A NOVEL AFM TECHNIQUE FOR SIMULTANEOUS NON-CONTACT IMAGING OF TOPOGRAPHY AND SURFACE POTENTIAL IN SOLUTION

A Thesis in
Chemical Engineering

by
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ABSTRACT

A novel Atomic Force Microscopy (AFM) technique is presented that can simultaneously image surface topography and local electrical potential in liquid without mechanical contact between the AFM tip and the sample. This new technique is called Liquid Environment Electroactuation Force Microscopy (LEEFM). The operation of LEEFM is similar to Scanning Polarization Force Microscopy (SPFM) in air. An AC voltage at frequency $\omega$ is applied to the AFM tip/cantilever, generating an electrical potential difference between the tip and sample. The electrical double layer does not screen out the electrostatic interactions, even in water containing added ions, because the voltage is switching polarity too fast for the electric field or the double layer to fully form. The resulting capacitive coupling causes an attractive force between the cantilever and sample, so the cantilever vibrates at the applied frequency ($1\omega$) and twice this frequency ($2\omega$), with a distinct vibration amplitude at each frequency. Non-contact imaging of topography is accomplished by feedback controlling the amplitude of the $2\omega$ vibration, which depends on the tip-sample separation in the range of 1~10 nm. The $1\omega$ vibration amplitude and phase shift are simultaneously collected to form maps of the properties of the surface. The exact relationships between the surface properties (e.g. charge) and the cantilever vibration behavior are not yet fully understood.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Pages</th>
</tr>
</thead>
<tbody>
<tr>
<td>List of Figures</td>
<td>vi</td>
</tr>
<tr>
<td>Acknowledgements</td>
<td>x</td>
</tr>
<tr>
<td>Chapter 1 Introduction</td>
<td>1</td>
</tr>
<tr>
<td>Background and Motivation</td>
<td>1</td>
</tr>
<tr>
<td>Project Goals</td>
<td>4</td>
</tr>
<tr>
<td>Chapter 2 Instrumentation</td>
<td>6</td>
</tr>
<tr>
<td>2.1 Synopsis</td>
<td>6</td>
</tr>
<tr>
<td>2.2 The Atomic Force Microscope (AFM)</td>
<td>7</td>
</tr>
<tr>
<td>2.2.1 History of AFM</td>
<td>7</td>
</tr>
<tr>
<td>2.2.2 AFM Principles</td>
<td>8</td>
</tr>
<tr>
<td>2.2.3 Dynamic AFM</td>
<td>12</td>
</tr>
<tr>
<td>2.3 The Scanning Polarization Force Microscope (SPFM)</td>
<td>14</td>
</tr>
<tr>
<td>2.3.1 Experimental Setup</td>
<td>14</td>
</tr>
<tr>
<td>2.3.2 Electrostatic Driving Force</td>
<td>15</td>
</tr>
<tr>
<td>2.3.3 Related Techniques</td>
<td>18</td>
</tr>
<tr>
<td>2.4 The Liquid Environment Electroactuation Force Microscope</td>
<td>20</td>
</tr>
<tr>
<td>2.4.1 Experimental Setup</td>
<td>20</td>
</tr>
<tr>
<td>2.4.2 LEEFM and SPFM Vibration Signals</td>
<td>21</td>
</tr>
<tr>
<td>2.4.2.1 – Voltage Dependence</td>
<td>22</td>
</tr>
<tr>
<td>2.4.2.2 – Frequency Dependence</td>
<td>23</td>
</tr>
<tr>
<td>2.4.2.3 – Distance Dependence</td>
<td>24</td>
</tr>
<tr>
<td>Chapter 3 LEEFM Imaging Results</td>
<td>29</td>
</tr>
<tr>
<td>3.1 Synopsis</td>
<td>29</td>
</tr>
<tr>
<td>3.2 Resolution Enhancement</td>
<td>30</td>
</tr>
<tr>
<td>3.3 Chemical Sensitivity</td>
<td>33</td>
</tr>
<tr>
<td>3.4 Hydrophobic Samples</td>
<td>34</td>
</tr>
<tr>
<td>3.5 Non-Conducting Samples</td>
<td>39</td>
</tr>
<tr>
<td>3.6 Discussion</td>
<td>42</td>
</tr>
<tr>
<td>Chapter 4 The Driving Force</td>
<td>45</td>
</tr>
<tr>
<td>4.1 Summary</td>
<td>45</td>
</tr>
<tr>
<td>4.2 Surface Charge and the Electrical Double Layer</td>
<td>46</td>
</tr>
<tr>
<td>4.3 AC Electrostatic Actuation in Liquids</td>
<td>49</td>
</tr>
<tr>
<td>4.4 Dielectrophoresis</td>
<td>52</td>
</tr>
<tr>
<td>4.5 Supporting Data</td>
<td>58</td>
</tr>
<tr>
<td>4.5.1 Voltage Dependence</td>
<td>58</td>
</tr>
<tr>
<td>4.5.2 The Probe</td>
<td>60</td>
</tr>
<tr>
<td>Section</td>
<td>Page</td>
</tr>
<tr>
<td>---------</td>
<td>------</td>
</tr>
<tr>
<td>4.5.3 The Substrate</td>
<td>63</td>
</tr>
<tr>
<td>4.5.4 The Medium</td>
<td>66</td>
</tr>
<tr>
<td>4.6 Discussion</td>
<td>69</td>
</tr>
<tr>
<td>Chapter 5 Conclusions</td>
<td>71</td>
</tr>
<tr>
<td>References</td>
<td>73</td>
</tr>
<tr>
<td>Appendix A Mathematica Simulations of LEEFM</td>
<td>79</td>
</tr>
<tr>
<td>Appendix B NSF EAPSI Proposal</td>
<td>84</td>
</tr>
</tbody>
</table>
LIST OF FIGURES

Figure 2.1: A descriptive schematic showing the major components of an AFM. The components are not nearly to scale: for example, the piezoelectric actuator is ~ 10 cm tall, while the cantilever is about 200 µm long. .................................................................9

Figure 2.2: An idealized Force-Distance (FD) curve, with the deflection of the cantilever vs. the displacement of the piezoelectric actuator. (1) Approaching the surface with no force felt by the tip; (2) Tip snap-in; (3) Cantilever bending due to mechanical contact with surface; (4) Tip retraction beyond neutral force due to adhesion; (5) Tip snap-off; (6) Retraction with no force felt by the tip. The slope of the line in region (3) is the deflection sensitivity used to calibrate the position sensitive photodetector. ....10

Figure 2.3: Experimental setup of the SPFM.................................................................15

Figure 2.4: A snapshot of the vibration profile of the tip. The black line is the voltage applied to the tip from the function generator. The purple line is the actual vertical position of the tip, with respect to time, output by the PSD. The blue and red lines are drawn to show the deconvolution of the $1\omega$ and $2\omega$ vibrations, respectively. ...........18

Figure 2.5: Experimental setup of the LEEFM............................................................21

Figure 2.6: The cantilever behavior in LEEFM as a function of the applied voltage. The green line is the constant deflection, and the $1\omega$ and $2\omega$ vibration amplitudes represented as blue and red error bars, respectively, centered on the constant deflection line. The frequency applied was 4 kHz, which was the $2\omega$ resonance frequency for this tip, and the tip was situated ~ 300 nm above a clean silicon surface in DI water. ..........................................................................................................22

Figure 2.7: Frequency dependence of the cantilever motion. (a) Constant deflection (green line) with the $1\omega$ and $2\omega$ vibrational amplitudes plotted as blue and red error bars, respectively, for LEEFM cantilever vibration in DI water. (b) Comparison of $1\omega$ and $2\omega$ vibrational amplitudes in LEEFM (solid lines) and SPFM (dotted lines). All data were collected ~ 300 nm over a silicon surface with 1 V applied to the tip. ......24

Figure 2.8: Distance dependence of the cantilever $2\omega$ vibration amplitude. (a) Comparison between vibration of LEEFM in water (red line with circle points) and SPFM in air (black line with diamond points) over 100 nanometers. (b) LEEFM $2\omega$ vibration amplitude over 100 micrometers. The curves in (a) and (b) are for the tip approaching the surface, not retraction. The data were collected over silicon with 1 V applied to the tip at the $2\omega$ resonance frequency (4 kHz in water, 30 kHz in air). ......25

Figure 2.9: Modeling the distance-dependence of the electrostatic force in AFM using the approximations found in [29]. (a) A representation of the approximation, where the tip is separated into three components: the cantilever, modeled as a plate (red); the bulk of the probe (blue), modeled as a cone; and the apex of the probe (green), modeled as a sphere. (b) The electrostatic force acting on the tip components in
SPFM/KPFM in air. (c) The electrostatic force acting on the tip components in LEEM in water; the only difference between the models for (c) and (b) is dielectric constant of the medium – 1 for air, 80 for water. For (b) and (c), the tip-sample separation is measured from the apex. The simulation parameters were: cantilever dimensions = 100 μm long x 20 μm wide; cone height = 20 μm; cone angle = 20°; the angle between the cantilever and the sample = 11°; the radius of the apex = 20 nm; and the voltage applied to the tip = 1 V.

Figure 3.1: Images of a hexagonal etched well on silicon imaged by (a) SEM, (b) contact mode AFM, (c) SPFM in ambient air, (d) LEEM in DI water. These are not the same well in each image, but a single well from a sample containing many. The AFM images are all right-to-left scans. The contact mode image was collected with a 6.7 nN normal force. The SPFM image was collected with at a tip-sample separation distance of ~ 30 nm. The LEEM image was collected at ~ 5 nm separation, which corresponded to 50% damping of the 2ω vibration amplitude feedback signal from 1.2 nm to 0.6 nm. The resolution enhancement is demonstrated in a cartoon—not to scale—showing the tip-sample electrical interactions, shown as red lines, spreading from the point of the tip when it is farther from the surface (e) as when using SPFM, and when closer to the surface (f) as when using LEEM. The color scale on the right side corresponds to the feature height in (b), (c) and (d), while the depth scales to the left of each of these images correspond to the line scan depth profile superimposed on each as a red line.

Figure 3.2: LEEM images of gold surfaces covered with self-assembled monolayers (SAMs) of (a) Au-SC11H22COOH and (b) Au-SC11H22NH2. A 1 μm × 1 μm area of the SAM was damaged by the AFM tip using a high load (~ 300 nN) contact scan. A 4 μm × 4 μm area centered on the damaged region was then imaged with LEEM, using the 2ω amplitude for feedback control while monitoring the 1ω amplitude and phase.

Figure 3.3: Images of Polystyrene (PS) domes deposited on silicon wafer. (a) Cartoon showing a (PS) particle (orange sphere) that is melted to form a dome shape. (b) The true topography of the surface was imaged with contact mode AFM. The LEEM topography (c), 1ω amplitude (d) and 1ω phase (e) images of the same sample show strange features as a result of poor feedback control of the 2ω amplitude. The 2ω amplitude was ~ 0.6 nm without damping. All AFM images are 5 μm x 5 μm, and the right-to-left scans are shown.

Figure 3.4: FD Curves of the time-averaged cantilever deflection (left axes) and the 1ω and 2ω amplitudes (right axes) performed on a silicon sample with polystyrene (PS) domes on it. (a) Untreated Si, (b) untreated PS, (c) plasma cleaned Si, (d) plasma cleaned PS.

Figure 3.5: Images of Polystyrene (PS) domes deposited on silicon wafer after a few seconds of exposure to oxygen plasma. (a) Topography from contact mode AFM. (b) Topography, (c) 1ω amplitude, and (d) 1ω phase from LEEM. The 2ω amplitude was used for feedback control with a setpoint of 1 nm, 25% damping from the undamped vibration of 1.3 nm. All images are 5 μm x 5 μm, and the right-to-left scans are shown.
Figure 3.6: Frequency sweeps on (a) silicon and (b) sapphire. The same tip was used for both, with 1 V applied 300 nm above the surface.................................40

Figure 3.7: Images of PS domes on sapphire. (a) Contact mode AFM, (b) LEEFM topography using 1ω amplitude as feedback, (c) LEEFM 2ω amplitude. Contact mode was performed with 0.5 nN applied normal force. The applied signal for LEEFM was 0.5 V at 2 kHz. The 1ω amplitude feedback setpoint was 1.3 nm from the undamped vibration of 6 nm. All images are 5 µm x 5 µm, and the right-to-left scans are shown..................................................41

Figure 3.8: Relationship between the isoelectric point of the probed surface and the 1ω phase. All data were collected with the same tip 300 nm from the surface with 1 V applied at 4 kHz, which was the 2ω resonance frequency.........................43

Figure 4.1: A simple model of the electrical double layer showing the ion distribution (top) and electrical potential (bottom) near a charged plate. (1) The charged surface, (2) the Stern layer of bound counterions, (3) the diffuse Gouy-Chapman layer of ions, (4) bulk solution. ..............................................................48

Figure 4.2: (a) SEM image of a MEMS comb drive actuator; (b) non-dimensionalized displacement of the free electrode as a function of frequency in different media (circles are in water), with a line drawn over one set of data to emphasize the sigmoidal shape; (c) the water data from (b) redimensionalized and replotted with cantilever deflection data from LEEFM. (a) and (b) and the comb drive deflection data in (c) are reproduced from ref. [85].................................................................51

Figure 4.3: Theoretical and experimental data changing (a) applied voltage, (b) applied frequency, and (c) tip-sample separation distance. Solid lines are experimental data, dotted lines are modeled data; blue – 1ω amplitude, red – 2ω amplitude, green – time-averaged deflection.................................................................55

Figure 4.4: Frequency dependence of the 1ω (blue lines) and 2ω (red lines) vibration amplitudes from theoretical modeling (dotted lines) and experimental data (solid lines). The theoretical model used here included the frequency dependent behavior of the relative permittivity of water. ................................................................................57

Figure 4.5: (a) LEEFM experimental data showing cantilever deflection (green line; left axis) and 1ω and 2ω vibration amplitudes (blue and red lines, respectively; right axis) as functions of the applied voltage. (b) Comb drive deflection in various liquids (AC) and air (DC, inset) as a function of the square of the applied voltage. ....58

Figure 4.6: Frequency sweeps in (a) air and (b) water showing the 1ω and 2ω vibration (blue and red lines, respectively) amplitudes (solid lines; left axes) and phase shifts (dotted lines; right axes). The 1ω phases are shifted by 180° in each case when the 1 V driving voltage is applied to a silicon sample instead of the silicon cantilever. The phase change that occurs at resonance is a well-known effect, but not relevant to the present discussion. ...........................................................................59
Figure 4.7: The change in vibration amplitudes due to changing properties of the AFM probe. The four materials represented are shown at the top in their respective color: Silicon is blue, silicon nitride is gray, gold is (creatively) gold, and nail polish is purple. Silver paste is not shown, but it was used in all cases except (b). The magnitudes of the vibration amplitudes observed are represented as the size of the text to the right of each probe. (a) A standard silicon probe with the individual components labeled and the baseline vibration amplitudes. (b) Nail polish used instead of silver paste to affix the cantilever to the gold spring – no vibration. (c) Nail polish on the outside of the gold spring – no change in vibration from baseline. (d) Si$_3$N$_4$ cantilever and tip – significantly reduced 1$\omega$ amplitude and an extremely faint 2$\omega$ vibration. (e) Si$_3$N$_4$ cantilever and tip with a gold film covering the back – faint 2$\omega$ vibration but huge 1$\omega$ vibration. Note that the cartoons of the probes are not to scale: the cantilever is 225 µm long and a few µm thick, while the chip is ~ 1 mm long and a few tenths of a mm thick. The scale of the gold spring compared to the chip is reasonable (though not exact), as is the scale of the tip compared to the cantilever.

Figure 4.8: Frequency dependence of the LEEFM (a) 1$\omega$ and (b) 2$\omega$ vibration amplitudes for a regular Si probe (blue lines), a Si$_3$N$_4$ cantilever and tip (gray lines), and a Si$_3$N$_4$ cantilever and tip coated with gold on the side facing away from the surface (orange line). 1 V was applied to the gold spring in all cases.

Figure 4.9: The 1$\omega$ (blue line) and 2$\omega$ (red line) LEEFM vibration amplitudes on silicon surfaces with thermally grown oxides. The applied signal was 1 V at 5.5 kHz, which was the 2$\omega$ resonance frequency, though the behavior was consistent at other applied frequencies. The Si tip was positioned 300 nm above the surfaces.

Figure 4.10: Cantilever deflection (left axis) due to an applied square wave voltage (black line, right axis) for a silicon tip 300 nm above: silicon with a native oxide layer (blue line), 50 nm (red line) and 110 nm (purple line) thermally grown oxides on silicon, and a glass slide (green line).

Figure 4.11: Cantilever deflection due to an applied +/- 0.5 V square wave in air (black line), decane (red line) and water (blue line).

Figure 4.12: The 1$\omega$ (blue line) and 2$\omega$ (red line) LEEFM vibration amplitudes vs. the concentration of KCl in the solution. The applied signal was 1 V at 4 kHz and the Si tip was positioned 300 nm above a Si surface.
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Chapter 1

Introduction

Atomic Force Microscopy (AFM) and its derivative techniques have been used to image many different properties of many different samples. But no AFM technique yet exists which allows non-contact imaging of both topography and surface potential in water. Such a technique would be very useful for imaging the structure and chemical configuration of soft and easily deformable surfaces, such as cells in biologically relevant conditions. This thesis deals with the development of that technique, which is called Liquid Environment Electroactuation Force Microscopy (LEEFM).

