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A NOVEL APPROACH FOR MEASURING THERMAL CONDUCTIVITY OF ELECTRO-SPUN NANOFIBERS

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A NOVEL APPROACH FOR MEASURING THERMAL CONDUCTIVITY OF
ELECTRO-SPUN NANOFIBERS

MASTER OF SCIENCE THESIS

BY

NICHOLAS BONATT

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2018

Abstract

The ability to replace metals, ceramics, and composites with polymer nanofibers can lead to more desirable applications in heat exchangers, energy storage, and biomedical fields. Research into thermal transport within polymer nanofibers has increased for such applications, with the need to develop new techniques to measure and understand such properties.

Polymers with high thermal conductivity have been a growing asset in desired heat transfer devices. Much effort has gone into developing advanced thermal conductivity measurement techniques; however, there is still a lack of fundamental understanding between the relationship of structures and thermal transport properties in polymer nanofibers.

The purpose of this thesis is to contribute to the further understanding of the thermal effects and conductivity capabilities of polymer nanofibers, and to supply a novel method of measurement to the research community.

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Contents

Abstract	ii
Acknowledgments	iii
List of Tables	vi
List of Figures	vii
1 Introduction	1
1.1 Thermal Transport Effects in Nanostructures	2
1.1.1 Thermal Properties of Polymer Nanofibers	2
1.2 Measurement Techniques	5
1.3 Proposed Method	8
1.3.1 Use for Electro-Spinning	9
1.3.2 AFM Use	11
1.3.3 Use of Bi-Material and Silicon Cantilevers	15
1.4 Thesis Outline	16
2 Design and Modeling	18
2.1 Heat Transfer and Conduction	19
2.2 Thermal Modeling of a Fin	21
2.3 Thermal Modeling of the Heating Prong	24
2.3.1 Heating Prong Fluxes $q_{p1}(x_1)$ and $q_{p2}(x_1)$	27
2.3.2 Thermal Modeling of a Single Nanofiber	29
2.4 Applied Temperature with AFM Integration	32
2.4.1 Bi-Material Cantilever Temperature Profile	33

2.4.2	Bi-Material Natural Beam Deflection Theory	34
2.4.3	AFM Displacements	37
3	Experimental Apparatuses	41
3.1	Sample Plates	42
3.1.1	Plate Design	42
3.1.2	Plate Creation	44
3.2	Fiber Creation	46
3.3	Electrospinning Apparatus	49
3.4	Appending a Fiber	52
3.5	AFM Setup	56
4	Methodology and Calibration	59
4.1	Measuring Force Constant and Resonance Frequency	60
4.2	Setting System Parameters	61
4.3	Procedural Setup and Alignment	66
5	Measurement Results and Discussion	69
5.1	Introduction	70
5.2	Deflection Results	70
5.2.1	Identifying V/nm and AFM-Tipless Cantilever Natural De- flection Recordings	71
5.2.2	Calibrated Deflection Recordings	76
5.2.3	Appended Fiber Deflection Recordings	79
5.3	Obtaining Fiber Thermal Conductivity	81
6	Summary and Future Work	83
6.1	Chapter Summaries	84
6.2	Future Work	85
A	Prong, Cantilever, and Fiber Properties	88
B	MATLAB Code	89

List of Tables

5.1	Appended fiber recorded temperatures (cantilever ambient, prong ambient, prong base, and prong tip respectively) and theoretical (prong end fiber and cantilever tip temperatures respectively). . . .	81
5.2	List of assumed and recorded flux into the fiber per heat step. All fluxes are multiplied by $10^5(W/m^2)$; $q_{Recorded}$ is the flux determined at the prong end of the fiber; qf_{25} and qf_{105} provide minimal and maximum assumed thermal conductivity where $q_{Recorded}$ falls between. Values are 0 at scan 100 since temperatures at this scan were set to zero.	82
A.1	Bi-Material and Silicon Tipless Cantilever Properties	88
A.2	Aluminum Heating Prong and Polycaprolactone (PCL) Single Nanofiber Properties.	88

List of Figures

1.1	Design of the gel-spinning process [21]	4
1.2	Suspended Micro-device [24]	6
1.3	Single Cantilever Technique [1]	7
1.4	Dual Cantilever Technique [25]	8
1.5	Design and Model of the Probe-to-Probe Technique	9
1.6	Typical AFM System	13
2.1	Uni-direction conduction through a beam with internal heat generation	20
2.2	Total Flux through the Heating Prong to the Nanofiber	25
2.3	Schematic of the Nanofiber	29
2.4	Heat Transfer through Bi-Material Cantilever modeled as a rectangle	33
2.5	Bi-material and AFM cantilever deflection: a) Natural beam deflection z_{nat} only from thermal expansion. b) Applied resistance from the AFM cantilever, where Δz is the change in deflection	39
3.1	Parts Used for Sample Plates	44
3.2	Completely constructed sample plates	45
3.3	Electrospinning Apparatus	50
3.4	Sample Plate Held Attached to the Microscope	52
3.5	a) Tweezers loading single fiber to prong and microscope tweezer, b) Appending fiber to tip of cantilever with Van der Waal attractive force	54
3.6	PCL nanofiber jumping to a cantilever tip due to Van der Waal's attractive force. This cantilever is a traditional silicon cantilever with probe which is not part of the probe-to-probe system	54
3.7	PCL nanofiber appended to the bi-material cantilever that was put through testing	55

3.8	Alternate variations of a single appended PCL nanofiber to the bi material cantilever. a) Shows a fiber only suspended between both cantilevers. b) Shows Van der Waal attractive force. c) and d) are alternate append fibers bridging both cantilevers. These were appended to a test bi-material cantilever sample plate and were not tested.	55
3.9	Soldering iron and AFM setup. The multimeters are replaced with a LabView DAQ recorder.	57
3.10	Close up image of the sample plate within the system.	57
4.1	Scan Tab Settings	64
4.2	System Tab Settings	65
4.3	Topo Scan Settings	65
4.4	a) Bi-Material Cantilever Base Contact using AFM-tipless silicon cantilever. b) Probe-to-Probe Contact	67
5.1	Average deflections of each measurement stage.	71
5.2	Natural AFM-tipless cantilever and Photo-diode deflections versus temperature.	73
5.3	The Photo-diode response to AFM-Tipless cantilever deflection. Obtained from dividing slopes from Figure 5.2 utilizing natural deflection results.	73
5.4	Theoretical versus Measured AFM-Tipless cantilever deflections. . .	75
5.5	Average recorded natural deflection temperatures after reaching steady state.	76
5.6	Theoretical versus measured calibration Results.	77
5.7	Average recorded Probe-to-Probe calibration temperatures after reaching steady state.	78
5.8	True measured fiber deflection results, subtracting appended fiber recordings from calibration recordings.	80
5.9	Average recorded Probe-to-Probe appended fiber temperatures after reaching steady state.	80
6.1	Park Systems SThM System	86

Chapter 1

Introduction

Polymers with high thermal conductivity are a growing asset in heat transfer devices. The ability to replace metals and ceramics can lead to more desirable applications in heat exchangers and energy storage. Bulk polymers are poor heat conductors, with a thermal conductivity around 0.1 W/mK . Studies into nanofibers have shown thermal conductivity to be as high as 104 W/mK , which is larger than about half of the pure metals [1]. Due to the highly oriented polymer chains and enhanced crystalline structure, a fiber with high thermal conductivity can be produced using high voltage [2]. The best known way is to use the electrospinning method to create these nanofibers. Creating a device to measure these nanofibers is a challenge.

1.1 Thermal Transport Effects in Nanostructures

With an increased demand for small technological devices and processed materials, including structures on the nanometer scale, a greater understanding of thermal transport of nanoscale devices and individual nanostructures arise [3, 4]. Novel thermal properties arise in low-dimensional nanostructures versus in bulk materials. Properties such as abnormal heat conduction, size dependence of thermal conductivity, phonon boundary internal and edge scatterings effect these one-dimensional structures [5, 6].

1.1.1 Thermal Properties of Polymer Nanofibers

Thermal transport within nonmetallic systems, such as polymers, transport heat via phonons. Phonons are a quasiparticle associated with vibration of a crystal lattice. While these phonons span a broad range of frequencies, those with mean free paths $< 100nm$ at room temperature are typically the main contributors to thermal conduction [3]. However, structures within this scale no longer adequately follow the thermal transport for bulk models [7, 8], unless taking into account the energies across boundaries [4].

The low thermal conductivity of bulk polymers comes from their structure due to random orientations and weak couplings of the polymer chains. Imperfections within bulk materials such as voids and entanglements, generate high thermal resistance between the crystalline domains; high frequency phonon modes within must transfer from high to lower frequencies modes across domains [9]. It

has been found through many studies that polymer nanofibers with highly aligned polymer chains can have much higher thermal conductivities and Young's modulus than typical bulk values [1, 2, 3, 9, 10, 11]. As the degree of crystallinity, increases so does the thermal conductivity [12, 13, 14]. Through techniques such as the draw and electro-spinning methods, polymer chain alignments and crystallinity can be enhanced. Attaining oriented and stretched polymer chains, as well as increased crystal sizes, can enhance mechanical strength and adversely affect thermal conductivity.

Zhong et al. were able to measure thermal conductivity of single Nylon-11 nanofibers fabricated utilizing electro-spinning [9]. Using a micro-device platform, the thermal conductivity of fibers between 50-400nm in diameter were measured to be between 0.35 - 1.6 W/mK , compared to the bulk form, which measured between 0.2 - 0.25 W/mK . Zhong was also able to measure the crystallinity using Wide-Angle X-ray Scattering (WAXS). This technique specifically refers to the analysis of Bragg peaks scattered to wide angles ($2\theta > 1^\circ$) within sub-nanometer structures. They found the crystallinity to be $\approx 35\%$; however such measurements require a collection of fibers and cannot be utilized on single fibers.

Studies by Yao and Papkov, Dmitry, et al. showed that the electro-spinning method for producing such nanofibers suggested that since the process involves rapid evaporation of the solvent, the subsequent solidification of nanofibers inhibits polymer crystallization [15, 16]. This was suggested due to the relaxation times and residual solvents remaining within after the fiber has been spun; this can accelerate chain relaxation and lead to shorter relaxation times [17, 18]. This

can also be seen for polymers with high glass Transition temperature (T_g) values [19]. However, with polymers and polyesters with lower T_g values, such as PCL ($T_g \sim -60^\circ\text{C}$), takes longer time to crystallize [20]. A gel-spinning process can fix this dilemma by applying a post-drawing once the fiber is in solid state below the melting temperature to prevent chain relaxation after orientation [21, 15]; the design is seen in 1.1.

Figure 1.1: Design of the gel-spinning process [21]

A similar method to the gel-spinning process is the ultra-drawing method which was utilized by Sheng Shen et al. in 2010. Shen fabricated and measured the thermal conductivity of single polyethylene nanofibers showing an increase in thermal conductivity compared to that of bulk polyethylene from 0.1 W/mK to values as high as 104 W/mK [1]. These fibers ranged from $50 - 500\text{nm}$ diameters and lengths up to tens of millimetres.

Despite these recent advancements in thermal conductivity enhancement

via drawing, there is still a lack of fundamental understanding of the relationship between the structures and attained thermal transport properties in polymer nanofibers.

1.2 Measurement Techniques

Much effort has gone into developing advanced thermal conductivity measurement techniques. On more of a macro scale, there exists the $3w$ technique. This traditional method is meant to measure polymer thin films using an AC current at frequency w through the sample leading to output voltage oscillations. The first reported use of the $3w$ method to measure the thermal conductivity of solids was by Cahill (Cahill and Pohl 1987). Cahill’s $3w$ technique utilizes a micro-fabricated metal line that acts as a heater/thermometer. “When an alternating current (AC) voltage signal is used to excite the heater at a frequency w , periodic heating generates oscillations in the electrical resistance of the metal line at a frequency of $2w$. In turn, this leads to a third harmonic ($3w$) in the voltage signal, which is used to infer the magnitude of the temperature oscillations” [22]. However, this technique is difficult to implement on a single nano-structure.

Another technique used a micro device that suspended carbon nanotubes between two silicon nitride plates. Current was passed through one generating a heat input, where the induced temperature change was measured through the other [23]. These plates were fabricated using an electron beam, photolithography, metal coating, and etching. Each island consisted of a platinum thin film resistor. This served as a heater to increase the temperature. Since the tempera-

ture changed with a change in their resistance, these could also be used to measure the temperature of each island [24]. Carbon nanotubes were then bridged between the two suspended islands using a similar method used to fabricate Atomic Force Microscope (AFM) scanning probe tips. This technique is used throughout industries to measure the thermal conductance of carbon nanotubes. However, it is not used for single polymer nanofibers.

Figure 1.2: Suspended Micro-device [24]

In more recent years two measurement methods were able to measure the thermal conductivity of a single polymer nanofiber: Shen [1] and Canetta [25]. Shen utilized a bi-material cantilever to directly draw a polymer wire from a droplet from a soldering iron tip. Shen constructed an optical system within a vacuum to measure the deflections from the bi-material cantilever once the tip of the iron was heated, seen in Figure 1.3. A fiber thermal conductivity could be known since the temperature of the heated tip and calculations of beam deflections due to temperature changes were known.

Figure 1.3: Single Cantilever Technique [1]

Canetta used a slightly different approach. Instead of drawing out a fiber onto a cantilever he designed the dual-cantilever technique, seen in Figure 1.4. This technique utilized two fabricated bi-material cantilevers, one for laser heating and the other for deflection sensing. Similar to Shen, Canetta constructed an optical system within a vacuum. Polymer nanofibers were electrically spun and then bridged between both cantilevers. Once one cantilever was heated with a known power, the deflection of the sensing cantilever was known.

Figure 1.4: Duel Cantilever Technique [25]

1.3 Proposed Method

In combination with both Shen and Canetta’s designs, my novel design will use two cantilevers in forced actuation, as seen in Figure 1.5. This design will take a look at a new thermal conductivity measurement design that focuses on a mechanical system rather than an optical method. The reason to create such a design is to mitigate complexity in measuring polymer nanofibers by joining two independent subsystems. This allows the underlining bi-material cantilever and fiber sample to be easily loaded into a traditional AFM without modification or cost.

A sample plate, which is loaded into the AFM, includes a heated prong, bi-material cantilever, and electro-spun nanofiber, where as the AFM will only include a tipless silicon cantilever and operated normally. Both cantilevers will be placed tip to tip, once temperature is added to the system, the temperature sensitive bi-material cantilever will force the AFM’s cantilever to deflect. The deflection will then be recorded, which will then be used to obtain the fibers thermal conductivity. This will be known as the Probe-to-Probe Technique.

Figure 1.5: Design and Model of the Probe-to-Probe Technique

1.3.1 Use for Electro-Spinning

One of the most common and traditional methods to create nano sized polymer fibers is the use of an electro-spinning apparatus. Electro-spinning has regained more attention due to a surging interest in nanotechnology since various polymers with diameters down to submicrons or nanometers can be easily fabricated [26]. It is currently the only method that allows the fabrication of continuous fibers with diameters down to a few nanometers [17].

Electro-spinning is a process by which polymer nanofibers with diameters between 0.05 and 5 microns can be produced using an electro-statically driven jet of polymer solution using high voltage electric fields [27, 28]. In general, a fluid solution is pumped through an electrode to a grounding plate or a collector plate. When a high electric field is applied to the droplet of fluid, which may be a melt or solution coming out from the tip, this acts as one of the electrodes [29]. “When an external electric field is applied to a solution, the positive and negative ions in the polymer fluid tend to move in opposite directions. Negative ions are forced

toward the positive electrode, and positive ions are forced toward the negative electrode [19].” This leads to the droplet deformation and finally to the ejection of a charged jet from the tip of the cone accelerating towards the counter electrode leading to the formation of continuous fibers [30, 31].

