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Investigation of the Acoustic Response of a Confined Mesoscopic Water Film Utilizing a
Combined Atomic Force Microscope and Shear Force Microscope Technique

by

Monte Allen Kozell

A thesis submitted in partial fulfillment of the
requirements for the degree of

Master of Science
in
Physics

Thesis Committee:
Andres La Rosa, Chair
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Portland State University
2018

Abstract

An atomic force microscopy beam-like cantilever is combined with an electrical tuning fork to form a shear force probe that is capable of generating an acoustic response from the mesoscopic water layer under ambient conditions while simultaneously monitoring force applied in the normal direction and the electrical response of the tuning fork shear force probe. Two shear force probes were designed and fabricated. A gallium ion beam was used to deposit carbon as a probe material. The carbon probe material was characterized using energy dispersive x-ray spectroscopy and scanning transmission electron microscopy. The probes were experimentally validated by demonstrating the ability to generate and observe acoustic response of the mesoscopic water layer.

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Chapter 1: A Brief Introduction to Probing Microscopy

Surfaces and material properties have been investigated for much of the 20th century. The development of the scanning electron microscope, the transmission electron microscope, the maturity of energy dispersive x-ray spectroscopy, crystallography, the invention of the scanning probe microscope in its many variances and many other microscopy techniques have propelled the current technological revolution that we currently enjoy. It can be stated that age of nanotechnology has arrived, however, the field of acoustics has hardly progressed much towards being a truly nanoscale discipline. Nano-acoustic interactions, as a form of sample manipulation or for sample characterization, has the potential to evolve into a powerful tool to characterize and manipulate biological surfaces and investigate subsurface material properties. To develop such tool, we will investigate the fundamentals of generating and monitoring nano-acoustics of surface interactions.

Section 1.1: Previous Scanning Probe Research

The field of shear force microscopy is still a relatively new and progressing field. In shear force microscopy, a nanometer sized probe is adhered to a tuning fork oscillator and electrically driven to oscillate at a free amplitude resonance frequency while the probe is allowed to interact with a sample substrate. The mechanical or electrical response of the tuning fork is typically monitored as a control parameter, allowing the ability to maintain a fixed set point of height or force between a probe and substrate. Typical benefits of such

interaction are that the probe can interact with the substrate at a fixed height above the substrate, operating in a shear motion, removing a direct probe-sample interaction typical of tapping mode, contact mode and intermittent contact mode of atomic force microscopy (AFM). By removing a direct mechanical interaction, in theory, a probe will avoid mechanically impacting a sample surface, extending probe lifespan and avoiding sample damage.

To measure relative separation distance between a sample and probe, the shear force microscope employs tunneling current of electrons between a probe and the sample surface. Researchers label an arbitrary tunneling current as the sample surface, usually a current of 1nA used to designate the probe-surface contact¹. The tunneling distance measurement method limits samples to clean and conductive samples.

AFM, by contrast, is directly able to mechanically measure and detect a probe-sample interaction using a flexible beam cantilever with a probe fabricated on the end. Both insulating and conducting samples can be used since the afm method is based upon a mechanical interaction. An afm can achieve sub-nanometer height resolution by using a laser reflected off of an afm cantilever and onto a position sensitive photodiode (pspd). As the afm probe is allowed to interact with the sample, the cantilever and subsequently, the reflected laser are proportionately deflected. Figure 1.1 below gives a schematic representation of afm operation. Considering that the afm feedback is cantilever based, it can easily measure many properties of a sample-probe interactions, such as normal force, lateral force and an amplitude-phase response of a vertically oscillating cantilever. A direct

mechanical observation of the probe-surface interaction is a fundamental capability that shear force microscopy lacks and with which the shear force investigation of a wider class of samples would be possible while maintaining the ability to correlate shear force results with probe-sample separation distance.

Figure 1.1: Schematic of AFM Operation. **Image A** Illustrates the standard scanning head configuration. A cantilever is mounted on a z-piezoelectric scanner, with a laser reflected off of the cantilever and onto a position sensitive photodiode. A force applied to the cantilever will result in a deflection of the laser spot across the pspd. Control electronics, not shown, operate a feedback loop to control the force applied to the cantilever tip while scanning with the x-y scanners. **Image B** illustrates the laser reflecting off of the cantilever onto a pspd detector. Notice how the pspd is divided into quads a, b, c, d. Vertical deflections are defined as A-B, with $A = (a+b)$, $B = (c+d)$, and lateral deflections defined as C-D, with $C = (a+c)$, $D = (b+d)$. A pspd gives an electrical signal proportional to measured light intensity and the relative positioning on the pspd. Image A & B from P.J. Eaton and P. West, *Atomic force microscopy* Oxford University Press, Oxford, 2014. pp.23-24.²

The nature of the shear force interaction is a source of controversy in the field of shear force microscopy. Traditionally, there have been two interpretations of the shear interaction. The first interpretation is that the shear force interaction and tuning fork dampening is driven by a probe ‘knocking’ on the sample surface before solid mechanical

contact is established, Ulbrich³. Ulbrich et. al. and others⁴ find that the degree of tuning fork dampening is directly dependent upon probe radius and the relative angle between the oscillatory motion of the probe and the sample surface. Ulbrich also demonstrates that there exists a direct relation between tuning fork drive amplitude and the distance over which the tuning fork is dampened, i.e. dampening occurs over increasingly larger distances as shear amplitude is increased. It is noted that Ulbrich operates the tuning fork at large shear amplitudes, of approximately 6-30nm. In a second interpretation, Karrai, and others,⁵ while operating at sub-nanometer tuning fork drive amplitudes¹ are not able to observe the ‘knocking’ between a probe and sample surface as observed by Ulbrich. Karrai is able to fit his observations using a standard driven harmonic oscillator, while Ulbrich fits his observations using a non-linear model.

Acoustics in shear force microscopy is a new and relatively unexplored field. In recent publications⁶ there have been attempts to complement shear force microscopy by the inclusion of the acoustic observation of the tuning fork probe and the 3rd body medium interactions. It has been observed that the probe-water interaction exhibits a dampening effect on tuning fork amplitude and acoustic observations are direct mechanical observations of probe-water interactions. The figure 1.2 below illustrates the tuning fork probe and sample surface interaction occurring under ambient conditions. The generation of an acoustic response is illustrated in figure 1.2-C.

Figure 1.2: Schematic demonstrates mesoscopic layer-probe interaction **Image A** shows the typical NSOM experimental setup. A probe is adhered to a quartz tuning fork (QTF) and the probe is allowed to interact with a sample surface where a mesoscopic water layer is present. The separation distance is maintained by measuring the electrical response of the QTF as the probe-mesoscopic layer interact. As the interaction occurs, the electrical response of the tuning fork changes. **Image B** shows the probe-sample interaction mediated through a mesoscopic water layer. The probe is stationary in this image. **Image C** shows a probe that is driven parallel to a sample surface. The probe-mesoscopic interaction generates an acoustic signal as depicted as radiating waves which travel both through the open air and through the sample. Acoustic response is detected in the near field regime.

It is the purpose of this thesis to merge complementary aspects of the two fields of microscopy, afm and shear force microscopy, by fabricating and characterizing a tuning fork with a flexible afm beam cantilever adhered onto a tuning fork tine. This will allow the direct ability to mechanically observe the true sample separation height, while maintaining the ability to investigate the dampening nature of the shear interaction of a probe and the mesoscopic water layer. The inclusion of an acoustic sensor will allow the direct ability to observe viscous and/or elastic interactions. Previous work has allowed the implementation of shear motion in conjunction with normal force measurements⁷ with the use of a piezoceramic mounted beneath the sample substrate. In such work, lateral force measurements were made with the afm, however, acoustics signals were not observed.

Section 1.2: Proposed Cantilever Fabrication

It was decided to incorporate a force sensitive cantilever onto a tuning fork as one modular apparatus because there are instances in which it may not be feasible to piezoelectrically vibrate a large sample, i.e. full wafer analysis, in situ biological experiments. Incorporating the cantilever furnished the option to place an acoustic sensor beneath the sample substrate, reducing the acoustic losses from an otherwise increased acoustic travel distance.

We have built two separate apparatuses, the first of which is an afm cantilever directly adhered to a tuning fork. This apparatus is seen in the figure 1.3 below. The second apparatus is a tuning fork which has a beam cantilever directly milled into a tine on the tuning fork using the focused ion beam (FIB) milling process. This apparatus is seen in figure 1.4 below. Ideal cantilevers will be force sensitive and used to acoustically excite the mesoscopic region. The two apparatuses will have a carbon nanoprobe acting as a afm tip/probe, which is ion beam deposited (IBD) onto the cantilever. The use of a custom probe allows the fabrication of a geometrically repeatable devices. It has been previously demonstrated that tip geometry plays a crucial role in tip-sample interaction force ⁸, therefore it greatly affords flexibility in experimental design to have the ability to tune tip geometry.

Cantilever Configuration #1

Figure 1.3: Illustrates an afm cantilever directly applied to a tuning fork to act as a force sensor (**Image A**). **Image B** is a close up of the cantilever. Fabrication will be described in later sections.

Cantilever Configuration #2

Figure 1.4 Illustrates a cantilever that was focused ion beam milled into a tuning fork to act as a force sensor (**Image A**). **Image B** is a close up that shows the milled cantilever and the ion beam deposited tip. Fabrication will be described in later sections.

Section 1.3: Cantilever & Tip Fabrication Requirements

To fabricate an afm cantilever that is able to investigate normal force interactions, a few key design parameters must be conceptually investigated. The primary considerations for probe design are the mechanical advantage of the system, which is directly related to cantilever sensitivity, cantilever geometries such as cantilever length, width and thickness, which are directly related to the stiffness for the cantilever, and the tip probe material and tip probe radius, which are related to normal forces which dictate whether the probe will comply with the sample surface upon interaction. Each parameter will be discussed with the goal of offering insight into how changes in each parameter affect the ability of the afm cantilever to measure normal force and generate an acoustic signal.

Section 1.4: Interaction Forces in AFM

Before we begin to describe the process of probe fabrication, it is useful to discuss the interaction forces that we expect to encounter during our experiment. There are many probe-surface interaction mechanisms. Table 1 below describes many of the interaction mechanisms found in probing microscopy, with the approximate interaction strength and the effective range of the interaction labeled. It is clear that there exists significant overlap between many interaction mechanisms, and interaction strengths. It is difficult to isolate one particular force as being the dominant factor as a function of distance. This contributes greatly to the uncertainty in interpreting force measurements. It is often left up to the experimenter to use best judgement and a scrupulously designed experiment to estimate the forces present and to estimate the magnitude of each force. We will do the same, while

acknowledging the inadequacies of such method. The main forces present in our experiment are expected to be Van der Waals dipole forces, possibly surface charges with electrostatic interactions, and the capillary forces from the formation of a mesoscopic layer.

Table 1: Range of Interaction		
Type of Force	Dependence of energy on distance (d)	Range (nm)
Intramolecular (Ionic or Covalent)	$1/d$	<1
London Dispersion	$1/d^6$	0.5 to 5
H-bonding	$1/d^3$	0.5 to 3
Dipoles	$1/d^3$	0.5 to 3
Electrostatic	e^{-d}	10s to 100s
Van der Waals	$1/d$	5 to 10
Solvation	e^{-d}	<5
Hydrophobic	e^{-d}	10s to 100s

Ref P.A. Maurice, Environmental surfaces and interfaces from the nanoscale to the global scale (Wiley, Hoboken, 2009, P. 94.)^{8,9}

Section 1.5: Capillary Forces

The main purpose of our experiment is to generate an acoustic signal from the interaction with the mesoscopic water layer. We will be conducting our experiments in high humidities conditions, at 60%+. At high humidities, there will be a mesoscopic water layer present on both the afm probe and sample surface¹⁰ with assumption that both surfaces are hydrophilic. To gain an appreciation of the capillary interaction, a typical schematic is shown illustrating the formation of a capillary bridge between an afm probe and a sample surface in the figure 1.5. Figure 1.5 is typically used for capillary force

modeling using the Derjaguin, Muller, Toporov (DMT) model. This model will not be used in our work due to the scale of our experiment but the schematic is mentioned here to illustrate the capillary formation between a probe and a hydrophilic surface.

Figure 1.5: Illustrates the formation of a liquid capillary bridge between a sample substrate and an afm probe approximated as a sphere. Critical dimensions are labeled. Figure reproduced by following M. Rosoff, *Nano-Surface chemistry* (Dekker, New York, 2002), P. 23. ¹¹

Section 1.6: Electrostatic Forces

Electrostatic forces are observed in the presence of charge on the afm probe and/or the sample substrate. These forces can be either attractive or repulsive depending upon the magnitude of charge present. In our experiment, our sample substrates are SiO₂ and mica. The SiO₂ is insulative in nature and does not inherently carry a net charge. Mica has been shown to contain K⁺ ions in the presence of a mesoscopic water layer¹⁰. Additionally, we will be producing a gallium ion beam deposited (Ga-IBD) carbon tip as an afm probe. Through EDX, we find that the (Ga-IBD) carbon probe contains 25% Ga atoms in

composition, which is in agreement with other findings¹². Therefore, the possibility of free Ga ions remaining in the probe is present. Having a sample surface which can contain free K⁺ ions and an afm probe which can contain Ga⁺ ions, there exists the possibility of ion-ion repulsion.

Section 1.6: Van der Waals Forces

Van der Waals forces are representative of induced dipole and quadrupole interactions. Van der Waals forces arise from quantum mechanical distribution of electrons and are generally non-localized in nature. Van der Waals forces are long range, attractive, and are said to be a weak interaction force. Most direct measurements of Van der Waals forces are performed in high vacuum systems where other interaction mechanisms are reduced, however, the Van der Waals force is present under ambient conditions as well⁹.

Chapter 2: Normal Force Models

To properly model the measured normal force, it is necessary to choose an appropriate model that fits the experimental geometries such as probe radius, interaction distances and environmental conditions involved. Our experiments will be performed from the mechanical contact point with the sample surface, up to a distance of about 100nm above a sample surface. The experiment will be performed under ambient conditions with enhanced humidity to promote the formation of a mesoscopic water layer. In our experiments, we used an afm tip of approximately 100-250 nm in radius. Therefore, it is useful to investigate a model that is able to represent normal forces in both the short range and the long-range regions, while approximating in ambient conditions. Such “complete” force models do not exist; therefore, we will attempt of model only parts of the interaction force curve where models are well defined and experimental conditions match the experiment domain.

Section 2.1: Sphere-Plane (SP) Force Model

To model the long-range interaction forces (Van der Waals) between the probe and substrate, we will consider the Sphere-Plane (SP) model which was derived by Hamaker in 1937¹³. Hamaker was able to obtain a relation that represents a geometrically simplified approximation of an afm tip-surface interaction, with the afm tip being approximated as a sphere and the sample surface as a flat plane. The force F_{sp} relation for the sphere-plane model is given as ¹³

$$F_{sp} = -2AR^3/3z^2(z+2R)^2 \quad (EQ 2.1)$$

where A is the Hamaker constant with units of energy, R is the probe radius and Z is the distance between the spherical tip and the planar surface under static conditions. The Hamaker constant is an energy scalar that is used to represent the molecule to molecule interactions. Hamaker shows that A can be expanded to represent n number of materials, allowing for the modeling of complex multilayer interfaces, such as the long range (non-contact region) afm force interactions between a tip, a mesoscopic layer and a lower substrate. The SP model is not valid for contact regions since it cannot model mechanical contact, and as such, it should not be applied within contact regions.

To use the SP model to correctly fit experimental data, we will need to directly measure the Hamaker constant A for the specific experimental materials and atmospheric conditions used. The Hamaker constant is dependent upon tip material, sample substrate material and the specific humidity conditions. Different combinations of tip and substrate materials will have different Hamaker constants. Critics of the Hamaker constant point out that it depends highly upon experimental conditions, such as a change in humidity. In Hamaker's landmark paper of 1937, he describes the Hamaker constant as a fitting parameter that can be used to describe the attractive force component between two objects separated by an arbitrary distance. He describes the Hamaker parameter as being able to represent an object that is a composite of multiple layers, such as a substrate with a mesoscopic film present. Hamaker gives an example of two different composition particles embedded in a third material, a fluid, giving the Hamaker constant in an expanded form,

$$A = \pi^2 \{ q_1 q_2 \lambda_{12} + q_{02} \lambda_{00} - q_{01} q_{02} \lambda_{01} - q_{01} q_{02} \lambda_{02} \} \quad (EQ 2.2)$$

With q_i being atom densities, and the λ_i being the London-van der Waals constants for the pairs of atoms indicated by the indices¹³. This expansion of the Hamaker constant is used to justify the validity for applying the Hamaker force model in multi-layered interactions. A direct measurement of the Hamaker constant and experimental fitting with the SP model will be performed in chapter 5 for our experimental conditions.

Section 2.2: Introduction to a simple force-displacement curve

A force-displacement curve is obtained as a cantilever is slowly lowered to interact with a sample substrate while the normal force (vertical cantilever deflection) is monitored and recorded. A typical afm force-displacement curve is shown below. The relative cantilever bending motion is illustrated.

Figure 2.1: The figure illustrates the typical force curve with adhesion hysteresis present in the retraction curve. Notice that attractive forces result in a cantilever bending towards the sample substrate, while repulsive forces result in a bending away from the surface. Plot is taken from page 65, Atomic Force Microscopy, by Peter Eaton, Paul West.¹⁵

Notice that as the afm probe approaches the sample surface, the attractive van der Waals forces pull the tip into contact with the sample substrate. This is known as a snap-to-contact point and is labeled as point B in the figure above. A cantilever acts as a spring, as force is applied, the cantilever exerts a restoring force, maintaining an equilibrium at large tip-to-sample distances. At point B, the cantilevers restoring force is overcome and the tip snaps into mechanical contact with the sample substrate. This effect is known as snap-to-contact and it prevents the probe from fully sampling the attractive forces as a function of tip-to-sample separation distance. One of the chief experimental considerations of our experiment is the ability to characterize the mesoscopic water layer. This layer exists close to the sample surface where forces are strong and attractive, therefore, it is decided that our cantilever should be “stiff” so as to avoid a snap-to-contact. Our definition of a “stiff” cantilever is a cantilever that has a large spring constant in the vertical direction. Parameters that define a cantilevers spring constant will be discussed in a later section and a quantitative estimate of a stiff spring constant will be provided.