Background and Motivation

The term “microscopy” is usually thought of in terms of optical or electron microscopy, where one “looks” at a surface by shooting photons or electrons at it then analyzing what bounces off. Atomic Force Microscopy (AFM) is a technique that uses a sharp probe to “touch” a surface instead, and can directly collect high resolution images of topographical image through mechanical contact [6]. A plethora of AFM-based techniques have been developed for probing all sorts of surface properties, such as surface charge [7-10], surface chemical groups [11], friction, adhesion and mechanical properties [12-15], electrostatic forces [16-18], magnetic forces [19-22], and others. Even more varied are the surfaces which have been studied via these myriad AFM techniques, such as cells and cell structures [23, 24], hard drives and electronics [25, 26], nanotubes and nano-structured materials [27-29], DNA and chromosomes [30-32], and many, many more.

The electrostatic properties of materials have been studied extensively using Electrostatic Force Microscopy (EFM) [8, 16, 18, 33, 34], Kelvin Probe Force Microscopy (KPFM) [35-39] and
Scanning Polarization Force Microscopy (SPFM) [40-45]. SPFM and KPFM are very similar techniques which allow non-contact imaging of both topography and surface potential for surfaces in air. Electrostatic properties can be probed in air or water via EFM, but requires two scans: the trace and re-trace method requires a contact scan to image the topography, then the tip is lifted above the surface and scanned along the same topographic map while detecting the electrostatic force between the tip and sample. Lacking among these myriad AFM techniques is one which allows non-contact imaging of both topography and surface potential in water. Non-contact imaging is required for soft samples such as cells, which can be damaged or destroyed by the high contact pressures exerted by the sharp AFM tip. Imaging surface potentials is particularly important in water, where surfaces develop a charge due to ion adsorption and ionization of the surface chemical groups if their isoelectric point is different from the pH of the water [46]. Surface charge in an aqueous solution can dictate the behavior of a system by affecting key processes, such as DNA adhesion [47-49], colloid adsorption and aggregation [50-53], and polymer swelling [54]. Surface charge also profoundly affects the function of cells, since the cell membrane is responsible for all interaction with the environment. For example, some bacteria and fungi cannot attach to their targeted host cell if their surface potential is not within the correct range [49, 55, 56]. It has been shown that the relative negative charge of some disease-causing bacteria (e.g. *E.coli*) is directly related to their attachment to meat, and is more important than their hydrophobicity – another important surface characteristic [55].

The average surface charge or $\zeta$ potential of particles or cells can be measured in a variety of ways, such as through the electrophoretic mobility, but the charge non-uniformity of a surface or particle often dominates its behavior [57-59]. The cell surface can have significant charge inhomogeneity; the lipid membrane has areas of concentrated proteins and polysaccharides, and these molecules can carry a net charge [60]. These areas where molecules aggregate to perform a function for the cell are called lipid rafts, and the exclusion or inclusion of specific molecules in the lipid rafts means that they can have a different surface charge than the surrounding membrane. Lipid rafts are
thought to be responsible for many processes, such as signal transduction, molecular assembly, and membrane protein trafficking [61-64]. However, the exact structure, function and distribution in the cell membrane are still poorly characterized. Jacobson et al. sum up the problem in [60]: “It is our contention that the lipid-raft field is at a technical impasse, largely because the tools to study biological membranes as liquids structured in space and time are rudimentary.” The technique described in this thesis would be capable of studying cell membranes and model liquid membranes through non-contact imaging, and would yield data on the topography and surface charge, hopefully giving new insights into these poorly-characterized structures.

This technique has in fact been successfully developed and is called Liquid Environment Electroactuation Force Microscopy (LEEFM). LEEFM could be useful for studying many systems, including those outlined above. A specific example of a biological system that could be studied with LEEFM is the attack of the fungus *Fusarium oxysporum* on the cells of the plant *Arabidopsis thaliana*. *F. oxysporum* causes diseases in many industrially important plants, including *A. thaliana*, which is one of the best-characterized plant species [65-67]. Different ecotypes of *A. thaliana* are resistant to different strains of *F. oxysporum*, though the mechanisms and structure-function relationships are still poorly understood [68, 69]. LEEFM would be able to study the cell surface topography and charge distribution at varying stages of the fungal attack without disturbing the cells through mechanical contact. The information gathered may yield new insight into the mechanism for fungal resistance, ultimately enabling an improvement in the resistance of crops to some diseases. Thus, in many ways, LEEFM could advance the understanding of the cell membrane and the specific processes which occur there, which are topics of great fundamental importance.
Project Goals

1. **Use model samples to show proof-of-concept for the desired capabilities of LEEFM**
   
The technique aims to image topography and surface potential, so these capabilities must be demonstrated before proceeding with development. Imaging results presented in Chapter 3 show that LEEFM can image topography and local potential.

2. **Determine the principles underlying the operation of the technique**
   
The mechanism which drives the cantilever vibration in LEEFM is not yet fully understood. The hypotheses of electrostatic and dielectrophoretic forces are discussed in Chapter 4.

3. **Quantify the relationships between surface properties and the signals output by LEEFM**
   
   So far, LEEFM can only detect changes in surface properties; it cannot quantify those changes or determine specific values, such as surface potential at a specific location. Some ways of elucidating surface property–LEEFM signal relationships are discussed in Chapter 3 as future work.

4. **Determine the limitations of LEEFM, such as resolution, sensitivity, and sample restrictions**
   
   A grasp of what the technique cannot do is as important as what it can do, otherwise time can be wasted trying to use the technique in an inappropriate way. In Chapter 3 it was shown that LEEFM may have trouble with insulating or hydrophobic samples, though these may not be absolute limitations. Other effects of the tip, sample, and medium are discussed in chapter 4. The ultimate spatial resolution still needs to be determined, and ways to do this are discussed in the future work of Chapter 3.
5. Apply LEEFM to relevant biological and physical systems

Applying the technique is the most important part in its development. The LEEFM will be used for imaging cell surfaces as discussed above and will hopefully yield new information about some other interesting biological systems such as lipid rafts. Another application is probing the characteristics of physical surfaces with surface charge inhomogeneities, such as colloids, self-assembled monolayers or ion-containing polymers.
Chapter 2

Instrumentation

2.1 Synopsis

The necessary background information for understanding the setup and operation of the LEEFM are discussed. Background and basic principles of the Atomic Force Microscope (AFM) are presented along with a description of its major components in section 2.2. The basic AFM imaging techniques – contact mode, tapping mode and non-contact mode – are described along with a mathematical treatment of the mechanics of the cantilever, which can be modeled as a springboard in static mode and a forced, damped oscillator in dynamic mode.

Many AFM techniques have been developed for specific applications, such as probing the chemical, magnetic or electrical properties of the surface [7, 9, 33, 54, 70]. The Scanning Polarization Force Microscope (SPFM) uses electrostatic interactions between the tip and sample, generated by an AC voltage applied to the tip, to drive cantilever vibration. This technique can image both topography and surface potential without touching the sample by monitoring and controlling the vibration of the cantilever. The setup of the SPFM and the properties of the electrostatic driving force are discussed in detail in section 2.3.

SPFM has only been used for imaging surfaces in air [40-44]. A new technique is proposed that uses the same setup as the SPFM but operates in a liquid environment; this technique, described in section 2.4, is called Liquid Environment Electroactuation Force Microscope (LEEFM). Like SPFM, the vibration of the cantilever is the critical element of LEEFM. The vibration signals from LEEFM and SPFM are compared with respect to changing the applied voltage and frequency, as well as their dependencies on the distance between the tip and sample.
2.2 The Atomic Force Microscope (AFM)

2.2.1 History of AFM

Gerd Binnig and Heinrich Rohrer invented the Scanning Tunneling Microscope (STM) in 1981 in an attempt to establish a technique for vacuum tunneling and local spectroscopy. In STM, an atomically sharp, conducting tip is scanned over a conducting surface. A bias voltage applied to the tip causes electronic tunneling to the surface; the tunneling current, which decays exponentially with separation, is used as a feedback signal to control the tip height. The resolution of the technique is so high that Binnig and Rohrer were able to collect images showing, for the first time ever, individual atoms [71].

Binnig and Roher initially encountered resistance from the scientific community as few believed their machine was actually collecting atomic-scale images. After about four years, they came out with an image of the 7x7 reconstruction of gold [72], thereby convincing the scientific community that the technique did indeed work as advertised. Even in that early stage the power of the STM was evident and, in a testament to its power, Binnig and Rohrer shared half of the Nobel Prize in Physics for 1986 – only a year after proving the technique’s efficacy. To put this swift timeline into perspective, the other half of the prize went to Ernst Ruska for his pioneering work on electron microscopy almost 40 years before.

In 1986 Binnig joined with Calvin Quate and Christoph Gerber to develop the Atomic Force Microscope (AFM), an offshoot of the STM which uses a probe in direct, physical contact with the surface [6]. Feedback control is accomplished by using the normal force acting on the probe instead of a tunneling current. By 1989 AFMs became commercially available, and since then the AFM has become ubiquitous in science and engineering research due to its wide range of capabilities and relatively low price.
2.2.2 AFM Principles

A descriptive schematic (not nearly to scale) of an AFM is shown in Figure 2.1. A sharp probe is mounted at the end of a flexible cantilever, which is attached to a piezoelectric actuator. This actuator contains a piezoelectric crystal that mechanically deforms a predictable amount due to an applied voltage. The actuator (herein referred to as the piezo, for brevity) is designed with multiple crystals in tandem so that it can produce displacements in X, Y and Z directions.

A laser beam is focused at the end of the cantilever and a position sensitive photo-detector (PSD) monitors the position of the reflected beam. Any bending of the cantilever due to normal or torsional forces from the surface is detected by the PSD. The PSD output signal is read by feedback electronics, which control the position of the piezo. The PSD is split into four quadrants, and the output signal is a voltage dependent on the difference of laser intensities between the top two and bottom two quadrants. There is also an output voltage for the left to right intensity that monitors cantilever torsion due to frictional drag, though this effect is unimportant for the current study. The PSD voltage can be converted to the amount of cantilever bending by a proportionality constant called the deflection sensitivity, D. Many AFM systems automatically convert the PSD signal to deflection, or convert even further to applied normal force on the cantilever, but monitoring the raw signal can be more reliable and more informative, especially when developing a new technique.
Figure 2.1: A descriptive schematic showing the major components of an AFM. The components are not nearly to scale: for example, the piezoelectric actuator is ~10 cm tall, while the cantilever is about 200 µm long.

The deflection sensitivity is found experimentally from a Force-Distance (FD) curve, where the cantilever deflection is monitored as a function of the piezo displacement. The piezo displacement ($z_p$) is the controllable height presented as the distance between tip and sample when the cantilever feels no force and is unbent, while the cantilever deflection ($z_c$) is the bending of the cantilever from its neutral position and is measured by the PSD; the total tip-sample separation distance is $z=z_c+z_p$.

Figure 2.2 shows an idealized FD curve for a tip in air. Initially, the piezo approaches the surface with no contact between the tip and surface, so there is no cantilever deflection or force (1). When the tip gets very close to the surface, interaction forces (mainly van der Waals and electrostatic) cause the tip to quickly jump into contact with the surface, or “snap-in” (2). The piezo continues to move towards the surface, causing the cantilever to linearly bend under the applied force (3). This linear bending region is the direct relation between piezo displacement and cantilever bending, so the slope of the line is the deflection sensitivity, $D$. After a set displacement, the piezo begins to retract the tip and the
cantilever unbends following (3). Adhesion forces prevent the tip from disengaging at the same point as snap-in, so the cantilever continues to bend past the neutral position of (1) as the piezo begins pulling the cantilever from the surface rather than pushing into it (4). When the retraction force exceeds the adhesion force the tip suddenly snaps off (5). The height of (5) is thus a direct measure of the adhesion force between tip and sample, so the FD curve is frequently used for studying adhesion forces, even of single molecules [73, 74].

Figure 2.2: An idealized Force-Distance (FD) curve, with the deflection of the cantilever vs. the displacement of the piezoelectric actuator. (1) Approaching the surface with no force felt by the tip; (2) Tip snap-in; (3) Cantilever bending due to mechanical contact with surface; (4) Tip retraction beyond neutral force due to adhesion; (5) Tip snap-off; (6) Retraction with no force felt by the tip. The slope of the line in region (3) is the deflection sensitivity used to calibrate the position sensitive photodetector.

With the deflection sensitivity [nm/V] the PSD signal [V] can be converted to tip deflection [nm], but it is often desired to convert tip deflection into the force on the tip (as in the case of Force-Distance curves, as the name implies). The cantilever acts as a simple spring, so the tip deflection and force are related linearly by Hooke’s law,

\[ F = -kz_c, \]  

(2.1)
where $F$ is the spring force, $z_c$ is the cantilever deflection, and $k$ is the spring constant. A mechanical analysis of a cantilever of rectangular cross-section yields a simple relationship to determine the spring constant,

$$k = \frac{EwL^3}{4L^5},$$

(2.2)

where $E$ is the elastic modulus of the cantilever, and $L$, $w$, and $t_c$ are the length, width, and thickness of the cantilever, respectively [75]. This equation is, unfortunately, essentially useless for determining the spring constant of a cantilever for two reasons. First, the cantilever is not a simple beam, but a beam with a mass at the end in the form of a probe, which typically has a mass of about 20% of the cantilever. Second, the thickness of the cantilever and the exact size of the probe are not well characterized. Most AFM tips are produced from silicon by laser lithography to trace the cantilever and chemical etching to produce the sharp probe. The lithography process gives very well-controlled cantilever length and width, but there is significant variation in the thickness – by about a factor of two – even among tips produced in the same batch. Since the spring constant varies with the cube of the thickness, the uncertainty in the thickness is compounded and can lead to an order of magnitude difference in spring constants. Thus, in practice, the spring constant is usually determined experimentally.

A convenient method to determine the spring constant is through a hydrodynamic function, developed by Sader et al. [76], which calculates the spring constant from inputs of the cantilever length and width, and its resonance frequency and quality factor. The resonance frequency is found by a frequency sweep, where the tip is oscillated and the vibration amplitude is monitored as the vibration driving frequency is changed. The quality factor describes the damping of the system, and is calculated as the resonance frequency divided by the full width at half maximum of the resonance peak. With the spring constant determined by this method and the deflection sensitivity calculated from the FD curve the voltage output by the PSD can be converted into force on the cantilever.
The most basic AFM imaging method, or “mode,” relies on a constant tip deflection or applied force. In this “contact mode” the tip is brought into contact with the surface so that the cantilever deflects to a setpoint value. The piezo scans the tip in an X-Y raster while the feedback electronics adjust the Z position of the piezo to maintain a constant deflection. If the tip deflects upward due to a high feature the piezo pulls away from the surface to decrease the deflection, and vice versa for a low feature. Contact mode is very simple to understand and use due to this very simple feedback scheme. Compared to other AFM modes, it yields high resolution images very quickly and with high consistency. However, contact mode does have a few drawbacks. A typical AFM tip has a radius of curvature of tens of nm, so even though the applied force is on the order of a few nN, the Hertzian contact pressure can be as high as a few GPa. At such high contact pressures the tip can deform or damage soft surfaces. The shear force due to friction during scanning can also lead to tip degradation, causing the imaging resolution to decrease as the tip dulls.

2.2.3 Dynamic AFM

Many other AFM imaging techniques have been developed as new applications are realized. Most of these techniques—and all that will herein be discussed—are “dynamic” imaging modes, which rely on perturbations to a vibrating cantilever instead of its absolute deflection. Since the tip and cantilever form a spring, the physical description of dynamic AFM is the same as a forced, damped oscillator. According to Newton’s second law, the sum of forces acting on the cantilever equal the mass times acceleration. For a forced, damped oscillator there are three acting forces: a time-dependent driving force $F(t)$, a Hookean spring force, and a damping force. In a viscous fluid such as air or water the damping force is a general function of the cantilever velocity, $a\cdot v + b\cdot v^2 + c\cdot v^3 + \ldots$, though in most cases it can be approximated with the first order term only [77]. The force balance therefore becomes [78]
where \( z_c \) is the cantilever deflection, \( t \) is time, \( m \) is the mass of the cantilever and probe, and \( b \) is a constant. Rearranging yields a more convenient expression,

\[
\frac{d^2 z_c}{dt^2} + \frac{\omega_0}{Q} \frac{dz_c}{dt} + \omega_0^2 z_c = \frac{f(t)}{m},
\]

(2.4)

where \( \omega_0 = \sqrt{\frac{k}{m}} \) is the natural resonance frequency of the system and \( Q \) is the quality factor, which characterizes the damping. There are analytical solutions to eq. 2.4 for some special cases (e.g. a sinusoidal driving force), but for realistic cases (e.g. a distance-dependent force) it must be solved numerically.

Intermittent contact mode, also known as tapping mode, is the simplest dynamic AFM technique [78]. It was developed to lessen some of the disadvantages of contact mode. The piezo is vibrated near the resonance frequency of the cantilever so that the tip is moving through a \( \sim 100 \text{nm} \) arc. The tip comes into contact with the surface at the bottom of the arc, and the surface forces damp the vibration, so the vibrational amplitude is a function of the tip-sample separation. The vibration amplitude can thus be used as a feedback signal for topographical imaging. The phase shift between the sinusoidal applied force and the cantilever vibration is also useful because it has been shown to correlate to mechanical properties of the surface, especially the modulus of elasticity [12, 79, 80]. Tapping mode greatly reduces the damaging shear forces present in contact mode, preserving the sharpness of the tip and the integrity of the sample, and eliminating imaging artifacts due to friction. For these reasons, tapping mode has become the de facto standard for AFM imaging.