At a traditional needle tip where the droplets or strands are produced, a Taylor Cone is formed. This is a consequence of electrical forces that form a conical protrusion [19, 32]. This theory was first described by Taylor in 1964 [33]. As charged liquid is pumped out of the needle, surface tension keeps the droplet appended until the surface charges of the droplet are overcome by the grounding electrode. As the intensity of the electric field is increased, the hemispherical surface of the fluid at the tip of the needle elongates to form a conical shape known as a Taylor Cone. Taylor studied these electric fields E and their influence on surface tension σ ,

$$\frac{1}{2}\varepsilon_o E^2 = \frac{\sigma}{r \tan\alpha} \quad (1.1)$$

where ε_o is the permittivity of free space (Fm^{-1}), $r \tan\alpha$ is the curvature of a cone, and α is the half cone angle [34, 35]. He predicted that it only took an angle of 49.3° . However, Taylor’s Cone angle should be 33.5° instead of 49.3° , as reported from Yarin et al (2001) [26], due to the Taylor Cone being a specific self-similar solution, meaning a flow which ‘looks the same’ either at all times or at the same scale. Moreover, there do exist non-self-similar solutions that do not tend toward a Taylor Cone [36]. The surface tension, viscoelasticity, and charge density within the ejected polymer are the key influences in proper fiber formation [37].

The discharged liquid solution jet undergoes an instability and elongation process, which allows the jet to become long and thin. Meanwhile, the solvent evaporates, leaving behind a charged polymer fiber. In the case of the melt, the discharged jet solidifies when it travels in the air [26]. The discharged polymer solution jet undergoes a whipping process wherein the solvent evaporates, leaving behind the charged polymer fiber, which tends to the grounding plate [28].

1.3.2 AFM Use

The Atomic Force Microscope (AFM/SFM) is within the family of the Scanning Probe Microscopes (SPMs). Other probe microscopes, such as Scanning Tunneling Microscopy (STM) or Scanning Near-field Optical Microscopes (SNOM) focus on quantum tunneling and short range electromagnetic fields, which are not useful with this proposed research [38]. An AFM utilizes force interactions to measure the structure of roughness of a surface. The instrument is able to collect information on the arrangement of individual molecules and even individual atoms in a sample with high accuracy and detailed resolution [39]. AFMs are useful for measuring magnetic fields, friction gradients, piezo response, temperature, nanoscale forces, and elasticity of samples. Additional surface characterization techniques such as Scanning Electron Microscopes (SEMs), allow for resolutions of about 25 Angstroms utilizing an electron beam rather than a light source [40]. However, polymers exhibit weak electron scattering and poor contrast and act essentially like organic materials within this system. Secondly, polymers typically have low electrical conductivity leading to rapid accumulation of negative charges, which dramatically decreases resolution [41]. SEMs may also damage polymers due to

their high power; AFMs only utilize the inter-atomic forces, a non-destructive technique for surface measurements [42]. The AFM will be used based on its ability to detect the small temperature-mechanical displacement variations implemented into the system and utility compared to previously mentioned instruments.

AFM Components

The main components of an AFM consist of a cantilever probe, piezoelectric scanner, force sense, laser, Proportional Integral and Derivative (PID) controller, and a photo diode signal detector, as seen in Figure 1.6 [43]. A probe is attached to a cantilever beam that is used to read the roughness of a surface as the probe scans in XY coordinates and interacts with the sample. As the cantilever is deflected due to forces exerted from the sample, a focused laser senses this change and sends a signal to the photo-diode detector. Once the detector notices this change, either the piezo stage moves to counter at the variation or stays static and records the bending moment, depending on the mode type.

Figure 1.6: Typical AFM System

AFM Mode

The AFM has a few different operating modes to use and consider for the novel measurement design. The operating modes are split into dynamic or static modes with attractive and net-repulsive interactions, contact or non-contact within modes. Dynamic, or tapping modes, measure the changes in the vibrational properties of the cantilever measuring: resonance frequency, oscillation amplitude, and phase between the cantilever oscillations, simply intermittent contact. Static mode can operate either in applying constant force or constant deflection by just adjusting

the z-piezo axis of the cantilever. However, in this case, since the sample will not be moving nor have the need for vibrational properties and the need for variable force change, the design will use a net-repulsive contact static mode, non-vibrating mode. The system will be held at a constant position and not allow the cantilever to re-position once deflection is noticed.

AFM System Parameters

Without constructing an external optical system as seen in prior designs, AFMs are programmed to be optimized, adjusted, and calibrated to certain preferences. This allows the PID gains controller and High Voltage (HV) gains of the system piezos to adjusted to particular parameters, depending on the need.

A sample is typically fixed on the top of a 3-axes piezoelectric stage that moves the sample under the tip, where the movements X and Y are controlled by the computer that generates two synchronized voltage ramps (gains) [44]. Once in contact, a force transducer sensor senses the force between the tip and the surface, allowing the feedback controller to feed a signal from the transducer back to the piezoelectric stage. This allows the AFM to maintain a fixed force between tip and sample. Typically, the expansion coefficient for a single piezoelectric device is on the order of 0.1nm per applied volt. Therefore, if the voltage to excite the piezoelectric stage is 2 volts, then the material will expand about 0.2nm [39].

The z-piezoelectric stage and the force transducer are linearly mirrored. Therefore to get the most data out of the AFM in use (can only record two devices at once), the XY piezo gains and force transducer gain will be zeroed. Zeroing

the transducer gains allows the piezo stage not to respond to photo-diode signals. Secondly, turning off the X and Y piezo stage gains hinders the scanning in X and Y directions, but still allows sensing detection from the photo-diode. Additionally, the PID gain controls can also be adjusted to scale the system properly, such that the feedback loop will respond quickly to topography changes. More on these settings will be discussed in Chapter 4.

1.3.3 Use of Bi-Material and Silicon Cantilevers

The reason for using a bi-material cantilever is because it has high sensitivity due to small dimensions and thermal mass [45]. A bi-material cantilever beam is comprised of two material layers. Typically bi-material cantilevers are made of silicon and coated with gold or aluminum to improve reflectivity for AFM sensing. Once a temperature change is introduced, the cantilever will deflect due to the difference in Coefficients of Thermal Expansion (CTE) of both layers. These types of bi-material cantilevers have shown the ability to detect deflections at 3 μm resolution with the measurement of temperature, optical power, and energy with 2 μK , 76 pW , and 15 fJ resolution, respectively [46].

Typical silicon heated cantilevers have spring constants ranging from 0.01 to 10 N/m, and resonant frequencies ranging from 50 to 300 kHz and are calibrated using the thermal noise method [47]. Raman microspectroscopy characterizes them with spatial and temperature resolutions of 1 μm and 3°C [47, 48]. Additional research of laser heated cantilevers, shows that contact thermal conductivity is typically in the range 0.1–100 nW/mK; and for probe tip radii of 30

nm, a typical contact diameter is about 10 nm providing a contact force of 10 nN. The spreading contact conductivity due to 10 nm contact on a polymer sample becomes 2 nW/mK [48]. This may be useful when determining conductivity of the cantilevers utilized within this thesis.

Furthermore, the heat transfer coefficient air gap h_{airgap} may be noticed when determining heat transfer from fiber to cantilever. As seen in equation 1.2, the h_{airgap} would be on the order of $10 \text{ kW}/\text{m}^2\text{K}$ for a tip height of 1–10 μm . Similarly, the probe being utilized within this thesis has a $15\mu\text{m}$ diameter. In continuing works, this may be useful. Moreover, $10 \text{ kW}/\text{m}^2\text{K}$ will also be utilized for the heat transfer coefficient for the fiber.

$$h_{airgap} = \frac{k_{air}}{d} \quad (1.2)$$

More on the properties of the cantilevers can be seen in the Appendix.

1.4 Thesis Outline

The purpose of this thesis is to further understand the thermal effects and conductivity capabilities of polymer nanofibers and to supply a novel method of measurement to the research community. With the use of temperature sensitive bi-material cantilevers and AFMs, one can obtain the thermal conductivity of electro-spun nanofibers.

Chapter 2 reviews introductory thermodynamics, along with the theoret-

ical design of the Probe-to-Probe measurement system. This design incorporates a two cantilever force interactive relationship. The reason to create such a design is to mitigate complexity in the measurement of polymer nanofibers by joining two independent subsystems. This allows the underlining bi-material cantilever and fiber sample to be easily loaded into a traditional AFM without modification or cost. Detailed modeling of this conjoined system design can be seen [here](#).

Chapter 3 focuses on the experimental apparatus, fiber creation, and equipment used. It will review the electro-spinning apparatus used for fiber fabrication, the experimental setup and creation of sample plates, fiber appending, measurement and alignment, and AFM integration for the measurement process.

Chapter 4 describes the procedural measurement of the system and outlines how the system was calibrated, along with how each of the system settings was determined.

Chapter 5 details all the results from testing, including: natural deflections, pre-appended fiber calibrations, and appended fiber recordings. Each review incorporates findings and comparisons of measured results to theoretical expectations, along with explanations and discussions.

Chapter 6 provides a summary of descriptions and conclusions from each chapter, along with a discussion of what can be done in future experiments to provide expected results.

Chapter 2

Design and Modeling

This chapter will review introductory heat transfer and the thermal modeling of the system in use. As seen in figure 1.5 the system utilizes a heating prong, a silicon tipless AFM cantilever, and a bi-material AFM cantilever. As heat is sent through the base of the heating prong it is transferred through the fiber to the tip of the bi-material cantilever. Due to the thermal expansion of gold versus silicon nitride, the gold deflects and adversely bends the tipless AFM cantilever. The AFM cantilever deflects, and the laser from the AFM records this beam deflection. As seen from natural beam deflection theory and Hooke's Law this deflection can be used to obtain the temperature output T_{ct} from the fiber at the tip of the bi-material cantilever. In congruence, the flux q_f and temperature T_f into the fiber from the heating prong is obtained through the use of thermocouples. The thermal conductivity of the nanofiber k_f can be found after finding the temperatures at both ends of the fiber.

The system will be modeled as a one-dimensional time-independent steady state problem. This allows the modeling and measurements to be simplified. Subscripts p , f , and c , and directions x_1 , x_2 , and x_3 represent the prong, fiber, and

bi-material cantilever respectively throughout this paper.

2.1 Heat Transfer and Conduction

Before reviewing the thermal models through the proposed system, the first step is to briefly explain heat transfer fundamentals for one-dimensional systems. Heat transfer by conduction is the flow of thermal energy within a solid and non-flowing fluids driven by a non-uniform temperature field. Heat transfer Q and work W are the two types of energy interactions that make up the internal energy E . These interactions are known as the first Law of Thermodynamics for a closed system or the conservation of energy:

$$\partial E = Q - W \quad (2.1)$$

Internal energy is associated with the disorderly motion of molecules transferring kinetic and potential energies, where heat is transferred by conduction. Work is the transfer of energy resulting from a force acting through a distance and heat is the energy transferred as the result of a temperature difference [49]. In terms of unidirectional and per-time equivalent through a insulated beam with heat generation from equation 2.1, internal energy can be simplified as

$$\frac{\partial E}{\partial t} = Q_{in} - Q_{out} + W \quad (2.2)$$

or

$$\frac{\partial E}{\partial t} = Aq_x - Aq_{x+\Delta x} + W \quad (2.3)$$

as a heat transfer rate q with some output change Δx in terms of heat

flux $q_x = Q/A$ (W/m^2). This is also known as Fourier's Law of heat conduction which reads

$$q_x(x, t) = -k \nabla T(x, t) \quad (2.4)$$

where k is the thermal conductivity and ∇T is the temperature gradient [50]. This is the assumption that the material is isotropic and homogeneous where the thermal conductivity is constant.

Figure 2.1: Uni-direction conduction through a beam with internal heat generation

As seen in Fig.2.1 when considering heat being conducted through a one-dimensional cube, $Aq_x - Aq_{x+\Delta x}$ is the longitudinal conduction, work W can resemble $(A\Delta x)\dot{q}$, where $\dot{q}$ is the volumetric rate of internal heat generation, and $\frac{\partial E}{\partial t} = pcA\Delta x \frac{\partial T}{\partial t}$ as thermal inertia. This is assumed that the temperature variation along the beam is very small so that the specific heat, c is small and that internal energy change is proportional to its temperature change. Rewriting equation (2.3) substituting the previously stated replacements, the following equation (2.5) can

be re-solved as the thermal inertia.

$$pcA\Delta x \frac{\partial T}{\partial t} = Aq_x - Aq_{x+\Delta x} + A\Delta x \dot{q} \quad (2.5)$$

However, this equation takes into account non-steady state with internal heat generation. Since the modeling and experimentation require steady state and there exists zero internal heat generation, the internal energy equation reduces to only terms of conduction. Simplifying equation 2.5 and substituting Fourier's Law 2.4 in x -direction obtains equation 2.6 called heat conduction, to be utilized later.

$$Q_{cond} = Aq_x - A(q_x + \frac{\partial q_x}{\partial x} \Delta x) \quad (2.6)$$

2.2 Thermal Modeling of a Fin

For both 1D beams and rods, or cantilevers and fibers respectively, the heat transfer through these systems can be modeled as fins including Newtons Law of Cooling. Steady state is defined as the process of unchanging time which will be considered zero since the collection of experimental data will be assumed to be steady state. The heat generated term will be considered the heat sink for cooling fins. Reviewing equation 2.5 and noting that in steady state all the heat that is being generated inside the fins must be transferred to the fluid around the fin, in this case the fluid is air. The temperature distribution $T(x)$ reaches a steady state because the surface of the fins are bathed in an ambient temperature T_∞ where the heat transfer coefficient h is uniformly surrounding the perimeters P by

a change of length Δx . As seen in equation 2.7 the lateral heat convection can be written:

$$Q_{conv} = -Ph\Delta x(T(x) - T_{\infty}) \quad (2.7)$$

The fins can be modeled as 1D because the conduction through the axis the y and radial directions respectively are much lower than in the lengths of each model. Using the dimensionless quantity of the Biot number, the thermal contact of the surface of the fins to the fluid can be shown to be 'poor', or that the fins are good thermal conductors. If the Biot number in equation 2.8 is $\ll 1$ over the length of the fin, than the boundary temperature is nearly the same as the temperature in the center of the fin. A typical AFM cantilever has a Boit number less than 10^{-4} , confirming it can be modeled as 1D [48, 51]. This also works for each subsystem (prong, fiber, and both cantilevers).

$$Bi = \frac{hL}{k} \quad (2.8)$$

Again with assuming steady state and that each part of the system is modeled as individual fins, the heat balance for each fin problem will be similar. Combining equations 2.6 and 2.7 the heat balance equation becomes:

$$Aq_x - A(q_x + \frac{\partial q_x}{\partial x}\Delta x) - Ph\Delta x(T(x) - T_{\infty}) = 0 \quad (2.9)$$

Taking the $\lim_{\Delta x \rightarrow 0}$, equation 2.9,:

$$\lim_{\Delta x \rightarrow 0} A \frac{\partial q_x}{\partial x} - Ph(T(x) - T_{\infty}) = 0 \quad (2.10)$$

Then substituting the modified Fourier Law as heat flux and taking the derivative with respect to x gives:

$$q_x = -k \frac{\partial T}{\partial x} \quad \rightarrow \quad \frac{\partial q_x}{\partial x} = -k \frac{\partial^2 T(x)}{\partial x^2} \quad (2.11)$$

Combining equations 2.10 and 2.11 the governing equation of a fin becomes:

$$\frac{\partial^2 T(x)}{\partial x^2} - m^2(T(x) - T_\infty) = 0 \quad (2.12)$$

where

$$m^2 = \frac{Ph}{Ak} \quad (2.13)$$

The constants m , P , and A will represent the perimeters and cross sectional area respectively in each of the three fin systems. For the heating prong and bi-material cantilever the perimeter $P = w + s$ and the area $A = ws$, where w and s are the width and thickness respectively. For a fiber it is modeled as a cylinder so $P_f = \pi d$ and $A_f = \pi(\frac{d}{2})^2$, where d is the measured diameter of the fiber. Therefore the general solution temperature profile of a fin is equation 2.14 where C_a and C_b will represent variable constants, a and b represent multiple constants.

$$T(x) = C_a e^{-mx} + C_b e^{mx} + T_\infty \quad (2.14)$$

This will be utilized throughout modeling each fin. After the boundary conditions are defined, the constants can be found.