Section 2.3: A Double jump-to-contact

The previous section described a force curve that was representative of a force-displacement interaction involving solely Van der Waals forces. Under ambient conditions there exists a mesoscopic water layer present upon hydrophilic surfaces. As an afm probe performs an approach curve onto a hydrophilic surface in high humidity conditions (Humidity > 60%), it must pass through two distinct boundaries; initially it must pass

through the mesoscopic water layer and secondly, it will interact with the underlying substrate, SiO₂ or Mica in our experiments. Therefore, it will experience two distinct and observable snap-to-contacts¹⁶. An example of a double snap-to-contact is shown below in figure 2.2. In the figure below, the initial snap-to-contact is labeled as A. This corresponds to the tip-mesoscopic layer interaction. The second snap-to-contact is labeled as B, this represents the tip-sample interaction. Notice that the force at point B is not zero, even though the tip is in direct contact with the sample surface. The zero-force point is located approximately 6nm to the left. At point B, the cantilever can be thought of as being bent downward into mechanical contact with the sample surface, with the source of attraction provided by Van der Waals and capillary forces. As the cantilever approaches, further toward the substrate, a repulsive electron-electron force (Pauli Exclusion Principle) counteracts the attractive forces and a force equilibrium is temporarily achieved at the zero-force point. This zero-force point is identified as the intersection of a dotted horizontal line and a solid vertical line in figure 2.2.

Figure 2.2: The figure shows an approach curve illustrating a double jump-to-contact, with the initial jump-to-contact labeled as point A, and the subsequent jump-to-contact labeled as point B. At point A, the interface is a transition from air to water. At point B, the interface is water to mica. The **lower** plot has the relative positioning and observed forces at each interface. This approach curve was obtained with humidity of 63.8%. A non-contact cantilever of spring constant $\sim 40\text{N/m}$ was used.

Section 2.4: Estimating the initial snap-to-contact point

Predicting where a snap-to-contact point will occur is handled by Soma Das, Sreeram and Raychaudhuri¹⁷. It is found that the snap-to-contact position is related to the tip radius, the cantilever spring constant in the normal direction, and the material interaction parameter, the Hamaker constant. The relation has the form

$$H_j^3 = 27/24 \cdot (H \cdot R_t / K_c) \quad (\text{EQ 2.3})$$

with H_j being the jump into contact position, H being the Hamaker interaction constant, R_t is the radius of the tip and K_c is the cantilever spring constant in the normal direction. This relation assumes only van der Waals interaction and a large radius tip is used. To get an estimate the snap-to-contact position of a Si_3N_4 cantilever on a mica surface, Somas Das, et al, used a tip radius $R_t = 35\text{nm}$, cantilever spring constant $K_c = 0.1\text{N/nm}$, and a Hamaker $H = 0.64 \times 10^{-19}\text{J}$. A jump-into-contact position of 2.9nm was found. A general trend that was observed was that the snap-to-contact position is both dependent upon the tip radius and the tip cantilever spring constant. The Hamaker interaction parameter acts as a scalar and is highly dependent upon humidity. Uncertainty in the snap-to-contact point is highly dependent upon the zero-force point and the relative positioning of the sample surface, the zero-distance point.

Using equation 2.2 and solving for the Hamaker constant, the experimental observation of a force curve can be used to obtain the Hamaker constant between two known surfaces. This allows the modeling of the attractive forces before the probe directly contacts these surfaces. In chapter 5, we will use this approach to obtain an estimated Hamaker constant between mica and an ion beam deposited IBD carbon probe.

To fabricate a cantilever that is able to probe down to the surface contact point without a snap-to-contact point, we need an estimate of the required spring constant for such cantilever. Using equation 2.2, we will try to estimate the snap-to-contact point for a standard non-contact Si_3N_4 afm cantilever on a mica surface with a 100nm radius and a spring constant of varying values. We will use the same Hamaker constant as Somas Das,

$H = 0.64 \times 10^{-19} \text{ J}$ since the materials are the same. The results are displayed in the table 2 below. It is evident that the initial snap-to-contact will not occur until the tip is within a sub nanometer of the sample surface given that the spring constant is sufficiently large.

Table 2: Estimated snap-to-contact point	
Spring Constant K	Snap-to-contact point
1 N/m	1.93 nm
10 N/m	0.89 nm
20 N/m	0.71 nm
30 N/m	0.62 nm
Parameters: $H = 0.64 \times 10^{-19} \text{ J}$, Surface=Mica, Tip= Si_3N_4 , $R_t = 100 \text{ nm}$	

Since we are using a custom tip, which we do not yet know the Hamaker constant, this is only a guide for suggested cantilever spring constant values. Hamaker constants can vary from low values 10^{-21} J to larger values 10^{-18} J . Using these Hamaker values with the above relation (EQ. 2.2), we can refine our estimate of the snap-to-contact point in an attempt to predict a range of cantilever spring constants that are sufficient to prevent a snap-to-contact for the probe we are designing.

As shown in the table below, it is observed that at low Hamaker constants, $\sim 10^{-21} \text{ J}$, the interaction energy between the tip and sample is low, therefore, softer spring constant cantilevers may be used. However, with large Hamaker constants $> 10^{-18} \text{ J}$, the snap-to-contact point occurs 10 times further away, i.e. there is a larger interaction energy between the tip and sample. In our experiment, there will be a capillary force present which is an

attractive force in addition to the attractive Van der Waals forces. These forces are additive in nature. In order to prevent a premature snap-to contact by these two attractors, it is decided that a cantilever with a spring constant of a minimum of $K = 50 \text{ N/m}$ will be used.

Table 3: Estimated snap-to-contact point			
Spring Constant (K) with Low Hamaker 10^{-21} J	Snap-to-contact point	Spring Constant (K) with High Hamaker 10^{-18} J	Snap-to-contact point
1 N/m	0.41 nm	1 N/m	4.16 nm
10 N/m	0.19 nm	10 N/m	1.93 nm
20 N/m	0.15 nm	20 N/m	1.53 nm
30 N/m	0.13 nm	30 N/m	1.34 nm
50 N/m	0.11 nm	50 N/m	1.13 nm
Parameters: Surface=Mica, Tip= Si_3N_4 , $R_t=100\text{nm}$			

It should be noted that this relation for predicting jump-to-contact point is only valid for the first jump-to-contact point and cannot be used for the second jump to contact point since the relation only accounts for Van der Waals forces and excludes complex capillary effects that are present once the tip has entered the mesoscopic region.

Section 2.5: Cantilever “Stiffness” Introduced

In the previous section, it was illustrated that in order to fully characterize the mesoscopic layer, a “stiff” cantilever is needed. A cantilever spring constant is given as a functions of cantilever material, and geometries. The vertical spring constant of an afm cantilever is given as

$$K_{ver} = w * E / 4 * (t / L)^3 \quad (\text{EQ 2.4})$$

with K_{ver} being the vertical spring constant of the cantilever, w being the cantilever width, E being the Young's modulus of the cantilever, t being the cantilever thickness, and L being the cantilever length¹⁵. We will be fabricating our cantilevers out of silicon and quartz, so the Young's modulus will be a fixed early on. We are left with cantilever geometry as our tuning parameters to fabricate a cantilever with a desired stiffness.

Section 2.6: Mechanical Amplification

In narrowing our cantilever geometries down, we will consider the role of cantilever length on cantilever sensitivity. These two properties are linked by a process known as mechanical amplification. The XE-120 afm used in our experiment utilizes an optical mechanical amplification to increase the pspd sensitivity to a cantilever displacement.

An ideal mechanical lever, is a lever that ideally never flexes, and only bends; thus, an afm cantilever, being of crystalline material, is a close approximation. The mechanical advantage of a lever is defined as the ratio of two lengths that pivot around some central point. On an afm, these two lengths correspond to the cantilever length and the optical path that the laser takes once reflected from the cantilever to the pspd. This is shown in the figures 2.3, 2.4 below. In the context of an afm system, mechanical advantage has the following form,

$$\text{Mechanical Advantage} = \text{Optical Path Length} / \text{Cantilever Length}$$

$$(\text{MA}) = (L1/L2)$$

Figure 2.3 gives two examples of mechanical advantage, with one apparatus producing no mechanical advantage and the other apparatus producing a gain of 3. Such gains are achieved by altering the ratio of path lengths. In the figure 2.4, it is illustrated how an afm optical path and the cantilever constitute a system that exhibits mechanical amplification.

Figure 2.3: Schematic illustrating mechanical amplification. **Top** Shows an example of mechanical amplification with a 1:1 ratio, both lengths are equal. **Bottom** Shows that mechanical amplification can be modified by changing the relative lengths of each side. Here L1 is increased to 1.5 and L2 is decreased to 0.5. The mechanical advantage is increased by a factor of 3.

Figure 2.4: Demonstrates optical path length and mechanical amplification of an afm scanning head. **(Top)** Shows the standard afm geometry. **(Below)** Shows the optical path (red dots) and the cantilever length (green line). Notice how both lengths pivot around the afm tip. As the cantilever is lowered while in contact with the substrate, the cantilever displacement distance is amplified by the mechanical advantage, producing a larger displacement of the laser spot on the pspd.

Source of image: Park AFM XE-120 user manual page 29.¹⁸

By applying the principle of mechanical advantage to the afm cantilever and the optical path length of the laser, one can gain insight into choosing a cantilever length. Consider the standard afm tapping mode cantilever, which typically have a length of about 125um. The optical path length of

the XE-120 afm is estimated to be between 4.0-5.0 cm, with an average 4.5 cm. Using these geometries, the mechanical advantage of the tapping mode cantilever is estimated to be 360 (optical path / cantilever length, = 4.5cm/125um = 360). The relationship between laser deflection and cantilever deflection is related by the mechanical amplification of the system and thus the laser displacement is determined by

$$\text{Laser Displacement} = \text{Cantilever Displacement} * \text{Mechanical Advantage}$$

Now, applying a 10nm displacement to the cantilever and is it found that the afm laser will deflect approximately 3.6 um on the pspd.

$$3.6\mu\text{m (Laser Displacement)} = 10\text{nm (Cantilever Displacement)} * 360 * (\text{Mechanical Amplification})$$

The XE-120 afm manufacturer PSIA states that the pspd itself is sensitive to laser deflections of approximately 1nm^{19} , therefore, the standard afm cantilever performs well as a force sensor.

Now we would like consider other cantilever lengths, such as a 50 um cantilever and a 1.4 mm cantilever. The 50um cantilever is potentially representative of an ion beam milled cantilever and the 1.4 mm cantilever is representative of a tuning fork tine as cantilever without modification. By considering these two geometries, one can compare how a cantilever that has been ion beam milled into a tuning fork will perform versus how a tuning fork tine unmodified will perform as a force sensor. Using the same optical path (4.5 cm) length for these cantilevers as before, the mechanical advantages were found to be 900 ($4.5\text{cm}/50\mu\text{m}=900$) for the milled cantilever and 32 ($4.5\text{cm}/1.4\text{mm}=32$) for the tuning fork cantilever. To make the comparison consistent, we again apply a 10 nm cantilever displacement to each cantilever, and it is found that the expected laser deflection for a 50 um milled cantilever is 9.0um and the laser deflection for the 1.4mm tuning fork tine is 320 nm. These three cantilever sensitivities are summarized in the table below.

Table 4: Varying Cantilever Length				
L1 : Cantilever Length (um)	L2 : Optical Path Length (cm)	Estimated Mechanical Advantage	Applied Cantilever Displacement (nm)	Expected Laser Displacement of PSPD (um)
125 um	4.5 cm	360.0	10nm	3.60 um
50 um	4.5 cm	900	10nm	9.0 um
1400 um	4.5 cm	32.15	10nm	321.5 nm

Comparing the mechanical amplification of the standard non-contact afm cantilever of 125 um length with the ion milled cantilever of 50 um length, a 250% increase in laser deflection is observed with the shorter cantilever. Comparing the standard afm cantilever to the longer tuning fork tine, a 91% decrease in laser deflection is observed for the longer tuning fork tine. This illustrates that a shorter cantilever is a more sensitive force sensor.

In our experiment, our cantilever is fabricated onto a QTF tine which subsequently had to be mounted on the afm resulting in a variance in mounting height and thus a change in optical path length. Therefore, it is of interest to examine the effect that an increased optical path length will have on a cantilever sensitivity. The cantilever and QTF was mounted approximately 100um lower than the standard afm cantilever. This results in a net increase in the overall optical path length. This is depicted in the figure 2.5 below, a QTF is mounted lower, thus the optical path length is increased. The table 5 below shows how such an increase in optical path will change the total mechanical amplification for each cantilever. It is found that a change in 100 um of the optical path results in a 2.2% increase in laser displacement.

Figure 2.5: Illustrates how decreasing the mounting height of a cantilever in the z-axis results in an increase in the optical path length (red dots). The **left** image depicts a standard afm cantilever mounted at the standard height. The **right** image depicts a tuning fork cantilever mounted at a lower z-height D, with an increased optical path length.

Table 5: Varying Optical Path Length				
L1 : Cantilever Length (um)	L2 : Optical Path Length (cm)	Mechanical Advantage	Cantilever Displacement (nm)	Laser Displacement of PSPD (um)
125 um	4.6 cm	368.0	10nm	3.68 um
50 um	4.6 cm	920	10nm	9.2 um
1400 um	4.6 cm	32.85	10nm	328.5 nm

Comparing changes in cantilever length and optical path length, it is found a change in cantilever length will result in large changes in mechanical amplification, while changes in optical path length result in minimal changes in mechanical amplification. Therefore, since the optical path length is rigid distance on a commercial afm, the largest contributor to afm sensitivity is cantilever length. Based on these factors, it was decided that an ideal

cantilever would have a length between 50-100um to maintain force sensitivity and stiffness.

Section 2.7: Lateral Spring Constant

The next parameter to investigate is cantilever width. Cantilever width plays an important role in afm measurements. A typical afm non-contact mode cantilever width is between 22-37um (Nanosensors, NCH-W). The cantilever width plays a key role in the lateral spring constant of cantilever design. Lateral spring constant designates the stiffness of a cantilever to bending parallel to the scan direction. Our experiment will involve a cantilever that is being oscillated parallel to a sample surface, therefore it will encounter a lateral force as the probe interacts with the mesoscopic water layer and sample surface. Our interest is to characterize the normal force while generating an acoustic interaction with the mesoscopic layer, hence a cantilever that is rigid in the shear dimension is necessary. Shear motion is parallel to a sample surface. The equation for the lateral spring constant has a similar form as the normal spring constant, except the thickness and width parameters are exchanged. The lateral spring constant is given as

$$K_{lat} = t^*E/4*(w / L)^3 \quad (EQ 2.5)$$

with K_{lat} being the lateral spring constant, t, w, L being cantilever thickness, width, and length¹⁵. Notice that after having chosen a fixed range of cantilever lengths in the previous section, that the cantilever width has the largest overall impact on lateral spring constant, with a cubic power. To tune the lateral spring constant for rigidity, it was decided to fabricate a cantilever on the higher side of the commercial cantilever width dimensions, a

width of at least 35 μ m would be fabricated. In a later section, once the cantilever thickness is chosen, we will estimate the lateral spring constant.

Section 2.8: Laser Alignment and Interference

One potential design issue pertaining to cantilever width, is the instance when the afm laser spot size is larger than the cantilever is wide and spills over the edges of the cantilever and onto the sample surface below¹⁵. This laser spot is then reflected off of the sample surface and back onto the pspd, creating laser interference. As the z-piezoelectric is extended and retracted, a periodic laser signal of minimum and maximum intensities is observed¹⁶. A typical approach curve, as displayed in the figure 2.6, shows such laser interference. The standard method for remediating laser interference is re-aligning the laser on the cantilever or repositioning the sample. By using a custom cantilever, care must be taken to fabricate a device to minimize laser interference. Our choice of fabricating a cantilever of a minimum width of 35 μ m should be sufficient at minimizing laser interference.

Figure 2.6: A typical normal force approach curve that illustrates laser interference. Sample substrate was V1 grade Mica mounted perpendicular.

Chapter 3: Cantilever and Tip Fabrication

We now have enough to fabricate a cantilever with a geometry that allows the probing of the mesoscopic layer with both normal force sensitivity and rigidity in the shear dimension for the generation of an acoustic signal. The following sections will recap equations describing cantilever stiffness, and then, the fabrication process for each cantilever will be described. As previously stated, two separate designs were fabricated, a FIB milled cantilever into a tuning fork tine and a commercial afm cantilever was attached to a tuning fork tine. Both cantilevers had a Ga ion beam deposited carbon tip fabricated on the cantilever to act as a geometrically repeatable probe.

Section 3.1.1: Method #1-Focused Ion Beam Milled Cantilever Fabrication

To fabricate a cantilever onto a tuning fork tine, a dual beam (Focused Ion Beam/Scanning Electron Microscope) FIB-SEM FEI Helios 400s tool was used. A beam cantilever was ion milled into a tuning fork tine as shown in figure 3.1. The critical dimensions of the beam cantilever were the length, width, thickness and tip height. These four parameters are used to tune the cantilever spring constants in the normal direction, lateral direction and torsional direction. Only the torsional spring constant is dependent upon the tip height, and as such, the tip height will be discussed in the tip fabrication section 3.1.4.

Equations showing the relation between spring constants and cantilever dimensions are shown in table 6. The milled cantilever beam dimensions are shown in table 7. A cantilever length of approximately $L = 76 \text{ } \mu\text{m}$ was chosen to enhance cantilever sensitivity. A cantilever width of approximately $W = 35 \text{ } \mu\text{m}$ was used.