The intermittent mechanical contact between the tip and sample in tapping mode still exposes the sample to very high contact pressures, so soft samples can still be damaged in tapping mode. The membrane of a cell in liquid, for example, could be pierced by the AFM tip, causing the cell to lyse [81, 82]. For soft samples, an imaging technique was developed in which the tip never actually
touches the surface; this technique is called non-contact mode. Non-contact mode is very similar to intermittent contact mode, except the vibration amplitude is much smaller at a few nm. Tip-surface interactions increase as the tip approaches the surface; these forces damp the vibration, so the vibration amplitude can still be used for feedback control and topographical imaging [83]. Like tapping mode, the phase of the non-contact vibration can be used to probe surface properties. Many more non-contact techniques have been developed for specific applications, such as probing the chemical, magnetic or electrical properties of the surface.

2.3 The Scanning Polarization Force Microscope (SPFM)

The scanning polarization force microscope (SPFM) is a non-contact AFM technique in which an AC voltage is applied to a conducting tip and the electrostatic forces generated are used to effect cantilever vibration instead of shaking the piezo [41]. SPFM produces a map of surface potential in addition to the standard topographical image of non-contact AFM. The setup and operation of the SPFM will be discussed in detail as it is the basis of the setup and operation of LEEFM.

2.3.1 Experimental Setup

Figure 2.3 shows the experimental setup of the SPFM. All of the components of an AFM as shown in Figure 2.1 are present, though not all are shown, and some extra components have been added. An AC voltage of frequency $\omega$ is applied to a conducting cantilever from a function generator (built into a lock-in amplifier). The signal from the PSD goes through two lock-in amplifiers before being fed to the feedback control and data acquisition systems. The lock-in amplifiers selectively find and amplify sinusoidal vibrations occurring at the frequency of the applied
voltage, $1\omega$, and twice this frequency, $2\omega$. Subtracting these two vibration signals from the raw PSD signal yields the time-averaged deflection of the cantilever, i.e. the deflection about which the cantilever vibrates. The $2\omega$ amplitude is used as a feedback signal to control the separation between the tip and sample, producing a topographical image, while the $1\omega$ amplitude and phase are recorded as separate images.

\[ U_{\text{cap}} = \frac{1}{2} CV^2, \]  

**2.3.2 Electrostatic Driving Force**

The vibration of the cantilever is driven by electrostatic forces. When a voltage is applied to the conducting cantilever it becomes charged and forms a capacitor with the sample. Charging the cantilever causes electrical energy to be stored in the capacitor in the form of an electric field. The energy stored in the field is described by the familiar equation
where $U_{cap}$ is the energy stored in the capacitor, $C$ is the capacitance of the system, and $V$ is the voltage difference between the two electrodes \cite{41, 84}. By definition, the force is the negative gradient of the energy, so the capacitive force between the tip and sample can be found by taking the negative derivative in the $z$-direction, which yields

$$ F_{cap} = -\frac{1}{2} \frac{\partial C}{\partial z} V^2. \quad (2.6) $$

Since the sample has an effectively infinite mass, this force acts on the cantilever, causing it to vibrate according to eq. 2.4. The voltage in eq. 2.6 is externally applied so it does not depend on the tip position. The capacitance, however, is a function of tip-sample separation, $z$, which is critically important because the force gradient results in the gradient of damping that is used for feedback control. For two parallel plates of area $A$ and separation $z$ the capacitance is simply $C = \varepsilon \frac{A}{z}$, so $\frac{\partial C}{\partial z}$ is easily calculable. But the actual geometry of the system—a cone mounted to a flat plate above an infinite plate—is much more complex, and there is no analytical expression for the capacitance. The derivative of the capacitance with respect $z$ has been shown to follow the form

$$ \frac{\partial C}{\partial z} = -8\pi \varepsilon_0 \varepsilon_s - \varepsilon_m \frac{\varepsilon_s - \varepsilon_m}{\varepsilon_s + \varepsilon_m} f\left(\frac{R}{z}\right), \quad (2.7) $$

where $\varepsilon_0$ is vacuum permittivity, $\varepsilon_s$ and $\varepsilon_m$ are the dielectric constants of the sample and medium, respectively, and $R$ is the radius of the tip. Useful approximations of $f\left(\frac{R}{z}\right)$ have been made for modeling purposes, but the exact forms are not important for understanding SPFM \cite{85}.

The functional form of the voltage is much more important to understanding SPFM as it demonstrates the origin of the multiple-frequency cantilever vibration. The voltage in eq. 2.6 is the total voltage difference between the tip and sample

$$ V = V_{tip} - \phi, \quad (2.8) $$

where $\phi$ is the natural surface potential difference between the two surfaces and $V_{tip}$ is the voltage applied to the tip by the function generator. The applied voltage is in the form of a sine wave of
frequency $\omega$ and root-mean-square voltage of $V_{RMS}$, so that the time-dependent voltage between the two surfaces is

$$V = V_{AC} \sin(\omega t) - \phi.$$  \hfill (2.9)

The capacitive force of eq. 2.6 depends on $V^2$, so squaring eq. 2.9 and expanding yields

$$V^2 = V_{RMS}^2 \sin^2(\omega t) - 2 V_{RMS} \phi \sin(\omega t) + \phi^2$$  \hfill (2.10)

The first term in eq. 2.10 can be expanded using a trigonometric identity,

$$\sin^2(\omega t) = \frac{1 - \cos(2\omega t)}{2}$$ \hfill (2.11)

to yield

$$V^2 = -\frac{1}{2} V_{AC}^2 \cos(2\omega t) + 2 \phi V_{AC} \sin(\omega t) + (\phi^2 + V_{AC}^2).$$  \hfill (2.12)

Combining eqs. 2.4, 2.6 and 2.12 gives the total mathematical description of cantilever vibration in SPFM as

$$\frac{d^2z_c}{dt^2} + \frac{\omega_d d^2z_c}{Q dt} + \omega_d^2 z_c = -4\pi \epsilon_0 \epsilon_s - \epsilon_m f \left( \frac{R}{z} \right) \frac{1}{2} \left[ V_{AC}^2 \cos(2\omega t) - 2 \phi V_{AC} \sin(\omega t) - (\phi^2 + V_{AC}^2) \right].$$ \hfill (2.13)

This equation shows that there are three components of the force that will act at twice the applied frequency $F(2\omega)$ through the first term, at the applied frequency $F(1\omega)$ through the second term, and a time-independent term $F(0\omega)$ through the last term. These three components are separated by the lock-in amplifiers shown in Figure 2.3.

A visualization of these components as a snapshot in time is shown in Figure 2.4. A 1 V sine wave applied from the function generator at a frequency $\omega$ is shown as the top, black line with the left axis. The purple line is the corresponding $z$ position of the cantilever as read by the PSD. This purple line can be deconvoluted into the three components: the red line at twice the frequency of the applied signal; the blue line, equal to the applied signal; and a constant offset (not shown) about which the vibrations occur. The lock-in amplifiers output the amplitude and phase shift of the $1\omega$ and $2\omega$ vibrations and the value of the constant offset. Equation 2.13 can be used to determine the effects that
changing experimental parameters, such as the driving voltage or frequency, have on the cantilever vibration. Modeling of the cantilever vibration has been done using eq. 2.13, and the models agree with experimental observations. Some of these experimental observations are shown in the next section with comparisons to the corresponding LEEFM data.

![Graph](image)

**Figure 2.4:** A snapshot of the vibration profile of the tip. The black line is the voltage applied to the tip from the function generator. The purple line is the actual vertical position of the tip, with respect to time, output by the PSD. The blue and red lines are drawn to show the deconvolution of the $1\omega$ and $2\omega$ vibrations, respectively.

### 2.3.3 Related Techniques

There are a few other AFM techniques that rely on electrostatic interactions, collectively called Electrostatic Force Microscopy (EFM) [86]. Kelvin Probe Force Microscopy (KPFM) is one EFM technique that is very closely related to SPFM, except it uses an additional DC bias applied on top of the AC (sine wave) bias. The total voltage difference between the tip and the sample in KPFM is
\[ V = V_{AC} \sin(\omega t) + V_{DC} - \phi \]  \hspace{1cm} (2.14)

where \( V_{AC} \) is the voltage of the applied AC signal, \( V_{DC} \) is the voltage of the applied DC voltage, and \( \phi \) is still the surface potential difference between the tip and sample. Plugging this voltage into the electrostatic force equation, eq. 2.6, yields

\[
F_{cap} = \frac{1}{2} \frac{\partial C}{\partial z} \left[ \frac{1}{2} V_{AC}^2 \cos(2\omega t) + 2(V_{DC} - \phi)V_{AC} \sin(\omega t) + \left( V_{DC}^2 - 2V_{DC}\phi + \phi^2 \right) \right].
\]  \hspace{1cm} (2.15)

KPFM uses the 2\( \omega \) amplitude to feedback control the separation distance, as in SPFM. But instead of monitoring the 1\( \omega \) amplitude and phase, it uses an additional feedback loop that minimizes the 1\( \omega \) amplitude by changing \( V_{DC} \); when \( V_{DC} = \phi \) the 1\( \omega \) vibration disappears. KPFM therefore yields a topographical map through the 2\( \omega \) feedback, and a map of the surface potential through the 1\( \omega \) feedback [34-37, 85, 86].

EFM can also be performed with a single feedback loop. In this double pass mode, or lift mode, the topography is first scanned using traditional AFM (tapping mode or non-contact mode) and saved into the software. The tip is retracted by \( \sim \) tens of nm and then scanned following the saved topography, so the tip-sample separation remains constant during the scan. A voltage is applied forming a force as in SPFM or KPFM, though without the distance dependence of the capacitance affecting the signal [86]. The disadvantages of this technique are reduced resolution of electrostatic domains because of the large separation, and possible drift in the images due to the extra movement of the tip during scanning.

There is also a static version of EFM which can be used to directly measure the electrostatic force [87]. The cantilever can be charged by functionalizing it with charged species such as phospholipids. When an FD curve is performed with the tip there will be a higher adhesion force than normal if the surface has the opposite charge of the cantilever, and a lower adhesion force if the surface has the same charge.
2.4 The Liquid Environment Electroactuation Force Microscope

SPFM has only been used for imaging surfaces in air. A new technique is proposed that uses the same setup as the SPFM but in a liquid environment; this technique is called Liquid Environment Electroactuation Force Microscopy (LEEFM).

2.4.1 Experimental Setup

The experimental setup of the LEEFM is shown in Figure 2.5. The setup is the same as SPFM, shown in Figure 2.3, but the cantilever and sample are now submerged in liquid. The AFM used in this study was a Molecular Imaging Pico-SPM (Scanning Probe Microscope) with an RHK controller. Rectangular, silicon AFM probes from Vista Probes were used which typically had a spring constant of $\sim 0.1$ N/m and resonance frequency in air of $\sim 30$ kHz. The deflection sensitivity of the system was typically $\sim 0.03$ V/nm. The values of these three parameters were found for each tip before experiments. The cantilevers were n-doped with conductivity $\sim 50$-100 S/cm, and electrical contact was made by first scratching the native oxide layer (using a carbide glass cutter) on the chip to which a cantilever was fabricated, then coating the area with conducting silver paste and affixing a gold electrode. The electrode was attached to a mount so that the cantilever was held in the proper place for the AFM, while also acting as the connection point for the function generator. The mounted probe was cleaned for 20 minutes before each experiment with UV ozone.
2.4.2 LEEFM and SPFM Vibration Signals

LEEFM, like SPFM, functions by monitoring the vibration of the cantilever. In order to better understand the vibration, the signals from LEEFM and SPFM are analyzed and compared with respect to changing the applied voltage, the frequency of the applied voltage, and the distance between the tip and sample. A firm grasp of the behavior of the cantilever will be needed to understand the data presented in subsequent chapters.

Figure 2.5: Experimental setup of the LEEFM.
2.4.2.1 – Voltage Dependence

Figure 2.6 shows the voltage dependence of the cantilever vibration in LEEFM. The green line is the time-averaged deflection of the cantilever, while the $1\omega$ and $2\omega$ vibration amplitudes are graphically represented as blue and red error bars, respectively. This arrangement stresses the physical situation of the cantilever vibrating with two (coupled) amplitudes about an average position, which itself is a function of the driving force. Since the applied voltage is the cause of the interactions causing vibration, it is logical that increasing the voltage increases the vibration. Eq. 2.13 predicts this behavior in SPFM—the $2\omega$ amplitude and time-avg bending increase with $V^2$, the $1\omega$ amplitude increases with $V$—so it seems SPFM and LEEFM are similar in their voltage dependence; the effect of voltage on the LEEFM cantilever motion will be discussed further in chapter 4.

Figure 2.6: The cantilever behavior in LEEFM as a function of the applied voltage. The green line is the constant deflection, and the $1\omega$ and $2\omega$ vibration amplitudes represented as blue and red error bars, respectively, centered on the constant deflection line. The frequency applied was 4 kHz, which was the $2\omega$ resonance frequency for this tip, and the tip was situated ~300 nm above a clean silicon surface in DI water.
2.4.2.2 – Frequency Dependence

The dependence of the LEEFM cantilever vibration on the frequency of the applied signal is shown in Figure 2.7. In (a) the vibration amplitudes are presented similarly to Figure 2.6, with the vibration amplitudes represented as error bars. Unlike the voltage dependence, where increasing the voltage lead to both higher amplitudes and more time-averaged deflection, increasing the frequency causes an increase in time-averaged deflection (towards the surface) but a decrease in the vibration amplitudes. This behavior cannot be explained using the theory behind SPFM alone, as shown in Figure 2.7 (b), which compares the vibration amplitudes in LEEFM and SPFM. Since LEEFM is performed in water, the viscosity is much higher than in air, so there is much greater viscous damping. A solely mechanical analysis would predict the vibration resonance peaks in water to be lower in frequency, broader in peak width, and lower in amplitude when compared to air. The former two predictions are supported by the data: the $1\omega$ and $2\omega$ resonance peaks shift from 29 kHz and 14.5 kHz to about 7 kHz and 3.5 kHz, respectively, and the peaks are significantly broader. The resonance peaks were confirmed to be purely mechanical – not due some electrically-driven process such as the motion of ions – because they did not shift when the conductivity of the solution was changed by adding electrolyte, but they did shift when media of different viscosities were used. The extent of the resonance peak broadening is difficult to measure, because the resonance peaks in LEEFM are obscured by a sharp increase in amplitudes as the frequency decreases. Similar behavior is seen in SPFM, which shows a small increase in the amplitudes as the frequency drops below 5 kHz. This feature is normally ignored since imaging in SPFM is performed near the $2\omega$ resonance peak, well above the 5 kHz region, to take advantage of the increased amplitudes. But in water, this low frequency increase in amplitude dominates the mechanical resonance behavior. Practically, this behavior means imaging can be done in LEEFM at any frequency where the vibration amplitudes are high; the resonance behavior of the cantilever can essentially be ignored. Scientifically, the low frequency increase shows that the driving force itself
depends on the frequency. In SPFM, the driving force was essentially constant, with the two large peaks present purely because of mechanical amplification (cantilever mechanical resonance). Thus the frequency dependence of the LEEFM driving force presents another mystery, which will be discussed, along with the frequency dependence of the time-averaged deflection, in chapter 4.

2.4.2.3 – Distance Dependence

The dependence of the cantilever vibration on distance from the surface is absolutely critical to the operation of LEEFM and SPFM: feedback control of the vibrational amplitude could not be achieved if that amplitude did not smoothly vary with the distance. Eq. 2.13 suggests that the driving force in SPFM is inversely related to the tip-sample distance; Figure 2.8 (a) shows the actual effect of distance on the 2ω vibration amplitude in SPFM and LEEFM. The cantilever approaches the surface from 100 nm until contact. In SPFM, the vibration amplitude increases as the tip approaches the surface, and the increase becomes more rapid as the distance decreased, as expected for an inverse relationship. At ~ 8 nm separation, tip-sample interaction forces overcome the spring force of the
cantilever and cause the tip to snap in, as described by Figure 2.2. The tip cannot vibrate when it is in physical contact with the surface, so the amplitude immediately becomes zero. The distance dependence of the LEEFM vibration is completely different than that of SPFM. The amplitude is nearly constant from 100 nm to ~ 10 nm, at which point the amplitude slowly decreases to zero at contact; there is no tip snap in because the attractive tip-sample forces are mitigated by water. It would be illogical for the vibration amplitude to increase as the separation distance increased arbitrarily high, so the $2\omega$ vibration in LEEFM was monitored over a much longer range. Figure 2.8 (b) shows that, over 1000x the distance of (a), the vibration does indeed decrease as expected.

![Figure 2.8](image)

**Figure 2.8:** Distance dependence of the cantilever $2\omega$ vibration amplitude. (a) Comparison between vibration of LEEFM in water (red line with circle points) and SPFM in air (black line with diamond points) over 100 nanometers. (b) LEEFM $2\omega$ vibration amplitude over 100 micrometers. The curves in (a) and (b) are for the tip approaching the surface, not retraction. The data were collected over silicon with 1 V applied to the tip at the $2\omega$ resonance frequency (4 kHz in water, 30 kHz in air).