2.3 Thermal Modeling of the Heating Prong

When it comes to appending a fiber to the system it is difficult to get it directly in the same position along the heating prong every time a new fiber is added. The best method is to theoretically model the flux at any point to the fibers position on the prong. Since the fiber can sit anywhere along the prong, the heat flux, temperature, and length to the fiber from the base, all vary. As seen in Figure. 2.2 the equation

$$Q_f(x_2) = Q_{p1}(x_1) - Q_{p2}(x_1) \Rightarrow A_f q_f(x_2) = A_p q_{p1}(x_1) - A_p q_{p2}(x_1) \quad (2.15)$$

or

$$k_f \frac{\partial T_f(x_2)}{\partial x_2} = k_p \frac{\partial T_{p1}(x_1)}{\partial x_1} - k_p \frac{\partial T_{p2}(x_1)}{\partial x_1} \quad (2.16)$$

can be used to measure the heat flux at any position where $q_f(x_2)$ is the flux into the fiber, $q_{p1}(x_1)$ is the input flux at the fiber location on the prong and $q_{p2}(x_1)$ is the output flux to the rest of the prong. In this case $A_f = A_p$ since fluxes in the contact cross sectional areas are the same. Since flux into the fiber is represented from equation 2.15, a change in temperature along the fiber will also need to be found. Equation 2.16 is the general form in which to solve for k_f .

Figure 2.2: Total Flux through the Heating Prong to the Nanofiber

Since the flux into the fiber can not be solved directly, temperature values can be recorded at both ends of the heating prong. This allows a theoretical determination of the temperature into the fiber T_f .

Within calibration, the flux at any point along the heating prong is known since the base T_{po} and tip T_{ptCal} temperatures are measured. Once a fiber is appended, both the base T_{po} and the new tip temperature T_{pt} are recorded. Taking both T_{ptCal} and T_{pt} values, new fluxes q_{p1} and q_{p2} will be obtained and solved for T_{fCal} and T_f respectively. T_{fCal} represents the theoretical value calculated with no appended fiber. In theory, T_{fCal} and T_f may equal the same value. This is mainly in place to confirm if there is a difference or not, but difficult to determine from ambient heating and recording. In Chapter 5, T_{fCal} and T_f are approximated to be equal for this thesis. However, in other systems, this may not be the case.

The first part for modeling the system is to obtain the temperature profile of the heating prong at $T_p(l_1) = T_{fCal}$ without an appended fiber where l_1 is the

length from the base of the prong to the fiber. From equation 2.14, $T_p(x_1)$ is represented as,

$$T_p(x_1) = C_1 e^{-m_p x_1} + C_2 e^{m_p x_1} + T_{\infty p}. \quad (2.17)$$

Utilizing boundary conditions:

$$T_p(0) = T_{po} \quad (2.18)$$

$$T_p(l_1 + l_2) = T_{ptCal} \quad (2.19)$$

Solving for constants C_1 and C_2 :

$$C_1 = (T_{po} - T_{\infty p}) - C_2 \quad (2.20)$$

$$C_2 = \frac{(T_{ptCal} - T_{\infty p}) - (T_{po} - T_{\infty p})e^{-m_p(l_1 + l_2)}}{2\sinh(m_p(l_1 + l_2))} \quad (2.21)$$

Combining equation 2.17 and constants C_1 and C_2 at $T_p(l_1) = T_{fCal}$ and re-writing the profile in terms of T_{fCal} becomes:

$$T_{fCal} = [(T_{ptCal} - T_{\infty p})\sinh(m_p l_1) + (T_{po} - T_{\infty p})\sinh(m_p l_2)]\operatorname{csch}(m_p(l_1 + l_2)) + T_{\infty p} \quad (2.22)$$

Again this temperature value is represented as the heat flux q_{p1} at any temperature T_{fCal} along the heating prong.

2.3.1 Heating Prong Fluxes $q_{p1}(x_1)$ and $q_{p2}(x_1)$

Obtaining fluxes q_{p1} and q_{p2} are the next steps to solving the thermal conductivity of a single nanofiber using equation 2.16. To find both fluxes q_{p1} and q_{p2} , the temperature profiles will be split into two separate systems as seen in Figure 2.2. Again, the T_f obtained here will be compared with the T_{fCal} to show similarity.

Heating Prong Flux, $q_{p1}(x_1)$:

The governing equation can be written as:

$$\frac{\partial^2 T_{p1}(x_1)}{\partial x_1^2} - m_p^2(T_{p1}(x_1) - T_{\infty p}) = 0 \quad (2.23)$$

where the temperature profile from equation 2.14 becomes

$$T_{p1}(x_1) = C_3 e^{-m_p x_1} + C_4 e^{m_p x_1} + T_{\infty p} \quad (2.24)$$

Utilizing boundary conditions:

$$T_{p1}(0) = T_{po} \quad (2.25)$$

$$T_{p1}(l_1) = T_f \quad (2.26)$$

After applying boundary conditions, the constants are found to be:

$$C_3 = (T_{po} - T_{\infty p}) - C_4 \quad (2.27)$$

$$C_4 = \frac{(T_f - T_{\infty p}) - (T_{po} - T_{\infty p})e^{-m_p l_1}}{2 \sinh(m_p l_1)} \quad (2.28)$$

Combining equations 2.16 and 2.3.1, and rearranging the constants solving for $q_{p1}(l_1)$ gives:

$$q_{p1} = -k_p \frac{\partial T_{p1}(l_1)}{\partial x_1} = k_p m_p [(T_f - T_{\infty p}) \coth(m_p l_1) - (T_{po} - T_{\infty p}) \operatorname{csch}(m_p l_1)] \quad (2.29)$$

Heating Prong Flux, $q_{p2}(x_1)$:

The flux from the second part of the prong is similarly solved as q_{p1} however, with reverse direction. Referencing back to Figure 2.2 and equation $T_{p2}(x_1)$ governing equation can be written as:

$$\frac{\partial^2 T_{p2}(x_1)}{\partial x_1^2} - m_p^2 (T_{p2}(x_1) - T_{\infty p}) = 0 \quad (2.30)$$

where the temperature profile becomes

$$T_{p2}(x_1) = C_5 e^{-m_p x_1} + C_6 e^{m_p x_1} + T_{\infty p} \quad (2.31)$$

Applying boundary conditions:

$$T_{p2}(0) = T_{pt} \quad (2.32)$$

$$T_{p2}(l_2) = T_f \quad (2.33)$$

Again this tip temperature T_{pt} is when a fiber is appended. The temperature exiting and entering into the second portion of the prong and fiber should all be the same temperature T_{fCal} . After applying boundary conditions constants are found to be:

$$C_5 = (T_{po} - T_{\infty p}) - C_6 \quad (2.34)$$

$$C_6 = \frac{(T_f - T_{\infty p}) - (T_{pt} - T_{\infty p})e^{-m_p l_2}}{2\sinh(m_p l_2)} \quad (2.35)$$

Combining equations 2.16 and 2.31, and rearranging the constants solving for $q_{p2}(l_2)$ gives:

$$q_{p2} = k_p \frac{\partial T_{p2}(l_1)}{\partial x_1} = -k_p m_p [(T_f - T_{\infty p})\coth(m_p l_2) - (T_{pt} - T_{\infty p})\operatorname{csch}(m_p l_2)] \quad (2.36)$$

2.3.2 Thermal Modeling of a Single Nanofiber

Figure 2.3: Schematic of the Nanofiber

The next step is to find the temperature profile of the nanofiber as seen in Figure 2.3. The modeling of the fiber is similar to a traditional 1D fin problem, however, there is an additional ambient temperature change over the length of the fiber. This can be measured, seen in calibration from the prong to the bi-material cantilever. Therefore the change of ambient temperature was treated as a linear decline since $T_{\infty p}$ at the prong has a higher temperature than $T_{\infty c}$ at the cantilevers. The governing equation of $T_f(x_2)$ including $T_{\infty}(x_2)$ is written as

$$\frac{\partial^2 T_f(x_2)}{\partial x_2^2} - m_f^2 T_f(x_2) = -m_f T_{\infty}(x_2) \quad (2.37)$$

Since $T_{\infty}(x_2)$ is similar to a forcing function for this second order non-homogeneous differential equation, the temperature profile $T_f(x_2)$ will have to be split into a homogeneous and particular solutions [52]. Using

$$y = y_h + y_p \quad (2.38)$$

where $y = T_f(x_2)$, y_h is the homogeneous solution, and y_p is the particular solution.

The solution to the homogeneous solution of the temperature profile is

$$y_h = C_7 e^{-m_f x_2} + C_8 e^{m_f x_2} \quad (2.39)$$

when $y_p = 0$, which is similar to that of previous fin solutions. Allowing $T_{\infty}(x_2)$ to be a linear function represented as

$$T_{\infty}(x_2) = C_9 x_2 + C_{10} \quad (2.40)$$

Referencing Figure 2.3 the boundary conditions are:

$$T_{\infty}(0) = T_{\infty p} \quad (2.41)$$

$$T_{\infty}(L_f) = T_{\infty c} \quad (2.42)$$

where constants C_9 and C_{10} can be simply solved as

$$C_9 = \frac{T_{\infty c} - T_{\infty p}}{L_f} \quad (2.43)$$

$$C_{10} = T_{\infty p} \quad (2.44)$$

The particular equation solution reduces to:

$$y_p = C_9 x_2 + C_{10} \quad (2.45)$$

Adding the homogeneous equation 2.39 and particular 2.45 solutions to obtain equation 2.46, keeping C_9 and C_{10} for simplification.

$$T_f(x_2) = C_7 e^{-m_f x_2} + C_8 e^{m_f x_2} + C_9 x_2 + C_{10} \quad (2.46)$$

After applying boundary conditions:

$$T_f(0) = T_f \quad (2.47)$$

$$T_f(L_f) = T_{ct} \quad (2.48)$$

C_7 and C_8 can be found:

$$C_7 = (T_f - T_{\infty p}) - C_8 \quad (2.49)$$

$$C_8 = \frac{(T_{ct} - T_{\infty c}) - (T_f - T_{\infty p})e^{-m_f L_f}}{2\sinh(m_f L_f)} \quad (2.50)$$

Using equation 2.46 and substituting constants 2.49, 2.50, 2.43, 2.44 and solving equation 2.15 for $q_f = -k_f \frac{\partial T_f(0)}{\partial x_2}$, q_f is

$$q_f = k_f m_f [(T_f - T_{\infty p})\coth(m_f L_f) - (T_{ct} - T_{\infty c})\operatorname{csch}(m_f L_f) + \frac{(T_{\infty p} - T_{\infty c})}{m_f L_f}] \quad (2.51)$$

Now that all the fluxes of equation (2.15) have been obtained, all but the thermal conductivity of the fiber k_f and the tip temperature of the bi-material cantilever T_{ct} are known.

2.4 Applied Temperature with AFM Integration

Since flux into the fiber is represented from equation 2.15, all the fluxes 2.29, 2.36, and 2.51 have been solved. Next is to obtain the output temperature T_{ct} to be substituted into equation 2.51 where the thermal conductivity k_f of the fiber can be found. This temperature is found through the bi-material cantilever deflection with an applied force at the tip. The applied force is due to the resistance from the above AFM cantilever; the natural beam deflection, where only thermal expansion is acting on it. Since the natural bi-material deflection is a function of the temperature profile $T_c(x_3)$ the next set of modeling will be split into three sections: temperature profile, natural beam deflection, and acting force displacement from Hooke's Law.

2.4.1 Bi-Material Cantilever Temperature Profile

Starting with the temperature profile of the bi-material cantilever, as seen in Figure 2.4, the x_3 direction is now from the base of the cantilever T_{co} to the tip of the cantilever T_{ct} of some L_c . The cantilevers in use are a triangle form. However, this can be simply modeled as a rectangle [45].

Figure 2.4: Heat Transfer through Bi-Material Cantilever modeled as a rectangle

Modifying equation 2.9, two fluxes from the base of the cantilever from each material that have different thickness, perimeters, and areas. As seen from equation 1.5, the Au layer is t_1 and the S_3N_4 top layer is t_2 . When adding both input fluxes the heat balance equation becomes:

$$A_1 q_1 - A_1 \left(q_1 + \frac{\partial q_1}{\partial x_3} \Delta x_3 \right) + A_2 q_2 - A_2 \left(q_2 + \frac{\partial q_2}{\partial x_3} \Delta x_3 \right) - h(P_1 + P_2) \Delta x (T_c(x_3) - T_{\infty c}) = 0 \quad (2.52)$$

Conducting the same steps as in section 2.2 for the thermal modeling of a fin the temperature profile is

$$T_c(x_3) = C_9 e^{-m_c x_3} + C_{10} e^{m_c x_3} + T_{\infty c} \quad (2.53)$$

where m_c^2 was solved when the width was much greater than the thickness t :

$$m_c^2 = \frac{2h}{k_1 t_1 + k_2 t_2} \quad (2.54)$$

Utilizing the boundary conditions

$$T_c(0) = T_{co} \quad (2.55)$$

$$T_c(L_c) = T_{ct} \quad (2.56)$$

the constants are solved as:

$$C_{11} = T_{co} - T_{\infty c} - C_{12} \quad (2.57)$$

$$C_{12} = \frac{(T_{ct} - T_{\infty c}) - (T_{co} - T_{\infty c})e^{-m_c L_c}}{2 \sinh(m_c L_c)} \quad (2.58)$$

where the complete temperature profile of the bi-material cantilever is:

$$T_c(x_3) = [(T_{ct} - T_{\infty c}) - (T_{co} - T_{\infty c})e^{-m_c L_c}] \left[\frac{\sinh(m_c x_3)}{\sinh(m_c L_c)} \right] + (T_{co} - T_{\infty c})e^{-m_c x_3} + T_{\infty c} \quad (2.59)$$

2.4.2 Bi-Material Natural Beam Deflection Theory

This section will cover a bi-material natural beam deflection when there is no force added to the tip of the cantilever. In the below equations, three assumptions were made. One is that a linear strain distribution existed through the thickness of the beam, second that both materials are perfectly bonded at the interface, and

third, that the temperature distribution within the cantilever is uniform. Upon temperature change, the bi-material cantilever will deflect due to the bending moment generated by thermal expansion (α) of the two materials. As seen similarly from Shen et al. the natural beam deflection equation can be written as equation 2.60 [53, 54, 45, 55]. From beam theory, the bending moment is related to the moment of inertia multiplied by Young's Modulus and the curvature radius of the beam [56], where the double derivative is relevant to this curvature.

$$\frac{\partial^2 z_{nat}}{\partial x_3^2} = N(T_c(x_3) - T_o) \quad (2.60)$$

where

$$N = \frac{6(a_2 - a_1)(t_1 + t_2)}{t_2^2 G} \quad (2.61)$$

and

$$G = 4 + 6\frac{t_1}{t_2} + 4\left(\frac{t_1}{t_2}\right)^2 + \frac{E_1}{E_2}\left(\frac{t_1}{t_2}\right)^3 + \frac{E_2}{E_1}\frac{t_2}{t_1} \quad (2.62)$$

where E is Young's Modulus and T_o is the temperature at which the cantilever has zero deflection throughout, $\frac{\partial^2 z_{nat}}{\partial x_3^2} = 0$ [57]. Since the cantilever has the fixed and free end boundary conditions, below only considers the fixed end where the slope and deflection are zero.