To tune the cantilever spring constants for desired performance, the only parameter remaining was cantilever thickness t . Ultimately, a cantilever of $5 \text{ } \mu\text{m}$ thickness was produced. This resulted in a cantilever with a stiffer normal spring constant than a standard tapping mode cantilever. A tapping mode cantilever has a spring constant ranging from 20-70 N/m, while the fabricated cantilever has a normal spring constant of approximately 170 N/m. This will allow the fabricated cantilever the ability to probe closer to the sample surface while simultaneously delaying the jump-to-contact point closer to the surface. The lateral spring constant was found to be 10,900 N/m and the torsional spring constant was

17,959 N/m. Both torsional and lateral spring constants are sufficiently large that displacement in either dimension will be small compared to normal displacement. Table 8 shows the material properties used for determining the spring constants and contains material properties of the tuning fork (SiO_2) and the ion beam deposited carbon used to fabricate the tip. Table 9 summarizes the estimated spring constants of the fabricated cantilever.

Table 6: Equations for Spring Constants	
Normal Force Constant K_{ver}	$K_{ver}=w*E/4*(t/l)^3$
Lateral Force Constant K_{lat}	$K_{lat}=t*E/4*(w/l)^3$
Torsional Force Constant K_{tor}	$K_{tor}=w*(G/3)*(t^3/l)*I/(H+t/2)^2$
t=thickness, w = width, l= length, H = tip height; Source ¹⁵	

Table 7: FIB Milled Cantilever Dimensions					
Tuning fork Cantilever Dimensions	Length (l)	Width (w)	Thickness (t)	Tip Height (H)	Tip Radius (R)
	76.67 um	34.67 um	4.854 um	5.77 um	124 nm

Table 8: Material Properties of QTF and IBD Carbon		
Quartz Tuning Fork (SiO ₂)	Young's Modulus E(Perp) & E(Para) Shear Modulus G	E(perp) = 78.7 GPa ²⁰ E(para) = 98.2 GPa G = 31.14 GPa ²¹
IBD Carbon (Used as the probe tip material)	Shear Modulus G	G = 70 GPa ²²

Table 9: FIB Milled Cantilever Spring Constants		
K_{ver}	K_{lat}	K_{tor}
173 N/m	11,019 N/m	17959 N/m

Section 3.1.2: Reflective Laser Pad

On the top side of the FIB milled cantilever, an ion beam deposited platinum was fabricated into a rectangle. The role of this platinum pad was to increase the reflectivity of the cantilever to increase laser reflection. The deposition process entailed the use of the in-chamber gas injection system. The dimensions of this pad were approximately $35 \times 45 \mu\text{m}^2$. This platinum pad is shown in the figure 3.2-Image C. Fabrication is shown in figure 3.1-3.2.

Section 3.1.3: Tip Base and Tip Fabrication

Afm tips have been fabricated using a FEI Helios 400s dual beam SEM-FIB with an integrated carbon gas injection system (GIS). Tips with radius of $\sim 100\text{nm}$ radius have been fabricated using ion beam deposition. Naphthalene, C_{10}H_8 , was the carbon gas source for all carbon probe depositions (FEI, Helios 400s User Manual). Before the carbon tip was fabricated, a rectangular platinum base was fabricated to serve as a structure onto which a probe can be deposited. A Gallium ion beam deposited platinum was deposited onto the tuning fork using an in-situ platinum gas injection system, constituting the rectangular tip-base. The platinum precursor gas was (methylcyclopentadienyl) trimethyl platinum, $\text{C}_9\text{H}_{16}\text{Pt}$ (FEI, Helios 400s User Manual). The rectangular base, as seen in the figure 3.2-Image E, figure 3.3-image B below has a pyramid geometry. The platinum base was fabricated to be $8 \times 8 \mu\text{m}^2$.

The base was built by sequentially deposited platinum layers that were reduced in width by 500 nm per layer deposition. 13 layers of platinum were deposited. Once the

width of the base was 1.5 μm , gallium ion deposited carbon was applied. The final tip was deposited using spot mode, i.e. the raster scanning was disabled. Tip growth occurs rapidly, often taking less than 30sec. The total height, (base height + tip height) was $\sim 5\mu\text{m}$ in height. The final tip material was ion beam deposited carbon. The current density for Pt deposition is 2-6p A/ μm^2 , and the current density for Carbon deposition is 1-10p A/ μm^2 .²³

Section 3.1.4: Electron and Gallium Ion Beam Deposited Carbon Tips

Electron beam carbon deposition onto tuning forks composed of the highly insulating quartz material proved difficult due to electron charge build-up. Charge buildup is a problem when performing electron beam deposition on insulating materials. Such charge buildup results in a repulsive electric field developing on the tuning fork tine, causing electron beam induced tip growth to be skewed, resulting in angled tips. Proper grounding of the tuning fork electrodes using silver paint (Ted Pella, conductive silver paint) allowed charge build-up to be reduced, but not always eliminated.

Due to this obstacle, it was decided to produce Gallium ion deposited carbon tips for experimental use. Gallium ions are 127,000 times more massive (Gallium 69.723u, Electron $5.485 \times 10^{-4}\text{u}$) than electrons, therefore, charge build-up has a lesser deflective effect on gallium ion beam path. A gallium ion, being opposite charge of an electron, is attracted to surfaces with built-up electron charge, therefore both negligible beam deflection results and the positive ions act to neutralize the negative charge build up. Due to the limited resolution of the ion beam, tip radius of 100nm were reliably produced. The

table 10 below shows the deposition parameters used for final carbon tip fabrication. The figures 3.1, 3.2, 3.3 the fabrication process for the FIB milled cantilever with a laser platinum pad and (IBD) carbon tip.

Table 10: Summary of Electron-Beam and Ion-beam Tip Deposition Parameters			
Deposition Parameters	Accelerating Voltage	Beam Current	Deposition time
EBD Carbon Tip	25 kv	25pA	65 sec
IBD Carbon Tip	30 kv	13pA	15 sec

Figure 3.1: A schematic illustration showing the tuning fork with a beam cantilever that was fabricated using a gallium Focused Ion Beam (FIB). **Image 1** shows the tuning fork with a corner of the tuning fork tine ion beam milled away. Red dots show the volume to be removed. **Image 2** illustrates the tuning fork tine post FIB milling. Red dots illustrate another milled region that allows the cantilever the ability to flex in the vertical direction. **Image 3** illustrates a cantilever that flexes vertically. **Image 3B** shows the cantilever range of motion. **Image 4** illustrates the cantilever after an ion beam deposited platinum pad was deposited on the top of the cantilever. The purple color represents an ion beam deposited platinum pad used for laser reflection. **Image 5** The cantilever is flipped over so that a carbon probe can be fabricated on the bottom of the cantilever. **Image 6** and **6B** illustrates the ion beam deposited probe (green color) onto the end of the beam cantilever.

Figure 3.1-1: Schematic illustrates the FIB milling of the cantilever onto the tuning fork tine. **(A)** The tuning fork is aligned parallel to the ion beam. **(B)** A beam cantilever is milled into the tuning fork tine. **(C)** Shows the resulting beam cantilever. Ion beam (Accelerating voltage) currents ranged from (30kv) 65nA for rough milling, to (30kv) 1nA for fine polishing.

Figure 3.1-2: Schematic illustrates the ion beam deposition of a reflective platinum pad on the top of the beam cantilever. **(A)** The tuning fork is rotated 180 degree so that the beam cantilever is aligned perpendicular to the ion beam path, with the **top of the cantilever normal to the ion beam**. **(B)** The platinum gas injection needle is inserted. **(C)** A (Acceleration voltage 30KV) 5nA ion beam was used to deposit a reflective platinum pad used for increasing laser reflectivity.

Figure 3.1-3: Schematic illustrates the top side of the FIB milled beam cantilever before (A) ion beam platinum deposition of the laser reflective pad and (B) after. The platinum laser pad is shown in purple.

Figure 3.1-4: Schematic illustrates the ion beam deposition of a platinum base and then, a carbon tip. The tuning fork is removed from the SEM chamber and flipped over so that the **bottom of the cantilever** is now normal to the ion beam. **(A)** The tuning fork is aligned perpendicular to the ion beam. **(B)** The platinum/carbon gas injection needle is inserted. A (Acceleration voltage 30KV) 25pA-1nA ion beam currents were used to deposit the platinum base of the tip and subsequently, the carbon tip.

Figure 3.1-3: Schematic illustrates the bottom of the FIB milled beam cantilever (**A**) before and (**B**) after the ion beam platinum/carbon deposition of the base and the tip. (**C**) Is a close-up of the deposited tip.

Figure 3.2: Schematic show the resulting FIB fabricated beam cantilever on tuning fork tine. Images are false colored to show material. (A), (B) Bottom of the tuning fork. (C) Gallium-Ion Beam Deposited (Ga-IBD) platinum pad (purple) on top of cantilever for increased laser signal. (D)-(E) Shows the first version of

a Ga-IBD deposited platinum base (purple) with carbon tip (green). Subsequent versions show improvement in symmetry and height. **(F)** Shows Ga-IBD carbon tip (green) with radius of 100 nm.

Figure 3.3: Shows the refined iteration, a platinum tip base and the final carbon deposited tip. **Image A** shows the FIB milled cantilever and a platinum pyramid base fabricated with Ga IBD deposition. **Image B** shows a higher magnification image of the platinum base (purple) and the carbon tip (green). **Image C** shows the carbon tip. A tip radius of 112 nm was achieved.

Section 3.2: Method #2-Commercial AFM Cantilever Adhered to Tuning Fork Tine

This section will describe the fabrication of the second cantilever design. To fabricate the new design, a commercial afm cantilever needed to be adhered to a tuning fork. The figure below shows a simplified description of how the tuning fork-afm cantilever combination was fabricated. Figure 3.4-Image A shows an unmodified afm cantilever and afm chip. The afm chip is a component attached to the afm cantilever to make macroscopic handling of the cantilever possible, otherwise, the chip has no functional role in the afm data collection. Figure 3.4-Image B shows the process in which the afm cantilever is cut free from the chip. Figure 3.4-Image C shows the process in which the afm cantilever is welded onto the tuning fork. The tuning fork used was from manufacturer Abracon, part number AB26TRQ-32.768KHz-T. The AFM cantilever used was from manufacturer Nanosensors, part number NCH-W.

Figure 3.4: Schematic illustrates afm cantilever transfer process. **Image A** shows an unmodified afm cantilever and afm chip. This is how it arrives from the manufacturer. **Image B** shows that the afm cantilever is cut free from the chip. **Image C** shows that the afm cantilever is welded onto the tuning fork tine.

The actual fabrication process utilized a dual-beam FIB-SEM FEI Helios 400s microscope. The tool was equipped with a platinum and carbon gas injection system (GIS) that was used for afm cantilever welding and tip growth. The tool had an Omni-Probe system integrated, which is simply a platinum needle that has been etched down to a tip with a micron diameter and has motor control in all three axes, x-y-z, allowing sub-micron feature manipulation. The Omni-probe system allows the user the ability to extract a sample from a surface and reattach it at another location using electron or ion beam welding via gas deposition. After the commercial afm cantilever is adhered to the tuning fork tine, a Ga IBD carbon tip is fabricated on the cantilever using the same IBD carbon tip growth process previously described.

Figure 3.5 illustrates the removal process of a commercial afm cantilever from a cantilever chip using the FIB-SEM FEI Helios 400s, platinum GIS and an Omni-probe lift-out procedure.

Figure 3.6 illustrates the platinum gas injection welding of the afm cantilever onto a tuning fork tine using the FIB-SEM FEI Helios 400s, platinum GIS and an Omni-probe re-weld procedure.

Figure 3.7 shows SEM images of the fabricated device with platinum welds and Ga IBD carbon tip labeled.

Figure 3.5: Illustrates the extraction of the afm cantilever inside the vacuum chamber of a FIB-SEM FEI Helios 400s. **(A)** The Omni-Probe nanomanipulator is inserted above the afm chip and cantilever. **(B)** The nanomanipulator is lowered until approximately 0.5-1um above the afm cantilever surface. **(C)** The platinum gas injection needle is inserted. **(D)** A platinum gas is injected into the chamber while the ion beam weld is patterning. This welds the nanomanipulator to the afm cantilever. **(E)** Shows the resulting Ga ion platinum weld. **(F)** The Focused Ion Beam is used to cut the afm cantilever free from the afm chip. The nanomanipulator is raised 300um above the sample and retracted.

Figure 3.6: Illustrates the welding of the afm cantilever onto a tuning fork tine inside the vacuum chamber of a FIB-SEM FEI Helios 400s. **(A)** The nanomanipulator is reinserted into the chamber above the tuning fork tine. **(B)** The nanomanipulator is lowered to a distance of approximately 0.5-1 μ m above the tuning fork tine. **(C)** The platinum gas injection needle is inserted. **(D)** A platinum gas is injected into the chamber while the electron beam weld is patterning. This welds the afm cantilever to the tuning fork tine. Many platinum welds were made to insure a secure attachment. **(E)** Shows the resulting electron beam welds. Electron beam deposition was used due to irregular gas flow caused by the large afm cantilever geometry impeding platinum gas flow. Ion deposition attempts resulted in ion etching instead of deposition. **(F)** Once welded, the nanomanipulator is FIB cut free, then lifted and retracted.

Figure 3.7 Above: (A) Shows the actual tuning fork tines with an afm cantilever attached with electron beam platinum welds. (B) A higher magnification image of the afm cantilever. Note the platinum weld at the center of the cantilever was used to temporarily adhere to the nanomanipulator. The afm tip is at the top, near the apex of the afm cantilever. (C) Shows the platinum welds adhering the cantilever to the tuning fork tine. (D) A higher magnification image of the end of the cantilever. (E) A top down image of the pyramid structure of the afm, with a carbon tip that was Ga ion beam deposited. Tip deposition was the same as previously described. (F) A 52-degree tilted image of the IBD carbon tip.

Table 11: Adhered Cantilever Dimensions					
Tuning fork Cantilever Dimensions	Length (l)	Width (w)	Thickness (t)	Tip Height (H)	Tip Radius (R)
	93.3 μm	38 μm	3.5-5 μm	15.00 μm	110 nm

Table 12: Cantilever Material properties		
Si_3N_4 AFM Cantilever	Young's Modulus E	$E = 150 \text{ GPa}^{24}$

Table 13: Adhered Cantilever Spring Constants
K_{ver}
73.5-219 N/m

Notice that only the vertical spring constant is calculated. The lateral and torsional spring constants were not presented due to the inability in identifying in literature the Young's modulus of silicon nitride in alternate crystal orientations. There was also found to be a large variance in the published Young's modulus, with values ranging from 130-150 GPa^{25, 26}.

Chapter 4: Formatting data and sampling techniques

Section 4.1: Force Distance Zero Line

Now that the cantilever fabrication process has been covered, it is useful to review the process of post-processing force-displacement data. Three adjustments are required to have meaningful data.

- First, the force-displacement data captured from the experimentation process has an arbitrary force offset applied to the acquired normal force data caused by a vertical offset inherent to the laser positioning on the photodiode. The offset is the form of a DC voltage value resulting from the difference between pspd quads A-B, with non-zero values resulting from, laser misalignment or laser drift as humidity is increased. This offset can be reduced by correcting the laser alignment before experimentation, but there always exists a small dc component that still must be removed in post processing. This process is called locating the zero force point. Simply stated, this is removing the laser misalignment from force data.
- Second, after the locating the zero-force point, the zero distance point should be found, i.e. where is the surface. The zero-distance point is defined as the intersection of the zero force point with the force-displacement curve. At this point, the cantilever is in an equilibrium contact with the sample surface and the observed force on the cantilever is zero. In other words, this is finding z-displacement point where there is tip and sample are in contact, and there is zero force measured with the cantilever.

- Third, the force data needs to be scaled using the proper spring constant. Most commercial afms allow the user to select a commercial cantilever from a predefined library, however, rarely do these values match the actual cantilever. Since we fabricated our own custom cantilever, we need to rescale the force appropriately.

Section 4.2: Normal Dimension Zero Force Point

Following the work of Cappella et. al¹⁶, it is established that the zero point ($F_n=0$) of normal force component is defined as being a distance far from the sample surface, where there is essentially no observable normal force present on the tip. In our experiments, we will define the zero point distance as approximately 50 nm from the surface ($F_n=0$, $Z=50\text{nm}$). The justification behind this can be found using the simple sphere-plane (SP) model of the afm normal force,

$$F_N = -H \cdot R^2 / (6 \cdot Z^2 \cdot (R+Z)) \quad (\text{EQ 4.1})$$

with H being the Hamaker constant, R is the tip radius and Z is the z-axis height from the sample surface. Letting an estimated Hamaker constant be $H = 5 \cdot 10^{-18} \text{ J}$, $R = 100 \text{ nm}$, using a tip to sample height of $Z = 50 \text{ nm}$, the observed force from the afm tip and surface interaction is $F_N = -22 \text{ pN}$, an attractive force. To compare this to thermal noise at ambient conditions, we can reference Cappella¹⁶; the thermal fluctuations in the normal component of force F_t ,

$$F_t \leq 30 \text{ pN}$$

These thermal fluctuations are larger than the observed surface-tip interaction forces at 50 nm in height. It is plausible to assign the normal force zero point at a distance $\geq 50 \text{ nm}$

from the surface. The zero-force point is marked as a horizontal line A on the plot shown figure 4.1 below. It intersects points on the force curve where the cantilever experiences zero force.

Section 4.3: Z-height Zero Point

The zero point ($Z_0=0$) of the z axis is defined as the point where the force curve intersects with the horizontal line A. For improved clarity, this is illustrated in the figure 4.1 above as point B. At point B, the tip and sample are in direct contact and the observed force is zero.