The distance dependence of the electrostatic force responsible for cantilever vibration in SPFM/KPFM can be modeled using various approximations. Early models assumed the probe to be spherical [88, 89], but this can be a very poor assumption and more complicated models are often needed [90]. Gil et al. proposed a better model where the complex geometry of the tip is separated
into three parts: the macroscopic cantilever, the mesoscopic tip cone, and the nanoscopic tip apex [34], as shown in Figure 2.9 (a). The result of using this model is shown in an electrostatic force vs. tip-sample separation profile, Figure 2.9 (b). The total force should – and does – look similar to the SPFM vibration amplitude, Figure 2.8 (a), though the tip snap-in behavior is not modeled. The contribution from the cantilever is approximately constant within ~ 10 μm of the surface, measured between the apex and the surface, because the tall cone of the tip means the cantilever will never be closer than 20 μm from the surface. The contribution from the cone of the probe is constant in the nearest few hundred nanometers to the surface, since this portion extends from 20 μm to ~ 50 nm above the apex. The apex contribution is trivial until less than 100 nm separation, and then becomes dominant over the other two components at ~ 10 nm. However, SPFM imaging is normally performed 20 – 30 nm from the surface to avoid tip snap-in, so the apex contribution is comparable to that from the cantilever and cone, which are both constant in this range. SPFM images thus have quite low lateral resolution because the information detected by the apex, which is close to the surface, is averaged with the constant background of the cantilever and cone, which are far from the surface. This effect will be demonstrated in Chapter 3.

Figure 2.9 (c) shows the results of applying the same model to a cantilever in water; the only difference between (c) and (b) is the dielectric constant of the medium – 1 for air, 80 for water. The scale is expanded so that the figure is comparable with Figure 2.8 (b), and both show similar behavior. The high dielectric constant of water means the electrostatic force is stronger and acts over a longer range than in air. But LEEFM imaging is actually performed closer to the surface than SPFM, where the apex contribution completely dominates the total force, so LEEFM has higher imaging resolution. This model may not necessarily be applicable to LEEFM, since its vibration may not depend completely on electrostatic interactions, as will be discussed in Chapter 4.
2.9: Modeling the distance-dependence of the electrostatic force in AFM using the approximations found in [34].

(a) A representation of the approximation, where the tip is separated into three components: the cantilever, modeled as a plate (red); the bulk of the probe (blue), modeled as a cone; and the apex of the probe (green), modeled as a sphere. (b) The electrostatic force acting on the tip components in SPFM/KPFM in air. (c) The electrostatic force acting on the tip components in LEEFM in water; the only difference between the models for (c) and (b) is dielectric constant of the medium – 1 for air, 80 for water. For (b) and (c), the tip-sample separation is measured from the apex. The simulation parameters were: cantilever dimensions = 100 μm long x 20 μm wide; cone height = 20 μm; cone angle = 20°; the angle between the cantilever and the sample = 11°; the radius of the apex = 20 nm; and the voltage applied to the tip = 1 V.

The distance dependent electrostatic force means that the vibration amplitudes in SPFM and LEEFM are also distance dependent, and so they can be used for feedback control. The feedback control electronics in SPFM monitor the $2\omega$ amplitude and adjust the piezo position to maintain a setpoint. The electronics interpret an increase above the setpoint as the tip moving closer to the surface and vice versa for a decrease. If the same control scheme were used for LEEFM, the vertical sensitivity would be on the order of microns instead of nanometers, rendering the method essentially useless. But the feedback controls can use any gradient in the vibration amplitude, not just an increase as the distance decreases. So in LEEFM the decrease in amplitude very close to the surface can be used...
instead; the feedback electronics are switched to interpret an increase in amplitude as an increase in
distance. This control scheme has an advantage over SPFM with respect to snap in behavior. In SPFM,
a decrease in amplitude causes the piezo to move the tip closer to the surface, which is the desired result
for any distances above 10 nm. But below this distance the tip snaps in and the vibration becomes zero,
which the feedback electronics interpret at the tip being very far from the surface. So if the tip touches a
high surface feature at any point during imaging with SPFM, the feedback electronics just move the
piezo towards the surface, and push the tip even further into the surface. The only way to rectify this
problem is to stop imaging and manually retract the tip, which must be done quickly to prevent the
cantilever from completely breaking under the mounting stress. Collecting an SPFM image can take as
long as an hour, depending on conditions, so this inconsistent feedback behavior can be very
inconvenient. Consequently, SPFM imaging must be done far enough from the surface to avoid coming
within ~ 8 nm of any features. The opposite feedback control utilized in LEEFM avoids these issues.
When the vibration amplitude decreases, even if it completely disappears due to contact, the electronics
pull the tip away from the surface. As a result, LEEFM imaging is much more stable than SPFM and
can be accomplished at much smaller separation distances. Images demonstrating this advantage are
presented in the next chapter.
Chapter 3

LEEFM Imaging Results

3.1 Synopsis

The purpose of developing the LEEFM is for its imaging capabilities, so this chapter outlines some of those capabilities, and some limitations, found by imaging model samples. The ability to image topography with LEEFM is shown in section 3.2. A hexagonal etched pit in silicon was imaged using contact AFM, SPFM in air, and LEEFM in water, and the images show that the LEEFM has much higher spatial resolution than SPFM. Section 3.3 details the technique’s ability to discern local changes to the chemical properties of the surface while simultaneously imaging topography. Self-assembled monolayers terminated with charged groups were imaged after purposefully damaging a small area. The LEEFM images showed a small depression in the topography and a large increase in the amplitude of the $1\omega$ vibration in the damaged region compared to the undamaged substrate.

Polystyrene (PS) colloidal particles were partially melted to form “domes” and imaged under different conditions in sections 3.4 and 3.5 to show some limitations of the technique. Section 3.4 shows that the domes cannot be reliably imaged when they are hydrophobic. Hydrophobic interactions between the tip and PS domes cause the tip to snap in near the surface, eliminating the gradual damping of the $2\omega$ vibration amplitude necessary for effective feedback control. Treating the sample to make the surface hydrophilic prevented the hydrophobic interactions, so the amplitude gradient reappeared and imaging was successful.

Section 3.5 demonstrates the ability of the LEEFM to image insulating samples. The $2\omega$ vibration disappears on insulators but the $1\omega$ vibration remains, so the $1\omega$ amplitude was used for
feedback control instead of the $2\omega$ amplitude. The topography was correctly reproduced using this scheme, though the lack of amplitude and phase images cripples the technique. It seems that LEEFM is limited to hydrophilic samples mounted on conducting substrates, but future work suggested in section 3.6 may overcome these limitations.

### 3.2 Resolution Enhancement

In section 2.4, it was shown that feedback control in LEEFM works differently than in SPFM, so LEEFM imaging can be accomplished closer to the surface. Figure 3.1 shows images of hexagonal nanowells etched into silicon imaged with SPFM (in air) and LEEFM (in water), as well as contact mode AFM and Scanning Electron Microscopy (SEM) for comparison. The nanowells were formed by wet etching (111) silicon using reactive 520 nm amidine functionalized polystyrene latex colloidal particles [91]. The nanowells are hexagonal, with a flat center and slanted edges corresponding to the (100) and (110) planes, as can be seen in the SEM image, Figure 3.1 (a). Contact mode AFM in (b) gives an accurate topographical reproduction of the surface, with six sloped sides and a flat center ~ 160 nm deep. A superimposed depth profile emphasizes these features. These nanowells are an ideal sample for demonstrating the difference between SPFM and LEEFM because there are topographic features without any change in bulk or surface properties that may artificially affect the cantilever vibration.

The LEEFM topography image in Figure 3.1 (d) is very similar to (b): all six sides are clearly seen, and the line scan shows flat topography in the center, though the depth is underestimated slightly as ~ 140 nm. The edges are slightly blurred, indicating that the electrical interactions between the tip and sample are averaged over a sampling area. This effect is illustrated in (f), where the red lines represent the tip-sample interactions. The SPFM nanowell image in (c) looks drastically different from the contact mode and LEEFM images. The shape is
blurry and circular instead of hexagonal, and the line profile shows a curved shape with no flat center and a depth of only ~ 60 nm. SPFM images far from the surface at ~ 30 nm, so the sampling area for the electrostatic interactions is very large compared to the sample features. Furthermore, the cone of the probe and the cantilever also contribute to the electrostatic force, as discussed in section 2.4.2.3, and at ~ 30 nm separation the magnitude of those contributions is about the same as the contribution from the probe apex. So the feature being imaged – in this case a hexagonal nanowell – is detected by the probe apex and averaged with the large surface area detected by the cantilever. It is clear that, by imaging closer to the surface, LEEFM achieves much higher lateral and depth imaging resolution than SPFM by sampling a much smaller area.
Figure 3.1: Images of a hexagonal etched well on silicon imaged by (a) SEM, (b) contact mode AFM, (c) SPFM in ambient air, (d) LEEFM in DI water. These are not the same well in each image, but a single well from a sample containing many. The AFM images are all right-to-left scans. The contact mode image was collected with a 6.7 nN normal force. The SPFM image was collected with a tip-sample separation distance of ~30 nm. The LEEFM image was collected at ~5 nm separation, which corresponded to 50% damping of the \(2\omega\) vibration amplitude feedback signal from 1.2 nm to 0.6 nm. The resolution enhancement is demonstrated in a cartoon—not to scale—showing the tip-sample electrical interactions, shown as red lines, spreading from the point of the tip when it is farther from the surface (e) as when using SPFM, and when closer to the surface (f) as when using LEEFM. The color scale on the right side corresponds to the feature height in (b), (c) and (d), while the depth scales to the left of each of these images correspond to the line scan depth profile superimposed on each as a red line.
3.3 Chemical Sensitivity

The ability of the LEEFM to distinguish local charge/surface potential would best be demonstrated using model samples with very large changes in surface potential, but small changes in topography. Such model samples were produced using two self-assembled monolayers (SAMs), one negatively charged and the other positively charged, which used a thiol group to bind the SAM molecules to a gold film deposited on a silicon wafer. The negatively charged SAM was made using SHC$_{11}$H$_{22}$COOH, which had a thickness of $\sim 2$ nm, measured by ellipsometry, and a zeta potential of $\zeta_{\text{COOH}} = -20$ mV. The positively charged SAM was made using SHC$_{11}$H$_{22}$NH$_2$, which had $\zeta_{\text{NH}_2} = +20$ mV and thickness $= \sim 2.2$ nm.

The change in surface properties (e.g. surface charge/potential) of the SAMs on gold was accomplished by damaging a small area of the SAM using physical contact with the AFM tip. A 1 µm $\times$ 1 µm area was scanned in contact mode in water with a high applied load of $\sim 300$ nN, corresponding to a maximum Hertzian contact pressure of $\sim 5.5$ GPa. A 4 µm $\times$ 4 µm region centered on the contact-scanned area was imaged using LEEFM with 2$\omega$ amplitude as feedback control. The imaging results for both SAMs are shown in Figure 3.2 (a) and (b). In both cases, the topography shows the scratched region slightly lower than the baseline with some debris piled around. The 1$\omega$ vibration amplitude images show an increase in the amplitude in the scratched region for both samples, though the increase was more distinct on the $-$NH$_2$ sample at $\sim 0.3$ nm than on the $-$COOH sample at $\sim 0.1$ nm. Interestingly, there was a $\sim 40^\circ$ decrease in the 1$\omega$ phase in the scratched region of the $-$COOH sample, but no change on the $-$NH$_2$ sample. This indicates that the phase is also sensitive to the surface properties, but might be sensitive to different properties than the 1$\omega$ amplitude.
Figure 3.2: LEEFM images of gold surfaces covered with self-assembled monolayers (SAMs) of (a) Au-SC$_{11}$H$_{22}$COOH and (b) Au-SC$_{11}$H$_{22}$NH$_{2}$. A 1 µm × 1 µm area of the SAM was damaged by the AFM tip using a high load (~ 300 nN) contact scan. A 4 µm × 4 µm area centered on the damaged region was then imaged with LEEFM, using the 2ω amplitude for feedback control while monitoring the 1ω amplitude and phase.

3.4 Hydrophobic Samples

It was found that LEEFM has difficulty imaging hydrophobic samples. A model sample was produced with polystyrene (PS) “domes” on a silicon surface. 520 nm spherical PS colloidal particles were deposited onto a silicon wafer and then heated in air at 120°C for one hour, which caused the particles to melt slightly and form a dome shape. The domes were imaged, without further treatment, using contact-mode AFM and LEEFM; these images are shown in Figure 3.3.
The contact-mode image (a) clearly shows domes shapes about 200 nm tall. The LEEFM topography image (b) shows mostly undistinguishable streaky features starting on the right side and moving left (these images are the right-to-left scan), and the $1\omega$ amplitude (c) and phase (d) images show strange, jagged features corresponding to the beginning of the streaks. Closer investigation of the images indicated that the tip could not be properly feedback controlled when it was above a PS dome: it would jump into contact, then pull far away from the surface, then approach quickly and jump back into contact, and pull away again.

Figure 3.3: Images of Polystyrene (PS) domes deposited on silicon wafer. (a) Cartoon showing a (PS) particle (orange sphere) that is melted to form a dome shape. (b) The true topography of the surface was imaged with contact mode AFM. The LEEFM topography (c), $1\omega$ amplitude (d) and $1\omega$ phase (e) images of the same sample show strange features as a result of poor feedback control of the $2\omega$ amplitude. The $2\omega$ amplitude was ~ 0.6 nm without damping. All AFM images are 5 µm x 5 µm, and the right-to-left scans are shown.
FD curves on this sample are shown in Figure 3.4 and can explain the strange imaging behavior. The contact-mode image was used to position the tip for separate FD curves on silicon (a) and on a PS dome (b). The behavior expected in these curves can be inferred from Figure 2.2, which shows that the cantilever deflection relates to mechanical contact between the tip and sample as well as any snap-in or snap-off behavior, and Figure 2.8, which shows that the LEEFM vibration amplitudes should steadily decrease near the surface. Figure 3.4 (a) is consistent with the expected behavior. On the approach curves, both amplitudes slowly decrease until mechanical contact, and the tip does not snap-in because the attractive forces are mitigated in water. On the retraction curve, the slope deflection is different in the contact region, and the point where the tip disengages is offset from where it engaged; this is probably due to hysteresis in the piezo, and does not significantly affect the imaging behavior. There is also a small snap-out—adhesion forces are expected if the surface is dirty—so the vibration amplitudes suddenly reappear. It would still be possible to image based on this FD curve, though the snap-out would cause some imaging artifacts where the tip contacted the surface. Figure 3.4 (b), however, shows why the feedback scheme completely failed when trying to image the untreated PS domes. On approach, there is a small snap-in and so the vibration amplitudes immediately drop to zero without any gradual decrease. Upon retraction, there is a very large snap-off due to adhesion. This behavior is consistent with electrostatic and van der Waals interactions between the tip and sample normally seen in air, but these interactions should be mitigated in water. Instead, this behavior is due to hydrophobic interactions between the tip and sample, a normally hydrophobic hydrocarbon polymer [92]. A quick measurement after the experiment showed a bulk contact angle of ~ 60-90° on this untreated surface, confirming that the particles were indeed hydrophobic.
It seems the LEEFM cannot be used to image hydrophobic samples, but this restriction was circumvented by treating the surface to make it hydrophilic. One way of making a surface hydrophilic is by surface oxidation via oxygen plasma. Irradiating oxygen molecules with radio waves creates oxygen radicals. These radicals readily react with surface species to form oxides, which can then take part in hydrogen bonding with water, so the surface becomes hydrophilic. Figure 3.4 (c) and (d) are FD curves on silicon and a PS dome, respectively, on the same sample as (a) and (b) but after a few seconds of exposure to oxygen plasma. The reason for the increase of the $2\omega$ amplitude and decrease of the $1\omega$ amplitude is unclear, as is the nature of the increase in
1ω amplitude before the damping region in (d), but the changes are likely due to the different surface properties. On both the Si and PS, the cantilever deflection shows that there is no longer snap-off due to adhesion, indicating that hydrophobic interactions are no longer present. A contact angle measurement showed almost full wetting of the surface, proving that it was rendered hydrophilic by the oxygen plasma treatment. The tip vibration behaves in the required manner above the now-hydrophilic surface, in that there is a gradual decrease in the amplitudes as the tip approaches the surface, and a gradual increase as the tip retracts. These amplitude gradients should make it possible to properly feedback control the tip position for imaging.

The images in Figure 3.5 show that it is indeed possible to image the PS domes when they are hydrophilic. The topography of the surface from contact mode imaging, shown in (a), looks very similar to the contact mode topography in Figure 3.3 (a), confirming that the plasma treatment did not greatly damage the surface. The topography from LEEFM imaging, Figure 3.5 (b), looks similar to both contact mode images, showing that the feedback control scheme functioned properly. All three properly imaged topographies show features ~ 200 nm tall. The LEEFM 1ω amplitude and phase images, Figure 3.5 (c) and (d), respectively, follow the topography closely. The images shown are right-to-left scans, so the strange features on the right side of each dome are probably feedback control artifacts where the tip touched the surface, which can be expected when imaging ~ 200 nm tall features from ~ 5 nm away. Unfortunately, besides these artifacts, the amplitude and phase images do not seem to provide any additional information about the surface, but this is unsurprising: the entire surface was oxidized, so the surface properties of the silicon and PS are probably more similar than they normally would be. There may be more subtle changes that could be detected by the amplitude and phase images, such as the change in dielectric constant between domains, but any such changes seem to be overshadowed by the large topographical features.
Figure 3.5: Images of Polystyrene (PS) domes deposited on silicon wafer after a few seconds of exposure to oxygen plasma. (a) Topography from contact mode AFM. (b) Topography, (c) $1\omega$ amplitude, and (d) $1\omega$ phase from LEEFM. The $2\omega$ amplitude was used for feedback control with a setpoint of 1 nm, 25% damping from the undamped vibration of 1.3 nm. All images are 5 µm x 5 µm, and the right-to-left scans are shown.