$$z_{nat}(0) = 0 \quad (2.63)$$

$$\frac{\partial z_{nat}(0)}{\partial x_3} = 0 \quad (2.64)$$

Integrating equation 2.60 with the temperature profile equation 2.59 and applying

boundary equation 2.64 the first constant d_1 can be found as

$$d_1 = \frac{N}{m_c} [(T_{co} - T_{\infty c}) \coth(m_c L_c) - (T_{ct} - T_{\infty c}) \operatorname{csch}(m_c L_c)] \quad (2.65)$$

Integrating again using equation 2.63, d_2 is

$$d_2 = -\frac{N}{m_c^2} (T_{co} - T_{\infty c}) \quad (2.66)$$

Instead of writing out the the deflection at some $z(x_3)$ since only the deflection at the free end of the cantilever is needed, the full equation at $z_{nat}(L_c)$ becomes:

$$z_{nat}(L_c) = \frac{N}{m_c^2} (T_{ct} - T_{co}) (1 - m_c \operatorname{csch}(m_c L_c)) + \frac{N}{m_c^2} (T_{co} - T_{\infty c}) m_c L_c \coth(m_c L_c) + \frac{N L_c^2}{2} (T_{\infty c} - T_o) \quad (2.67)$$

This is the general form however, this model can be reduced when $T_{co} = T_{\infty c}$ to equation 2.68. This assumption can be made since in this case the cantilever has non-uniform temperature distribution due to the heat at the tip of the cantilever. This non-uniformity can be kept small from the temperature output of the fiber [53].

$$z_{nat}(L_c) = \frac{N}{m_c^2} (T_{ct} - T_{\infty c}) (1 - m_c \operatorname{csch}(m_c L_c)) + \frac{N L_c^2}{2} (T_{\infty c} - T_o) \quad (2.68)$$

This deflection is only taking into account a natural beam deflection with no applied force at the free end. Solving equation 2.68 for T_{ct} simplifies to:

$$T_{ct} = \frac{m_c^2}{(1 - m_c \operatorname{csch}(m_c L_c))} \left[\frac{z_{nat}}{N} - \frac{L_c^2}{2} (T_{\infty c} - T_o) \right] + T_{\infty c} \quad (2.69)$$

2.4.3 AFM Displacements

Individual Zero Deflection

Before discussing forced beam deflection, the individual AFM cantilevers in use will be reviewed to obtain a T_o value. Again this value is temperature at which there is zero deflection, which is more complex to find depending on the cantilever in question considering each cantilever has an individual intrinsic bending moment. If referring to a basic Pyrex-Nitride Probe (PNP) cantilever, which are probes that have silicon nitride cantilevers with very low force constants, then these are optimized for a bending less than 2° at room temperature for a long cantilever, a 100um will be less theoretically, as referenced by NanoAndMore USA Corp. But due to the fact that nitride and gold have different thermal expansion coefficients each cantilever has an individual zero deflection on a different temperature and drift as a function of temperature.

The cantilever bending angle is the angle between the tangent to the cantilever at its free end (tip) and the support chip surface in degrees. A positive algebraic sign a is used for bending towards the detector side and a negative sign for bending towards the tip side. A rough estimation of the bending angle may be calculated from the cantilever length l and the total deflection h ; this is only valid for small angles.

$$|a| = 2 \arctan \frac{h}{l} \quad (2.70)$$

This may be useful when dealing with the calibration seen in Chapter 4,

however if a 2° or larger angle was to be used in a theoretical case, the deflection determined can be subtracted from final displacements. However, we can assume that since AFM cantilevers are optimized to have near zero deflection in room temperature, this small angle will be considered zero deflection at room temperature. So $23^\circ C$, which is a standard scientific value of room temperature, will be used for T_o throughout calibrations and measurements. Moreover, T_o may be optimized in calibration, dropping to zero, since all temperatures will be zeroed for simplification.

Forced Beam Deflection

As seen in Chapter 4 when the system is calibrated, the AFM cantilever will interact with the bi-material cantilever. Both cantilevers will interact at the horizontal plan with the AFM cantilever fixture tilt at 10 degrees. In calibration, the cantilevers will undergo two different forces. The first force interacts in less than a few angstroms, this is known as the repulsive force. This results from a charge overlap between both cantilever tips. This force is very localized, and involves only a few near field interacting atoms. The other force is up to hundreds of angstroms known as the attractive force, called the van der Waals (vdW) force. This results from a change in dipole moment induced interaction [58, 59]. In calibration it can be seen that these cantilevers can be adjusted to account for these forces. The assumption can be made when knowing the 'jump-to-contact' distance an additional jog on the AFM can be applied to infer that the net force on the system can be zeroed and both cantilevers attend to a horizontal plane again minimizing large angle deformations.

Once in final contact a total net force can be zero. This can relate to the recorded AFM cantilever beam displacements that can sync to natural beam deflection theory. As described by Hooke's Law, the force acting on both cantilevers can be seen in equations 2.71 and 2.72 where K_{afm} and K_{Bi} are the force constants, and δ_{afm} and δ_{Bi} are the cantilever displacements of the AFM and bi-material cantilevers respectfully [60].

$$F_{afm} \sin(10) = K_{afm}(\delta_{afm}) \quad (2.71)$$

$$F_{Bi} = -K_{Bi}(\delta_{Bi}) \quad (2.72)$$

Figure 2.5: Bi-material and AFM cantilever deflection: a) Natural beam deflection z_{nat} only from thermal expansion. b) Applied resistance from the AFM cantilever, where Δz is the change in deflection

By forcing the system to be stationary when the cantilevers are in contact the net force is zero [60], we can see that the displacement of one adversely affects the other as

$$\delta_{Bi} = \frac{K_{afm}}{K_{Bi}\sin(10)}\delta_{afm} \quad (2.73)$$

Now that Hooke's Law has been applied it must be referenced back to natural beam deflection to obtain T_{ct} needed considering a change of temperature. When calibrated, natural beam deflection is already occurring. As seen in Figure 2.5, we can see that

$$\delta_{afm} = z_{nat} - \delta_{Bi} \quad (2.74)$$

where the difference from natural deflection to the displaced bi-material beam is equivalent to the change in displacement from the AFM cantilever [61]. When a force is applied from varied temperature of the bi-material cantilever to the AFM cantilever a change in δ_{afm} occurs, $d\delta_{afm}$, where additionally z_{nat} changes, dz_{nat} . This $d\delta_{afm}$ change is the recorded displacement from the AFM photo-diode laser. Both these values will be compared later after obtaining calibrated and appended fiber measurements for zeroing and acquiring the T_{ct} value. Combining equations 2.73 and 2.74 for z_{nat} in terms of the recorded displacement value δ_{afm} gives

$$z_{nat} = \delta_{afm} \left[\frac{K_{afm}}{K_{Bi}\sin(10)} + 1 \right] \quad (2.75)$$

Utilizing both equations 2.69 and 2.75 will give the temperature value T_{ct} needed to implement back into equation 2.51.

Chapter 3

Experimental Apparatuses

This chapter will review the electrospinning apparatus used for fiber fabrication, the experimental setup of sample plates, and AFM integration for the measurement process.

3.1 Sample Plates

3.1.1 Plate Design

A transitioning device and system play a key role to measure the thermal conductivity of a single nanofiber. Thermally sensitive commercially obtained bi-material cantilevers have been shown to successfully measure and conduct polymeric nanofibers [62]. In addition to their abilities, they are traditionally used in nano-instrumentation as actuators and sensors [63]. AFM's are typically useful in measuring small optical cantilever beam deflections and are able to detect these small thermal changes. However, with the use of an AFM, a few complications can arise. AFMs utilize a sensing laser to measure these small deflections. Depending on the AFM, the lasers power may differ however, this power may effect ambient temperature measurements due to radiation and adversely modeled cantilever beam deflections. Additionally, for the practicality and advantages that an AFM provides, it can be difficult to calibrate if one was to construct an apparatus in tandem. By designing and creating a simple sample plate device one can limit optical interference and to utilize an AFM as easily as possible.

The sample plates were created to account for a few parameters. The first is that the plates have to conform to the traditional use of the AFM where the convective heat from the soldering iron and heating prong will not effect the AFM laser or lack of hindrance from the thermocouples. This also includes the AFM's cantilever for the use of detection. Again since this thesis focuses on not using power lasers for heating, the sample plate utilizes separate cantilevers for detection.

The bi-material cantilever is attached to the sample plate with the sphere facing up and the other is a tipless silicon nitride cantilever already calibrated in the AFM before use as seen in Chapter 4.

The second parameter is the working distance from the bi-material cantilever to the heating prong. The prong is heated using a ZENY 862D+ soldering iron which has a working lowest temperature of 100°C with an upper limit of 480°C. Since the system will undergo calibration and appending fiber steps where the bi-material cantilever will deflect due to ambient variations, an optimal heating prong distance from the cantilever must be obtained. Moreover, a proper thermal resistance from the soldering iron and measurable ambient differences must be achieved. Since the lowest controlled temperature of the soldering iron is 100°C, this will be the starting point value when measuring the temperature from the heating prong. Keeping in mind that the value of the prong base should not exceed the maximum melting temperature of the nanofiber once appended, where the melting temperature of the polymer. It was found that through measuring the experimental system at steady state and varying the soldering temperature that about 7mm was an optimal distance. This allowed the soldering iron and thermocouples not to interact with the workings of the AFM. Meaning that the ambient temperatures around the bi-material cantilever are very small compared to the heating temperature of the soldering iron. This calibration will be noted in Chapter 4.

3.1.2 Plate Creation

As seen in Figures 3.1 and 3.2, are the parts and a constructed sample plate. A glass slide is first used as a base, cut to about a third of the original size. Cement epoxy glue is used to attach a 90° AFM Sample Mount from TED PELLA, INC which serves as a raised ledge for the bi-material cantilever. A small strip of aluminum is placed on the right of this to provide the heating prong to be level with the cantilever. Since the AFM utilizes a magnet to hold test samples in place, PELCO Tabs are used to attach a steel disk to the underside of the plate. A spade terminal connector from Neiko Tools, used in electrically devices, is used as the heating prong, sniping of the right prong to limit conduction elsewhere. The end of an alligator clip is then soldered to the back end of the terminal. This clip is used to heat the prong from the soldering iron as well for holding a stationary position under the microscope when appending a fiber.

Figure 3.1: Parts Used for Sample Plates

Figure 3.2: Completely constructed sample plates

Additional terminal connectors are used to align the thermocouples to keep them in place. These are first coated in "heat shrink" for insulation and then slid through the connector tubes which aid in stability for the glue to hold the plate. Four thermocouples are attached to the plates. Two record the temperatures at the base and the tip of the heating prong, one records the ambient above the heating prong, and one records the ambient of the above the attached cantilever. Since the tip of the cantilever can not be measured directly, the tip of the cantilever T_{ct} can be calculated as reviewed in Chapter 2.

The bi-material cantilever is then appended with UV glue upside down to the AFM sample mount 7mm from the heating prong while also allowing the probe to hang well over the curvature of the mount. This is to avoid complications when

loading a fiber to the probe and AFM for measurements. To not potentially break break a probe, the cantilever should be appended just before fiber appending.

3.2 Fiber Creation

As explained previously in section (1.1) morphology and fiber properties are key in obtaining uniform thermally conductive nanofibers. The molecular chain length and the molecular weight of a polymer is vital when choosing a "good" solvent to use [64, 65]. The first step for creating nanofibers is to properly formulate a solution for different polymers needed for measurement. Depending on the polymer being used for spinning, there are certain solvent carriers that work best with the polymer. This is due to the ability of the solvent to fully dissolve the polymer.

The polymer to be used for spinning and alternatively measuring the thermal conductivity needs to be determined. There are many different polymers to choose from depending on the use. Electrospun nanofibers can be useful in such fields as electrical or even biomedical. In the biomedical field, these fiber matrices have shown morphological similarities to natural extra-cellular matrices, characterized by ultrafine continuous fibers, high surface-to-volume ratio, high porosity and variable pore-size distributions [66]. Solution properties such as solution viscosity, conductivity, dielectric constant, and surface tension may go into the decision on a polymer needed.

In the proposed experiment, the chosen polymer is polycaprolactone (PCL) with a density (p_x) of $1.145g/mL$ at room temperature and a melting

point of 60°C. The reason for using polycaprolactone is due to the biomedical usage. PCL is known as a synthetic biodegradable aliphatic polyester for uses in tissue engineering, scaffolds, nerve guides, and drug delivery systems [67]. Since acetone is the working solvent, PCL works best [68]. Additionally acetone is the low end of the spectrum of toxicity, where solvents such as dimethylformamide (DMF) or tetrahydrofuran (THF) have high ratings of such toxicity. Keep in mind the melting point of PCL, this factors into the heating limit of the heating prong and the fiber itself. There are additional solvent and polymer combinations that produce more consistent and uniform fibers, that are more thermally conductive and have a higher melting point. However, note that this is also not to say that the method of creating a solution, the spinning process, or measuring the thermal conductivity is any different. Further details of the produced fiber properties can be seen in the Appendix.

With the chosen polymer we can move on to calculating a proper equation to use for determining a useful weight of solute needed for the concentration. Using a concentration of the polymer solution as $w/v\%$, a sought after typical percentage would be between 7.5% and 10% for this solution [68].

$$\frac{w}{v}\% = \frac{\text{mass of the solute } w_x}{\text{volume of the solution}} \times 100 \quad (3.1)$$

The optimization of electrospun fibers versus electrospraying is fundamental for electrospinnability. The determination of how the fibers are produced depends a lot on the concentration of the solution itself. There is a certain minimal concentration value that must be reached, which, if below this value, electrospray-

ing occurs or the formation of droplets only [69, 70]. This is because under high voltage or electrical force the charge density of a droplets surface at the evaporation point increases, the coulomb repulsion overcomes the surface tension and several smaller droplets are formed. This is theorized by Rayleigh instability phenomena [71, 72]. The higher the concentration the more stable the string of droplets become [64]. On the other hand, if the concentration is too high and thus becomes more viscous, uniform fibers will no longer be produced [73]. As the concentration of polymer increases, an overlapping of macromolecular chains occurs and becomes important. The relative viscosity of solution increases significantly with an increase in concentration, up to a critical concentration. This region, called the semi-dilute regime, is found in the dimensionless concentration range of 1.0 to 10.0 [74, 75]. The Martin equation best describes the viscosity-concentration relationship in concentrated polymer solutions [76, 74],

$$\frac{n_{sp}}{c[n]} = e^{K_m c[n]} \quad (3.2)$$

where n_{sp} is the specific viscosity, c is the concentration of polymer solution, $[n]$ is the intrinsic viscosity of the polymer, and K_m is a constant and it is a measure of polymer-polymer and polymer-solvent interactions [74, 77].

Knowing what concentrations to use, next is to determine how much solute is needed. As seen in equation 3.3 the weight (w_x) of polymer in grams to use can be found utilizing 3.1 and rewritten in a general form,

$$w_x = \frac{v_y}{\frac{1}{P} - \frac{1}{p_x}} \quad (3.3)$$

where v_y is the volume of solvent being used and P is the fraction of the concentration wanted.

In this experiment, 20mL of acetone and a 10% PCL concentration was used providing 2.191g of solute at 1.145g/mL. To obtain a proper solution, acetone and the PCL were heated to about 40°C on a hot plate until dissolved. The boiling point of acetone is 56°C so 40°C is enough to help dissolve the polymer. This took about 40 minutes to dissolve. This was also taking into account a solvent volume of 20mL.