Figure 4.1: A schematic representation of the approach and retraction curve. The **point A** represents the zero point of the normal force component. The **point B** represents the zero point of the z-axis distance component. Notice that the force at point B is zero. The definition of the surface is accepted to be the intersection of measured force curve and the zero normal force line [1]. The **point C** is the snap-to-contact point. Image from ^{27]}

Section 4.4: Normal Force Scaling

To scale the experimentally obtained data, one simply multiplies the observed force by the theoretical spring constant, and divides by the experimentally observed spring constant. The experimentally observed spring constant is the slope of the force curve in the contact region. The theoretical spring constant is obtained from SEM cantilever measurements. Corrected force has the following form,

$$F_c = F_m * K_{\text{theory}} / K_{\text{measure}} \quad (\text{EQ 4.2})$$

with F_c being the corrected force, F_m being the measured force, K_{theory} being the estimated cantilever spring constant from SEM measurement and K_{measure} is the slope of the force curve in the contact region.

Section 4.5: Cantilever Deflection Amplitude

In shear force experiments, it is useful to have an estimate of tuning fork amplitude in terms of actual displacement distances. Traditionally, this is measured using interferometric techniques. In this thesis, we attempt to directly measure the tuning fork amplitude displacement by mechanically contacting a vertically oscillating tuning fork tine with an afm tip while simultaneously monitoring the laser deflection voltage. We are able to convert the laser deflection voltage into a tuning fork displacement distance by obtaining a scalar that relates laser deflection voltage to tuning fork deflection distance. The parameter relating laser deflection voltage to cantilever deflection is known as the deflection sensitivity. In section 4.6 we will briefly cover deflection sensitivity in

anticipation of performing such experiment in chapter 5 to estimate tuning fork deflection distances as a function of tuning fork drive voltage.

Section 4.6: Deflection Sensitivity

To obtain the deflection sensitivity parameter, a laser deflection-displacement curve is needed. A laser deflection curve is obtained in the same manner as a force curve, with the difference being that the afm records a voltage that is proportional to the position of the laser beam spot as it is deflected across the position sensitive photodiode as the z-piezoelectric is extended toward the sample surface. The parameter known as the deflection sensitivity, β , has units of nm/V. Distance here is cantilever displacement and volts are the output from the pspd. The deflection sensitivity values are not readily available to afm users, therefore a method to obtain them is necessary. The deflection sensitivity parameter can be obtained by performing a laser-displacement curve (A force curve while observing the laser voltage instead of force) and recording the slope in the contact region. In this contact region, the deflection of the cantilever is directly proportional to the z-piezoelectric displacement. The slope of the laser-displacement curve in the contact region has units of V/nm. Taking the inverse of this, one obtains the deflection sensitivity parameter, β . Typical values of β range from 10-100 nm/v^{27,28}.

Section 4.7: AFM Scanner Calibration

The process to obtain a meaningful approach and retraction curve requires a properly calibrated tool. For reference to the full scanner calibration procedure, please see afm manual from Park (Park Systems Corporation, XE-120 High Accuracy Biological Sample SPM, User Manual Version 1.8.4, (2013), p. 127.)¹⁹ A properly calibrated tool requires that the z-axis be calibrated with respect to a known distance. To calibrate this dimension, a cleaved piece of silicon wafer (2cm²) was masked with a piece of tape and partially sputtered with iridium to a known thickness, (13.5nm). This value was verified by performing a scanning transmission electron microscope (STEM) measurement using an FEI Helios 400s, figure 4.4. For x-y calibration, a checkerboard patterned calibration stub (MicroMesh, TGX series 1, 10um pitch) was used.

The XE120 AFM operates the x, y, z scanning piezo electrics in low voltage mode and high voltage mode. The XE-120 afm uses a 16bit digital-to-analog converter (DAC) which allows 2¹⁶, 65,536 addresses. In high voltage mode, the z piezoelectric has a displacement of 12um and in low voltage mode, it has a displacement of 1.7um. By operating in two separate modes, the afm is able to achieve resolutions of 1.83Å and 0.26Å for high voltage and low voltages respectively. This z-resolution is easily found with

$$(Total (x,y,z) \text{ piezo displacement}) / (number \text{ of DAC addresses}) = \\ (x,y,z) \text{ resolution}$$

$$i.e. 12um / 65,536 \text{ voltage addresses} = 1.83\text{\AA} = Z \text{ high voltage resolution}$$

$$1.7um / 65,536 \text{ voltage addresses} = 0.26\text{\AA} = Z \text{ low voltage resolution}$$

In high voltage mode, the x-y piezoelectrics have a displacement of 100 μm and in low voltage mode, it has a displacement of 10 μm . The effective resolutions for x-y piezoelectrics for high voltage and (low voltages) modes are 15.2 $\text{\AA}$ and (1.52 $\text{\AA}$) respectively (XE-120 manual pg. 71)¹⁹. The XE-120 manual recommends that the afm be calibrated in the size scales that will be used within the experiment, therefore, the z-dimension should be calibrated with atomic dimensions if possible. The x-y scanner will not be used in our experiments, but it was calibrated within the micron domain for consistency. The calibration procedure was to obtain a topography image while maintaining proper tracking. For the z-axis calibration, since the measurement was sub-nanometer in scale, a fresh tip was used. If an old tip is used, a dull tip will not be able to properly sample small cracks and hole-like features, resulting in the substrate appearing to be smoother than actuality. Images were obtained with a tapping mode cantilever (Nanosensors, NCH-W) with a spring constant of approximately 40N/m.

Figure 4.2: High Voltage Z-Calibration Profile. Measured Profile was found to be 21.73nm, Accurate value was expected as 13.50 nm $\pm$ 0.5nm. Notice the large perturbation ($\sim$ 75nm height) at the interface between the iridium coated sample region (right) and the bare silicon region (left). Using the STEM procedure, this was found to be a glue artifact from the masking procedure.

Figure 4.3: Low Voltage Z-Calibration Profile. Measured Profile was found to be 14.0nm, Accurate value was expected as 13.50 nm. Notice the large perturbation at the interface between the iridium coated sample region (right) and the bare silicon region (left). Using the STEM procedure, this was found to be an artifact from the masking procedure.

It is interesting to note the large (height) perturbation at the interface between the iridium coated sample region (right) and the bare silicon region (left) in the figures 4.2 & 4.3 above. The z-axis calibration stub was fabricated by applying scotch tape as a mask to half of the sample and then coating the sample with iridium. In theory, removing the mask afterwards would result in a step height interface suitable for atomic calibration. Scanning Transmission Electron Microscopy (STEM) procedure was applied to verify the iridium coating thickness. In the STEM images shown below, the large perturbation appears bright, indicating that the material is a low atomic weight material. Notice that the perturbation is embedded beneath the iridium coating. This supports the conclusion that the perturbation is ‘glue’ from the masking procedure. By using a large scan area where the glue regions are disregarded, a step height between the clean silicon and iridium coating can be obtained to calibrate the z-axis of the afm.

Figure 4.4: The STEM image shows the interface between iridium and bare silicon z-axis calibration standard. In the center of the image is a large low-z material ‘glue’ embedded under the iridium coating. This suggests that it is from the masking procedure. (1) Protective Electron Beam Deposited Platinum (2) Protective Electron Beam Deposited Carbon. (3) Bare silicon substrate (4) Low-z material (5) Iridium coating is the thin black line.

Figure 4.5: A high resolution STEM image of the low-z 'glue' perturbation. It measures 74nm in height. AFM measurements indicate a 75-100nm height of the interface perturbation.

Figure 4.6: High Voltage X-Y Calibration Profile. Measured Profiles were $x = 39.919\mu\text{m}$ and $y = 40.02\mu\text{m}$. Expected profile was (x-y) $40.00 \times 40.00\mu\text{m}$. Feature spacing was $10\mu\text{m}$.

Section 4.8: Measurements with a Lock-In Amplifier

To make a measurement of an oscillating tuning fork amplitude or an oscillating acoustic signal, one needs to make use of a lock-in amplifier. For a thorough introduction to lock-in amplifier theory, it is recommended that one reads literature covering the subject. The SR850 instruction manual provides key insights into lock-in theory²⁹. The university of Pittsburgh has compiled a great introductory tutorial covering the subject³⁰. Following DeVore, et al. from the University of Pittsburgh in deriving the output of a lock-in amplifier, the expected output of a lock-in amplifier before a low pass filter has the form

$$V_{mx} = 1/2G * \{ \cos(2\pi(F_r - F_s)t + \phi) + \cos(2\pi(F_r + F_s)t + \phi) \} \quad (\text{EQ 4.3})$$

and

$$V_{my} = 1/2G * \{ \sin(2\pi(F_r - F_s)t + \phi) + \sin(2\pi(F_r + F_s)t + \phi) \} \quad (\text{EQ 4.4})$$

where V_{mx} (V_{my}) is the voltage in the x-quadrant (y-quadrant) after the mixer/multiplier, G is the gain of the amplifier, F_r is the reference signal, F_s is the experiment signal, ϕ is the phase delay. Notice the ideal case of $F_r = F_s$, the experiment signal exactly matches the reference signal. In this case, $F_r - F_s$ is zero and $F_r + F_s = 2F_r$. This gives an output of

$$V_{mx} = 1/2G * \{ \cos(\phi) + \cos(2\pi(2F_r)t + \phi) \} \quad (\text{EQ 4.5})$$

and

$$V_{my} = 1/2G * \{ \sin(\phi) + \sin(2\pi(2F_r)t + \phi) \} \quad (\text{EQ 4.6})$$

where the first term in each expression is a DC component and the second term in each expression is an AC component that rapidly oscillates. To obtain only the DC component, a low pass filter is used such that the higher $2F_r$ component is filtered. On a lock-in

amplifier, to control filtering, one has the ability to designate a time constant that is proportional a cut-off frequency. This relation has the form

$$T = 1/(2 \pi F_c) \quad (\text{EQ 4.7})$$

where T is the time constant, F_c is the cut off frequency at -3db. In our experiments, we use a reference frequency around 32,768hz (+/- 300hz depending on geometry and mass of attached tip), the $2f$ component is approximately 65kHz. To filter the $2f$ component would require a cutoff frequency below this value. Letting a cutoff frequency be 60kHz, one would choose a time constant of $T = 2.65 \text{ us}$. Any shorter time constants would result in passing for the $2f$ component. Lowering the cutoff frequency has the effect of increasing the time constant. For long time constants, on the order of 500ms, the cutoff frequency is 0.31Hz. Such long time constants are able to remove noisy signals around our frequency of interest, but at the cost of adding a long time delay to our signal. Further, such long time constants result in a slow response to rapidly changing signals. In the experiments described in sections 5.5 & 5.6, we use a short time constant of 3ms to filter out the $2f$ component of the tuning fork signal.

Section 4.9: Lock-in Amplifier Sampling Rate

The z resolution of signals tracked with a lock-in amplifier are directly proportional to sample rate and afm approach speed. Our afm approach velocity is limited to a minimum approach speed of 10 nm/sec. To obtain a z resolution of 0.5nm, would require a sample rate of 20 samples per second. A lock-in amplifier needs 5X the time constant T to obtain

a single data point. This $5X$ is known as the settling time or the averaging time. Therefore, we can estimate the maximum time constant based on the above sampling rate and approach velocity. A single data point should be sampled every $1/20$ th of a second, but the sampling procedure takes $5 * T$ seconds. Therefore, the maximum time constant is $1/5$ of the sampling rate, $1/(\text{Sample Rate} * 5)$ seconds, or 10ms.

Section 4.10: AFM Noise Level

The noise level of the XE-120 afm was obtained by analyzing an afm force approach curve in the contact region. In the contact region, the slope of the force curve follows Hooke's law and is constant. By performing a linear fit in this region and removing the slope from the experimental data, we are able to project the noise into either the normal force axis or in the z-axis. Plots below show the resulting noise signals in each axis. The standard deviation of the noise is used as measure of the noise level. It was found that there exist a 0.22nm noise level in the z-axis and a 11nN noise in the normal force. Please note, this is a considerable noise signal, while small compared to our experimental findings, it could possibly be caused be a result of an environmental noise, an unbalanced air table or both.

Figure 4.7: Shows z-axis afm noise. Shows the resulting contact normal force data projected onto $z=0$. The standard deviation of the z-axis is 0.22nm.

Figure 4.8: Shows afm normal force noise. Shows the resulting contact normal force data projected onto $F_n=0$. The standard deviation of the normal force-axis is 11nN.

Chapter 5: Experimental Procedures:

The purpose of chapter 5 is to experimentally verify four key properties related to the investigation of surface forces. The four experiments that were performed are:

Section 5.1: List of Experiments:

1. Experiment 1: An experiment to measure the tuning fork lateral displacement using an afm laser-displacement curve. The goal is to estimate the tuning fork displacement as a function of driving voltage.
2. Experiment 2: AFM force curves are obtained using a non-contact afm cantilever with the intent of directly observing the snap-to-contact vertical position. By observing the snap-to-contact position, it is possible to obtain an estimate for the Hamaker constant for a Carbon tip and a Mica surface.
3. Experiment 3: EDX analysis is performed on the electron and ion beam deposited carbon tip material. Material is deposited as a thin film and then characterized with edx to determine the relative elemental concentrations.
4. Experiment 4: The FIB milled cantilever is driven to oscillate parallel to the sample surface and is interacted with a sample surface to generate normal force, tuning fork amplitude, and acoustic signals.
5. Experiment 5: A laterally oscillating tuning fork with a commercial afm cantilever attached is interacted with a sample surface to generate and observe normal force, tuning fork amplitude, lateral displacement and acoustic signal.

Section 5.2: Experiment 1: Directly Measuring Tuning Fork Oscillation Amplitude

Previous shear force experiments by Karrai and Gregor used interferometry to observe tuning fork displacement distance. We will attempt to directly measure tuning fork displacement distance using a direct contact afm method. We will compare measure tuning fork displacements with the interferometric results to assess the validity of such approach.

To measure the tuning fork displacement distance using an afm, a tuning fork was mounted vertically with the oscillator's motion constrained up and down in the z-axis as seen in the figure 5.1 below. A non-contact NanoSensor (NCH-W) afm cantilever with spring constant of ~ 40 nN/nm was then contacted with the tuning fork while the tuning fork was driven at resonance. The tuning fork tines were mounted perpendicular to the afm tip and were electrically driven to oscillate up and down in a vertical motion, causing the afm tip to deflect vertically. By obtaining a deflection sensitivity value, it is possible to convert the observed afm laser deflection (voltage (v)) values into tuning fork deflection (distance (nm)) values. The tuning fork was mounted using cyanoacrylate onto a aluminum cylinder of height approximately 8-10 mm. A small cylinder was chosen to maintain sufficient afm tip clearance between the afm head and the sample mount.

Figure 5.1: **Image A** Illustrates an afm cantilever in direct contact with a stationary tuning fork. **Image B** illustrates an afm cantilever in direct contact with a tuning fork electrically driven to oscillate in the vertical direction. This vertical tuning fork deflection results in a laser deflection proportional to tuning fork deflection amplitude.

The tuning fork (TF) current (I_1) and driving voltage (V_1) were observed with a SR850 digital lock-in. The tuning fork oscillation amplitude was directly observed by operating the afm in contact mode without feedback. There is concern that operating with feedback would result in the feedback loop constantly adjusting to maintain the force set point, negating tuning fork deflection amplitude measurements. This concern can be relaxed since the tuning fork operates at 32 KHz, a much faster rate than the feedback loop. The feedback loop would in essence observe the cantilever as being stationary. Operating in direct contact without feedback could result in a linear drift in the observed laser voltage as a sloping DC voltage. This slope could be measured and subtracted from the data.

Figure 5.2: Schematic illustrates experiment setup for measuring tuning fork displacement. A digital lock-in (SR850) is used to electrically excite a tuning fork. The tuning fork is oscillated vertically causing vertical displacement of the afm cantilever. The afm cantilever displacements are observed by monitoring the laser deflection with the pspd of the XE-120 afm. The (PSPD Quads A-B) vertical laser deflections of the pspd voltage (AC) component is passed through a signal access module (SAM) with a standard BNC to a Tektronix TCD 2024B oscilloscope for observation.

During the experiment, the afm cantilever is directly mechanically coupled to the tuning fork and oscillates at the same frequency as the tuning fork. By isolating this frequency on an oscilloscope, it is possible to measure the laser (AC) deflection voltage, V_{pp} . However, it is not a voltage value that we are interested in, but the actual deflection height of the tuning fork, therefore, the deflection sensitivity (β) will be needed.

To pass and record the laser voltages on the oscilloscope, the laser deflection voltages were transferred from the XE-120 afm to the oscilloscope using an intermediary breakout box known as the XE Signal Access Module (SAM). The SAM allows users the ability to access control voltages supplied to and from the hardware of the afm. It allows the user to act as a “man in the middle” and gives them the ability to copy critical drive signals to external hardware for custom experiments. The SAM was used to pass the vertical deflection component from the PSPD to a Tektronix TCD 2024B oscilloscope where it was recorded. The oscilloscope was triggered externally by the lock-in amplifier driving the tuning fork. For clarity, the vertical deflection components were the voltage difference between quadrants A and quadrant B of the pspd. As previously mentioned, $A = a+b$, and $B = c+d$, where a, b are the upper two quadrants on the pspd and c, d are the lower two quadrants on the pspd. See Figure 1.1 for clarity of pspd functionality. Therefore, subtracting the upper quadrants from the lower quadrants will give a voltage difference proportional to vertical laser deflection. The range of output voltages from the SAM were ± 10 V.

The sensitivity parameter is obtained by performing a force distance curve on a non-deformable hard sample. In our experiment, the laser deflection voltage is recorded instead of force. See figure 5.3 for a laser deflection voltage vs distance plot. (The recorded voltage here is the laser deflection voltage induced by the cantilever deflection and should not be confused with the driving voltage of the tuning fork which is recorded with the SR850 lock-in amplifier). This will result in a laser deflection voltage versus displacement curve (LDV-D) that would have slope units of V/nm. Deflection sensitivity is the inverse of the slope of the LDVD-D curve, with units of nm/V. The single crystalline quartz tuning

fork was used as a hard sample surface to obtain β . It should be noted here that sensitivity values depend upon cantilever mounting height, afm cantilever length, and laser spot positioning on the cantilever. Therefore, for accurate scaling of cantilever deflection voltages, it is recommended that one should obtain a deflection sensitivity value after every direct displacement experiment. Tip damage can occur with direct contact, so deflection sensitivity parameters should be obtained after the experiment has been performed.