3.5 Non-Conducting Samples

All of the data and images shown until this point have been of samples mounted on silicon wafers (a gold film on Si wafer for the SAMs). As will be shown in the next chapter, a high dielectric constant substrate (conductor or semi-conductor) is required to generate an appreciable $2\omega$ vibration. On insulators, such as glass or sapphire (Al$_2$O$_3$), the $2\omega$ vibration amplitude vanishes. This is demonstrated in Figure 3.6, which shows frequency sweeps in water.
on (a) silicon wafer and (b) sapphire, holding all other conditions constant. The $1\omega$ amplitude is reduced almost by half on sapphire compared to Si, but is still appreciable. The $2\omega$ amplitude, however, is about an order of magnitude smaller on sapphire. The amplitude is so low, in fact, that the lock-in amplifier was unable to consistently isolate the signal, so imaging was impossible using the $2\omega$ amplitude as feedback. But, the $1\omega$ amplitude is still high enough to be used for feedback control. Feedback controlling the $1\omega$ amplitude and monitoring the $2\omega$ amplitude and phase is essentially the same as controlling the $2\omega$ and monitoring the $1\omega$ in practice—the only change to the experimental setup is switching the respective wires—but the images acquired would provide different information.

![Figure 3.6: Frequency sweeps on (a) silicon and (b) sapphire. The same tip was used for both, with 1 V applied 300 nm above the surface.](image)

The capability to use the $1\omega$ amplitude as feedback is demonstrated in Figure 3.7. PS domes were produced on sapphire and plasma cleaned to make them hydrophilic. Figure 3.7 (a) is a contact-mode AFM image of the domes and, expectedly, looks the same as the contact mode images of domes on Si. The topography image from LEEFM in (b) is a very good match to the contact mode topography, and the features are the correct height of ~200 nm, proving that the $1\omega$
amplitude can be used effectively for feedback control. The $2\omega$ amplitude image (c) shows a faint outline of the domes, but the change in amplitude is barely above the noise level. The $2\omega$ phase image showed nothing but noise and is not shown. Thus it seems it is possible to image on insulators using LEEFM, but with much less effectiveness.

Figure 3.7: Images of PS domes on sapphire. (a) Contact mode AFM, (b) LEEFM topography using $1\omega$ amplitude as feedback, (c) LEEFM $2\omega$ amplitude. Contact mode was performed with 0.5 nN applied normal force. The applied signal for LEEFM was 0.5 V at 2 kHz. The $1\omega$ amplitude feedback setpoint was 1.3 nm from the undamped vibration of 6 nm. All images are 5 µm x 5 µm, and the right-to-left scans are shown.
3.6 Discussion

The preceding results have shown that LEEFM is capable of accurately imaging topographical features, and it has a significantly higher spatial resolution than SPFM in air. The clarity of the ~ 1 μm hexagonal nanowell suggests that the spatial resolution is much better than 1 μm; determining the imaging resolution of the LEEFM will be the subject of future work. Some work was done to this effect using scratched regions of SAMs—like those used to show chemically-sensitive imaging—of progressively smaller sizes. The act of scratching the surface under high-load contact significantly dulls the AFM tip, so features smaller than 250 nm could not be seen using this method. Samples with small features have been prepared, but were not imaged by the time of this writing. These include PS domes using 100 nm colloidal particles instead of the 520 nm particles shown above, and it is expected that the LEEFM will easily discern these features. Also in preparation are cellulose nanowhiskers, chains of cellulose a few μm long but only ~ 10 nm wide, which are probably close to or beyond the limit of resolution for the LEEFM.

The ability of the LEEFM to simultaneously detect local surface potential changes while recording the topography was demonstrated. The $1\omega$ amplitude increased in the region where charged SAMs were damaged, but the $1\omega$ phase only responded to the damage on the negatively charged SAM. Figure 3.8 extends on this data and shows that the phase seems to consistently depend on the charge of the surface. The DI water used for the LEEFM experiments had a pH ~ 5.5 due to dissolved carbonate, so the surfaces with an isoelectric point (pI) > 5.5 would be positively charged due to adsorbed H+ ions, and surfaces with pI < 5.5 would be negatively charged. More surfaces need to be tested to confirm this trend, but if the trend is consistent then it could be used to predict surface charge based on the $1\omega$ phase. This idea can be extended for the vibration amplitudes and the time-averaged deflection value as functions of surface charge and
other properties. Hopefully, smooth trends will emerge so that other surface properties can be predicted by the cantilever behavior. It is expected that the dielectric constant of the surface affects the $1\omega$ vibration, as predicted by eq. 2.13 for SPFM. Samples are in preparation which have two electrodes separated by different dielectric materials, so the electrode can be used as a baseline to compare the signals for the different samples and the $1\omega$ vibration will (hopefully) change above the different dielectric materials. The change in vibration due to a change in surface charge/potential will be tested by selectively charging a sample surface with an externally applied DC voltage. The samples prepared for this study have a thin gold film deposited on silicon; the gold film will be externally charged, while the underlying silicon—not affected by the applied voltage because of its insulating native oxide layer—acts as a control.

![Figure 3.8](image.png)

**Figure 3.8:** Relationship between the isoelectric point of the probed surface and the $1\omega$ phase. All data were collected with the same tip 300 nm from the surface with 1 V applied at 4 kHz, which was the $2\omega$ resonance frequency.

A few limitations for LEEFM imaging were presented, and it seems that LEEFM is most appropriate for hydrophilic samples on conducting/dielectric substrates. Feedback control failed
on hydrophobic surfaces because hydrophobic interactions caused tip snap in. Oxidizing the surface to make it hydrophilic solved this problem, but eliminated any changes in local surface potential, eliminating one of the primary reasons for using LEEFM. There may be ways to circumvent this issue by treating the tip or solution instead of the surface. For example, the tip could be functionalized with highly charged species so that it is highly hydrated and reduces hydrophobic interactions, or a small amount of surfactant could be added to the solution to coat hydrophobic regions.

The LEEFM also had difficulty imaging on an insulating substrate. This limitation can easily be avoided by mounting samples of interest to a conducting/dielectric substrate, but obviously this would not apply to samples fabricated from an insulator. It was shown that topographical imaging is possible with LEEFM on insulators, but this is a moot point since the purpose of LEEFM is to image topography and surface potential; other AFM techniques already exist which can obtain the topography of a surface in liquid via non-contact imaging. For insulating samples, it may be possible to artificially induce a $2\omega$ vibration by laying a conducting grid over the insulator. Feedback control is possible as long as there is a $2\omega$ vibration, no matter what the origin of that vibration. Imaging in the grid spaces might yield surface information from the $1\omega$ vibration, as long as the naturally produced vibration is not overpowered by the grid-induced vibration.

The experiments presented were performed as proof-of-concept for imaging topography and surface properties in LEEFM, and the future work mainly involves quantifying these LEEFM signals. But the motivation for developing the technique, outlined in Chapter 1, is its ability to image biological samples and produce surface property information. Thus the most important work yet to be done is the imaging of biological samples, such as *F. oxysporum* as it attacks *A. thaliana*, which will hopefully lead to a better understanding of the cell surface and its interactions with the environment.
Chapter 4
The Driving Force

4.1 Summary

The hypothesis concerning the origin of the forces driving cantilever vibration in LEEFM is discussed. The primary contribution seems to be from electrostatic interactions between the charged tip and an image charge produced on the sample. There also may be electrokinetic force acting, such as dielectrophoresis and electrophoresis.

Section 4.2 introduces charged surfaces in solution and the electrical double layer (EDL). The EDL is normally thought to screen electrical charges in solution, so electrostatic forces become insignificant far from the surface (a few µm in pure water). There is still significant cantilever vibration in LEEFM even 100 µm from the surface, which discourages the electrostatics hypothesis at first thought. But the LEEFM uses an alternating (AC) electrical signal applied to the cantilever, so the dynamics of EDL formation around the cantilever become important. Section 4.3 discusses electric field and EDL dynamics and shows that electrostatic forces can act over long range if the frequency of the applied AC signal is high enough to avoid full electric field or double layer formation. Supporting evidence from an outside source is presented and compared to LEEFM data.

Section 4.4 presents dielectrophoresis (DEP), another possible phenomenon contributing to cantilever vibration. In an electric field, a dielectric particle will polarize in response to the field, and the field will exert a force on each side of the dipole. These forces are unbalanced in a non-uniform field, so a net force on the particle will cause it to migrate. When a dielectrophoretic force is applied to the force balance for a cantilever instead of a particle, it predicts $1\omega$ and $2\omega$
vibrations and a time-averaged deflection of the cantilever, so DEP is a plausible driving force. The validity of the DEP driving force is supported by theoretical modeling accomplished in Mathematica, which predicts many of the experimentally observed trends.

LEEFM data is compared to the behavior predicted by the theory developed for SPFM in section 4.5. A consistent trend appeared from changing the conditions of the cantilever, the substrate and the medium: the $2\omega$ vibration amplitude follows the predicted behavior for electrostatic or dielectrophoretic forces, but the $1\omega$ vibration does not. It seems that electrostatic or dielectrophoretic interactions are driving the $2\omega$ vibration and contributing to the $1\omega$ vibration, but another as-yet-unknown process is also affecting the $1\omega$ vibration. A few possibilities for the other force driving the $1\omega$ vibration are presented, though no conclusion has yet been reached.

### 4.2 Surface Charge and the Electrical Double Layer

Surfaces generally become charged when they are submersed in water (or another high dielectric constant liquid) due to the transport of ions. Some functional groups will ionize in the presence of water, such as the silanol groups (-Si-OH $\rightarrow$ -Si-O$^{-}$ + H$^{+}$) and carboxylic acid groups (-COOH $\rightarrow$ -COO$^{-}$ + H$^{+}$), which become negatively charged, or amine groups (-NH$_{2}$ + H$^{+}$ $\rightarrow$ NH$_{3}^{+}$), which become positively charged. These reactions occur in pure water, but in general a surface will become positively or negatively charged according to its isoelectric point (pI) and the pH of the solution. A surface will be positively charged if the solution pH is lower than the pI, and negatively charged if the pH is higher than the pI. Electrolytes adsorbing to the surface from solution can also generate a net charge. Charged surfaces exert electrostatic forces on each other: like-charged surfaces repel each other, while – as the saying goes – opposites attract. Electrostatic repulsion is extremely important in preventing particle coagulation, which would otherwise occur due to the always-attractive van der Waals forces. Many important processes and products rely on
particle stability due to electrostatics, including anything involving colloidal dispersions [53] (such as milk, without which the cookie industry would be crippled), so electrostatic phenomena have been intensely studied.

The behavior of charged surfaces in solution is not as simple as in air, vacuum, or even inert liquids. Ions in solution interact with the electric field generated by the charged surface, so that ions of like charge are repelled and ions of opposite charge (counterions) are attracted. The charged surface and oppositely charged atmosphere are collectively referred to as the electrical double layer (EDL) [53, 93]. Figure 4.1 shows a simple model of the EDL with a corresponding graphical representation of the surface potential, which decreases due to the opposite potential generated from the counterions. The charged surface (1) starts with a potential of $\varphi_0$. Some counterions bind to the surface in the innermost layer, called the “Stern layer” (2), resulting in a sharp decrease in the electrical potential. The diffuse layer or “Gouy-Chapman layer” (3) is a cloud enriched in counterions, where the excess concentration of counterions (and the potential) decays exponentially, following a Boltzmann distribution, until the potential equalized with the bulk solution (4). More complicated models of the EDL exist, but this simplified description is sufficient for the discussion to follow.
Figure 4.1: A simple model of the electrical double layer showing the ion distribution (top) and electrical potential (bottom) near a charged plate. (1) The charged surface, (2) the Stern layer of bound counterions, (3) the diffuse Gouy-Chapman layer of ions, (4) bulk solution.

The characteristic distance required for the potential to drop by $1/e$ is called the Debye length,

$$\kappa^{-1} = \sqrt{\frac{\varepsilon_0 \varepsilon_r k_B T}{2 N_A e^2 I}}$$

(4.1)

where $\varepsilon_0$ is the permittivity of free space, $\varepsilon_r$ is the dielectric constant of the solution, $k_B$ is the Boltzmann constant, $T$ is the temperature, $N_A$ is the Avagadro constant, $e$ is the elementary charge, and $I$ is the ionic strength in the solution in units of mole/m$^3$. Electrostatic forces are almost completely screened out at distances greater than $\sim$ a few times the Debye length. The screening effect is strongest when there are electrolytes in solution ($\kappa^{-1} \approx 10$ nm in 1 mM
monovalent salt), but even in pure water the hydronium and hydroxide ions eventually screen the charges ($\kappa^{-1} = \sim 1 \text{ µm water at pH 7}$). Deionized water will absorb CO$_2$ from the atmosphere to have an equilibrium pH $= \sim 5.5$, corresponding to $\kappa^{-1} = \sim 200 \text{ nm}$. When the EDL is considered, it seems impossible for the cantilever vibrations in LEEFM to be driven by electrostatic forces – as they were in SPFM – since significant vibrations were seen at distances above even 100 µm in equilibrated water.

### 4.3 AC Electrostatic Actuation in Liquids

This model of the EDL does not address the dynamics of double layer formation; it takes time for the ions to diffuse into a Boltzmann distribution. The characteristic screening time $t_s$ depends on the distance the ions need to diffuse, characterized by the Debye length, and the speed at which they diffuse, characterized by the ion diffusion coefficient $D$, as

$$t_s \propto \frac{1}{\kappa^2 D}. \quad (4.2)$$

For surfaces charged naturally by ionization or ion adsorption the electrical potential is constant once the charging reaction is complete, so the dynamics of the double layer can often be ignored. But surfaces can also be charged by an externally applied electrical potential, which can change magnitude or polarity quickly and arbitrarily. If an alternating (AC) potential is applied to the surface, the dynamic response of the EDL may dominate the screening behavior. If the alternating voltage changes much slower than $t_s$, the double layer will have time to form and it will screen the surface charge. If the voltage switches much faster than the double layer can form, then the electrostatic potential will not be screened at all. When the time scales are similar, there is a smooth transition between the two extremes – the effective voltage increases as frequency increases – forming a sigmoidal relationship, and details of the system are needed to determine the extent of the screening behavior.
The electrical double layer forms in response to an electric field, but the electric field also takes a finite time to form. For electrodes covered in an insulating oxide, such as the silicon tip and a silicon sample in LEEFM, the characteristic time scale for the electric field formation \( t_e \) can be calculated as [94]

\[
t_e \propto \frac{\varepsilon_{ox}\varepsilon_0}{\sigma} \frac{d}{2t},
\]

where \( \varepsilon_{ox} \) is the dielectric constant of the oxide (\( \varepsilon_{SiO_2} = 3.5 \)), \( \varepsilon_0 \) is the permittivity of free space (8.85 \times 10^{-12} \text{ F/m}), \( \sigma \) is the conductivity of the medium (\( \sigma_{H_2O} \) at pH 5.8 is 5.5 \times 10^{-6} \text{ S/m}), \( d \) is the electrode separation distance (20 \( \mu \text{m} \)), and \( t \) is the surface oxide thickness (2 nm). Under these typical conditions for LEEFM experiments \( t_e \approx 2.8 \times 10^{-2} \text{ s} \), so if the applied AC voltage varies faster than \( \sim 35 \text{ Hz} \), there will not be complete electrical field formation, and so the electrical double layer will not be able to form in response.

Sounart et al. demonstrated the ability to use an AC signal to electrostatically actuate electrodes in liquid [94]. They used an interdigitated silicon comb-drive actuator, a common component in microelectromechanical systems (MEMS), which has “fingers” of two electrodes to increase the surface area. A (usually DC) voltage is applied to the lower, fixed electrode, and the resulting electrostatic force draws the top, free comb towards the bottom. An SEM image of their comb drive is shown in Figure 4.2 (a). These devices are not usually used in water due to concerns of electrode polarization, but they showed that, like LEEFM, electrostatic actuation is possible in water when AC drive signals are used. They monitored the time-averaged deflection (\( \sim \mu \text{m} \text{ scale} \)) of the movable electrode as a function of the applied voltage and frequency in water and other liquids. They did not report any vibration behavior, so the vibration amplitudes were probably very small due to viscous damping, as seen for LEEFM cantilever vibration in Figure 2.7 (a). The deflection corresponds directly to the strength of the electrostatic force through a Hookean relationship, so trends in the deflection can be interpreted directly as trends in the
electrostatic force. Figure 4.2 (b), reproduced from the paper, shows a sigmoidal relationship between the applied frequency and the deflection, the effect expected from the EDL dynamics argument above. The frequency dependence of the comb drive deflection was replotted (so that increasing deflection is down) and compared to LEEFM data in Figure 4.2 (c). The green line (left axis) is the LEEFM cantilever deflection – the same data as in Figure 2.7 (a) – and the orange line (right axis) is comb drive deflection. The magnitude of the comb drive deflection is, by design, much greater than the cantilever deflection, but the important feature of the graph is that the shapes of the curves are very similar. Both the cantilever and comb drive move towards the counterelectrode as the applied frequency increases, so the LEEFM behavior also matches the expectations from EDL formation dynamics. This hypothesis of an electrostatic driving force is supported in section 4.5.