The reason for creating such a higher volume than needed is that the total volume of the solution is that similar to the volume of the solvent. Therefore when obtaining a concentration to use, the weight of the solute to the volume of the solution is small. This infers that if the polymer homogenizes in to the solvent that only the volume of the solvent would have to be used. Moreover, in other cases requiring a higher concentration or smaller solution volumes, the volume of the solute or polymer should be taken into account. In this case, using PCL, the acetone is poor at dissolving PCL properly, therefore the general form of equation 3.3 should be used. However in the case of using other polymers and solvents a $wt\%$ should be used; this is because the solution will become homogeneous. Once the solution is made the next step is to set up the solution for spinning.

3.3 Electrospinning Apparatus

For a traditional electrospinning apparatus only a few general items are needed, a high voltage power supply up to 30kV, a syringe pump, electrode connected to a

needle, and a grounding collector. As seen in Figure 3.3 is the constructed custom electrospinning apparatus.

Figure 3.3: Electrospinning Apparatus

Electrospinning systems can be setup for sheet collection as well as for a single nanofiber. Many traditional methods utilize spinning for thin film matrices, using flat, cylindrical rotating drum, or even 3D columnar collector plates [78]. However, due to the instability and chaotic motion of the electrically charged fibers it can be a challenge to collect a single nanofiber. Additional methods such as magnetic fields can produce alignment of fibers [79] or the utilization of a drawing method, other than electrospinning, to combat this problem as seen from Shen et al. (2010). The proposed system uses two steel rods in series with the grounding source perpendicular with the needle. As the charged stream of fiber tends to the grounding source, the fibers append between them creating a fiber web. To avoid collecting too many fibers and creating a thin film, the system should only be run for a few seconds. The PCL nanofibers were spun at 10kV with .3mA and

a working electrode distance of 9cm.

Using a chosen solution, the syringe is placed into the syringe pump. Depending on the viscosity or concentration of the solution, a correct needle and flow rate for spinning should be determined. With a flow rate applied, the fluid should drip out at a consistent rate, as a drip flows out, a second drop should replace it immediately. The smaller the needle, the lower the concentration should be and vice-versa. In the case of using a 10% weight/volume solution of acetone and PCL a needle gauge of 20AWG at a flow rate of 1 mL/min is recommended. However, the applied voltage also needs to work in tandem with this flow rate. The voltage applied depends on the distance of the needle to the collector. With this, a critical voltage V_c can be expressed to determine the electric field needed to develop fluid instability. Taylor (1964) also showed that this can be expressed as:

$$V_c^2 = 4 \frac{H^2}{L^2} (\ln \frac{2L}{R} - 1.5) (0.117\pi R\sigma) \quad (3.4)$$

where H is the distance between the needle tip and collector, L is the length of the needle, R is the radius of the needle, and σ is the surface tension of the liquid [30, 26, 80]. Equation 3.4 may be useful in determining a proper applied voltage. A voltage around 10kVDC was found to be the workable amount to spin PCL polymer nanofibers. Once the fibers are spun, they can be collected, measured for dimensions, and appended to the sample plates.

3.4 Appending a Fiber

Once a web of fibers has been amended between both steel rods the next step is to append a single fiber to the sample plate. A calibrated 10x OMax microscope will be used to measure and aid in appending a single strand as seen in Figure 3.4. The microscopes XY-axis slide is removed and a held positioning screw is added. The alligator clip, of the sample plate, is clamped to the screw which aligns well in view under the microscopes camera. A pointed tweezer prong is attached to XYZ-axis stages; these can also be pivoted around the microscope for easier fiber loading.

Figure 3.4: Sample Plate Held Attached to the Microscope

Prior to grabbing a suspended fiber from the electrospinning apparatus, use UV glue to coat the tips of the heating prong and pointed tweezer, without using a UV light to solidify the glue yet. The thermal conductivity of the glue on the heating prong is taken into account in calibration in Chapter 4.

Loading tweezers are used to then grab suspended fibers from the steel rods. Depending on the thickness of the fibers produced the fibers may not naturally append to the tweezers by Van der Waal forces. In this case, UV glue and light source can be used on the tips to stick the desired fiber. The fiber is then brought to the microscope and attached as seen in Figure 3.5.

First, the fiber is attached to the heating prong, the glues' surface tension is able to hold this in place; then the fiber is attached to the microscope pointed tweezer. The UV light source is used on the both the heating prong and microscope tweezer to hold the fiber in place. The microscope tweezer is then swung slowly towards the cantilever, using the XYZ stages. Once close enough, the fiber will jump to the tip of the cantilever by Van der Waals forces as seen in Figure 3.6 (this cantilever is not the one used within the design, it is an alternate testing cantilever with probe). Figure 3.7 provides the final appended PCL fiber used in testing. Alternative appended fibers can be seen in Figure 3.8; these existed on another older model of sample plate, therefore were not tested. Again, these are purchased bi-material cantilevers which come with two cantilevers, 100um and 200um; the gold coating is deposited on both cantilevers however, on the cantilever of choice obtains the probe micro-sphere.

Figure 3.5: a) Tweezers loading single fiber to prong and microscope tweezer, b) Appending fiber to tip of cantilever with Van der Waal attractive force

Figure 3.6: PCL nanofiber jumping to a cantilever tip due to Van der Waal's attractive force. This cantilever is a traditional silicon cantilever with probe which is not part of the probe-to-probe system

Figure 3.7: PCL nanofiber appended to the bi-material cantilever that was put through testing

Figure 3.8: Alternate variations of a single appended PCL nanofiber to the bi material cantilever. a) Shows a fiber only suspended between both cantilevers. b) Shows Van der Waal attractive force. c) and d) are alternate append fibers bridging both cantilevers. These were appended to a test bi-material cantilever sample plate and were not tested.

A soldering iron is used to cut the ends of the fiber leaving only the fiber suspended between the cantilever and the heating prong; keeping in mind the temperature of the iron since the polymers melting temperature is 60°C . While carefully unloading the sample plate and placed into a carrying container, it is taken to the AFM for measurement.

3.5 AFM Setup

Once the sample plate with appended fiber is ready, it is moved to the AFM for measurement, Figures 3.9 and 3.10 show the AFM setup. An 'AFM Workshop' Table Top AFM (TT-AFM) with a 1 *mW* laser will be used. It is suspended as a pendulum with a large open door which makes it easy for loading and hooking up external equipment. Further required specifications and details on the AFM and measurement will be noted within Chapter 4.

Figure 3.9: Soldering iron and AFM setup. The multimeters are replaced with a LabView DAQ recorder.

Figure 3.10: Close up image of the sample plate within the system.

A tipless silicon cantilever is loaded into the AFM as for typical use, this is the AFM-tipless cantilever. The sample plate is then slid onto the stage with the alligator clip facing out underneath the AFM cantilever. During measurement, the cantilevers should line up as seen back in Figure 1.5. This alignment will be seen further in Chapter 4. A simple stand and clamp is used to hold the soldering iron. This should be brought to level with the sample plate, and fixed to the alligator clip seen in Figure 3.10. The stand is on the pendulum platform due to consistent swaying from camera and laser re-positioning and alignments; this eliminates the sample plate from shifting out of position. The sample plates' four thermocouples are then plugged into a LabView DAQ system. The chamber door is then closed to limit air flow. The AFM is now setup for testing.

Chapter 4

Methodology and Calibration

This chapter reviews the system settings and parameters used, along with how to conduct and measure the thermal conductivity of electrospun nanofibers. Before any measurements are to be recorded, the AFM cantilevers responses and settings will first need to be understood. The resonance frequency will initially be measured, to validate that its force constant is indeed lower than that of the bi-material cantilever. Once this is proven, the cantilever will be tested in contact with bi-material cantilevers silicon base to show baseline changes in nm/C values, seen in Chapter 5. This will first, show how the AFM cantilever will react under varied temperatures without the bi-material cantilever and secondly, indicate proper PID settings needed.

After the AFM cantilever parameters and settings have been determined, the Probe-to-Probe system will then be set up to determine the calibrated temperature vs deflection recordings; results of these recordings can be seen in Chapter 5.

4.1 Measuring Force Constant and Resonance Frequency

The force constant can be simply known by measuring the resonance frequency of the cantilever itself. The purchased cantilevers all come with supplied force constants and resonance frequencies. However, some cantilevers such as the tipless cantilevers used as the AFM cantilever provide a range between 0.02-0.77 N/m and 6-21 kHz respectively whereas the bi-material cantilever only provides single values of 0.32 N/m and 67 kHz respectively. Although the online catalog for the tipless cantilevers states that the average force constant is 0.2 N/m, one can not follow this when working with such closely similar values. The AFM cantilevers force constant will need to be lower than that of the bi-material cantilever to be able to see a response. The AFM itself has two different modes to work in, vibrating and contact modes. The vibrating mode will only be used to measure the resonant frequency of the tipless cantilever. Additionally, since the bi-material cantilever is coated in gold, the laser could not be aligned at all due to reflectively issues and therefore cannot be measured for confirmation.

The ratio from the resonant frequency to the force constant can be compared to indicate the proper force constant; if lower than the bi-material, the cantilever can be used. Equation 4.1 can also be used to obtain the resonance frequency [81].

$$k = \frac{2\pi^3 w (f_o L \sqrt{\rho})^3}{\sqrt{E}} \quad (4.1)$$

Also in good practice, before recording all cantilever deflections, one

should obtain the voltage-deflection V/nm response from the photo-diode, which additionally aids in the measured of force constant. Traditionally the force distance curve portion of the AFM would be used to determine this V/nm response however, this is not currently functioning properly; utilizing applied force and known force constant. Due to this limitation, alternate methods were determined. These results can be seen in Chapter 5.

4.2 Setting System Parameters

The next step is to confirm how altering the PID and voltage gains effect the stability of the system with varied heat and its feedback loop. Using the same AFM cantilever with known force constant; several scans were performed using alternate PID and gain settings. The XY HV Gains are always set to zero to hinder any XY movement from the piezo stage. Alterations included system changes to Z Drive (1-15 HV Gain), XY percentage gains (1-100%) which represent the Z Sense response, varied PID settings, and varied feed back loop. As a side note, the Z Drive should mirror the Z sense values (force transducer verse the piezo stage sensor); either the Z Drive or Z Sense can be used for simplicity. A few objectives were to be determined after testing various settings:

1. The first was to determine if a feed back loop was needed; meaning that the system can either be held in constant deflection or the system can just be set to a user defined value and a change in voltage can be recorded. If one was to have no feedback loop, the Z Drive may be turned to zero for simplicity, and the Z Sense used.

2. The second was to confirm that the PID settings will accurately respond to temperature increase and that the stage or force transducer are not auto adjust/auto correct linearly showing a phantom force response. As an example, in the case of not using a feedback loop, the piezo stage may increase linearly without push back or balancing from the Z Drive. The piezo stage is programmed with a constant linear gain value as low as .0001V, this can not be changed to zero, however the other PID settings can be. As recommend from AFM Workshop, the PID settings should be set to zero leaving the gain value at its original .5V setting. Again, the fore-mentioned settings will indicate if these changes are accurate.
3. The third was to confirm that the stage piezo is not responding to conduction from the heated stage. To test this, the system is heated instantly to 400C and run for 40mins; no change in the Z Sense should be noticed. AFM piezos are also created to withstand conduction temperatures below 150C, so there should be no difference however, if a change is noticed between the Z Drive and Z Sense due to temperature increase, the Z Sense recordings will not be used.

By the end of testing key settings were defined. Starting with the first objective, the system should include a feedback loop. It was noticed that once in Probe-to-Probe contact, without a feedback loop, that the T-B and L-R photodiode sensors would shift without external heating; meaning the cantilevers were slipping. This may be due to an imperfect gluing of a bi-material cantilever on the sample plate or alignment of the AFM cantilever; working at nanoscale may

provide these challenges.

With a change in the first objective, requiring a feedback loop, the second determined to simply use the original PID, Z Drive and Z Sense HV gain settings for this feedback. It is known that the higher the Z Drive HV gain the faster the response, however increasing voltage may have lead to more noise. Throughout testing various gain responses and feedback loops, the original PID and Z Drive values can be used. Lower values under 10 HV however, may lead to imprecise and weak contact. A linear response still existed creating noise within the system however, were considered very low and were to be subtracted out when comparing the calibrated recordings to the appended fiber recordings; results on this are seen in Chapter 5.

A major problem that surfaced from testing was that there existed a power draw from the soldering iron to the rest of the system. This was discovered when the soldering iron was turned on, a voltage gain was noticed within the Z Drive and Z Sense. Increasing the output temperature quickly on the soldering iron also showed this spike. This was a considerable problem. Since the soldering iron uses a power regulator to control the temperature supplied, it would also draw power from the AFM itself both from the Z piezo stage and from the force transducer once the cantilevers interacted. This type of error produced many problems with inconsistent drowned out data. This problem was easily fixed by disconnecting the soldering iron from the sample plate; only allowing ambient heating. The down side of doing this may lead to a lower power through the fiber in addition to having to increase the heating steps of the soldering iron to achieve higher ambient heating temperatures throughout. However, all temperatures within the system

are still recorded the same way; so the current modeling is still accurate.

Referencing back to the third objective, it was determined that the stage piezo was not interacting with the change to external ambient temperature however, if the soldering iron was connected to the sample plate, differential power steps can be seen. Again, showcasing that the power regulator of the soldering iron plays a large role in noise drowning out any results.

The final system settings can be seen below. The AFM can only record two sensors at once. The T-B voltage and Z Drive will be recorded since the Z Sense was shown to mirror the Z Drive.

Figure 4.1: Scan Tab Settings

Figure 4.2: System Tab Settings

Figure 4.3: Topo Scan Settings

4.3 Procedural Setup and Alignment

This section reviews how the probe-to-probe system is set up and run however, it does not include how to initially set up the AFM for traditional use or laser alignment. On instructions on how to set up the AFM for traditional use, the AFM's operators manual can be referenced. Any alterations to the manual are mentioned. This also includes the procedural steps for the prior mentioned calibration parameters.

1. Setup a tipless AFM cantilever traditionally and align the laser normally.
2. Once the AFM cantilever has been placed into the AFM and laser aligned, the sample plate is placed onto the magnetic stage making sure of clearance to the AFM cantilever seen in Figure 3.10. Set the magnification focused to the small 100um length cantilever or base depending on either conducting a probe-to-probe or silicon base contact scan.
3. Prior to Probe-to-Probe contact, the AFM cantilever is jogged down to the silicon "under belly" or now the top surface of the bi-material cantilever as seen below. Both the XY axis sample plate and AFM cantilever Z axis will have to be turned and adjusted. This helps to figure out how close the cantilevers are to each other without accidentally breaking both cantilevers.
4. The XY HV gain is set to zero.
5. Set the AFM mode to vibrating and obtain the resonance frequency/force constant.

6. The automatic tip approach is used, and the AFM cantilever is set to jog slowly down to the surface at a rate of $.3\mu\text{m/s}$ to make contact. Again, depending on the surface, either Probe-to-Probe or base contact can be seen in Figure 4.4. Seen in (b), the laser is offset to the bi-material cantilever, this is the positioned tip of the tipless AFM-tipless cantilever. Since the laser can only cover a circular portion of the tip when aligning in step one, the true tip is actually positioned onto the tip of the bi-material cantilever.

Figure 4.4: a) Bi-Material Cantilever Base Contact using AFM-tipless silicon cantilever. b) Probe-to-Probe Contact

The T-B sensor should read a steady 0.1V lower than the original value once in feedback; this can be set to other forced values however, it is not required. If the L-R signal reads greater or less than its original value after contact, the cantilever is jogged up and the sample plate's XY axis is adjusted. This is done until the L-R signal does not change after proper contact. In addition, it is possible during scanning that the stages' Z range will end. If the range of the stage ends, an increase in a T-B value will be noticed during a scan. If this happens, stop the current scan, jog up, and slide the sample plate

further centered on the magnetic stage. The entire scan will have to be started over.