A value of $\beta = 22.48 \text{ nm/V}$ was observed. Typical sensitivity values range from 10-100 nm/V.³¹ In the figure below, a laser-displacement curve is plotted to find the deflection sensitivity parameter; notice that only the contact region is plotted, this is so that a linear fit can be used to obtain an inverse slope value for the deflection sensitivity parameter.

Figure 5.3: A laser deflection voltage to displacement curve. A sensitivity value is the inverse of slope, which gives Beta $\beta = 22.48 \text{ nm/V}$.

Multiplying the deflection sensitivity β by the laser deflection voltages V_{pp} that were observed with the oscilloscope, a TF displacement distance is obtained. The TF displacement distance is plotted against the recorded tuning fork drive voltages and drive currents in the figure 5.4 below. The plot to the left in figure 5.4 is the TF displacement distance versus measured TF current and the plot to the right is the TF displacement distance versus TF drive voltage. At the lowest drive voltages, 4mV, a TF displacement of approximately 1nm was observed. At higher drive voltages, 50mV, a TF displacement of approximately 5.4nm was observed. A linear relationship for (TF-displacement versus drive-voltage) and (TF-displacement versus TF-current) is observed. It is found that for every increase of 10mV drive voltage, there is an increased tuning fork displacement of approximately 1nm or simply 100 pm/mV. Previous work by Grober, et al. have directly measured physical tuning fork amplitude displacements of 59.6+/-0.1 pm/mV from interferometric measurements³². Our experiment used a different tuning fork than Grober, et al, but the comparable results seem to suggest that direct mechanical observation using an afm cantilever yields a good estimate of the tuning fork displacement.

Figure 5.4: Demonstrates relation between tuning fork displacements and measured electrical response. **(Left)** Shows the relation between TF displacement and measured TF current. **(Right)** shows the relation between TF displacement and TF drive voltage. Notice the linear relation between observed tuning fork displacement and observed electrical characteristics.

It should be noted that this TF displacement distance is a reduced value. By the nature of the experiment, the afm cantilever applies a small restoring force to the tuning fork, reducing the total amplitude to some reduced amplitude. The amount of force applied can be estimated by applying Hooke's law, $F = -kx$, with k being the afm cantilever spring constant, and x being the total observed displacement. With $K \sim 40 \text{ nN/nm}$ and x ranging from 1-20nm, the applied force ranges 40-800nN. For future cantilever deflection measurements, it is recommended to use low K cantilevers, such that only small restoring force is applied and thus limited tuning fork damping occurs. Contact mode cantilevers have spring constants well below 1nN/nm, such as $K = 0.05 \text{ nN/nm}$. If used, a maximum force of approximately 1nN could be expected while driving a tuning fork amplitudes of 20nm. However, even with stiff cantilevers, such as the one used in our experiment, as long as the deflection distances are small, so too will be the resulting dampening force.

Section 5.3 Experiment 2: AFM Normal force curves to obtain Hamaker's Constant

This section covers the experimental process for obtaining a normal force curve. A force model will be used to obtain an estimated Hamaker constant for an IBD carbon tip with radius of 100nm with a mica surface at high humidity (>40%).

The force model used follows the work of Soma Das, et al.¹⁷ The procedure proposed by Das's group utilizes a force curve interaction to directly measure the Hamaker constant by deriving a relation between the snap-to-contact point of an afm force curve, the tip radius, the cantilever spring constant, and the Hamaker constant. They make use of a simplified model of the afm force interaction using the sphere-plane (SP) approximation to represent the afm tip and sample substrate. The relation obtained by Das is

$$A = (24/27) * (K_c/R_t) * h_j^3, \quad (\text{EQ 5.1})$$

where A is the Hamaker constant, K_c is the normal spring constant, R_t is the tip radius and h_j is the experimentally measured jump to contact position. This function is valid in the domain of $z > a_0$, with a_0 being an atomic distance, generally defined as $a_0 = 0.15\text{nm}$. By operating at heights larger than 0.15 nm, the system is well approximated by Van der Waals forces. A note of caution, at high humidities, there is a mesoscopic water layer present and such model is invalid within contact with this region, therefore, the Hamaker constant will only be obtained for regions above the mesoscopic water interaction.

Section 5.3.1: Experimental Force Curves

A series of force curves were obtained using a regular afm cantilever with a spring constant of $K_c = \sim 40$ nN/nm. A IBD carbon tip with a radius of 100 nm was fabricated onto the afm tip using the ion deposition procedure previously described. A maximum force set point of 100 nN was defined. A 10mm v1 grade mica surface was used (Ted Pella Inc, Highest Grade V1 AFM Mica Discs, 10mm). Humidity was 45-47%. The XE-120 afm was operated in force-displacement mode.

The force curve data presented below uses the method previously described in section 4.2 to define the zero force point and then uses the intersection of this force height with the z-displacement to find the zero-distance point as well. A well-defined snap-to-contact point at $Z_0 = 2.5$ nm and $F_n = -70$ nN is observed. Using the jump-to-contact point in conjunction with the (EQ 5.1), it is possible to estimate the Hamaker constant. This is illustrated in the table 14 below.

Figure 5.5: This figure shows the observed normal force with the zero force and zero distance points. Points of interest labeled with solid black horizontal and dotted vertical lines. The snap-to-contact point is labeled and found to be 2.57 nm with an attractive force of 70 nN. The approach curve is then parsed into a region before surface/mesoscopic interaction (blue line) and a region after mesoscopic layer and surface interaction (red line).

Section 5.3.2: Estimated Hamaker Constant

Table 14: Hamaker Constants for IBD Carbon Tip and Mica Surface	
Hamaker using Snap-to-contact Model	$6.03 \times 10^{-18} \text{ J (} Z_{\text{snap}} = 2.57 \text{ nm)}$
	$6.03 \times 10^{-18} \text{ J (} Z_{\text{snap}} = 2.71 \text{ nm)}$
Parameters used in EQ 5.1: $h_j = 2.57\text{-}2.71\text{ nm}$, $R_t = 100\text{ nm}$, $K_c \sim 40\text{ N/m}$	

These measured values for the Hamaker constant are reasonable. Typical Hamaker constants are generally of magnitudes (10^{-21} to 10^{-18}) J. Examining the obtained force curves shows a perturbation at approximately the 5-7nm position, which is caused by the probe-mesoscopic layer interaction to improve the accuracy of this Hamaker constant,

future experiments should make use of a contact mode cantilever (low spring constant cantilever) to reduce the interaction duration with the mesoscopic water layer. Lower humidity conditions would reduce contributions of the water layer to the observed normal force.

Section 5.3.3: Probe Reliability

To investigate the probe reliability, a probe was used to acquire 10 normal force curves without a shear oscillation applied. Normal force curves were acquired to obtain the Hamaker constant between a mica surface and a IBD carbon tip. Before and after SEM images show that tip wear was minimal. Figure 5.5-1. When a shear force was applied, tip wear was observed. Figure 5.5-2.

Figure 5.5-1: Left SEM image is before and **right** is after acquiring 10 normal force curves without a shear force applied. A force set point of 100nN was used. 10 force curves were acquired to obtain the Hamaker constant between a mica surface and IBD carbon tip.

Figure 5.5-2: Image shows an example of probe wear after many (10's to 100s) normal force approach curves while a shear oscillation is applied. The final probe is approximately 415nm in radius.

Section 5.3.4: STEM Analysis of IBD carbon

A STEM analysis of IBD carbon was performed. See literature for STEM preparation procedure. The figure below shows the resulting bright-field image of the grain structure from the ion beam deposited carbon. Notice that the IBD carbon structure shows nanoparticles and an amorphous structure is present. The nanoparticles are estimated to be between 1-5 nm in diameter, without long range structure. It is not known if these particles are diamond like carbon.

Figure 5.5-3: A bright-field STEM image showing the nano-structure of IBD carbon.

Section 5.4: Experiment 3: EDX characterization of EBD and IBD carbon materials

Section 5.4.1: EDX Characterization of Electron and Ion deposited Carbon

An energy dispersive x-ray spectra (EDX) was acquired to characterize the ion implantation that occurs while performing a Ga ion carbon tip deposition. A series of carbon thin films were deposited onto a freshly cleaved silicon wafer using both electron beam deposition (EBD) and ion beam deposition (IBD) using an FEI Helios 400s SEM-FIB dual-beam with an integrated naphthalene gas injection system and a Bruker instrument spectrometer with 133 eV resolution.

An EDX signal is composed of two main components, the bremsstrahlung x-rays which are considered background noise and the characteristic x-ray peaks, which are used for elemental identification. Bremsstrahlung noise is generated when electrons and x-rays scatter as they interact with a substrate lattice. A Bremsstrahlung signal is an x-ray signal that is generally lower in x-ray counts and covers an energy range that broadly spans the total sampled energy spectrum. Characteristic x-rays are the result of direct electron transitions that occur when an electron fills a shell vacancy left after the incident electron beam scatters a lattice electron. X-rays that make it directly to the detector without energy loss contain information that is unique to the scattering atom, thus they are ideal for atomic elemental identification.

Electron beam accelerating voltage and beam current play a critical role in the EDX characterization of unknown specimens. Electron beam accelerating voltage controls the maximum excitation energy, and beam penetration depth. Both the standard 15 kv and also, a lower 5 kv acceleration voltage were used. At 5kv, many atomic elements have unique characteristic x-rays available for identification. A 15kv acceleration voltage is able to probe higher electron energies and is used to verify elemental identification by exciting higher energy transitions.

Section 5.4.2: Electron Beam Acceleration of 5k Volts

Choosing a 5 kv acceleration voltage was an attempt to limit the sample penetration depth to only the carbon film and to observe the lower K-alpha energies of carbon, silicon and L-alpha of gallium. A 5 kv acceleration voltage produced a spectra with low x-ray counts and subsequently a high degree of uncertainty in elemental identification.

Section 5.4.3: Electron Beam Acceleration of 15k Volts

The 15 kv beam provided sufficient x-ray counts for reliable elemental identification and also a direct excitation of both L-alpha and K-alpha energies in Gallium.

Table 15 contains the beam conditions used for thin film depositions of electron beam and ion beam deposited carbon. The last row of table 15 shows the beam conditions (acceleration voltage, beam current and sampling time) used for edx characterization.

Table 16 lists the excitation energies for the elements identified from EDX. Table 17 contains a summary of atomic percentages from each thin film edx sampling.

Table 15: Summary of Electron-Beam and Ion-beam thin film Deposition Parameters			
Deposition Parameters	Accelerating Voltage	Beam Current	Deposition time
EBD Thin Film Carbon	20 kv	11nA	300 sec
IBD Thin Film Carbon	30 kv	30pA	300sec
EDX Parameters (Spot sampling)	5 kv and 15 kV	1.4nA	EDX sample time: 120 sec

Table 16: Energy Table for EDX analysis				
Carbon (C)	Silicon (Si)	Gallium (Ga)	Aluminum (Al)	Tin (Sn)
K- Alpha:0.277keV	K- Alpha:1.793keV	K- Alpha:9.241keV L- Alpha:1.098keV	K- Alpha:1.486keV	L-Alpha:3.443keV
Source ³³				

Table 17: Summary of EDX characterization				
Material	Atomic % Carbon K-Series	Atomic % Gallium K/L-Series	Atomic % Si K-Series	Atomic % Trace Elements
EBD Thin Film Carbon	28.18% (1 sigma 1.97%)	N/A	71.14% (1 sigma 3.60%)	Al-K-Series 0.32% (1 sigma 0.04%) Sn-L-Series 0.36% (1 sigma 0.08%)
IBD Thin Film Carbon	62.5% (1 sigma 4.37%)	17.48% (1 sigma 2.16%)	20.47% (1 sigma 1.21%)	N/A

Section 5.4.4: EDX Results

It was found that electron beam deposited carbon thin-films were 99% carbon if impurities are ignored and 97.6% pure if Al and Sn impurities are considered. It was found that Gallium ion beam deposited carbon contained 25% gallium and 75% carbon with no impurities detected. All results disregard the background Silicon signal.

Comparing the EBD and the IBD edx results, one can conclude that the naphthalene gas was of high purity, >97.6%. This conclusion is obtained by noting that the IBD signal contained no impurities while the EBD signal contained trace impurities. A possible source of impurities was the silicon substrate. The penetration depth of electrons at 15 kV is 1.8um in carbon³⁴ given by the Kanaya-Okayama range. It should be noted that the EBD carbon

film thickness was less than the Kanaya-Okayama range, and since a strong silicone peak was observed, it can be concluded that sampling of the silicon substrate occurred. Since IBD carbon deposited faster¹², a thicker carbon layer was formed for similar deposition times, therefore it is plausible that there was less sampling of the silicon substrate. This is supported by examining the EDX spectra of both EBD and IBD. It is clear that a larger silicon peak is observed for the EBD edx spectra.

Since it was observed that there were no trace elements found in the IBD edx analysis, this supports the idea that the trace elements were contaminants of the silicon substrate and not the carbon precursor gas. Inspecting the elements in the energy table for edx analysis, it can be observed that all elements are well separated in energy excitation levels, thus it is improbable that the gallium peak is obscuring the trace elements. Again, disregarding the silicon peak as background, one finds a carbon concentration of 75% and a gallium concentration of 25%. This corresponds well with observed values in literature, Lemoine et al.,¹² which observed values of gallium implantation in IBD carbon of 20-25%.

Following the work of Lemoine et al., they observed the material properties of IBD carbons tips to have a Young's modulus between $E=120-130$ GPa. An intrinsic hardness was observed to be approximately $H=9-10$ GPa. Comparing the Hardness values of silicon ($9-12.4$ GPa)³⁵, and mica (5.12 GPa)³⁶ with that of IBD carbon ($9-10$ GPa), it is found that IBD carbon is softer than crystalline silicon but harder than mica.

Figure 5.6: Shows the EDX spectra for IBD carbon (Top) and EDB carbon (Bottom).

Section 5.5: Experiment 4 Surface interaction using FIB milled Cantilever

Section 5.5.1: Experimental design

The objective of this experiment is to observe simultaneously the normal force and shear force while obtaining approach and retraction curves using a custom designed cantilever and probe. The tuning fork ultrasound signal was also observed using an acoustic emission transducer. This experiment will use a cantilever that has been FIB milled into a tuning fork tine. Results will discuss the observed findings and experimental limitations.

Section 5.5.2: Measuring Normal Force

To observe the normal force, a rectangular cantilever was focused ion beam milled into the tine of the 32.768kHz tuning fork and a carbon tip was ion beam deposited onto the cantilever as previously described. The milling process removed mass from the tuning fork, increasing the resonant frequency to 33.109kHz. The tuning fork and probe were then mounted (adhered with cyanoacrylate) on the AFM such that the tuning fork tines would oscillate parallel to the sample surface, see figure 5.7 below. The XE-120 afm laser was aligned top of the cantilever such that interactions with the normal forces would cause a direct vertical laser deflection on the A-B quads of the position sensitive photodiode. The XE-120 electronics will record the normal force data as the force curve is obtained. The vertical spring constant of the FIB milled cantilever was found to be approximately 170 N/m. For calculation of the spring constant, see section 3.1.1, table 6.

Figure 5.7: Illustrates the tuning fork oscillating motion relative to the sample surface (**Image 1**). This oscillation motion is constrained to be parallel to the sample surface, in the x-axis. **Image 2** illustrates a cantilever before contact with the sample surface. Sides A, B,C are labeled for dimensional clarity. **Image 3** illustrates a cantilever interacting with a sample surface and bending as force is applied. Notice the laser deflection as the cantilever bends.

Section 5.5.3: Measuring the Shear Force

To observe the shear force, the tuning fork was driven electrically with a digital lock-in amplifier (Stanford Research SR-850). The tuning fork was driven at 50mV, estimated 5nm amplitude. While being driven, the piezo-electrically generated current from the tuning fork was observed using the same digital lock-in amplifier. The drive signal was generated and phase locked monitored using the internal frequency source of the lock-in amplifier. Sensitivity of the lock-in amplifier was set to 1uA. A time constant of 3ms was used. The SR-850 digital lock-in then output the magnitude (R) of the measured tuning fork current as a DC voltage through channel 1 output. This DC voltage is then passed to the analog-to-digital-converter (ADC#1) on the XE-120 afm using a standard bnc. Channel

1 has an output range of $\pm 10\text{V}$, with a maximum 10mA output. The ADC#1 accepts an input of $\pm 10\text{V}$, with a $50\text{k}\Omega$ impedance.

Section 5.5.4: Measuring the Acoustic Response

The commercially available acoustic emission transducers AET R15 (Physical Acoustic Group, R15a) was used to record the acoustics generated from the tuning fork. In the following experiment, a different acoustic sensor is used, specifically the SE40-Q (Score Dunegan, SE40-Q). This was an attempt to improve the acquired acoustic signal. In the current experiment, the R15a acted as a bottom sensor, i.e. it was mounted beneath the substrate, as seen in the figure 5.8 below. The acoustic signal was monitored using a second digital lock-in amplifier (SR-850). The SR-850 used an external trigger from the first lock-in amplifier. The measurement was a phase locked current measurement with a sensitivity of 20nA . A time constant of 3ms was used. The acoustic sensor's current was sampled similarly to the tuning fork signal, it was passed from the channel 1 output of the lock-in amplifier into the ADC#2 on the XE-120 afm. ADC#2 has the same power considerations as ADC#1.