Figure 4.2: (a) SEM image of a MEMS comb drive actuator; (b) non-dimensionalized displacement of the free electrode as a function of frequency in different media (circles are in water), with a line drawn over one set of data to emphasize the sigmoidal shape; (c) the water data from (b) redimensionalized and replotted with cantilever deflection data from LEEFM. (a) and (b) and the comb drive deflection data in (c) are reproduced from ref. [94].
4.4 Dielectrophoresis

An electrical bias can cause other forces besides electrostatic interactions, such as the dielectrophoretic force. Dielectrophoresis (DEP) is the motion of a particle due to the polarization forces imposed by an external, inhomogeneous electric field [53, 93, 95, 96]. Thales of Miletus, a philosopher in Greece in ~ 600 B.C., first noticed the effect as bits of leaf and straw were pulled towards a piece of charged amber [97]. In 1978 – more than 2500 years later – Herbert Pohl named the force using the Greek word phorein, meaning “carry,” by virtue of dielectric properties, in his thorough treatment of the phenomenon [98]. In a uniform electric field a particle in solvent will polarize to form a dipole, and the electric field will produce a force that is equal and opposite on each side of the particle/dipole. A non-uniform field, however, will act more strongly on one side of the particle, producing a net force across the particle that causes it to move. The solvent suspending the particle will also be polarized by the electric field, so the difference in dielectric properties – which determines the strength of the induced dipole – will determine the net behavior: if the particle is more polarizable (higher permittivity/dielectric constant) than the solvent it will move towards regions of stronger electric fields, and vice versa for particles with lower permittivity than the solvent. Since the DEP force depends only on field strength, and not field polarity, DEP is possible in DC or AC electric fields.

An expression for the DEP force has been derived in many places as

$$F_{DEP}(t) = V_{eff} \varepsilon_0 \varepsilon_m Re[K(\omega)] \nabla E^2(t)$$  \hspace{1cm} (4.4)

where $V_{eff}$ is the effective volume of the particle, $\varepsilon_m$ is the relative permittivity of the medium, $E$ is the amplitude of the electric field, and $Re[K(\omega)]$ is the Clausius-Mossoti (CM) factor,

$$K(\omega) = \frac{\varepsilon_p^* - \varepsilon_m^*}{\varepsilon_p^* + 2\varepsilon_m^*}$$  \hspace{1cm} (4.5)
where $\varepsilon_p^*$ and $\varepsilon_m^*$ are the complex permittivities, where of the particle and medium, respectively. The complex permittivity $\varepsilon^* = \varepsilon + \frac{\sigma}{i\omega}$, where $\sigma$ is the conductivity, $i$ is the imaginary number, and $\omega$ is the frequency of the electric field, describes the frequency dependent dielectric behavior of the material. The real part of the CM factor describes the frequency dependent dielectric behavior of the system, i.e. whether the medium or the particle is more polarizable, with values bounded by $-\frac{1}{2}$ for a conducting medium and 1 for a conducting particle.

The DEP force, eq. 4.4, can be used in the dynamic AFM force balance, eq. 2.4, though a few approximations are needed to simplify the expression. The electric field can be very roughly approximated using the expression for parallel plates, $V/z$, where $z$ is the tip sample separation. Only the $z$ component of the gradient of the field needs to be considered for vertical vibration, and the voltage does not depend on $z$, so the gradient of $E^2$ becomes $\nabla E^2 \approx \frac{d}{dz} \left( \frac{V^2}{z^2} \right) \approx \frac{V^2}{z^3}$.

Combining this expression with eq. 4.4, replacing $Re[K(\omega)]$ with an appropriate constant CM, and plugging the whole expression into the dynamic AFM force balance eq. 2.4 yields

$$\frac{d^2 z_c}{dt^2} + \frac{\omega_0}{Q} \frac{dz_c}{dt} + \omega_0^2 z_c = \frac{g V_{eff} \varepsilon_1 CM}{m} \left( \frac{V_{RMS}^2 \sin^2(\omega t)}{z^3} - 2 \frac{V_{RMS} \phi \sin(\omega t) + \phi^2}{z^3} \right)$$

(4.6)

where $g$ is a factor that accounts for the system geometry with a value on the order of 10 [99, 100], $z_c$ is the cantilever deflection and $z = z_c + d_0$ is the tip-sample separation for some imaging distance $d_0$. This expression shows that the DEP force can produce $1\omega$ and $2\omega$ vibrations and a time-averaged deflection with some dependence on the frequency and distance, so it is a plausible driving force for the LEEFM.

Modeling was done based on eq. 4.6 to determine if DEP theory could predict the cantilever vibration behavior. A Mathematica program was written which would solve the differential equation for a set of conditions, then fit the resultant “vibration” with a time-averaged offset and two sine waves of frequencies $1\omega$ and $2\omega$. Experimental data could be mimicked by...
looping through relevant conditions, such as changing the applied frequency to produce a frequency sweep. Figure 4.3 shows the results of this modeling for changing (a) the applied voltage and (b) the tip-sample separation distance, and compares each to corresponding experimental data. It should be noted that the parameters in the force balance were manipulated slightly in each case to fit the data better; the purpose of the modeling at this stage was just to check that the cantilever behavior qualitatively matched the theoretical predictions, not obtain rigorously accurate estimates of the vibration. In (a), the vibration follows very closely with the expected $V^2$ dependence for the $2\omega$ amplitude and time-averaged deflection, and the expected $V$ dependence for the $1\omega$ amplitude, as was seen Figure 4.3. The approach curve in (b) shows the increase in vibration as the tip approaches the sample. Here, the $2\omega$ amplitude does seem to depend on $1/z^3$ as predicted by DEP theory, but no conclusion about the accuracy of the model can be drawn from this result. The distance dependence of the electrostatic force will be different than for DEP because they depend on the electric field differently, and in both cases the electric field is very poorly modeled by assuming that the tip/cantilever and sample are parallel, flat plates. The comparison between the $1\omega$ and $2\omega$ is more important, because once again these two vibrations act differently, giving further support to the multiple driving force hypothesis. The $1\omega$ amplitude decays much faster with distance than the $2\omega$, indicating a different dependence on the electric field, as would be expected for a different driving force. If an accurate model can be constructed, it might be possible to glean information about the origin of the $1\omega$ vibration by adjusting specific parts of the model (e.g. the dependence on the electric field) to see what functional form best fits the $1\omega$ data. Better approximations of the electric field near the AFM tip have been made [34, 85], and will be applied to the model, along with the appropriate AC electrostatics equations, in the future.
Figure 4.3: Theoretical and experimental data changing (a) applied voltage, (b) applied frequency, and (c) tip-sample separation distance. Solid lines are experimental data, dotted lines are modeled data; blue – $1\omega$ amplitude, red – $2\omega$ amplitude, green – time-averaged deflection.

Figure 4.4 shows the frequency dependence of the vibration amplitudes from experiments and modeling. Eq. 4.6 does not predict any frequency dependence of the driving force, but the vibration amplitude is frequency dependent due to mechanical resonance. The model fits the data well at frequencies higher than resonance, but below resonance the vibration amplitude continually increases as the frequency decreases. This low frequency increase cannot be explained by either DEP or the AC electrostatics hypothesis, the latter of which would actually predict a decrease in the vibration amplitude at lower frequency because the double layer has longer to form and can screen the charge more effectively before the polarity changes. One possible explanation is that the driving force is increasing at low frequency because the electric
field is stronger due to an increase in the dielectric constant. It has been shown that the dielectric constant of water increases at low frequency as

$$\varepsilon(\omega) \approx \varepsilon_\infty \left(1 + \frac{\kappa^3 D^2}{\omega^2 h}\right),$$

(4.7)

where $\omega$ is the frequency, $\varepsilon(\omega)$ is the frequency-dependent permittivity, $\varepsilon_\infty$ is the dielectric constant (at 0 Hz), $\kappa$ is the inverse of the Debye length, $D$ is the ion diffusion coefficient, and $h$ is the separation between the electrodes [101, 102]. Figure 4.4 (b) shows the modeling results when this equation is used to modify the dielectric constant. In this case, the model over-predicts the low frequency increase of the vibration amplitude. But if this model were combined with an expression for the electric field and double layer formation dynamics, which would decrease the effective voltage as the frequency decreases, then an accurate model may result.
Figure 4.4: Frequency dependence of the $1\omega$ (blue lines) and $2\omega$ (red lines) vibration amplitudes from theoretical modeling (dotted lines) and experimental data (solid lines). The theoretical model used here included the frequency dependent behavior of the relative permittivity of water.
4.5 Supporting Data

4.5.1 Voltage Dependence

If the LEEFM driving force is in part electrostatic in nature then some of its behavior should be predictable using the same equations developed for SPFM. The cantilever force balance derived for SPFM in Chapter 2 is reproduced here for convenience:

\[
\frac{d^2 z}{dt^2} + \omega_1^2 \frac{dz}{dt} + \omega_2^2 z = -4 \pi \varepsilon_0 \varepsilon_r \frac{\varepsilon_m}{\varepsilon_r + \varepsilon_m} f \left( \frac{k}{k_o} \right) \left[ \frac{1}{2} V_{RMS}^2 \cos(2 \omega t) - 2 \phi V_{RMS} \sin(\omega t) - (\phi^2 + V_{RMS}^2) \right].
\] (2.13)

This equation predicts that the \(2 \omega\) amplitude will increase with \(V^2\), the \(1 \omega\) amplitude will increase (the sign does not affect the amplitude) with \(V\), and the time-averaged deflection will increase (towards the surface, in the negative direction) with \(V^2\). Figure 4.5 (a) presents LEEFM experimental data showing exactly these relations and (b) shows the \(V^2\) dependence of comb drive deflection both in air (DC) and liquids (AC) from ref. [94].

Figure 4.5: (a) LEEFM experimental data showing cantilever deflection (green line; left axis) and \(1 \omega\) and \(2 \omega\) vibration amplitudes (blue and red lines, respectively; right axis) as functions of the applied voltage. (b) Comb drive deflection in various liquids (AC) and air (DC, inset) as a function of the square of the applied voltage.
The predicted dependence of the $2\omega$ vibration and the time-averaged deflection on $V^2$ means these signals should be unaffected by a change in the polarity of the applied voltage. But the $1\omega$ vibration should depend on $V$, so the polarity would affect the vibration. The polarity of the applied AC signal can be reversed by applying the voltage to the sample instead of the cantilever. If, for example, the peak of the $1\omega$ sine wave vibration occurs when the voltage applied to the cantilever is at its peak, then the phase shift between the two waves would be zero. Applying the voltage to the sample would switch the polarity of the electrodes (applied positive voltage to the sample means the cantilever is the negative electrode), so the peak of the $1\omega$ vibration should occur at the trough of the applied voltage for a phase shift of $180^\circ$. Figure 4.6 shows the results of this experiment for both SPFM in air (a) and LEEFM in water (b). In both cases, there was no change in the phase of the $2\omega$ vibration, but there was a $180^\circ$ phase shift of the $1\omega$ vibration.

![Figure 4.6: Frequency sweeps in (a) air and (b) water showing the $1\omega$ and $2\omega$ vibration (blue and red lines, respectively) amplitudes (solid lines; left axes) and phase shifts (dotted lines; right axes). The $1\omega$ phases are shifted by $180^\circ$ in each case when the 1 V driving voltage is applied to a silicon sample instead of the silicon cantilever. The phase change that occurs at resonance is a well-known effect, but not relevant to the present discussion.](image-url)
These data do not necessarily prove that electrostatics are the driving force, but the functional form of the voltage in eq. 2.13 must describe the process that is occurring. Further credence to this point comes from the fact that no higher harmonic vibrations (3ω, 4ω, etc.) are ever seen in LEEFM.

4.5.2 The Probe

The argument for an electrostatic driving force requires that the charged electrode is the tip and cantilever, but with the complex geometry of the LEEFM tip – silicon probe attached to the end of a silicon cantilever attached to the end of a silicon chip with a layer of silver paste affixing the whole thing to a gold spring – it would be prudent to confirm that this is the case. Figure 4.7 summarizes a series of simple experiments that were performed to verify the electrode. A tip prepared normally, as described in the experimental section (Chapter 2), was used to get a baseline of the expected vibration amplitudes, which are represented as the size of the text of “1ω” and “2ω” to the right of each tip cartoon. When the chip was isolated from the electrode, using insulating nail polish to affix the chip to the gold spring instead of conducting silver paste, there was no cantilever vibration (b). When the tip was scratched and affixed with silver paste, as normal, but the gold electrode coated with nail polish on the outside, there was no change to the vibration signal from baseline (c). Clearly, the gold spring passes the applied voltage to the chip without affecting the behavior of the system in any other way.

Probes were purchased with the same dimensions as the standard Si probes but fabricated with silicon nitride, Si₃N₄, cantilevers and tips (d). Si₃N₄ is an electrical insulator commonly used as an insulating layer in silicon microelectronics, and has a dielectric constant of ~ 7 compared to ~ 12 for Si. There should be no electrostatic driving force from a non-conducting cantilever/tip, so any tip vibration could not be due to electrostatics. If the Si₃N₄ tip has vibration amplitudes
about half of the Si tip it would indicate some dielectric-based force, such as dielectrophoresis. The frequency sweeps in Figure 4.8 show essentially no $2\omega$ vibration with the $\text{Si}_3\text{N}_4$ tip, which supports an electrostatic driving force. But there is a significant $1\omega$ vibration compared to the baseline Si case, so the $1\omega$ vibration may not be due to electrostatics; the two vibration modes may be caused by different driving forces.

Additional tips were purchased with a $\text{Si}_3\text{N}_4$ cantilever/probe and a thin gold layer coating the top of the cantilever (e). The gold coating is normally used as a practical consideration to increase the reflectivity of the cantilever, making it easier to focus the AFM laser beam on the cantilever. Here, the gold is used as an electrode since any applied potential would reach the top of the cantilever through the film. This electrode, however, is facing away from the surface and is separated from the underside of the cantilever by a few microns of $\text{Si}_3\text{N}_4$. The frequency sweep with this tip shows a small $2\omega$ amplitude at very low frequency (below 1 kHz), but the $1\omega$ vibration is huge – almost an order of magnitude higher than the Si base case. Again, the $2\omega$ vibration seems to follow the expected behavior for an electrostatic driving force, but the $1\omega$ vibration certainly does not. This behavior is further explored below by adding an insulating layer to the substrate, which acts as the other electrode in the system.
Figure 4.7: The change in vibration amplitudes due to changing properties of the AFM probe. The four materials represented are shown at the top in their respective color: Silicon is blue, silicon nitride is gray, gold is (creatively) gold, and nail polish is purple. Silver paste is not shown, but it was used in all cases except (b). The magnitudes of the vibration amplitudes observed are represented as the size of the text to the right of each probe. (a) A standard silicon probe with the individual components labeled and the baseline vibration amplitudes. (b) Nail polish used instead of silver paste to affix the cantilever to the gold spring – no vibration. (c) Nail polish on the outside of the gold spring – no change in vibration from baseline. (d) Si$_3$N$_4$ cantilever and tip – significantly reduced 1ω amplitude and an extremely faint 2ω vibration. (e) Si$_3$N$_4$ cantilever and tip with a gold film covering the back – faint 2ω vibration but huge 1ω vibration. Note that the cartoons of the probes are not to scale: the cantilever is 225 µm long and a few µm thick, while the chip is ~ 1 mm long and a few tenths of a mm thick. The scale of the gold spring compared to the chip is reasonable (though not exact), as is the scale of the tip compared to the cantilever.
4.5.3 The Substrate

Altering the characteristics of the probe had drastic effects on the LEEFM signal, so it would follow that altering the surface - the other electrode in the system – would also greatly affect the signal. The effect of introducing an insulating layer between the tip and conducting substrate was studied using silicon surfaces with thick oxide layers grown on them. The native oxide layer on silicon is 2 nm thick, but baking silicon at high temperature causes the oxide layer to grow. The electrostatic force relies on an image charge generated in a conducting sample, so it is expected that introducing an insulating oxide layer between the electrodes would reduce the electrostatic force, and thus the vibration amplitude. Figure 4.9 shows the vibration amplitudes measured above silicon surfaces as a function of the oxide thickness. As expected, the $2\omega$ vibration amplitude decreases as the thickness of the insulating layer increases. The $1\omega$ vibration amplitude, however, behaves in the opposite manner. Yet again, the differing behavior of the two vibration modes indicates a separate driving force acting at $1\omega$. 

Figure 4.8: Frequency dependence of the LEEFM (a) $1\omega$ and (b) $2\omega$ vibration amplitudes for a regular Si probe (blue lines), a $\text{Si}_3\text{N}_4$ cantilever and tip (gray lines), and a $\text{Si}_3\text{N}_4$ cantilever and tip coated with gold on the side facing away from the surface (orange line). 1 V was applied to the gold spring in all cases.
Figure 4.9: The $1\omega$ (blue line) and $2\omega$ (red line) LEEFM vibration amplitudes on silicon surfaces with thermally grown oxides. The applied signal was 1 V at 5.5 kHz, which was the $2\omega$ resonance frequency, though the behavior was consistent at other applied frequencies. The Si tip was positioned 300 nm above the surfaces.