7. Once contact has been made, the Topo Scan tab will be used. The scan rate is set to 0.42 Hz recording for about two 40 min scans, each containing 1024 scan lines; the AFM can only record so many scan lines within a given time. Additionally, LabView is set up to record the thermocouples at a rate of 0.42 Hz.
8. Then hit start on both devices. Once the number of scan lines reaches increments of 256, the soldering iron is increased 50C. This gives about 10mins for each temperature increase to attain steady state.
9. Once each set of scans are complete, the LabView program is stopped; the values are automatically saved off.
10. After both scans, the soldering iron is turned off and cooled for 20mins, ready for another set of scans.

Chapter 5

Measurement Results and Discussion

This chapter compares all theoretical and measured results to determine the thermal conductivity of the nanofibers. This also reviews recorded values for voltage and natural deflection calibration results.

5.1 Introduction

There exist two different models to consider when obtaining measurements, theoretical and measured/recorded. Calibrated values and recordings are first conducted in order to make sure recorded measurements match theoretical results. The calibrated recordings of the Probe-to-Probe system without a fiber are compared to the measured/recorded deflections with an appended fiber.

The theoretical values are obtained using the modeled functions from Chapter 2, whereas the recorded values are sent to an Excel spreadsheet. Both the theoretical and measured/recorded values are generated/called in to a MATLAB program where depictions are shown. The theoretically calculated bi-material cantilever temperatures T_{ct} , where T_{ct} is output temperature from the fiber to the bi-material cantilever, will need to be theoretically generated since they can not be measured. A difference in T_{ct} should be noticed once a fiber is appended. The temperature into the fiber from the heating prong, T_f , are also numerically generated; the approximation for this is seen in Chapter 2 but the values are shown further in this chapter. Once both T_{ct} and T_f temperatures are known, the heat conducted through the appended fiber k_f will be known.

5.2 Deflection Results

The preceding recordings will showcase all measurements and theoretical results of cantilever deflection with and without a fiber. Figure 5.1 shows the average deflection with ambient temperature values reaching steady state after 8 minutes;

averaging the last 2 minutes of the 10 minute individual stepped scans. Six full scan sets exist for the AFM-tipless cantilever natural deflection and calibrated Probe-to-Probe contact, and only two for the appended fiber probe-to-probe contact. A difference in the calibrated versus appended values can be seen; the following sections will delve in to the individual recordings and discussions.

Figure 5.1: Average deflections of each measurement stage.

5.2.1 Identifying V/nm and AFM-Tipless Cantilever Natural Deflection Recordings

Measuring the natural deflection of the AFM cantilever in V/nm can further determine if the system is indeed responding properly and is not at all deflecting at all temperature variations. Considering that the force distance curve function could not be utilized to record both cantilevers on the this AFM system, the

voltage and deflection had to be recorded by two separate recording methods; the slopes of these methods can still be compared to show that the AFM-tipless cantilever reacts properly within the system. Moreover, considering that the bi-material cantilevers natural deflection could not be measured due to the gold reflectively and poor laser itself, the AFM-tipless cantilever was used.

The first method, part 1, was to only record the photo-diode's voltage output whereas part 2 only records the natural deflection, via a held constant forced deflection, zeroed voltage. Showcasing both these graphs as V/C and nm/C respectively, provides V/nm . To measure V/C , the AFM cantilever was held just above the sample plates' bi-material cantilever and heated. To measure nm/C , the AFM cantilever was held in forced contact on the base of the bi-material cantilever, zero voltage displacement, and heated; this provides the natural deflection of the cantilever. More on how to set up and align these setups can be seen in the procedural section within Chapter 4. Results can be seen in Figures 5.2 and 5.3.

Figure 5.2: Natural AFM-tipless cantilever and Photo-diode deflections versus temperature.

Figure 5.3: The Photo-diode response to AFM-Tipless cantilever deflection. Obtained from dividing slopes from Figure 5.2 utilizing natural deflection results.

From these results, in Figure 5.2, one can see that the AFM cantilever actually does indeed respond to small temperature variations during a system scan. Once the scan was complete and temperature turned off, one can notice that over time the cantilever will revert back to its original state via the photo-diode, which does not require a set scan to display. This is considerable considering that even a long silicon cantilever could be further utilized in measurements and future work. Figure 5.2 above not only shows how the photo-diode responds to deflections but also shows that there is no linear gain applied to the system from the stage since the nm/C slope is similar to V/C slope. More on this gain value is seen in Chapter 4, System Settings. Slope V/C in Figure 5.2 however, also represents very limited data points; more data should still be supplied.

One can also utilize the following second method to measure V/nm . The AFM functions traditionally by sensing a deflection response from the photo-diode, sending a signal to the force transducer and the piezo in the stage telling both systems to balance and hold a constant set deflection provided by the user. In this case, the AFM will be told not to hold this deflection and instead force the piezo stage to move the cantilever. This is done by jogging the cantilever down to make contact rather than utilizing the automatic tip approach which initiates the feedback loop response. The Z-Drive is turned on as well, but the piezo within the drive is told not to respond since the feedback loop is not used. Once the scan is started, the stage will supply a linear decrease pulling the contacted cantilever along with it. The scan will record both Z-Sense position and T-B signal in time. Dividing the slope of the photo-diode by the stage's movement provides the V/nm slope. However this method was not used or required within this thesis,

the procedure can still applied to future works.

Figure 5.4 below shows how the AFM-tipless cantilever itself responded to temperature variations when compared to its theoretical values. From the displayed results of V/C , from Figure 5.2, one can clearly notice change in deflection.

Figure 5.4: Theoretical versus Measured AFM-Tipless cantilever deflections.

There are no statements from the purchased cantilever manufacturer that the silicon cantilever should respond to higher than normal variations in temperature, only that they should not deflect in regular ambient room temperature. Traditional uses of AFM do not include increases to ambient normally, so scans would typically ignore this since ambient usually does not change. The system was also tested by removing the AFM cantilever, then heating the system; no change in the photo-diode was noticed. However, the actual theoretical result does match expected results seen from Chapter 1, showing silicon cantilever temperature res-

olutions of about $1\ \mu\text{m}$ and 3°C . This is promising considering it showcases that the thermal model from Chapter 2 is near accurate.

Figure 5.5 provides the average temperatures for all recorded scans at steady state during calibrated measurements. Step 0 were temperatures recorded at room temperature and were just used as a test run; these values were also inconsistent, but were still removed.

Figure 5.5: Average recorded natural deflection temperatures after reaching steady state.

5.2.2 Calibrated Deflection Recordings

The values generated from this procedure are used in tandem with the appended fiber recordings seen in the following section. These calibrated recorded values are compared to their theoretical generated values, seen in Figure 5.6. Both the-

oretical results showcase how each cantilever (bi-material or AFM-tipless) would react under this Probe-to-Probe system, meaning considering the values measured, which cantilever is actually causing the deflection/forcing seen. Referencing back to natural beam deflection and Hooke's Law from Chapter 2, and utilizing each cantilevers' properties with the recorded temperatures in Figure 5.7 from calibration, one can obtain the theoretical values for this calibration step. How the equations are utilized can further be seen within the MATLAB code provided in the Appendix.

Figure 5.6: Theoretical versus measured calibration Results.

Figure 5.7: Average recorded Probe-to-Probe calibration temperatures after reaching steady state.

One can note that since the AFM-tipless theoretical results more closely resemble the measured/recorded results, that the AFM-tipless cantilever is out forcing/deflecting the bi-material cantilever. This further provides comparable analysis to Figure 5.4 when looking at the recorded results. The measured natural deflection and forced calibration of the AFM-tipless cantilever are similar, meaning that the bi-material is having a minimal effect. This may be due to a few possible scenarios: either a) the bi-material cantilever is not sensitive enough to record temperature change, b) the ambient temperature is not hot enough to provide deflection, or c) it does not have an accurately stated force constant of 0.32 N/nm ; meaning its actually lower than the AFM-tipless cantilever (seen from Chapter 4 equation 4.1); the measured force constant was 0.23 N/nm . Considering research

conducted on the sensitivity of bi-material cantilevers, seen from Chapter 1, the former should not be the case.

5.2.3 Appended Fiber Deflection Recordings

After recording deflection and temperature values once a fiber was appended, the recorded slope must be subtracted from the recorded calibrated slope; this zeros out data to provide a true deflection versus change in ambient temperature solution seen in Figure 5.8. These new deflections are used within the MATLAB program to supply the T_f and T_{ct} values required; again, the theoretical values utilize equations 2.22 and 2.69 respectively, assuming $T_f = T_{fCal}$. In this experiment, when the fiber was appended to the sample plate, the prong end of the fiber was connected directly to the prong tip; this makes the assumption negated and $T_f = T_{fCal} = T_{pt}$ and $q_f = q_{p1}$ provide equation simplification. Figure 5.9 provides the averaged recorded temperatures.

Figure 5.8: True measured fiber deflection results, subtracting appended fiber recordings from calibration recordings.

Figure 5.9: Average recorded Probe-to-Probe appended fiber temperatures after reaching steady state.

Table 5.1 provides T_f and T_{ct} compared to the recorded temperatures.

These temperatures will be used to determine the heat flux into the fiber to obtain the thermal conductivity of the fiber seen in the following section.

Recorded Temperatures with Appended Fiber °C							
Solder Temp	Tambp	Tpo	Tpt	Tf	Tambc	Tct	Tct-Tambc
100	0	0	0	0	0	0	0
150	1.4151	0.85987	0.54005	0.54005	0.42494	0.42494	5.08E-07
200	3.0192	1.8575	1.1809	1.1809	0.97729	0.97729	1.17E-06
250	4.7307	3.016	1.986	1.986	1.6543	1.6543	1.98E-06
300	6.4784	4.389	2.9301	2.9301	2.4063	2.4063	2.88E-06
350	8.2314	5.9458	4.026	4.026	3.2395	3.2395	3.87E-06
400	10.18	7.7851	5.2942	5.2942	4.2176	4.2176	5.04E-06

Table 5.1: Appended fiber recorded temperatures (cantilever ambient, prong ambient, prong base, and prong tip respectively) and theoretical (prong end fiber and cantilever tip temperatures respectively).

When reviewing Table 5.1, note that the ambient temperature over the cantilevers is similar to the input tip temperature of the bi-material cantilever. This may show that there is very limited heat conducted to the tip of the bi-material cantilever, if none at all, or the use of ambient heating is overcoming any heat transfer. It is possible that Figure 5.1 may be providing an illusion of change even though there is no additive temperature to the cantilever. The thermocouple position was consistent and accurate between scans when adjusted to the system however, it is possible position was not ideal, and ambient recordings varied.

5.3 Obtaining Fiber Thermal Conductivity

Taking the temperature values from 5.1, Table 5.2 provides fluxes utilized when obtaining the thermal conductivity k_f . The equations used can be seen in Chapter 2 and the MATLAB code provided in the Appendix. Since the MATLAB version

in use did not include a $f(\text{solve})$ function, which is provided in a extra Simulink Tool Kit, an alternate method to determining the thermal conductivity was used.

Ranged Flux ($\cdot 10^5$)(W/m^2) and $k_f(W/mK)$ Linear Solution				
Solder Temp	qf_{25}	qf_{105}	$qf_{Recorded}$	k_f
100	0	0	0	0
150	-1.2762	-1.9511	-1.3177	29.92
200	-2.6933	-4.1508	-2.7874	30.17
250	-4.0126	-6.1603	-4.243	33.58
300	-5.1563	-7.8338	-6.0067	50.41
350	-6.0575	-9.0588	-7.9009	74.14
400	-6.9842	-10.302	-10.247	103.67

Table 5.2: List of assumed and recorded flux into the fiber per heat step. All fluxes are multiplied by $10^5(W/m^2)$; $q_{Recorded}$ is the flux determined at the prong end of the fiber; qf_{25} and qf_{105} provide minimal and maximum assumed thermal conductivity where $q_{Recorded}$ falls between. Values are 0 at scan 100 since temperatures at this scan were set to zero.

Table 5.2 shows only two flux sets, qf_{25} and qf_{105} , where the values for each scan fall between, $(qf_{25} \leq q_{Recorded} \leq qf_{105})$. This shows that the thermal conductivity of the fiber may fall between 25 and 105 (W/mK). This is assuming that the recorded difference between T_{ambc} and T_{ct} , seen in Table 5.1, is indeed significant enough to showcase this range, but in a large ambient bath, with such similar values. Using a linear solution from the fluxes provided, the thermal conductivity was determined. Furthermore, the change in flux between each scan is larger as the system is heated; due to increases in temperatures, the gap between ambient temperatures increases, as seen from Figure 5.9. Given the testing parameters and constraints of the current system, one can state that highest recorded thermal conductivity is 103.67 (W/mK).

Chapter 6

Summary and Future Work

The chapter details end thesis conclusions and takeaways along with design ideas that can be incorporated in future works.

6.1 Chapter Summaries

This section reviews each chapter, the resulting conclusions and details noticed.

Chapter 1 - Provided background information on nanoscale thermal transport, past measurement techniques, and defined the proposed Probe-to-Probe design.

Chapter 2 - Defined introductory heat transfer along with the detailed modeled design of the Probe-to-Probe system. It further provided listed equations to obtain unknowns such as system and fiber fluxes, system cantilever and prong temperatures, and forced and natural deflections, all of which required to solve for the thermal conductivity of an appended nanofiber.

Chapter 3 - Focused on the experimental apparatus, fiber and sample plate creation, and equipment used. System properties such as bi-material cantilever, AFM-tipless cantilever, and electrospun PCL nanofibers were obtained, which are further seen in the Appendix.

Chapter 4 - Reviewed the procedural measurement of the system and outlined how the system was calibrated, along with how each system setting were determined. It was found that the bi-material cantilevers' natural deflection to ambient changes could not be measured due to inert reflectively possibly due to the strength and focus of the laser. A voltage draw was also noticed when in a conductive heat transfer system. This was fixed by disconnecting the soldering iron from the sample plate and recording all temperatures as normal.

Chapter 5 - Detailed all the results from testing including: natural deflections, pre-appended fiber calibrations, and appended fiber recordings. Each section reviewed findings and comparisons of measured results to theoretical expectations, along with explanations and conclusions. Minimal deflection was seen from the bi-material cantilever due to unexpected deflections from AFM-tipless cantilever. Results matching this seen deflection do not coincide with theoretical results. However, theoretical silicon cantilever natural deflection results match expected results seen from Chapter 1 showing silicon cantilever temperature resolutions of about $1\ \mu m$ and $3^{\circ}C$. This was promising considering it showcases that the thermal model from Chapter 2 is near accurate; measured results do not match.

Furthermore, thermal conductivity values were determined to be between 25 and 105 (W/m^2) when comparing flux. Following, given the testing parameters and constraints of the current system, one can state that highest recorded thermal conductance is 103.67 (W/m^2). This was assuming that the extra temperature at T_{ct} is indeed significant enough to showcase this range, but in a large ambient bath, with such similar values.

6.2 Future Work

A lot can be done to modify the Probe-to-Probe design; the first thing to consider is the AFM itself. The AFM is still a very useful tool in measuring nanoscale technology, however, the particular AFM model utilized within this thesis was a simple model. There exists AFMs that can implement a Scanning Thermal

Microscopy (SThM) mode which was developed to probe thermal properties at the nanoscale levels specifically. Such systems, from Park Systems, contain two modes: Temperature Contrast Microscopy (TCM) and Conductivity Contrast Microscopy (CCM). TCM allows the measurement of the temperature variations on a sample surface and CCM utilizes the measurement of variations to define the thermal conductivity of a sample surface. The thermal probe essentially forms one leg of a Wheatstone bridge, seen in Figure 6.1.