Section 5.5.5: Substrate Preparation

The substrate that was used was a 1cm^2 silicon wafer cleaned with ipa. A native oxide layer was present on the silicon substrate. The edge of the sample (within $20\mu\text{m}$ of edge) was used for force curve collection. This was an attempt to avoid unwanted contact of the tuning fork and the substrate. It is only desired that the probe tip and substrate have interaction.

The sample was adhered to the acoustic emission sensor using vacuum grease (Dow Corning, High Vacuum Grease).

The afm is enclosed inside of an acrylic enclosure with an air feed through line to control atmospheric humidity. Humidity was increased from ambient conditions (10-45% humidity) to approximately 60% by pumping air at 12-15 psi through a bubbler in a beaker of deionized water. Humidity was maintained between 55-65%.

Figure 5.8: Experiment Schematic illustrating the normal force, shear force and acoustic interaction measurements. The tuning fork/probe was mounted on the XE-120 afm in place of a regular afm cantilever. To measure shear force, the tuning fork was electrically driven using an SR-850 digital lock-in amplifier. This caused the tuning fork to oscillate parallel to the sample surface while generating an acoustic signal with a tip-sample interaction. The tuning fork's electrical current was measured. An acoustic sensor (R15) was placed beneath the sample surface to measure the tip-sample acoustic signal. The acoustic sensor's electrical current was measured with a second SR-850 digital lock-in amplifier. Both SR-850 lock-in amplifiers passed a dc voltage (proportional to measured signal current) to the XE-120 afm. To measure normal force, the XE-120 afm's laser was reflected off the tuning fork cantilever and aligned onto a position sensitive photodiode. The XE-120 performed approach and retraction curves while recording the three signals.

Section 5.5.6: Performing a measurement with a Lock-in Amplifier (SR850)

An approach and retraction speed of 10 nm/sec was chosen (slowest approach value) on the XE-120 AFM. To achieve a minimum sampling at every 0.5nm in z-displacement, a sample rate of 20hz is needed, ($10 \text{ nm}/0.5 \text{ nm} \cdot \text{sec} = 20\text{hz}$). This corresponds to a maximum time constant of $T_c = 10\text{ms}$, assuming a settling time of 5 times the time constant, $T_c = 1/20 \cdot 5 \text{ hz} = 1\text{s}/100 = 10\text{ms}$. To use longer time constants, a slower approach speed would be needed.

Section 5.5.7: XE-120 AFM considerations

The afm was operated in nanoindentation mode which allows direct control of the z-piezo displacement distance. The tool was further operated in maintenance mode to override insufficient laser intensity signal. This was required in part because the tool has a minimum required laser intensity to operate scanning modes and for using the automated approach software. The minimum required laser signal known as the sum peak is 1.1 volts, (Quadrants (A+B) values from the pspd). While utilizing a custom cantilever with a platinum pad for increased laser signal, a 0.175v (A+B) laser signal was obtained.

The procedure for obtaining force curves is to manually approach the sample surface while monitoring the TF shear force signal on the digital lock-in amplifier. Once the probe encounters the surface/mesoscopic layer, the tuning fork signal is observed to decrease. At this time, the probe is manually retracted using software to rest above the surface of the sample (within a 1um). The tool then is allowed to extend and retract the probe onto and off of the surface at a constant speed of 10 nm/s. The total distance that the

probe travels is 500nm-1.5 μ m. During the approach and retraction process, the normal force, the shear force and the acoustic signal are obtained simultaneously.

Section 5.5.8: Experimental Results

The measured normal force, tuning fork amplitude and acoustic emission transducer signal is plotted in the figures 5.9, 5.10, 5.11 below. Spring constant was estimated to be approximately 170N. The zero-force point was found by averaging the pre-contact normal force signal over approximately 300nms. The zero-distance point was found by plotting the zero normal force line until it intersected the normal force curve in the contact region. This method is described in more detail in the background section.

The snap-to-contact was not observed. This could be attributed to the fact that the model used to predict a snap-to-contact is based on purely van der Waals interactions. Once a tip starts to interact with the mesoscopic water layer, the model is no longer valid. It seems that the acoustic interaction occurs before the probe contacts the surface; this is concluded from the observation that the acoustic signal is observed in the region of 1-15nm, a region before the cantilever experiences a linear contact force. Once the probe enters the contact region, there is a large acoustic signal that is observed. It is suspected that this is the result of the carbon tip bending as it interacts with the sample surface.

Figure 5.9: Experimental results for Trial #1 observing normal force, shear force and acoustic signal. The upper plot is the observed normal force as a function of z-displacement. Notice there is not observed snap-to-contact. In the lower plot, both the tuning fork amplitude (**red**) and the acoustic signal (**blue**) are plotted with arbitrary units.

Figure 5.10: Experimental results for Trial #2 observing normal force, shear force and acoustic signal. The top plot is the observed normal force as a function of z-displacement. Notice there is not observed snap-to-contact. In the lower plot, both the tuning fork amplitude (**red**) and the acoustic signal (**blue**) are plotted with arbitrary units. The acoustic signal is observed to be diminished when compared to trial #1.

Figure 5.11: Experimental results for Trial #3 observing normal force, shear force and acoustic signal. The top plot is the observed normal force as a function of z-displacement. Notice there is not observed snap-to-contact. In the lower plot, both the tuning fork amplitude (**red**) and the acoustic signal (**blue**) are plotted with arbitrary units. The acoustic signal is observed to be diminished when compared to trial #1 and #2.

Section 5.5.9: Experimental Discussion

This experiment used a purposely "stiff" cantilever to avoid jump-to-contact, with the result being a cantilever which exhibits little force variance as the cantilever approaches the sample surface. Although this allows the ability to acoustically sample through the mesoscopic region without a snap-to-contact, it does not give detailed information regarding normal force within the approach region (0-50nm). Looking at the observed acoustic data, one finds that the positioning of what is believed to be the mesoscopic water layer is seemingly offset from the sample surface. The positioning of the acoustic signal is shifted away from the surface to a distance of 5-15nm.

The stiff normal force measurements from this experiment give little in terms of data to validate the location of the water signal which was acoustically observed. An alternate experiment was performed with a lower spring constant afm cantilever in an attempt to confirm the location of the mesoscopic water layer relative to the surface of the sample. This experiment consisted of performing a simple approach and retraction curve with a standard non-contact mode afm cantilever with a spring constant of approximately 40N/m, ~63% humidity, on a cleaved v1 grade mica surface. This experiment used the same procedure as described in section 5.2 for obtaining a force curve. No tuning fork or acoustic signals were gathered in this experiment, only a standard approach and retraction force curve was obtained. By performing a force-displacement curve at similar humidities (60%+), but with a more sensitive (flexible) cantilever, the positioning of the mesoscopic water layer can be obtained and compared. Results of the comparison between the acoustic

approach curve and the subsequent normal force curve are in agreement in that the relative positioning of the mesoscopic water layer is offset from the surface by approximately 6-7nm. Figure 5.12 shows this comparison.

To estimate the mesoscopic water layer thickness from the approach curve, a measurement was made at the first jump-to-contact point and also at the second jump-to-contact point on the approach curve. This is labeled in the two lower plots of figure 5.12 below. The first jump-to-contact point is the mesoscopic layer, the second jump-to-contact is the mica surface. It should be stated that for both the acoustic signal and the normal force curve presented in figure 5.9-5.11, the same procedure to find the zero-force point ($F_n=0$) and zero-surface point ($Z_o=0$) was used. This procedure is described in the background sections 4.2 and 4.3.

Figure 5.12: Illustrates a comparison of the relative positioning of the acoustic response obtained in current experiment and the double snap-to-contact positioning normal force curve obtained in a verification experiment. The **top** two plots show the acoustic signal (**blue**) illustrating the offset of the acoustic signal from the sample surface. The tuning fork signal (**red**) (shown in the two upper plots) approaches a decreased constant amplitude within the contact region. The **lower** two plots show the double jump-to-contacts points

found on the normal force curve performed to verify the mesoscopic water layer position. The agreement found between the positioning of the acoustic signal and the normal force signal is of interest. To be clear, the presented acoustic signal and normal force curves were obtained from two separate experiments, with separate cantilevers, with separate spring constants. Again, the normal force curve is used here to confirm the mesoscopic water layer positioning.

Section 5.5.10: Experimental Limitations

The experiment described in the previous section had quite a few experimental limitations that resulted in constrained data collection. The first shortfall was a low laser intensity on the pspd. We were operating a commercial afm, which has a minimum required laser intensity measured at the pspd of 1.1V to operate in normal conditions. The custom cantilever had a voltage of 0.175v. This reduced laser signal was the result of reflecting off an irregular surface caused either by the etch manufacturing process of the tuning fork tine, or the GIS deposited platinum pad. Another shortfall from using a commercial afm, was the inability to approach the sample surface at a speed less than 10 nm/sec. An afm manufacturer generally has no reason to have a slower approach speed for collecting force curve data due to sample drift at low approach speeds. In our case, slow approach speeds would allow the collection of acoustic data with long time constants. A long time constant is an excellent tool to filter noise around a frequency of interest allowing the ability to isolate the small acoustic signal.

Section 5.6: Shear force experiments using a Commercial AFM cantilever

The objective of this experiment is to observe simultaneously the (1) afm normal force, (2) afm lateral force (C-D on the pspd), (3) tuning fork shear interaction and (4) tuning fork acoustic signal while obtaining approach and retraction curves using a commercial afm cantilever that has been joined with tuning fork tine. Specifically, this experiment will use a commercial afm cantilever that has been electron beam platinum welded onto a tuning fork tine. The tuning fork will be oscillated parallel to the sample surface as shown in the figure 5.13.

Section 5.6.1: Experimental Design

A series of force curves will be obtained while the tuning fork drive voltage is incrementally varied from 14mV to 400mV (estimated 1.4-40nm Tuning Fork amplitude). The purpose is to observe how an increasing tuning fork drive voltage and thus an increase of the shear amplitude of the afm cantilever changes the observed normal force, the lateral force, the tuning fork amplitude, and the tuning fork acoustic signal. It is anticipated that a larger driving voltage will result in an increased acoustic response of the afm tip interacting in a shear motion with the mesoscopic water layer. The afm is enclosed inside of an acrylic enclosure with an air feed through line to control atmospheric humidity. Humidity was increased from ambient conditions (10-45% humidity) to approximately 60% by pumping air at 12-15 psi through a bubbler in a beaker of deionized water. Humidity was maintained between 55-65%.

Figure 5.13: Illustrates the tuning fork oscillation direction relative to the sample surface (**Image 1**). The tuning fork is driven parallel to the sample surface. **Image 2** illustrates the commercial afm cantilever with no normal force applied. **Image 3** illustrates the cantilever with a normal force applied, notice the cantilever bending in the normal direction and the laser deflection.

Section 5.6.2: Measuring Normal Force

To observe normal force, the afm laser will be reflected off of the afm cantilever that has been welded onto a 32,768 Hz tuning fork and the laser will be aligned onto the center of the pspd. Laser sum voltage (A+B) on the pspd was 1.35V, sufficient for standard operating conditions. Vertical deflections to the afm cantilever will cause a DC voltage to be observed in the A-B quads on the pspd, figure 1.1 illustrates pspd operation. The geometry of the afm cantilever was measured with SEM and found to be length is 94 μ m, width is 38 μ m, and thickness is 3.5-5 μ m. With Young's modulus of 130-150 GPa, the normal spring constant was found to be between 73.5-219 N/m. For calculation of the spring constant, see section 3.1.

Section 5.6.3: Measuring the Shear Force

To observe the shear force, the tuning fork was driven electrically with a digital lock-in amplifier (Stanford Research SR-850). The tuning fork was driven at voltages ranging from 14-400mV. While being driven, the piezo-electrically generated current from the tuning fork was observed using the same digital lock-in amplifier. The drive signal was generated and phase locked monitored using the internal frequency source of the lock-in amplifier. Sensitivity of the lock-in amplifier was set to 1uA. A time constant of 3ms was used. The SR-850 digital lock-in output the magnitude (R) of the measured tuning fork current as a DC voltage through channel 1 output. This DC voltage is then passed to the analog-to-digital-converter (ADC#1) on the XE-120 afm. Channel 1 has an output range of +/-10v, with a maximum 10mA output. The ADC#1 accepts an input of +/-10v, with a 50k Ω impedance.

Section 5.6.4: Acoustic Amplitude and Lateral Displacement Voltage Measurements

It is noted here that the commercial afm is built with 3 ADCs, however, nano-indentation mode only allows recording normal force, and two ADCs simultaneously. To observe 4 signals with 3 channels, we needed to alternate recording a single channel between two signals. The normal force was constantly recorded. The tuning fork amplitude was always recorded on ADC#1. Thus, ADC#2 was used to record either the acoustic amplitude or the lateral displacement voltages in an alternating manner. This means that each experiment was performed twice in order to observe both signals for later comparison. While inconvenient to perform experiments twice, it allows verification of experimental repeatability.

Section 5.6.5: Measuring the Acoustic Response

The commercially available acoustic emission transducers SE40-Q (Score Dunegan, SE40-Q) was used to record the acoustics generated from the shear interaction of the afm tip and mesoscopic layer. This is a different acoustic sensor than the one used in the previous experiment. Changing acoustic sensors was an attempt to increase acoustic signal to noise ratio. The SE40-Q was used as a bottom sensor and was mounted beneath the substrate as seen in the figure 5.14. The acoustic signal was monitored using a second digital lock-in amplifier (SR-850). The SR-850 used an external trigger from the first lock-in amplifier as a reference frequency signal. The measurement was a phase locked voltage measurement with a sensitivity of 20mV. A time constant of 3ms was used. The acoustic signal was sampled similarly to the tuning fork signal in that it was passed from the channel 1 output of the lock-in amplifier into the ADC#2 on the XE-120 afm. ADC#2 has the same power considerations as ADC#1.

Section 5.6.6: Measuring the Lateral Displacement Voltage

The lateral force will be observed as a voltage value since the lateral spring constant has not been calibrated. Calibration of the lateral displacement cannot be treated as standard since the tuning fork has a sheared oscillatory motion applied; no longer is the lateral displacement purely a result of lateral friction forces, but it includes a driven oscillatory shear component. In our experiment, the lateral displacement is proportional to the laser deflection on the C-D quadrants on the pspd, i.e. voltage signal results from horizontal displacements of the laser spot on the pspd. The lateral displacement voltage is recorded by passing the raw lateral force voltage component from the pspd out to a second

SR850 lock-in amplifier using a signal access module (SAM) to share the voltage between the afm electronics and the lock-in amplifier. The lock-in amplifier is used to track the shear lateral oscillation that results from the motion of the oscillating tuning fork. A 3ms time constant and a sensitivity was 1V was used by the lock-in amplifier. The magnitude (R) of the lateral displacement voltage was passed from the channel 1 output of the lock-in amplifier into the ADC#2 on the XE-120 afm.

Section 5.6.7: Substrate Preparation

A cleaved mica (PELCO Mica Disc 9.9mm, Grade V1) surface was used. The mica was cleaved using the scotch-tape method, such that a single layer of mica is peeled away revealing a pristine surface free of non-native surface contaminants. The probe tip was aligned near the edge of the mica sample (within 50um of the edge). This was an attempt to avoid unwanted contact of the tuning fork and the substrate. It is only desired that the probe tip and substrate have interaction. The sample was adhered to the acoustic emission sensor using vacuum grease (Dow Corning, High Vacuum Grease).

The two schematic figures below illustrate the two separate experimental procedures needed to measure the 4 signals of interest. Figure 5.14 illustrates the experimental procedure for measurement of normal force, tuning fork amplitude and acoustic amplitude. Figure 5.15 illustrates the experimental procedure for measurement of normal force, tuning fork amplitude and lateral displacement voltage.

Figure 5.14: This schematic shows the basics of the experiment where normal force, tuning fork amplitude and acoustic amplitude are measured. The laser is aligned on the afm cantilever that has been welded onto a tuning fork. The tuning fork is driven at open air resonance with displacement being parallel to the sample surface. A mica surface is used. The two lock-in amplifiers measure the tuning fork amplitude and acoustic amplitude. These measurements were passed to the afm on adc#1 and adc#2 of the XE-120 afm control electronics. The XE-120 afm also recorded the normal force-displacement curve.

Figure 5.15: The schematic shows the basics of the experiment where normal force, tuning fork amplitude and lateral displacement voltages are measured. The PSPD records voltages proportional to vertical and lateral laser displacements. The XE-120 afm records the vertical laser deflections. A signal access module is used to output the lateral displacement voltage to lock-in amplifier #2. The two lock-in amplifiers measure the tuning fork amplitude and lateral displacement voltages respectively. These measurements are passed to the afm on adc#1 and adc#2 of the XE-120 afm control electronics. The XE-120 afm also recorded the normal force-displacement curve.

Section 5.6.8: Performing a measurement with a Lock-in Amplifier (SR850)

An afm cantilever approach and retraction speed of 10 nm/sec was chosen (slowest approach velocity) on the XE-120 AFM. To achieve a minimum sampling at every 0.5nm in z-displacement, a sample rate of 20hz is needed, ($10\text{nm} / 0.5\text{nm} \cdot \text{sec} = 20\text{hz}$). This corresponds to a maximum time constant of $T_c = 10\text{ms}$, assuming a settling time of 5 times the time constant, $T_c = 1/(20 \cdot 5) \text{ hz} = 1\text{sec}/100 = 10\text{ms}$. To use longer time constants, a slower approach speed would be needed or concessions on the Z-axis sampling resolution. We use a 3ms time constant for all lock-in measurements.

Section 5.6.9: XE-120 AFM considerations

The afm was operated in nanoindentation mode which allows direct control of the z-piezo displacement distance. The procedure for obtaining force curves is to bring the afm cantilever to a distance of approximately 100um above the sample surface. The software performed the final approach automatically, engaging the sample surface and maintaining a fixed force on the sample surface, at a set point of 350nN. The tool then is allowed to extend and retract the probe onto and off of the surface at a constant speed of 10 nm/s. The total distance that the probe travels is 500nm-1.5um. During the approach and retraction process, the normal force, the shear force and the acoustic signal or lateral force are obtained. After each approach and retraction curve is obtained, the probe is removed from the surface and the surface is re-approached for each subsequent curve collection in an attempt to reduce probe wear.