A different type of experiment was constructed to better understand the differing behavior of the $1\omega$ and $2\omega$ vibrations. All of the data presented until this point have been a result of the dynamic conditions of a sinusoidal (AC) applied voltage, so the LEEFM setup was modified to monitor the response of the cantilever to a constant (DC) voltage. The lock-in amplifiers were removed and replaced with an oscilloscope, allowing direct monitoring of the bending of the cantilever rather than the amplitudes and phases of its vibrations and its time-averaged offset. A function generator that could output a square wave (a DC voltage switching between two values at a given frequency) was connected to the tip. The applied voltage and the resultant cantilever bending for the different oxide thicknesses on silicon are shown in Figure 4.10. For the native oxide silicon base case, it seems that there is an attraction every time the voltage is switched, either negative-to-positive or positive-to-negative. This behavior is analogous to the second harmonic vibration, where there is an attractive force at both the peak and trough of the applied sine wave. The behavior of the 50 and 110 nm thick oxides seems to mimic the
behavior of a 1ω vibration, where there is one attractive and one repulsive interaction in every period of the wave. The cantilever bends away from the surface when there is a negative voltage applied, indicating electrostatic repulsion from the surface, which is consistent with the negative charge developed by silicon oxide surfaces in solution. For the silicon and the two oxide thicknesses there is a peak in the deflection immediately after the voltage switches, which is followed by a relaxation due to the double layer forming and screening the charge. The glass slide deflection does not show an initial spike or relaxation: it looks like simple electrostatic repulsion in an inert, non-ionic medium. The reason for this strange behavior remains unclear.

Figure 4.10: Cantilever deflection (left axis) due to an applied square wave voltage (black line, right axis) for a silicon tip 300 nm above: silicon with a native oxide layer (blue line), 50 nm (red line) and 110 nm (purple line) thermally grown oxides on silicon, and a glass slide (green line).
4.5.4 The Medium

The three components in an electrostatic interaction are the two electrodes and the medium in between them. Having covered the two electrodes, the medium is now considered. Figure 4.9 shows the cantilever bending due to an applied square wave in air, decane and water. Air and decane contain no ions, so no EDL can form to screen the charge, and the cantilever just deflects towards or away from the surface as expected of a surface with static charge. Decane has a higher dielectric constant, $\varepsilon_{\text{decane}} = 2$, than air, $\varepsilon_{\text{air}} = 1$, so the energy density of the electric field is higher in decane, resulting in a larger electrostatic force and the larger deflection observed. But in both air and decane there is no “$2\omega$” attractive force, due to the $V^2$ term, occurring every time the voltage changes like in water. The $V^2/2\omega$ term should manifest itself as a constant deflection in this type of experiment, since the applied square wave is essentially a constant voltage with changing polarity, and the polarity does not affect the $V^2$ term. The data in Figure 4.11 are artificially centered on zero bending because system limitations made it difficult to calibrate the cantilever deflection so that 0 corresponded exactly to no bending. Consequently, any time-averaged deflection due to the $V^2/2\omega$ term is not represented in the data, so these square wave experiments do not fully represent the physical situation that they were designed to test.
The properties of the medium can also be changed by the addition of ions, which would decrease the Debye length and allow the double layer to form faster, as described by eq. 4.2. The surface potential would be screened to a greater extent, so the electrostatic force would decrease as would the vibration amplitudes. Figure 4.12 shows the $1\omega$ and $2\omega$ vibration amplitudes as a function of the salt concentration and, once again, the $2\omega$ behavior follows what is expected for an electrostatic driving force but the $1\omega$ does not. In this case, the $1\omega$ does not act in the opposite way of the $2\omega$, as it did when changing the probe and substrate. The $1\omega$ amplitude does initially increase, but then both it and the $2\omega$ amplitude disappear above 10 mM KCl. Whatever process is driving the $1\omega$ vibration seems to stop working at this high salt concentration, possibly because the solution begins to conduct electricity, which completely changes the nature of the system.
Figure 4.12: The $1\omega$ (blue line) and $2\omega$ (red line) LEEFM vibration amplitudes vs. the concentration of KCl in the solution. The applied signal was 1 V at 4 kHz and the Si tip was positioned 300 nm above a Si surface.
4.6 Discussion

There are two main conclusions to draw from this chapter: from the theory, both AC electrostatic/capacitive coupling and dielectrophoretic interactions could be responsible for cantilever vibration; but from the data, there must also be another driving force acting only in $1\omega$. It is not surprising that there are multiple driving forces acting when the complexity of the system is considered with the plethora of phenomena that occur when electrical potentials are applied in solution. Some examples are the myriad electrokinetic phenomena, including dielectrophoresis and others such as electrophoresis, electroosmosis, and their induced-charged counterparts. These phenomena can be sorted by their dependence on the electric field or applied voltage: a quadratic dependence (i.e. dielectrophoresis and electrostatics) would yield $2\omega$ terms, while a linear dependence (e.g. electrophoresis) would yield $1\omega$ terms.

The data in this chapter follow the general trends expected for an electrostatic or dielectrophoretic driving force. Determining which one is acting – or if both are acting, to what extent – is critical to advance the understanding of the technique. But the similarities of these driving forces, since both allow for $1\omega$ and $2\omega$ vibrations and a time-averaged deflection, means that decoupling the two will be very difficult. More accurate modeling of the system may help, so future work will include combining many separate models into one coherent system. The modeling process described for dielectrophoresis will be expanded to include the complex geometry outlined in the distance dependent modeling of Chapter 2 and the electrical field and electrical double layer formation dynamics shown in Chapter 4.

Future work will also involve investigating the nature of the other force driving the $1\omega$ vibration. A few other phenomena have been considered, but will require closer study. The most likely effect is related to electrophoresis (EP), the movement of charged species in a uniform electric field. EP is normally thought of as a method of sorting particles (especially DNA)
according to their charge, but its underlying principle may affect LEEFM. In EP, a Coulombic force is exerted by the electric field on the charged particles, but there is also a counter-balancing force on the opposite charges in the EDL called electrophoretic retardation (EPR). A force very similar to EPR is electroosmosis (EO), which is the movement of liquid due to a Coulombic force exerted on the ions in the EDL by an electric field [93, 96, 103]. While there are no particles to move due to EP in LEEFM, there are certainly double layers forming at the electrode interfaces, so some effect related to EPR and EO could feasibly cause a force on the cantilever. EO, EP and EPR are all considered DC effects, because in an AC field the motion of the particle (EP/EPR) or fluid (EO) would oscillate with the field, yielding no net movement. (There is also an AC variant of electroosmosis – not-so-creatively called AC electroosmosis – which causes a steady fluid flow due to electroosmosis acting more strongly in one direction of a non-uniform field.) But in LEEFM the oscillation is the critical result, not a time-averaged displacement, so these forces are plausible.

Even if all the acting phenomena in both $1\omega$ and $2\omega$ are determined, the complexity of the system suggests that theory alone may not be able to accurately predict the response of the cantilever vibration to different surface properties. The quantification of properties, such as surface charge, is central to the applicability of LEEFM, so correlations between the surface properties and the cantilever vibration behavior are critical. If these correlations cannot be found via theoretical modeling, then a heuristic approach will be used, as outlined in Chapter 3. Ideally, the theoretical and heuristic approaches will corroborate each other, giving more confidence to measurements from the LEEFM.
Chapter 5
Conclusions

The development of a novel Atomic Force Microscopy (AFM) technique was presented. It is a dynamic technique that uses AC electrical interactions in solution to generate vibration of the cantilever. Electrostatic interactions are normally thought to be screened out in water due to the formation of an electrical double layer of counter-charged ions, which is central to the well-known DLVO theory. But it was shown that AC electrostatic interactions are possible if the polarity of the voltage/electric field is switched faster than the time needed to fully form the electric field and electrical double layer. Dielectrophoretic forces may also be contributing to cantilever vibration, but the similarity in functional forms of the electrostatic and dielectrophoretic forces makes it very difficult to decouple the two phenomena and determine to what extent they are acting. There also seems to be another force acting only on the $1\omega$ vibration, implying a linear dependence on the electric field instead of the quadratic dependence of the electrostatic and dielectrophoretic. This force may be an electrokinetic force such as electrophoresis or electroosmosis, though more control experiments and theoretical modeling are required to determine the exact nature of the force. Due to the uncertainty in which of these myriad forces are acting, the movement of the cantilever driven by the suite of electrical interactions is referred to with the general term “electroactuation.” This AFM imaging technique is thus called Liquid Environment Electroactuation Force Microscopy (LEEFM).

The underlying physical mechanisms of the LEEFM may not yet be fully understood, but it is still a viable technique. Model samples were used to show proof-of-concept for the ability of LEEFM to discern topographical features as well as local changes in the chemical nature of the surface. The LEEFM has a higher spatial resolution than SPFM, its counterpart technique for imaging in air; the ultimate resolution is not yet known, but seems to be on the order of 10s of
nanometers. The LEEFM can qualitatively distinguish areas of different surface properties, and certain components of the LEEFM signal seem to correlate with certain properties, but the ability to quantify surface properties using the LEEFM signal has not yet been realized. There are some significant limitations for the types of samples that can be imaged and in which media. The electrically induced cantilever vibration is not very effective on insulating samples – the topography can be imaged but no surface property detection is possible. This problem could be circumvented by strategically placing ground electrodes on the sample, though this method has not yet been tested. Difficulty was also encountered when imaging hydrophobic samples because hydrophobic interactions would cause the tip to snap into the sample. This problem was partially rectified by treating the surface to make it hydrophilic, which does eliminate the problematic hydrophobic interactions, but also homogenizes the surface so the property changes of interest are no longer present. The medium in which the sample is immersed is also very important. The tip and sample act as electrodes, so in a conducting medium current will flow between them, and the electrical interactions that drive cantilever vibration will not be present. The electrical interactions are proportional to the dielectric constant of the medium, so the dielectric constant must be high to allow large enough driving forces to cause cantilever vibration. So LEEFM works best with hydrophilic samples that are dielectric or conducting (or mounted on such a substrate) immersed in dielectric solutions such as water or alcohols. These are significant limitations and the LEEFM requires some further development, but it will hopefully become a useful tool for the characterization of myriad samples such as MEMS electrodes, polymers, or cells.
References


Appendix A
Mathematica Simulations of LEEFM

(*LF-DEPFM Simulation: Frequency Sweep*)
(*Written June 28, 2010*)

\[ \omega_0 = 11000 \] (*Resonance frequency in water- multiplied by \(2\pi\) to convert from time domain to angular frequency*);
\[ r_0 = 70 \times 10^{-6} \] (*m - distance from the lowest end of the chip to the substrate *);
\[ Q = 2 \] (*Q damping factor in water*);
\[ m = 1 \times 10^{-11} \] (*kg - Mass of cantilever+tip*);
\[ V_{\text{rms}} = 1 \] (*V - Driving voltage*);
\[ \phi = 0.03 \] (*V - Surface potential difference between tip and sample*);
\[ V = 1 \times 10^{-14} \] (*Volume of cantilever+tip*);
\[ \varepsilon_0 = 8.85 \times 10^{-12} \] (*F/m - Free space permittivity*);
\[ \varepsilon_r = 78 \] (*Dielectric constant of water*);
\[ CM = 1 \] (*CM Factor*);
\[ G = 20 \] (*The geometric prefactor for the DEP force (= about 20 for cone-plate)*);
\[ d_0 = 300 \times 10^{-9} \] (*Tip-sample separation for frequency sweep*);
\[ q_{\text{tip}} = 8 \times 10^{-15} \] (*Coulomb - total charge on surface of tip*);
\[ F = 96485 \] (*C/mol - Faraday constant*);
\[ R = 8.314 \] (*J/mol-K - Gas constant*);
\[ C_0 = 1 \times 10^{-3} \] (*Molar concentration of electrolyte*);
\[ T = 300 \] (*K - Water temperature*);
\[ D_c = 1.6 \times 10^{-9} \] (*m^2/s - Diffusion coefficient for NaCl*);
\[ \kappa = (2 F^2 C_0)/(\varepsilon_0 \varepsilon_r R T)^{1/2} \] (*1/Debye length*);

\[ \omega_r = \omega_0 \left(1 - \frac{1}{2Q^2}\right)^{1/2}/N \] (*Reduced resonance frequency - with no tip-sample interaction, \( \omega_{\text{eff}} = \omega_r \));
Print["\( \omega_r = \) ", \( \omega_r \) , " Hz"];
init=0.01;  fin = 0.012;  step = 0.00001;  n=(fin-init)/step; initn=.1; (*init and fin = starting and ending time (s) of fitting, n = number of steps required*)
\[ zsa=zsan=Table[0,{i,1,n+1}] \]; (*Create a table for the fitting of the solution from NDSolve that is filled with n points*)
\[ \varepsilon_{pp}[\omega_] := \varepsilon_0 (1+(3\times D_c^2)/(\omega^2 d_0)); \]
Plot[\[\varepsilon_{pp}[\omega],\{\omega,1,jf\},PlotRange\rightarrow\{\{0,jf\},\{0,300\}\}]\];
\[ \omega_r = 10289.6 \] Hz

(*The loop: solve the differential equation at each frequency step (resonance and non-resonance parts)*)

ji=0;  jf=20000;  jstep=500;  jn=Round[(jf-ji)/jstep]; (*initial and final values for the frequency sweep, step size, and number of steps*);
A1=P1=A2=P2=DC=A1n=P1n=A2n=P2n=DCn=Table[0,{j,1,jn}]; (*Create a table as long as the number of steps in the loop for each parameter*);
A1[[1]]=A2[[1]]=A1n[[1]]=A2n[[1]]=10^-9; P1[[1]]=P2[[1]]=P1n[[1]]=P2n[[1]]=1;
A2[[1]]=10^-9; DC[[1]]=DCn[[1]]=0;(*Initial guesses for each parameter*);

Do[
ω=(jstep*(j-1)+ji);(*Step the frequency*)
εp[ω_]:=εr*(1+(κ3 DC2)/(ω2 d0));(*Calculate the frequency dependence dielectric constant*)
sol=NDSolve[{z''[t]+(2π ωr/Q)*z'[t]+(2π ωr)^2* z[t]==(2 G V εp[ω] CM)/(Vrms Sin[2π*ω t]+ϕ)^2/(d0)^3; z[0]==.1*10^-9, z'[0]==-10^5}, z, {t,init,fin},MaxStepSize->0.0001,MaxSteps->200000,AccuracyGoal→9,PrecisionGoal→9];(*Solve the force balance differential equation*)
zs[t_]:=Evaluate[z[t]/.sol];
Do[zs[[i]]:=zs[init+(i-1)*step]; {i,1,n}];
zsaa=Flatten[Table[zs[[i]], {i,1,n+1}]];
zstable=Table[zs[init+(i-1)*step], {i,1,n}];
fit=NonlinearModelFit[zstable,a1*Sin[2π ω x+p1]+a2*Sin[2π 2 ω x+p2]+dc, {a1,A1[[j-1]]}, {p1,P1[[j-1]]}, {a2,A2[[j-1]]}, {p2,P2[[j-1]]}, {dc,DC[[j-1]]}], x];(*Fit 1ω and 2ω amplitudes and phases and time-avg deflection to the solved equation*)
fits=fit["BestFitParameters"];A1[[j]]=a1/.fits; P1[[j]]=p1/.fits; A2[[j]]=a2/.fits; P2[[j]]=p2/.fits; DC[[j]]=dc/.fits;

(*Check the fit of the data*)

plot1=Plot[zs[t], {t,init,fin}, PlotStyle→Blue]; plot2=ListPlot[zstable,PlotStyle→Red]; plot3=Plot[fit[t], {t,init,fin}, PlotStyle→{Green,Dashed}]; Show[plot1,plot2,plot3]
(*Plot the results from the frequency sweep*)

expt1wtable=Import["C:\Users\David\Desktop\Research\DEPFM\Modeling\Experimental data\Frequency Sweep expt 1w.txt","Table"];(*Import experimental data*)
expt2wtable=Import["C:\Users\David\Desktop\Research\DEPFM\Modeling\Experimental data\Frequency Sweep expt 2w.txt","Table"];
expt1wplot=ListPlot[expt1wtable,PlotStyle->{Darker[Blue],Thick,Dashed},PlotRange->All];(*Plot experimental data*)
expt2wplot=ListPlot[expt2wtable,PlotStyle->{Darker[Red],Thick,Dashed},PlotRange->All];(*Plot experimental data*)
Show[{expt1wplot,expt2wplot},PlotRange->{0,jf},{0,All}]

(*Form tables of simulated data*)
A1table=Table[{(j*jstep+ji),Abs[A1[[j]]]*10^9},{j,2,jn}];
A2table=Table[{(j*jstep+ji),Abs[A2[[j]]]*10^9},{j,2,jn}];
P1table=Table[{(j*jstep+ji),P1[[j]]*180/\[Pi]},{j,2,jn}];
P2table=Table[{(j*jstep+ji),P2[[j]]*180/\[Pi]},{j,2,jn}];
D1table=Table[{(j*jstep+ji),DC[[j]]},{j,2,jn}];
DCltable=Table[{(j*jstep+ji),DCn[[j]]*10^9},{j,2,jn}];