Figure 6.1: Park Systems SThM System

The Wheatstone bridge provides feedback, adjusts, and balances the bridge voltage in order to measure the probe's temperature (in TCM) or maintain a constant probe temperature (in CCM) [82]. Similarly to a traditional AFM, a SThM cantilever tip serves as a resistance thermometer, or as a heater in CCM mode. The resistivity of the SThM tip is then changed according to the temperature of the surface in contact; the tip to sample heat transfer changes the tip temperature, which is used to calculate the temperature or thermal properties

of the sample at contact [83]. This would be very useful when determining the thermal conductivity of a nanofiber rather than a planar surface. This may be a promising technique when used in tandem with a vacuum. Kim et al. have utilized an Ultra-High Vacuum (UHV)-based SThM technique that was capable of quantitatively mapping temperature fields with about 15 mK temperature resolution and 10 nm spatial resolution [84]. However, the thermal transport around the nanoscale contact area between a SThM probe tip and sample is still an issue in SThM [85].

The second option would be to mitigate all ambient temperature utilizing a vacuum with the current system or an SThM. Again, this would limit thermal noise and excess heat into the system to provide only conductive heat transfer. Considering the issue seen in Chapter 4 with voltage draw, this calibration would have been more easily noticed if the system was not in an ambient bath skewing data.

The third would be to utilize alternate silicon or bi-material cantilevers. This thesis utilized tipless silicon cantilevers however, there do exist lower consistent force constant cantilevers that include probes. The rationale for placing the probe on the bi-material cantilever instead was due to the purchasing ability; these could not be purchased tipless.

Appendix A

Prong, Cantilever, and Fiber Properties

Cantilever Properties		
Property	Bi-Material Cantilever (Si, Au)	Tipless Cantilever
Length	100 (um)	450 (um)
Thickness	(Si) 540, (Au) 60 (nm)	2 (um)
Co. Thermal Expansion	(Si) 3, (Au) 14.2 (um/mK)	3(um/mK)
Supplied Force Constant	0.32 (N/m)	0.02-0.77 (N/m)
Resonance Frequency	67 (kHz)	6-21 (kHz)
Thermal Conductivity	(Si) 32, (Au) 320 (W/mK)	(Si) 32 (W/mK)

Table A.1: Bi-Material and Silicon Tipless Cantilever Properties

Prong and Fiber Properties		
Property	(Al) Heating Prong	(PCL) Single Fiber
Length	5 (mm)	7.7 (mm)
Thickness	0.6 (mm)	0.75 (um)
Density	N/A	1.145 (g/mL)
Melting Point	N/A	60 (°C)
Thermal Conductivity	205 (W/mK)	Figure (5.2)

Table A.2: Aluminum Heating Prong and Polycaprolactone (PCL) Single Nanofiber Properties.

Appendix B

MATLAB Code

```
%%Imported Temperatures and Deflections
clear
filename = 'Master2.xlsx';

AFMdeflection=xlsread(filename,1,'A5:A11');
%Natural deflections of AFM cantilever
AFMSTDErr=xlsread(filename,1,'B5:B11');
Probedeflection=xlsread(filename,1,'C5:C11');
%Probe-to-probe Contact deflections
ProbeSTDErr=xlsread(filename,1,'D5:D11');
Fiberdeflection=xlsread(filename,1,'E5:E11');
%Probe-to-probe contact with fiber
FiberSTDErr=xlsread(filename,1,'F5:F11');
%Probe-to-Probe Temps with fiber appended
Tpo=xlsread(filename,1,'AA5:AA11'); %Fiber Prong Base
TpoErr=xlsread(filename,1,'AB5:AB11');
Tamp=xlsread(filename,1,'Y5:Y11'); %Fiber Prong Ambient
TampErr=xlsread(filename,1,'Z5:Z11');
Tambc=xlsread(filename,1,'W5:W11'); %Fiber Cant Ambient
TambcErr=xlsread(filename,1,'X5:X11');
Tpt=xlsread(filename,1,'AC5:AC11'); %Fiber Prong Ambient
TptErr=xlsread(filename,1,'AD5:AD11');
%Cal Probe-to-Probe Temps without fiber
TptCal=xlsread(filename,1,'U5:U11'); %Prong Tip
TptCalErr=xlsread(filename,1,'V5:V11');
TpoCal=xlsread(filename,1,'S5:S11'); %Prong Base
TpoCalErr=xlsread(filename,1,'T5:T11');
TampCal=xlsread(filename,1,'Q5:Q11'); %Prong Ambient
TampCalErr=xlsread(filename,1,'R5:R11');
TambcCal=xlsread(filename,1,'O5:O11'); %Cant Ambient
TambcCalErr=xlsread(filename,1,'P5:P11');
%AFM cantilever Natural Deflection Temps
TptAFM=xlsread(filename,1,'M5:M11'); %Prong Tip
TptAFMErr=xlsread(filename,1,'N5:N11');
TpoAFM=xlsread(filename,1,'K5:K11'); %Prong Base
TpoAFMErr=xlsread(filename,1,'L5:L11');
```

```

TambpAFM=xlsread(filename,1,'I5:I11'); %Prong Ambient
TambpAFMErr=xlsread(filename,1,'J5:J11');
TambcAFM=xlsread(filename,1,'G5:G11'); %Cant Ambient
TambcAFMErr=xlsread(filename,1,'H5:H11');

SolderTemp=xlsread(filename,1,'AE5:AE11');
%New nm/C Slope after subtracting calibrated
%from fiber appended results
SlopeDeltaDefl=xlsread(filename,1,'AI5:AI11');
SlopeDeltaTemp=xlsread(filename,1,'AJ5:AJ11');
%should be the Tct measured value from slope subtraction
PolyDefl=xlsread(filename,1,'AK5:AK11');
Tco=Tambc;

%%prong properties
Lp=5E-3; %prong length
l2=0; %prong 2 length
l1=Lp-l2; %prong 1 length
kp=205; %prong thermal conductivity (Al)
tp=.6E-3; %prong thickness
hp=10;
mp=sqrt((2*hp)/((kp*tp)));

%%Fiber properties
hf=10;%3900nano scale coef.
ep=1;%constant
sig=5.670367E-8;%constant
d=.75E-6;%fiber diameter
Lf=7.7E-3;%length
A=pi*(d^2)/4;

%%Bi-Material Cantilever Properties
Lc=100E-6; %Length
t2=540E-9; t1=60E-9;
a2=3E-6; a1=14.2E-6;
E2= 271E9; E1= 78E9;
k2=32; %S3N4 Thermal Conductivity
k1=320; %gold Thermal Conductivity
hc=10; %3900for nanoscale
mc = sqrt((2*hc)/((k1*t1 + k2*t2)));
G = 4+6*(t1/t2)+4*((t1/t2)^2) +
    (E1/E2)*((t1/t2)^3) + (E2/E1)*(t2/t1);
N=6*(a2-a1)*(t1+t2)/(((t2)^2)*G);
kBi=0.32; %Given Force Constant

%%AFM Cantilever Properties
b=50E-6; %%width
tafm=2E-6; %%thickness

```



```

Eafm=271E9; %or 1.69E11;
Lafm=450E-6;
a3=3E-6;
k3=32; %Si3N4 Thermal Conductivity
p=2350; %Si3N4 density
f=15500; %frequency
%kafm=.238; %Measured stiffness,
kafm=(2*(pi^3)*b*(f*Lafm*(sqrt(p)))^3)/(sqrt(Eafm));
%theoretical force constant-stiffness

hafm=10; %3900 for nanoscale
mafmsqrt=(2*hafm)/(k3*tafm);
Nafm=(3*a3)/(2*tafm);

%Voltage/nm
Voltage=xlsread(filename,1,'AF5:AF11');
TambcVolt=xlsread(filename,1,'AG5:AG11');
NewVolt=-xlsread(filename,1,'AR5:AR11');

figure(1)
[hAx,hLine1,hLine2]=plotyy(TambcAFM, AFMdeflection,
    TambcVolt, Voltage);
title('Natural AFM-Tipless Cantilever and
    Photo-diode Deflection')
legend('Deflection per temp','Voltage per temp')
xlabel('Ambient Temp (C)')
ylabel(hAx(1),'Tipless-AFM-Natural Deflection (m)')
ylabel(hAx(2),'Voltage (V)')
grid

figure(2)
plot(AFMdeflection, NewVolt);
title('AFM-Tipless Cantilever V/m Deflection')
xlabel('Deflection (m)')
ylabel('Voltage (V)')
grid

Time=[1,2,3,4,5,6,7];
figure(3)
errorbar(Time,TambcAFM,TambcAFMErr)
hold on
errorbar(Time,TampAFM,TampAFMErr)
errorbar(Time,TpoAFM,TpoAFMErr)
errorbar(Time,TptAFM,TpoAFMErr)
title('Natural Deflection Temperature Recordings
    per Time Step')
legend('Cantilever Ambient','Prong Ambient',
    'Prong Base','Prong Tip')

```

```

xlabel( 'Time_Step_Interval' )
ylabel( 'Temperature_(C)' )
hold off
grid

figure(4)
errorbar( Time, TambcCal, TambcCalErr )
hold on
errorbar( Time, TambpCal, TambpCalErr )
errorbar( Time, TpoCal, TpoCalErr )
errorbar( Time, TptCal, TpoCalErr )
title( 'Calibration_Temperature_Recordings_per_Time_Step' )
legend( 'Cantilever_Ambient', 'Prong_Ambient',
        'Prong_Base', 'Prong_Tip' )
xlabel( 'Time_Step_Interval' )
ylabel( 'Temperature_(C)' )
hold off
grid

figure(5)
errorbar( Time, Tambc, TambcErr )
hold on
errorbar( Time, Tambp, TambpErr )
errorbar( Time, Tpo, TpoErr )
errorbar( Time, Tpt, TpoErr )
title( 'Appended_Fiber_Temperature_Recordings
      _per_Time_Step' )
legend( 'Cantilever_Ambient', 'Prong_Ambient',
        'Prong_Base', 'Prong_Tip' )
xlabel( 'Time_Step_Interval' )
ylabel( 'Temperature_(C)' )
hold off
grid

figure(6)
errorbar( TambcAFM, AFMdeflection, AFMSTDerr )
hold on
errorbar( TambcCal, Probedeflection, ProbeSTDerr )
errorbar( Tambc, Fiberdeflection, FiberSTDerr )
title( 'Change_of_Deflection_vs_Change
      _in_Cantilever_Ambient' )
legend( 'Tipless_AFM_Natural_Deflection',
        'Probe-to-Probe_Calibration', 'Probe-to-Probe_Fiber' )
xlabel( 'Delta_Ambient_Temp_(C)' )
ylabel( 'Delta_Natural_Deflection_(m)' )
hold off
grid

```

```

figure(7)
plot(Tambc, SlopeDeltaDefl);
title( 'Appended_Fiber_Deflection_per
      Ambient_Temperature_Change' )
legend( 'Appended_Fiber_Deflection_vs_Tambc' )
xlabel( 'Cantilever_Ambient_Temp_(C)' )
ylabel( 'Deflection_(m)' )
grid

%recorded Tct with Using new slope (dx/dT)
To=0;
Deltaznat = SlopeDeltaDefl*((kafm/(sin(10)*kBi)) + 1);
%Convert to Bi material Natrual deflection
display(Deltaznat)
Tct=Tambc + (((mc^2)/(1-mc*csch(mc*Lc)))*((Deltaznat/N)
      -((Lc^2)*(Tambc-To)/2)));
%Find tip temp at change in deflection
%recorded value, should be less than Tf
      %and greater than Tambc

%Theorectial Tct
      %Temp at l1 without fiber (Only Prong Beam)
      %using Tf temp profile
Tf=((Tpt-Tampb)*sinh(mp*l1)+(Tpo-Tampb)*
sinh(mp*l2))*csch(mp*(l1+l2))+Tampb;

kf=105; %assumption
display(kf)
%mf=(sqrt((hf)/(d*kf)));
qfSimple=-(kf/Lf).*(Tf-Tct);
%simple flux using kf assumption
qf=kf.*( sqrt((hf)/(d.*kf)))
      .*((Tf-Tampb).*coth((sqrt((hf)/(d.*kf)))*Lf)
      -(Tct-Tambc).*csch((sqrt((hf)/(d.*kf)))*Lf)
      +((Tampb-Tambc)./((sqrt((hf)/(d.*kf)))*Lf)));
%theorectical flux using recorded Tct and
%kf assumption at cantilever end

%Fluxes with Fiber
qp1=kp*mp*((Tf-Tampb)*coth(mp*l1)
      -(Tpo-Tampb)*csch(mp*l1));
      %qp1 should always be the same in either case
qp2=kp*mp*((Tf-Tampb)*coth(mp*l2)
      -(Tpt-Tampb)*csch(mp*l2));
      %this is zero in this measured case
      %since fiber is at prong tip
qfTH=qp1;%recorded flux from prong end of
%the fiber (should match qf on other end),

```

```

%used to obtain kf

%%
for m=1:length(Tf)
    fun = @(kfb) kfb*(sqrt((hf)/(d*kfb)))*((Tf(m)-Tampb(m))
        *coth((sqrt((hf)/(d*kfb)))*Lf)-(Tct(m)
        -Tambc(m))*csch((sqrt((hf)/(d*kfb)))*Lf)
        +((Tampb(m)-Tambc(m))/((sqrt((hf)/(d*kfb)))*Lf))) - qfTH(m);
    kfv(m) = fzero(fun, 105);
end
kf_Recorded=transpose(kfv);
display(kf_Recorded)
%%
q_Fourier=qfSimple*10E-5;
q_Assumed=qf*10E-5;
q_Recorded=qfTH*10E-5;
Extra_Tct=Tambc-Tct;
W=table(SolderTemp, Tambc, Tampb, Tpo, Tpt, Tf, Extra_Tct);
Y=table(q_Assumed, q_Recorded, kf_Recorded);
display(W)
display(Y)

%Natural Tipless-AFM cantliver deflections with
%AFM temps TcoAFM=TambcAFM=TctAFM
TcoAFM=TambcAFM;
TctAFM=TcoAFM;
xafm=Lafm;
znatTHafm=Nafm*((TambcAFM-To)*(xafm^2)/2);

figure(9)
plot(TambcAFM, znatTHafm, TambcAFM, AFMdeflection);
title('AFM-Tipless_Natural_Cantilever_Deflections')
legend('Theoretical', 'Measured')
xlabel('Cantilever_Ambient_Temp_(C)')
ylabel('Natural_Deflection_(m)')
grid

%theoretical calibrated deflections using
%N, Lc, and Cal temps
znatTHCal=N*((TambcCal-To)*(Lc^2)/2);
CalDeflTH = znatTHCal/((kafm/((sin(10)*kBi)) + 1);
%theoretical calibrated deflections using
%Nafm, Lafm, and Cal temps
znatTHCalafm=Nafm*((TambcCal-To)*(Lafm^2)/2);
CalDeflTHafm = znatTHCalafm/((kafm/((sin(10)*kBi)) + 1);
figure(10)
plot(TambcCal, CalDeflTH, TambcCal,

```

```

    CalDeflTHafm, TambcCal, Probedeflection);
title('Calibrated_Theoretical_vs_Measured
      _Cantilever_Deflections')
legend('Theoretical:_Bi-Cant_Properties',
        'Theoretical:_AFM/Tipless-Cant_Properties','Measured')
xlabel('Cantilever_Ambient_Temp_(C)')
ylabel('Deflection_(m)')
grid

```

Bibliography

- [1] Sheng Shen et al. “Polyethylene nanofibres with very high thermal conductivities”. In: *Nature nanotechnology* 5.4 (2010), pp. 251–255.
- [2] Jian Ma et al. “Thermal conductivity of electrospun polyethylene nanofibers”. In: *Nanoscale* 7.40 (2015), pp. 16899–16908.
- [3] David G Cahill et al. “Nanoscale thermal transport”. In: *Journal of Applied Physics* 93.2 (2003), pp. 793–818.
- [4] David G Cahill et al. “Nanoscale thermal transport. II. 2003–2012”. In: *Applied Physics Reviews* 1.1 (2014), p. 011305.
- [5] Nuo Yang et al. “Thermal transport in nanostructures”. In: *AIP Advances* 2.4 (2012), p. 041410.
- [6] Sebastian G Volz and Gang Chen. “Molecular dynamics simulation of thermal conductivity of silicon nanowires”. In: *Applied Physics Letters* 75.14 (1999), pp. 2056–2058.
- [7] Yunfei Chen et al. “Monte Carlo simulation of silicon nanowire thermal conductivity”. In: *Journal of Heat Transfer* 127.10 (2005), pp. 1129–1137.