Section 5.6.10: Experimental Results

Two sets of data are plotted below. The first data set shows the normal force, tuning fork amplitude and the acoustic amplitude. The second data set shows the normal force, tuning fork amplitude and the lateral displacement voltage. General trends will be discussed. Humidity was approximately 55-60%.

Data Set #1

Plots show the normal force, tuning fork amplitude and the acoustic amplitude:

1. Normal Force: Figure 5.16, Figure 5.17
2. Tuning Fork Amplitude: Figure 5.18, Figure 5.19
3. Acoustic Amplitude: Figure 5.20
4. Low Amplitude (50mV) and High Amplitude (300mV) Comparison:
 - a. Figure 5.21- Low tuning fork drive voltage
 - b. Figure 5.22- High tuning fork drive voltage

Figure 5.16: Data-Set#1 A series of normal Force vs. Z-Displacement approach curves plotted as tuning fork drive voltage is increased from 50mV to 400mV. Tuning fork (TF) drive voltage is labeled in the top right of each plot. Notice a large force builds near the sample surface as the tuning fork drive voltage is increased. Notice that a low tuning fork drive voltage has a corresponding force curve that resembles a standard force curve with two snap-to-contact points. The two snap-to-contact points are representative of the beginning and the end of the mesoscopic layer. Notice at low TF drive voltages (50-100mV) that the normal force curve is attractive before surface contact and at large TF amplitudes ($>100\text{mV}$) the normal force is repulsive.

Figure 5.17: Data-Set#1 The series of Normal Force vs. Z-Displacement approach curves plotted overlapping as tuning fork drive voltage is increased from 50mV to 400mV. Tuning fork drive voltages are labeled in the top right of the plot. Notice a large force builds near the sample surface and expands further from the sample surface as the tuning fork drive voltage is increased.

Figure 5.18: Data-Set#1 A series of Tuning Fork Amplitude vs. Z-Displacement approach curves plotted as tuning fork drive voltage is increased from 50mV to 400mV. Tuning fork drive voltage is labeled in the lower right of each plot. The most interesting trend observed is that initially there is a large temporary tuning fork amplitude decrease near the sample surface, after which the amplitude rebounds and continues to decrease linearly. This dip in the tuning fork amplitude corresponds spatially exactly in the sample region as the normal force bump.

Figure 5.19: Data-Set#1 The series of Tuning Fork Amplitude vs. Z-Displacement approach curves are overlapped to illustrate the general trends of increased tuning fork amplitude damping. Notice the amplitude dependency of the dampening distance, i.e. the distance Δz at which tuning fork signal is attenuated is directly dependent upon initial tuning fork amplitude. This was observed in non-linear force models proposed by M.J. Gregor et al. in (1995).

Figure 5.20: Data-Set#1 A series of Acoustic Amplitude vs. Z-Displacement approach curves plotted as tuning fork drive voltage is increased from 50mV to 400mV. Tuning fork drive voltage is labeled in the lower right of each plot. At low tuning fork driving voltages, 50mV-116mV, there is little acoustic response as the afm cantilever is interacted with the mesoscopic water layer near the sample surface. As the tuning fork amplitude is increased above 130mV, an acoustic response is observed. The acoustic signal shows an increase in magnitude between the sample surface and 25nm. This region corresponds to an increase in observed normal force and a decrease in tuning fork amplitude, as described in the previous plots.

Figure 5.21: A low amplitude tuning fork approach curve with distinct interaction regions labeled. **Region (A)** is the complete contact region, **(B)** is the ‘knocking’ contact region, **(C)** is the 3rd body contact region, **(D)** is the Van der Waals region, and **(E)** is the long range non-contact region. **Top** plot is the normal force curve, **middle** plot is the tuning fork amplitude, and the **bottom** plot is the observed acoustic signal. The drive voltage of the tuning fork was 50mv, or approximately an estimated 5nm drive amplitude. Region B spans approximately 16nm, region C spans 16nm. The Van der Waals region D was extended arbitrarily to the 50nm region, but the forces extend weakly beyond. Labeled point **(1)** is the kink point, point **(2)** is the sample surface, point **(3)** is the initial contact point with the mesoscopic layer.

Figure 5.22: A high amplitude tuning fork approach curve with distinct interaction regions labeled. The drive voltage of the tuning fork was 300mv, or approximately an estimated 30nm drive amplitude. **Region (A)** is the complete contact region, **(B)** is the 'knocking' contact region, **(C)** is the 3rd body contact region, **(D)** is a weakly repulsive region, and **(E)** is the long range non-contact region. **Top** plot is the normal force curve, **middle** plot is the tuning fork amplitude, and the **bottom** plot is the observed acoustic signal. Region B spans approximately 29.7nm, region C spans 16nm. The region D here does not follow the attractive van der waals behavior; this regions weakly repulsive region extends about 50nms. Labeled point **(1)** is the kink point, point **(2)** is the sample surface, point **(3)** is the contact point with the mesoscopic layer, point **(4)** is the beginning of the repulsive interaction. Notice the well-defined acoustic response in region C.

Data Set #2

Plots shows the normal force, tuning fork amplitude and the lateral displacement:

1. Normal Force: Figure 5.23, Figure 5.24
2. Tuning Fork Amplitude: Figure 5.25, Figure 5.26
3. Lateral Displacement: Figure 5.27, Figure 5.28
4. Low Amplitude (25mV) and High Amplitude (350mV) Comparison:
 - a. Figure 5.29-Low tuning fork drive voltage
 - b. Figure 5.30-High tuning fork drive voltage

Figure 5.23: Data-Set#2 A series of normal Force vs. Z-Displacement approach curves plotted as tuning fork drive voltage is increased from 14mV to 350mV. Tuning fork drive voltage is labeled in the top/lower right of each plot. Notice a large force builds near the sample surface as the tuning fork drive voltage is increased. Notice that a low tuning fork drive voltage has a corresponding force curve that resembles a standard force curve with two snap-to-contact points. The two snap-to-contact points are representative of the beginning and the end of the mesoscopic layer. Notice that at low shear amplitudes (14-74mV), the normal force is attractive and at high amplitudes (>74mV), the normal force is purely repulsive.

Figure 5.24: Data-Set#2 The series of Force vs. Z-Displacement approach curves plotted overlapping as tuning fork drive voltage is increased from 14mV to 350mV. Tuning fork drive voltages are labeled in the upper right of the plot. Notice a large force builds near the sample surface and expands further from the sample surface as the tuning fork drive voltage is increased.

Figure 5.25: Data-Set#2 A series of Tuning Fork Amplitude vs. Z-Displacement approach curves plotted as tuning fork drive voltage is increased from 14mV to 350mV. Tuning fork drive voltage is labeled in the lower right of each plot. Similar to data set #1, the tuning fork signal exhibits a damped bump near the sample surface.

Figure 5.26: Data-Set#2 The series of Tuning Fork Amplitude vs. Z-Displacement approach curves are overlapped to illustrate general trends of increased tuning fork amplitude damping. Dampening occurs further from the sample surface as tuning fork drive voltage is increased. This corresponds to the increased normal force bump observed further from the sample surface.

Figure 5.27: Data-Set#2 A series of Lateral Displacement vs. Z-Displacement approach curves plotted as tuning fork drive voltage is increased from 14mV to 350mV. Tuning fork drive voltage is labeled in the upper right of each plot. Two interesting trends are observed in the lateral force approach curves. Initially at low tuning fork drive voltages, (14mV-74mV), the lateral force is constant while the afm tip is above the sample surface and increases to a larger constant value once tip-surface contact is established. As the tuning fork drive voltages are increased above 100mV, the lateral displacement rapidly decreases once the afm tip enters the mesoscopic region (0-25nm) and increases again once surface contact occurs. The region of rapid decrease in lateral displacement signal corresponds directly to the observed increase in normal force, the decrease in tuning fork amplitude and an increase in acoustic response.

Figure 5.28: Data-Set#2 The series of Lateral Displacement vs. Z-Displacement approach curves are overlapped to illustrate the increase in lateral displacement dampening as the tuning fork drive voltage is increased. Tuning fork drive voltage is labeled in the lower right. Lateral displacement is proportional to friction forces, and it is observed that during tip-sample contact a large friction force is present. All curves are aligned to the dampened axis as the zero point, with the assumption that the lateral displacement is constant in this region regardless of initial TF drive voltage.

Figure 5.29: A low amplitude tuning fork approach curve with distinct interaction regions labeled. **Region (A)** is the complete contact region, **(B)** is the ‘knocking’ contact region, **(C)** is the 3rd body contact region, **(D)** is the van der waals region, and **(E)** is the long range non-contact region. **Top** plot is the normal force curve, **middle** plot is the tuning fork amplitude, and the **bottom** plot is the observed lateral displacement signal. The drive voltage of the tuning fork was 25mv, or approximately a 2.5nm drive amplitude. Region B spans approximately 7nm, region C spans 8.3nm. The van der waals region D was extended arbitrarily to the 50nm region, but the forces extend weakly beyond. Labeled point **(1)** is the kink, point **(2)** is the sample surface, point **(3)** is the 3rd body initial contact point.

Figure 5.30: A high amplitude tuning fork approach curve with distinct interaction regions labeled. **Region (A)** is the complete contact region, **(B)** is the ‘knocking’ contact region, **(C)** is the 3rd body contact region, **(D)** is the van der Waals region, and **(E)** is the long range non-contact region. **Top** plot is the normal force curve, **middle** plot is the tuning fork amplitude, and the **bottom** plot is the observed lateral displacement signal. The drive voltage of the tuning fork was 350mv, or approximately a 35nm drive amplitude. Region B spans approximately 30.2nm, region C spans 25.8nm. The region D here does not follow the attractive van der Waals behavior; this region’s weakly repulsive region extends about 50nms. Labeled point **(1)** is the kink, point **(2)** is the sample surface, point **(3)** is the 3rd body initial contact point.

Figure 5.31: Illustrates the observed ‘kink’ in the normal force curve and the static ‘clamping’ effect for the tuning fork amplitude. The ‘kink’ and static ‘clamping’ occur simultaneously at the transition between the complete contact region A and the ‘knocking’ region B. The tuning fork drive amplitude was 350mV, ~35nm amplitude.

Section 5.6.11: A ‘Kink’ in the Normal Force Curve

The normal force approach curve exhibits a kink, figure 5.31 which is described as a sudden change in slope between regions A & B. In literature³, this kink is the point where mechanical contact with the probe and sample surface is initiated.

Section 5.6.12: A ‘Static Clamping’ of the Tuning Fork

Static clamping is the mechanical clamping of the probe to the sample surface. At this point in the tuning fork approach curve, shown above, the tuning fork amplitude spontaneously decreases to a minimum. This is attributed to micro-surface roughness of the sample and probe³.

Section 5.6.13: Estimated Tip Velocities

Table 18: Tuning Fork Shear Velocity (Estimated)		
Tuning Fork Drive Voltage	Tuning Fork Displacement (A ₀)	*Shear Velocity (Vel)
14mv	1.4nm	288 um/sec
25mv	2.5nm	514 um/sec
50mv	5.0nm	1030 um/sec
74mv	7.4nm	1524 um/sec
100mv	10nm	2059 um/sec
116mv	11.6nm	2389 um/sec
150mv	15nm	3091 um/sec
200mv	20nm	4119 um/sec
250mv	25nm	5149 um/sec
350mv	35nm	7207 um/sec
<p>Relation for Tuning fork Drive Voltage and Tuning fork Displacement: ~10mv/nm Tuning fork Drive Frequency: F_{Resonance} = 32,801 Hz. Tuning fork Displacement = A₀ $W = 2\pi * F_{\text{Resonance}}$ *Vel = -A₀*w*sin(wt) *Velocity equation obtained by differentiating Simple Harmonic Oscillator (SHO) position equation</p>		

Section 5.6.14: Region A: Complete Contact Region

Region A is accepted as the direct mechanical contact between the tip and substrate. Normal force is observed to follow Hooke's law and linearly increase with z-piezo displacement. The tuning fork amplitude is dampened to a constant amplitude. The acoustic signal in this region is observed to be constant in amplitude. The observed lateral displacement signal is a maximum in this region. A constant, but maximum lateral displacement could be indicative of a tip in frictional shear motion with the surface, possibly indicating that the tip maintains a constant dampened shear motion while direct contact occurs, as has been observed by previous experiments⁵.

Section 5.6.15: Region B: The 'Knocking' and Partial Contact Region

Region B corresponds to a region where the tip is in an increasingly dampened motion as probe height is decreased, resulting from a 'knocking' which occurs between the tip and sample surface. The 'knocking' term is used to describe the tip tapping the surface. At the transition between regions A and B there occurs a kink in the normal force curve, as demonstrated in figure 5.31. This kink is observed as a change in slope of the force curve into a constant Hooke's law regime. A previous study by M.J. Gregor et. al. describes this kink in the force curve as being indicative of the initial tip-sample contact³. This is in subtle disagreement to what we observe. We observe a dampening of the tuning fork amplitude occurring throughout region B, indicative of a probe tapping the sample surface, and at the kink point, a firm mechanical contact is established between the probe and surface, resulting in a completely dampened tuning fork amplitude and a linear force. Once again, referencing Gregor et. al., within a nanometer of the kink region, the tuning fork was shown

to exhibit a spontaneous jump-to-zero amplitude; a point at which it is said that a ‘static clamping’ of the probe occurs, caused by the ‘micro-roughness’ of the sample surface³.

The acoustic response in region B mirrors that of the tuning fork amplitude, indicating that the tuning fork remains in motion. The lateral displacement is observed to increase in magnitude as tip-sample ‘knocking’ increases in intensity. This corresponds to a probe encountering a shear dampening, indicative of a cantilever exhibiting increased torsional and lateral motion from lateral friction interactions.

Section 5.6.16: Region C: The 3rd Body Contact Region

The primary question of interest of this thesis is, what is occurring in region C, a region defined roughly from the surface, $z=0$, to approximately 15-25 nm from the surface. It is best to examine this region under two separate conditions, a low tuning fork drive amplitude (14-50mV) and a large tuning fork drive amplitude (300mV).

At low tuning fork drive amplitudes (drive voltage 14-50mV, estimated shear amplitude of 1-5nm), the normal force curve exhibits the typical attractive forces and double snap-to-contact points characteristic for the presence of a water layer, Figure 5.29. It is observed that the normal force in this region is negative and attractive. Such attractive conditions are not characteristic of a double layer repulsion effect. The tuning fork amplitude exhibits a dampening with a slope different from the ‘knocking’ of region B and the dampened region A, possibly indicative of a different medium supplying the dampening interaction. There is no acoustic response observed at these low drive amplitudes. The lateral displacement is observed to decrease in this region, indicating a low shear interaction or correspondingly, a decrease in tip shear motion.

At increasingly higher tuning fork drive amplitudes, (drive voltage 100-300mV, estimated shear amplitude 10-30nm), the normal force is observed to increase and transitions from a net attractive force to a net repulsive force, Figure 5.30. Also, a large ‘bump’ appears in the same region as the mesoscopic water layer that was previously observed at low tuning fork drive amplitudes. This ‘bump’ in the force curve has observed force values approaching 1500nN at large shear amplitudes. This bump has a peak at approximately the midpoint of region C and it’s exact position is seemingly dependent upon the tuning fork drive amplitude. After the peak, the normal force is observed to decrease until a ‘knocking’ contact with the surface is established at the point between region B and C, Figure 5.30. The tuning fork amplitude is observed to decrease in the sample spatial region that the increase in the normal force occurs. A local minimum, a dip, in the tuning fork amplitude is observed to occur at the same point as the peak in the normal force. After this tuning fork dip is observed, the tuning fork recovers to a less dampened state. The acoustic response in this region is observed to follow that of the normal force. As the probe moves through region C, an increase in acoustic signal is found to correspond to a decrease in tuning fork amplitude, possibly indicative of a mechanical dampening interaction resulting in the generation of an acoustic response. The lateral displacement is observed to decrease and exhibits a minimum corresponding spatially to the tuning fork amplitude minimum. The observed lateral displacement is expected to decrease in relation to a decrease in tuning fork amplitude with small friction force, or increase in the presence of a large frictional force. It appears that the former condition is present in this region, i.e. a dampened tuning fork motion in the presence of a small friction force provided by the probe-mesoscopic layer interaction.

Section 5.6.17: Region D: The Mid-Range Interaction Region

At low drive amplitudes (14-50mV), this region exhibits the typical behavior of van der Waals forces, as observed in the normal force plots of figure 5.29. At high drive amplitudes (300mV), this region exhibits a long range repulsive force, figure 5.30. Long range repulsion is typical of electronic repulsion. Section 5.6.20 speculates sources for this observed transition from attractive to repulsive forces.

Section 5.6.18: Region E: The Long Range Non-Interaction Region

This is loosely defined as the far region where van der Waals forces or repulsive forces are below thermal background force levels.

Section 5.6.19: Plausible Explanations for the Observed ‘Bump’ in Region C

It has been shown in previous experiments by Peter M. Hoffmann, et. al.³⁷ that a sharp transition occurs from viscous (fluid like) to elastic (solid like) response of a confined liquid which is highly dependent upon vertical probe compression rates. Hoffmann termed this material response dynamic solidification, observing a high elastic response in the atomically ordered water layers closest to the sample surface. Hoffmann found that at a vertical approach velocity of 8 Angstroms per second, the remaining two layers of water exhibited a large elastic response and in addition, finding that at a vertical approach velocity of 14 Angstroms per second, the remaining 4 water layers exhibited a large elastic response. In essence, Hoffmann illustrated a dynamic solidification where the viscous and elastic response was highly dependent upon vertical probe approach velocity. He illustrated a threshold vertical compression rate of 8 angstroms per second, showing that elastic

behavior is exhibited when compression rates are greater than this and a viscous response at compression rates below this threshold. Hoffmann interpreted the large elastic response as the water layers exhibiting a solid-like behavior. In our experiment, the probe's vertical compression rate was approximately 7 times larger than Hoffmann's largest, at 100 Angstroms per second, or 10nm/s. At these rapid compression rates, it is plausible that the ordered liquid layers could exhibit a high elastic stiffness.

