perform resonance experiments.
VI. References