- [8] LN Maurer et al. “Universal features of phonon transport in nanowires with correlated surface roughness”. In: *Applied Physics Letters* 106.13 (2015), p. 133108.
- [9] Zhenxin Zhong et al. “Structure-induced enhancement of thermal conductivities in electrospun polymer nanofibers”. In: *Nanoscale* 6.14 (2014), pp. 8283–8291.
- [10] Teng Zhang, Xufei Wu, and Tengfei Luo. “Polymer nanofibers with outstanding thermal conductivity and thermal stability: fundamental linkage between molecular characteristics and macroscopic thermal properties”. In: *The Journal of Physical Chemistry C* 118.36 (2014), pp. 21148–21159.
- [11] Xiaojia Wang et al. “Thermal conductivity of high-modulus polymer fibers”. In: *Macromolecules* 46.12 (2013), pp. 4937–4943.
- [12] AG Gibson et al. “Thermal conductivity of ultrahigh-modulus polyethylene”. In: *Journal of Polymer Science Part C: Polymer Letters* 15.4 (1977), pp. 183–192.
- [13] CL Choy, WH Luk, and FC Chen. “Thermal conductivity of highly oriented polyethylene”. In: *Polymer* 19.2 (1978), pp. 155–162.
- [14] DB Mergenthaler et al. “Thermal conductivity in ultraoriented polyethylene”. In: *Macromolecules* 25.13 (1992), pp. 3500–3502.
- [15] Jian Yao, Cees WM Bastiaansen, and Ton Peijs. “High strength and high modulus electrospun nanofibers”. In: *Fibers* 2.2 (2014), pp. 158–186.
- [16] Dimitry Papkov et al. “Simultaneously strong and tough ultrafine continuous nanofibers”. In: *ACS nano* 7.4 (2013), pp. 3324–3331.

- [17] Andreas Greiner and Joachim H Wendorff. “Electrospinning: a fascinating method for the preparation of ultrathin fibers”. In: *Angewandte Chemie International Edition* 46.30 (2007), pp. 5670–5703.
- [18] Dan Li and Younan Xia. “Electrospinning of nanofibers: reinventing the wheel?” In: *Advanced materials* 16.14 (2004), pp. 1151–1170.
- [19] Darrell H Reneker et al. “Bending instability of electrically charged liquid jets of polymer solutions in electrospinning”. In: *Journal of Applied physics* 87.9 (2000), pp. 4531–4547.
- [20] Avinash Baji et al. “Electrospinning of polymer nanofibers: effects on oriented morphology, structures and tensile properties”. In: *Composites science and technology* 70.5 (2010), pp. 703–718.
- [21] PJ Lemstra, CWM Bastiaansen, and HEH Meijer. “Chain-extended flexible polymers”. In: *Macromolecular Materials and Engineering* 145.1 (1986), pp. 343–358.
- [22] David De Koninck. “Thermal conductivity measurements using the 3-omega technique: application to power harvesting microsystems”. PhD thesis. McGill University, 2008.
- [23] Philip Kim et al. “Thermal transport measurements of individual multi-walled nanotubes”. In: *Physical review letters* 87.21 (2001), p. 215502.
- [24] Keith Schwab et al. “Measurement of the quantum of thermal conductance”. In: *Nature* 404.6781 (2000), p. 974.
- [25] Carlo Canetta. *Bi-material microcantilever-based thermal sensing techniques*. Columbia University, 2014.

- [26] Zheng-Ming Huang et al. “A review on polymer nanofibers by electrospinning and their applications in nanocomposites”. In: *Composites science and technology* 63.15 (2003), pp. 2223–2253.
- [27] Jayesh Doshi and Darrell H Reneker. “Electrospinning process and applications of electrospun fibers”. In: *Industry Applications Society Annual Meeting, 1993., Conference Record of the 1993 IEEE*. IEEE. 1993, pp. 1698–1703.
- [28] Audrey Frenot and Ioannis S Chronakis. “Polymer nanofibers assembled by electrospinning”. In: *Current opinion in colloid & interface science* 8.1 (2003), pp. 64–75.
- [29] Seema Agarwal, Joachim H Wendorff, and Andreas Greiner. “Use of electrospinning technique for biomedical applications”. In: *Polymer* 49.26 (2008), pp. 5603–5621.
- [30] Geoffrey Taylor. “Electrically driven jets”. In: *Proceedings of the Royal Society of London A: Mathematical, Physical and Engineering Sciences*. Vol. 313. 1515. The Royal Society. 1969, pp. 453–475.
- [31] Michael Bognitzki et al. “Nanostructured fibers via electrospinning”. In: *Advanced Materials* 13.1 (2001), pp. 70–72.
- [32] Darrell H Reneker and Iksoo Chun. “Nanometre diameter fibres of polymer, produced by electrospinning”. In: *Nanotechnology* 7.3 (1996), p. 216.
- [33] GI Taylor. “Cavitation in hydrodynamic lubrication”. In: *Cavitation in real liquids* (1964), pp. 80–101.

- [34] GMH Meesters et al. “Generation of micron-sized droplets from the Taylor cone”. In: *Journal of aerosol science* 23.1 (1992), pp. 37–49.
- [35] Juan Fernández de La Mora. “The fluid dynamics of Taylor cones”. In: *Annu. Rev. Fluid Mech.* 39 (2007), pp. 217–243.
- [36] Alexander L Yarin, Sureeporn Koombhongse, and Darrell Hyson Reneker. “Taylor cone and jetting from liquid droplets in electrospinning of nanofibers”. In: *Journal of applied physics* 90.9 (2001), pp. 4836–4846.
- [37] H Fong, I Chun, and DH Reneker. “Beaded nanofibers formed during electrospinning”. In: *Polymer* 40.16 (1999), pp. 4585–4592.
- [38] Ernst Meyer, Hans Josef Hug, and Roland Bennewitz. *Scanning probe microscopy: the lab on a tip*. Springer Science & Business Media, 2013.
- [39] Peter Eaton and Paul West. *Atomic force microscopy*. Oxford University Press, 2010.
- [40] Brandon Cheney. “Introduction to scanning electron microscopy”. In: *Materials Engineering department San Jose State University* (2007).
- [41] Cedric Gaillard et al. “Practical method for high-resolution imaging of polymers by low-voltage scanning electron microscopy”. In: *Scanning* 26.3 (2004), pp. 122–130.
- [42] RN Jagtap and AH Ambre. “Overview literature on atomic force microscopy (AFM): Basics and its important applications for polymer characterization”. In: (2006).
- [43] Jaime Castillo-León, Winnie Edith Svendsen, and Maria Dimaki. *Micro and nano techniques for the handling of biological samples*. CRC Press, 2011.

- [44] Michele Giocondo et al. “Atomic Force Spectroscopies: A Toolbox for Probing the Biological Matter”. In: *Atomic Force Microscopy Investigations into Biology-From Cell to Protein*. InTech, 2012.
- [45] JR Barnes et al. “A femtojoule calorimeter using micromechanical sensors”. In: *Review of Scientific Instruments* 65.12 (1994), pp. 3793–3798.
- [46] J Lai et al. “Optimization and performance of high-resolution micro-optomechanical thermal sensors”. In: *Sensors and Actuators A: Physical* 58.2 (1997), pp. 113–119.
- [47] Jungchul Lee et al. “Electrical, thermal, and mechanical characterization of silicon microcantilever heaters”. In: *Journal of Microelectromechanical Systems* 15.6 (2006), pp. 1644–1655.
- [48] William P King et al. “Heated atomic force microscope cantilevers and their applications”. In: *Annual Review of Heat Transfer* 16.16 (2013).
- [49] HEAT TRANSFER THERMODYNAMICS. “DOE FUNDAMENTALS HANDBOOK”. In: (1992).
- [50] Liqiu Wang, Xuesheng Zhou, and Xiaohao Wei. *Heat conduction: mathematical models and analytical solutions*. Springer Science & Business Media, 2007.
- [51] William P King et al. “Atomic force microscope cantilevers for combined thermomechanical data writing and reading”. In: *Applied Physics Letters* 78.9 (2001), pp. 1300–1302.

- [52] William E Boyce, Richard C DiPrima, and Charles W Haines. *Elementary differential equations and boundary value problems*. Vol. 9. Wiley New York, 1969.
- [53] Sheng Shen et al. “Thermal conductance of bimaterial microcantilevers”. In: *Applied Physics Letters* 92.6 (2008), p. 063509.
- [54] Masaya Toda et al. “Evaluation of bimaterial cantilever beam for heat sensing at atmospheric pressure”. In: *Review of Scientific Instruments* 81.5 (2010), p. 055104.
- [55] Wen-Hwa Chu, Mehran Mehregany, and Robert L Mullen. “Analysis of tip deflection and force of a bimetallic cantilever microactuator”. In: *Journal of Micromechanics and Microengineering* 3.1 (1993), p. 4.
- [56] JN Reddy. “On locking-free shear deformable beam finite elements”. In: *Computer Methods in Applied Mechanics and Engineering* 149.1 (1997), pp. 113–132.
- [57] Arvind Narayanaswamy and Ning Gu. “Heat transfer from freely suspended bimaterial microcantilevers”. In: *Journal of Heat Transfer* 133.4 (2011), p. 042401.
- [58] Frank O Goodman and Nicolas Garcia. “Roles of the attractive and repulsive forces in atomic-force microscopy”. In: *Physical Review B* 43.6 (1991), p. 4728.
- [59] Seung-woo Lee and Wolfgang M Sigmund. “AFM study of repulsive van der Waals forces between Teflon AFTM thin film and silica or alumina”. In:

Colloids and Surfaces A: Physicochemical and Engineering Aspects 204.1 (2002), pp. 43–50.

- [60] Brunero Cappella and Giovanni Dietler. “Force-distance curves by atomic force microscopy”. In: *Surface science reports* 34.1 (1999), pp. 1–104.
- [61] Akihiro Torii et al. “A method for determining the spring constant of cantilevers for atomic force microscopy”. In: *Measurement Science and Technology* 7.2 (1996), p. 179.
- [62] Arvind Narayanaswamy, Sheng Shen, and Gang Chen. “Near-field radiative heat transfer between a sphere and a substrate”. In: *Physical Review B* 78.11 (2008), p. 115303.
- [63] RJF Bijster, J de Vreugd, and H Sadeghian Marnani. “Dynamic characterization of bi-material cantilevers”. In: (2013).
- [64] SY Gu, J Ren, and GJ Vancso. “Process optimization and empirical modeling for electrospun polyacrylonitrile (PAN) nanofiber precursor of carbon nanofibers”. In: *European polymer journal* 41.11 (2005), pp. 2559–2568.
- [65] Sachiko Sukigara et al. “Regeneration of Bombyx mori silk by electrospinning. Part 2. Process optimization and empirical modeling using response surface methodology”. In: *Polymer* 45.11 (2004), pp. 3701–3708.
- [66] SG Kumbar et al. “Electrospun nanofiber scaffolds: engineering soft tissues”. In: *Biomedical Materials* 3.3 (2008), p. 034002.
- [67] Bahareh Azimi et al. “Poly (ϵ -caprolactone) Fiber: An Overview”. In: *Journal of Engineered Fabrics & Fibers (JEFF)* 9.3 (2014).

- [68] Lucy A Bosworth and Sandra Downes. “Acetone, a sustainable solvent for electrospinning poly (ϵ -caprolactone) fibres: effect of varying parameters and solution concentrations on fibre diameter”. In: *Journal of Polymers and the Environment* 20.3 (2012), pp. 879–886.
- [69] CJ Luo, M Nangrejo, and M Edirisinghe. “A novel method of selecting solvents for polymer electrospinning”. In: *Polymer* 51.7 (2010), pp. 1654–1662.
- [70] Matthew G McKee, Casey L Elkins, and Timothy E Long. “Influence of self-complementary hydrogen bonding on solution rheology/electrospinning relationships”. In: *Polymer* 45.26 (2004), pp. 8705–8715.
- [71] BJ Haupt, TJ Senden, and Edith M Sevick. “AFM evidence of Rayleigh instability in single polymer chains”. In: *Langmuir* 18.6 (2002), pp. 2174–2182.
- [72] C HENDRICK et al. “PHOTOMICROGRAPHY OF ELECTRICALLY SPRAYED HEAVY PARTICLES”. In: ().
- [73] Pankaj Gupta and Garth L Wilkes. “Some investigations on the fiber formation by utilizing a side-by-side bicomponent electrospinning approach”. In: *Polymer* 44.20 (2003), pp. 6353–6359.
- [74] Mohammad R Kasaai, Gérard Charlet, and Joseph Arul. “Master curve for concentration dependence of semi-dilute solution viscosity of chitosan homologues: the Martin equation”. In: *Food research international* 33.1 (2000), pp. 63–67.
- [75] William W Graessley. “The entanglement concept in polymer rheology”. In: *The Entanglement Concept in Polymer Rheology*. Springer, 1974, pp. 1–179.

- [76] Won Keun Son et al. “The effects of solution properties and polyelectrolyte on electrospinning of ultrafine poly (ethylene oxide) fibers”. In: *Polymer* 45.9 (2004), pp. 2959–2966.
- [77] John L Richards. “Viscosity and the shapes of macromolecules: a physical chemistry experiment using molecular-level models in the interpretation of macroscopic data obtained from simple measurements”. In: *J. Chem. Educ* 70.8 (1993), p. 685.
- [78] Daming Zhang and Jiang Chang. “Electrospinning of three-dimensional nanofibrous tubes with controllable architectures”. In: *Nano letters* 8.10 (2008), pp. 3283–3287.
- [79] Dayong Yang et al. “Fabrication of aligned fibrous arrays by magnetic electrospinning”. In: *Advanced materials* 19.21 (2007), pp. 3702–3706.
- [80] Christopher J Buchko et al. “Processing and microstructural characterization of porous biocompatible protein polymer thin films”. In: *Polymer* 40.26 (1999), pp. 7397–7407.
- [81] Ben Ohler. “Practical advice on the determination of cantilever spring constants”. In: *Bruker Application Note# AN94 1* (2007).
- [82] Grzegorz Wielgoszewski et al. “A high-resolution measurement system for novel scanning thermal microscopy resistive nanoprobe”. In: *Measurement Science and Technology* 22.9 (2011), p. 094023.
- [83] Li Shi and Arunava Majumdar. “Thermal transport mechanisms at nanoscale point contacts”. In: *Journal of Heat Transfer* 124.2 (2002), pp. 329–337.

- [84] Kyeongtae Kim et al. “Ultra-high vacuum scanning thermal microscopy for nanometer resolution quantitative thermometry”. In: *Acs Nano* 6.5 (2012), pp. 4248–4257.
- [85] Joost Duvigneau, Holger Schonherr, and G Julius Vancso. “Nanoscale thermal AFM of polymers: transient heat flow effects”. In: *ACS nano* 4.11 (2010), pp. 6932–6940.