In our experiment, in addition to high vertically applied compressive loads, we applied a shear interaction at various velocities. Table 18 shows the estimated probe velocities given as a function for tuning fork drive amplitudes. In estimating shear velocity, we differentiated a simple harmonic oscillator (SHO) to establish a velocity relation. We found that as the shear velocity increased above a threshold, the observed interaction exhibited an elastic response characteristic of a compressed, solid-like material. Under our experimental conditions, it is estimated that the threshold velocity for a shear dynamic solidification occurs at tuning fork drive voltage of 116mv or an estimated tuning fork amplitude of 11.6nm. This corresponds to an estimated probe shear velocity of 2389 um/sec from table 18. Though a high uncertainty exists in the actual shear displacement and velocity at which the threshold for which this transition occurs, qualitatively, it is shown that there exists a distinct transition between a viscous water medium at low shear amplitudes and an elastic solid-like medium at high shear amplitudes.

Evidence for an elastic response of the 3rd body or water layer observed in region C is evident when analyzing the normal force and the acoustic response data. At high shear

amplitudes, the normal force was observed to have a large bump that can be interpreted as the probe ‘compressing’ a solid-like material. Correspondingly, the acoustic response in shows an increase in amplitude, which could be an elastic interaction between the probe and the 3rd body in region C. An elastic interaction between the probe and the 3rd body would exhibit a subsequent dampening of the tuning fork amplitude, which is observed in this region.

Interestingly, as the probe is moved through the 3rd body towards the surface, the dampening is gradually decreased until the transition from region C to B occurs. At this point, the tuning fork amplitude is no longer dampened and the ‘bump’ in the normal force has disappeared. One possible interpretation of this observation could be that the 3rd body medium is ‘squeezed out’ between the probe and the sample surface. Our data illustrates that the dampening subsides at the transition from region C into B. Recall, region B corresponds to the tip making mechanical knocking-contact with the sample surface, leaving scant space for a 3rd body. This supports the possible squeezing out of the 3rd body medium.

Section 5.6.20: Transition from Attractive to Repulsive Response

Examining the normal force response as the tuning fork amplitude is increased figure 5.23, it is observed that the normal force is attractive in nature in the pre-contact regions C & D while operating at low shear amplitudes. However, as the tuning fork drive voltage was increased, the observed normal force transitions into purely a repulsive response. One possible explanation for this response entails the phase response of the tuning fork oscillator as a function of tuning fork drive amplitude. In studies on the amplitude and

phase response of tapping mode afm, ³⁸, ³⁹, it was observed that “if the free oscillation amplitude exceeds a critical threshold, that the amplitude-distance and phase-distance curves exhibit a distinct transition from a net attractive force between the tip and sample, to a net repulsive response” ³⁹. Zitzler reasoned this effect “can be explained by assuming the intermittent formation and rupture of a capillary neck in each oscillation cycle of the AFM cantilever”.

In our experiment, we attempted to drive the cantilever parallel to the sample surface, however, any misalignment results in a vertical component in the oscillation vector. Thus, any increase in the shear driving voltage could result in a similar tapping of the mesoscopic layer effect observed in the tapping mode experiments by Garcia, Paulo and Zitzler, with the probe tapping in the normal direction.

Chapter 6: Future Experiments

The use of acoustics for sample characterization on the nanoscale is becoming a mature technology. It is useful to consider possible uses for acoustics for semiconductor characterization of surface roughness, defects and void identification. In addition to characterization, investigation of surface manipulation with acoustics should be explored.

Section 6.1: Future Force Curve Experiments.

A couple experiments that would clarify the nature of shear force microscopy are:

- Compare the Amplitude-Frequency response (Frequency Sweep) as function of distance above a sample. Previous work by Karrai¹ and Gregor³ exhibit inconsistencies resulting from both experiments operating at two drastically different amplitudes regimes, with Karrai observing a simple harmonic oscillator response and Gregor observing a non-linear response. By performing frequency sweeps at small tuning fork amplitudes (<1nm) and increasing the amplitude to large tuning fork amplitudes (>30nm) in small steps, it is possible to illustrate both parties are correct within their respective experimental domains. This would illustrate that the shear force is a result of a knocking between the probe and sample surface or 3rd body medium.
- Another series of experiments to perform in the future would be a repeat our previous experiment described in section 5.6 while also capturing the phase response as the probe moves through the bump region. Zitzler's tapping mode experiment predicts a negative change in phase response when the probe is in the repulsive force region. By investigating the probe while it is interaction in the bump, region C, it is possible to isolate the role that phase plays in the cantilever dynamics.

Section 6.2: Future Experiment #1: Subsurface void localization

Section 6.2.1: Proposal

It has been shown in previous work that it is possible to use nearfield acoustics to localize subsurface voids within many materials. However, most previous work has only explored the localization of either large subsurface voids (10's of μm^2) located under shallow substrate or nanoscale defects ($\sim 1\text{nm}^2$) under atomically thin substrate such as graphene. There is a need to develop subsurface acoustic imaging across a spectrum of void sizes and void depths. Further, the investigation of alternative substrate materials is warranted, i.e.

explore a Cu, Oxide substrates, as well as many different substrate materials which are used in semiconductor device fabrication.

Section 6.2.2: Implementation

Subsurface void localization has been implemented using the XE-120 afm. A sample was mounted on top of a vertically oscillating piezo-electric. The sample and piezoelectric are driven together to oscillate at resonance (about 70-80 kHz) using a SR850 lock-in amplifier with drive voltages ranging from 50 mV to 500 mV. A contact mode afm cantilever of low spring constant ($<0.5\text{ nN/nm}$) is scanned across the sample to obtain an image. The afm cantilever will have a vertical deflection oscillation component that is unique to the Young's modulus of the sample substrates chemical composition and geometry. The lock-in amplifier is used to measure the vertical deflection of the afm laser spot (A-B) on the pspd. The laser signal is passed from the signal access module to the lock-in, where both the amplitude and phase of the laser signal is tracked. Output channels 1 and 2 of the lock-in amplifier are used to pass the DC components to the afm control and scan electronics where it is plotted as the afm cantilever is raster scanner across the sample surface. It is found that a slow afm scan speed (0.2Hz) give a well-defined ultrasonic amplitude and phase signals.

Section 6.2.3: Sample Fabrication

A geometrically known subsurface feature was fabricated using electron/ion-beam deposition and milling. This made use of a dual-beam FEI Helios 400s with gas injection systems for platinum and carbon deposition. On a freshly cleaved silicon substrate a series of box outlines of decreasing sizes were deposited and/or milled onto the surface. The box outline sizes were $500\times 500\text{ nm}^2$, $1\times 1\text{ }\mu\text{m}^2$, $2\times 2\text{ }\mu\text{m}^2$, $3\times 3\text{ }\mu\text{m}^2$, $4\times 4\text{ }\mu\text{m}^2$, $5\times 5\text{ }\mu\text{m}^2$. Three sets of boxes were fabricated. Set #1 was fabricated using electron-beam platinum deposition using a low resolution electron beam at 2kV, 340pA. Set #2 was fabricated using high resolution electron beam platinum deposition 2kV, 340pA. The difference between low resolution electron beam deposition and high resolution deposition is the use of an in-lens secondary electron detector for high resolution imaging, which has far higher resolution due to field enhancement that channels electrons to the detector. Low resolution imaging is accomplished using in chamber detectors which typically utilize a bias voltage to filter and collect electrons of various energies. Set #3 was fabricated using ion beam milling at 30kV, 300pA. Once the three sets of box outlines were fabricated, they were covered with ion beam deposited carbon. Ion beam conditions were 30kV, 1nA. The fabrication of the box outlines is shown in the figure 6.1 below. The carbon capping of the features is shown in the figure 6.2 below.

Figure 6.1: Demonstrates electron and ion beam fabrication of subsurface features. **Green** boxes illustrate the box outlines that were deposited using low resolution electron beam platinum deposition. **Grey** boxes illustrate the box outlines that were deposited using high resolution electron beam platinum deposition. **Yellow** boxes illustrate the box outlines that were fabricated using ion beam milling. Box outlines were organized in order of increasing size and the 3 sets were fabricated within a 30um² area.

Figure 6.2: This illustrates the ion beam deposited carbon capping of the fabricated box outlines. The **upper diagram** shows the carbon capping of the first set of box outlines. The grey outline is used to signify a carbon deposition. The **middle diagram** shows the center set of box outlines being carbon capped. Notice the overlapping depositions, this was an attempt to minimize changes in topographic height. The **lower diagram** illustrates the carbon capping of the final set of box outlines.

Figure 6.3: Shows a schematic outline of the fabricated features that have been buried under an ion beam deposited carbon layer (**Image A**). The **dotted red** outline is used to show the afm scan orientation with respect to the features. **Image B** is a topographic afm scan of the fabricated features. Notice that the carbon layers have a small height difference at the overlap region. Also, the low-resolution electron beam features are visible.

Figure 6.4: Image illustrates a measurement of the carbon cap height of approximately 500nm (**Left**). (**Right**) image illustrates a measurement of the 3x3 box outline. It is found to be 2.85 μm wide.

Figure 6.5: A 3D topographic afm image of the scanned features. Low resolution electron beam deposited (LrEBD) features are the foremost features and the middle region is the high-resolution electron beam deposited (HrEBD) feature set and the back set of features are the IBD features. This image is used to illustrate the ion beam deposited capping, capping overlap, and surface height of the subsurface feature. Notice that LrEBD features are easily visible on the surface topography, while HrEBD and IBD features are not visible.

Figure 6.6: Shows a schematic outline of the fabricated features that have been buried under a ion beam deposited carbon layer (**Above**) **Image A**. The **dotted red** outline is used to show the afm scan orientation with respect to the features. **Image B** is a topographic afm scan of the fabricated features. **Image C** is a normal force image. **Image D** is a lateral force image. Notice the presence of the fabricated features, vertical lines from the ion beam carbon deposition, and regions of high lateral force from the afm tip dragging surface debris as the image is scanned. **Image E** is the ultrasonic amplitude image obtained by lock-in tracking the vertical laser deflection. Subsurface features are identifiable in all three regions, low resolution EBD, high resolution EBD, and ion milled box outlines. **Image F** is the ultrasonic phase image obtained by lock-in tracking the vertical laser deflection. Again, components of all sets of features are identifiable.

Figure 6.7: (Above) The same images as the previous figure, but with the subsurface features labeled with red dotted outlines.

Section 6.2.4: Experimental Results

The goal was to fabricate features that were predominantly subsurface to verify that the UAFM technique is sensitive to subsurface defects. It was found that the fabrication process resulted in small but identifiable surface features that were identified using topographic afm. It was found that subsurface features are identifiable using the UAFM technique, specifically, the by monitoring the amplitude and phase.

Section 6.2.5: AFM Topography

In the observed topographic image, Figure 6.7 Image B, the vertical set of rectangles to the left is the low resolution EBD features, the middle set was the high resolution EBD features and the set to the right was the ion milled features. In the topographic image only the low resolution EBD features were easily identifiable.

Section 6.1.6: AFM Normal Force Image

The normal force image Figure 6.7 Image C is used as the error signal while scanning in contact mode, therefore, it is expected to have a low contrast and low sensitivity to surface features. It does exhibit high contrast at the transition from silicon substrate to IBD carbon capping pad, and once more at the overlap region between capping pads, identified as bright vertical lines in image C. This was likely caused by the gain parameter being too low. All three sets of box outlines are visible to a varying degree. Similar to the topographic image, the low resolution electron beam deposited LrEBD features are easiest to identify, while HrEBD and IBD features are less defined.

Section 6.1.7: AFM Lateral Force Image

The LFM image Figure 6.7 Image D is sensitive to lateral forces that induce a cantilever torsion. In image D, material changes, height changes produce image contrast. In the image LFM there exists a “debris trail” that resulted from a piece of surface debris being dragged across the IBD capping pad and is visible as a white streak across the image. The high contrast of this debris trail indicates that it produces a large friction force on the cantilever as it is contact mode scanned across the sample surface. This feature is not visible in the topographic image. The three sets of subsurface features are visible to varying degrees. All features for LrEBD boxes are visible, while $1 \times 1 \mu\text{m}^2$ features or larger are visible in the HrEBD and IBD feature sets. Feature visibility is summarized in the table 19.

Section 6.2.8: UFM Amplitude Image

The UFM amplitude image figure 6.7-Image D is sensitive to changes in material properties such as Young’s modulus and surface topography. Image E has high contrast regions in areas exhibiting large changes in surface height (Overlapping IBD capping regions), in the region containing the “debris trail”, and in regions containing subsurface features. Similar subsurface feature visibility to the LFM images is noted. Submicron features are not well defined. Feature visibility is summarized in the table 19.

Section 6.2.9: UFM Phase Image

The UFM phase image is sensitive to phase changes that are induced as the afm cantilever and vertically oscillating surface interact. Feature visibility is similar to LFM and UFM amplitude. Feature visibility is summarized in the table 19.

Table 19: Summary of Feature Visibility							
	Deposition Type	500x500nm ²	1x1 μm^2	2x2 μm^2	3x3 μm^2	4x4 μm^2	5x5 μm^2
Topography	LrEBD	X	X	X	X	X	X
	HrEBD						
	IBD						
Normal Force	LrEBD	X	X	X	X	X	X
	HrEBD			/	/	/	
	IBD	/	/	/	/	/	
Lateral Force	LrEBD	X	X	X	X	X	X
	HrEBD			/	/	/	/
	IBD		/	/	/	/	/
UFM Amplitude	LrEBD	X	X	X	X	X	X
	HrEBD		/	/	/	/	/
	IBD		/	/	/	/	/
UFM Phase	LrEBD	X	X	X	X	X	X
	HrEBD		/	/	/	/	/
	IBD		/	/	/	/	/
X = Visible Feature, / = Partially Visible Feature, Blank = non-Visible Feature							

Section 6.3: Future Experiment #2: Defect Adhesion

Through the analysis of the afm tip-substrate interaction, it was realized that adhesion energy is a function of surface area of interaction. In the semiconductor industry, the presence of particle defects can cause device failure and reduce production yields. By exploring particle size distributions, methods can be developed for particle removal or particle adhesion mitigation. In ambient conditions, the major contributor for particle adhesion is due to capillary forces due to high humidity. In low vacuum conditions such as those used in atomic layer deposition (ALD), plasma enhanced chemical vapor deposition, capillary forces are reduced, and the major interaction force of non-charged particles is van der Waals. Controlling humidity could have a large effect on defect numbers.

Section 6.3.1: Defect Prevention

By directly measuring adhesion forces as a function of surface area, one can estimate binding energies and therefore the work required to remove defect debris. It is theorized that by acoustically exciting a sample surface or wafer at a mechanical resonance, that defect adhesion energy can be overcome. Perhaps by acoustically exciting a sample during processing, defects can be reduced or directed with acoustic nodes to controlled sacrificial regions. Perhaps wafers could also be acoustically cleaned, reducing process time and cost. Please note, the method described here is not ultrasonic bath cleaning, which works on the basis of the formation of air bubbles that supersonically collapse to apply force to particle debris. Such method can damage $1\mu\text{m}^2$ areas of substrate and are not ideal for the current submicron feature. The process described above would make use of passing acoustic waves

through the wafer, which then are transferred in the normal direction onto surface defects in both ambient and vacuum conditions.

Figure 6.8: Schematic illustrating using an acoustic sensor-transducer to apply a force to the surface of a wafer with surface debris present. Such acoustic cleaning could transfer an acoustic signal through the wafer using direct mechanical contact, allowing the process to be applied in both ambient and vacuum conditions.

Section 6.4: Surface Nano-Roughness Characterization using Acoustics

Section 6.4.1: Proposal

In the semiconductor field, surface roughness analysis is typically performed to characterize resistivity of a nanofilm, and verify uniformity of Atomic Layer Deposition (ALD) processing. A surface roughness analysis is performed using an afm and the results are dependent upon tip radius. As an afm tip is used to process multiple samples, the tip becomes blunted and loses its ability to characterize small cracks and voids in a sample surface. Afm tips can be expensive and it is time consuming to change tips after multiple samples. A method that is able to reliably measure surface roughness without contact is needed. It is proposed here that the relationship between nano/sub-nano roughness and surface acoustic reflectivity be investigated to see if a useful correlation is present. It has been shown by Nagy and Alder⁴⁰ that the acoustic reflection from a sample surface is significantly attenuated by a rough surface. It has been shown that the surface roughness changes of 3-4nm of a thin-film resonator results in a drastic reduction in the Q-factor from 350 down to 150⁴¹. This suggests that acoustic reflectivity losses are sensitive to nanometer roughness to changes.

Section 6.4.2: Implementation

A tuning fork driven to oscillate at resonance is mounted a fixed distance above a sample surface and is driven such that motion is perpendicular or oblique (angled) to the sample surface. An acoustic emission transducer (Acoustic Sensor) is mounted at a fixed angle and distance from the sample and tuning fork. The experiment could utilize a simple glass slide

half coated with metal deposition and half without a metal deposition as a test surface. AFM and SEM imaging can be used for direct roughness measurements and topographic surface analysis.

Figure 6.9: (A) Illustrates an acoustic wave is incident upon a smooth surface that exhibits specular reflection. (B) An acoustic wave is incident upon a rough surface and the acoustic signal is diffusely scattered.

Section 6.4.3: Estimated Results

It is expected that there will be a relationship between surface acoustic reflectivity and the nano-surface roughness. However, the magnitude and usefulness of this relation remains unknown.

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