(*Plot all of simulated data*)
Plot[\[Epsilon]p[\[Omega]],\{\[Omega],1,20000\},PlotRange->{0,jf},{0,10}];
A1plot = ListLinePlot[A1table, PlotStyle -> {Blue, Thick}, PlotRange -> {{0, jf}, {0, All}}];
A2plot = ListLinePlot[A2table, PlotStyle -> {Red, Thick}, PlotRange -> {{0, jf}, {0, All}}];
Show[{A1plot, A2plot}];
Show[{A1plot, A2plot, expt1wplot, expt2wplot}, AxesLabel -> {"Frequency (Hz)", "Pk-Pk Vibrational Amplitude (nm)"}, PlotRange -> {{0, jf}, {0, 5}}]
Show[{A1plot, expt1wplot}, PlotRange -> {{0, jf}, {0, 5}}]
Show[{A2plot, expt2wplot}, PlotRange -> {{0, jf}, {0, 5}}]

P1plot = ListLinePlot[P1table, PlotStyle -> {Blue, Thick, Dashed}, AxesLabel -> {"Frequency (Hz)", "Resonance Phase (degree)"}, PlotRange -> {{0, jf}, All}];
P2plot = ListLinePlot[P2table, PlotStyle -> {Blue, Thick}, AxesLabel -> {"Frequency (Hz)", "Resonance Phase (degree)"}, PlotRange -> {{0, jf}, All}];
Show[{P1plot, P2plot}, PlotLabel -> "Blue=2w, Red=1w"];

DCplot = ListLinePlot[DCtable, PlotStyle -> {Green, Thick}, AxesLabel -> {"Frequency (Hz)", "DC Offset (nm)"}, PlotRange -> {{0, jf}, {0, Automatic}}]
(*Export the data*)

resultstable = Table[{(j*jstep+ji)/1000., (Abs[A1[[j]]]+Abs[A1n[[j]]])*10^9, (Abs[A2[[j]]]+Abs[A2n[[j]]])*10^9, P1[[j]]*180/\[Pi], P2[[j]]*180/\[Pi]}, {j, 2, jn}];

Export["C:\Users\David\Desktop\Research\DEPFMModeling\Output\FreqSweep.txt", resultstable, "Table"];
Appendix B

NSF EAPSI Proposal

The following proposal was recently accepted by the NSF East Asia and Pacific Summer Institutes (EAPSI) program. The program will fund 8 weeks of research in China over summer 2011.
Understanding Silicon Protrusion and Wear Due to Nanoasperity Frictional Contact

**Intellectual Merit**

The tribology of nanoasperity contacts plays an important role in design and operation of microelectromechanical systems (MEMS) with moving components. Recent nanofretting experiments using an atomic force microscope (AFM) to rub a Si ball against a Si(100) substrate in vacuum showed that the substrate protrudes out in the rubbed area forming a nanoscopic “hillock”, which is a counterintuitive effect [1-3]. In contrast, an identical experiment conducted in air showed substrate wear. The hillock height increases with fretting amplitude; without lateral sliding, no protrusion is formed. These observations lead to a hypothesis that protrusion formation is due to friction, as is wear, but it remains unclear why one result is favored over the other. This proposal intends to (1) test the friction-induced substrate deformation hypothesis and (2) quantify the wear prevention effect at the nanoscale. The study will utilize alcohol vapor phase lubrication (VPL)—continuous supply of lubricating molecules through the vapor phase [7, 8]—as a means to mitigate friction at a constant applied load. For this study, the PI will bring together VPL and AFM expertise from Penn State and MEMS and nanotribology expertise from Tsinghua University (the host institution in China) and Southwest Jiaotong University (a collaborator with the Tsinghua group). The knowledge obtained from this study will augment fundamental understanding of mechanisms behind these nanoscale tribological effects.

**Background**

As devices become smaller, their surface-to-volume ratio increases, changing the physics governing their operation conditions. This shift is clearly seen in MEMS devices, where friction and adhesion of microscale surfaces make it difficult to utilize full mechanical motions with conventional lubrication strategies [9, 10]. MEMS devices without these motions are already widely-used in everyday life; examples include accelerometers that detect car crashes to deploy airbags and actuators that control the flow of ink in an inkjet printer. Enabling the full range of motion in MEMS would open the door to more complicated and more exciting mechanical applications at the microscale.

MEMS devices are usually fabricated with Si using lithography and surface machining techniques. Nanoscale roughness is inevitable on the silicon MEMS surfaces, which leads to asperity contacts at MEMS interfaces rather than continuous contact as described in Hertzian contact mechanics [11]. Figure 1a is a scanning electron microscopy (SEM) image of a MEMS device used for tribology research, and an AFM image of the surface from such a device, which

![Fig. 1](image)

**Fig. 1** (a) SEM image of a MEMS sidewall tribometer. Electrical comb actuators are used to load the post (A) against the sidewall, which is sheared with the B actuators. Inset is a close-up of the contact area (circled region). (b) AFM image of a MEMS contact surface. The arrows point to nano-asperities, which may dominate tribological properties of this device [6].

![Fig. 2](image)

**Fig. 2** (a) Hillock formation in vacuum and (b) wear in ambient air. Both results are from comparable mechanical conditions [3].
shows two nanoscale asperities dominating the landscape, is given in Figure 1b. These asperities govern the tribological interaction with other surfaces, so studying their friction and wear can shed light on the tribological properties of microscale surfaces in general.

MEMS operation can involve continuous reciprocating motion with very small amplitudes. This cyclical sliding motion is called fretting, and can cause fatigue and wear that greatly reduce device lifetime [12]. In MEMS devices, vibration amplitudes are on the order of nanometers, so the motion is called “nanofretting” [13, 14]. Nanofretting of a single asperity contact can be modeled and studied with AFM [1, 2]. Nanofretting usually results in wearing of the components, but a counterintuitive effect was observed in a recent AFM study for a Si ball rubbing against a Si substrate: the substrate swelled in the sliding contact region forming a small hill (Figure 2a) [3]. The formation of this protrusion or “hillock” was observed only in vacuum; experiments conducted with the same mechanical load and fretting amplitude but in ambient air demonstrated substrate wear (Figure 2b) [3]. The hillock height increased with fretting amplitude in the stick regime and leveled off in the slip regime (Figure 3a); no hillock formation is observed if a normal load is applied without any lateral displacement (such as nanoindentation tests). Thus, it can be hypothesized that protrusion formation is a result of the friction of the sliding interface.

Many other factors were shown to affect hillock formation. The substrate wears, instead of forming hillocks, at higher contact pressures [2]. This indicates that there is some balance between enough friction producing hillocks and too much friction plowing the substrate. The chemical environment at the interface is also vitally important: the chemical treatment of the substrate and the test environment affect whether hillocks will be formed or wear will occur. As shown in Figure 3b, hillock formation occurs preferentially on hydrophobic surfaces in vacuum, while more severe nano-wear occurs on hydrophilic surfaces in humid air [3].

These results lead to the hypothesis that both hillock formation and nano-wear under nano-fretting motion are due to sliding friction, but their severity depends on the interfacial chemistry and environmental conditions. This work proposes to test this hypothesis with alcohol vapor phase lubrication (VPL), an innovative way of controlling the interfacial friction without changing the applied load [8]. Another important task is to quantify the effects of alcohol VPL for prevention of protrusion formation and the nano-wear process.

Alcohol VPL can dramatically affect surface chemistry and tribological processes [4, 7, 8, 15].
Alcohol molecules form hydrogen bonds to the –OH groups present on silicon oxide, and form a monolayer over a wide range of alcohol vapor pressure, as shown in Figure 4 [5]. At atmospheric pressure conditions, the collision frequency of these molecules with the surface is so high that the monolayer will form within a fraction of a microsecond. The resulting monolayer film will have the hydrophobic tail of the alcohol molecules pointing outward, which lowers the interfacial energy and leads to the lubricating effects. Alcohol VPL has been shown to work over a wide range of length scales; nano-, micro- and macro-scale tests have all been successful (Figure 5). The macro-scale test provides a slide track big enough for surface chemical analysis. Infrared vibration spectroscopy and time-of-flight secondary ion mass spectroscopy analyses found that tribochemical reactions can take place in the wear track in alcohol vapor conditions, forming high molecular weight polymeric species [4]. However, these tribo-chemical reaction products do not seem to be the main contributor to the lubrication effect. In fact, they seem to be a by-product of the substrate wear process, which can occur at high mechanical loads or if the alcohol vapor supply is insufficient [16]. The underlying mechanism of alcohol VPL was explored using density functional theory calculations, which modeled wear as dissociation of the Si-O-Si bonds at the SiO2 surface. The calculations showed that the activity of the surface oxide bonds is significantly reduced when they are terminated with an alkoxyl group, compared to the hydroxyl termination case [17].

The effectiveness of VPL has been made especially clear in MEMS tribo-tests [4]. The data shown in Figure 5b were obtained using a MEMS tribometer wherein a curved post was controllably loaded against a flat surface that sled perpendicularly to the post. In dry N2, the device failed due to wear of the initially-coated organic monolayer (without which the friction becomes too high for the post to slide) in less than 10^4 cycles (< 2 minutes at 100 Hz operation); in alcohol vapor environments, the device did not fail even after 11 days. These data were generated by the PI’s group at Penn State in collaboration with Dr. M. T. Dugger at the Sandia National Laboratories. The MEMS tribometer had a low curvature post, which resulted in a nominal contact pressure of only 20 MPa.

The alcohol VPL effects need to be studied with higher curvature (smaller radius) devices or using a single asperity contact (such as AFM), which mimics actual asperity contacts and the resulting very high asperity contact pressures (on the order of a few GPa). Preliminary proof-of-concept tests conducted by the PI’s group at Penn State demonstrated that VPL is effective even at nanoscale single asperity contacts. Figure 5c shows the results of scratching a silicon AFM tip against a silicon wafer (both of which were coated with a native oxide layer). Wear of the substrate (and tip) was observed after scratching in humid air, but there was no wear from scratching in an alcohol vapor environment.
These results are, however, only qualitative – wear or no wear. More systematic and quantitative studies of VPL effectiveness at the nanoscale are needed for molecular-level understanding of the role of adsorbed alcohol molecules in friction and wear reduction of asperity contacts. Such studies can also be used to investigate the origins of the protrusion formation observed for silicon substrates due to nanofretting. The facilities that will enable these studies are available at the State Key Laboratory of Tribology, Tsinghua University (THU) and the Key Laboratory for Advanced Technology of Materials of the Ministry of Education, Southwest Jiaotong University (SWJTU) [1, 18]. These are the proposed studies for the NSF EAPSI fellowship for the summer of 2011.

Research Plan

The proposed research seeks to address three questions: (i) Will hillock formation and wear by nanofretting be mitigated by the introduction of VPL for single asperity contacts? (ii) Will the hillocks be more susceptible to mechanical and/or chemical wear than the bulk substrate, and can this wear also be mitigated by VPL? (iii) How efficient is alcohol VPL for a MEMS tribometer with a high curvature (small radius), multi-asperity contact? n-Pentanol will be the lubricating molecule for this study, allowing for comparison of these studies with previous studies of VPL in MEMS. This section briefly describes the experimental plans that will answer these questions.

As discussed previously, the formation of hillocks seems to be driven by the interfacial friction, as is wear. VPL will be used to reduce the friction at the nanoasperity contact. If friction is indeed the cause of hillock formation, then reducing the friction via VPL should reduce hillock formation at the same applied load or increase the critical load needed to induce hillock formation upon sliding. The effects of changing the applied load (which controls the contact pressure and friction force), displacement amplitude (stick/slip behavior), number of cycles (total frictional energy dispersed), substrate surface chemistry, environment (vacuum and air), and ball/tip size (Hertzian contact area) have already been studied [1-3]. These results can be used to guide the appropriate choices of experimental parameters for the VPL study. Obviously, VPL cannot be employed in vacuum, so all experiments will be conducted in an atmospheric argon environment containing a controlled partial pressure of alcohol vapor. Also, we are limited to oxide terminated silicon to allow for hydrogen bonding. Among the remaining parameters, only the load and displacement amplitude will be explored due to the time limitation.

Hillock formation was observed at applied loads up to about 2 µN for a ~0.5 µm diameter ball, and wear was observed at higher loads [1, 2]. The friction force is the product of the friction coefficient and applied load, as described by Amontons’ 1st Law of Friction. So, if friction is the cause for hillock formation, then reducing the coefficient of friction (COF) should directly increase the maximum applied load which still causes hillock formation. VPL studies at the microscale and macroscale show that the coefficient of friction can be reduced by factor of ~3-4 [4], so hillocks should form under applied loads up to ~6-8 µN. If this maximum applied load does not change due to VPL, then the friction force—which is now 3-4 times smaller—must not be the controlling factor in whether hillock formation or wear occurs; other parameters, such as contact pressure, would then be considered to elucidate the controlling factor.

Hillock height was observed to increase with fretting amplitude in the stick regime and level off in the slip regime. Reducing the COF by VPL would allow the tip to slip at a lower applied lateral force (torque at the surface), so the maximum hillock heights should decrease under alcohol VPL conditions at the same applied load (e.g., 2 µN). If it turns out that alcohol VPL has no or negligible effects on hillock formation under nano-fretting conditions, then it could imply that the friction (or frictional energy dissipation) is not the main cause; this would
mean that simply rubbing the substrate with a sharp tip at a high enough normal load must be the main cause. Distinguishing these two hypotheses experimentally will greatly contribute to future theoretical studies of this nano-fretting behavior.

The observation of hillocks from nanofretting in vacuum (inert environment with no chemical reactions) raises an interesting new point. Since the hillock grows out of the substrate (volume increase), a simple mass balance argument suggests that the density of the hillock will be lower than that of the bulk substrate. In addition, the hillock is likely an amorphous form. Thus, hillocks may wear differently than the pristine substrate surface. Hillocks will be produced in a controlled way and then subjugated to wearing conditions as outlined above. It is expected that they will wear more readily than the pristine crystal surface in argon atmosphere. Once this is confirmed, then VPL can be tested to see if it can prevent or reduce the wear of hillocks. Of specific interest (and importance) is the wear prevention of hillocks using alcohol vapor in humid environments, since water molecules will greatly increase their susceptibility to wear. This will be studied by testing the hillock wear in argon environments containing both water and alcohol vapors at varying ratios.

One of the most important applications for nanotribology knowledge is improvement of the tribological properties of MEMS. The insights attained from these nanoasperity studies will be tested using a MEMS tribometer with a high curvature contact surface design. Such a MEMS device has already been fabricated at Tsinghua University and can be used for the proposed study in the summer of 2011. The main focus of the work is to compare the friction force (direct output from the MEMS device) and degree of wear (post-operation analysis with SEM) of MEMS devices in dry argon, humid argon, and alcohol-containing argon environments. It is very important to evaluate and confirm the efficacy of the alcohol VPL for high-curvature MEMS devices to bridge the knowledge of nanotribology to micro- and macro-scale tribological phenomena. The results of the high-curvature MEMS tribometer study should lie somewhere between the single asperity AFM studies and the low-curvature MEMS tribometer study, and would help complete the picture of VPL efficacy.

**Qualifications and Feasibility**

The main focus of the proposed EAPS work is to initiate collaboration between the PI’s group at Penn State and the research teams at THU and SWJTU, which can be continued by the PI at Penn State and other graduate students at THU and SWJTU long after the PI’s return from China. This ongoing collaboration would result in a greater outcome than completing a narrower scope study while the PI is in China; for this reason, the PI will closely interact with their graduate students and perform initial studies of the three subjects outlined in the Research Plan, even though all of the experiments may not be finished within the allotted time.

Although the Key Laboratory at THU (the biggest tribology laboratory in China) has all the mechanical test facilities needed for the proposed study, they do not have controlled vapor generation/flow systems; the PI has the necessary expertise to construct and use such systems. Additionally, the PI has considerable experience with macroscale tribometers and various imaging modes of AFM, which will allow him to quickly learn AFM nanofretting techniques from the researchers at SWJTU, and quickly and efficiently initiate the proposed research.
Letters of Reference will be provided by:

Anand Jagota  
Professor, Chemical Engineering  
Lehigh University  
PI’s Undergraduate Research Advisor,  
Jan 2007 – May 2009

Seong H. Kim  
Associate Professor, Chemical Engineering  
The Pennsylvania State University  
PI’s Graduate Research Advisor,  
Dec 2009 – Present

**Broader Impacts**

Understanding the tribological properties of nanoasperity contacts will directly benefit MEMS technology with the goal of attaining full mechanical motions. Fully functional microscale machines would have a profound effect across a great breadth of technological applications. The insights obtained from this research will be broadly disseminated through journal publications and presentations at chemical and mechanical engineering conferences held in the US and Asia.

Conducting the proposed research in China will also give the PI insight into Chinese culture and thought processes. The morals, social behavior, and general thought processes of the people of the Western world are very different from those of East Asia and China: the former derive mostly from Judeo-Christian beliefs, whereas the latter come from Confucianism; and it is likely that this philosophical difference in thinking results in a different approach to scientific problem solving. Immersion into research in China will introduce the PI to the Chinese scientific method and foster multifaceted thinking. Indeed, psychologists have shown that living abroad makes one more creative and generally better at problem solving [19]. The PI will share his experiences with peers and collaborators in the hopes of increasing their creativity and productivity. The PI will also learn an appreciation of Chinese history and culture by exploring the modern city of Beijing (THU)—which contains Tiananmen Square, the Forbidden City, the Summer Palace, and a section of the Great Wall—and the more traditional, remote city of Chengdu (SWJTU)—a Mecca of Chinese Buddhism in the southwest of the country. Understanding Chinese culture, and thus being able to more easily interface with Chinese people, will become an ever more important skill as China becomes a world economic and scientific power.
References